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KORNBLUM, Zvi Chaim, 1949-
ISOTOPE EFFECT ON THE ZERO POINT ENERGY
SHIFT UPON CONDENSATION.

City University of New York, Ph.D., 1977
Chemistry, physical

Xerox University Microfilms, Ann Arbor, Michigan 48106

ISOTOPE EFFECT
ON THE
ZERO POINT ENERGY SHIFT
UPON CONDENSATION

by

Zvi Chaim Kornblum

A dissertation submitted to the
Graduate Faculty in Chemistry
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy,
The City University of New York

1977

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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The City University of New York

Abstract

ISOTOPE EFFECT
ON THE
ZERO POINT ENERGY SHIFT
UPON CONDENSATION

by

Zvi Chaim Kornblum

Adviser: Professor Takanobu Ishida

The various isotope-dependent and independent atomic and molecular properties that pertain to the isotopic difference between the zero point energy (ZPE) shifts upon condensation have been derived. The theoretical development of the change of the ZPE associated with the internal molecular vibrations, due to the condensation of the gaseous molecules, has been presented on the basis of Wolfsberg's second-order perturbation treatment of the isotope-dependent London dispersion forces between liquid molecules.

The isotope effect on the ZPE shift is related to the difference between the sums of the integrated intensities of the infrared absorption bands of the two gaseous isotopic molecules. Each intensity sum is expressed, in part, in terms of partial derivatives of the molecular dipole moment with respect to atomic cartesian coordinates. These derivatives are related to the isotope-independent effective charges of the atoms, which are theoretically calculated by means of a modified CNDO/2 computer

program. This program is based on a quantum mechanical semi-empirical molecular orbital theory. The effective atomic charges are also calculated from available experimental infrared intensity data.

The effects of isotopic substitutions of carbon-13 for carbon-12 and/or deuterium for protium, in ethylene, methane, and the fluorinated methanes, CH_3F, CH_2F_2, CHF_3, and CF_4, on the ZPE shift upon condensation are calculated. These results compare well with the Bigeleisen B-factors, which are experimentally obtained from vapor pressure measurements of the isotopic species.

Each of the following molecular properties will tend to increase the isotopic difference between the ZPE shifts upon condensation: (1) large number of highly polar bonds, (2) high molecular weight, (3) non-polar (preferably) or massive molecule, (4) non-hydrogenous molecule, and (5) closely packed liquid molecules. These properties will result in stronger dispersion forces in the liquid phase between the lighter molecules than between the isotopically heavier molecules.

To My Favorite Mathematician, Dearest Debby,

"Ahavat Olam Ahavteech"

ACKNOWLEDGMENTS

With heartfelt appreciation, the author would like to acknowledge the assistance and guidance that was given by Professor Takanobu Ishida of Brooklyn College during the course of this research. It has been a privilege to have conducted this research under such an accomplished and energetic scientist. It has also been gratifying to have Professor Vojtech Fried of Brooklyn College and Professor Louis Massa of Hunter College on the thesis committee. Their invaluable assistance and helpful suggestions were instrumental in this research. Special thanks are also due to Professor James Howell of Brooklyn College for making his version of the CNDO/2 computer program available to this author. Messrs. Benjamin Klein of the City University Computer Center and Armand Gazes of the Brooklyn College Data Acquisition Facility have been extremely helpful. The author would also like to express his sincere appreciation to the City University of New York Graduate School, to Brooklyn College, and to their faculties and staffs for the educational opportunity that they provided. The author is grateful to his wife, Deborah, for reading the entire manuscript several times and offering many helpful mathematical and grammatical suggestions, and for the patience that she has shown during the course of this research.

The funding that was provided for this research by the United States Energy Research and Development Administration and the City University of New York Faculty Awards Program has been most helpful.

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I. INTRODUCTION

This dissertation presents a theoretical formulation and interpretation of the isotopic phase dependence of the molecular zero point energy (ZPE) produced by the internal vibrational motions. The formulation permits calculations of the change in the ZPE upon condensation for a pair of isotopic molecules.

The zero point energy shift upon condensation of a gas molecule is an important phenomenon in the studies of molecular forces in the condensed phase, because the shift is a consequence of the change in the intramolecular forces upon condensation and of the influence of the intermolecular forces in the condensed phase. In the simplest form of the theory of the vapor pressure isotope effect (VPIE) originally developed by J. Bigeleisen, the logarithm of the ratio of the vapor pressures of the light isotopic molecule to that of the heavier isotopic molecule, at a given temperature, is expressible as a sum of two opposing terms. The positive term is due to the isotopic difference in the first-order quantum correction to the reduced partition function, and the negative term is caused by the isotopic difference in the ZPE shift upon condensation. Thus, the ZPE shift upon condensation plays a central role in the theory of vapor pressure isotope effects.

In particular, as the magnitude of the negative ZPE-shift term increases, the interesting phenomenon of the "crossover" of the VPIE into the inverse VPIE occurs. That is, the vapor pressure of the heavier molecule becomes higher than the vapor pressure of the lighter molecule. This phenomenon is not only interesting and useful from the standpoint of the theory of the liquid phase, but it is also important for the industrial application of the VPIE theory. The cost of the fractionation of stable isotopes such as heavy water, ^{13}C, ^{15}N, etc., by a low-temperature distillation process has been predicted to be less if the plant is operated at temperatures at which the VPIE is inverse rather than normal.

At the present state of art, the isotope effect on the ZPE shift upon condensation can be obtained experimentally from the measurements of the vapor pressure isotope effect. On the theoretical side, however, the best one can do at present is to calculate it directly from the spectroscopic data on the gas and liquid molecules. However, the spectroscopic data of condensed phases are complete and reliable for only a handful of molecules. For these few species, one can calculate the normal frequencies of the isotopic liquid molecules from an established force constant matrix and, consequently, obtain the ZPE shifts. For the majority of molecules, reliable liquid force fields have not been mapped out. The purpose of this dissertation has been to establish a theory by which a priori evaluations of the isotope effect on the ZPE shift upon condensation can be made without relying on experimentally obtained force fields of condensed phases.

This dissertation consists of five main parts, Sections II-VI. Section II presents the general theory of chemical isotope effects, especially as it pertains to equilibrium systems. The quantum statistical mechanical origin of the reduced partition function ratio of a pair of isotopic molecules, one of the most important factors of isotope chemistry, is presented. Various simplifying approximations of this ratio are reviewed, so as to give an insight into the role of molecular forces in isotope effects.

Section III reviews the development of the VPIE formalisms. The Bigeleisen formulation of this problem is emphasized with respect to the internal and external modes of vibration of both the gaseous and condensed molecules. The discussion of the VPIE concludes with a description of the intermolecular forces in the liquid, with special emphasis given to the Wolfsberg derivation of the ZPE shift upon condensation.

Section IV is the commencement of this investigator's original research in the field of isotope effects. The isotope effect on the ZPE shift upon condensation is related to readily available, or calculable, atomic and molecular properties. This is accomplished by means of various matrix transformations of the molecular dipole moment derivatives, which are related to infrared absorption intensities. The relationship between the above isotope effect and the effective charge(s) of the isotopically substituted atom(s) is emphasized.

Section V discusses the computational methods used to obtain the effective atomic charges. The computer program utilized for this purpose is based on a semi-empirical molecular orbital theory. This program is outlined and the necessary modifications are described.

The computer program is furnished in the appendix.

Section VI presents the results of the calculations of the isotope effects on the ZPE shift upon condensation, and interprets them. Both specific and general analyses are performed on these results.

A brief conclusion, Section VII, and appendix complete the body of the text.

II. THEORY OF CHEMICAL ISOTOPE EFFECTS

II.A. Quantum Statistical Mechanical Foundations of Isotope Chemistry: the Reduced Partition Function Ratio

In the examination of equilibrium or kinetic isotope effects on reactions, an important relation which appears in the study of such effects is Bigeleisen and Mayer's (1-5) reduced partition function ratio for two isotopic species, (s/s')f. This ratio is defined as

$$\frac{s}{s'} f \equiv \frac{(Q/Q')_{qm}}{(Q/Q')_{cl}} = \frac{(Q_{qm}/Q_{cl})}{(Q_{qm}/Q_{cl})'} = \frac{Q_r}{Q_r'} \quad . \tag{1}$$

According to Bigeleisen and Mayer's convention the primed (') species denotes the lighter isotope and the un-primed isotope denotes the heavier species. Thus, s and s' are the symmetry numbers of the heavier and lighter molecules, respectively. Q_{qm} and Q_{cl} are the quantum mechanical and classical molecular partition functions, respectively. Therefore, Eqn.(1) represents a ratio of reduced partition functions of two isotopic species; reduced in the sense that a quantum statistical machanical partition function is divided by its classical counterpart.

The importance of the reduced partition function ratio is that it provides an absolute measure of isotopic fractionations. Isotope effects on equilibrium constants and, in fact, isotopic differences for all thermodynamic functions, can be expressed in terms of these reduced partition function ratios, since thermodynamic properties are functions of partition functions. The isotopic ratio of the molecular partition functions is a simple explicit function of normal frequencies, under a set of simplifying assumptions and approximations. Since this ratio forms the basis of this thesis, the formulation of the partition function ratio, based on the work of Bigeleisen and Mayer (5), will be recorded in subsections II.A.1, II.A.2, and II.A.3.

II.A.1. Approximations for Isotope Effect Studies

Several simplifying approximations are made in order to facilitate the calculation of the partition functions.

II.A.1.a. Born-Oppenheimer approximation

This is the basic approximation that is fundamental to theoretical isotope effect studies. Quantum mechanically, the electronic and nuclear motions of a molecule may be separated, due to the large mass difference between the electrons and nuclei. The electronic problem is then solved for fixed nuclear positions, nuclear charges, the number of electrons in the system, and for the potential which does not involve nuclear masses. The resulting electronic energy surface is the potential energy for the motion of the nuclei. Therefore, under the Born-Oppenheimer approximation, the force field in which the nuclei vibrate is isotope independent. Isotope effects are, consequently, nuclear mass effects resulting from the motion of different nucleic masses on the same potential energy surface. This assumption is valid for polyatomic molecules. However, for the hydrogenous molecule, the Born-Oppenheimer approximation is partially invalidated. Hence, from the separability notion,

$$Q \simeq Q_{el}Q_{nuc} \quad , \tag{2}$$

and from the isotopic invariance of the electronic partition function,

$$Q_{el}' \simeq Q_{el} \; , \tag{3}$$

one obtains for the isotopic molecular partition function ratio

$$Q/Q' \simeq Q_{nuc}/Q_{nuc}' \; . \tag{4}$$

II.A.1.b. Freely translating rigid rotor

The nuclear partition function is simplified by approximately separating the nuclear motion into three motions, i.e., translation, rotation, and vibration. Thus, the nuclear contribution to the partition function is

$$Q_{nuc} \simeq Q_{tr} Q_{rot} Q_{vib} \,. \tag{5}$$

II.A.1.c. Harmonic oscillator approximation

Neglecting anharmonicities in the internal vibrations, one obtains for the quantum-mechanical vibrational partition function,

$$(Q_{vib})_{qm} = \prod_{i}^{3N-6} \frac{e^{-u_i/2}}{1-e^{-u_i}} \,, \tag{6}$$

where u_i is a dimensionless energy defined as

$$u_i \equiv \frac{hc}{k} \frac{\omega_i}{T} = \frac{h\nu_i}{kT} \,, \tag{7}$$

N is the number of atoms in the molecule, h is Planck's constant, c is the speed of light, k is Boltzmann's constant, ω_i is the i-th harmonic frequency in cm^{-1}, ν_i is the frequency in sec^{-1}, and T is the temperature in ^{o}K. The zero of the energy is chosen at the minimum of the potential energy curve, because this places isotopic molecules on a common ground, so that isotopic differences may be treated without ambiguity.

At high temperatures or low u_i, the vibrational partition function approaches the classical limit:

$$(Q_{vib})_{cl} = \prod_{i}^{3N-6} \frac{1}{u_i} \; . \tag{8}$$

II.A.1.d. Classical translations and rotations

For the translational and rotational motions, the spacing between energy levels is sufficiently small, so that classical statistical mechanics may be employed at temperatures above, say, 100^{o} K. Consequently,

$$(Q_{tr})_{qm} \simeq (Q_{tr})_{cl} \tag{9}$$

and

$$(Q_{rot})_{qm} \simeq (Q_{rot})_{cl} \quad . \tag{10}$$

However, the last relation is not appropriate for small molecules, such as hydrogen, so that a non-classical correction must be taken into account (5, 13).

II.A.2. Standard Form of the Reduced Partition Function Ratio

Substituting the previous equations into Eqn.(1) yields

$$\frac{s}{s'}f = \prod_{i}^{3N-6} \frac{u_i}{u_i'} \frac{e^{-u_i/2}}{e^{-u_i'/2}} \frac{1-e^{-u_i'}}{1-e^{-u_i}} \quad . \tag{11}$$

(s/s')f is thus composed of three contributions. The ratio of the u_i's results from the classical vibrational partition functions. The ratio of the $e^{-u_i/2}$'s results from the vibrational zero point energy. The last ratio of the $(1-e^{-u_i})$'s results from the vibrational excitation.

II.A.3. Equilibrium Isotope Effects: Classical Vs. Quantum

The effect of isotopic substitutions on equilibrium (and kinetic) reactions has been the subject of experimental and theoretical investigations since the 1930s (5-10). Classical statistical mechanics, however, does <u>not</u> lead to isotopic enrichments.

Classically,

$$(Q/Q')_{tr,cl} = (M/M')^{3/2} \tag{12}$$

and

$$(Q/Q')_{rot,cl} = (s'/s)(I_aI_bI_c/I_a'I_b'I_c')^{1/2} \ , \tag{13}$$

where M and M' are the molecular masses of the heavy and light isotopic molecules, respectively, and the I's are the principal moments of inertia. Thus, using the separability assumption, Eqn. (5), and Eqns. (8), (12), and (13), one obtains

$$\left(\frac{Q}{Q'}\right)_{cl} = \left(\frac{M}{M'}\right)^{3/2} \left(\frac{s'}{s}\right) \left(\frac{I_aI_bI_c}{I_a'I_b'I_c'}\right)^{1/2} \prod_i^{3N-6} \frac{u_i'}{u_i} \ . \tag{14}$$

In addition, from the Teller-Redlich product rule (72,73),

$$\prod_{i}^{3N-6} \frac{u_i'}{u_i} = \prod_{i}^{3N-6} \frac{\omega_i'}{\omega_i} \tag{15a}$$

$$= \left(\frac{M'}{M}\right)^{3/2} \left(\frac{I_a'I_b'I_c'}{I_aI_bI_c}\right)^{1/2} \prod_{\alpha}^{N} \left(\frac{m_\alpha}{m_\alpha'}\right)^{3/2} , \tag{15b}$$

the classical partition function ratio becomes

$$(Q/Q')_{cl} = (s'/s)\prod_{\alpha}^{N}(m_\alpha/m_\alpha')^{3/2} , \tag{16}$$

where m_α and m_α' are the masses of the heavy and light atoms α and α', respectively.

The classical equilibrium constant, K_{cl}, can be calculated for the isotope exchange equilibrium

$$AX + BX' \rightleftarrows AX' + BX, \tag{17}$$

where A and B are any polyatomic groups, and X and X' are the isotopic atoms. Thus,

$$K_{cl} = \left\{Q(AX')Q(BX)/Q(AX)Q(BX')\right\}_{cl} \tag{18}$$

$$= \left[\frac{Q(BX)/Q(BX')}{Q(AX)/Q(AX')}\right]_{cl} = \left[\frac{(Q/Q')_{BX}}{(Q/Q')_{AX}}\right]_{cl} . \tag{19}$$

Substituting Eqn.(16) into (19), one obtains

$$K_{cl} = \frac{(s'/s)_{BX}}{(s'/s)_{AX}} , \tag{20}$$

since all the atomic masses cancelled, due to the fact that between two sides of a balanced chemical equation all the atomic masses must be preserved. Therefore, the classical equilibrium constant for an isotope exchange reaction is simply a ratio of symmetry numbers.

The symmetry number s of a molecule is defined as the number of different values of the rotational coordinates which all correspond to one orientation of the molecule, remembering that the identical atoms are indistinguishable. Thus, the symmetry number ratio provides no mechanism for isotopic preferences. Rather, this ratio is an important statistical correction for the probabilities of forming symmetrical vs. asymmetrical molecules of the same configuration. Therefore, the classical situation always corresponds to a random distribution of isotopes, i.e., no isotope effect.

Hence, an isotope effect is a direct manifestation of quantum mechanical energy levels as expressed by Eqn. (6). Classical mechanics is adequate when the spacing between energy levels is amall compared with kT. The quantum mechanical equilibrium constant for the isotope exchange equilibrium, Eqn. (17), is

$$K_{qm} = \left(\frac{(Q/Q')_{BX}}{(Q/Q')_{AX}}\right)_{qm} \quad . \tag{21}$$

In addition, the isotope separation factor α, given by

$$\alpha \equiv \frac{\text{isotopic atom ratio in chemical species BX}}{\text{isotopic atom ratio in chemical species AX}} \quad , \tag{22}$$

is the isotope effect on the exchange equilibrium. Thus,

$$\alpha = K_{qm}/K_{cl} = \left(\frac{(Q/Q')_{qm}}{(Q/Q')_{cl}}\right)_{BX} / \left(\frac{(Q/Q')_{qm}}{(Q/Q')_{cl}}\right)_{AX} \tag{23}$$

$$= \left(\frac{s}{s'}f\right)_{BX} / \left(\frac{s}{s'}f\right)_{AX} \tag{24}$$

and

$$K_{qm} = \left[\frac{s'}{s}\left(\frac{s}{s'}f\right)\right]_{BX} \Big/ \left[\frac{s'}{s}\left(\frac{s}{s'}f\right)\right]_{AX} \quad . \tag{25}$$

If $\alpha \equiv 1$, there is no isotopic separation. An isotope effect occurs when $\alpha \neq 1$. It is seen from Eqns.(24) and (25) that both the isotope effect on an equilibrium reaction, and the equilibrium constant itself, can be expressed in terms of Bigeleisen and Mayer's reduced partition function ratio of Eqn.(11).

II.B. Approximations of the Reduced Partition Function Ratio

A number of approximations of (s/s')f of Eqn. (11) have been developed, so as to give more physical significance to the reduced partition function ratio. These approximations are especially important for explaining the role of molecular forces in isotope chemistry and will be referred to later in this work.

II.B.1. First Order Approximations

II.B.1.a. Bigeleisen and Mayer's G(u)-function (5)

This is a first-order approximation of (s/s')f and is appropriate for small frequency shifts

$$\delta u_i \equiv u_i' - u_i \ . \tag{26}$$

Eqn. (11) can be rearranged to yield

$$\frac{s}{s'}\,f = \left(\left(1 + \frac{\delta u_i}{u_i}\right)^{-1}\right)\left(e^{\delta u_i/2}\right)\left(\left(1-e^{-(u_i+\delta u_i)}\right) \Big/ \left(1-e^{-u_i}\right)\right) \ . \tag{27}$$

Each of these three parts is expanded through a Taylor series in powers of δu_i,and only terms up to the first order in δu_i are retained. Thus, Eqn. (27) becomes

$$\frac{s}{s'} f \simeq 1 + \sum_{i}^{3N-6} G(u_i)\delta u_i \ , \tag{28}$$

where

$$G(u_i) \equiv \frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1} \ . \tag{29}$$

Since δu_i is small, Eqn. (28) can be further simplified to

$$\ln\left(\frac{s}{s'} f\right) \simeq \sum_{i}^{3N-6} G(u_i)\delta u_i \ . \tag{30}$$

The G(u) function still retains all the original contributions to (s/s')f. The "$\frac{1}{2}$" corresponds to the zero-point energy term; $1/u_i$ is the classical contribution; and $1/(e^{u_i}-1)$ is the excitational term. This approximation is a superb one, since all isotopic differences are factored out as a single factor, δu_i. In addition, G(u) is a monotonic positive function with the following limiting values :

$$\lim_{u\to 0} G(u) = 0 \qquad \text{(classical case)} \quad , \tag{31}$$

$$G(u) \simeq u/12 \qquad \text{(small u)} \quad , \tag{32}$$

and

$$\lim_{u\to\infty} G(u) = 1/2 \ . \tag{33}$$

Hence, Eqn. (30) becomes

$$\ell n\left(\frac{s}{s'} f\right)_{u\ \text{large}} = \frac{1}{2} \sum_{i}^{3N-6} \delta u_i \propto \frac{1}{T} \tag{34}$$

and

$$\ell n\left(\frac{s}{s'} f\right)_{u\ \text{small}} = \frac{1}{12} \sum_{i}^{3N-6} u_i \delta u_i \tag{35a}$$

$$\simeq \frac{1}{24} \sum_{i}^{3N-6} \delta u_i^{\,2} \propto \frac{1}{T^2} \quad , \tag{35b}$$

where

$$\delta u_i^2 \equiv u_i'^2 - u_i^2 \quad . \tag{36}$$

Eqn. (36) was obtained from the fact that if u_i is small, then

$$\delta u_i^2 \simeq 2u_i \delta u_i \quad . \tag{37}$$

Eqn. (34) represents the zero point energy approximation of $\ln\left(\frac{s}{s'} f\right)$, while the contributions from the strong vibrations (with high frequencies) at relatively low temperatures, i.e., large u_i's, vary with temperature according to 1/T. Eqn. (35) represents the first-order quantum correction to the classical partition function, while the contributions from the weak vibrations (with low frequencies) at relatively high temperatures, i.e., small u_i's, vary with temperature as $1/T^2$.

II.B.1.b. Bigeleisen's $\bar{\gamma}$ method (6, 11)

This approximation is a semi-empirical modification of the first quantum correction, Eqn. (35). The G(u) approximation, Eqn. (30), can be written as

$$\ell n\left(\frac{s}{s'} f\right) = \frac{1}{12} \sum_{i}^{3N-6} \gamma_i u_i \delta u_i \quad , \tag{38}$$

where

$$\gamma_i \equiv 12\ G(u_i)/u_i \quad . \tag{39}$$

Since γ_i is a slowly varying function of u_i, one could use an average value for γ_i, i.e., $\bar{\gamma}$, which is chosen to be independent of u_i, if all the frequencies of the molecule were in a narrow frequency range. Thus, Eqns. (38) and (37) yield

$$\ell n\left(\frac{s}{s'} f\right) \simeq \frac{\bar{\gamma}}{24} \sum_{i}^{3N-6} \delta u_i^{\ 2} \quad , \tag{40}$$

which is a modification of Eqn. (35) in that Eqn. (40) is appropriate for large and small u. Some values of $\gamma(u)$ are $\gamma(0)=1$, $\gamma(9.5)=0.50$, $\gamma(25)=0.221$, and $\gamma(\infty)=0$. Unfortunately, the average value for $\bar{\gamma}$ is difficult to evaluate (12).

II.B.1.c. Low-temperature approximation (18)

At low temperatures and strong frequency vibrations, i.e., large u, Eqn. (11) becomes

$$\ell n\left(\frac{s}{s'} f\right) = \frac{1}{2} \sum_{i}^{3N-6} \delta u_i - \sum_{i}^{3N-6} \delta \ell n\, u_i \quad , \tag{41}$$

where

$$\delta \ell n\, u_i \equiv \ell n\, u_i' - \ell n\, u_i = \ell n \frac{u_i'}{u_i} \quad . \tag{42}$$

The excitation terms do not contribute to Eqn. (41). In addition, the second term, $\delta \ell n\, u_i$, is temperature - independent since $\ell n(u_i'/u_i) = \ell n(\omega_i'/\omega_i)$. The temperature-dependent term represents the isotope effect on the zero-point energies. This approximation becomes poor for low-frequency normal vibrations, such as out-of-plane motions, at room temperature and above.

II.B.2. Higher Order Approximations: $(\delta u_i)^n$

II.B.2.a. Extension of the G(u)-function

II.B.2.a.i. Bigeleisen's third order (6,14)

The retention of the terms $(\delta u_i)^2$ and $(\delta u_i)^3$ in the Taylor series expansion of (s/s')f, in addition to the δu_i term, yields

$$\ell n\left(\frac{s}{s'}f\right) = \sum_i^{3N-6} G(u_i)\left\{1 + \frac{S(u_i)}{2G(u_i)}\,\frac{\delta u_i}{u_i} + \left(\frac{C(u_i)-2S(u_i)}{6G(u_i)}\right)\left(\frac{\delta u_i}{u_i}\right)^2 + \ldots\right\}\delta u_i \;. \qquad (43)$$

In Eqn. (43),

$$S(u) \equiv \frac{1}{u} - \frac{ue^u}{(e^u-1)^2} \qquad (44)$$

and

$$C(u) \equiv \frac{2u^2 e^{2u}}{(e^u-1)^3} - \frac{u(u+2)e^u}{(e^u-1)^2} \quad . \tag{45}$$

II.B.2.a.ii. Vojta's n-th order (15)

Vojta extended (s/s')f to higher orders. Thus,

$$\ln\left(\frac{s}{s'}\,f\right) = \sum_{i}^{3N-6} G(u_i)\delta u_i + \sum_{i}^{3N-6} \sum_{n=2}^{\infty} (-1)^n \left[\left(n u_i^{\,n}\right)^{-1} - (n!)^{-1} \sum_{m=1}^{\infty} m^{n-1}\, e^{-mu_i}\right] (\delta u_i)^n \quad . \tag{46}$$

This is an absolutely convergent series for all u_i.

II.B.2.b. Urey's hyperbolic expansion (29,30)

Eqn. (11) can be rewritten as

$$\ln\left(\frac{s}{s'}\,f\right) = - \sum_{i}^{3N-6} \delta\ln\left(b(u_i)\right) = \sum_{i}^{3N-6} \left[\ln\left(b(u_i)\right) - \ln\left(b(u_i')\right)\right], \tag{47}$$

where

$$b(u_i) \equiv u_i e^{-u_i/2} / (1-e^{-u_i}) \quad . \tag{48}$$

In addition, b(u) can be expressed as

$$b(u) = \frac{u}{2} / \sinh\left(\frac{u}{2}\right) \quad . \tag{49}$$

Thus, Eqn. (47) becomes

$$\ell n\left(\frac{s}{s'} f\right) = \sum_{i}^{3N-6} \ell n\left(\frac{u_i}{u_i'}\right) + \sum_{i}^{3N-6} \ell n\left(\frac{\sinh(u_i'/2)}{\sinh(u_i/2)}\right) \quad . \tag{49a}$$

The second term is expanded in terms of the frequency shift, Eqn. (26), and thus

$$\ell n\left(\frac{s}{s'} f\right) = \sum_{i}^{3N-6} \ell n\left(\frac{u_i}{u_i'}\right) + \sum_{i}^{3N-6} \left(\frac{\delta u_i}{2}\coth(x_i) + \frac{(\delta u_i)^3}{96}\coth(x_i)(\coth^2(x_i)-1)+\ldots\right) \quad , \tag{49b}$$

where

$$x_i \equiv \delta u_i/4 + u_i/2 \quad . \tag{49c}$$

II.B.3. Higher Order Approximations: δu_i^{2n}

II.B.3.a. Bigeleisen's Bernoulli series expansion (6,16)

This is a Taylor expansion of $\ell n\left(\frac{s}{s'} f\right)$ and is valid for $u_i' < 2\pi$ but is not restricted to small δu_i's.

From Eqn. (49), one obtains

$$\ell n\left(b(u)\right) = - \sum_{k=1}^{\infty} \ell n \left(1+\left(\frac{u}{2\pi k}\right)^2\right) \quad , \tag{50}$$

where this infinite series is absolutely convergent for any value of u. In addition, if the absolutely convergent Taylor series

$$\ell n(1+x) = \sum_{m=1}^{\infty} (-1)^{m+1} \frac{x^m}{m}; \quad \left(|x|<1\right), \tag{51}$$

is substituted into Eqn. (50), and a relation for Riemann's zeta function,

$$z(m) \equiv \sum_{k=1}^{\infty} \frac{1}{k^{2m}} = \frac{2^{2m-1} \pi^{2m} B_{2m-1}}{(2m)!} , \tag{52}$$

is used, one obtains

$$\ell n \left[b(u) \right] = - \sum_{m=1}^{\infty} \frac{(-1)^{m+1} B_{2m-1}}{2m(2m)!} u^{2m} . \tag{53}$$

In Eqn. (52), the B's are Bernoulli numbers, e.g., $B_1 = 1/6$, $B_3 = 1/30$, and $B_5 = 1/42$. Substituting Eqn. (53) into Eqn. (47) and taking isotopic differences, one obtains

$$\ell n \left(\frac{s}{s'} f \right) = \sum_{m=1}^{\infty} (-1)^{m+1} \frac{B_{2m-1}}{2m(2m)!} \sum_{i}^{3N-6} \delta u_i^{2m} \quad \left(u_i' < 2\pi \right) , \tag{54}$$

where

$$\delta u_i^{2m} \equiv u_i'^{2m} - u_i^{2m} . \tag{55}$$

The inequality for Eqn. (54) was obtained from the convergence condition of Eqn. (51), i.e., $(u/2\pi k)^2 < 1$ for all integral values of k. Thus, the first three terms of Eqn. (54) are

$$\ln\left(\frac{s}{s'}\, f\right) = \frac{1}{24}\sum_{i}^{3N-6} \delta u_i^{\,2} - \frac{1}{2880}\sum_{i}^{3N-6} \delta u_i^{\,4} + \frac{1}{181440}\sum_{i}^{3N-6} \delta u_i^{\,6} \quad . \tag{56}$$

The major disadvantage with Eqn. (54) is that a frequency of 3000 cm^{-1} at room temperature corresponds to $u=15$, which is more than double the allowed limit for u. Thus, the Bernoulli series is inapplicable to all H-containing molecules.

II.B.3.b. Orthogonal polynomial expansion (17-25)

The difference between this method and the previous one is that the Bernoulli series is modified mainly through the use of an orthogonal polynomial expansion of $\ln(1+x)$, Eqn. (51), instead of the Taylor expansion. This extends the range of validity of the Bernoulli series up to $u \leq u'_{max}$, the largest u involved in a given problem. The reason that the radius of convergence for a Taylor series expansion is small ($u_i' < 2\pi$) is that all the information needed for such a series is obtained at a point about which the function is to be expanded, and values of the function at other points are extrapolated from that single point. Thus, the accuracy of this approximation becomes progressively worse as the point moves away from the center of expansion. However, in the orthogonal polynomial expansion, one concedes the existence of an error term in the polynomial approximation before the expansion is employed. The error is forced to be proportional to an n-th order orthogonal polynomial which, when properly chosen, oscillates on both sides of the zero point, rather than yielding a null error at the center of expansion, with the result of an increasingly larger error as the point moves away from the origin.

In place of Eqn. (51), the Taylor expansion for the logarithmic function,

$$\ell n\ (1+x) \equiv y(x) \quad , \tag{57}$$

one uses the orthogonal expansion as follows. The following differential equation is obtained:

$$(1+x)\ \frac{dy}{dx} = 1 + \tau P_n(x) \quad . \tag{58}$$

The τ method leads to an inclusion of the error term $\tau P_n(x)$, since one admits that the linear differential equation

$$(1+x)\frac{dy}{dx} = 1 \tag{59}$$

cannot be solved exactly. τ is an <u>a priori</u> undetermined coefficient and $P_n(x)$ is an n-th order orthogonal polynomial of x.

The τ method approximates Eqn. (11) as

$$\ell n\left(\frac{s}{s'} f\right) = \sum_{j=1}^{n} W_j A_j \sum_{i}^{3N-6} \delta u_i^{\,2j} , \tag{60}$$

where the A_j's are the same factors that appear in the Bernoulli series, Eqn. (54),

$$A_j \equiv \frac{(-1)^{j+1}\, B_{2j-1}}{2j(2j)!} \quad . \tag{61}$$

The W_j's are modulating coefficients defined as follows:

$$W_j = W_j(n,j,\, u'_{max},L) \tag{62}$$

$$= T\,(n,j,R_{L+1}) + \frac{1}{z(j)} \sum_{k=1}^{L} \frac{T(n,j,R_k) - T(n,j,R_{L+1})}{k^{2j}} , \tag{63}$$

where z(j) is Riemann's zeta function, Eqn. (52),

$$T(n,j,R) = \frac{\sum_{p=j}^{n} (-1)^p \, C_n^{\,p} / R^p}{\sum_{p=0}^{n} (-1)^p \, C_n^{\,p} / R^p} \quad , \tag{64}$$

$$R_k = \frac{R_1}{k^2} = \left(\frac{u}{2\pi k} \right)^2 \quad , \quad k=1,\ 2, \ldots, \ L, \tag{65}$$

and

$$R_k = R_{L+1} = \frac{R_1}{(L+1)^2} \qquad \left\{ \text{all } k \geq L+1 \right\} \quad . \tag{66}$$

In Eqn. (64), $C_n^{\,p}$ is the coefficient of the p-th order term of an n-th order orthogonal polynomial, $P_n\ (x)$ of Eqn. (58), i.e.,

$$P_n\ (x) = \sum_{p=0}^{n} C_n^{\,p} \, x^p \quad . \tag{67}$$

The orthogonal polynomials used are the Jacobi polynomials, such as Legendre, Laguerre, Hermite, and Chebyshev polynomials, which depend on two parameters γ and δ in that

$$P_n^{(\gamma,\delta)}(x) = F(-n,n+\gamma+\delta-1,\gamma;x) \tag{68}$$

$$= 1 + \sum_{m=1}^{n} x^m \prod_{k=o}^{m-1} \frac{(-n+k)(n+\gamma+\delta-1+k)}{(\gamma+k)(1+k)} \;, \tag{69}$$

where F is the Gaussian hypergeometric function. δ may assume any real value, while γ can be any positive real number. By varying γ and δ, a "best" Jacobi polynomial has been chosen for each selected range of u which minimizes the root mean square error of the corresponding approximation for $\ell n\, b(u)$.

The modulating coefficients W_j vary from zero to unity and, as can be seen from Eqn. (62), depend on the order of the expansion (n), the term number in the expansion (j), the largest u involved (u'_{max}), and a positive integer (L) chosen to yield the best approximation. As the value of L increases, the approximation improves, but a value of L=5 is sufficient. Thus, the first three terms of Eqn. (60) are:

$$\ell n\left(\frac{s}{s'} f\right) = \frac{W_1}{24} \sum_i \delta u_i^{\,2} - \frac{W_2}{2880} \sum_i \delta u_i^{\,4} + \frac{W_3}{181440} \sum_i \delta u_i^{\,6} \quad . \tag{70}$$

II.B.4. Wolfsberg's Second Order Perturbation Theory (26-28)

This method is unlike any of the others, both in the initial formulation of the approximation and in the final expression of (s/s')f. The harmonic vibrational Hamiltonian of a molecule is divided into a diagonal part, the zeroeth order, and an off-diagonal part, the perturbation. The molecular vibrational partition function, calculated by Schwinger perturbation theory, is composed of the unperturbed partition function, corresponding to uncoupled oscillators, plus the perturbation to the partition function, corresponding to coupled oscillators.

The quantum mechanical partition function of a molecule, Q_{qm}, is the "Slater sum," i.e., the trace of the matrix representation of the operator $e^{-\beta H}$. Thus,

$$Q = \mathrm{Tr}\left(e^{-\beta H}\right) \quad , \tag{71}$$

where

$$\beta = 1/kT \quad , \tag{72}$$

and, according to Schwinger perturbation theory for partition functions, the Hamiltonian operator H is separated into unperturbed and perturbed Hamiltonians, H_0 and H_1, respectively, so that

$$H = H_0 + H_1 \quad . \tag{73}$$

For the ideal gas-phase molecular vibrational problem, the Hamiltonian is given by

$$H = T + V \quad , \tag{74}$$

where T and V are the kinetic and potential energies of the molecule, respectively, and, in addition (31),

$$T = \frac{1}{2} \sum_{i}^{3N-6} \sum_{j}^{3N-6} g_{ij} p_i p_j \quad , \tag{75}$$

and

$$V = \frac{1}{2} \sum_{i}^{3N-6} \sum_{j}^{3N-6} f_{ij} q_i q_j \quad . \tag{76}$$

In Eqns. (75) and (76), the q_i's are the internal displacement coordinates, the p_i's are the corresponding conjugate momenta,

where

$$p_i = \partial q_i/\partial t = \dot{q}_i \quad , \tag{77}$$

the f_{ij}'s are the harmonic force constants of the molecular force field, i.e., the elements of the $\underset{\sim}{F}$ matrix, and the g_{ij}'s are the elements of Wilson's $\underset{\sim}{G}$ matrix. The quantum mechanical representation of H is obtained by replacing p_i with $-i\hbar\partial/\partial q_i$, where $\hbar \equiv h/2\pi$.

From Eqns. (73) - (76), H_0 and H_1 are given by

$$H_0 = \frac{1}{2}\sum_{i}^{3N-6} g_{ii}p_i^2 + \frac{1}{2}\sum_{i}^{3N-6} f_{ii}q_i^2 \tag{78}$$

and

$$H_1 = \sum_{i<j}\sum g_{ij}p_ip_j + \sum_{i<j}\sum f_{ij}q_iq_j \quad . \tag{79}$$

Thus, the unperturbed Hamiltonian H_0 corresponds to a collection of uncoupled oscillators with "unperturbed" frequencies

$$\nu_i^0 = (2\pi)^{-1}(f_{ii}g_{ii})^{1/2} \quad , \tag{80}$$

and the perturbation H_1 contains the coupling terms.

Therefore, the partition function is given by

$$Q = Q_0 + Q_1 + Q_2 + \cdots , \tag{81}$$

where the first term is the zeroeth order approximation and successive terms contain successively higher powers of the perturbation H_1. The solution of Eqn.(71) yields

$$Q_0 = \prod_{i}^{3N-6} \frac{e^{-u_i^0/2}}{1-e^{-u_i^0}} , \tag{82}$$

where

$$u_i^0 = h\nu_i^0/kT . \tag{83}$$

The first order correction, Q_1, vanishes, and the first nonvanishing term is the second order correction, Q_2, where

$$Q_2 = Q_0 D , \tag{84}$$

$$D \equiv \beta^2 \sum_{i<j}\sum \left\{ \frac{1}{(1-e^{-u_i^0})(1-e^{-u_j^0})} \left[B_{ij}^2 \frac{1-e^{-(u_i^0+u_j^0)}}{u_i^0 + u_j^0} + C_{ij}^2 \frac{e^{-u_i^0} - e^{-u_j^0}}{u_j^0 - u_i^0} \right] \right\} , \tag{85}$$

$$B_{ij} \equiv -\frac{h}{2} g_{ij} \left(\frac{\nu_i^0 \nu_j^0}{g_{ii} g_{jj}} \right)^{\frac{1}{2}} + \frac{h}{8\pi^2} f_{ij} \left(\frac{g_{ii} g_{jj}}{\nu_i^0 \nu_j^0} \right)^{\frac{1}{2}} , \tag{86}$$

and

$$C_{ij} \equiv \frac{h}{2} g_{ij} \left(\frac{\nu_i^0 \nu_j^0}{g_{ii} g_{jj}} \right)^{\frac{1}{2}} + \frac{h}{8\pi^2} f_{ij} \left(\frac{g_{ii} g_{jj}}{\nu_i^0 \nu_j^0} \right)^{\frac{1}{2}} . \tag{87}$$

Thus, to second order,

$$(Q_{vib})_{qm} = Q_0 + Q_2 = Q_0(1 + D) = \left(\prod_{i}^{3N-6} \frac{e^{-u_i^0/2}}{1-e^{-u_i^0}} \right) (1 + D) , \tag{88}$$

which is comparable to Eqn.(6).

The classical vibrational partition function is obtained for $T \to \infty$, i.e., $u^0 \to 0$, so that

$$(Q_{vib})_{cl} = \left(\prod_{i}^{3N-6} \frac{1}{u_i^0} \right) (1 + E) , \tag{89}$$

where

$$E \equiv \sum_{i}^{3N-6} \underset{<}{} \sum_{j}^{3N-6} \frac{1}{2} \left(\frac{g_{ij}^2}{g_{ii} g_{jj}} + \frac{f_{ij}^2}{f_{ii} f_{jj}} \right) . \tag{90}$$

Hence, within the approximations in section II.A.1, the ideal gas-phase reduced partition function is given by

$$Q_{red} = Q_{qm}/Q_{cl} = \left(\prod_{i}^{3N-6} \frac{u_i^0 e^{-u_i^0/2}}{1-e^{-u_i^0}} \right) \left(\frac{1 + D}{1 + E} \right). \tag{91}$$

One could empirically improve Eqns.(88), (89), and (91) by substituting e^D and e^E for 1+D and 1+E, respectively, where the latter are the first two terms in the expansion of e^D and e^E. This is only valid if D and E, the second order corrections to the quantum mechanical and classical vibrational partition functions, respectively, are very small. Otherwise, this procedure is arbitrary, since higher order terms are being introduced into the perturbation without justification. However, this new formulation does lead to better agreement with exact values of Q_{vib} than does Eqn.(88). Thus, Eqns.(88), (89), and (91) become

$$(Q_{vib})_{qm} = \left(\prod_{i}^{3N-6} \frac{e^{-u_i^0/2}}{1-e^{-u_i^0}} \right) e^D , \tag{92}$$

$$(Q_{vib})_{cl} = \left(\prod_{i}^{3N-6} \frac{1}{u_i^0} \right) e^E , \tag{93}$$

and

$$Q_{red} = \left(\prod_{i}^{3N-6} \frac{u_i^0 e^{-u_i^0/2}}{1-e^{-u_i^0}} \right) e^{D-E} . \tag{94}$$

Therefore, the reduced partition function ratio for a pair of isotopic molecules becomes

$$\frac{s}{s'}f = \left\{ \prod_{i}^{3N-6} \frac{u_i^0}{u_i'^0} \left(e^{\delta u_i^0/2} \right) \frac{1-e^{-u_i'^0}}{1-e^{-u_i^0}} \right\} e^{(\delta E - \delta D)} , \qquad (95)$$

where the "δ" notation is the same as in Eqn.(26), i.e., the light species minus the heavy species.

Hence, according to this second order perturbation theory, the first factor of Eqn.(95), the zeroeth order term, is a function of ν_i^0, $\nu_i'^0$, and T, and the second factor, the perturbation, is a function of ν_i^0, $\nu_i'^0$, ν_j^0, $\nu_j'^0$, g_{ij}, g_{ij}', f_{ij}, and T.

II.C. Intramolecular Forces and the Reduced Partition Function Ratio

In order to calculate the exact reduced partition function ratio, Eqn.(11), one must determine the individual normal mode vibrational frequencies of the two isotopic molecules. This can be accomplished through the use of the secular equation

$$|\underset{\sim}{H} - \lambda \underset{\sim}{E}| = 0 \ , \qquad (96)$$

where

$$\underset{\sim}{H} = \underset{\sim}{F}\,\underset{\sim}{G} \ , \qquad (97)$$

and $\underset{\sim}{E}$ is the identity matrix. The 3N-6 non-zero eigenvalues λ_i are the roots of the secular equation and are related to the frequencies ν_i according to

$$\lambda_i = 4\pi^2 \nu_i^2 \ . \qquad (98)$$

Thus, with a given harmonic force field, i.e., $\underset{\sim}{F}$, and a corresponding equilibrium geometry, i.e., $\underset{\sim}{G}$, together with a digital computer, the 3N-6 vibrational frequencies can be calculated (32).

However, this procedure does not yield important physical information regarding the role of specific force constants in isotope effects. In addition, in "prehistorical" times, when digital computers were not widely available, approximations were needed to permit quick and accurate numerical evaluations of isotope effects. Thus, the expansions based on the G(u) function (II.B.1.a. and 2.a.) were suited for quick calculations. On the other hand, the $\overline{\gamma}$ method (II.B.1.b.), the low-temperature approximation (II.B.1.c.), the Bernoulli series (II.B.3.a.), the orthogonal polynomial expansion (II.B.3.b.), and the perturbation theory (II.B.4.) are especially designed to explain isotope effects.

The expansion of (s/s')f in terms of sums of even powers of the vibrational frequencies, as in the $\overline{\gamma}$ method, the Bernoulli series, and the orthogonal polynomial expansion, is extremely useful. These sums are directly expressible in terms of harmonic constants, atomic masses, and the molecular geometry through the $\underset{\sim}{F}$ and $\underset{\sim}{G}$ matrices. These force relationships will be given below and will be referred to later in this work.

II.C.1. Method of Moments

From Eqns. (7) and (98), one obtains

$$\sum_{i}^{3N-6} \delta u_i^{2n} = (h/2\pi kT)^{2n} \sum_{i}^{3N-6} \delta \lambda_i^{n} , \tag{99}$$

where the sum of the 3N-6 roots is just the trace of $\underset{\sim}{H}$, i.e. (6),

$$\sum_{i}^{3N-6} \lambda_i^{n} = \mathrm{Tr}\left[(\underset{\sim}{H})^{n} \right] , \tag{100}$$

where, according to Eqn.(97),

$$(\underset{\sim}{H})^n = (\underset{\sim}{F}\ \underset{\sim}{G})^n \ . \tag{101}$$

Therefore, for isotopic differences, one obtains

$$\sum_{i}^{3N-6} \delta\lambda_i = \sum_{i}^{3N-6} \sum_{j}^{3N-6} f_{ij}\delta g_{ij} \tag{102}$$

$$= \sum_{\alpha}^{N} A_\alpha \delta\mu_\alpha \ , \tag{103}$$

where the first relation is in terms of internal coordinates and the second is in cartesian coordinates. A_α is the sum of the three diagonal force constants for the three cartesian coordinate displacements of atom α, and μ_α is the reciprocal mass of atom α, i.e.,

$$\mu_\alpha = 1/m_\alpha \ . \tag{104}$$

Similarly, the second order trace yields

$$\sum_{i}^{3N-6} \delta\lambda_i^{\,2} = \sum_{i}\sum_{j}\sum_{k}\sum_{\ell} f_{ik}f_{j\ell}\delta(g_{kj}g_{\ell i}) \tag{105}$$

$$= \sum_{\alpha}^{N}\sum_{\beta}^{N} A_{\alpha\beta}^2 \ \delta(\mu_\alpha\mu_\beta) \ , \tag{106}$$

which now includes interaction terms between atoms α and β. $A^2_{\alpha\beta}$ is the sum of the squares of the nine force constants for the combined cartesian displacements of atoms α and β.

Thus, Eqn.(99), either Eqn.(102) or (103), and either Eqn.(105) or (106) can be substituted into the first two terms of the orthogonal polynomial expansion, Eqn.(70), for a direct correlation of isotope effects with molecular forces.

II.C.2. Zero Point Energy (ZPE) Approximations

In the low-temperature approximation, Eqn.(41), the termperature-dependent term, $\sum_i \delta u_i$, can be approximated through Bigeleisen and Goldstein's Taylor series expansion of the isotopic zero point energies (33, 78), or through Wolfsberg's perturbation treatment (26-28).

II.C.2.a. Bigeleisen and Goldstein's Taylor series expansion (33, 78)

The isotope effect on the ZPE can be approximated as a sum of isotopic differences in the traces, i.e.,

$$\frac{1}{\omega_0}\sum_{i}^{3N-6}\delta\omega_i = \frac{1}{2\lambda_0}\sum_{i}^{3N-6}\delta\lambda_i$$

$$+ \sum_{p=2}^{\infty}\frac{(-1)^{p+1}}{2^{2p-1}}\,\frac{(2p-2)!}{(p-1)!}\sum_{j=0}^{p-1}\frac{(-1)^j}{j!(p-j)!}\,\frac{1}{\lambda_0^{\,p-j}}\sum_{i}^{3N-6}\delta\lambda_i^{\,p-j}, \qquad (107)$$

where

$$\lambda_0 = 4\pi^2 c^2 \omega_0 \ , \tag{108}$$

$$\delta\lambda_i^{p-j} \equiv \lambda_i'^{p-j} - \lambda_i^{p-j} \ , \tag{109}$$

and ω_0 is an isotope-independent characteristic frequency of the isotopic set. This series is absolutely convergent when

$$\frac{\lambda_i'}{\lambda_0} - 1 \leqq 1 \ , \tag{110}$$

which restricts λ_0 to

$$\lambda_0 \geq \frac{\lambda'_{max}}{2} \ . \tag{111}$$

From Eqn.(7), one obtains

$$\sum_{i}^{3N-6} \delta u_i = \frac{hc}{kT} \sum_{i}^{3N-6} \delta\omega_i \ . \tag{112}$$

Thus, by using the ZPE approximation, Eqn.(107), together with either Eqns.(102) or (103) and either (105) or (106), one can relate the first term of the low-temperature approximation, Eqn.(41), in terms of molecular forces.

II.C.2.b. Wolfsberg's perturbation treatment

Through the use of a perturbation treatment, as discussed in section II.B.4., one obtains up to second order and at low temperatures,

$$\mathrm{ZPE} = \frac{1}{2}\,hc\left(\sum_{i}^{3N-6} \omega_i\right) \simeq \frac{1}{2}\,h\left(\sum_{i}^{3N-6} \nu_i^0\right) - kTD\ , \tag{113}$$

where ν_i^0 and D are given by Eqns.(80) and (85), respectively. However, the temperature must not be so low as to make D significantly large compared with unity. Therefore, after taking isotopic differences, $\delta(\mathrm{ZPE})$, and substituting into Eqn.(41), one can again relate the reduced partition function ratio at low temperatures in terms of molecular forces, without explicitly solving the secular equation, Eqn.(96), for the individual frequencies.

III. THEORY OF VAPOR PRESSURE ISOTOPE EFFECTS (VPIEs)

III.A. Historical Background (2, 34)

The first quantitative formulation of an isotope effect (specifically for vapor pressures) was independently given by Stern and Lindemann (Lord Cherwell) (39-41). They considered the equilibrium between a monatomic Debye solid (10, 49) and an ideal gas composed of monatomic substances, and the following assumptions were made: (1) the oscillations in a solid lattice are harmonic, (2) the potential energy is isotope invariant, and (3) an oscillator has a zero point energy. The only degrees of freedom for monatomic molecules are the three translational ones. Thus, their VPIE equation was

$$\ell n\frac{P'}{P} = \frac{3}{40}\left(\frac{\Theta}{T}\right)^2\left(\frac{M-M'}{M'}\right) , \tag{113a}$$

where $\Theta/T < 2\pi$ is a reduced temperature and Θ, the Debye temperature of the heavy isotope, is given by

$$\Theta \equiv h\nu_m/k . \tag{113b}$$

Later, corrections for the gas imperfections and the difference between the Gibbs and Helmholtz free energies for an incompressible solid were included in the above formulation by Scott et al. (42). Roth and Bigeleisen (43, 44) later reinvestigated the above VPIE equation and confirmed its validity.

A more general expression for the effect of isotopic substitution on the vapor pressures of condensed phases of monatomic substances was derived by Herzfeld and Teller (45). Through the use of the Wigner quantum correction to the Boltzmann distributions (46), they obtained

$$\ell n \frac{P'}{P} = \frac{1}{24} \left(\frac{\hbar}{kT}\right)^2 \left(\frac{1}{M'} - \frac{1}{M}\right) \left[\langle\nabla^2 U\rangle_c - \langle\nabla^2 U\rangle_g\right] , \qquad (113c)$$

where $\langle\nabla^2 U\rangle_c$ is the mean value of the Laplacian of the intermolecular interaction potential in the condensed phase. For an ideal gas,

$$\langle\nabla^2 U\rangle_{g(\mathrm{ideal})} = 0 , \qquad (113d)$$

and, in the harmonic oscillator approximation,

$$\langle\nabla^2 U\rangle_c = a_x + a_y + a_z \qquad (113e)$$

is just the sum of the three external forces corresponding to the three translations in the condensed phase. The mean Laplacian $\langle\nabla^2 U\rangle$ may be theoretically calculated for simple monatomic systems from radial distribution functions (35, 37, 38). For a harmonic Debye lattice,

$$\left(\frac{\hbar}{k}\right)^2 \langle\nabla^2 U\rangle \frac{1}{M} = \Theta_D^{\ 2} . \qquad (113f)$$

However, these VPIE relationships are only applicable to monatomic substances and, in addition, they do not explain the phenomenon of the inverse VPIE, i.e., the heavy isotope having the higher vapor pressure. The VPIE equations presented this far predict that the lighter isotope would always have the higher vapor pressure, i.e., the normal effect. The "crossover" phenomenon, i.e., the normal VPIE at a low temperature and the inverse effect at a higher temperature, will not be predicted by theories which relate the effect of isotopic substitution on the condensed phase equation of state only to the molecular weight, but not to the molecular structure (47-49). Thus, the theories of de Boer (50), Friedman, White, and Johnston (51), and Libby and Barter (52) are inappropriate. Bigeleisen (36) gave the first clear and general quantitative treatment of VPIEs that incorporated the role of the molecular structure in the difference between the thermodynamic properties of isotopic molecules in the condensed phase.

III.B. Bigeleisen's Statistical Thermodynamics Treatment

The objective of this section is to record Bigeleisen's treatment of the VPIE (36), which expresses the vapor pressure ratios of a pair of isotopic molecules in terms of the reduced partition function ratios of both the gas and condensed phases. The condensed phase is considered to be in equilibrium with its vapor, so that the equilibrium condition is

$$G_c = G_g \, , \tag{114}$$

where G_c and G_g are the Gibbs free energies for the condensed and gas phases, respectively.

III.B.1. Simple Cell Model for the Condensed Phase

The simple cell model is assumed for the liquid phase, where the molecules are considered to be located at the centers of the lattice points of a cell. Thus, the average liquid molecule is surrounded by its neighbors and constrained to move in a space, or a cell. Normally, the potential energy that this molecule experiences is a function of its position in the cell and of the positions of its neighbors. However, in this theoretical cell model description of the liquid phase, one assumes that the average potential on a molecule is caused by some equilibrium or average positions of the molecules surrounding the cell. Thus, the potential will not explicitly depend on the instantaneous positions of individual neighboring molecules, and every molecule in the condensed system experiences the same potential energy. In addition, in the sense that the motion of each molecule in a cell does not depend on other molecular positions, this system is composed of independent non-interacting molecules.

The molar Gibbs free energy for the condensed phase is given by

$$G_c = -kT\ell nQ + PV_c \ , \tag{115}$$

where Q, P, and V_c are the molar partition function for an assembly of N_0 molecules, the vapor pressure, and the molar volume of the condensed phase, respectively. If one defines an average molecular partition function $(Q_c)_{av}$ for the condensed phase as

$$Q_c \equiv (Q_c)_{av} = Q^{1/N_0} \ , \tag{116}$$

Eqn.(115) becomes

$$G_c = -RT\ell nQ_c + PV_c \ . \tag{117}$$

III.B.2. Gas Phase Properties

The molar Gibbs free energy for the gas phase is

$$G_g = -kT\ell nQ_g + PV_g \ . \tag{118}$$

In addition, if the molecules are non-interacting and indistinguishable, then,

$$Q = (qe/N_0)^{N_0} \ , \tag{119}$$

where q is the complete molecular partition function, i.e.,

$$q = q_{tr}Q_i \ . \tag{120}$$

In Eqn.(120), Q_i is an average molecular partition function for the internal motions, i.e., vibrations and rotations. Thus,

$$Q_i \equiv q_{rot}q_{vib} \ . \tag{121}$$

Therefore, Eqn.(118) becomes

$$G_g = -RT\ell n\left(Q_{i,g}\frac{q_{tr}e}{N_0}\right) + PV_g \ . \tag{122}$$

In addition,

$$\ell n\left(\frac{q_{tr}e}{N_0}\right) = \frac{3}{2}\,\ell nM + \frac{5}{2}\ell nT - \ell nP - K_{ST}\ , \tag{123}$$

where K_{ST} is the Sackur-Tetrode constant and is defined as

$$K_{ST} = \ell n\left\{h^3/(2\pi k)^{3/2}ke\right\}\ , \tag{124}$$

and M is the molecular weight. Also, the gas imperfection leads to the following gaseous equation of state

$$\frac{PV_g}{RT} = 1 + B_0P + \frac{1}{2}\,C_0P^2\ , \tag{125}$$

where B_0 and C_0 are the second and third virial coefficients. After substituting Eqn.(125) and (123) into Eqn.(122), one obtains for the Gibbs free energy of the gas

$$G_g = RT(K_{ST} + \ell nP - \frac{5}{2}\,\ell nT - \frac{3}{2}\,\ell nM - \ell nQ_{i,g})$$

$$+ (1 + B_0P + \frac{1}{2}\,C_0P^2)\ . \tag{126}$$

III.B.3. VPIE and the Reduced Partition Function Ratios of the Condensed and Gas Phases

Substitution of Eqns.(126) and (117) into the equilibrium condition, Eqn.(114), yields

$$\ell nP = \ell n(Q_{i,g}M^{3/2}/Q_c) + \frac{5}{2}\ell nT + \frac{PV_c}{RT} - (1 + B_0P + \frac{1}{2}C_0P^2) - K_{ST} \ . \quad (127)$$

After taking isotopic differences between two species at the same temperature, Eqn.(127) becomes

$$\ell n\frac{P'}{P} = \ell n\left(\frac{Q'_{i,g}M'^{3/2}/Q_{i,g}M^{3/2}}{Q'_c/Q_c}\right) + \frac{1}{RT}(P'V'_c - PV_c)$$

$$- (B_0P + \frac{1}{2}C_0P^2)' + (B_0P + \frac{1}{2}C_0P^2) \ . \quad (128)$$

In addition,

$$Q'_{i,g}M'^{3/2}/Q_{i,g}M^{3/2} = Q'_g/Q_g \ , \quad (129)$$

where Q_g is the complete quantum mechanical partition function for the gas.

It is convenient to compare the isotopic species at the same molar volume V. Thus,

$$\ln(Q'_c)_{V'} = \ln(Q'_c)_V + \frac{1}{RT}\int_V^{V'} P'dv \; . \qquad (130)$$

Recalling the classical definition for isotopic partition function ratios, Eqn.(16),

$$\left(\frac{Q_c}{Q'_c}\right)_{c\ell} = \frac{s'}{s}\prod_{\alpha}^{N}\left(\frac{m_\alpha}{m'_\alpha}\right)^{3/2} = \left(\frac{Q_g}{Q'_g}\right)_{c\ell} \; , \qquad (131)$$

and by using Eqns.(129) and (130), one obtains the following form for the first term of Eqn.(128):

$$\ln\left[\frac{Q'_g/Q_g}{Q'_c/Q_c}\right]_{qm} = \ln\frac{\left((Q_c)_V/(Q'_c)_V\right)_{qm}}{\left(Q_c/Q'_c\right)_{c\ell}} - \ln\frac{\left(Q_g/Q'_g\right)_{qm}}{\left(Q_g/Q'_g\right)_{c\ell}}$$

$$- \frac{1}{RT}\int_V^{V'} P'dV \; . \qquad (132)$$

The first two terms of Eqn.(132) are simply the logarithms of the reduced partition function ratios, (s/s')f, of the condensed (since the molar volumes of the isotopic pair are measured at the same V) and gas phases, respectively. Upon subsitution of Eqn.(132) into Eqn.(128), one obtains the overall effect on the vapor pressure upon isotopic substitution:

$$\ell n \frac{P'}{P} = \ell n\left(\frac{s}{s'} f\right)_c - \ell n\left(\frac{s}{s'} f\right)_g + \frac{1}{RT}\left(P'V'_c - PV_c\right)$$

$$- \left(B_0P + \frac{1}{2} C_0P^2\right)'_g + \left(B_0P + \frac{1}{2} C_0P^2\right)_g$$

$$- \frac{1}{RT} \int_V^{V'} P'dV \ . \tag{133}$$

The physical significance of the various terms in Eqn.(133) are now summarized. The reduced partition function ratio difference, $\ell n\left((s/s')f\right)_c - \ell n\left((s/s')f\right)_g$, is the quantum effect difference in the condensed and gaseous states. The virial coefficients B_0 and C_0 represent the gaseous non-ideality, and B_0' and C_0' represent the quantum effects on the equation of state of the gas. The third, fourth, and fifth terms can be combined into a form

$$\frac{1}{RT}\,\delta\left(PV_c\right) - \frac{1}{RT}\,\delta\left(PV_g\right)_{real} \ , \tag{134}$$

where

$$\delta\left(PV_c\right) \equiv P'V'_c - PV_c \tag{135}$$

and

$$\delta\left(PV_g\right)_{\text{real}} = \left(B_0P + \frac{1}{2}\,C_0P^2\right)'_g - \left(B_0P + \frac{1}{2}\,C_0P^2\right)_g \,. \qquad (136)$$

Thus, the correction terms, Eqn.(134), represent the difference between the Gibbs and Helmholtz (A) free energies for the condensed and gas phases of both isotopes, i.e.,

$$\delta\left((G - A)_c - (G - A)_g\right) = \delta(PV_c) - \delta(PV_g) \,. \qquad (136a)$$

It is the effect on the vapor pressure that occurs when the condensed phase is subjected to a pressure and volume change from PV_c to $P'V'_c$ and the nonideal gases are compressed to P and P'. The final term is a second order correction to $\ell n\left(\frac{s}{s'}\,f\right)_c$, due to the fact that the molar volumes of the two isotopic condensed phases are not the same. These corrections are necessary because the separated isotopic samples are being compared at the same temperature but at different pressures.

Eqn.(133) can be further simplified by assuming that $V_c \cong V'_c$, $B_0 \cong B'_0$, and that C_0 is isotope-independent and/or negligible. Also, if $\delta P/P$ and $B_0 - V_c/RT$ are small, then through Taylor expansions, one obtains

$$\ell n\,\frac{P'}{P} = \left[\ell n\left(\frac{s}{s'}f\right)_c - \ell n\left(\frac{s}{s'}f\right)_g\right]\left[1 - P\left(B_0 - \frac{V_c}{RT}\right)\right] \,. \qquad (137)$$

Alternatively, if

$$P'V'_c \cong PV_c \ , \tag{138}$$

in addition to $V_c \cong V'_c$, $B_0 \cong B'_0$, and $\int_V^{V'} P'dV \cong 0$, then the vapor pressure isotope effect equation takes its simplest expression, i.e.,

$$\ell n\left(\frac{P'}{P}\right) = \ell n\left(\frac{s}{s'}f\right)_c - \ell n\left(\frac{s}{s'}f\right)_g \ . \tag{139}$$

III.C. Separation of the Internal and External Modes

The gas phase molecules consist of 3N-6 (or 3N-5 for linear species) non-zero vibrational frequencies per molecule, as a result of the forces that hold the atoms together. In addition, there are 6 (or 5) zero frequencies due to the freely (unhindered) translating and rotating molecule in the gaseous state. Monatomic molecules possess just 3 translations per species.

In the condensed phase, three manifestations must be considered. First, the 3N-6 internal vibrational frequencies are either raised or lowered with respect to their corresponding gas phase values, depending on the type of oscillation and molecule. This is due to the intermolecular forces in the condensed phase which perturb the energy levels of the internal oscillator energies, and thus alter the internal force field. This shift of an internal frequency upon condensation is also due to the interaction between the internal and external modes of vibration, which will be described as the third effect below. The internal frequency shift was originally discussed by Topley and Eyring (74).

Secondly, these same intermolecular interactions quantize the translations and rotations, which are classical in the gas phase. Thus, the 6 external motions of the condensed molecule are now loosely bound and somewhat hindered (75, 76), especially the rotational motions (54-59), so that they may be considered as loose harmonic lattice oscillations of entire molecules about their respective equilibrium positions in the cell. The molecule is assumed to oscillate slowly under the influence of an isotropic external force, a resultant of all forces exerted by all the surrounding molecules. However, these external lattice frequencies are much smaller than the "large" internal frequencies, since intermolecular forces are much weaker than intramolecular forces.

Furthermore, an external oscillation may couple with another external mode or with an internal vibration. Therefore, this leads to the existence of symmetry-allowed internal-external interactions (28, 53, 57-62, 79), i.e., vibration-rotation and/or vibration-translation couplings, as well as translation-rotation interactions (48, 79, 63-70). These interactions stem from the fact that the very motions that cause the change in the internal coordinates also tend to produce a change in the external motions and, thus, these two motions must be intimately coupled. These interactions do not contribute as much as the other two condensed phase effects to the VPIE. However, Gordon (64) and Fang and Van Hook (71) proposed theories that assume the separability of the internal vibrations from the external motions of molecules.

The frequencies can be separated into two groups: one is the 3N-6 "large" internal frequencies of both the gas and condensed phases, and the second group consists of 6 "small" external frequencies of the condensed phase. Thus, using Eqns.(139) and (11), the full expression for the vapor pressure ratio in terms of internal and external (condensed) frequencies is obtained:

$$\frac{p'}{p} = \frac{\left(\frac{s}{s'}f\right)_c}{\left(\frac{s}{s'}f\right)_g} = \frac{\left[\left(\frac{s}{s'}f\right)_{int}\left(\frac{s}{s'}f\right)_{ext}\right]_c}{\left(\frac{s}{s'}f\right)_g}$$

$$= \left[\left(\frac{s}{s'}f\right)_c \Big/ \left(\frac{s}{s'}f\right)_g\right]_{int}\left[\left(\frac{s}{s'}f\right)_c\right]_{ext} \tag{140}$$

$$= \prod_{i}^{3N-6}\left[\left(\frac{(u_i/u_i')_c}{(u_i/u_i')_g}\right)\left(\frac{e^{\delta(u_i)_c/2}}{e^{\delta(u_i)_g/2}}\right)\left(\frac{\left(1-e^{-(u_i')_c}\right)\Big/\left(1-e^{-(u_i)_c}\right)}{\left(1-e^{-(u_i')_g}\right)\Big/\left(1-e^{-(u_i)_g}\right)}\right)\right]$$

$$\times \prod_{e}^{6}\left(\frac{u_e}{u_e'}\, e^{\delta u_e/2}\, \frac{1-e^{-u_e'}}{1-e^{-u_e}}\right)_c . \tag{141}$$

This results from the fact that there are no translational and rotational contributions to the reduced partition function ratio in the gas phase, because the potential for these modes is zero.

In the following subsections, various temperature approximations of the full VPIE expression, Eqn.(141), are given. The low temperature approximation is especially important as it involves, in part, the isotope effect on the ZPE shift upon condensation, which is the basis of this dissertation.

III.C.1. Zero Point Energies and the First Order Quantum Correction

At low temperatures, the first bracketed term in Eqn. (141), the ratio of frequency product ratios for the internal vibrations, is less significant than the second bracketed term in Eqn. (141), the ratio of the exponentials of the zero point energies. Thus,

$$\ell n \frac{(u_i/u_i')_c}{(u_i/u_i')_g} << \frac{1}{2}\left[\delta(u_i)_c - \delta(u_i)_g\right] . \qquad (142)$$

In addition, the excitation terms in internal vibrations, the $(1-e^{-u_i})$'s, tend toward unity, since the u_i's are large under the low temperature approximation (section II.B.1.c.). Consequently, only the zero point energy term, $e^{\delta u/2}$, remains significant for the internal vibrations. For the external contributions to the vapor pressure isotope effect, $\left[\left(\frac{s}{s'}f\right)_c\right]_{ext}$, one can use the Bernoulli approximation (section II.B.3.a.), since the u_e's are so small and certainly less than 2π.

At ordinary temperatures, say, 100-400°K, Eqn. (139) can be simplified to (36, 81)

$$\ell n \frac{P'}{P} = \frac{A}{T^2} - \frac{B}{T} , \qquad (143)$$

where

$$A \equiv \frac{1}{24}\left(\frac{hc}{k}\right)^2 \sum_e^6 \delta\omega_e^{\,2} \qquad (144)$$

and

$$B \equiv \frac{1}{2}\left(\frac{hc}{k}\right)\sum_{i}^{3N-6}(\Delta\omega_i - \Delta\omega_i') \tag{145}$$

$$\equiv \frac{1}{2}\left(\frac{hc}{k}\right)\sum_{i}^{3N-6}\left[\delta\omega_i(g) - \delta\omega_i(c)\right] . \tag{146}$$

In Eqn.(144),

$$\delta\omega_e^2 \equiv \omega_e'^2 - \omega_e^2 , \tag{147}$$

and in Eqn.(145), $\Delta\omega_i$ represents the shift in the i-th internal frequency on condensation, i.e.,

$$\Delta\omega_i \equiv \omega_i(c) - \omega_i(g) . \tag{148}$$

Thus, "δ" represents an isotopic shift, whereas "Δ" represents a phase shift. All the ω's are in cm^{-1}.

The A term is therefore the first order quantum correction to the 6 low frequencies of the external modes of the condensed-phase molecule. The B factor is the isotope effect on the shift of the zero point energies of the internal vibrations on condensation. B can be rewritten as

$$B = \frac{1}{2}\left(\frac{hc}{k}\right)\sum_{i}^{3N-6}\left[-\delta(\Delta\omega_i)\right] = \frac{1}{2}\left(\frac{hc}{k}\right)\sum_{i}^{3N-6}\left[-\Delta(\delta\omega_i)\right] . \tag{149}$$

Both A and B are positive. A is positive according to Eqns.(144) and (147), because $\omega_e' > \omega_e$. The positiveness of B will be discussed in section VI.E.2.b.

The simplified VPIE expression, Eqn.(143), thus predicts the "crossover" phenomenon. The A factor, which represents the hindered translations and rotations, favors the normal isotope effect, i.e., P' > P, where the light species has the higher vapor pressure. The B factor will tend toward the inverse effect (P > P') at a higher temperature range. In addition, the inverse VPIE will be enhanced if the internal force constants of the molecule are smaller in the condensed phase than in the vapor phase, which is the usual occurrence.

In the absence of internal-external interactions in the condensed phase of polyatomic molecules, the A term can be written as

$$A \equiv A_{tr} + A_{rot} \tag{150}$$

$$\simeq \frac{1}{24}\left(\frac{h}{k}\right)^2 3\left[(\delta\mu_2)_{tr} + (\delta\mu_2)_{rot}\right] , \tag{151}$$

where $(\mu_2)_{tr}$ and $(\mu_2)_{rot}$ are the second moments of the translation and rotation of the frequency spectrum of the condensed-phase molecule (36). The second moment is just the sum of the squared frequencies. For a Debye frequency distribution, one obtains

$$A_{tr} = \frac{3}{40}\,\delta\Theta^2 = \frac{3}{40}\,(\Theta'^2 - \Theta^2) \;, \tag{152}$$

where Θ is the Debye temperature (10, 49).

The translational contribution to A has been obtained from low-temperature heat capacity data and the three rotational force constants have also been estimated, in part, by assuming that they are proportional to the relative volumes swept out by the isotopic molecule about its three principal axes (59). In addition, A_{tr} and A_{rot} are given by the following proportionalities (77):

$$A_{tr} \propto \left(\frac{M-M'}{M}\right)\Theta'^2 \tag{153}$$

and

$$A_{rot} \propto \prod_{a}^{3} \left(\frac{I_a - I_a'}{I_a}\right) (\mu_2')_{rot} \;, \tag{154}$$

where M is the molecular weight and I_a is one of the three principal moments of inertia.

Thus, for polyatomic molecules that are heavy and complex, the A factor becomes less important, while the B factor becomes more significant, which would favor the inverse VPIE.

III.C.2. Various Temperature Approximations

Four different temperature categories will be studied in order to determine the possible occurrence of the inverse VPIE within these temperature ranges. Thus, from Eqns.(141) and (142), one obtains

$$\ell n\frac{P'}{P} = \frac{1}{2}\sum_{i}^{3N-6}\left[(\delta u_i)_c - (\delta u_i)_g\right] + \sum_{i}^{3N-6}\ell n\left[\frac{\left(1-e^{-(u_i')_c}\right)\Big/\left(1-e^{-(u_i)_c}\right)}{\left(1-e^{-(u_i')_g}\right)\Big/\left(1-e^{-(u_i)_g}\right)}\right]$$

$$+ \sum_{e}^{6}\ell n\frac{u_e}{u_e'} + \sum_{e}^{6}\frac{1}{2}(\delta u_e) + \sum_{e}^{6}\ell n\left[\frac{1-e^{-u_e'}}{1-e^{-u_e}}\right] . \tag{155}$$

III.C.2.a. Very low temperatures

For very large u's, $1-e^{-u} \rightarrow 1$, and $\ell nu << u/2$. Therefore, all internal and external excitation terms, as well as the classical external terms, cancel, so that in this limit, Eqn.(143) is not applicable and Eqn.(141) takes the form

$$\ell n\left(\frac{P'}{P}\right)_{T\rightarrow 0} \approx \left(\frac{hc}{2k}\right)\frac{1}{T}\left[\sum_{i}^{3N-6}\left(\delta\omega_i(c) - \delta\omega_i(g)\right) + \sum_{e}^{6}\delta\omega_e(c)\right] . \tag{156}$$

This may lead to the normal effect (P' > P) due to the presence of the external (lattice) frequencies in the liquid.

III.C.2.b. Low temperatures

As the temperature is increased somewhat, the large internal frequencies still contribute zero-point energy terms, whereas the small external frequencies now contribute according to the first-order quantum correction ($1/T^2$). Thus,

$$\ell n\left(\frac{P'}{P}\right)_{\text{low }T} \simeq \frac{A}{T^2} - \frac{B}{T}\,, \tag{157}$$

where A and B were given previously. Therefore, this effect may be normal or inverse (P' < P) depending on the magnitudes of the two terms.

III.C.2.c. High temperatures

At this temperature range, the excitation terms for all the frequencies become significant and the isotope effect decreases. Therefore, inverse effects will go through maxima.

III.C.2.d. Very high temperatures

For very low u's, all terms contribute according to a first-order quantum correction. Thus,

$$\ln\left(\frac{P'}{P}\right)_{T\to\infty} \simeq \frac{1}{24}\left(\frac{hc}{k}\right)^2 \frac{1}{T^2}\left[\left(\sum_{i}^{3N-6} \delta\omega_i(c)^2 + \sum_{e}^{6} \delta\omega_e(c)^2\right) - \sum_{i}^{3N-6} \delta\omega_i(g)^2\right] . \tag{158}$$

This could lead to normal or inverse effects. If the condensed phase properties (ω^2) are larger than the gas phase squared frequencies, then any inverse effect exhibited at lower temperatures will become normal again before approaching the classical limit at infinite temperatures. Thus, a second crossover at high temperatures may be possible.

Figure 1 represents the plots of the isotopic vapor pressure ratios of ethylene vs. the tri-deutero and the carbon-13 species, respectively. Thus, for a $^{12}C/^{13}C$ substitution, the normal effect is preserved; whereas, for an H/D substitution, the inverse effect is preserved and there is no second crossover.

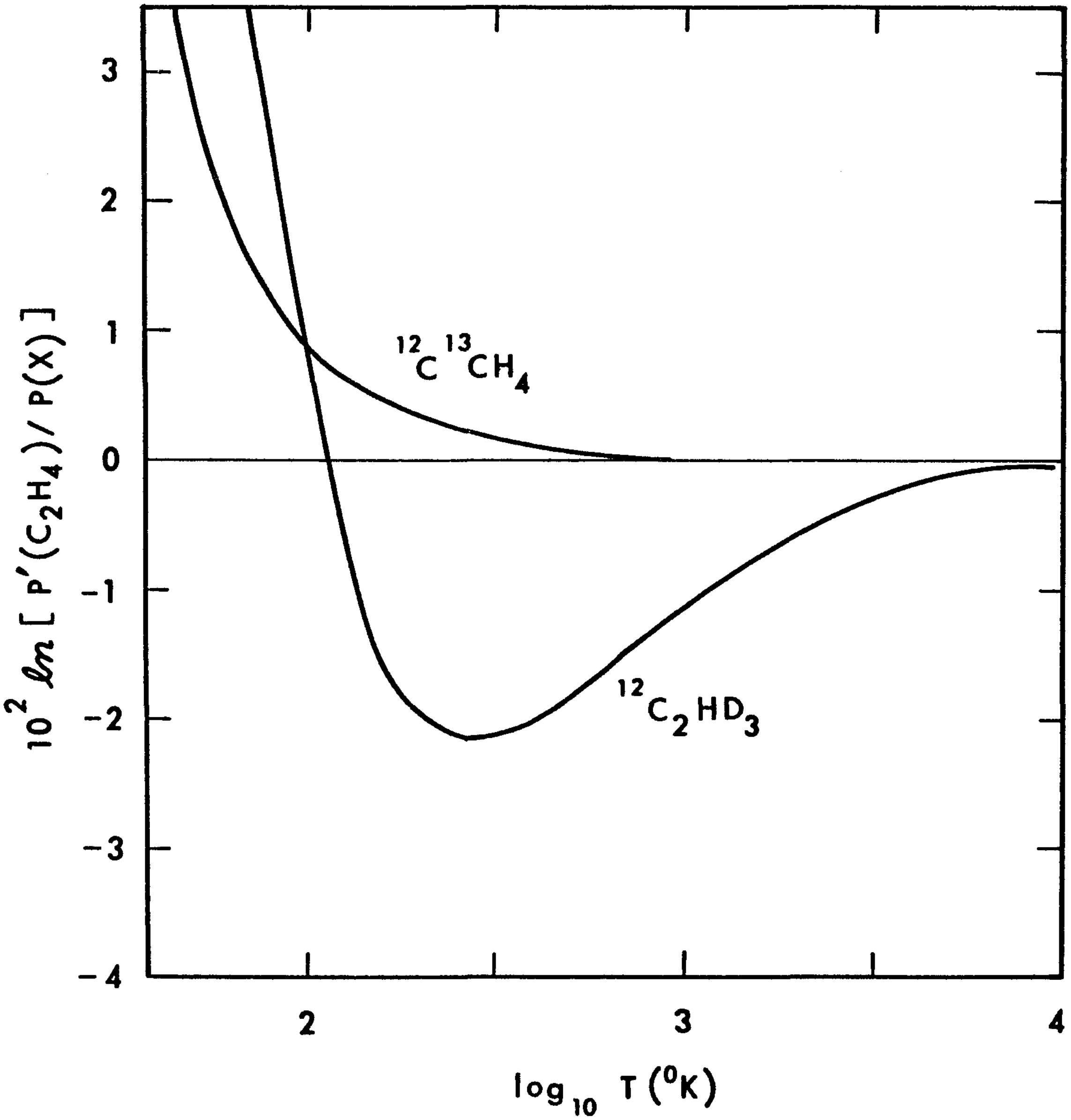

Figure 1. Isotopic vapor pressures in ethylene. (See Reference (53)).

III.D. Examination of the Assumptions

A summary and criticism of some of the assumptions that were used heretofore is given below. The effect of isotopic substitution on the vapor pressure of a condensed phase is determined through a "difference of differences," i.e., the isotopic differences between the changes in the frequencies on condensation. Thus, the ordinary difficulties involved with the usual application of the simple cell model for the evaluation of various thermodynamic properties would tend to cancel when determining vapor pressure isotope effects. This is true because the various multiplicative counting factors cancel for the difference of differences (150). The simple cell model of the condensed phase is perhaps the most questionable of all the approximations used in VPIEs studies. The assumption of an average molecule is not physically realistic since it only crudely recognizes the fact that the motions of neighboring molecules are intimately coupled through intermolecular forces. However, Pollin and Ishida recently showed by means of the medium cluster model of the liquid that a consideration of molecular interactions confirms the results of the cell model calculations for the isotopic methanes (150, 151). Furthermore, the harmonic approximation, though suitable for the internal motions, may be unrealistic for the external motions, since these latter motions have much larger amplitudes. Molecular associations in the condensed phase and thermal expansion of the liquid lead to difficulties in the theoretical investigations of vapor pressure isotope effect studes.

The VPIE theory described heretofore assumed only one kind of molecule in the liquid and that the liquid behaves like a solid. The significant structure theory of Eyring and co-workers was used by Grosh et al. (80) to calculate vapor-pressure differences between isotopic liquids. This theory pictures the liquid as consisting of solid-like molecules and holes.

III.E. Intermolecular Forces in the Liquid

The liquid phase isotopic frequencies differ from the gas phase oscillations, due to the fact that intermolecular interactions are present in the condensed phase. The intermolecular interactions, which are, in general, important for ground-state molecules without electronic charges, are the long-range attractive van der Waals forces and the short-range repulsive chemical (or valence) forces. In general, all these forces cause the shift in the frequencies upon condensation of the molecule.

The chemical forces arise when two molecules come close together for their electron clouds to overlap and thus repel each other. The van der Waals forces may include Keesom's orientation (or electrostatic) forces between two molecules with permanent electric dipole moments, Debye's induction forces between a molecule with a permanent dipole moment and another molecule, which may or may not be polar, and London's dispersion forces between two molecules, which may or may not possess permanent electric dipole moments. The van der Waals forces are effective at larger intermolecular separations and are attractive.

The orientation forces arise when two dipoles in rapid thermal motion are oriented so as to have a net attractive interaction energy. Thus, for a large separation r_{AB} between molecules A and B, and for "ideal" (or point) dipoles P_A and P_B (where the distance between the two charges is made to approach zero, while the charges are increased in order to keep the value of the electric dipole moment constant), and after averaging over all molecular orientations, one obtains the orientation energy between two molecules (82)

$$E_{orn} = - \frac{2}{3kT} \frac{P_A^2 P_B^2}{r_{AB}^6} . \qquad (159)$$

The induction forces result from the attractive interactions between a permanent dipole moment and an induced dipole produced in another molecule. Thus, if both molecules A and B have permanent point dipoles then the induction energy, averaged over all orientations of the molecule, is (82)

$$E_{ind} = - \frac{P_A^2 \alpha_B + P_B^2 \alpha_A}{r_{AB}^6} , \qquad (160)$$

where α is the average molecular polarizability. The induction effect is, generally, the weakest of the van der Waals forces.

The dispersion forces between two molecules result from the mutual attractions of an instantaneous dipole and an induced dipole of another molecule produced by that instantaneous moment. An instantaneous dipole is created in a molecule when the electron cloud, which, on the average, is spherically symmetric, becomes distorted and creates a momentary dipole with a certain orientation. Instantaneous dipoles of the two molecules do not interact to produce an attractive potential, due to the fact that there is insufficient time for the instantaneous moments to line up with one another, and thus there will be repulsion as often as attraction. This interaction is a purely quantum mechanical effect. Thus, for large separations, one obtains (82) for the dispersion energy between molecules A and B, after averaging over all molecular orientations,

$$E_{dis} = -\frac{3}{2}\frac{I_A I_B}{I_A+I_B}\frac{\alpha_A \alpha_B}{r_{AB}^6}, \tag{161}$$

where I is the molecular ionization potential. The dispersion interaction is always significant and often is the strongest of the van der Waals forces. The above equation is not applicable to long conjugated double-bond or aromatic molecules, because of the very large separations between the positive and negative charges in these molecules.

Thus, if one assumes that no interactions between molecules exist in the gas phase, then the potential energy of a liquid molecule relative to that of a gas molecule, due to the molecular interactions, becomes

$$\Delta E = E_\ell - E_g \tag{162}$$

$$= \Delta E_{rep} + \Delta E_{att} \tag{163}$$

$$= (\Delta E_{val}) + (\Delta E_{orn} + \Delta E_{ind} + \Delta E_{dis}) . \tag{164}$$

The valence, orientation, and induction forces are purely electrostatic in origin, and, within the framework of the Born-Oppenheimer approximation, are isotope-independent. However, the dispersion forces, which are quantum mechanical in origin, are isotope dependent, due to the vibrational excitation terms (28). Thus, in the study of isotope effects on intermolecular interactions in the liquid, only the London dispersion forces are important.

III.F. Wolfsberg's Dispersion Energy Treatment and the Zero Point Energy Shift upon Condensation

The problem of interest is the interaction between two liquid molecules A and B, where the separation, S, of the centers of mass of the two molecules is sufficiently large so that it is not necessary to antisymmetrize the wave functions with respect to the electronic coordinates. The zeroeth order wave function of this interacting system is assumed to be a product of the wave functions of the two free (separated) non-translating molecules, i.e., gaseous molecules. The perturbation potential resulting from the electrostatic interaction is expanded in inverse powers of the intermolecular separation S. Thus, after averaging over all orientations, the second order perturbation treatment yields the London dispersion energy (28, 82):

$$\Delta E_{dis} = - \frac{2}{3} \frac{e^4}{S^6} \sum_{k_A \neq 0} \sum_{k_B \neq 0} \frac{\sum_a^3 |(0|D_a|k_a)|^2 \sum_b^3 |(0|D_b|k_B)|^2}{(E_{kA} - D_{0A}) + (E_{kB} - E_{0B})} \ . \qquad (165)$$

In the above equation, e is the electronic charge, k_A and k_B represent the set of quantum numbers of the excited states of molecules A and B, respectively, with corresponding energies E_{kA} and E_{kB}, and the 0's represent the ground states of the two molecules, with corresponding energies E_{0A} and E_{0B}, respectively. D_a represents the x, y, or z component of the dipole moment operator for molecule A, and D_b is the operator for molecule B. Thus,

$$D_{a=x} = D_x^A = \sum_{\alpha}^{\text{atoms}} Z_\alpha^A x_\alpha^A - \sum_{i}^{\text{electrons}} x_i^A , \qquad (166)$$

or

$$D = D_{\text{nuclear}} - D_{\text{electronic}} , \qquad (167)$$

where the superscripts refer to molecule A, Z_α is the nuclear charge of the α-th nucleus with x_α, y_α, z_α as its center-of-mass molecule-fixed cartesian coordinates, and x_i, y_i, z_i as the corresponding electron coordinates. In addition,

$$(0|D_a|k_A) \equiv \int \psi_{0A}^* D_a \psi_{kA} d\tau , \qquad (168)$$

where the molecular wave function is of the form

$$\psi = \psi(\text{electronic})\psi(\text{vibrational}) . \qquad (169)$$

Thus, k refers to an electronically and/or vibrationally excited state. Furthermore, the quantum states of molecules A and B, k_A and k_B, must change simultaneously (82).

At this point, one considers each of the cases where k refers to electronic or vibrational excitations. For the case where k_A, $k_B \neq 0$ refer to excited electronic states, summation over the various vibrational levels belonging to each electronic state results in the lack of nuclear contributions to the interaction energy. Thus, electronic excitations of the two molecules transform Eqn.(165) into

$$(\Delta E_{dis})_{el} = -\frac{3}{2}\frac{I_A I_B}{I_A+I_B}\frac{\alpha_A\alpha_B}{S^6}\ . \tag{170}$$

In the above equation, α_A is the electronic polarizability of molecule A in its ground state, and is given by

$$\alpha_A \equiv \frac{2}{3}e^2 \sum_{k_A\neq 0}\frac{1}{E_{kA}-E_{0A}}\sum_{a}^{3}|(0|D_a^{el}|k_A)|^2 \tag{171}$$

$$\simeq \frac{2}{3}\frac{e^2}{I_A}\sum_{k_A\neq 0}\sum_{a}^{3}|(0|D_a^{el}|k_A)|^2\ , \tag{172}$$

and I_A is some average excitation energy, usually taken as the ionization potential of molecule A.

For the case where k_A and k_B correspond to vibrational excitations without electronic excitations, i.e., $k_A=V_A$ and $k_B=V_B$, the dipole moment operator becomes

$$D_a = P_a^0 + \sum_{i=1}^{3N-6}\left(\frac{\partial P_a}{\partial Q_i}\right)_0 Q_i + \text{higher terms}, \tag{173}$$

where P_a^0 is the x, y, or z component of the electric dipole moment possessed by the molecule in its equilibrium configuration, Q_i is the i-th normal coordinate, and $(\partial P_a/\partial Q_i)_0$ is the dipole moment derivative evaluated at the equilibrium position. In addition,

$$(V_{ia}|D_a|V'_{ia}) \equiv \left(\psi_{V_{ia}}(Q_i)|D_a|\psi_{V'_{ia}}(Q_i)\right)$$

$$\equiv \int \psi^*_{V_{ia}}(Q_i)\, D_a\, \psi_{V'_{ia}}(Q_i)\, d\tau \ , \tag{174}$$

and from Eqn.(173) one obtains (31)

$$\sum_{V'_{iA}} \sum_{a}^{3} |(V_{iA}|D_a|V'_{iA})|^2 = \frac{h(2V_{ia}+1)}{8\pi^2 \nu_{iA}} \sum_{a}^{3} \left(\frac{\partial P_a}{\partial Q_{iA}}\right)_0^2 \ , \tag{175}$$

where ν_{iA} is the i-th fundamental frequency of vibration of molecule A associated with Q_{iA}, and V_{iA} and V'_{iA} are two vibrational quantum numbers associated with the i-th normal coordinate of molecule A, Q_{iA}. Eqn.(175) represents the sum of vibrational dipole transition probability integrals for the state V_i of molecule A. Thus, the total perturbation (dispersion) energy for the interaction between two molecules A and B in the liquid phase is (28)

$$(\Delta E_{dis})_{total} = -\frac{3}{2}\frac{I_A I_B}{I_A+I_B}\frac{\alpha_A \alpha_B}{s^6} - \sum_{i}^{3N-6} \frac{h(2V_{iA}+1)}{8\pi^2 \nu_{iA}} \sum_{a}^{3} \left(\frac{\partial P_a}{\partial Q_{iA}}\right)_0^2 \frac{\alpha_B}{s^6}$$

$$- \sum_{j}^{3N-6} \frac{h(2V_{jB}+1)}{8\pi^2 \nu_{jB}} \sum_{b}^{3} \left(\frac{\partial P_b}{\partial Q_{jB}}\right)_0^2 \frac{\alpha_A}{s^6} \ , \tag{176}$$

provided that the electronic excitation energy is greater than the vibrational excitation energy, and that the higher order terms of Eqn.(173) are negligible. All of the properties on the right-hand side of the last equation, except for S, the intermolecular separation, are those of the <u>unperturbed</u> molecules, i.e., the <u>gaseous</u> molecules. If all the molecules are in their ground states, then $V_{iA} = V_{jB} = 0$, and Eqn.(176) becomes

$$(\Delta E_{dis})_{total} = \left[-\frac{3}{2}\,\frac{I_A I_B}{I_A + I_B}\,\frac{\alpha_A \alpha_B}{S^6} \right] + \left[-\frac{\alpha_B}{S^6}\,\frac{h}{8\pi^2} \sum_{i}^{3N-6} \frac{1}{\nu_{iA}} \sum_{a}^{3} \left(\frac{\partial P_a}{\partial Q_{iA}} \right)_0^2 \right.$$

$$\left. -\frac{\alpha_A}{S^6}\,\frac{h}{8\pi^2} \sum_{j}^{3N-6} \frac{1}{\nu_{jB}} \sum_{b}^{3} \left(\frac{\partial P_b}{\partial Q_{jB}} \right)_0^2 \right] \qquad (177)$$

$$= (\Delta E_{dis})_{el} + (\Delta E_{dis})_{vib} \;, \qquad (178)$$

where both the electronic and the vibrational excitation contributions to the energy of the intermolecular interaction have been indicated.

Since the molecules are in their ground states, the second term of Eqn.(178) represents the change in the vibrational zero point energy (ZPE) of both molecules due to the interactions in the liquid phase. Thus,

$$(\Delta E_{dis})_{vib} = \Delta(\mathrm{ZPE})_A + \Delta(\mathrm{ZPE})_B \;, \qquad (179)$$

where

$$\Delta(\mathrm{ZPE})_A = \Delta\left(\sum_i^{3N-6} \frac{1}{2} h\nu_{iA}\right) = \frac{h}{2} \sum_i^{3N-6} \Delta\nu_{iA} \tag{180}$$

$$= -\frac{h}{8\pi^2}\frac{\alpha_B}{S^6}\sum_i^{3N-6}\frac{1}{\nu_{iA}}\sum_a^3\left(\frac{\partial P_a}{\partial Q_{iA}}\right)_g^2 . \tag{181}$$

The latter equation was obtained through Eqn.(177). Therefore, the sum of the shifts of the vibrational frequencies of molecule A upon condensation is

$$\sum_i^{3N-6} \Delta\nu_{iA} = \sum_i^{3N-6}\left(\nu_{iA}(\ell)-\nu_{iA}(g)\right) = -\frac{1}{4\pi^2}\frac{\alpha_B}{S^6}\sum_i^{3N-6}\frac{1}{\nu_{iA}}\sum_a^3\left(\frac{\partial P_a}{\partial Q_{iA}}\right)_g^2 . \tag{182}$$

In addition, since $\lambda_i = 4\pi^2\nu_i^2$, Eqn.(98), where λ_i is the i-th force constant associated with the normal vibrational coordinate Q_i, one obtains for the shift

$$\Delta\lambda_i \simeq 8\pi^2\nu_i\,\Delta\nu_i . \tag{183}$$

This equation is valid, because the vibrational frequency shift upon condensation, $\Delta\nu_i$, has been experimentally measured to be, indeed, small (53). Thus, substituting Eqn.(183) into (182) yields

$$\sum_{i}^{3N-6} \Delta\lambda_{iA} = \sum_{i}^{3N-6} \left[\lambda_{iA}(\ell)-\lambda_{iA}(g)\right] = -2\,\frac{\alpha_B}{S^6} \sum_{i}^{3N-6} \sum_{a}^{3} \left(\frac{\partial P_a}{\partial Q_{iA}}\right)_g^2 , \qquad (184)$$

which represents the sum of the 3N-6 shifts of the vibrational force constants on condensation. Consequently, the interaction between molecules A and B results in a change in the frequency sum or in the force constant sum of molecule A, represented by Eqn.(182) or by Eqn.(184), respectively, while a corresponding change occurs for molecule B.

The previous results, Eqns.(182) and (184), may also be obtained in the following way (28). The potential energy for the nuclear motions (vibrations) is given by

$$V = \sum_{i}^{3N-6} \frac{1}{2}\lambda_i Q_i^2 . \qquad (185)$$

If the internal configuration of molecule A deviates from the equilibrium configuration (at which all Q_i's are zero) along the i-th normal coordinate, Q_i, then this displacement causes the following two changes. One is that the potential energy is increased from zero to $\frac{1}{2}\lambda_i Q_i^2$. In addition, this displacement creates a new dipole moment vector

$$(\vec{P}_{new})_A = (\partial\vec{P}/\partial Q_i)_A \, Q_{iA} , \qquad (186)$$

where

$$(P_{new})_A^2 = \sum_{a}^{3} (\partial P_a/\partial Q_{iA})^2 \, Q_{iA}^2 . \qquad (187)$$

This dipole will induce an additional dipole in molecule B, which creates an additional interaction energy, i.e., Debye's induction energy (dipole--induced-dipole), Eqn.(160). The induction term yields

$$(\Delta E_{ind})_A = -\frac{1}{S^6}\sum_a^3 \left(\frac{\partial P_a}{\partial Q_{iA}}\right)^2 Q_{iA}{}^2 \alpha_B \ . \tag{188}$$

Therefore, the total change in the vibrational interaction energy for molecule A is

$$(\Delta E_{vib})_A = \frac{1}{2}\sum_i^{3N-6} \lambda_{iA} Q_{iA}{}^2 - \sum_i^{3N-6} \sum_a^3 \left(\frac{\partial P_a}{\partial Q_{iA}}\right)^2 Q_{iA}{}^2 \frac{\alpha_B}{S^6} \tag{189}$$

$$= \frac{1}{2}\sum_i^{3N-6} \left(\lambda_{iA} - 2\sum_a^3 \left(\frac{\partial P_a}{\partial Q_{iA}}\right)^2 \frac{\alpha_B}{S^6}\right) Q_{iA}{}^2 \tag{190}$$

$$= \frac{1}{2}\sum_i^{3N-6} \lambda_{iA}(\text{liq})\ Q_{iA}{}^2 \ . \tag{191}$$

Hence, the sum of the shifts of the 3N-6 normal coordinate force constants is

$$\sum_i^{3N-6} \Delta\lambda_{iA} = \sum_i^{3N-6} \left(\lambda_{iA}(\ell) - \lambda_{iA}(g)\right) = -2\frac{\alpha_B}{S^6}\sum_i^{3N-6}\sum_a^3 \left(\frac{\partial P_a}{\partial Q_{iA}}\right)_g^2 \ , \tag{192}$$

which is the same as Eqn.(184).

Eqns.(182) and (184) do lead to isotope effects due to the isotope dependence of the normal coordinates. Thus, the isotope effect on the zero point energy shift on condensation, the B term in Eqn.(145), may be evaluated if one knows the isotopic dependence solutions to Eqns.(182) or (184). This would lead to a better understanding of the inverse phenomenon of the vapor pressure isotope effect, Eqn.(143), and of condensed phase chemical isotope effects, in general.

IV. ISOTOPE EFFECT ON THE ZERO POINT ENERGY SHIFT UPON CONDENSATION

IV.A. Interactions of the Liquid Reference Molecule

The shift that is due to the attractive London dispersion forces between two liquid molecules, in the trace of the vibrational eigenvalues upon condensation, was developed above, Eqn.(192). This shift for a liquid molecule A, which is a result of its interaction with molecule B, is given by

$$\sum_{i}^{3N-6} \Delta\lambda_{iA} = -2\,\frac{\alpha_B}{S_{AB}^{6}} \sum_{i}^{3N-6} \left(\frac{\partial\vec{P}}{\partial Q_i}\right)^2_{A(g)} , \qquad (193)$$

where $\vec{P}$ is the molecular dipole moment vector of A, and S_{AB} is the separation between liquid molecules A and B. Another equation given by Wolfsberg (his Eqn.[6] in Ref.[28]),

$$\Delta\lambda_i = -2\,\frac{\alpha}{S^6}\left(\frac{\partial\vec{P}}{\partial Q_i}\right)^2_g , \qquad (194)$$

is actually inappropriate, because it infers that every liquid eigenvalue (or frequency) is always less than the corresponding gaseous value. However, there are cases where the frequency shift, represented by Eqn.(194), is in fact positive (53). It is the sum of these shifts, as represented by Eqn.(193), that is negative; i.e., the sum of the liquid eigenvalues is smaller than the gaseous sum.

For this investigation, the simple cell model is assumed for the liquid state. The liquid phase has a closely packed structure that is very similar to the solid state (82, 83). Thus, the total intermolecular potential of one molecule must be evaluated with respect to its interactions with all the other molecules.

If V_{ij} is the van der Waals interaction between molecules i and j, then the total energy of any one molecule i is

$$V_i = \sum_{j \neq i}^{\infty} V_{ij} , \qquad (195)$$

where i can be considered to be a reference liquid molecule in the system. Therefore, the attractive part of the potential energy of one molecule in the system, which is due to all the other molecules, is

$$V_i = \sum_{j \neq i}^{\infty} V_{ij} \propto \sum_{j \neq i}^{\infty} r_{ij}^{-6} = CS^{-6} . \qquad (196)$$

In the above equation, r_{ij} is the distance between reference molecule i and any other molecule j, S is the nearest-neighbor separation, and C is the Lennard-Jones and Ingham crystal potential constant (82, 84-86). This constant is a function of the particular crystal structure and of the potential energy form (i.e., the particular exponential dependence on the intermolecular distance r). It accounts for the sum of contributions of all outer-shell molecules to the potential at the position of the central molecule. The Lennard-Jones and Ingham constant is similar to the Madelung constant for ionic crystals, except that the former applies to molecular crystals. Molecular liquids (or crystals) are those in which the molecules are held together by van der Waals forces, and these molecules tend to pack together as closely as possible (83).

Some of these constants are tabulated in Table I. Thus, as the intermolecular force becomes more short-ranged, the outer-shell neighbors become less important with respect to the interactions with the central reference molecule, until C approaches its limiting value, the coordination number of the crystal. For the van der Waals energy ($1/r^6$ dependence), and for the closest-packed configuration, the value for the constant is

$$C = 14.455 \ . \tag{197}$$

Therefore, the total shift in the trace of the vibrational Hamiltonian, which is a result of the interaction of any one molecule in the condensed phase with all the others, is given by Eqns.(193) and (196); i.e.,

$$\sum_{i}^{3N-6} \Delta\lambda_i = -2C \frac{\alpha}{S^6} \sum_{i}^{3N-6} \left(\frac{\partial \vec{P}}{\partial Q_i}\right)_g^2 \ . \tag{198}$$

Table I

Lennard-Jones and Ingham Crystal Potential Constants, C, for Various Crystal Structures and Potential Energy Forms(a)

Potential Energy Exponent n in r^{-n}	Simple Cubic	Body-Centered Cubic	Face-Centered Cubic (Cubic Close-Packed)	Hexagonal Close-Packed
4	16.5323	22.6387	25.3383	....
5	10.3775	14.7585	16.9675	....
6	8.4019	12.2534	14.4539	14.4549
8	6.9458	10.3552	12.8019	12.8028
10	6.4261	9.5644	12.3112	12.3119
12	6.2022	9.1142	12.1319	12.1323
30	6.0004	8.0802	12.0002	....

(a) References (82), (84) - (86).

The above equation is applicable for a pure liquid, which contains only identical molecules.

IV.B. Isotopic Difference between the Vibrational Eigenvalue Shifts upon Condensation

Eqn.(107) expresses the isotope effect on the ZPE as a sum of isotopic differences of various orders of eigenvalue sums. The p=1 limit of this Bigeleisen and Goldstein (33, 78) Taylor series expansion yields

$$\sum_{i}^{3N-6} \delta\omega_i \simeq \frac{1}{8\pi^2 c^2} \frac{1}{\omega_0} \sum_{i}^{3N-6} \delta\lambda_i \ . \tag{199}$$

Upon substitution of Eqn.(199) into Eqn.(146), one obtains the following expression for B in terms of isotopic differences between the eigenvalue shifts upon condensation:

$$B \simeq \frac{1}{(4\pi)^2} \frac{h}{ck} \frac{1}{\omega_0} \sum_{i}^{3N-6} (\Delta\lambda_i - \Delta\lambda_i') \tag{200}$$

$$\simeq \frac{1}{(4\pi)^2} \frac{h}{ck} \frac{1}{\omega_0} \sum_{i}^{3N-6} \left[\delta\lambda_i(g) - \delta\lambda_i(\ell)\right] \ . \tag{201}$$

In addition, substituting Eqn.(198) into Eqn.(200) yields

$$B \simeq \frac{1}{8\pi^2} \frac{h}{ck} \frac{C}{\omega_0} \frac{\alpha}{S^6} \sum_{i}^{3N-6} \left[\left(\frac{\partial\vec{P}}{\partial Q_i'}\right)^2 - \left(\frac{\partial\vec{P}}{\partial Q_i}\right)^2\right]_g \ . \tag{202}$$

Thus, the B term, which represents the isotope effect on the zero point energy shift upon condensation, is related to the sum of the isotopic differences between the dipole moment derivatives in normal coordinates. The derivative is isotope-dependent, even though the molecular dipole moment is, according to the Born-Oppenheimer approximation, isotopically invariant. This isotopic property is due to the mass-dependence of the normal coordinates.

In Eqn.(202), the molecular polarizability is a function of the electronic structure and is therefore isotope-independent (similar to $\vec{P}$). Similarly, the crystal potential constant is independent of isotopic substitutions. The characteristic frequency of Bigeleisen and Goldstein, ω_0, was taken to be constant for the entire isotopic molecular series, as mentioned previously.

S, which is the separation of the centers of mass of two nearest-neighbor molecules, may be isotope dependent. However, the average separation is the one that minimizes the electronic energy of the system, and the isotopic difference for this separation is a second order effect (28,87). In fact, if the intermolecular potential is harmonic, then S must be isotope-independent, according to the Born-Oppenheimer approximation. Only when the intermolecular potential is anharmonic, would the difference between the amplitudes of the external oscillations of isotopic molecules lead to a prediction of an isotope-dependent S. Therefore, to the first order, the average value of S may be considered to be isotope-independent.

The isotope-independent characteristic frequency, ω_0, must satisfy the constraint

$$\omega_0 \geq 2^{-\frac{1}{2}}\omega_{\max} , \tag{203}$$

according to Eqns.(108) and (111). $\omega_{\max}$ is the largest harmonic frequency of the lightest isotopic molecule in the molecular series. Semi-empirically, it was found (78, 152, 153) that the best choice for ω_0 is

$$(\omega_0)_{\text{best}} = 2^{-\frac{1}{2}}\omega_{\max} . \tag{204}$$

IV.C. Dipole Moment Derivatives in the Normal Coordinates and Infrared Intensities

The dipole moment derivatives with respect to normal coordinates, $\partial\vec{P}/\partial Q_i$, which appeared in Eqn.(202), are related to the absorption intensities of infrared bands (88-96). The band area or the absorption "cross section" for an infrared transition from state p to q, $\Gamma_{p,q}$, is given by (88-95)

$$\Gamma_{p,q} \equiv \frac{1}{n\ell} \int_{\text{band}} \ln\left(\frac{I_0}{I}\right) d\ln\nu \tag{205}$$

$$= \frac{8\pi^3 N_0}{3hc} <p|\hat{P}|q>^2 \, Q_v^{-1} \left[\exp(-E_p/kT) - \exp(-E_q/kT)\right] . \tag{206}$$

The latter equation is obtained by integrating and then summing over the rotational fine structure of the vibrational absorption band. In the above equations, I_0 and I are the incident and transmitted intensities, respectively, at a frequency ν; and n and ℓ are the molar concentration and the optical path length, respectively, of the sample in the absorption cell. In addition, N_0 is Avogadro's number; Q_v is the molecular vibrational partition function,

$$Q_v = \sum_i \exp(-E_i/kT) \; ; \tag{207}$$

and the dipole moment matrix element for states p and q is given by

$$<p|\hat{P}|q> = \int \psi_p^* (Q_i)\hat{P}\psi_q(Q_i)dQ_i \ , \tag{208}$$

where $\hat{P}$ is the electric dipole moment operator.

In order to obtain the transition integral for a fundamental transition from the ground vibrational state, V=0, to the first excited state, V=1, $\vec{P}$ is expanded in a Taylor series in the normal coordinate Q_i, as in Eqn.(173). Thus,

$$\vec{P}(Q_i) = \vec{P}_0 + \sum_i^{3N-6} \left(\frac{\partial \vec{P}}{\partial Q_i}\right) Q_i + \frac{1}{2} \sum_i^{3N-6} \sum_j^{3N-6} \left(\frac{\partial^2 \vec{P}}{\partial Q_i \partial Q_j}\right) Q_i Q_j + \ldots , \tag{209}$$

and the transition integral becomes (31)

$$<0|\hat{P}|1> = \frac{\partial \vec{P}}{\partial Q_i} \int \psi_0^* Q_i \psi_1 dQ_i = \left(\frac{h}{8\pi^2 c\omega_i}\right)^{\frac{1}{2}} \frac{\partial \vec{P}}{\partial Q_i} \ . \tag{210}$$

The last equation was obtained by neglecting all the non-linear terms in the dipole moment expansion, Eqn.(209). ω_i is the <u>harmonic</u> frequency (in cm^{-1}) of the i-th mode and $\vec{P}_0$ is the dipole moment at the equilibrium molecular configuration.

Eqn.(206) can be simplified because

$$Q_v^{-1} \left(\exp(-E_p/kT) - \exp(-E_q/kT)\right) \simeq 1 \ . \tag{211}$$

In addition, since the increase in induced emission exactly cancels the absorption from the excited states, one can ignore the contributions of the hot bands (i.e., absorptions from excited states, 1→2, 2→3, etc.) to the absorption of the fundamental region. Thus, integrated fundamental intensities can be determined as if all the sample molecules are in their ground states (95).

Therefore, upon substitution of Eqns.(210) and (211) into Eqn.(206), one obtains for the integrated intensity of the i-th fundamental absorption band (88-95)

$$\Gamma_i = \frac{N_0 \pi}{3c^2} \frac{g_i}{\omega_i} \left(\frac{\partial \vec{P}}{\partial Q_i} \right)^2 . \tag{212}$$

The mechanical and electrical anharmonicities have been neglected in the above equation, i.e., the harmonic oscillator and linear dipole moment approximations, respectively, have been employed. The degeneracy of the i-th fundamental is given by g_i. As a result of the above approximations, contributions from the overtone and combination bands to the fundamental intensities are disregarded.

Vibrational intensities may also be expressed by a relationship that is similar to Eqn.(205), i.e, (88-95),

$$A_{p,q} \equiv \frac{1}{n\ell} \int_{\text{band}} \ell n \left(\frac{I_0}{I} \right) d\nu \ , \tag{213}$$

where, in this case, the integration is carried out over the frequency itself and not over the logarithm of the frequency. Thus Γ and A are related to each other according to the following approximate equation:

$$A_i \simeq \nu_i \Gamma_i \ , \tag{214}$$

where ν_i is the observed frequency (in cm^{-1}) of the i-th band center. The i-th integrated intensity, A_i, becomes

$$A_i = \left(\frac{N_0 \pi}{3c^2}\right) g_i \left(\frac{\nu_i}{\omega_i}\right) \left(\frac{\partial \vec{P}}{\partial Q_i}\right)^2 \ . \tag{215}$$

The anharmonic correction factor, ν_i/ω_i, is often neglected, because it is generally very close to unity. Therefore, the integrated intensity of the i-th fundamental infrared absorption band is simply

$$A_i \simeq \left(\frac{N_0 \pi}{3c^2}\right) \left(\frac{\partial \vec{P}}{\partial Q_i}\right)^2 \ , \tag{216}$$

assuming a value of unity for the state multiplicity g_i.

Using this last relationship between dipole moment derivatives with respect to normal coordinates and integrated intensities of infrared absorption bands, one can reformulate the isotope effect on the zero point energy shift upon condensation, the B factor, in terms of intensities. Thus, Eqn.(202) becomes

$$B \simeq \frac{3}{(2\pi)^3} \frac{hc}{N_0 k} \frac{C}{\omega_0} \frac{\alpha}{S^6} \sum_i^{3N-6} (A_i{}'-A_i)_g \ , \tag{217}$$

where the only isotopic difference is expressed in the gaseous (g) infrared intensities of the lighter (A_i') and heavier (A_i) species.

IV.D. Experimental Determination of Gas-Phase Integrated Infrared Absorption Intensities

This section is provided in order to record various experimental methods for the determination of the infrared intensities. These experimentally derived intensities will be compared with theoretically calculated absorption intensities, later in this work. An understanding of the experimental procedures and shortcomings will enable a critical evaluation of the measured intensities to be made.

IV.D.1. Wilson-Wells Method (88, 95, 97-99)

The true value of the intensity A of Eqn.(213) cannot be determined directly, because the monochromator does not transmit radiation of only the selected frequency. Instead, the resolving power of the monochromator determines the width of the narrow band of frequencies that are, in actuality, transferred. Thus, the observed integrated intensity, A_{obs}, is related to the true value through

$$\lim_{n\ell \to 0} A_{obs} = A \ , \tag{218}$$

where,

$$A_{obs} \equiv \frac{1}{n\ell}\int \ell n\left(\frac{T_0}{T}\right) d\nu \ , \tag{219}$$

and T_0 and T are the measured intensities of the incident and transmitted radiation, respectively. Hence, a plot of $A_{obs}n\ell$ against $n\ell$, followed by an extrapolation to $n\ell=0$, would yield the <u>true</u> integrated intensity, A. However, there is considerable uncertainty in determining the slope of the tangent near the origin, because, in practice, the curve is non-linear. In addition, the evaluation of the apparent intensity, A_{obs}, must necessarily rely heavily on low absorption data, which inherently contain the greatest relative errors in the concentration n and in the observed absorption. Furthermore, because of the absorption of radiation by atmospheric CO_2 and water vapor, rapid fluctuations in I and I_0 occur.

IV.D.2. Pressure Broadening Technique

In order to keep I constant over the narrow band of frequencies transmitted by the monochromator, the pressure broadening technique is employed. The pressure in the absorption cell is increased to a sufficiently high pressure, so that the rotational spectral lines are broadened (100), and thus produce a smoothened band contour. This increase in pressure is produced by the use of a foreign infrared-transparent gas, at a high enough pressure so as to yield a linear (98) Beer's Law plot of $A_{obs}n\ell$ vs. $n\ell$. This linearity reduces the errors that are due to the extrapolation to zero. However, precautions must be taken in order to prevent the inadequate mixing of the two gases, and the adsorption on the cell walls. In addition, very high pressures may be needed (e.g., 100 atmospheres) for the complete broadening of the absorption band, and lower pressures may result in serious errors in the determination of the intensities (95).

IV.D.3. Complications

There are two major complications that are encountered with the graphical integration of the infrared absorption bands. It is difficult to accurately measure the intensities of the fairly extensive band wings, due to the low optical density of these wings. However, they do make a significant contribution to the intensity.

The other considerable difficulty is the overlap of two or more bands. The separation into individual band intensities is a rather arbitrary procedure because the band may be unsymmetrical.

IV.E. Transformations of the Normal Coordinate Dipole Moment Derivatives

The integrated intensities of the fundamental infrared absorption bands are proportional to the squares of the absolute magnitudes of the derivatives of the molecular dipole moment with respect to the normal vibrational coordinates (see Eqn.[216]). In addition, the isotopic differences of these (gas-phase) derivatives or intensities can determine the isotope effect on the zero point energy shift upon condensation (Eqns.[202] or [217]), which, in turn, determines the inverse vapor pressure isotope effect (Eqn.[143]). The derivatives $\partial\vec{P}/\partial Q_i$ are properties of the molecule as a whole, but physico-chemical properties would be better suited for interpretations if they were related to the individual parts of the molecule, e.g., bonds, angles, and/or atoms. Thus, as one of the major achievements of this research, the derivatives in the normal coordinates were first transformed to be expressed in terms of internal coordinates, and then in terms of atomic cartesian coordinates (154).

IV.E.1. Dipole Moment Derivatives with Respect to Internal Coordinates

Setting

$$K \equiv \frac{N_0\pi}{3c^2} \quad , \qquad (220)$$

will lead to the following expression for A_i of Eqn.(216):

$$A_i = K\left|\frac{\partial\vec{P}}{\partial Q_i}\right|^2 . \tag{221}$$

Furthermore,

$$\left|\frac{\partial\vec{P}}{\partial Q_i}\right|^2 = \left(\frac{\partial P_x}{\partial Q_i}\right)^2 + \left(\frac{\partial P_y}{\partial Q_i}\right)^2 + \left(\frac{\partial P_z}{\partial Q_i}\right)^2 , \tag{222}$$

$$= \sum_x^3 \left(P_{xQ_i}\right)^2 = \underset{\sim}{P}_{Q_i}{}^t \, \underset{\sim}{P}_{Q_i} = \mathrm{Tr}\left(\underset{\sim}{P}_{Q_i}\underset{\sim}{P}_{Q_i}{}^t\right) , \tag{223}$$

where,

$$P_{xQ_i} \equiv \frac{\partial P_x}{\partial Q_i} , \tag{224}$$

and

$$\underset{\sim}{P}_{Q_i} \equiv \begin{pmatrix} P_{xQ_i} \\ P_{yQ_i} \\ P_{zQ_i} \end{pmatrix} . \tag{225}$$

If the molecule has fairly high symmetry, then the change in the dipole moment during the normal vibration, Q_i, may lie along a certain characteristic direction associated with the molecule; thus, only one of the three components of $\partial\vec{P}/\partial Q_i$ will not vanish.

The 3N-6 internal coordinates,

$$\underset{\sim}{R} = \begin{pmatrix} R_1 \\ R_2 \\ \cdot \\ \cdot \\ \cdot \\ R_i \\ \cdot \\ \cdot \\ \cdot \\ R_{3N-6} \end{pmatrix} , \tag{226}$$

are related to the 3N-6 column matrix $\underset{\sim}{Q}$, representing the normal coordinates, according to

$$\underset{\sim}{R} = \underset{\sim}{L}\,\underset{\sim}{Q} \tag{227}$$

or

$$R_j = \sum_{i}^{3N-6} L_{ji}Q_i , \tag{228}$$

where $\underset{\sim}{L}$ is the (3N-6) x (3N-6) matrix that transforms the normal coordinates to internal ones. In addition,

$$\frac{\partial P_x}{\partial Q_i} = \sum_j^{3N-6} \frac{\partial P_x}{\partial R_j} \frac{\partial R_j}{\partial Q_i} , \tag{229}$$

and, according to Eqn.(228),

$$\frac{\partial R_j}{\partial Q_i} = L_{ji} . \tag{230}$$

Thus, substituting Eqn.(230) into Eqn.(229), one obtains

$$P_{xQ_i} \equiv \frac{\partial P_x}{\partial Q_i} = \sum_j^{3N-6} \frac{\partial P_x}{\partial R_j} L_{ji} = \sum_j^{3N-6} P_{xR_j} L_{ji} \tag{231}$$

or

$$\underset{\sim}{P}_{xQ} = \underset{\sim}{L}^t \underset{\sim}{P}_{xR} , \tag{232}$$

where

$$P_{xR_j} \equiv \frac{\partial P_x}{\partial R_j} , \tag{233}$$

$$\underset{\sim}{P}_{xQ} \equiv \begin{pmatrix} P_{xQ_1} \\ P_{xQ_2} \\ \cdot \\ \cdot \\ \cdot \\ P_{xQ_i} \\ \cdot \\ \cdot \\ \cdot \\ P_{xQ_{3N-6}} \end{pmatrix} , \tag{234}$$

and

$$\underset{\sim}{P}_{xR} \equiv \begin{pmatrix} P_{xR_1} \\ P_{xR_2} \\ \cdot \\ \cdot \\ \cdot \\ P_{xR_i} \\ \cdot \\ \cdot \\ \cdot \\ P_{xR_{3N-6}} \end{pmatrix} . \tag{235}$$

Thus, from Eqns.(221), (222), and (231), and from the rules of matrix multiplication, one obtains

$$A_i = K\left[\left(\underset{\sim}{L}^t\ \underset{\sim}{P}_{xR}\right)_{il}^{2} + \left(\underset{\sim}{L}^t\ \underset{\sim}{P}_{yR}\right)_{il}^{2} + \left(\underset{\sim}{L}^t\ \underset{\sim}{P}_{zR}\right)_{il}^{2}\right] . \qquad (236)$$

It is therefore necessary to know the $\underset{\sim}{L}$ matrix, if the individual band intensity, A_i, is to be determined from the dipole moment derivatives with respect to the internal coordinates. The evaluation of $\underset{\sim}{L}$ can be accomplished if the internal force constants for the vibrations are known (31). However, the B term of Eqn.(217) is a function of the <u>total</u> intensity, i.e., the sum of all the A_i's:

$$\sum_{i}^{3N-6} A_i = K \sum_{i}^{3N-6} \left|\frac{\partial \vec{P}}{\partial Q_i}\right|^2 . \qquad (237)$$

Therefore, Eqns.(222) and (223) become

$$\sum_{i}^{3N-6} \left|\frac{\partial \vec{P}}{\partial Q_i}\right|^2 = \sum_{i}^{3N-6} \sum_{x}^{3} \left(\frac{\partial P_x}{\partial Q_i}\right)^2 = \sum_{i}\sum_{x} \left(P_{xQ_i}\right)^2 \qquad (238)$$

$$= \underset{\sim}{P}_Q^{\,t}\ \underset{\sim}{P}_Q = \mathrm{Tr}\left(\underset{\sim}{P}_Q\ \underset{\sim}{P}_Q^{\,t}\right) \qquad (239)$$

$$= \sum_{x}^{3} \underset{\sim}{P}_{xQ}^{\,t}\ \underset{\sim}{P}_{xQ} = \sum_{x}^{3} \mathrm{Tr}\left(\underset{\sim}{P}_{xQ}\ \underset{\sim}{P}_{xQ}^{\,t}\right) \qquad (240)$$

$$= \sum_{i}^{3N-6} \underset{\sim}{P}_{Q_i}^{\,t}\ \underset{\sim}{P}_{Q_i} = \sum_{i}^{3N-6} \mathrm{Tr}\left(\underset{\sim}{P}_{Q_i}\ \underset{\sim}{P}_{Q_i}^{\,t}\right) . \qquad (241)$$

In Eqn.(239), $\underset{\sim}{P}_Q$ is a (3N-6) x 3 matrix that is composed of 3N-6 submatrices according to

$$\underset{\sim}{P}_Q \equiv \begin{pmatrix} \underset{\sim}{P}_{Q_1}{}^t \\ \underset{\sim}{P}_{Q_2}{}^t \\ \cdot \\ \cdot \\ \cdot \\ \underset{\sim}{P}_{Q_i}{}^t \\ \cdot \\ \cdot \\ \cdot \\ \underset{\sim}{P}_{Q_{3N-6}}{}^t \end{pmatrix} , \qquad (242)$$

where $\underset{\sim}{P}_{Q_i}$ is a 3 x 1 column matrix defined by Eqn.(225). In addition, Wilson's $\underset{\sim}{G}$ matrix (31) is related to the transformation matrix $\underset{\sim}{L}$ according to

$$\underset{\sim}{L}\,\underset{\sim}{L}^t = \underset{\sim}{G} \; . \qquad (243)$$

Hence, substituting Eqn.(232) into Eqn.(240) and using Eqn.(243), one obtains for the total intensity, Eqn.(237),

$$\sum_{i}^{3N-6} A_i = K \sum_{x}^{3} \underset{\sim}{P}_{xR}{}^t \, \underset{\sim}{G} \, \underset{\sim}{P}_{xR} \; . \qquad (244)$$

Thus, the evaluation of the *total* intensity through the dipole moment derivatives does not have to depend on the availability of vibrational force constants; the $\underset{\sim}{G}$ matrix is merely a function of the atomic masses and of the equilibrium molecular geometry.

IV.E.2. Dipole Moment Derivatives with Respect to Cartesian Coordinates

The transformation of the total intensity into an expression involving internal coordinates has been presented in the previous section. Now the sum of all 3N-6 individual intensities will be expressed as a function of the cartesian coordinates of the N atoms in the molecule. The following coordinate transformations (102) are needed for the new intensity representation:

$$\underset{\sim}{R} = \underset{\sim}{B}\,\underset{\sim}{X}\ , \tag{245}$$

$$\underset{\sim}{\rho} = \underset{\sim}{\beta}\,\underset{\sim}{X}\ , \tag{246}$$

and

$$\underset{\sim}{X} = \underset{\sim}{A}\,\underset{\sim}{R} + \underset{\sim}{\alpha}\,\underset{\sim}{\rho}\ . \tag{247}$$

In the above equations, $\underset{\sim}{R}$, $\underset{\sim}{\rho}$, and $\underset{\sim}{X}$ are the column matrices of the 3N-6 internal, the 6 external, and the 3N cartesian coordinates, respectively. $\underset{\sim}{R}$ is given by Eqn.(226),

$$\underset{\sim}{\rho} \equiv \begin{pmatrix} T_x \\ T_y \\ T_z \\ R_x \\ R_y \\ R_z \end{pmatrix}, \tag{248}$$

which represents the 3 translations and the 3 rotations of the whole molecule, and $\underset{\sim}{X}$ is a 3N x 1 column matrix that is composed of N submatrices according to

$$\underset{\sim}{X} \equiv \begin{pmatrix} \underset{\sim}{X}_1 \\ \underset{\sim}{X}_2 \\ \cdot \\ \cdot \\ \cdot \\ \underset{\sim}{X}_\alpha \\ \cdot \\ \cdot \\ \cdot \\ \underset{\sim}{X}_N \end{pmatrix}, \tag{249}$$

where

$$\underset{\sim}{X}_{\alpha} \equiv \begin{pmatrix} X_{\alpha} \\ Y_{\alpha} \\ Z_{\alpha} \end{pmatrix} \tag{250}$$

is the matrix representation of the displacement vector of the α-th atom. In addition, $\underset{\sim}{B}(3N-6 \times 3N)$ and $\underset{\sim}{\beta}(6 \times 3N)$ are the transformation matrices from the cartesian displacement coordinates to the internal and to the external coordinates, respectively; they are composed of N submatrices according to

$$\underset{\sim}{B} = \begin{pmatrix} \underset{\sim}{B}(1) & \underset{\sim}{B}(2) & \ldots & \underset{\sim}{B}(\alpha) & \ldots & \underset{\sim}{B}(N) \end{pmatrix} \tag{251}$$

and

$$\underset{\sim}{\beta} = \begin{pmatrix} \underset{\sim}{\beta}(1) & \underset{\sim}{\beta}(2) & \ldots & \underset{\sim}{\beta}(\alpha) & \ldots & \underset{\sim}{\beta}(N) \end{pmatrix} , \tag{252}$$

where $\underset{\sim}{B}(\alpha)$ and $\underset{\sim}{\beta}(\alpha)$ are $(3N-6) \times 3$ and 6×3 submatrices, respectively. Furthermore, if the external motions of the molecule are occurring relative to the principal axes a, b, and c, with the origin at the center of mass of the molecule, then (96)

$$\underset{\sim}{\beta}(\alpha) \equiv \begin{pmatrix} m_\alpha M^{-\frac{1}{2}} & 0 & 0 \\ 0 & m_\alpha M^{-\frac{1}{2}} & 0 \\ 0 & 0 & m_\alpha M^{-\frac{1}{2}} \\ 0 & -m_\alpha c_\alpha I_a^{-\frac{1}{2}} & m_\alpha b_\alpha I_a^{-\frac{1}{2}} \\ m_\alpha c_\alpha I_b^{-\frac{1}{2}} & 0 & -m_\alpha a_\alpha I_b^{-\frac{1}{2}} \\ -m_\alpha b_\alpha I_c^{-\frac{1}{2}} & m_\alpha a_\alpha I_c^{-\frac{1}{2}} & 0 \end{pmatrix} . \qquad (253)$$

In the above equation, m_α is the mass of the α-th atom, M is the molecular mass, i.e.,

$$M = \sum_{\alpha}^{N} m_\alpha , \qquad (254)$$

I_a, I_b, and I_c are the moments of inertia about the respective equilibrium principal axes, and a_α, b_α, and c_α are the equilibrium coordinates of the α-th atom along the principal axes, measured from the center of mass of the molecule. The above form of $\underset{\sim}{\beta}(\alpha)$ insures the orthonormality of $\underset{\sim}{\delta}$,

$$\underset{\sim}{\delta} = \left[\underset{\sim}{\delta}(1) \; \underset{\sim}{\delta}(2) \; \ldots \; \underset{\sim}{\delta}(\alpha) \; \ldots \; \underset{\sim}{\delta}(N) \right] , \qquad (255)$$

where (31)

$$\underset{\sim}{\delta}(\alpha) = m_{\alpha}^{-\frac{1}{2}} \underset{\sim}{\beta}(\alpha) \ . \tag{256}$$

(Note: some authors (28, 53) use M^{-1} and I^{-1} as the "normalizing" coefficients, instead of $M^{-\frac{1}{2}}$ and $I^{-\frac{1}{2}}$, which were used here.) The matrices $\underset{\sim}{A}$(3N x 3N-6) and $\underset{\sim}{\alpha}$(6 x 3N) of Eqn.(247), transform the 3N-6 internal and the 6 external coordinates, respectively, to the 3N cartesian coordinates.

If the internal, external, and cartesian coordinates each represent a linearly independent set, then the following relationships would exist among the transformation matrices $\underset{\sim}{A}$, $\underset{\sim}{\alpha}$, $\underset{\sim}{B}$, and $\underset{\sim}{\beta}$, resulting in either the unit or null matrices, $\underset{\sim}{E}$ or $\underset{\sim}{0}$, respectively:

$$\underset{\sim}{A}\underset{\sim}{B} + \underset{\sim}{\alpha}\underset{\sim}{\beta} = \underset{\sim}{E}(3N \text{ x } 3N) \ , \tag{257}$$

$$\underset{\sim}{B}\underset{\sim}{A} = \underset{\sim}{E}(3N-6 \text{ x } 3N-6), \tag{258}$$

$$\underset{\sim}{\beta}\underset{\sim}{\alpha} = \underset{\sim}{E}(6 \text{ x } 6), \tag{259}$$

$$\underset{\sim}{\beta}\underset{\sim}{A} = \underset{\sim}{0}(6 \text{ x } 3N-6) \ , \tag{260}$$

and

$$\underset{\sim}{B}\underset{\sim}{\alpha} = \underset{\sim}{0}(3N-6 \text{ x } 6). \tag{261}$$

From the rules of partial differentiation, one obtains

$$\frac{\partial P_x}{\partial X_c} = \sum_{i}^{3N-6} \frac{\partial P_x}{\partial R_i} \frac{\partial R_i}{\partial X_c} + \sum_{e}^{6} \frac{\partial P_x}{\partial \rho_e} \frac{\partial \rho_e}{\partial X_c} , \qquad (262)$$

where c=1, 2, ..., 3N. Furthermore, differentiation of Eqns.(245) and (246) yields the following respective coefficients:

$$\frac{\partial R_i}{\partial X_c} = B_{ic} \qquad (263)$$

and

$$\frac{\partial \rho_e}{\partial X_c} = \beta_{ec} . \qquad (264)$$

Thus, with these substitutions, Eqn.(262) becomes

$$P_{xc} = \sum_{i}^{3N-6} P_{xR_i} B_{ic} + \sum_{e}^{6} P_{xe} \beta_{ec} \qquad (265)$$

or

$$\underset{\sim}{P}_{xX}^{\;t} = \underset{\sim}{P}_{xR}^{\;t} \underset{\sim}{B} + \underset{\sim}{P}_{x\rho}^{\;t} \underset{\sim}{\beta} , \qquad (266)$$

where

$$P_{xc} \equiv \frac{\partial P_x}{\partial X_c} \tag{267}$$

and

$$P_{xe} \equiv \frac{\partial P_x}{\partial \rho_e} \; . \tag{268}$$

Moreover, $\underset{\sim}{P}_{xR}$ is given by Eqn.(235), $\underset{\sim}{P}_{xX}$(3N x 1) and $\underset{\sim}{P}_{x\rho}$(6 x 1) are given by

$$\underset{\sim}{P}_{xX} \equiv \begin{pmatrix} \partial P_x/\partial X_1 \\ \partial P_x/\partial Y_1 \\ \partial P_x/\partial Z_1 \\ \partial P_x/\partial X_2 \\ \vdots \\ \partial P_x/\partial X_\alpha \\ \partial P_x/\partial Y_\alpha \\ \partial P_x/\partial Z_\alpha \\ \vdots \\ \partial P_x/\partial Z_N \end{pmatrix} , \tag{269}$$

and similarly,

$$\underset{\sim}{P}_{x\rho} \equiv \begin{pmatrix} \partial P_x/\partial T_x \\ \partial P_x/\partial T_y \\ \partial P_x/\partial T_z \\ \partial P_x/\partial R_x \\ \partial P_x/\partial R_y \\ \partial P_x/\partial R_z \end{pmatrix} . \tag{270}$$

In Eqn.(244), the $\underset{\sim}{G}$ matrix is a 3N-6 by 3N-6 representation of the interactions between the internal coordinates. It is one of four submatrices of the overall 3N x 3N $\underset{\sim}{G}^{CC}$ matrix, which represents the interactions between the cartesian (C) coordinates; thus,

$$\underset{\sim}{G}^{CC} = \left|\begin{array}{c|c} \hline \underset{\sim}{G}^{II} & \underset{\sim}{G}^{IE} \\ \hline \underset{\sim}{G}^{EI} & \underset{\sim}{G}^{EE} \\ \hline \end{array}\right| , \tag{271}$$

where,

$$\underset{\sim}{G}^{II}(3N-6 \times 3N-6) = \underset{\sim}{B}\underset{\sim}{M}^{-1}\underset{\sim}{B}^{t} , \tag{272}$$

$$\underset{\sim}{G}^{IE}(3N-6 \text{ x } 6) = \underset{\sim}{B}\underset{\sim}{M}^{-1}\underset{\sim}{\beta}^{t} \ , \tag{273}$$

$$\underset{\sim}{G}^{EI}(6 \text{ x } 3N-6) = \underset{\sim}{\beta}\underset{\sim}{M}^{-1}\underset{\sim}{B}^{t} = \left(\underset{\sim}{G}^{IE}\right)^{t} \ , \tag{274}$$

$$\underset{\sim}{G}^{EE}(6 \text{ x } 6) = \underset{\sim}{\beta}\underset{\sim}{M}^{-1}\underset{\sim}{\beta}^{t} \ , \tag{275}$$

and $\underset{\sim}{M}^{-1}$ is a 3N x 3N diagonal matrix of the reciprocal atomic masses. $\underset{\sim}{G}^{IE}$, $\underset{\sim}{G}^{EI}$, and $\underset{\sim}{G}^{EE}$ represent the internal-external, external-internal, and external-external interactions, respectively. Thus, Eqn.(244) can be rewritten as

$$\sum_{i}^{3N-6} A_i = K \sum_{x}^{3} \underset{\sim}{P}_{xR}{}^{t} \ \underset{\sim}{G}^{II} \ \underset{\sim}{P}_{xR} \ . \tag{276}$$

IV.E.2.a. Effective atomic charges and atomic polar tensors

The cartesian coordinate representation can now be presented by substituting Eqns.(272) and (266) into Eqn.(276). Thus,

$$\sum_{i}^{3N-6} A_i = K \sum_{x}^{3} \left[\underset{\sim}{P}_{xX}{}^{t} \underset{\sim}{M}^{-1} \underset{\sim}{P}_{xX} - 2\underset{\sim}{P}_{x\rho}{}^{t} \underset{\sim}{\beta}\underset{\sim}{M}^{-1} \underset{\sim}{P}_{xX} + \underset{\sim}{P}_{x\rho}{}^{t} \underset{\sim}{G}^{EE} \underset{\sim}{P}_{x\rho} \right] \ . \tag{277}$$

A further substitution of Eqn.(266) into Eqn.(277) is made, in order to rewrite the second term in the brackets of Eqn.(277). Thus, Eqn.(277)

becomes

$$\sum_{i}^{3N-6} A_i = K\left(\sum_{\alpha}^{N} \mu_\alpha \xi_\alpha^{\,2} - \Omega - 2D\right) . \qquad (278)$$

In the above equation, Ω and D represent the external-external and the internal-external interactions, respectively. These contributions are subtracted from the overall intensity term, $\Sigma\mu_\alpha\xi_\alpha^{\,2}$, because only the intensities of the genuine vibrations are desired, according to the left-hand side of Eqn.(278). Ω and D are given by

$$\Omega \equiv \sum_{x}^{3} \underset{\sim}{P}_{x\rho}\,{}^{t}\underset{\sim}{G}^{EE}\underset{\sim}{P}_{x\rho} \qquad (279)$$

and

$$D \equiv \sum_{x}^{3} \underset{\sim}{P}_{x\rho}\,{}^{t}\underset{\sim}{G}^{EI}\underset{\sim}{P}_{xR} \qquad (280)$$

$$= \sum_{x}^{3} \underset{\sim}{P}_{x\rho}\,{}^{t}\underset{\sim}{\beta}\underset{\sim}{M}^{-1}\underset{\sim}{P}_{xX} - \Omega . \qquad (281)$$

In Eqn.(281),

$$(M^{-1})_{ab} = \mu_\alpha \delta_{ab} , \qquad (282)$$

where $a = \alpha, x$; $b = \beta, y$; $\alpha, \beta = 1, \ldots, N$; $x, y = 1, 2, 3$; δ_{ab} is the Kronecker delta; and μ_α is the reciprocal mass of atom α, and is given by Eqn.(104). In addition, ξ_α is the "effective charge" of atom α (31, 96, 101, 103), which can be considered to be the charge produced on an atom during its vibrational motion, while it is not directly related to the equilibrium nuclear charge. This charge is a result of the new atomic position and of the consequent change of the electron distribution about that atom (31). ξ_α is an isotope-independent atomic property, and is given by the following equivalent expressions:

$$\xi_\alpha \equiv \left| \frac{\partial \vec{P}}{\partial \vec{r}_\alpha} \right| \tag{283}$$

and

$$\xi_\alpha^{\,2} = \left(\frac{\partial \vec{P}}{\partial X_\alpha} \right)^2 + \left(\frac{\partial \vec{P}}{\partial Y_\alpha} \right)^2 + \left(\frac{\partial \vec{P}}{\partial Z_\alpha} \right)^2 = \mathrm{Tr}\left(\underset{\sim}{P}_X(\alpha)\ \underset{\sim}{P}_X(\alpha)^t \right) , \tag{284}$$

where $\underset{\sim}{P}_X(\alpha)$ is the "atomic polar tensor" for atom α (96, 103-110),

$$\underset{\sim}{P}_X(\alpha) \equiv \begin{pmatrix} \frac{\partial P_x}{\partial X_\alpha} & \frac{\partial P_x}{\partial Y_\alpha} & \frac{\partial P_x}{\partial Z_\alpha} \\ \frac{\partial P_y}{\partial X_\alpha} & \frac{\partial P_y}{\partial Y_\alpha} & \frac{\partial P_y}{\partial Z_\alpha} \\ \frac{\partial p_z}{\partial X_\alpha} & \frac{\partial P_z}{\partial Y_\alpha} & \frac{\partial P_z}{\partial Z_\alpha} \end{pmatrix} . \tag{285}$$

IV.E.2.b. Gas-phase infrared intensities and the non-rotation correction

For gas-phase intensities, the D term in Eqn.(278) vanishes, because of the (assumed) non-existent internal-external interactions for gas molecules; thus

$$\underset{\sim}{G}^{EI}(\text{gas}) = \underset{\sim}{0} \; , \tag{286}$$

which leads to a null D term, Eqn.(280). Hence, the total gas-phase intensity is

$$\sum_{i}^{3N-6} A_i(g) = K\left(\sum_{\alpha}^{N} \mu_\alpha \, \xi_\alpha{}^2 - \Omega \right), \tag{287}$$

where the non-rotation correction, Ω, may be evaluated from Eqn.(279) in the following way. If the normalizing coefficients for $\underset{\sim}{\beta}(\alpha)$ are as given in Eqn.(253), then, from Eqn.(275), $\underset{\sim}{G}^{EE}$ becomes a 6 x 6 unit matrix $\underset{\sim}{E}$, and the 6 x 1 column matrix $\underset{\sim}{P}_{x\rho}$ of Eqn.(270) can be considered to be one of three sumatrices of the molecular $\underset{\sim}{P}_\rho$ (6 x 3) matrix. Thus,

$$\underset{\sim}{P}_\rho \equiv \left(\underset{\sim}{P}_{x\rho} \; \underset{\sim}{P}_{y\rho} \; \underset{\sim}{P}_{z\rho} \right) \; , \tag{288}$$

which yields (96, 102, 104)

$$\underset{\sim}{P}_{\rho} = \left[\begin{array}{ccc} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \hline 0 & -P_c I_a^{-\frac{1}{2}} & P_b I_a^{-\frac{1}{2}} \\ P_c I_b^{-\frac{1}{2}} & 0 & -P_a I_b^{-\frac{1}{2}} \\ -P_b I_c^{-\frac{1}{2}} & P_a I_c^{-\frac{1}{2}} & 0 \end{array}\right] , \qquad (289)$$

where the subscripts a, b, and c refer to the principal axes of the molecule. This is the matrix representation of the change in the molecular dipole moment, this change being a result of the external motions, i.e., translations and rotations. Thus, the upper 3 x 3 block of Eqn.(289) consists entirely of null elements, because a rigid translation of the whole molecule will not alter the dipole moment. The vanishing diagonal elements of the lower 3 x 3 block are due to the fact that a rotation about the a- (or b- or c-) axis will not change the a (or b or c) component of the molecular dipole moment. Therefore, in terms of the principal axes, Ω becomes

$$\Omega = (P_b^2 + P_c^2)I_a^{-1} + (P_a^2 + P_c^2)I_b^{-1} + (P_a^2 + P_b^2)I_c^{-1} \ . \qquad (290)$$

However, both Ω and D vanish for non-polar molecules, according to Eqns.(279) and (280), because $\underset{\sim}{P}_{x\rho}$ is a null matrix for these molecules.

If the normalizing coefficients of Eqn.(253) were M^{-1} and I^{-1} instead of $M^{-\frac{1}{2}}$ and $I^{-\frac{1}{2}}$, respectively, then $\underset{\sim}{G}^{EE}$ would not be a unit matrix, rather, it would become

$$\underset{\sim}{G}^{EE} = \begin{pmatrix} M^{-1} & & & & & \\ & M^{-1} & & & 0 & \\ & & M^{-1} & & & \\ & & & I_a^{-1} & & \\ & 0 & & & I_b^{-1} & \\ & & & & & I_c^{-1} \end{pmatrix} , \qquad (291)$$

where M^{-1} is the reciprocal molecular mass, Eqn.(254). Thus, the moment of inertia factors, $I^{-\frac{1}{2}}$, would not appear in Eqn.(289), and Ω would again be given by Eqn.(290).

The non-rotation term, Ω, is a property of the molecule as a whole, and may be expressed in any coordinate reference frame, according to the following relation (104):

$$\Omega = \mathrm{Tr}\left(\underset{\sim}{P}\ \underset{\sim}{I}^{-1}\ \underset{\sim}{P}^{t}\right) . \qquad (292)$$

$\underset{\sim}{P}$ is given by

$$\underset{\sim}{P} \equiv \begin{pmatrix} 0 & P_z & -P_y \\ -P_z & 0 & P_x \\ P_y & -P_x & 0 \end{pmatrix} , \qquad (292a)$$

and it is an anti-symmetric dipole-moment tensor, i.e.,

$$\underset{\sim}{P} = -\underset{\sim}{P}^{t} , \tag{293}$$

and

$$\underset{\sim}{I} \equiv \begin{pmatrix} I_x & -I_{xy} & -I_{xz} \\ -I_{xy} & I_y & -I_{yz} \\ -I_{xz} & -I_{yz} & I_z \end{pmatrix} , \tag{294}$$

is the symmetric moments-of-inertia tensor. The subscripts x, y, and z refer to <u>any</u> cartesian coordinate axes with the origin at the center of mass of the particular isotopic molecule, and do not necessarily refer to the principal axes of the particular molecular species. Since the trace of a tensor is invariant with respect to a coordinate transformation, Ω and ξ_α, as given by Eqns.(292) and (284), are fundamental molecular and atomic properties, respectively, and are not dependent on a particular coordinate system chosen for the molecule.

In order to determine $\delta\Omega$, the isotopic difference in Ω, the expression for Ω in Eqn.(292) is simplified by choosing a parallel set of axes for the two isotopic molecules. This choice is done in such a way that the molecular dipole moment $\vec{P}$ lies along one of the axes, say, the z-axis; thus,

$$P_z = P_0 = |\vec{P}| = |\vec{P}'| , \tag{295}$$

while $P_x=P_y=0$. Upon substitution of these latter null values into the expanded expression for Ω, one obtains for the isotope-dependent Ω',

$$\Omega' = P_0^2\left[(\underset{\sim}{I}'^{-1})_{11} + (\underset{\sim}{I}'^{-1})_{22}\right] , \tag{296}$$

if

$$\vec{P} = P_0\vec{k} , \tag{297}$$

$$\vec{P}' = P_0\vec{k}' , \tag{298}$$

and

$$\vec{k} \cdot \vec{k}' = 1 , \tag{299}$$

where $\vec{k}$ is a unit vector directed along the z axis. The primed (') and unprimed properties refer to the lighter and to the heavier isotopic molecules, respectively. In Eqn.(296), $(\underset{\sim}{I}^{-1})_{11}$ is the (1,1)- element of the $\underset{\sim}{I}^{-1}$ matrix and is given by

$$(\underset{\sim}{I}^{-1})_{11} = \frac{1}{\det I}(I_{yy}I_{zz} - I_{yz}^2), \tag{300}$$

and

$$(\underset{\sim}{I}^{-1})_{22} = \frac{1}{\det I}(I_{xx}I_{zz} - I_{xz}^2) , \tag{301}$$

where det I is the determinant of matrix $\underset{\sim}{I}$ of Eqn.(294). Thus, if the axes x, y, and z are the principal axes of the molecule, a, b, and c, then

$$I_a = I_{xx},\ I_b = I_{yy},\ I_c = I_{zz}\ , \tag{302}$$

and $I_{yz} = I_{xz} = 0$, which leads to Eqn.(290).

The isotope effect on the zero point energy shift upon condensation, the B-factor, can now be expressed in terms of both the fundamental properties of the two isotopic molecules, and of the contributions from atomic parameters. Thus, the last factor of Eqn.(217) becomes

$$\delta \sum_{i}^{3N-6} A_i(g) = \sum_{i}^{3N-6} \delta A_i(g) = \frac{N_0 \pi}{3c^2}\left(\sum_{\alpha}^{N} \xi_\alpha{}^2 \delta\mu_\alpha - \delta\Omega \right) . \tag{303}$$

The isotopic difference for the ZPE shift upon condensation of the gaseous molecules is directly related to the square of the effective charge(s) of the isotopically substituted atom(s).

IV.E.2.c. Condensed-phase infrared intensities

For liquid-phase infrared absorption band intensities, the D term of Eqn.(278) does not vanish. This is due to the presence of internal-external contributions to the total intensity, which result from the intermolecular interactions. In addition, the potential energy of the condensed phase, unlike that of the gas-phase, cannot be adequately described without the inclusion of force constants that involve the external coordinates $\underset{\sim}{\rho}$ of Eqn.(246) (28, 53). However, these external coordinates depend on isotopic masses, according to the $\underset{\sim}{\beta}$ matrix, Eqn.(253), and this would be in direct conflict with one of the major concepts of isotope-effect studies, the Born-Oppenheimer approximation. The isotopic dependence would cause the potential energy surface to be dependent on isotopic substitution. This dilemma was solved by using six isotope-independent external coordinates that correspond to one of the isotopic molecules, the "basis" molecule, for *all* the isotopic species of that molecule (28, 53). Thus, the $\underset{\sim}{\beta}$ matrix that is to be used is that of the basis molecule; hence, $\underset{\sim}{\beta}^0$ contains the isotope-independent elements m^0, $I_a{}^0$, $I_b{}^0$, and $I_c{}^0$.

The total liquid-phase intensity becomes

$$\sum_{i}^{3N-6} A_i(\ell) = K\left(\sum_{\alpha}^{N} \mu_\alpha \xi_\alpha{}^2 - \Omega(\ell) - 2D(\ell)\right) , \tag{304}$$

where

$$\Omega(\ell) \equiv \sum_{x}^{3} \underset{\sim}{P}_{x\rho}{}^t \, \overset{EE}{\underset{\sim}{G}}(\ell) \, \underset{\sim}{P}_{x\rho} \quad , \tag{305}$$

$$\overset{EE}{\underset{\sim}{G}}(\ell) \equiv \underset{\sim}{\beta}^0 \, \underset{\sim}{M}^{-1} \, \underset{\sim}{\beta}^{0^t} \quad , \tag{306}$$

$$D(\ell) \equiv \sum_{x}^{3} \underset{\sim}{P}_{x\rho}^{\,t} \, \underset{\sim}{G}^{EI}(\ell) \, \underset{\sim}{P}_{xR} \, , \tag{307}$$

$$= \sum_{x}^{3} \underset{\sim}{P}_{x\rho}^{\,t} \, \underset{\sim}{\beta}^{0} \, \underset{\sim}{M}^{-1} \, \underset{\sim}{P}_{xX} - \Omega(\ell) \, , \tag{308}$$

and

$$\underset{\sim}{G}^{EI}(\ell) = \underset{\sim}{\beta}^{0} \, \underset{\sim}{M}^{-1} \, \underset{\sim}{B}^{t} \, . \tag{309}$$

The isotope independence of the $\underset{\sim}{\beta}$ matrix could also have been deduced from the transformations of Eqns.(257) - (261). If the $\underset{\sim}{\beta}$- matrix were isotope-dependent, then it would follow that $\underset{\sim}{A}$ must also be isotope-dependent, due to Eqn.(260). Therefore, $\underset{\sim}{B}$ would be isotope-dependent because of Eqn.(258). However, the last statement is false, because the internal coordinates $\underset{\sim}{R}$ of Eqn.(245) are isotope-independent (31). Thus, the $\underset{\sim}{\beta}$- matrix must be isotope-independent and the concept of the "basis" molecule is necessary for condensed-phase intensities.

V. EFFECTIVE ATOMIC CHARGES FROM "CNDO" MOLECULAR ORBITAL THEORY

The isotope-independent effective charge of atom α, ξ_α, may be calculated from molecular orbital theory by first theoretically calculating the polar tensors for each atom, Eqn.(285), and then applying Eqn.(284) for ξ_α^2 (96, 107, 108). Each element of the polar tensor expresses the change in a component of the dipole moment when the atom undergoes a displacement in a cartesian direction. Thus, the method is to evaluate the molecular dipole moment for several atomic configurations, and thereby to calculate these dipole moment derivatives with respect to cartesian displacements. (Some authors calculate the dipole moment derivative with respect to an internal coordinate or to a symmetry coordinate [111-113].)

V.A. General Theory of the CNDO/2 Approach

The dipole moment was calculated by means of a modified CNDO/2 (Complete Neglect of Differential Overlap) program (111, 114-117). It is based on an approximate semi-empirical molecular orbital theory that is based on a self-consistent-field (SCF) approach. This method explicitly includes the electronic interaction between valence electrons, and it systematically neglects electron repulsion integrals that nearly vanish, especially those involving the overlap distribution of atomic orbitals, $\phi_\mu(1)\phi_\nu(1)$, $\mu \neq \nu$. This latter assumption is known as the zero-differential overlap (ZDO) approximation. CNDO/2 also makes some use of experimental data in selecting values for other integrals. The great advantage of this method is that no new parameters, other than the molecular geometry, are needed for the calculation of the dipole moment derivatives, since all empirical quantities have been previously selected in order to enable the approximate theory to agree as closely as possible with the full SCF-MO results on a number of diatomic molecules.

Incorporating these and other simplifying approximations into the CNDO/2 version, the matrix elements $F_{\mu\nu}$ of the effective one-electron Fock hamiltonian operator $\hat{F}$ of the eigenvalue problem

$$\hat{F}\psi = E\psi \tag{310}$$

can be given. In Eqn.(310), E and ψ are the eigenvalues and the eigenfunctions of the system, respectively. Hence,

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \gamma_{AB}; \quad (\mu \neq \nu,\ \phi_\mu \text{ on A},\ \phi_\nu \text{ on B}) \tag{311}$$

and

$$F_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) - \left[Q_A + \tfrac{1}{2}(P_{\mu\mu} - 1)\right]\gamma_{AA} - \sum_{B(\neq A)} Q_B \gamma_{AB}; \quad (\phi_\mu \text{ on A}). \tag{312}$$

The definitions of the terms in the above two equations are given below:

μ and ν refer to atomic orbitals (AOs);

A and B refer to atoms;

$$\beta^0_{AB} = \text{bonding parameters} = \tfrac{1}{2}(\beta^0_A + \beta^0_B); \tag{313}$$

$$S_{\mu\nu} = \text{overlap integrals} = \int \phi_\mu(1)\phi_\nu(1)d\tau_1 \ ; \tag{314}$$

$$P_{\mu\nu} = \text{bond order} = 2 \sum_{i}^{\text{occupied}} c_{\mu i} c_{\nu i} \ ; \tag{315}$$

$c_{\mu i}$ are the elements of the transformation matrix for

AO → MO as follows: the molecular orbital ψ_i^{MO} is given as a linear combination of the (valence-shell Slater-type) atomic orbitals ϕ_μ^{AO} by

$$\psi_i = \sum_\mu c_{\mu i} \phi_\mu \ ; \tag{316}$$

$$\gamma_{AB} = \text{coulomb integral} = \iint \left(\phi_{sA}(1)\right)^2 \frac{1}{r_{12}} \left(\phi_{sB}(2)\right)^2 d\tau_1 \, d\tau_2 \; ; \tag{317}$$

I_μ is the atomic ionization potential from the μ-th orbital;

A_μ is the atomic electron affinity of the μ-th orbital;

$$Q_A = \text{net charge on atom A} = Z_A(\text{eff}) - P_{AA} \; , \tag{318}$$

where $Z_A(\text{eff})$ is the effective nuclear charge of atom A, and is given by

$$Z_A(\text{eff}) = Z_A - n \begin{pmatrix} n = 2 \text{ for first-row elements} \\ n = 10 \text{ for second-row elements} \end{pmatrix} , \tag{319}$$

Z_A is the nuclear charge of atom A, and P_{AA} is the total valence electron density on atom A, i.e.,

$$P_{AA} = \sum_{\mu_A} P_{\mu\mu} \; . \tag{320}$$

V.B. Equilibrium Molecular Dipole Moments

The molecular dipole moment, within the CNDO approximations, is given by a sum of two terms (111, 114-117):

$$\vec{P} = \vec{P}_{chg} + \vec{P}_{mix} \ . \tag{321}$$

The first gives the contributions from the net atomic charges located at the nuclear positions, i.e.,

$$\vec{P}_{chg}(\text{Debyes}) = 2.5416 \sum_{A} Q_A \vec{R}_A \ , \tag{322}$$

where $\vec{R}_A$ is the position vector of nucleus A. The second contribution is due to atomic dipoles that result from the mixing of s and p orbitals on the same atom; thus,

$$P_{x,mix}(\text{Debyes}) = -7.3370 \sum_{A} \zeta_A^{-1} P_{2s(A),2px(A)} \ , \tag{323}$$

where ζ_A is the orbital exponent of the valence orbitals on atom A, and $P_{\mu\nu}$ is defined by Eqn.(315). This latter hybridization term measures the contribution due to the displacement of charge away from the center of the nuclear position.

V.C. Subroutines of the Quantum Mechanical Computer Program, CNDO/2

Figure 2 is a flow chart of the CNDO/2 quantum mechanical computer program, showing the linkage among the various subroutines of the program. The complete program listing is included in the appendix.

MAIN consists of the readings of the input data, i.e., the kind and number of atoms, the molecular geometry, and the variation of the molecular configuration. This variation scheme will be described in the next section.

COEFFT assigns the coefficients that are used in the calcualtion of the reduced overlap integrals (Subroutine SS), which determine the overlap and coulomb integrals.

INTGRL computes the overlap integral matrix ($\underset{\sim}{S}$) and the coulomb integral matrix ($\underset{\sim}{\gamma}$). The basis functions on each atom are specified by filling arrays that indicate the number of the atom on which the basis function is centered, the principal, azimuthal, and magnetic quantum numbers, and the orbital exponents.

RELVEC calculates the relative unit vector along the internuclear axis of atoms A and B.

FACT computes the factorial of a number.

SS determines the reduced overlap integrals which are a part of the overlap and coulombic integrals.

AINTGS and BINTGS evaluate the A and B integrals, which constitute the reduced overlap integrals, in part.

HARMTR forms the rotation matrix, which transforms the overlap integrals in the atomic frame back to the molecular coordinate system.

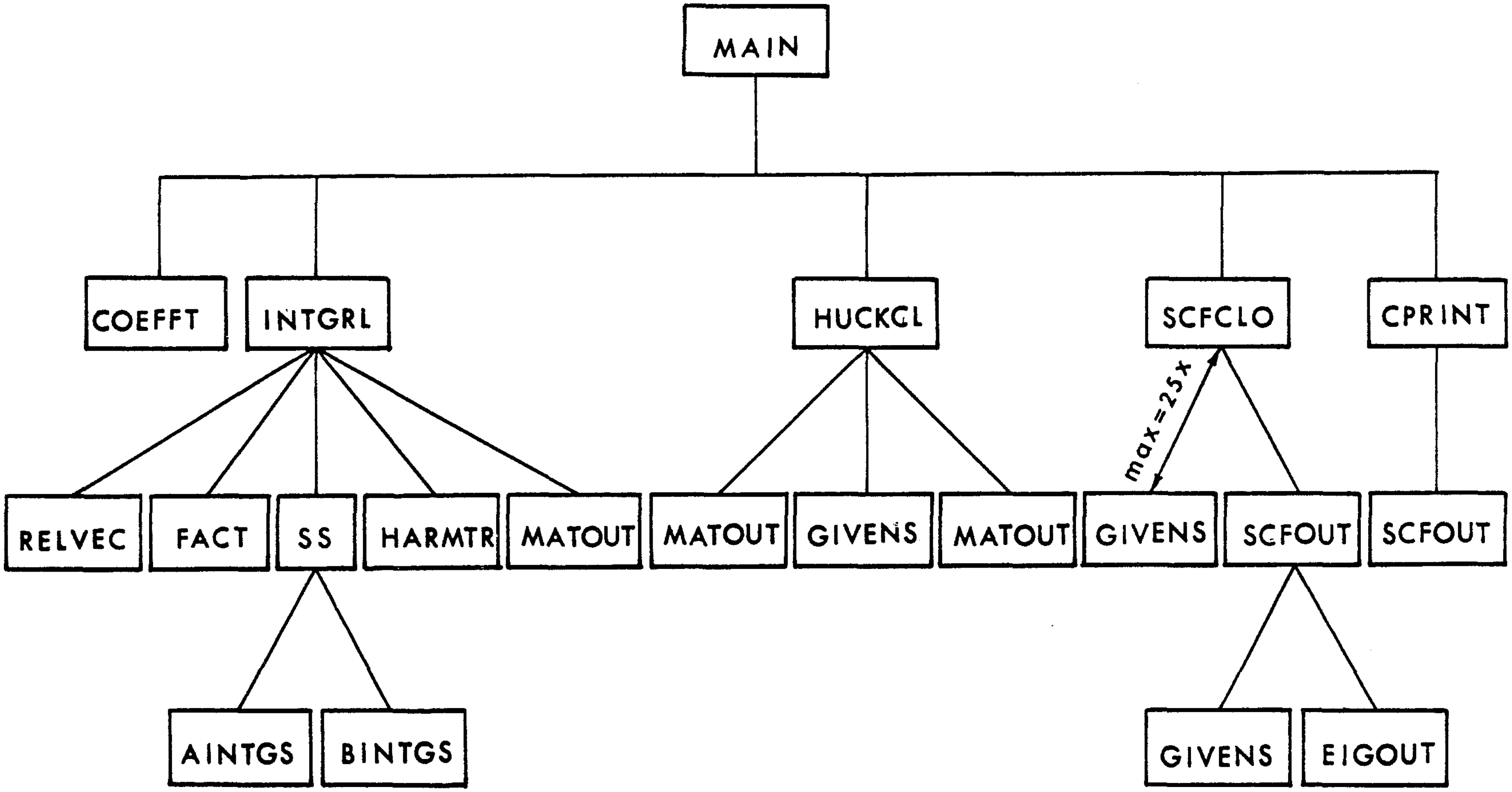

Figure 2. CNDO/2 subroutine flowchart for closed-shell molecules.

MATOUT, when called by INTGRL, prints the overlap integral matrix and the coulomb integral matrix.

HUCKCL forms a zero-differential-overlap (ZDO) extended Hückel-type (156) approximation to the Fock matrix for closed-shell molecules; thus,

$$F_{\mu\mu}^{(0)} = -\tfrac{1}{2}(I_{\mu} + A_{\mu}) \tag{324}$$

and

$$F_{\mu\nu}^{(0)} = \beta_{AB}^{0}\, S_{\mu\nu}, \quad \mu \neq \nu \, . \tag{325}$$

MATOUT, when called by HUCKCL for the first time, prints the bonding parameters β_{AB}^{0}.

GIVENS, when called by HUCKCL, diagonalizes the approximate Fock matrix $\underset{\sim}{F}^{(0)}$, and constructs an initial density matrix from the coefficients of the occupied MOs. Corrections to the hamiltonian are now added for the CNDO/2 calculations.

MATOUT, when called by HUCKCL for the second time, prints the core hamiltonian matrix.

SCFCLO is a self-consistent-field procedure for closed-shell molecules. It takes as input the initial density matrix and the CNDO/2 core hamiltonian, and forms the Fock matrix by adding the CNDO integrals. At this point, the electronic energy is computed and printed.

GIVENS, when called by SCFCLO, diagonalizes the Fock matrix and forms a new density matrix, which is used to construct a new Fock matrix by SCFCLO.

The SCFCLO-GIVENS procedure is repeated (with a maximum of 25 iterations) until successive cycles yield electronic energies that are within 10^{-6} eV of each other. Afther this self-consistency is reached, the coefficients $c_{\mu i}$ in the LCAO-MO theory are determined.

SCFOUT prints the final Fock matrix, and after this matrix has been diagonalized once more by GIVENS, the resulting eigenvectors are printed.

EIGOUT prints the eigenvalues.

CPRINT computes and prints the dipole moments, the atom densities, and the nuclear repulsion energy.

V.D. Modification of the CNDO/2 Program for the Calculation of the Atomic Polar Tensors

The MAIN program of the CNDO/2 scheme necessitated certain modifications for the calculation of the derivatives of the dipole moment with respect to an atomic cartesian displacement. The x-component of the molecular dipole moment can be expanded about the equilibrium position, by means of a Taylor series in any one of the three cartesian displacement coordinates of any atom α. Thus,

$$P_x = P_x^0 + a_0(\Delta Y_\alpha) + a_1(\Delta Y_\alpha)^2 + a_2(\Delta Y_\alpha)^3 + \cdots , \tag{326}$$

where

$$a_0 = \left(\frac{\partial P_x}{\partial Y_\alpha}\right)_0 = \lim_{\Delta Y_\alpha \to 0} \left(\frac{\Delta P_x}{\Delta Y_\alpha}\right)_0 , \tag{327}$$

$$a_1 = \frac{1}{2}\left(\frac{\partial^2 P_x}{\partial Y_\alpha^2}\right)_0 , \tag{328}$$

and

$$a_2 = \frac{1}{6}\left(\frac{\partial^3 P_x}{\partial Y_\alpha^3}\right)_0 . \tag{329}$$

In the above equations, P_x^0 represents the equilibrium x-component of the dipole moment for the undistorted molecule, ΔY_α is the displacement of atom α from the equilibrium position Y_α^0, i.e,

$$\Delta Y_\alpha = Y_\alpha - Y_\alpha^0 , \tag{330}$$

and a_0, a_1, a_2 represent the first, second, and third partial derivatives, with respect to the displacement in the Y direction, respectively, evaluated at the equilibrium position (0). Thus, Eqn.(326) becomes (77)

$$\frac{\Delta P_x}{\Delta Y_\alpha} = a_0 + a_1(\Delta Y_\alpha) + a_2(\Delta Y_\alpha)^2 , \tag{331}$$

where

$$\Delta P_x = P_x - P_x^0 . \tag{332}$$

In Eqns.(326) to (332), x may be replaced by y or z, and Y may be replaced by X or Z, in order to obtain other partial derivative expressions.

Consequently, Eqn.(327) represents the (1,2) element of the polar tensor $\underset{\sim}{P}_X(\alpha)$ of atom α, Eqn.(285). Each such element was calculated by the method described below. Only one cartesian coordinate of one atom at a time was varied slightly, while keeping the other two coordinates of that atom, and all the coordinates of the other atoms, fixed at their undistorted equilibrium configurations. A new dipole moment was evaluated for each new cartesian coordinate position of the displaced atom. This was done for both positive and negative cartesian displacements. Thus, one obtains several corresponding values for ΔY_{α} and $\Delta P_{x}/\Delta Y_{\alpha}$. A least-squares fit was applied for these points, so that the coefficients a_0, a_1, and a_2 of Eqn.(331) can be determined. Subsequently, the polar tensors were ascertained.

VI. RESULTS AND DISCUSSION

VI.A. Molecular Geometries and Inertial Constants

The molecules that were investigated include ethylene, methane, and the four fluoromethanes $CH_{4-n}F_n$ (n=1, •••, 4). The bond lengths and bond angles that were used in the investigation of these molecules are summarized in Table II. The right-handed cartesian axes that were chosen for these species are depicted in Figure 3. These are "aerial views" of the molecules, so that the C atom is "buried" by either an H or F atom in some of the molecules. Thus, in CH_4, for example, the representation

indicates that H_3 is projected downward from the central atom, C, which is overshadowed by the apex atom, H_4. The C atom is at the origin of the cartesian coordinate system for methane and the fluoromethanes. In addition, the C-H and C-H_4 bonds in CHF_3 and CH_4, respectively, and the C-F and C-F_4 bonds in CH_3F and CF_4, respectively, lie on the (positive) z-axis. In CH_2F_2, the H-C-H and F-C-F angles are bisected by the positive and negative directions, respectively, of the z-axis.

These axes are not necessarily the principal axes of the molecules.

Table II

Molecular Geometries of Ethylene, Methane, and the Fluoromethanes

Bonds and Angles	Molecule (Reference)					
	C_2H_4 (125)	CH_4 (123)	CH_3F (119)	CH_2F_2 (120-122)	CHF_3 (118)	CF_4 (118)
R(C-C) [(a)]	1.353	.....	.....	.....	.....	.....
R(C-H) [(a)]	1.071	1.091	1.106	1.092	1.098	.....
R(C-F) [(a)]	.....	.....	1.3853	1.358	1.332	1.321
∡ (H-C-H)	119°55'	109°28'	109°59'	111°52'	....	....
∡ (H-C-F) [(b)]	....	....	108°57'	....	110°08'	....
∡ (F-C-F)	....	....	....	108°17'	108°48'	109°28'

(a) Ångstrom units.

(b) Calculated from the given data.

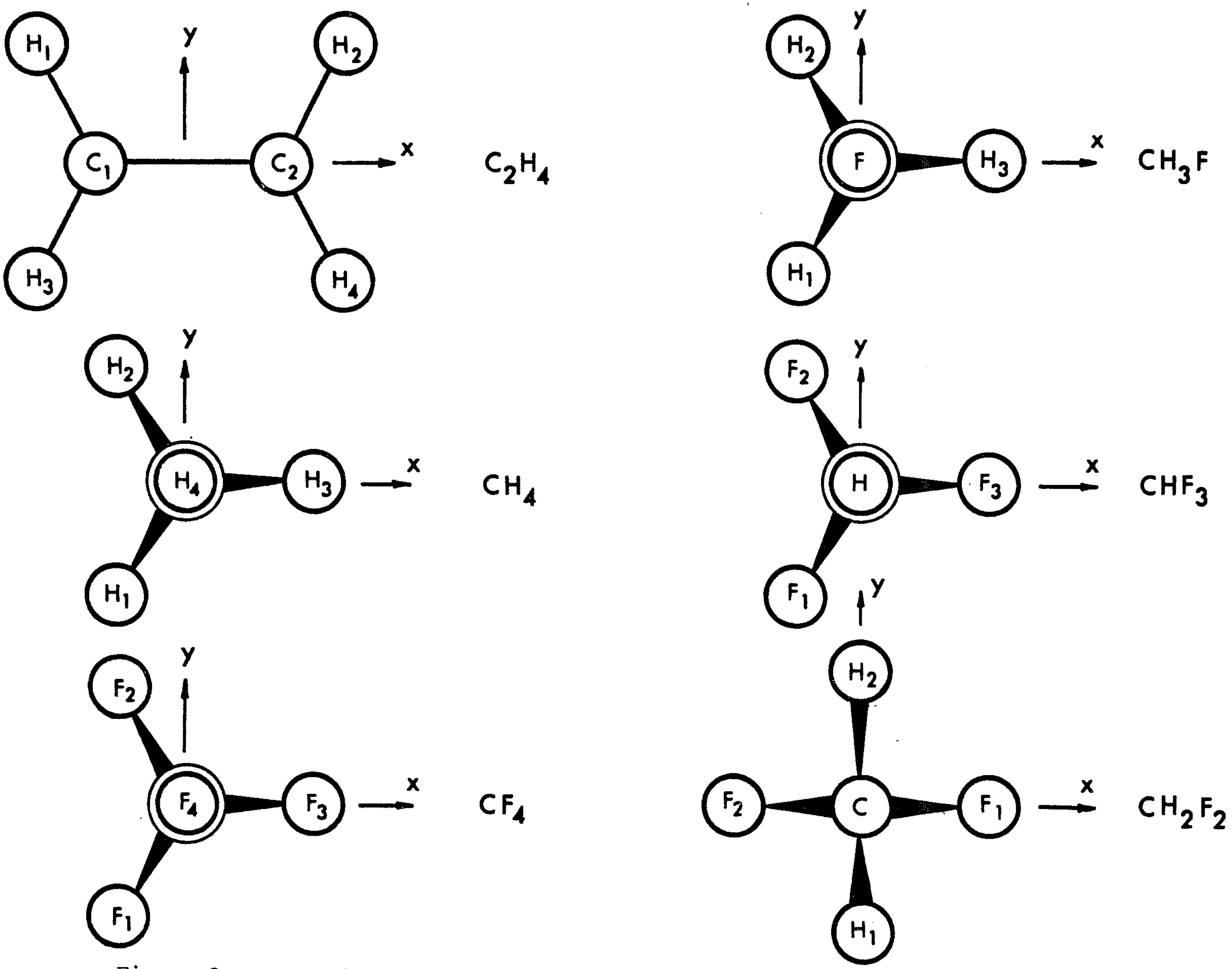

Figure 3. Cartesian axis systems for ethylene, methane, and for the fluoromethanes.

In addition, the directions of these axes are chosen to be isotope-independent throughout the calculations.

The moments of inertia tensor $\underset{\sim}{I}$, Eqn.(294), is necessary for the evaluation of the non-rotation correction Ω, Eqns.(292) or (290). Thus, for the polar molecules CHF_3, CH_2F_2, and CHF_3, the moments of inertia tensor with respect to the arbitrarily chosen coordinate system of Figure 3, as well as the principal moments, have been calculated by using the molecular geometries given by Table II and Figure 3. The results have been tabulated in Tables III-V. In addition, the center of mass of each species, relative to the axis system of Figure 3, has been included. The above calculations were done for each isotopic species of the polar fluoromethanes with respect to carbon-13 and/or deuterium substitutions. The atomic masses of the isotopes of interest are given below (124):

$$^{1}H = 1.007825 \text{ amu},$$

$$^{2}H \equiv D = 2.0140 \text{ amu},$$

$$^{12}C = 12 \text{ (exactly) amu},$$

$$^{13}C = 13.00335 \text{ amu},$$

and

$$^{19}F = 18.99840 \text{ amu}.$$

Table III

Calculations of the Molecular Mass, the Center of Mass, and the Moments of Inertia of the Carbon-13 and Deuterium Isotopes of CH_3F

Isotope	Molecular Mass (amu)	Center of Mass (see Figure 3) (Å)	Moments of Inertia Tensor, $\underset{\sim}{I}$ (amu·Å^2)	Principal Moments of Inertia: I_a, I_b, and I_c (amu·Å^2)
$^{12}CH_3F$	34.021875	$\begin{pmatrix} 0 \\ 0 \\ -0.741650 \end{pmatrix}$	$\begin{pmatrix} 19.789744 & 0 & 0 \\ 0 & 19.789744 & 0 \\ 0 & 0 & 3.308232 \end{pmatrix}$	19.789744 19.789744 3.308232
$^{13}CH_3F$	35.025225	$\begin{pmatrix} 0 \\ 0 \\ -0.720404 \end{pmatrix}$	$\begin{pmatrix} 20.325822 & 0 & 0 \\ 0 & 20.325822 & 0 \\ 0 & 0 & 3.308232 \end{pmatrix}$	20.325822 20.325822 3.308232
$^{12}CH_2DF$	35.028050	$\begin{pmatrix} -0.030047 \\ 0 \\ -0.710027 \end{pmatrix}$	$\begin{pmatrix} 20.974160 & 0 & 1.125395 \\ 0 & 22.043475 & 0 \\ 1.125395 & 0 & 4.377546 \end{pmatrix}$	21.050124 22.043475 4.301582
$^{13}CH_2DF$	36.031400	$\begin{pmatrix} -0.029210 \\ 0 \\ -0.690255 \end{pmatrix}$	$\begin{pmatrix} 21.465902 & 0 & 1.104585 \\ 0 & 22.536097 & 0 \\ 1.104585 & 0 & 4.378427 \end{pmatrix}$	21.537010 22.536097 4.307319

(continued)

Table III (continued)

$^{12}CHD_2F$	36.034225	$\begin{pmatrix}-0.014604\\-0.025295\\-0.680170\end{pmatrix}$	$\begin{pmatrix}22.895081 & 0.490032 & 0.546985\\0.490032 & 23.460921 & 0.947406\\0.546985 & 0.947406 & 5.479368\end{pmatrix}$	23.809132 22.612161 5.414077
$^{13}CHD_2F$	37.037575	$\begin{pmatrix}-0.014208\\-0.024610\\-0.661744\end{pmatrix}$	$\begin{pmatrix}23.347312 & 0.489671 & 0.537289\\0.489671 & 23.912736 & 0.930612\\0.537289 & 0.930612 & 5.480200\end{pmatrix}$	24.256944 23.064600 5.418703
$^{12}CD_3F$	37.040400	$\begin{pmatrix}0\\0\\-0.651935\end{pmatrix}$	$\begin{pmatrix}24.801359 & 0 & 0\\0 & 24.801359 & 0\\0 & 0 & 6.611047\end{pmatrix}$	24.801359 24.801359 6.611047
$^{13}CD_3F$	38.043750	$\begin{pmatrix}0\\0\\-0.634742\end{pmatrix}$	$\begin{pmatrix}25.216555 & 0 & 0\\0 & 25.216555 & 0\\0 & 0 & 6.611047\end{pmatrix}$	25.216555 25.216555 6.611047

Table IV

Calculations of the Molecular Mass, the Center of Mass, and the Moments of Inertia of the Carbon-13 and Deuterium Isotopes of CH_2F_2

Isotope	Molecular Mass (amu)	Center of Mass (see Figure 3) (Å)	Moments of Inertia Tensor, $\underset{\sim}{I}$ (amu·Å^2)	Principal Moments of Inertia: I_a, I_b, and I_c (amu·Å^2)
$^{12}CH_2F_2$	52.012450	$\begin{pmatrix} 0 \\ 0 \\ 0.557429 \end{pmatrix}$	$\begin{pmatrix} 10.286660 & 0 & 0 \\ 0 & 54.664840 & 0 \\ 0 & 0 & 47.676982 \end{pmatrix}$	10.286660 54.664840 47.676982
$^{13}CH_2F_2$	53.015800	$\begin{pmatrix} 0 \\ 0 \\ 0.546879 \end{pmatrix}$	$\begin{pmatrix} 10.592528 & 0 & 0 \\ 0 & 54.970707 & 0 \\ 0 & 0 & 47.676982 \end{pmatrix}$	10.592528 54.970707 47.676982
$^{12}CHDF_2$	53.018625	$\begin{pmatrix} 0 \\ -0.017167 \\ 0.535242 \end{pmatrix}$	$\begin{pmatrix} 12.443569 & 0 & 0 \\ 0 & 56.014023 & -1.043920 \\ 0 & -1.043920 & 48.484707 \end{pmatrix}$	12.443569 56.156080 48.342650
$^{13}CHDF_2$	54.021975	$\begin{pmatrix} 0 \\ -0.016848 \\ 0.525301 \end{pmatrix}$	$\begin{pmatrix} 12.725964 & 0 & 0 \\ 0 & 56.296128 & -1.034872 \\ 0 & -1.034872 & 48.484997 \end{pmatrix}$	12.725964 56.430909 48.350216

(continued)

Table IV (continued)

$^{12}CD_2F_2$	54.024800	$\begin{pmatrix} 0 \\ 0 \\ 0.513881 \end{pmatrix}$	$\begin{pmatrix} 14.581473 & 0 & 0 \\ 0 & 57.312952 & 0 \\ 0 & 0 & 49.323682 \end{pmatrix}$	14.581473 57.312952 49.323682
$^{13}CD_2F_2$	55.028150	$\begin{pmatrix} 0 \\ 0 \\ 0.504511 \end{pmatrix}$	$\begin{pmatrix} 14.841600 & 0 & 0 \\ 0 & 57.573079 & 0 \\ 0 & 0 & 49.323682 \end{pmatrix}$	14.841600 57.573079 49.323682

Table V

Calculations of the Molecular Mass, the Center of Mass, and the Moments of Inertia of the Carbon-13 and Deuterium Isotopes of CHF_3

Isotope	Molecular Mass (amu)	Center of Mass (see Figure 3) (Å)	Moments of Inertia Tensor, $\underset{\sim}{I}$ (amu·Å^2)	Principal Moments of Inertia: I_a, I_b, and I_c (amu·Å^2)
$^{12}CHF_3$	70.003025	$\begin{pmatrix} 0 \\ 0 \\ 0.357499 \end{pmatrix}$	$\begin{pmatrix} 48.820361 & 0 & 0 \\ 0 & 48.820361 & 0 \\ 0 & 0 & 89.140323 \end{pmatrix}$	48.820361 48.820361 89.140323
$^{13}CHF_3$	71.006375	$\begin{pmatrix} 0 \\ 0 \\ 0.352447 \end{pmatrix}$	$\begin{pmatrix} 48.946783 & 0 & 0 \\ 0 & 48.946783 & 0 \\ 0 & 0 & 89.140323 \end{pmatrix}$	48.946783 48.946783 89.140323
$^{12}CDF_3$	71.009200	$\begin{pmatrix} 0 \\ 0 \\ 0.336875 \end{pmatrix}$	$\begin{pmatrix} 50.921716 & 0 & 0 \\ 0 & 50.921716 & 0 \\ 0 & 0 & 89.140323 \end{pmatrix}$	50.921716 50.921716 89.140323
$^{13}CDF_3$	72.012550	$\begin{pmatrix} 0 \\ 0 \\ 0.332181 \end{pmatrix}$	$\begin{pmatrix} 51.033995 & 0 & 0 \\ 0 & 51.033995 & 0 \\ 0 & 0 & 89.140323 \end{pmatrix}$	51.033995 51.033995 89.140323

Inertial data was not necessary for the non-polar species C_2H_4, CH_4, and CF_4, since $\Omega=0$ as a result of the vanishing dipole moment.

VI.B. Dipole Moments and Derivatives, Polar Tensors, and Effective Charges

VI.B.1. CNDO/2 and Experimental Equilibrium Dipole Moments

The equilibrium dipole moments for the polar fluoromethanes, CH_3F, CH_2F_2, and CHF_3, have been evaluated according to the CNDO/2 scheme, Eqns.(321)-(323), and are tabulated in Tables VI and VII. The agreement between the experimental and theoretically derived values is quite satisfactory. The experimental methods only yield the absolute magnitude of the equilibrium dipole moment vector $\vec{P}_0$, whereas the quantum mechanical procedure determines the components of this vector.

The dipole moment vector is defined to be positive if it is directed <u>from</u> the negative to the positive end of the molecule, i.e.,

$$- \xrightarrow{\vec{P}} + \, .$$

Thus, from the CNDO/2 values of P_z for the polar fluoromethanes, and from Figure 3, it is seen that the dipole moment vector of the undistorted molecule is oriented from the fluorine atom(s) to the hydrogen atom(s). That signifies that the fluorines have a partial negative charge, while the hydrogens obtain a partial positive charge. Thus, the polar fluoromethanes have the following equilibrium dipoles:

$$\overset{-}{} F_n CH_{4-n}^{+}, \; n=1,\ 2, \text{ and } 3 \, .$$

Table VI

Experimental and CNDO/2 Equilibrium Dipole Moments of Gaseous CH_3F

Experimental[(a)]

Year of Publication	Temperature (^oC)	Dipole Moment, P_0[(b)] (Debye)
1953	NS[(c)]	1.79 ± 0.02
1934	-50 to 225	1.822 ± 0.01
1966	NS	1.8471
1936	-80 to 95	1.85
1970	50 to 140	1.851 ± 0.005
1970	NS	1.8549 ± 0.0010
1963	NS	1.8555 ± 0.0015
1965,66	NS	1.8572 ± 0.001
1970	NS	1.8580 ± 0.001
1966	NS	1.858 ± 0.001
1966	NS	1.8583
1965,66	NS	1.8682

Average, P_0 = 1.85

CNDO/2, P_z[(d)] = -1.71833

(a) References (126) and (127).

(b) P_0 is the absolute magnitude of $\vec{P}_0$.

(c) Temperature not specified.

(d) Also $P_x = P_y = 0$, relative to axes of Figure 3.

Table VII

Experimental and CNDO/2 Equilibrium Dipole Moments of Gaseous CH_2F_2 and CHF_3

Experimental [(a)]			CNDO/2
Year of Publication	Temperature (°C)	Dipole Moment, P_0 [(b)] (Debye)	Dipole Moment, P_z [(d)] (Debye)
		CH_2F_2	
1952	NS[(c)]	1.96 ±0.02	1.94301
		CHF_3	
1949	NS	1.59	
1935	-80 to 95	1.60	
1955	25 to 225	1.62	
1952	NS	1.64 ±0.02	
1951	NS	1.645 ±0.009	
1966	NS	1.6458	
1966	NS	1.6461	
1966	NS	1.6468	
1966	NS	1.6471	
1970	50 to 140	1.649 ±0.005	
1961	80, 160	1.65 ±0.01	
	Average	1.63	1.67547

(a) See footnote (a) of Table VI.

(b) See footnote (b) of Table VI.

(c) See footnote (c) of Table VI.

(d) See footnote (d) of Table VI.

VI.B.2. CNDO/2 Dipole Moment Derivatives

The physical significance of a dipole moment derivative can be seen by looking at the diatomic molecule AB, where the following charges exist at equilibrium:

$$^{-}A \text{——} B^{+} .$$

If the internuclear axis is on the z-axis, then the effect on the molecular dipole moment, due to the stretching vibrational motion r_{AB}, can be expressed as

$$\partial\vec{P}/\partial r_{AB} = (\partial P_z/\partial r_{AB})\vec{k} , \tag{333}$$

where $\vec{k}$ is the unit vector in the direction of the z-axis, and

$$\frac{\Delta P_z}{\Delta r_{AB}} \simeq q_0 + r_{AB} \frac{\Delta q}{\Delta r_{AB}} , \tag{333a}$$

where q is the equilibrium value of the magnitude of the charge. Thus, if $\Delta P/\Delta r > q_0$ (which is positive), then B becomes more positive as the A-B bond is stretched; if $\Delta P/\Delta r < q_0$, or if the dipole derivative is negative, then B becomes less positive than its equilibrium value, during this stretching motion.

According to the CNDO/2 scheme, there are three basic factors (111, 128) that contribute to the dipole moment derivatives, $\partial P/\partial R$, i.e., the change in the molecular dipole moment upon the distortion from its equilibrium geometry. Thus,

$$\frac{\partial P}{\partial R} = q_0 + \Delta q + q_{sp} \quad . \tag{334}$$

The first term, q_0, is due to the equilibrium charges of the atoms. The second contribution, Δq, is an intramolecular charge transfer term that leads to a change in the equilibrium charge as a result of the change in the atomic hybridization. The last term, q_{sp}, is the change in the atomic dipole moment. This change is due to the variation in the sp-type polarization of the electrons about the nuclei of the atoms.

The derivative of one of three components of the dipole moment vector with respect to one of three cartesian displacements of each atom, $\partial P_x/\partial Y_\alpha$, was calculated from the modified CNDO/2 program according to the variation scheme described in section V.D. Thus, a cartesian coordinate of an atom was altered from its equilibrium configuration by successive increments of 0.002Å for 10 positive and 10 negative displacements, while keeping all other coordinates fixed. This coordinate variation led to maximum displacements of ±0.02Å from the equilibrium value, for each atomic coordinate. A least-squares fit was applied to the functional form of Eqn.(331), which yielded the first-, second-, and third-order coefficients, a_0, a_1, and a_2. The polar tensor $\underset{\sim}{P}_X(\alpha)$, Eqn.(285), is composed of the first-order coefficients. For a molecule containing 5 atoms, the total number of variations that were needed per molecule was

(9 elements/tensor) (20 variations/element) (5 tensors/molecule)
= 900 variations.

It was found that variation of an atomic coordinate by ±0.02Å, rather than by ±0.002Å, decreased the accuracy of each tensor element by 3 to 4 orders of magnitude. This is due to the facts that the curvature at the origin is not negligible and that the smaller increment better resembles the realistic magnitudes of the vibrational amplitude. Figures 4 and 5 depict the change in the x-component of the dipole moment, ΔP_x of CH_4, which is due to the change in the x-coordinate of the H_1 atom, $\Delta X(H_1)$, for relatively large (±0.1Å) and small (±0.02Å) atomic displacements, respectively. The solid line in Figure 5 represents the more detailed plot near the equilibrium configuration, $\Delta X=0$, and it is seen that although the variation of $\vec{P}$ is almost linear, the determination of the slope at the origin, based on the displacement increments of ±0.02Å, would lead to a significant error (cf: the dashed lines in Figure 5). In addition, the plots are non-symmetric with respect to the positive and negative values of $\Delta X(H_1)$; this is expected in light of the chosen axis system of Figure 3. This tensor element, $\partial P_x/\partial X(H_1)$, represented the "worst" deviation from linearity of all the molecules that were studied in this investigation.

VI.B.3. CNDO/2 Atomic Polar Tensors

The atomic polar tensors obtained from the CNDO/2-derived first

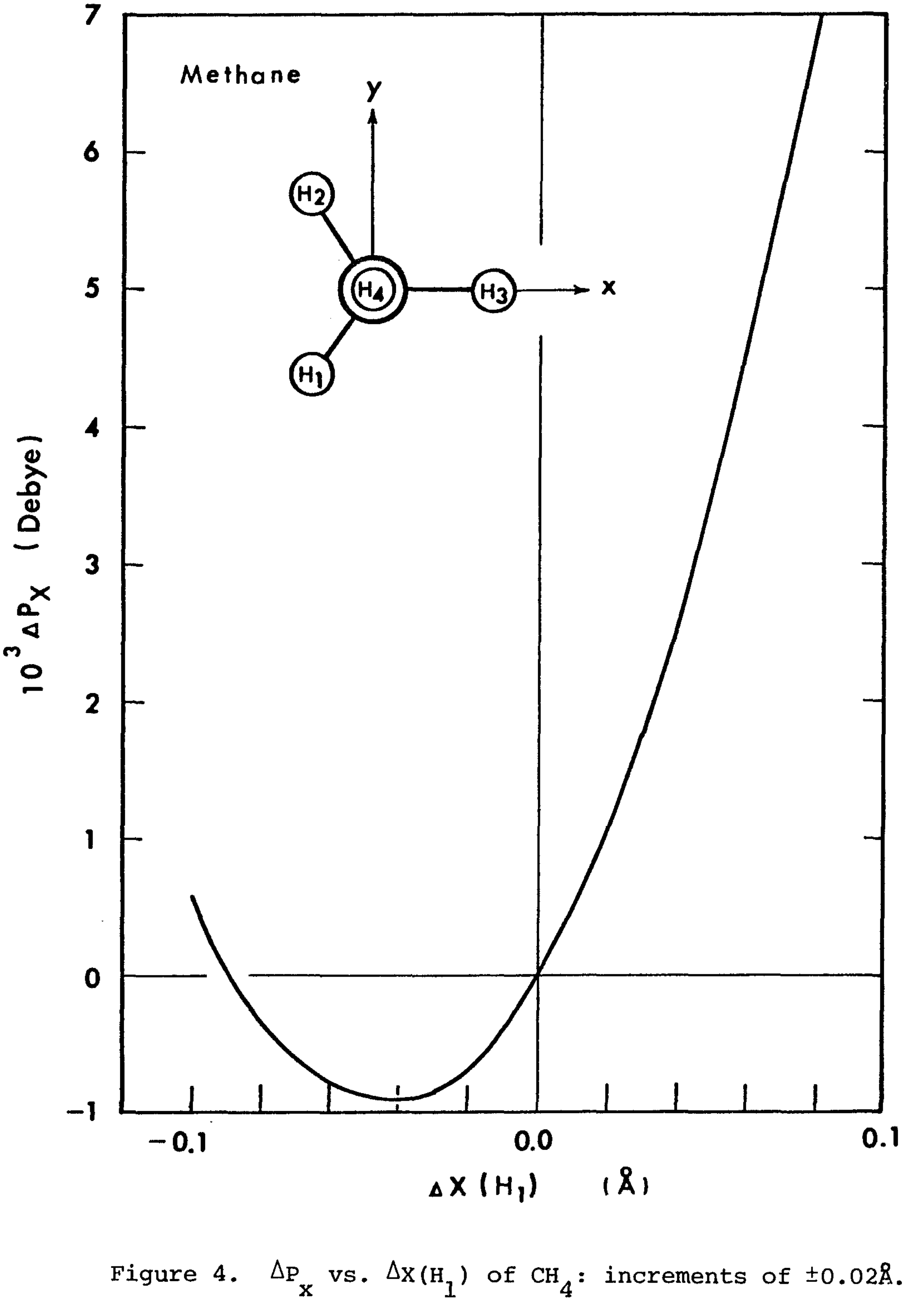

Figure 4. ΔP_x vs. $\Delta X(H_1)$ of CH_4: increments of ±0.02Å.

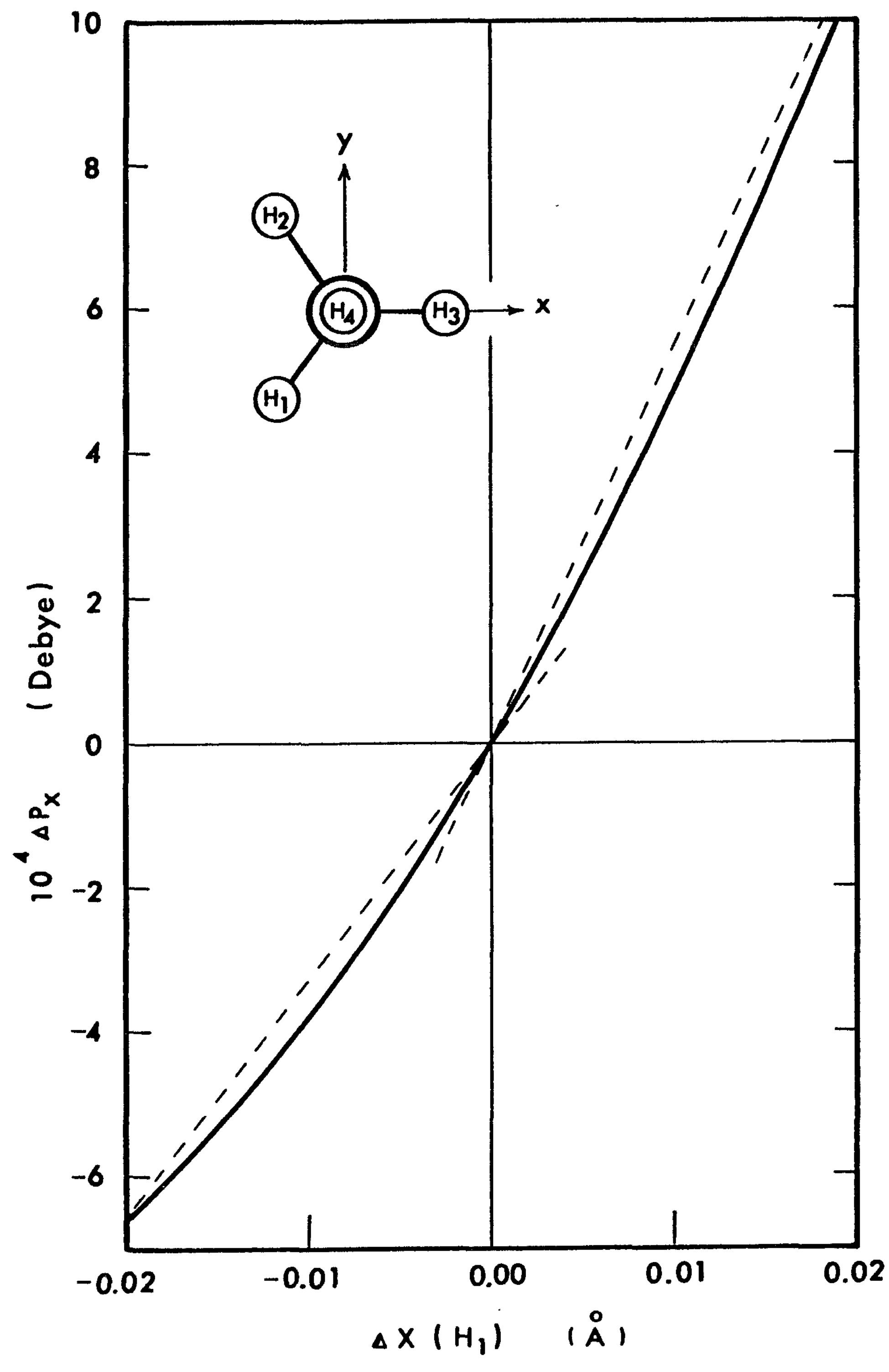

Figure 5. ΔP_x vs. $\Delta X(H_1)$ of CH_4: increments of ±0.002Å.

order cartesian dipole moment derivations are given in Tables VIII-XIII for the molecules C_2H_4, CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4, respectively.

These polar tensors depend on the coordinate frame that is chosen for the molecule, but not on the inherent isotopic nature of the molecular species. Thus, since the identical axes were used for all the isotopes of a molecule, these polar tensors are isotope-independent. This is true because the electron cloud can be assumed to be distorted in the same manner during the corresponding vibrational motions of two isotopic molecules (Born-Oppenheimer approximation). The coordinate axes that were used are those of Figure 3.

The atomic polar tensors are not necessarily symmetrical. However, due to the spherical symmetry about the C atom in CH_4 and CF_4, the polar tensor for carbon in these molecules is a scalar tensor, i.e., a diagonal matrix with identical elements (157).

The precision of the least-squares fit, Eqn.(331), is excellent. This is apparent from Tables VIII-XIII in that the discrepancy in the tensor elements never occurs before the seventh decimal place for any element. This is especially due to the small atomic displacements of ±0.002Å.

The polar tensors of all the atoms of a molecule are not independent of one another. The translational condition leads to the following vanishing sum requirement for each molecule (104):

$$\sum_{\alpha}^{N} \underset{\sim}{P}_X(\alpha) = \underset{\sim}{0} \ , \qquad (335)$$

Table VIII

Atomic Polar Tensors for C_2H_4

α	$\underset{\sim}{P}_X(\alpha)$*	ξ_α
H_1	$\begin{pmatrix} -0.1122635 & 0.3252726 & 0 \\ 0.4184010 & -0.4316963 & 0 \\ 0 & 0 & 0.4984523 \end{pmatrix}$	0.8533939
H_2	$\begin{pmatrix} -0.1122635 & -0.3252726 & 0 \\ -0.4184010 & -0.4316963 & 0 \\ 0 & 0 & 0.4984523 \end{pmatrix}$	0.8533939
H_3	$\begin{pmatrix} -0.1122635 & -0.3252726 & 0 \\ -0.4184010 & -0.4316963 & 0 \\ 0 & 0 & 0.4984523 \end{pmatrix}$	0.8533939
H_4	$\begin{pmatrix} -0.1122635 & 0.3252726 & 0 \\ 0.4184010 & -0.4316963 & 0 \\ 0 & 0 & 0.4984523 \end{pmatrix}$	0.8533939
C_1	$\begin{pmatrix} 0.2245271 & 0 & 0 \\ 0 & 0.8633927 & 0 \\ 0 & 0 & -0.9969047 \end{pmatrix}$	1.3377885
C_2	$\begin{pmatrix} 0.2245271 & 0 & 0 \\ 0 & 0.8633927 & 0 \\ 0 & 0 & -0.9969047 \end{pmatrix}$	1.3377885

* Relative to axes of Figure 3.

Table IX

Atomic Polar Tensors for CH_4

α	$P_{\underset{\sim}{X}}(\alpha)$*	ξ_α
H_1	$\begin{pmatrix} 0.0431696 & -0.2891963 & -0.1180639 \\ -0.2891963 & -0.2907655 & -0.2044926 \\ -0.1180639 & -0.2044926 & 0.1266534 \end{pmatrix}$	0.6174390
H_2	$\begin{pmatrix} 0.0431696 & 0.2891963 & -0.1180639 \\ 0.2891963 & -0.2907655 & 0.2044926 \\ -0.1180639 & 0.2044926 & 0.1266534 \end{pmatrix}$	0.6174390
H_3	$\begin{pmatrix} -0.4577330 & 0 & 0.2361278 \\ 0 & 0.2101372 & 0 \\ 0.2361278 & 0 & 0.1266534 \end{pmatrix}$	0.6174390
H_4	$\begin{pmatrix} 0.2101372 & 0 & 0 \\ 0 & 0.2101372 & 0 \\ 0 & 0 & -0.5412168 \end{pmatrix}$	0.6174390
C	$\begin{pmatrix} 0.1612565 & 0 & 0 \\ 0 & 0.1612566 & 0 \\ 0 & 0 & 0.1612566 \end{pmatrix}$	0.2793046

* Relative to axes of Figure 3

Table X

Atomix Polar Tensors for CH_3F

α	$\underset{\sim}{P}_X(\alpha)$*	ξ_α
H_1	$\begin{pmatrix} -0.1226182 & -0.2632983 & -0.0180205 \\ -0.2632983 & -0.4266489 & -0.0312124 \\ -0.1121836 & -0.1943077 & -0.1416799 \end{pmatrix}$	0.6383019
H_2	$\begin{pmatrix} -0.1226182 & 0.2632983 & -0.0180205 \\ 0.2632983 & -0.4266489 & 0.0312124 \\ -0.1121836 & 0.1943077 & -0.1416799 \end{pmatrix}$	0.6383019
H_3	$\begin{pmatrix} -0.5786643 & 0 & 0.0360410 \\ 0 & 0.0293971 & 0 \\ 0.2243672 & 0 & -0.1416799 \end{pmatrix}$	0.6383019
F	$\begin{pmatrix} -1.4132402 & 0 & 0 \\ 0 & -1.4132402 & 0 \\ 0 & 0 & -2.5652375 \end{pmatrix}$	3.2519132
C	$\begin{pmatrix} 2.2371411 & 0 & 0 \\ 0 & 2.2371410 & 0 \\ 0 & 0 & 2.9902773 \end{pmatrix}$	4.3533156

* Relative to axes of Figure 3.

Table XI

Atomic Polar Tensors for CH_2F_2

α	$\underset{\sim}{P}_X(\alpha)$*	ξ_α
H_1	$\begin{pmatrix} -0.2714725 & 0 & 0 \\ 0 & -0.5907212 & 0.0939032 \\ 0 & 0.2805795 & -0.3145578 \end{pmatrix}$	0.7804730
H_2	$\begin{pmatrix} -0.2714725 & 0 & 0 \\ 0 & -0.5907212 & -0.0939032 \\ 0 & -0.2805795 & -0.3145578 \end{pmatrix}$	0.7804730
F_1	$\begin{pmatrix} -2.4391999 & 0 & 0.7294150 \\ 0 & -1.5687109 & 0 \\ 0.2825507 & 0 & -2.0772647 \end{pmatrix}$	3.6520488
F_2	$\begin{pmatrix} -2.4391999 & 0 & -0.7294150 \\ 0 & -1.5687109 & 0 \\ -0.2825507 & 0 & -2.0772647 \end{pmatrix}$	3.6520488
C	$\begin{pmatrix} 5.4213452 & 0 & 0 \\ 0 & 4.3188642 & 0 \\ 0 & 0 & 4.7836451 \end{pmatrix}$	8.4218069

* Relative to axes of figure 3.

Table XII

Atomic Polar Tensors for CHF_3

α	$\underset{\sim}{P}_X(\alpha)$*	ξ_α
H	$\begin{pmatrix} -0.4391015 & 0 & 0 \\ 0 & -0.4391015 & 0 \\ 0 & 0 & -0.7243704 \end{pmatrix}$	0.9541136
F_1	$\begin{pmatrix} -2.1508433 & -0.3711670 & -0.2920408 \\ -0.3711670 & -2.5794301 & -0.5058295 \\ -0.0736194 & -0.1275126 & -2.0193259 \end{pmatrix}$	3.9994530
F_2	$\begin{pmatrix} -2.1508433 & 0.3711670 & -0.2920408 \\ 0.3711670 & -2.5794301 & 0.5058295 \\ -0.0736194 & 0.1275126 & -2.0193259 \end{pmatrix}$	3.9994530
F_3	$\begin{pmatrix} -2.7937234 & 0 & 0.5840816 \\ 0 & -1.9365500 & 0 \\ 0.1472388 & 0 & -2.0193259 \end{pmatrix}$	3.9994530
C	$\begin{pmatrix} 7.5345118 & 0 & 0 \\ 0 & 7.5345118 & 0 \\ 0 & 0 & 6.7823483 \end{pmatrix}$	12.6308344

* Relative to axes of Figure 3.

Table XIII

Atomic Polar Tensors for CF_4

α	$\underset{\sim}{P}_X(\alpha)$*	ξ_α
F_1	$\begin{pmatrix} -2.2815510 & -0.2803410 & -0.1144487 \\ -0.2803410 & -2.6052610 & -0.1982310 \\ -0.1144489 & -0.1982311 & -2.2006236 \end{pmatrix}$	4.1349213
F_2	$\begin{pmatrix} -2.2815510 & 0.2803410 & -0.1144487 \\ 0.2803410 & -2.6052610 & 0.1982311 \\ -0.1144487 & 0.1982311 & -2.2006236 \end{pmatrix}$	4.1349213
F_3	$\begin{pmatrix} -2.7671160 & 0 & 0.2288975 \\ 0 & -2.1196961 & 0 \\ 0.2288975 & 0 & -2.2006236 \end{pmatrix}$	4.1349213
F_4	$\begin{pmatrix} -2.1196961 & 0 & 0 \\ 0 & -2.1196961 & 0 \\ 0 & 0 & -2.8480435 \end{pmatrix}$	4.1349213
C	$\begin{pmatrix} 9.4499144 & 0 & 0 \\ 0 & 9.4499143 & 0 \\ 0 & 0 & 9.4499144 \end{pmatrix}$	16.3677315

* Relative to axes of Figure 3.

where the summation is over all the atoms in the molecule, and $\underset{\sim}{P}_X(\alpha)$ is given by Eqn.(285). This results from the fact that if the cartesian motion of all the atoms corresponds to a rigid translation of the whole molecule, then this motion would have no effect on the dipole moment. The data in Tables VIII-XIII prove that Eqn.(335) is satisfied to the seventh decimal place for each molecule.

If the cartesian motion is a rigid rotation of the molecule, then this motion would have the effect of rotating the components of the dipole moment. Thus (104),

$$\underset{\sim}{P}_X(\alpha)\underset{\sim}{r}_\alpha = \underset{\sim}{P} \ , \tag{336}$$

where $\underset{\sim}{P}$ is given by Eqn.(292a) and $\underset{\sim}{r}_\alpha$, like $\underset{\sim}{P}$, is an antisymmetric tensor:

$$\underset{\sim}{r}_\alpha \equiv \begin{pmatrix} 0 & Z^0_\alpha & -Y^0_\alpha \\ -Z^0_\alpha & 0 & X^0_\alpha \\ Y^0_\alpha & -X^0_\alpha & 0 \end{pmatrix} , \tag{337}$$

where X^0_α, Y^0_α, and Z^0_α are the equilibrium coordinates of atom α. Eqn. (336) is still valid even if the origin of the axis system is <u>not</u> at the center of mass of the molecule. Again, the atomic polar tensors of Tables VIII-XIII satisfy the rotational condition, Eqn.(336).

Another relationship among the polar tensors that was obtained by this investigation is one that relates the tensors of electronically equivalent atoms, within the Born-Oppenheimer approximation. Thus, the polar tensors for equivalent atoms, say, α_1 and α_2, of a molecule, where α_1 and α_2 could be isotopes of one another, are related through

$$\underset{\sim}{P}_X(\alpha_1) = \underset{\sim}{T}\,\underset{\sim}{P}_X(\alpha_2)\,\underset{\sim}{T}^t , \tag{338}$$

where $\underset{\sim}{T}$ is the rotational tensor that transforms the coordinates of atom α_2 to those of atom α_1. The rows (or columns) of $\underset{\sim}{T}$ form a set of orthogonal normalized vectors. Therefore, once the polar tensor for one atom in a set of equivalent atoms is known, the tensors for the other atoms in the set can be determined according to Eqn. (338). In addition, the vanishing polar tensor sum, Eqn. (335), relates the sums of equivalent sets to each other. Once again, the consistency of the CNDO/2-derived polar tensors was reaffirmed by the application of the equivalence relationship, Eqn. (338).

VI.B.4. Effective Atomic Charges

VI.B.4.a. CNDO/2 and experimentally derived charge values

The effective atomic charges ξ_α are given with the polar tensors in Tables VIII-XIII and are summarized in Table XIV for all the non-equivalent atoms of C_2H_4, CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4. The squared charges $\xi_\alpha{}^2$ are first calculated from the polar tensors $\underset{\sim}{P}_X(\alpha)$ by means of

Table XIV

CNDO/2 Calculation of ξ_α *

Species	ξ_H	ξ_F	ξ_C
C_2H_4	0.8533939	....	1.3377885
CH_4	0.6174390	....	0.2793046
CH_3F	0.6383019	3.2519132	4.3533156
CH_2F_2	0.7804730	3.6520488	8.4218069
CHF_3	0.9541136	3.9994530	12.6308344
CF_4	....	4.1349213	16.3677315

* Units of Debyes/Ångstrom

Eqn.(284) and thereafter the values for ξ_α are obtained, which are all positive.

Tables VIII-XIII show that the effective charges of equivalent atoms are, in fact, equivalent, even if the polar tensors of these atoms are not. This is due to the fact that the polar tensors depend on the particular choice of coordinate axes for the molecule, whereas the effective charges of equivalent atoms are equal, due to Eqns.(284) and (338), and to the orthonormality of $\underset{\sim}{T}$, i.e.,

$$\underset{\sim}{T}\,\underset{\sim}{T}^t = \underset{\sim}{T}^t\,\underset{\sim}{T} = \underset{\sim}{E} \;, \tag{339}$$

where $\underset{\sim}{E}$ is the unit tensor. Thus, the effective atomic charge represents an intrinsic isotope-independent molecular property, which is not dependent on the particular molecular reference frame.

The theoretically derived effective atomic charges compare quite favorably with the few available experimentally deduced values for C_2H_4, CH_4, and CH_3F. The possible experimental values of ξ_α for C_2H_4 and CH_4 have been tabulated in Tables XV and XVI, respectively. Table XVII summarizes the "best" experimental values that are obtained from the former two tables.

The effective atomic charges of Tables XV and XVI were calculated from the available literature values of the total infrared absorption intensities of various isotopic species of C_2H_4 and CH_4 (see Tables XXVII and XXVIII), by means of Eqn.(303). In order to solve for all the isotope-independent ξ_α's of a molecule that contains n sets of electronically non-equivalent atoms, the intensities of n isotopes of

Table XV

Comparison of Possible Experimental and CNDO/2 Values of ξ_α for C_2H_4(a)

	Experimental			
Source	This Investigation			King et al.(b)
	ξ_C^2	ξ_C	ξ_H	ξ_H
1. C_2H_4,C_2D_4(c)	......	0.739	0.866	0.818
2. C_2H_4,cis-$C_2H_2D_2$(c)	......	3.021	0.624	0.563
3. C_2D_4,cis-$C_2H_2D_2$(c)	-3.747	(imag.)	1.054	1.010
4. C_2D_4,trans-$C_2H_2D_2$(c)	-0.382	(imag.)	0.910	0.865
5. C_2H_4,trans-$C_2H_2D_2$(c)	......	1.550	0.820	0.767
6. Polar tensors of C_2H_4(d)	......	1.513	0.774	.....
	CNDO/2			
		ξ_C	ξ_H	
7. Person and Newton(e)		1.343	0.859	
8. This investigation		1.338	0.853	
9. "Best" experimental		1.51 ± 0.04	0.82 ± 0.04	

(continued)

Table XV (continued)

(a) ξ_α in units of Debye/Ångstrom.

(b) Calculated in Reference (101).

(c) ξ_α is calculated from the experimental total intensities of this isotopic pair of Reference (129), Table XXVII, by means of Eqn. (303).

(d) ξ_α is calculated from the experimentally deduced polar tensors of Reference (96) by means of Eqn. (284).

(e) Reference (96).

Table XVI

Comparison of Possible Experimental and CNDO/2 Values of ξ_α for CH_4 *

Source	Experimental			
	This Investigation			King et al.(b)
	ξ_C^2	ξ_C	ξ_H	ξ_H
1. CH_4,CH_3D(c)	......	3.181	0.634	0.655
2. CD_4,CD_3H(c)	......	2.650	0.571	0.576
3. CH_4,CD_3H(c)	-4.207	(imag.)	0.839	0.859
4. CD_4,CH_3D(c)	-1.357	(imag.)	0.823	0.831
5. CH_3D,CD_3H(c)	-8.685	(imag.)	0.924	0.666
6. CH_3D,CH_2D_2(d)	-3.231	(imag.)	0.805	.....
7. CH_3D,CD_3H(d)	-1.242	(imag.)	0.775	.....
8. CH_4,CD_4(c)	......	0.532	0.780	0.798
9. CH_2D_2,CD_3H(d)	......	0.424	0.743	.....
	CNDO/2			
		ξ_C	ξ_H	
10. This investigation		0.279	0.617	
11. "Best" experimental		0.48 ± 0.06	0.76 ± 0.02	

(a) ξ_α in units of Debye/Ångstrom.

(b) Calculated in Reference (101).

(c) ξ_α is calculated from the experimental total intensities of this isotopic pair of Reference (130), Table XXVIII, by means of Eqn. (303).

(d) Same as (c), except that Reference (131) was used.

Table XVII

"Best" Experimental ξ_α for C_2H_4, CH_4, and for CH_3F

Species	ξ_H	ξ_C	ξ_F	Source
C_2H_4	0.82 ± 0.04	1.51 ± 0.04	....	Table XV
CH_4	0.76 ± 0.02	0.48 ± 0.06	....	Table XVI
CH_3F	0.78 ± 0.04	5.12 ± 0.10	4.81 ± 0.20	Reference (107)

this molecule are needed. Since C_2H_4 (or CH_4) contains only two different types of atoms, C and H, the intensity data for a pair of isotopic ethylenes (or methanes) would suffice. However, some of these calculated charges yield unrealistic values for the effective charge on an atom.

Thus, the first two sets of values of Table XV (1. and 2.) are rejected because they yield a value for ξ_C of C_2H_4 that is either too low (0.739) or too high (3.021), as compared with the theoretically derived value of about 1.34 D/Å. The third and fourth sets of values of Table XV are also rejected because they both yield imaginary values for ξ_C. Thus, a comparison of the last two remaining experimental sets of values (5. and 6.) with the corresponding CNDO/2 values, leads to the particular choice for the "best" experimental values for ξ_C and ξ_H of C_2H_4.

The rejection of several sets of values is also the situation for the data for CH_4 in Table XVI. The first two sets of charge values (1. and 2.) yield values that are too high for ξ_C of CH_4 (3.181 and 2.650), especially when compared with the low theoretical value of 0.279. The next five sets (3. to 7.) all result in imaginary values for ξ_C. Only the last two sets remain without any objections and they determine the choice for the "best" experimental ξ_C and ξ_H of CH_4.

The somewhat large discrepancy for ξ_C between the experimental (0.48) and theoretical (0.28) values suggests that it may be difficult to accurately predict very low values of effective atomic charges, as is the case with ξ_C of CH_4. It appears that ξ_C of CH_4 is very sensitive to the equilibrium molecular geometry. This particular effective charge is strongly dependent on the equilibrium value of the carbon-hydorgen bond length, R_0(C-H), whereas the effective hydrogen charge, ξ_H, is rather insensitive. Table XVIII tabulates the calculated values of ξ_H and ξ_C, each as a function of the C-H bond length. This table indicates that for a +0.002Å deviation from the original choice of R_0(C-H) = 1.091Å, ξ_C deviates by +6.4%, whereas ξ_H is changed by only -0.08%. For a unit increase in the equilibrium bond length, ξ_C is increased by approximately 8.9 charge units, whereas ξ_H decreases by only 0.2 charge units. This extreme sensitivity is undoubtedly due to the small value of the effective carbon charge of methane.

It should also be emphasized that the experimentally derived ξ_C may be somewhat unreliable. This is because the experimental value was obtained from Eqn.(303) as a difference between two relatively large numbers, which resulted in a small number.

In order to obtain a more reliable result for the CNDO/2 value of ξ_C for CH_4, a least-squares procedure was employed. Table XIV suggests that an approximate linear relationship exists between ξ_C and the number of fluorines, n_F, in the fluoromethanes. Thus, a linear fit was obtained by inputting the ξ_C values for the n_F = 1, ..., 4 species:

$$\xi_C = (4.025 \pm 0.068)n_F + (0.380 \pm 0.186) \ . \qquad (340)$$

For methane, $n_F = 0$ and $\xi_C = 0.380 \pm 0.186$. This theoretical value is in closer agreement with the experimental quantity of 0.48 (Table XVII), although the latter (experimental) value may be in error.

Figures 6, 7, and 8 are graphic representations of the effective charges of the atoms in methane and in the fluoromethanes. Figure 6 is

Table XVIII

Effect of R_o(C-H) on ξ_H and ξ_C of CH_4*

R_o(C-H)	ξ_H	ξ_C
1.097	0.616049	0.332751
1.095	0.616473	0.314973
1.093	0.616937	0.297158
1.091	0.617439	0.279305
1.089	0.617981	0.261412
1.087	0.618562	0.243481
1.085	0.619183	0.225510

*R in units of Ångstroms,
and ξ in units of Debyes/Å.

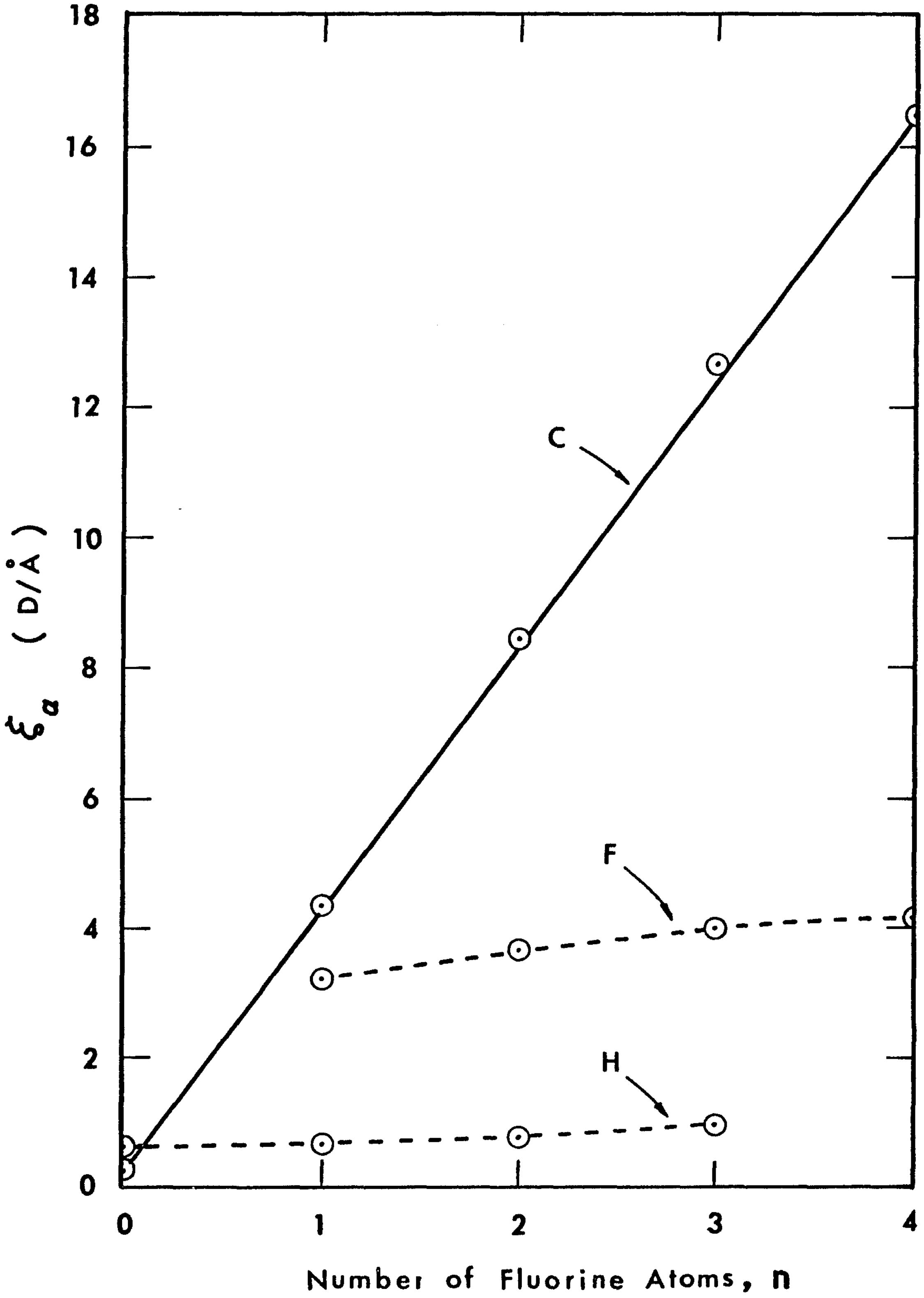

Figure 6. CNDO/2 calculated effective atomic charges for C,H, and for F in $CH_{4-n}F_n$, n = 0, ..., 4.

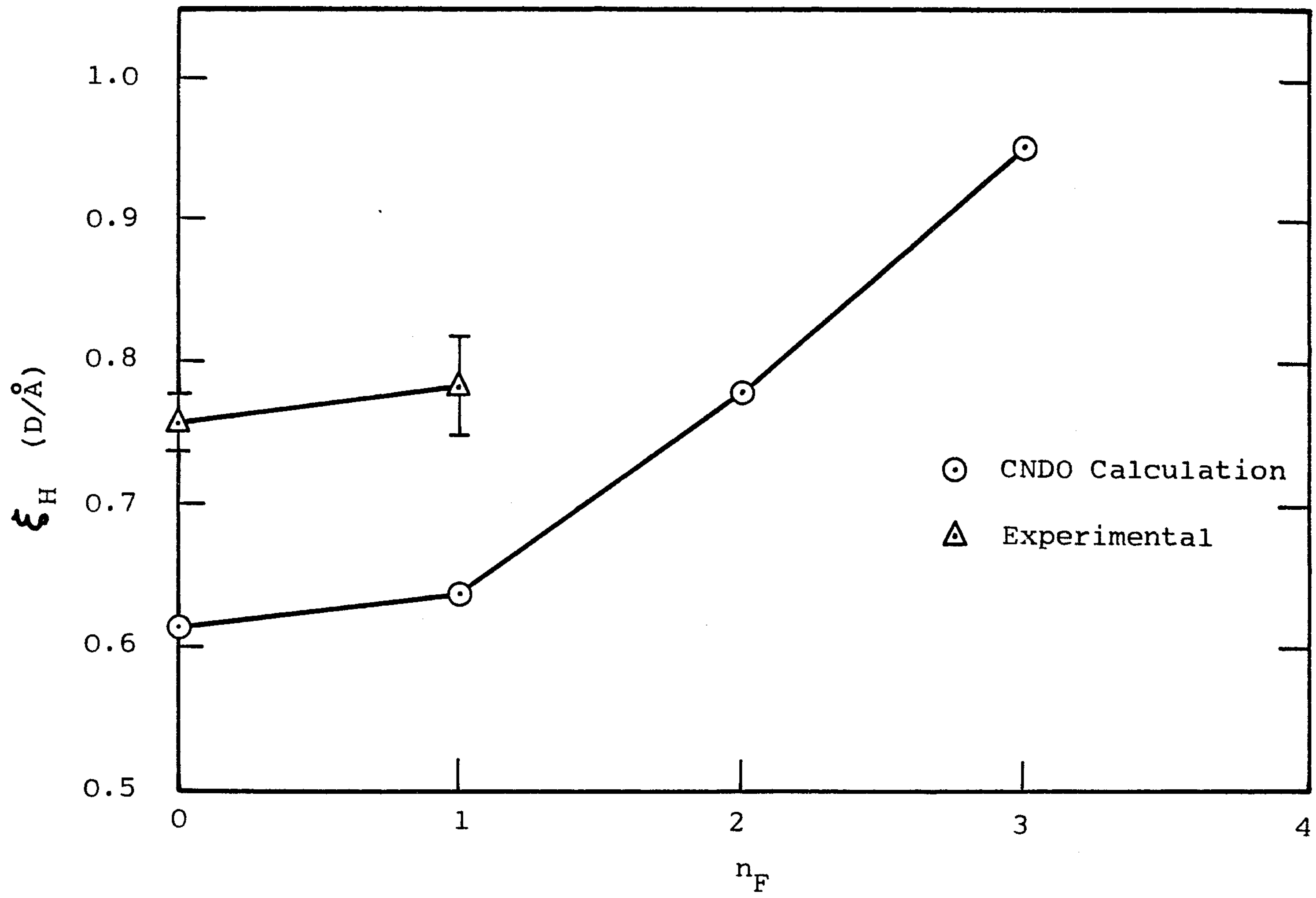

Figure 7. CNDO/2 calculated effective atomic charges of H in $CH_{4-n}F_n$, n = 0, 1, 2, 3.

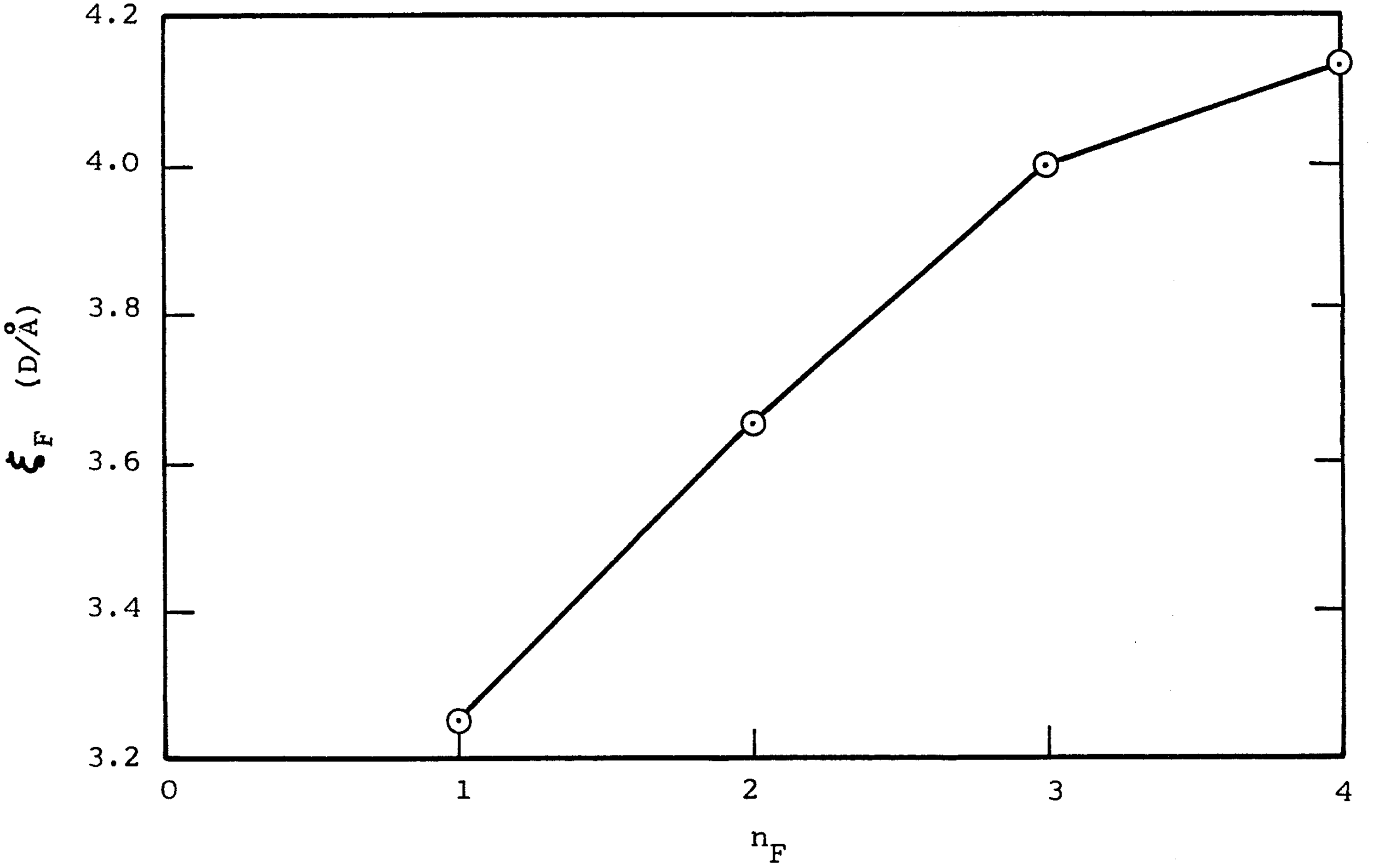

Figure 8. CNDO/2 calculated effective atomic charges of F in $CH_{4-n}F_n$, n = 1, 2, 3, 4.

a plot of ξ_C, ξ_H, and ξ_F, of $CH_{4-n}F_n$, each against the number of fluorines n in the species. It is seen that as the very electronegative fluorine atoms replace the hydrogens, in going from CH_4 to CF_4, the effective charge on the central carbon atom is dramatically increased. This is due to the strong electron-withdrawing inductive effect of the fluorine atoms that are directly bonded to the carbon atom. The near linear relationship between ξ_C and n is borne out by the straight line that is drawn according to the least-squares fit, Eqn.(340). Most of the ξ_C values lie exactly on this line.

Besides this primary inductive effect upon the central atom, there is a slight secondary inductive effect on the terminal hydrogen and fluorine atoms. Figure 6 indicates that, compared to the sharp increase in ξ_C with increasing the fluorine substitutions, the effective charges on hydrogen and fluorine remain relatively constant (with a slight increase) with respect to direct substitution on the central carbon. Thus, in going from CH_4 to CF_4, ξ_C increased by about 5,400%, ξ_H by approximately 54% and ξ_F by 27%; i.e., the ratio of increases is

$$\xi_C : \xi_H : \xi_F = 200 : 2 : 1 .$$

The detailed graphs of ξ_H and ξ_F with respect to the number of fluorines in the molecule, Figures 7 and 8, respectively, indicate that in both cases there is an approximate linear relationship for the medium values of n, i.e., n=1, 2, and 3. However, at the left extreme of ξ_H, n=0 to 1, and at the right extreme of ξ_F, n=3 to 4, the rate of increase of the respective effective charges is sharply reduced.

VI.B.4.b. Sum rules for the effective charges

Although there are direct relationships among the atomic polar tensors $\underset{\sim}{P}_X(\alpha)$ of a molecule, Eqns.(335) and (336), there is no simple exact relationship among the effective charges of non-equivalent atoms of a molecule. However, certain empirical relationships, which could be called sum rules, may exist among the effective charges of a specific atom that appears in different molecules of a homologous series (105, 106, 109). A sum rule would be reliable if it involved at least three different molecules, and, better, if it involved four different molecular species with the same molecular symmetry.

From the CNDO/2 values of the effective charges, Table XIV, the following empirical sum rules can be written for the fluoromethane series:

$$\xi_\alpha(CH_3F) + \xi_\alpha(CHF_3) = 2\xi_\alpha(CH_2F_2), \qquad \alpha = H \text{ or } C \text{ or } F \tag{341}$$

and

$$\xi_C(CH_4) + \xi_C(CF_4) = 2\xi_C(CH_2F_2) \; . \tag{342}$$

These relationships are applicable within a relative error of 2%. Other such sum rules can be written for numerous molecular series.

VI.C. Total Infrared Absorption Intensities

VI.C.1. CNDO/2 Intensities

Once the isotope-independent effective atomic charges ξ_α are known for a molecule, the intensity sums of all the gas-phase isotopic species of this molecule can be generated according to Eqn.(287). Thus, the charges, which are obtained from Table XIV, and the reciprocal atomic masses μ_α, from section VI.A, will yield the first term on the right-hand side of Eqn.(287), $\sum_{\alpha}^{N}\mu_\alpha\xi_\alpha^2$. For non-polar molecules, such as C_2H_4, CH_4, and CF_4, the non-rotation condition Ω, Eqn.(296), vanishes. For the polar molecules, CH_3F, CH_2F_2, and CHF_3, Ω is obtained from the equilibrium dipole moments of Tables VI and VII, and from the inertial constants of Tables III-V. Tables XIX-XXIII list the total intensities of the isotopes of ethylene, methane, and the fluoromethanes, which were obtained in this manner. The intensities for each chemical species are tabulated in descending order, and, in addition, the contributions to each total intensity are given for each set of electronically equivalent atoms in the isotopic molecule.

From Tables XIX and XX it can be seen that for non-polar molecules, the total intensity ΣA_i of a molecule that has been isotopically substituted with the heavier atom(s) of only one isotopic type, will always be smaller than that of its lighter counterpart. Thus, for the hypothetical non-polar molecule, $A_aB_bC_c$, the total intensity of $A_{a-n}A^*_nB_bC_c$, $n \leq a$, where A^* is a heavy isotope of A, will be smaller than that of $A_{a-m}A^*_mB_bC_c$, $m < n$.

Table XIX

CNDO/2 Gas-Phase Infrared Absorption Intensities of the Isotopes of C_2H_4

Isotope	$\xi_H^2(n_H\mu_H+n_D\mu_D)$	$\xi_C^2(n_{12}\mu_{12}+n_{13}\mu_{13})$ (a)	$\sum_{\alpha}^{6}\xi_\alpha^2\mu_\alpha$	ΣA_i (b)
	$(D^2/Å^2\cdot amu)$			(cm/mmole)
$^{12}C_2H_4$	2.89051	0.29828	3.18879	13,476.3
$^{12}C^{13}CH_4$	2.89051	0.28677	3.17728	13,427.6
$^{13}C_2H_4$	2.89051	0.27526	3.16577	13,379.0
$^{12}C_2H_3D$	2.52949	0.29828	2.82777	11,950.5
$^{12}C^{13}CH_3D$ (c)	2.52949	0.28677	2.81626	11,901.9
$^{13}C_2H_3D$	2.52949	0.27526	2.80475	11,853.3
$^{12}C_2H_2D_2$ (d)	2.16847	0.29828	2.46675	10,424.8
$^{12}C^{13}CH_2D_2$ (e)	2.16847	0.28677	2.45524	10,376.2
$^{13}C_2H_2D_2$ (d)	2.16847	0.27526	2.44373	10,327.5
$^{12}C_2HD_3$	1.80745	0.29828	2.10573	8,899.1
$^{12}C^{13}CHD_3$ (c)	1.80745	0.28677	2.09422	8,850.5
$^{13}C_2HD_3$	1.80745	0.27526	2.08271	8,801.8
$^{12}C_2D_4$	1.44644	0.29828	1.74472	7,373.4
$^{12}C^{13}CD_4$	1.44644	0.28677	1.73321	7,324.8
$^{13}C_2D_4$	1.44644	0.27526	1.72170	7,276.1

(continued)

Table XIX (continued)

(a) n_{12} is the number of ^{12}C atoms, which have a reciprocal mass of μ_{12}, that are present in the isotopic species; n_{13} and μ_{13} are similarly defined for the ^{13}C species.

(b) See Eqn. (287); 1 $D^2/\text{Å}^2$ = 6022.52 amu·cm^3/sec^2, and K = (4226.135 amu $\text{Å}^2/D^2$) cm/mmole.

(c) Any of two isotopic isomers.

(d) Any of three isotopic isomers.

(e) Any of four isotopic isomers.

Table XX

CNDO/2 Gas-Phase Infrared Absorption Intensities of the Isotopes of CH_4 and CF_4

Isotope	$\xi_H^{2}(n_H\mu_H+n_D\mu_D)$	$\xi_F^{2}(4\mu_F)$	$\xi_C^{2}(\mu_{12}$ or $\mu_{13})$ (a)	$\sum_{\alpha}^{5}\xi_\alpha^{2}\mu_\alpha$	ΣA_i (b)
	$(D^2/\mathrm{\AA}^2 \cdot amu)$				(cm/mmole)
$^{12}CH_4$	1.51289	....	0.00639	1.51928	6420.7
$^{13}CH_4$	1.51289	....	0.00590	1.51879	6418.6
$^{12}CH_3D$	1.32394	....	0.00639	1.33033	5622.2
$^{13}CH_3D$	1.32394	....	0.00590	1.32984	5620.1
$^{12}CH_2D_2$	1.13498	....	0.00639	1.14137	4823.6
$^{13}CH_2D_2$	1.13498	....	0.00590	1.14088	4821.5
$^{12}CHD_3$	0.94602	....	0.00639	0.95241	4025.0
$^{13}CHD_3$	0.94602	....	0.00590	0.95192	4022.9
$^{12}CD_4$	0.75707	....	0.00639	0.76346	3226.5
$^{13}CD_4$	0.75707	....	0.00590	0.76297	3224.4
$^{12}CF_4$	....	3.59993	22.32595	25.92588	109,566
$^{13}CF_4$	....	3.59993	20.60326	24.20319	102,286

(a) See footnote (a) of Table XIX.

(b) See footnote (b) of Table XIX.

Table XXI

CNDO/2 Gas-Phase Infrared Absorption Intensities of the Isotopes of CH_3F

Isotope	$\xi_H^2(n_H\mu_H+n_D\mu_D)$	$\xi_F^2\mu_F$	$\xi_C^2(\mu_{12}$ or $\mu_{13})$	$\sum_{\alpha}^{5}\xi_\alpha^2\mu_\alpha$	$\Omega_E^{(a)}$	$\Omega_T^{(b)}$	$(\Sigma A_i)_E^{(c)}$	$(\Sigma A_i)_T^{(c)}$
	($D^2/Å^2\cdot$amu)						(cm/mmole)	
$^{12}CH_3F$	1.21279	0.55665	1.57905	3.34849	0.34806	0.29840	12,680	12,890
$^{13}CH_3F$	1.21279	0.55665	1.45721	3.22665	0.33888	0.29053	12,204	12,408
$^{12}CH_2DF$	1.01082	0.55665	1.57905	3.14652	0.32072	0.27669	11,942	12,128
$^{13}CH_2DF$	1.01082	0.55665	1.45721	3.02468	0.31340	0.27038	11,458	11,640
$^{12}CHD_2F$	0.80886	0.55665	1.57905	2.94456	0.29694	0.25618	11,189	11,361
$^{13}CHD_2F$	0.80886	0.55665	1.45721	2.82272	0.29118	0.25120	10,699	10,868

(continued)

Table XXI (continued)

$^{12}CD_3F$	0.60689	0.55665	1.57905	2.74259	0.27773	0.23810	10,417	10,584
$^{13}CD_3F$	0.60689	0.55665	1.45721	2.62075	0.27315	0.23418	9,921	10,086

(a) Calculated based on the experimental (E) equilibrium dipole moment.

(b) Calculated based on the theoretical (T), i.e., CNDO/2-derived, moment.

(c) See (a) and (b) above and footnotes (a) and (b) of Table XIX.

Table XXII

CNDO/2 Gas-Phase Infrared Absorption Intensities of the Isotopes of CH_2F_2

Isotope	$\xi_H^2(n_H\mu_H+n_D\mu_D)$	$2\xi_F^2\mu_F$	$\xi_C^2(\mu_{12}$ or $\mu_{13})$	$\sum_{\alpha}^{5}\xi_\alpha^2\mu_\alpha$	Ω_E(a)	Ω_T(b)	$(\Sigma A_i)_E$(c)	$(\Sigma A_i)_T$(c)
	$(D^2/\mathring{A}^2\cdot amu)$						(cm/mmole)	
$^{12}CH_2F_2$	1.20890	1.40402	5.90944	8.52236	0.44373	0.43607	34,141	34,174
$^{12}CHDF_2$	0.90692	1.40402	5.90944	8.22038	0.37733	0.37082	33,146	33,173
$^{13}CH_2F_2$	1.20890	1.40402	5.45346	8.06638	0.43256	0.42509	32,262	32,293
$^{12}CD_2F_2$	0.60495	1.40402	5.90944	7.91841	0.33049	0.32478	32,068	32,092
$^{13}CHDF_2$	0.90692	1.40402	5.45346	7.76440	0.37014	0.36375	31,249	31,276
$^{13}CD_2F_2$	0.60495	1.40402	5.45346	7.46243	0.32557	0.31995	30,161	30,185

(a) See footnote (a) of Table XXI.

(b) See footnote (b) of Table XXI.

(c) See footnote (c) of Table XXI.

Table XXIII

CNDO/2 Gas-Phase Infrared Absorption Intensities of the Isotopes of CHF_3

Isotope	$\xi_H^2(\mu_H$ or $\mu_D)$	$3\xi_F^2\mu_F$	$\xi_C^2(\mu_{12}$ or $\mu_{13})$	$\sum_{\alpha}^{5}\xi_\alpha^2\mu_\alpha$	$\Omega_E^{(a)}$	$\Omega_T^{(b)}$	$(\Sigma A_i)_E^{(c)}$	$(\Sigma A_i)_T^{(c)}$
	$(D^2/Å^2 \cdot amu)$						(cm/mmole)	
$^{12}CHF_3$	0.90324	2.52527	13.29308	16.72159	0.10884	0.11500	70,208	70,182
$^{12}CDF_3$	0.45199	2.52527	13.29308	16.27034	0.10435	0.11026	68,320	68,295
$^{13}CHF_3$	0.90324	2.52527	12.26737	15.69588	0.10856	0.11470	65,874	65,848
$^{13}CDF_3$	0.45199	2.52527	12.26737	15.24463	0.10412	0.11001	63,986	63,961

(a) See footnote (a) of Table XXI.

(b) See footnote (b) of Table XXI.

(c) See footnote (c) of Table XXI.

However, comparisons of total intensities cannot be made between two isotopic molecules that differ by more than one type of isotopic atom, e.g., $A_{a-1}A^*B_bC_c$ vs. $A_aB_{b-1}B^*C_c$. Thus, even if the former species is heavier than the latter, the total intensity of $A_{a-1}A^*B_bC_c$ could still be greater. This is due to the magnitude of the effective charge of ξ_A relative to that of ξ_B, and to the relative mass change in each type of electronically equivalent set of atoms. From Table XIX it is seen that, for example, the intensity of $^{12}C^{13}CH_4$ is greater than that for $^{13}C_2H_4$, because this is a substitution of only one isotopic type, ^{13}C for ^{12}C, and the latter molecular species is heavier. However, $^{13}C_2H_4$ has a greater intensity than $^{12}C_2H_3D$, even though the former is more massive. This is an example of a substitution of two different isotopic types, ^{12}C for ^{13}C and D for H. The percent change of the total of the reciprocal masses of all the carbon atoms, in going from $^{13}C_2H_4$ to $^{12}C_2H_3D$, is +7.8%, whereas the percent change of the reciprocal masses of the total hydrogen set is almost twice as great, -14.4%. Thus, the contribution to the total intensities from the hydrogen set is much more pronounced, and its mass drop is too large to be made up by the mass increase from the carbon set, as can be seen from Table XIX. In addition to this mass effect, there is also a charge factor involved. Thus, even though $\xi_C^{\ 2}$ is 57% larger than $\xi_H^{\ 2}$, the carbon effective charge is still not large enough to counter the hydrogen contributions.

For both the ethylene and methane isotopic intensities, the major contributions to the total intensity come from the hydrogen set. In Table XIX for C_2H_4, the carbon set contribution varies from about 10-20%

of that for the hydrogen set. This is due to the effective charge of carbon in C_2H_4 (see Table XIV), which is only slightly more than ξ_H, and to the much smaller reciprocal mass of carbon. In methane, the effective charge of carbon is smaller than that for hydrogen by 55% (Table XIV). That fact and the small reciprocal mass of carbon tend to make the carbon contributions to the total intensity of methane almost negligible.

For the fluorinated methanes, on the other hand, the carbon set contributes more to the total intensity of each species than do either the hydrogen or fluorine sets (see Tables XX-XXIII). This is due to the dramatic increase of the carbon effective charge in the fluorinated methanes (see Table XIV and Figure 6), while the effective charges of H and F remain relatively constant. The fluorine set of the first fluorocarbon of the methyl fluoride series contributes less to the total intensity of this isotopic series than does the hydrogen set. However, in the methylene fluoride and the fluoroform series, the fluorine contribution predominates over that of the hydrogen set.

The non-rotation condition Ω is directly related to the reciprocal function of the moments of inertia of the isotopic molecule, according to Eqn.(296). This is verified by Tables XXI-XXIII for the polar species. A heavy isotopic substitution near the center of mass of the molecule will decrease Ω by only a slight amount, because the moments of inertia increase slightly. This is the situation for ^{13}C substitutions. However, an isotopic substitution with a heavier atom at a terminal position, away from the principal axes, will increase the moments of inertia substantially, and thus Ω would be significantly decreased. This occurs for D substitutions in the polar fluoromethanes. The contributions of Ω to the overall intensity is relatively small, however. The value of Ω in the polar species ranges from a maximum of about 10% of the total charge contributions in CH_3F, to 5% in CH_2F_2, and to a minimum of less than 1% in CHF_3.

For the CH_3F series, the intensity of the $^{13}CH_{3-m}D_mF$ (m = 0,1,2) species is greater than the corresponding $^{12}CH_{2-m}D_{m+1}F$ species. However, for the other fluoromethane with the same molecular symmetry, CHF_3, the reverse is true, i.e., the intensity of $^{12}CDF_3$ is larger than that of $^{13}CHF_3$. In the methyl fluoride pairs, the contribution of the hydrogen set in the ^{13}C species is the determining factor. However, in the fluoroform pair, the contribution of the carbon set in the ^{12}C species determines the overall intensity.

The CH_2F_2 series has characteristics of both the CH_3F and CHF_3. The intensities of the methylene fluoride species fall according to

$$^{12}CD_2F_2 < {}^{13}CH_2F_2 < {}^{12}CHDF_2 \ .$$

Thus, the first inequality, $^{12}CD_2F_2 < {}^{13}CH_2F_2$, is similar to the methyl fluoride series, where a carbon-12 and two deuterium atoms are substituted for a carbon-13 and two hydrogen species, respectively, i.e., $^{12}CHD_2F < {}^{13}CH_3F$ and $^{12}CD_3F < {}^{13}CH_2DF$. The last inequality for the methylene fluoride series, $^{13}CH_2F_2 < {}^{12}CHDF_2$, resembles the fluoroform series, where a carbon-13 and a hydrogen atom are substituted with a carbon-12 and a deuterium species, respectively, i.e., $^{13}CHF_3 < {}^{12}CDF_3$.

It should be mentioned that for these polar molecules, the order of intensities within a series is not at all dictated by the rotational correction, Ω. In fact, the trend is completely determined by $\sum_{\alpha}\xi_{\alpha}^{2}\mu_{\alpha}$ for every series. Furthermore, the isotopic variation of intensities for a polar molecular series is not as pronounced as it is for the non-polar ethylene and methane series. Thus, the minimum intensity values for the methane and for the ethylene series are 50% and 46%, respectively, of the maximum series values. However, the corresponding values for CHF_3, CH_2F_2, and CH_3F are 9%, 12%, and 22%, respectively.

VI.C.2. Experimental Intensities

The total intensities can also be generated from the "best" experimental effective atomic charges of Table XVII for C_2H_4, CH_4, and CH_3F. The intensities are calculated according to Eqn.(287) and are tabulated in Tables XXIV-XXVI. It is seen that the trends, i.e., the order of the isotopic intensities, within each series for the calculated and the CNDO/2 intensities are in agreement. The agreement between the calculated and the CNDO/2 values for the ethylene series is very good. The CNDO/2 intensities for CH_4 and for CH_3F are less than the experimentally calculated intensities, because of the lower CNDO/2 effective atomic charges for these species.

The total intensities derived from the experimentally measured individual band intensities for some of the isotopic species of ethylene and methane, and for the fluorinated methanes, are given in Tables

Table XXIV

Derived Gas-Phase Infrared Absorption Intensities of the Isotopes of C_2H_4 from the Experimental ξ_α's of Table XVII

Isotope	$\xi_H^2(n_H\mu_H+n_D\mu_D)$ (D²/Å²·amu)	$\xi_C^2(n_{12}\mu_{12}+n_{13}\mu_{13})^{(a)}$ (D²/Å²·amu)	$\sum_\alpha^6 \xi_\alpha^2\mu_\alpha$ (D²/Å²·amu)	$\Sigma A_i^{(b)}$ (cm/mmole)
$^{12}C_2H_4$	2.66872	0.38002	3.04874	12,884.4
$^{12}C^{13}CH_4$	2.66872	0.36536	3.03408	12,822.4
$^{13}C_2H_4$	2.66872	0.35069	3.01941	12,760.4
$^{12}C_2H_3D$	2.33540	0.38002	2.71542	11,475.7
$^{12}C^{13}CH_3D^{(c)}$	2.33540	0.36536	2.70076	11,413.8
$^{13}C_2H_3D$	2.33540	0.35069	2.68609	11,351.8
$^{12}C_2H_2D_2^{(d)}$	2.00208	0.38002	2.38210	10,067.1
$^{12}C^{13}CH_2D_2^{(e)}$	2.00208	0.36536	2.36744	10,005.1
$^{13}C_2H_2D_2^{(d)}$	2.00208	0.35069	2.35277	9,943.1
$^{12}C_2HD_3$	1.66877	0.38002	2.04879	8,658.5
$^{12}C^{13}CHD_3^{(c)}$	1.66877	0.36536	2.03413	8,596.5
$^{13}C_2HD_3$	1.66877	0.35069	2.01946	8,534.5
$^{12}C_2D_4$	1.33545	0.38002	1.71547	7,249.8
$^{12}C^{13}CD_4$	1.33545	0.36536	1.70081	7,187.9
$^{13}C_2D_4$	1.33545	0.35069	1.68614	7,125.9

(continued)

Table XXIV (continued)

(a) See footnote (a) of Table XIX.

(b) See footnote (b) of Table XIX.

(c) See footnote (c) of Table XIX.

(d) See footnote (d) of Table XIX.

(e) See footnote (e) of Table XIX.

Table XXV

Derived Gas-Phase Infrared Absorption Intensities of the Isotopes of CH_4 from the Experimental ξ_α's of Table XVII

Isotope	$\xi_H^2(n_H\mu_H+n_D\mu_D)$ (D^2/Å^2·amu)	$\xi_C^2(\mu_{12}$ or $\mu_{13})^{(a)}$ (D^2/Å^2·amu)	$\sum_\alpha^5 \xi_\alpha^2\mu_\alpha$ (D^2/Å^2·amu)	$\Sigma A_i^{(b)}$ (cm/mmole)
$^{12}CH_4$	2.29246	0.01920	2.31166	9769.4
$^{13}CH_4$	2.29246	0.01772	2.31018	9763.1
$^{12}CH_3D$	2.00614	0.01920	2.02534	8559.4
$^{13}CH_3D$	2.00614	0.01772	2.02386	8553.1
$^{12}CH_2D_2$	1.71982	0.01920	1.73902	7349.3
$^{13}CH_2D_2$	1.71982	0.01772	1.73754	7343.1
$^{12}CHD_3$	1.43349	0.01920	1.45269	6139.3
$^{13}CHD_3$	1.43349	0.01772	1.45121	6133.0
$^{12}CD_4$	1.14717	0.01920	1.16637	4929.2
$^{13}CD_4$	1.14717	0.01772	1.16489	4923.0

(a) See footnote (a) of Table XIX.

(b) See footnote (b) of Table XIX.

Table XXVI

Derived Gas-Phase Infrared Absorption Intensities of the Isotopes of CH_3F from the Experimental ξ_α's of Table XVII

Isotope	$\xi_H{}^2(n_H\mu_H+n_D\mu_D)$	$\xi_F{}^2\mu_F$	$\xi_C{}^2(\mu_{12}$ or $\mu_{13})$[(a)]	$\sum_\alpha^5 \xi_\alpha{}^2\mu_\alpha$	Ω	ΣA_i[(b)]
	($D^2/\text{Å}^2\cdot$amu)					(cm/mmole)
$^{12}CH_3F$	1.81103	1.21779	2.18453	5.21335	0.34806	20,561
$^{13}CH_3F$	1.81103	1.21779	2.01597	5.04479	0.33888	19,888
$^{12}CH_2DF$	1.50944	1.21779	2.18453	4.91176	0.32072	19,402
$^{13}CH_2DF$	1.50944	1.21779	2.01597	4.74320	0.31340	18,721
$^{12}CHD_2F$	1.20785	1.21779	2.18453	4.61017	0.29694	18,228
$^{13}CHD_2F$	1.20785	1.21779	2.01597	4.44161	0.29118	17,540
$^{12}CD_3F$	0.90626	1.21779	2.18453	4.30858	0.27773	17,035
$^{13}CD_3F$	0.90626	1.21779	2.01597	4.14002	0.27315	16,342

(continued)

Table XXVI (continued)

(a) See footnote (a) of Table XIX.

(b) See footnote (b) of Table XIX.

XXVII-XXIX. In the literature, either A_i or Γ_i are given for the i-th absorption band intensity. In the latter case, the Γ_i are converted to A_i through the frequency of that band, according to Eqn.(214).

From Table XXVII it is seen that the experimental intensities of the cis and trans isomers of the dideutero-ethylene isotope are not equivalent. On the other hand, the CNDO/2 intensities and those calculated from the "best" experimental ξ_α's are the same for these isomers. This is the situation because of Eqn.(287); i.e., ξ_α is the effective charge of an atom, considered individually, without regarding its relationship to the other atoms. Thus, all the hydrogens (or deuteriums) on ethylene have equivalent effective charges. In addition, it should be remembered that Eqn.(287) is based on two assumptions: the harmonic oscillator approximation and the linear dipole moment approximation. However, the mechanical and electrical anharmonicities, which are present during the vibrational motions, may lead to different values for the cis and trans isomeric intensities.

From Tables XXVIII and XXIX, one can see that as the methane molecule becomes more fluorinated, the CNDO/2 intensities, in general, better approximate the experimental values.

VI.C.3. Sum Rules for the Intensities

Since the total intensities within an isotopic series vary with the reciprocal masses μ_α, while the ξ_α's remain constant (see Eqn.287), first order sum rules can be written among the total intensities of an isotopic

Table XXVII

Experimental Gas-Phase Infrared Absorption Intensities (in cm/mmole) of Some of the Isotopes of C_2H_4

Isotope	Experimental						Derived(d)	CNDO/2(e)
	Thorndike et.al.(a)		Hammer(b)		Golike et.al.(c)			
	Fundamental Bands	Fundamentals and Overtones	Fundamental Bands	Fundamentals and Overtones	Fundamental Bands	Fundamentals and Overtones		
C_2H_4	18,230	19,350	12,330	14,480	12,846	12,961	12,884	13,476
cis-$C_2H_2D_2$	......	......	......	......	10,988	11,322	10,067	10,425
trans-$C_2H_2D_2$	......	......	......	......	9,841	10,145	10,067	10,425
C_2D_4	......	......	......	......	6,678	......	7,250	7,373

(continued)

Table XXVII (continued)

(a) See Reference (89).

(b) See Reference (132).

(c) See Reference (129).

(d) See Table XXIV.

(e) See Table XIX.

Table XXVIII

Experimental Gas-Phase Infrared Absorption Intensities (in cm/mmole) of Some of the Isotopes of CH_4

Isotope	Experimental							Derived[g]	CNDO/2[h]
	Rollefson and Havens[a]	Thorndike[b]	Welsh et al.[c]	Armstrong and Welsh[d]	Heicklen and Ruf[e]	Hiller and Straley[f]	Average		
CH_4	10,578	10,088	11,560	10,887	10,312	.....	10,685	9,769	6,421
CH_3D	......	......	......	......	9,469	8,370	8,920	8,559	5,622
CH_2D_2	......	......	......	......	......	7,013	7,013	7,349	4,824
CHD_3	......	......	......	......	5,893	5,856	5,875	6,139	4,025
CD_4	......	......	......	......	5,210	.....	5,210	4,929	3,227

(continued)

Table XXVIII (continued)

(a) See Reference (133).

(b) See Reference (134).

(c) See References (135) and (136).

(d) See Reference (137).

(e) See Reference (130).

(f) See Reference (131).

(g) See Table XXV.

(h) See Table XX.

Table XXIX

Experimental Gas-Phase Infrared Absorption Intensities (in cm/mmole) of the Fluoromethanes

Isotope	Experimental							Derived[(g)]	CNDO/2[(h)]
	Barrow and McKean[(a)]	McKean[(b)]	Morcillo et al.[(c)]	Morcillo et al.[(d)]	Schwin[(e)]	Schatz and Hornig[(f)]	Average		
CH_3F	20,769	19,812	......	....	....	....	20,291	20,561	12,680
CH_2F_2	......	......	44,203	....	....	....	44,203	......	34,141
CHF_3	......	......	......	101,222	....	....	101,222	......	70,208
CF_4	......	......	......	....	121,013	102,613	111,813	......	109,566

(continued)

Table XXIX (continued)

(a) See Reference (138).

(b) See Reference (139).

(c) See Reference (140).

(d) See Reference (141).

(e) See Reference (142).

(f) See Reference (92).

(g) See Table XXVI.

(h) See Tables XX - XXIII.

series of non-polar molecules. Sum rules could also be written for polar molecules, except that these rules would not involve the total intensities, ΣA_i, but would employ the effective charge term $\Sigma \xi_\alpha^2 \mu_\alpha$. The effective intensity (143) is denoted by

$$I \equiv K \sum_\alpha^N \mu_\alpha \xi_\alpha^2 \, , \tag{343}$$

which is equal to $\Sigma A_i(g)$ for non-polar molecules, because $\Omega = 0$. Thus, for a molecular species consisting of, e.g., a equivalent A atoms and b equivalent B atoms, i.e., $A_a B_b$, one can write the following general first-order intensity sum rule:

$$\begin{aligned} &I(A'_i A_{a-i} B'_j B_{b-j}) + I(A'_k A_{a-k} B'_\ell B_{b-\ell}) \\ &\qquad = I(A'_m A_{a-m} B'_n B_{b-n}) + I(A'_p A_{a-p} B'_q B_{b-q}) \, , \end{aligned} \tag{344}$$

where $p \equiv i + k - m$, $q \equiv j + \ell - n$; and $i, k, m, p = 1, 2, \ldots, a$, and $j, \ell, n, q = 1, 2, \ldots, b$. A' and B' represent the isotopes of A and B, respectively. The validity of Eqn.(344) can be verified by the use of all the intensity tables for the ^{13}C and/or deuterium substitutions in the ethylene, the methane, and the fluorinated methanes isotopic series.

VI.D. Calculation of the Isotope Effect on the Zero Point Energy Shift upon Condensation

Since the effective atomic charges ξ_α and the molecular intensities ΣA_i have been evaluated, the B term of Eqn.(145), which represents the isotope effect on the zero point energy (ZPE) shift upon condensation, can be determined according to Eqns.(217) and (303). These two equations are very important for this investigation and thus they are rewritten below:

$$B = \frac{3}{(2\pi)^3} \frac{hc}{N_0 k} \frac{C}{\omega_0} \frac{\alpha}{S^6} \delta \left[\sum_i^{3N-6} A_i(g) \right] , \tag{345}$$

where

$$\delta \left[\sum_i^{3N-6} A_i(g) \right] = \frac{N_0 \pi}{3c^2} \left[\sum_\alpha^N \xi_\alpha^2 \delta\mu_\alpha - \delta\Omega \right] . \tag{346}$$

The only remaining quantities that are needed to be evaluated are ω_0, α, and S, which represent the characteristic frequency of an isotopic series, the molecular polarizability, and the intermolecular separation, respectively. The Lennard-Jones and Ingham crystal potential constant, C, is given in Eqn.(197).

VI.D.1. Characteristic Frequency, ω_0

The isotope-independent values for the Bigeleisen and Goldstein characteristic frequency were calculated for the molecular species studied in this investigation, according to Eqn.(204), and are tabulated in Table XXX. ω_0 is dependent on the largest frequency of the isotopic series. Thus, for the C_2H_4, CH_4, CH_3F, CH_2F_2, and CHF_3 molecules, the largest vibrational frequency in these species is due to the C-H bond stretch, which, as can be seen from Table XXX, is fairly constant. The harmonic frequency involving a C-H stretch is approximately 3100-3200 cm^{-1}. Therefore, for the species containing a C-H bond, ω_0 is about 2200 cm^{-1}. However, for a molecule without any C-H bonds, such as CF_4, ω_0 is drastically reduced by a factor of 2.3 from the ω_0 of a molecule that contains a C-H bond.

Since the harmonic frequencies are generally larger than the fundamental values, the ω_0 values that were used for the fluoromethanes were adjusted accordingly.

VI.D.2. Molecular Polarizabilities and Intermolecular Separations in the Liquid Phase

The value for the intermolecular separation S is difficult to obtain, unlike that of the molecular polarizability α. The nearest-neighbor distance between liquid molecules may be obtained from various inter-

Table XXX

Bigeleisen and Goldstein's Characteristic Frequencies, ω_0, for Ethylene, Methane, and the Fluorinated Methanes

Species	ω_{max}	$2^{-1/2}\omega_{max}$	ω_0 Used
		(cm^{-1})	
C_2H_4	3110(a)	2199	2200
CH_4	3154(b)	2230	2230
CH_3F	3006(c)	2126	2200
CH_2F_2	3013(c)	2131	2200
CHF_3	3035(c)	2146	2200
CF_4	1283(c)	907	950

(a) Harmonic frequency taken from Reference (53).

(b) Harmonic frequency taken from References (144) and (145).

(c) Fundamental frequencies of Reference (146).

molecular properties that yield information about the molecular diameter. This diameter may be obtained from each of the various properties that are listed below (82, 83): gas viscosities, self-diffusion, van der Walls' b, molecular refractions, closest-packing structures, second virial coefficients, and Joule-Thomson coefficients. In addition, a different value may be obtained by each of these methods, depending on the particular intermolecular potential energy form that is used. Thus, all these combinations tend to make a proper evaluation of S rather uncertain. This is particularly true since it is S^{-6} that is needed and not simply S: a one percent uncertainty in S will create a six percent uncertainty in S^{-6}. Therefore, S was not determined directly, but the indirect approach of Wolfsberg (28) was employed.

For a molecular crystal, the energy of cohesion is the heat of vaporization. Thus, from the London dispersion energy, Wolfsberg (28) obtained for α/S^6,

$$\frac{\alpha}{S^6} = \frac{8\ \Delta H_{vap}}{3I\alpha}\ , \tag{347}$$

where I is the first ionization potential of the molecule. The isotope-independent values of α/S^6 for the molecules studied in this investigation are presented in Table XXXI.

Table XXXI

Evaluation of α/S^6 for Ethylene, Methane, and the Fluorinated Methanes

Species	Normal Boiling Point (^{o}C)	ΔH_{vap} at n.b.p. (kcal/mole)	$I^{(d)}$ (eV)	$\alpha^{(e)}$ ($\AA^3$)	α/S^6 (cm^{-3})
C_2H_4	$-103.7^{(a)}$	$3.221^{(a)}$	10.5	4.26	8.6×10^{21}
CH_4	$-161.5^{(a)}$	$1.956^{(a)}$	12.6	2.60	7.2×10^{21}
CH_3F	$- 78.4^{(b)}$	$4.1^{(c)}$	12.85	2.67	13.8×10^{21}
CH_2F_2	$- 51.6^{(b)}$	$4.6^{(c)}$	12.9	2.74	15.0×10^{21}
CHF_3	$- 82.0^{(a)}$	$4.007^{(a)}$	13.0	2.81	12.8×10^{21}
CF_4	$-128.0^{(a)}$	$2.859^{(a)}$	13.0	2.89	8.9×10^{21}

(a) See Reference (147).

(b) See Reference (124).

(c) Calculated from Kistiakowsky's rule, Reference (158), and from the data for CHF_3 and CF_4 of (a) above.

(d) See Reference (124).

(e) See References (82) and (159).

VI.D.3. Calculations from Effective Charges and from Experimental Intensities

The B values for the ethylene, the methane, and the fluormethane isotopes have been calculated, according to Eqn.(345), in three ways: using the available experimental total intensities, the "best" experimentally derived effective atomic charges, and by using the CNDO/2 quantum mechanically derived effective atomic charges. These values have been tabulated in Tables XXXII-XXXV, and are compared with the available values obtained experimentally from vapor pressure measurements. In these tables, the B value for an isotopic species is given relative to the lightest isotope in the series. Thus, $^{12}C_2H_4$, $^{12}CH_4$, $^{12}CH_3F$, $^{12}CH_2F_2$, $^{12}CHF_3$, and $^{12}CF_4$ are the basis molecules for their respective series.

From Table XXXII it is seen that the B values for the isotopic ethylenes are best reproduced by the CNDO method. However, for the isotopic methanes, Table XXXIII, the experimental total intensities yield the best results for the calculated B values, as compared with the experimentally determined B's.

It is seen from Tables XXXII and XXXIII that Eqn.(345) consistently predicts low results for the B values of methane and ethylene. The experimentally obtained total intensity does not depend on the quantum mechanical assumptions and approximations, yet this experimental data also leads to the low B values. Thus, it is apparent that Eqn.(345), although ideally proper, does not reflect additional corrections that are needed to account for the discrepancy in the B values by a factor of 1.3-2.8. However, it is gratifying that the present formulation of

Table XXXII

B Values for the Isotopic Ethylenes*

	Calculated			Experimental			
		From Effective Charges					
Species	From Experimental Intensities (a)	"Best" Experimental (b)	CNDO/2 (c)	Vapor Pressure Measurements	$\frac{B(exp)}{B(a)}$	$\frac{B(exp)}{B(b)}$	$\frac{B(exp)}{B(c)}$
$^{12}C^{13}CH_4$	....	0.1012	0.0794	0.281	....	$2.78^{(f)}$	$3.54^{(f)}$
$^{13}C_2H_4$	....	0.2024	0.1588	.....	....	....	....
$^{12}C_2H_3D$	....	2.2999	2.4910	3.687	....	1.60	1.48
$^{12}C^{13}CH_3D$	....	2.4011	2.5704	.....	....	....	....
$^{13}C_2H_3D$	....	2.5023	2.6498	.....	....	....	....
trans-$^{12}C_2H_2D_2$	4.45	4.5998	4.9821	6.713	1.51	1.45	1.35

(continued)

Table XXXII (continued)

cis-$^{12}C_2H_2D_2$	2.56$^{(e)}$	4.5998	4.9821	6.966	....	1.51	1.40
gem-$^{12}C_2H_2D_2$	....	4.5998	4.9821	7.081	....	1.54	1.42
$^{12}C^{13}CH_2D_2$	....	4.7010	5.0615	......	....	....	....
$^{13}C_2H_2D_2$	....	4.8022	5.1409	......	....	....	....
$^{12}C_2HD_3$	....	6.8997	7.4731	10.284	....	1.49	1.38
$^{12}C^{13}CHD_3$	....	7.0009	7.5525	......	....	....	....
$^{13}C_2HD_3$	....	7.1021	7.6319	......	....	....	....
$^{12}C_2D_4$	10.0	9.1996	9.9642	13.124	1.31	1.43	1.32
$^{12}C^{13}CD_4$	....	9.3008	10.0436	......	....	....	....
$^{13}C_2D_4$	....	9.4020	10.1229	......	....	....	....
	Average				1.41	1.50	1.39

(continued)

Table XXXII (continued)

* B in units of ^{o}K; basis molecule is $^{12}C_2H_4$.

(a) See Table XXVII.

(b) See Table XXIV.

(c) See Table XIX.

(d) See References (53), (58), (59), and (79).

(e) This value is rejected.

(f) Not used for the average.

Table XXXIII

B Values for the Isotopic Methanes*

	Calculated			Experimental			
		From Effective Charges					
Species	From Experimental Intensities (a)	"Best" Experimental (b)	CNDO/2 (c)	Vapor Pressure Measurements(d)	$\frac{B(exp)}{B(a)}$	$\frac{B(exp)}{B(b)}$	$\frac{B(exp)}{B(c)}$
$^{13}CH_4$	....	0.0085	0.0053	0.535	....	....	....
$^{12}CH_3D$	2.45	1.6317	1.0770	2.995	1.22	1.84	2.78
$^{13}CH_3D$	....	1.6402	1.0823	.....	....	....	....
$^{12}CH_2D_2$	5.00	3.2635	2.1540	5.854	1.17	1.79	2.72
$^{13}CH_2D_2$	....	3.2719	2.1594	.....	....	....	....
$^{12}CHD_3$	6.56	4.8952	3.2310	8.687	1.32	1.77	2.69

(continued)

Table XXXIII (continued)

$^{13}CHD_3$	....	4.9037	3.2364	.....	....	....	....
$^{12}CD_4$	7.45	6.5270	4.3080	11.097	1.49	1.70	2.58
$^{13}CD_4$	....	6.5354	4.3134	.....	....	....	....
	Average				1.30	1.78	2.69

* B in units of ^{o}K; basis molecule is $^{12}CH_4$.

(a) See Table XXVIII.

(b) See Table XXV.

(c) $\xi_C = 0.380$ D/Å was used according to section VI.B.4.a, and ξ_H is from Table XIV.

(d) See References (55), (148), and (149).

Table XXXIV

Calculated B Values (in ^{o}K) for the Isotopes of CH_3F*

Species	From Effective Charges	
	"Best" Experimental (a)	CNDO/2 (b)
$^{13}CH_3F$	1.7632	1.2471
$^{12}CH_2DF$	3.0364	1.9335
$^{13}CH_2DF$	4.8206	3.2015
$^{12}CHD_2F$	6.1122	3.9062
$^{13}CHD_2F$	7.9147	5.1900
$^{12}CD_3F$	9.2377	5.9288
$^{13}CD_3F$	11.0533	7.2283

* Basis Molecule is $^{12}CH_3F$.

(a) See Table XXVI.

(b) See Table XXI.

Table XXXV

Calculated B Values (in $^{\circ}K$) for the Isotopes of CH_2F_2, CHF_3, and CF_4

Species	Basis Molecule	B from CNDO/2 (a)
$^{12}CHDF_2$	$^{12}CH_2F_2$	2.8335
$^{13}CH_2F_2$	$^{12}CH_2F_2$	5.3508
$^{12}CD_2F_2$	$^{12}CH_2F_2$	5.9033
$^{13}CHDF_2$	$^{12}CH_2F_2$	8.2356
$^{13}CD_2F_2$	$^{12}CH_2F_2$	11.3338
$^{12}CDF_3$	$^{12}CHF_3$	4.5871
$^{13}CHF_3$	$^{12}CHF_3$	10.5307
$^{13}CDF_3$	$^{12}CHF_3$	15.1185
$^{13}CF_4$	$^{12}CF_4$	28.5187

(a) See Tables XXII, XXIII, and XX for methylene fluoride, fluoroform, and tetrafluoromethane, respectively.

the B-factor has yielded better than merely order-of-magnitude agreements.

VI.D.4. First Order Sum Rules for the B's

From Eqns.(345) and (346), and from Tables XXXII and XXXIII, it is seen that for non-polar molecules ($\Omega = 0$), the B value for an isotopic pair is proportional to the isotopic difference(s) between the reciprocal masses of the substituted atom(s). Thus, numerous first order sum rules can be written for the molecular species of a non-polar isotopic series. Taking ethylene as an example, sum rules such as the ones below can be written:

$$B({}^{12}C_2H_3D) + B({}^{12}C{}^{13}CH_4) = B({}^{12}C{}^{13}CH_3D) \ , \tag{348}$$

$$B(\text{cis-}C_2H_2D_2) = B(\text{gem-}C_2H_2D_2) = B(\text{trans-}C_2H_2D_2) \ , \tag{349}$$

and

$$B(C_2D_4) = \frac{4}{3}B\,(C_2HD_3) = 2B(C_2H_2D_2) = 4B(C_2H_3D) \ , \tag{350}$$

where each B is relative to the lightest isotopic molecule of the series, i.e., the basis molecule, ${}^{12}C_2H_4$. These relationships demonstrate the basic rules for the B values of a non-polar molecular series: (1) the B values of successive isotopic substitutions are additive and cumulative, (2) the B values of equivalent isotopic isomers are equal, and (3) the rule of the mean among B values of successive isotopic substitutions at equivalent positions. As seen from Table XXXII, the experimental results closely satisfy these relations. However, these relations are not exactly followed, because Eqn.(345) was derived on the basis of an isotropic external field, while the actual B value is dependent on the symmetry-allowed interactions between the external molecular motions and the internal modes of vibration (53).

From the intensity sum rule, Eqn(344), and from Eqns.(345) and (346), one can derive the following general sum rules for the isotopic species of the non-polar molecule X_xY_y, which consists of x equivalent X atoms and y equivalent Y atoms:

$$B(X'_iX_{x-i}Y'_jY_{y-j}) + B(X'_kX_{x-k}Y'_rY_{y-r})$$

$$= B(X'_mX_{x-m}Y'_nY_{y-n}) + B(X'_pX_{x-p}Y'_qY_{y-q}) \qquad (351)$$

and

$$q\ B(X_kX'_{x-k}Y_rY'_{y-r}) = r\ B(X_kX'_{x-k}Y_qY'_{y-q})\ . \qquad (352)$$

Each B value is relative to the basis molecule of this isotopic series, $X'_xY'_y$, where X' and Y' are the lighter isotopes. The subscripts of the above relationships are given by $p \equiv i + k - m$, $q \equiv j + r - n$; and $i, k, m, p = 1, 2, \ldots, x$, and $j, r, n, q = 1, 2, \ldots, y$.

The fact that the present formulation of the B-factor rigorously leads to these sum rules is a flaw, rather than a success, of the present treatment. This is because this formulation did not include the internal-external interactions among the real liquid molecules. Thus, the sum rules in the B values must be followed only approximately (53).

VI.E. Molecular Properties that Increase the Isotope Effect on the Zero Point Energy Shift upon Condensation

From the previous results, the various isotopic dependent and independent atomic and molecular properties that tend to increase the B value for an isotopic pair can be deduced. Consequently, these properties will also increase the inverse vapor pressure isotope effect. The following factors, each of which will increase the isotope effect on the zero point energy shift upon condensation by varying degrees, will be analyzed in light of Eqns.(345) and (346).

VI.E.1 Individual Properties

VI.E.1.a. Large number of highly polar bonds

From Eqns.(345) and (346), one can see that the B value for an isotopic pair is, in part, directly proportional to the square of the effective charge(s) of the isotopically substituted atom(s). The effective atomic charge ξ_α increases in magnitude if the molecule possesses a large number of highly polar bonds. This can be seen from Table XIV, where the effective charges of all the atoms of a molecule increase as the number of C-F bonds increases. As discussed in section VI.B.4.a., Figure 6 showed that the greatest increase in the effective charge occurs for the central atom, i.e., the atom that is involved with many of these polar bonds. The increase in the effective charge of the central atom would be more apparent if highly electronegative atoms or groups of atoms are substituted on a weakly electronegative element. Thus, the carbon atom in CF_4 has a greater effective charge than the carbon in CCl_4. Furthermore, one would also expect that Si in SiF_4 would have an even greater effective charge than C in CF_4 due to the lower electronegativity of Si. Therefore, the greater electronegativity difference for the Si-F bond, as compared with the C-F bond, results in SiF_4 having more-polar bonds. This leads to a strong electron-withdrawing inductive effect, which would yield a very large effective charge on Si during the vibrational motions of the tetrafluorosilicon molecule.

From Tables XXXII-XXXV, it is therefore seen that the B value for a single $^{13}C/^{12}C$ substitution is greatest for $B(^{13}CF_4)$, the fully fluorinated methane (Table XXXV). The reason for this is that, of all the fluoromethanes, the CF_4 species has the largest effective charge on carbon. Similarly, for a single D/H substitution, $B(^{12}CDF_3)$ would have the largest B value, because this species has the largest effective charge on hydrogen.

VI.E.2.b. High molecular weight

Another way of looking at the B values is through Eqn.(345). The B value for an isotopic pair is, in part, proportional to the difference between the infrared absorption intensities of the two isotopic molecules. Thus, as the intensities of isotopic species decrease within a series, the B values (relative to the basis molecule of that series) increase. As can be seen from Tables XIX-XXIII, the intensity will generally (but not always) decrease, as the molecules within an isotopic series become more massive. Thus, in the majority of cases, the B values for an isotopic series will increase as the molecular mass increases. This can be verified by Tables XXXII-XXXV.

VI.E.1.c. Non-polar (preferably) or massive molecule

According to Eqns.(345) and (346), the B value will be decreased from the effective charge term $\Sigma\xi_\alpha^{\;2}\delta\mu_\alpha$ by an amount equal to $\delta\Omega$. This isotopic difference, $\delta\Omega$, is determined through

$$\delta\Omega = \Omega(\text{basis}) - \Omega \geq 0 \ , \tag{353}$$

where Ω(basis) is the non-rotational correction term for the basis molecule, which is the lightest isotopic species of the series. As can be seen from Eqn.(296), Ω is directly related to the square of the magnitude of the equilibrium dipole moment, $P_0^{\;2}$, and inversely related to the moments of inertia of the isotopic molecule.

Thus, for a non-polar molecule, $\Omega = 0$ for all the isotopic species of that molecule, because the isotope independent P_0 vanishes. Hence, $\delta\Omega = 0$ and the B value will not be decreased by this amount.

If the molecule is polar, $\Omega \neq 0$, but $\delta\Omega$ could still be a negligible amount if the molecule is slightly polar. In addition, since Ω decreases with increasing moments of inertia, Ω will usually decrease as the molecular mass increases within an isotopic series, as P_0 remains constant. Consequently, if Ω itself is small, then the difference between two small Ω's, $\delta\Omega$, will also be small. This can be seen from the Ω values of Table XXIII for the CHF_3 series, which is more massive than the CH_3F or the CH_2F_2 series, and thus has small Ω and $\delta\Omega$ values.

Even if the molecule is strongly polar, the value of Ω can be minimized if the isotopic substitution in the basis molecule occurs near the center of mass of that molecule. This is especially true if the basis molecule is massive. Thus, the isotope effect on the non-rotational correction, $\delta\Omega$, for a $^{12}C/^{13}C$ substitution is, in fact, small, whereas, $\delta\Omega$ for an H/D substitution is significantly larger (see Tables XXI-XXIII). An isotopic substituion near the center of mass of the basis molecule will alter the moments of inertia only slightly and thus $\delta\Omega$ will be minimized.

The $\delta\Omega$ term can be highly significant when comparing the B value of $^{13}CH_2F_2$ with $^{12}CD_2F_2$ and with $^{13}CHD_2F$. Therefore, for the considerations of only the effective charge and the non-rotational contributions to the B factor, one obtains

$$B(X) - B(^{13}CH_2F_2) \propto \left(\delta Z(X) - \delta Z(^{13}CH_2F_2)\right) - \left(\delta\Omega(X) - \delta\Omega(^{13}CH_2F_2)\right), \tag{354}$$

where X could be either $^{12}CD_2F_2$ or $^{13}CHD_2F$,

$$\delta Z(X) \equiv \sum_\alpha \xi_\alpha^{\,2}\delta\mu_\alpha(X) = \sum_\alpha \xi_\alpha^{\,2}\mu_\alpha(\text{basis of X}) - \sum_\alpha \xi_\alpha^{\,2}\mu_\alpha(X) \;, \tag{355}$$

and

$$\delta\Omega(X) \equiv \Omega(\text{basis of } X) - \Omega(X) \ . \qquad (356)$$

The basis molecule for $^{13}CH_2F_2$ and for $^{12}CD_2F_2$ is $^{12}CH_2F_2$, while the basis molecule for $^{13}CHD_2F$ is $^{12}CH_3F$. These values have been tabulated in Table XXXVI.

The following discussion will involve only the intensity contributions to the B value. From Table XXXVI, it is seen that both B($^{12}CD_2F_2$) and B($^{13}CHD_2F$) would tend to be larger than B($^{13}CH_2F_2$), due to the contributions from the effective charges (see item 3. in Table XXXVI). However, the non-rotational term (see item 4. in that table), which must be subtracted from the effective charge term, according to Eqn.(354), almost nullifies the charge contributions. Thus B($^{12}CD_2F_2$) - B($^{13}CH_2F_2$) $\propto$ 0.14797 - 0.10207 and B($^{13}CHD_2F$) - B($^{13}CH_2F_2$) $\propto$ 0.06979 - 0.04571. Consequently, even though the non-rotational term Ω does not reverse the trend exhibited by the effective charge contributions, Ω may still be very significant, at least as far as reducing the charge contributions. Furthermore, the Ω term may counteract and actually predominate over the ξ term, although this effect did not occur with the species studied in this investigation.

It should be mentioned that $\delta\Omega(^{13}CH_2F_2)$, as seen from Table XXXVI, is rather small. This is a result of an isotopic substitution near the center of mass of the basis molecule $^{12}CH_2F_2$.

Table XXXVI

Comparison of the Contributions of the Effective Charge* and the Non-Rotational Term* to $B(^{12}CD_2F_2)$, $B(^{13}CHD_2F)$, and $B(^{13}CH_2F_2)$

Quantity$^{(c)}$	X $^{12}CD_2F_2$ (a)	 $^{13}CHD_2F$ (b)	 $^{13}CH_2F_2$ (a)
1. $\delta Z(X)$	0.60395	0.52577	0.45598
2. $\delta\Omega(X)$	0.11324	0.05688	0.01117
3. $\delta Z(X) - \delta Z(^{13}CH_2F_2)$	0.14797	0.06979	....
4. $\delta\Omega(X) - \delta\Omega(^{13}CH_2F_2)$	0.10207	0.04571	....
5. 3. - 4.	0.04590	0.02408	....

* Units are $D/\text{Å}^2 \cdot$amu.

(a) Basis molecule is $^{12}CH_2F_2$.

(b) Basis molecule is $^{12}CH_3F$.

(c) See text.

VI.E.1.d. Non-hydrogenous molecule

According to Eqn.(345), the B value would increase if the characteristic frequency ω_0 of the entire isotopic series is small. From Eqn.(204), therefore, a small ω_{max}, the maximum harmonic vibrational frequency of the lightest isotopic molecule of the series, would yield a small characteristic frequency.

In section VI.D.1 and Table XXX, it was observed that the ω_0 for a molecule that contains at least one C-H bond, i.e., $CH_{4-n}F_n$, where n = 0,1,2, or 3, is more than twice as large as the characteristic frequency of CF_4. Thus, with respect to the characteristic frequency of a species, the B value for CF_4 isotopic pairs would be increased by a factor of approximately 2.3 over the B value for the $CH_{4-n}F_n$ isotopic pairs. Thus, everything else being the same, non-hydrogenous molecules would tend to have a larger B value than hydrogenous molecules.

VI.E.1.e. Closely packed liquid molecules

The B value for an isotopic pair, according to Eqn.(345), is directly related to the Lennard-Jones and Ingham crystal potential constant C, and inversely related to the sixth power of the nearest-neighbor distance S. The parameters C and S are taken to be isotope-independent, at least to the first approximation, and involve the liquid molecules of the basis species, which represents the isotopic pair in question. C, in part, is a measure of the number of molecules that surround any particular liquid molecule, i.e., the coordination number of a reference molecule in the condensed-phase. Thus, as the liquid molecules attain a close-packed structure, the number of neighbors about a reference molecule will increase C and thus B. In addition, as the condensed-phase molecules become more closely packed, the nearest-neighbor intermolecular distance S decreases. A decrease in S would also contribute to the increase of the B value, the isotope effect on the ZPE shift upon condensation.

VI.E.2. Resultant Property: Stronger Dispersion Forces in the Liquid Phase between the Lighter Molecules than between the Isotopically Heavier Molecules

As discussed in Section III.E, the zero point energy (ZPE) is lowered upon condensation of the gaseous molecules. This energetically more stable state is due to the (attractive) van der Waals forces between the liquid molecules. Of these forces, however, only the dispersion force is isotope-dependent (section III.F). Consequently, when considering the isotopic difference between the ZPE shifts upon condensation, only the dispersion forces need to be considered with this overall effect. The isotope effect on the dispersion forces in the liquid phase can be regarded as being caused by the molecular properties that were discussed in the previous section. Therefore, the following section will analyze the net result of the isotope effect on the ZPE shift upon condensation in terms of the isotopic difference between the dispersion forces.

If an equation similar to Eqn.(199) is written for a phase shift rather than for an isotopic difference, then

$$\sum_{i}^{3N-6} \Delta\omega_i \cong \frac{1}{8\pi^2 c^2} \frac{1}{\omega_0} \sum_{i}^{3N-6} \Delta\lambda_i \ , \tag{357}$$

where "Δ" represents a condensed-phase property minus the gas-phase property, and is given by Eqn.(148). Eqn.(198) represents the sum of the shifts of the vibrational eigenvalues, where these shifts are caused by all the intermolecular forces in the liquid. Substituting Eqn.(198) into Eqn.(357) will yield

$$\frac{2}{hc} \Delta(\mathrm{ZPE}) = \sum_{i}^{3N-6} \Delta\omega_i \simeq - \frac{1}{(2\pi c)^2} \frac{C}{\omega_0} \frac{\alpha}{S^6} \sum_{i}^{3N-6} \left(\frac{\partial \vec{P}}{\partial Q_i} \right)^2 , \tag{358}$$

where Δ(ZPE) represents the zero point energy shift upon condensation. From Eqns.(237) and (303), it is seen that the intensity of the lighter isotope (primed) is greater than the intensity of the heavier species (unprimed), i.e.,

$$\sum_{i}^{3N-6} \left(\frac{\partial \vec{P}}{\partial Q'_i} \right) > \sum_{i}^{3N-6} \left(\frac{\partial \vec{P}}{\partial Q_i} \right)^2 . \tag{359}$$

Therefore, from Eqns. (358) and (359), one obtains

$$\Delta(\mathrm{ZPE}) \equiv (\mathrm{ZPE})_{\ell} - (\mathrm{ZPE})_{g} < 0 \ , \tag{360}$$

which implies that the attractive intermolecular forces in the liquid state (and not the repulsive forces) predominate, and thereby cause the ZPE of the liquid to decrease from its original value in the gas phase, where the intermolecular forces are assumed not to exist.

From the previous arguments it can be seen that the B value will always be positive. Thus, using Eqns.(145) and (358)-(360), one obtains for B

$$B \propto \Delta(\mathrm{ZPE}) - \Delta(\mathrm{ZPE})' \propto \left(\frac{\partial\vec{P}}{\partial Q'_i}\right)^2 - \left(\frac{\partial\vec{P}}{\partial Q_i}\right)^2 > 0 \ . \tag{361}$$

The previous relationship imples that

$$\Delta(\mathrm{ZPE}) > \Delta(\mathrm{ZPE})' \tag{362}$$

or

$$\left((\mathrm{ZPE})_g - (\mathrm{ZPE})_{\ell}\right) < \left((\mathrm{ZPE})_g - (\mathrm{ZPE})_{\ell}\right)' \ . \tag{363}$$

Thus, the dispersion forces of the van der Waals (attractive) intermolecular forces between the lighter liquid molecules are greater than those forces between the liquid molecules of the heavier isotope. For a large B value, therefore, this difference should be as large as possible, i.e., the dispersion forces between the light molecules should be greater than the dispersion forces between the heavier liquid species.

A pictorial representation of this effect is given in Figure 9. It is seen from this figure that the ZPE of the gas phase is greater than the liquid phase value, for both isotopes, according to Eqn.(360). This implies that the attractive intermolecular forces in the liquid phase decrease the ZPE. However, since the intermolecular dispersion forces between the lighter molecules are greater than those between the heavier species, the shift of the ZPE for the lighter isotope is greater than for the heavier species (see Eqn.(363)).

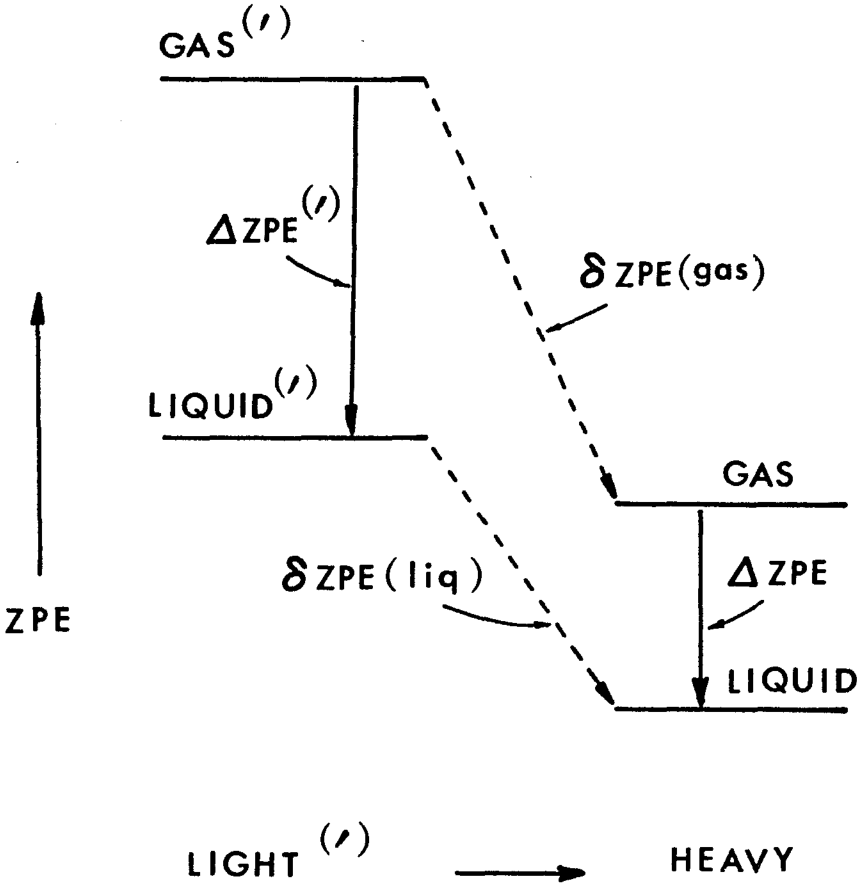

Figure 9. Isotope effect on the zero point energy (ZPE) shift upon condensation.

VII. CONCLUSION

The isotopic difference between the zero point energy (ZPE) shifts upon condensation, the Bigeleisen B-factor, was expressed in terms of atomic and molecular properties. This isotope effect was shown to be directly related to the effective charge(s) of the isotopically substituted atom(s). The effective charges of the atoms of ethylene, methane, and of the fluorinated methanes were calculated by means of a modified CNDO/2 quantum mechanical computer program. Satisfactory agreement has been obtained between the theoretically derived effective atomic charges of a molecule, and those obtained from the experimental total infrared absorption intensities of the particular molecular species. Subsequently, the isotope effect on the change in the ZPE upon condensation was calculated from the effective atomic charges and other gaseous and liquid molecular properties. The theoretically calculated Bigeleisen B-factors for the molecules mentioned above compared well with the available experimental values.

The isotope effect on the ZPE shift upon condensation is due to the stronger (attractive) dispersion forces in the liquid phase between the ligher molecules than between the isotopically heavier molecules. This effect can be increased by the following molecular properties: (1) large number of highly polar bonds (especially if the central atom is isotopically substituted), (2) high molecular weight, (3) non-polar molecule (preferably), or a massive molecule with isotopic substitution near the center of mass, (4) non-hydrogenous molecule, and (5) closely packed liquid molecules.

Future research in condensed phase isotope effects and in infrared absorption intensities (i.e., effective atomic charges) will be discussed below.

The isotope effect on the ZPE shift upon condensation can be investigated by means of the gas and condensed phase "atomic force parameters," A_{α} and $A_{\alpha\beta}^{2}$ of Eqns.(103) and (106), respectively (155). These isotope-independent force constants permit interatomic interactions (while the present effective charge treatment does not), which would explain the non-equivalent Bigeleisen B-factors of isotopic isomers. In addition, the atomic force parameters would significantly reduce the number of idependent force terms that are involved with isotope effect studies, compared with the usual number of force constants.

The effective atomic charges can be theoretically calculated by means of quantum mechanical computer programs other than CNDO/2, which was used for the present calculations. The effective charges of each atom within a homologous series can be determined in order to find a general quantitative relationship between the effective charge on an atom and the electronegativity difference between that atom and the atom that is bonded to it. Thus, if this relationship were known, then the effective charges could be determined for complex atoms that are not amenable to quantum mechanical calculations.

VIII. APPENDIX: CNDO/2 COMPUTER PROGRAM FOR THE CALCULATION OF THE ATOMIC POLAR TENSORS

```
C
C
C         INPUT DATA-
C         FIRST CARD-TITLE AND INDICATE FORMULA OF MOLECULE
C         SECOND CARD-NH,NA,NTIMES,CINCRM,ICHOIS (3I3,F6.3,I3)
C           NH IS THE NUMBER OF HYDROGEN ATOMS, NA IS THE NUMBER OF
C           MAIN ATOMS. NTIMES IS THE NUMBER OF TIMES THAT CINCRM, THE
C           VALUE OF THE COORDINATE INCREMENT, WILL BE VARIED.
C           MAXIMUM NUMBER OF VARIATIONS OF EACH COORDINATE IS 50.
C           THEREFORE MAX NTIMES IS 25. MAX NATOMS IS 15 AND, IN
C           ADDITION, NH+4NF+9NS .LE. 80, WHERE NF AND NS ARE THE
C           NUMBER OF FIRST AND SECOND ROW ATOMS, RESPECTIVELY.
C           IF ICHOIS=0 ONLY THE DIPOLE MOMENTS ARE PRINTED OUT.
C           IF LUMPX=0, GRAPHS OF P(X),P(Y),....,P(T) HAVE GREATEST DETAIL.
C           IF LUMPDX=0, GRAPHS OF DP(X),....,DP(T) ARE SHOWN.
C         NEXT CARDS- X,Y,Z COORDINATES OF ATOMS, HYDROGENS FIRST(3F15.8)
C         LAST CARD-ATOMIC SYMBOLS OF MAIN ATOMS, RIGHT JUSTIFIED(15A2).
C
C
```

```
NOUFLO       START 0
             USING NOUFLO.15
             L     15.MASK
             SPM   15
             SR    15.15
             BR    14
CON          DS    0F
MASK         DC   BL4'110100'
             END
*  FORMS THE DOT PRODUCT OF TWO VECTORS
*  EACH OF LENGTH LIMIT + 1
*  THIS VERSION FOR LIMIT LESS THAN 99
         MACRO
         DOTP     &INDEX.&PROD.&SUM
         LD       &PROD.&INDEX.(2)  LOAD A(I)
         MD       &PROD.&INDEX.(3)  MULTIPLY A(I)*B(I)
         ADR      &SUM.&PROD        DOUBLE PRECISION ADD A(I)*B(I) TO SUM
         MEND
         LCLA     &I
DOTTER START
*  IBM SYSTEM 360 ASSEMBLY LANGUAGE FUNCTION
*  THE FORTRAN EQUIVALENT OF THIS PROGRAM FOLLOWS
*     DOUBLE PRECISION FUNCTION DOT(A.B)
*     DIMENSION A(1).B(1)
*     COMMON /VECTOR/ FACTOR.LIMIT
*     ITOP = LIMIT + 1
*     DOT = 0.D0
*     DO 10 I=1.ITOP
*  10 DOT = DOT + A(I)*B(I)
*     RETURN
*     END
```

```
OLDSAVE EQU     13
RETURN  EQU     14
BASE    EQU     15
ARGLOC  EQU     1
A       EQU     2
B       EQU     3
RLIMIT  EQU     15
SUM     EQU     0
PROD    EQU     2
*  THE FOLLOWING STATEMENT SETS A MAXIMUM LIMIT OF 98=784/8
&I      SETA    1600
        ENTRY   DOT
DOT     SAVE    (2.3)
        USING   DOT.BASE
        L       2.LIMIT              PICK UP LOCATION OF LIMIT
        L       2.5(2)               LOAD VALUE OF LIMIT
        LR      3.2                  THE FOLLOWING FOUR STATEMENTS MULTIPLY
*                                    LIMIT BY 10
        AR      3.3
        SLL     2.3(0)
        AR      2.3
        LA      RLIMIT.REF           PICK UP REFERENCE LOCATION
        SR      RLIMIT.2             SUBTRACT 10*LIMIT FROM REFERENCE
        LM      2.3.0(ARGLOC)        PICK UP ADDRESSES OF ARGUMENTS A AND B
        LD      SUM.0(0.A)           LOAD A(1)
        MD      SUM.0(0.B)           MULTIPLY BY B(1)
        BCR     15.RLIMIT            BRANCH TO START OF DOT PRODUCT
.LOOP   ANOP
        DOTP    &I.PROD.SUM
&I      SETA    &I-8
        AIF     (&I GT 0).LOOP
REF     RETURN  (2.3).RC=0
LIMIT   DC      V(VECTOR)
        END
*  ADDS FACTOR*B TO A. WHERE A AND B ARE VECTORS OF LENGTH LIMIT+1
*  THIS VERSION FOR LIMIT LESS THAN 99
        MACRO
        VSUM    &INDEX
        LDR     0.2                      LOAD FACTOR
        MD      0.&INDEX.(3)             MULTIPLY FACTOR*B(I)
        AD      0.&INDEX.(2)             ADD A(I) + FACTOR*B(I)
        STD     0.&INDEX.(2)             STORE RESULT IN A(I)
        MEND
        LCLA    &I
VCSM    START
*  IBM SYSTEM 360 ASSEMBLY LANGUAGE SUBROUTINE
*  THE FORTRAN EQUIVALENT OF THIS PROGRAM FOLLOWS
*     SUBROUTINE VECSUM(A.B)
*     DIMENSION A(1).B(1)
*     COMMON /VECTOR/ FACTOR.LIMIT
*     ITOP = LIMIT + 1
*     DO 10 I=1.ITOP
*  10 A(I) = A(I) + FACTOR*B(I)
*     RETURN
*     END
```

```
OLDSAVE EQU     13
RETURN  EQU     14
BASE    EQU     15
ARGLOC  EQU     1
A       EQU     2
B       EQU     3
RLIMIT  EQU     15
SUM     EQU     0
FACTOR  EQU     2
*  THE FOLLOWING STATEMENT SETS A MAXIMUM LIMIT OF 98=784/8
&I      SETA    1600
        ENTRY   VECSUM
VECSUM  SAVE    (2,3)
        USING   VECSUM,BASE
        L       2,LIMIT             PICK UP LOCATION OF LIMIT
        LD      FACTOR,0(2)         PICK UP VALUE OF FACTOR
        L       2,8(2)              PICK UP VALUE OF LIMIT
        LR      3,2                 THESE 4 STATEMENTS MULTIPLY LIMIT*14
        AR      3,3
        SLL     2,4(0)
        SR      2,3
        LA      RLIMIT,REF          PICK UP REFERENCE LOCATION
        SR      RLIMIT,2            SUBTRACT 14*LIMIT FROM REFERENCE
        LM      2,3,0(ARGLOC)       PICK UP ADDRESSES OF ARGUMENTS A AND B
        BCR     15,RLIMIT           BRANCH TO START OF VECTOR SUM
.LOOP   VSUM    &I
&I      SETA    &I-8
        AIF     (&I GT 0).LOOP
REF     LDR     SUM,FACTOR          LOAD FACTOR
        MD      SUM,0(0,B)
        AD      SUM,0(0,A)
        STD     SUM,0(0,A)
        RETURN  (2,3),RC=0
LIMIT   DC      V(VECTOR)
        END
*  FORMS A VECTOR PRODUCT USED BY GIVENS
DSUMD   START
*  IBM 360 ASSEMBLY LANGUAGE FUNCTION
*  FORTRAN EQUIVALENT FOLLOWS
*      DOUBLE PRECISION FUNCTION DSUM(B,A,IPI,LIMIT)
*      DIMENSION B(1),A(1)
*      JJ = 1
*      DSUM = 0.D0
*      DO 180 II=IP1,LIMIT
*      DSUM = DSUM + B(II+1)*A(JJ)
* 180  JJ = JJ + II
*      RETURN
*      END
```

```
OLDSAVE EQU     13
RETURN  EQU     14
BASE    EQU     15
ARGLOC  EQU     1
B       EQU     1
A       EQU     2
INDEX   EQU     3
INCR    EQU     4
RLIMIT  EQU     5
JJ      EQU     6
        ENTRY   DSUM
DSUM    SAVE    (2,6)
        USING   DSUM,BASE
        LM      1,4,0(ARGLOC)   PICK UP ADDRESSES OF ARGUMENTS
        L       INDEX,0(3)      LOAD VALUE OF THIRD ARGUMENT, IP1
        SLL     INDEX,3(0)      MULTIPLY INDEX*8
        L       RLIMIT,0(4)     LOAD VALUE OF FOURTH ARGUMENT, LIMIT
        SLL     RLIMIT,3(0)     MULTIPLY LIMIT*8
        SR      JJ,JJ           SET INITIAL VALUE OF JJ = 0
        SDR     0,0             ZERO DSUM
        LA      INCR,8(0)       LOAD INCREMENT=8
LOOP    LD      2,0(INDEX,B)    LOAD B(II+1)
        MD      2,0(JJ,A)       MULTIPLY B(II+1)*A(JJ)
        ADR     0,2             ADD PRODUCT TO DSUM
        AR      JJ,INDEX        ADD II INTO JJ
        BXLE    INDEX,INCR,LOOP END OF DO LOOP
        RETURN  (2,6),RC=0
        END
```

```
ROT     START
*  PERFORMS A PLANE ROTATION ON EACH OF THE COLUMNS OF THE MATRIX V
*  C AND S ARE THE COSINE AND SINE OF THE ROTATION
*  FORTRAN EQUIVALENT FOLLOWS
*        SUBROUTINE ROTATE(V,C,S,NJX,JTOP)
*        DIMENSION V(1)
*        JLIM=JTOP+1
*        DO 10 J=1,JLIM,NJX
*        TA=V(J)
*        TB=V(J+1)
*        V(J)=TA*C+TB*S
*     10 V(J+1)=TB*C-TA*S
*        RETURN
*        END
OLDSAVE EQU     13
RETURN  EQU     14
BASE    EQU     15
ARGLOC  EQU     1
V       EQU     1
J       EQU     3
NJX     EQU     4
JTOP    EQU     5
C       EQU     0
S       EQU     2
        ENTRY   ROTATE
ROTATE  SAVE    (2,5)
        USING   ROTATE,BASE
        LM      1,5,0(ARGLOC)      PICK UP ADDRESSES OF ARGUMENTS
        LD      C,0(2)             LOAD VALUE OF COSINE
        LD      S,0(3)             LOAD VALUE OF SINE
        L       NJX,0(4)           LOAD VALUE OF NJX
        L       JTOP,0(5)          LOAD VALUE OF JTOP
        SR      J,J                ZERO J
        SLL     NJX,3(0)           MULTIPLY NJX*8
        SLL     JTOP,3(0)          MULTIPLY JTOP*8
LOOP    LDR     4,C                LOAD COSINE
        LDR     6,S                LOAD SINE
        MD      4,0(J,V)           MULTIPLY C*V(J)
        MD      6,8(J,V)           MULTIPLY S*V(J+1)
        ADR     4,6                ADD C*V(J)+S*V(J+1)
        LDR     6,S                LOAD SINE
        MD      6,0(J,V)           MULTIPLY S*V(J+1)
        STD     4,0(J,V)           STORE NEW V(J)
        LDR     4,C                LOAD COSINE
        MD      4,8(J,V)           MULTIPLY C*V(J+1)
        SDR     4,6                SUBTRACT C*V(J+1)-S*V(J)
        STD     4,8(J,V)           STORE NEW V(J+1)
        BXLE    J,NJX,LOOP         BRANCH TO START OF DO LOOP
        RETURN  (2,5),RC=0
        END
```

```
      BLCCK DATA
      CCMMCN/CRB/ORB(9)
      CCMMCN/PERTBL/EL(18)
      COMMON/DIRXN/DIRXN(4)
      INTEGER DIRXN
      INTEGER ORB,EL
      DATA ORB/'   S','  PX','  PY','  PZ',' DZ2',' DXZ',' DYZ','DX-Y',
     1 ' DXY'/
      CATA EL/'   H','  HE','  LI','  BE','   B','   C','   N','   O',
     1 '   F','  NE','  NA','  MG','  AL','  SI','   P','   S','  CL',
     2 '  AR'/
      CATA DIRXN/'X','Y','Z','T'/
      END
```

```
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/INFO/NATOMS,AN(15),C(15,3),N
      COMMON/INFO1/CZ(15),U(80),ULIM(15),LLIM(15),NELECS,OCCA,OCCB
      COMMON/VARY/CINCRM,NTIMES
      COMMON/MTXPTS/CONTDP(51,5),NTHROW
      COMMON/DIRXN/DIRXN(4)
      COMMON/MAJIC/MAGIC,MAJ
      COMMON/CHOICE/ICHOIS,ICHCOZ
      COMMON/SLOPE/SLOPE(15,3,4,3),EFFCHG(2),SLOPE2(4,3),DERIV(15,3,4,4)
      COMMON/DX/DX(51,5)
      COMMON/DPDX/DPDX(51,5)
      COMMON/DPDXAV/DPDXAV(25,4),AVG2(25,4)
      DIMENSION Y(50),EY(50),X(50,5),A(5),EINT(5),EEXT(5)
      INTEGER AN,CZ,U,ULIM,OCCA,OCCB,AB(14)
      INTEGER*2 SYMBOL(15),AC(15),CHIK(15)
      INTEGER DIRXN
      DATA SYMBOL/' C',' N',' O',' F','SI',' P',' S','CL','LI','BE',
     * ' B','NA','MG','AL',' H'/
      DATA AB/6,7,8,9,14,15,16,17,3,4,5,11,12,13/
      DATA BLANKS/' '/


      CALL NCUFLO
  100 READ (5,11,END=200) (AN(I), I=1,20)
   11 FORMAT(20A4)
      READ(5,5000) NH,NA,NTIMES,CINCRM,ICHOIS,LUMPX,LUMPDX
 5000 FORMAT(3I3,F6.3,3I3)
      NVARYS=NTIMES*2
      NATOMS=NH+NA
      WRITE (6,13) (AN(I), I=1,20)
   13 FORMAT(/'1'/,20A4)
      WRITE(6,1234) NATOMS,NVARYS,CINCRM
 1234 FORMAT(//////,5X,'CNDO/2 PROGRAM FOR A CLOSED SHELL MOLECULE WITH
     1CHARGE=0, MULTIPLICITY=1, AND NUMBER OF ATOMS =',I3,'. '/,5X,'TOTA
     2L NUMBER OF VARIATIONS OF EACH COORDINATE =',I3,', AND EACH COORDI
     3NATE WILL BE VARIED BY + AND -',F6.3,'.')
      WRITE(6,5252)
 5252 FORMAT(//,20X,'THESE ARE THE EQUILIBRIUM COORDINATES OF THE ATOMS
     1IN ANGSTROMS')
```

```
      DO 21 I=1,NATOMS
   21 READ (5,14) C(I,1),C(I,2),C(I,3)
   14 FORMAT(3F15.8)
      READ (5,15) AC
   15 FORMAT(15A2)
   23 DO 27 I=1,NA
      J=NH+I
      DO 24 K=1,14
      IF(SYMBOL(K).EQ.AC(I)) GO TO 26
   24 CONTINUE
      WRITE (6,16)
   16 FORMAT(' UNIDENTIFIED HEAVY ATOM--STOP')
      STOP
   26 AN(J)=AB(K)
   27 CONTINUE
      WRITE (6,17)
   17 FORMAT(1H0,'ATOM NUMBER',11X,'X',19X,'Y',19X,'Z')
      IF(NH.EQ.0) GO TO 29
      DO 28 I=1,NH
      AN(I)=1
   28 WRITE (6,18) SYMBOL(15),I,C(I,1),C(I,2),C(I,3)
   18 FORMAT(1H0,A2,3X,I3,3F20.8)
   29 DO 30 I=1,NA
      J=NH+I
   30 WRITE (6,18)  AC(I),J,C(J,1),C(J,2),C(J,3)
      DO 31 I=1,NATOMS
      DO 31 J=1,3
   31 C(I,J)=C(I,J)/0.529167D0
      WRITE(6,2626)
 2626 FORMAT('1',5X,'THIS SEGMENT USES THE UNALTERED EQUILIBRIUM GEOMETR
     1Y'//)
      CALL COEFFT
      CALL INTGRL
   80 CALL HUCKCL
      MAGIC=5
      ICHOOZ=1
      CALL SCFCLO
      NTHROW=NTIMES+1
      CALL CPRINT
      IF(NTIMES.EQ.0) GO TO 484
C
C  VARIATION PART OF PROGRAM STARTS
C
      IF(NH.EQ.0) GO TO 4792
      DO 4791 J=1,NA
 4791 CHIK(J)=AC(J)
      DO 4790 I=1,NA
      J=NH+I
 4790 AC(J)=CHIK(I)
      DO 4792 I=1,NH
      AC(I)=SYMBOL(15)
 4792 CONTINUE
C     TESTING FOR ATOMIC SYMBOLS
      WRITE(6,33221) (AC(MOLG),MOLG=1,NATOMS)
33221 FORMAT(/' TEST FOR ATOMIC SYMBOLS: AC(1),....,AC(5)',5A2,/)
C     END OF TEST
```

```
      ITHATM=1
      ICHOOZ=ICHOIS
 1111 JCRDNT=1
  999 CFIXED=C(ITHATM,JCRDNT)
      MAGIC=0
      NTHROW=NTIMES+1
      CONTDP(NTHROW,1)=CFIXED*0.529167D0
      NSTART=NTIMES+2
      NEND=NTIMES*2+1
      DO 777 INCMNT=NSTART,NEND
      NTHROW=INCMNT
      C(ITHATM,JCRDNT)=C(ITHATM,JCRDNT)*0.529167D0 + CINCRM
      CONTDP(NTHROW,1)=C(ITHATM,JCRDNT)
      VARYBY=DFLOAT(INCMNT-NSTART+1)*CINCRM
      MAGIC=MAGIC+1
C  TO SKIP PRINTING OF INDIVIDUAL COMPONENTS OF DIPOLE MOMENT
      ISKIP=1
      IF(ISKIP.EQ.1) GO TO 389
      IF(ICHOOZ.NE.0) GO TO 385
      MAGTST=MAGIC-1
      MAGTST=(MAGTST/4)*4
      IF(MAGTST.NE.MAGIC-1) GO TO 380
  385 WRITE(6,383)
  383 FORMAT('1',1H )
  380 WRITE(6,222) MAGIC,ITHATM,AC(ITHATM),DIRXN(JCRDNT),VARYBY,C(ITHATM
     1,JCRDNT)
  222 FORMAT(1X,I3,'--- ATOM #',I3,1X,A2,' --- ',A1,' COORDINATE WILL BE
     1 VARIED BY',F7.3,' TO THE NEW VALUE',F13.3)
  389 C(ITHATM,JCRDNT)=C(ITHATM,JCRDNT)/0.529167D0
      CALL COEFFT
      CALL INTGRL
      CALL HUCKCL
      CALL SCFCLO
      CALL CPRINT
  777 CONTINUE
      CINC=-CINCRM
      C(ITHATM,JCRDNT)=CFIXED
      DO 779 INCMNT=1,NTIMES
      C(ITHATM,JCRDNT)=C(ITHATM,JCRDNT)*0.529167D0 + CINC
      NTHROW= NTIMES+1-INCMNT
      CONTDP(NTHROW,1)=C(ITHATM,JCRDNT)
      VARYBY=DFLOAT(INCMNT)*CINC
      MAGIC=MAGIC+1
      IF(ICHOOZ.NE.0) GO TO 925
      MAGTST=MAGIC-1
      MAGTST=(MAGTST/4)*4
      IF(ISKIP.EQ.1) GO TO 9845
      IF(MAGTST.NE.MAGIC-1) GO TO 921
  925 WRITE(6,383)
  921 WRITE(6,222) MAGIC,ITHATM,AC(ITHATM),DIRXN(JCRDNT),VARYBY,C(ITHATM
     1,JCRDNT)
 9845 C(ITHATM,JCRDNT)=C(ITHATM,JCRDNT)/0.529167D0
      CALL COEFFT
      CALL INTGRL
      CALL HUCKCL
      CALL SCFCLO
```

```
      CALL CPRINT
  779 CONTINUE
C START OF SEGMENT FOR PRINTING AND PLOTTING OF DIPOLE MOMENT COMPONENTS
      WRITE(6,135) AC(ITHATM),ITHATM,DIRXN(JCRDNT),CINCRM
  135 FORMAT('1',' VARIATION OF MOLECULAR DIPOLE MOMENT WITH AN ATOMIC D
     1ISPLACEMENT OF ',A2,' (',I2,') IN THE ',A1,' DIRECTION BY',F6.3,'
     2INCREMENTS')
      WRITE(6,270) DIRXN(JCRDNT)
  270 FORMAT(//' VARY #',6X,A1,' COORDINATE',10X,'P(X)',16X,'P(Y)',16X,'
     1P(Z)',16X,'P (TOTAL)'/)
      DO 2772 ICRDNT=1,NTIMES
      WRITE(6,350) ICRDNT,(CONTDP(ICRDNT,JDIPOL),JDIPOL=1,5)
  350 FORMAT(2H (,I2,1H),5F20.10)
 2772 CONTINUE
      LABEL1=NTIMES+1
      WRITE(6,6310) (CONTDP(LABEL1,JDIPOL),JDIPOL=1,5)
 6310 FORMAT(/,' (EQ)',5F20.10,/)
      DO 2774 ICRDNT=NSTART,NEND
      IROW=ICRDNT-1
      WRITE(6,350) IROW,(CONTDP(ICRDNT,JDIPOL),JDIPOL=1,5)
 2774 CONTINUE
C
C
  911 DO 913 KST=1,NEND
      DO 913 LST=1,5
  913 DX(KST,LST)=CONTDP(KST,LST)-CONTDP(NTIMES+1,LST)
      DO 395 IMARK=1,NEND
      DO 395 JOO=1,4
      IF(DX(IMARK,1).NE.0.D0) GO TO 6790
      DPDX(IMARK,JOO+1) = BLANKS
      GO TO 395
 6790 DPDX(IMARK,JOO+1)=DX(IMARK,JOO+1)/DX(IMARK,1)
  395 CONTINUE
C
      WRITE(6,135) AC(ITHATM),ITHATM,DIRXN(JCRDNT),CINCRM
      WRITE(6,390) DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDNT)
  390 FORMAT(//,10X,' DP(I) = P(I) - P(EQ)     AND     D',A1,'(I) = ',A1,'
     1(I) - ',A1,'(EQ)'//)
      WRITE(6,392) DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDN
     1T),DIRXN(JCRDNT)
  392 FORMAT(//,'    I    ',3X,'D',A1,8X,'DP(X)',10X,'DP(Y)',10X,'DP(Z)',8
     1X,'DP(TOT)',8X,'DP(X)/D',A1,7X,'DP(Y)/D',A1,7X,'DP(Z)/D',A1,6X,'DP
     1(TOT)/D',A1,/)
      DO 394 IMARK=1,NTIMES
  394 WRITE(6,396) IMARK,(DX(IMARK,JOO),JOO=1,5),(DPDX(IMARK,J),J=2,5)
      WRITE(6,397) (DX(NTIMES+1,JOO),JOO=1,5)
  397 FORMAT(/,5H (EQ),F8.3,4F15.10,/)
      DO 393 IMARK=NSTART,NEND
      IROW=IMARK-1
  393 WRITE(6,396) IROW,(DX(IMARK,JOO),JOO=1,5),(DPDX(IMARK,J),J=2,5)
  396 FORMAT(2H (,I2,1H),F8.3,8F15.10)
  914 DO 445 JEW=1,4
      DO 445 JMARK=1,NTIMES
      DPDXAV(JMARK,JEW)=0.D0
      AVG2(JMARK,JEW)=(DPDX(NTIMES-JMARK+1,JEW+1)+DPDX(NTIMES+JMARK+1,JE
     1W+1))/2.D0
```

```
      NEND=2*JMARK+1
      DO 443 IMARK=1,NEND
      DPDX(NTIMES+1,JEW+1)=0.D0
  443 DPDXAV(JMARK,JEW)=DPDXAV(JMARK,JEW)+DPDX(NTIMES-JMARK+IMARK,JEW+1)
  445 DPDXAV(JMARK,JEW)=DPDXAV(JMARK,JEW)/DFLOAT(2*JMARK)
C
      WRITE(6,448) DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDN
     1T),DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(JCRDNT),DIRXN(J
     2CRDNT)
  448 FORMAT(///'    J    ',3X,'D',A1,6X,'DP(X)/D',A1,7X,'DP(Y)/D',A1,7X,'
     1DP(Z)/D',A1,7X,'DP(T)/D',A1,7X,'DP(X)/D',A1,7X,'DP(Y)/D',A1,7X,'DP
     2(Z)/D',A1,7X,'DP(T)/D',A1)
      WRITE(6,450) DIRXN(JCRDNT),DIRXN(JCRDNT)
  450 FORMAT(' ',14X,12(1H-),'AVERAGE: FROM - TO + D',A1,', INCLUSIVE',1
     112(1H-),2X,14(1H-),'AVERAGE: - AND + D',A1,', EXCLUSIVE',14(1H-)/)
      DO 451 JMARK=1,NTIMES
      JAD=NTIMES+JMARK +1
      WRITE(6,449) JMARK,DX(JAD,1),(DPDXAV(JMARK,JEW),JEW=1,4),(AVG2(JMA
     1RK,JOO),JOO=1,4)
  449 FORMAT(2H (,I2,')',F8.3,8F15.10)
  451 CONTINUE
C  PLOT OF DP  VS.  DX
      WRITE(6,370) DIRXN(JCRDNT),AC(ITHATM),ITHATM
  370 FORMAT('1',15X,' PLOT OF  DP(X), DP(Y), DP(Z), AND DP(T)  VS.  D',
     1A1,' OF ATOM ',A2,' (',I2,')',10X,'(TURN PAGE 90 DEGREES TO THE LE
     2FT)'/)
      IF(LUMPDX.NE.0) GO TO 503
      CALL MYPLOT(DX,NEND,5,LUMPX)
      WRITE(6,370) DIRXN(JCRDNT),AC(ITHATM),ITHATM
      CALL MYPLOT(DX,NEND,5,1)
C
C  END OF PRINTING SEGMENT
C START OF LEAST SQUARES FIT SEGMENT
  912 DO 313 KST=1,NTIMES
      EY(KST)=1.D0
      X(KST,1)=1.D0
      X(KST,2)=DX(KST,1)
      X(KST,3)=DX(KST,1)**2
      X(KST,4)=0.D0
      X(KST,5)=0.D0
  313 CONTINUE
      NP=2*NTIMES
      NART=NTIMES+1
      DO 503 KST=NART,NP
      EY(KST)=1.D0
      X(KST,1)=1.D0
      X(KST,2)=DX(KST+1,1)
      X(KST,3)=DX(KST+1,1)**2
      X(KST,4)=0.D0
      X(KST,5)=0.D0
  503 CONTINUE
      DO 793 KOP=2,5
      IF((CONTDP(NTIMES,KOP)-CONTDP(NTIMES+2,KOP)).GT..00000001D0) GO T
     1O 505
      IF((CONTDP(NTIMES+2,KOP)-CONTDP(NTIMES,KOP)).GT..00000001D0) GO T
     1O 505
```

```
      A(1)=0.D0
      GO TO 498
  505 DO 321 IOP=1,NTIMES
  321 Y(IOP)=DPDX(IOP,KOP)
      DO 307 IOP=NART,NP
  307 Y(IOP)=DPDX(IOP+1,KOP)
  476 WRITE(6,480) AC(ITHATM),ITHATM,DIRXN(KOP-1),DIRXN(JCRONT),DIRXN(JC
     1RONT),DIRXN(JCRONT),DIRXN(KOP-1),DIRXN(JCRONT),DIRXN(JCRONT),DIRXN
     2(JCRONT),NP
  480 FORMAT('1',' ',A2,'(',I2,')',9X,' DP(',A1,')/D',A1,' = A(1) + A(2)
     1*D',A1,' + A(3)*D',A1,'**2',10X,'( DP(',A1,')/D',A1,' ) AT ',A1,'=
     2',A1,'(EQ)= A(1)          NUMBER OF POINTS = ',I2)
C
      CALL LSF(Y,EY,X,3,NP,1,0,A,EINT,EEXT)
  498 DERIV(ITHATM,JCRONT,KOP-1,1)=A(1)
C
  793 CONTINUE
      DO 453 MI=1,3
      DO 453 KPXYZ=1,4
  453 SLOPE(ITHATM,JCRONT,KPXYZ,MI)=DPDXAV(MI,KPXYZ)
      C(ITHATM,JCRONT)=CFIXED
      JCRONT=JCRONT+1
      IF(JCRONT.LE.3) GO TO 999
      ITHATM=ITHATM+1
      IF(ITHATM.LE.NATOMS) GO TO 1111
      DO 399 NIP=1,3
      WRITE(6,409) NIP
  409 FORMAT('1',' TRIAL NUMBER = ',I1,'  FOR AVERAGE METHOD'/)
      WRITE(6,403)
  403 FORMAT('          POLAR TENSORS HAVE THE FOLLOWING ELEMENTS :',//,17
     1X,'DP(X)/DX',4X,'DP(X)/DY',4X,'DP(X)/DZ'/,17X,'DP(Y)/DX',4X,'DP(Y)
     2/DY',4X,'DP(Y)/DZ'/,17X,'DP(Z)/DX',4X,'DP(Z)/DY',4X,'DP(Z)/DZ'//,1
     37X,'DP(T)/DX',4X,'DP(T)/DY',4X,'DP(T)/DZ')
      WRITE(6,405)
  405 FORMAT(///,' ATOM  # ',13X,'ATOMIC POLAR TENSOR',10X,'EFFECTIVE CH
     1ARGE',18X,'ATOMIC POLAR TENSOR',10X,'EFFECTIVE CHARGE')
      WRITE(6,407)
  407 FORMAT(14X,1H ,13(1H-),'IN UNITS OF DEBYE/ANGSTROM',13(1H-),11X,8(
     11H-),'IN UNITS OF E, THE ELECTRONIC CHARGE',8(1H-))
      DO 400 I1=1,NATOMS
      SUM=0.D0
      DO 398 K1=1,3
      DO 398 J1=1,3
  398 SUM=SUM+SLOPE(I1,J1,K1,NIP)**2
      EFFCHG(1)=DSQRT(SUM)
      DO 419 KLOP=1,4
      DO 419 ISLOP=1,3
  419 SLOPE2(KLOP,ISLOP)=SLOPE(I1,ISLOP,KLOP,NIP)*0.208204D0
      EFFCHG(2)=0.208204D0*EFFCHG(1)
      WRITE(6,413) AC(I1),I1,(SLOPE(I1,J1,1,NIP),J1=1,3),EFFCHG(1),(SLOP
     1E2(1,ISLOP),ISLOP=1,3),EFFCHG(2)
  413 FORMAT(///' ',A2,' (',I2,')',6X,3F12.7,5X,F12.7,10X,3F12.7,5X,F12.
     17)
      DO 422 K1=2,3
  422 WRITE(6,423) (SLOPE(I1,J1,K1,NIP),J1=1,3),(SLOPE2(K1,ISL),ISL=1,3)
  423 FORMAT(1H ,13X,3F12.7,27X,3F12.7)
```

```
      WRITE(6,425)
  425 FORMAT(1H )
      WRITE(6,423) (SLOPE(I1,J1,4,NIP),J1=1,3),(SLOPE2(4,ISL),ISL=1,3)
      IF(I1.LE.6) GO TO 400
      WRITE(6,411)
  411 FORMAT(1H ,'1')
  400 CONTINUE
  399 CONTINUE
      JIP =1
      WRITE(6,496) JIP
  496 FORMAT('1',' TRIAL NUMBER = ',I1,'  FOR LSF METHOD'/)
      WRITE(6,403)
      WRITE(6,405)
      WRITE(6,407)
      DO 488 I1=1,NATOMS
      SUM=0.D0
      DO 490 K1=1,3
      DO 490 J1=1,3
  490 SUM=SUM+DERIV(I1,J1,K1,JIP)**2
      EFFCHG(1)=DSQRT(SUM)
      DO 492 KLOP=1,4
      DO 492 ISLOP=1,3
  492 SLOPE2(KLOP,ISLOP)=DERIV(I1,ISLOP,KLOP,JIP)*0.208204D0
      EFFCHG(2)=0.208204D0*EFFCHG(1)
      WRITE(6,413) AC(I1),I1,(DERIV(I1,J1,1,JIP),J1=1,3),EFFCHG(1),(SLOP
     1E2(1,ISLOP),ISLOP=1,3),EFFCHG(2)
      DO 494 K1=2,3
  494 WRITE(6,423) (DERIV(I1,J1,K1,JIP),J1=1,3),(SLOPE2(K1,ISL),ISL=1,3)
      WRITE(6,425)
      WRITE(6,423) (DERIV(I1,J1,4,JIP),J1=1,3),(SLOPE2(4,ISL),ISL=1,3)
      IF(I1.LE.6) GO TO 488
      WRITE(6,411)
  488 CONTINUE
  434 CONTINUE
      GO TO 100
  200 STOP
      END
```

```
      SUBROUTINE MYPLOT(A,NROWS,M,LUMP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(51,5)
      DIMENSION OUT(121),YPR(13),ANG(4),YSCAL(4),YMIN(4)
      DATA BLANK,ANG(1),ANG(2),ANG(3),ANG(4)/' ','X','Y','Z','T'/
    2 FORMAT(1H ,F9.4,1X,121A1)
    3 FORMAT(1H )
    7 FORMAT(1H ,1X,13(9X,1H.),/)
    8 FORMAT(1H0,3X,12F10.4,F9.4)
    9 FORMAT(1H0,3X,A1,F9.4,11F10.4,F9.4)
C           FIND SCALE FOR CROSS-VARIABLES
      IF(LUMP.EQ.0) GO TO 14
      MR=2
      GO TO 16
   14 MR=M
   16 DO 42 JS=2,MR
      YMIN(JS-1)=A(1,JS)
      YMAX=YMIN(JS-1)
      MJ=1
      IF(LUMP.EQ.0) GO TO 44
      MJ=M
      GO TO 18
   44 MJ=JS
   18 DO 40 K=JS,MJ
      DO 40 J=1,NROWS
      IF(A(J,K)-YMIN(JS-1)) 28,26,26
   26 IF(A(J,K)-YMAX) 40,40,30
   28 YMIN(JS-1)=A(J,K)
      GO TO 40
   30 YMAX=A(J,K)
   40 CONTINUE
      YSCAL(JS-1)=(YMAX-YMIN(JS-1))/120.D0
C           PRINT CROSS-VARIABLE NUMBERS
      YPR(1)=YMIN(JS-1)
      DO 90 KN=1,11
      IF(YSCAL(JS-1).LE.0.000000001D0) GO TO 42
   90 YPR(KN+1)=YPR(KN)+YSCAL(JS-1)*10.D0
      YPR(13)=YMAX
      IF(LUMP.EQ.0) GO TO 32
      WRITE(6,8) (YPR(IP),IP=1,13)
      GO TO 42
   32 WRITE(6,9) ANG(JS-1),(YPR(IP),IP=1,13)
   42 CONTINUE
      WRITE(6,7)
      MY=M-1
C           FIND CROSS-VARIABLES
      DO 95 L=1,NROWS
      DO 55 IX=1,121
   55 OUT(IX)=BLANK
      DO 60 J=1,MY
      IF(LUMP.EQ.0) GO TO 84
      JS=2
      GO TO 46
   84 JS=J+1
      IF(YSCAL(JS-1).LE.0.000000001D0) GO TO 60
   46 JP=(A(L,J+1)-YMIN(JS-1))/YSCAL(JS-1) + 1.5D0
```

```
      OUT(JP)=ANG(J)
   60 CONTINUE
C           PRINT LINE AND CLEAR OR SKIP
      WRITE(6,2) A(L,1),(OUT(IX),IX=1,121)
   65 IF(NROWS.GT.16) GO TO 63
      WRITE(6,3)
   63 IF(NROWS.GT.25) GO TO 95
      WRITE(6,3)
   95 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE LSF(Y,EY,X,NI,NP,IFPT,IFSE,A,EINT,EEXT)
C         LSF-PROGRAM IN FORTRAN IV FOR B.C. COMPUTER (IBM360/40 WITH
C         32K MEMORY).  IN THE LIST OF ARGUMENTS ABOVE, Y THRU IFSE ARE
C         INPUT TO THE SUBROUTINE, AND THE LAST 3 ARE OUTPUT.
C         MAX. NUMBER OF EXPT'L PTS IS 50.
C         Y(I)   = DEPENDENT VARIABLE, I-TH POINT.
C         EY(I)  = DEVIATION ON Y(I)
C         X(I,J) = J-TH INDEPENDENT VARIABLE, I-TH PT.  J UP TO 5.
C         NI     = NO. OF INDEP. VARIABLES.
C         NP     = NO. OF EXPT'L PTS.
C         IFPT   = 1 IF X(I,J) ARE TO BE PRINTED.
C         IFSE   = 1 IF THE SIMULTANEOUS EQN'S ARE TO BE PRINTED.
C         A(J)   = J-TH BEST-FIT COEFFICIENT
C         EINT(J)= INTERNAL DEVIATION ON A(J)
C         EEXT(J)= EXTERNAL DEVIATION ON A(J)
      DOUBLE PRECISION Y(50),EY(50),X(50,5),A(5),EINT(5),EEXT(5),W(50),
     1P(5,10),Q(5),B(5,50),S(50),E(50),DC(50)
      DIMENSION NG(2)
      IF(IFPT)3,3,1
    1 WRITE(6,3001)
 3001 FORMAT(//79H0   I      X(I,1)        X(I,2)        X(I,3)        X
     1(I,4)        X(I,5)     I)
      NPMIN1=NP-1
      DO 2 I=1,NP,NPMIN1
    2 WRITE(6,3002)I,(X(I,J),J=1,5),I
 3002 FORMAT(I5,5F14.8,I4)
    3 DO 4 I=1,NP
    4 W(I)=1.0D0/EY(I)**2
      DO 6 J=1,NI
      DO 6 K=J,NI
      P(J,K)=0.0D0
      DO 5 I=1,NP
    5 P(J,K)=P(J,K)+W(I)*X(I,J)*X(I,K)
      P(K,J)=P(J,K)
    6 CONTINUE
      NI1=NI+1
      DO 11 J=1,NI
      DO 11 K=NI1,10
   11 P(J,K)=0.0D0
      IF(IFSE)12,12,7
    7 DO 9 K=1,NI
      Q(K)=0.0D0
      DO 8 I=1,NP
    8 Q(K)=Q(K)+W(I)*Y(I)*X(I,K)
    9 CONTINUE
      WRITE(6,3003)
 3003 FORMAT(//57H THE SIMULTANEOUS EQUATIONS FOR COEFFICIENTS A(J) FOLL
     1OW.)
      WRITE(6,3004)
 3004 FORMAT(//110H       *A(1)              *A(2)              *A(3)
     1           *A(4)              *A(5)            =   CONSTANTS)
      DO 10 K=1,NI
   10 WRITE(6,3005)(P(K,J),J=1,5),Q(K)
 3005 FORMAT(2X,E15.8,4(4X,E15.8),5H    =E15.8)
   12 NG(1)=NI
      NG(2)=-1
```

```
      CALL GAJC3(NG,P)
      DO 14 J=1,NI
      JA=J+NI
      DO 13 K=1,NI
   13 P(K,J)=P(K,JA)
   14 CONTINUE
      DO 16 J=1,NI
      DO 16 I=1,NP
      B(J,I)=0.0D0
      DO 15 K=1,NI
   15 B(J,I)=B(J,I)+P(K,J)*X(I,K)
   16 CONTINUE
      DO 18 J=1,NI
      A(J)=0.0D0
      DO 17 I=1,NP
   17 A(J)=A(J)+B(J,I)*W(I)*Y(I)
   18 EINT(J)=DSQRT(P(J,J))
      DO 20 I=1,NP
      S(I)=0.0D0
      DO 19 J=1,NI
   19 S(I)=S(I)+A(J)*X(I,J)
      E(I)=Y(I)-S(I)
   20 DC(I)=E(I)/EY(I)
      AK=NP-NI
      AJ=0.0D0
      DO 21 I=1,NP
   21 AJ=AJ+W(I)*E(I)**2
      DO 22 J=1,NI
   22 EEXT(J)=DSQRT(AJ*P(J,J)/AK)
      WRITE(6,3006)
 3006 FORMAT(////80H COMPARISON OF INPUT DATA WITH THE BEST-FIT CURVE FO
     1LLOWS.  RESIDUE = Y(I) - LSF)
      WRITE(6,3007)
 3007 FORMAT(//64H     I    INPUT Y(I)      INPUT EY(I)  RESIDUE/EY(I)   Y FR
     1OM LSF     I)
      DO 23 I=1,NP
   23 WRITE(6,3008)I,Y(I),EY(I),DC(I),S(I),I
 3008 FORMAT(I5,F13.8,F13.6,F15.8,F15.8,I4)
      WRITE(6,3009)
 3009 FORMAT(////74H THE LEAST-SQUARES FIT COEFFICIENTS A(J) AND INT. &
     1EXT DEVIATIONS FOLLOW.)
      WRITE(6,3010)
 3010 FORMAT(//49H                  A(J)          INT.DEV.      EXT.DEV.)
      DO 24 J=1,NI
   24 WRITE(6,3011)A(J),EINT(J),EEXT(J)
 3011 FORMAT(/8X,E16.8,E13.4,E13.5)
      RETURN
      END
```

```
      SUBROUTINE GAJ03(NG,AMAT)
CGAJ03    THIS IS A MODIFICATION OF GAJ03 ORIGINALLY WRITTEN BY S. EHREN
C     -SON IN FORTRAN II AND IS TO BE CALLED BY LSFAM.
      DOUBLE PRECISION AMAT(5,10),A
      DIMENSION NG(2),K1C(5)
    1 NS1=1
      DO 17 NC=1,15
      N=NG(NC)
      IF(N)12,12,6
    6 M=N+1
      IF(NG(2))2,3,3
    2 K=2*N
      DO 5 I=1,N
      L=I+N
      DO 4 J=M,K
    4 AMAT(I,J)=0.0D0
    5 AMAT(I,L)=1.0D0
      M=K
    3 NSN=NS1+N-1
      DO 9 L=1,N
      A=0.0D0
      DO 7 K=1,N
      I=K+NS1-1
      IF(DABS(AMAT(I,K))-DABS(A))7,7,8
    8 K1=K
      A=AMAT(I,K1)
    7 CONTINUE
      K1C(L)=K1
      K2=K1+NS1-1
      DO 9 I=NS1,NSN
      IF(I-K2)10,9,10
   10 DO 11 J=1,M
      DO 13 L1=1,L
      IF(K1C(L1)-J)13,11,13
   13 CONTINUE
      IF(K)14,14,15
   15 AMAT(K2,J)=AMAT(K2,J)/A
   14 AMAT(I,J)=AMAT(I,J)-AMAT(I,K1)*AMAT(K2,J)
   11 CONTINUE
      K=0
    9 AMAT(I,K1)=0.0D0
   17 NS1=NS1+N
   12 RETURN
      END
```

```
      SUBROUTINE SCFCLO
      IMPLICIT REAL*8(A-H,O-Z)
C     CNDO/2 CLOSED SHELL SCF SEGMENT
C     GAMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q AND
C     UPPER TRIANGLE OF A, AND INITIAL DENSITY MATRIX CONTAINED IN B
      COMMON/INFO/NATOMS,AN(15),C(15,3),N
      COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)
      COMMON/GAB/XXX(480),G(15,15),Q(80),YYY(80),ROOT(80),ENERGY
      COMMON/INFO1/CZ(15),U(80),ULIM(15),LLIM(15),NELECS,OCCA,OCCB
      COMMON/MAJIC/MAGIC,MAJ
      COMMON/CHOICE/ICHOIS,ICHOOZ
      INTEGER OCCA,OCCB,UL,ULIM,U,AN,CZ,Z
      DIMENSION G1(18),F2(18)
         IT=25
      G1(3)=.092012D0
      G1(4)=.1407  D0
      G1(5)=.199265D0
      G1(6)=.267708D0
      G1(7)=.346029D0
      G1(8)=.43423 D0
      G1(9)=.532305D0
      F2(3)=.049865D0
      F2(4)=.089125D0
      F2(5)=.13041 D0
      F2(6)=.17372 D0
      F2(7)=.219055D0
      F2(8)=.266415D0
      F2(9)=.31580 D0
      Z=0
      NEIG=OCCA
   10 CONTINUE
      Z = Z+1
      ENERGY = 0.D0
C     TRANSFER CORE HAMILTONIAN TO LOWER TRIANGLE OF A
      DO 20 I=1,N
      A(I,I)=Q(I)
      DO 20 J=I,N
   20 A(J,I)=A(I,J)
      DO 30 I=1,N
      II=U(I)
      A(I,I)=A(I,I)-B(I,I)*G(II,II)*0.5D0
      DO 30 K=1,N
      JJ=U(K)
   30 A(I,I)=A(I,I)+B(K,K)*G(II,JJ)
      NM=N-1
      DO 40 I=1,NM
      II=U(I)
      LL=I+1
      DO 40 J=LL,N
      JJ=U(J)
   40 A(J,I)=A(J,I)-B(J,I)*G(II,JJ)*0.5D0
      DO 100 I=1,N
  100 ENERGY=ENERGY+0.5D0*B(I,I)*(A(I,I)+Q(I))
      DO 105 I=1,NM
      LL=I+1
      DO 105 J=LL,N
```

```
  105 ENERGY=ENERGY+B(I,J)*(A(I,J)+A(J,I))
      IF(ICHOOZ.EQ.0) GO TO 115
      WRITE(6,110) ENERGY
  110 FORMAT(10X,22H ELECTRONIC ENERGY     ,F16.10)
  115 IF(DABS(ENERGY-OLDENG).GE..00000100) GO TO 150
  120 Z=IT+10
      NEIG=N
      IF(ICHCOZ.EQ.0) GO TO 145
  130 WRITE(6,140)
  140 FORMAT(5X,18H ENERGY SATISFIED /)
  145   K=NATCMS-1
      CO 55 I=1,K
        L=I+1
      DC 55 J=L,NATCMS
      RAD=DSQRT((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2
     1          +(C(I,3)-C(J,3))**2)
   55 ENERGY=ENERGY+(DFLCAT(CZ(I))*DFLCAT(CZ(J)))/RAD
      ERGY=ENERGY*27.204D+00
      IF(ICHCCZ.EQ.0) GO TO 155
      WRITE (6,65) ERGY
   65 FCRMAT(//,10X,16H TCTAL ENERGY = ,F16.8,' EV')
  155 GO TO 170
  150 CCNTINUE
  160 CLDENG=ENERGY
  170 CONTINUE
      CALL GIVENS(N,NEIG)
      IF (Z.LE.IT) GO TO 240
      CO 200 I=1,N
  200 RCCT(I)=RCOT(I)*27.204C0
      IF(ICHOOZ.EQ.0) GO TO 240
      MAJ=MAGIC
      MAJ=(MAJ/5)*5
      IF(MAJ.NE.MAGIC) GO TO 240
  220 WRITE(6,230)
  230 FCPMAT(1X,28HEIGENVALUES AND EIGENVECTORS)
      CALL SCFCUT(1,2)
  240 CCNTINUE
C     EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
      DO 280 I=1,N
      DO 260 J=I,N
      XXX(J)=0.0D0
      CO 250 K=1,OCCA
  250 XXX(J)= XXX(J)+B(I,K)*B(J,K)*2.0D0
  260 CCNTINUE
      DC 270 J=I,N
  270 B(I,J)= XXX(J)
  280 CONTINUE
      DO 290 I=1,N
      CO 290 J=I,N
  290 B(J,I)=B(I,J)
      IF (Z.LE.IT) GO TO 10
  300 CCNTINUE
      RETURN
      END
```

```
      SUBROUTINE COEFFT
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/ARRAYS/S(80,80),Y(9135),Z( 765),XX(2900)
      DO 1 I=1,9135
    1 Y(I)=0.0D0
      DO 2 I=1,765
    2 Z(I)=0.0D0
C     LOAD NON-ZERO Y COEFFICIENTS
      Y(7039)=    64.D0
      Y(7040)=    64.D0
      Y(7049)=   -64.D0
      Y(7032)=  -128.D0
      Y(7041)=   -64.D0
      Y(7033)=  -128.D0
      Y(7042)=   128.D0
      Y(7025)=    64.D0
      Y(7034)=   128.D0
      Y(7026)=    64.D0
      Y(7035)=   -64.D0
      Y(7027)=   -64.D0
      Y(6904)=   -96.D0
      Y(6913)=    32.D0
      Y(6896)=  -192.D0
      Y(6905)=   192.D0
      Y(6906)=   288.D0
      Y(6915)=   -96.D0
      Y(6889)=   192.D0
      Y(6907)=  -192.D0
      Y(6890)=    96.D0
      Y(6899)=  -288.D0
      Y(6891)=  -192.D0
      Y(6900)=   192.D0
      Y(6892)=   -32.D0
      Y(6901)=    96.D0
      Y(2854)=   -16.D0
      Y(2863)=    16.D0
      Y(2847)=    32.D0
      Y(2856)=   -16.D0
      Y(2865)=   -16.D0
      Y(2840)=   -16.D0
      Y(2849)=   -16.D0
      Y(2858)=    32.D0
      Y(2842)=    16.D0
      Y(2851)=   -16.D0
      Y(2710)=    48.D0
      Y(2719)=   -48.D0
      Y(2711)=    48.D0
      Y(2720)=   -96.D0
      Y(2729)=    48.D0
      Y(2703)=   -48.D0
      Y(2712)=   -48.D0
      Y(2721)=    96.D0
      Y(2704)=   -48.D0
      Y(2713)=    48.D0
      Y(2722)=    48.D0
      Y(2731)=   -48.D0
```

```
Y(2705)=    96.00
Y(2714)=   -48.00
Y(2723)=   -48.00
Y(2706)=    48.00
Y(2715)=   -96.00
Y(2724)=    48.00
Y(2707)=   -48.00
Y(2716)=    48.00
Y(5329)=    64.00
Y(5322)=  -128.00
Y(5340)=   -64.00
Y(5315)=    64.00
Y(5333)=   128.00
Y(5326)=   -64.00
Y(5185)=   -96.00
Y(5194)=    32.00
Y(5186)=   -96.00
Y(5195)=    64.00
Y(5204)=    32.00
Y(5178)=    96.00
Y(5187)=    32.00
Y(5196)=    64.00
Y(5179)=    96.00
Y(5188)=   -32.00
Y(5197)=    32.00
Y(5206)=   -96.00
Y(5180)=   -64.00
Y(5189)=   -32.00
Y(5198)=   -96.00
Y(5181)=   -32.00
Y(5190)=   -64.00
Y(5199)=    96.00
Y(5182)=   -32.00
Y(5191)=    96.00
Y(4375)=  -144.00
Y(4384)=    96.00
Y(4393)=   -16.00
Y(4368)=   144.00
Y(4386)=   -48.00
Y(4395)=    96.00
Y(4370)=   -96.00
Y(4379)=    48.00
Y(4397)=  -144.00
Y(4372)=    16.00
Y(4361)=   -96.00
Y(4390)=   144.00
Y(1900)=   144.00
Y(1909)=  -144.00
Y(1893)=  -144.00
Y(1920)=   144.00
Y(1895)=   144.00
Y(1922)=  -144.00
Y(1906)=  -144.00
Y(1915)=   144.00
Y( 955)=   -16.00
Y( 964)=    32.00
```

```
Y( 973)=   -16.00
Y( 948)=    16.00
Y( 966)=   -48.00
Y( 975)=    32.00
Y( 950)=   -32.00
Y( 959)=    48.00
Y( 977)=   -16.00
Y( 952)=    16.00
Y( 961)=   -32.00
Y( 970)=    16.00
Y(8155)=    64.00
Y(8156)=   -64.00
Y(8165)=   -64.00
Y(8148)=   -64.00
Y(8157)=    64.00
Y(8149)=    64.00
Y(8158)=    64.00
Y(8150)=   -64.00
Y(8020)=   -96.00
Y(8029)=    32.00
Y(8021)=   128.00
Y(8013)=    96.00
Y(8031)=   -96.00
Y(8014)=  -128.00
Y(8015)=   -32.00
Y(8024)=    96.00
Y(7084)=   -64.00
Y(7076)=  -128.00
Y(7085)=    64.00
Y(7086)=   128.00
Y(7069)=   128.00
Y(7070)=    64.00
Y(7079)=  -128.00
Y(7071)=   -64.00
Y(3205)=   -16.00
Y(3214)=    16.00
Y(3206)=    16.00
Y(3215)=   -16.00
Y(3198)=    16.00
Y(3216)=   -16.00
Y(3199)=   -16.00
Y(3217)=    16.00
Y(3200)=   -16.00
Y(3209)=    16.00
Y(3201)=    16.00
Y(3210)=   -16.00
Y(7579)=    64.00
Y(7580)=   -64.00
Y(7572)=  -128.00
Y(7573)=   128.00
Y(7565)=    64.00
Y(7566)=   -64.00
Y(5680)=    64.00
Y(5681)=   -64.00
Y(5673)=   -64.00
Y(5691)=   -64.00
```

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Y(5674)=     64.00
Y(5692)=     64.00
Y(5684)=     64.00
Y(5685)=    -64.00
Y(7435)=    -96.00
Y(7444)=     32.00
Y(7436)=    -96.00
Y(7445)=    160.00
Y(7428)=     96.00
Y(7437)=    128.00
Y(7446)=    -96.00
Y(7429)=     96.00
Y(7438)=   -128.00
Y(7447)=    -96.00
Y(7430)=   -160.00
Y(7439)=     96.00
Y(7431)=    -32.00
Y(7440)=     96.00
Y(5545)=    -96.00
Y(5554)=     32.00
Y(5546)=     32.00
Y(5555)=     32.00
Y(5538)=     96.00
Y(5556)=     32.00
Y(5539)=    -32.00
Y(5557)=    -96.00
Y(5540)=    -32.00
Y(5549)=    -32.00
Y(5541)=    -32.00
Y(5550)=     96.00
Y(3070)=     48.00
Y(3079)=    -48.00
Y(3071)=    -48.00
Y(3080)=     48.00
Y(3063)=    -48.00
Y(3081)=     48.00
Y(3064)=     48.00
Y(3082)=    -48.00
Y(3065)=     48.00
Y(3074)=    -48.00
Y(3066)=    -48.00
Y(3075)=     48.00
Y(8200)=    -64.00
Y(8201)=     64.00
Y(8193)=     64.00
Y(8194)=    -64.00
Y(7615)=    -64.00
Y(7616)=    -64.00
Y(7625)=     64.00
Y(7608)=     64.00
Y(7617)=     64.00
Y(7609)=     64.00
Y(7618)=    -64.00
Y(7610)=    -64.00
Y(3250)=     16.00
Y(3259)=    -16.00
```

```
      Y(3243)=   -16.D0
      Y(3261)=    16.D0
      Y(3245)=    16.D0
      Y(3254)=   -16.D0
      Y(5725)=   -64.D0
      Y(5718)=    64.D0
      Y(5736)=    64.D0
      Y(5729)=   -64.D0
C     LOAD NON-ZERO Z COEFFICIENTS
      Z(341)=    -1.D0
      Z(343)=     3.D0
      Z(345)=    -3.D0
      Z(347)=     1.D0
      Z(664)=    -1.D0
      Z(665)=     5.D0
      Z(666)=   -10.D0
      Z(667)=    10.D0
      Z(668)=    -5.D0
      Z(669)=     1.D0
      Z(154)=    -1.D0
      Z(156)=     5.D0
      Z(158)=   -10.D0
      Z(160)=    10.D0
      Z(162)=    -5.D0
      Z(164)=     1.D0
      Z(222)=    -1.D0
      Z(223)=     1.D0
      Z(224)=     4.D0
      Z(225)=    -4.D0
      Z(226)=    -6.D0
      Z(227)=     6.D0
      Z(228)=     4.D0
      Z(229)=    -4.D0
      Z(230)=    -1.D0
      Z(231)=     1.D0
      Z(307)=    -1.D0
      Z(308)=     2.D0
      Z(309)=     2.D0
      Z(310)=    -6.D0
      Z(312)=     6.D0
      Z(313)=    -2.D0
      Z(314)=    -2.D0
      Z(315)=     1.D0
      Z(409)=    -1.D0
      Z(410)=     3.D0
      Z(411)=    -1.D0
      Z(412)=    -5.D0
      Z(413)=     5.D0
      Z(414)=     1.D0
      Z(415)=    -3.D0
      Z(416)=     1.D0
      Z(528)=    -1.D0
      Z(529)=     4.D0
      Z(530)=    -5.D0
      Z(532)=     5.D0
      Z(533)=    -4.D0
```

```
      Z(534)=    1.D0
      Z(562)=   -1.D0
      Z(563)=    2.D0
      Z(565)=   -2.D0
      Z(566)=    1.D0
      Z(732)=   -1.D0
      Z(733)=    1.D0
      Z(545)=    1.D0
      Z(546)=   -3.D0
      Z(547)=    2.D0
      Z(548)=    2.D0
      Z(549)=   -3.D0
      Z(550)=    1.D0
      Z(579)=    1.D0
      Z(580)=   -1.D0
      Z(581)=   -1.D0
      Z(582)=    1.D0
      Z(596)=   -1.D0
      Z(598)=    1.D0
      Z(443)=   -1.D0
      Z(444)=    1.D0
      Z(445)=    2.D0
      Z(446)=   -2.D0
      Z(447)=   -1.D0
      Z(448)=    1.D0
      Z(698)=   -1.D0
      Z(699)=    3.D0
      Z(700)=   -3.D0
      Z(701)=    1.D0
      Z(324)=    1.D0
      Z(325)=   -1.D0
      Z(326)=   -3.D0
      Z(327)=    3.D0
      Z(328)=    3.D0
      Z(329)=   -3.D0
      Z(330)=   -1.D0
      Z(331)=    1.D0
      Z(460)=    1.D0
      Z(462)=   -2.D0
      Z(464)=    1.D0
      RETURN
      END
```

```
      SUBROUTINE INTGRL
      IMPLICIT REAL*8(A-H,O-Z)
C     ATOMIC INTEGRALS FOR CNDO CALCULATIONS
      COMMON/ARRAYS/S(80,80),Y(9,5,203),Z(17,45),XX(2900)
      COMMON/INFO/NATOMS,AN(15),C(15,3),N
         COMMON /STO/ MU
      COMMON/INFO1/CZ(15),U(80),ULIM(15),LLIM(15),NELECS,OCCA,OCCB
      COMMON/GAB/XXX(399),T(9,9),GAMMA(15,15),PAIRS(9,9),TEMP(9,9),
     *C1(3),C2(3),YYY(73)
      COMMON/AUXINT/A(17),B(17)
      DIMENSION MU(18),NC(18),LC(9),MC(9),E(3)
      DIMENSION P(80,80)
      EQUIVALENCE (P(1),Y(1))
      REAL*8 MU,NUM,K1,K2
      INTEGER AN,ULIM,ULK,ULL,CZ,U,ANL,ANK,OCCA,OCCB
C     DETERMINATION OF SIZE OF AO BASIS IN AND CORE CHARGE CZ
      N=0
      DO 60 I=1,NATOMS
      LLIM(I) = N+1
      K=1
      IF (AN(I).LT.11) GO TO 20
   10 N=N+9
      CZ(I)=AN(I)-10
      GO TO 50
   20 IF (AN(I).LT.3) GO TO 40
   30 N=N+4
      CZ(I) = AN(I)-2
      GO TO 50
   40 N=N+1
      CZ(I)= AN(I)
   50 CONTINUE
      ULIM(I) = N
   60 CONTINUE
C     FILL U ARRAY---U(J) IDENTIFIES THE ATOM TO WHICH ORBITAL J IS
C     ATTACHED E.G. ORBITAL 32 ATTACHED TO  ATOM 7, ETC.
      DO 70 K=1,NATOMS
      LLK = LLIM(K)
      ULK = ULIM(K)
      LIM = ULK+1-LLK
      DO 70 I=1,LIM
      J = LLK+I-1
   70 U(J) = K
C     ASSIGNMENT OF ORBITAL EXPONENTS TO ATOMS BY SLATERS RULES
      MU(2)=1.7D0
      MU(1)=1.2D0
      NC(1)=1
      NC(2)=1
      DO 80 I=3,10
      NC(I)=2
   80 MU(I)=.325D0*DFLOAT(I-1)
      DO 90 I=11,18
      NC(I)=3
   90 MU(I)=(.65D0*DFLOAT(I)-4.95D0)/3.D0
C     ASSIGNMENT OF ANGULAR MOMENTUM QUANTUM NOS. TO ATOMIC ORBITALS
      LC(1)=0
      LC(2)=1
```

```
      LC(3)=1
      LC(4)=1
      LC(5)=2
      LC(6)=2
      LC(7)=2
      LC(8)=2
      LC(9)=2
      MC(1)=0
      MC(2)=1
      MC(3)=-1
      MC(4)=0
      MC(5)=0
      MC(6)=1
      MC(7)=-1
      MC(8)=2
      MC(9)=-2
C     STEP THRU PAIRS OF ATOMS
      DO 320 K=1,NATOMS
      DO 320 L=K,NATOMS
      DO 100 I=1,3
      C1(I) = C(K,I)
  100 C2(I) = C(L,I)
C     CALCULATE UNIT VECTOR ALONG INTERATOM AXIS,E
      CALL RELVEC(R,E,C1,C2)
      LLK = LLIM(K)
      LLL = LLIM(L)
      ULK = ULIM(K)
      ULL = ULIM(L)
      NORBK=ULK-LLK+1
      NORBL=ULL-LLL+1
      ANK=AN(K)
      ANL=AN(L)
C     LOOP THRU PAIRS OF BASIS FUNCTIONS, ONE ON EACH ATOM
      DO 200 I=1,NORBK
      DO 200 J=1,NORBL
      IF(K.EQ.L) GO TO 160
  110 IF(MC(I).NE.MC(J)) GO TO 150
  120 IF(MC(I).LT.0) GO TO 140
  130 PAIRS(I,J)=DSQRT((MU(ANK)*R)**(2*NC(ANK)+1)*(MU(ANL)*R)**(2*NC(ANL
     1)+1)/(FACT(2*NC(ANK))*FACT(2*NC(ANL))))*(-1.D0)**(LC(J)+MC(J))
     2*SS(NC(ANK),LC(I),MC(I),NC(ANL),LC(J),MU(ANK)*R,MU(ANL)*R)
      GO TO 190
  140 PAIRS(I,J)=PAIRS(I-1,J-1)
      GO TO 190
  150 PAIRS(I,J)=0.0D0
      GO TO 190
  160 IF (I.EQ.J) GO TO 170
  180 PAIRS(I,J)=0.0D0
      GO TO 190
  170 PAIRS(I,J)=1.0D0
  190 CONTINUE
  200 CONTINUE
      LCULK=LC(NORBK)
      LCULL=LC(NORBL)
      MAXL=MAX0(LCULK,LCULL)
      IF(R.GT.0.000001D0) GO TO 220
```

```
  210 GO TO 250
C     ROTATE INTEGRALS FROM DIATOMIC BASIS TO MOLECULAR BASIS
  220 CALL HARMTR(T,MAXL,E)
      DO 230 I=1,NORBK
      DO 230 J=1,NORBL
      TEMP(I,J) = 0.D0
      DO 230 KK=1,NORBL
      TEMP(I,J) = TEMP(I,J)+T(J,KK)*PAIRS(I,KK)
  230 CONTINUE
      DO 240 I=1,NORBK
      DO 240 J=1,NORBL
      PAIRS(I,J) = 0.D0
      DO 240 KK=1,NORBK
      PAIRS(I,J) = PAIRS(I,J)+T(I,KK)*TEMP(KK,J)
  240 CONTINUE
C     FILL S MATRIX
  250 CONTINUE
      DO 260 I=1,NORBK
      LLKP=LLK+I-1
      DO 260 J=1,NORBL
      LLLP=LLL+J-1
  260 S(LLKP,LLLP)=PAIRS(I,J)
C     COMPUTATION OF 1-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIONS
      N1=NC(ANK)
      N2=NC(ANL)
      K1=MU(ANK)
      K2=MU(ANL)
      IF(K.NE.L) GO TO 290
  270 TERM1 = FACT(2*N1-1)/((2.D0*K2)**(2*N1))
      TERM2 = 0.D0
      LIM = 2*N1
      DO 280 J=1,LIM
      NUM =DFLOAT(J)*(2.D0*K1)**(2*N1-J)*FACT(4*N1-J-1)
      DEN = FACT(2*N1-J)*2.D0*DFLOAT(N1)*(2.D0*(K1+K2))**(4*N1-J)
      TERM2 = TERM2 + NUM/DEN
  280 CONTINUE
      GO TO 310
C     COMPUTATION OF 2-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIONS
  290 TERM1=(R/2.D0)**(2*N2)*SS(0,0,0,2*N2-1,0,0.D0,2.D0*K2*R)
      TERM2 = 0.D0
      LIM = 2*N1
      DO 300 J=1,LIM
  300 TERM2 = TERM2+(DFLOAT(J)*(2.D0*K1)**(2*N1-J)*(R/2.D0)**(2*
     1N1-J+2*N2))/ (FACT(2*N1-J)*2.D0*DFLOAT(N1))*SS(2*N1-J,0,0,2*N2-1,0
     2,2.D0*K1*R,2.D0*K2*R)
  310 GAMMA(K,L) = ((2.D0*K2)**(2*N2+1)/FACT(2*N2))*(TERM1-TERM2)
  320 CONTINUE
C     SYMMETRIZATION OF OVERLAP AND COULOMB INTEGRAL MATRICES
      DO 330 I=1,N
      DO 330 J=I,N
  330 S(J,I) = S(I,J)
      DO 340 I=1,NATOMS
      DO 340 J=I,NATOMS
  340 GAMMA(J,I) = GAMMA(I,J)
      RETURN
      END
```

```
      SUBROUTINE HARMTR(T,MAXL,E)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION T(9,9),E(3)
      COST = E(3)
      IF((1.DO-COST**2).GT.1.D-10          ) GO TO 20
   10 SINT = 0.DO
      GO TO 30
   20 SINT=DSQRT(1.DO-COST**2)
   30 CONTINUE
      IF(SINT.GT.0.000001DO)  GO TO 50
   40 COSP = 1.DO
      SINP = 0.DO
      GO TO 70
   50 COSP = E(1)/SINT
   60 SINP = E(2)/SINT
   70 CONTINUE
      DO 80 I=1,9
      DO 80 J=1,9
   80 T(I,J) = 0.DO
      T(1,1) =1.DO
      IF (MAXL.GT.1) GO TO 100
   90 IF (MAXL.GT.0) GO TO 110
      GO TO 120
  100 COS2T = COST**2-SINT**2
      SIN2T = 2.DO*SINT*COST
      COS2P = COSP**2-SINP**2
      SIN2P = 2.DO*SINP*COSP
C     TRANSFORMATION MATRIX ELEMENTS FOR D FUNCTIONS
      SQRT3=DSQRT(3.DO)
      T(5,5) = (3.DO*COST**2-1.DO)/2.DO
      T(5,6) = -SQRT3   *SIN2T/2.DO
      T(5,8) = SQRT3   *SINT**2/2.DO
      T(6,5) = SQRT3   *SIN2T*COSP/2.DO
      T(6,6) = COS2T*COSP
      T(6,7) = -COST*SINP
      T(6,8) =-T(6,5)/SQRT3
      T(6,9) = SINT*SINP
      T(7,5) = SQRT3   *SIN2T*SINP/2.DO
      T(7,6) = COS2T*SINP
      T(7,7) = COST*COSP
      T(7,8) = -T(7,5)/SQRT3
      T(7,9) = -SINT*COSP
      T(8,5) = SQRT3   *SINT**2*COS2P/2.DO
      T(8,6) = SIN2T*COS2P/2.DO
      T(8,7) = -SINT*SIN2P
       T(8,8) = (1.DO+COST**2)*COS2P/2.DO
      T(8,9) = -COST*SIN2P
      T(9,5) = SQRT3   *SINT**2*SIN2P/2.DO
      T(9,6) = SIN2T*SIN2P/2.DO
      T(9,7) = SINT*COS2P
      T(9,8) = (1.DO+COST**2)*SIN2P/2.DO
      T(9,9) = COST*COS2P
  110 CONTINUE
C     TRANSFORMATION MATRIX ELEMENTS FOR P FUNCTIONS
      T(2,2) = COST*COSP
      T(2,3) = -SINP
```

```
      T(2,4)  =  SINT*COSP
      T(3,2)  =  COST*SINP
      T(3,3)  =  COSP
      T(3,4)  =  SINT*SINP
      T(4,2)  =  -SINT
      T(4,4)  =  COST
  120 CONTINUE
      RETURN
      END
```

```
      SUBRCUTINE CPRINT
      IMPLICIT REAL*8(A-H,O-Z)
C     CNDO SCF CLCSED SHELL- PRINTOUT SEGMENT
      COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)
      CCMMON/GAB/XXX(480),G(15,15),Q(80),YYY(80),ROOT(80),ENERGY
      COMMCN/INFC/NATCMS,AN(15),C(15,3),N
      COMMON/INFO1/CZ(15),U(80),ULIM(15),LLIM(15),NELECS,OCCA,OCCB
      COMMON/PERTBL/EL(18)
      CCMMCN/MTXPTS/CCNTDP(51,5),NTHROW
      COMMCN/VARY/CINCRM,NTIMES
      COMMON/MAJIC/MAGIC,MAJ
      COMMON/CHOICE/ICHOIS,ICHOOZ
      INTEGER AN,U,ULIM,EL,OCCA,OCCB,UL,CZ,ANI
      CIMENSION DPM(3),DM(3),DMSP(3),DMPO(3)
      DIMENSION ATENG(18)
      ATENG(1)=-0.6387302462  DO
      ATENG(3)=-.2321972405   DO
      ATENG(4)=-1.1454120355  DO
      ATENG(5)=-2.9774239048  DO
      ATENG(6)=-6.1649936261  DO
      ATENG(7)=-11.0768746252 DO
      ATENG(8)=-18.0819658651 DO
      ATENG(9)=-27.5491302880 DO
      ATENG(11)=-.1977009568  DO
      ATENG(12)=-.8671913833  DO
      ATENG(13)=-2.0364557744 DO
      ATENG(14)=-3.8979034686 DO
      ATENG(15)=-6.7966009163 DO
      ATENG(16)=-10.7658174341DO
      ATENG(17)=-16.0467017940DO
   30 CCNTINUE
      K=NATCMS-1
      IF(ICHOOZ.EQ.0) GO TO 45
      IF(MAJ.NE.MAGIC) GO TO 45
      WRITE(6,40)
   40 FORMAT('1',1X,15H DENSITY MATRIX)
      CALL SCFCUT(0,2)
   45 DO 70 I=1,NATCMS
      ANI=AN(I)
   70 ENERGY=ENERGY-ATENG(ANI)
      ERGY=ENERGY*27.204D+00
      IF(ICHCCZ.EC.0) GO TO 85
      WRITE (6,80) ERGY
   80 FORMAT(//,10X,16HBINDING ENERGY= ,F16.8,' EV')
   85 DO 110 I=1,NATCMS
      TCHG = 0.DO
      LL=LLIM(I)
      UL=ULIM(I)
      DO 90 J=LL,UL
   90 TCHG = TCHG+B(J,J)
      ANI=AN(I)
      IF(ICHOOZ.EQ.0) GO TO 105
      WRITE(6,100) I,EL(ANI),TCHG
  100 FORMAT(I3,A4,8X,F7.4)
  105 XXX(I)=TCHG
  110 CONTINUE
```

```
      DO 120 I=1,3
      DM(I)=0.0D0
      DMSP(I)=0.0D0
  120 DMPD(I)=0.0D0
      DO 200 J=1,NATOMS
      IF (AN(J).LT.3) GO TO 180
  130 IF (AN(J).LT.11) GO TO 140
  160 SLTRI=(.65D0*DFLOAT(AN(J))-4.95D0)/3.D0
      FACTOR=2.5416D0*7.D0/(DSQRT(5.D0)*SLTRI)
      INDEX=LLIM(J)
      DO 170 K=1,3
  170 DMSP(K)=DMSP(K)-B(INDEX,INDEX+K)*10.27175D0/SLTRI
      DMPD(1)=DMPD(1)-FACTOR*(B(INDEX+2,INDEX+8)+B(INDEX+3,INDEX+5)
     1  +B(INDEX+1,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+1,INDEX+4))
      DMPD(2)=DMPD(2)-FACTOR*(B(INDEX+1,INDEX+8)+B(INDEX+3,INDEX+6)
     1  +B(INDEX+2,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+2,INDEX+4))
      DMPD(3)=DMPD(3)-FACTOR*(B(INDEX+1,INDEX+5)+B(INDEX+2,INDEX+6)
     1  +2.D0/DSQRT(3.D0)*B(INDEX+3,INDEX+4))
      GO TO 180
  140 INDEX=LLIM(J)
      DO 150 K=1,3
  150 DMSP(K)=DMSP(K)-B(INDEX,INDEX+K)*7.33697D0/
     1 (.325D0*DFLOAT(AN(J)-1))
  180 DO 190 I=1,3
  190 DM(I)=DM(I)+(DFLOAT(CZ(J))-XXX(J))*C(J,I)*2.5416D0
  200 CONTINUE
      DO 210 I=1,3
  210 DPM(I)=DM(I)+DMSP(I)+DMPD(I)
      IF(ICHOOZ.EQ.0) GO TO 275
      WRITE(6,220)
  220 FORMAT(//,30X,16H  DIPOLE MOMENTS,/)
      WRITE(6,230)
  230 FORMAT(15X,11H COMPONENTS,3X,2H X,8X,2H Y,8X,2H Z)
      WRITE(6,240)DM(1),DM(2),DM(3)
  240 FORMAT(15X,10H DENSITIES,3(1X,F9.5))
      WRITE(6,250)DMSP(1),DMSP(2),DMSP(3)
  250 FORMAT(15X,4H S.P,6X,3(1X,F9.5))
      WRITE(6,260)DMPD(1),DMPD(2),DMPD(3)
  260 FORMAT(15X,4H P.D,6X,3(1X,F9.5))
      WRITE(6,270)DPM(1),DPM(2),DPM(3)
  270 FORMAT(15X,6H TOTAL,4X,3(1X,F9.5),/)
  275 DP=DSQRT(DPM(1)**2+DPM(2)**2+DPM(3)**2)
      IF(ICHOOZ.EQ.0) GO TO 285
      WRITE(6,280) DP
  280 FORMAT(13X,15H DIPOLE MOMENT=,F9.5,7H DEBYES,//)
  285 CONTOP(NTHROW,2)=DPM(1)
      CONTOP(NTHROW,3)=DPM(2)
      CONTOP(NTHROW,4)=DPM(3)
      CONTOP(NTHROW,5)=DP
      RETURN
      END
```

```
      SUBROUTINE HUCKCL
      IMPLICIT REAL*8(A-H,O-Z)
C     EXTENDED HUCKEL THEORY FOR CLOSED SHELLS
C     OVERLAPS ARE IN MATRIX A,COULOMB INTEGRALS(GAMMA) ARE IN MATRIX G
      COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)
      COMMON/INFO/NATOMS,AN(15),C(15,3),N
      COMMON/INFO1/CZ(15),F(80),ULIM(15),LLIM(15),NELECS,OCCA,OCCB
      COMMON/GAB/XXX(480),G(15,15),Q(80),YYY(80),ROOT(80),ENERGY
      DIMENSION ENEG(18,3),BETAO(18)
         DIMENSION BETA(17,17)
      DIMENSION G1(18),F2(18)
         DIMENSION S(80,80)
         EQUIVALENCE(S(1,1),A(1,1))
      INTEGER OCCA,OCCB,UL,AN,CZ,F,ULIM,ANI
         SQ3=DSQRT(3.D0)
      G1(3)=.092012      D0
      G1(4)=.1407        D0
      G1(5)=.199265      D0
      G1(6)=.267708      D0
      G1(7)=.346029      D0
      G1(8)=.43423       D0
      G1(9)=.532305      D0
      F2(3)=.049865      D0
      F2(4)=.089125      D0
      F2(5)=.13041       D0
      F2(6)=.17372       D0
      F2(7)=.219055      D0
      F2(8)=.266415      D0
      F2(9)=.31580       D0
      ENEG(1,1)=7.1761   D0
      ENEG(3,1)=3.1055   D0
      ENEG(3,2)=1.258    D0
      ENEG(4,1)=5.94557  D0
      ENEG(4,2)=2.563    D0
      ENEG(5,1)=9.59407  D0
      ENEG(5,2)=4.001    D0
      ENEG(6,1)=14.051   D0
      ENEG(6,2)=5.572    D0
      ENEG(7,1)=19.31637D0
      ENEG(7,2)=7.275    D0
      ENEG(8,1)=25.39017D0
      ENEG(8,2)=9.111    D0
      ENEG(9,1)=32.2724  D0
      ENEG(9,2)=11.08    D0
      ENEG(11,1)=2.804   D0
      ENEG(11,2)=1.302   D0
      ENEG(11,3)=0.150   D0
      ENEG(12,1)=5.1254  D0
      ENEG(12,2)=2.0516  D0
      ENEG(12,3)=0.16195D0
      ENEG(13,1)=7.7706  D0
      ENEG(13,2)=2.9951  D0
      ENEG(13,3)=0.22425D0
      ENEG(14,1)=10.0327D0
      ENEG(14,2)=4.1325  D0
      ENEG(14,3)=0.337   D0
```

```
      ENEG(15,1)=14.0327D0
      ENEG(15,2)=5.4638 D0
      ENEG(15,3)=0.500  D0
      ENEG(16,1)=17.6496D0
      ENEG(16,2)=6.939  D0
      ENEG(16,3)=0.71325D0
      ENEG(17,1)=21.5906D0
      ENEG(17,2)=8.7081 D0
      ENEG(17,3)=0.97695D0
      BETA0(1)= -9.     D0
      BETA0(3)= -9.     D0
      BETA0(4)= -13.    D0
      BETA0(5)= -17.    D0
      BETA0(6)= -21.    D0
      BETA0(7)= -25.    D0
      BETA0(8)= -31.    D0
      BETA0(9)= -39.    D0
      BETA0(11)=-7.7203 D0
      BETA0(12)=-9.4471 D0
      BETA0(13)=-11.3011D0
      BETA0(14)=-13.065 D0
      BETA0(15)=-15.070 D0
      BETA0(16)=-18.150 D0
      BETA0(17)=-22.330 D0
C... EXPAND THE BETA MATRIX
         DO 511 I=1,17
         DO 511 J=1,I
         BETA(I,J)=.5D0*(BETA0(I)+BETA0(J))
         BETA(J,I)=BETA(I,J)
511      CONTINUE
C     FIND NELECS AND FILL H CORE(DIAGONAL) WITH (I+A)/2
      NELECS=0
      DO 60 I=1,NATOMS
      NELECS=NELECS+CZ(I)
      LL =LLIM(I)
      UL =ULIM(I)
      ANI=AN(I)
      L=0
      DO 50 J=LL,UL
      L=L+1
      IF (L.EQ.1) GO TO 10
   20 IF (L.LT.5) GO TO 40
   30 A(J,J)=-ENEG(ANI,3)/27.21D0
      GO TO 50
   40 A(J,J)=-ENEG(ANI,2)/27.21D0
      GO TO 50
   10 A(J,J)  =-ENEG(ANI,1)/27.21D0
   50 CONTINUE
   60 CONTINUE
      OCCA=NELECS/2
C     FORM HUCKEL HAMILTONIAN IN A (OFF DIAGONAL TWO CENTER TERMS)
      DO 90 I=2,N
         D(I,I)=A(I,I)
      K=F(I)
      L=AN(K)
      UL=I-1
```

```
      DO 90 J=1,UL
      KK=F(J)
      LL=AN(KK)
      IF ((L.GT.9).OR.(LL.GT.9)) GO TO 70
80       A(I,J)=A(I,J)*BETA(L,LL)/27.21D0
      A(J,I)=A(I,J)
         GOTO 90
70       A(I,J)=0.75D0*A(I,J)*BETA(L,LL)/27.21D0
      A(J,I)=A(I,J)
   90 CONTINUE
      DO 100 I=1,N
  100 Q(I)=A(I,I)
      CALL GIVENS(N,OCCA)
C     EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
      DO 140 I=1,N
      DO 120 J=I,N
      XXX(J)=0.0D0
      DO 110 K=1,OCCA
  110 XXX(J)= XXX(J)+2.D0*B(I,K)*B(J,K)
  120 CONTINUE
      DO 130 J=I,N
  130 B(I,J)= XXX(J)
  140 CONTINUE
      DO 150 I=1,N
      DO 150 J=I,N
  150 B(J,I)=B(I,J)
C     ADD V(AB) TO HCORE--CNDO
      DO  170  I=1,N
      J=F(I)
      Q(I)=Q(I)  +0.5D0*G(J,J)
      DO 160 K=1,NATOMS
  160 Q(I)=Q(I)-DFLOAT(CZ(K))*G(J,K)
  170 CONTINUE
      DO 310 I=1,N
         A(I,I)=Q(I)
      DO 300 J=I,N
  300 A(J,I)=A(I,J)
310      CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SCFOUT(CP,MOP)
      IMPLICIT REAL*8(A-H,O-Z)
C     THIS ROUTINE PRINTS THE ARRAY IN COMMON/ARRAYS/ WHICH IS DESIGNATE
C     MOP. IF OP = 1 THE EIGENVALUES CONTAINED IN COMMON/1/ ARE ALSO
C     PRINTED. IF OP= 0 THE EIGENVALUES ARE NOT PRINTED
      COMMON/ARRAYS/A(80,80,3)
      COMMON/INFO/NATOMS,AN(15),C(15,3),N
      COMMON/INFO1/CZ(15),U(80),ULIM(15),LLIM(15),NELECS,OCCA,OCCB
      COMMON/ORB/ORB(9)
      COMMON/PERTBL/EL(18)
      INTEGER CP,AN,ANII,CZ,U,ORB,ULIM,EL,OCCA,OCCB
      DO 120 M=1,N,11
      K=M+10
      IF (K.LE.N) GO TO 30
   20 K=N
   30 CONTINUE
      WRITE(6,100)
      IF (OP.EQ.1) GO TO 40
      GO TO 50
   40 CALL EIGOUT(M,K)
   50 CONTINUE
      WRITE(6,60) (I,I=M,K)
   60 FORMAT(13X,50I9)
      DO 110 I=1,N
      II=U(I)
      ANII=AN(II)
      L=I-LLIM(II)+1
   70 WRITE(6,80) I,II,EL(ANII),ORB(L),(A(I,J,MOP),J=M,K)
   80 FORMAT(1X,I2,I3,A4,1X,A4,50(F9.4))
      IF (I.EQ.ULIM(II)) GO TO 90
      GO TO 110
   90 WRITE(6,100)
  100 FORMAT(1X)
  110 CONTINUE
  120 CONTINUE
      WRITE(6,100)
      WRITE(6,100)
      RETURN
      END
```

```
      SUBROUTINE EIGOUT(M,K)
      IMPLICIT REAL*8(A-H,O-Z)
C     THIS ROUTINE IS CALLED IN SCFOUT TO PRINT THE EIGENVALUES M TO K
      COMMON/GAB/XXX(865),EPSILN(80),YYY
      WRITE(6,10) (EPSILN(I),I=M,K)
   10 FORMAT(//,15H EIGENVALUES---,20(F9.4),//)
      RETURN
      END
```

```
      SUBROUTINE GIVENS(NX,NROOTX)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ARRAYS/AB(80,80),VECT(80,80),X(80,80)
      COMMON/GAB/B(80,6),XYZ(385),ROOT(80),ABCD
      DIMENSION A(3240),BA(3160)
      EQUIVALENCE (AB(1),BA(1)),(AB(3161),A(1))
      NJX=80
      NROOTX=NX
      DO 600 I=1,NX
      DO 600 J=1,NX
  600 VECT(I,J)=AB(I,J)
      L=1
      DO 601 J=2,NX
      K=J-1
      DO 601 I=1,K
      BA(L)=VECT(I,J)
  601 L=L+1
      L=1
      DO 602 J=1,NX
      DO 602 I=1,J
      A(L)=VECT(J,I)
  602 L=L+1
      CALL GIVEN(NX,NX,NJX,A,B,ROOT,VECT)
      L=NX*(NX-1)/2
      DO 603 I=2,NX
      K=NX-I+2
      K1=K-1
      DO 603 J=1,K1
      J1=K1-J+1
      AB(J1,K)=BA(L)
  603 L=L-1
      N=NROOTX/2
      DO 604 I=1,N
      J=NROOTX-I+1
      TEMP=ROOT(I)
      ROOT(I)=ROOT(J)
      ROOT(J)=TEMP
      DO 604 K=1,NX
      TEMP=VECT(K,I)
      VECT(K,I)=VECT(K,J)
  604 VECT(K,J)=TEMP
      RETURN
      END
```

```
      SUBROUTINE GIVEN(NX,NROOTX,NJX,A,B,ROOT,VECT)
C       CALCULATES EIGENVALUES AND EIGENVECTORS OF REAL SYMMETRIC MATRIX
C       STORED IN PACKED UPPER TRIANGULAR FORM.
C
C
C       THE PARAMETERS FOR THE ROUTINE ARE:
C           NX     ORDER OF MATRIX
C           NROOTX NUMBER OF ROOTS FOR WHICH EIGENVECTORS ARE WANTED.
C                  IF NO VECTORS ARE WANTED, MAKE NROOTX NEGATIVE.
C           NJX    ROW DIMENSION OF VECT ARRAY.  SEE 'VECT' BELOW.
C                  NJX MUST BE NOT LESS THAN NX.
C           A      MATRIX STORED BY COLUMNS IN PACKED UPPER TRIANGULAR
C                  FORM, I.E. OCCUPYING NX*(NX+1)/2 CONSECUTIVE
C                  LOCATIONS.
C           B      SCRATCH ARRAY USED BY GIVENS.  MUST BE AT LEAST
C                  NX*6 CELLS.
C           ROOT   ARRAY TO HOLD THE EIGENVALUES.  MUST BE AT LEAST
C                  NX CELLS LONG.  THE ROOTS ARE ORDERED LARGEST FIRST
C                  IN THIS ARRAY.
C           VECT   EIGENVECTOR ARRAY.  EACH COLUMN WILL HOLD AN
C                  EIGENVECTOR FOR THE CORRESPONDING ROOT.  MUST BE
C                  DIMENSIONED WITH 'NJX' ROWS AND AT LEAST 'NJX'
C                  COLUMNS, UNLESS NO VECTORS ARE REQUESTED (NEGATIVE
C                  NROOTX).  IN THIS LATTER CASE, THE ARGUMENT VECT
C                  IS JUST A DUMMY, AND THE STORAGE IS NOT USED.
C                  THE EIGENVECTORS ARE NORMALIZED TO UNIT LENGTH.
C
C       THE ARRAYS A AND B ARE DESTROYED BY THE COMPUTATION.  THE RESULTS
C       APPEAR IN ROOT AND VECT.
C       FOR PROPER FUNCTIONING OF THIS ROUTINE, THE RESULT OF A FLOATING
C       POINT UNDERFLOW SHOULD BE A ZERO.
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /VECTOR/ FACT,IDIF
      DIMENSION B(NX,6),A(1),ROOT(NX),VECT(NJX,NROOTX)
C
C       THE ORIGINAL REFERENCE TO THE GIVENS TECHNIQUE IS IN OAK RIDGE
C       REPORT NUMBER ORNL 1574 (PHYSICS), BY WALLACE GIVENS.
C       THE METHOD AS PRESENTED IN THIS PROGRAM CONSISTS OF FOUR STEPS,
C       ALL MODIFICATIONS OF THE ORIGINAL METHOD...
C       FIRST, THE INPUT MATRIX IS REDUCED TO TRIDIAGONAL FORM BY THE
C       HOUSEHOLDER TECHNIQUE (J. H. WILKINSON, COMP. J. 3, 23 (1960)).
C       THE EIGENVALUES OF THE TRIDIAGONAL MATRIX ARE THEN FOUND USING
C       THE QR TRANSFORM METHOD.  SEE J. H. WILKINSON, THE ALGEBRAIC
C       EIGENVALUE PROBLEM(1965) FOR A DESCRIPTION OF THIS ALGORITHM.
C       THE EIGENVECTORS OF THE TRIDIAGONAL FORM ARE THEN EVALUATED
C       (J. H. WILKINSON, COMP. J. 1, 90 (1958)), BY THE METHOD OF
C       INVERSE ITERATION, FOR NONDEGENERATE MATRICES.
C       FOR MATRICES WITH DEGENERATE OR NEAR-DEGENERATE EIGENVALUES,
C       THE EIGENVECTORS ARE EVALUATED INSTEAD BY FURTHER QR TRANSFORMS.
C       THIS METHOD GIVES ORTHOGONAL VECTORS EVEN FOR DEGENERATE ROOTS.
C       FINALLY THE TRIDIAGONAL VECTORS ARE ROTATED TO VECTORS OF THE
C       ORIGINAL ARRAY (FIRST REFERENCE).
C       THE INVERSE ITERATION PORTION OF THIS PROGRAM WAS ADAPTED
C       FROM THE QUANTUM CHEMISTRY PROGRAM EXCHANGE NUMBER 62.1, BY
C       FRANKLIN PROSSER.  THE EIGENVALUE SUBROUTINE (EVQR) WAS WRITTEN
C       BY WALTER NIELSEN.
```

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C       RUY GORDON,  SEPT., 1969
C
C       AN EXCELLENT PRESENTATION OF THE GIVENS TECHNIQUE IS FOUND IN
C       J. M. ORTEGA'S ARTICLE IN 'MATHEMATICS FOR DIGITAL COMPUTERS,'
C       VOLUMC 2, ED. BY RALSTON AND WILF, WILEY (1967), PAGE 94.
C
C **                                                                   *
      ETA = 1.D-16
      THETA = 1.D75
C ** * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      DEL1 = ETA/1.D2
      DELTA = ETA**2*1.D2
      SMALL = ETA**2/1.D2
      DELBIG = THETA*DELTA/1.D3
      THETA1 = 1.D3/THETA
C       TOLER IS A FACTOR USED TO DETERMINE IF ANY ROOTS ARE CLOSE
C       ENOUGH TOGETHER TO BE CONSIDERED DEGENERATE FOR PURPOSES OF
C       CALCULATING EIGENVECTORS.  FOR THE MATRIX NORMED TO UNITY, IF THE
C       DIFFERENCE BETWEEN TWO ROOTS IS LESS THAN TOLER, THEN THE
C       QR TRANSFORMATION IS USED TO FORM THE EIGENVECTORS.
      TOLER = 1.D2*DSQRT(ETA)
C       EMAG IS A TOLERANCE FOR NEGLIGIBLE ELEMENTS IN THE QR ITERATION
C       FOR EIGENVECTORS FOR DEGENERATE EIGENVALUES.
      EMAG = ETA
C
      N = NX
      FLOATN = DFLOAT (N)
      NROOT = IABS(NROOTX)
      IF (NROOT.EQ.0) GO TO 1001
      IF (N-1) 1001,1003,105
 1003 ROOT(1) = A(1)
      IF (NROOTX.GT.0) VECT(1,1) = 1.D0
      GO TO 1001
  105 CONTINUE
C       NSIZE     NUMBER OF ELEMENTS IN THE PACKED ARRAY
      NSIZE = (N*(N+1))/2
      NM1 = N-1
      NM2 = N-2
      NP1 = N+1
C
C  COMPUTE TRACE
      TRACE = 0.D0
      JUMP = 1
      DO 1 J=2,NP1
      TRACE = TRACE + A(JUMP)
    1 JUMP = JUMP + J
      TRACE = TRACE/FLOATN
C  SUBTRACT TRACE FROM DIAGONAL ELEMENTS TO GIVE A MORE RELIABLE NORM
C  WHEN THERE ARE LARGE DIAGONAL ELEMENTS
      JUMP = 1
      DO 2 J=2,NP1
      A(JUMP) = A(JUMP) - TRACE
    2 JUMP = JUMP + J
C  SCALE MATRIX TO EUCLIDEAN NORM OF 1.  SCALE FACTOR IS ANORM.
      FACTOR = 0.D0
```

```
      DO 70 I=1,NSIZE
   70 FACTOR = DMAX1(FACTOR,DABS(A(I)))
      IF (FACTOR.NE.0.D0) GO TO 72
C  NULL MATRIX.  FIX UP ROOTS AND VECTORS, THEN EXIT.
      DO 78 I=1,NROOT
      IF (NROOTX.LT.0) GO TO 78
      DO 77 J=1,N
   77 VECT(J,I) = 0.D0
      VECT(I,I) = 1.D0
   78 ROOT(I) = 0.D0
      GO TO 1001
   72 ANORM = 0.D0
   66 SCALE = DSQRT(2.D0)/FACTOR
      DO 80 I=1,NSIZE
   80 ANORM = ANORM + (A(I)*SCALE)**2
C  SUBTRACT DIAGONAL CONTRIBUTIONS, WHICH WERE COUNTED TWICE
      SCALE = 1.D0/FACTOR
      JUMP = 1
      DO 81 J=2,NP1
      ANORM = ANORM -(A(JUMP)*SCALE)**2
   81 JUMP = JUMP + J
   83 ANORM = FACTOR*DSQRT(ANORM)
      SCALE = 1.D0/ANORM
      DO 91 I=1,NSIZE
   91 A(I) = A(I)*SCALE
      ALIMIT = 1.D0
C
C  TRIDIA SECTION.
C  TRIDIAGONALIZATION OF SYMMETRIC MATRIX
      ID = 0
      IA = 1
      IF (NM2.EQ.0) GO TO 201
      DO 200 J=1,NM2
C  J        COUNTS ROW OF A-MATRIX TO BE DIAGONALIZED
C  IA       START OF NON-CODIAGONAL ELEMENTS IN THE ROW
C  ID       INDEX OF CODIAGONAL ELEMENT ON ROW BEING CODIAGONALIZED.
      IA = IA+J+2
      ID = ID+J+1
      JP2 = J + 2
      J1 = J + 1
C  FIND LIMITS FOR BAND OF SIGNIFICANT MATRIX ELEMENTS
      LIMIT = J1
      II = IA
      DO 99 I=JP2,N
      B(I,5) = A(II)
      IF (DABS(B(I,5)).GT.DEL1) LIMIT = I
   99 II = II + I
      DTEMP = A(ID)
      IF (LIMIT.GT.J1) GO TO 110
C  NO TRANSFORMATION NECESSARY IF ALL THE NON-CODIAGONAL
C  ELEMENTS ARE TINY.
  120 B(J,1) = DTEMP
      A(ID) = 0.D0
      GO TO 200
C  SUM SQUARES OF SIGNIFICANT NON-CODIAGONAL ELEMENTS OF ROW J
  110 IDIF = LIMIT -JP2
```

```
      SUM = DOT(B(JP2,5),B(JP2,5))
C  NOW COMPLETE THE SUM OF OFF-DIAGONAL SQUARES
      SUM = DSQRT(SUM + DTEMP**2)
C  NEW CODIAGONAL ELEMENT
      B(J,1) = -DSIGN(SUM,DTEMP)
C  FIRST NON-ZERO ELEMENT OF THIS W-VECTOR
      B(J+1,2) = DSQRT((1.D0 + DABS(DTEMP)/SUM)*5.D-1)
C  FORM REST OF THE W-VECTOR ELEMENTS
      TEMP = DSIGN(5.D-1/(B(J+1,2)*SUM),DTEMP)
      II = IA
      DO 130 I=JP2,LIMIT
      B(I,2) = A(II)*TEMP
  130 II = II + I
C  FORM P-VECTOR AND SCALAR.  P-VECTOR = A-MATRIX*W-VECTOR.
C  SCALAR = W-VECTOR*P-VECTOR.
      DAK = 0.D0
C  IC        LOCATION OF NEXT DIAGONAL ELEMENT
      IC = ID + 1
C  I         RUNS OVER THE NON-ZERO P-ELEMENTS
C  CASES FOR I LESS THAN LIMIT
      LIMLES = LIMIT - 1
      DO 188 I=J1,LIMLES
C  FORM FIRST PART OF P ELEMENT
      IDIF = I - J1
      DTEMP = DOT(B(J1,2),A(IC))
C  MOVE IC TO TOP OF NEXT A-MATRIX 'ROW'
      IC = IC + I
C  COMPLETE P ELEMENT
C  CHANGE INCREMENTING MODE AT THE DIAGONAL ELEMENT
  178 IP1 = I + 1
      JJ = IC + IDIF
      DTEMP = DTEMP + DSUM(B(N,1),A(JJ),IP1,LIMIT)
C  BUILD UP THE K-SCALAR (AK)
      DAK = DAK + DTEMP*B(I,2)
  188 B(I,1) = DTEMP
C  CASE FOR I = LIMIT
      IDIF = LIMIT - J1
      DTEMP = DOT(B(J1,2),A(IC))
      DAK = DAK + DTEMP*B(LIMIT,2)
      B(LIMIT,1) = DTEMP
      IDIF = LIMIT - J1
C  TEST TO SEE IF ANY I VALUES REMAIN
      IF (LIMIT.EQ.N) GO TO 190
      IC = IC + LIMIT
      LIMLO = LIMIT + 1
C  DO REMAINING I VALUES
      DO 189 I=LIMLO,N
      B(I,1) = DOT(B(J1,2),A(IC))
      B(I,2) = 0.D0
  189 IC = IC + I
C  FORM THE Q-VECTOR
  190 FACT = -DAK
      CALL VECSUM(B(J1,1),B(J1,2))
C  TRANSFORM THE REST OF THE A-MATRIX
C  JJ        START-1 OF THE REST OF THE A-MATRIX
      JJ = IC
```

```
C  MOVE W-VECTOR INTO THE OLD A-MATRIX LOCATIONS TO SAVE SPACE
C  I         RUNS OVER THE SIGNIFICANT ELEMENTS OF THE W-VECTOR
      DO 160 I=J1,N
      A(JJ) = B(I,2)
      IF (I.GT.LIMIT) GO TO 161
      B2 = B(I,2)
      FACT = -B2 - B2
      IDIF = I - J1
      CALL VECSUM(A(JJ+1),B(J1,1))
  161 B1 = B(I,1)
      FACT = -B1 - B1
      IDIF = MIN0(I,LIMIT) - J1
      CALL VECSUM(A(JJ+1),B(J1,2))
  160 JJ = JJ + I
C  STORE AWAY LIMIT FOR LATER USE IN BACK TRANSFORMATION
  200 B(J,6) = LIMIT
C  MOVE LAST CODIAGONAL ELEMENT OUT INTO ITS PROPER PLACE
  201 CONTINUE
      B(NM1,1) = A(NSIZE-1)
      A(NSIZE-1) = 0.D0
C
C  USE QR TRANSFORM METHOD TO FIND EIGENVALUES OF THE TRIDIAGONAL MATRIX
C  MOVE DIAGONAL ELEMENTS OF THE TRIDIAGONAL MATRIX INTO ROOT ARRAY
C  THIS IS A MORE CONVENIENT INDEXING POSITION.
C  ALSO, PUT SQUARE OF CODIAGONAL ELEMENTS IN THIRD N ELEMENTS.
      JUMP = 0
      DO 320 J=1,NM1
      JUMP = JUMP + J
      ROOT(J) = A(JUMP)
  320 B(J,3) = B(J,1)**2
      ROOT(N) = A(NSIZE)
      CALL EVCR(ROOT,B(1,3),N,30,SMALL)
C  ROOT NOW CONTAINS THE SHIFTED AND SCALED EIGENVALUES
C  STORE EIGENVALUES FOR POSSIBLE LATER USE AS SHIFTS, IN
C  EVALUATING EIGENVECTORS FOR DEGENERATE MATRICES.
      DO 325 J=1,N
  325 B(J,2) = ROOT(J)
C  SORT THE EIGENVALUES INTO DESCENDING ALGEBRAIC ORDER
      DO 330 I=1,NM1
      IP1 = I + 1
      DO 330 J=IP1,N
      IF (ROOT(I).GE.ROOT(J)) GO TO 330
      TEMP = ROOT(I)
      ROOT(I) = ROOT(J)
      ROOT(J) = TEMP
  330 CONTINUE
C  QUIT NOW IF NO VECTORS WERE REQUESTED.
      IF (NROOTX.LT.0) GO TO 1002
C  IF ONLY ONE VECTOR WAS REQUESTED, DEGENERACY DOESN'T MATTER
      IF (NROOTX.EQ.1) GO TO 807
C  TEST FOR DEGENERACY OR NEAR DEGENERACY OF EIGENVALUES FOR WHICH
C  EIGENVECTORS WERE REQUESTED
      NTOP = NROOT - 1
      DO 400 I=1,NTOP
      IF (DABS(ROOT(I+1)-ROOT(I)).LE.TOLER) GO TO 410
  400 CONTINUE
```

```
C  THIS IS REACHED IF ALL EIGENVALUES FOR WHICH EIGENVECTORS WERE
C  REQUESTED ARE WELL SEPARATED.
      GO TO 807
C
C  THE FOLLOWING IS REACHED IF THERE ARE ANY DEGENERATE CLUSTERS
C  OF EIGENVALUES.  USE FURTHER QR TRANSFORMS TO EVALUATE
C  THE EIGENVECTORS OF THE TRIDIAGONAL MATRIX.  THIS METHOD
C  GIVES ORTHOGONAL EIGENVECTORS EVEN WHEN THE EIGENVALUES ARE
C  DEGENERATE.  HOWEVER, IT TAKES MORE ARITHMETIC THAN THE METHOD
C  OF INVERSE ITERATION (AT LEAST AT LARGE N).
C
C  PUT DIAGONAL ELEMENTS OF TRIDIAGONAL MATRIX INTO ROOT
C  PUT OFF-DIAGONAL ELEMENTS INTO B(I,3)
  410 JUMP = 0
      DO 440 J=1,NM1
      JUMP = JUMP + J
      ROOT(J) = A(JUMP)
  440 B(J,3) = B(J,1)
C  LAST DIAGONAL ELEMENT
      ROOT(N) = A(NSIZE)
C
C  INITIALIZE VECTORS TO A UNIT MATRIX
      DO 450 I=1,N
      DO 445 J=1,N
  445 VECT(J,I) = 0.D0
C  DIAGONAL ELEMENT
  450 VECT(I,I) = 1.D0
C
C  FORM EIGENVECTORS OF TRIDIAGONAL MATRIX, FOR DEGENERATE MATRICES.
      CALL QRTN(ROOT,B(1,3),VECT,B(1,2),N,25,EMAG,NJX)
C  TRANSPOSE THE VECTORS
      DO 456 I=1,NM1
      IP1 = I + 1
      DO 455 J=IP1,N
      FLIP = VECT(I,J)
      VECT(I,J) = VECT(J,I)
  455 VECT(J,I) = FLIP
  456 CONTINUE
C  IF ROOTS WERE NOT LOCATED IN DESCENDING ORDER, INTERCHANGE ROOTS
C  AND VECTORS.
      ITOP = NROOT-1
      DO 480 I=1,ITOP
      IP1 = I+1
      DO 480 J=IP1,N
      IF (ROOT(I).GE.ROOT(J)) GO TO 480
C  ROOTS OUT OF ORDER.  INTERCHANGE.
      TEMP = ROOT(I)
      ROOT(I) = ROOT(J)
      ROOT(J) = TEMP
C  INTERCHANGE VECTORS
      DO 470 K=1,N
      TEMP = VECT(K,I)
      VECT(K,I) = VECT(K,J)
  470 VECT(K,J) = TEMP
  480 CONTINUE
C  DEGENERATE VECTORS ARE NOW COMPLETE
```

```
      GO TO 940
C
C  EIGENVECTORS OF TRIDIAGONAL MATRIX, FOR NONDEGENERATE MATRICES
  807 CONTINUE
C  INITIALIZE VECTOR ARRAY.
      DO 705 I=1,NROOT
      DO 15 J=1,N
   15 VECT(J,I) = 1.D0
  705 CONTINUE
      DO 700 I=1,NROOT
C  USE INVERSE ITERATION TO FIND VECTORS
  701 AROOT = ROOT(I)
      ELIM1 = A(1) - AROOT
      ELIM2 = B(1,1)
      JUMP = 1
      DO 750 J=1,NM1
      JUMP = JUMP + J + 1
C  GET THE CORRECT PIVOT EQUATION FOR THIS STEP.
      IF (DABS(ELIM1).LE.DABS(B(J,1))) GO TO 760
C  FIRST (ELIM1) EQUATION IS THE PIVOT THIS TIME.  CASE 1.
      B(J,2) = ELIM1
      B(J,3) = ELIM2
      B(J,4) = 0.D0
      TEMP = B(J,1)/ELIM1
      ELIM1 = A(JUMP) - AROOT - TEMP*ELIM2
      ELIM2 = B(J+1,1)
      GO TO 755
C  SECOND EQUATION IS THE PIVOT THIS TIME.  CASE 2.
  760 B(J,2) = B(J,1)
      B(J,3) = A(JUMP) - AROOT
      B(J,4) = B(J+1,1)
      TEMP = 1.D0
      IF (DABS(B(J,1)).GT.THETA1) TEMP = ELIM1/B(J,1)
      ELIM1 = ELIM2 - TEMP*B(J,3)
      ELIM2 = -TEMP*B(J+1,1)
C  SAVE FACTOR FOR THE SECOND ITERATION.
  755 B(J,5) = TEMP
  750 CONTINUE
      B(N,2) = ELIM1
      B(N,3) = 0.D0
      B(N,4) = 0.D0
      B(NM1,4) = 0.D0
      ITER = 1
C  BACK SUBSTITUTE TO GET THIS VECTOR.
  790 L = N + 1
      DO 780 J=1,N
      L = L - 1
  786 CONTINUE
      ELIM1 = VECT(L,I)-VECT(L+1,I)*B(L,3)-VECT(L+2,I)*B(L,4)
C  IF OVERFLOW IS CONCEIVABLE, SCALE THE VECTOR DOWN.
C  THIS APPROACH IS USED TO AVOID MACHINE-DEPENDENT AND SYSTEM-
C  DEPENDENT CALLS TO OVERFLOW ROUTINES.
      IF (DABS(ELIM1).GT.DELBIG) GO TO 782
      TEMP = B(L,2)
      IF (DABS(B(L,2)).LT.DELTA) TEMP = DELTA
      VECT(L,I) = ELIM1/TEMP
```

```
      GO TO 780
C  VECTOR IS TOO BIG.  SCALE IT DOWN.
  782 DO 784 K=1,N
  784 VECT(K,I) = VECT(K,I)/DELBIG
      GO TO 786
  780 CONTINUE
      GO TO (820,900), ITER
C  SECOND ITERATION
  820 ITER = ITER + 1
  890 ELIM1 = VECT(1,I)
      DO 830 J=1,NM1
      IF (B(J,2).EQ.B(J,1)) GO TO 840
C  CASE ONE.
  850 VECT(J,I) = ELIM1
      ELIM1 = VECT(J+1,I) - ELIM1*B(J,5)
      GO TO 830
C  CASE TWO.
  840 VECT(J,I) = VECT(J+1,I)
      ELIM1 = ELIM1 - VECT(J+1,I)*TEMP
  830 CONTINUE
      VECT(N,I) = ELIM1
      GO TO 790
C  NORMALIZE THE VECTOR
  900 ELIM1 = 0.D0
      DO 904 J=1,N
  904 ELIM1 = DMAX1(DABS(VECT(J,I)),ELIM1)
      TEMP = 0.D0
      DO 910 J=1,N
      ELIM2 = VECT(J,I)/ELIM1
  910 TEMP = TEMP + ELIM2**2
      TEMP = 1.D0/(DSQRT(TEMP)*ELIM1)
      DO 920 J=1,N
      VECT(J,I) = VECT(J,I)*TEMP
      IF (DABS(VECT(J,I)).LT.DEL1) VECT(J,I) = 0.D0
  920 CONTINUE
  700 CONTINUE
C
C  SIMVEC SECTION.
C  ROTATE THE CODIAGONAL VECTORS INTO VECTORS OF ORIGINAL ARRAY
C  LOOP OVER ALL THE TRANSFORMATION VECTORS
  940 IF (NM2.EQ.0) GO TO 1002
      JUMP = NSIZE - NP1
      IM = NM1
      DO 950 I=1,NM2
      LIMIT = IDINT(B(IM-1,6))
      J1 = JUMP
C  MOVE A TRANSFORMATION VECTOR OUT INTO BETTER INDEXING POSITION.
      DO 955 J=IM,LIMIT
      B(J,2) = A(J1)
  955 J1 = J1 + J
      IDIF = LIMIT - IM
C  MODIFY ALL REQUESTED VECTORS.
      DO 960 K=1,NROOT
C  FORM SCALAR PRODUCT OF TRANSFORMATION VECTOR WITH EIGENVECTOR
      TMP = DOT(B(IM,2),VECT(IM,K))
      FACT = -TMP - TMP
```

```
      CALL VECSUM(VECT(IM,K),B(IM,2))
  960 CONTINUE
      JUMP = JUMP - IM
  950 IM = IM - 1
 1002 CONTINUE
C  RESTORE ROOTS TO THEIR PROPER SIZE AND ADD BACK TRACE
      DO 95 I=1,N
   95 ROOT(I) = ROOT(I)*ANORM + TRACE
 1001 RETURN
      END
```

```
      SUBROUTINE EVQR(A,B,N,M,TOL)
C  QR TRANSFORM FOR REAL SYMMETRIC TRIDIAGONAL MATRICES
C  ON ENTERING, A CONTAINS THE N DIAGONAL ELEMENTS OF THE TRIDIAGONAL
C  MATRIX.  B CONTAINS THE SQUARES OF THE N-1 OFF-DIAGONAL ELEMENTS.
C  ITERATES UNTIL THE SQUARES OF THE OFF-DIAGONAL ELEMENTS ARE LESS
C  THAN TOL.
C  TYPICALLY, LESS THAN TWO ITERATIONS PER EIGENVALUE ARE REQUIRED.
C  THUS THE UPPER LIMIT M TO THE NUMBER OF ITERATIONS PER EIGENVALUE
C  MAY SAFELY BE SET AT 20 OR SO
C  ON RETURNING, A CONTAINS THE N EIGENVALUES
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(1),B(1)
      NX = N
      NI = 1
      SH = 0.D0
C  K COUNTS THE NUMBER OF ITERATIONS PER EIGENVALUE
      K = 0
      IF (NX-2) 50,60,85
C  EACH NEW ITERATION BEGINS HERE
  100 K = K + 1
      IF (K.LT.M) GO TO 101
      WRITE (6,1000) K
 1000 FORMAT(35H NO CONVERGENCE OF QR ALGORITHM IN   ,I4,11H ITERATIONS)
      CALL EXIT
C  SOLVE THE TWO BY TWO IN THE LOWER RIGHT CORNER, AND USE SMALLER ROOT
C  AS THE NEXT SHIFT
  101 AT = A(NX) + A(NX-1)
      ST = AT*5.D-1
      DISC = AT**2 - 4.D0*(A(NX)*A(NX-1)-B(NX-1))
      IF (DISC.LE.0.D0) GO TO 15
      ST = ST - DSIGN(DSQRT(DISC),ST)*5.D-1
C  INCREASE THE TOTAL SHIFT BY THE TEMPORARY SHIFT
   15 SH = SH + ST
C  THIS LOOP SUBTRACTS THE TEMPORARY SHIFT FROM THE DIAGONAL ELEMENTS
      DO 20 I=1,NX
   20 A(I) = A(I) - ST
C  INITIALIZE
      G = A(NI)
      PS = G**2
      RS = PS + B(NI)
      SX = B(NI)/RS
      CXS = 1.D0
      CX = PS/RS
      U = SX*(G+A(NI+1))
      A(NI) = G + U
      NTOP = NX - 2
C  THIS LOOP COMPLETES ONE ITERATION, THAT IS ONE QR TRANSFORM
      DO 10 I=NI,NTOP
C  G IS THE GAMMA, IN THE NOTATION OF WILKINSON
      G = A(I+1) - U
      IF (CX.GT.TOL) GO TO 12
      PS = B(I)*CXS
      GO TO 16
   12 PS = G**2/CX
   16 RS = PS + B(I+1)
C  THIS ROTATES AN OFF-DIAGONAL ELEMENT
```

```
      B(I) = SX*RS
      SX = B(I+1)/RS
      CXS = CX
      CX = PS/RS
      U = SX*(G+A(I+2))
C  ROTATE A DIAGONAL ELEMENT
      A(I+1) = G + U
   10 CONTINUE
C  COMPUTE THE LAST DIAGONAL ELEMENT
      A(NX) = A(NX) - U
C  COMPUTE THE LAST OFF-DIAGONAL ELEMENT
      IF (CX.GT.TOL) GO TO 112
      PS = B(NTOP+1)*CXS
      GO TO 116
  112 PS = ((A(NX))**2)/CX
  116 B(NTOP+1) = SX*PS
C  THIS ENDS ONE ITERATION
   85 IT = NX
C  CHECK UPWARD THROUGH THE OFF-DIAGONAL ELEMENTS TO FIND THOSE LESS
C  THAN TOL.
C  THESE THREE STATEMENTS CONSTITUTE A BACKWARD LOOP
   30 IT = IT-1
      IF (DABS(B(IT)).LE.TOL) GO TO 40
C  IF NO OFF-DIAGONAL ELEMENTS LESS THAN TOL ARE FOUND, WE PERFORM
C  ANOTHER ITERATION
      IF (IT-NI) 100,100,30
C  THIS CONDITIONAL BRANCHES ACCORDING TO WHETHER THE MATRIX ISOLATED
C  BY THE SMALL OFF-DIAGONAL ELEMENT IS OF DIMENSION ONE, TWO, OR MORE
   40 IF (NX-IT-2) 50,60,70
C  THIS EXTRACTS THE EIGENVALUE OF A ONE BY ONE MATRIX, BY
C  ADDING BACK THE SHIFT
   50 A(NX) = A(NX) + SH
C  THIS DECREASES THE SIZE OF THE PORTION OF THE MATRIX AFFECTED BY
C  LATER ITERATIONS
      NX = NX-1
C  THIS RESETS THE ITERATION COUNTER
      K = 1
      GO TO 80
C  THIS SECTION EXTRACTS THE EIGENVALUES FROM A TWO BY TWO MATRIX.
   60 AL = B(NX-1)
      AM = 5.D-1*(A(NX-1)-A(NX))
      AMS = AM**2
      SAM = DSIGN(1.D0,AM)
      AN = DSQRT(AL+AM**2)
      CX = (AN+DABS(AM))/(2.D0*AN)
      SX = B(NX-1)/(4.D0*AN**2*CX)
      TA = A(NX-1)
      TB = A(NX)
      TC = B(NX-1)
      I = NX
C  ROTATE THE DIAGONAL ELEMENTS
      A(NX-1) = TA*CX+TB*SX+TC*SAM/AN+SH
      A(NX) = TA*SX+TB*CX-TC*SAM/AN+SH
C  ROTATE THE OFF-DIAGONAL ELEMENT
      B(NX-1) = 4.D0*AMS*CX*SX-DABS(AM)*TC/AN+TC*(CX-SX)**2
C  RESET THE ITERATION COUNTER
```

```
      K = 1
C  DECREASE THE SIZE OF THE PORTION OF THE MATRIX AFFECTED BY THE LATER
C  ITERATIONS
      NX = NX-2
      GO TO 80
C  THIS STATEMENT IS REACHED WHEN THE PORTION OF THE MATRIX
C  ISOLATED IS GREATER THAN TWO BY TWO.  IT CHANGES THE LOWER LIMIT
C  OF THE ITERATION SO THAT ONLY THIS PORTION WILL BE AFFECTED BY
C  SUBSEQUENT ROTATIONS, UNTIL ALL ITS EIGENVALUES ARE FOUND
   70 NI = IT + 1
C  TRANSFER TO BEGINNING OF ANOTHER ITERATION
      GO TO 85
C  THIS STATEMENT IS REACHED AFTER EITHER ONE OR TWO EIGENVALUES
C  HAVE JUST BEEN FOUND.  IT TRANSFERS IF ALL THE EIGENVALUES IN
C  THIS PORTION OF THE MATRIX HAVE BEEN FOUND.
   80 IF (NX.LT.NI) GO TO 90
C  THIS BRANCH TRANSFERS ACCORDING TO WHETHER ONE, TWO, OR MORE
C  EIGENVALUES REMAIN TO BE FOUND IN THIS PORTION
   95 IF (NX-NI-1) 50,60,85
C  THIS CONDITIONAL IS REACHED WHEN ALL EIGENVALUES IN THIS PORTION
C  OF THE MATRIX HAVE BEEN FOUND.  IT RETURNS IF THIS IS THE LAST
C  PORTION OF THE MATRIX.
   90 IF (NI.EQ.1) RETURN
C  THIS ENLARGES THE PORTION OF THE MATRIX BEING TREATED TO INCLUDE
C  THE BEGINNING OF THE MATRIX
      NI = 1
      GO TO 95
      END
```

```
      SUBROUTINE QRTN (A,B,V,EIG,N,M,TOL,NJX)
C     QR TRANSFORM FOR REAL SYMMETRIC TRIDIAGONAL MATRICES
C     N IS THE DIMENSION OF THE MATRIX
C     A CONTAINS THE N DIAGONAL ELEMENTS OF THE TRIDIAGONAL MATRIX
C     B CONTAINS THE N-1 OFF-DIAGONAL ELEMENTS
C     M IS THE MAXIMUM NUMBER OF ITERATIONS ALLOWED (SAY 20)
C     NJX IS THE PHYSICAL ROW DIMENSION OF THE EIGENVECTOR MATRIX V
C     THE EIGENVALUES OF THE MATRIX ARE ASSUMED KNOWN, AND PLACED
C     IN THE FIRST N   ELEMENTS OF THE ARRAY EIG.
C     N VECTORS V (EACH OF LENGTH N) ARE TRANSFORMED INTO THE BASIS
C     IN WHICH THE MATRIX IS DIAGONAL
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(1),B(1),V(1),EIG(1)
      NX = N
      NNM1 = NJX*(NX-1)
      NI = 1
C  SET INITIAL TOTAL SHIFT
      SH = 0
      IF (NX-2) 50,60,1
C  K COUNTS THE NUMBER OF ITERATIONS PER EIGENVALUE
    1 K=0
C  SET INITIAL TEMPORARY SHIFT
   98 ST = EIG(NX)-SH
C  CHECK FOR SMALL OFF-DIAGONAL ELEMENTS.
      IT = NX
   99 IT = IT-1
      IF (DABS(B(IT)).LE.TOL) GO TO 40
      IF (IT.GT.NI) GO TO 99
C  NO SMALL OFF-DIAGONAL ELEMENTS FOUND.  ITERATE.
C  EACH NEW ITERATION BEGINS HERE
  100 K = K + 1
      IF (K.LT.M) GO TO 11
      WRITE (6,1000) K
 1000 FORMAT(35H NO CONVERGENCE OF QR ALGORITHM IN   ,I4,11H ITERATIONS)
      CALL EXIT
   11 IF (K.EQ.1) GO TO 15
C  SOLVE THE TWO BY TWO IN THE LOWER RIGHT CORNER, AND USE SMALLER ROOT
C  AS THE NEXT SHIFT
   12 AT = A(NX) + A(NX-1)
      ST = AT*5.D-1
      DISC = AT**2-4.D0*(A(NX)*A(NX-1)-B(NX-1)**2)
      IF (DISC.LE.0.D0) GO TO 15
      ST = ST-DSIGN(DSQRT(DISC),ST)*5.D-1
C  INCREASE THE TOTAL SHIFT BY THE TEMPORARY SHIFT
   15 SH = SH + ST
C  THIS LOOP SUBTRACTS THE TEMPORARY SHIFT FROM THE DIAGONAL ELEMENTS
      DO 20 I=1,NX
   20 A(I) = A(I) - ST
      R = DSQRT(A(NI)**2+B(NI)**2)
      S = B(NI)/R
      CS = S
      C = A(NI)/R
      U = (S**2)*(A(NI)+A(NI+1))
      A(NI) = A(NI) + U
      CALL ROTATE(V(NI),C,S,NJX,NNM1)
```

```
      NTOP = NX - 2
C  THIS LOOP COMPLETES ONE ITERATION, THAT IS ONE QR TRANSFORM
      DO 10 I=NI,NTOP
C  G IS THE GAMMA, IN THE NOTATION OF WILKINSON
      G = A(I+1) - U
C  Q IS THE P, IN THE NOTATION OF WILKINSON
      Q = C*A(I+1) - CS*B(I)
      R = DSQRT(Q**2+B(I+1)**2)
C  THIS ROTATES AN OFF DIAGONAL ELEMENT
      B(I) = S*R
C  FIND THE NEW SINE FOR THE JACOBI ROTATION
      S = B(I+1)/R
      CS = C*S
C  FIND THE NEW COSINE
      C = Q/R
C  COMPUTE A NEW U
      U = (S**2)*(G+A(I+2))
C  ROTATE A DIAGONAL ELEMENT
      A(I+1) = G + U
C  ROTATE THE VECTORS
      CALL ROTATE (V(I+1),C,S,NJX,NNM1)
   10 CONTINUE
C  COMPUTE THE LAST OFF DIAGONAL ELEMENT
      B(NTOP+1) = S*(C*A(NX)-CS*B(NTOP+1))
C  COMPUTE THE LAST DIAGONAL ELEMENT
      A(NX) = A(NX) - U
C  THIS ENDS ONE ITERATION
   85 IT = NX
C  CHECK UPWARD THROUGH THE OFF DIAGONAL ELEMENTS TO FIND THOSE LESS
C  THAN TOL.
C  THESE THREE STATEMENTS CONSTITUTE A BACKWARD LOOP
   30 IT = IT - 1
      IF (DABS(B(IT)).LE.TOL) GO TO 40
C  IF NO OFF DIAGONAL ELEMENTS LESS THAN TOL ARE FOUND, WE PERFORM
C  ANOTHER ITERATION
      IF (IT-NI) 100,100,30
C  THIS CONDITIONAL BRANCHES ACCORDING TO WHETHER THE MATRIX ISOLATED
C  BY THE SMALL OFF DIAGONAL ELEMENT IS OF DIMENSION ONE, TWO, OR MORE
   40 IF (NX-IT-2) 50,60,70
C  THIS EXTRACTS THE EIGENVALUE OF A ONE BY ONE MATRIX, BY ADDING
C  BACK THE SHIFT
   50 A(NX) = A(NX) + SH
C  THIS DECREASES THE SIZE OF THE PORTION OF THE MATRIX AFFECTED BY
C  LATER ITERATIONS
      NX = NX - 1
C  THIS RESETS THE ITERATION COUNTER
      K = 0
      GO TO 80
C  THIS SECTION EXTRACTS THE EIGENVALUES FROM A TWO BY TWO MATRIX,
C  AND PERFORMS THE CORRESPONDING ROTATIONS ON THE VECTORS
   60 AL = -B(NX-1)
      AM = 5.D-1*(A(NX-1)-A(NX))
      AN = DSQRT(AL**2+AM**2)
      C = DSQRT((AN+DABS(AM))/(2.D0*AN))
      S = DSIGN(5.D-1,AM)*AL/(AN*C)
      TA = A(NX-1)
```

```
      TB = A(NX)
      TC = B(NX-1)
      CX = C**2
      SX = S**2
      CS = C*S
C  ROTATE THE DIAGONAL ELEMENTS
      A(NX-1) = TA*CX+TB*SX-2.D0*TC*CS+SH
      A(NX) = TA*SX+TB*CX+2.D0*TC*CS+SH
C  ROTATE THE OFF DIAGONAL ELEMENTS
      B(NX-1) = 2.D0*AM*CS+TC*(CX-SX)
      I = NX-1
C  ROTATE THE VECTORS
      S = -S
      CALL ROTATE (V(I),C,S,NJX,NNMI)
C  RESET THE ITERATION COUNTER
      K = 0
C  DECREASE THE SIZE OF THE PORTION OF THE MATRIX AFFECTED BY THE LATER
C  ITERATIONS
      NX = NX-2
      GO TO 80
C  THIS STATEMENT IS REACHED WHEN THE PORTION OF THE MATRIX
C  ISOLATED IS GREATED THAN TWO BY TWO.  IT CHANGES THE LOWER LIMIT
C  OF THE ITERATION SO THAT ONLY THIS PORTION WILL BE AFFECTED BY
C  SUBSEQUENT ROTATIONS, UNTIL ALL ITS EIGENVALUES ARE FOUND
   70 NI = IT + 1
C  TRANSFER TO BEGINNING OF ANOTHER ITERATION
      GO TO 100
C  THIS STATEMENT IS REACHED AFTER EITHER ONE OR TWO EIGENVALUES
C  HAVE JUST BEEN FOUND.  IT TRANSFERS IF ALL THE EIGENVALUES IN
C  THIS PORTION OF THE MATRIX HAVE BEEN FOUND.
   80 IF (NX.LT.NI) GO TO 90
C  THIS BRANCH TRANSFERS ACCORDING TO WHETHER ONE, TWO, OR MORE
C  EIGENVALUES REMAIN TO BE FOUND IN THIS PORTION
   95 IF (NX-NI-1) 50,60,98
C  THIS CONDITIONAL IS REACHED WHEN ALL EIGENVALUES IN THIS PORTION
C  OF THE MATRIX HAVE BEEN FOUND.  IT RETURNS IF THIS IS THE LAST
C  PORTION OF THE MATRIX.
   90 IF (NI.EQ.1) RETURN
C  THIS ENLARGES THE PORTION OF THE MATRIX BEING TREATED TO INCLUDE
C  THE BEGINNING OF THE MATRIX
      NI = 1
      GO TO 95
      END
```

```
      SUBROUTINE RELVEC(R,E,C1,C2)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION E(3),C1(3),C2(3)
      X = 0.D0
      DO 10 I=1,3
      E(I) = C2(I)-C1(I)
      X = X+E(I)**2
   10 CONTINUE
      R=DSQRT(X)
      DO 40 I=1,3
      IF (R.GT..000001D0) GO TO 30
   20 GO TO 40
   30 E(I) =E(I)/R
   40 CONTINUE
      RETURN
      END
```

```
      FUNCTION FACT(N)
      IMPLICIT REAL*8(A-H,O-Z)
      PRODT = 1.DO
   20 DO 30 I=1,N
   30 PRODT=PRODT*DFLOAT(I)
   40 FACT=PRODT
      RETURN
      END
```

```
      SUBROUTINE BINTGS(X,K)
      IMPLICIT REAL*8(A-H,O-Z)
C     FILLS ARRAY OF B-INTEGRALS. NOTE THAT B(I) IS B(I-1) IN THE
C     USUAL NOTATION
C     FOR X.GT.3                        EXPONENTIAL FORMULA IS USED
C     FOR 2.LT.X.LE.3 AND K.LE.10       EXPONENTIAL FORMULA IS USED
C     FOR 2.LT.X.LE.3 AND K.GT.10       15 TERM SERIES IS USED
C     FOR 1.LT.X.LE.2 AND K.LE.7        EXPONENTIAL FORMULA IS USED
C     FOR 1.LT.X.LE.2 AND K.GT.7        12 TERM SERIES IS USED
C     FOR .5.LT.X.LE.1 AND K.LE.5       EXPONENTIAL FORMULA IS USED
C     FOR .5.LT.X.LE.1 AND K.GT.5        7 TERM SERIES IS USED
C     FOR X.LE..5                        6 TERM SERIES IS USED
C     *****************************************************************
      COMMON/AUXINT/A(17),B(17)
      IO=0
      ABSX=DABS(X)
      IF(ABSX.GT.3.D0) GO TO 120
   10 IF(ABSX.GT.2.D0) GO TO 20
   40 IF(ABSX.GT.1.D0) GO TO 50
   70 IF(ABSX.GT..5D0) GO TO 80
  100 IF(ABSX.GT..000001D0) GO TO 110
      GO TO 170
  110 LAST=6
      GO TO 140
   80 IF(K.LE.5) GO TO 120
   90 LAST=7
      GO TO 140
   50 IF(K.LE.7) GO TO 120
   60 LAST=12
      GO TO 140
   20 IF(K.LE.10) GO TO 120
   30 LAST=15
      GO TO 140
  120 EXPX=DEXP(X)
      EXPMX=1.D0/EXPX
      B(1)=(EXPX-EXPMX)/X
      DO 130 I=1,K
  130 B(I+1)=(DFLOAT(I)*B(I)+(-1.D0)**I*EXPX-EXPMX)/X
      GO TO 190
  140 DO 160 I=IO,K
      Y=0.D0
      DO 150 M=IO,LAST
  150 Y=Y+(-X)**M*(1.D0-(-1.D0)**(M+I+1))/(FACT(M)*DFLOAT(M+I+1))
  160 B(I+1)=Y
      GO TO 190
  170 DO 180 I=IO,K
  180 B(I+1)=(1.D0-(-1.D0)**(I+1))/DFLOAT(I+1)
  190 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE AINTGS(X,K)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/AUXINT/A(17),B(17)
      A(1) =DEXP(-X)/X
      DO 10  I=1,K
   10 A(I+1) =(A(I)*DFLOAT(I)+DEXP(-X))/X
      RETURN
      END
```

```
      FUNCTION SS(NN1,LL1,MM,NN2,LL2,ALPHA,BETA)
      IMPLICIT REAL*8(A-H,O-Z)
C     PROCEDURE FOR CALCULATING REDUCED OVERLAP INTEGRALS
      COMMON/ARRAYS/S(80,80),Y(9,5,203),Z(17,45),XX(2900)
      COMMON/AUXINT/A(17),B(17)
      INTEGER ULIM
      N1=NN1
      L1=LL1
      M=MM
      N2=NN2
      L2=LL2
      P =(ALPHA + BETA)/2.D0
      PT=(ALPHA - BETA)/2.D0
      X = 0.D0
      M=IABS(M)
C     REVERSE QUANTUM NUMBERS IF NECESSARY
      IF((L2.LT.L1).OR.((L2.EQ.L1).AND.(N2.LT.N1))) GO TO 20
   10 GO TO 30
   20 K = N1
      N1= N2
      N2= K
      K= L1
      L1= L2
      L2= K
      PT=-PT
   30 CONTINUE
      K = MOD((N1+N2-L1-L2),2)
C     FIND A AND B INTEGRALS
      CALL AINTGS(P,N1+N2)
      CALL BINTGS(PT,N1+N2)
      IF((L1.GT.0).OR.(L2.GT.0)) GO TO 60
C     BEGIN SECTION USED FOR OVERLAP INTEGRALS INVOLVING S FUNCTIONS
C     FIND Z TABLE NUMBER L
   40 L = (90-17*N1+N1**2-2*N2)/2
      ULIM = N1+N2
      LLIM = 0
      DO 50 I=LLIM,ULIM
      NNII=N1+N2-I+1
   50 X=X+Z(I+1,L)*A(I+1)*B(NNII)/2.D0
      SS=X
      GO TO 80
C     BEGIN SECTION USED FOR OVERLAPS INVOLVING NON-S FUNCTIONS
C     FIND Y TABLE NUMBER L
   60 L=(5-M)*(24-10*M+M**2)*(83-30*M+3*M**2)/120+
     1  (30-9*L1+L1**2-2*N1)*(28-9*L1+L1**2-2*N1)/8+
     2  (30-9*L2+L2**2-2*N2)/2
      LLIM = 0
      DO 70 I=LLIM,8
      ULIM=4 - MOD(K+I,2)
      DO 70 J=LLIM,ULIM
      IIII=2*J+MOD(K+I,2)+1
   70 X=X+Y(I+1,J+1,L)*A(I+1)*B(IIII)
      SS = X*(FACT(M+1)/8.D0)**2*DSQRT(DFLOAT(2*L1+1)*FACT(L1-M)*
     1 DFLOAT(2*L2+1)*FACT(L2-M)/(4.D0*FACT(L1+M)*FACT(L2+M)))
   80 CONTINUE
      RETURN
```

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