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**A study of the surface Raman spectra of triphenylmethane dyes
on colloidal silver**

Persaud, Indira Vedawatee, Ph.D.

City University of New York, 1990

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A

**A STUDY OF THE SURFACE RAMAN SPECTRA OF
TRIPHENYLMETHANE DYES ON COLLOIDAL SILVER**

BY

INDIRA VEDAWATEE PERSAUD

**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**

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Approval

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

7/18/90

Date

William E. Grossman
Chair of Examining Committee7/30/90

Date

Neil R.
Executive OfficerRonald L. Burke
J. R. Faldut
Max Lamm

Supervisory Committee

The City University of New York

ABSTRACT**A STUDY OF THE SURFACE RAMAN SPECTRA
OF TRIPHENYLMETHANE DYES
ON COLLOIDAL SILVER****by****Indira V. Persaud**

Adviser: Professor William E.L. Grossman

The usefulness of Surface Enhanced Raman Scattering (SERS) as a viable analytical technique has been explored in this study. This investigation was carried out by a study of the structural changes that some of the triphenylmethane dyes undergo when complexed to a silver surface. An assessment of the solution and surface vibrational spectra has led to the conclusion that the dye molecules are most likely lying parallel to the sol surface and adopting C_3 symmetry. It is not evident that a new surface complex is formed when these dyes are adsorbed onto the silver surface, but there is evidence for interactions between the Ag sol and the dyes. Very few changes are noted for the N-phenyl stretching mode; most of the vibrational changes are localized at the C^+-C bonds; hence we have concluded that the central carbonium ion is the major center of interaction.

The utility of SERS as a quantitative tool has been also examined. The SERS intensity of the analyte peaks were measured relative to the O-H stretching band of water and corrected for absorption. A linear calibration curve over a wide concentration range is not observed. SERS intensities were found to be independent of the concentration from $5 \times 10^{-7} \text{M}$ to $5 \times 10^{-5} \text{M}$. The intensity of the dye peaks in the surface Raman spectra were found to be dependent on a number of factors including the sol's age. It would appear that some degree of aggregation is necessary before a surface Raman spectrum could be observed at concentrations $\leq 10^{-6} \text{M}$ for crystal violet and pararosaniline. A limit of detection of $5 \times 10^{-8} \text{M}$ was obtained for all of the three dyes studied.

Surface enhancement factors have been estimated by a comparison of the relative Raman cross-section of the dyes in solution and adsorbed on the sol. After correcting for absorption and for the number of molecules actually lying on the sol's surface (assuming monolayer coverage), enhancement factors ranging from 10^5 - 10^6 were obtained.

DEDICATION

The year 1988 was indeed the "year of anniversaries". It marked the centennial anniversary of C.V. Raman's (1888-1970) birth and the sixtieth anniversary of his discovery of the Raman effect. More important to me was that it marked the one hundred and fiftieth anniversary of the immigration of East Indians to Guyana. On May 5, 1838, the ships Whitby and Hesperus landed in British Guiana with 396 indentured workers. This was the start of a process whereby at least half a million Indian workers migrated to the Caribbean through the port of Calcutta, India. Brought to a foreign land to work in a system that was rooted upon slavery, these Indians soon produced a middle class of small farmers and shop owners. By their hard work, diligence, courage and hope, they managed to start educating their children and future generations. I am proud to consider myself an educated member of the third generation. I would like to dedicate this thesis to the beloved memories of my courageous forefathers and foremothers who struggled under an inhuman system and years of suppression as indentured laborers. The stories of their sacrifices for their children's education are not published but deep in our hearts we all know about them.

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My sincerest gratitude is expressed to my mentor, Professor Grossman for all his help, encouragement, criticisms and all the time he spent with me discussing research issues. His high standards will always be an inspiration to me.

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Finally, but not least, I acknowledge the patience and kindness of my wonderful family. Nal, Sav and Shan you are all wonderful human beings. I am most grateful to my mother who displayed tremendous courage when she defied all odds and traditional bondage and successfully educated her daughters. To my grandparents, I thank them for the greatest gift of all: sustenance of life. From my beloved Nana I learnt to be patient and from my late grandmother I learnt the lessons of humility and simplicity. Today I share my honor with them.

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LIST OF ABBREVIATIONS

Ar	=	Aromatic ring
BF	=	Basic Fuchsin
CARS	=	Coherent anti Stokes Raman Scattering
CV	=	Crystal violet
CSA	=	Cross-sectional area
DMA	=	Dimethylaniline
def	=	deformation
EHMO	=	Extended Huckel Molecular Orbital
EV	=	Ethyl violet
FIA	=	Flow Injection Analysis
FT	=	Fourier Transform
GVFF	=	General Valence Force Field
HPTLC	=	High Performance Thin Layer Chromatography
ip	=	In plane
IR	=	Infra-red
LOD	=	Limit of detection
NCA	=	Normal Coordinate Analysis
oop	=	Out-of plane
PED	=	Potential Energy Distribution
Ph	=	Phenyl
PR	=	Pararosaniline
RE	=	Relative Enhancement
R6G	=	Rhodamine 6G
RS	=	Raman Scattering
RRS	=	Resonance Raman Scattering

SERS = Surface Enhanced Raman Scattering
S/N = Signal : Noise
SR = Surface Raman
SRS = Surface Raman Scattering
str = Stretch
TLC = Thin Layer Chromatography
TPM = Triphenylmethane
UBFF = Urey Bradley Force Field
vib = Vibration

CHAPTER 1: AN OVERVIEW OF RAMAN SPECTROSCOPY

1.1 INTRODUCTION:

The study of molecules at interfaces and as adsorbed species can be a stimulating experience for a new graduate student. Molecules on a surface can exhibit physical and chemical properties that are quite different from their solution counterparts. Surface scientists have a basic aim in monitoring these changes and to detect these "sorbed species". Over the years various techniques have been applied to the study of surfaces. Ellipsometry and attenuated total reflection are probably two of the oldest techniques utilized in surface studies. Infrared (IR) absorption spectroscopy has also been applied and there has been much success in its use. The study of the vibrational spectra of an adsorbed species provides a multitude of information concerning the structure, bonding and reactivity of the species in all phases of matter (1). However in this technique all absorbers present will contribute to the absorption spectrum. In addition water absorbs IR radiation very strongly and its interference with the analyte absorption is inevitable. Sophisticated IR reflection techniques have been developed and these have found useful applications. A second method of obtaining a vibrational spectrum is by utilizing Raman spectroscopy which is a scattering phenomenon. This technique is proving to be an excellent tool for the study of vibrations of adsorbed

molecules on various surfaces. It is not restricted to ultra high vacuum conditions but can be also applied to catalytic surfaces and liquid-solid interfaces (2). The discovery of surface enhanced Raman spectroscopy has served only to enhance the sensitivity of this technique. In the rest of Chapter 1 a brief review of Raman spectroscopy will be presented along with its applications and some theoretical explanations for this phenomenon.

RAMAN SPECTROSCOPY

1.2.1 HISTORICAL BACKGROUND:

On February 28, 1928, Chandrashekara Venkata Raman, while studying the scattering of light in liquids, observed the presence of new spectral lines which were not components of the exciting light source but rather were characteristic of the scattering medium, that is, the frequency of the scattered light was dependent on the sample and not on the light source (3-5). These new lines were described by C.V. Raman simply as "a new type of secondary radiation" (3), but the phenomenon was later dubbed the Raman effect and it won for C.V. Raman the Nobel prize in Physics in 1930.

The Raman effect was immediately recognized worldwide by both physicists and chemists to be a powerful tool for structural investigations. In the U.S., R.W. Wood most

probably initiated the research in Raman spectroscopy. He had observed evidence of the effect while studying the resonance fluorescence of various simple molecules. It has been reported that Wood subsequently published thirty articles on the effect in the decade beginning in 1928 (6).

But Raman spectroscopy remained a very unpopular technique mainly because convenient equipment was not available as it was for IR spectroscopy. With the advent of World War II, military needs led to the development of the photomultiplier tube which replaced the photographic plate as a detector and Raman spectroscopy benefited. Further, in 1953, the resonance Raman effect was discovered. Now colored materials could be examined at very low concentrations by exciting within the region of an electronic absorption band. In 1961, the laser was introduced as a new light source and it initiated what is commonly referred to as the renaissance of Raman spectroscopy. The laser, an intense source with a high degree of collimation and polarization, was the ideal source for Raman spectroscopy which is an inherently weak effect - one in every 10^{10} photons incident on a sample is Raman scattered. The laser undoubtedly established Raman spectroscopy as a vibrational technique for probing a wide variety of molecules. In addition to normal and resonance Raman spectroscopy, the laser was also used to stimulate non-linear effects in coherent Raman spectroscopy.

Just when it was thought that all Raman techniques were exploited, it was discovered, largely through the work of Fleischmann and coworkers (7), Jeanmaire & Van Duyne (8) and Creighton et al. (9,10) that molecules adsorbed on specially prepared silver surfaces produced enhanced Raman spectra that are at times a million fold more intense than expected. This surface enhanced effect has served to stimulate further progress in Raman spectroscopy. In an effort to give a theoretical explanation for this phenomenon both chemists and physicists have focussed their interest on the classical electromagnetic theory. A large number of researchers are now using this technique for vibrational studies of molecules on surfaces. Presently, interest is being directed at Fourier transform surface enhanced Raman spectroscopy.

A modest scattering experiment carried out sixty two years ago initiated a new era in the field of spectroscopy. Amazingly, Raman spectroscopy still remains alive with the emergence of new Raman techniques, instrumental advances and practical applications. Predictably, it will remain a fascinating subject for spectroscopists in the years to come.

1.2.2 NATURE OF THE RAMAN EFFECT:

The Raman effect belongs to a large class of light scattering phenomena all of which have their origin in the fact that a beam of light when passed through a non absorbing

medium is found to be attenuated by the medium. The light can be scattered elastically or inelastically, the former being Rayleigh scattering and the latter Raman or Brillouin scattering. Light scattering arises from dipole moments induced in atoms or molecules by the incident field through the polarizability of the molecule. The static polarizability leads to Rayleigh scattering while the modulation of the polarizability by electronic, vibrational or rotational motion leads to Raman scattering. Brillouin scattering arises from the modulation of the incident light by acoustical waves. If the frequency of the scattered radiation is analyzed, it will be observed that a portion of the scattered beam lies at the frequency of the exciting light source and smaller portions lie at fixed frequencies above and below that of the excitation source. In molecular systems, these frequency shifts are found to correlate to the energies associated with rotational, vibrational and electronic levels.

To understand the Raman process, consider Fig. 1. Monochromatic radiation of frequency ν_0 is incident on a sample. The incident radiation raises the molecule to a virtual excited state. As the electromagnetic wave passes, the polarized molecule returns to the ground state in a very short time - 10^{-14} seconds (11). The electric field produced by the polarized molecule oscillates at the same frequency as the electromagnetic wave. When the molecule

relaxes to the original vibrational level associated with the ground state, frequency of the incident radiation is emitted. This is Rayleigh scattering. If the molecule re-emits by returning not to the original vibrational level but to a higher vibrational level, the emitted radiation is of lower frequency than the incident radiation. Moreover, the difference in frequency or the frequency shift is equal to a natural vibrational frequency of the electronic ground state. This is Raman scattering. Raman lines arising from this relaxation pathway are called Stokes lines. In the third case, a few of the molecules will interact with the radiation while they are in an excited vibrational level and can decay to a lower energy level. The frequency of the scattered radiation is now higher than the incident radiation. Again the Raman frequency shifts will correspond to natural vibrational frequencies of the electronic ground state. Such lines are referred to as anti-Stokes lines. Thus a scanned spectrum will consist of the frequency unshifted Rayleigh component of scattering and two weak components corresponding to the Stokes and anti-Stokes lines. For purposes of chemical analyses, only the Stokes lines are considered. These are more intense because under ordinary circumstances, most molecules are initially in the lowest vibrational level. The vibrational frequencies observed in Raman spectroscopy are those of the ground electronic state, since the scattering process starts and

terminates in the ground state.

1.3 THEORY OF THE RAMAN EFFECT:

1.3.1 CLASSICAL DESCRIPTION OF THE RAMAN EFFECT:

A simple description of the classical theory of Raman spectroscopy is given in ref. (12) and a summary of this presentation will be given here.

When a molecule is placed in an electric field, its electrons are displaced relative to its nuclei, thus developing an electric dipole moment. The induced dipole moment, U_i , is proportional to the field strength, E , where,

$$U_i = \alpha E \dots\dots\dots(1)$$

α is a measure of the polarizability of the molecule: that is, the ease with which the electron cloud of the molecule can be distorted.

Associated with the incident electromagnetic radiation is an electric field which can be expressed as:

$$E = E^0 \cos 2\pi t \nu_0 \dots\dots\dots(2)$$

where,

E^0 = equilibrium field strength, and

ν_0 = angular frequency of the radiation.

The electromagnetic radiation will induce a fluctuating dipole of frequency ν_0 in the molecule. The induced dipole

can emit or scatter radiation of frequency ν_0 . This results in Rayleigh scattering.

Consider the case of a diatomic molecule vibrating with frequency ν_v . If it performs simple harmonic vibrations, then, a coordinate q_v along the axis of vibration can be defined as: (12)

$$q_v = q_0 \cos 2\pi \nu_v t \dots\dots\dots (3)$$

If the polarizability changes during the vibration, its value for a small amplitude of vibration is given by:

$$\alpha = \alpha^0 + \left| \frac{\delta \alpha}{\delta q} \right|_0 q_v \dots\dots\dots (4)$$

$$= \alpha^0 + \left| \frac{\delta \alpha}{\delta q_v} \right|_0 q_0 \cos 2\pi \nu_v t \dots\dots\dots (5)$$

Suppose incident radiation of frequency ν_0 interacts with a molecule then the induced dipole moment U_i can be expressed as:

$$U_i = \alpha E = \alpha E^0 \cos 2\pi \nu_0 t \dots\dots\dots (6)$$

$$= [\alpha^0 + \left| \frac{\delta \alpha}{\delta q_i} \right|_0 q_0 \cos 2\pi \nu_v t] E^0 \cos 2\pi \nu_0 t \dots\dots\dots (7)$$

$$= \alpha^0 E^0 \cos 2\pi \nu_0 t + \left| \frac{\delta \alpha}{\delta q_i} \right|_0 q_0 E^0 \cos 2\pi \nu_v t \cos 2\pi \nu_0 t \dots\dots\dots (8)$$

$$= \alpha^0 E^0 \cos 2\pi \nu_0 t + \left| \frac{\delta \alpha}{\delta q_i} \right|_0 \frac{E^0 q_0}{2} \times$$

$$[\cos 2\pi (\nu_0 + \nu_v) t + \cos 2\pi (\nu_0 - \nu_v) t] \dots\dots\dots (9)$$

The first term in equation (9) gives an expression for the Rayleigh scattering, the second for Stokes scattering and the third for anti-Stokes scattering. In addition it

indicates that for Raman scattering to occur $(\delta\alpha/\delta q_i) \neq 0$: that is, the polarizability of the molecule must change during a vibration if that vibration is to be Raman active. From classical electromagnetic theory, the energy scattered per unit time is proportional to $(\ddot{U}_i)^2$ (11). Differentiating equation (9) twice and squaring the result leads to the conclusion that the classical theory, apart from predicting the Raman effect, also gives the dependence of the Raman intensity on the fourth power of the frequency of the incident radiation. However, it does not yield any selection rules or predict which vibrational modes will give rise to Raman scattering. This can be deduced from the quantum mechanical analysis.

1.3.2 QUANTUM MECHANICAL DESCRIPTION OF THE RAMAN EFFECT:

The quantum mechanical description starts from a calculation of the dipole moment associated with the transition between two states, ϕ_n and ϕ_m , when a molecule is perturbed by an electromagnetic field of frequency ν_0 . This approach considers the perturbation of the wavefunctions and defines an expression for the induced transition moment P_{nm} as follows (13):

$$P_{nm} = \int \phi_m P \phi_n dt \dots\dots\dots (10)$$

where P is the induced dipole moment, ϕ_n and ϕ_m are time independent wavefunctions of the states and the integration

is carried out over the whole range of coordinates. The quantum mechanical result of P_{nm} is:

$$P_{nm} = \frac{1}{h} \sum_r \left(\frac{M_{nr} M_{rm}}{\nu_{rn} - \nu_0} + \frac{M_{nr} M_{rm}}{\nu_{rm} + \nu_0} \right) E \dots\dots (11)$$

where,

h = Planck's constant

r = complete set of electronic levels belonging to a molecule

ν_{rn}, ν_{rm} = frequencies corresponding to different states denoted by the subscripts.

M_{nr}, M_{rm} = transition moments

E = Electric vector of the incident light

The intensity of the scattered light varies as the square of P . Thus the intensity of the Raman line involving the transition from n to m is given by:

$$I = C(\nu_0 + \nu_v)^4 P_{nm}^2 \dots\dots\dots (12)$$

where,

$$C = \frac{64\pi^2}{3c^2} \dots\dots\dots (13)$$

c = velocity of light

When $n = m$, $\nu_{nm} = 0$ and Rayleigh scattering will occur. When $n \neq m$, the Raman effect occurs. In normal Raman spectroscopy, ν_0 is small compared to both ν_{rn} and ν_{rm} . Under these circumstances both terms will contribute equally to the Raman intensity, I_{nm} , which will also be proportional to the fourth power of the incident radiation fre-

quency.

Suppose ν_0 lies near to a particular absorption frequency, ν_{rm} , then the term $1/(\nu_{rm} - \nu_0)$ will dominate and resonance Raman scattering is observed. The resonantly enhanced intensity may be $10^2 - 10^6$ times the normal Raman intensity values and follows a complex frequency dependence.

This equation still does not indicate which vibrations are resonantly enhanced. Using the Born-Oppenheimer adiabatic approximation, the total wavefunctions can be separated into products of electronic and vibrational parts. If the electronic wavefunction is then expanded in a Taylor series in terms of the nuclear displacement, two main terms, the A and B, are arrived at (14):

$$P_{nm} = A + B$$

The A term involves vibrational interaction with a single excited electronic state by way of a Franck - Condon overlap integral. These integrals are non-zero for totally symmetric vibrations. In resonance Raman spectroscopy, it is usually found that only totally symmetric vibrations are enhanced. The non-totally symmetric vibrations can be resonantly enhanced when the incident radiation interacts with two or more coupled electronic transitions.

1.4 APPLICATIONS AND LIMITATIONS OF RAMAN SPECTROSCOPY:

In Raman spectroscopy the observed frequency shifts of the Raman bands correspond to the normal vibrational modes of the electronic ground state of a molecule. Thus a Raman spectrum is essentially a vibrational spectrum. It is therefore not surprising that Raman spectroscopy has found wide applications in studying the vibrational structure of various molecules. Moreover, the scattering intensity can be increased by orders of magnitude as large as 5 when the resonance Raman effect (RRE) is encountered, thus increasing the sensitivity of this technique. Since an electronic absorption is often more or less localized in one part of a molecule, selectively enhanced bands can be probed using the RRE. Resonance Raman spectroscopy has been used extensively to study biological samples at low concentrations (15,16).

However, analytical applications of RRS are still limited; this is because the technique suffers from a number of setbacks: the fluorescence background produced when exciting in the absorption band of a compound can negate the enhancement advantages of RRS. Secondly since the compounds can absorb the scattered light a linear relationship between the Raman intensity and the concentration does not exist. To understand why fluorescence can be a problem consider Fig. 2. In fluorescence, relaxation to the lowest vibrational level of the excited state precedes fluores-

cence emission and the whole process takes place in 10^{-9} sec. In Raman scattering, the molecule relaxes by immediately returning to the ground state and the whole process occurs in 10^{-12} sec. More important here is the fact that both the fluorescence emission and the Raman scattered Stokes lines occur on the lower energy side of the incident radiation frequency. Since both processes give rise to radiation in the same spectral region, interference is likely. In fact fluorescence can appear as a broad background signal and obscure the Raman bands completely.

The problem of fluorescence has continually plagued Raman spectroscopists and much attention has been given to developing methods to overcome the detrimental effects of luminescence in Raman scattering. If the fluorescence arises from impurities, the sample can be purified with the use of conventional clean-up techniques such as chromatography, recrystallization, distillation and filtration (17). This can often be done without a great deal of effort. The classical drain-quench technique can be applied but this is quite time consuming (17). These two methods will only work when the source of the fluorescence is due to an impurity. More complex instrumental approaches are used when the sample itself fluoresces. These include coherent anti-Stokes Raman spectroscopy (CARS) (18,19), time resolved spectroscopy (20-22) and Fourier transform (FT) methods (23-25). All these techniques require complex

hardware. CARS yields good spatial and spectral resolution of fluorescence, but the non-resonant background severely limits its sensitivity and since it is a non-linear technique, the signal is not generally proportional to concentration. Time resolved spectroscopy utilizes the temporal difference between fluorescence and Raman scattering. This technique requires pulsed lasers and gated detectors and some success has been reported (22). FT-Raman has recently emerged as a viable technique for eliminating fluorescence. The experiment is performed with a near IR laser and an interferometer. A few spectra have been reported with good reduction of fluorescence (23-25). One significant advantage of FT-Raman lies in the use of low energy IR light sources. This results in the inaccessibility of an electronic transition and thus eliminates the occurrence of fluorescence.

Surface Enhanced Raman spectroscopy (SERS) is yet another technique that can be used to overcome the fluorescence problems in Raman spectroscopy. By studying the vibrational spectra of molecules adsorbed on special metal surfaces an enhanced Raman spectrum is obtained and, in addition, the metal provides a pathway for the radiationless transfer of energy from the excited molecule, thus quenching the fluorescence of the adsorbed molecule. This technique will be discussed in detail in Chapter 2.

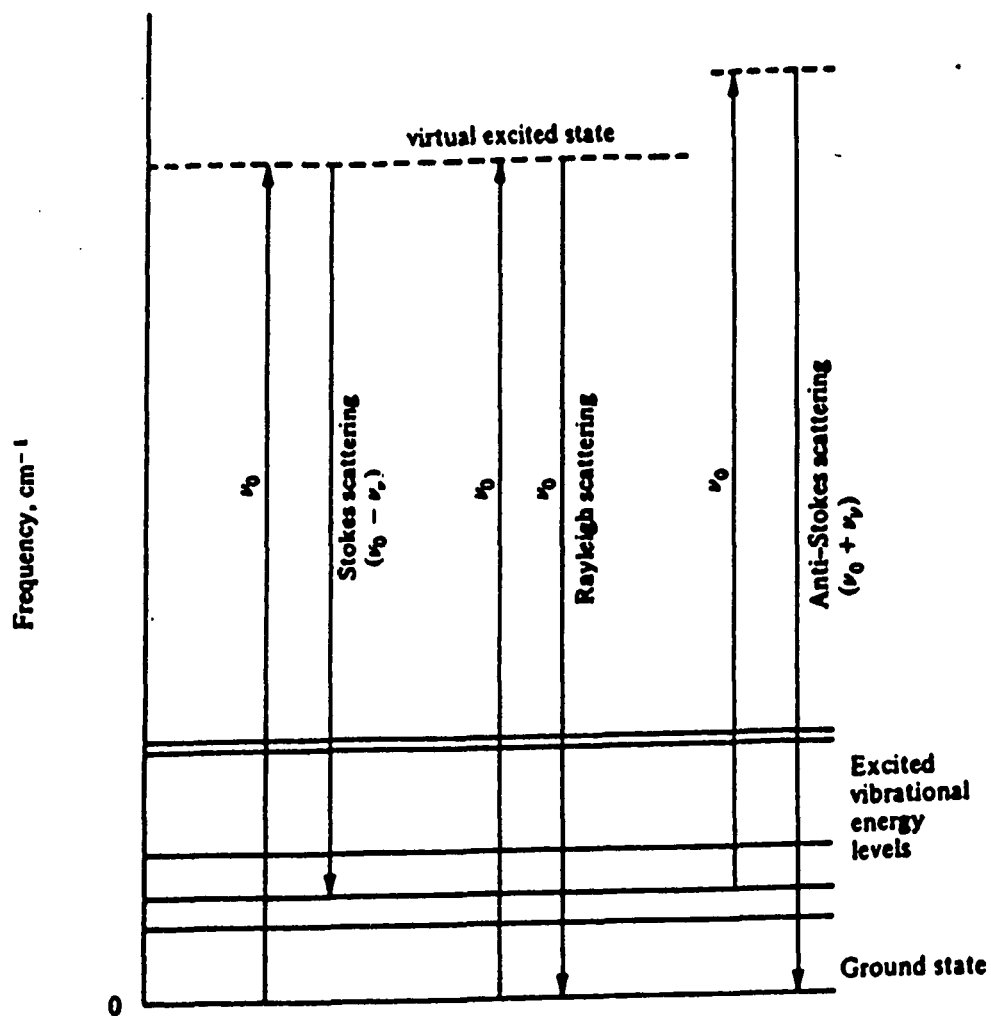


Figure 1. Energy level diagram illustrating the Raman scattering processes.

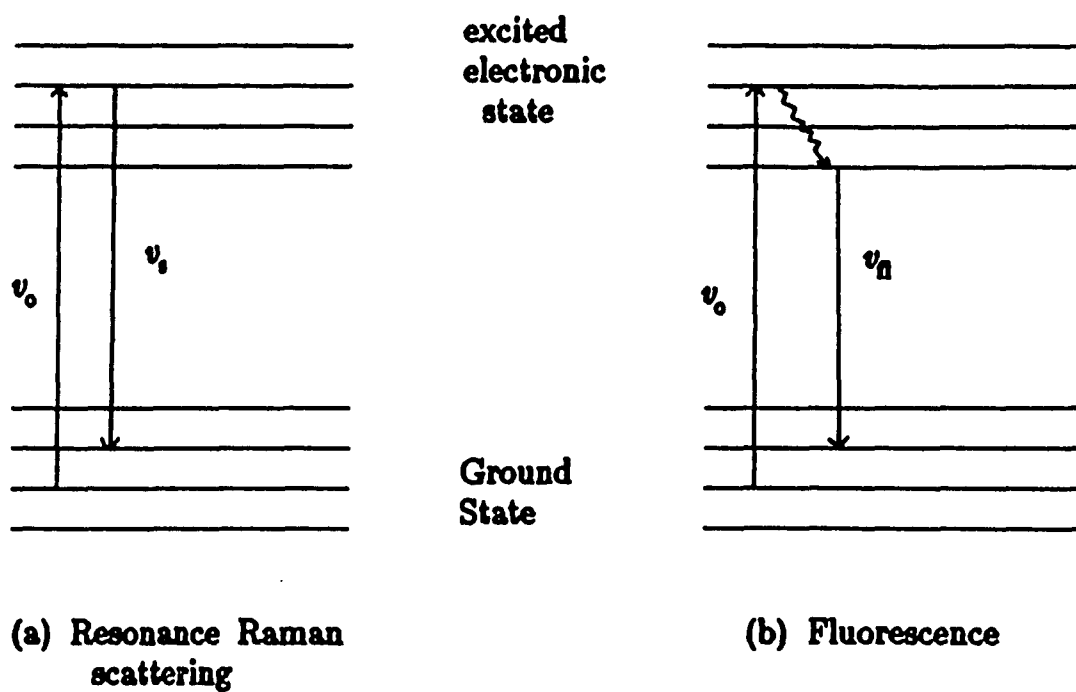


Figure 2. Energy level diagrams showing the difference between (a) resonance Raman scattering and (b) fluorescence.

CHAPTER 2: SURFACE ENHANCED RAMAN SPECTROSCOPY

2.1 INTRODUCTION:

In 1974 Fleischmann and coworkers were the first researchers to report the Raman signal of pyridine adsorbed on a silver electrode (7). This signal was thought to be due to the large surface area produced by the roughened silver electrode. However by 1977 it was shown by Van Duyne & Jeanmaire (8) and Creighton et al. (9,10) that the large surface area alone could not account for the large increase in intensity. Their results also indicated that the signals from pyridine on a Ag electrode were enhanced by a factor of $10^4 - 10^6$ relative to that of liquid pyridine. This enhancement effect quickly gained the title of Surface Enhanced Raman Spectroscopy (SERS) and it has had a dramatic impact on the field of surface science. Numerous scientists were led to investigate various SERS "active" systems and to offer various theoretical explanations for the nature of this phenomenon. To date, over two thousand papers have been written on the subject.

2.2 NATURE OF THE SERS EFFECT.

A large number of excellent reviews exist on this subject (26-28). An attempt will be made here to discuss the major characteristics of SERS which are:

1. The observation of SERS has been limited to a small number of metal surfaces. Silver remains the most effi-

cient SERS scatterer and the most extensively studied surface. Cu and Au have been shown to exhibit enhancements but these are much lower than those observed on a silver metal.

2. Numerous molecules have shown a SERS signal and all these species do seem to have the potential of coordinating to the metal surfaces. A wide variety of species types have been investigated, these include nitrogen heterocyclics (29), anionic ligands such as CN^- , SCN^- (26 and refs. therein) and CrO_4^- (30), aliphatic and aromatic amines (31), alkenes, alkynes and arenes (32-34) and non polar compounds such as benzene (35). SERS has also been extended to the study of biological compounds such as cytochrome c and DNA bases (36,37).

3. Enhancements of 4-6 orders of magnitude have been observed for molecules which are adsorbed on a metal surface. This observation has been reported for molecules that do not exhibit resonant Raman scattering.

4. While surface roughness is not a prerequisite for observing SERS, its presence is essential for increased enhancement.

5. The intensity of the SERS band deviates from the fourth power dependency on the frequency observed in normal Raman scattering.

6. For metals that exhibit enhancement, any adsorbate that is on the surface would exhibit SERS. The intensities

of the signals from different adsorbates can vary because of the differences in their molecular polarizabilities.

7. A background continuum has been observed in SERS. There is a potential dependence of this continuum and it has been attributed to luminescence. On Ag surfaces, the background is pronounced between $1300 - 1600 \text{ cm}^{-1}$.

8. SERS vibrational modes are depolarized. The band intensities of the molecular vibrations of different symmetry types are independent of the direction of the polarization of the exciting light.

9. Many SERS bands show vibrational shifts when compared to the peaks in the solution spectrum. Generally these shifts are not large. Relative intensities of the SERS bands can also be different from those of the free molecule. New bands in the SERS spectra may also appear. However in most cases, the spectra are similar enough so that molecular identification is possible.

10. The enhancement is limited to those molecules immediately on the surface or to those molecules in close proximity to it.

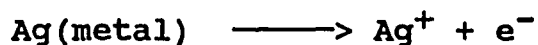
2.3 SERS ACTIVE SUBSTRATES

Much attention has been focussed in this area after it had been established that SERS seems to be most intense when excited on metal surfaces containing many microscopic metal domains. Various systems have been explored and the

most common of these include electrodes, colloids, and island films. Some of these will be discussed here:

2.3.1 ELECTRODE SURFACES

Since the first observation of SERS was in an electrochemical environment, it seems only natural that various electrode systems have been subsequently investigated. SERS studies have been carried out on Cu (38), Ag (8,29,33,39), Au (35,38-40) and Pt (41) electrodes subjected to oxidation-reduction cycles. During the oxidation half cycle, a metal salt, usually a halide, is formed at the electrode surface. In the case of silver, the reaction would be (42):



In the reduction process, the metal does not redeposit itself uniformly over the electrodes, but instead, forms clusters of the metal at the surface:



The average size of these clusters has been reported to be $\leq 200 \text{ \AA}$ (27). SERS studies on semiconductor electrodes have also been reported. These include a silver-modified n-GaAs electrode (43) and a p type InP electrode (44). Nonaqueous SERS has also been investigated in an electrochemical environment (45,46).

2.3.2 COLLOIDAL SYSTEMS

Creighton et al. were the first researchers to exploit the unique optical properties of colloidal silver in SERS (47). Unlike electrochemically modified surfaces or island films, the surface roughness is provided by the microstructure of the colloids themselves. Colloids are most commonly prepared by the reduction of a solution of a metal salt by means of an appropriate reducing agent in either an aqueous (47) or non-aqueous medium (48,49); for example, silver sols can be obtained by reducing silver nitrate with sodium borohydride. The resulting sols usually have a narrow size distribution with a diameter of a few hundred angstroms (50). Other reducing agents such as citrate and hydrogen have also been used (50). The most intense SERS signals are obtained from aggregated metal sols, consisting of large assemblies of individual colloidal particles each about several hundred angstroms in size. Apart from Ag colloids, studies have been carried out on Au (51- 52), Cu (53), and Pt-Au (54) colloids. Lepp and Siiman have studied SERS on silver ethanosols (48,49). "Photocolloids" have also been generated by photoreduction using laser irradiation (55). Matrix isolated colloids have been produced by quenching the metal vapor in a noble gas matrix or by cocondensation of the metal vapor and the noble gas on a cold substrate (42). Colloidal silver has also been produced at the surface of silver chloride grains (56).

Silver ions in the silver halide grains are reduced by electron transfer from the halide ions. It has been argued that the colloidal surface is advantageous for SERS studies because it provides a well controlled system in terms of sphericity, size and monodispersity. This system can be characterized using electron microscopy or absorption spectroscopy. It has been impossible in some cases to observe SERS on a colloid because of the inability to induce adsorption. In the case of an electrode surface, the application of a potential can successfully induce adsorption. However, the electrochemical cells used for SERS require the presence of a supporting electrolyte that often interferes with the species of interest. Sols are perhaps the simplest SERS active system available however, there are problems associated with their stabilities and reproducibilities. Some workers have reported some success in dealing with these problems (57).

2.3.3 METAL ISLAND FILMS

These island films have been prepared by depositing an appropriate metal vapor on a cold (34,58) or a warm substrate (59). Glass and quartz are the most commonly used substrate although the use of cellulose has also been reported (60). This process usually results in the formation of a rough metal film. The higher temperature of the substrate increases the metal atom mobility, causing the nuclei to grow into islands. Analogously, the colder

substrate reduces the mobility of the metal atoms and leads to the formation of a rough metal film. While Ag island films are the most commonly studied surfaces in this category, studies have also been carried out on Indium films (61) and vapor deposited sodium (62).

2.3.4 OTHER SYSTEMS

A number of other potentially active systems have been reported. Metals have been roughened by means of ion bombardment in vacuo, mechanical polishing and acid etching. Rough Ag has also been produced when AgBr films have been exposed to UV radiation in vacuo, releasing halogen vapor and leaving behind a rough metal (27). Lithographically produced metal domains are yet another type of surface applied to the study of SERS (63).

2.4 THEORETICAL EXPLANATION FOR SERS

While one group of researchers has focussed on studying experimental systems for the observation of SERS, another group has concentrated on proposing theoretical explanations for the observation of this effect. Many explanations have been put forward as possible mechanisms and there has been a lot of controversy as to which mechanism is responsible for SERS. However, some consensus has been reached and it can now be said that theories accounting for SERS can be grouped into two categories: those that are electro-

magnetic in nature and those that promote chemical interaction between the adsorbate and the metal surface. Reviews of these theories are available (27,64-67) and only a brief insight into them will be given here.

2.4.1 ELECTROMAGNETIC (EM) ENHANCEMENT:

This approach is based on the classical electromagnetic effect. The electromagnetic field at the surface of a metal is dramatically changed from that of the incident field because of the influence of the metal. These effects are more well defined when the surface contains rough features whose dimensions are much less than the wavelength of the incident light. These length scales are typically 50 to 2000 Å (68). For such a feature, modeled as an isolated sphere, the induced electric field, E_i , is related to the incident field, E_o , as follows (69):

$$E_i = \left(\frac{1}{1 + [\epsilon(w)/\epsilon_o - 1]A} \right) E_o$$

A = depolarization factor and is assumed to be size independent and shape dependent. $A = 0.33$ for a sphere.

$\epsilon(w)$ = dielectric constant of the bulk metal
 $= \epsilon_1 + i\epsilon_2$

ϵ_o = dielectric constant of the surrounding medium.

There is a resonant response of the sphere when the real part of the denominator is zero that is when $\epsilon_1 = -2\epsilon_o$. At

this resonance, E_1 gains a very high value, only if the associated ϵ_2 is small. The second requirement for a large enhancement is that the frequency of the incident light should match the plasma resonance frequency of the substrate's rough feature. This frequency depends on the size and shape of the particle. By virtue of the first requirement, the noble metals, Ag, Au and Cu are predicted to be strong SERS scatterers since ϵ_2 is small for these metals. Moreover, the stipulation that the $\epsilon_1 = -2\epsilon_0$ can be satisfied for all these three metals in the visible region where laser excitation sources are readily available. In fact the energies correspond to the blue region for Ag and to the red for Au and Cu. Since for Cu and Au, the energies are much lower and the ϵ_2 values are also somewhat larger than that of Ag; then Ag would cause an adsorbate to experience a greater intensity enhancement. It should be noted that the EM approach also predicts that theoretically other metals should also provide a high degree of enhancement in other regions of the spectrum for example Ga and Pt in the IR region (69).

The excitation of plasma resonances results in a large increase in the electric field intensity within a metal and a corresponding increase in the field intensity just outside of the metal. Apart from the plasma resonance effect, the shape of the rough feature and the mismatch between the dielectric function within the metal and the surrounding

medium are two more important contributing factors. This mismatch results in the concentration of the electric field at points or tips or regions where the surface curvature is a maximum and it has been called the "lightning rod effect" (67). Both the plasma resonances and the lightning rod effect are mechanisms which promote the concentration of the field intensity on small regions on the surface. Enhancement of the emitted signal is predicted because of the increased intensity of the excitation field and because the emitted signal is radiated more effectively through coupling to the metal. SER scattering intensity depends roughly on the fourth power of the field intensity - a power of two from the enhancement of the incident field and another two from the enhancement of the Raman shifted field.

To date, the EM theory can account for a large number of experimental results. The actual enhancements attributed to the EM effects range from 10^3 to 10^6 . There are however some limitations to this theory and these include: (a) the necessity of some form of roughness; this would preclude the smooth surfaces that have been studied in UHV experiments and (b) the requirement of a well defined electronic plasma resonance at energies accessible with the most commonly used lasers; this stipulation would limit the most efficient surfaces to those of the free electron metals such as Au, Ag, Cu, Na, Li and K.

2.4.2 CHEMICAL INTERACTIONS

This approach takes into account the possibility of a change in the Raman polarizability of a molecule that can occur when it is adsorbed on a metal and which can result in an increase in the Raman scattering cross-section. This change in polarizability has been explained in terms of (a) adatoms (69), (b) the existence of special active sites (69), (c) the existence of new electronic energy levels caused by the mixing of those of the adsorbate and the metal (13) and (d) the interaction of the adsorbate with the metal electrons either through some form of charge transition (64) or simply through the Coulombic interaction between the molecular electrons and the electron gas of the molecule.

These effects, all chemical in nature are thought to contribute factors of $10 - 10^2$ to the total enhancement. There are also experimental results which can account for the chemical interactions; for example, the observation that the enhancement factor for the first adsorbed layer is much greater than for the subsequent layers. This would imply that the first layer is first enhanced by the short range chemical interactive process.

Most experimental results seem to indicate that both theories are contributing to the SERS enhancement mechanism and this finding has also been universally accepted.

2.5 ANALYTICAL POTENTIAL OF SERS

Since the enhancement factor for SERS can be as high as 10^6 , it would seem to be the ideal technique to be used for the detection of analyte species at low concentrations. It has also been proposed that resonance enhancement effects and surface enhancement effects should be multiplicative in a system where the species can absorb at the excitation wavelength. Theoretically, this should lead to enhancements of 10^8 . Further it has been found that the metal surface can effectively quench the fluorescence of adsorbed molecules. This is thought to arise from the nonradiative transfer of energy from the excited molecule to the metal (13). A number of workers have exploited these properties of SERS and have applied it to: (a) the study of adsorbate-metal interaction, (b) the use of SERS as a trace analytical technique and (c) the study of SERS as a method of detection for FIA and chromatography.

C.D. Tran (70) was one of the earliest workers to investigate the figures of merit of SERS as an analytical technique. By depositing Ag sols and various dyes on filter paper supports and then scanning the Raman spectra, detection limits ranging from 500 pg to 240 ng were obtained for a number of dyes. The calibration plot in this study exhibited a linear response over a wide range of concentrations. Pemberton and Buck (71), while studying the dithiozone anion at a Ag electrode surface reported accept-

able S/N ratios for concentrations ranging from 10^{-2}M to 10^{-9}M . Vo Dinh et al have investigated the detection of polyaromatic organic compounds using Ag coated spheres deposited on filter paper (72). The detection limits were at the nanogram level. Similar detection limits were reported for N-containing drugs and organophosphorus compounds (73,74). Vo Dinh et al (72) also reported a linear calibration curve for concentrations ranging from 10^{-6}M to 10^{-3}M for benzoic acid. In an effort to extend the practical usefulness of SERS, Alak and Vo-Dinh have reported some success in using SERS to analyze a real life soil sample deliberately contaminated (73). In this study a dynamic range of 10^2 - 10^3 was reported. Lee et al. have reported detection limits of $3 \times 10^{-3}\text{M}$ for catecholamines studied at a silver electrode (75). Brandt (76), in an analysis of dyes in photographic films obtained detection limits of 2×10^{-6} mol and a linear intensity versus coverage over the range of 0.05 to 1 monolayer. Carrabba and coworkers (77) investigated the use of SERS in the identification of water contaminants and found no interferences from the presence of humic materials in the water or from any background fluorescence. The limit of detection was reported to be 700 ppb for quinoline. As can be seen from this short review, a wide range of materials are being investigated in an effort to establish SERS as a viable analytical technique in determining compounds at trace levels.

A growing interest now lies in the use of SERS as a method of detection in flow injection analysis (FIA) and chromatography (57, 78-81). Freeman carried out a FIA study on SERS using colloidal silver prepared by citrate reduction. Linearity for the SERS signals of pararosaniline hydrochloride was reported along with a reproducibility of 1% and a detection limit of 2 ng. Freeman has also promoted SERS as a potential detector for HPLC (78). Berthod, using Ag sols prepared by borohydride reduction, reported the precision of the SERS signal in FIA as 5% and a detection limit of ppb for paraminobenzoic acid (79). In contrast to Freeman's finding, it was found that SERS signals were not linearly proportional to the concentrations. Forcé (80), using electrodes as a detector of eluents in FIA, obtained a 7% reproducibility for intensities which were linear over three order of magnitude and a detection limit of 250 ng. Perhaps the simplest system was demonstrated by Séquaris and Koglin (81) who have applied SERS to analyze directly HPTLC spots of nucleic purine derivatives. After the HPTLC plates were dried and the chromatograms developed, Ag colloidal solution was sprayed using an atomizer. Spots of 2-4 mm i.d. were then analyzed using a conventional 90° scattering arrangement. High quality spectra using sample sizes of 30 ng were reported.

Although there is an increasing interest in exploring the analytical potential of SERS, there are some drawbacks

to this technique. Three major limitations have been well described by R.L. Garrell in a recent article (82). Firstly, the availability of active surface area sets an upper limit on the measurable concentration. In addition, the analyte adsorption equilibria can set a lower limit to the detection. The second problem lies with the linearity of this technique. In reality, a linear calibration curve over a wide range of concentration has been obtained for only a few molecules. Such a curve would not be applicable to other analytes or for species undergoing competitive adsorption, since the Raman scattering cross-sections and the adsorptivities are different for various molecules. Despite the fact that structural information is available from SERS, it cannot be used for unambiguous identification of a particular chemical species and complementary techniques may have to be used. However, in this respect, SERS is not different from other vibrational techniques.

SERS, despite its limitations, is still experiencing a continuous interest in its possible applications. Presently, the SERS process is being investigated with the use of a FT-Raman spectrometer and a Nd: YAG laser (38,39). Its applications as a chromatographic detector and as a tool for studying adsorption on catalytic surfaces are still being investigated.

CHAPTER 3: RESEARCH APPROACH AND EXPERIMENTAL DETAILS

In this chapter an outline of the research approach taken will be presented along with details of the experiments that were carried out. Results and discussions of the absorption data will follow in Chapter 4. An analysis of the solution and surface vibrational spectra of the dyes will be given in Chapters 5,6 & 7. An attempt will also be made to interpret the changes between the solution and surface spectra in terms of the interactions that might be taking place and to gather some conclusions concerning the interaction sites on the dye molecules and the geometries adopted by them when adsorbed on to the colloidal surface.

3.1 RESEARCH OBJECTIVE:

Since Fleischmann, Hendra and McQuillan (7) reported the first enhanced Raman spectrum of pyridine, a vast amount of effort has been expended to explain the large increase in the observed intensity in SERS. This work has been largely successful. The mechanisms responsible for SERS are well established and understood now. However, practical application of SERS are still few and the analytical potential of SERS has yet to be justified. This research was undertaken with two objectives in mind: to investigate the usefulness of SERS to study the structural changes that the TPM dyes undergo when complexed to metal ions and to study the limitations of this technique as a quantitative and

qualitative tool for characterizing highly fluorescing compounds at low concentrations where it would be impossible to observe normal Raman scattering.

It seemed only logical to begin a study on silver, since it has been established as an efficient SERS scatterer. The reasons for choosing colloidal silver are threefold: (a) colloidal systems have been successfully demonstrated as SERS active systems, (b) colloidal systems are very simple and easy to prepare; the surface roughness necessary for the observation of SERS is already provided by the microstructure of the colloids, quite unlike other substrates where the surface roughness is provided by an external means of pretreatment and (c) the sizes of the colloids can be monitored using electron microscopy and absorption spectroscopy.

The dyes chosen to be studied were crystal violet (CV), ethyl violet (EV) and pararosaniline chloride (PR). Their structures are shown in Fig.3. These compounds form a useful series of molecules having similar structures. They all belong to the class of cationic dyes and are useful as acid-base indicators especially in non-aqueous media (83). They are also applied as biological stains and as dyes in the textile and printing industry (84). CV has been used in the analysis of heavy metal ions. This application stems from the ability of the dye to complex metal ions (85). It has also been reported that CV is capable of

forming a charge transfer complex with a donor molecule with resulting changes in its spectral characteristics (86). Thus we find these group of dyes spectroscopically interesting molecules.

Previous Raman spectroscopic study on the TPM dyes have focussed mainly on CV. Jeanmaire & Van Duyne reported the first surface spectrum of CV on a Ag electrode (8). Pettinger and Watanabe carried out a comparative study of the RRS and SERS spectra of CV on a Ag electrode (87). Burstein et al reported the resonant Raman scattering of CV adsorbed on Ag and Au surfaces (88). Other workers have investigated CV on substrates such as Ag island films (89). The spectrum of a related compound, basic fuchsin (see Fig.3), has been reported on silver island films (59). While a number of workers might have successfully demonstrated that it is possible to observe the surface Raman spectrum of some of these dyes, a detailed analysis of the mode of interaction between the metal and the molecule has not been carried out.

SERS is ideally suited for vibrational studies of highly colored compounds. This stems from the fact that in addition to obtaining an enhanced spectrum, fluorescence quenching can also take place at the metal surface. With these two factors strongly favoring SERS, we proceeded to investigate the interactions that the TPM dyes exhibit while adsorbed on a silver surface. This was done by

carrying out an analysis of the Raman spectra of the dyes in the presence and absence of silver hydrosols and by correlating the absorption spectra of the free dyes with those of the dyes adsorbed on the surface of the colloid.

3.2 EXPERIMENTAL:

Crystal violet, CV, (CI42555) and ethyl violet, EV, (CI42600) were purchased as the chloride salts from Kodak and used without further purification. Pararosaniline chloride, PR, (CI42500) was purchased from Sigma Chemicals. This compound had to be doubly recrystallized from a 1:4 mixture of ethanol and water before the Raman spectrum at an excitation wavelength of 514.5 nm could be observed. All other spectra of this sample were obtained using the 'crude' sample that was obtained from the manufacturer.

All solutions were prepared with distilled, deionized water. Prior to use all the glassware was scrupulously cleaned by rinsing with concentrated nitric or sulfuric acids and then with distilled, deionized water. The glassware was usually left to soak overnight in distilled water to ensure all traces of acids had been removed.

Stock solutions of the dyes were prepared by dissolving the appropriate amounts of dyes necessary for a 10^{-4} M solution. CV and EV dissolved immediately at room temperature. It was necessary to warm the PR solution to 75° to promote dissolution. From these stock solutions, other concentrations were prepared by diluting as required.

Colloidal solutions of silver were prepared following a variation of the recipe of Creighton et al. using a sodium borohydride reduction of Ag^+ (47). Sodium borohydride was purchased from Fischer Scientific Company while the silver nitrate was bought from Alfa. They were both used without further purification. A stock solution of silver nitrate, of concentration $5 \times 10^{-3}\text{M}$, was prepared and stored in an amber bottle for further use. AgNO_3 solutions of concentrations $1 \times 10^{-3}\text{M}$ were prepared from this stock. The NaBH_4 solution had to be freshly prepared and used immediately because of its instability. Usually, a $2 \times 10^{-2}\text{M}$ NaBH_4 solution was prepared and this was diluted to obtain a $2 \times 10^{-3}\text{M}$ solution. The latter was placed in an ice bath immediately to slow down any decomposition.

Prior to the preparation of the silver sol both the $1 \times 10^{-3}\text{M}$ AgNO_3 and $2 \times 10^{-3}\text{M}$ NaBH_4 were ice cooled. Silver sols were then prepared by adding the AgNO_3 solution dropwise to the solution of NaBH_4 . The sol mixture was kept ice cold in an ice bath and vigorously stirred while it was being prepared. The volume ratio of AgNO_3 to NaBH_4 used was 1:3.

Dye-sol mixtures were prepared by adding the necessary volume of dye to a fixed amount of sol. Final adjustment of the volumes was carried out in a volumetric flask. Dilution factors were calculated such that even if the dye concentration varied the concentration of the sol remained

constant. The absorption and Raman spectra were scanned immediately after preparation of the dye-sol mixtures.

The absorption spectra were scanned using a Varian uv-vis 634 spectrophotometer and recorder. Raman spectra were scanned with a home built Raman spectrometer. A schematic diagram of this instrument is given in Fig.4. The instrumental set up consisted of a Coherent Ar⁺ ion Innova 70-2 laser as the light source, along with the necessary focussing and collection optics, a Jarrell-Ash 25-100 Double Czerny-Turner one meter scanning monochromator controlled by a North Star computer and a photomultiplier tube (PMT) as the detector. Signals from the PMT could have been recorded using dc amplification or photon counting. Most often the latter mode of detection was used: that is, the individual pulses from the tube were first preamplified with a fast preamplifier, Tektronix model 9301; then further amplified with an Ortec Model 454 Timing filter amplifier; then passed through an Ortec Model 436 discriminator, digitally counted and finally stored on data disks, enabling the user to retrieve the spectral data at any time. Spectra were plotted with the aid of a Hewlett Packard 7210A digital plotter.

The sample compartment consisted of a cuvette holder sealed to a movable mount which enabled adjustments to be made in the horizontal and vertical directions. The samples were held in a 0.5 cm glass fluorescence cell polished on

the bottom and the sides. The same cuvettes were used to acquire the absorption spectra of the samples. The laser beam was focussed through the bottom of the sample cell with the aid of a system of lens and mirrors. The scattered radiation was collected in a direction at 90° to that of the incident radiation. Using an $f/1$ lens, the scattered light was collimated and then focussed on the entrance slit of the monochromator with an $f/10$ lens.

Optical and sample alignments were carried out to maximize the signal output. Since all of the solutions were optically absorbing, it was necessary to optimize the distance traveled by the scattered light through the sample. This was done by setting the monochromator at a line corresponding to a Raman peak of the sample and then moving the sample so that the laser beam was as close as possible to the edge of the cell while at the same time obtaining the maximum signal output. This distance was usually 0.25 cm for concentrations $\leq 10^{-5}M$ and 0.21 cm for a $5 \times 10^{-5}M$ solution. Optimum optical alignment was obtained by adjusting the position of the collecting lens laterally and parallel to the optical bench until the maximum signal output for the analyte peak was observed. Once the positions of the sample and the collection lens were optimized, the Raman spectra were scanned. For the dye spectra, multiple scanning of single samples was done in order to obtain better S/N ratios. Raman spectra of CV,

EV, and PR at various concentrations were obtained using an excitation wavelength of 514.5 nm. In addition, the spectrum of PR was scanned at 488.0 nm and 457.9 nm. Laser power used for the dye samples was ~ 30 mW at the sample. The solution spectra of the dyes were recorded at intervals of 1 cm^{-1} and an integration time of 2.5 - 3 seconds/ cm^{-1} was used.

The same procedures were utilized for obtaining the Raman spectra of the dye-sol mixtures. The laser power used for these samples was ~ 12 mW at the sample. For the PR-Ag sol mixtures some changes had to be made because of the rapid precipitation of the sol in the presence of this dye. Solution mixtures of this dye and sol were very unstable and only 1 or 2 scans of a single sample could be obtained. Therefore, single Raman scans for a number of PR-Ag sol mixtures were obtained and these were then coadded into a single spectrum and used for further analysis. This procedure was necessary for studies at concentrations $\geq 10^{-5}\text{M}$. At lower concentrations ($\leq 10^{-6}$) the dye-sol mixture was stable enough to enable the user to obtain multiple scans of a single sample. For CV and EV, their mixtures with the Ag sol were stable enough to obtain several Raman spectra of a single sample. All of the Raman spectra were scanned over the same spectral range: from 125 to 1700 cm^{-1} . The water peak was scanned from 2900 cm^{-1} to 3800 cm^{-1} in each spectrum. The spectra of the dye-sol mixtures were recorded

at intervals of 1 cm^{-1} and an integration time of 2 .seconds/ cm^{-1} was used.

The absorption spectra of all samples were routinely scanned before and after the recording of the Raman spectra as a check for sample deterioration.

The activity of the Ag sol was verified by quickly scanning a Raman spectrum of a mixture of Ag sol and pyridine between 950 and 1050 cm^{-1} and observing the enhanced peaks at 990 cm^{-1} and 1010 cm^{-1} . An example of such a spectrum is shown in Fig.5.

The calibration of the monochromator was routinely checked by monitoring the position of the 459 cm^{-1} peak of a sample of carbon tetrachloride. This was especially necessary when the excitation wavelengths were altered.

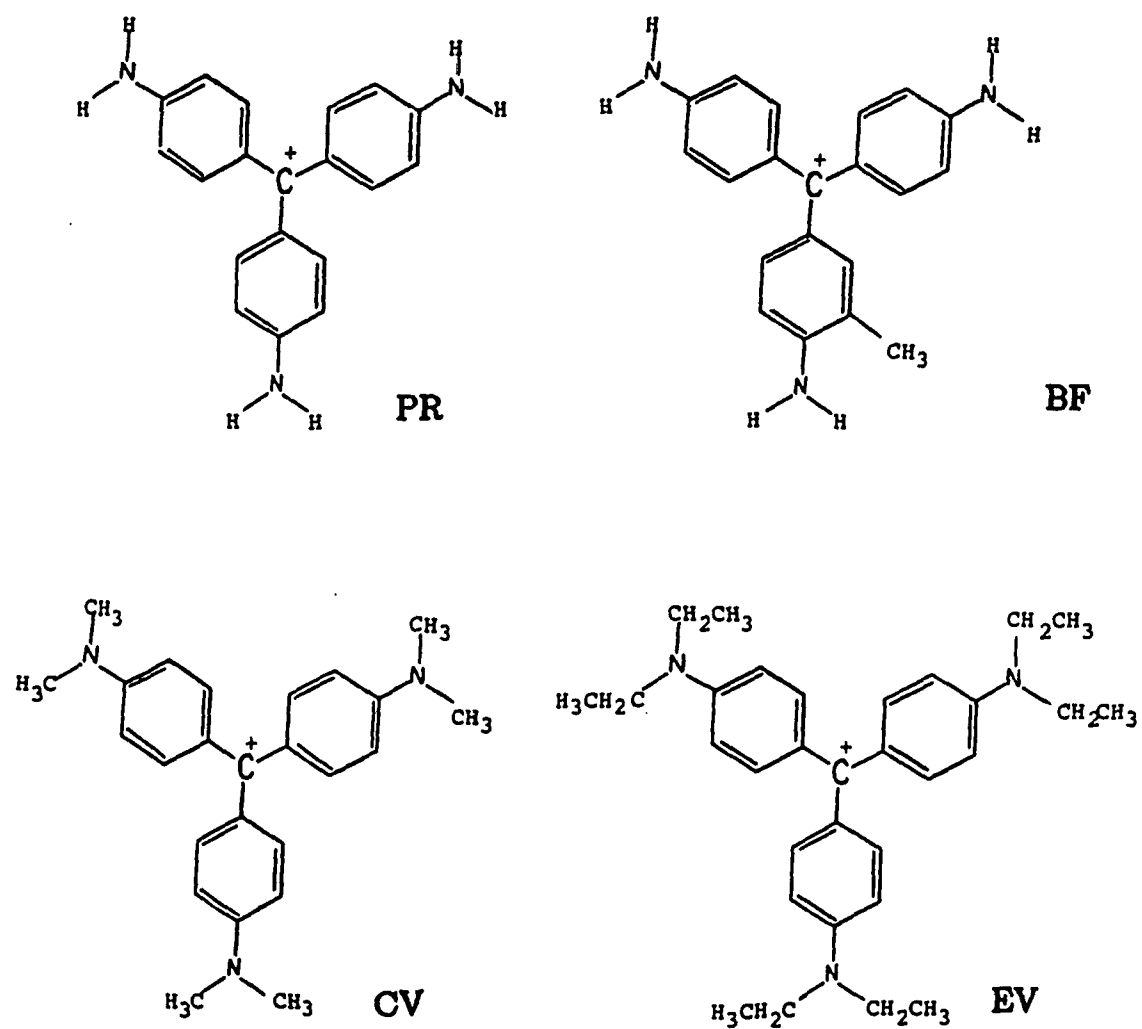


Figure 3. Structures of triphenylmethyl dye; PR = pararosaniline, BF = Basic Fuchsia, CV = Crystal Violet, EV = Ethyl Violet.

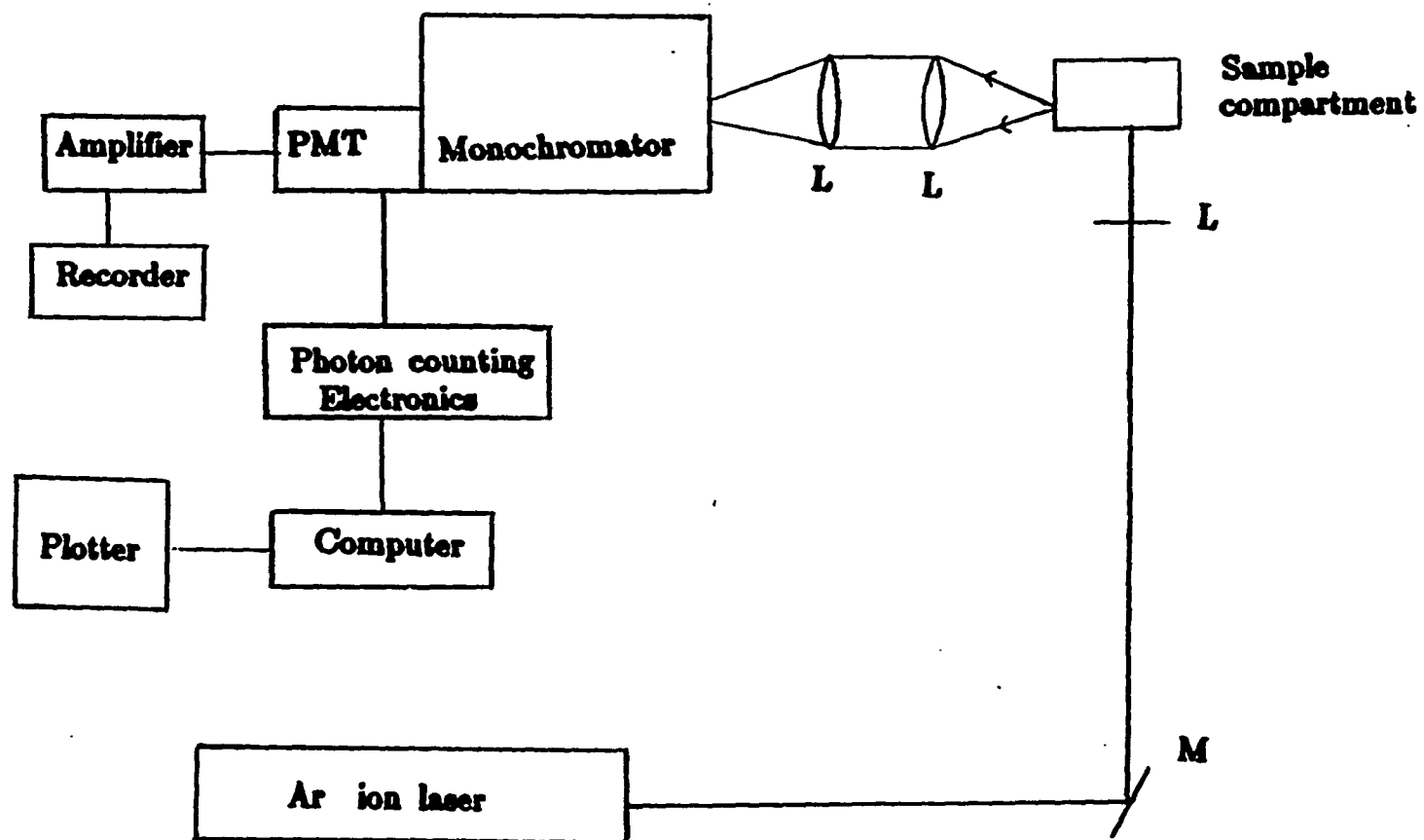


Figure 4. Schematic diagram of the Raman spectrometer;
L = Lens and M = mirror.

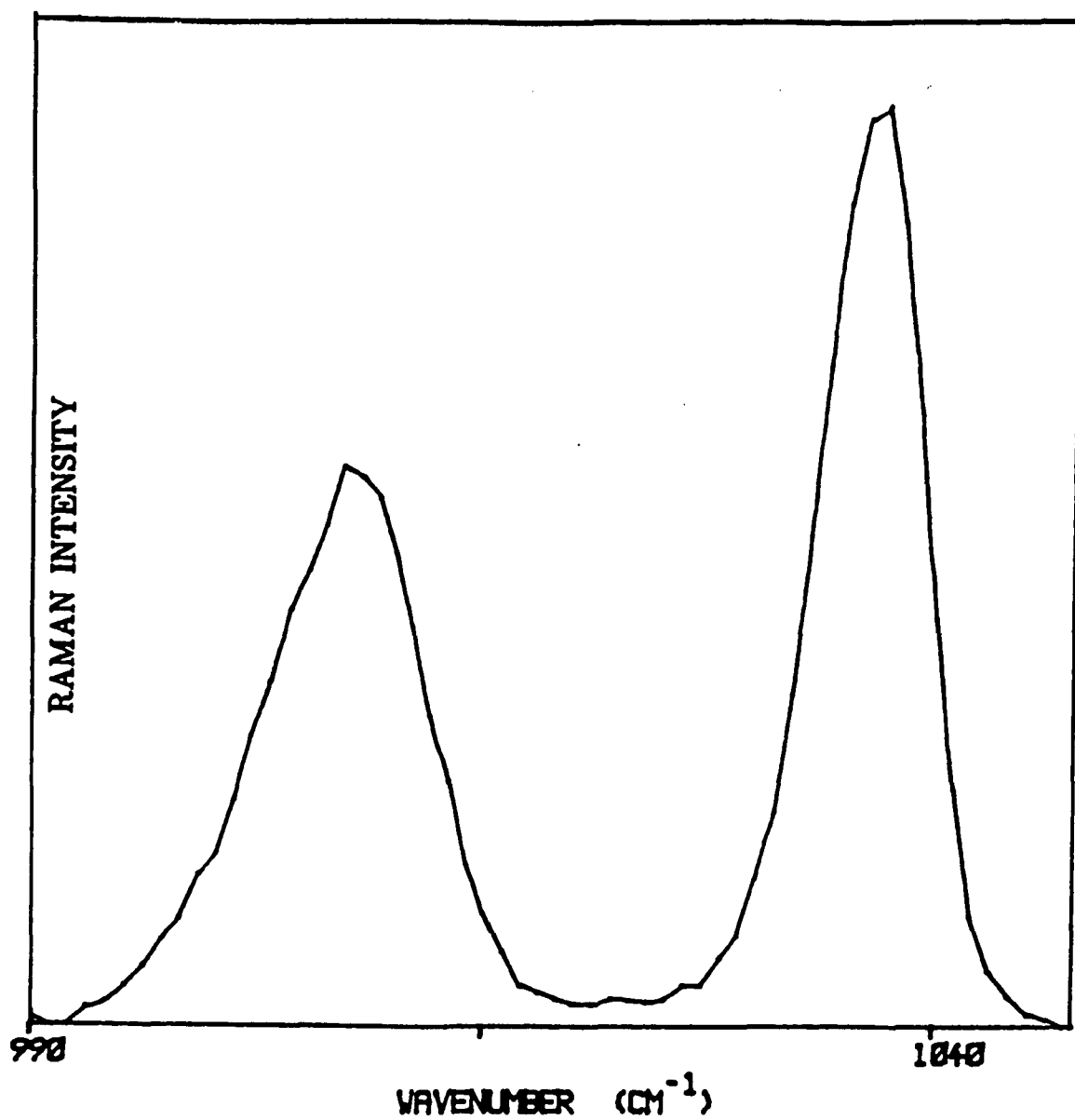


Figure 5. Surface Raman spectrum of 2.5×10^{-4} M pyridine adsorbed on colloidal silver. Laser power = 100 mW at sample. Excitation wavelength = 514.5 nm.

CHAPTER 4: RESULTS AND DISCUSSION OF THE ABSORPTION SPECTRA OF THE DYES AND DYE-AG SOL MIXTURES

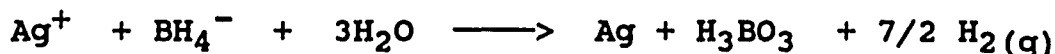
4.1 ABSORPTION DATA:

The absorption spectra of the TPM dyes , CV, EV and PR are shown in Fig.6. Table I lists some of the spectral parameters associated with these dyes. The absorption spectra of the dyes at $5 \times 10^{-5}M$ are identical to those at $1 \times 10^{-6}M$ hence we deduce that no evidence for dimerization is present. The relevant spectra for the dyes over this concentration range are shown in Figs.7 -9.

All three dyes are deeply colored, EV and CV are of a strong violet color while PR is fuchsia in color. A strong absorption band along with a shoulder at a lower wavelength are observed in the 500-700 nm region of the absorption spectra of the dyes. These dyes are alternate hydrocarbons with an even number of atoms involved in conjugation and with a 24π electron system. The last two occupied orbitals have been reported to be nonbonding and degenerate (90-92). Hopkinson and Wyatt have assigned the two absorption bands (408 and 434 nm) observed for the TPM carbonium ion to transitions to the first empty orbital from the highest occupied doubly degenerate orbitals (90). They have proposed that the doubly degenerate orbitals become separated owing to a distortion of the D_3 symmetry; hence the observation of two bands. They also claimed that

the introduction of π electron donating groups on the rings would further split the degeneracy of the two highest filled orbitals. Chu and Weissman have also proposed the splitting of the degenerate orbitals in the TPM cation (91). While most workers have assigned these two bands to $n - \pi^*$ or $\pi - \pi^*$ others have attributed the second band at higher energy to the unsymmetrical isomer proposed by Lewis et al. (93). It seems most reasonable to assign the absorption bands to $n - \pi^*$ transitions, since spectroscopic evidence for the existence of the rotational isomer is limited (see Chapter 5, Section 5.1).

The absorption spectra of the silver sols prepared by reduction of a $1 \times 10^{-3}M$ silver nitrate solution by a $2 \times 10^{-3}M$ sodium borohydride solution are shown in Figs.10 -12. (Although these spectra will be referred to as absorption spectra, they originate from the loss of light intensity due to light scattering by the sol particles.) The chemical reactions taking place have been reported to be (79) :



Hydrogen is also produced by the reduction of water :



This sol is usually yellow to yellowish brown in color at room temperature and a sharp absorption band is observed at 390 nm. The size of these sols have been previously reported to be in the range of 100-300 Å (50). After preparation they are usually stable for long periods without any

signs of precipitation. The activity of the sol does not remain constant with time. Evidence for the activity of the sol is provided by the enhanced Raman spectra observed for a 1:3 mixture of $10^{-1}M$ pyridine and the sol (Fig.5).

From a comparison of the spectra of the dyes and those of the dye-sol mixtures (see Figs.10-12) it can be deduced that there are signs of interaction between the sol and dye. Clearly, the spectra of the sol-dye mixtures are not the simple sum of their individual absorption spectra as is expected from Beer's law. Instead, the intensity of the sol spectrum has decreased considerably, especially from the solutions where concentrations of the dyes $\geq 10^{-5}M$. There is also a noticeable rise in the background of the spectrum of the solution mixture when compared to either the spectrum of the dye only or that of the sol only. The spectral features, notably the peak shape and the peak's position in the region of 500-700 nm, can be attributed to the dye in solution since these do bear a strong resemblance to those in the spectrum of the dyes only. It should be noted, however, that even though the spectral features are the same, the absorbance values differ.

At lower concentrations, notably those $\leq 10^{-6}M$, the dye peak is almost absent and the spectrum is now dominated by an intense sol peak at 390 nm. The spectral features of the dye in the region 500-700 nm are not retained in the spectrum of the dye-sol mixture; only a hump is observed

(see Figs.13-15). The spectra of the dye-sol mixtures are not the simple sum of the spectrum of the dye and the sol.

We note also that while certain spectral features of the dye and the sol are retained in the spectra of the sol-dye mixtures, no new bands are observed; a slight shift to lower wavelength is observed for the sol peak.

4.1.1 TIME VARIATION OF THE ABSORPTION SPECTRA

The absorption spectra of the dyes did not change appreciably during the time that the Raman spectra were scanned; though a slight decrease in absorbance values was observed. That there was not a significant change in the absorption spectra indicated that sample deterioration did not take place due to exposure of the laser beam. By contrast, changes were observed for the dye-sol mixtures. In general the absorbance values decreased with time. This effect is not due to laser exposure but to the natural deterioration of the sample mixtures themselves. Ultimately all mixtures of the dyes and sol at concentrations $\geq 10^{-5}M$ show signs of sol precipitation although the rate of precipitation varied with each dye (see later). We conclude that addition of the dye molecules induces aggregation of the sol particles ultimately leading to precipitation of the sol. When this process has taken place both the sol peak and the dye peaks absorbances decrease (see Figs. 16 & 17). That the dye peak also disappears when the sol precipi-

tated is evidence that the dye particles are also being precipitated and that the dye molecules must be closely associated with the sol particles.

At concentrations $\leq 10^{-6}\text{M}$, the occurrence of precipitation was rare. Whenever it did occur we attributed it to unclean glassware. At these concentrations, we observed that as the sol-dye mixture aged, the absorbance values increased between the region 500-700 nm while the absorbance of the sol peak at 390 nm showed a simultaneous decrease and a slight broadening (see Figs. 18-20). This we interpret as a sign of slow induced aggregation of the sol particles.

4.1.2 STABILITY OF THE AG SOL-DYE MIXTURES

The stability of the dye-sol mixtures at concentration $\geq 10^{-5}\text{M}$ varied for each dye. This was very surprising considering the similarities among the structures of the dyes. The order of stability was found to be $\text{EV} > \text{CV} \gg \text{PR}$. The solution mixtures of PR and Ag sol were the least stable. After mixing this dye and the sol, there was a distinct darkening of the solution and the color changed from pink to pinkish-gray and finally to gray with signs of precipitation. These mixtures would be almost completely precipitated in 3-4 hours. There was an accompanying deterioration of the absorption spectra of this sample. As the sol aged it was observed that the solution mixtures remained more stable. The sample took longer to completely precipi-

tate and had a higher absorbance value after recording the Raman spectra (compare Fig.17 & 21). However the increased stability observed with the aged sol was not significant enough to allow acquisition of multiple Raman scans of one sample and therefore scanning a number of freshly prepared sample mixtures using the same sol was the preferred method. By contrast, solutions of CV and EV were stable relative to PR. After a 24 hour period, signs of precipitation were observed in the sol-dye mixtures; although for EV the extent of deterioration was much less. An accompanying decrease in the absorbance values was also observed. Again as for PR, sample mixtures did improve in stability when they were prepared with a sol that had been aged for at least 24 hours, but the increased stability was not significant. However mixtures of these dyes and sol were stable long enough to allow multiple scanning of a single sample; although we did observe each individual Raman spectrum deteriorating with time.

Dramatic changes were not observed among the absorption spectra for mixtures prepared with an aged and a freshly prepared sol. Usually the absorbance values of the sol peak in the sol-dye spectra increased with the age of the sol. This increase however was not large, usually it was about 25% and it took place during the first 24 hours after preparation. An accompanying increase in absorbance is usually observed in the spectra of the Ag sol.

DYE	pH TRANSITION		COLOR		λ_{MAX} (NM)
	INTERVAL	ACID	BASE		
PR	1.0 - 3.1	purple	red	544	
CV	0.8 - 2.6	green	blue	590	
	0.0 - 1.5	yellow	blue		
EV	0.0 - 2.4	yellow	blue	596	

Table I: Characteristics of PR, CV and EV

(λ_{max} = wavelength of maximum absorption)

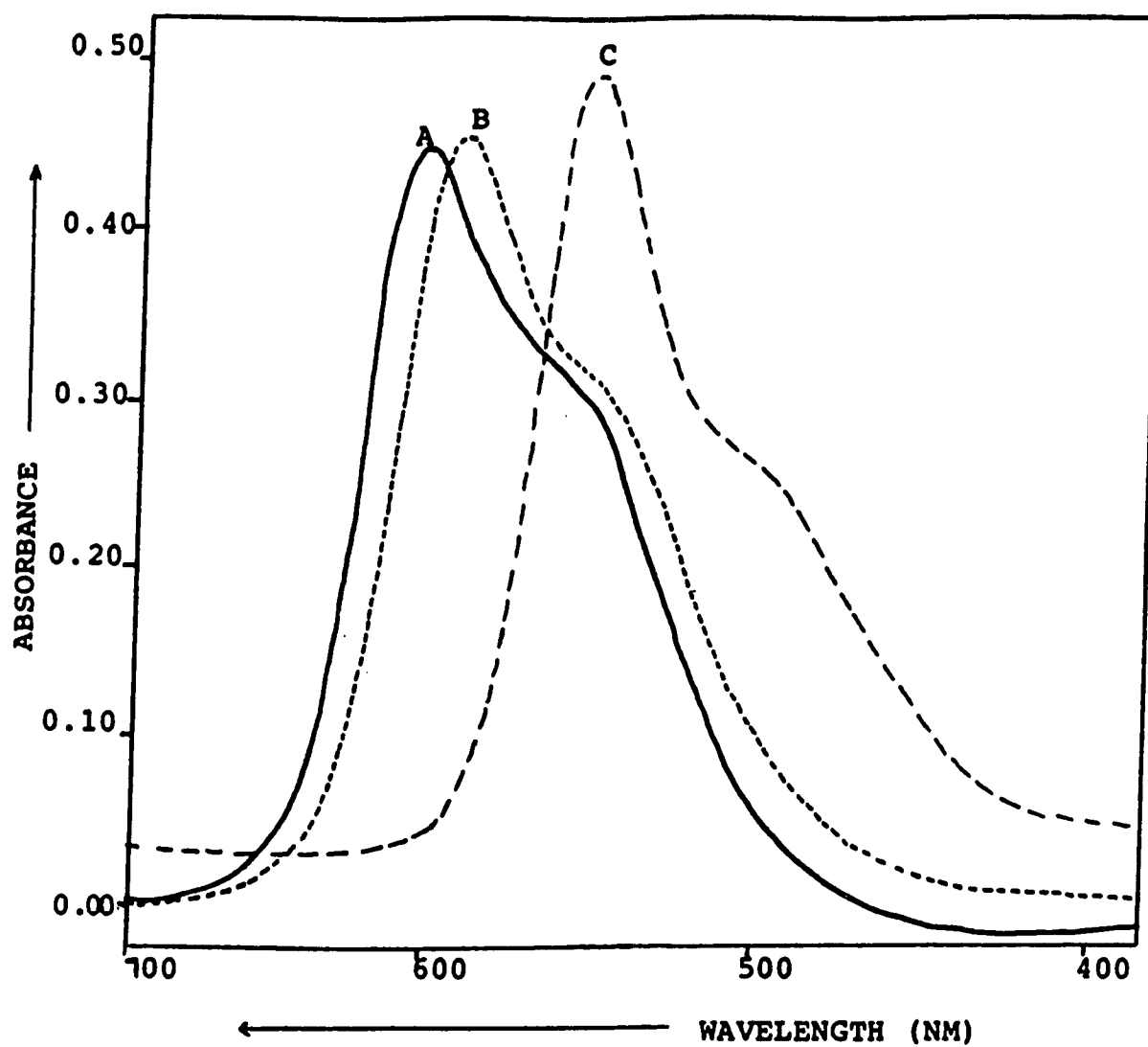


Figure 6. Absorption spectrum of dye solutions, $10^{-5}M$.
A: EV, B: CV, C: PR.

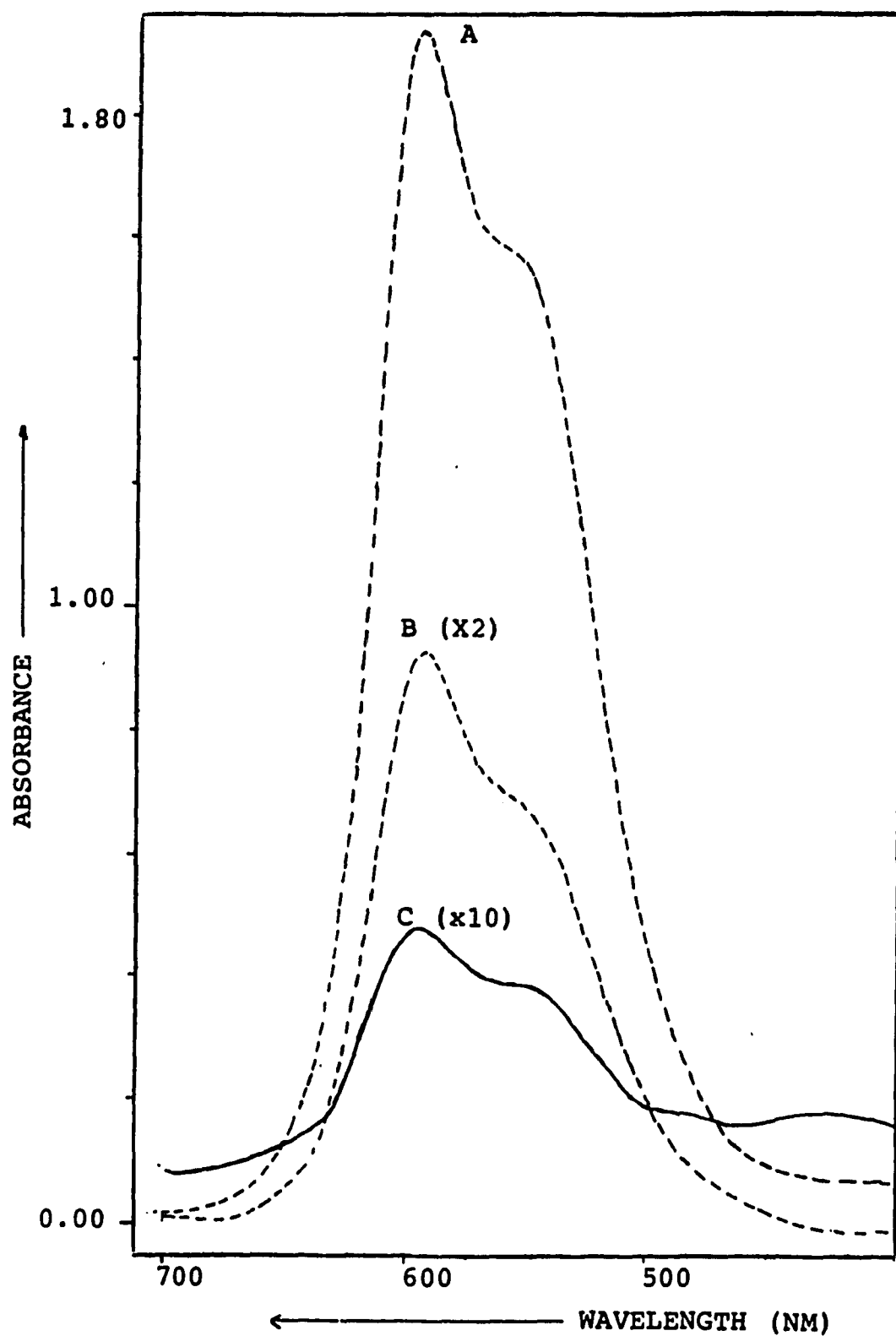


Figure 7. Absorption spectrum of EV solutions: (A) $5 \times 10^{-5}M$, (B) $1 \times 10^{-5}M$, (C) $1 \times 10^{-6}M$. Absorbance scale refers to spectrum A only.

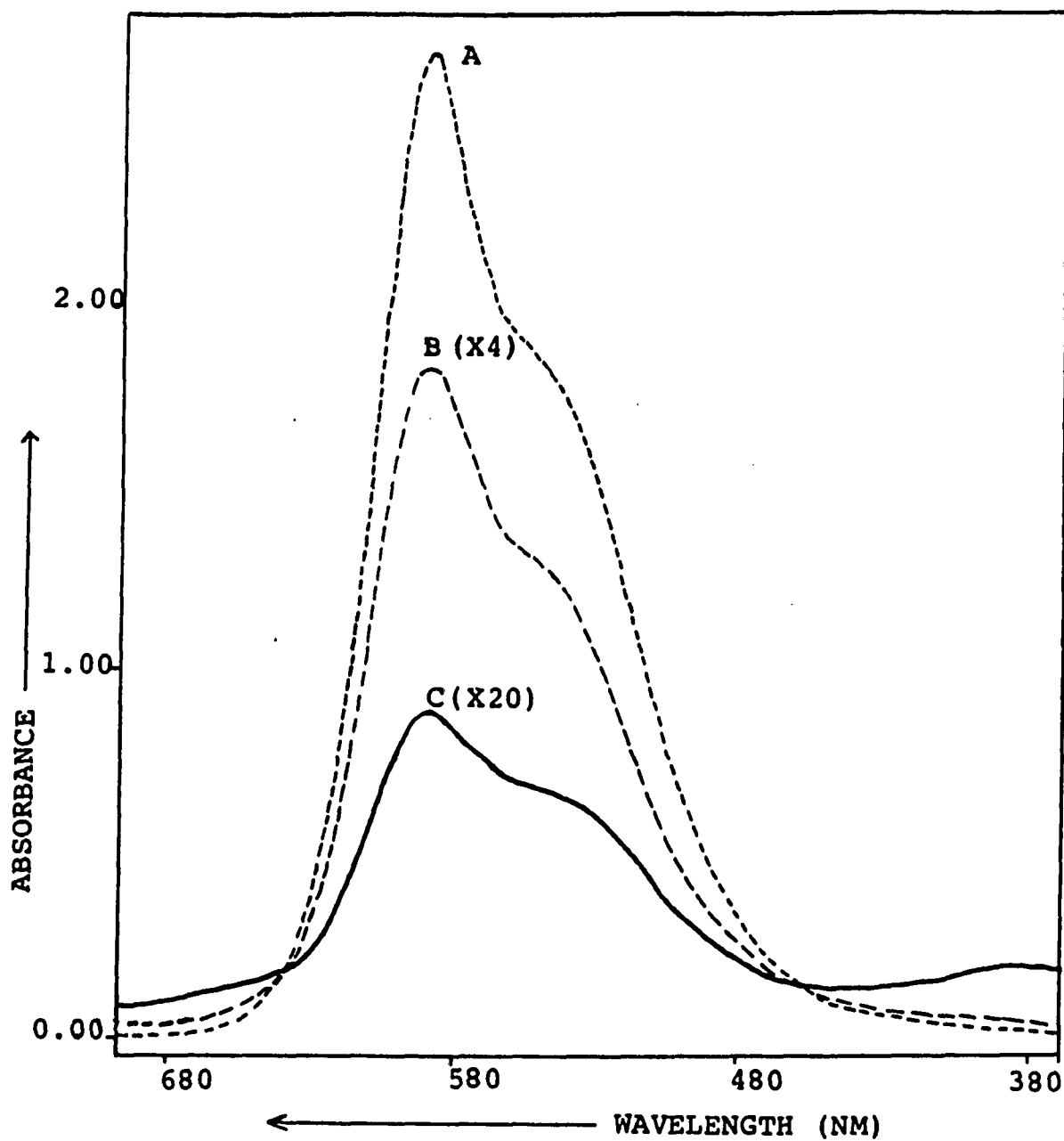


Figure 8. Absorption spectra of CV solutions. (A) $5 \times 10^{-5}M$, (B) $1 \times 10^{-5}M$, (C) $1 \times 10^{-6}M$. Absorbance scale refers to spectrum A only.

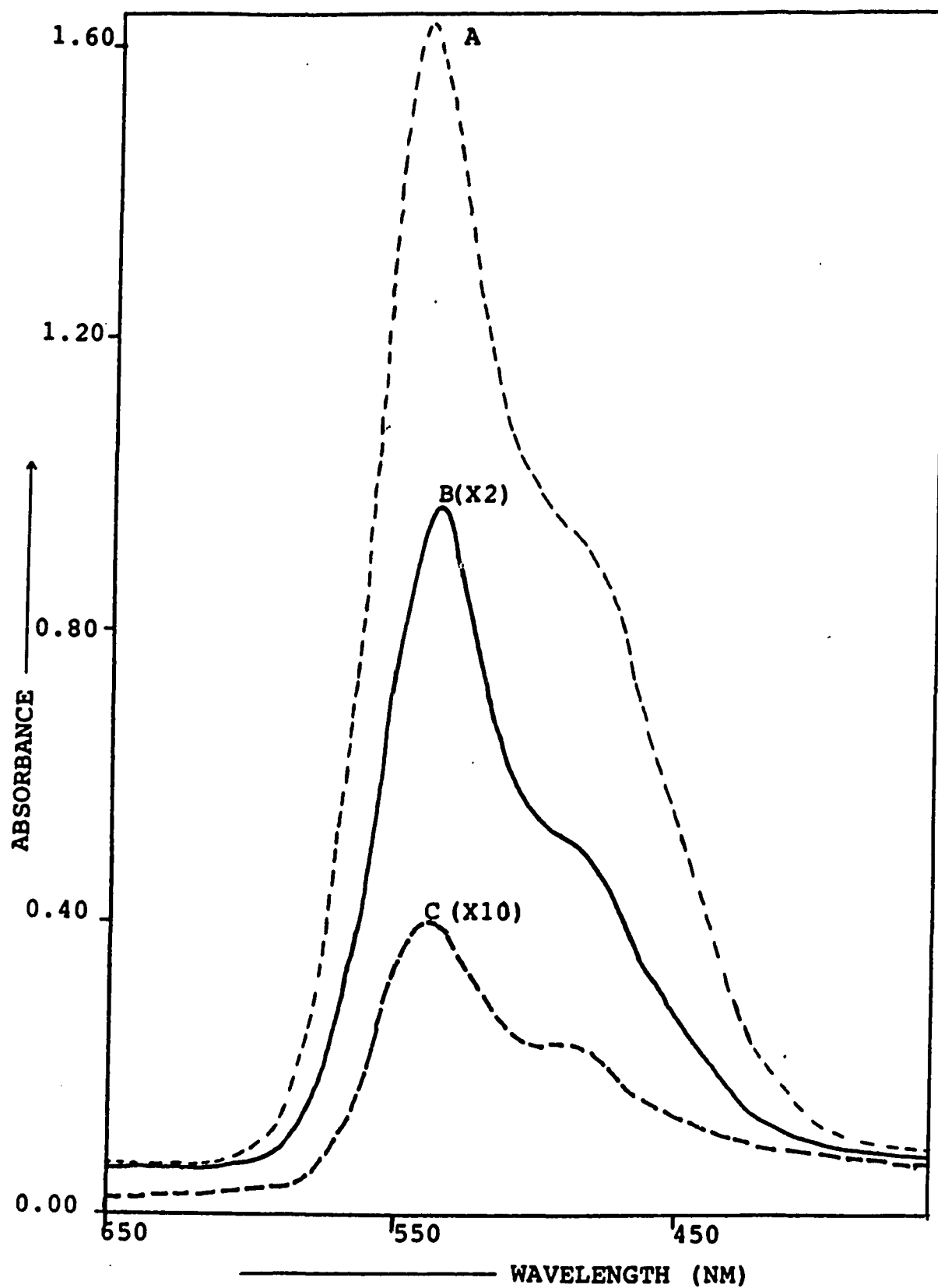


Figure 9. Absorption spectra of PR solutions. (A) $5 \times 10^{-5}M$, (B) $1 \times 10^{-5}M$, (C) $1 \times 10^{-6}M$. Absorbance scale refers to spectrum A only.

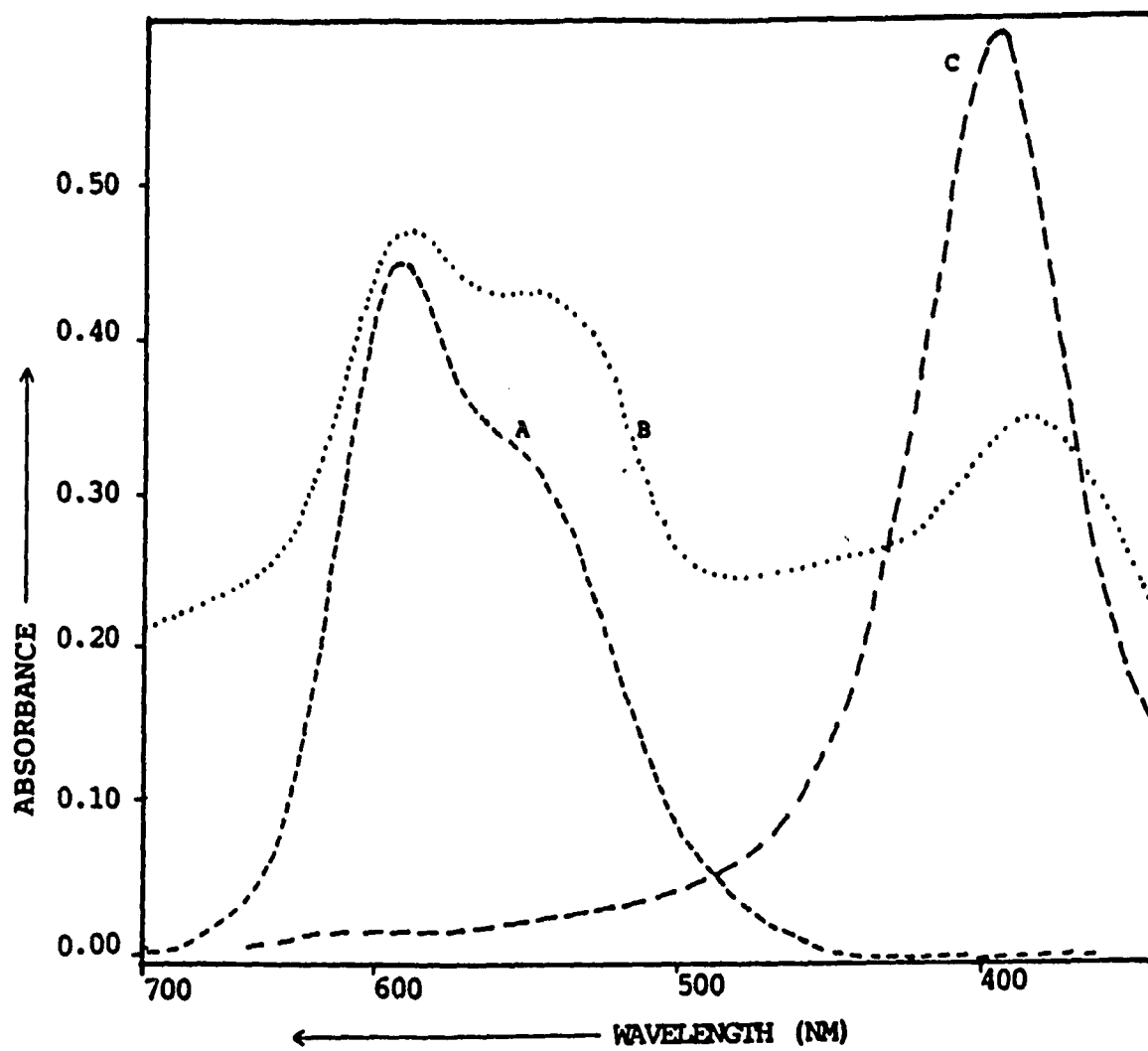


Figure 10. Absorption spectrum of A: EV, 10^{-6}M ,
B: EV + Agsol mixture (10^{-6}M in EV), C: Agsol, freshly prepared.

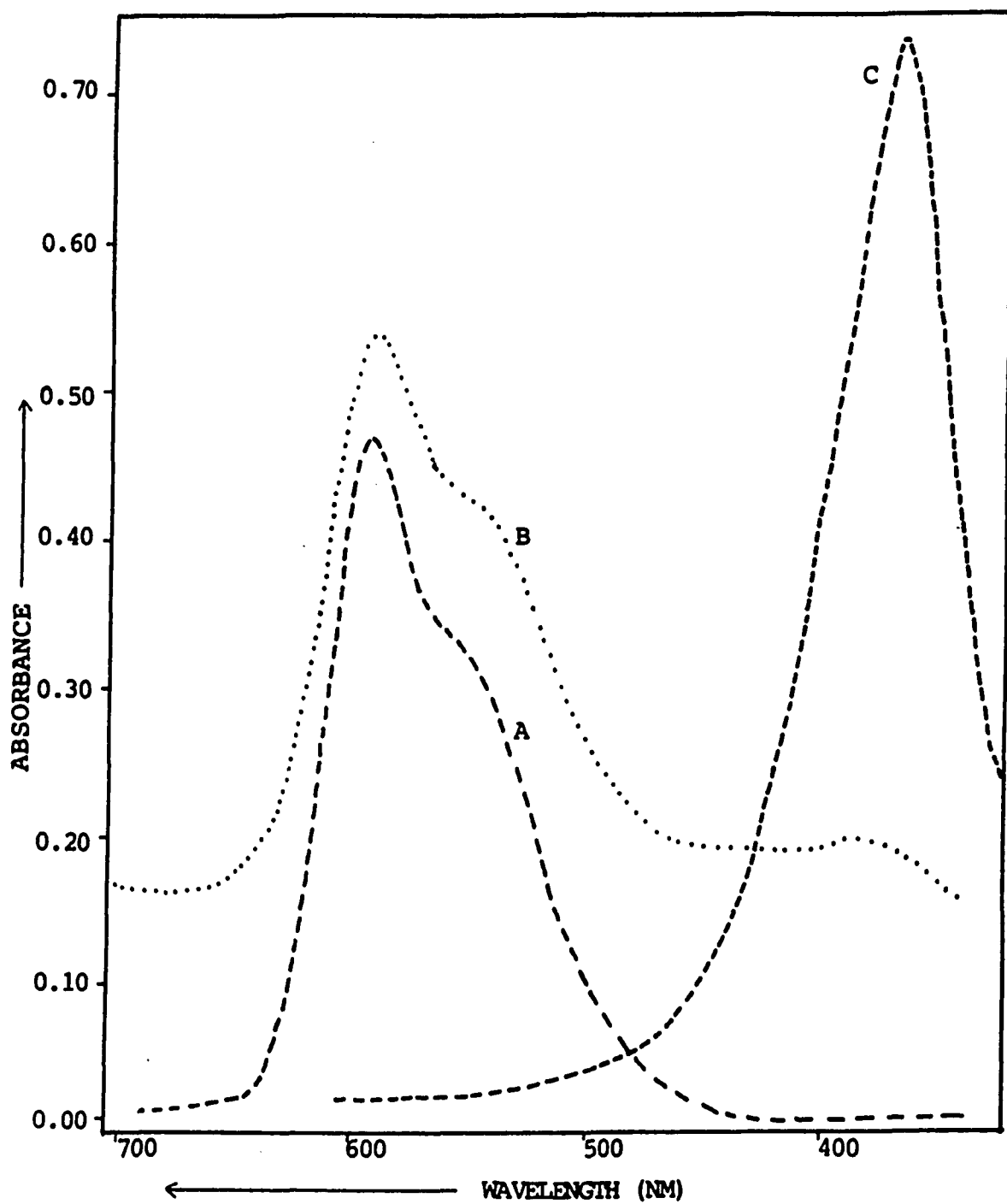


Figure 11. Absorption spectrum of A: CV, 10^{-6}M ,
B: CV + Agsol mixture (10^{-6}M in CV), C: Agsol, freshly prepared.

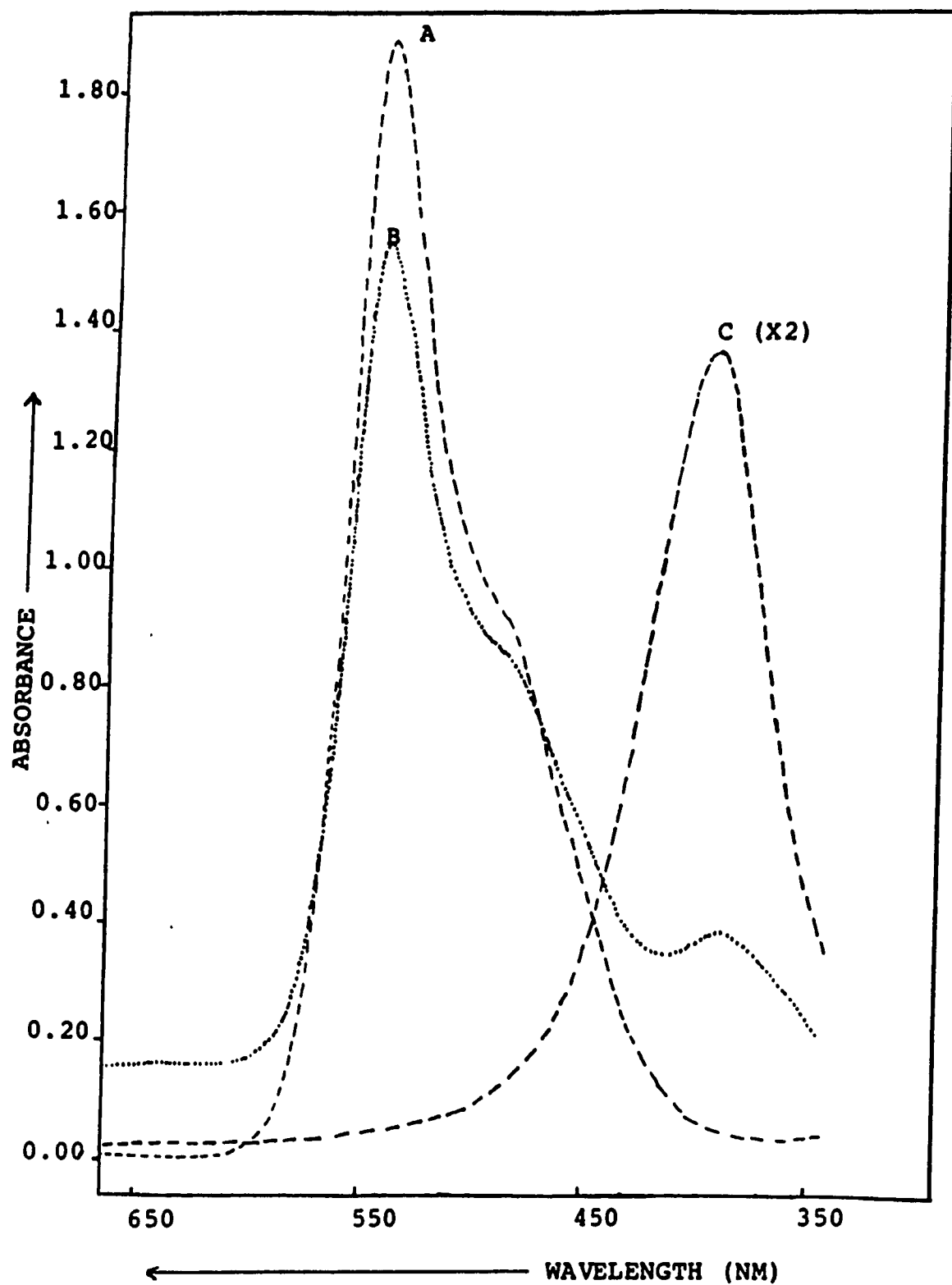


Figure 12. Absorption spectrum of A: PR, $5 \times 10^{-5}M$, B: PR + Agsol mixture ($5 \times 10^{-5}M$ in PR), C: Agsol. Absorbance scale refers to spectrum A and B only.

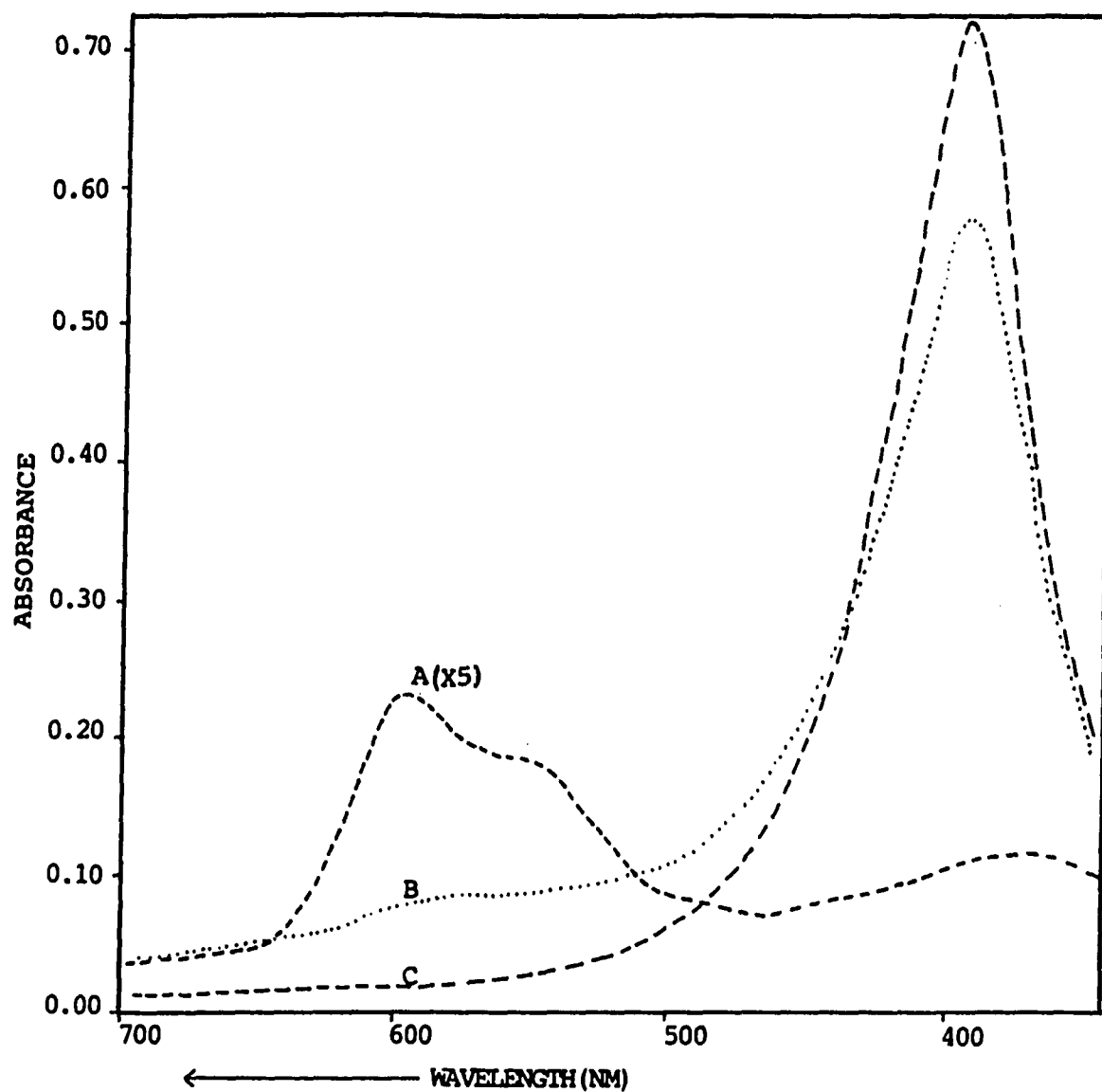


Figure 13. Absorption spectrum of A: EV, 10^{-6}M , B: EV + Agsol mixture (10^{-6}M in EV), C: Agsol. Absorbance scale refers to spectrum B and C only.

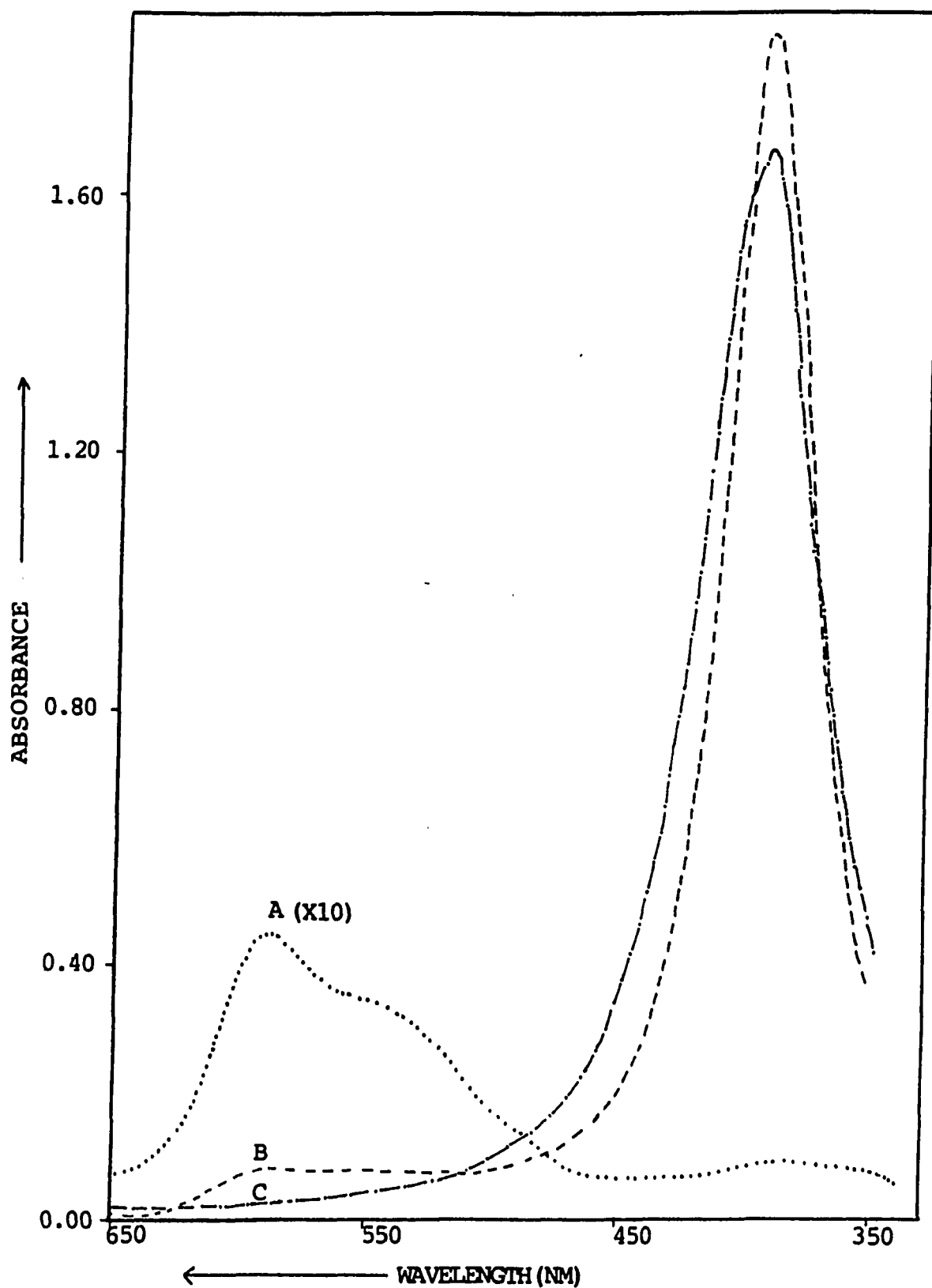


Figure 14. Absorption spectrum of A: CV, 10^{-6} M, B: CV + Agsol mixture (10^{-6} M in CV), C: Agsol. Absorbance scale refers to spectrum B and C only

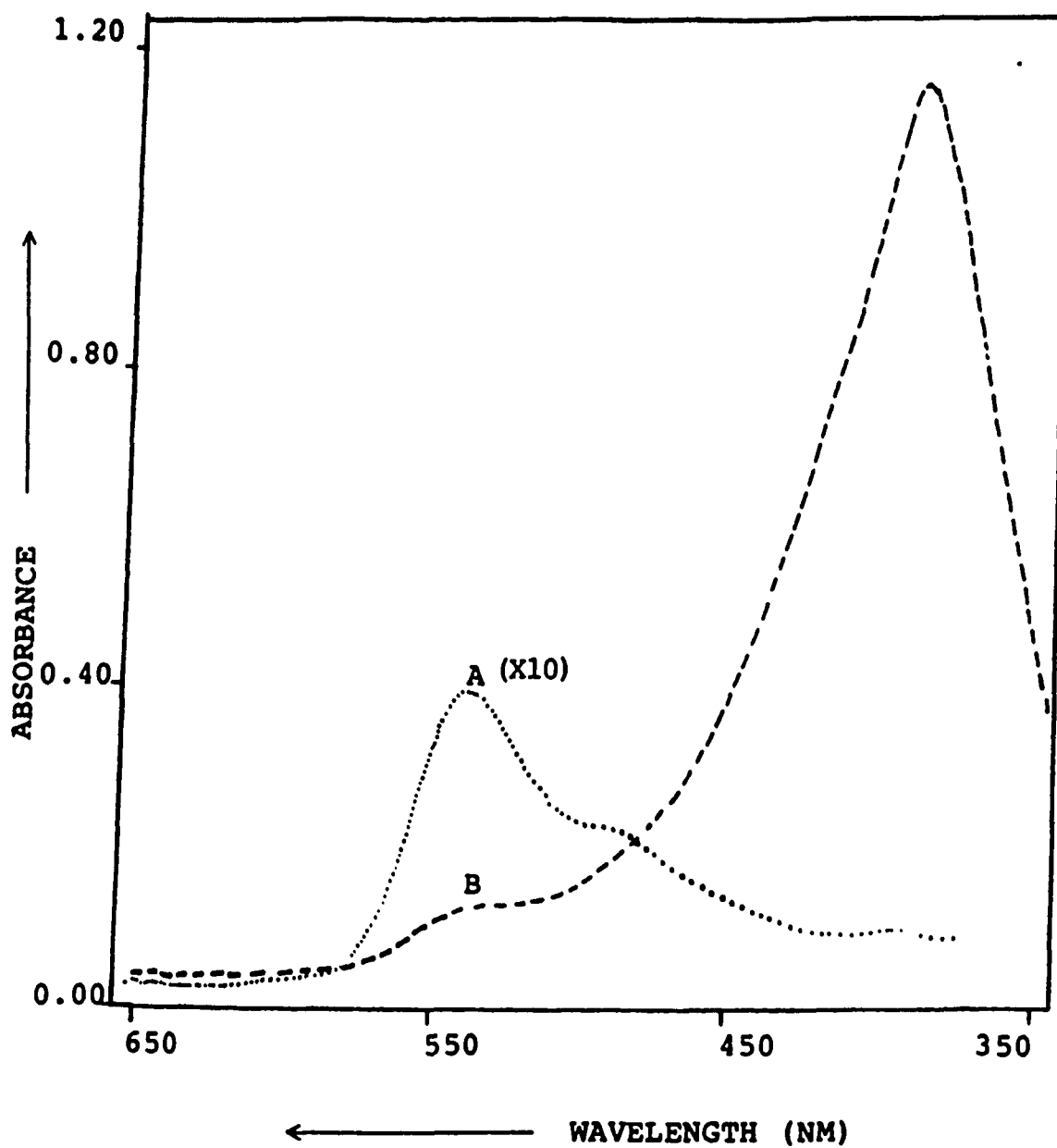


Figure 15. Absorption spectrum of A: PR, 10^{-6} M, B: PR + Agsol mixture (10^{-6} M in PR). Absorbance scale refers to spectrum B only.

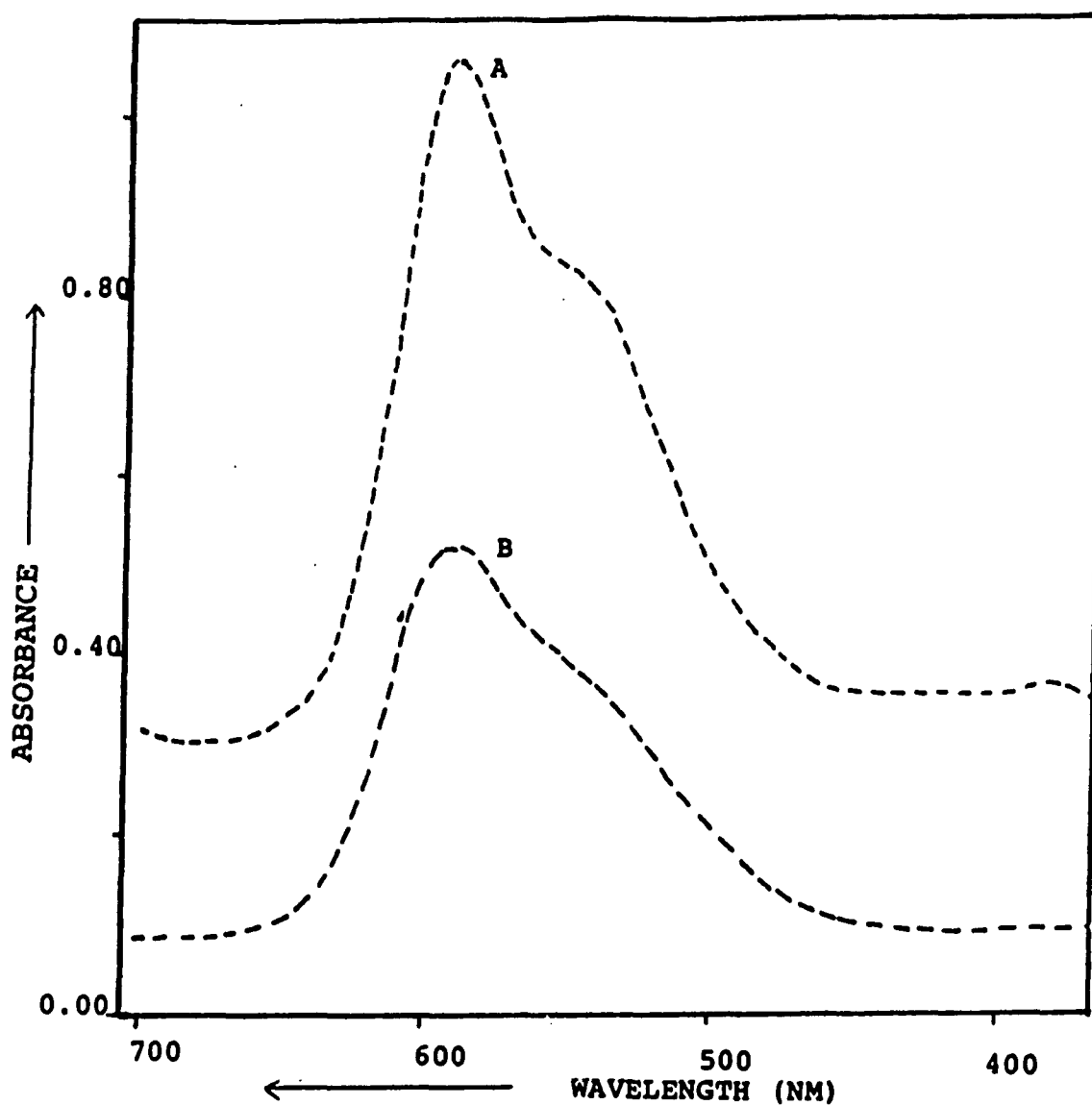


Figure 16. Absorption spectrum of CV + Agsol mixture (10^{-5} M in CV) A: freshly prepared, B: after 30 hours.

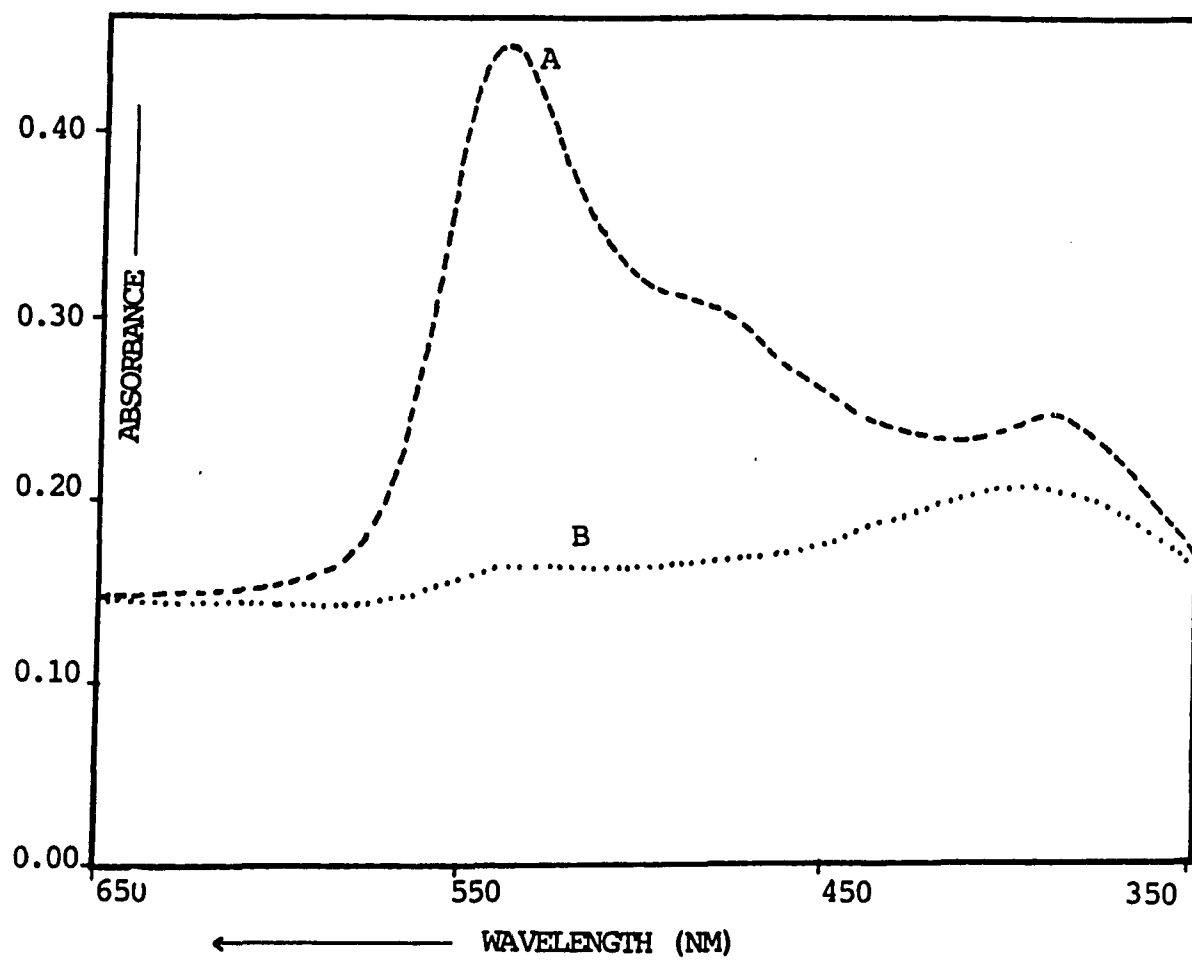


Figure 17. Absorption spectrum of PR + Agsol mixture (10^{-5} M in PR) A: freshly prepared, B: after 85 minutes.

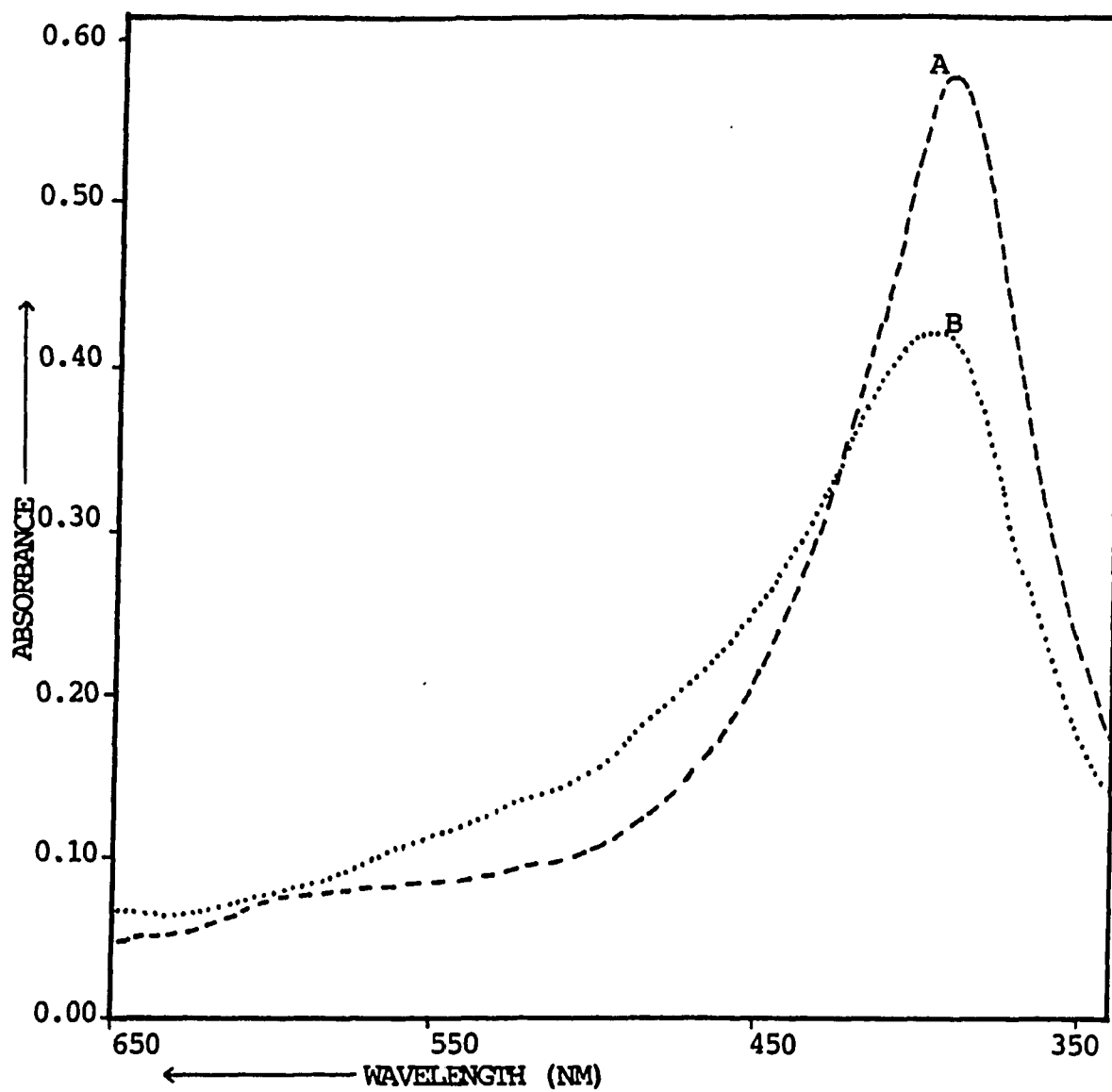


Figure 18. Absorption spectrum of EV + Agsol mixture (10^{-6} M in EV); A: freshly prepared, B: after 24 hours.

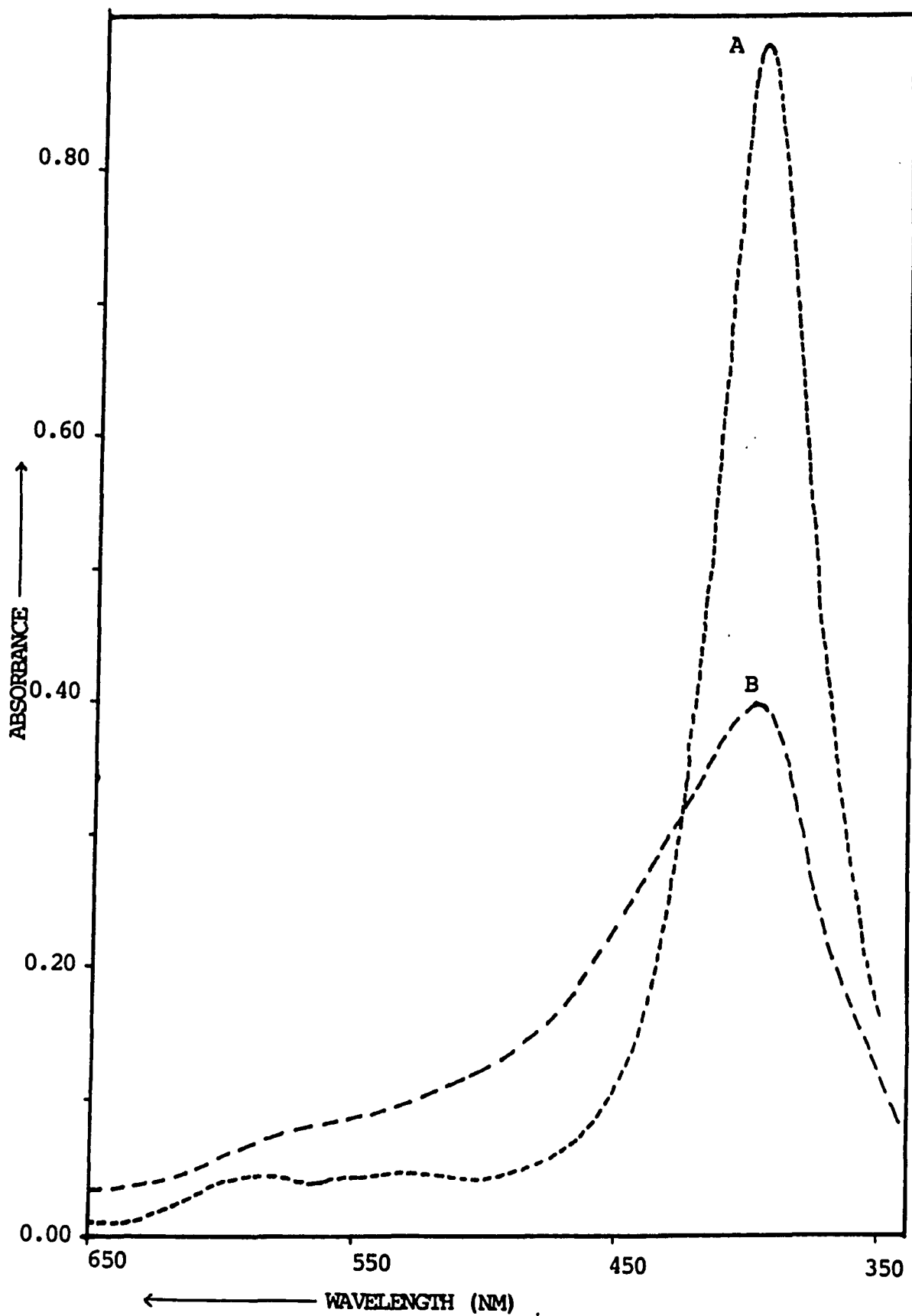


Figure 19. Absorption spectrum of CV + Agsol mixture (10^{-6} M in CV); A: freshly prepared, B: after 24 hours.

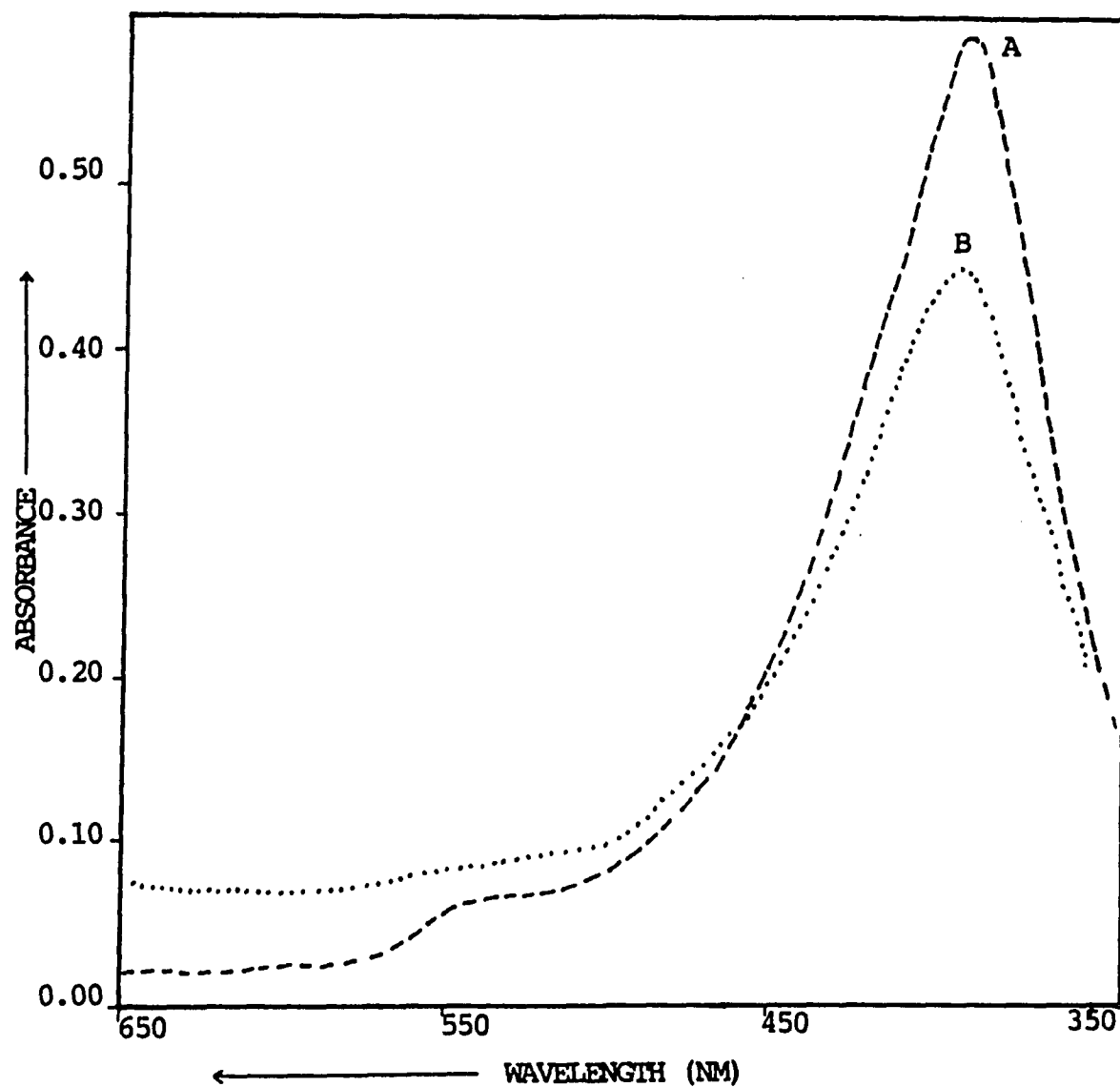


Figure 20. Absorption spectrum of PR + Agsol mixture (10^{-6} M in PR); A: freshly prepared, B: after 24 hours.

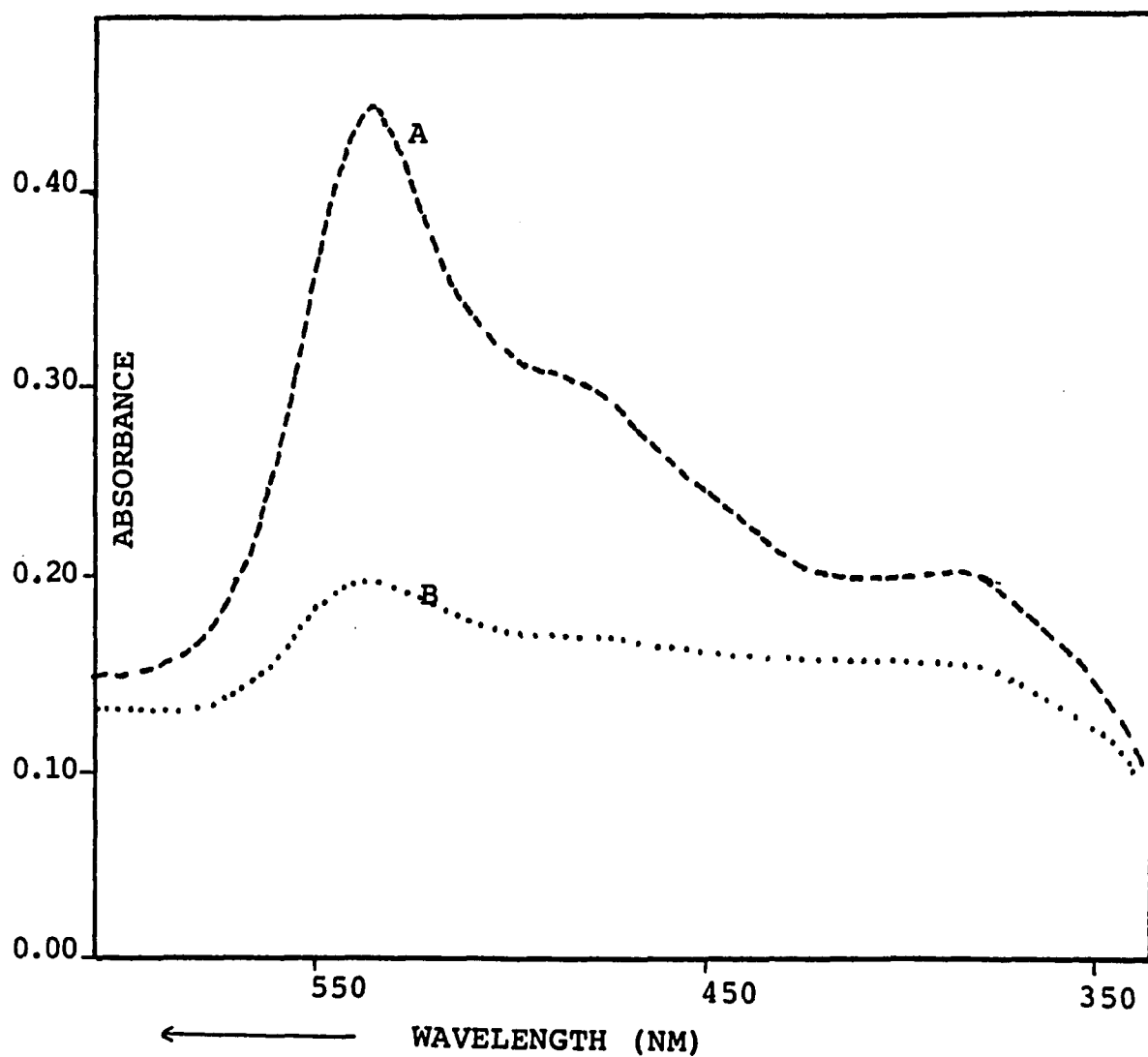


Figure 21. Absorption spectrum of PR + Agsol mixture (10^{-5} M in PR; Agsol, 24 hours old); A: 2 minutes after preparation, B: 85 minutes after preparation.

CHAPTER 5: RESULTS AND DISCUSSION OF THE SOLUTION AND SURFACE VIBRATIONAL SPECTRA OF THE DYES

5.1 STRUCTURE OF THE TPM CATION:

Before attempting an analysis of the results we will consider briefly the structures of the triphenylmethyl dyes studied in this work and outline a brief review of the previous vibrational assignments.

The molecular structures of CV, EV and PR are shown in Fig. 22. The triphenylmethyl (TPM) carbonium ion would have the same structure, but without any substituent groups present on the phenyl rings (Fig. 23). From a consideration of the structure shown in Fig. 22, it can be deduced that if the three rings and all six ortho hydrogens were to lie in the same plane, then the molecular symmetry would be D_{3h} . But it is clear that with the molecule having a horizontal plane, severe steric hindrance between the rings would occur. In fact Lewis *et al.* have pointed out that if the CV molecule were to be planar, then the two adjacent hydrogens (positions 2 and 6" for example) would be only 0.5 Å apart and the amount of repulsion between two such hydrogens would be quite considerable (93). This strain would be best relieved if the molecule were to assume a non-planar structure in which two adjacent ortho hydrogens have moved far enough from each other so that the force of repulsion is minimized. If atoms 2, 2' and 2" were to lie above the plane and atoms 6, 6' and 6" below the plane, it

is possible to relieve the strain in the molecule and a structure analogous to a windmill or a propeller of three blades would then be obtained. This form of the TPM ion, usually referred to as a symmetrical helical structure, would have D_3 symmetry. If one of the rings is further rotated through 180° , one would obtain a form like a propeller of three blades in which one of the blades is turned in the opposite sense from the other two. This form is referred to as the distorted helical structure and it should have no symmetry. Lewis *et al.* have predicted that this unsymmetrical helical structure should be higher in energy and exist as a rotational isomer (93). The existence of this isomer has been proposed on the basis of the occurrence of two bands in the visible absorption spectrum (93,94). However, to date no vibrational studies have proven the existence of two rotamers. Proof that only one species exists in solution has been deduced from the close resemblance between the IR spectrum of the solid and that of the solution for CV (95).

An X-ray diffraction study of the perchlorate salt of the TPM ion has established that the ion has D_3 symmetry with the central C^+-C bonds being coplanar (96). The lengths of each C^+-C bonds have been reported to be 1.454 Å, which is significantly less than 1.54 Å, the length of a C-C single bond. The three aromatic rings have been found to be twisted 32° out of the plane of the C^+-C bonds. This means

that the molecule is not flat and it will most likely assume a propeller shape. The C-C bond lengths within each ring differ slightly from those of benzene. These are 1.408 Å, 1.364 Å, and 1.372 Å for the C₁-C₂, C₂-C₃ and C₃-C₄ bond respectively (Fig. 23). In addition, the interbond angles of the ring are unequal. These are 115.3°, 123.5°, 116.1° and 125.3° for the C₂-C₁-C₆, C₁-C₂-C₃, C₂-C₃-C₄ and C₃-C₄-C₅ angles respectively. It would seem reasonable that related compounds such as the p-N,N' dialkylamino derivatives would adopt a similar geometry. An assessment of the vibrational data of CV by ref. (95) has led to the conclusion that this molecule does assume D₃ symmetry in solution.

5.2 VIBRATIONAL ASSIGNMENT

Previous SERS (8,59,87-89) RRS (86,95,97-100) and IR (101, 102) studies of CV and related compounds have been reported. Most workers have dealt with the assignment of the N,N' dialkylamino derivatives of the TPM ion by considering each aromatic ring as a paradisubstituted benzene with C_{2v} symmetry. This simplification has been justified by the fact that the frequencies of the v₈, v₉, v₁₆ and v₁₉ modes which are degenerate in benzene show removal of degeneracy in the RRS spectrum, just as is expected for paradisubstituted benzenes having C₂ symmetry. Additional evidence was found in the fact that the v₁₄ C-C stretching mode of benzene which is inactive in Raman and becomes

active under C_2 symmetry has been observed in the RRS spectrum of CV (86).

In addition to the ring vibrations, we expect to observe additional vibrations arising from the three central $C-C^+$ bonds. These would include the C^+ -phenyl stretching, which in the case of EV, CV and PR amounts to the molecular breathing vibrational modes. As shown in Fig.24, this mode can be symmetric (A) or doubly degenerate and anti symmetric (E). An in plane (ip) and an out of plane (oop) $C-C^+-C$ bending mode as well as the ring torsions, Ar_2-C^+-Ar , (Ar = aromatic ring) are the other vibrations that should arise from the central bonds. These vibrations are shown in Fig. 24 which has been adapted from ref. (101). Combinations of the ring vibrations can also occur. Weston et al. (101) have pointed out that under D_3 symmetry each normal vibration of a phenyl ring can combine either in phase or out of phase with the corresponding vibration of the other two rings to give rise to a symmetric vibration of a_1 or a_2 type and a doubly degenerate vibration belonging to the e type. Under threefold symmetry (C_{3v} , C_3 , D_{3h} , D_3), one would expect at the most, three components for each degenerate benzene vibration.

There seems to be a general consensus concerning the vibrational assignment of CV and related compounds. Apart from the N-phenyl (Ph) and C^+-Ph stretching modes all bands above 450 cm^{-1} have been assigned to vibrations of the

phenyl rings. Vibrations arising from the central carbon bonds, $C-C^+-C$, have been ascribed to the frequencies below 450 cm^{-1} . Various workers have assigned the vibrational spectrum of CV (86,87,95,97,98). One general approach involved is to compare the spectrum with those of model compounds such as dimethylaniline and the TPM cation. Frequency assignment of the TPM cation have been carried out by Weston et al. by analogy with assignments for monosubstituted benzenes (101). In this study, evidence for certain assignments were obtained by using ^{13}C and deuterium substitutions. Alexandrov et al. in their studies of the vibrational spectra of various TPM dyes used the spectra of dimethylaniline, aniline and the TPM cation as models. However, many of their assignments and peak positions do not concur with other studies (97). Gicquel et al., noting how similar the RRS spectrum of CV was to the IR spectrum of the TPM cation studied by Weston et al. (101) assigned the spectrum of CV by comparing it to the assignment of the IR spectrum of the TPM cation (86). Angeloni et al. noted that the RRS spectrum of CV was closely related to the RRS spectrum of the TPM cation reported by Maeda et al. (99) and proceeded to assign the vibrational spectrum of CV by attributing a D_3 symmetry to the ion and a C_2 symmetry for the dimethylanilinium groups and by comparing frequency assignments of disubstituted benzenes (95). Bernstein and Sunder (98) reported the deuterated spectrum

of CV and assigned the spectrum by comparing it to that of CV and dimethylaniline. There are some existing controversies among the assignments of the vibrational spectra of CV. These include the assignment of the phenyl-N stretching vibration. This vibration has been assigned by most workers to the doublet feature appearing at $\sim 1370 - 1390 \text{ cm}^{-1}$. In ref. (86), two shoulders at 1400 cm^{-1} and 1344 cm^{-1} have been attributed to the N-phenyl stretching modes. These features have not been reported by other workers. Angeloni et al. (95) argued that the RRS spectrum of CV closely resembled that of the TPM cation with the exception of the strong doublet at 1380 and 1395 cm^{-1} and concluded that the doublet arose from a stretching vibration of the N-phenyl bond. Bernstein and Sunder (98) did not concur with Angeloni et al. on the assignment of the second feature at 1395 cm^{-1} to a second vibration arising from the phenyl-N stretching. Based on the observed deuterium shift, they assigned the 1395 cm^{-1} peak to a vibration arising from the H atoms attached on the benzene rings (98).

A peak appearing at 917 cm^{-1} has been assigned to a C-H out of plane bending by Gicquel et al. (86). Alexandrov et al. (97) have assigned it to the ring breathing vibrational mode of the phenyl ring while in ref. (95), it has been attributed to the ring deformational mode, ν_{12} . Bernstein and Sunder claimed that this vibration did not involve the C-H atoms of the benzene rings since a significant deuteri-

um shift was not observed for this peak (98).

There appears to be some inconsistencies in the assignment of the C^+ -phenyl stretching mode. Weston et al. have reported the IR spectrum of the TPM cation and have assigned a strong band at 1359 cm^{-1} to the degenerate C^+ -phenyl stretching vibration (101). This assignment was verified by a $^{13}C^+$ substitution. By analogy to this assignment Gicquel et al. have attributed the Raman peaks at 1377 cm^{-1} and 1399 cm^{-1} to the $C-C^+$ symmetric and antisymmetric stretchings respectively in the CV molecule (86). Other workers have assigned a lower frequency band at 200 cm^{-1} to a molecular breathing vibrational mode of the entire CV molecule (87,95,98). A normal coordinate analysis (NCA) of a model compound, $(CH_3)_3C^+$, yielded a C^+-C stretching at 1298 cm^{-1} . This mode was little affected by deuterium substitution (103). It is tempting to form an analogy here and consider the TPM ion central bonds as $(Ph)_2-C^+-Ph$ and treat the stretching vibrations of the central bonds separately. However, this would entail treating the phenyl rings as rigid masses and these stretching vibrations may occur in the low frequency regions where vibrations of the substituents also occur so that a considerable degree of vibrational mixing can take place. Previous work on biphenyl has indicated that the Ph-Ph stretching modes are significantly affected upon deuteration of the rings; the ring-ring stretching mode had

shifted from 1274 cm^{-1} to 1180 cm^{-1} for biphenyl- d_{10} , indicating that the stretching motions of the central bonds are not independent of the ring motions (101).

From a comparison of previous vibrational assignments of CV, the spectra of dimethylaniline (97) and aniline (104), and a partial NCA of the $\text{C}^+(\text{C}_6\text{H}_4)\text{N}$ moiety (see Appendix II), we have assigned the Raman spectrum of CV. This is shown in Table II. The ring modes to which the assignments refer are shown in Figs. 25-27. These have been adapted from refs. (105 - 106).

Our normal coordinate analysis of the $(\text{X})_2\text{C}^+(\text{C}_6\text{H}_4)\text{N}$ moiety (see Appendix II) indicated that the stretching motions of the C^+-Ar bonds are combined with the aromatic ring stretches in the $1400 - 1600\text{ cm}^{-1}$ region. When the substituents, X, are added to the C^+ center and their masses adjusted to match those of the $(\text{C}_6\text{H}_4)\text{N}$ groups, a vibration at 263.5 cm^{-1} is obtained. This vibration has an 80% contribution from the $\text{C}-\text{C}^+$ stretching mode. An analysis of this vibration indicates that it involves a combined motion of all the atoms in this molecule. Thus we will concur with refs. (87,95,98) on their assignment of the Raman band at $\sim 200\text{ cm}^{-1}$ to the breathing mode of the entire molecule.

The N-phenyl stretching frequency has been reported for aniline and dimethylaniline (DMA) at 1273 cm^{-1} (104) and 1350 cm^{-1} (97) respectively. Lippitsch has also reported a

strong peak at 1346 cm^{-1} in the SERS spectrum of DMA as well as two peaks at 1378 cm^{-1} and 1400 cm^{-1} for methyl violet (107). We obtain two calculated frequencies at 1347 cm^{-1} and 1365.8 cm^{-1} in which there is some contribution (albeit small) from the N-Ph stretching mode; though there also appears to be some mixing of the aromatic ring stretching motions and the in plane C-H deformations. We will then assign the two observed frequencies at 1365 cm^{-1} and 1384 cm^{-1} to vibrations originating from the N-Ph stretching motions. We note also that there is considerable contribution from the ring C-H deformational mode to the 1365.8 cm^{-1} peak; this result concurs with Bernstein and Sunder's observation that there is a large deuterium shift for this peak in the Raman spectrum of CV-d₁₂ (98).

Like the N-Ph stretching vibration, the C⁺-C stretching is not well characterized in our NCA calculations. In fact we find that it is combined with a number of other modes, notably the aromatic C-C stretching. We do obtain a calculated mode at 1208.8 cm^{-1} in which there is a large contribution from the C-C⁺ stretching force constant. However the closest observed frequency is 1298 cm^{-1} and this yields a large percentage error of ~7%. This band is usually assigned to the v14 ring vibrational mode. Because of the ambiguity in assigning this band, we will retain the previous assignment of the 1299 cm^{-1} peak to the v14 mode.

We have obtained calculated frequencies at 1174.1 cm^{-1} ,

1142 cm^{-1} , 901.5 cm^{-1} , 891.6 cm^{-1} and 917.0 cm^{-1} for vibrations involving ip CH deformations and we have assigned these vibrations accordingly. It should be noted that there is a considerable contribution to the calculated mode at 1174.1 cm^{-1} from the C-C⁺ stretching vibration.

The oop C-H deformations have been attributed to the frequency region between 630 cm^{-1} and 833 cm^{-1} because the NCA calculations indicate that the calculated modes in this region show a large contribution from the C-H torsions. These modes we have interpreted as deformations of the C-H bond out of the adjacent C-C-C plane of the ring.

The ring skeletal vibrations of radial orientation are not easily interpreted from our calculations. We approximated the calculated mode at 891.6 cm^{-1} as a skeletal vibration. This one probably corresponds to the observed frequency at 914 cm^{-1} . Two other calculated frequencies at 546.3 cm^{-1} and 534.2 cm^{-1} have been interpreted as in plane ring skeletal vibrations.

A calculated frequency at 470 cm^{-1} has been obtained and it has combined contributions from the oop ring motions and oop C-C⁺ deformations. The doublet at 417 cm^{-1} and 437 cm^{-1} has been previously assigned to the v16a and v16b oop ring skeletal vibrational modes (95). We are in agreement with Gicquel *et al.* who indicated that these modes might be coupled to the deformations arising from the C⁺-C bonds (86). Varsányi has also pointed out that the oop

skeletal vibrations v16a and v16b could involve an oop C-X vibration for a paradisubstituted benzene (106). So to this doublet we assign a combination of an oop ring skeletal vibration and a C-Ph bending mode.

Most of the aromatic ring stretching vibrational modes have been assigned to the frequency region ranging from 1400-1600 cm^{-1} . This overlaps with previous assignments (86,87,95,97,98).

We did not obtain a reasonable frequency for the ip C-C⁺ deformation. A calculated frequency was obtained at 217.9 cm^{-1} which could not be correlated to an observed frequency. We will retain the previous assignment of the ip C-C⁺ deformation to the 327 cm^{-1} band.

Generally, nearly all of the assignments of these bands overlap closely with those of Angeloni et al (95). However, we do not observe a peak at 990 cm^{-1} which has been attributed to the ring breathing mode.

5.3 COMPARISON OF THE RRS SPECTRUM AND SURFACE RAMAN (SR) SPECTRUM OF CV

The resonance Raman and the surface Raman spectra of CV were studied at 514.5 nm. Figs. 28-31 show the RRS spectrum and the SRS spectrum of CV on Ag sol at various concentrations, and Table II lists the peak positions in both spectra. Good coincidence is observed among the wavenumbers of the peaks in the RRS spectra and the corresponding peaks

in the SRS spectrum. This observation concurs with previous studies of CV on various SERS active substrates (87-89). Certain differences can be cited in terms of:

- (i) Fluorescence
- (ii) Relative Intensities of peaks
- (iii) Appearance of new peak
- (iv) Spectral shifts

The differences observed in each of these categories will be outlined first.

5.3.1 FLUORESCENCE:

While an intense fluorescence background is not observed in the RRS spectrum of CV scanned at 514.5 nm, there is some fluorescence observed in the spectral region ranging from 1000 to 1600 cm^{-1} and between 125 and 250 cm^{-1} . This luminescence is found to be quenched to a large extent in the SRS spectrum. (compare Fig. 28 & 29).

We note that as the dye concentration increases from $1 \times 10^{-5}\text{M}$ to $5 \times 10^{-5}\text{M}$ the fluorescence in the region from 3000 to 3700 cm^{-1} is not quenched in the SRS spectrum (compare Figs. 30 & 31).

5.3.2 RELATIVE INTENSITIES:

From a consideration of the surface and solution spectra (Figs. 28-31) it can be deduced that there is an apparent increase in the intensities of the dye peaks relative to the water peak in the SRS spectrum. Perhaps the most striking example is the 205 cm^{-1} peak which is observed in

the RRS spectrum as a very weak peak superimposed on a strong background. While in the SRS spectrum it is one of the most intense peaks. The very weak 327, 518, 553, 937, 977, 1299 and 1477 cm^{-1} peaks in the RRS spectrum are barely visible above the noise; while in the SRS spectrum, a large improvement in the signal to noise (S/N) ratio is seen and thus most of the peaks are well defined above the noise background.

The intensity of the 420 cm^{-1} peak increases beyond that of the 442 cm^{-1} peak in the SRS spectrum, while in the RRS spectrum, both peaks are of comparable intensity.

The splitting of the 1174 cm^{-1} peak observed in the RRS spectrum is not observed in the SRS spectrum. A similar observation has been reported with reference to a surface spectra of CV on a silver electrode (87).

5.3.3 NEW PEAKS

A new peak at 660 cm^{-1} is observed in the SRS spectrum. No counterpart for this peak is found in the RRS spectrum. Watanabe & Pettinger (87) have also reported the presence of a peak at 663 cm^{-1} in the SERS spectrum of CV on a silver electrode and have assigned it to the ν_{11} mode of the benzene ring which is essentially a C-H out-of-plane vibration (106).

5.3.4 SPECTRAL SHIFTS:

While there is good overlap among peak positions in the RRS spectrum and those in the SRS spectrum, there are some

observed shifts. Most peaks are shifted to higher wave numbers in the SRS spectrum. These shifts range from 1 to 9 cm^{-1} and the peaks showing significant upshifts are shown in Table III. Fewer peaks are shifted to lower wavenumbers and these are tabulated in Table IV. In general, peaks showing upshifts $\geq 5\text{ cm}^{-1}$ are concentrated between 190 and 600 cm^{-1} while those exhibiting negative shifts are localized between 800 and 1550 cm^{-1} .

5.4 INTERPRETATION OF VIBRATIONAL CHANGES OBSERVED

IN THE SRS SPECTRUM OF CV

The observed vibrations of CV can be categorized as follows:

- (a). The skeletal vibrations of the central C^+ -phenyl bond.
- (b). The skeletal vibrations of the phenyl rings. There are two types: the ip skeletal vibrations of radial orientation, which include the v6a, v6b & v12 modes and the oop skeletal vibrations to which modes v16a and v16b belong.
- (c). The oop C-H deformations; these include the v17a, v17b and v10a modes.
- (d). The ip C-H deformations which are involved in the v9a and v18a modes.
- (e). The C-C stretching motions of the rings. The v14, v19a, v19b, v8a & v8b modes are included in this vibrational type.

(f). The N-phenyl stretching.

5.4.1 THE C⁺ SKELETAL VIBRATIONS: (125-450 cm⁻¹)

The vibrations attributed to this frequency region include the oop and the ip deformational mode of the Ph-C⁺-Ph bonds with a possible combination of the oop ring deformational mode. A ring breathing mode of the entire molecule has also been assigned in this region. The changes observed in this region include (see Figs. 33 & 34):

(a). An exceptionally large increase in the S/N ratio for the 197 cm⁻¹ peak along with more moderate increases for the 327 cm⁻¹ peak and the doublet at 417 cm⁻¹ and 437 cm⁻¹.

(b). An upshift of 8 cm⁻¹ and 6 cm⁻¹ for the 197 cm⁻¹ and 327 cm⁻¹ peaks respectively.

(c). An increase in the intensity of the 417 cm⁻¹ peak relative to the 437 cm⁻¹ peak.

The fact that changes occur in the vibrational peaks attributed to the C-C⁺-C center imply that the carbonium ion is an interaction site. These vibrations are expected to be sensitive to molecular distortions; thus it is possible that some alteration of the geometry of the molecule at this center takes place when the molecule is adsorbed on the Ag surface. The degree of interaction can be measured by the extent of the changes that occur. The upshift of 8 cm⁻¹ for the 197 cm⁻¹ peak is the largest shift observed for any other peak in the surface spectrum. This peak also

exhibits the largest increase in S/N ratio. The molecular stretching mode has been assigned to this peak. The upshift in frequency would imply a strengthening of the C^+-Ph bond. An increase in electron density at the carbonium ion can be gained either through (i) conjugation or (ii) the formation of a fourth bond to the Ag atoms on the surface. We will reject the first explanation since a corresponding upshift in the frequency of the Ph-N stretching mode is expected if the molecule is conjugated on the surface and such a shift is not observed. The presence of the Ag atom at the central C^+ ion would seem a more reasonable interpretation. The upshift in frequency can be explained by the formation of a complex between CV and Ag where CV can act as an electron acceptor and Ag as an electron donor. Such complexes have been previously reported for CV (86). An interaction of this kind at this site is bound to affect the planarity of the three central Ph- C^+ bonds which would in turn affect the vibrations involving these bonds. The increase in the intensity of the 417 cm^{-1} is interpreted as a manifestation of the loss of planarity at the central bonds. Suppose the central part of the molecule is isolated and treated as: $(C)_3C^+$. To this part a symmetry of D_{3h} can be attributed. Loss of planarity would lead to a change in symmetry to C_{3v} . An examination of the symmetry of the vibrations under C_3 indicates that the oop C^+-Ph bending mode would become completely symmetrical, which would

probably explain the reinforcement of the 417 cm^{-1} peak relative to the 437 cm^{-1} peak and possibly the increase in the observed intensity of the 205 cm^{-1} which in the SRS spectrum may include some oop C-C⁺ deformational character. The asymmetry and the width of the peak in the SRS spectrum do attest to the fact that more than one vibration could be coupled in this region.

We do not believe that the peak at 205 cm^{-1} in the SRS spectrum to be due to a Ag-N or Ag-Cl stretching mode for the following reasons. Firstly, a corresponding peak at 197 cm^{-1} is observed in the solution spectrum of CV. While the 197 cm^{-1} peak is very weak in the RRS spectrum of CV at 10^{-5}M , it is more intense at higher concentrations of CV. (see Fig.34). Secondly, previous workers have assigned the Ag-N stretching mode to a frequency region ranging from 220 to 240 cm^{-1} (25, 108). In addition chloride ions are present in such small concentrations in the solutions that it is highly unlikely that a Ag-Cl stretching mode of such strength will be observed. However there exists the possibility that a vibration involving the Cl^{-} ions could be contributing to this low frequency peak.

An explanation promoting a chemisorptive bond between Ag and the nitrogen atoms of CV seems unlikely to account for the vibrational changes (vide supra). While an interaction between the C⁺ center and the Ag atom is favored, we do not propose that a new chemical bond is formed. The formation

of such a bond would alter the whole symmetry of the molecule. In fact one may expect the spectrum to closely resemble that of the HCV molecule where the hydrogen is attached to the central C^+ ion. A comparison between the SRS spectrum reported here (Fig.32A) and previously published RRS or SERS spectra of HCV (87,95) does not indicate any similarities.

5.4.2 RING SKELETAL VIBRATIONAL MODES

We have already pointed out that the v_{16a} and v_{16b} mode could be coupled with the oop $C-C^+-C$ deformations. The other skeletal vibrations v_{6a} , v_{6b} and v_{12} appear at 518, (599,558), and 937,914 cm^{-1} respectively. It is worthwhile to note that all of these have some ring deformational character and their frequencies are upshifted by 4-6 cm^{-1} in the SRS spectrum. The increases in the frequencies imply an increase in the restoring force for such a vibration. We suggest that such an effect would occur if the molecule assumes a configuration that involves parallel orientation of the phenyl rings to the Ag surface.

5.4.3 OOP C-H VIBRATIONS

These vibrations are involved in the v_{17b} , v_{17a} and v_{10a} modes. The v_{17b} mode has been assigned to the 722 cm^{-1} peak, the v_{17a} mode to 739 and 753 cm^{-1} peaks and the v_{10a} mode to the 807 cm^{-1} peak. We note a splitting of the 756 cm^{-1} peak in the surface spectrum, giving rise to a second peak at 765 cm^{-1} . A downshift of 5 cm^{-1} is observed for

the v10a mode. A new peak at 660 cm^{-1} in the SRS spectrum has been attributed to a C-H oop bending vibration. This is the only region where the appearance of new peaks and explicit splitting of peaks take place (see Fig.35). Whether these changes are significant is debatable since it is a very weak region in both the RRS and SRS spectrum. The 660 cm^{-1} band is also very weak in the surface spectrum. We note however that it was previously reported by Watanabe & Pettinger (87). An analogous peak is also observed in the SRS spectrum of EV (see later).

5.4.4 C-H IN PLANE DEFORMATION

The v18a and v9a modes are best described by this vibrational type. The v18a mode has been assigned to the 977 cm^{-1} peak and the v9a mode to a doublet at $1174, 1188\text{ cm}^{-1}$. The frequency position of the v8a mode is not changed. The split peaks observed for the v9a mode in the RRS spectrum appear as a single peak in the SRS spectrum (see Fig. 32). It would appear that this vibration becomes degenerate on the surface of the sol or the 1174 cm^{-1} has been downshifted. A weak shoulder is observed at 1130 cm^{-1} and it may be accounted for by a coupling of another vibration with the v9a mode.

5.4.5 RING C-C STRETCHING

The modes attributed to this character are the v14, v19a, v19b, v8b, & v8a. The v19a and v8a modes undergo no frequency shifts in the SRS spectrum. However, the v14, v19b

and v8b experience downshifts ranging from 3-5 cm^{-1} , which indicate a slight decrease in the C-C aromatic bond strength. It would be reasonable to expect a lowering of the C-C bond strengths if there exists an interaction involving donation of the π electrons in the phenyl rings to the Ag atoms on the surface.

5.4.6 N-PHENYL STRETCHING MODE:

A slight downshift of 3 cm^{-1} is observed for the N-phenyl stretching in the SRS spectrum. This indicates a very slight weakening of the phenyl-N bond and a small interaction between the nitrogen atoms and the Ag surface. The fact that a large red shift for this vibration is not observed would lead us to conclude that the CV cannot be attached "end on" to the Ag surface, that is, assuming what has been referred to as the pendant position. The latter is a commonly proposed configuration for substituted benzenes on SERS active surfaces.

5.5 MODE OF INTERACTION, BINDING SITE & MOLECULAR CONFIGURATION

5.5.1 MODE OF INTERACTION:

The question now arises as to the nature of the mode of interaction between CV and the Ag surface. There is evidence that an interaction has taken place since:

(i). The absorption spectrum of CV-sol mixture is not the simple sum of the spectrum of the sol and dye alone.

(ii). There is an abrupt decrease in the Raman intensities of the dye peaks when the sol precipitates.

(iii). An enhancement for all the bands is observed.

(iv). Quenching of fluorescence takes place at the sol surface.

(v). There are changes in the relative intensities of some of the vibrational bands in the surface spectrum.

(vi). Frequency shifts for some of the peaks are observed in the surface Raman spectrum. These are:

(a). A downshift in the C-C stretching frequency at 1299 cm^{-1} and the C-H deformational mode at 807 cm^{-1} .

(b). An upshift in the frequencies of the ring skeletal vibrations and the deformational vibrations of the $\text{C-C}^+\text{-C}$ bond.

Most of the peak positions are only slightly shifted. In fact, for most bands, there is a close correlation in terms of the peak positions and shape between the solution and the surface spectrum of CV. This implies that the vibrational environment of CV on the Ag surface is not much changed and that the CV molecules are not tightly bound to the sol surface. The largest red shift observed in any of the bands is only 5 cm^{-1} for the oop C-H ring bending at 807 cm^{-1} and the ring stretching mode ν_{14} at 1299 cm^{-1} . In addition no new strong band assignable to the Ag-CV stretching vibration is observed in the SRS spectrum. While there is evidence of interaction at the central C^+ ion, we

have observed no new bands that can be unambiguously ascribed to a Ag-C^+ vibration. The small red shifts and the absence Ag-ligand vibrational peaks in the surface spectrum would lead us to conclude that the interaction does not involve the formation of a Ag-CV charge-transfer type complex yet it would seem to be strong enough to promote enhancement and fluorescence quenching.

5.5.2 BINDING SITES AND MOLECULAR CONFIGURATION

Firstly consider the nature of the sol itself. It is likely that it will be negatively charged due to adsorption of the negative ions in solution. These could be NO_3^- or BH_4^- . Addition of the dye will also introduce Cl^- ions since CV was used as the chloride salt. Thus the primary layer should be negatively charged. As expected, positive charges would be attracted first. One source of positive charge is the central carbonium ion and we do have evidence for an interaction at this site. The positive charge can be further delocalized by resonance. Conjugation of the lone pairs of electrons on the nitrogens will result in the positive charge residing on the nitrogens, presenting yet another possible interaction site. If an interaction takes place at the C=N^+ one would expect that a nitrogen having a bond order of $\sim 1.5-2$ would exist. This should lead to an increase in the observed frequency of the N-Ph stretching. Since this is not seen it appears that conjugation is not

promoted on the sol surface. Thus the upshift of the C-C⁺-C deformational frequency cannot be explained by conjugative effects, since we would also expect an accompanying increase in the frequency of the N-Ph stretching mode.

The π electrons in the phenyl rings are another source of interaction. It has been reported that Ag with its low lying d orbitals can accept electrons and that certain alkenes and aromatic molecules can bind to the SERS metal surfaces through their π orbital systems (31,33,34,40). There is evidence that there is an involvement of the ring electrons judging from the changes that have taken place in the ring vibrations.

There is no evidence for the involvement of the lone pair of electrons on the nitrogen atoms. The only change observed in the N-Ph stretch is a slight downshift of 3 cm⁻¹. This is within the experimental error of $\pm 2-3$ cm⁻¹ and is not considered significant.

Both the "end on" and flat configurations of molecules adsorbed on metal substrates are well documented in the literature (31,40). The possibility of a ring molecule being tilted and lying on its side has also been proposed (27,40). Three possible orientation for the CV molecule can be considered in this case. These are depicted in Fig.36 A-C. Fig. 36A represents the "end on" position where each molecule is attached through one or two nitrogen atoms on

the phenyl rings. It can be argued that such an attachment is quite possible even though no significant change in N-Ph stretching mode is observed. We do have a large increase in the observed intensity of the C^+-Ph stretching mode. This mode is perpendicular to the Ag surface and is a totally symmetric (Angeloni has reported it as a polarized band in the RRS spectrum, ref.(95)) vibration, making it ideally suited for enhancement (via the electromagnetic effect). However we are unable to explain the upshift in the C^+-Ph stretching frequency and the deformational modes and the changes (albeit slight) in the ring vibrations.

Fig. 36B represents the CV molecule oriented parallel to the surface of the Ag sol and lying flat; it assumes D_{3h} symmetry. A flat configuration would imply that the π electrons of the ring would be readily available for interaction and no molecular distortion of the central bonds would occur. While we do have evidence for an interaction between the π electrons of the phenyl rings, this interaction is not a strong one. There are also steric hindrances between the ortho hydrogens which twist the rings out of the molecular plane and would prevent the molecule from assuming a planar configuration.

The most probable orientation is that shown in Fig. 36C. Here the CV molecule is parallel to the Ag surface. However, it is not lying flat. The phenyl rings are twisted to assume the propeller shape as described before, and the

central carbon bonds are not at 120° . Under such circumstances the symmetry of the molecule would be C_{3v} . Since the rings are non planar, only a small degree of interaction is expected between the π electrons of the phenyl rings and the Ag. This is borne out by the data. This parallel configuration of the CV molecules would account for the following conclusions:

- (a). The most significant changes occur in the vibrations involving the central $C-C^+-C$ bonds.
- (b). There exists only a small degree of interaction between the π electrons of the ring and the Ag.
- (c). There is no interaction between the lone pair of electrons on the nitrogen atoms and the Ag surface.

Hopkinson and Wyatt have carried out an Extended Huckel Molecular Orbital (EHMO) calculation for the TPM ion and related amino compounds (90). They have reported that the introduction of a pair of electrons in the lowest empty orbital results in a large concentration of electron density on the central carbonium ion and on the ortho and para carbons of the phenyl rings. If a transference of electron density takes place from the Ag to the CV molecule, it seems most likely that a parallel configuration would allow optimum overlap of the molecular orbitals on CV and those of Ag in order to effect such a charge distribution in the lowest orbital.

RRS (cm^{-1})	SBS (cm^{-1})	ASSIGNMENT	DESCRIPTION OF VIBRATION
197	205		breathing of the central bonds
327	333		ip C^+-Ph def
417, 437	420, 442	ν_{16a}, ν_{16b}	oop ring skeletal vib + oop $\text{C}-\text{C}^+$ def
518	524	ν_{6b}	ring skeletal vib of radial orientation
553	558	ν_{6a}	"
599	608	ν_{6a}	"
—	660	$\nu_{17b}(?)$	oop ring C-H bend
720	722	ν_{17b}	"
739	741	ν_{17a}	"
753	756, 765	ν_{17a}	"
807	802	ν_{10a}	"
914	913	ν_{12}	ring skeletal vib of radial orientation
937	941	ν_{12}	"
977	979	ν_{18a}	ip ring C-H bend
1174, 1188	1174, —	ν_{9a}	"
1299	1294	ν_{14}	ring C-C str
1368	1365		N-Ph str
1382	1384		N-Ph str + ring vib
1443	1448	ν_{19b}	ring C-C str + ring def
1477	1478	ν_{19a}	"
1540	1537	ν_{8b}	ring C-C str
1585	1585	ν_{8a}	"
1620	1620	ν_{8a}	"

Table II: CV peak frequencies and their assignments.

Abbreviations: ip = in-plane; def = deformation; oop = out-of plane; vib = vibration; str = stretch. Wilson's notation are used for the assignments.

RRS (cm^{-1})	SRS (cm^{-1})	SHIFT (cm^{-1})
197	205	8
327	333	6
417, 437	420, 442	3, 5
518	524	6
553	558	5
599	608	9
753, 763	756, 765	3, 2

Table III: Peaks of CV showing upshifts in the SRS spectrum.
 Table IV (below): Peaks of CV showing downshifts in the SRS spectrum.

RRS (cm^{-1})	SRS (cm^{-1})	SHIFT (cm^{-1})
807	802	5
914	913	1
1299	1294	5
1448	1443	5
1540	1537	3
1368	1365	3

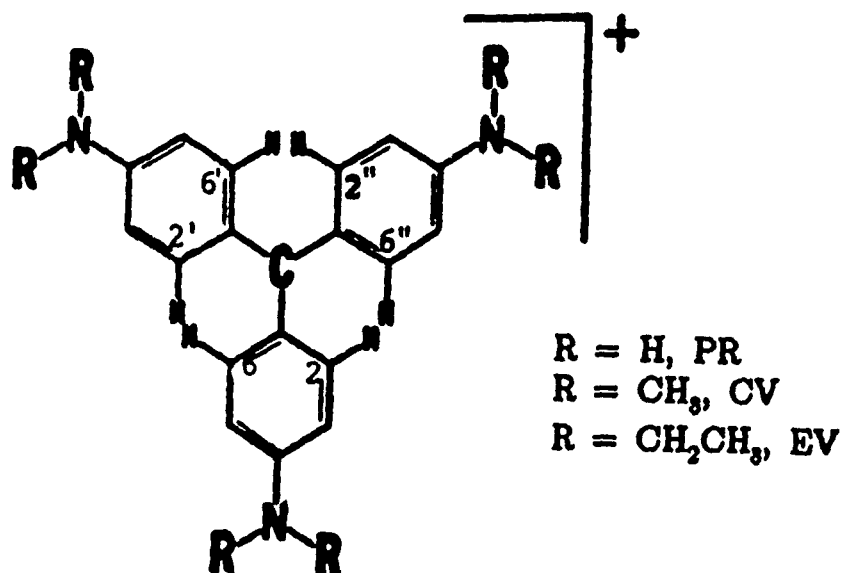


Figure 22. Representation of the CV, EV, & PR ion.

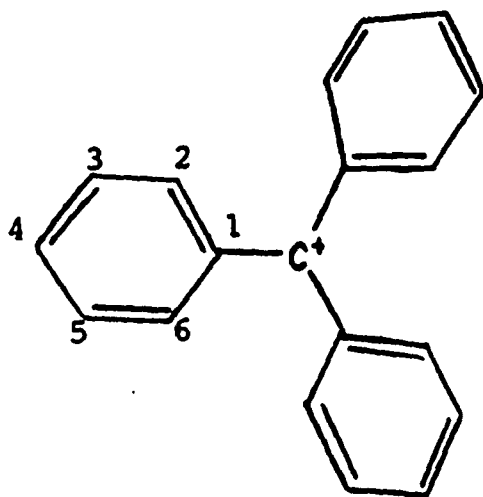


Figure 23. Representation of the triphenylmethyl (TPM) carbonium ion.

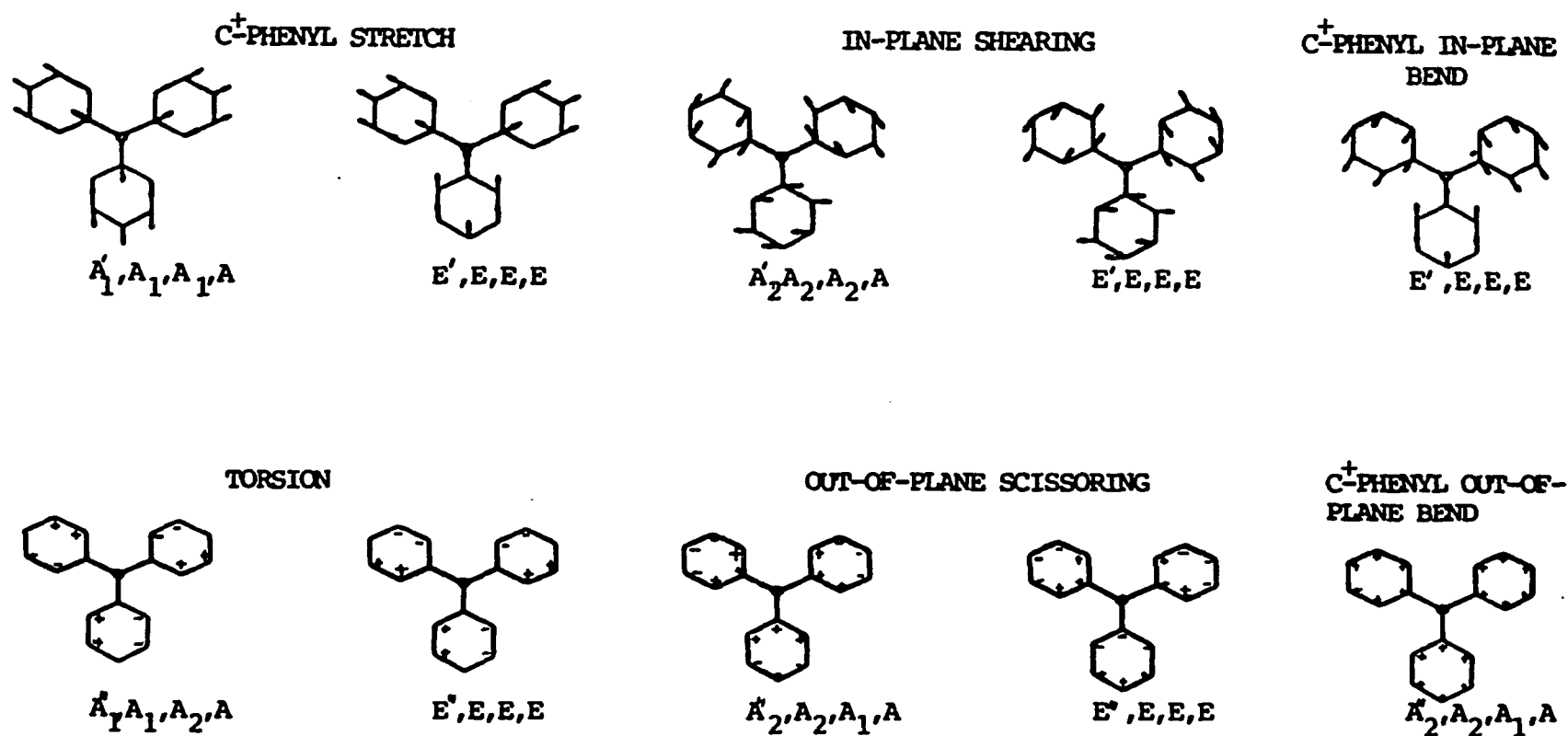


Figure 24. Skeletal vibrations of the triphenylmethyl group. The group is portrayed as planar with D_{3h} symmetry. The symmetry species below each vibration correspond to the point groups D_{3h} , D_3 , C_{3v} & C_3 respectively.

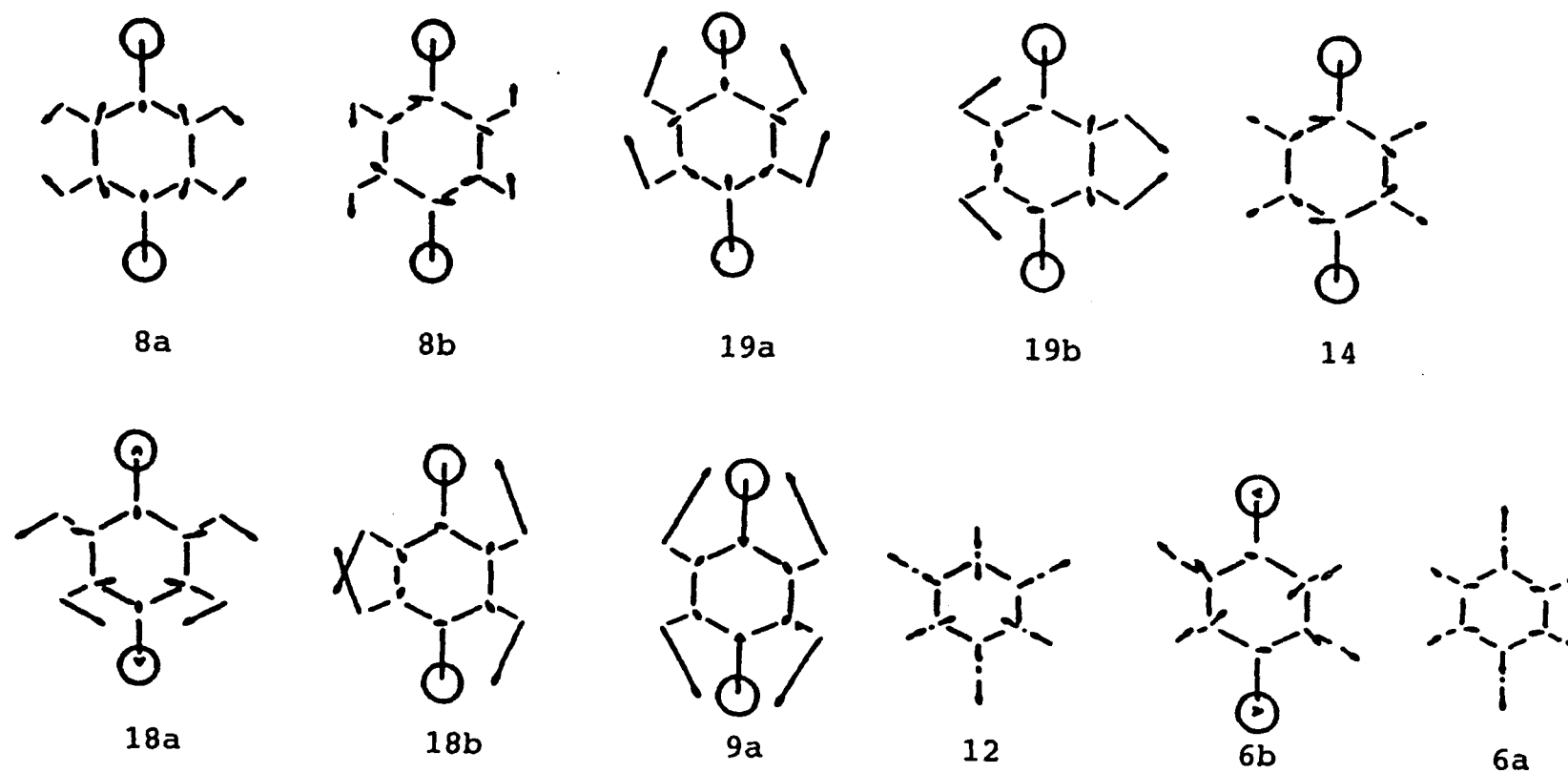


Figure 25. Ring vibrations of paradisubstituted benzene assigned to CV; modes 6a and 12 are taken from the vibrations of benzene.

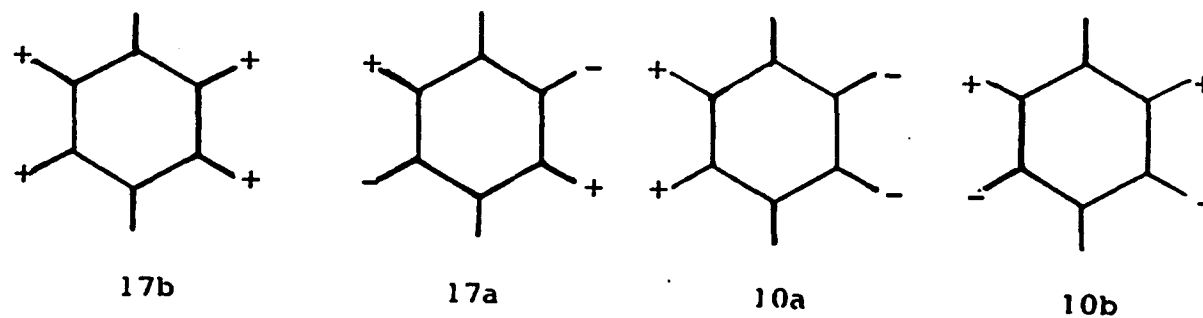


Figure 26. Vibrational forms of the CH out-of-plane bending modes in paradisubstituted benzenes.

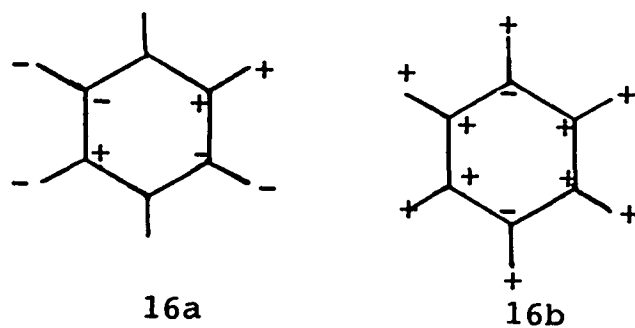


Figure 27. Vibrational forms of the 16a and 16b mode for paradisubstituted benzenes.

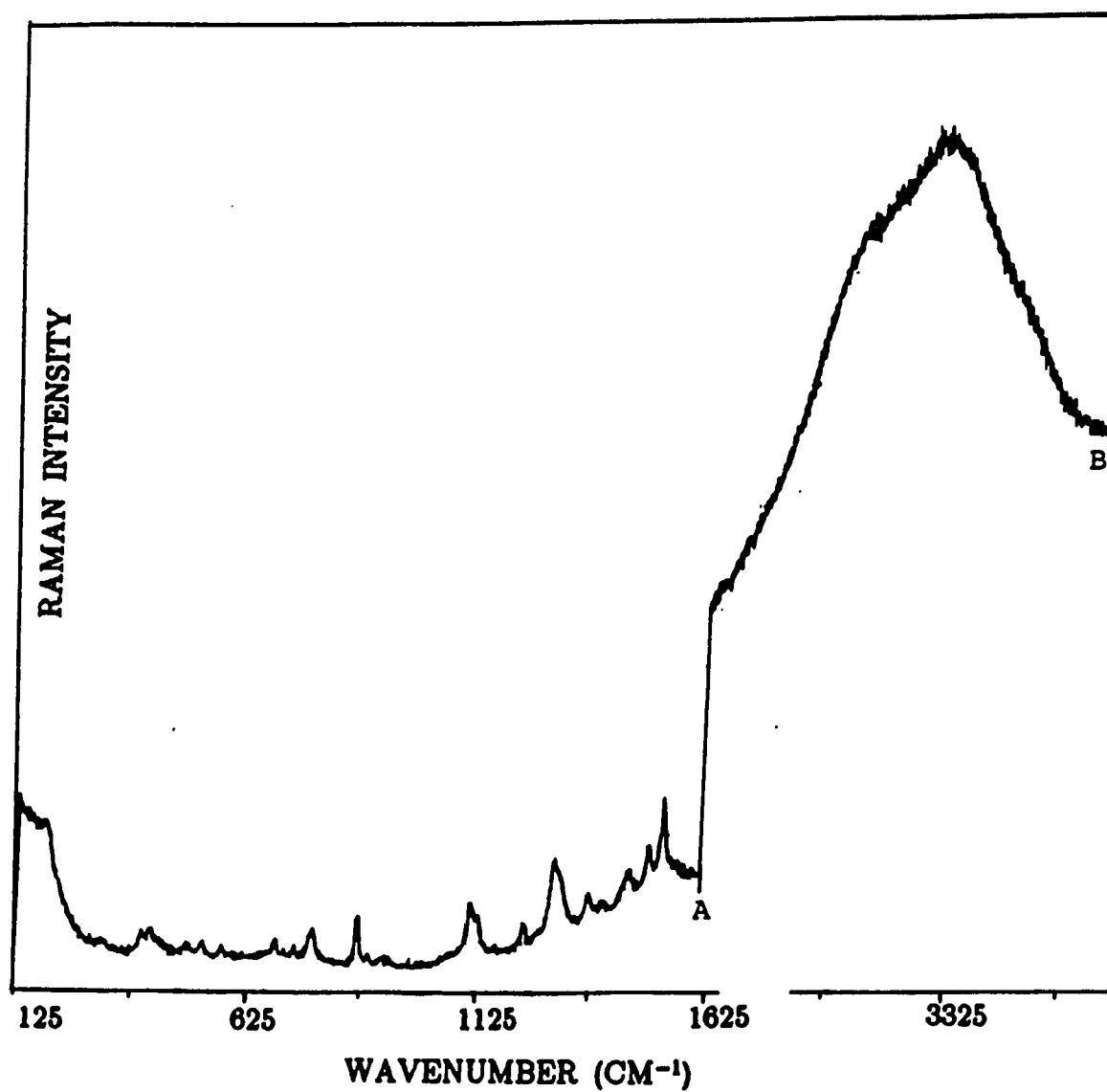


Figure 28. RRS spectrum of CV, $10^{-5}M$ in solution.
Region A - B represents the O-H stretching region of H_2O
(2900 - 3800 cm^{-1}).

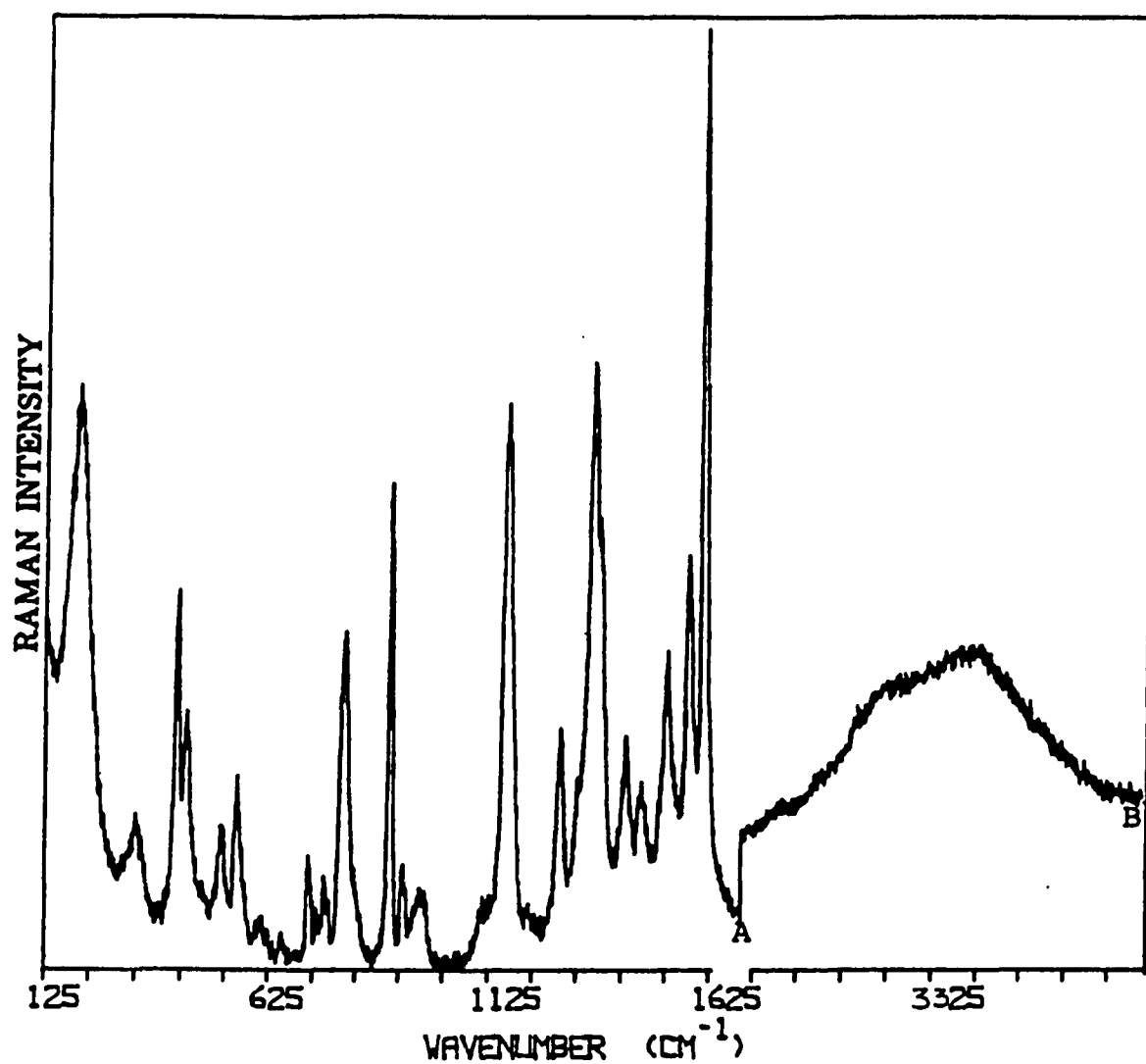


Figure 29. Surface Raman spectrum of CV on Agsol, 10^{-6} M . Region A - B represents the O-H stretching region of H_2O ($2900 - 3800 \text{ cm}^{-1}$).

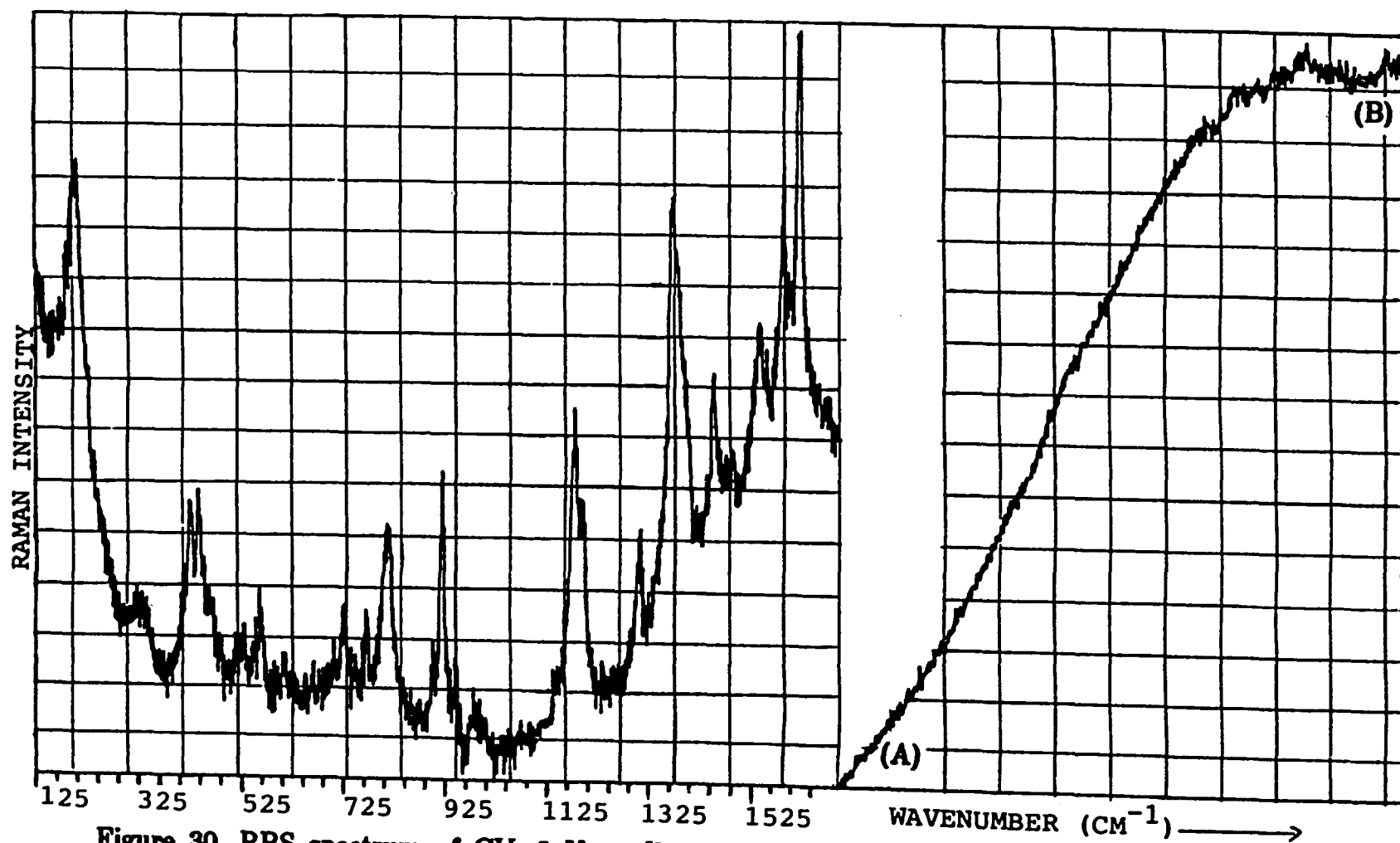


Figure 30. RRS spectrum of CV, $5 \times 10^{-5} \text{ M}$. Region A - B represents the O-H stretching region of H_2O , $2900 \text{ cm}^{-1} - 3800 \text{ cm}^{-1}$. Note that the spectral region, $125 - 1700 \text{ cm}^{-1}$ has been expanded by a factor of 9.

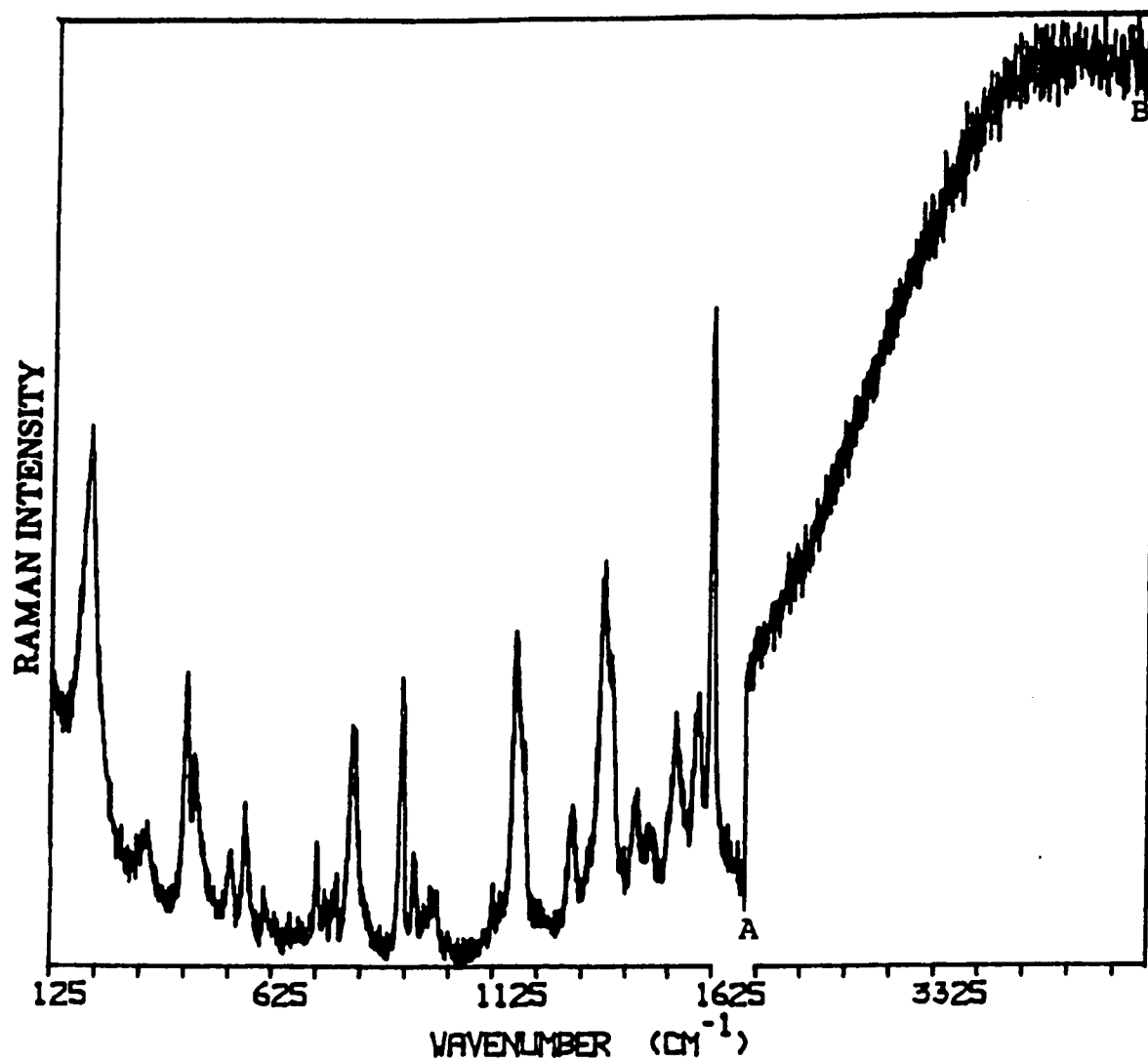


Figure 31. Surface Raman spectrum of CV on Agsol, $5 \times 10^{-5} \text{M}$. Region A - B represents the O-H stretching region of H_2O ($2900 - 3800 \text{ cm}^{-1}$).

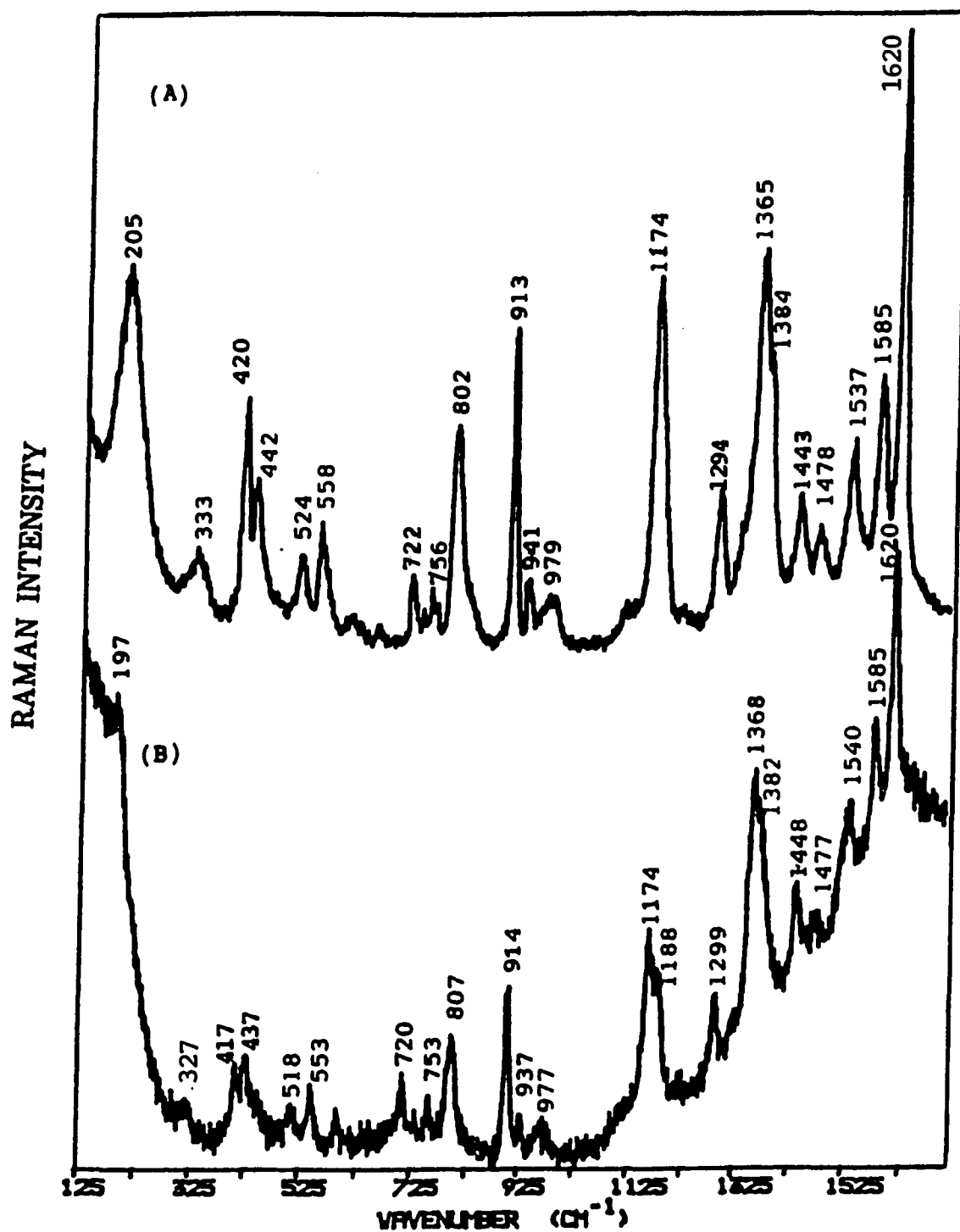


Figure 32. (A) Surface Raman spectrum of CV, 10^{-5}M on Agsol laser power = 12 mW at sample, exciting wavelength = 514.5nm. (B) RRS spectrum of CV, 10^{-5}M ; laser power = 50mW at sample, exciting wavelength = 514.5nm

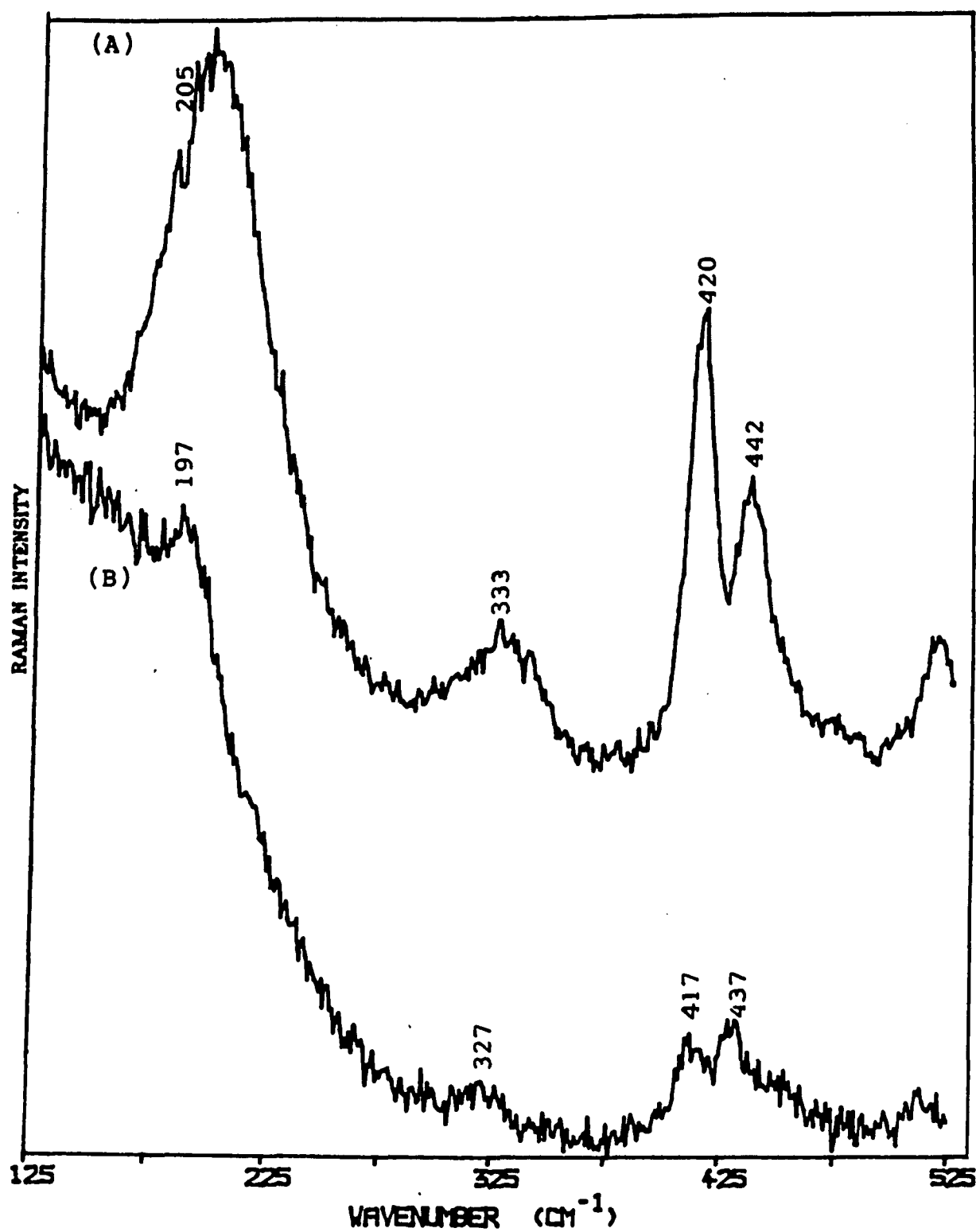


Figure 33. (A) Surface Raman spectrum of CV, 10^{-6}M on Agsol
(B) RRS spectrum of CV, 10^{-6}M .

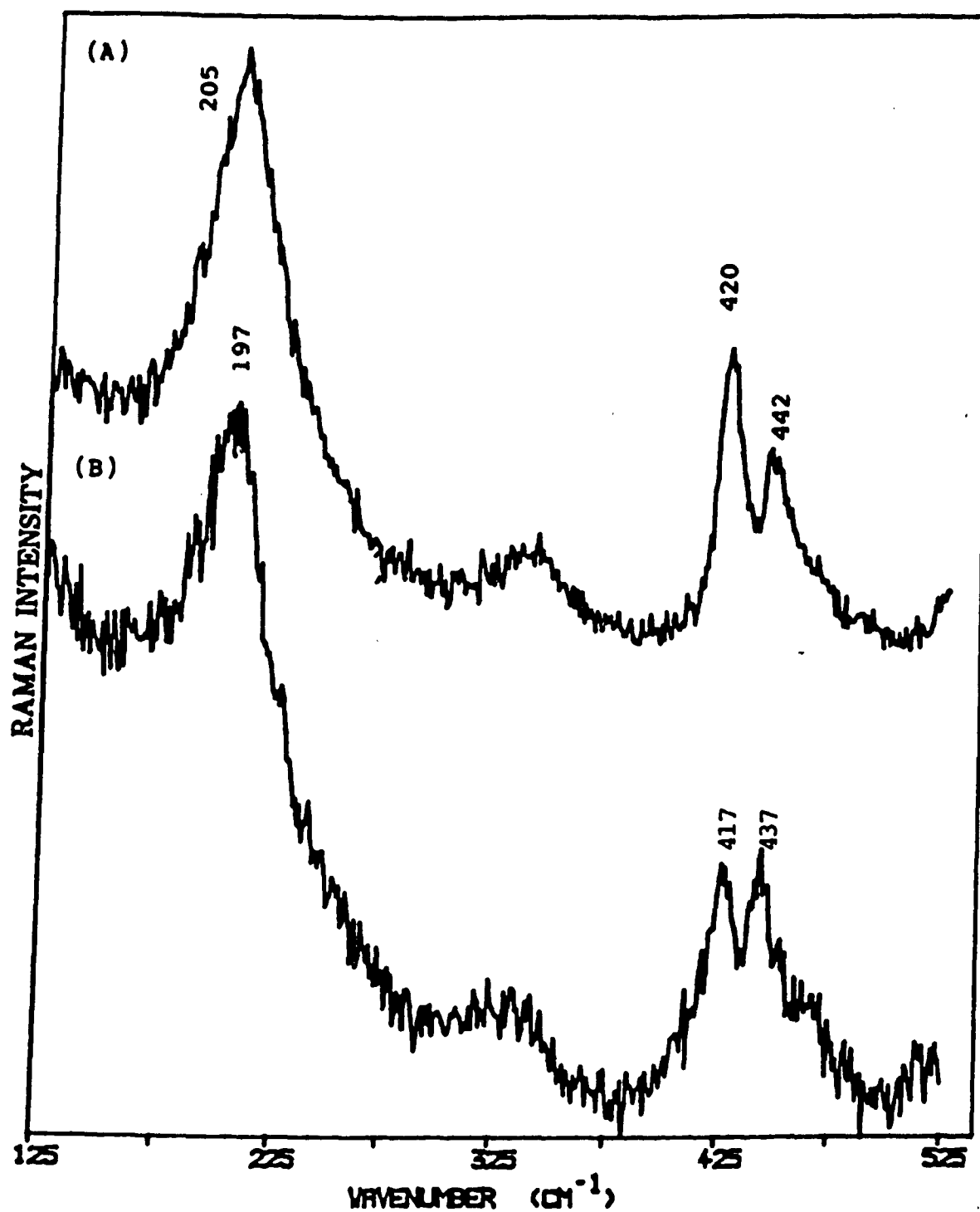


Figure 34. (A) Surface Raman spectrum of CV, $5 \times 10^{-5}\text{M}$ on Agsol. (B) RRS spectrum of CV solution, $5 \times 10^{-5}\text{M}$.

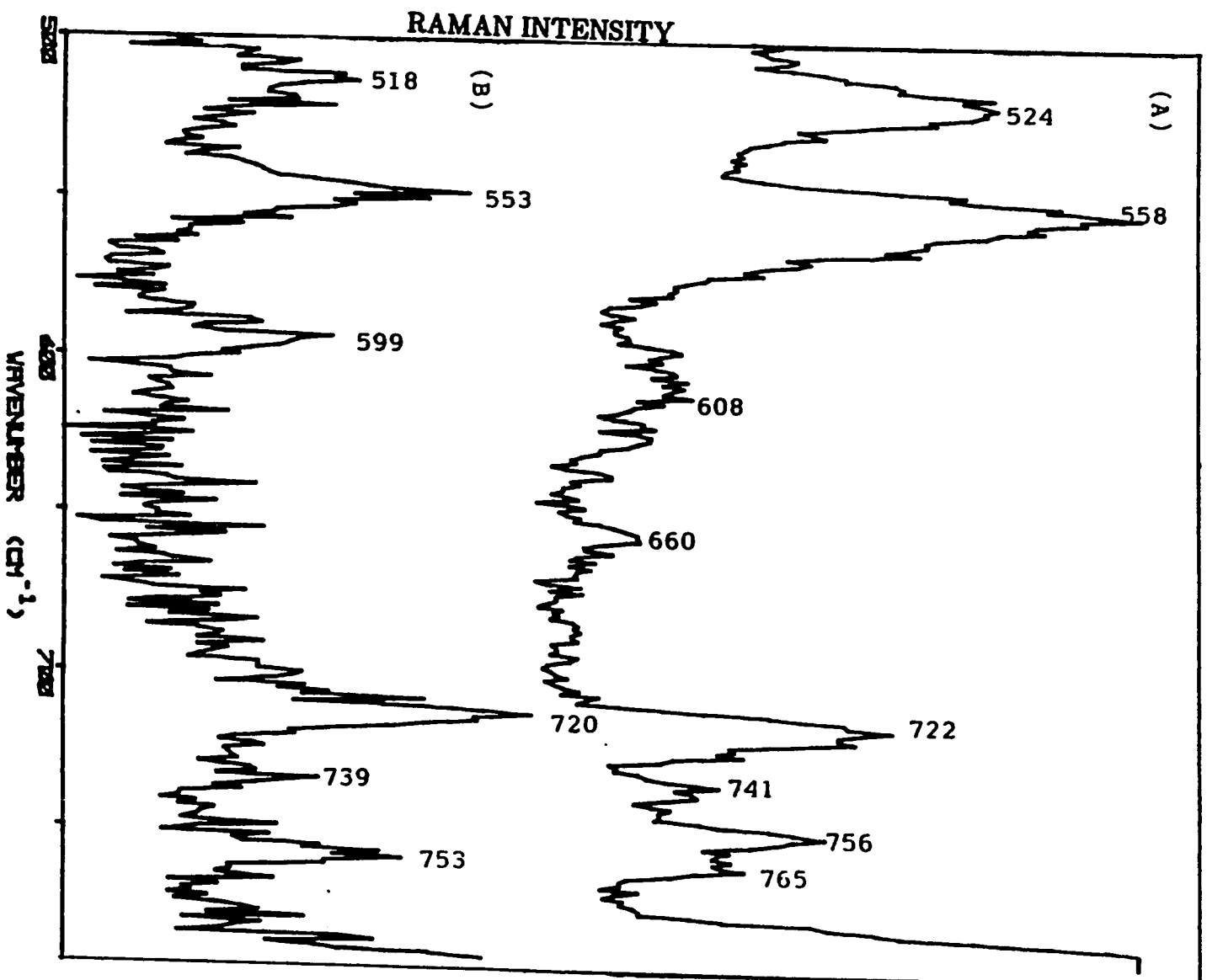


Figure 35. (A) Surface Raman spectrum of CV adsorbed on Agsol, 10⁻⁵M. (B) RRS spectrum of CV, 10⁻⁵M.

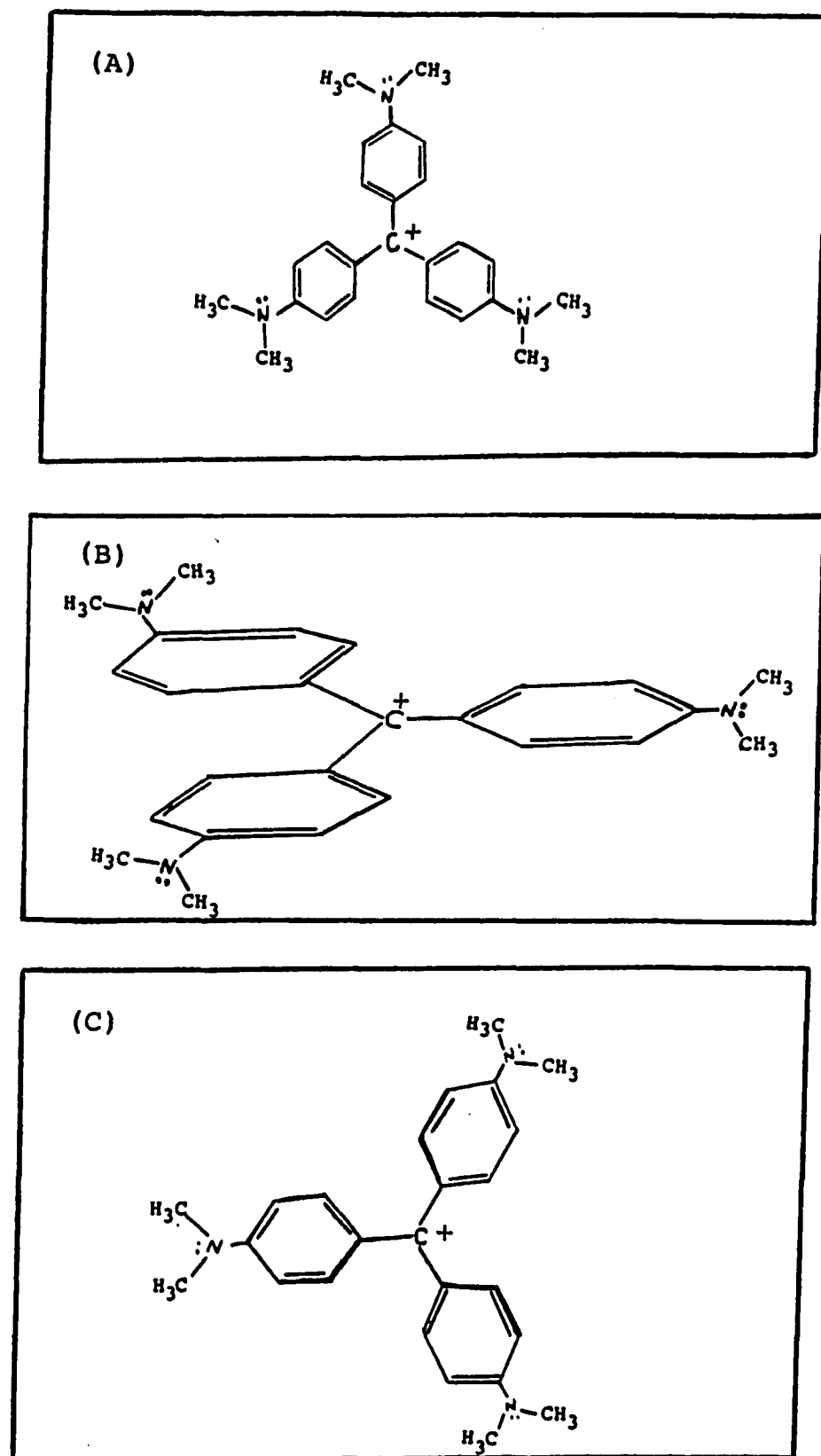


Figure 36. Various orientation proposed for CV adsorbed on Agsol.

CHAPTER 6: DISCUSSION AND ANALYSIS OF VIBRATIONAL RESULTS FOR ETHYL VIOLET

6.1 COMPARISON OF THE SURFACE RAMAN SPECTRUM AND THE RESONANCE RAMAN SPECTRUM:

Figs. 37-40 show the RRS spectra and SRS spectra of EV on Ag sol scanned at various concentrations. Table V lists the peak positions in both spectra. Again it is immediately obvious that there is a good coincidence between the positions of the peaks in the RRS spectra and those in the SRS spectra. Closer inspection indicates that there are differences in terms of :

- (i) Fluorescence
- (ii) Band intensities
- (iii) Appearance of new peaks
- (iv) Disappearance of peaks
- (v) Peak shifts

6.1.1 FLUORESCENCE:

A fairly large fluorescence background is observed in the RRS spectrum of EV scanned at $5 \times 10^{-5}M$ between 525 cm^{-1} and 1700 cm^{-1} and between 3000 and 3700 cm^{-1} . Some fluorescence is also observed in the RRS spectrum of EV, scanned at $10^{-5}M$ between 1000 and 1700 cm^{-1} (Figs.37 & 39). In the SRS spectra of both concentrations, the fluorescence background has diminished. However, the luminescence observed between 3000 and 3700 cm^{-1} in the RRS spectrum of

EV at $5 \times 10^{-5} \text{M}$ has not been quenched in the corresponding SRS spectrum (Figs. 38 & 40).

6.1.2 BAND INTENSITIES:

The changes in the intensities of the peaks relative to the water peak in the SRS spectra are perhaps the most striking differences observed between the SRS and the RRS spectra (compare Fig. 37 & 39 and Fig. 38 & 40). This change is greatest for the 205 cm^{-1} peak. Other peaks which show large increases in intensities include: 427, 442, 464, 810, 1163 and 1620 cm^{-1} . While the peaks at 310, 343, 526, 564, 601, 739, 747 and 763 cm^{-1} are weak in the RRS spectrum; in the SRS spectrum, they are clearly observed due to the large increase in S/N ratio in the surface spectrum (Fig.41).

Changes in relative intensities of some of the peaks are also observed. In the RRS spectrum, the 810 cm^{-1} peak is of a comparable intensity to that of the 919 cm^{-1} peak. However, it is more intense relative to the 919 cm^{-1} peak in the SRS spectrum (Fig.41).

The 1163 cm^{-1} peak appears as a weak splitting of the 1192 cm^{-1} peak in the RRS spectrum, while in the SRS spectrum it is much more intense relative to the 1188 cm^{-1} peak (Fig. 41).

The 1284 cm^{-1} peak is observed to be less intense than the 1304 cm^{-1} peak in the RRS spectrum; in the SRS spectrum their relative intensities are reversed (Fig.41).

6.1.3 APPEARANCE OF NEW PEAKS

There are a few peaks appearing in the SRS spectra for which there are no counterparts in the RRS spectra. These include two weak shoulders on the lower wavenumber side of the 1371 cm^{-1} peak in the SRS spectrum, a slight shoulder at 182 cm^{-1} on the 209 cm^{-1} peak and two new peaks at 620 cm^{-1} and 663 cm^{-1} (Fig.42).

6.1.4 DISAPPEARANCE OF PEAKS:

This phenomenon is unique to the spectra of EV. The 726 cm^{-1} peak in the RRS spectrum is clearly absent in the SRS spectrum (see Fig. 42).

6.1.5 PEAK SHIFTS:

There are no large red shifts in the SRS spectra, and most of the peak positions in both the RRS and SRS spectra coincide within $\pm 1 - 3\text{ cm}^{-1}$. However some of the peaks do show larger shifts and these are listed in Table VI.

6.2 ANALYSIS OF THE RRS AND SRS DATA FOR EV

6.2.1 VIBRATIONAL ASSIGNMENT:

The vibrational assignments of the peaks appearing in the spectra of EV are shown in Table V. These assignments have been made by comparison to those of CV. The RRS spectrum of EV closely resembles that of CV with the exception of the appearance of new peaks at 1078 cm^{-1} and

1422 cm^{-1} . Dollish et al. have reported that alkyl substituted benzenes usually show a peak at 1075 cm^{-1} which is assignable to the n-alkyl substituents (105). On this basis we assign the 1078 cm^{-1} to the oop deformation of the $-\text{CH}_2-$ group in the ethyl side chain. The 1422 cm^{-1} is probably due to the hydrogen bending vibration of the ethyl group since alkanes generally show C-H bending vibrations in the 1300- 1475 cm^{-1} region (109). A larger degree of peak splitting is also observed in the spectrum of EV; the peaks for which this phenomenon is observed are shown in Table VII. The larger degree of splitting may imply a larger degree of interactions between the rings of EV than for CV.

6.3 INTERPRETATION OF VIBRATIONAL CHANGES OCCURRING ON THE COLLOIDAL SURFACE

The changes observed for EV on the sol surface are very similar to those for CV; however, there are some differences and we think it best to discuss them separately.

6.3.1 SKELETAL VIBRATIONS OF THE CENTRAL BONDS, 125 cm^{-1} -450 cm^{-1}

The strong peak located at 209 cm^{-1} in the surface spectrum has been assigned to the breathing motion of the entire molecule. This peak, although very weak in the 10^{-5}M solution spectrum is observable at higher concentrations of

EV (see Fig.43) and we would therefore associate it with a vibration due to the EV molecule itself and not to a ligand vibration. A shoulder is observed at 182 cm^{-1} and there are various possible assignments for it: a Ag-N, Ag-Cl, or Ag-C⁺ stretching mode or a second vibration arising from the deformation of the central carbon bonds would all have frequencies in this region. An unambiguous assignment of this shoulder cannot be made here. The in plane deformational mode of the central C⁺-C bonds has been attributed to the doublet at 301 and 343 cm^{-1} . These are degenerate under threefold symmetry but may be split due to ring interactions as previously described. The v16a and v16b modes assigned to the triplet at 427, 442 and 464 cm^{-1} could also involve an oop C⁺-phenyl vibrational motion as suggested for CV since it is expected that the frequency of this vibration would also lie in this region. The changes observed in this region are the same as for CV and we interpret them similarly. These include:

(a). The upshift of 9 cm^{-1} for the 200 cm^{-1} peak along with a large enhancement for this peak in the surface spectrum (see Fig.42).

(b). The appearance of the doublet at 310, 343 cm^{-1} in the surface spectrum while they are not visible in the solution spectrum of EV (see Fig.42).

(c). In the solution spectrum, the triplet peaks at 427, 442, 464 cm^{-1} are of comparable intensity, while in

the surface spectrum, the 427 and 443 cm^{-1} peaks appear more intense relative to the 464 cm^{-1} . (see Fig.42). As argued for CV, this can indicate a loss of planarity of the central C^+-C bonds leading to a lowering of symmetry from D_{3h} to C_{3v} .

We interpret the changes occurring for the vibrations of the central molecular bonds as evidence that EV is interacting with the Ag surface through the central carbonium ion. We suggest that molecular distortion of the central bonds is taking place when EV is adsorbed on the sol surface because of the observed changes in the deformational modes. These modes are expected to be sensitive to molecular distortions.

6.3.2 RING SKELETAL VIBRATIONS

In contrast to CV no frequency shifts are observed in the ν_{12} and ν_{16} ring vibrations. The ν_{6a} and ν_{6b} modes undergo a very small upshift of 3 cm^{-1} which is not considered significant since it is within the wavenumber measurement error. The ν_{6b} mode at 526 cm^{-1} is split when EV is adsorbed on the Ag sol surface; again this may be due to a lowering of degeneracy of the ring vibrations since each ring can interact differently with the surface on which EV is adsorbed as compared to when it is in solution.

6.3.3 C-H DEFORMATIONAL MODES

In general, the peaks assigned to the C-H deformational modes experience downshifts in frequencies and a larger

degree of splitting on the surface of the sol. The ν_{7a} mode assigned to the 747 cm^{-1} in the solution spectrum is observed as a doublet at 737 and 747 cm^{-1} in the surface spectrum. The second peak at 763 cm^{-1} assigned to the ν_{17a} mode is very weak in the solution spectrum, but appears much stronger relative to the doublet in the surface spectrum (see Fig. 42). A downshift of 4 cm^{-1} is also observed for this peak. The ν_{10a} mode at 810 cm^{-1} experiences a downshift of 6 cm^{-1} in the surface spectrum (the same observation is noted for the corresponding peak in the surface spectrum of CV). The change in the ν_{9a} mode for CV differs from that observed for EV. The splitting of the 1163 cm^{-1} and 1192 cm^{-1} is more pronounced in the surface spectrum of EV with the 1162 cm^{-1} peak being more intense relative to the 1192 cm^{-1} band. The latter also undergoes a downshift of 4 cm^{-1} .

6.3.4 C-C RING STRETCHING VIBRATIONS

A slight downshift of 4 cm^{-1} is observed for the ν_{8a} stretching mode when EV is adsorbed on the surface of the sol. This observation indicates only a slight lowering of the C-C bond strength in the rings. The 1449 cm^{-1} peak undergoes an upshift of 8 cm^{-1} . By contrast this peak underwent a downshift for CV. This vibrational mode also consists of some ring deformational character and it may well be that it is this part of the motion that is being

affected by the presence of the silver. It can also be argued that the change may not be significant since the peaks are weak in both the solution and surface spectrum.

6.3.5 N-PHENYL STRETCHING

A downshift of 4 cm^{-1} is observed for this stretching mode, indicating a slight lowering of the bond strength. Two shoulders on the lower frequency side of this band appear more clearly in the surface spectrum. This may not be significant, however, since the corresponding peak in the solution spectrum does appear to be asymmetric on the lower frequency side (see Figs. 41 & 43).

6.4 CONCLUSION

We conclude that for EV the most significant changes occur for the vibrations involving the central carbon bonds and the C-H deformations of the phenyl rings. The skeletal and the C-C stretching vibrations of the phenyl rings as well as the N-phenyl stretching mode undergo minimal changes. From the changes occurring it can be inferred that the most important site of interaction would be the central carbonium ion. There is also an involvement of the rings judging from the changes involved in the C-H deformational modes. The interaction of the nitrogen lone pair of electrons would seem minimal as is also the case for CV.

We stress that the band shifts, with the possible exception of the 200 cm^{-1} peak, are small thus indicating that

the molecule is not tightly bound to the surface. All previous arguments for CV concerning the geometry of the molecule and its interaction on the surface will also apply here; thus, we conclude that like CV, EV adopts an orientation that is parallel to the sol surface and assumes a C_{3v} symmetry.

RFS (cm^{-1})	SRS (cm^{-1})	ASSIGNMENT	DESCRIPTION OF VIBRATION
200	182,209		breathing of the central bonds
296	301		ip C^+-Ph bend
338	343		ip C^+-Ph bend
427,442, 464	428,442, 464	ν_{16a}, ν_{16b}	oop ring skeletal vib + $\text{C}-\text{C}^+$ def
-,526	513,529	ν_{6b}	ring skeletal vib of radial orientation
584	567	ν_{6a}	"
601	599	ν_{6a}	"
---	620		ring C-H oop def
---	663		"
707	708	ν_{17b}	"
747	737,747	ν_{17a}	"
763	759	ν_{17a}	"
810,825	804,828	ν_{10a}	"
905,919	905,917	ν_{12}	ring skeletal vib of radial orientation
981,994, 1010	979,992, 1009	ν_{18a}	ip ring C-H def
1078	1076		ip C-H def of $-\text{CH}_2\text{CH}_3$ group
1163,1192	1162,1188	ν_{9a}	ip ring C-H def
1284,1304	1284,1302	ν_{14}	ring C-C str
1375	1371		N-Ph str
1422	1423		N-Ph str + ring vib
1449	1457	ν_{19b}	ring C-C str + ring def
1494	1492	ν_{19a}	"
1536	1535	ν_{8b}	ring C-C str
1588	1584	ν_{8a}	"
1620	1621	ν_{8a}	"

Table V: EV peak positions and their assignments; for explanations of abbreviations, refer to Table II.

RRS (cm^{-1})	SRS (cm^{-1})	Shift (cm^{-1})
200	209	+9
763	759	-4
810	804	-6
1192	1188	-4
1375	1371	-4
1449	1457	+8
1588	1584	-4

Table VI: EV peaks exhibiting shifts greater than 3 cm^{-1} in the SRS spectrum.

EV (cm^{-1})	CV (cm^{-1})
301, 343	327
427, 442, 464	417, 437
810, 825	807
905, 919	914
981, 994, 1010	977
1284, 1304	1299

Table VII: EV peaks exhibiting a larger degree of splitting in the RRS spectrum.

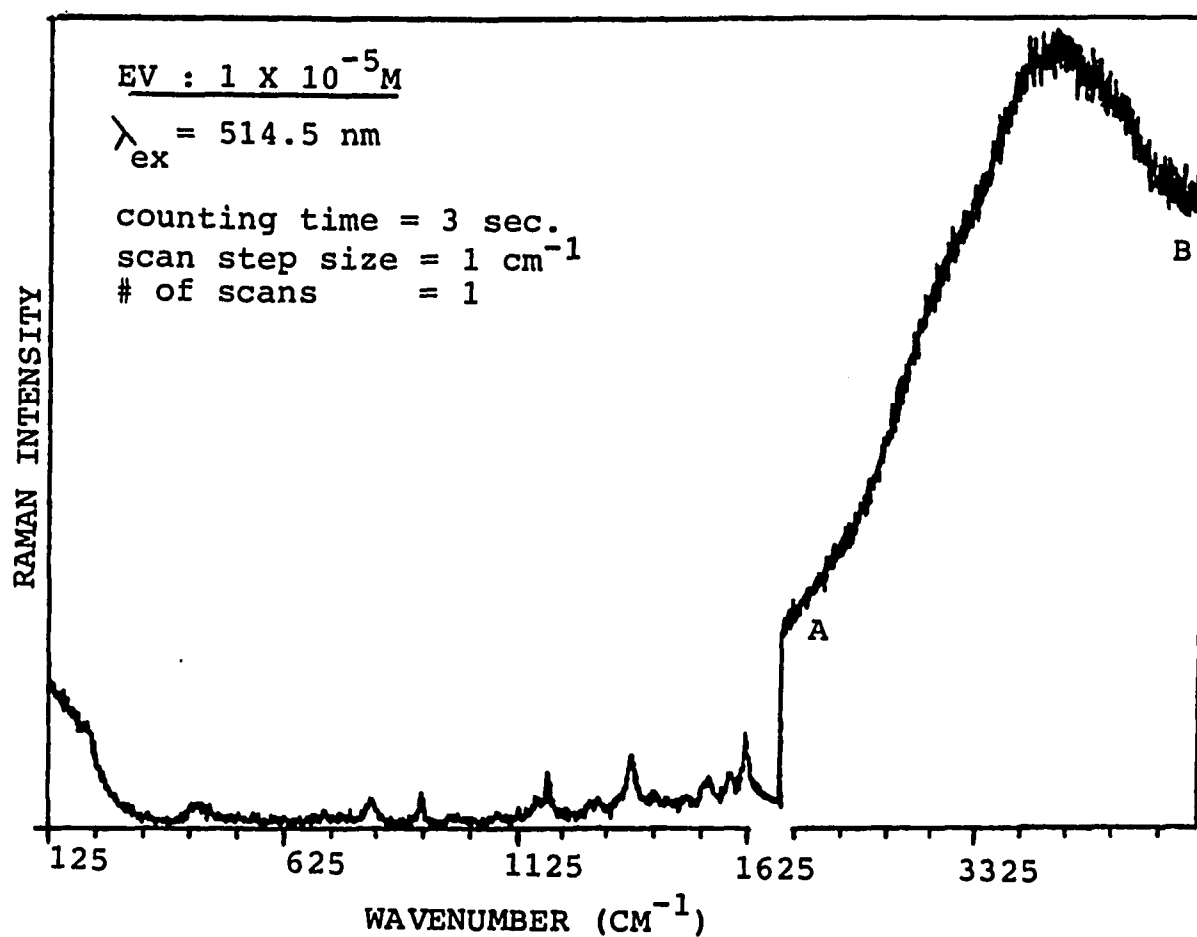


Figure 37. RRS spectrum of EV, 10^{-5} M . Region A-B represents the O-H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$. Laser power @ sample = 30 mW.

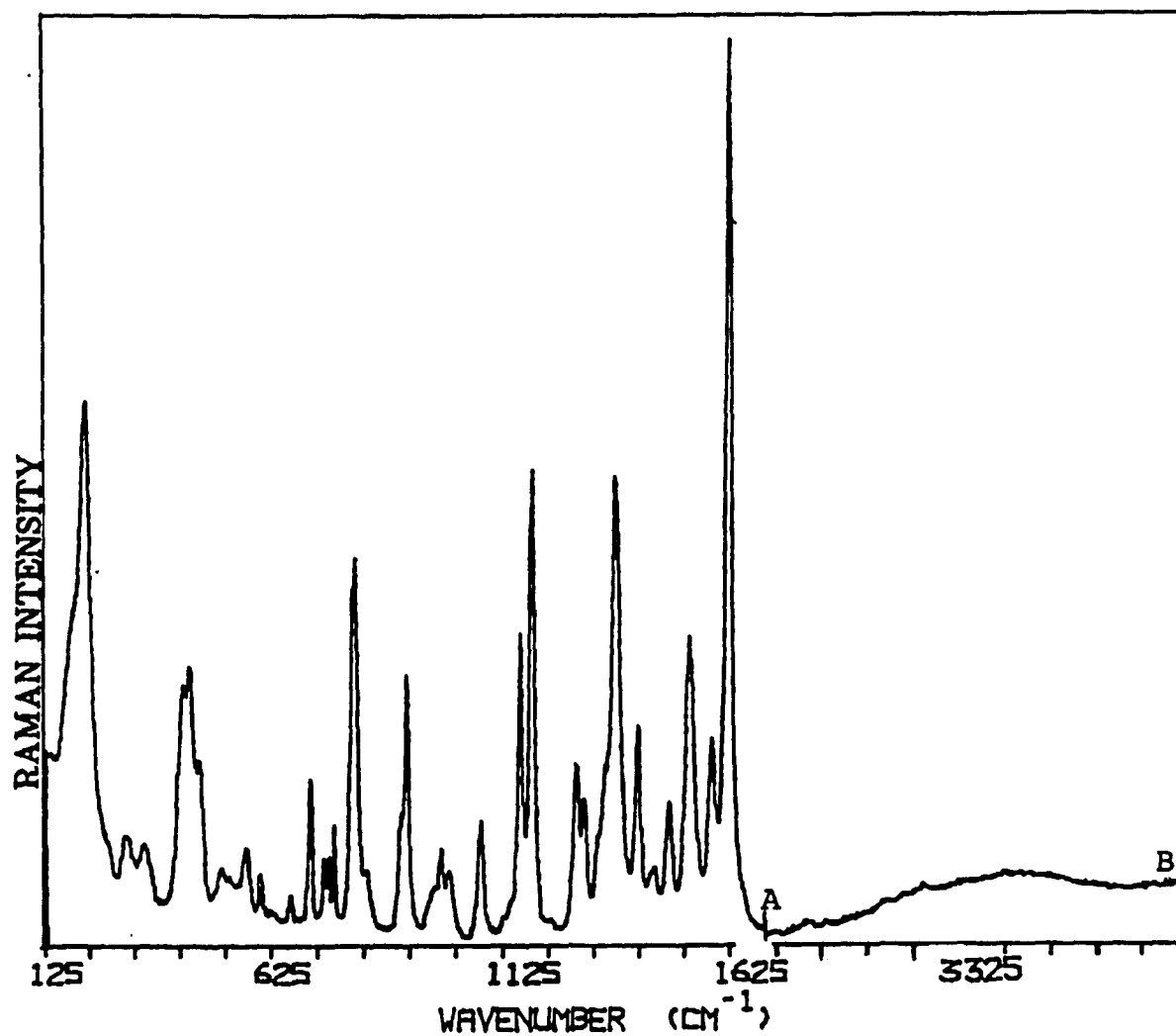


Figure 38. Surface Raman spectrum of EV on Agsol, 10^{-6}M . Region A - B represents the O-H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$. Exciting wavelength = 514.5nm ; laser power @ sample = 12mW .

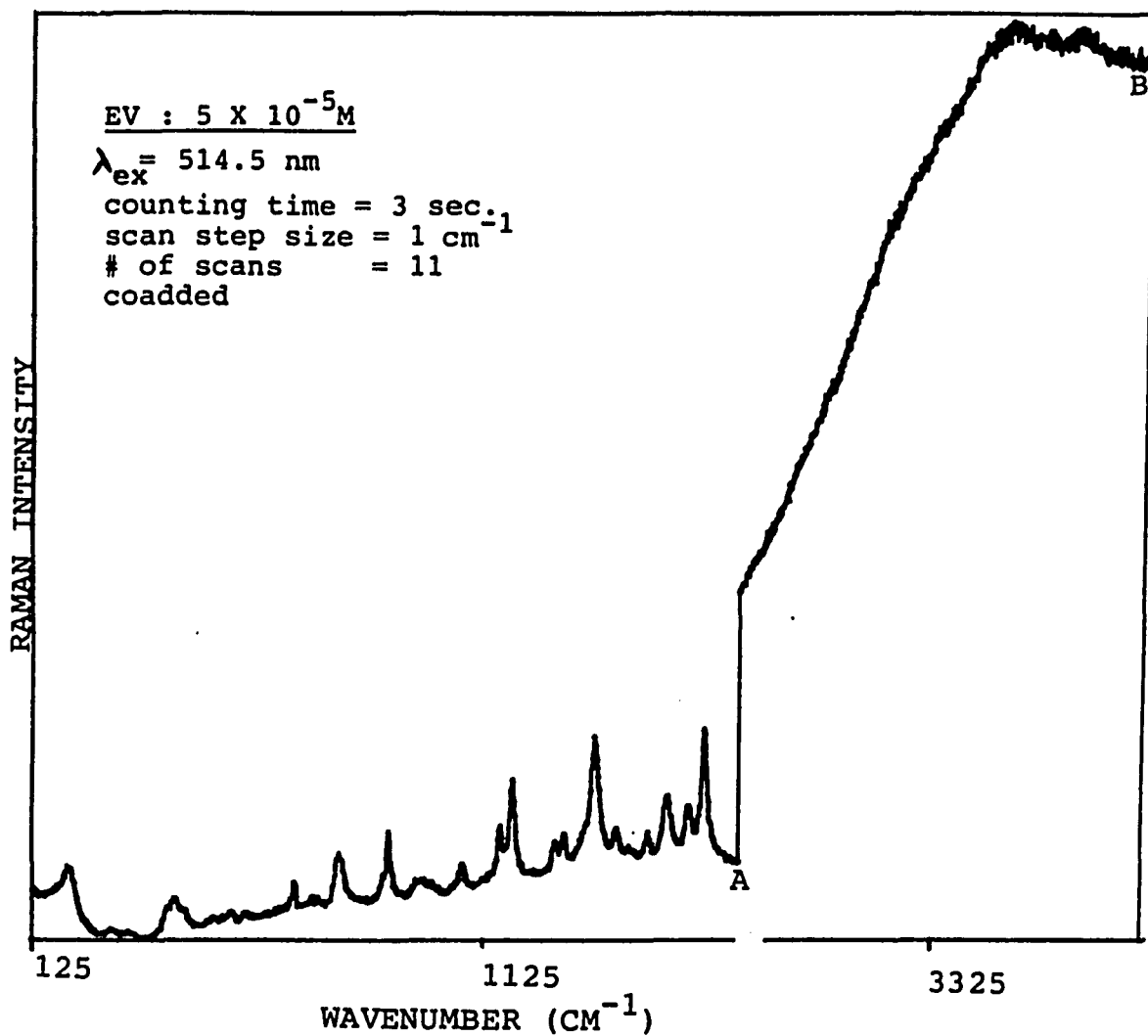


Figure 39. RRS spectrum of EV, $5 \times 10^{-5} \text{ M}$. Region A – B represents the O–H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$
 Laser power @ sample = 30 mW

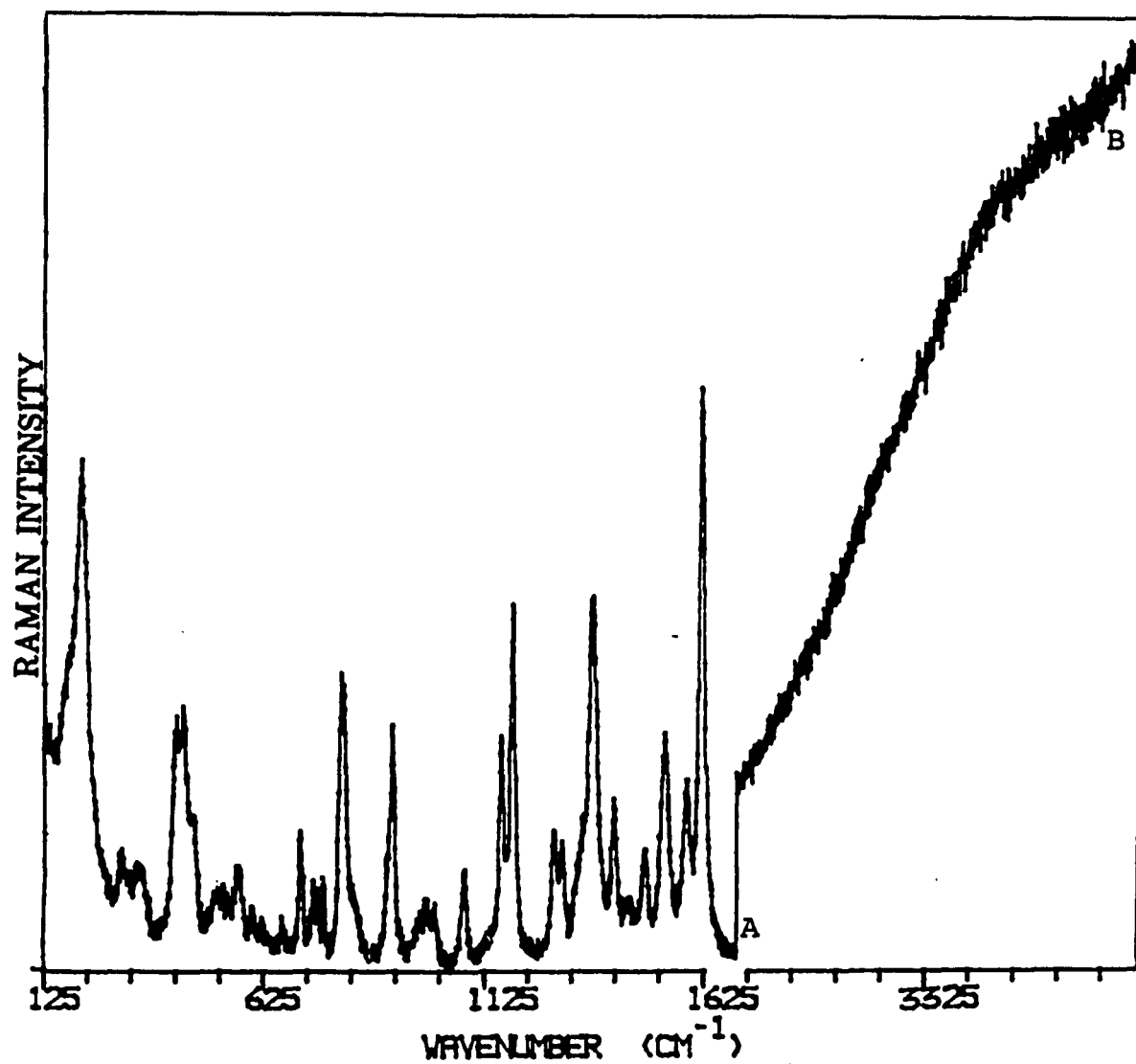


Figure 40. Surface Raman spectrum of EV on Agsol, 5×10^{-6} M. Region A - B represents the O-H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$. Exciting wavelength = 514.5 nm ; laser power @ sample = 12 mW .

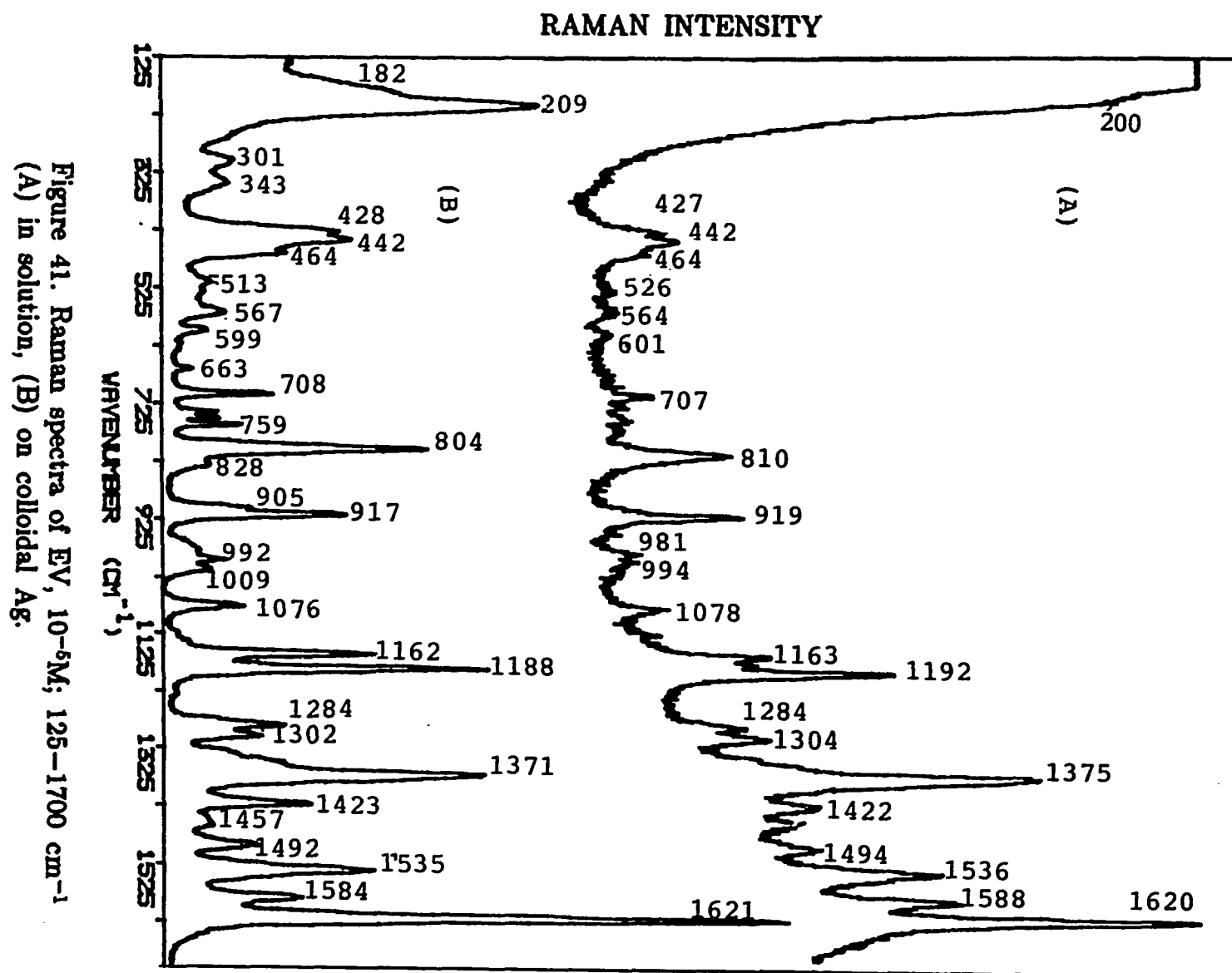
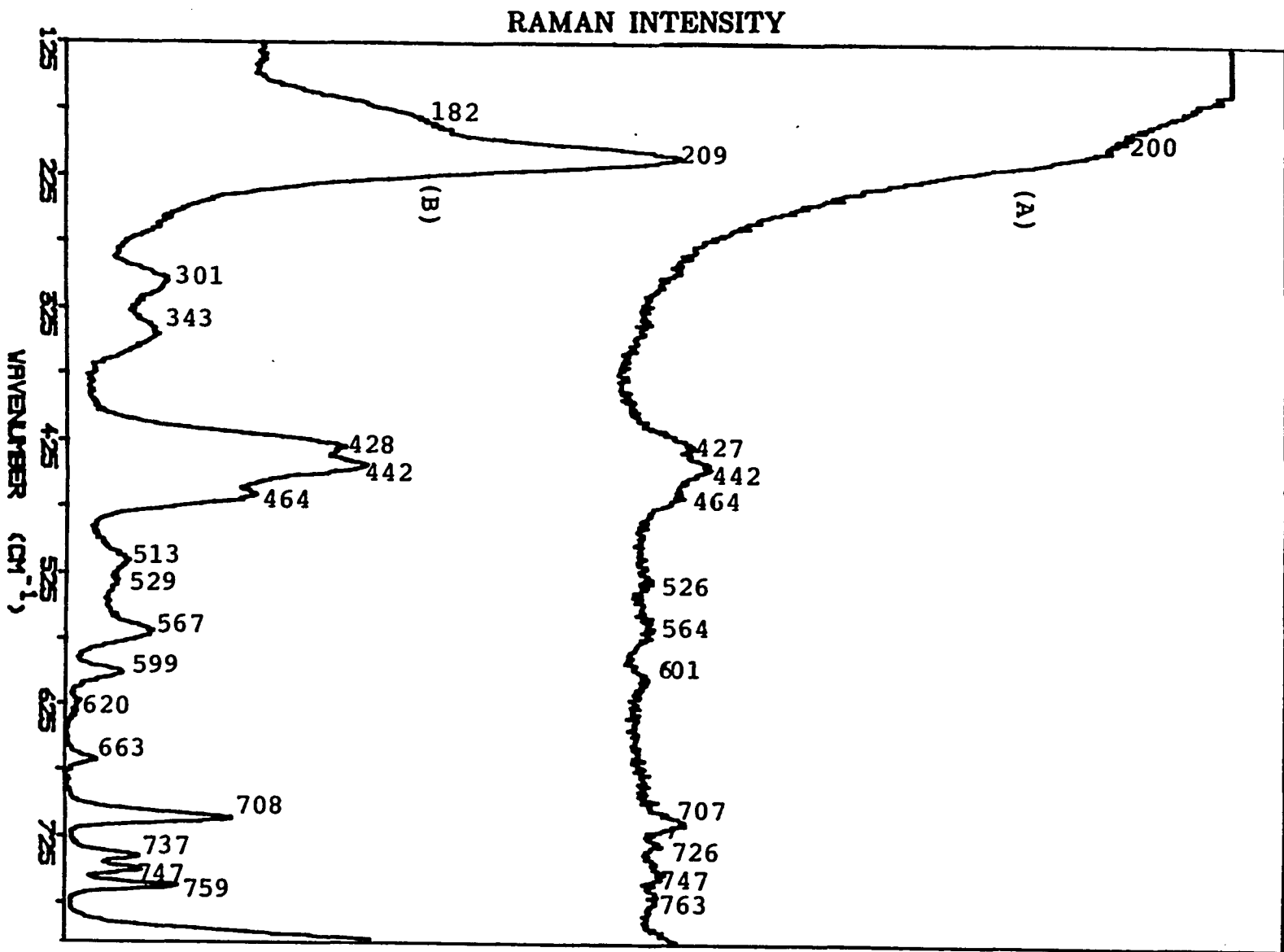


Figure 42. Raman spectra of EV, $10^{-6}M$; 125 - 800 cm^{-1}
 (A) in solution, (B) on colloidal Ag.



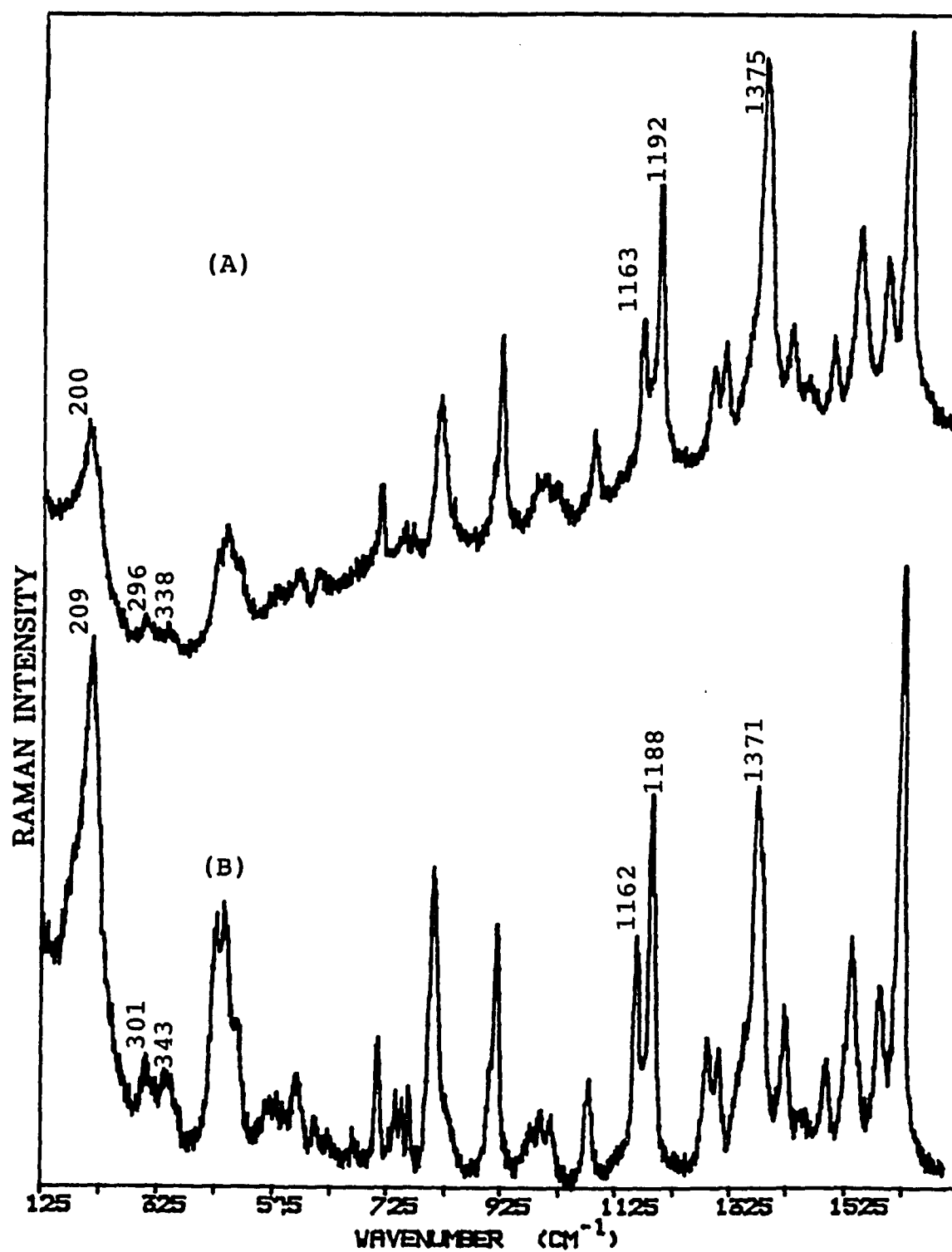


Figure 43. Raman spectra of EV, $5 \times 10^{-6} \text{M}$; $125-1700 \text{cm}^{-1}$
(A) in solution, (B) on colloidal Ag.

CHAPTER 7: DISCUSSION AND ANALYSIS OF VIBRATIONAL DATA FOR PARAROSANILINE

The surface Raman (SR) spectra and Resonance Raman (RR) spectra of PR are shown in Figs.44-46. Table VIII gives a summary of the wavenumbers of the peaks observed. For the peaks that are present in both the SRS and RRS spectra, a fairly good coincidence is observed among the peak positions in both spectra. Some of the relative intensities of the peaks also remain the same in both spectra.

The surface Raman spectrum of PR at 514.5 nm compares well in terms of peak positions and relative intensities with previously published surface spectra of a related compound, Basic Fuchsin (BF), on Ag island films (59). BF is a closely related compound to PR, differing only in having an extra methyl group attached ortho to the amino substituent on one of its phenyl rings (Fig. 3). Soper & Kuwana (57) have reported the SERS spectra of PR adsorbed on Cary Lea Ag sols in solution and on a TLC plate at a concentration of 10^{-6}M and 514.5 nm excitation. While there is good overlap of the spectral features in both spectra we observe a strong peak at 1449 cm^{-1} for PR at 10^{-5}M while Kuwana & Soper do not report this to be a major peak. Two side bands also appear on either side of the 1189 cm^{-1} peak in our surface spectrum. The relative intensities of the 1593 cm^{-1} and the 1526 cm^{-1} peaks are also different in the SRS spectrum reported herein.

The wavelength of maximum absorption for PR occurs at 545 nm. This is closer to 514.5 nm than any of the other wavelength maxima for EV or CV. The broad fluorescence background observed in the RRS spectrum observed for PR at 514.4 nm is therefore not very surprising. Fig. 44B shows the RRS spectrum of PR scanned at an excitation wavelength of 514.5 nm and it is clear that this is not the ideal spectrum for an analysis of any kind. Weak Raman peaks are observed and these are superimposed on a broad fluorescence background. This spectrum was observable only after the sample had been doubly recrystallized. Thus, in addition to the sample's fluorescence there seemed to be fluorescence from impurities as well. That there is fluorescence quenching is evident when a comparison is made with the surface Raman spectra of PR on colloidal silver (see Fig. 44A & B). The broad and sloping fluorescence background is no longer visible in the surface Raman spectrum. This spectrum does indicate the potential usefulness of SERS for vibrational studies. It should also be noted that the PR sample adsorbed on the silver sol was the crude sample, so it would seem that the fluorescence arising from the impurities is also quenched on the silver surface.

Since the RRS spectrum of PR scanned at 514.5 nm is of such poor quality it is difficult to analyze whether spectral changes observed in the corresponding SRS spectrum can be attributed to the presence of the sol. We therefore

found it necessary to obtain better quality RRS spectra of PR at other excitation wavelengths. Using an Ar^+ ion laser as the excitation source it was possible to obtain Raman data at 488.0 nm and 457.9 nm. The spectra obtained at these excitation wavelengths are shown in Figs. 45 & 46. As the excitation wavelengths are decreased a dramatic drop in the fluorescence background is observed in the RRS spectra of PR. The peaks are also more intense than those observed in the 514.5 nm RRS spectrum. Although the level fluorescence is low in the 457.9 nm spectrum the intensities of the peaks are lower than those in the 488.0 nm spectrum. This might be explained by the fact that the 457.9 nm line lies further away from the absorption band of PR and we are moving into an 'off resonance' situation.

The RRS spectrum of PR at 457.9 nm does appear to resemble the Raman spectrum of 10^{-3}M BF in ethanol at 457.9 nm reported by Weitz *et al.* (59) though in the latter spectrum the peaks in the region of 300-500 nm do appear to be more intense. This might be due to the fact that the concentration was two orders of magnitude greater than that used in this study.

Though the RRS spectra at these two excitation wavelengths are of much better quality than that obtained at 514.5 nm, the SRS spectra at these wavelengths are of superior quality when compared to their RRS counterparts, especially in terms of the signal to noise ratio. The peak

positions are clearly defined and the sloping backgrounds observed in the 125-925 cm^{-1} regions of the RRS spectra are not observed in the SRS spectra. In all three SRS spectra there is a background observed between 1300-1600 cm^{-1} ; this has been attributed to the scattering of the silver sol itself (26).

Though all three SRS spectra are of similar quality, The absolute peak intensities are higher in the 514.5 nm spectrum. This is in accordance with previous calculations which have indicated that the 514.5 nm excitation line would be the most efficient line for Raman studies on Ag surfaces. There exist no major differences among these three spectra especially when the positions (Table VIII) and relative intensities of the peaks are compared.

7.2 COMPARISON OF THE RRS AND SRS SPECTRA OF PR

Apart from fluorescence other differences can be cited when the RRS spectra of PR at 488.0 nm and 457.9 nm are compared with the corresponding surface spectra on the colloidal silver. These are:

- (a). Changes in relative intensities of peaks.
- (b). Appearance of new peaks.
- (c). Band shifts.

7.2.1 CHANGES IN RELATIVE INTENSITIES:

A comparison of the intensities of the peaks in the solution and surface spectrum indicates that there is an apparent increase in the intensity of all of the peaks relative

to the water peak (Fig.47 & 48). This increase seems greatest for the 1620 cm^{-1} and the 250 cm^{-1} peaks. The two peaks at 411 cm^{-1} and 438 cm^{-1} appearing as a doublet are of comparable intensity. However in the surface spectra, the 411 cm^{-1} peak intensity is greater than that of the 438 cm^{-1} peak.

7.2.2 APPEARANCE OF NEW PEAKS:

Two distinct (albeit small) side peaks are observed on the sides of the 1177 cm^{-1} band in the SRS spectra. These are not observed in the RRS spectrum. No counterpart for the 760 cm^{-1} peak in the SRS spectra can be found in any of the RRS spectra. A weak band is observed on the low frequency side of the 1293 cm^{-1} peak. What is perhaps the most striking difference between the RRS spectra and the SRS spectra is the absence of the 1452 cm^{-1} peak.

7.2.3 PEAK SHIFTS:

As a rule large red shifts in peaks are not observed. Wavenumbers are slightly lowered in the SRS spectra. In the 488.0 nm SRS spectrum the 1298 cm^{-1} peak is downshifted by 5 cm^{-1} . In the 457.9 nm spectrum, a downshift of 8 cm^{-1} is observed for the analogous 1301 cm^{-1} peak. In the 457.9 nm SRS spectra, a downshift of 5 cm^{-1} is observed for the 917 cm^{-1} peak. A smaller shift of 3 cm^{-1} is observed in the 488 nm spectra for the corresponding peak at 916 cm^{-1} . The shifts (if any) seem to be concentrated between the region of $820 - 1290\text{ cm}^{-1}$.

7.3 TIME DEPENDENCE OF THE RRS AND SRS SPECTRAL INTENSITY

For improvement of S/N ratio multiple scans of a single sample of PR were coadded and the final spectrum obtained was used for further analyses. A comparison of the first and last scans did not indicate any changes in peak positions or relative peak intensities. From this, it can be inferred that no sample deterioration took place.

By contrast, as the Ag sol-PR mixture aged, the quality of the SRS spectrum declined. The signal to noise ratio decreased dramatically, the spectrum was plagued with spikes and was very noisy, and the dye's peaks were barely visible. This deterioration was attributed to the sample's instability. Addition of PR to the sol induced precipitation rapidly. The rapid precipitation of the sol precluded effective focussing of the laser beam into the sample. Simultaneous precipitation was also observed in the stock mixture which was not exposed to the laser beam. Thus the deterioration of the sample could not be attributed to the laser. This problem was overcome by scanning several spectra of freshly prepared sample mixtures using the same sol for a particular batch study. These spectra were coadded to yield a final averaged spectrum (as shown in Figs.47 & 48).

It was found however that the spectral features of the surface spectrum did change with the age of the sol. This was quite unique to PR. Sols were not used for extensive

periods of time. For 10^{-5}M and $5 \times 10^{-5}\text{M}$ solution mixtures, the sol was used over a period of five days. An assessment of the individual spectrum scanned over a period of time on the same sol indicated the following: on day 1 when the sol is freshly prepared, the resulting spectrum is weak in the $125 - 1100 \text{ cm}^{-1}$ region while in the $1100-1600 \text{ cm}^{-1}$, very strong peaks at 1182 , 1449 and 1594 cm^{-1} dominate (see Fig. 49). Similar observations are noted at all three wavelength of excitation used (Fig. 50); peaks at 255 , 411 and 519 cm^{-1} though visible are weak. No splitting of the 411 cm^{-1} peak is observed as yet.

By the second day however there is a phenomenal rise in the intensities of some of the peaks (Fig. 49B & 50B). The following observations are noted for the peaks: the 255 cm^{-1} peak which is weak in the 514.5 nm spectrum and absent in the 488.0 and 457.9 nm spectra scanned on the first day now appears as an intense peak in the SRS spectra and moreover it remains as one of the most intense peaks over the time period investigated.

The 568 cm^{-1} peak is virtually absent in the SRS spectrum scanned on the first day. However, by the second day its intensity increases beyond that of the 517 cm^{-1} peak which was more intense on the first day.

The 411 cm^{-1} peak splits only after the sol has aged for some time. With the 488.0 nm excitation it has been observed six hours after preparation of the sol.

The 1375 cm^{-1} peak which is almost absent in the first Raman scan starts increasing in intensity while the 1452 cm^{-1} peak decreases. Moreover the 1375 cm^{-1} peak increases to become one of the most intense peaks observed in the 514.5 nm spectrum, and a medium strong peak in the 488.0 and 457.8 nm SRS spectra. An increase is also observed for the 1520 cm^{-1} peak. This band is absent in the spectra scanned at 457.8 nm and 488.0 nm and barely visible in the 514.5 nm spectrum scanned on the first day. With time it does seem to increase as the 1452 cm^{-1} peak decreases.

It is clear that changes among the spectra scanned at different times are related to the aging of the sol. On a freshly prepared sol only certain peaks appear, while on an aged sol, all the normal peaks associated with PR appear; in fact the surface spectrum does appear to look closely like the solution spectrum only after the first twenty-four hours of sol aging.

7.4 VIBRATIONAL ASSIGNMENT:

The assignments of the RRS and SRS peaks of PR are given in Table IX. These assignments were done on the same basis as for CV. The RRS spectrum of PR displays close similarity to those of EV and CV in its set of vibrational frequencies but differs in peak intensity distribution. The doublet lines for example at $\sim 1600\text{ cm}^{-1}$ show an inversion of relative intensities for PR. This observation has been previously made by Alexandrov et al. (97). The peak at 250 cm^{-1}

is the analogy to the 197 cm^{-1} and 200 cm^{-1} peaks of CV and EV respectively. This frequency does seem higher, but Angeloni *et al.* (95) have pointed out that this peak (a molecular breathing mode) should be very sensitive to mass and should shift to higher frequencies as the masses are lowered. This concurs with our observation for PR. The N-Ph stretching mode is assigned to the 1346 cm^{-1} and the 1375 cm^{-1} peaks although the latter may also include some ring vibrations as pointed out for CV. The 1346 cm^{-1} band frequency is also lower than those observed for CV or EV. But this seems to correlate well with Colthup's assignment of the N-Ph stretching frequencies of secondary amines (109). It does appear much higher than the 1276 cm^{-1} peak assigned to the N-Ph stretching motion in aniline (104), but overlaps with the peak at 1346 cm^{-1} reported for N,N' dimethylamine (107).

An unambiguous assignment of the 1454 cm^{-1} peak cannot be made at this stage without any isotopic substitution studies. In both EV and CV very weak peaks appear at 1449 cm^{-1} and these have been assigned to the ν_{19b} ring stretching vibrational mode. It is highly unlikely that this weak peak could be so strong in the surface spectrum. At this point we can only say that it is associated with the Ag-PR complex and possibly involves a combination of both the C-C stretching and N-Ph stretching modes; since frequencies assignable to both of these modes are found in this fre-

quency region.

7.5 INTERPRETATION OF CHANGES IN THE VIBRATIONS OCCURRING ON THE SOL SURFACE

As for CV and EV we will attempt to rationalize the changes occurring on the surface of the sol in terms of the interaction of PR and the sol. That there is an interaction is evidenced from the following facts:

1. The difference between the absorption spectra of the PR-Agsol mixtures and those of the dye and sol only.
2. The loss in the Raman intensity of the dye peaks when the sol precipitates in the sol-dye mixture.
3. The quenching of the fluorescence that occurs on the sol surface.
4. The changes observed between the surface Raman spectra and the solution Raman spectra. These are discussed in more detail below for the 488.0 nm spectra:

7.5.1 VIBRATIONS OF THE CENTRAL CARBON BONDS,

125 cm^{-1} - 450 cm^{-1}

The vibrational changes involved for PR in this frequency region are similar to those for EV and CV. The breathing mode of the $\text{Ph-C}^+-\text{Ph}$ bonds at 249 cm^{-1} is upshifted by 6 cm^{-1} . The magnitude of the upshift is slightly lower than those of EV and CV, possibly indicating less interaction of the C^+ center with the surface. Again we do not ascribe the 255 cm^{-1} peak in the surface spectrum to a Ag-ligand vibration since there is a corresponding peak found at 249

cm^{-1} in the RRS solution spectrum. A weak peak appears at 195 cm^{-1} in the surface spectrum and as pointed out for EV various Ag-ligand vibrations can be attributed to this peak. The ip deformational mode assigned to the 334 cm^{-1} peak undergoes a slight upshift of 3 cm^{-1} in the 488.0 nm surface spectrum; it also appears to split into three components, again indicating a lowering of degeneracy. For the doublet at 409 cm^{-1} and 433 cm^{-1} we observe an increase in the intensity of the 409 cm^{-1} relative to that of the 433 cm^{-1} . These changes overlap with the observations for CV and EV and the interpretations are the same.

7.5.2 RING SKELETAL VIBRATIONAL MODES:

In contrast to EV and CV, these modes do not undergo any appreciable shifts. The only change observed is for the v6b mode at 515 cm^{-1} . In the surface Raman spectrum this peak appears more intense than the v6a mode at 567 cm^{-1} . In the solution spectrum the v6b mode is less intense than the v6a modes.

7.5.3 C-H DEFORMATIONAL MODES:

We have assigned the v7a mode to the 736 cm^{-1} peak; in the surface spectrum a new peak appears at 760 cm^{-1} which could be a second vibration arising from the v7a mode. A slight downshift of 4 cm^{-1} is observed for the v10a mode. The observation of this downshift for the v10a mode is consistent for all three compounds. The in plane C-H deformational mode, v18a, at 973 cm^{-1} remains weak in both

spectra. The most dramatic change is observed for the v_{9a} mode at 1179 cm^{-1} which is another ip C-H deformational mode. Two side bands appear on either side of this peak in the surface spectrum. This vibration of all three rings is probably degenerate in the solution where the orientation of PR is most likely random; while on the surface because of the orientation adopted by the molecule each ring can interact differently with the surface, thereby giving rise to three bands. A similar observation has been reported for the C-H bending mode of the rhodamine 6G dye (108).

7.5.4 N-PH STRETCH:

This stretching mode when it appears in the surface spectrum shows a slight down shift of 3 cm^{-1} , indicating only a slight weakening of the N-Ph bond. This would indicate very little interaction at the site. But we would note that this peak is time dependent and its appearance varies with the age of the sol (vide infra).

7.5.5 C-C STRETCHING MODE:

A downshift of 5 cm^{-1} is observed for the v_{14} mode at 1293 cm^{-1} . A downshift of 7 cm^{-1} is observed for the v_{8b} mode in the 488.0 nm surface spectrum. These downshifts are indicative of a weakening of the C-C bonds in the phenyl rings.

7.6 CONCLUSION:

From a consideration of the changes occurring in the vibrations we conclude that the most significant interac-

tion occurring on the surface involve the central carbonium ion and the phenyl rings. However this conclusion is drawn only from a comparison of the solution spectrum and the surface spectrum of PR scanned on an aged sol (at least 48 hours old). There is a time dependency involved which may be interpreted in various ways. One proposal is that the molecule may be changing its orientation. Significant changes were not observed in the absorption spectra of the sol over the time period during which the Raman data was collected. This means that the changes are not due to changes in the sizes of the sol particles. However, it is known that a sol can reshape itself and form rods, chains and random coils and yet retain its primary particle size (110) and this may be the factor that is responsible for the variation in orientation of the dye. The nature of this orientation can only be surmised at this point. It is possible that the PR molecule stands "end on" on the freshly prepared sol; and as it ages, it adopts a parallel orientation. We conclude that the final orientation is parallel because the changes observed in the vibrations of the central carbonium ion and the phenyl rings are similar to those observed for EV and CV and we have argued that these molecules would most likely be lying parallel to the surface.

EXCITING WAVELENGTH (NM)					
514.5	488.0	457.9	514.5	488.0	457.9
RRS (CM ⁻¹)			SRS (CM ⁻¹)		
251	249	249	254	255	255
337	334	336	337	337	335
408,442	409,433	411,423, 440	410,439	410,437	412,422, 439
517	516	516	521	520	515
570	568	567	571	567	567
639	639	640	640	640	642
—	—	—	761	761	760
837	829	834	832	825	821
920	916	917	920	913	912
979	973	965	978	975	968
-,1182,-	-,1179,-	-,1181,-	1143, 1179,1196	1144, 1177,1197	1144, 1180,-
1299	1298	1301	1297	1293	1293
1347,1378	1348,1373	-,1376	1342,1372	1345,1376	1375
—	—	—	1449	1454	1454
1594	1591	1595	1591	1591	1595
1616	1618	1624	1616	1611	1623

Table VIII: Peak frequencies of PR at various exciting wavelengths.

RRS (CM^{-1})	SRS (CM^{-1})	ASSIGNMENT	DESCRIPTION OF VIBRATION
249	254		breathing mode of the central bonds
334	337, 378, 365		ip C^+ -Ph def
409, 433	410, 437	ν_{16a}, ν_{16b}	oop ring skeletal + oop C^+ -C def
516	515	ν_{6b}	ring skeletal vib. of radial orientation
568	567	ν_{6a}	"
639	640	ν_{6a}	"
736	736	ν_{17a}	oop C-H def
—	761	ν_{17b}	"
829	825	ν_{10a}	"
916	913	ν_{12}	ring skeletal vib of radial orientation
973	975	ν_{18a}	ip C-H bend
-, 1179, -	1144, 1177, 1197	ν_{9a}	"
1298	1293	ν_{14}	ring C-C str
1348, 1373	1345, 1370		N-Ph str
—	1454		C-C + N-Ph(?)
1524	1523	ν_{19a}	ring str + ring def
1591	1591	ν_{8b}	ring C-C str
1618	1611	ν_{8a}	ring C-C str

Table IX: Vibrational assignment of the Raman peaks of PR.
Exciting wavelength = 488.0 nm. For explanations of abbreviations
refer to Table II.

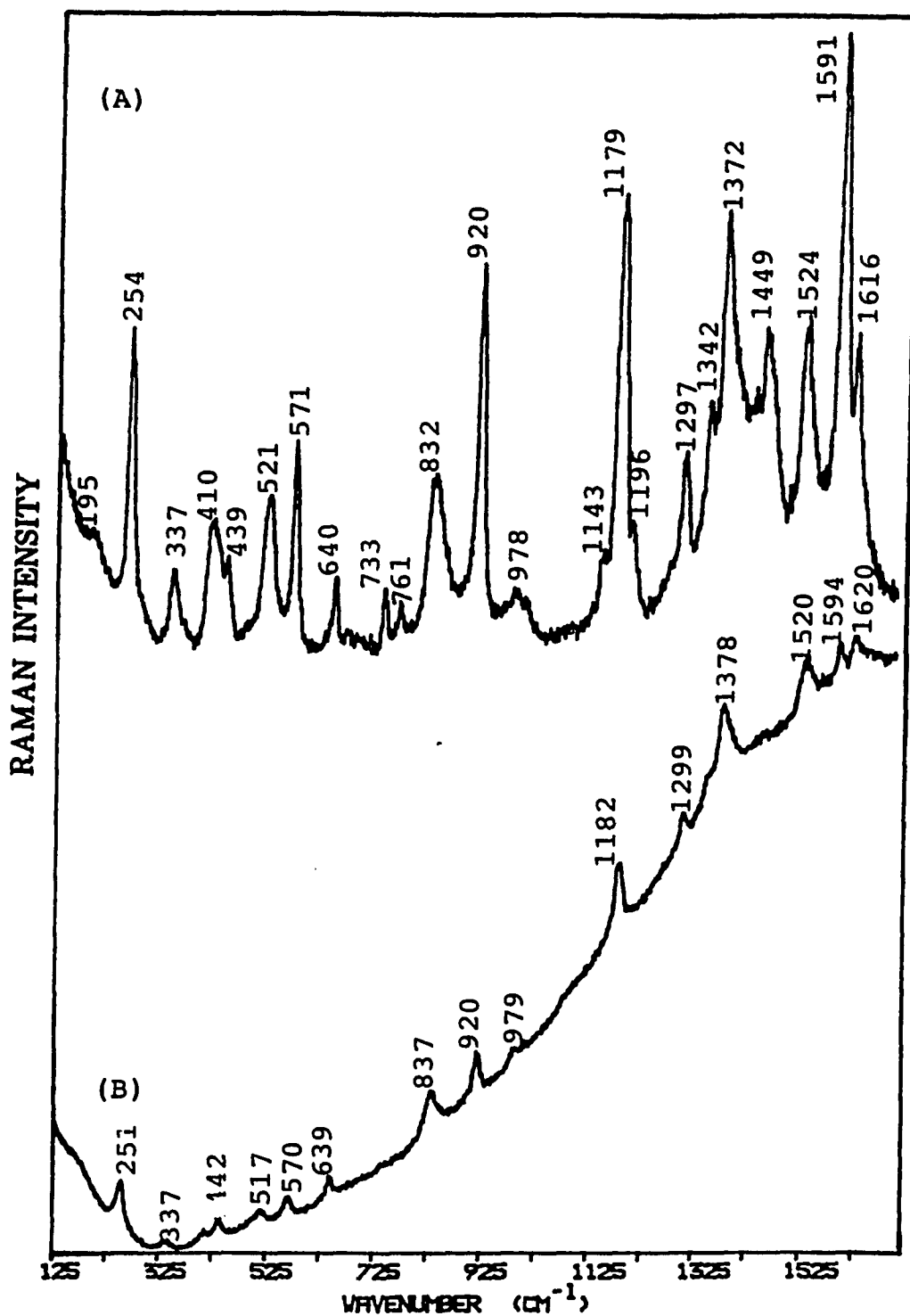


Figure 44. Raman spectra of PR, 10^{-5}M ; 125–1700 cm^{-1} ; exciting wavelength = 514.5nm (A) on colloidal Ag, laser power @ sample = 12mW (B) in solution, laser power = 30mW @ sample.

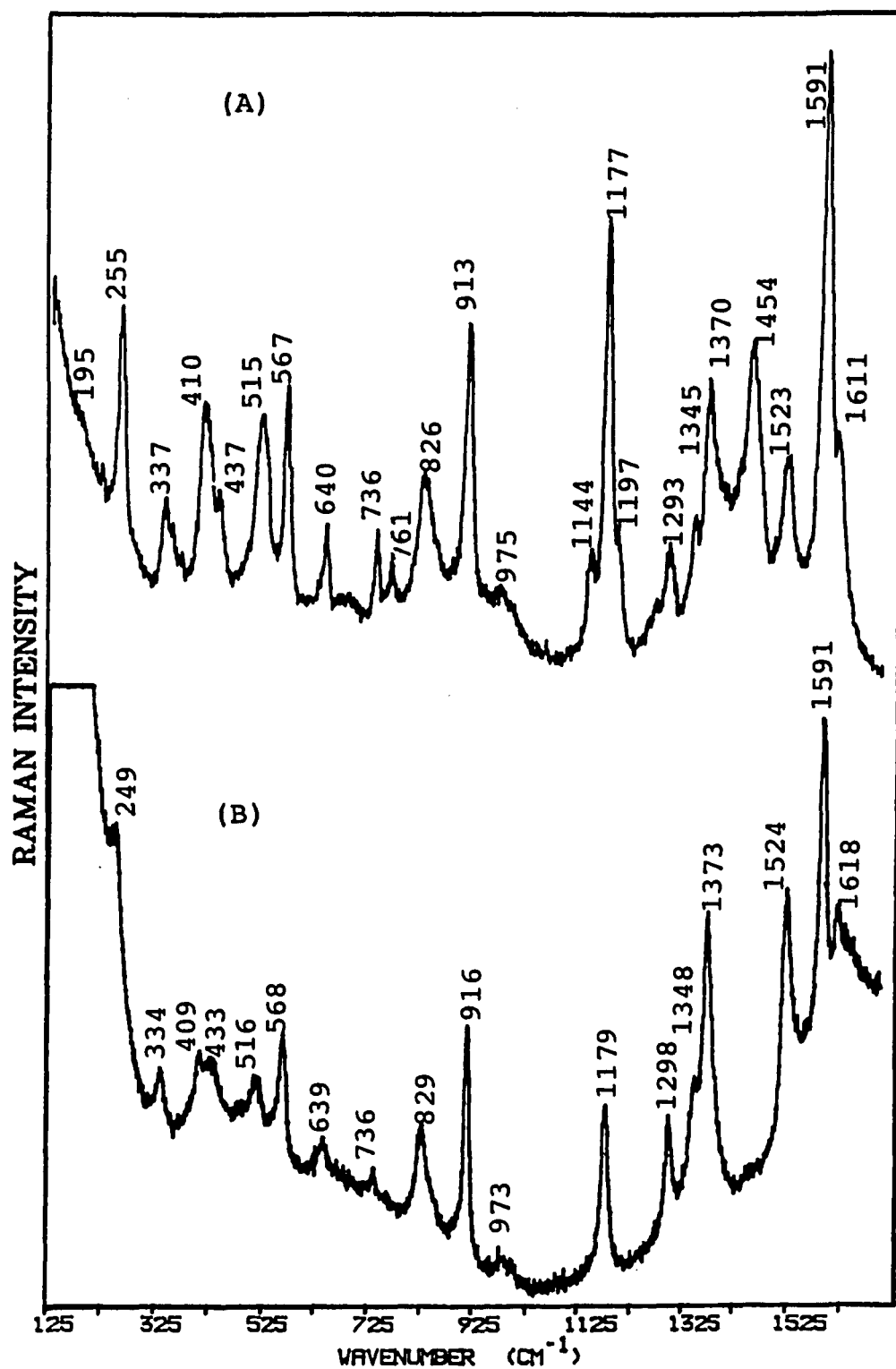


Figure 45. Raman spectra of PR, 10^{-5}M ; $125\text{--}1700\text{cm}^{-1}$; exciting wavelength = 488.0nm (A) on colloidal Ag, laser power @ sample = 12mW (B) in solution, laser power = 30mW @ sample.

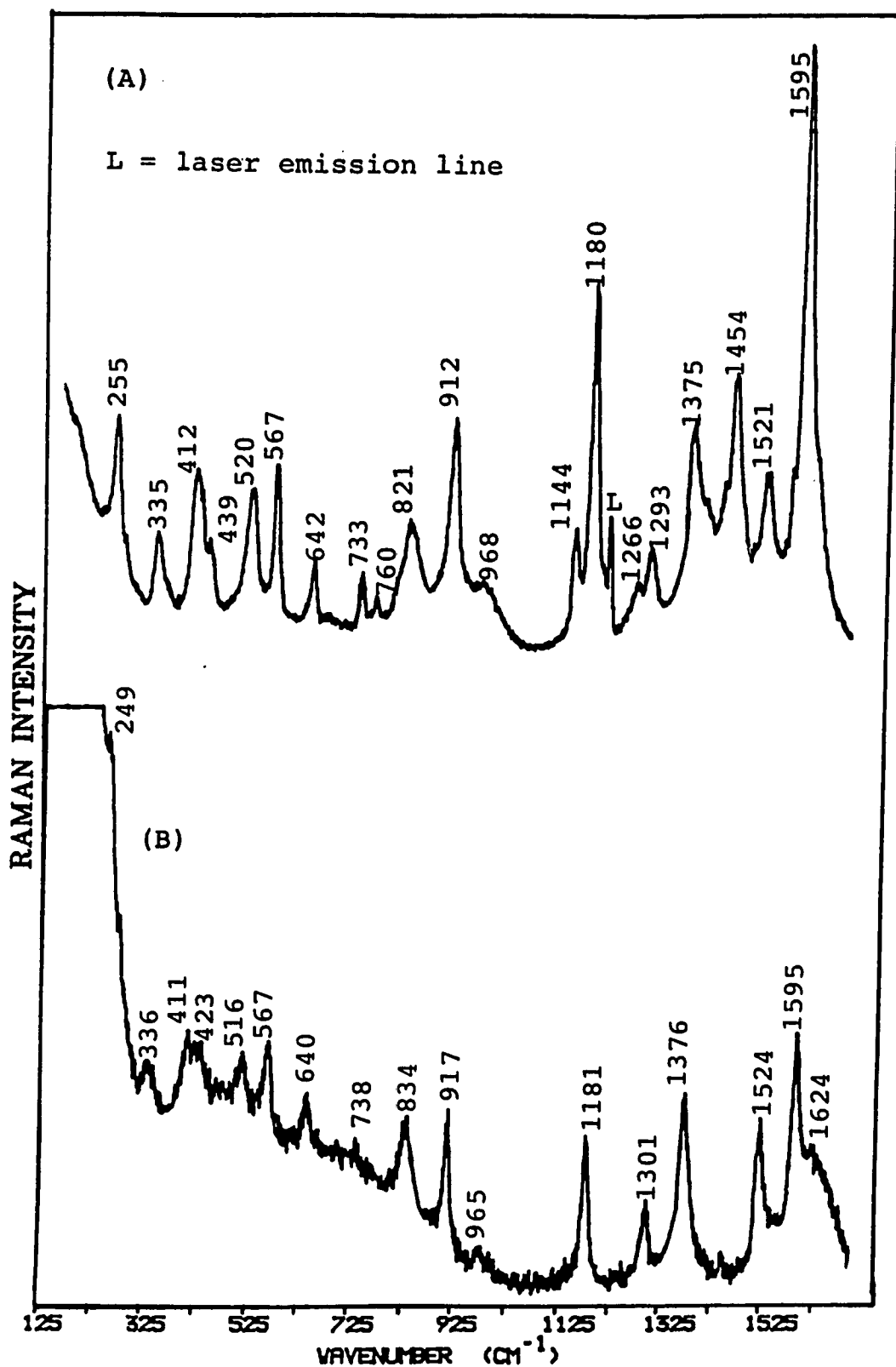


Figure 46. Raman spectra of PR, 10^{-5}M ; $125\text{--}1700\text{cm}^{-1}$; exciting wavelength = 457.9nm (A) on colloidal Ag, laser power @ sample = 12mW (B) in solution, laser power = 30mW @ sample.

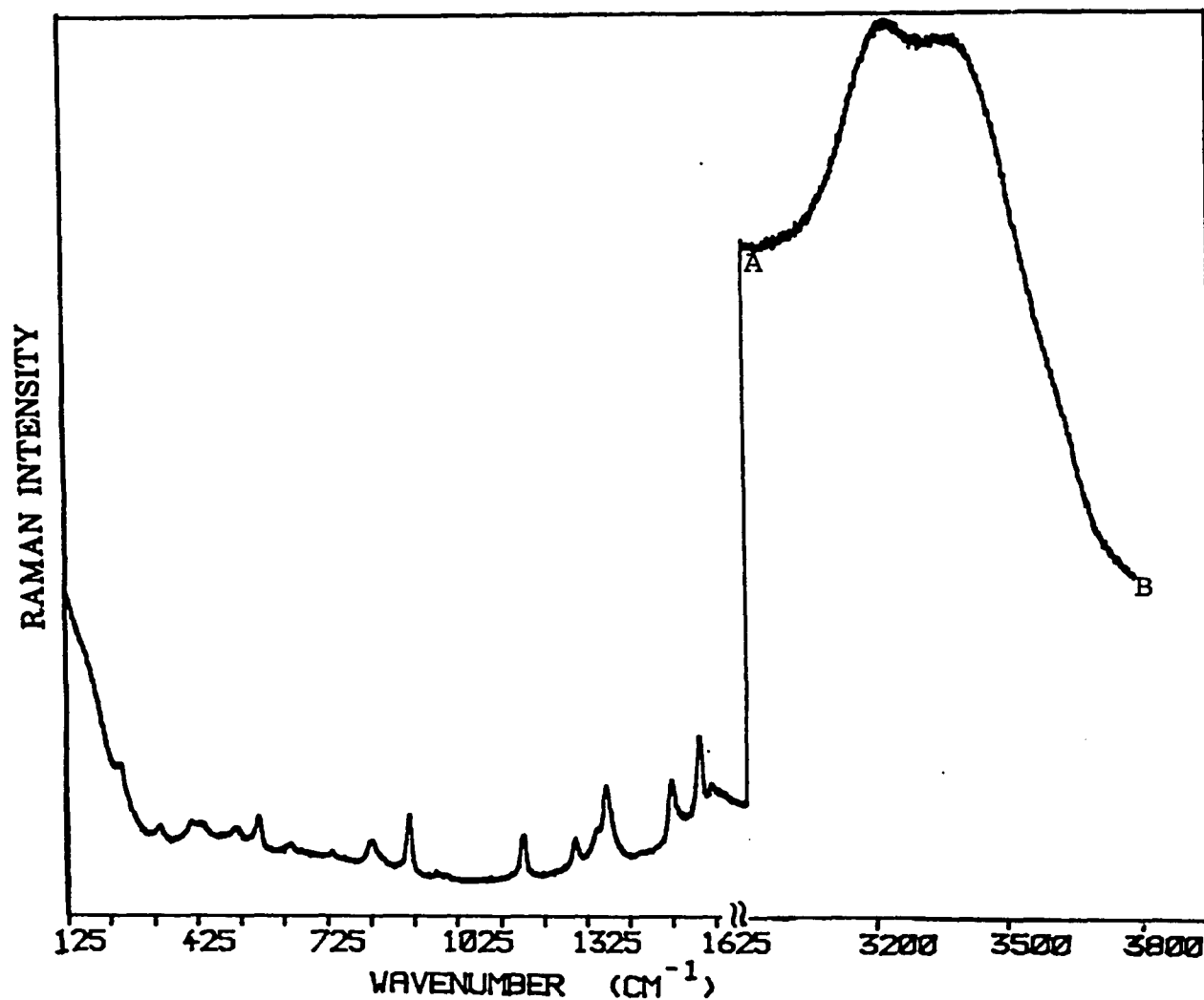


Figure 47. RRS spectrum of PR, 10^{-5}M , laser power @ sample = 30 mW
exciting wavelength = 488.0nm. Region A-B represents the O-H stretching region
of H_2O , 2900–3800 cm^{-1} .

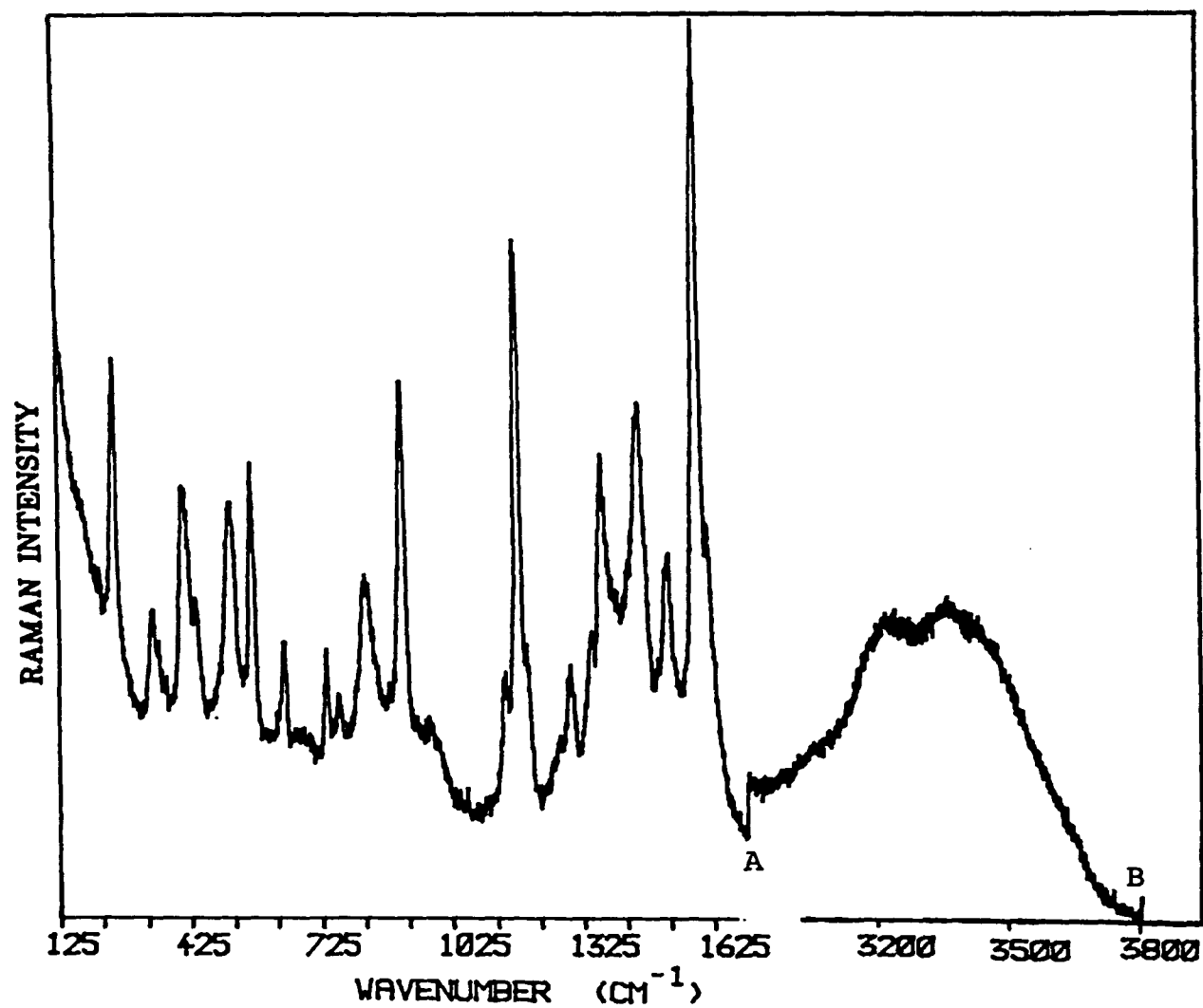


Figure 48. Surface Raman spectrum of PR, 10^{-5}M , laser power @ sample = 12 mW, exciting wavelength = 488.0nm. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800\text{cm}^{-1}$.

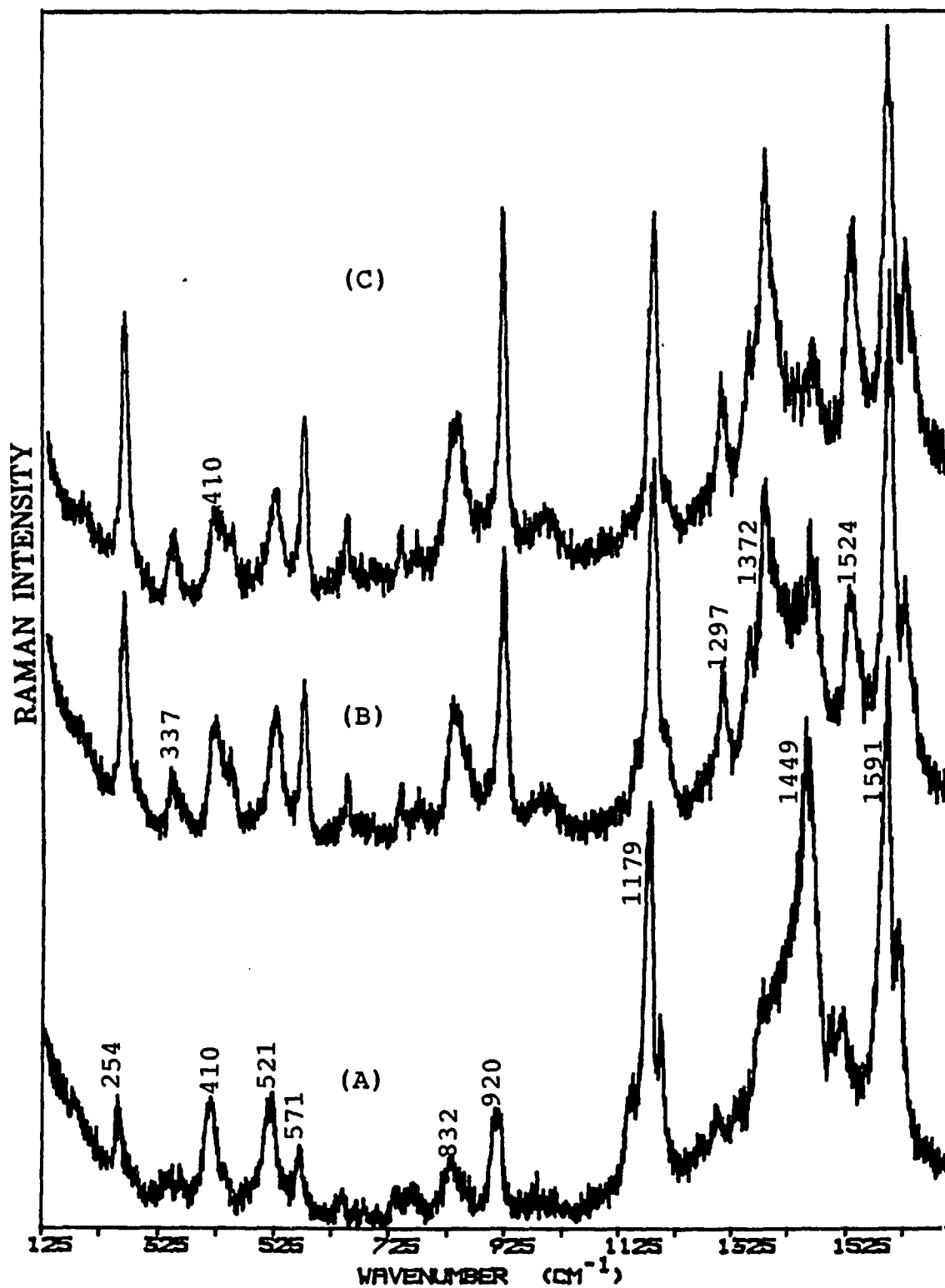


Figure 49. Surface Raman spectra of PR on Agsol, 10^{-5}M , excitation wavelength = 514.5nm (A) sol freshly prepared (B) sol 24 hours old (C) sol 48 hours old.

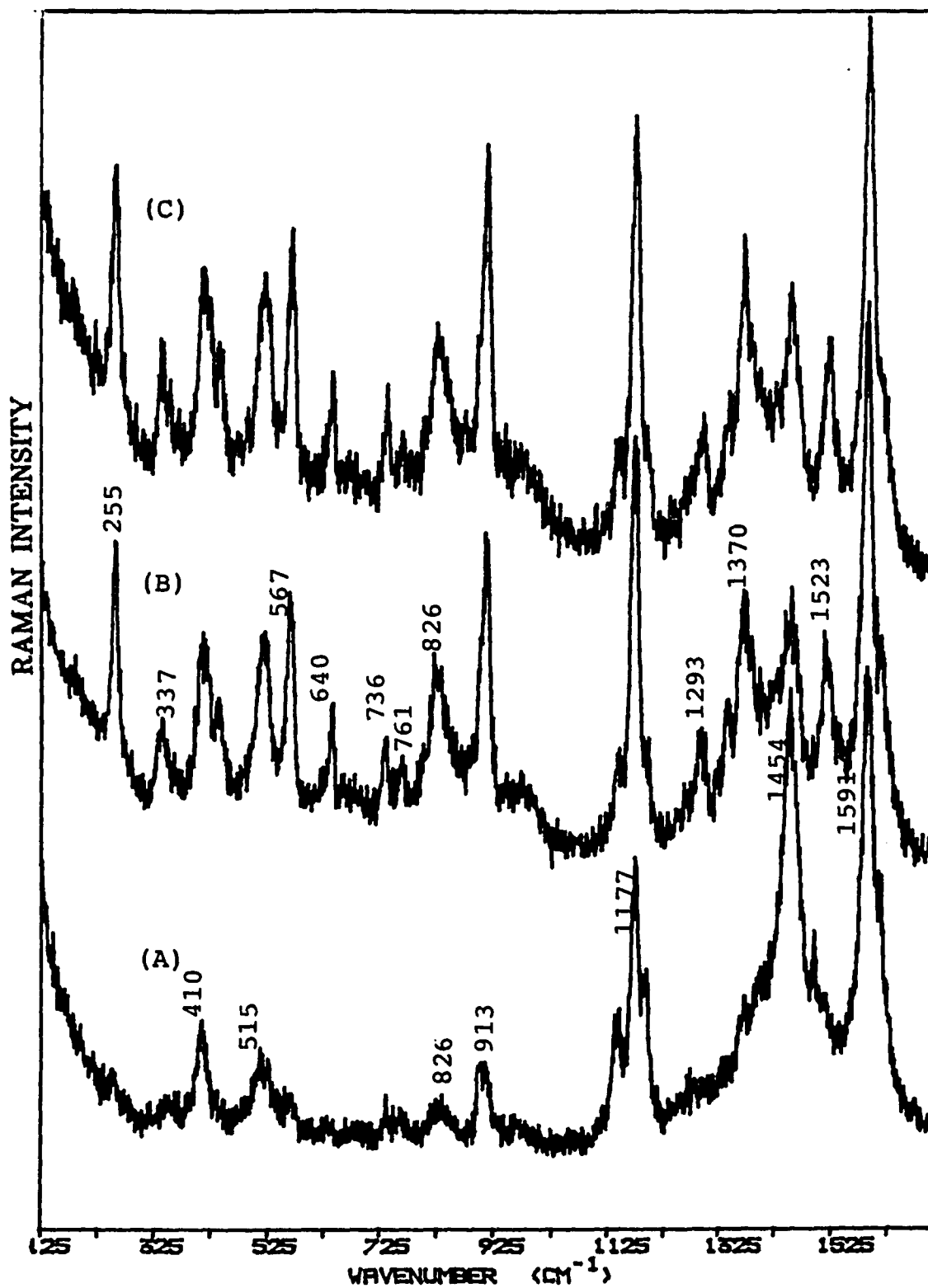


Figure 50. Surface Raman spectra of PR on Agsol, 10^{-5}M , excitation wavelength = 488.0nm (A) sol freshly prepared (B) sol 48 hours old (C) sol 96 hours old.

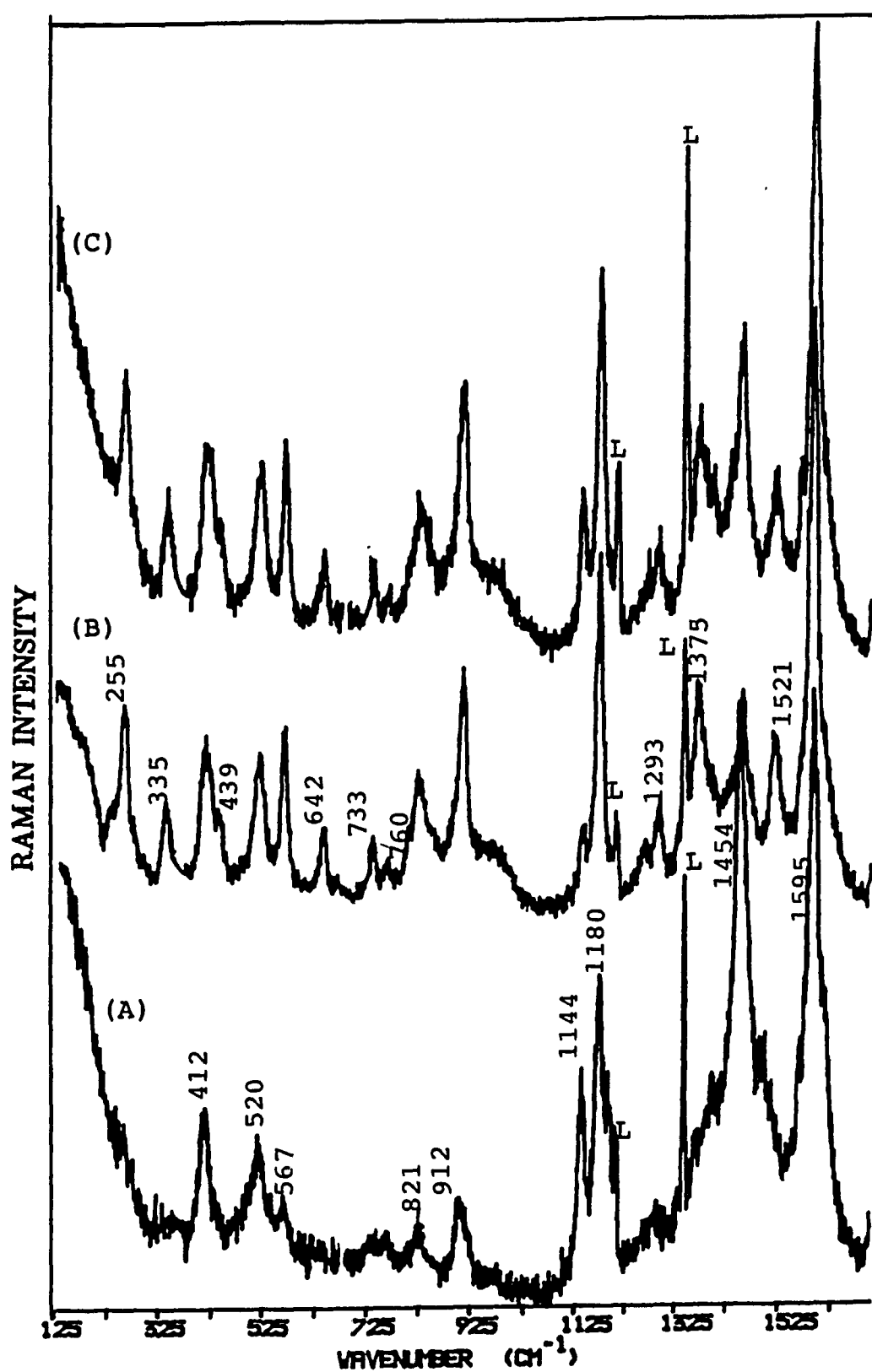


Figure 51. Surface Raman spectra of PR on Agsol, 10^{-6}M , excitation wavelength = 457.9nm (A) sol freshly prepared, (B) sol 48 hours old (C) sol 96 hours old; L = laser emission line.

CHAPTER 8 SURFACE ENHANCED RAMAN SPECTROSCOPY: QUANTITATIVE ANALYSIS

8.1 SURFACE ENHANCEMENT:

To calculate the relative enhancements of the Raman peaks in the surface Raman spectra of the dyes adsorbed on colloidal silver, the following procedure was adopted: the Raman cross-sections of the dye peaks ($\alpha_{(\text{dye})}$) in the solution spectra were calculated relative to the Raman cross-section of the water peak ($\alpha_{(\text{wat})}$). An identical calculation was carried out for the dye peaks in the surface Raman spectra of the dyes adsorbed on to the silver colloid. These two cross sections were then ratioed to obtain a value for the relative enhancement (RE):

$$\text{RE} = \frac{\text{cross-section of dye adsorbed on Ag colloid}}{\text{cross-section of dye in solution}}$$

The values of the cross-sections were calculated from a consideration of the Raman intensities of the peaks corrected for absorption and the concentration of the dyes in solution. The relevant equations are taken from refs. (111-112):

$$I_s = I_0 \alpha_s C_s 10^{-C_s (b_1 \epsilon_i + b_2 \epsilon_s)} , \dots\dots\dots (1)$$

where,

I_s = Observed Raman intensity

I_0 = Incident laser intensity

α_s = Effective Raman scattering cross-section

C_s = Concentration

- ϵ_i = Molar absorptivity at the incident laser frequency
 ϵ_s = Molar absorptivity at the Raman scattered frequency
 b_1 = Distance traveled by the incident beam to the region of scattering (see Fig.52).
 b_2 = Distance traveled by the scattered beam to leave the sample (see Fig.52).

The water peak under the O-H stretching region was used as an internal standard. The peak areas were used as measures of the peak intensities. Equation (1) can be rearranged to obtain expressions for the scattering cross-sections of water, α_{wat} and the dye, α_{dye} :

$$\alpha_{\text{wat}} = \frac{I_{\text{wat}}}{I_0 C_s(\text{wat}) 10^{-[C_s(\text{dye}) \{b_1 \epsilon_i + b_2 \epsilon_{v(\text{wat})}\}]}} \dots (2)$$

where,

- I_{wat} = Intensity of the water peak
 $C_s(\text{wat})$ = Concentration of water (55.555M)
 $C_s(\text{dye})$ = Concentration of the dye solution
 $\epsilon_{v(\text{wat})}$ = Molar absorptivity at the Raman scattered water peak frequency.

I_0 , b_1 , b_2 and ϵ_i have been previously defined, and

$$\alpha(\text{dye}) = \frac{I(\text{dye})}{I_0 C_s(\text{dye}) 10^{-[C_s(\text{dye}) (b_1 \epsilon_i + b_2 \epsilon_{v(\text{dye})})]}} \dots (3)$$

where,

- I_s = Intensity of the dye peak

$\epsilon_v(\text{dye})$ = Molar absorptivity at the Raman scattered
dye peak frequency

From 2 & 3 and using the Beer's law relationship:

$$\epsilon_v = \frac{A_v}{bC} \dots\dots\dots (4)$$

where,

A_v = Absorbance at frequency v

C = concentration of the absorbing species

b = cell path length (= 0.50 cm in these experiments)

one obtains:

$$\frac{\alpha(\text{dye})}{\alpha(\text{wat})} = \frac{I_s(\text{dye}) C_s(\text{wat})}{I_s(\text{wat}) C_s(\text{dye})} 10^{-(C_s(\text{dye}) b_2 [\epsilon_v(\text{wat}) - \epsilon_v(\text{dye})])} \dots\dots\dots (5)$$

$$= \frac{I_s(\text{dye}) 55.555}{I_s(\text{wat}) C_s(\text{dye})} 10^{-2b_2 [(A_{v(\text{wat})} - A_{v(\text{dye})})]} \dots\dots\dots (6)$$

where,

$A_{v(\text{wat})}$ = Absorbance at the Raman peak frequency of the
water = $\epsilon_v(\text{wat}) b C_s(\text{wat})$

$A_{v(\text{dye})}$ = Absorbance at the Raman peak frequency of the
dye = $\epsilon_v(\text{dye}) b C_s(\text{dye})$

So, for each peak, the intensity was measured from the integrated peak area, the absorbance value at the peak frequency was read from the absorption spectrum, and the distance b_2 was measured for each sample scanned. Once these values were obtained they were substituted into equation (6) and a value for the relative scattering cross-section was computed for each peak. Finally the relative

enhancement for each peak was calculated by ratioing $\alpha_{\text{dye-sol}} / \alpha_{\text{dye}}$.

Measurement of the absorbance at the water peak frequency presented a problem. It was found that for all the spectra, the water peak spanned a wide frequency range: from 3000 - 3700 cm^{-1} . For PR, the absorbance values across this region are constant for all three excitation wavelengths used. However for EV and CV the absorbance values changed dramatically sometimes by as much as 60% over this frequency range; thus, it was not accurate enough to just average the values at 3000 cm^{-1} and at 3700 cm^{-1} . Instead the following method was adopted: first a baseline for the water peak was constructed. From this, vertical lines were drawn from the baseline to the peak at intervals of 25 cm^{-1} and the line heights were measured from the baseline to the points of intersection on the water peak. Absorbance values were measured from the absorption spectra at the frequencies corresponding to each line. Each line height was corrected for the absorbance at that particular line frequency using the equation:

$$H_{\text{corrected}} = H_{\text{measured}} \times 10^{2b_2 A_v}$$

where,

$H_{\text{corrected}}$ = line height corrected for absorbance at frequency, ν

H_{measured} = measured line height uncorrected for absorbance

b_2 has been previously defined.

Using the corrected line heights, a new water peak was reconstructed and its area measured, and this value was used as the peak intensity corrected for absorbance. Fig. 53(B) shows an example of a water peak uncorrected for absorbance and Fig. 53(A) shows the reconstructed water peak whose integrated peak area was used as the intensity corrected for absorbance.

If multiple scanning of a single sample was done, the absorbance value at each dye peak frequency was read from the absorption spectra scanned immediately before recording of the Raman spectra. The peak intensities were measured from the spectra resulting from a coaddition of the individual Raman scans.

If single scanning of multiple samples were carried out as in the case of PR-Ag sol mixtures, the absorbance spectrum of each sample mixture was usually scanned before the Raman spectrum. The absorbance at each peak frequency was read from each individual absorption spectrum and the average value of these absorbances was used to correct for the absorption at the peak frequencies. The individual Raman scans were coadded and the peak areas were measured from these coadded spectra.

8.2 RELATIVE INTENSITY

The relative intensities of the peaks were calculated and corrected for absorption at various concentrations.

This relative intensity refers to the ratio: $I_{\text{dye}} / I_{\text{water}}$.

From equation (1), it can be deduced that this ratio =

$$\frac{I_{\text{dye (meas.)}}}{I_{\text{wat (meas.)}}} \times 10^{-2b_2[A_v(\text{wat}) - A_v(\text{dye})]}$$

where $I_{\text{meas.}}$ = integrated peak area

Again with EV and CV, the water peaks were reconstructed as described before and an intensity corrected for absorbance was computed. This correction was necessary at concentrations $\geq 10^{-5}\text{M}$. The above equation is then reduced to:

$$\text{Relative Intensity} = \frac{I_{\text{dye (meas.)}} \times 10^{2b_2 A_v(\text{dye})}}{I_{(\text{water})\text{corrected for absorption}}}$$

All that was required was to substitute the necessary values for the variables and compute the value for the relative intensity.

For concentrations $\leq 10^{-6}\text{M}$, the absorbances were low and the variations across the O-H stretching region were not large. Thus it was not necessary to reconstruct a new water peak.

8.3 SURFACE ENHANCEMENT FACTORS FOR EV, CV & PR

RESULTS & DISCUSSION

Tables X -XII list the surface enhancement factors calculated for peaks in the surface Raman spectra of CV, EV and PR at a concentration of $10^{-5}M$. In calculating these values, no correction has been made for the number of dye molecules present on the surface of the silver colloid. A rough calculation (see Appendix I) using the basic assumption of monolayer coverage indicates that the ratio:

$$\frac{\text{Number of dye molecules on Ag surface}}{\text{Number of dye molecules in } 10^{-5}M \text{ solution}} = 10^{-4}$$

Since 1 in every 10^4 molecules is present on the sol's surface then at $10^{-5}M$ the effective surface enhancements for CV and PR are on the order of 10^5 and 10^6 for EV. The value of 10^5 for CV is 2 orders of magnitude greater than the values previously reported (8,87,89). This is a bit surprising especially since the basic assumption of monolayer coverage was made by us and by ref.(87) However no details were given for the calculated value of 10^3 . Chou et. al. (89) studied the spectrum of CV on Ag films and calculated the enhancements of the Raman scattering cross-sections by comparing the Raman intensities per adsorbed molecule with the Raman intensities per CV molecule in solution. The ratio of the number of adsorbed molecules to the number of molecules exposed to the laser spot in a

solution of CV was reported to be 10^{-2} which is two orders of magnitude higher than our value. The intensities of the SERS peaks were reported to be 1 order of magnitude greater than the RRS peaks; this corresponds to our calculations. Apparently none of the previous studies have corrected for the absorption of the analyte species or measured the intensities relative to an internal standard.

An assessment of the values for PR in Table XII indicates that most of the peaks show a trend of decreasing enhancement with decreasing wavelength of excitation. The 250 cm^{-1} peak is a notable exception, showing the largest enhancement when the exciting wavelength was shifted to 457.9 nm. For each exciting wavelength, a different peak shows maximum enhancement; at 514.5 nm, it is the 1593 cm^{-1} at 488.0 nm, the 409 cm^{-1} peak and at 457.9 nm, it is the peak at 250 cm^{-1} . Thus as the energy of the exciting light decreases the frequency of the peak exhibiting maximum enhancement increases. There are two factors to consider here (59): the frequency dependence of the electromagnetic enhancement and the frequency dependence of the molecular resonance. As the exciting frequency is shifted away from the surface plasmon frequency of Ag it is expected that less enhancement due to electromagnetic effects will be observed. As the frequency shifts away from the absorption peak (540 nm for PR) less enhancement due to resonant scattering will be observed. However, it must be empha-

sized that there is not a large variation among these enhancement values: it is obvious that no single peak is enhanced significantly more than another. This observation is borne out for all of the three compounds. It is interesting that even with the correction for absorbance of the sample, these enhancement values fall far below the hypothetical values which can be as large as 10^8 - 10^{10} if it is considered that the molecular resonance enhancement can combine multiplicatively with the surface enhancement.

8.4 SERS: FIGURES OF MERIT AND DEMERIT

In the course of this study a number of striking features of SERS stood out. It is difficult to generalize and the author thinks it best to discuss these features under the following headings:

- (a). SERS and RRS spectra versus concentration
- (b). Time dependent changes among the intensities of the SERS spectra.
- (c). SERS intensity versus concentration

8.4.1 SERS AND RRS SPECTRA VERSUS CONCENTRATION

It was not possible to observe a RRS spectrum of EV, CV or PR at concentrations $\leq 10^{-6}M$ (see Figs. 54 & 55). By contrast a SERS spectrum could be observed at $5 \times 10^{-8}M$ for all three compounds. However, for CV and PR the observation of a SERS spectrum at concentrations $\leq 10^{-6}M$ required

that the sol be aged first (vide infra). Surface Raman spectra of EV were observed on freshly prepared sols for concentrations ranging from $5 \times 10^{-5}M$ to $1 \times 10^{-7}M$. The aging time required for each concentration and compound are shown in Table XIII. A possible explanation for EV exhibiting a SERS spectrum before the other compounds lies in it having a larger molecular polarizability or its stronger binding to the sol surface. We recall that the EV-sol mixtures were the most stable and took longer to precipitate.

8.4.2 TIME DEPENDENT CHANGES AMONG THE INTENSITIES OF THE SERS SPECTRA

The intensity of the dye peaks were monitored for various concentrations of dye-sol mixtures prepared with sols of various ages. A new sol was prepared for each concentration and compound; the time dependent studies were carried out on the same sol. In these studies a fixed amount of sol was used and only the dye concentration was varied. The observed changes will be discussed for each compound and its respective concentrations.

8.4.2.1 ETHYL VIOLET: $5 \times 10^{-5}M$ - $1 \times 10^{-6}M$

Significant changes in the intensities of the dye peaks measured relative to the water peak are not observed across these concentration ranges. A slight increase is observed as the sol ages to 2-3 days and this is followed by a

slight drop. Fig. 56 (A) shows a plot of the intensity versus time for the 10^{-5}M concentration. Enhanced spectra were observed for the $5 \times 10^{-5}\text{M}$, $1 \times 10^{-5}\text{M}$ and $1 \times 10^{-6}\text{M}$ solutions of EV-sol mixtures immediately after the sol's preparation. The maximum time covered in this study was seven days.

8.4.2.2 ETHYL VIOLET: $5 \times 10^{-7}\text{M}$ - $1 \times 10^{-7}\text{M}$

A strong spectrum was observed for $5 \times 10^{-7}\text{M}$, however a much more intense spectrum is observed as the sol ages to 3 days. The change in relative intensities of the dye peaks are much greater than those at higher concentrations. This observation is clear in the plot shown in Fig. 56(B). While a surface Raman spectrum is observed for $1 \times 10^{-7}\text{M}$ on a freshly prepared sol, it is a weak spectrum. Pronounced enhancement is not observed until the sol has been aged for 7 days (compare Fig. 57 & 58). As with the other concentrations, an increase in the intensity is observed followed by a decrease. The differences among the intensities are much larger (see Fig. 59).

8.4.2.3 ETHYL VIOLET : $7.5 \times 10^{-8}\text{M}$ - $5 \times 10^{-8}\text{M}$

A surface Raman spectrum was not observed for EV at 10^{-8}M ; instead, intermediate concentrations were investigated. It was found that to observe peaks at a concentration of $7.5 \times 10^{-8}\text{M}$, the sol had to be aged for at least seven days. An intense spectrum was not observed until the

sol had been aged for 20 days (Fig.60). The intensity of the peaks decreased as the sol was further aged. At $5 \times 10^{-8}\text{M}$, the sol had to be aged for 30 days before a weak spectrum could be observed. The spectrum is shown in Fig. 61. No further study of this concentration was carried out beyond this time limit.

8.4.2.4 CRYSTAL VIOLET: $5 \times 10^{-5}\text{M}$ - $1 \times 10^{-5}\text{M}$

Large changes among the intensities of the peaks were not observed for these concentrations when the sol was allowed to age. The quality of the spectra did decline - appearing more noisy as the sol aged.

8.4.2.4 CRYSTAL VIOLET: $1 \times 10^{-6}\text{M}$ - $5 \times 10^{-7}\text{M}$

A very weak surface spectrum is observed for CV at 10^{-6}M when it is scanned on a freshly prepared sol. When the sol is aged for 24 hours, a phenomenal change in the relative intensity of the bands is observed (compare Fig.62 & 63). This increase in intensities continues to be observed in the spectrum scanned in the next 48 hours. By the seventh day the intensity of the peaks begin to decrease. Fig.64 gives the relevant plots. For the $5 \times 10^{-7}\text{M}$ mixture, an enhanced spectrum is not observed until the sol has been aged for 5 days. Again the intensities increase and then decrease with time.

8.4.2.5 CRYSTAL VIOLET 1×10^{-7} - $5 \times 10^{-8}M$

The time dependence of the surface Raman peak intensity at $10^{-7}M$ was monitored for a period of 26 days. A spectrum was not observed until the sol was aged for at least 7 days. The quality of the spectrum does improve with time and then starts deteriorating. From Fig. 65 we observe that the dramatic changes in the intensities observed for the previous concentrations are not observed; in fact the intensities are much more constant and the improvement in S/N is not large. It should be noted that of all the three compounds studied, CV exhibited the weakest spectrum at $1 \times 10^{-7}M$ (see Fig.66). For the $5 \times 10^{-8}M$ a weak surface spectrum is not observed until the sol has been aged for 11 days (Fig.67). Fewer peaks are observed at this concentration. Unsuccessful attempts were made to obtain surface Raman spectra at lower concentration.

8.2.4.6 PARAROSANILINE $5 \times 10^{-5}M$ - $5 \times 10^{-8}M$

Some of the spectral changes occurring for PR were described in Chapter 7. Just as for CV and EV, changes among the peak intensities were observed as the sol aged. At $10^{-5}M$ the observed changes were not the same; while for EV and CV the intensities were relatively constant, for PR large changes in the intensities were observed especially during the first 48 hours (see Fig. 68). This was also observed at the various exciting wavelengths used. Although a surface spectrum is observed for PR, $10^{-6}M$, on a freshly

prepared sol, an enhanced spectrum is not observed until the sol has been aged for 2-3 days (compare Figs. 69 & 70). An enhanced spectrum for the 10^{-7}M solution mixture is not observed on a freshly prepared sol; in fact the Raman spectrum observed (see Fig. 71) is identical to that of the sol alone. An enhanced spectrum is observed after the sol has been aged for three days (Fig. 72). The changes observed among the relative peak intensities at this concentration indicate an increase with time followed by a decrease (Fig. 73). For the 10^{-8}M mixture, the spectrum was monitored for 30 days, but no enhanced Raman spectrum of PR was observable. The observed spectrum resembles that of the sol only (Fig. 74).

8.4.3 VARIATION OF SERS INTENSITY WITH CONCENTRATION

To evaluate the potential of SERS as a quantitative tool, the intensities of the dye bands were measured at various concentrations of the dyes, using a fixed concentration of the silver colloid. (In all the mixtures, 2 ml were sampled and these contained 1 ml of $2.5 \times 10^{-4}\text{M}$ Ag colloid.

Figs. 75-77 show the log plots of relative intensities versus concentrations of EV, CV and PR. A discussion of the change in relative intensity with time preceded this section and an important question arises as to which intensity should be considered. In this study SERS intensity for the peaks at $5 \times 10^{-5}\text{M}$ and $1 \times 10^{-5}\text{M}$ were measured from

the coadded spectra of the various sol-dye mixtures obtained over 2-7 days. At concentrations $\leq 10^{-6}\text{M}$ where it was observed that there were larger variations among the intensities the SERS intensity was measured from the strongest spectrum obtained over the time period studied.

A linear variation with concentration is not observed even though the intensities have been corrected for absorption. Linearity is observed for EV and CV at concentrations $\leq 5 \times 10^{-7}\text{M}$. The lowest concentration studied was 10^{-8}M and while a surface Raman spectrum could not be observed at this concentration, one could be observed at $5 \times 10^{-8}\text{M}$. The latter concentration thus marks a cutoff point for a detection limit for SERS, using this particular concentration of sol and this silver colloid. The intensity values remain almost constant at concentrations $\geq 5 \times 10^{-7}\text{M}$; probably indicating a saturation point. A linear variation is observed for concentrations $\leq 5 \times 10^{-7}\text{M}$. This observation overlaps with Tran's quantitative studies of the SERS signals of CV at the nanogram level (70) (we estimated the concentration ranges in ref.(70) to be $\sim 10^{-6}$ - $5 \times 10^{-8}\text{M}$). Burstein et al. (88) reported that the SERS signals for CV on a Ag electrode were independent of the concentrations between 10^{-7} and 10^{-4}M ; a linear variation was observed at concentrations below 10^{-7}M . These observations are in accordance with ours, although a study of the 10^{-4}M concentration was not done by us. In contrast to our

results, Vo-Dinh et al. (72) have reported linear SERS signals of 1-aminopyrene on Ag-sphere-coated filter paper for concentrations ranging from $5 \times 10^{-6} \text{M}$ to $2 \times 10^{-4} \text{M}$. Linear calibration curves were also reported for benzoic acid from 10^{-6}M to 10^{-3}M and for carbazole from 10^{-7}M to 10^{-3}M .

The plot for PR (Fig.77) indicates a dramatic decrease in SERS intensity when the concentration is lowered from 10^{-5}M to 10^{-6}M . This is attributed to the fact that enough time was not allotted to obtain the "most enhanced" spectrum at this concentration of PR. Spectral data was obtained only over a period of three days and it is quite possible that it could have required a longer time to obtain a larger degree of enhancement.

The lowest detectable concentration in this study was $5 \times 10^{-8} \text{M}$; this does not represent an impressive limit of detection (LOD), but it does not deviate from previous reports. It should be noted that no attempts were made to "activate" the sol by introducing foreign ions like Cl^- . Hildebrandt & Stockburger (108) studied R6G on Ag sols, and reported intensities for concentrations as low as 10^{-8}M . For a R6G/sol/ Cl^- systems, concentrations as low as 10^{-11}M could be studied. Taylor et al. have recently reported an impressive LOD of 10^{-12}M for a CV/citrate sol/ Cl^- system (113). These observations certainly point out the complexity of the adsorption process of the dyes on the SERS

substrate.

That the SERS intensities are not constant with time remains the limiting factor to the use of SERS on silver colloids for quantitative analyses. It is evident that the silver colloids are changing with time - possibly aggregating. However such a process is not obvious from the lack of changes in the absorption spectra of the sol which are monitored over the time period during which the sol is being used. The only changes observed are (1) a rise in the absorbance values at the wavelength of maximum absorption and (2) a slight broadening of the spectrum; no significant shifts in the absorption peak frequencies are observed.

The problem of the variation in SERS intensities is not unique to this work, rather it is one that has plagued a number of previous workers investigating SERS on Ag colloids. It should be noted, however, that Soper and Kuwana have reported recently that by depositing the Ag sol-dye mixture onto a supporting matrix such as aluminum oxide, stable SERS signals could be obtained for long periods (57).

SERS cm ⁻¹	RRS cm ⁻¹	ENHANCEMENT FACTOR
205	197	47.33
333	327	75.97
420	417	42.87
524	518	42.77
558	553	40.92
608	599	29.60
722	720	43.28
741	739	71.01
756	753	34.33
802	807	48.47
913	914	36.59
941	937	60.69
979	977	30.45
1174	1174	34.43
1294	1299	21.33
1365	1368	30.63
1443	1448	20.00
1478	1477	23.28
1537	1540	24.60
1585	1585	68.12
1620	1620	44.84

Table X: Calculated enhancement factors for peaks of CV.

RRS cm ⁻¹	SERS cm ⁻¹	ENHANCEMENT FACTOR
200	209	534.94
442	442	226.98
526	513,529	181.57
564	567	146.67
601	599	81.10
707	708	216.88
747	747	257.70
763	759	218.13
825	828	227.11
919	917	184.0
994	992	216.96
1078	1076	199.05
1163	1162	262.33
1192	1188	221.94
1304	1302	157.11
1375	1371	112.29
1422	1423	234.00
1449	1457	70.59
1494	1492	156.65
1536	1535	151.32
1588	1584	94.81
1620	1621	210.34

Table XI: Calculated enhancement factors for peaks of EV.

RRS (cm^{-1})	SERS (cm^{-1})	514.5 (nm)	488.0 (nm)	457.9 (nm)
250	255	20.79	20.99	62.85
336	336	36.33	17.51	15.17
409,438	411,438	41.04	37.76	13.17
516	519	42.14	31.81	19.15
568	568	27.83	12.11	12.20
639	641	11.24	9.37	7.21
733	734	no	13.62	18.76
833	826	14.56	10.42	12.84
918	915	29.60	10.12	12.81
1181	1179	32.43	27.57	18.82
1299	1294	19.58	8.64	14.02
1348, 1376	1343, 1372	9.96	4.51	6.04
1523	1523	13.33	4.26	5.60
1593	1592	57.81	15.45	26.72
1619	1617	6.73	6.40	vw

Table XII: Calculated enhancement factors for PR.
 (The averaged wavenumber positions are reported here).
 vw = very weak, no = not observed.

CONCENTRATION (M)	AGE OF SOL NECESSARY TO OBSERVE A SURFACE RAMAN SPECTRUM		
	CV	EV	PR
5×10^{-5}	fresh sol	fresh sol	fresh sol
1×10^{-5}	fresh sol	fresh sol	fresh sol
1×10^{-6}	fresh sol	fresh sol	fresh sol
5×10^{-7}	6 days	fresh sol	NS
1×10^{-7}	7 days	fresh sol	2 days
7.5×10^{-8}	NS	7 days	NS
5×10^{-8}	32 days	30 days	30 days

Table XIII. Comparison of the sol's age necessary for the observation of a surface Raman spectrum for CV, EV, & PR at various concentrations.

(NS = not studied).

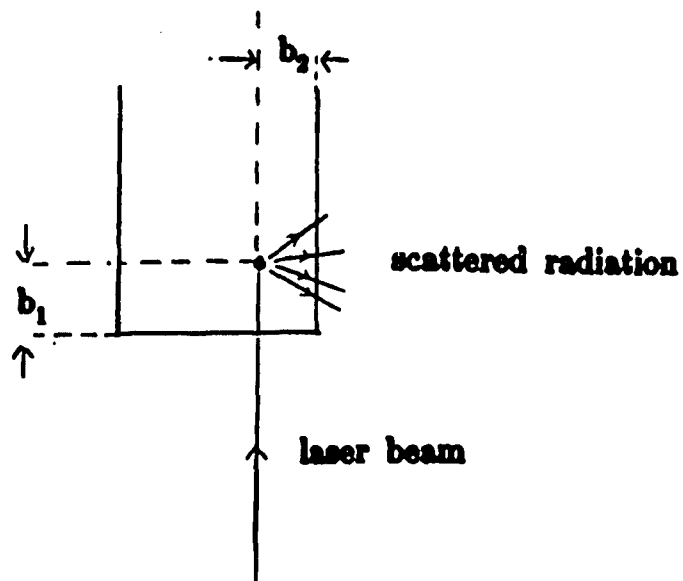


Figure 52. Definition of b_1 and b_2 .

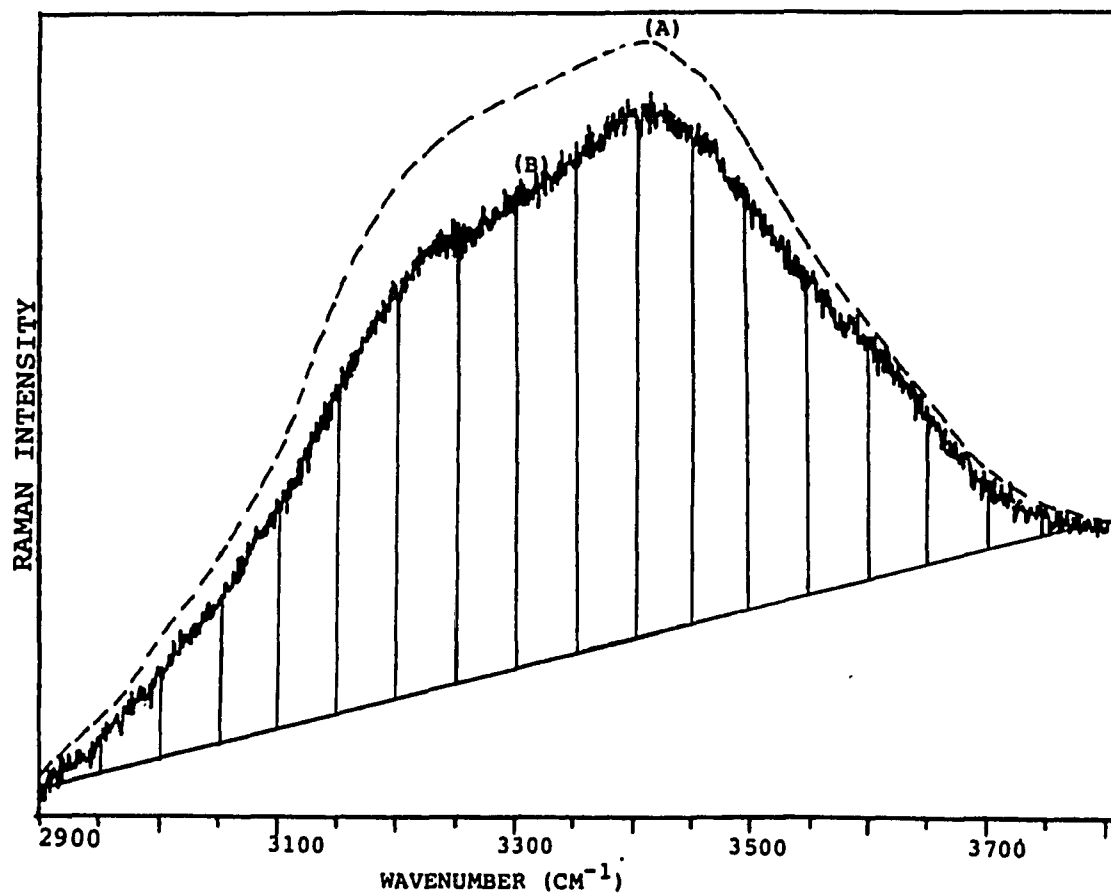


Figure 53. Water peak of CV, $10^{-6}M$, (A) after correction for absorbance & (B) before absorbance correction.

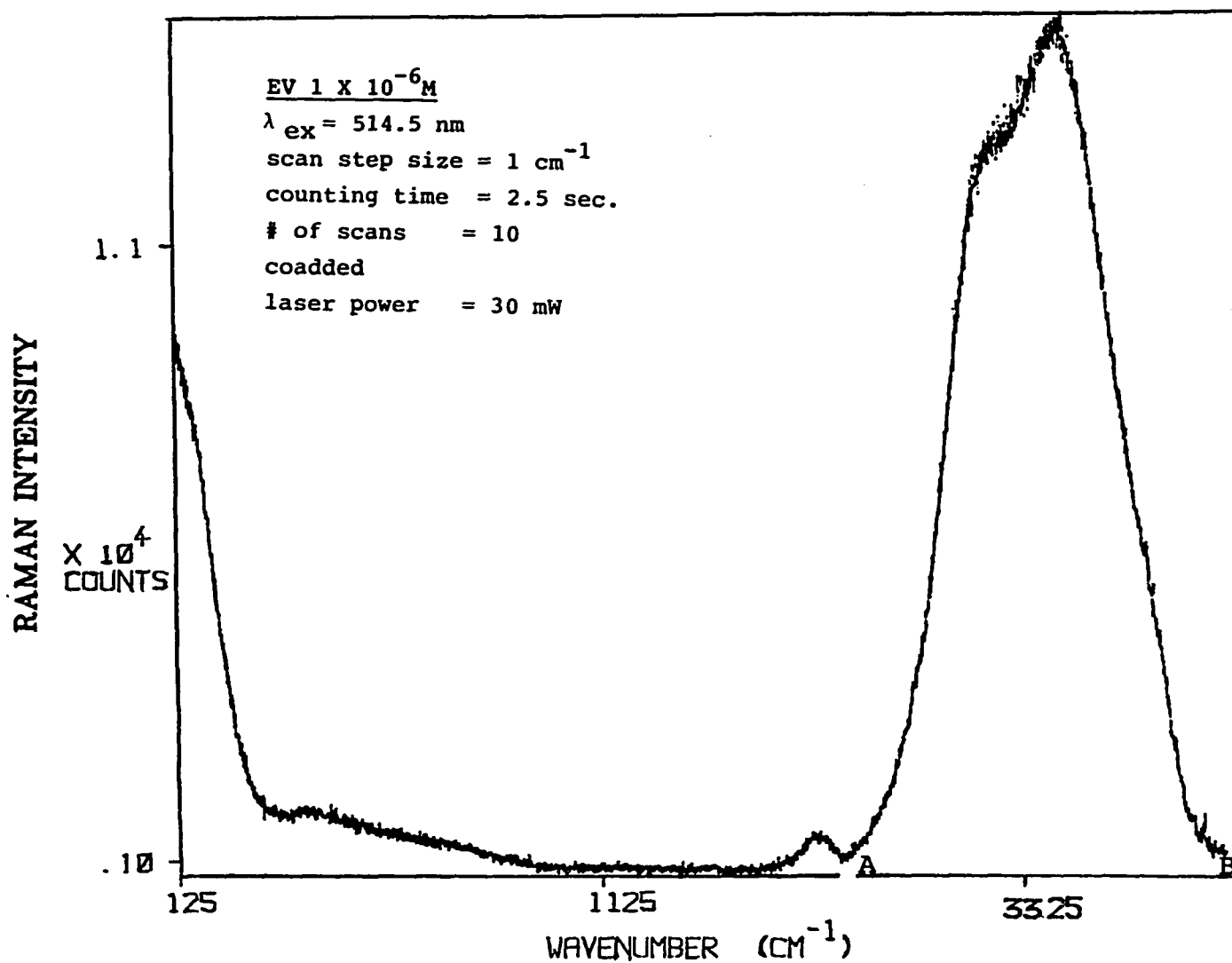


Figure 54. Solution RRS spectrum of EV, $1 \times 10^{-6}M$. Region A-B represents the O-H stretching region of H_2O , $2900 - 3800\text{ cm}^{-1}$.

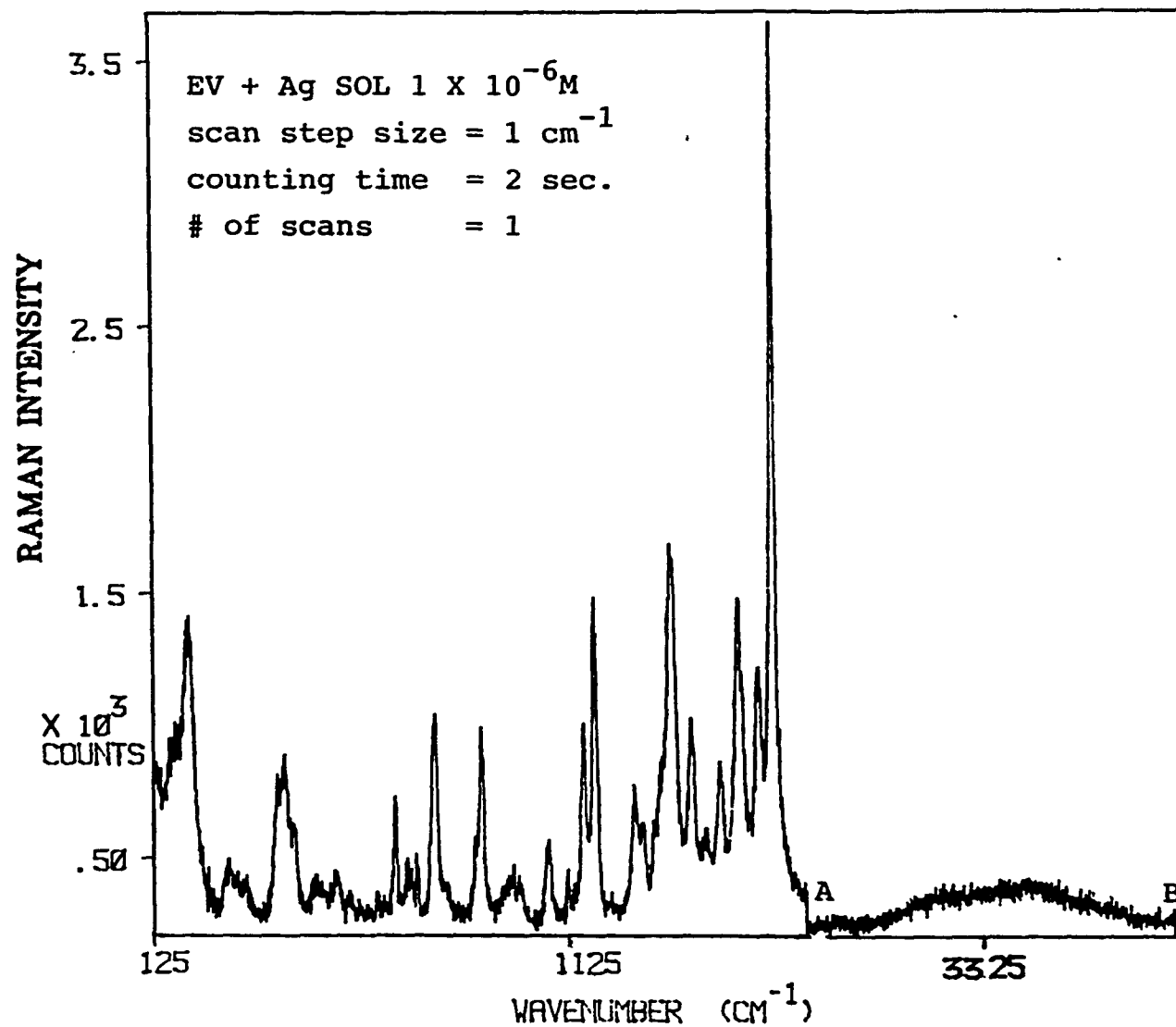


Figure 55. SERS spectrum of EV, 10^{-6}M on freshly prepared Ag sol. Region A-B represents the O-H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$.

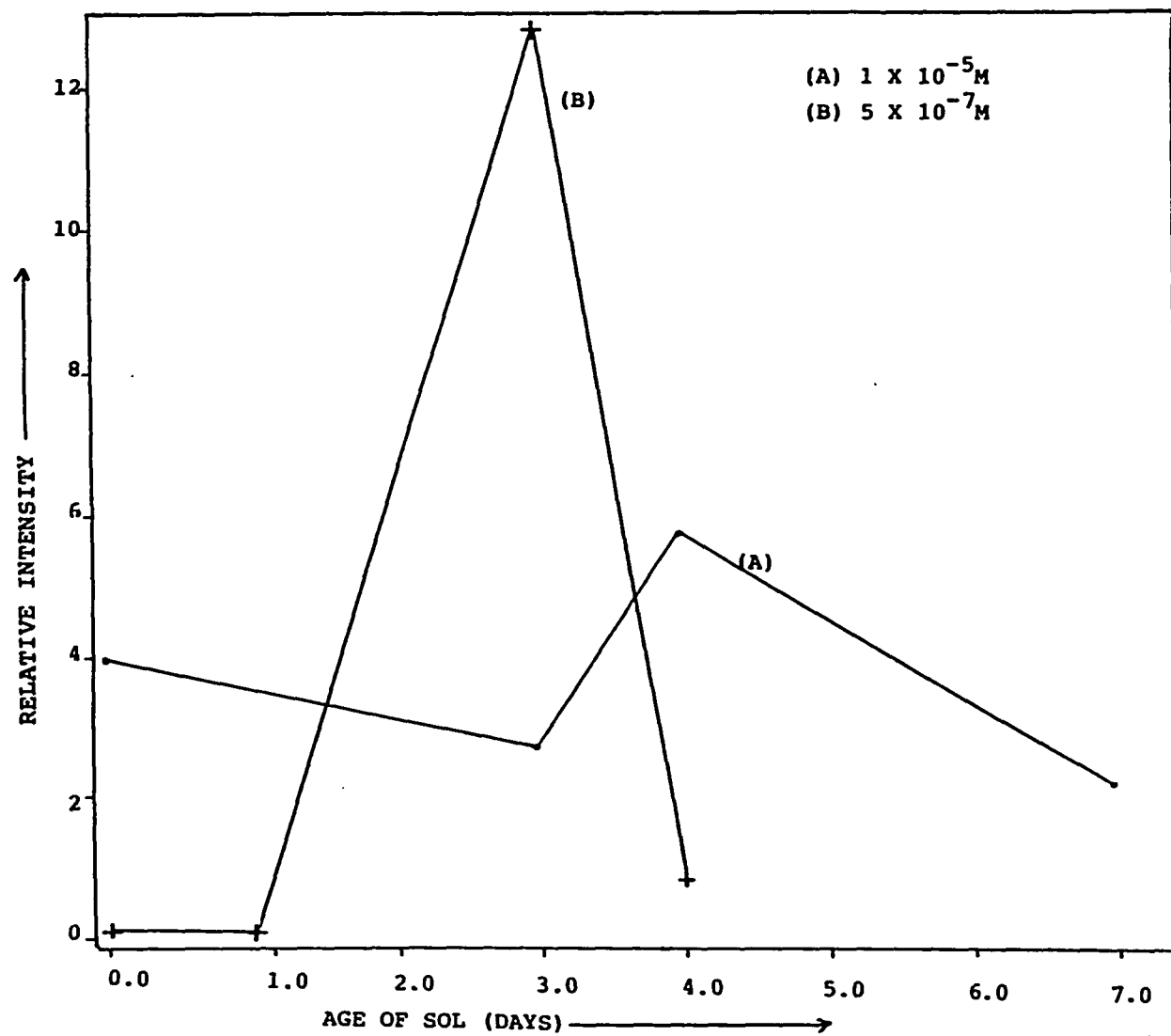


Figure 56. Variation of SERS intensity with sol's age for the 1620 cm^{-1} peak.

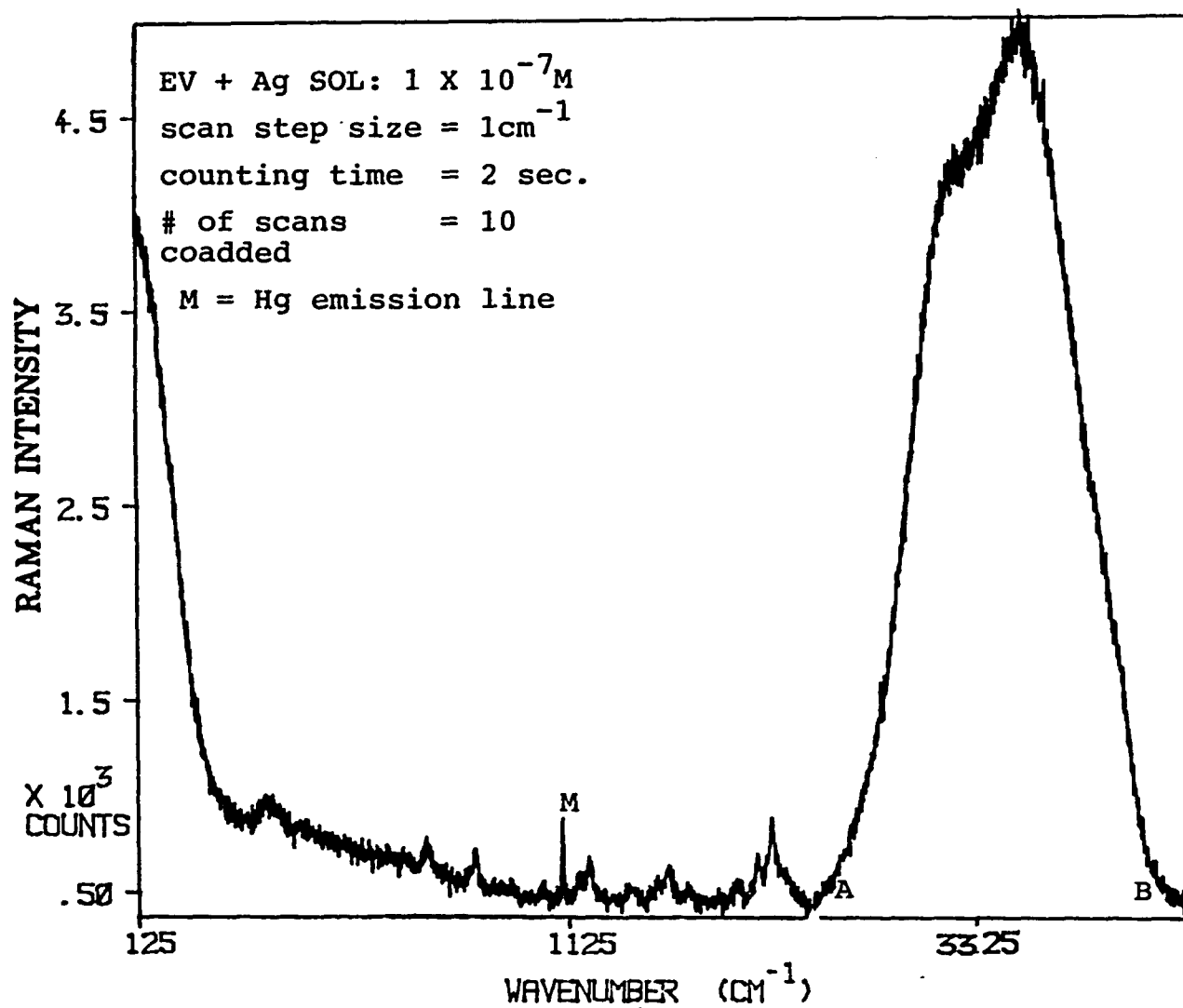


Figure 57. SERS spectrum of EV, $10^{-7} M$ on freshly prepared Ag sol.
 Region A-B represents the O-H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$

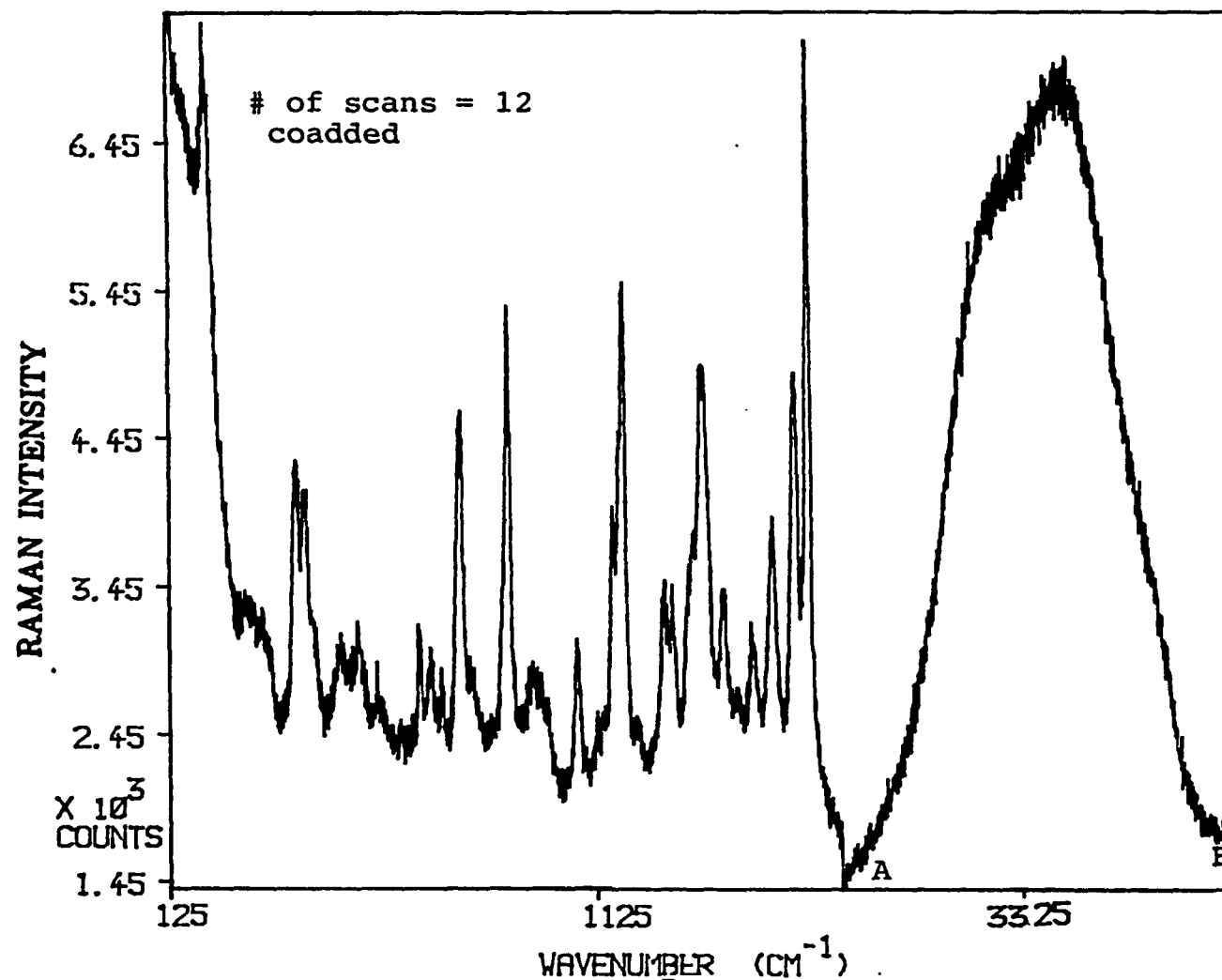


Figure 58. SERS spectrum of EV, 10^{-7} M on Ag sol. Age of sol = 7 days. Region A-B represents the O-H stretching region of H_2O , $2900 - 3800 \text{ cm}^{-1}$. Scanning conditions: as in Figure 57.

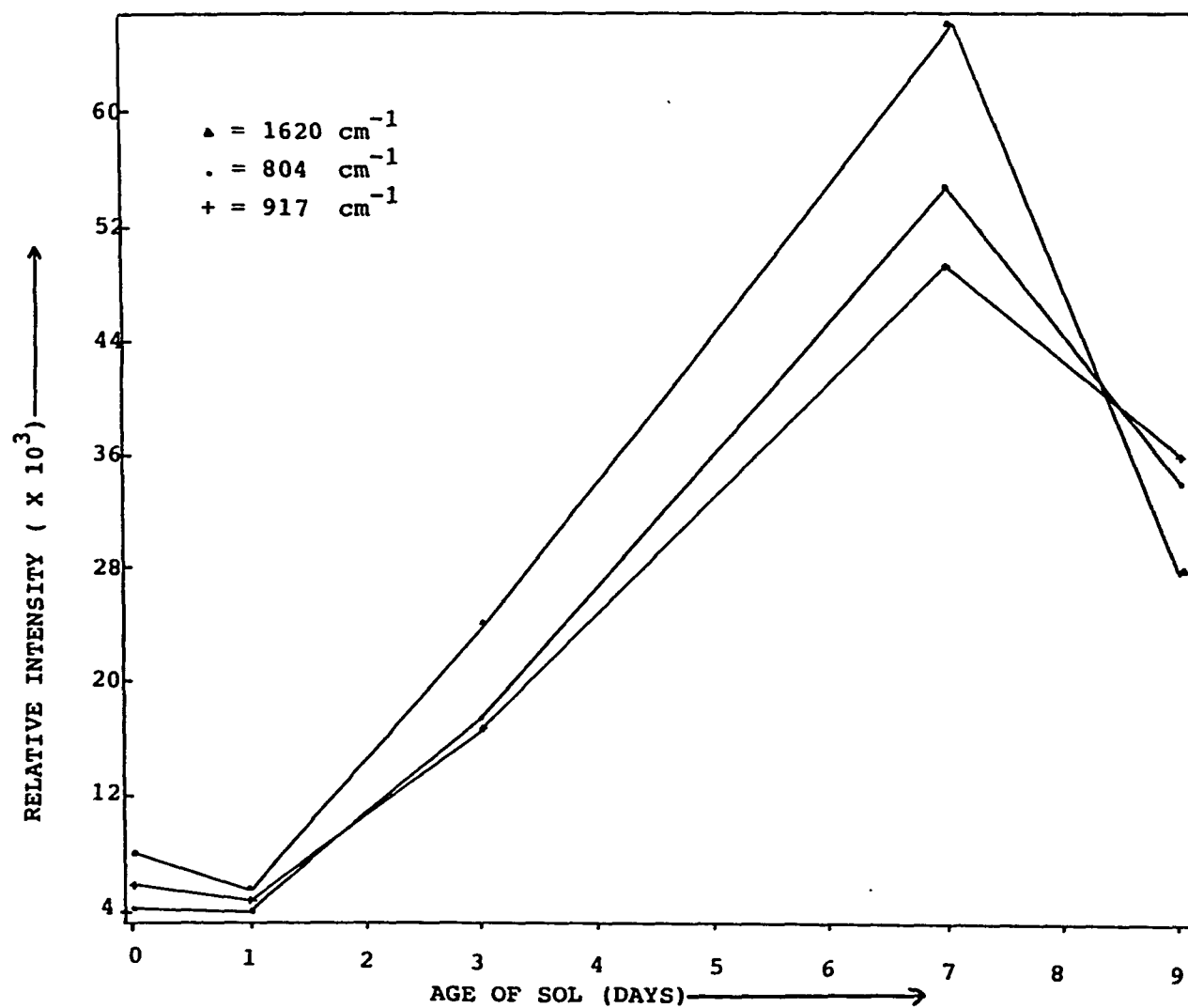


Figure 59. SERS intensity versus sol's age for peaks of EV, 10^{-7}M on Ag sol.

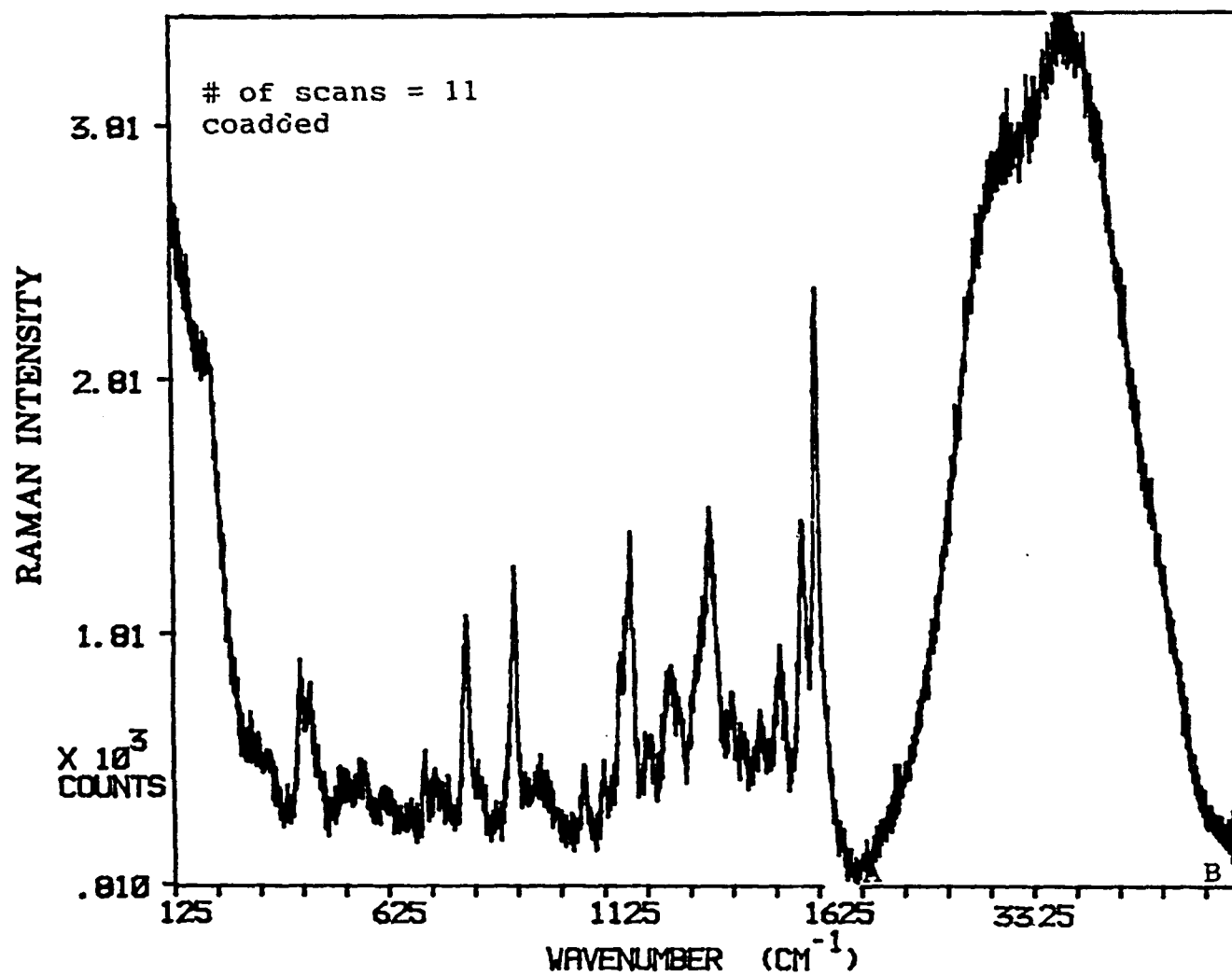


Figure 60. SERS spectrum of EV, $7.5 \times 10^{-8} \text{ M}$ on Ag sol. Age of sol = 20 days. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800 \text{ cm}^{-1}$.

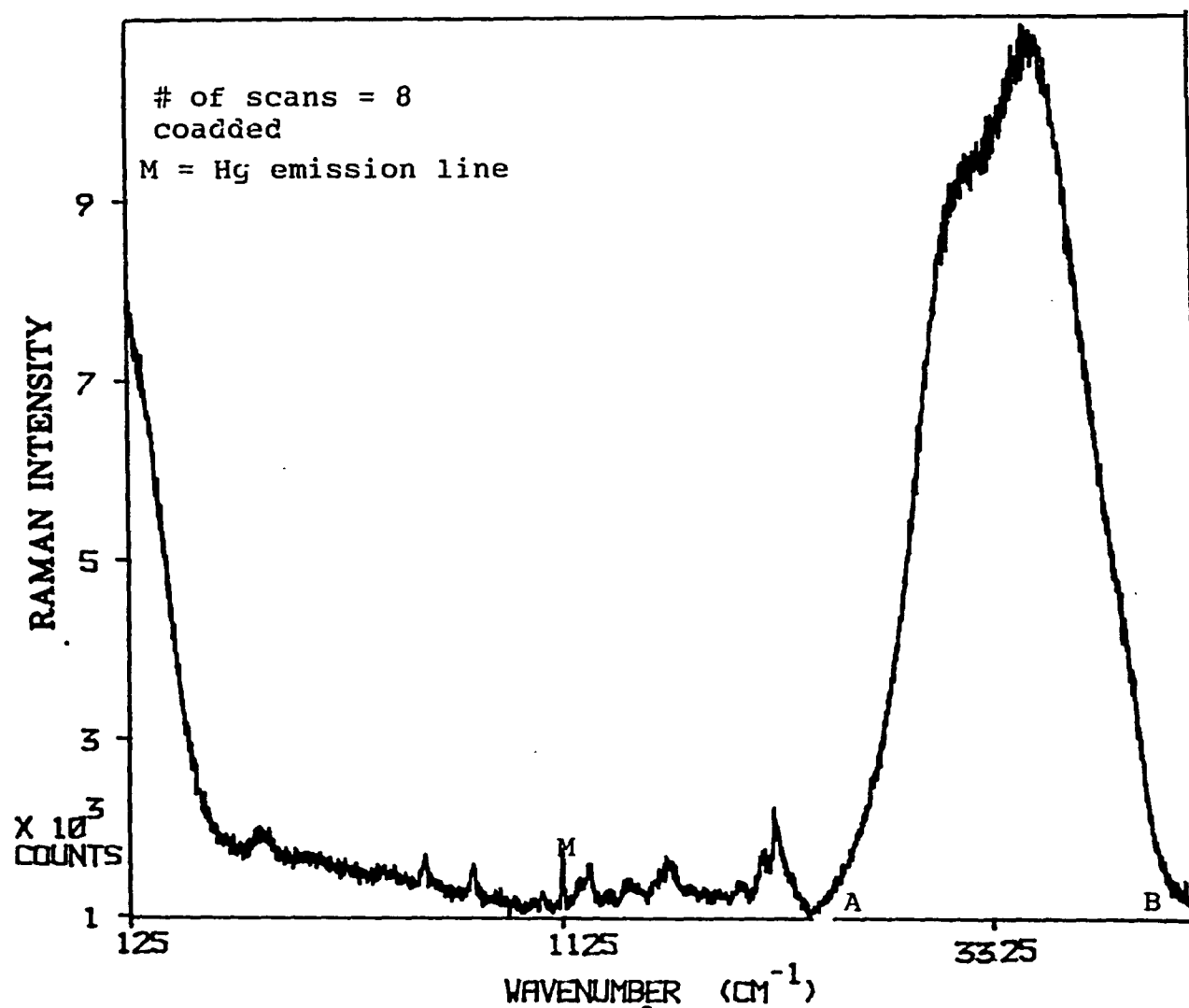


Figure 61. SERS spectrum of EV, $5 \times 10^{-8} \text{M}$ on Ag sol. Age of sol = 30 days. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800 \text{ cm}^{-1}$.

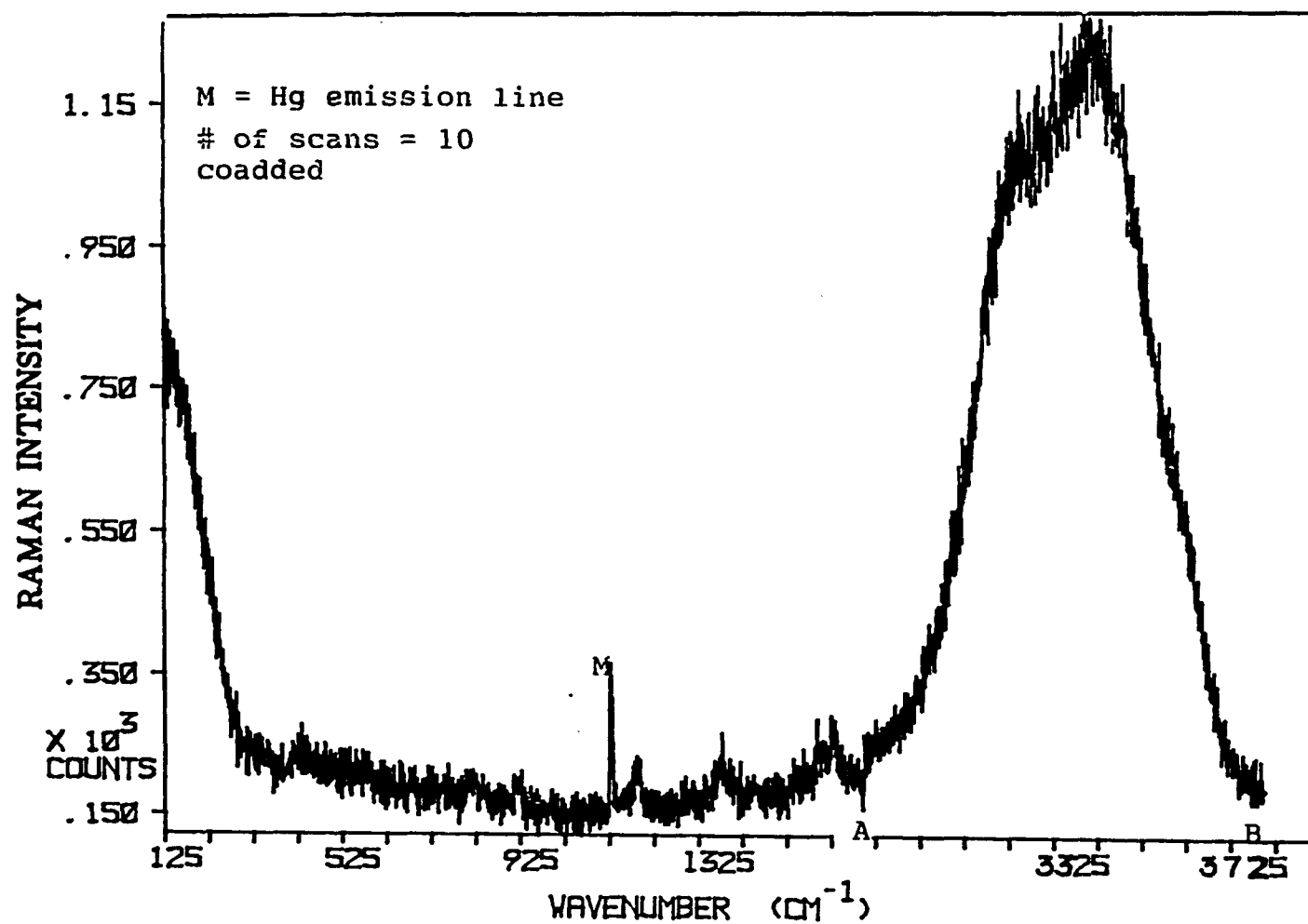


Figure 62. SERS spectrum of CV, 10^{-6} M on freshly prepared Ag sol.
 Region A-B represents the O-H stretching region of H_2O , $2900-3800\text{ cm}^{-1}$.

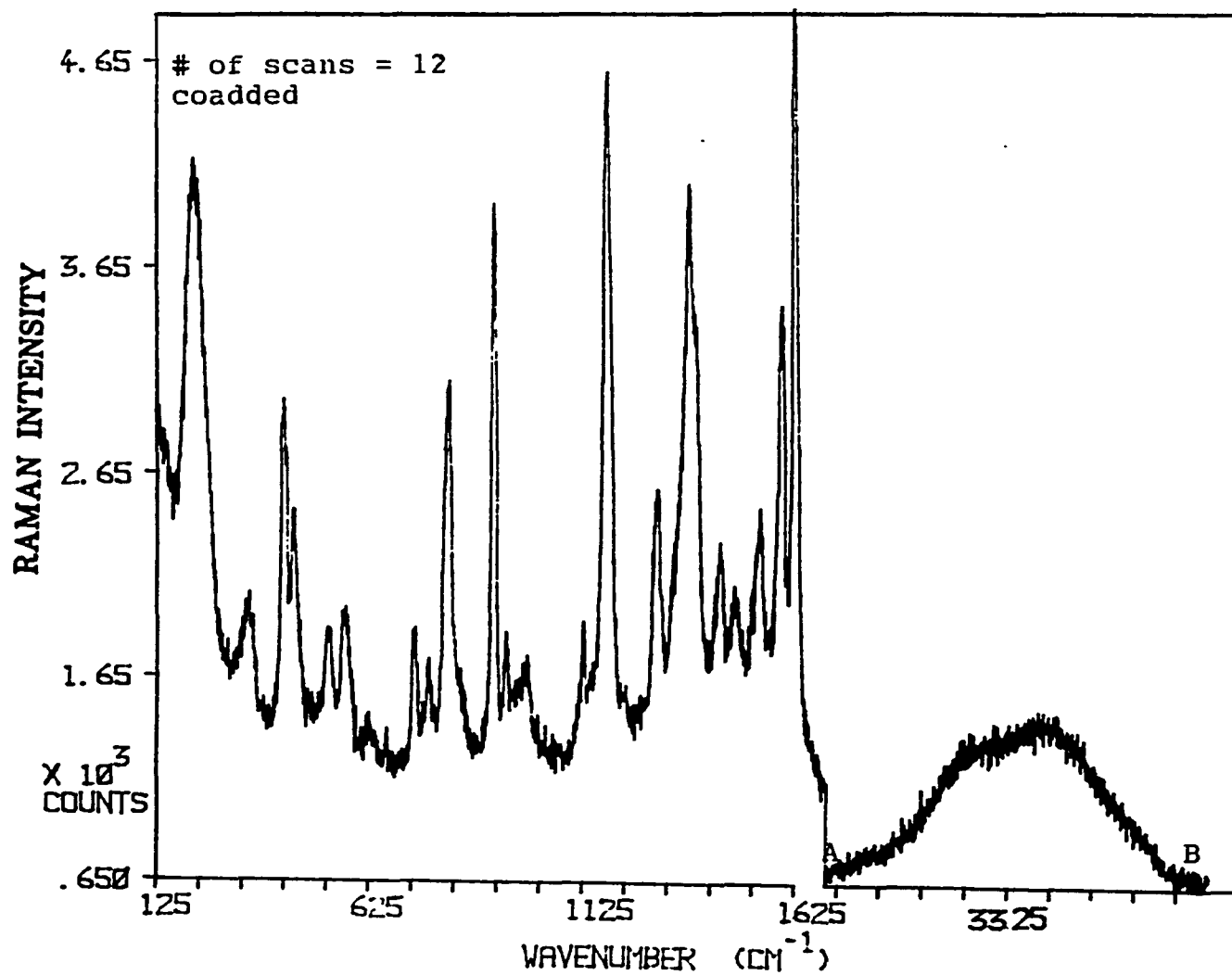


Figure 63. SERS spectrum of CV, 10^{-6}M on Ag sol. Age of sol = 24 hours. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800\text{ cm}^{-1}$.

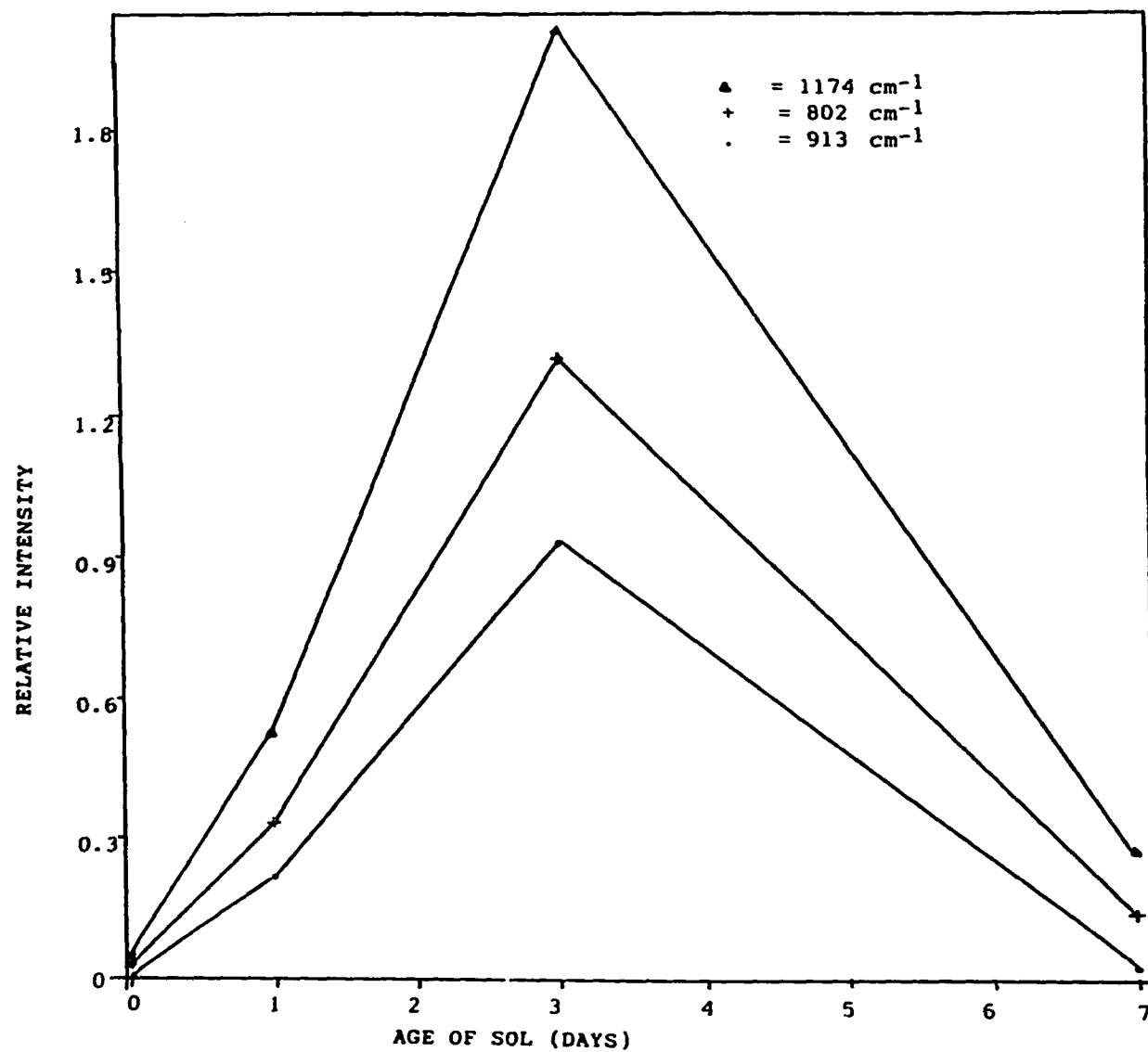


Figure 64. SERS intensity versus sol's age for peaks of CV, 10^{-6} M on Ag sol.

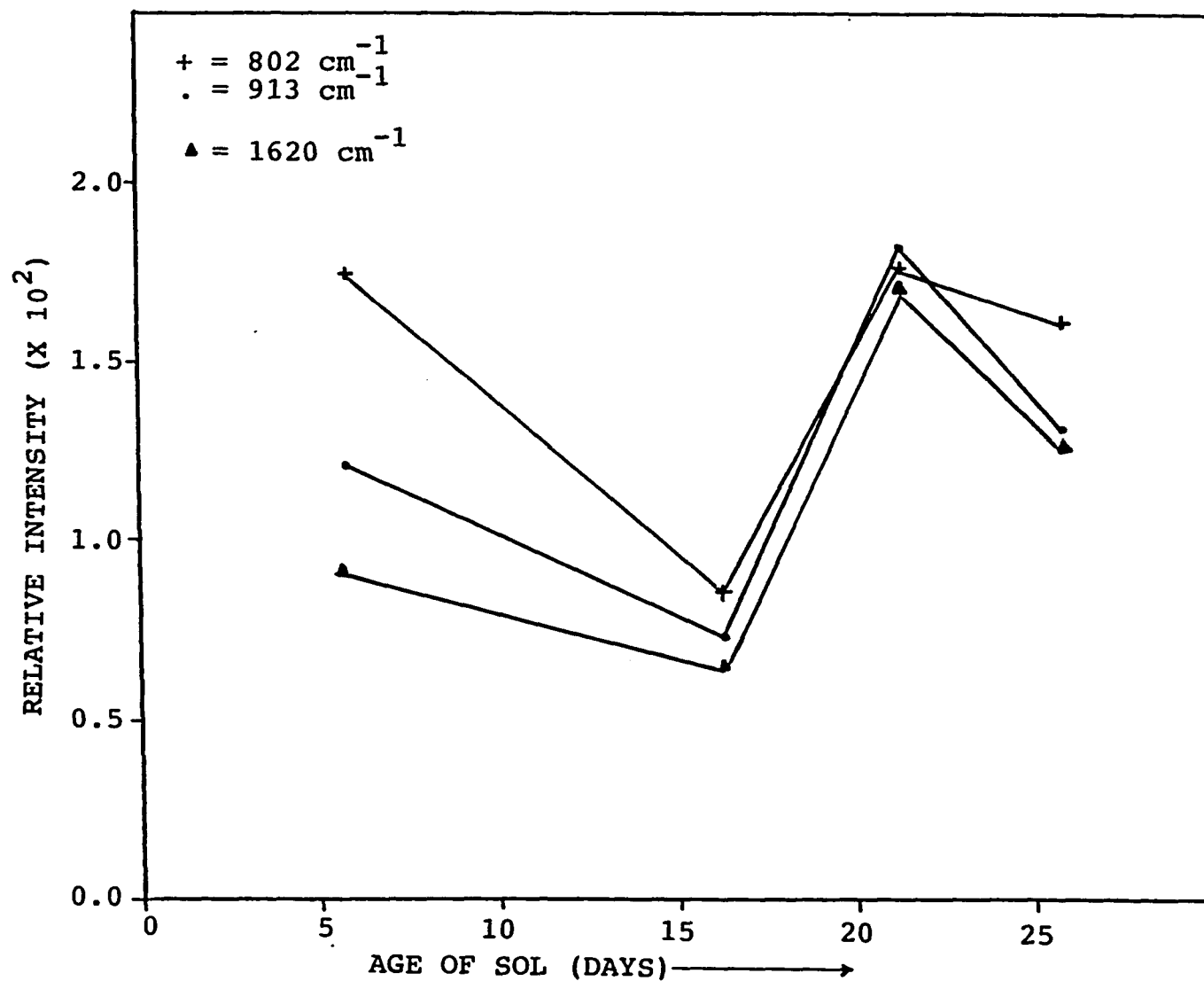


Figure 65. SERS intensity versus sol's age for peaks of CV, 10^{-7}M on Ag sol.

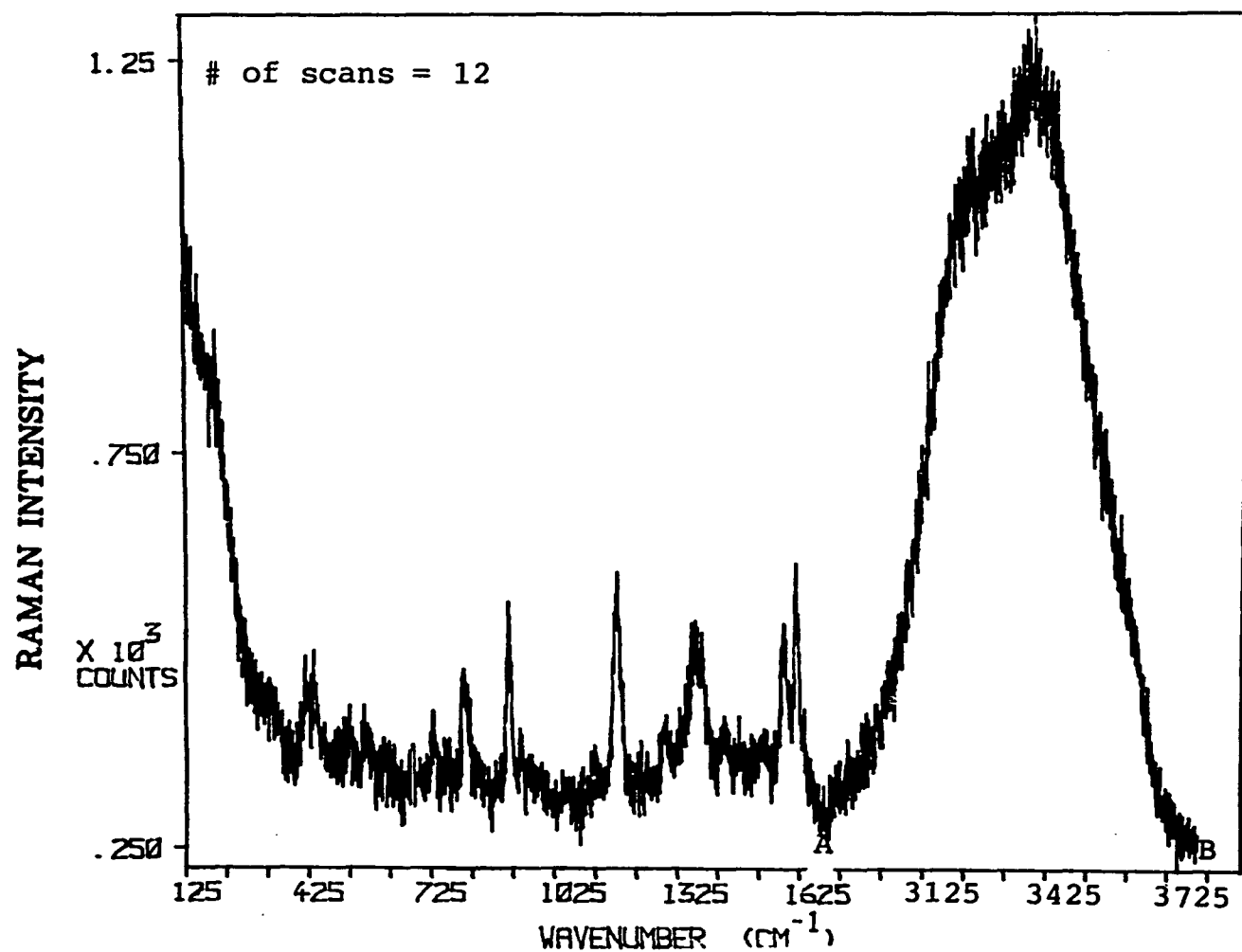


Figure 66. SERS spectrum of CV, $1 \times 10^{-7} \text{M}$ on Ag sol. Age of sol = 7 days. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800 \text{ cm}^{-1}$.

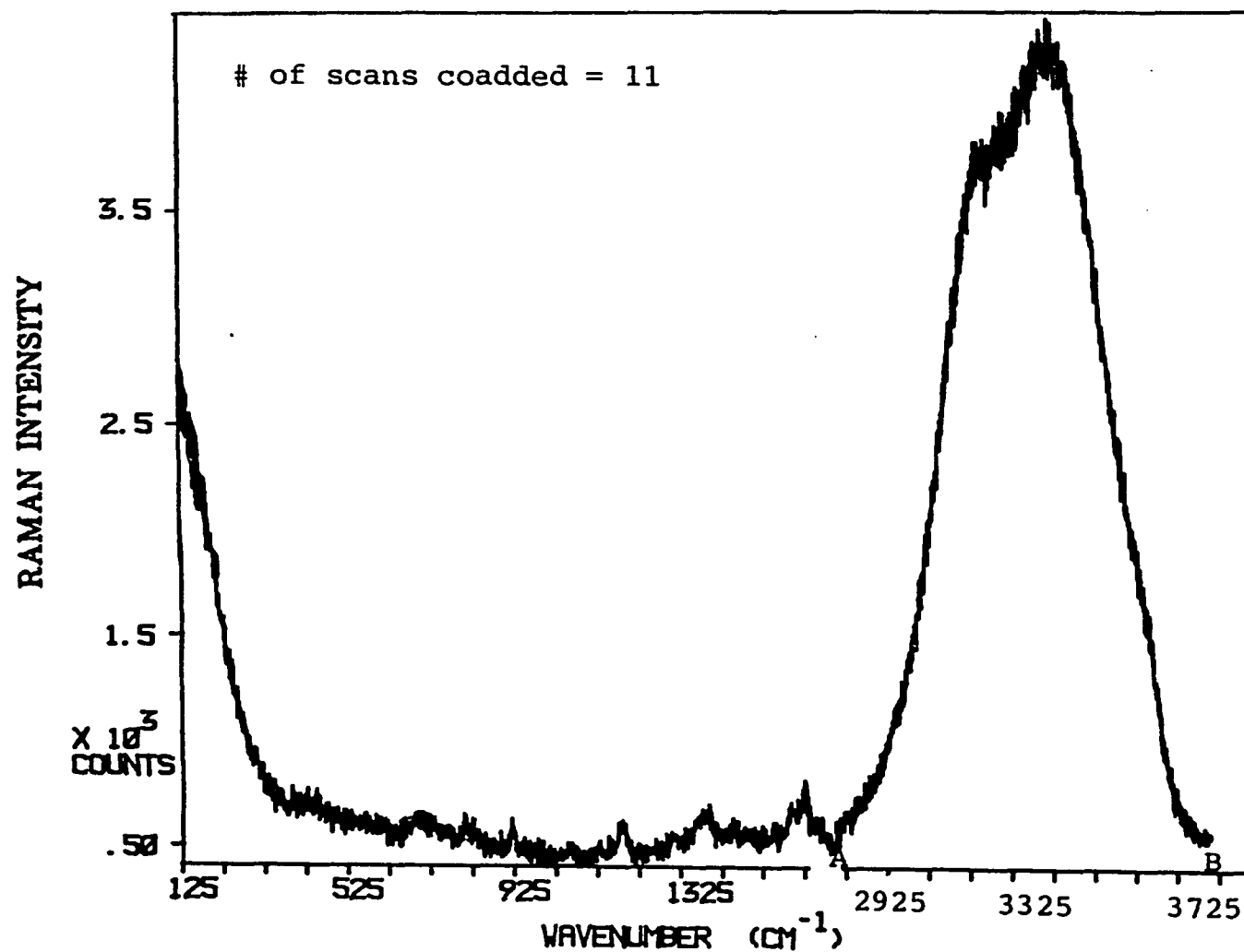


Figure 67: SERS spectrum of CV, $5 \times 10^{-8} \text{M}$ on Ag sol. Age of sol = 11 days. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800 \text{ cm}^{-1}$.

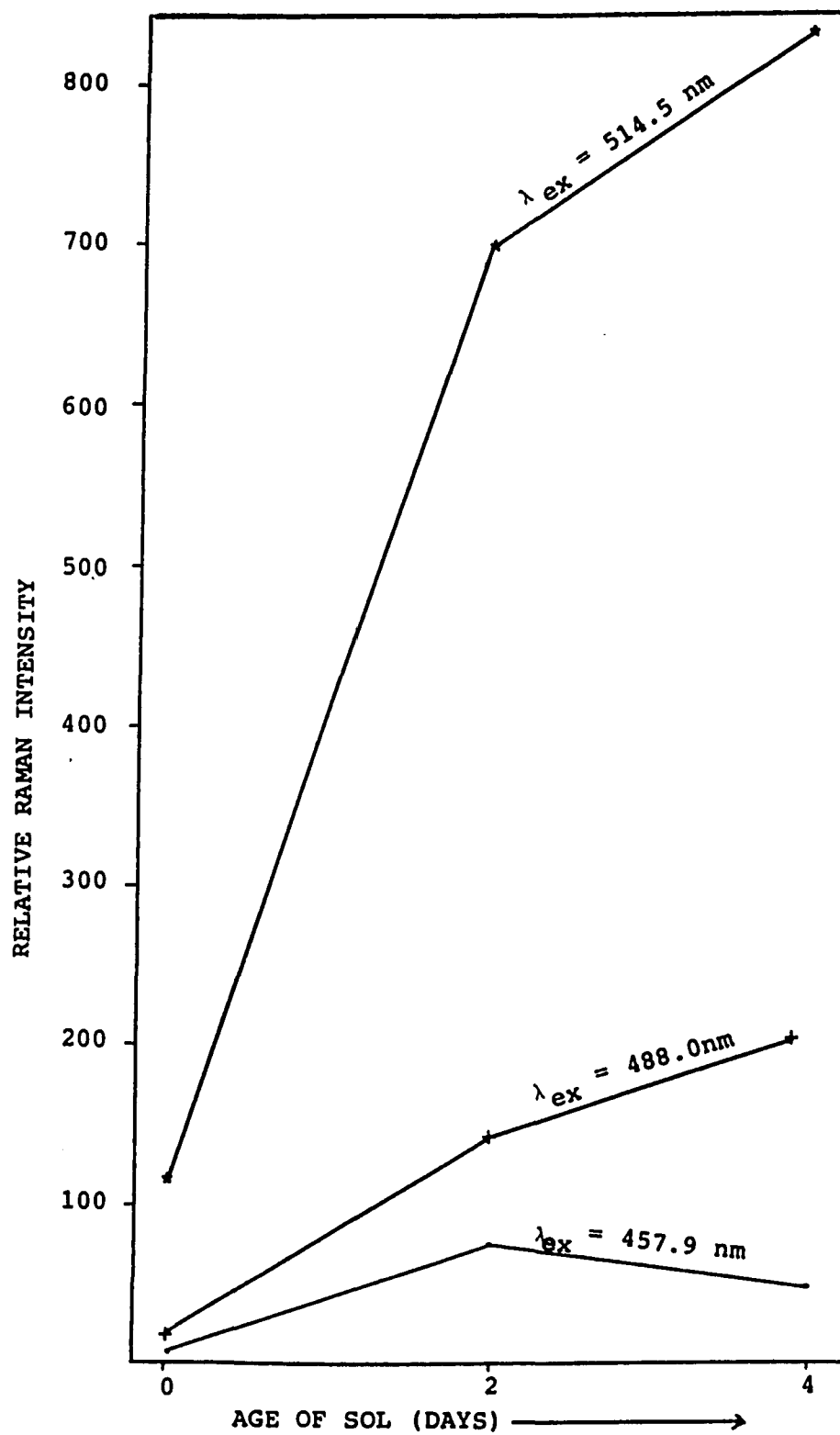


Figure 68. Variation of the SERS intensity of the 260 cm^{-1} peak of PR, 10^{-5}M , on Ag sol at various exciting wavelengths.

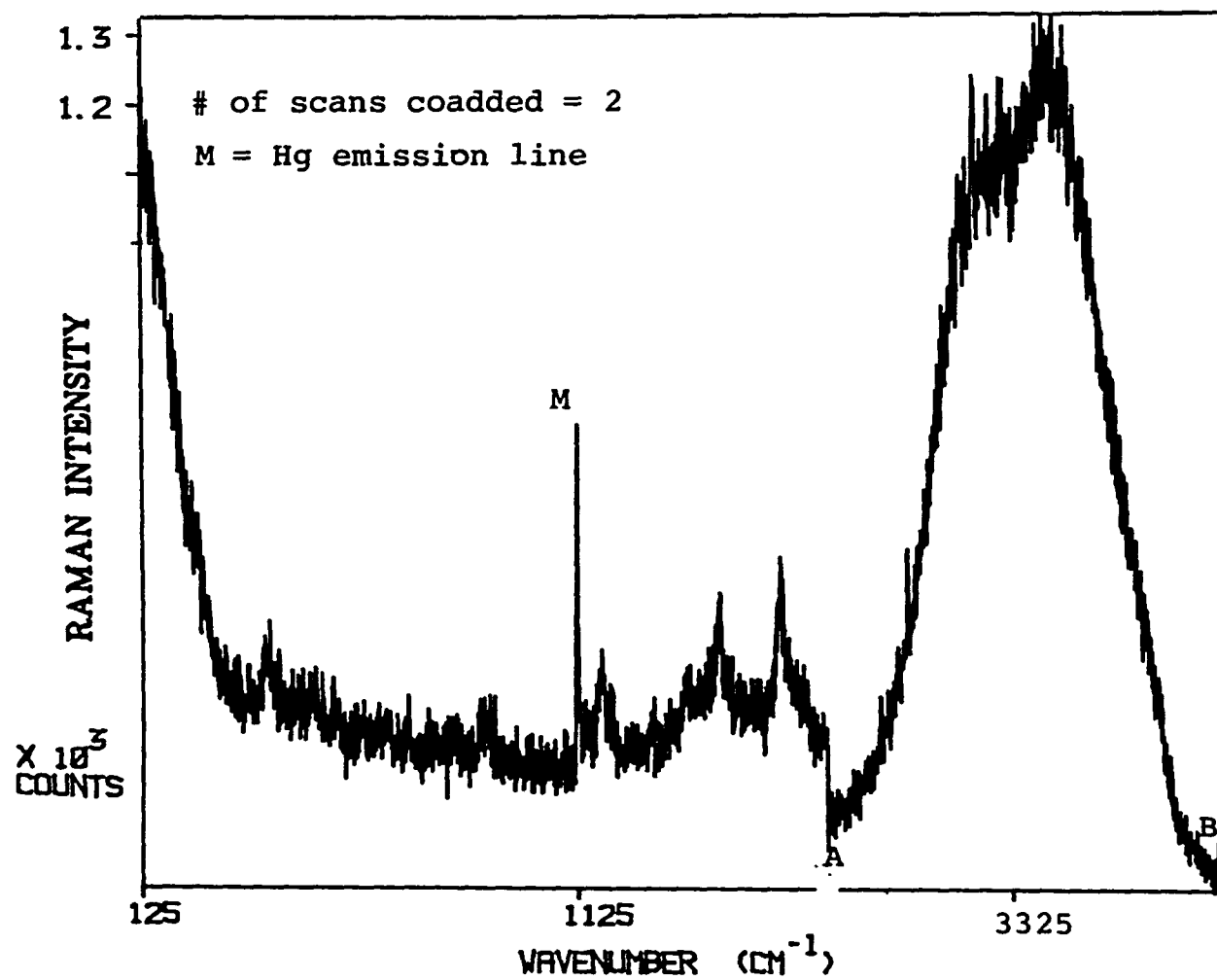


Figure 69. SERS spectrum of PR, 10^{-6}M , on freshly prepared Ag sol.
Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800\text{ cm}^{-1}$.

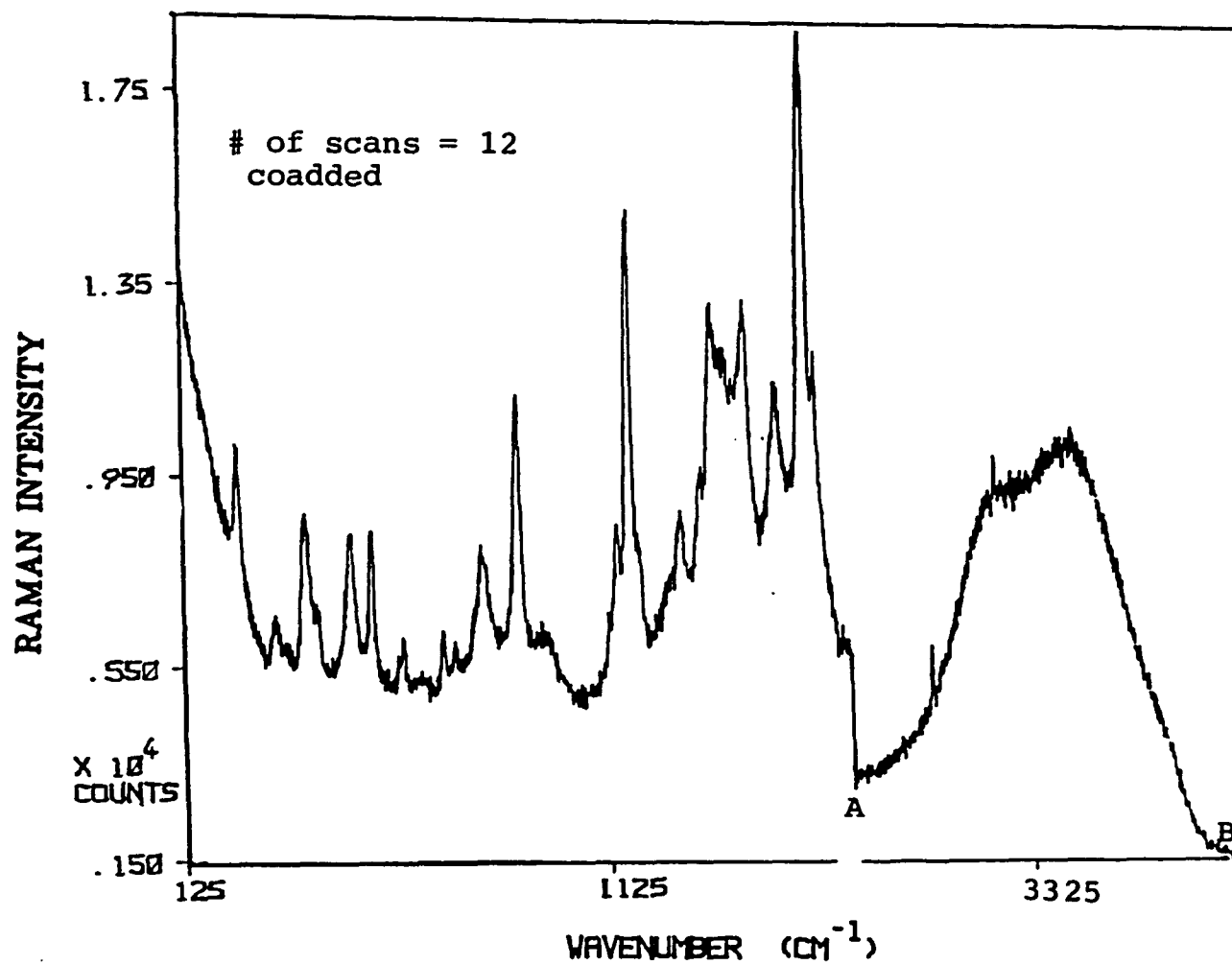


Figure 70. SERS spectrum of PR, 10^{-6}M , on Ag sol. Age of sol = 3 days. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800\text{ cm}^{-1}$.

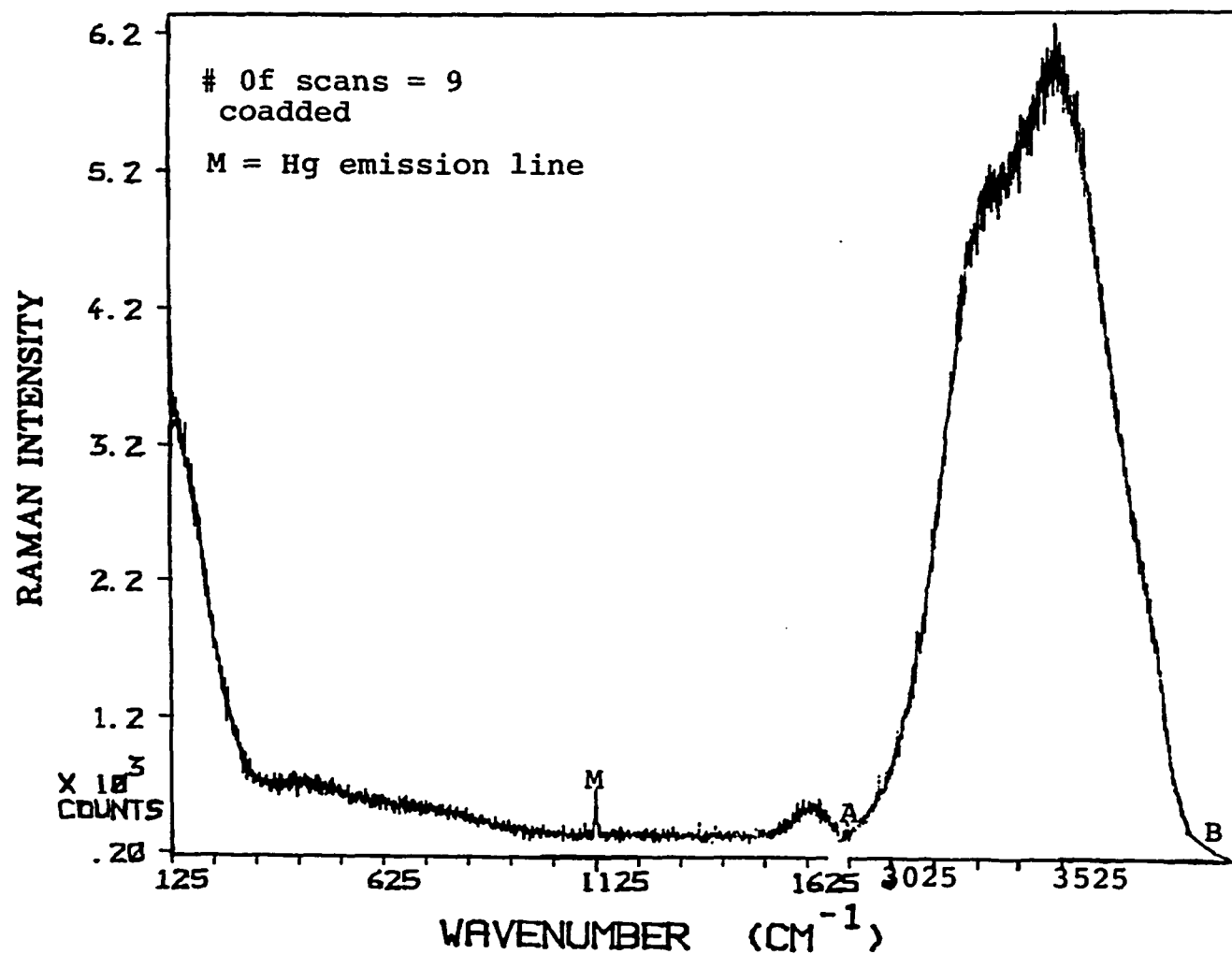


Figure 71. SERS spectrum of PR, 10^{-7} M, on freshly prepared Ag sol.
Region A-B represents the O-H stretching region of H₂O, 2900-3800 cm⁻¹.

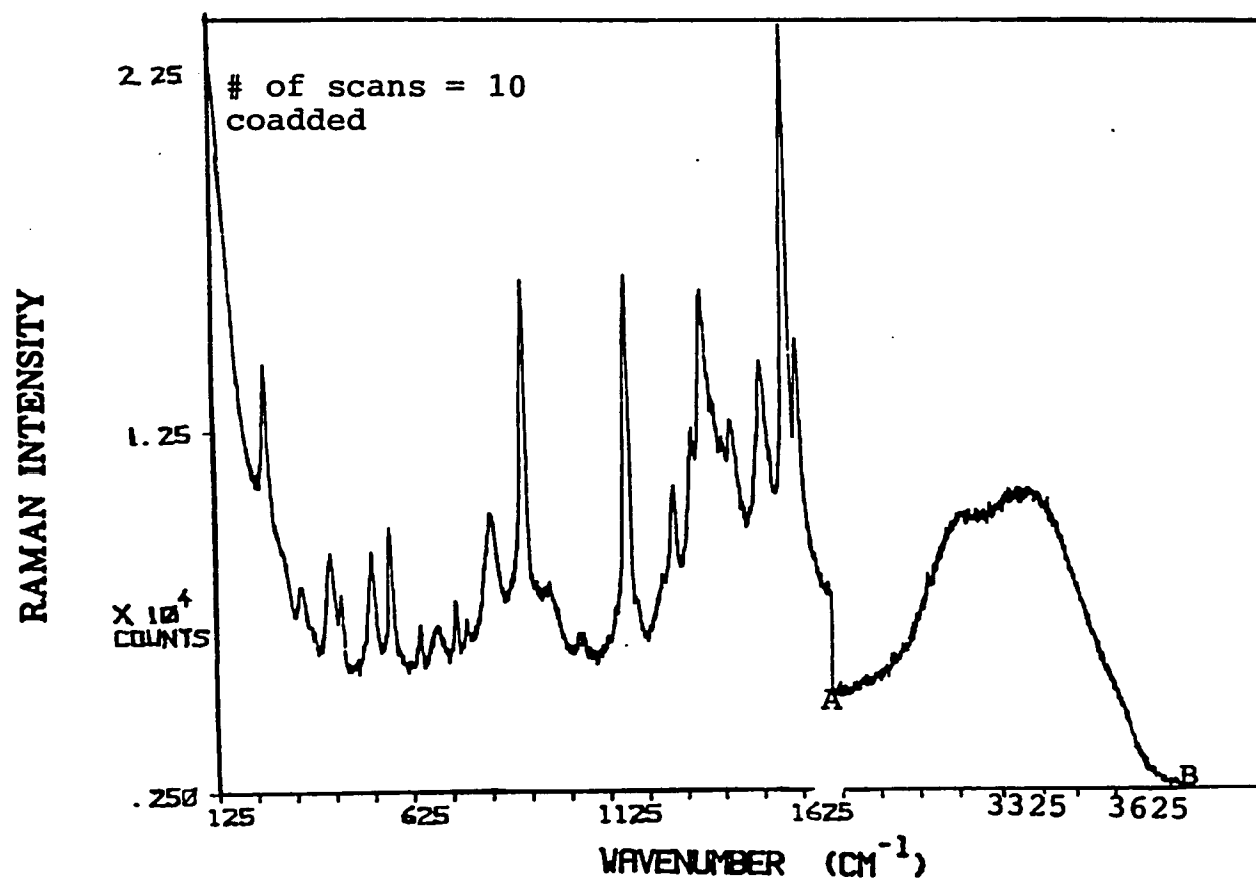


Figure 72. SERS spectrum of PR, 10^{-7} M on Ag sol. Age of sol = 3 days. Region A-B represents the O-H stretching region of H_2O , 2900-3800 cm^{-1} .

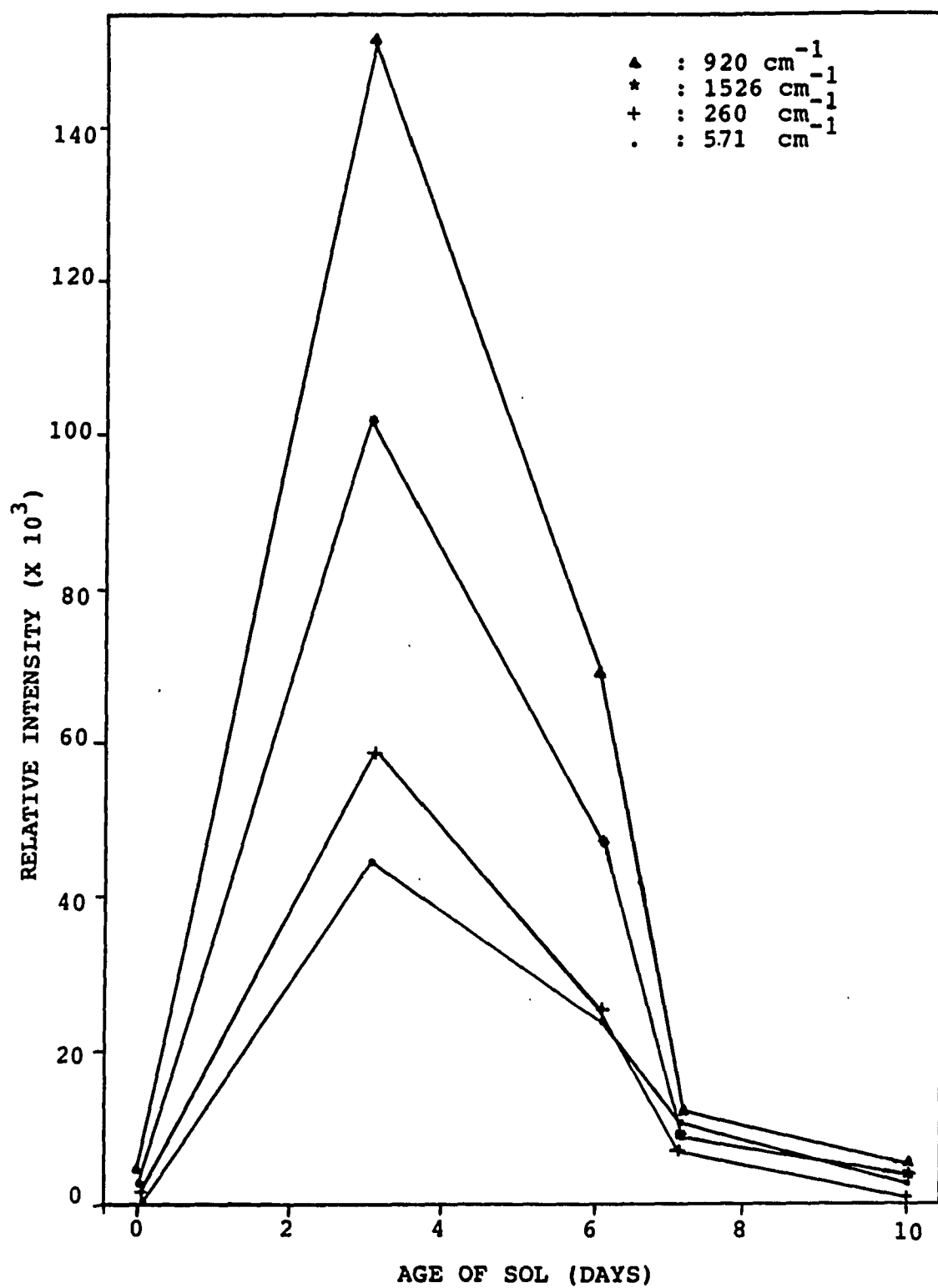


Figure 73. SERS intensity versus sol's age for peaks of PR, 10^{-7}M , on Ag sol.

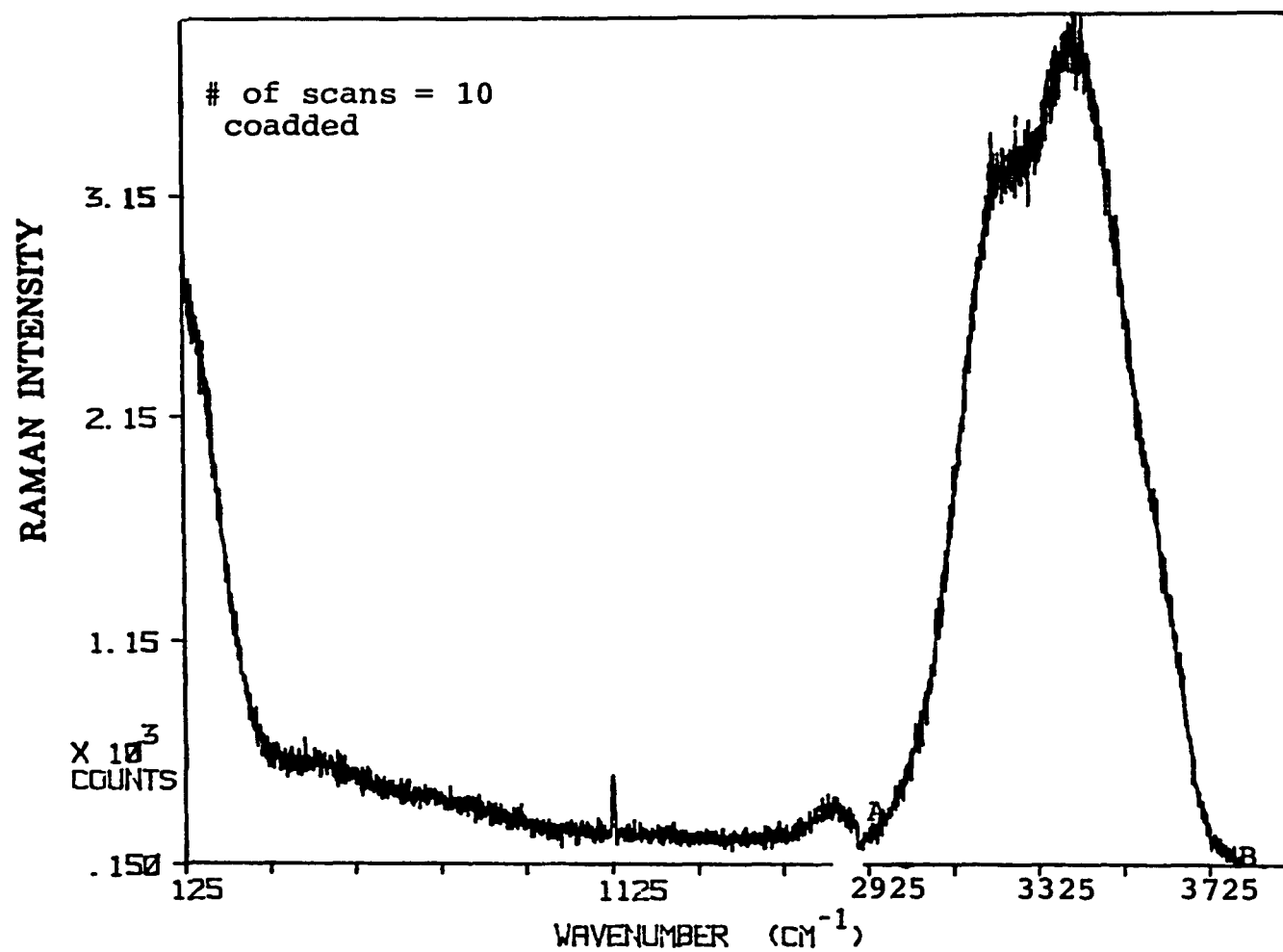


Figure 74. Surface Raman spectrum of PR, 10^{-8}M , on freshly prepared Ag sol. Region A-B represents the O-H stretching region of H_2O , $2900\text{--}3800\text{ cm}^{-1}$.

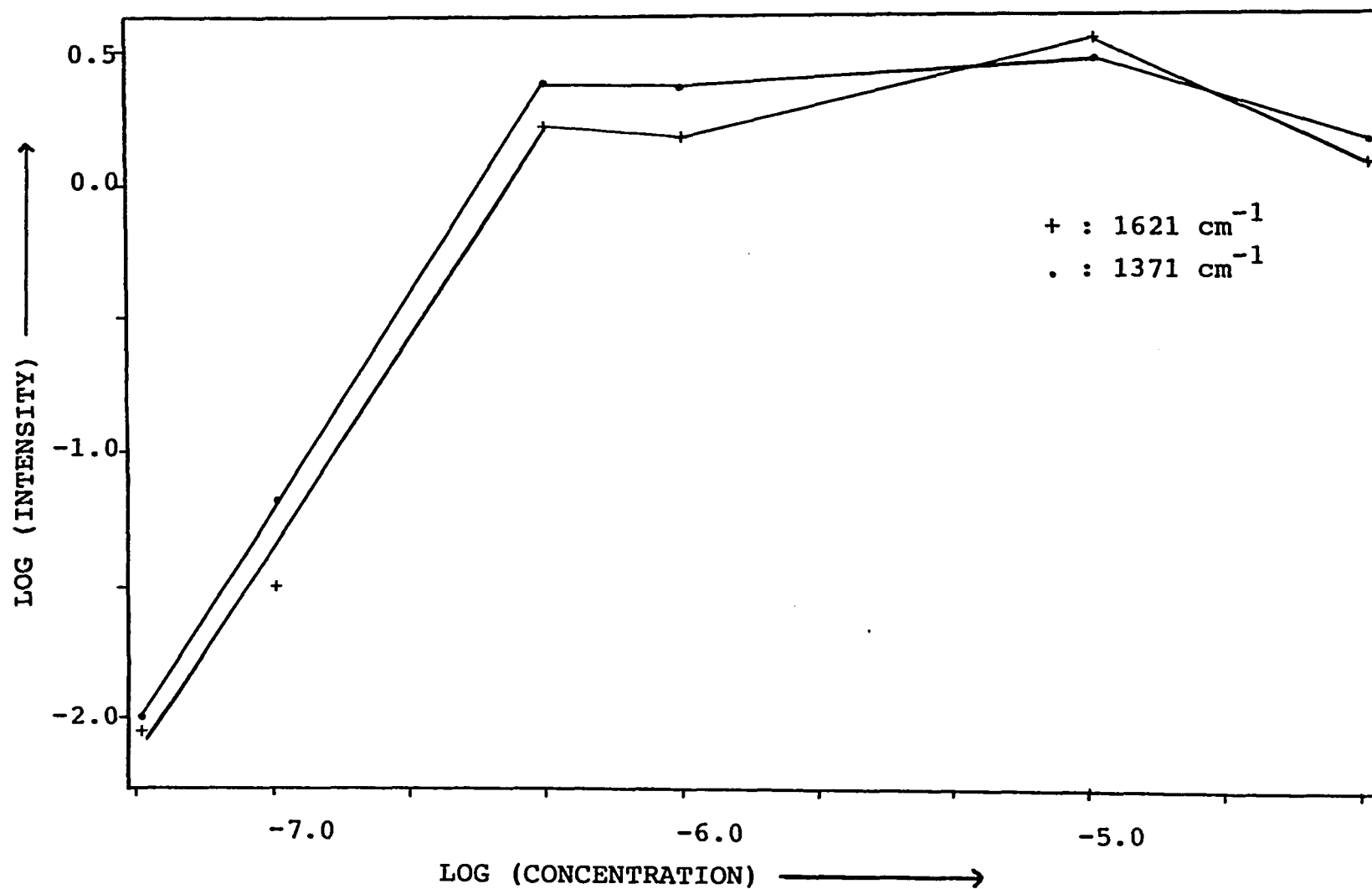


Figure 75. Plot of log [SERS intensity] versus log [concentration] for peaks of EV on Ag sol.

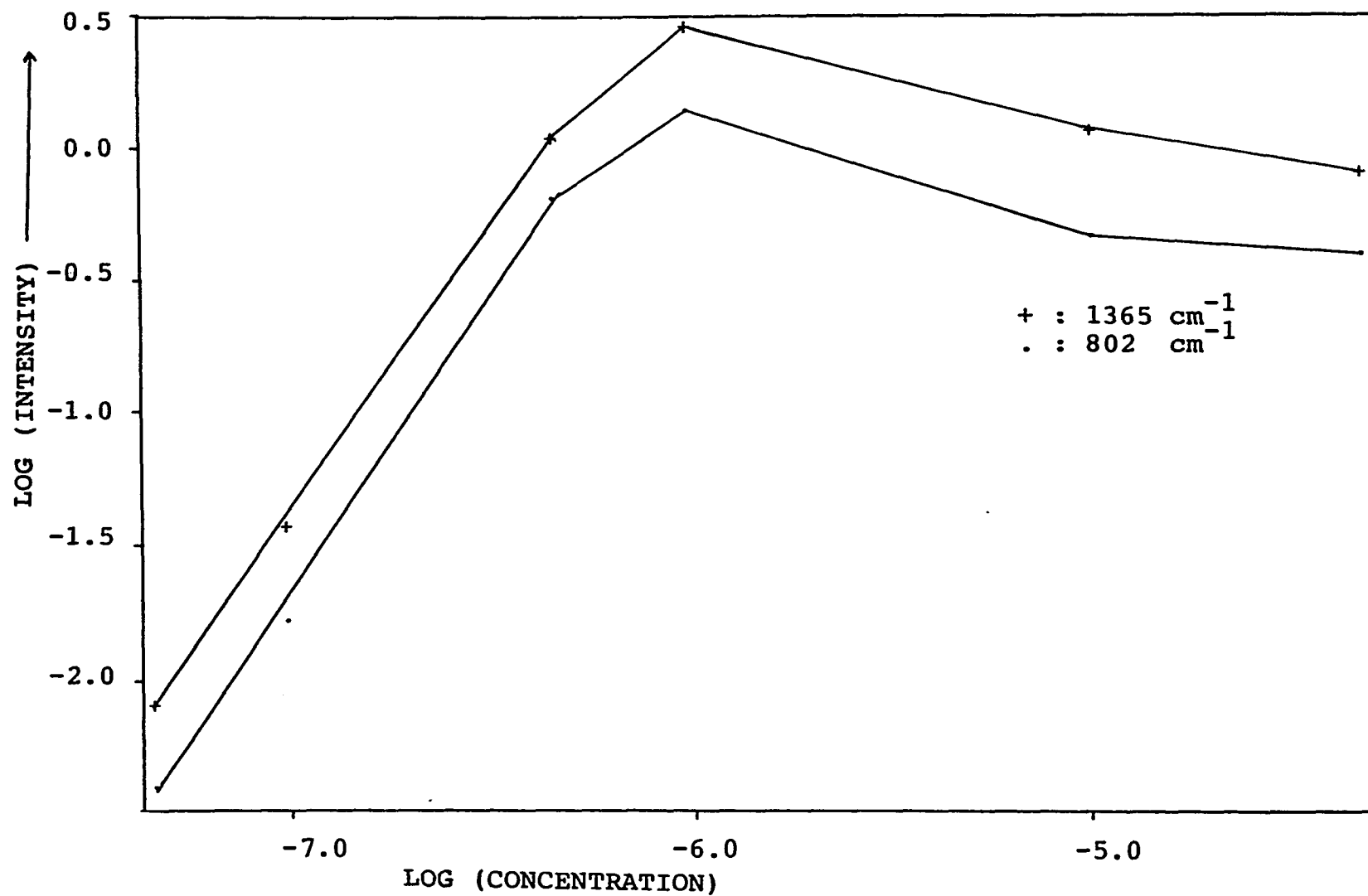


Figure 76. Plot of log (SERS intensity) versus log (concentration) for peaks of CV on Ag sol.

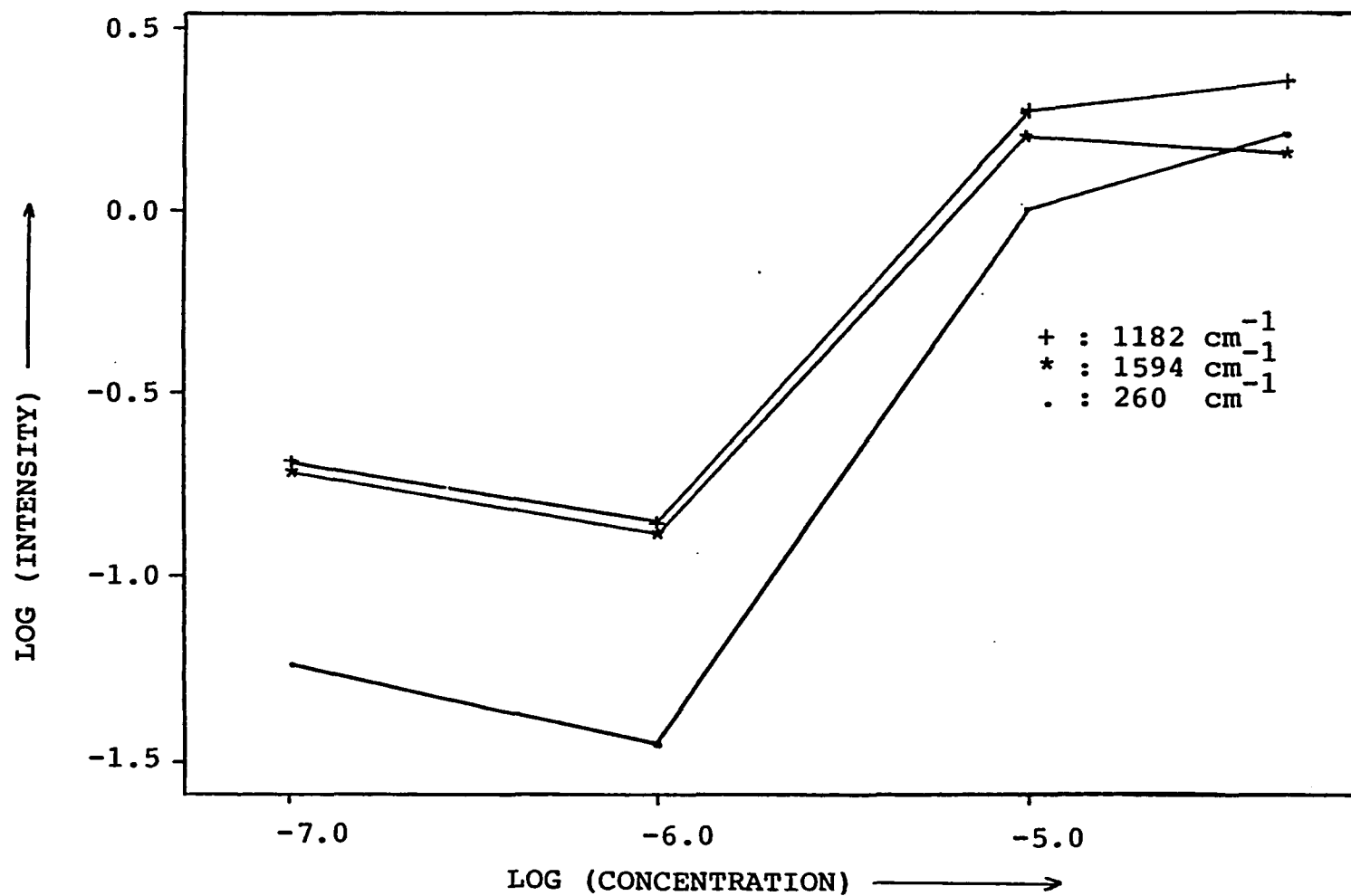


Figure 77. Plot of log (SERS intensity) versus log (concentration) for peaks of PR on Ag sol.

APPENDIX I

**CALCULATION FOR THE NUMBER OF DYE MOLECULES ADSORBED
ON THE COLLOIDAL SILVER SURFACE, ASSUMING MONOLAYER
COVERAGE.**

It has been reported that silver sols exhibiting a wavelength of maximum absorption at 390 nm have a radius of 200-300 Å (50). Taking the atomic radius of a Ag atom as being 1.75 Å, the # of silver atoms per colloidal particle

$$= \frac{\text{Volume of colloidal particle}}{\text{Volume of Ag atom}}$$

Recalling, $V = 4/3\pi r^3$, this ratio =

$$\frac{[200\text{\AA}]^3 / \text{sol particle}}{[1.75\text{\AA}]^3 / \text{Ag atom}}$$

$$= 1.49 \times 10^6 \text{ Ag atoms/sol particle}$$

Concentration of Ag colloid = $2.5 \times 10^{-4} \text{M}$ and 1 ml is sampled. Total number of atoms in this 1 ml =

$$\frac{1 \text{ ml} \times 2.5 \times 10^{-4} \text{ moles/L} \times 6.022 \times 10^{23} \text{ atoms/mole}}{1000 \text{ ml/L}}$$

$$= 1.51 \times 10^{17} \text{ Ag atoms/ml of Ag sol}$$

so, # of colloidal particle/ml =

$$\frac{1.51 \times 10^{17} \text{ Ag atoms/ml of sol}}{1.49 \times 10^6 \text{ Ag atoms/colloidal particle}}$$

$$= 1.01 \times 10^9 \text{ colloidal particles/ml of Ag sol}$$

Assuming sphericity, total surface area of the colloidal particle

$$= 4\pi r^2 \times 1.01 \times 10^9 = 4\pi(200\text{\AA})^2 \times 1.01 \times 10^9$$

$$= 1.6 \times 10^{14} \pi (\text{\AA})^2$$

Now it is required to calculate the cross-sectional area (CSA) of a dye molecule. Refer to Fig.78, the radius of a PR molecule is shown to be 7.88Å. Thus,

$$\text{CSA} = \pi r^2 = \pi (7.88\text{\AA})^2 = 62.1(\text{\AA})^2/\text{dye molecule.}$$

Total number of dye molecules required for complete sol coverage

$$= \frac{1.6 \times 10^{14}}{62.1} = 2.6 \times 10^{12}$$

This corresponds to :

$$\frac{2.6 \times 10^{12} \text{ molecules}}{6.0233 \times 10^{23} \text{ molecules /mole}} = 4.32 \times 10^{-12} \text{ moles}$$

For 1 ml 10^{-5}M solution of PR, total # of dye molecules present in solution =

$$\frac{1 \text{ ml} \times 2.0 \times 10^{-5} \text{ moles} \times 6.022 \times 10^{23} \text{ /mole}}{1000 \text{ ml}} = 1.2 \times 10^{16}$$

thus,

$$\begin{aligned} & \frac{\text{\# of dye molecules on sol surface}}{\text{\# of dye molecules in } 10^{-5}\text{M solution}} \\ &= \frac{2.6 \times 10^{12}}{1.2 \times 10^{16}} \\ &= 10^{-4} \end{aligned}$$

Thus, 1 in every 10^4 molecules is present on the sol's surface.

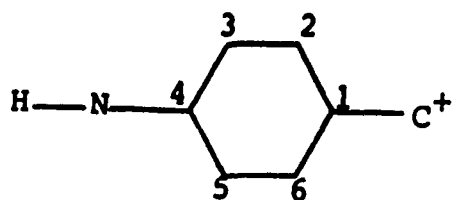


Figure 78. Structure of PR used to calculate its total radius.

$$C^+-C_1 = 1.454\text{\AA}$$

$$C_1-C_2 = 1.408\text{\AA}$$

$$C_2-C_3 = 1.364\text{\AA}$$

$$C_3-C_4 = 1.372\text{\AA}$$

$$C_4-N = 1.000\text{\AA}$$

$$N-H = 1.43\text{\AA}$$

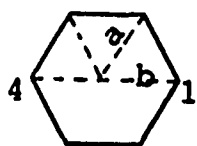
$$\text{van der Waal's} = 1.200\text{\AA}$$

radius of H

Total radius of PR =

$$\begin{aligned} & (C^+-C_1) + (C_1-C_4)^* + (C_4-N) + (N-H) + \text{vdW radius (H)} = \\ & (1.45) + (2.80) + (1.00) + (1.43) + (1.20) = \\ & 7.88\text{\AA} \end{aligned}$$

* to calculate the distance C_1-C_4 , I assumed the phenyl ring to be a regular hexagon with dimensions 1.40 Å



$$a = b = 1.40\text{ \AA}$$

$$C_1-C_4 = 2 \times 1.40\text{ \AA} = 2.80\text{\AA}$$

APPENDIX II: NORMAL COORDINATE ANALYSIS CALCULATION

All normal coordinate analysis (NCA) calculations have as a basic aim to mathematically calculate the vibrational frequencies and the atomic displacements for each normal mode of vibration. This process involves two steps: (a) setting up the classical expressions for the kinetic energy (T) and the potential energy (V) in terms of convenient coordinates of the atoms and (b) using these expressions to solve for the normal frequency of the vibrations and the displacements of the nuclei. The potential energy expression is usually formulated by using empirical expressions derived from assuming a particular force field. To date a number of force fields have been proposed and the general valence force field (GVFF) (114) and the Urey-Bradley force field (UBFF) (114,115) are two of the most popular. In the GVFF approximation, forces resisting motions such as stretching, bending, or torsions of the valence bonds are considered. These motions can be described in terms of time dependent changes of the coordinates and are limited by the $3N$ degrees of freedom allowed for that molecule ($N = \#$ of atoms). The UBFF approximation modifies the VFF potential function by including central terms which account for the repulsive forces operating between the non bonded atoms. The magnitudes of the interaction constants are sometimes assumed to be determined by the magnitude of the other constants. Simanouti (116), for example, considered

that the geminal and cis interaction constants are 1/10 of the value of the appropriate diagonal constant.

We will briefly consider a description of the appropriate coordinate systems which are used to describe the motions of the atoms and used to formulate the expressions for T and V. This discussion is an abbreviated version of that found in refs. (106 & 114). Four commonly used coordinate systems are: (a) Cartesian coordinates, (b) mass-adjusted Cartesian coordinates, (c) internal coordinates and (d) normal coordinates.

A. CARTESIAN COORDINATES

The motion of the system is described by a total of $3N$ coordinates: $x_1, y_1, z_1 \dots x_n, y_n, z_n$. These can be relabeled simply as: $X_1, X_2, X_3 \dots X_{3N}$. The potential energy, V , can be defined in terms of these coordinates:

$$V(X_1, X_2, \dots, X_{3N}) \dots \dots \dots (1)$$

The force acting on the i th particle is given by:

$$f_i = - \left| \frac{\partial V}{\partial X_i} \right| \dots \dots \dots (2)$$

$$f_i = m_i \left| \frac{d^2 X_i}{dt^2} \right| = -m_i \ddot{X}_i \dots \dots \dots (3)$$

The kinetic energy expression is:

$$2T = \sum_i m_i \left| \frac{dX_i}{dt} \right|^2 = \sum_i m_i \dot{X}_i^2 \dots \dots \dots (4)$$

The potential energy can be expanded and expressed in terms of a Taylor series:

$$2V = V_0 + \sum_i \left| \frac{\partial V}{\partial X_i} \right|_0 X_i + \frac{1}{2} \sum_{ij} \left| \frac{\partial^2 V}{\partial X_i \partial X_j} \right|_0 X_i X_j + \\ + \frac{1}{6} \sum_{ijk} \left| \frac{\partial^3 V}{\partial X_i \partial X_j \partial X_k} \right|_0 X_i X_j X_k + \dots \quad (5)$$

In this expression, cubic and higher terms can be neglected using the harmonic approximation; the constant term can be set to zero by choosing the zero energy as that of the equilibrium configuration of the atoms. When all the atoms are in their equilibrium positions, their energies are at a minimum, thus the second term vanishes. The final expression for V becomes:

$$2V = \sum_{ij} \left| \frac{\partial^2 V}{\partial X_i \partial X_j} \right|_0 X_i X_j \quad \dots \dots \dots (6)$$

These second derivatives are force constants of the potential energy function which can be expressed in terms of the Cartesian coordinates:

$$2V = \sum_{ij} f_{ij} X_i X_j \quad \dots \dots \dots (7)$$

B.MASS WEIGHTED COORDINATES. The mass weighted coordinates, q 's are defined as:

$$q_i = m_i^{1/2} X_i \quad \dots \dots \dots (8)$$

T and V can now be expressed as:

$$2T = \sum_i \dot{q}_i^2 \quad \dots\dots\dots(9)$$

$$2V = \sum_{ij} C_{ij} q_i q_j \quad \dots\dots\dots(10)$$

In matrix notation:

$$2T = \dot{q}^T \dot{q} \quad \dots\dots\dots(11)$$

$$2V = q^T C q \quad \dots\dots\dots(12)$$

where q^T is the transpose of q ; C is the force constant matrix in mass weighted Cartesian coordinates.

Newton's equation of motion can be expressed as:

$$\frac{d}{dt} \left| \frac{\partial T}{\partial \dot{q}_j} \right|_0 + \left| \frac{\partial V}{\partial q_j} \right|_0 = 0; j = 1, 2 \dots 3N \quad \dots\dots\dots(13)$$

Substituting the mass weighted coordinates into this equation leads to 3N second order homogeneous differential equations:

$$\ddot{q}_i + \sum_j C_{ij} q_j = 0; j = 1 \dots 3N \quad \dots\dots\dots(14)$$

The solution is of the form:

$$q_i = A_i \sin(t \lambda^{\frac{1}{2}} + \epsilon) \quad i = 1 \dots 3N \quad \dots\dots\dots(15)$$

A_i , λ and ϵ are all constants.

If the solutions are resubstituted into the equation above the following equations are arrived at:

$$\sum_j C_{ij} A_j - \lambda A_i = 0 \quad i = 1 \dots 3N \quad \dots\dots\dots(16)$$

$$\sum_{j \neq i} C_{ij} A_j + A_j (C_{ii} - \lambda) = 0 \quad \dots\dots\dots(17)$$

Such a simultaneous equation can only have non-trivial solutions if the determinant of the coefficients vanishes:

$$\begin{vmatrix} C_{11} - \lambda & C_{12} & C_{13} & \dots & C_{1,3N} \\ C_{21} & C_{22} - \lambda & C_{23} & \dots & C_{2,3N} \\ \vdots & \vdots & \vdots & & \vdots \\ C_{3N,1} & C_{3N,2} & C_{3N,3} & \dots & C_{3N,3N} - \lambda \end{vmatrix} = 0 \quad \dots \dots \dots (18)$$

Solutions to equation (18) yield $3N$ roots for λ_i . Each value of λ represents the harmonic vibration of a particle having frequency ν which is the normal frequency of vibration.

Suppose the root λ_k is substituted into equation (17); a relationship between the amplitudes $A_{1,k} \dots A_{3N,k}$ and the k th normal frequency is obtained. In fact $3N$ simultaneous equations will result:

$$\begin{aligned} C_{11}A_{1k} + C_{12}A_{2k} + \dots - \lambda_k A_{1k} &= 0 \\ C_{21}A_{1k} + C_{22}A_{2k} + \dots - \lambda_k A_{2k} &= 0 \\ \vdots & \\ C_{3N,1}A_{1k} + C_{3N,2}A_{2k} + \dots - \lambda_k A_{3N,k} &= 0 \end{aligned} \quad \dots \dots \dots (19)$$

The solutions to these equations do not yield unique values for the A 's; rather only ratios of A_{1k} , A_{2k} etc. are obtained. Only relative displacements of the atoms are deducible. To yield a physical value for the A 's, the following procedure is adopted:

Define $3N$ coefficients, l_{ik} , such that

$$\sum_i l_{ik}^2 = 1 \quad \text{and} \quad \dots \dots \dots (20)$$

$$A_i = K_k l_{ik}, \text{ where } \dots\dots\dots (21)$$

A_i represents the relative amplitude and K_k represents the transformation coefficient.

Using these coefficients l_{ik} and K_k , equations for equation (19) can be constructed and the resulting matrix for l_{ik} is:

$$\begin{array}{ccccccc} l_{11} & l_{12} & \dots\dots\dots & l_{1,3N} & & & \\ l_{21} & l_{22} & \dots\dots\dots & l_{2,3N} & & & \\ \cdot & & & & & & \\ \cdot & & & & & & \\ l_{3N,1} & l_{3N,2} & \dots\dots\dots & l_{3N,3N} & \dots\dots\dots & & \end{array} \quad (22)$$

Where each l_{ik} is proportional to the amplitude of A .

The above example gives the basic calculations involved in solving the expressions for T and V , that is, solution of the secular equation: $|C - \lambda E| = 0$, where E is a unit matrix. The solutions ultimately lead to the vibrational forms and normal coordinates.

C.INTERNAL CO-ORDINATES. The analogous expressions for the kinetic and potential energies are as follows:

$$2V = \sum_{tt''} F_{tt''} R_t R_{t''} \quad \dots\dots\dots (23)$$

$$2T = \sum_{tt''} G^{-1}_{tt''} \dot{R}_t \dot{R}_{t''} \quad \dots\dots\dots (24)$$

The secular equation is of the form :

$$|F - (G^{-1}) \lambda| = 0 \quad \dots\dots\dots (25)$$

Computationally, it is easier to calculate:

$$|GF - E \lambda| = 0 \quad \dots\dots\dots (26)$$

Thus the basic calculations involve the determination of the G matrix elements.

D.NORMAL COORDINATES. Solving the expressions for T and V in terms of general or mass weighted coordinates can be rather complicated because of the cross terms in the secular equation. It is found to be more convenient to use a coordinate system consisting of the $3N-6$ parameters. This is most convenient since it gives both the kinetic energy and potential energy expressions in a diagonal form.

The normal coordinates are defined as follows:

$$Q_1, Q_2 \dots Q_{3N-6} \dots (27)$$

The analogous expressions for T and V becomes:

$$2T = \sum_i \dot{Q}_i^2 \dots (28)$$

$$2V = \sum_i Q_i^2 \lambda \dots (29)$$

The equation of motion becomes:

$$\ddot{Q} + \lambda Q = 0 \dots (30)$$

The solutions to this equation are of the form:

$$Q_i = Q_i^0 \sin(\lambda_i^{1/2} + \epsilon) \dots (31)$$

The secular equation will be:

$$|\Lambda - \lambda E| = 0 \dots (32)$$

which will have $3N-6$ roots. Each λ_i will represent a normal mode of vibration. Q_i^0 represents the amplitude of the i th normal vibration.

CO-ORDINATE TRANSFORMATIONS

As seen from the discussion above, the expressions for T and V and the vibrational forms can be expressed in a variety of co-ordinate systems. For convenience, the kinetic energy is usually expressed in Cartesian coordinates and the potential energy in terms of internal coordinates. The equation of motion must be dealt with in a single coordinate system; and in such cases the energy expressions usually have to be transformed to the preferred system. It is not surprising that transformation coefficients and the matrix of transformation coefficients play a major role in the routine of any normal coordinate analysis calculation.

A normal coordinate analysis was carried out for the moiety $N(C_6H_4)C^+(X)_2$. The assumed structure is shown in Fig. 79 A. A UBFF force field adapted from Simanouti (116) was used. The computation programs were written by Schachtschneider (117) and some of these were rewritten by M. Diem (118). There are four programs which are labeled: "CART", "BMAT", "UBZM" and "NOCO". The purpose of each program will be discussed and in the course of this discussion the method of calculation will be outlined.

METHOD OF CALCULATION

The four programs are executed sequentially and the output data obtained consist of calculated vibrational frequencies, potential energy distributions (PED) and the

relative atomic displacements. This program recognizes six internal coordinates and four of these were relevant to the calculations; these are: bond stretching, angular bending, oop wag and torsions. The first program "CART" calculates the equilibrium coordinates from given input parameters of the molecule. These include the bond distances, bond angles and atom positions. The data are entered in a specified format and the actual data for $\text{N}(\text{C}_6\text{H}_4)\text{C}^+(\text{X})_2$ is shown in Table XIV. The output data for this molecule is shown in Table XV.

Once the equilibrium Cartesian coordinates have been calculated, the program "BMAT" is executed. This program calculates the transformation matrix, B, which transforms the Cartesian displacement coordinates to internal coordinates:

$$R = BX$$

where R = internal coordinate and X = Cartesian displacement coordinates (contained in the X matrix in Table XV). Thus the B matrix gives a description of the internal coordinates in terms of the Cartesian displacement coordinates. As expected the input data for this program include the Cartesian displacement coordinates (calculated from "CART":) and the internal coordinates viz. the stretching, bending, wagging etc.. All redundancies are included as well and the atoms involved in the vibrations have to be defined. The sample input data for this mole-

cule is shown in Table XVI and the output B matrix is shown in Table XVII.

It is now required to express the potential energy in terms of the internal coordinates; recall equation (23):

$$2V = \sum_{tt''} F_{tt''} R_t R_{t''}$$

or,

$$2V = R^T F R$$

Similarly T can be expressed as: (cf. equation (24))

$$2T = \sum_{tt''} G^{-1}_{tt''} \dot{R}_t \dot{R}_{t''}$$

It should be noted that the transformation of T to internal coordinates is not carried out in these calculations since the kinetic energy matrix is already diagonalized in mass weighted Cartesian coordinates. Instead the potential energy defined in internal coordinates (R) is transformed back to mass weighted Cartesian coordinates space and the remaining computations are carried out in Cartesian coordinates. It has been argued that this method saves a lot of time (117).

One logical question that arises is how is the F matrix defined? it is clear that the force constants for chemically equivalent bonds will be the same and the values will have to be repeated. The purpose of the "UBZM" program is to transform the force constants from UB space to general space. In doing so a "Z" matrix is calculated such that: $F_{tk} = \sum Z_{tk} \omega_k$, where ω is a one dimensional

vector of force constants and Z = a matrix which will define the position of $\mathbf{Q}$.

The input data required for this program include the definition of the Urey-Bradley force constants; the off diagonal force constants are also required. These have to be weighted and the calculations of the weighting constants in the UB field is carried out by the program "UBZM". The input data are shown in Tables XVIII & XIX. The computed Z matrix is in Table XX.

Finally the program "NOCO" calculates the vibrational frequencies, the PED's and the atomic displacement vectors. Before executing "NOCO", the values of the force constants and the masses of the atoms are required. These data are listed in Table XXI.

Recall that the F matrix is constructed via the "UBZM" program in internal coordinates. It is first transformed into Cartesian space:

$$A = B^T F B$$

Then it is transformed into mass-weighted Cartesian coordinates via the transformation coefficient W : ($W = m^{-\frac{1}{2}}$)

$$H = W^T A W$$

which can be rewritten as:

$$H = W^T B^T F B W$$

In terms of the secular equation, this is essentially:

$$|H - \lambda E| = 0,$$

where the eigenvectors of H are proportional to the vibra-

tional frequency. At this stage H is not diagonalized. It is required to transform it to normal coordinate space. The matrix C is computed which would diagonalize H :

$$\Lambda = C^T H C$$

The matrix C carries out the transformation from mass weighted coordinates, q , to normal coordinates, Q , thus:

$$Q = Cq$$

It has been mentioned that coordinate systems can be converted via linear transformations. Consider for example the transformation from Cartesian coordinates, X , to normal coordinates. Let S be defined as the transformation matrix which will carry out this transformation. Clearly,

$$S = WC$$

$$X = SQ$$

The transformation from internal coordinates, R , to normal coordinates, Q , is carried out by L where,

$$R = LQ$$

$$L = BS$$

$$L = BWC$$

With H diagonalized, the λ values obtained from the secular equation: $|\Lambda - \lambda E| = 0$ are the eigen values which are proportional to the vibrational frequencies. The potential energy distribution calculates the fractional contribution of force constant F_{jk} for example to a normal vibration λ_i ; this is calculated as:

$$l_{ji} l_{ki} F_{jk} / \lambda_i \quad \text{for } j \neq k$$

(See equation (20) for explanation of the l 's).

The atomic displacements are output in Cartesian coordinates and these are contained in the S matrix. Recall that it is their relative amplitudes that are calculated and these are normalized to unit displacement lengths. As an example the S vector output is shown for a vibration in Table XXII.

NCA CALCULATIONS OF $X_2C^+(C_6H_4)N$:

The strategy in carrying out any NCA is to obtain a reasonable set of force constants. It is not usual to calculate force constants from the observed frequencies but rather to start with a reasonable set of assumed force constants and to refine these to fit the experimental frequency data. Some of the force constants used here were adapted from those reported by Califano and Crawford (119) who had previously reported the UBFF calculations of benzene. Some were also taken from those of Ingold and Mair-Honig which have been cited in ref. (106). The results of the PED's obtained with the force constants listed in Table XXI are shown below. The observed frequencies cited are those from the RRS and SERS spectrum of PR scanned at 488.0 nm. We have attempted to interpret the vibrations in terms of the following categories: aromatic C-C stretch, skeletal vibrations of the phenyl rings, ring C-H deformations,

substituent stretching motions and molecular breathing motions.

OUTPUT DATA OBTAINED AFTER EXECUTION OF THE "NOCO" PROGRAM:

I. Calculated frequency : 3249.1 cm^{-1}

PED:

K (C-H) 89% ; f(C..H) 11%

II. Calculated frequency : 3236.1 cm^{-1}

PED:

K (C-H) 89% ; f(C..H) 11%

III. Calculated frequency : 3066.1 cm^{-1}

PED:

K (C-H) 100%

IV. Calculated frequency: 3064.5 cm^{-1}

PED:

K (C-H) 100%

V. Calculated frequency: 1644 cm^{-1}

Observed frequency: 1619 cm^{-1}

PED:

K (C-C) 66 % ; K (C-C⁺) 20 % ; H (CCH) 14 %

Interpretation: aromatic ring stretching.

VI. Calculated frequency: 1592.7 cm^{-1}

Observed frequency : 1591 cm^{-1}

PED:

K (C-C) 100%

Interpretation: aromatic ring stretching

VII. Calculated frequency: 1579.7 cm^{-1}

PED: K(C-C) 46% ; K (Ph-N) 15% ; H (CCH) 25% f(C..H) 14%

VIII. Calculated frequency: 1534.9 cm^{-1}

Observed frequency: 1524 cm^{-1}

PED:

K (C-C) 100%

Interpretation: aromatic C-C stretch

IX. Calculated frequency: 1409 cm^{-1}

Observed frequency: 1454 cm^{-1}

PED:

K (C-C) 21% ; K (C-C⁺) 34% ; H (CCH) 24% ; f(C..H) 20%

X. Calculated frequency: 1365.8 cm^{-1}

Observed frequency: 1373 cm^{-1}

PED:

K(Ph-N) 20% ; K(C-C) 17% ; H(CCH) 35% ; f(C..H) 28%

XI. Calculated frequency: 1347 cm^{-1}

Observed frequency: 1348 cm^{-1}

PED:

K (Ph-N) 26% ; K (C-C) 43% ; H (CCH) 18% ; f(C..H) 13%

XII. Calculated frequency: 1208.8 cm^{-1}

Observed frequency: 1298 cm^{-1}

PED:

K (C-C) 14% ; K(C-C⁺) 57% ; H (CCH) 14% ; f(C..H) 15%

XIII. Calculated frequency: 1174.1 cm^{-1}

Observed frequency : 1179.0 cm^{-1}

PED: K (C-C) 30% ; K (C-C⁺) 38% ; H(CCH) 32%

XIV. Calculated frequency: 1143.4 cm^{-1}

PED: W (HCCC) 40% ; T (CCCC) 60%

XV. Calculated frequency: 1142.1 cm^{-1}

Observed frequency: 1144 cm^{-1}

PED:

K (C-C) 28% ; K (C-C⁺) 24% ; H(CCH) 48%

Interpretation: in plane ring C-H deformation

XVI. Calculated frequency: 917 cm^{-1}

Observed frequency: 973 cm^{-1}

PED:

K (C-C) 35% ; H (CCH) = 65%

Interpretation: in plane ring C-H deformation

XVII. Calculated frequency: 901.5 cm^{-1}

Observed frequency: 916 cm^{-1}

PED:

K (C-C) 56% ; H (CCH) 44%

XVIII. Calculated frequency: 891.6 cm^{-1}

PED:

K (C-C) 43% ; H (CCH) 57%

XIX. Calculated frequency: 881.1 cm^{-1}

Observed frequency: 829 cm^{-1}

PED:

W (HCCC) 75% ; T (CCCC) 25%

XX. Calculated frequency: 785.8 cm^{-1}

Observed frequency: 761 cm^{-1}

PED: W (HCCC) 62% ; T (CCCC) 38%

XXI. Calculated frequency: 752.4 cm^{-1}

Observed frequency: 736 cm^{-1}

PED: K ($\text{C}-\text{C}^+$) 17% ; H (CCC) 57% ; f(C..C) 27%

XXII. Calculated frequency: 633.8 cm^{-1}

Observed frequency : 639 cm^{-1}

PED: W (HCCC) 100%

XXIII. Calculated frequency: 546.3 cm^{-1}

Observed frequency: 568 cm^{-1}

PED: H (CCH) 20% ; H(CCC) 53% ; f(C..C) 27%

XXIV. Calculated frequency: 534.2 cm^{-1}

Observed frequency: 516 cm^{-1}

PED: K ($\text{C}-\text{C}^+$) 42% ; H(CCC) 39% ; f(C..C) 19%

XXV. Calculated frequency: 509.4 cm^{-1}

PED: W(NCCC) 12% ; W(HCCC) 62% ; T(CCCC) 26%

XXVI. Calculated frequency: 470.7 cm^{-1}

Observed frequency: 433 cm^{-1}

PED: W(C^+CCC) 18% ; W(HCCC) 53% ; T(CCCC) 40%

Interpretation: oop ring skeletal vibration +
oop $\text{C}-\text{C}^+$ deformation.

XXVII. Calculated frequency: 410.9 cm^{-1}

Observed frequency: 409 cm^{-1}

PED: H(CCN) 51% ; f(C..N) 49%

XXVIII. Calculated frequency: 328.7 cm^{-1}

Observed frequency: 334 cm^{-1}

PED:

H(CCN) 51% ; f(C..N) 49%

XXIX. Calculated frequency: 263.5 cm^{-1}

Observed frequency: 249 cm^{-1}

PED: $K(C-C^+)$ 80% ; $H(CCC)$ 20%

Interpretation: molecular breathing motion (see table XXII).

XXX. Calculated frequency: 217.9 cm^{-1}

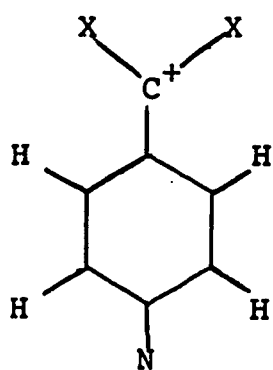
PED: $H(C^+CC)$ 64% ; $f(C^+..C)$ 36%

XXXI. Calculated frequency: 189.5 cm^{-1}

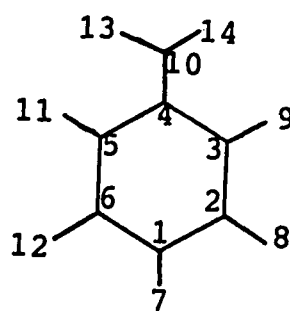
PED: $W(NCCC)$ 35% ; $W(C^+CCC)$ 46% ; $T(CCCC)$ 19%

XXXII. Calculated frequency. 99.4 cm^{-1}

PED: $W(NCCC)$ 34% ; $W(C^+CCC)$ 27% ; $T(CCCC)$ 40%



(A)



(B)

Figure 79. (A). Model of $(X)_2C^+(C_6H_4)N$ used for NCA calculations.

(B). Atom numbering used for NCA calculations.

ATOM #					BOND DIST. (N_a-N_b) (Å)	BOND ANGLE ($\angle N_a N_b N_c$)	DIHEDRAL ANGLE ($N_o-N_a-N_b-N_c$)
	N_o	N_a	N_b	N_c			
1							
2	1				1.372		
3	2	1			1.364	116.1	
4	3	2	1		1.408	123.5	000.0
5	4	3	2		1.408	115.3	000.0
6	1	2	3		1.372	125.3	000.0
7	1	2	3		1.428	120.0	180.0
8	2	3	4		1.080	120.0	180.0
9	3	4	5		1.080	120.0	180.0
10	4	3	9		1.454	120.0	000.0
11	5	6	1		1.080	120.0	180.0
12	6	1	2		1.080	120.0	180.0
13	10	4	5		1.454	120.0	000.0
14	10	4	3		1.454	120.0	000.0

Table XIV. Input data used to calculate the equilibrium Cartesian coordinates of $(X)_2C^+(C_6H_4)N$. For atom number and structure of the molecule refer to Figure 79.

Explanation: $N_o = 1$ defines the origin. The line from $N_o = 1$ to $N_o = 2$ defines the +X axis. Atoms $N_o = 1, 2, 3$ define the XY plane.

CALCULATION OF THE CARTESIAN EQUILIBRIUM COORDINATES

ATOM NO.	X	Y	Z
1	.000000	.000000	.000000
2	1.372000	.000000	.000000
3	1.972077	1.224910	.000000
4	1.259581	2.439329	.000000
5	-.142844	2.314165	.000000
6	-.792821	1.119741	.000000
7	-.713000	-1.234952	.000000
8	1.974365	-.896413	.000000
9	3.052051	1.232450	.000000
10	1.977772	3.703574	.000000
11	-.706276	3.235547	.000000
12	-1.868203	1.019981	.000000
13	1.241999	4.957669	.000000
14	3.431737	3.713725	.000000

X MATRIX:

```

1 2 1.372000000 1 3 1.972077000 2 3 1.224910000 1 4 1.259581000
2 4 2.439329000 1 5 -.142844500 2 5 2.314165000 1 6 -.792820600
2 6 1.119741000 1 7 -.713000100 2 7 -1.234952000 1 8 1.974365000
2 8 -.896413200 1 9 3.052051000 2 9 1.232450000 1 10 1.977772000
2 10 3.703574000 1 11 -.706275600 2 11 3.235547000 1 12 -1.868203000
2 12 1.019981000 1 13 1.241999000 2 13 4.957669000 1 14 3.431737000
2 14 3.713725000 -1 0 .000000000

```

Table XV. Output data for $(X)_2C^+(C_6H_4)N$ after execution of "CART".

N_I	N_C	N_1	N_2	N_3	N_4
1	1	2	8		
2	1	3	9		
3	1	5	11		
4	1	6	12		
5	1	1	7		
6	1	1	2		
7	1	2	3		
8	1	3	4		
9	1	4	5		
10	1	5	6		
11	1	6	1		
12	1	4	10		
13	1	10	14		
14	1	10	13		
15	2	1	2	8	
16	2	2	3	9	
17	2	4	5	11	
18	2	5	6	12	
19	2	1	6	12	
20	2	6	5	11	
21	2	4	3	9	
22	2	3	2	8	
23	2	1	2	3	
24	2	2	3	4	
25	2	3	4	5	
26	2	4	5	6	
27	2	5	6	1	
28	2	6	1	2	
29	2	3	4	10	
30	2	10	4	5	
31	2	2	1	7	
32	2	6	1	7	
33	3	7	1	2	6
34	3	10	4	5	3
35	3	8	2	1	3
36	3	9	3	2	4
37	3	11	5	6	4
38	3	12	6	1	5
39	4	2	3	4	5
40	4	2	1	6	5
41	4	3	2	1	6
42	4	3	4	5	6
43	4	4	5	6	1
44	4	4	3	2	1

EXPLANATIONS:

 N_I = Internal coordinate # N_C = Code # for vibration

= 1 for stretching

= 2 for bending

= 3 for oop wag

= 4 for torsion

 N_1, N_2, N_3, N_4 = atoms involved in a vibration.

(For explanation of atom # refer to Fig. 79)

Table XVI. Input data for calculation of the B matrix.

1 4	-.557745	1 22	.557745	1 5	.030012	1 23	-.030012
2 7	-.999976	2 25	.999976	2 8	-.006981	2 26	.006981
3 13	.521696	3 31	-.521696	3 14	-.853132	3 32	.853132
4 16	.995725	4 34	-.995725	4 17	.092370	4 35	-.092370
5 1	.500000	5 19	-.500000	5 2	.866025	5 20	-.866025
6 1	-1.000000	6 4	1.000000	7 4	-.439939	7 7	.439939
7 5	-.896028	7 8	.896028	8 7	.506034	8 10	-.506034
8 8	-.862513	8 11	.862513	9 10	.996041	9 13	-.996041
9 11	.008895	9 14	-.008895	10 13	.477986	10 16	-.477986
10 14	.870368	10 17	-.870368	11 16	-.577057	11 1	.577057
11 17	.816138	11 2	-.816138	12 10	-.493942	12 28	.493942
12 11	-.869495	12 29	.869495	13 28	-.999976	13 40	.999976
13 29	-.006982	13 41	.006982	14 28	.506034	14 37	-.506034
14 29	-.862514	14 38	.862514	15 22	.768530	15 4	-.768530
15 2	.728863	15 23	.516431	15 5	-1.245294	16 4	-.658378
16 25	-.006464	16 7	.664042	16 5	.322536	16 26	.925903
16 8	-1.248439	17 10	.063135	17 31	-.789937	17 13	.726802
17 11	-.707416	17 32	-.483052	17 14	1.190467	18 13	.645943
18 34	.005528	18 16	-.731471	18 14	-.351506	18 35	-.921968
18 17	1.273474	19 1	.594052	19 34	-.005528	19 16	-.509324
19 2	.421170	19 35	.921967	19 17	-1.343146	20 16	.645943
20 31	.789937	20 13	-1.435880	20 17	-.351506	20 32	.483052
20 14	-.131546	21 10	-.612581	21 25	.006464	21 7	.606116
21 11	-.359399	21 26	-.925903	21 8	1.285302	22 7	-.658378
22 22	-.768530	22 4	1.426908	22 8	.322536	22 23	-.516431
22 5	.193895	23 7	.658378	23 4	-.658378	23 2	-.728863
23 8	-.322536	23 5	1.051399	24 4	.658378	24 10	.612581
24 7	-1.270950	24 5	-.322536	24 11	.359399	24 8	-.036863
25 7	.612581	25 13	-.063135	25 10	-.549445	25 6	.359399
25 14	.707416	25 11	-1.066815	26 10	-.063136	26 16	-.645943
26 13	.709078	26 11	.707416	26 17	.351506	26 14	-1.058922
27 13	-.645943	27 1	-.594053	27 16	1.240795	27 14	.351506
27 2	-.421179	27 17	.069073	28 16	-.594053	28 1	.594053
28 17	-.421179	28 5	-.728863	28 2	1.150042	29 7	-.612581
29 28	-.598002	29 10	1.210503	29 8	-.359399	29 29	.339713
29 11	.019087	30 28	.598002	30 13	.063136	30 10	-.661138
30 29	-.339713	30 14	-.707416	30 11	1.047128	31 19	-.607311
31 1	.607311	31 5	.728863	31 20	.350631	31 2	-1.079494
32 16	.594053	32 10	.607311	32 1	-1.202163	32 17	.421179
32 20	-.350631	32 2	-.070548	33 21	.701262	33 6	.811356
33 18	.773416	33 3	-2.286034	34 30	.607758	34 15	.600331
34 9	.645050	34 12	-2.013947	35 24	-.925926	35 3	-.702889
35 9	-.677611	35 6	2.306426	36 27	-.925926	36 6	-.761394
36 12	-.762223	36 9	2.449542	37 33	.925926	37 18	.791693
37 12	.738918	37 15	-2.456537	38 36	.925926	38 3	.674290
38 15	.709463	38 18	-2.309679	39 6	-.079102	39 9	1.684994
39 15	.705570	39 12	-1.591390	40 6	.893064	40 3	-1.766921
40 15	-.819210	40 18	1.693074	41 9	.816387	41 6	-1.689516
41 18	-.893064	41 3	1.766194	42 9	-.785578	42 12	1.594140
42 18	.003458	42 15	-1.692020	43 12	-.853229	43 15	1.703817
43 3	.811947	43 18	-1.662535	44 12	.851788	44 9	-1.696121
44 3	-.811627	44 6	1.656040	-5 0	.000000		

Table XVII. B matrix elements obtained after execution of "EMAT".

I	F
1	1
2	1
3	1
4	1
5	2
6	3
7	3
8	3
9	3
10	3
11	3
12	4
13	4
14	4
15	5
16	5
17	5
18	5
19	5
20	5
21	5
22	5
23	6
24	6
25	6
26	6
27	6
28	6
29	7
30	7
31	8
32	8
33	9
34	10
35	11
36	11
37	11
38	11
39	12
40	12
41	12
42	12
43	12
44	12

EXPLANATION:

I = Internal coordinate # (= N_I in Table XVI)

F = Force constant #

Table XVIII. Input data for the "UBZM" program.

DEFINITION OF INTERACTION FORCE CONSTANTS													
1	4												N(OPT) = 1; N(COD) = 4
5	4	3	2	0									ATOM #'S
39	24	25	8	7	9	0	0	0	0	0			INTERNAL COORDINATE #
20	20	0	0	0	0	0	0	0	0	0			UB FORCE CONSTANT #
1	1												
3	4	10	0	0									
29	12	8	0	0	0	0	0	0	0	0			
16	16	0	0	0	0	0	0	0	0	0	0	0	0
1	1												
6	1	7	0	0									
32	5	11	0	0	0	0	0	0	0	0			
18	18	0	0	0	0	0	0	0	0	0	0	0	0
1	1												
12	6	1	0	0									
19	11	4	0	0	0	0	0	0	0	0			
17	17	0	0	0	0	0	0	0	0	0	0	0	0
17	17	0	0	0	0	0	0	0	0	0	0	0	0
1	1												
4	3	2	0	0									
24	7	8	0	0	0	0	0	0	0	0			
19	19	0	0	0	0	0	0	0	0	0	0	0	0

Table XIX. Input data for "UBZM" program. N(OPT) = options for weighting the coordinates. N(COD) = code for identifying the subroutine. N(COD) = 1 for geminal interaction, = 4 for a cis interaction.

NUMBER OF Z MATRIX ELEMENTS												225			
1	1	1	1.000000	2	2	1	1.000000	3	3	1	1.000000	4	4	1	1.000000
5	5	2	1.000000	6	6	3	1.000000	7	7	3	1.000000	8	8	3	1.000000
9	9	3	1.000000	10	10	3	1.000000	11	11	3	1.000000	12	12	4	1.000000
13	13	4	1.000000	14	14	4	1.000000	15	15	5	1.000000	16	16	5	1.000000
17	17	5	1.000000	18	18	5	1.000000	19	19	5	1.000000	20	20	5	1.000000
21	21	5	1.000000	22	22	5	1.000000	23	23	6	1.000000	24	24	6	1.000000
25	25	6	1.000000	26	26	6	1.000000	27	27	6	1.000000	28	28	6	1.000000
29	29	7	1.000000	30	30	7	1.000000	31	31	8	1.000000	32	32	8	1.000000
33	33	9	1.000000	34	34	10	1.000000	35	35	11	1.000000	36	36	11	1.000000
37	37	11	1.000000	38	38	11	1.000000	39	39	12	1.000000	40	40	12	1.000000
41	41	12	1.000000	42	42	12	1.000000	43	43	12	1.000000	44	44	12	1.000000
39	39	20	-.144788	24	24	20	1.519888	24	25	20	1.502904	8	24	20	1.174946
7	24	20	.420709	9	24	20	.491216	25	25	20	.917498	8	25	20	1.237193
7	25	20	.576855	9	25	20	.399677	8	8	20	.997359	7	8	20	.505587
8	9	20	.474900	7	7	20	.186574	7	9	20	.316329	9	9	20	.144175
44	44	20	-.144662	23	23	20	1.619323	23	24	20	1.498362	7	23	20	1.217469
6	23	20	.371318	8	23	20	.598016	24	24	20	.864547	7	24	20	1.191586
6	24	20	.479270	8	24	20	.467345	7	7	20	.999509	6	7	20	.460582
7	8	20	.532297	6	6	20	.131555	6	8	20	.320209	8	8	20	.213908
41	41	20	-.137158	28	28	20	1.471582	23	28	20	1.428722	6	28	20	1.151086
11	28	20	.458928	7	28	20	.478354	23	23	20	.912596	6	23	20	1.197892
11	23	20	.602247	7	23	20	.382322	6	6	20	.998411	6	11	20	.542841
6	7	20	.476760	11	11	20	.228431	7	11	20	.332625	7	7	20	.148888
40	40	20	-.136684	28	28	20	1.469110	27	28	20	1.423558	11	28	20	1.149905
6	28	20	.480162	10	28	20	.476915	27	27	20	.912707	11	27	20	1.194851
6	27	20	.602300	10	27	20	.379812	11	11	20	.998535	6	11	20	.544271
10	11	20	.476027	6	6	20	.229960	6	10	20	.332837	10	10	20	.146234
43	43	20	-.144347	26	26	20	1.563186	26	27	20	1.495675	10	26	20	1.190037
9	26	20	.469045	11	26	20	.479837	27	27	20	.921802	10	27	20	1.216538
9	27	20	.599639	11	27	20	.372705	10	10	20	.999482	9	10	20	.534019
10	11	20	.461861	9	9	20	.215999	9	11	20	.321531	11	11	20	.132803
42	42	20	-.144087	25	25	20	1.679040	25	26	20	1.486378	9	25	20	1.235617
8	25	20	.481541	10	25	20	.576760	26	26	20	.882835	9	26	20	1.170878
8	26	20	.491504	10	26	20	.419216	9	9	20	.997142	8	9	20	.476761
9	10	20	.505981	8	8	20	.145982	8	10	20	.317395	10	10	20	.187263
30	30	16	.681366	9	30	16	.524462	12	30	16	.533951	9	9	16	.755445
9	12	16	.808898	12	12	16	.770874	29	29	16	.665156	12	29	16	.563085
8	29	16	.551800	12	12	16	.733792	8	12	16	.774905	8	8	16	.718113
32	32	18	.787835	5	32	18	.579573	11	32	18	.583595	5	5	18	.692113
5	11	18	.737872	11	11	18	.667400	31	31	18	.635586	6	31	18	.538252
5	31	18	.551498	6	6	18	.714318	5	6	18	.774863	5	5	18	.735545
19	19	17	.473983	11	19	17	.582185	4	19	17	.431408	11	11	17	.787602
4	11	17	.769825	4	4	17	.657223	18	18	17	.433555	4	18	17	.417019
10	18	17	.476802	4	4	17	.698438	4	10	17	.796584	10	10	17	.809779
20	20	17	.478245	10	20	17	.499210	3	20	17	.431324	10	10	17	.785403
3	10	17	.770198	3	3	17	.659795	17	17	17	.521546	3	17	17	.441899
9	17	17	.532082	3	3	17	.618716	3	9	17	.742390	9	9	17	.770961
24	24	19	.579128	7	24	19	.515142	8	24	19	.524635	7	7	19	.745698
7	8	19	.798292	8	8	19	.761344	23	23	19	.658780	6	23	19	.553945
7	23	19	.551690	6	6	19	.693766	6	7	19	.747989	7	7	19	.698164

Table XX. Output Z matrix after execution of "UBZM" program.

FORCE CONSTANTS

5.110	K(C-H)	F1	C-H str
6.200	K(Ph-N)	F2	Ph-N str
5.552	K(C-C)	F3	aromatic C-C str
5.350	K(C-C ⁺)	F4	C-C ⁺ str
0.320	H(OCH)	F5	OCH def
0.450	H(OOC)	F6	ring OOC def
0.400	H(C+CC)	F7	C ⁺ CC def
0.400	H(CCN)	F8	NCC def
0.180	W(NCCC)	F9	NCCC wag
0.180	W(C+CCC)	F10	C ⁺ CCC wag
0.220	W(HCCC)	F11	HCCC ⁺ wag
0.230	T(OCCC)	F12	ring torsion
0.050	f(H..H)	F13	
0.050	f(C+.H)	F14	
0.050	f(N..H)	F15	geminal interaction
0.320	f(C+.C)	F16	force constants
0.550	f(C..H)	F17	
0.550	f(C..N)	F18	
0.300	f(C..C)	F19	
0.080	f(cis)	F20	cis interaction constant

MASSES OF ATOMS 1- 14

12.011	12.011	12.011	12.011	12.011	12.011
14.007	1.008	1.008	11.011	1.008	1.008
90.011	90.011	0.000	0.000	0.000	0.000

Table XXI. Input data for the "NOCO" program.
Abbreviations: str = stretch, def = deformation

MODE # XXIX

		DEL X	DEL Y	DEL Z
ATOM #	1	.0441	.0789	.0000
ATOM #	2	.0458	.0442	.0000
ATOM #	3	.0490	.0311	.0000
ATOM #	4	.0051	-.0030	.0000
ATOM #	5	.0096	.0543	.0000
ATOM #	6	.0193	.0625	.0000
ATOM #	7	.0384	.0891	.0000
ATOM #	8	.0346	.0367	.0000
ATOM #	9	.0492	.0528	.0000
ATOM #	10	-.0174	-.0303	.0000
ATOM #	11	.0294	.0664	.0000
ATOM #	12	.0208	.0475	.0000
ATOM #	13	.0280	-.0478	.0000
ATOM #	14	-.0565	-.0004	.0000

ASSIGNMENT: molecular breathing mode.

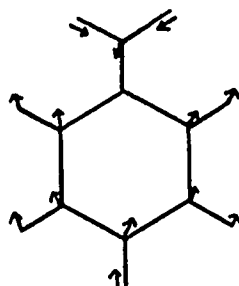


Table XXII. S vector output for calculated mode XXIX @ 263.5 cm^{-1} . The figure below represents the visual interpretation of this vibrational mode.

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