

**SPECTROSCOPY OF MASS-SELECTED
METAL CLUSTERS IN ARGON MATRICES**

By
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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.

2005

UMI Number: 3187393

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

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ABSTRACT

Spectroscopy of Mass-Selected Metal Clusters in Argon

Matrices

By

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The chemistry of metal clusters is a fascinating and expanding area of research. During the last three decades, the study of metal clusters and in particular transition metal clusters has been the subject of numerous experimental and theoretical investigations. The desire to understand the frontier between molecular chemistry and solid state physics, as well as to gain new insight into the chemical properties of the metal surfaces used in heterogeneous catalysis is one of the motivations for the extensive work done on metal clusters.

Absorption and Resonance Raman spectroscopy has been employed to interrogate mass-selected metal clusters in argon matrices. With the CCNY metal cluster deposition source, metal cluster cations (produced by bombardment) are mass selected using a velocity Wien Filter, and then co-deposited with rare gas on a cold window in the presence of low energy electrons. Neutralized cluster samples are interrogated by absorption, excitation, fluorescence and

Raman spectroscopy. Good quality Raman spectra of Heteronuclear Clusters such as dimers of Al_2 , Mo_2 and trimers of Cr_3 , Mo_3 , and tetramer of Sc are reported. At the same time, investigation of heteronuclear clusters resulted in reports on VCo , VFe , CuAg , CrFe , and TiCu_3 . The information about the geometry, electronic and vibrational structures, dissociation energies and force constants are determined from resonance Raman spectroscopy, absorption and Raman excitation profiles which turned out to be a very useful and fruitful method to assign all the optical transitions involved in each metal clusters. In fact Raman excitation profiles might even be a more sensitive method for obtaining cluster absorption spectra than direct measurements.

ACKNOWLEDGMENTS

I would like to thank all my colleagues during the research about this thesis. Dr. Li Fang, Dr. Bing Zhao and Dr. Wei Qing Xu, and Dr. Lei Yan who provide me a free space of learning and thinking; Prof. Ronald Birke and Prof. Louis Massa, who keep eyes on every improvement of me. Without them, I could not finish so far.

I am deeply indebted to Prof. John R. Lombardi, my academic mentor. He taught me not only the knowledge but also the art of science. His courage and support brought all my work through tough situations. His dedication to research and strictness in experiment will teach me all my life. Without him, I could never finish this work.

I really could not have done it without my family behind me. Especially my parents for their encouragement support and most of all they has never failed to be there for me. My parents in law for their continuous blessing.

At last but not the least I dedicated this thesis to my wife, her unconditional love and prayers have always helped me achieve my goals.

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CHAPTER I. INTRODUCTION

The nature, importance and potential applications of metal clusters are issues attracting wide attention by a large number of investigators working in quite diverse areas of research. Increasing the importance is the recent attention being paid to the field of nanotechnology.¹ This is especially evident from the proliferation of specialized symposia^{2, 3, 4, 5, 6} and review articles,^{7, 8, 9, 10} where contributions have ranged from nuclear and solid state physics through materials science and chemical synthesis. Thus, while the two extrema, the free atom and the bulk metal are quite well understood, much less is known about the transition region in between. One experimental approach involves growing increasingly smaller particles and looking for the appearance of "quantum size" effects. A second, complementary method is to start with the atom and then synthesize progressively larger cluster sizes, attempting to find the "onset" of bulk properties such as band structure, plasma resonances, ionization, phase transitions, crystalline habit, etc.

In the past 20 years or so, metal clusters without ligand support have come under both experimental and theoretical examination. The potential applications could

be in fields from solid state physics to chemical catalysis, or from material science to chemical synthesis.

The knowledge of clusters provides not only clues as to interaction within and between materials, but also provides a template for designing new materials. The technology developed on the way to achieving the knowledge such as molecular beam instrumentation, spectroscopy, as well as theoretical methods present a great contribution to all science fields.

An overwhelming array of techniques has been brought to bear in cluster science. Experimental studies have focused on absorption spectroscopy, excitation spectroscopy, surface scattering and depletion, ionization potential, stability and thermodynamic, photochemical process. In the following, we will focus on details of several previous experimental studies for the vibronic property of the cluster.

Knudson Effusion Mass Spectroscopy is probably the earliest investigation of clusters. The major concern of this method is to determine the dissociation energy by setting up thermal equilibrium between cluster and atom. Results for almost all transition metal dimers had been published 20 years ago¹¹. The second law is applied to the equilibrium constant vs. temperature which in turn gives

the dissociation energy D_e . Another way is to use the third law and to predict some parameter such as frequency, and degeneracy for both ground state and excited. The third law method always provides better and more reasonable results than second law. For the second law method, the relatively high deviation is from the uncertainty in the mass determination and therefore in the equilibrium constants. Furthermore, experiments are limited by a technology 20 years old so that there are problems in ionization, measurement, as well as purity. The equilibrium is a slow process and the result may be different from spectroscopic dissociation. The real process would not always be from the cluster ground state to atomic ground state.

Study of gas phase clusters is hampered by insufficient sensitivity. Nevertheless, there are still some elegant experiments. The following two methods change the essence of detection by ionization, substituting photon detection by more sensitive ion detection.

Photoelectron Spectroscopy of negative cluster ions provides information on the neutral cluster. It reveals the accurate electron affinity (EA) of a cluster. The ground state gas phase information from this experiment is always reliable. The vibrational frequency result for Cr_2 and Pd_2 ¹² is selected as our standard in the dimer periodical table.

Sometime even the anharmonicity constant could be quite similar to the matrix isolation result also. However, the frequency data acquired from this method is not as precise as from Raman spectroscopy. The method is also limited to those dimers whose diatomic anion may be formed from the discharge of a carbonyl complex. Zero Kinetic Energy (ZEKE) is a special way to detect a photoelectron, which is successfully applied in cluster investigation such as in Y_2 ¹³.

The review¹⁴ of Dr. Michael Morse summarized cluster investigation as of 1986. Soon after that, his group at the University of Utah began their studies on resonance two-photon ionization (R2PI) spectroscopy of clusters. From such studies they obtained information on molecular term symbols, dissociation energy through predissociation threshold measurements, equilibrium distance (r_e) between atoms by rotational resolved studies, precise force constant or vibrational frequency (ω) measurements by fluorescence and ionization energy for clusters. They provided the most reliable spectroscopic D_e . The precision of the parameters, around 0.2% deviation of ω , D_e and r_e , is astonishing. That is due to the application of extremely sensitive R2PI or fluorescence detection, as well as a 0.04 cm^{-1} line width scannable dye laser. They published numerous

results about several homonuclear¹⁵ and especially heteronuclear¹⁶ clusters. Such experiment on a gas phase cluster revealed the geometric information through rotational structure, and this has an advantage over matrix isolation. The obvious limitation of this method is that the resonance process must take place in the region where the dye laser can be continuously lasing. The assignment of electronic state energy levels is another problem.

A purely spectroscopic method with detection of photons always requires accumulation of the clusters such as in a deposition process. Fluorescence and resonance Raman are always applicable. Cu_2 , Mo_2 , and Pt_2 ¹⁷ are three special species only determined by fluorescence. Normally, the fluorescence spectrum is easier to detect due to its high intensity. Because of the huge number of excited states located between ground and the excitation state, and being a relatively slow process, fluorescence is often quenched in metal clusters. On the contrary, a faster process such as Raman Spectroscopy is more generally applicable. Fluorescence is so sensitive that gas phase clusters are sometimes detectable. The shortcoming of fluorescence is the uncertainty of the ground state assignment.

Resonance Raman spectroscopy is a powerful tool for the study of molecular vibrations that are coupled to electronic transitions in clusters. Much information can be obtained about the potential surfaces of both ground and excited states. Matrix Isolation and resonance Raman spectroscopy of clusters has been investigated by the Moskovits group. In the late 80's they almost finished the measurement of all the third row dimers and several trimers. By the furnace method they produced cluster mixtures of all sizes, analyzed and assigned the spectroscopy. Some other ambiguous but interesting results are obtained from varying working condition such as: cluster to matrix gas ratio, temperature, pressure, photo-dissociation and aggregation. Some of their assignments for absorption are successful especially those with Resonance Raman evidence. But some others, including features for clusters larger than a dimer failed. Their work provided a great incentive for further cluster studies.

In recent years considerable progress has been made in these areas by other techniques, such as photoelectron spectroscopy of metal cluster anions¹⁸ resonance enhanced multiphoton ionization photoelectron spectroscopy^{19,20,21}, and photodissociation spectroscopy of metal cluster cations.^{22,23} These techniques have been quite valuable in elucidating

the optical spectroscopy of transition metal clusters. Photoelectron spectroscopy yields vibrational spectra of ground states, but is of somewhat lower resolution than our Raman technique, and the spectra are often considerably more congested. The multiphoton ionization techniques provide considerable information about internuclear distances, especially when rotational resolution is obtained, but are often not sensitive to ground state vibrations. They have, however, found considerable utility in determining dissociation energies. The use of third law Knudsen effect measurements as well as spectroscopic measures of anharmonicities have well-known deficiencies in this regard²⁴, while Morse and co-workers have shown that under the right conditions, quite accurate measurements can be obtained by observing an abrupt predissociation threshold. On the other hand, the mass-selected resonance Raman spectra, proposed below are of sufficiently high resolution to provide quite accurate values for force constants. These are especially valuable as a complement to the known dissociation energies in understanding chemical bond strengths.

There are only three machines of neutralization matrix isolation of mass selected clusters in the world. The contribution of the first in Switzerland has been basic

mechanisms such as sputtering, neutralization, soft-landing, fragmentation and deposition process in Ag clusters²⁵. On the other hand, and we have studied clusters across the periodic table. A recent goal by the Moskovits group focuses their interest on size dependent bonding and geometry, especially from coinage metal clusters²⁶.

The configuration of electronic states is important knowledge for all clusters. Electron Spin Resonance (ESR) is another important way to go deeply into essence of bonding²⁷. This method focuses more on the electronic character, especially paramagnetic properties instead of nuclear vibration parameters. Normally, ESR is a very sensitive measurement in matrix isolation. Geometry is an indirect result of ESR analysis comparable with Raman results. However, ESR detects a slow process compared to molecular stretching so that it determines only the average geometry. Thus it is sometimes the case that ESR gives different structural conclusions from spectroscopy.

Besides those experimental methods mentioned above, there are a lot of other investigation about such topics as ionization potential, electron affinity, structure and internuclear distance, and potential application of cluster chemical reactions. They are all related to bonding characteristics.

Investigation in the cluster area has been divided into experimental and theoretical. Theoretical calculation predicts the results of experiment and the experimental results modify some of the theories. They are normally based on the traditional *ab initio* methods or semi-empirical methods. Calculation on metal clusters, especially for heavy element of third row, are challenging because of the large number of electrons, relativistic effects, electron spin orbital coupling effect, etc. There is no single calculation model that could explain all experimental results. During our studies, density functional calculations employing pseudopotentials with configuration interaction were applied in lanthanide dimers²⁸, and Complete Active Space Multi-Configuration Self-Interaction (CASSCF) + Multi-Reference Configuration Interaction (MRSDCI) made for trimer¹² energy levels and the symmetry appears more reliable. However, it is still hard to predict the correct parameters before experimental work.

The high sensitivity of ESR enables our neutralization method applicable for sample preparation. The mass-selected matrix isolation device can be modified for such an application. On the other hand, the heteronuclear properties have become attractive along with homonuclear cluster studies. The force constant, dissociation energy,

and even absorption character can be predicted from homonuclear dimer parameters. For example, the dissociation energy can be predicted by Pauling's rule, force constant is always believed to be between two component homonuclear dimers, excited states levels are sometimes foreseen especially for heteronuclear dimer by two atoms from same group. However, the experimental details are still so sparse that it is hard to summarize. It can be suggested that additional investigation of heteronuclear dimers with our experimental set-up should be undertaken.

Such investigations raise a host of rather intriguing questions. How in detail does the progression from atom through molecule to macroscopic sample take place? Do properties vary monotonically with cluster size? In what ways do the molecular and solid-state descriptions of matter merge? Do clusters possess special properties (e.g. shell and "supershell" structures), not to be found in molecules or bulk materials? Might such properties be of practical importance, as for instance in the fabrication of nanostructures? Could particular molecular arrangements, observed in cluster samples, provide a template for the design of new materials? Might cluster beams be a means of manufacturing macroscopic components or materials, for example as sources for epitaxial growth? Can nanophase

materials and quantum dot devices be assembled using clusters or even on an atom-by-atom basis?

Parallel to and interactive with these more fundamental concerns has been a search for applications of these novel compounds. In fact, much of the early interest in cluster chemistry was driven by the realization that catalytic behavior is related largely or in part to the properties of small metal particles.²⁹ The majority of present day industrial catalysts are heterogeneous in nature. In many cases the active site may be a molecular sized cluster or "raft". For certain "demanding" reactions, catalytic activity is markedly improved as the degree of dispersion (ratio of atoms present in the surface to the total number of atoms) is increased.^{30, 31} This effect arises not just from an increase in surface area, but also because small metal particles ($< 50 \text{ \AA}$) show a much greater activity than do larger particles. Certain bimetallic catalysts have a dispersion approaching unity, with particle sizes as small as 5 - 10 $\text{\AA}$. Recently,³² a Pt_3Ru_6 cluster complex has been shown to be an effective catalyst for hydrogenation reactions. More recently, platinum-tin and platinum-copper alloys have been shown to be highly effective in increasing oxidative dehydrogenation of ethane to ethylene.³³ Such studies have enormous implications for industrial processes.

A related effect is the observation³⁴ that smooth, perfectly grown Pt surfaces are relatively inactive as catalysts. However, Pt surfaces prepared with a large number of kinks, terraces and other irregularities show enhanced activity. Apparently, it is the nature of the imperfections on the surface, a class of features, which in many ways mimic small metal clusters.

One of the goals of this research is to help understand the nature of bonding in metal clusters. In the transition metals, bonding is dominated by the s - and d -electrons. The extent of the d -orbital contribution to bonding is largely dependent on the relative availability for bonding of the $(n+1)s$ electrons as compared with that of the nearly isoenergetic $(n)d$ electrons. The ratio of the expectation value of the orbital radii $\langle r_{nd} \rangle / \langle r_{(n+1)s} \rangle$ is found to decrease considerably with increasing atomic number within a particular transition metal row. Both nd and $(n+1)s$ orbitals contract as the nuclear charge increases, but the nd electrons are not shielded as effectively as the $(n+1)s$ electrons, and therefore contract more rapidly. Thus d -electrons tend to be spatially less available for chemical bonding in the late transition metals. In addition to spatial extent we must also account for energetic considerations. Many transition metal atoms possess ground

$d^m s^2$ configurations. These are relatively unsuitable for bonding since the s-orbital is filled. In order for a good bond to form between two metal atoms at least one must be promoted to the $d^{m+1} s^1$ configuration. The resulting bond strength is consequently reduced by the promotion energy required. Still further complications ensue when relativistic considerations, especially important for the heavier third row transition metals, are taken into account. Third row species also involve *f*-orbitals, although it is usually presumed that their contributions are slight. In recent years considerable progress has been made in these areas by other techniques, such as photoelectron spectroscopy of metal cluster anions³⁵ resonance enhanced multiphoton ionization photoelectron spectroscopy^{36, 37, 38}, photodissociation spectroscopy of metal cluster cations.^{39, 40} These techniques have been quite valuable in elucidating the optical spectroscopy of transition metal clusters. Photoelectron spectroscopy yields vibrational spectra of ground states, but is of somewhat lower resolution than our Raman technique, and the spectra are often considerably more congested. The multiphoton ionization techniques provide considerable information about internuclear distances, especially when rotational resolution is obtained, but are often not sensitive to ground state

vibrations. They have, however, found considerable utility in determining dissociation energies. The use of third law Knudsen effect measurements as well as spectroscopic measures of anharmonicities have well-known deficiencies in this regard⁴¹, while Morse and co-workers have shown that under the right conditions, quite accurate measurements can be obtained by observing an abrupt predissociation threshold. On the other hand, the mass-selected resonance Raman spectra, proposed below are of sufficiently high resolution to provide quite accurate values for force constants. These are especially valuable as a complement to the known dissociation energies in understanding chemical bond strengths.

Chapter II Experimental

2.1 overview

The cluster deposition source is shown schematically in Figure 2.1, and will be discussed thoroughly in the following sections. Briefly, A intense (typically 15 mA at 25 keV) argon ion beam from a "CORDIS" ion source sputters metal cluster ions from a water cooled target, which is maintained at about 300 V. Secondary ions were extracted with a modified Colutron model 200-B lens system and then mass selected using a Wein filter in conjunction with an approximately 175 mm long drift space and a 6.5 mm diameter aperture. After mass separation, the ion beam is bent by 10° (using deflector plates D2, mounted in a short bellows section) to eliminate neutral sputtered products, and then guided to the deposition region by two einzel-like lenses. The secondary beam line (extraction lens, Wein filter, drift space, etc.) was floated at about -1.5 kV to increase the extractable ion currents.

Cluster ions were then codeposited with Ar and electrons on to a CaF_2 substrate held at about 16K. Prior to deposition, the selected ions were slowed down by a surrounding "Faraday cage". Secondary current could be measured between metal target and a Faraday plate in the

deposition region. Matrices were grown at about 5-7 $\mu\text{m}/\text{hour}$ with an Ar:metal ratio of approximately $10^4:1$.

Matrix samples were interrogated *in situ* using absorption, excitation and Raman spectroscopy. For the first two measurements we employed a deuterium or a tungsten lamp, dispersed by a (computer controlled) Spex $\frac{1}{4}$ m monochromator (calibrated with a Hg lamp) and focused onto the matrix sample as indicated in Figure 2.1. The mirror (M in Figure 2.1) is mounted on a computer controlled stepping motor (Compumotor A5783), which allows the focused light to be scanned (in approximately 12 steps) across the 8 mm wide sample. All the measurements were made by collecting the light scattered at 90° to that incident using lens F in Fig 2.1. (F/1 optics). The absorption spectra were detected by a cooled (Hamamatsu R943-02) photomultiplier tube (PMT), which is mounted directly on the deposition chamber, and amplifier/discriminator using photon counting techniques and an AT386 compatible computer. The only difference between absorption and excitation measurements is that for the latter the emitted light was filtered by an appropriate long pass filter (LPF) before detected. Raman spectra were recorded using Ar^+ laser (Spectra Physics, Model 2045), a dye laser (Coherent, 599-02), or a titanium sapphire (TiS) laser (Lexel model 479)

with, typically, 30-80 mW focused down to an estimated 50 μm spot. Plasma lines were removed by predispersing the laser beam with a grating. Light scattered at 90° was focused onto a 0.6m Triplemate spectrometer (Spex model 1877E) and detected with a liquid nitrogen cooled CCD detector (SPEX model "Spectrum One"), and DM3000R series software.

2.2 Primary Ion Source

A CORDIS ion source⁴², designed and manufactured by Rokion Ionenstrahl-Technologie, is used to produce the primary beam. For the purpose of sputtering, medium and heavy inert gas ions (e.g. Ar, Kr) are employed.

CORDIS is a reflex discharge multicusp source with single stage discharge, featuring the cylindrical anode alone lined with magnets and both end plates of the discharge chamber on or close to cathode potential, see Figure 2.2. The Ar^+ are created by electron-impact ionization, forming plasma (typically 15mA at 25keV). Discharge is employed and maintained by a dc voltage (50-80V) between a thermionic cathode and an anode. The cathode is composed of Ta wires, and the typical working condition is 7 volts at 120 A. The pressure of Ar gas (Matheson, analytical grade, 99.9999%) during discharge, measured as in sputtering chamber, is maintained at about 1.5×10^{-5} Torr. The magnetic field, with a so-called minimum-B configuration, is used to confine the plasma and enhance the ionization rate per electron.

The primary beam was collimated by an 8mm aperture, which also serves to separate the ion source from the rest

of the apparatus. The ion source was pumped through and around this aperture, by a 500 l/s turbomolecular pump (Blazers TPU510) which supports the specially designed sputtering chamber (MDC Vacuum Products).

2.3 Sputtering

Metal cluster cations are formed by sputtering from a water-cooled, rotatable metal target using the intense, high energy Ar^+ beam of the "CORDIS" ion source. Compared with other ionization technique, the superiority of sputtering lies in the fact that any solid element, which is not an insulator at operating temperature, can be done by sputtering.⁴³ In principle, it is universal within our interest in transition metals.

Fig. 2.3.1 shows a simple scheme for producing a beam of ions by sputtering. It is a process of kinetic ejection of the particles of the bombarded substrate as a result of the momentum exchange between the impinging ion and the particles of the target lattice. This process may comprise various effects, which depends on such physical parameters as incident ion energy and mass, angle of incidence, target lattice or crystalline nature, ambient gas pressure, and target temperature. The extent to which these parameters influence sputtering is difficult to ascertain a priori.

The incident angle of Ar^+ beams adopted here is 50° , which is close to the optimum ejection angle⁴⁴, but a bit smaller than most other reported optimum angles for

sputtering yield that range from 60° to 80° ⁴⁵. Incident energy between 20keV and 25keV is employed to achieve maximum secondary current. Further increment of this energy has little effect on secondary current. As shown in Fig. 2.3.2, a typical qualitative sputtering ratio curve is mainly composed of threshold, linear portion, plateau, and back. This plateau generally extends from 10 to 30keV, and it is evident that the incident energy in our experiments fell into this region. The target holder is composed of copper, a good thermal conductor, and cooled by water to prevent metal sample from melting. It has been shown that the effect of target temperature on sputtering is generally small for temperatures not too close to the melting point.⁴⁶

An important parameter of this secondary ion source is the energy spread of the ions produced, that is the width of the energy distribution of the ions. This parameter is of special importance since the ion beam is to be acted on by a mass separator. A distribution in ion energy can result from a number of causes. Metal cluster cations may be created at different locations and thermal energy that is characteristic of the temperature of the cations. Ions created by sputtering also originate from an equipotential surface and have an energy distribution characteristic of secondary ions, which is peaked at about 5 eV and has a

low-intensity high-energy tail extending into the few hundreds of eV. At low bombarding energies, the energy distribution approaches Maxwellian, but at higher energies the distribution deviates significantly from Maxwellian, the high-energy tail becomes more predominant.

The sputtering yield is one of our major concerns, since enough sample has to be gathered for effective measurements. The following expression indicates the relationship between sputtering yield and some physical parameters.

$$Y(E, \theta, x) = 0.042 F_D(E, \theta, x) / NU_0$$

Here, x is the depth of the sputtering surface from the entrance point of the projectile, E is the projectile energy, and θ is the angle of incidence to the surface normal. $F_D(E, \theta, x)$ is the deposited energy depth distribution, and U_0 and N are the average surface-binding energy and the density of the target material, respectively. A necessary condition for the yield to be proportional to the deposited energy at the surface is that $E \gg U_0$.

With mass selection, as in our experiment, only clusters with one given energy (E_1) and charge state emitted into a given angle (Ω_1) can be measured, i.e., $\frac{\partial^3 Y}{\partial E_1 \partial^2 \Omega} \Delta E_1 \Delta \Omega_1$ is determined. It is worth pointing out that this quantity

is generally not directly proportional to the sputtering yield.⁴⁷

2.4 Wein Filter (Mass Spectroscopy)

The mass separator is the key element of this system, since the species and purity of the ion beam at deposition is of our major concern. For this purpose, a COLUTRON VELOCITY FILTER (Model 600-B) is used, which is a typical ExB separator, sometimes also called "velocity analyzer" or "Wein filter". The Wein filter makes use of an electric field normal to both the magnetic field and the ion trajectory to counter balance the Lorentz force on a particle of given velocity. Under this balance condition a selected class of ions will pass straight through the separator, while particles of different mass or velocity will be deflected.

Compared with other frequently used mass separators, a Wein filter's superiority lies in some of its main features: Straight beam line; Economical and lightweight; Controllability. A major draw back of this type of mass separator is the transmission of neutral species. In our system, the ion beam is bent by 10° after mass selection to prevent neutral species from entering the deposition chamber.

As illustrated in Fig. 2.4.1, the Wein filter is made up of a long magnet, along the axis of which the magnetic

field is uniform. Along the x direction, an electric field is created by the potential between two parallel electrostatic deflection plates. Because the width of the plates is comparable with their spacing, the electric field will be barrel shaped, with consequent distortion of a finite diameter beam, unless a field correction is applied. For this reason, a gradient on electrostatic field is introduced by means of electrically biased guardrings. The guardrings are made of stainless steel shims and each guardring is individually connected to a potentiometer which provides the right bias.

The Wein filter is cooled using a HFC-134a refrigerator (Model CU-1, Copeland Corp.). A thermal sensor is attached on the stainless steel that encapsulates the magnet coils. The pressure is adjusted during experiments so that the working temperature of Wein filter is below 60°F.

If the balance condition $v_o = E_o/B_o$ is set for a desired ion of mass m_o injected along the axis of the separator, it can be shown that the dispersion (D), or the distance off axis that an ion of mass m is deflected, is given by the equation

$$D = \Delta x = \frac{l \cdot a \cdot E}{2V_o} \left(1 - \sqrt{\frac{m_o}{m}} \right)$$

where l is the drift distance from the center of the filter, a is the length of the filter, E is the electric field strength, V_0 is the acceleration voltage. When $m \pm m_0 = \delta m \gg 1$, this relation can be simplified to

$$D = \Delta x = \frac{l \cdot a \cdot E}{4V_0} \frac{\delta m}{m}$$

Let us consider for example a separation for 1800eV Gd_2^+ . Using the Wein filter for which $E = 130\text{V} / 0.0178\text{m}$, $a = 0.152\text{m}$, $l = 0.251\text{m}$, $D = 0.00325\text{m}$, the calculated mass resolution $\delta m/m = 0.08$. The magnetic field strength B_0 can be derived from

$$B_0 = E \sqrt{\frac{m_0}{2qV_0}}$$

and is about 2200 Gauss.

The velocity dispersion or variation in velocity of the ions in Wein filter is an important quantity affecting its performance, which can reduce the mass dispersion sensitivity. Ions of desired mass m_0 can be deflected in the magnet even under supposedly balance conditions (i.e., $v_0 = E_0 / B_0$) if $\delta v \neq 0$. As discussed in the previous section, since the process of sputtering does not produce a monoenergetic beam, the actual mass resolution is somewhat lower than calculated above, but still sufficient to

separate atom and different size of clusters, as shown in Fig. 2.4.2.

2.5 The Deposition Chamber (Matrices)

The deposition chamber consists of an 8 in. conflat cube (MDC Vacuum Products) and is pumped by a 500 l/s turbomolecular pump. The 10° bend separates interested cluster ions from neutral sputtered products, whose flux may be comparable to or greater than that of the ions. In previous examination⁴⁸, neutral silver clusters both with and without a 10° bend were deposited, and it's estimated that only about 1% of the neutral species is deposited in our experiments.

The deposition region is shown in more detail in Figure 2.5.1. Cluster ions were confined and directed towards a 45 x 8 x 1 mm polished CaF_2 substrate by electrostatic lenses (denoted L2 and L3 in Fig. 2.1), where they were co-deposited (at about 16K) with Ar and electrons. The CaF_2 window is mounted on a closed cycle cryostat (APD Displex, 204SL/DMX-6) using Wood's metal and an in gasket. The cryostat temperature was measured by a Si diode in conjunction with a Scientific Instruments model 5500 temperature controller. This temperature controller can also be programmed to carry out annealing experiments. The CaF_2 substrate was largely enclosed by a conducting cage (shaded regions in Fig. 2.5.1) composed of two side plates

(with openings for optical measurements), the lower half of the cryostat radiation shield, the electron source, and the last lens element of L3 which was closed by a 90% transmitting Ni mesh. All these components were held at the same voltage and form a so-called "Faraday cage". This cage serves to decelerate the cluster ions, whose deposition energy (eV_{dep}) was controlled by altering the potential difference applied between the target and Faraday cage, which was held at approximately 10 eV. Secondary ion currents could be monitored using a Faraday plate (not shown) situated near the deposition window. Since the cryostat is rotatable, the Faraday plate and the window could easily be adjusted in order to measure ion currents, prepare matrix samples, or to record optical spectra. The kinetic energy distribution of the arriving ions, measured by applying a retarding potential to the Faraday plate, was centered close to $eV_{\text{dep}} = 0$ eV with a FWHM of about 10 eV. A typical deposition curve of the ion current and kinetic energy vs. voltage difference between the target and the Farady cage is shown in Fig. 2.5.2.

The ions were neutralized by a charge cloud of electrons maintained between the transmitting mesh and the substrate. The electron source consisted of a Philips electron microscope filament (0.13 mm tungsten) on a

ceramic base (Ladd Research Industries). This assembly was enclosed by a stainless steel box having an 8 x 1 mm slit positioned so that the electrons were introduced about 1-2 mm in front of the CaF_2 substrate. In order for sufficient, low-energy electrons to reach the matrix target, the filament was biased at about -3V with respect to the Faraday cage. This arrangement provides a self-regulating mechanism for the deposition process. Thus, the matrix is charged negative until this potential prevents the arrival of further electrons. Incoming cluster cations decrease this charge so allowing more electrons to reach the matrix. When cluster ionization potentials are large in comparison with the cluster bond energies, the neutralization step is believed to take place on, or very near to, the matrix surface.^{49,50}

Matrix argon gas (99.9995% Ar, Alphagaz) is introduced into deposition chamber through eight 0.5 mm diameter holes located on the last lens element of L3, forming a coaxial injector ring. Matrices were grown at 5-7 μ /hour with an Ar:metal dilution ratio of approximately $10^4:1$, i.e., sufficient to ensure that the dimers remain well isolated both from each other and (more difficult to achieve) from any impurity species. During deposition, the partial pressure of H_2O (the dominant background gas) in the

cryostat chamber was generally about 5×10^{-9} Torr, as measured on a residual gas analyzer (Leybold-Inficon, Quadruvac Q100). This translates into a better than 95% probability that a cluster will be surrounded by at least 12 nearest-neighbor argon atoms.

Fragmentation may be estimated by comparing the intensities of atomic excitation features in a dimer deposition with those obtained from depositions of the atom under similar conditions.

2.6 Absorption (Scattering Depletion Spectroscopy)

SDS (Scattering Depletion Spectroscopy) works as a substitute for absorption for optically thin matrix samples in which the scattering is relatively intense. For these measurements we employed a deuterium or a Tungsten lamp, dispersed by a (computer controlled) Spex $\frac{1}{4}$ m monochromator (calibrated with a Hg lamp) and focused onto the matrix sample. A mirror is mounted on a computer controlled stepping motor (Compumotor A5783), which allows the focused light to be scanned (in approximately 12 steps) across the 8 mm wide sample.

The SDS intensity is defined by the ratio of the "reference intensity" to the "signal intensity". The former corresponds to light scattered from an edge of the sample, whereas the latter pertains to that region near the center. The optical density profile of the sample was obtained by recording single beam scattering spectra as a function of lateral position the sample on the substrate. It is generally found that the sample is non uniform, with about twice as much absorption in the center as compared to near an edge. Compared with conventional absorption spectra, using the same signal and reference position but detecting

the light transmitted through the sample, the SDS signal is 20~50% more intense. Due to the relatively more flat background of scattering light, SDS should be more sensitive than normal absorption.

In our experience, the SDS signal is related to the thickness of matrix sample. Five to six hours deposition of sample and matrix gas provide suitable thickness for the scattering measurement. Another interesting characteristic is further deposition after 6 hours will not increase the scattering signal any more and the absorption curve vs. the deposition time will become flat. Such saturation may be brought by insufficient interaction of photon and sample caused by thickness.

Besides higher sensitivity, SDS is much more convenient to setup than normal absorption. Fluorescence spectroscopy, which is also important for spectroscopic identification and fragmentation estimation, can be applied without further optical setting. Another advantage over absorption is the possibility of using a nontransparent substrate such as an Al plate.

There is a broad background in the spectra. This is due to relatively small, but wavelength dependent, difference in scattering and/or collection efficiency in the reference and signal beams. It is not easy to pick

absorption peaks out from background if the absorption is too broad. Normally the absorption with less than 50nm width would not be a problem.

The SDS or absorption spectrum is an important indication of the location of resonances. It gives us a clue as to where to excite the sample with a laser. However, not all absorption regions will give high quality resonance Raman spectra. Sometimes the absorption of cluster is overlapped with that of atom. Strong atomic emission or fluorescence from impurities will diminish any dimer spectrum.

Most homonuclear transition metal dimers have been tried in our lab. Fig 2.6.1 and 2.6.2 show the SDS spectra of transition metal dimers. Some of them have strong absorption structure. However, there are also some metals giving good resonance Raman spectra even without obvious absorption. The appearance of resonance Raman is evidence for our assignment to absorption. If we assume the most probable spectroscopic impurity is from fragmented atoms, we can assign our spectra quantitatively by comparison to the deposition of an atom.

2.7 Resonance Raman Spectroscopy

An intense light source, normally a laser is applied to excite the sample for high quality resonance Raman spectra. An argon ion laser (Spectra Physics 2045), dye laser (Coherent, 599-02) and Ti-Sapphire laser will cover almost entire range from 360nm to 910nm. Typically, about 50 mW is focused down to an estimated 50 μ spot. Plasma lines are removed by dispersing the laser beam with a grating. The Raman spectrum is collected at 90° to the incident light with a Spex 1877E Triplemate Spectrometer (0.6m) and detected by a liquid nitrogen cooled CCD detector (Spex model "Spectrum One") with DM3000R software.

Resonance Raman spectra of metallic clusters are characterized as an overtone peak progression with almost the same interval for the totally symmetric vibrational mode. The intensity increment of resonance over nonresonance Raman is estimated to be 100 times. Although resonance excitation raises the scattering power of many substances by several orders of magnitude, resonance Raman can not always be observed with ease. The scattered radiation may be abnormally attenuated by simultaneously intensified absorption and possibly concealed by superimposed fluorescence emission. Moreover, photolysis may not only

destroy the sample but also produce unknown products. Those Raman lines with small shift lower than 100cm^{-1} are normally hard to detect due to the intense Rayleigh scattering background especially at short wavelength excitation.

Compared to the previous experimental data obtained with a double $\frac{1}{4}$ m monochromator combined with photomultiplier tube, the application of a Triplemate Spectrometer and detection of with a CCD increased the precision of our measurement. Furthermore, the experiment duration is greatly shortened and more exploration is possible. This is especially helpful when no obvious absorption character is shown in SDS, as with Rh_3 and Ru_3 trimers.

Raman spectra provide a lot of information on the ground state and low lying excited states, including force constant, anharmonicity, spectroscopic dissociation energy, and geometry information for clusters larger than dimer.

The Raman excitation profile is the relative Raman intensity vs. excitation wavelength. Such relative intensity can be the intensity ratio of Raman line to CaF_2 or the absolute intensity divided by the excitation laser intensity and CCD integration time. The Raman profile is often more sensitive than SDS (absorption), which reveals useful absorption detail. First of all, it provides proof

of our absorption assignment. It is also helpful in extracting the dimer absorption shape from the overlap band between dimer absorption and the more intense atomic absorption. Sometimes, fine structure involving vibrations of the electronic state can be achieved clearer than with absorption. For polyatomic metal clusters, when more than one normal mode is of concern, the excitation profile is especially useful. The excitation profile gives not only resolved exhibition of all modes but also information as to symmetry and transition polarizability, which is often a clue to the transition assignment.

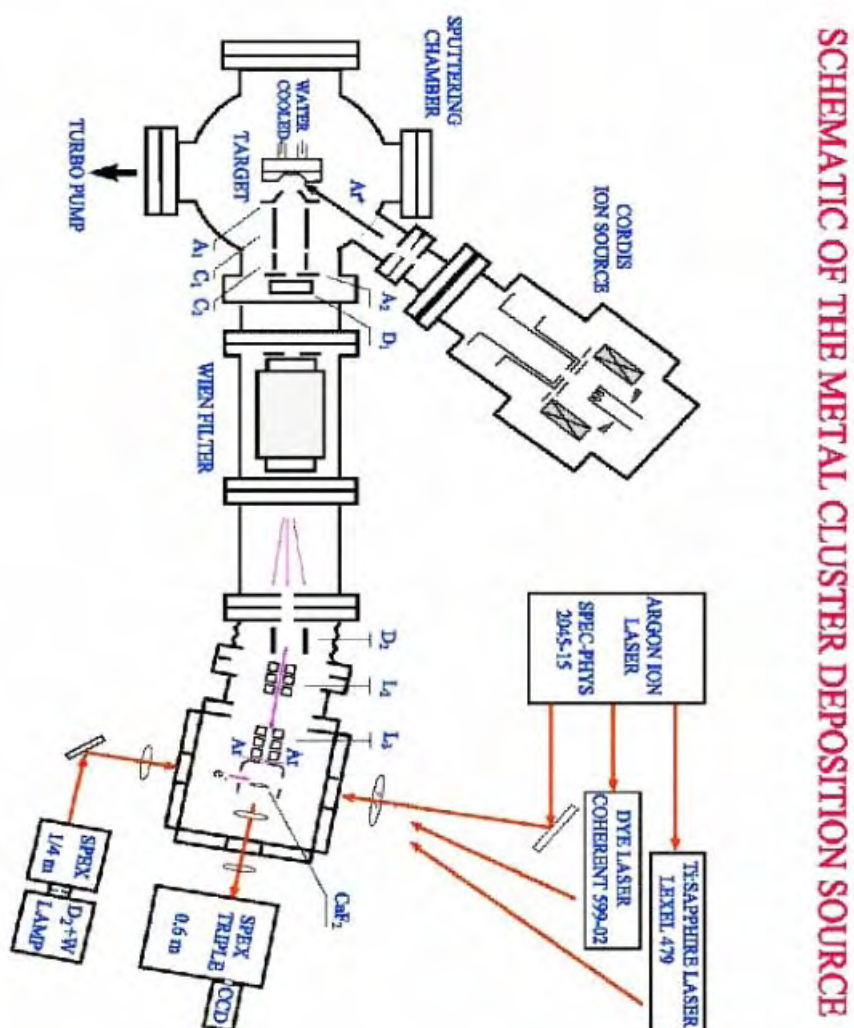


Figure 2.1 CCNY cluster deposition source

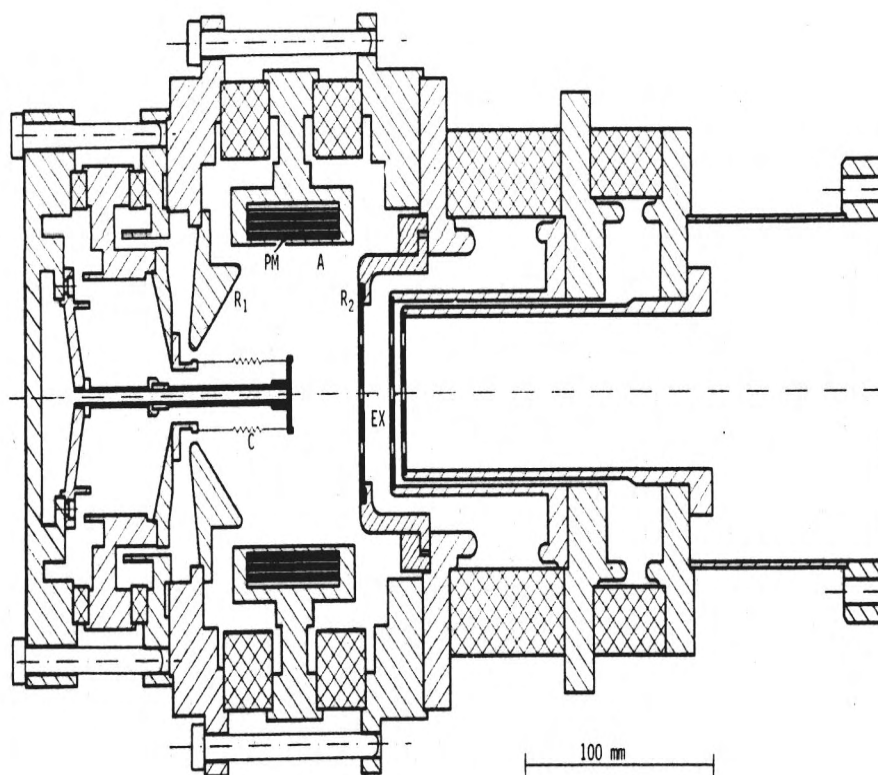


Figure 2.2 CORDIS ion source

A, anode; C, cathode filament; EX, accel-decel extraction system; PM, permanent magnet; R₁, R₂, reflector electrodes; R₂ acts as outlet electrode as well. The beam is extracted to the right.

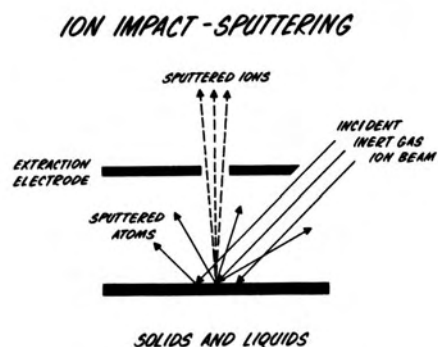


Figure 2.3.1 Illustration of ion creation by ion impact on
a solid or liquid surface

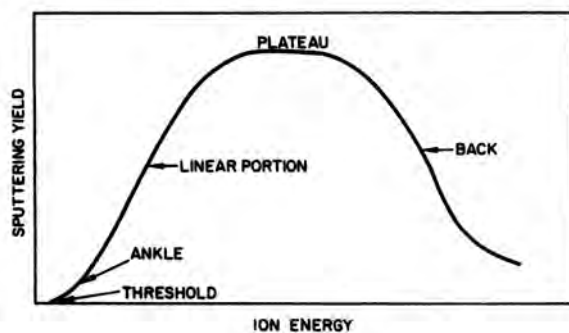


Figure 2.3.2 General feature of a typical sputtering yield
versus ion energy curve

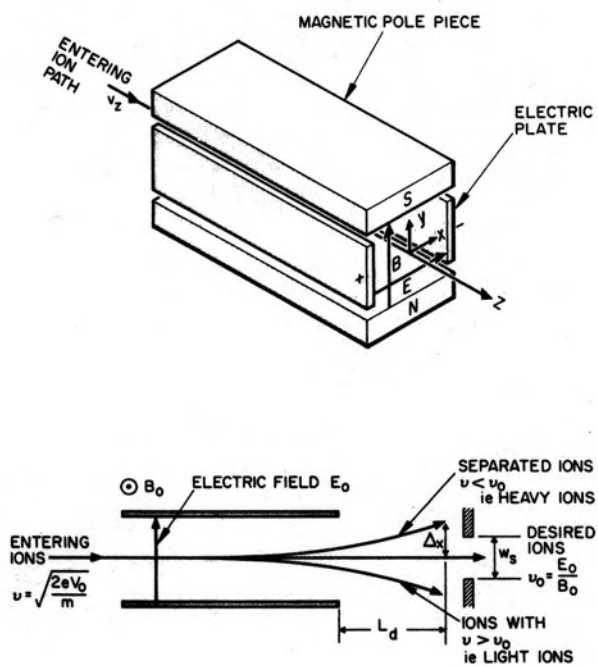


Figure 2.4.1 Geometry and mass separation in Wein filter

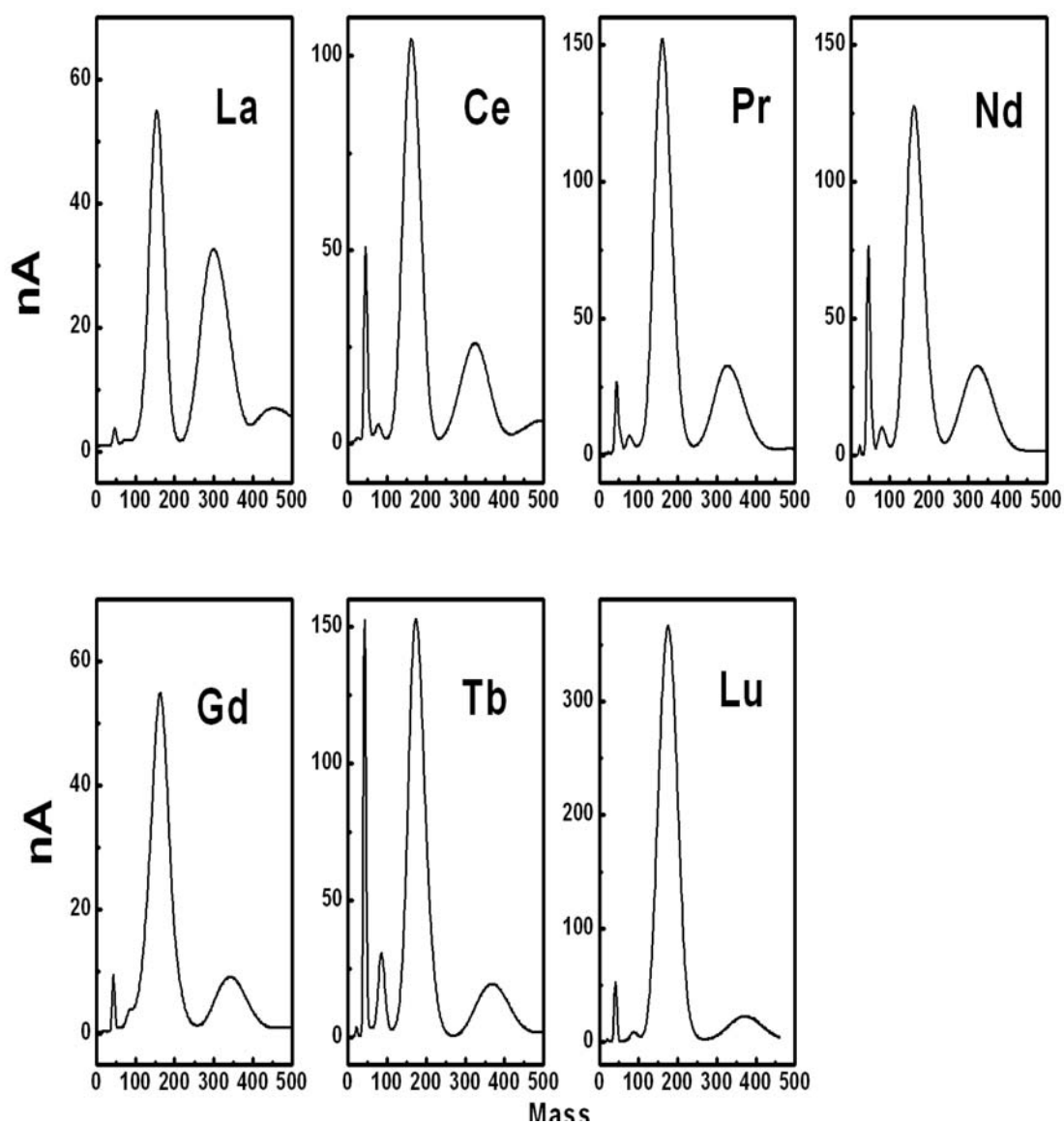


Figure 2.4.2 Mass spectra of some lanthanide elements from sputtering

DEPOSITION REGION

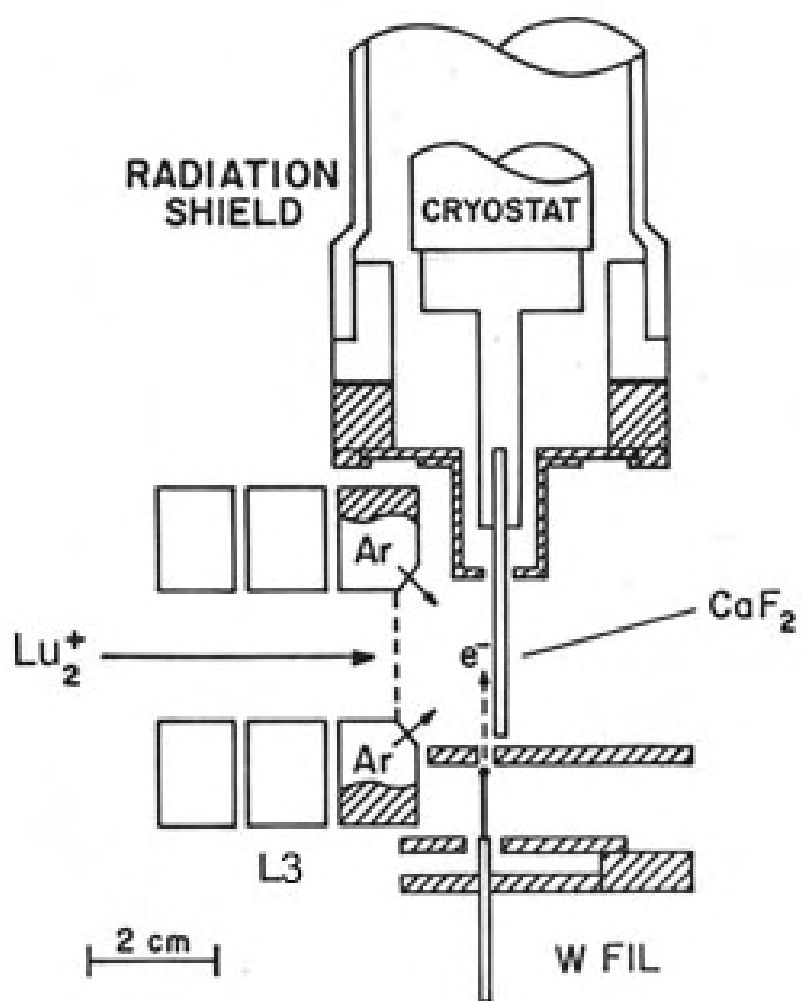


Figure 2.5.1 Illustration of deposition chamber

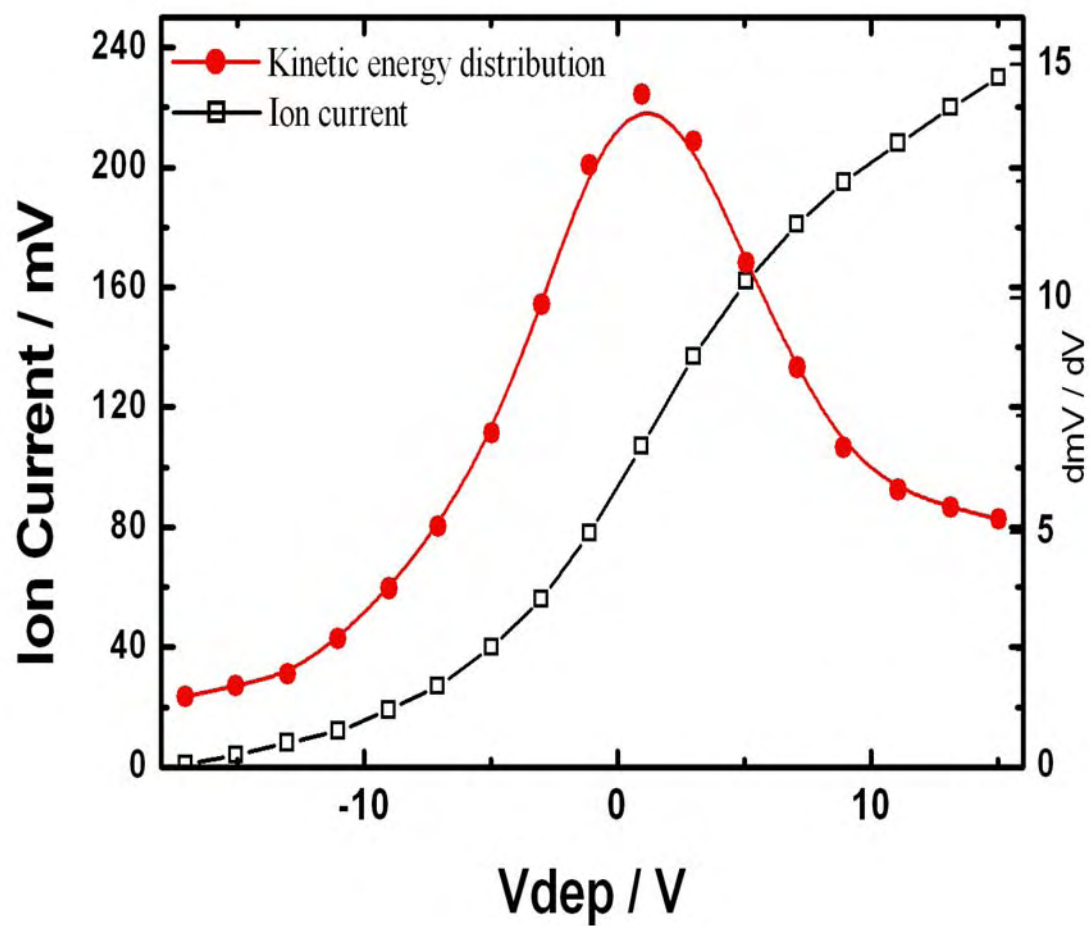


Figure 2.5.2 Ion current and kinetic energy distribution of cerium dimer in deposition

SDS of Transition Metal Dimers (early transition)

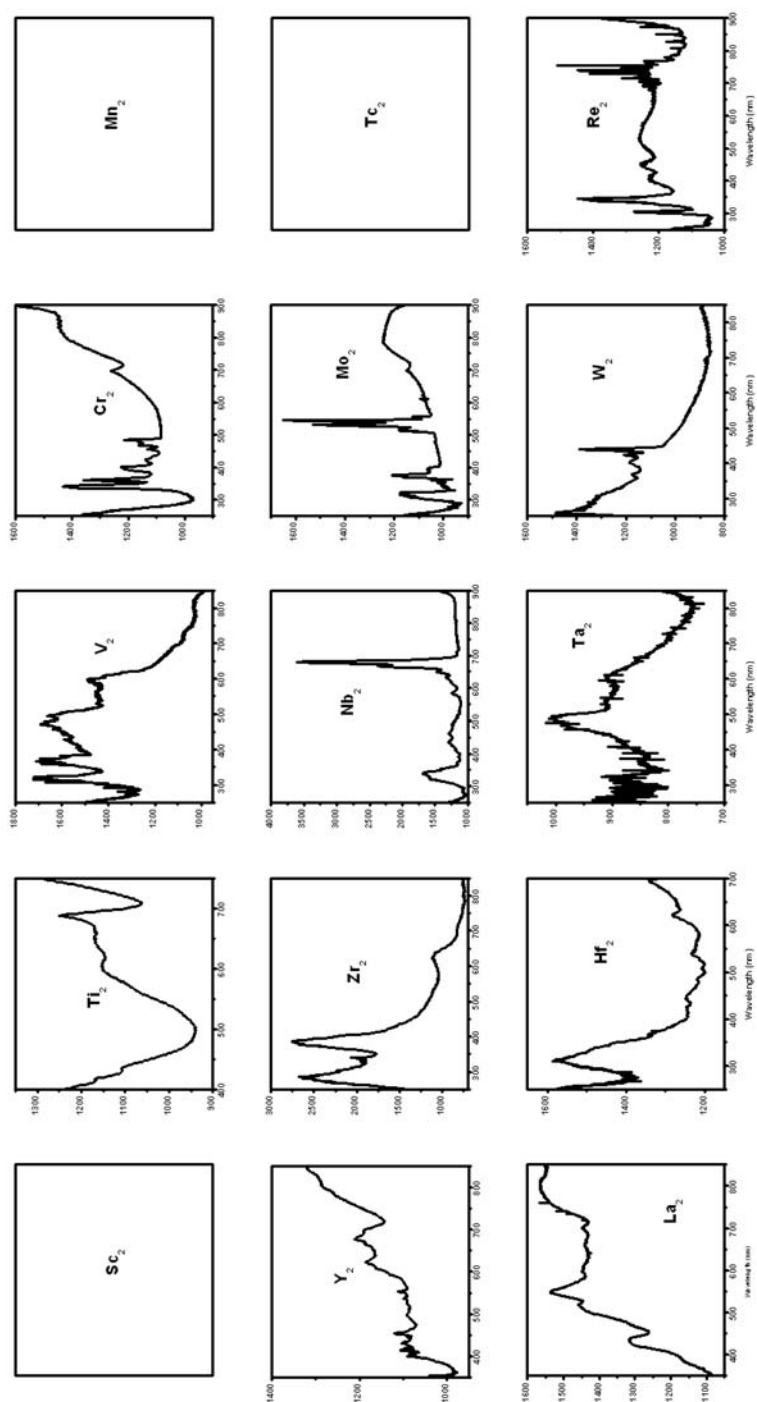


Fig.2.6.1

SDS of Transition metal Dimers (Late Transition)

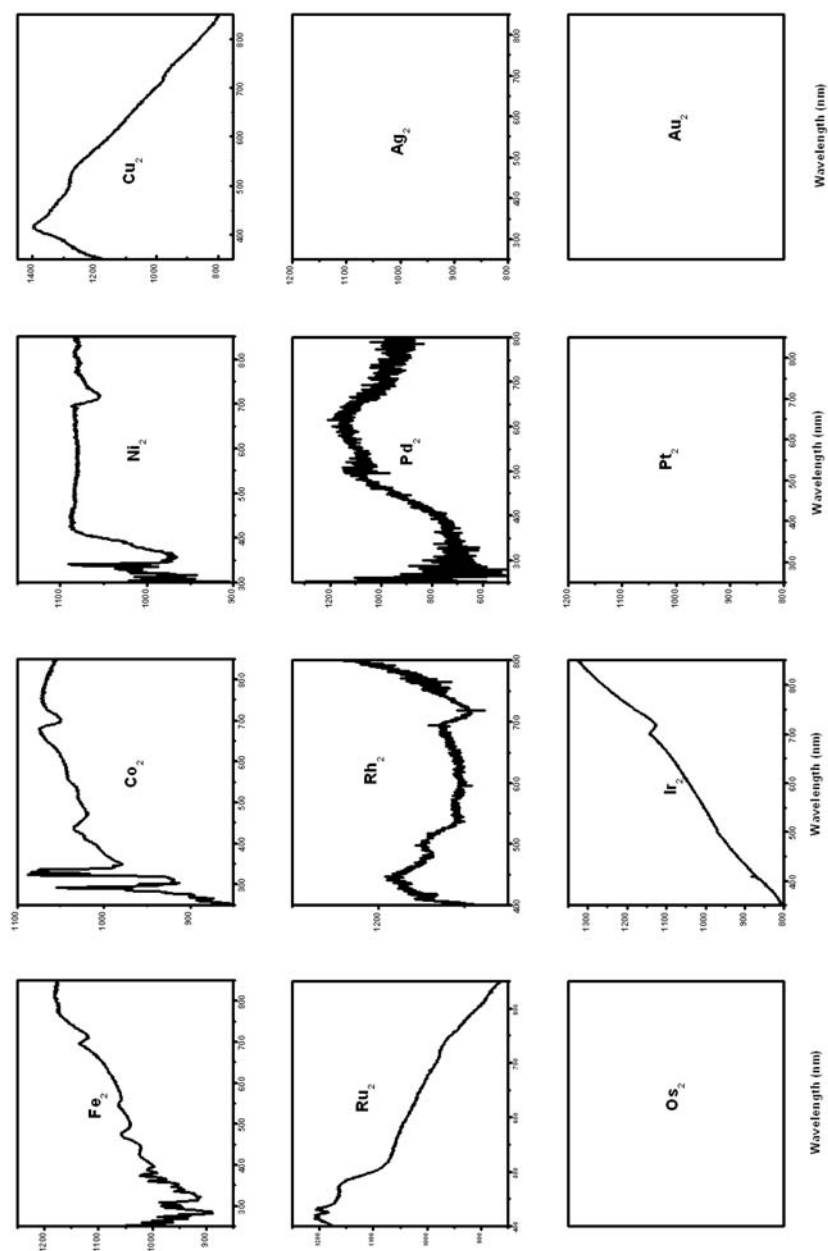


Fig.2.6.2

Chapter III. Theory

3.1 Raman Spectroscopy

3.1.1 Nature of Raman Effect

When electromagnetic radiation interacts with a molecule, the varying electric field $E(t)$ will induce a time dependent polarization $P(t)$ (dipole moment per unit volume). The magnitude of the induced polarization P may be expanded in increasing powers of electric field E as

$$P(t) = \chi^{51}E(t) + \chi^{52}E^2(t) + \chi^{53}E^3(t) + \dots \quad (3.1)$$

Here, $\chi^{(n)}$ is the susceptibility tensor of order n . While higher order susceptibilities are associated with nonlinearities, χ^{51} is responsible for linear effects (dispersion and absorption) and also called polarizability α . Most of what we normally consider spectroscopy is accounted for by considering this term.

The time varying polarization can act as new source of electromagnetic field. If the internuclear distance changes during the vibration i with frequency ν_i , obviously the polarizability α must also change, even if slightly. In turn, the induced polarization P will change not only with the frequency ν_0 of the incident light, but also with the frequencies $\nu_0 - \nu_i$ and $\nu + \nu_i$. The resultant light, scattered in

all directions, will contain both sum and difference frequencies and is responsible for the Raman effect. In quantum theory, this effect is explained by the term of energy exchange between scattering molecule and incident light, i.e. the light is scattered inelastically, and the Raman shifts give directly the energy differences between the stationary states of the molecule.

The study of the Raman spectrum supplies in many respects the same information about a molecule as the study of its infrared spectrum. However, different selection rules apply in these two cases. Raman effect is a two-photon process, which depends on the polarizability of the molecule but is entirely independent of the presence of a permanent dipole moment.

3.1.2 Anharmonic Oscillator Treatment

In classical mechanics an anharmonic oscillator has a vibrational frequency of

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (3.2)$$

for very small amplitudes, where k is the force constant and μ is the reduced mass. This frequency decreases slowly as the vibrational amplitude increases.

When anharmonicity is considered, the induced polarization P oscillates with $\nu_0 \pm 2\nu_i$, $\nu \pm 3\nu_i$, ... as well as $\nu \pm \nu_i$. For small anharmonicity of the oscillator, the energy values of the anharmonic oscillator are

$$E_v = hc\omega_e \left(v + \frac{1}{2}\right) - hc\omega_e x_e \left(v + \frac{1}{2}\right)^2 + hc\omega_e y_e \left(v + \frac{1}{2}\right)^3 + \dots, \quad (3.3)$$

or correspondingly the term values are

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \dots, \quad (3.4)$$

where $\omega_e y_e \ll \omega_e x_e \ll \omega_e$. Neglecting cubic terms the separation of successive levels is given by

$$\Delta G_{v+\frac{1}{2}} = G(v+1) - G(v) = \omega_e - 2\omega_e x_e - 2\omega_e x_e v. \quad (3.5)$$

A plot of $\Delta G_{1/2}$ vs. $2(v+1)$ gives approximately a straight line with a slope of $\omega_e x_e$ and intercept of ω_e^{51} . (see for example, the ΔG curve for the ground state of the Al_2

molecule as shown in Fig. 3.1). $\omega_e x_e$ is a measure of the anharmonicity of the oscillator, and ω_e gives the vibrational frequency (for the unrealizable state with $v = -1/2$) that the anharmonic oscillator would have classically for an infinitesimal amplitude.

From the vibrational frequency ω_e the force constant of the anharmonic oscillator for infinitesimal displacements is given by

$$k_e = 4\pi^2 \mu c^2 \omega_e^2 \quad (3.6)$$

If the actual potential curve of the molecule can be well described by Morse potential, and the higher terms in Eq. (3.4) are truly negligible, the dissociation energy can be expressed as

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} \quad (3.7)$$

Dissociation energies are good measures of bond strengths in that they are sensitive to the entire range of the potential curve, from its minimum to asymptote, and therefore have considerable thermodynamic utility. Force constants, on the other hand, are sensitive to the region of the potential near the minimum, and can, through Pauling's rule, be directly related to the bond order.⁵²

Thus, determination of force constants is more of use as a test of quantum mechanical considerations.

3.1.3 Raman Intensity

For a Raman Transition between two states $|g\rangle$ and $|f\rangle$ of a scattering system, the intensity of light scattered is

$$I_s = \frac{8\pi(\nu_0 \pm \nu_{gf})^4}{9c^4} I_0 \sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{gf}|^2, \quad (3.8)$$

where I_0 is the incident intensity at frequency ν_0 , ν_{gf} is the frequency of the Raman transition $|f\rangle \leftarrow |g\rangle$, and $(\alpha_{\rho\sigma})_{gf}$ is the transition polarizability tensor, which is equivalent to $\partial\alpha_{\rho\sigma}/\partial Q$, with incident and scattered polarization indicated by ρ and σ . Second order perturbation theory gives the following expression for the polarizability

$$(\alpha_{\rho\sigma})_{gf} = \frac{1}{\hbar} \sum_e \left(\frac{\langle f|\mu_\rho|e\rangle\langle e|\mu_\sigma|g\rangle}{\nu_{eg} - \nu_0 + i\Gamma_e} + \frac{\langle f|\mu_\sigma|e\rangle\langle e|\mu_\rho|g\rangle}{\nu_{ef} + \nu_0 + i\Gamma_e} \right), \quad (3.9)$$

where μ_ρ and μ_σ are dipole moment operators, and $|e\rangle$ is an excited state of half-bandwidth Γ_e , and ν_{eg} and ν_{ef} are transition frequencies.

Eq. (3.9) shows that two different dipole moment matrix elements must be simultaneously non-zero for a Raman active transition. It is evident that the components of the polarizability α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{xz} , α_{yz} transform as same

representations of a group as xx , xy , and so on. That is the reason why a Raman spectrum can also appear for molecules that have no infrared spectrum, like homonuclear diatomic molecules, for example.

Within the framework of the adiabatic Born-Oppenheimer approximation, the wave functions may be separated into electronic and vibrational parts, giving

$$\langle f | \mu | e \rangle = \langle j | M_{ef} | v \rangle \text{ and } \langle e | \mu | g \rangle = \langle v | M_{eg} | i \rangle ,$$

where $|j\rangle$, $|v\rangle$ and $|i\rangle$ are final, excited and initial vibrational states respectively. M_{ef} and M_{eg} are pure electronic transition moments. Assuming that the system is initially and finally in the ground electronic state, (i.e. a vibrational Raman transition is under consideration), M_{ef} and M_{eg} then represent the same term. When Born-Oppenheimer condition is valid, the electronic transition moment is a weakly varying function of on the nuclear coordinates, and may be expanded in a Taylor series around the equilibrium position as a function of the normal coordinate Q :

$$M_{eg} = M_{eg}^0 + (\partial M_{eg} / \partial Q)^0 Q + \dots \quad (3.10)$$

Under the condition of weak vibronic coupling, the Herzberg-Teller treatment is valid, and the derivative of the transition moment can be evaluated because the variation in the Hamiltonian with respect to the normal

coordinate Q can mix the state $|e\rangle$ with other states $|s\rangle$ of the appropriate symmetry, and Eq. (3.10) can be rewritten as:

$$M_{eg} = M_{eg}^0 + \sum_s M_{sg}^0 \frac{h_{es}}{\nu_s - \nu_e} Q + \dots \quad (3.11)$$

where $|s\rangle$ represents another excited state, and $h_{es} = \langle s | \partial H / \partial Q | e \rangle$.

Some Considerable simplification of the transition polarizability is possible for excitation under resonance conditions. The second term in Eq. (3.9) can be neglected since near resonance it is small in comparison to the first term due to the large resonance denominator. As ν_0 approaches some particular transition frequency ν_{eg} , the relevant excited state will dominate the sum over states. In addition for simplicity, the polarization is ignored, since Eq. (3.9) is completely general. Applying these considerations to Eq. (3.9) and incorporating the zeroth and first order terms in Eq. (3.11), the polarizability is given by:

$$\alpha = A + B + C + D \quad (3.12)$$

where

$$A = (M_{eg}^0)^2 \frac{1}{\hbar} \sum_v \frac{\langle j | \nu \rangle \langle \nu | i \rangle}{\nu_{vi} - \nu_0 + i\Gamma_v} \quad (3.13)$$

$$B = (M_{eg}^0)(M_{sg}^0) \frac{h_{es}}{\nu_s - \nu_e} \sum_{\nu} \frac{\langle j|Q|\nu\rangle\langle\nu|i\rangle + \langle j|\nu\rangle\langle\nu|Q|i\rangle}{\nu_{di} - \nu_0 + i\Gamma_{\nu}} \quad (3.14)$$

Term C and D are negligibly small⁵³, and hence will not be discussed here.

Usually, the A-term is the dominant contributor to resonance Raman intensity since for allowed transitions; M_{eg}^0 is larger than $\partial M_{eg}/\partial Q$. Only totally symmetric modes give rise to resonance enhancement via the A-term because for non-totally symmetric modes the Franck-Condon factors, $\langle j|\nu\rangle$ and $\langle\nu|i\rangle$, are equal to zero. In the case of diatomic molecules there is only one vibrational mode, which is totally symmetric. So, A-term resonance Raman scattering is extremely important for this category of molecules. However, when a change in molecular symmetry accompanies the electronic transition, the term totally symmetric applies no longer to the ground state point group, but to the "common group" formed by the operations that are common to both the ground state and excited state point groups. Thus non-totally symmetric fundamental vibrations may acquire some intensity from the A-term also. Eq. (3.13) shows clearly that the resonance enhancement of A-term depends on Franck-Condon factors. When there is a relatively large displacement between the potential energy minimum of ground

state and that of excited state, this factor may have appreciable size up to several quanta. Thus the A-term can give rise to overtones of intensity comparable to that of fundamental.

Considering Eq. (3.13) only, one would expect the intensities of the successive overtones to vary erratically depending on the magnitudes of the Franck-Condon overlap factors connecting the intermediate and final states. In contrast to this conclusion, the relative intensities of overtones observed in the resonance Raman spectra of transition metal clusters decrease smoothly along the progression in most cases. The same phenomenon has been observed previously in the gaseous I_2 spectrum when the excitation frequency is brought into the continuum region.⁵⁴ For excitation into a continuum the resonant denominator no longer picks out a single vibrational state transition. Instead all populated vibrational levels of the ground electronic state are at resonance with some continuum state (continuum can be deemed as infinitely narrow states). The overtones now are composed of a summation of lines resulting from Raman transitions from all the populated levels rather than resulted from a single vibrational transition. This large number of superimposed bands has an averaging effect on the overtone intensities and frequency

dependence. An additional averaging effect comes from the loose definition of "resonance denominator" in the case of continuum. Since the spacing of vibrational levels is infinitesimal in the continuum region, a transition can "borrow" some intensity from nearby continuum states that are only slightly off resonance. Discussion above also applies to the situation when there is a high density of excited states. It is more likely that the observed intensity pattern of overtones for transition metal clusters belongs to the latter case, since a large number of electronic configurations are expected for this category of species.

Unlike the A-term, which involves a single excited electronic state, the B-term arises from the vibronic coupling of the resonant state to other excited states. The major importance of the B-term mechanism is the intensity it allows to scattering by non-totally symmetric modes, because of the Q dependent vibrational integrals. It may become dominant in resonance with a weakly allowed transition that is vibronically coupled to a nearby intense transition, in which case $(M_{eg}^0) (M_{sg}^0) \gg (M_{eg}^0)^2$. The term h_{es} is a measurement of the strength of the vibronic coupling, and is related to Q . Thus striking enhancement can be observed for those modes which are particularly effective

in mixing the two transitions. Expressed group theoretically, for a non-totally symmetric coordinate Q_k to be B-term active, its irreducible representation, Γ_k , must be contained in the product $\Gamma_e \otimes \Gamma_s$. It is worth pointing out that B-term scattering contributes to totally symmetric modes as well as to non-totally symmetric modes. But for the former, it is necessary that the two excited states, $|e\rangle$ and $|s\rangle$, have the same symmetry.

In the case of strong vibronic coupling, the assumption of electron-nuclear separability begins to break down as the coupling states approach one another in energy. The Jahn-Teller effect can be considered an extreme form of vibronic coupling, in which the coupled states are degenerate. The Herzberg-Teller approach is no longer valid, and the vibronic wave functions must be determined by direct diagonalization of the Hamiltonian.⁵⁵ When the Jahn-Teller effect can not be ignored, A-term activity may arise for some non-totally symmetric modes if their irreducible representations are contained in the symmetric direct product $\{\Gamma_e \otimes \Gamma_e\}$. Consequently, the resonance Raman spectra may show combination band progressions involving quanta of totally symmetric modes plus one quantum or multiple quanta of JT active vibrations, as well as overtones of the latter.

3.1.4 Electronic Raman Effect

Notice in Eq. (3.9) that, $|f\rangle$ and $|g\rangle$ are not necessarily in the ground electronic state simultaneously. When $|f\rangle$ belongs to a low lying electronic states, Raman transitions between electronic states can thus be detected. A few experimental observations of the electronic Raman effect will be discussed in the following chapters. For instance, a band at 400 cm^{-1} was detected in the Raman spectrum of Rh_3 and assigned to the ${}^6\text{B}_2 \leftarrow {}^6\text{A}_1$ electronic transition of Rh_3 . The importance of electronic Raman spectroscopy lies in the nature of the selection rules, which differ from those operative in absorption or emission electronic spectroscopy. Thus transitions between states of the same parity, though forbidden by electric dipole selection rules, may be Raman active. By electronic Raman spectroscopy it is thus possible to measure transition frequencies which might otherwise be inaccessible spectroscopically.

3.1.5 Isotope Effect

For isotopic molecules the vibrational frequencies are different according to Eq. (2), since the reduced mass is different. For the purpose of evaluating this frequency difference, a constant ρ is defined as

$$\rho = \frac{\nu^i}{\nu} = \sqrt{\frac{\mu}{\mu^i}} \quad (3.15)$$

where the superscript i stands for an isotopic molecule. The formula for isotope shift is given by

$$\Delta\nu = \nu - \nu_i = (1 - \rho)\nu\Delta G_{\nu+\frac{1}{2}}. \quad (3.16)$$

Eq. (3.16) is in good approximation when ρ is only slightly different from 1.⁵¹

This vibrational isotope effect can be found in the Raman spectra of TiCu_3 . A Gaussian fit to the fundamental and overtones are shown in Fig. 3.2. Although there is no fine structure seen in the spectrum, the increasing peak width along the progression was successfully interpreted by isotope effects.

3.1.6 Matrix Effect

Rare gases are typical matrix materials. They are optically transparent from the far infrared to vacuum ultraviolet. When gaseous cluster ions are trapped in argon matrix, they are prevented from diffusion and rotation, but may vibrate with frequencies close to the gas-phase values. Thus the spectra are frequently much simpler than those obtained for any other state of matter, particularly if low temperatures are used, and the vibrational bands are sufficiently sharp to allow accurate frequency measurement. The lattice energy of argon solid is quite low (2 kcal/mole)⁵⁶, therefore the interaction between matrix atoms are weak, as are the interactions between matrix lattice and the metal clusters isolated in the host. As a consequence, the optical properties of the metal clusters are generally characteristic of the free clusters, and host-guest interactions exert only small distortions on the guest electron configuration. However, these small changes may bring about evident changes in the appearance of the spectrum, such as small frequency shifts and multiplet structure,^{57, 58} and interpretation of the vibrational spectra requires understanding of those perturbation effects caused by the matrix environment.

Matrix shift

The guest-host interaction in a matrix may result in either red shift or blue shift of the vibrational frequency, although the former is more commonly observed. At present there is a lack of sufficient successful theoretical model for treatment of the matrix shift effect. However, certain useful empirical predictions have been made on the basis of existing experimental matrix-shift data. It has been found that the red shift decreases with decreasing matrix polarizability and decreasing dipole moments of the trapped species. With comparison of more than two hundred pairs of observations, Jacox⁵⁹ reported that the argon-matrix shift for most diatomic molecules is less than 2%. For molecules with a substantial component of van der Waals bonding, the matrix shift may be significant. It is possible that the matrix may introduce a potential barrier to dissociation, which causes a considerable blue shift for weakly bonded molecules.

Site effect

In addition to the actual perturbation of vibrational states by the matrix, one also often observes a splitting or multiplet structure in the spectra. See, for example,

the Raman spectra of lanthanum dimer as shown in Fig. 4.2.1. This is currently believed to be due to the trapped species being located in several distinct sites. Site splitting is usually a few wave numbers in magnitude and is sometimes difficult to resolve. In many cases the splitting can either be reduced or eliminated by annealing of the matrix, which is an irreversible process. This is to be contrasted with the reversible temperature-dependent behavior of rotational structure.

The different sites in matrices may come from several origins. Assuming the argon solid has a structure of cubic closed packing with six nearest neighbors per atom and the unit cell is face-centered cubic, there are consequently two kinds of sites available for the embedded molecules. One is an octahedral site with a diameter of 1.55 Å, and the other is a tetrahedral site with a diameter of 3.76 Å.⁵⁶ These two sites are also called interstitial and substitutional sites respectively. When the molecular size exceeds the available space of a substitutional or interstitial site, the probability of the trapped species locating in a site where the cage also contains another molecule is increased. This cage will clearly perturb the trapped species by a different amount than a cage formed entirely by matrix molecules and thus will produce another

kind of effect known as an aggregation site effect. Furthermore, the grain boundaries between microcrystals are also possible matrix sites. The situation may become even more complicated when matrix lattice distortion is involved. As mentioned above, the lattice energy of argon solid is fairly low, and small host-guest forces may cause relatively large random lattice distortions.

It is obvious that molecules located in different sites experience different interactions with host matrix, which results in different potential energies. These molecules can be deemed as distributed to close states, and hence have different vibrational frequencies. Sites effect has been observed in the resonance Raman spectra of La_2 , Ce_2 , Pr_2 , etc.

3.2 Scattering Depletion Spectroscopy (SDS)

Raman spectroscopy is relatively insensitive and is currently feasible only in cases where the Raman signal is resonantly enhanced. In order to carry out such measurements it is first necessary to map out the optical absorption spectrum of the cluster (i.e. the coefficient M_{eg}^0 in Eq. 3.13 must be non zero). Normally this is accomplished by observing (as a function of wavelength) the light transmitted by or reflected through the matrix sample. However, matrices prepared by the mass-selected ion deposition technique are fairly dilute ($< 10^{16}$ dimers/cm²) and often highly scattering. To partially overcome these disadvantages, an alternative method, termed "Scattering Depletion Spectroscopy" (SDS), is employed. This involves detecting the light scattered at 90° to that incident.

When a sample consists of a number of absorbers embedded in a matrix which itself may scatter light (e. g. through microcrystallites), the intensity of light scattered at right angles to the incident light maybe depleted by absorption. Under proper conditions, therefore, dispersion of the scattered light provides an alternative means of detecting absorption. The ratio of scattered light

in absence of an absorber to that in the presence of an absorber is given by the "SDS response function";

$$R^{SDS} = 1 + \frac{\alpha_a}{\alpha_s} \frac{1 - \exp(-\alpha_s)}{1 - \exp(-\alpha_s - \alpha_a)} \quad (3.17)$$

Where α_a and α_s are absorption and scattering coefficients, proportional to the number of absorbers/scatters and the thickness. For strongly scattering samples, SDS has an advantage over normal absorption spectroscopy due to the flatter background of the former.

SDS spectra of several lanthanides are shown in Fig. 3.3. The ordinate in Fig. 3.3 (the "SDS signal") is the ratio of the "reference intensity" to the "signal intensity". The former corresponds to light scattered from a region near the center of the 8 mm wide sample, whereas the latter pertains to that scattered near an edge. Fig. 3.4 shows an optical density profile of the sample, which was obtained by recording single beam SDS spectra as a function of lateral position on the sample. It is obvious that the sample is non-uniform, with about three times as much absorption in the center as compared to near an edge. Thus the reference also contains absorption information but to a lesser degree than the signal. The rather significant baseline drift in Fig. 3.3 is due to a slight and smooth change of the sampling spot for both signal and reference.

That's because light with different wavelength is subject to different dispersion. A decrease in signal with accompany of an increase in reference will result in a baseline increasing in the ref./sig. ratio, and vice versa. The up or down drift of the baseline is determined by which one of the two edges are used to record the reference. Another evident feature in Fig. 3.3 is a bump around 700nm. That's because a different dispersion element is used for light further to red. Conventional absorption spectra, using the same signal and reference positions but detecting the light transmitted through the sample, also show the same features evident in Fig. 3.3. However, we find that absorption features in the scattered spectra are approximately 20-50% more intense than those observed in transmission, and thus SDS is a more sensitive technique for obtaining optical spectra.

3.3 Raman Excitation Profile

The plot of the intensities of the fundamental and overtone bands throughout the region of the resonant absorption band is called an excitation profile. An analysis of resonant Raman intensities like a Raman excitation profile can provide valuable information regarding the symmetry of vibronic transition.

When A-term scattering is the dominant contributor, the maximum of an excitation profile is expected at the origin of the resonant electronic transition and subsidiary peaks at successive excited state vibrational levels, the amplitudes depending on the successive Franck-Condon factors. Consequently, the symmetry of the vibration mode under consideration can be derived from the symmetry character of ground and excited electronic state, and vice versa. In the investigation of Cr_3 , for example, Raman excitation profile indicated clearly the non-totally symmetric nature of a low lying electronic state with term energy of 400 cm^{-1} .

Raman excitation profile can provide valuable information even for diatomic molecules, for which there is only one normal mode. Because of fragmentation during deposition, atomic features may appear in the absorption spectrum. Raman excitation profile helps to resolve the

observed transitions and give unambiguous assignment of bands.

Raman excitation profile differs markedly from the absorption spectrum if the vibrational fine structure of the latter is resolved. Where as absorption profiles are simply given by the superposition of the individual vibronic bands, Raman excitation profile involves cross-terms ($v \neq v'$) which produce interference between the contributions from different vibronic states.^{53,55} Thus theoretically, studies of Raman excitation profiles provides a possibility for the determination of excited state geometries, and lifetimes. However, an accurate measurement of the Raman excitation profile can be hardly done largely due to fluctuation of laser power during each scan.

Nevertheless, Raman excitation profile has been proven to be a powerful method in the assignment of absorption bands. Moreover, since our samples are optically thin, absorption spectra are sometimes hard to obtain and Raman excitation profiles often provide higher sensitivity.

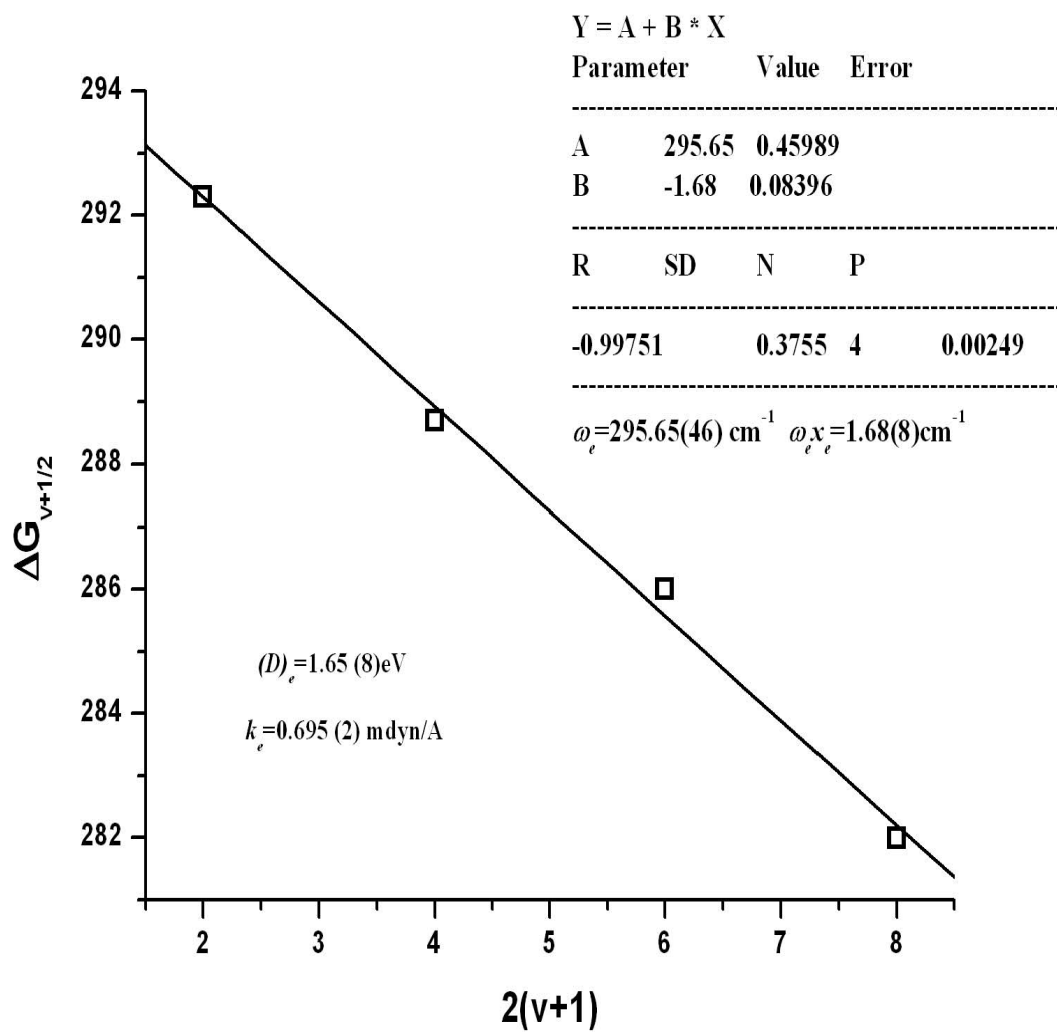


Figure 3.1 ΔG curve for the ground state of the Al_2 molecule

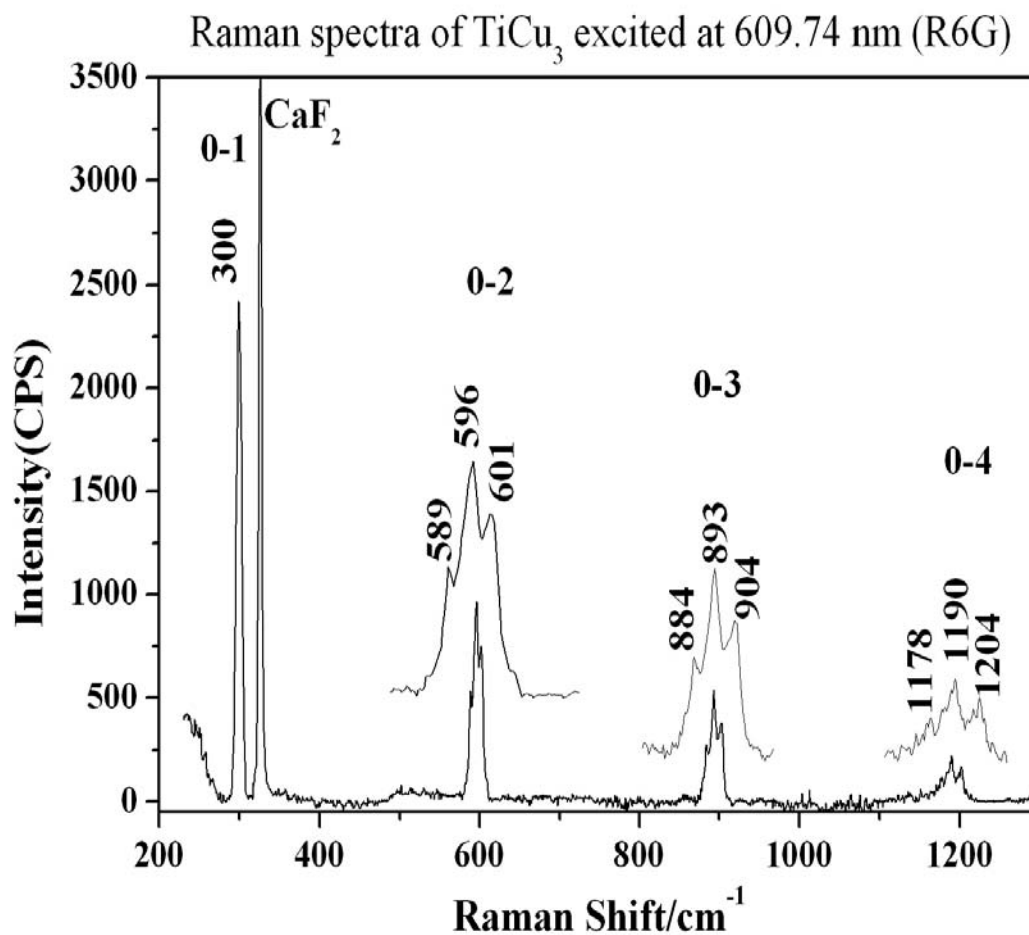


Figure 3.2 Details of TiCu_3 Raman spectrum showing simulated isotopic effect considering the contribution from 3 major isotopic combinations.

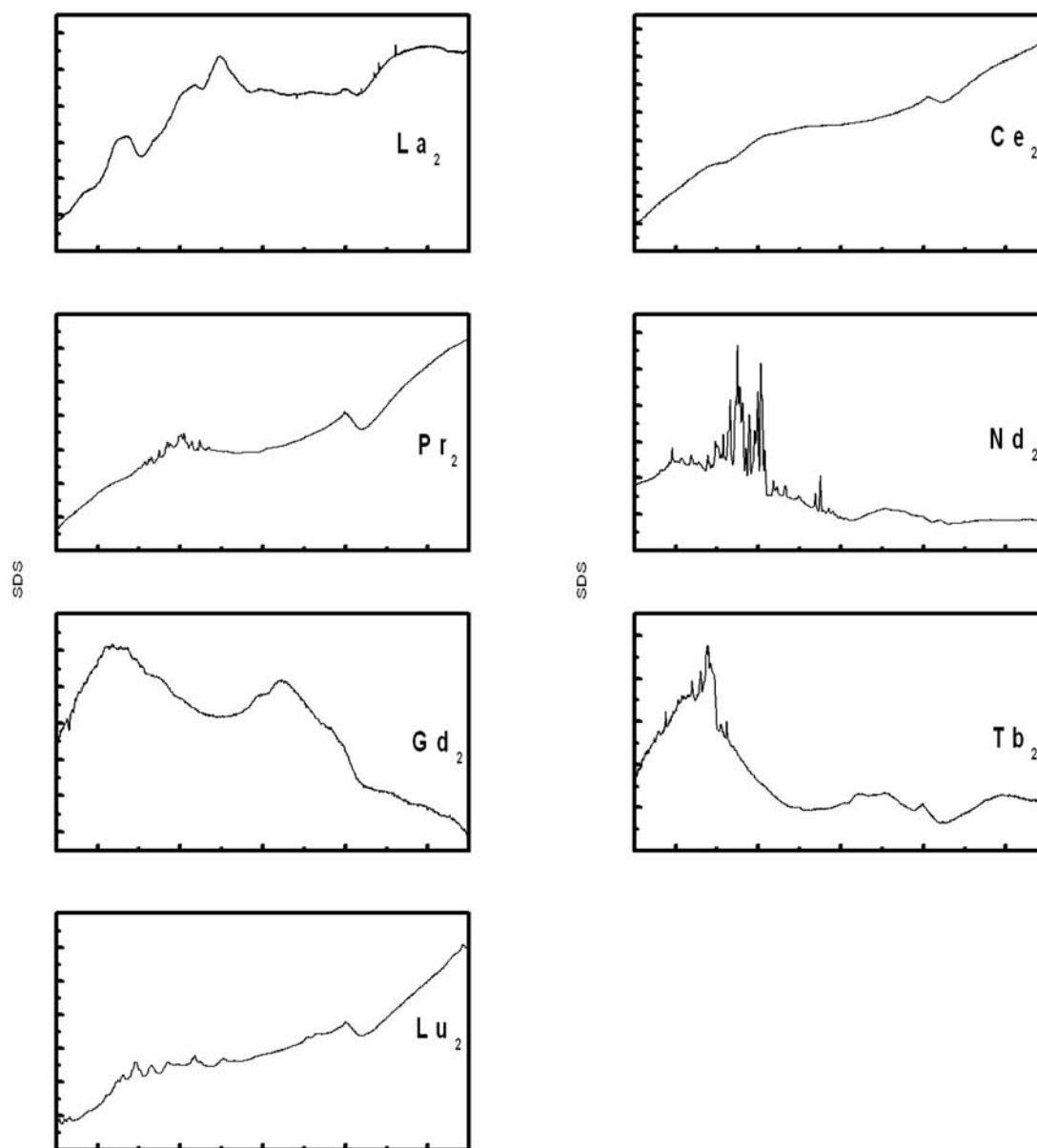


Figure 3.3 Absorption (SDS) spectra of some lanthanide dimers

Chapter IV Homonuclear metal Dimers and Trimers

4.1. Resonance Raman Spectroscopy of Mass Selected Al_2 in an Argon Matrix

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Abstract

In an excitation range of 620 nm to 760 nm, resonance Raman spectra of aluminum dimers (Al_2) in an argon matrix have been obtained for the first time. Temperature annealing experiments were performed to remove Raman lines attributed site effects caused by the Al_2/Ar matrix. We observe a single fundamental at $293.3 (5) \text{ cm}^{-1}$ along with a progression up to $1149 (1) \text{ cm}^{-1}$. Taking successive differences of band centers we obtain spectroscopic constants for the ground state fundamental, $\omega_e = 297.5 (5) \text{ cm}^{-1}$, the anharmonicity, $\omega_e x_e = 1.68 (8) \text{ cm}^{-1}$. Our results are in close agreement with previous experimental results for Al_2 which designate the ground state as a $^3\Pi_u$ state, and may be considered as confirmation of this assignment.

Introduction

In ars there has been confusion as to the quantum designation of the ground state of Al_2 . This was due to the various electronic configurations available for the ground state via $\sigma\sigma$, $\sigma\pi$, or $\pi\pi$ chemical bonding. Sound evidence was presented by Cai, Dzugan, and Bondybey⁶⁰, via fluorescence studies of laser vaporized aluminum, and Fu, Lemire, Bishea, and Morse⁶¹, via resonant two photon ionization of jet cooled aluminum dimers, that the ground state for Al_2 is of $^3\Pi_u$ symmetry. Cai et al.⁶² also report ground state frequency of 284.2 cm^{-1} for aluminum dimer.

In this paper we present the resonance Raman spectrum of aluminum dimers in an argon matrix. Exciting with various lines of the visible, and near infrared spectral regions we obtain a fundamental at 292.3 (5) cm^{-1} . This is accompanied by a progression of lines up to 1149 (1) cm^{-1} . The spectroscopic constants for the aluminum dimer were garnered by extrapolating successive differences of band centers of the resonance Raman spectrum of the dimer. This leads to a ground state vibration of $\omega_e = 295.7\text{ (5) cm}^{-1}$, an anharmonicity of $\omega_e x_e = 1.68\text{ (5) cm}^{-1}$. Our results are in agreement with the work of Cai et al. and Fu et al. and we add confirmation that the ground state of Al_2 is $^3\Pi_u$.

Experimental

The resonance Raman spectrum of Al_2 was acquired using the CCNY metal cluster deposition source. The design of this apparatus has been discussed in detail in other publications^{62,63}, but will be mentioned briefly here for the resonance Raman experimentation of Al_2 . An argon ion beam of 10 mA (at 25 eV) sputters a water cooled aluminum metal target, purchased from Alfa Aesar at 99.9% (REO). A series of einzel lenses collect the sputtered aluminum cluster ions from the metal sputtering region. A Wien filter mass selects the focussed aluminum cluster ions. Any neutral aluminum atoms produced during the sputtering process that pass through the mass selector are removed via a 10^0 bend in the path following the Wien filter. A second set of einzel lenses focus the mass selected aluminum dimer cations into the deposition region, which are then codeposited with electrons, for neutralization, onto a CaF_2 substrate. A cryostat pumps the deposition region to cool the surface of the substrate to ~ 16 K. To prevent degradation of the aluminum dimers upon impact with the CaF_2 substrate, Al_2 clusters are slowed to ~ 15 eV to ensure a soft landing on the substrate. The current under hard landing conditions was measured at 60 nA. The Al_2/Ar matrix had a growth rate of $\sim 6\mu\text{m/h}$. The argon : metal ratio was $\sim 10^4:1$. Resonance

Raman spectrum was recorded after a six hour deposition at a current of ~ 50 nA for Al_2 .

Resonance Raman spectroscopy was carried out *in situ* on the matrix sample. An absorption spectrum, in the form of a "scattering depletion spectrum" (SDS) was also obtained. The "SDS" absorption is a ratio between scattered light from the edge and center, where most of the sample is deposited, to that of the CaF_2 substrate. The scattered light is collected at a 90° angle from the incident radiant. The absorption spectrum was recorded after a six hour deposition at a current of ~ 50 nA for Al_2 . No obvious absorption band could be assigned to Al_2 .

The visible lines of a Spectra Physics 2045 argon ion laser, laser lines from a Coherent model CR599 dye laser, employing the dyes R6G, R110, and DCM, and near IR lines from a Lexel model 479 titanium sapphire laser were used to observe resonance Raman features of the mass selected aluminum dimers. The 327.0 cm^{-1} line of the CaF_2 substrate was used to calibrate all Raman shifts. The Raman excitation profile for Al_2 was generated by stepping the dye laser in increments of ~ 4 nm and observing the varying intensities of the Raman spectra. The detection system for the metal cluster beam consists of a Spex 1877E 0.6m

Triplemate Spectrometer coupled with a liquid nitrogen cooled CCD system (Spectrum One and CCD30).

Results

The resonance Raman spectrum of Al_2 in an argon matrix is shown in Fig.4.1.1. These bands are observed via probing the Al_2/Ar matrix with excitation frequencies that range from 620 to 760 nm. At an exciting wavelength of 660 nm, a total of nine bands were observed for the dimer ranging from 278 cm^{-1} to 1149 (1) cm^{-1} . Through temperature annealing of the resonance Raman spectrum Al_2 from 16 K to 38 K, it was concluded that the 278 and the 285 (5) cm^{-1} lines are side bands associated with the 292.3 cm^{-1} line arising from site effects of the Ar matrix. We assign the 292.3 (5) cm^{-1} line to the ground state vibration for aluminum dimer. This Raman line gives a progression up to 1149 cm^{-1} . Significant Raman enhancements of the 292.3 cm^{-1} line, in a spectral range of 660 nm to 730 nm (see insert Fig. 4.1.1), further confirms our designation of this line as the ground vibration. This band corresponds to the absorption observed by Douglas, Hauge, and Margrave at 699 nm. Taking successive differences of band centers in the spectrum, we obtain, using a least squares fit, $\omega_e = 295.7\text{ (5) cm}^{-1}$ and $\omega_e x_e = 1.68\text{ (8) cm}^{-1}$.

Discussion

In earlier work on Al_2 , there were ambiguities as to the designation of the ground state for aluminum dimer. The confusion for this assignment is due to the several electronic configurations Al_2 can attain by placing two 3p electrons in either a σ_g or π_u bonding orbital. With this, there are three reasonable designations for the ground state of Al_2 , a $^1\Sigma_g^+$ state from the σ_g^2 configuration, a $^3\Pi_u$ from the a $\sigma_g^1\pi_u^1$ configuration, and a $^3\Sigma_g^-$ from the π_u^2 configuration.

Previous gas phase work on Al_2 by Ginter et al.⁶⁴, using vaporization of aluminum metal in a graphite tube resistance furnace, gave rotational spectra that displayed a 7:5 ratio of alternating intensities of the spectral branches. This pattern is characteristic of a homonuclear diatomic molecule with a nuclear spin of $I = 5/2$. With their spectral observations and through interpretation of the rotational bands, Ginter et al. reasoned that the only allowable electronic transitions for Al_2 were of the $^3\Sigma_u^- \leftarrow ^3\Sigma_g^-$ and $^3\Sigma_g^+ \leftarrow ^3\Sigma_u^+$ type. Douglas et al.⁶⁵, in their observation and spectral interpretation of absorption characteristics of Al_2 isolated in a krypton matrix,

signated the ground state symmetry for aluminum dimer as a $^1\Sigma_g^+$.

Not until the work of Cai, Dzugan and Bondebey and Fu, Lemire, Bishea, and Morse was this problem resolved. Using fluorescence studies of laser vaporized aluminum, in a spectral range of 27,000 to 29,000 cm^{-1} , Cai observed vibronic bands in the form of triplets with unequal intensities and a constant spacing of $\sim 32 \text{ cm}^{-1}$. They observed a ground state vibrational frequency of 284.2 cm^{-1} . The unequal intensities observed in the triplet bands was attributed to thermal populations of the spin-orbit components in the lower state. Their experimental observations were taken as evidence for $^3\Pi_u$ as the ground state.

Through resonant two-photon ionization (R2PI) of jet cooled Al_2 molecules, Fu et al.⁶¹ also concluded that the ground state was unequivocally of $^3\Pi_u$ symmetry. Their R2PI rotational spectrum lacked the 7:5 intensity alternation of the spectral bands common for a $^1\Sigma \leftarrow ^1\Sigma$ homonuclear diatomic transition with nuclear spin $I = 5/2$. This led to their reasoning that the Al_2 electronic transition was of the $\Omega' = 0 \leftarrow \Omega'' = 0$ type, therefore eliminating the $^1\Sigma_g^+$ as the ground state. The $^3\Sigma_g^-$ state was eliminated as a

possibility for the ground state due to their observation of multiplet splittings of the upper states of the E, E'', F', and F band systems of their rotational spectra. Resolvable Λ doublets were observed, which imply the originating state has a triplet or higher multiplicity. Of the three symmetries, $^1\Sigma_g^+$, $^3\Pi_u$, and $^3\Sigma_g^-$, only the $^3\Pi_u$ state fulfills this requirement. They obtained $\omega_e = 285.8 \text{ cm}^{-1}$ for the ground state.

Since our observations are made at 16 K, the electronic transitions must originate from the ground state. We take our value of ω_e to display a reasonable matrix shift from the gas phase result obtained for the $^3\Pi_u$ state (as opposed to the value of 350 cm^{-1} for the $^3\Sigma_g^-$ state).⁶⁴ Our results therefore add confirmation to the assignment of the $^3\Pi_u$ as the ground state.

Acknowledgements

This work was financially supported by the Center for Analysis of Structures and Interfaces (CASI) in conjunction with IGERT grant DGE-9972892, National Science Foundation under Cooperative Agreement No. RII-9353488, Grant No. CHE-0091362, and by the City University of New York (CUNY) PSC-BHE Faculty Research Award Program.

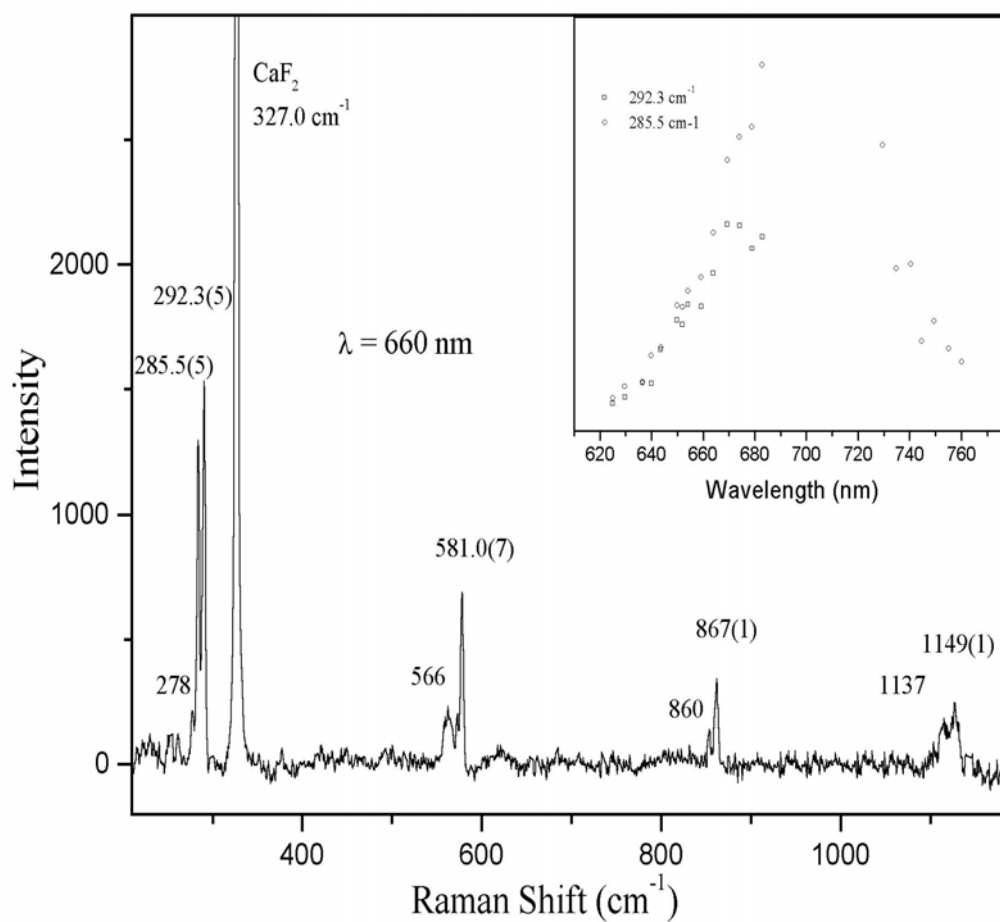


Fig.4.1.1. Resonance Raman spectrum of Al_2 in argon matrices.

The insert is the absorption (SDS) spectrum of aluminum dimmer in argon matrices in a spectral range of 610–770 nm.

4.2 Resonance Raman spectroscopy of mass selected chromium trimers in an argon matrix

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Abstract

The resonance Raman spectra of mass-selected chromium trimers (Cr_3) in argon matrices have been obtained. Five resonance Raman transitions were observed between 450 nm and 690 nm. Four of them are assigned to a totally symmetric (a_1') vibrational progression, from which we obtain a ground state harmonic frequency of $\omega_e = 432.2 \text{ cm}^{-1}$ with $\omega_e x_e = 16.3 \text{ cm}^{-1}$. The other Raman line, observed at 302.0 cm^{-1} , is assigned to the degenerate bending motion $\nu_2(e')$ of the triatomic metal cluster. The geometry of the ground state is that of an equilateral triangle (D_{3h}). These results provide a value of the stretching force constant of $k_e = 1.91 \text{ mdyne/\AA}$ and a spectroscopic atomization energy of 0.36 eV.

Introduction

This work is an extension of our previous studies on transition metal trimers⁶⁶. Cr is of special interest due to the great disparity between the relatively close d-orbitals and the diffuse nature of the s orbital. The ground state configuration of Cr atom is $3d^54s^1$, which provides ample opportunity for multiple bonding, and increasing sophistication of our ability to carry out accurate calculations on these species encourages us to obtain accurate spectroscopic properties.

Transition metal clusters present particular experimental problems in that it is often difficult to obtain a sample of a particularly chosen cluster, free of contamination from other clusters of nearby nuclearity. Spectroscopic studies of such samples often lead to uncertainty in the exact nature of the observed species. We have solved this problem by construction of our mass-selection apparatus, which has provided unambiguous spectroscopic results.

In this work we obtain the absorption, and resonance Raman spectrum of mass-selected chromium trimers. The Raman spectrum consists of five lines, four of which form a progression that can be assigned to the symmetric stretch

normal mode vibration. The remaining line can be assigned to the degenerate bend of an equilateral triangle (D_{3h}).

Experimental

Previous publications have described in great detail the instrumental setup of the CCNY metal cluster beam.^{67, 68} In this section we present a brief description of the experimental parameters employed by the apparatus for the formation, mass selection, deposition, and subsequent *in situ* resonance Raman spectroscopy of chromium trimers in an argon matrix. Chromium cluster cations are formed via argon ion plasma bombardment (at ~ 10 mA and accelerated at 25 keV) of a water-cooled chromium metal target (at 300 V) purchased from Goodfellow at 99.7% purity. A series of einzel lenses collect the chromium cluster ions from the sputtering region and focus the ions into the mass selection apparatus. Chromium trimers are then mass selected by a Wien filter. Most neutral chromium atoms produced during the sputtering process that traverse the Wien filter are lost to the system via a 10^0 bend of the path following mass selection.

Another set of einzel lenses focus the mass selected chromium trimer cations into the deposition region, where they are co-deposited with argon and electrons, for

neutralization, onto a CaF_2 substrate. The Cr_3/Ar matrix is formed under cryogenic conditions (~ 16 K). Before actual deposition of Cr_3 onto the CaF_2 substrate, the trimers are slowed to ~ 10 eV, with respect to the potential across the metal target, by a Faraday cage encompassing the cooled CaF_2 substrate. This is done to ensure a soft landing of the mass selected sample onto the CaF_2 substrate. The current under hard landing conditions was measured to be 40 nA.

The chromium trimers were probed *in situ* via resonance Raman and absorption spectroscopy. The absorption spectrum for Cr_3 is obtained using scattering depletion spectrum (SDS). SDS is an absorption measuring technique in which a ratio between scattered light from the center of the CaF_2 substrate, where a majority of the sample is deposited, and scattered light from the edge of the substrate is obtained 90° from the incident radiation. The absorption spectrum (SDS) of chromium trimer in an argon matrix was acquired after a five hour deposition of the molecule at an average current of 24 nA, giving a total concentration of ~ 120 nA-h. As a check on our results, we separately deposited Cr_2 with a total concentration of 100 nA-h. Although a distinct SDS spectrum of Cr_2 was obtained, no Raman intensity was observed. Consequently, we could not estimate the fragmentation ratio of Cr_3 to Cr_2 in the usual fashion.

Crude estimates from the SDS spectra give a maximum fragmentation ratio of 10%.

Resonance Raman experiments were performed employing the visible lines of a Spectra Physics 2045 argon ion laser, as well as dye lasers utilizing R6G (spectral range ~ 575 to 622 nm), and DCM (spectral range ~ 630 to 685 nm) dyes. All Raman lines were detected with a Spex 1877E 0.6m Triplemate Spectrometer coupled to a liquid nitrogen cooled CCD (Spectrum One and CCD30). All collected data was interpreted and displayed by DM3000R software interfaced with a computer.

Results

The resonance Raman spectrum of chromium trimer (Cr_3) isolated in an argon matrix at ~ 16 K is shown in Fig.4.2.1. All observed Raman frequencies are averaged over a maximum of 25 spectra in an exciting range of ~ 460 to 685 nm and are calibrated with respect to the 327 cm^{-1} Raman shift of the CaF_2 substrate. At an excitation wavelength of 476.5 nm, the isolated Cr_3 displays five distinct Raman lines. The observed frequencies of these lines are 302.0 (87) , 400.0 (7) , 766.1 (8) , $1,100.8\text{ (10)}$, and $1,438.7\text{ (16)}\text{ cm}^{-1}$. No other lines were observed down to 100 cm^{-1} . The Raman line located at 400.0 cm^{-1} is the most intense of all the observable bands in our spectrum and we attribute the three

Raman lines at higher frequencies, up to $1,438.7\text{ cm}^{-1}$, as a spectral progression in the 400.0 cm^{-1} frequency. Since this is the highest frequency fundamental, we assign the 400.0 cm^{-1} line to the totally symmetric stretch $\nu_1(a'_1)$ of chromium trimer.

Taking successive differences of Raman band centers and employing a least squares fit (we have left out the line at $1,438.7\text{ cm}^{-1}$ from this analysis, due to low signal-to-noise ratios), we obtain a ground state harmonic frequency for this mode of $\omega_e = 432.2\text{ (16)}\text{ cm}^{-1}$ with $\omega_e x_e = 16.3\text{ (37)}\text{ cm}^{-1}$. The other lower frequency Raman line, observed at 302.0 cm^{-1} , is assigned to the degenerate bending motion $\nu_2(e')$ of the triatomic metal cluster. The frequency ratio of the two fundamentals $432/302 = 1.43$ is sufficiently close to $\sqrt{2}$ to indicate that the symmetry of chromium trimer is D_{3h} , confirming the assignment to the degenerate bend. A summary of our assignment for this spectrum is given in Table 4.2.1, and values for all spectroscopic constants for this system, namely the ground state vibration for Cr_3 (ω_e), the anharmonicity ($\omega_e x_e$), the force constant (k_e), and the atomization energy (D_e^a) are given in Table 4.2.2. Note that, as in the dimer, the force constant for the trimer ($1.91\text{ mdyne/\AA}$) is rather large, suggesting considerable involvement of d-electrons in

bonding. However, the energy of atomization (0.36 eV) is quite low. Such considerations led Casey and Leopold⁶⁹ to suggest that the potential governing nuclear motions in the dimer deviates considerably from that of a Morse curve. It is likely that the trimer potential energy surface is similarly distorted.

We also observe an absorption spectrum for Cr_3 in the form of a scattering depletion spectrum, as shown in Fig4.2.2. The absorption of Cr_3 displays noticeable absorption bands in an exciting region of ~ 400 to 685 nm. The positions of these absorption bands are given in the figure. Plotted parallel with the SDS spectrum for chromium trimer are the resonance Raman excitation profiles of the 400.0 and 302.0 cm^{-1} lines. The excitation profiles show significant resonance Raman enhancement of the 400.0 cm^{-1} line in the absorption region of ~ 461 and 477 nm. We were unable to probe the absorption region between ~ 525 to 575 nm due to the unavailability of dyes in this region. The 302.0 cm^{-1} line, $\nu_2(\text{e}')$ vibration, shows relatively strong resonant enhancement at ~ 604 and 647 nm. This indicates the existence of strong vibronic coupling in the excited state of these two optical transitions.⁷⁰ This conclusion is also likely for the 477 nm transition.

Upon deposition of Cr_2 we found no Raman transitions despite an intensive search across the excitation region. We take this to mean that there is little or no resonance enhancement of the dimer lines. A portion of the absorption (SDS) spectrum is shown for Cr_2 in Fig.4.2.2. Note there is overlap of dimer and trimer absorption in the region of 450 to 500 nm, but that the spectra are clearly distinct. There is no measurable intensity for Cr_2 at longer wavelengths.

Discussion

Using resonance Raman spectroscopy, DiLella et al.⁷¹ examined a mixture of chromium metal clusters. These molecules were formed by sublimation and subsequent condensation with Ar, Kr, and Xe onto a polished aluminum surface (~ 12 K). Upon excitation at 514.5 nm, they observed 13 spectral lines that we have listed in Table4.2.1 along with our results. They found two major progressions that began with fundamentals located in their spectrum at 308 and 396 cm^{-1} .⁷¹ One progression (396 cm^{-1}) may be characterized by vibrational constants $\omega_e = 427.5 \text{ cm}^{-1}$ and $\omega_e x_e = 15.75 \text{ cm}^{-1}$ and was assigned to the dimer, and the other, based on a line at 308 cm^{-1} , gave vibrational constants $\omega_e = 313 \text{ cm}^{-1}$ and $\omega_e x_e = 2 \text{ cm}^{-1}$.⁷¹ Since this latter progression (along with lines at 226 cm^{-1} and 123 cm^{-1})

increased in intensity simultaneously upon illuminating a more metal rich portion of the sample; they assigned these lines to the trimer. In addition, a progression with an origin at 155 cm^{-1} was assigned (in a later work) to an excited state (A) of the dimer.⁷¹

Through pulsed YAG laser vaporization of chromium metal, Bondybey and English⁷² observed fluorescence excitation spectrum for Cr_2 . Based upon their interpretation of the high resolution spectrum, they were certainly viewing emission due to Cr_2 , i.e. alternate rotational lines were missing from the spectrum, and only the P and R branches were present. From their observed gas phase emission spectrum, Bondybey and English derived $\Delta G_{1/2} = 452.34\text{ cm}^{-1}$ and a ground state vibrational frequency for the dimer to be $\omega_e \sim 470\text{ cm}^{-1}$. Our inability to observe resonance Raman intensity in Cr_2 is also consistent with their observation that there is practically no change in bond length ($0.004\text{ \AA}$) in the X to A transition. This would imply extremely small Frank-Condon factors in the resonance Raman spectrum.

The above value for ω_e (470 cm^{-1}) was confirmed in the negative ion photoelectron spectroscopy of Casey and Leopold.⁷³ Their extensive study resulted in the conclusion that the ground state of Cr_2 has a potential curve that

deviates strongly from a Morse potential. In order to explain the observed vibrational spectrum, they had to assume a "shelf" like addition to the curve and required terms up to order $(v + 1/2)^6$ to obtain an adequate fit. Their value of $\omega_e = 474.3 \text{ cm}^{-1}$ is in excellent agreement with that of Bondybey and English and in marked contrast with that of DiLella et al. In a subsequent paper, Moskovits, Limm, and Mejean⁷⁴ revisited the spectrum of Cr_2 and concluded that the discrepancy between the gas phase results and their matrix isolation results ($\omega_e = 425 \text{ cm}^{-1}$) are due to an unusually large matrix shift. Usually matrix effects shift observed vibrational frequencies by 1-2 %, so that a shift of almost 10 % must be considered quite large.

Our results presented here clear up this discrepancy. With the advantages provided by mass selection we have shown that, in an argon matrix, Cr_2 has no resonance enhancement. The observation by DiLella et al⁷¹ of a progression based on 396 cm^{-1} and attributed to the dimer is nearly identical to the lines observed in our trimer spectrum (see Table 4.2.1). We recommend that our assignment of the 400.0 cm^{-1} progression as the totally symmetric stretch of chromium trimer is indeed the correct assignment for this progression. It is likely that the dimer was not

observed by DiLella et al., since we see no resonance enhancement in our mass-selected dimer deposit. Despite this conclusion, we should note that the analysis of DiLella et al. was strengthened by a careful isotope effect calculation (including the effects of mass on $\omega_e x_e$) of the high resolution spectrum they attributed to the dimer.⁷¹ A similar analysis for the (D_{3h}) trimer failed to fit their observed spectrum. We have been unable to confirm their results since we do not observe these isotopic lines in our spectrum. It is possible that their isotopic lines were complicated by matrix site effects which were persistent despite their attempts to anneal the sample, although this explanation requires a rather remarkable coincidence. Despite this discrepancy, we feel that the mass-selection afforded in our experiments remains strong evidence that we are in fact observing the trimer spectrum, and that DiLella et al. misassigned this as the dimer.⁷¹

It should be noted that the line we observe at 302.0 cm^{-1} , assigned to the e' vibration, is not the same as that observed by DiLella et al. at 308 cm^{-1} . The latter is considerably more intense relative to the 396 cm^{-1} in their spectrum. Our observed Raman line at 302.0 cm^{-1} is quite

weak, with respect to the 400.0 cm^{-1} line, and has a very different excitation profile (see Fig.4.2.2).

In a far IR study of matrix isolated Cr_3 , Ozin and Mitchell⁷⁵ observed over fifteen distinct lines in the range 95 to 325 cm^{-1} . They attributed these lines to numerous sites with distinct angular geometries. Since the totally symmetric vibration was not observed in their experiments, they had no independent measure of the stretching force constant, and assumed $f_r = 1.00\text{ mdyne/\AA}$, far lower than we observe here (Table4.2.3). However, our degenerate bending vibration falls within their range of observation. We only see evidence for one site. Because our Cr_3/Ar matrix is grown at a much slower rate than that of Ozin and Mitchell, most likely our samples had sufficient time to attain the most stable configuration.

In a recent work, Alex, Green, Millam, Villalta and Leopold⁷⁶ examined the negative ion photoelectron spectroscopy of mass-selected Cr_3 . They observed vibrational spacings in the lowest transition of $480(15)\text{ cm}^{-1}$ and $130(15)\text{ cm}^{-1}$, which differ considerably from the results observed here. Most likely they are observing transitions to a different state than we are, since the geometry derived

from these frequencies cannot be D_{3h} and the force constants should also be quite different.

Derouault and Dalibart⁷⁷ carried out experiments involving acquisition of UV-visible absorption spectra, Raman scattering spectra, and luminescence spectra of highly concentrated chromium fragments vapourized from a tungsten basket and cooled to 12 K in an argon matrix. Using factor analysis methods on the acquired data they resolved the spectra into seven absorption profiles labeled N1 to N7. Derouault and Dalibart assigned absorption spectra N2, N3, and N4, which gave absorption bands in the 330 nm range, to Cr atoms in different argon sites.⁷⁷ Absorption profile N1 was assigned to an excited state of Cr, and absorption spectrum N7 was attributed to Cr_2 . They made this assignment based on previous absorption profiles obtained by Klotzbucher and Ozin⁷⁸ on chromium dimers and trimers in argon matrices. Klotzbucher and Ozin observed low energy optical absorptions for Cr_2 at 460/469 nm and for Cr_3 at 477 nm.

Comparing our absorption (SDS) profiles for both chromium dimer and trimer to Derouault and Dalibart's absorption spectra N5 (assigned Cr_3), N6 (assigned Cr_2 -Cr), and N7 (assigned Cr_2), there are clear similarities. We observe

the 469 nm absorption band for Cr_2 in our absorption (SDS) spectrum, which they observe in their N6 (assigned $\text{Cr}_2\text{-Cr}$) absorption spectrum. The 477 nm absorption band that is observed for both chromium dimer and trimer in our absorption (SDS) spectrum is similar to Derouault and Dalibart's N7 (assigned Cr_2) absorption spectrum. It is therefore likely that the 477 nm absorption as initially observed and attributed to Cr_3 by Klotzbucher and Ozin is correct. This would imply the assignment of spectrum N7 to chromium trimer instead of chromium dimer. This is also consistent with our reassignment of the Raman spectrum of DiLella et al. This line of reasoning would also imply spectra N5 and N6 to a chromium molecule of higher nuclearity, possibly Cr_4 , and chromium dimer with a small mixture of the atom respectively.

Clearly, if the above analysis is correct, the lines at 123, 226, and 308 cm^{-1} assigned by DiLella et al., to the trimer of chromium, must be some other species. Since these Raman lines appear in regions of their chromium sample more rich in metal, it is likely that these lines are due to chromium clusters of higher nuclearity. The most likely candidate is the tetramer, Cr_4 . If the tetramer is a tetrahedron we expect three distinct fundamentals $\nu_1(a_1)$, $\nu_2(t)$, and $\nu_3(e)$, which should have the frequency ratios of

2: $\sqrt{2}$:1 respectively. However, $v_1/v_2 = 308/226 = 1.38$ and $v_1/v_3 = 308/126 = 2.46$, and thus the tetramer must deviate significantly from a tetrahedral structure. A square planar structure can also be eliminated since all the frequencies should be nearly equal. Another symmetric possibility is a planar rhombus (D_{2h}). For such a structure, there should be six distinct fundamentals. Two are of A_g symmetry and should be observed in resonance Raman spectroscopy, while those of B_{1g} , B_{2g} , and B_{3g} symmetry should be Raman active. Assuming all bonds have an equal force constant, the frequency ratios for $v_1(A_g): v_2(A_g): v_3(B_{1g})$ should be $3^{1/2} / \sqrt{2} / 1$, (i.e. 1.73/1.41/1), still considerably different from the observed ratios. Either there is a considerable difference between the rhomboidal diagonal bond force constant and the edge bond force constant, or other possible geometries must be considered.

Examining the ratios observed, we might guess that the correct geometry lies somewhere between a rhombus and tetrahedron. We can envision, for example, a planar rhombus in which one atom bends out of plane dihedrally in C_{2v} symmetry until it reaches an apex on top of the remaining three atoms forming a tetrahedron. Normal mode calculations indicate that the vibrational frequencies should vary monotonically between these two limits, but, as of now,

there is insufficient data observed to obtain a complete analysis.

In the two limits, however, it is possible to calculate bond stretching force constants assuming the totally symmetric stretch is at 308 cm^{-1} . For a tetrahedron we obtain $k_e^{(4)} = 1.29\text{ mdyne/\AA}$. For a rhombus (assuming all bonds with equal force constant) $k_e^{(4)} = 0.97\text{ mdyne/\AA}$. Using the rules of Ozin and McIntosh⁷⁹, as mentioned above, we can predict the expected force constants. For a tetrahedral cluster, $\text{Cr}_4\text{ (T}_d\text{)}$, we expect $k_e^{(4)} = 1/3\ k_e^{(2)} = 1.15\text{ mdyne/\AA}$. For a planar rhombus, $\text{Cr}_4\text{ (D}_{2h}\text{)}$, we expect $k_e^{(4)} = 1/3\ k_e^{(2)}$ ($1.15\text{ mdyne/\AA}$) for the diagonal bond and $k_e^{(4)} = 2/5\ k_e^{(2)} = 1.38\text{ mdyne/\AA}$ for the edge bonds. These results are summarized in Table 4.2.3. We see once again that neither the rhomboidal nor the tetrahedral geometry is likely, but that some intermediate (C_{2v}) geometry may be correct. Note, however, that the predicted force constants and the observed force constants are sufficiently close in magnitude to lend support for the assignment of these lines to the tetramer. The only other set of metal clusters for which so much information is known about the small cluster force constants is tantalum.

Acknowledgements

We wish to acknowledge Dr. Doreen Leopold for helpful conversations pertaining to this work, and for providing an advance copy of her manuscript on chromium trimer. We are also indebted to Martin Moskovits for helpful comments. These experiments were funded by the National Science Foundation under Cooperative Agreement No.RII-9353488, Grant No. CHE-9712031, and by the City University of New York (CUNY) PSC-BHE Faculty Research Award Program.

Frequencies (cm^{-1}) and assignments for mass selected Cr_3 (this work).			Frequencies (cm^{-1}) and assignments for non-mass selected Cr clusters.		
Frequencies	Cr_3 assn.		Frequencies	Cr_2 assn.	Cr_3 assn.
			123		ν_3
			145		
			155	A(0-0)	
			226		ν_2
302.0	$\nu_2(e')$				
			308		ν_1
400.0	$\nu_1(a_1)$		396	ν_1	
			439		
			548	A(0-1)	
			620		
766.1	$2\nu_1$		770	$2\nu_1$	
			919	A(0-2)	
1101.0	$3\nu_1$		1100	$3\nu_1$	
1439.0	$4\nu_1$		1410	$4\nu_1$	

Table 4.2.1. Summary of observed resonance Raman frequencies for Cr clusters from various laboratories.

ω_e (cm^{-1})	$\omega_e X_e$ (cm^{-1})	D_e^a (eV)	k_e (mdyne/ $\text{\AA}$)
432.2 (16)	16.3 (4)	0.36	1.90

Table 4.2.2 Spectroscopic constants obtained from Cr_3 resonance Raman spectra.

Cluster	Observed k_e (mdyne/ $\text{\AA}$)	Predicted k_e
Cr_2	3.45	(3.45)
Cr_3 (D_{3h})	1.91	1.73
Cr_4 (T_d)	1.29 ^a	1.15
Cr_4 (D_{2d})	0.97 ^a	1.15/1.38 ^b

Table 4.2.3 Summary of observed and predicted force constants, k_e , for various clusters of Cr. Note that predicted k_e values are based upon rules of Ozin and MacIntosh.¹⁴

- a) We are assuming the 308 cm^{-1} band represents the totally symmetric stretch of each symmetry and that all-stretching constants are equal.
- b) The predicted force constant values for diagonal/edge bonds of planar rhombus.

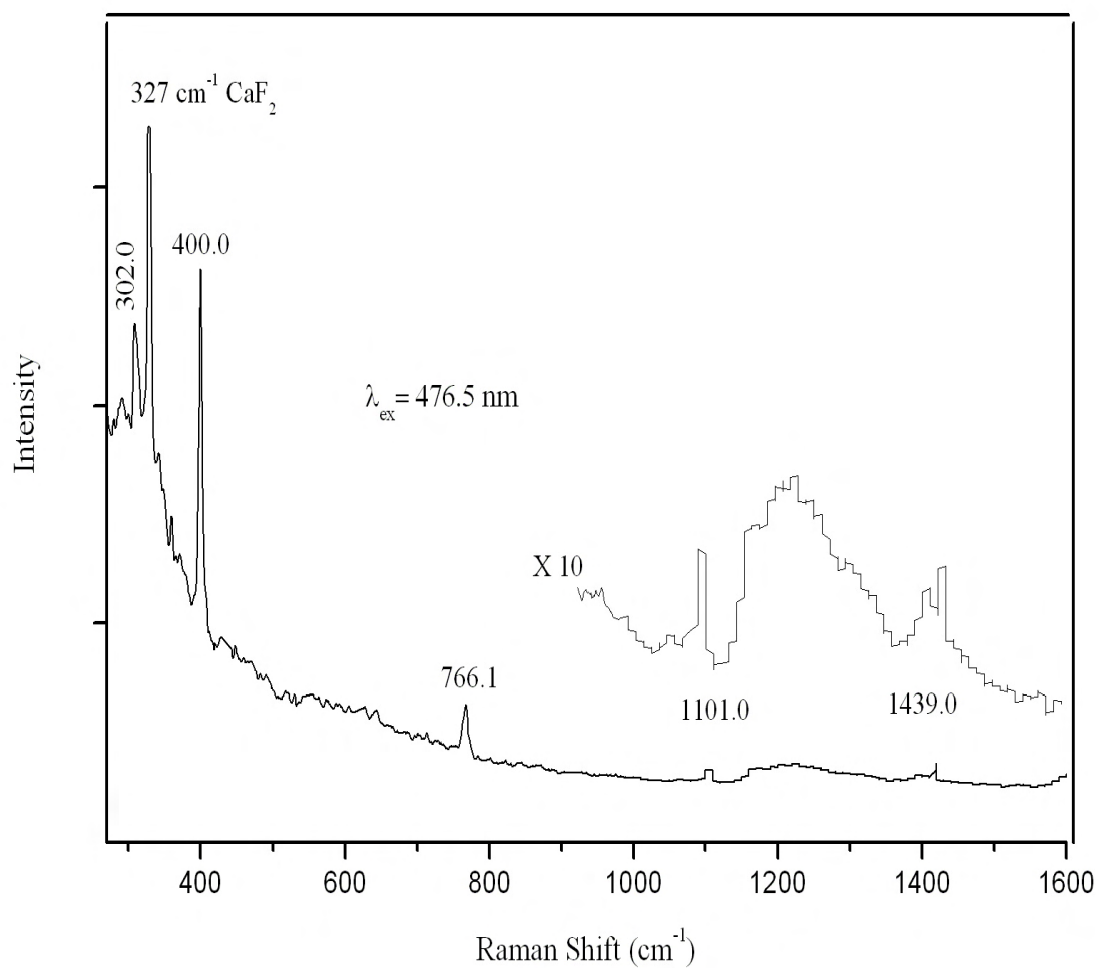


Fig.4.2.1 Resonance Raman spectrum of chromium trimer in an argon matrix at 16 K and excited at 476.5 nm. The line at 327 cm^{-1} is that of the CaF_2 substrate, and the band located at $\sim 1225 \text{ cm}^{-1}$ is attributed to fluorescence.

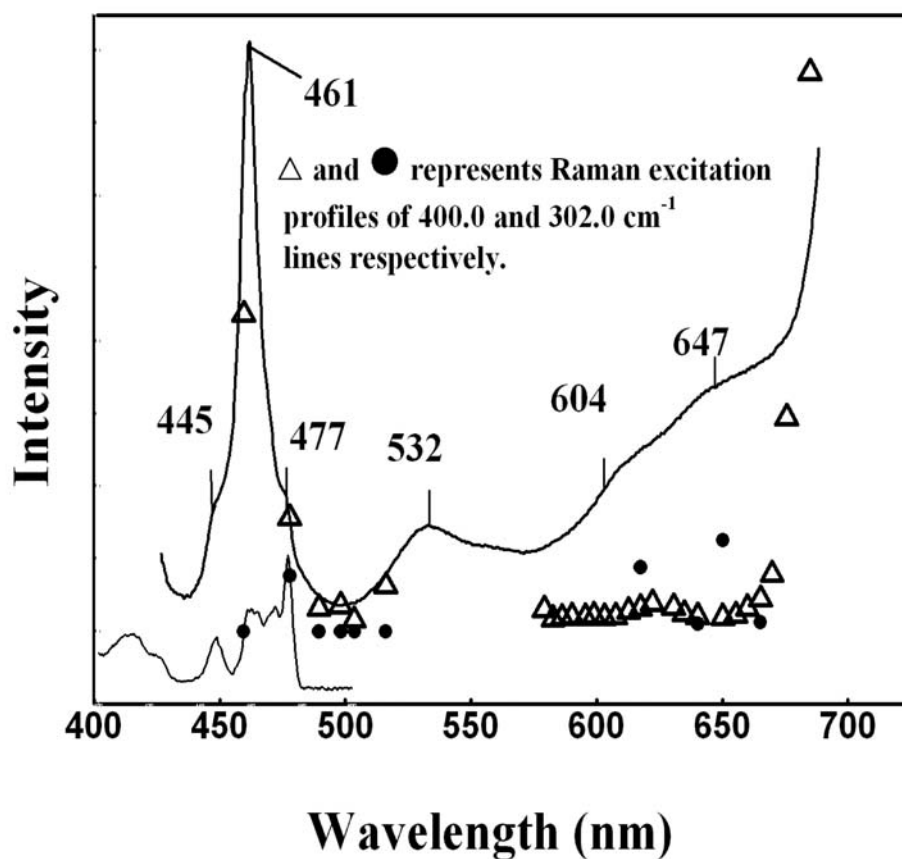


Fig.4.2.2 The absorption (SDS) spectrum of Cr_3 in an argon matrix. Plotted parallel with the trimer absorption spectrum is the resonance Raman excitation profile of the 400.0 (Δ) and 302.0 ($\bullet$) cm^{-1} lines. In the lower left corner, from 400 to 500 nm is a truncated absorption (SDS) spectrum of Cr_2 in an argon matrix at 16 K. The vertical lines refer to relative absorption maxima.

4.3 Resonance Raman spectra of mass-selected Mo₂ and Mo₃ in Argon matrices

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Abstract

We report on mass-selected molybdenum dimers (Mo₂) and trimers (Mo₃) in argon matrices via resonance Raman spectroscopy. The resonance Raman spectrum of Mo₂ displays lines at 394.5(12), 445.0(18), and 473.3(15) cm⁻¹, with several overtones observed for the most intense 394.5 cm⁻¹ line.

The trimer (Mo₃) displays absorption in the 575-625 nm regions with a maximum at ~600 nm. Excitation into this region gives Raman lines at 224.5(5), 236.2(8), 386.8(12), and 446.9(7) cm⁻¹. They are assigned to $\nu_3(a_1)$, $\nu_2(b_1)$, $\nu_1(a_1)$ (the bend, antisymmetric stretch, and symmetric stretch) and $2\nu_2$ respectively.

Introduction

Molybdenum dimer, Mo_2 , is noted for having one of the strongest metal-metal bonds with a likely bond order greater than four^{80,81} and it is worthwhile examining whether this strong bonding extends to the trimer. Efremov et al⁸² resolved vibrational and rotational frequencies of three electronic band systems of Mo_2 via flash photolysis of crystallized molybdenum hexacarbonyl. They found vibrational fundamentals in each of the states involved, from which they obtained the ground state fundamental of $\omega_e=477 \text{ cm}^{-1}$ for Mo_2 , as well as $\omega_e=443.4 \text{ cm}^{-1}$ for the first excited $A(^1\Sigma_u^+)$ state at 19303.7 cm^{-1} . Pellin et al⁸³ employing time resolved fluorescence techniques investigated Mo_2 in argon and krypton matrices. When exciting at various wavelengths ranging from 498 to 543 nm, they observed fluorescence from the dimer in a spectral range of ~724–850 nm. Their fluorescence spectra gave two sets of nearly identical emissions that were slightly shifted in spectral range from one another, which they termed red and blue emission attributed to the existence of two sites in the argon matrix. They determined the ground state fundamental of the red and blue emission to be $\omega_e=473.3$ and 477 cm^{-1} , respectively. Their findings were later confirmed by observation of a single Raman line at 475 cm^{-1} ⁸⁴.

In this Letter we present the resonance Raman and absorption characteristics of Mo_2 and Mo_3 in argon matrices. Exciting with laser lines 488, 496.5, or 501.7 nm as well as with dye lasers, we observe Raman features for Mo_2 in a spectral region of ~451-461 nm. The Raman spectrum of Mo_2 displays three distinct lines at 394.5(12), 445.0(81), and 473(15) cm^{-1} . The 394.5 cm^{-1} line is the most intense of the three and includes a series of three overtones up to 1547 cm^{-1} . We also detect fluorescence from Mo_2 when exciting in a region of 440-685 nm, which is the same as that observed by Pellin.

For Mo_3 , there are no previously reported resonance Raman experiments. In our experiments, the trimer displays a broad absorption band extending from ~575 to 625 nm, with an absorbance maximum around 600 nm. We excite near the absorbance maximum of Mo_3 and observe four resonance Raman lines at 224.5(5), 236.2(8), 386.8(12), and 446.9(7) cm^{-1} . We assign the 386.8 cm^{-1} peak as the ground state fundamental of the symmetric stretch $\nu_1(a_1)$. The lines at 236.5 and 224.5 cm^{-1} we attribute to the antisymmetric stretch $\nu_2(b_1)$ and the bend $\nu_3(a_1)$, respectively. The line at 446.9 cm^{-1} is assigned as an overtone to the antisymmetric stretch.

Experimental

The CCNY metal cluster deposition source has been described in detail in previous publications^{85, 86} but will be briefly detailed here. A 10 mA argon ion beam (at 25 keV) sputters a water-cooled molybdenum metal target, purchased from Alfa Aesar at 99.9% purity. A series of einzel lenses collect Mo_n^+ from the metal sputtering region and focuses the molecules to the Wien filter, where mass selection occurs. After mass selection, molybdenum clusters are focused onto the deposition region where Mo_2^+ , or Mo_3^+ , is codeposited with argon gas and electrons for neutralization, onto a CaF_2 substrate. Deposition occurs while the substrate is held at ~16 K. The argon/metal matrix is grown at ~6 m/h with an Ar:metal ratio of $\sim 10^4$:1. Upon comparison of atomic molybdenum excitation features with those of Mo_2 and Mo_3 , where molybdenum atoms are deposited under the same conditions, the fragmentation ratio for Mo_2 is estimated to be ~3% and for Mo_3 <1%.

Resonance Raman experiments are carried out using the visible lines of a Spectra Physics 2045 argon ion laser, which pumps a Coherent model CR599 dye laser employing the dyes R6G, Stilbene 3, R110, and DCM. All Raman shifts are calibrated using the 327.0 cm^{-1} line of the CaF_2 substrate.

Note also the weak CaF_2 line at 360 cm^{-1} . Observing the resonance Raman spectra of Mo_2 or Mo_3 , while tuning the dye laser in small increments, generates the resonance Raman excitation profile. The equivalent of optical absorption spectra are obtained in our ultra-thin samples by an alternative technique called "scattering depletion spectroscopy" (SDS), by which we measure decreases in the intensity of light scattered through the sample at 90° to the incident radiation.

Results and discussion: Mo_2

The resonance Raman spectrum of Mo_2 gives three unique Raman lines at 394.5 , 445.0 , and 473.3 cm^{-1} , with three overtones of 394.5 cm^{-1} at $783.0(52)$, $1167.0(49)$, and $1547(9)\text{ cm}^{-1}$ (Fig. 4.3.1). No Raman lines were observed below 300 cm^{-1} . Normally, only a single fundamental is observed for a diatomic molecule, unless tied to an origin of a low lying electronic state^{87, 88}. Surprisingly, we observe several lines with the same spectral origin (i.e., the Rayleigh line). The 394.5 cm^{-1} line is, by far, the most intense. Note, however, that two of these fundamentals (445 and 473 cm^{-1}) were previously observed in emission and absorption studies⁸² above^{3, 4, 5} and also that Pellin et al., exciting with several argon ion laser

lines, observed only one line at 475 cm^{-1} in a resonance Raman spectrum⁵. They reported only a small portion of the Raman spectrum due to fluorescence interference from atomic emission⁸⁹.

The Raman excitation profile of Mo_2 is shown as an inset of Fig.4.3.1. One weak absorption region is centered at $\sim 457\text{ nm}$, and the other region is near $\sim 500\text{ nm}$. In the region above 500 nm , fluorescence begins to obscure our Raman excitation profile. Note that the 395 cm^{-1} Raman line rises in intensity as it approaches the $\sim 500\text{ nm}$ region while the profiles arising from the other two lines remain relatively flat. This latter is in agreement with the observation of Pellin⁵ for the intensity variation of the 475 cm^{-1} line. This indicates that the 394.5 cm^{-1} line is most likely resonantly enhanced near the region of strong absorption (515 nm).

Our observation of the three different fundamentals in the Raman spectrum implies that we are observing spectra in three distinct states and leads us to inquire which corresponds to the ground state. Clearly all three cannot, and at these low temperatures our experiment can only be explained if at least two of these states are populated by some optical pumping mechanism. From vibrational analysis

of the observed emission of Mo_2 , Efremov ³ obtained $\omega_e=477.1 \text{ cm}^{-1}$ for the lowest state, which they designated, $X(^1\Sigma_g^+)$. For the excited states they found $\omega_e=443.4 \text{ cm}^{-1}$ $A(^1\Sigma_u^+)$, $\omega_e=412.0 \text{ cm}^{-1}$ $B(^1\Pi_u)$, and $\omega_e=408.0 \text{ cm}^{-1}$ $C(^1\Sigma_u^+)$ ⁴. Most likely our observed lines at 473.3 and 445.0 cm^{-1} correspond to the X and A states, but the state to which the most intense 394.5 cm^{-1} line belongs has not been previously identified. Perhaps one reason why the most intense line observed in our spectrum does not correspond to the ground state observed in fluorescence is due to the rather small (0.001 Å) change in internuclear distance observed ⁹⁰ leading to small Raman enhancement of the ground state fundamental. This is similar to the lack of observation of resonance enhancement in Cr_2 where ⁹¹ an unusually small change in internuclear distance (0.004 Å) is also observed. Clearly additional experiments are needed to arrive at a definite assignment for this line.

Results and discussion: Mo_3

The resonance Raman spectrum of a ~220 nA-h sample of Mo_3 in an argon matrix is shown in Fig.4.3.2. The absorption (SDS) spectrum and resonance Raman excitation profile, both shown in the inset of Fig.4.3.2, are in agreement and confirms our assignment of the spectrum of the mass-

selected sample to the trimer. The absorption of Mo_3 displays a broad band in the region of $\sim 575\text{--}625$ nm. The maximum for this absorption is in the region of ~ 600 nm. Exciting at 590 nm, we observe resonance Raman lines for Mo_3 at $224.5(5)$, $236.2(8)$, $386.8(12)$, and $446.9(7)$ cm^{-1} . We assign the highest frequency fundamental 386.8 cm^{-1} to the totally symmetric stretch $\nu_1(a_1)$ of triatomic molybdenum (C_{2v}). The vibrations at 236.2 and 225.5 cm^{-1} may then be assigned to the $\nu_2(b_1)$ antisymmetric stretch and the $\nu_3(a_1)$ bend, respectively. This ordering is consistent with previous assignments of transition metal trimers. The band observed at $\omega_e=446.9$ cm^{-1} is assigned as an overtone $2\nu_2(a_1)$. We make this assignment despite the fact that the bending fundamental is more intense, because we expect considerable anharmonicity in these vibrations and assignment to the overtone of the bend would imply virtually no anharmonicity in that mode.

In a recent density functional study of small Mo clusters Pis Diez⁹² predicted that the ground state of Mo_3 will be an equilateral triangle with a $^3A_2'$ state arising from a $1a_1'^2 1a_2''^2 1e'^4 2a_1'^2 3a_1'^2 1e''^2 2e'^2$ configuration. The vibrational frequencies for this state are 271 cm^{-1} (e') and 446 cm^{-1} (a_1^1), both somewhat larger than the assignments in this study. It might be tempting to assign our observed

line at 446.9 cm^{-1} to the symmetric stretch in agreement with the calculation, but then it would be impossible to assign the remaining three lines to a trimer, since only three fundamentals are expected.

In order to analyze the normal modes, it is useful to make the central force approximation. The number of independent frequencies observed does not justify assumption of a more sophisticated force field, and any attempt to fit the observed data with more elaborate descriptions results in serious inconsistencies. Lack of isotopic shifts is a special hindrance in this regard. This assumed force field is strictly valid for a highly symmetric equilateral triangle in which all three bonds have an equal force constant, and therefore must be considered subject to further analysis. However, this force field does enable us to obtain an approximate value of the symmetric stretch force constant, which is $k_e=2.82\text{ mdyne/\AA}$. As suggested by Ozin and McIntosh⁹³, the force constant for an equilateral triangle trimer should be $\sim 1/2$ that of the dimer ($k_e=6.33\text{ mdyne/\AA}$, assuming $\omega_e=473.3\text{ cm}^{-1}$), giving a predicted value of $3.17\text{ mdyne/\AA}$. This deviation ($3.17\text{ vs }2.82$) is in keeping with deviations observed in other trimers.

Note that as with the dimer, the observed force constant is one of the highest ever observed for a metal trimer. Only those observed in V_3 (2.21 mdyne/Å)⁹⁴ and Ta_3 (2.25 mdyne/Å)⁹⁵ are even close. It is apparent that the tendency toward strong multiple bonding, which was observed in Mo_2 , is also present in the trimer. This may also be seen by comparisons across the periodic table. The force constants for Zr_3 (1.19 mdyne/Å)⁹⁶ and Nb_3 (2.05 mdyne/Å)⁹⁷ show the effects of increasing availability of d-electrons for bonding. The atomic configuration of Mo is $4d^55s^1$, and to the extent that all valence electrons may be used in bonding, this provides 18 potential electrons for trimer bonds. The large observed stretching force constant indicates that, relative to other trimers, it is likely that bond order in the trimer of Mo is rather large in a fashion similar to the relative dimer bond orders.

Acknowledgements

We wish to acknowledge Dr. Michael Pellin and Dr. Steven Mitchell for helpful conversations pertaining to this work. We are especially grateful to Professors Michael Morse and Doreen Leopold for extensive and helpful comments concerning this manuscript. These experiments were funded by the National Science Foundation under Cooperative

Agreement No. RII-9353488, Grant No. CHE-0091362, and by the City University of New York (CUNY) PSC-BHE Faculty Research Award Program.

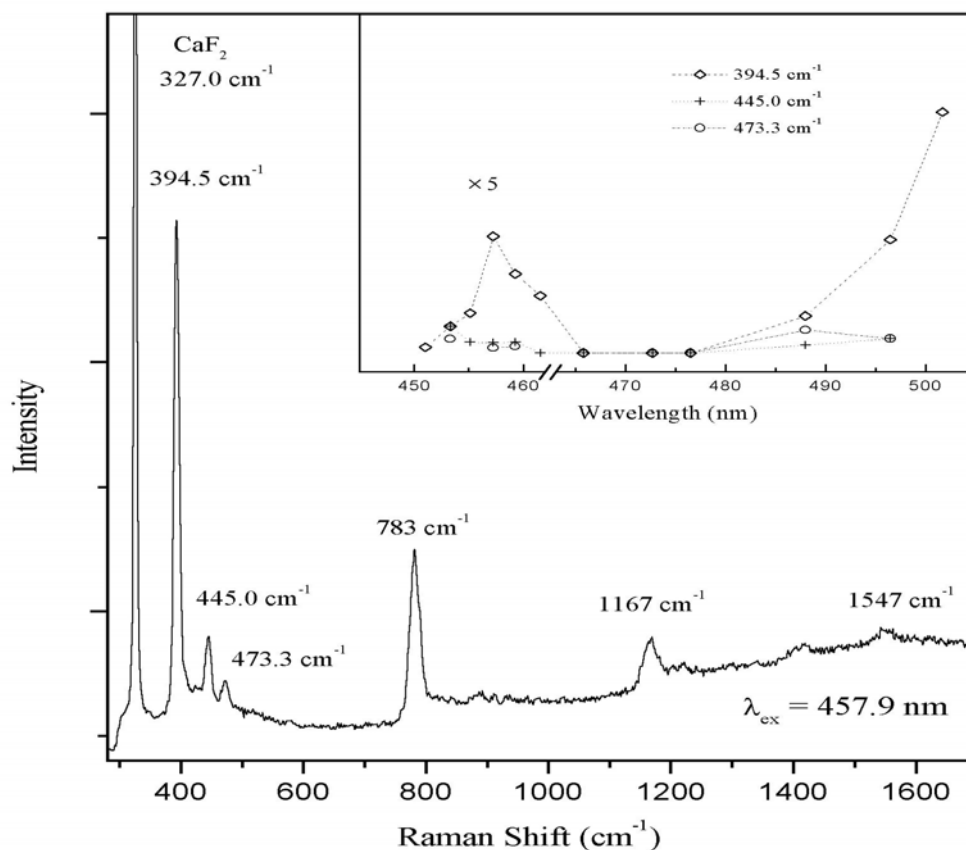


Fig.4.3.1 The resonance Raman spectrum of Mo₂ in argon matrix excited at 457.9 nm. Raman excitation profiles for the frequencies 394.5, 445.0, and 473.3 cm⁻¹ are shown in the inset for an excitation range of ~450–500 nm. Significant resonance enhancement of the 394.5 cm⁻¹ vibration may be observed, but little to no resonance enhancement of the 473.3 and 445.0 cm⁻¹ vibrations are apparent. No Raman lines were observed below the region shown.

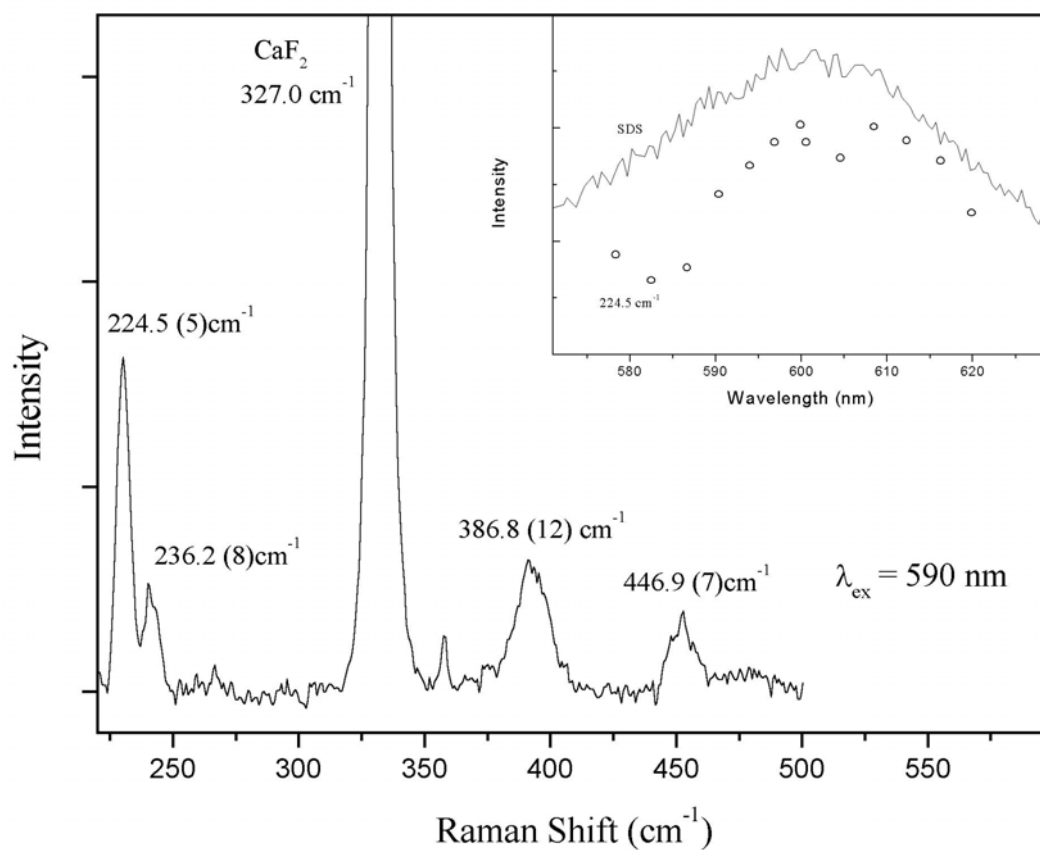


Fig.4.3.2. The resonance Raman spectrum of Mo_3 . The absorption (SDS) spectrum and excitation profile are shown as insets. No Raman lines were observed below the region shown.

Chapter V Homonuclear Transition Metal tetramers

5.1 Absorption and Raman Spectroscopy of Mass-Selected Scandium Tetramers in Argon Matrices

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10031

Abstract

We examine the absorption and resonance Raman spectra of mass-selected Sc clusters, and obtain the spectra of tetramers of Sc. Tetramers are produced in a sputtering source and mass filtered with a Wien filter, then neutralized and deposited in an Ar matrix. The absorption spectrum indicates several new optical transitions at 350, 451, 538, and 563 nm. Raman resonances were excited at 488 nm with transitions at 222, 166, and 103 cm^{-1} . These indicate a tetrahedral (Td) geometry, and we assign the observed frequencies to a singly degenerate totally symmetric stretch $\omega_1(\alpha_1)$, a triply degenerate mode $\omega_2(t)$, and a doubly degenerate $\omega_3(e)$. 2002 Elsevier Science B.V. All rights reserved.

Introduction

As the first and lightest member of the series of transition metals, Sc and its small clusters have received considerable theoretical and experimental attention^{98,99}. The optical absorption spectrum of Sc₂ was first obtained by Busby, Klotzbücher, and Ozin¹⁰⁰. In a sample of deposited Sc atoms, they found three broad transitions at 662, 470, and 335nm, which they attribute to the dimer. With Knudsen effusion mass-spectroscopy, Verhaegen, Smoes and Drowart¹⁰¹ determined the dissociation energy of the Sc₂ to be 1.12 eV, while Gingerich¹⁰² reported a value of 1.65 eV. Using ESR spectroscopy, Knight, Van Zee, and Weltner¹⁰³ showed that the ground state of Sc₂ is $^5\Sigma_u^-$, derived essentially from a $so^1do^1d\pi^2$ configuration. This conclusion was given theoretical support in a CASSCF/CI(SD) calculation by Walch and Bauschlicher¹⁰⁴ who showed that the dominant configuration is $4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^1 3d\pi^2$. The Raman spectra of scandium dimers and trimers in argon matrices have been obtained by Moskovits, DiLella, and Limm¹⁰⁵. They concluded that the dimer has vibrational constants $\omega''_e = 239.9\text{cm}^{-1}$ and $\omega''_ex''_e = 0.93\text{ cm}^{-1}$. The trimer is described as an equilateral (or near equilateral) triangle with a symmetric stretching (a'_1) vibrational frequency of 247 cm^{-1} and a degenerate (e')

vibrational frequency of 150cm^{-1} (which is split to 145 and 151 cm^{-1} at low temperatures). Knight and Van Zee¹⁰⁶, using ESR spectra at 4-30K confirmed that the trimer is an equilateral triangle with a likely $^2\text{A}'_1$ ground state. In a CASSCF/CI(SD) calculation on the trimer by Walch and Bauschlicher¹⁰⁷ indicate instead that strong bonding of the 3d electrons of Sc_3 leads to a $^2\text{A}''_2$ ground state.

These results suggest that it is worthwhile examining the tetramer of Sc, which until now, has not been observed. Our mass-selection apparatus employs a sputtering source, followed by a Wien filter for separation by mass. However, the filter, similar to most mass-selection devices, in reality is sensitive to the mass-to-charge ratio. It is thus possible to obtain clusters of larger mass when multiple ionized species are present. This was first observed in our apparatus in the study of Hf_3 , when significant currents of Hf_3^{+2} were obtained through our filter¹⁰⁸. In mass scans of various scandium clusters, we find evidence for the presence of Sc^{+2} as well as Sc_4^{+2} , the latter in confluence with Sc_2^+ . We report observation of absorption and resonance Raman spectra of various scandium clusters, confirming the previous results of Moskovits et al. on the dimer, and report new bands which we attribute

to the tetramer (at 350, 451, 538, and 563 nm in absorption and 222 cm^{-1} , 166 cm^{-1} , and 103 cm^{-1} in the Raman spectrum).

Experiment

The absorption and resonance Raman spectrum of various mass-selected Sc clusters were acquired using the CCNY metal cluster deposition source. The design of this apparatus has been discussed in detail in other publications^{109, 110} but will be described briefly here. An argon ion beam of 10 mA (at 25 eV) sputters a water-cooled scandium metal target, purchased from Alfa Aesar at 99.9% (REO). The scandium target was maintained at about 300V. A series of einzel lenses collects the sputtered scandium cluster ions from the metal sputtering region, and a Wien filter mass selects the focused cluster ions. Any neutral atoms or clusters produced during the sputtering process that pass through the mass selector are removed by a 10^0 bend in the path following the Wien filter. A second set of einzel lenses focuses the mass-selected cations into the deposition region, which are then codeposited with argon gas and electrons, for neutralization, onto a CaF_2 substrate. A cryostat cools the substrate to $\sim 16\text{ K}$. To prevent degradation upon impact with the CaF_2 substrate, focused ions are slowed to $\sim 10\text{ eV}$ to ensure a soft landing on the

substrate. The Sc_n/Ar matrix had a growth rate of $\sim 6\mu\text{m/h}$. The argon: cluster ratio was $\sim 10^4:1$. Several deposits were carried out, during which the current for a particular mass-to-charge (M/C in amu/electron charge) ratio was optimized. For $M/C = 45$ ($\text{Sc}^+/\text{Sc}_2^{+2}$) the optimized current was 360 nA, for $M/C = 90$ ($\text{Sc}_2^+/\text{Sc}_4^{+2}$) the current was 160 nA, and for $M/C = 135$ (Sc_3^+) the current was 60 nA. In all our scans the current for Sc_4^+ (i.e. at $M/C = 180$) was negligible.

Resonance Raman spectroscopy was carried out *in situ* on the matrix sample. An absorption spectrum, in the form of a "scattering depletion spectrum" (SDS) was also obtained. The "SDS" absorption is a ratio between scattered light from the edge and center, where most of the sample is deposited, to that of the CaF_2 substrate. The scattered light is collected at a 90° angle from the incident radiant.

The visible lines of a Spectra Physics 2045 argon ion laser and a Spectra Physics 2020 krypton ion laser, as well as laser lines from a Coherent model CR599 dye laser, employing the dyes R6G and DCM were used to observe resonance Raman features of the mass-selected species. The 327 cm^{-1} line of the CaF_2 substrate was used to calibrate all Raman shifts. The Raman detection system consists of a Spex 1877E 0.6m Triplemate Spectrometer coupled with a liquid nitrogen cooled CCD system (Spectrum One and CCD30).

The computer software DM3000R acquired, interpreted, and displayed spectral information from the CCD.

Results

Several deposits were obtained, during which the current for a particular mass-to-charge (M/C in amu / electron charge) ratio was optimized. In Figure.5.1.1, we show the scattering depletion spectra (SDS) of the samples obtained in each of the deposits. As discussed previously, the SDS spectrum is a more sensitive means of obtaining the absorption spectrum under conditions encountered in our apparatus. In table5.1.1, we list the absorption peaks observed in each of the deposits, next to the previous assignments of the atom, dimer and trimer. In addition to the previously observed bands, we observed several new bands, namely at 350, 451, 538, and 563 nm which we attribute to the tetramer. Note also the peaks at 327, 497, 614 and 624 nm are stronger than expected from the dimer spectrum, and we suggest that coincidences may exist for these bands with the tetramer. For the deposit with $M/C = 90$ (Sc_2^+/Sc_4^{+2}), we observe some lines attributed to the atomic spectrum, and calculate a fragmentation ratio for this deposit of about 20%.

In Figures 5.1.2 and 5.1.3 we present resonance Raman spectra obtained for the deposit at M/C of 90. Figure 5.1.2 shows the spectrum with excitation at the 676.5 nm line of the krypton laser. In addition to the CaF_2 line at 327 cm^{-1} (observed in all our spectra) there is the line at 234 cm^{-1} , which was observed by Moskovits and co-workers and assigned to the dimer. Exciting the same sample at 488 nm with an argon ion laser, we obtain the spectrum shown in figure 3. In addition to the (weak) line at 234 cm^{-1} , three new somewhat stronger lines appear at 223 cm^{-1} , 166 cm^{-1} , and 103 cm^{-1} , which we attribute to the tetramer.

Depositing with a mass-to-charge ratio of 135 and exciting at 488 nm, we were not able to observe the lines at 247, 151, and 145 cm^{-1} assigned to the trimer by Moskovits et al. It is likely that the trimer is not observed either because the resonance enhancement of the trimer is too low, or that severe fragmentation of the trimer occurs under the conditions of our apparatus. In figure 5.1.1(c), (the "SDS" of the M/C = 135) a rather large amount of intensity due to atomic lines is observed. Assuming this is due to fragmentation of the trimer, we calculate a fragmentation ratio of over 70% for this deposit. In each of the deposits, we carried out extensive

searches of other regions of the spectrum for additional Raman lines, but were unable to find any.

In summary, then we have observed three new Raman lines, not previously observed in spectra obtained for the dimer and trimer. These lines at 222 cm^{-1} , 166 cm^{-1} , and 103 cm^{-1} may be assigned to the tetramer of scandium.

Discussion

Our results confirm the previous observation of Sc_2 by Moskovits, DiLella, and Limm. To this we may add the present results in the tetramer (Sc_4). Observation of three lines at 222 cm^{-1} , 166 cm^{-1} , and 103 cm^{-1} for the tetramer suggest the possibility that the geometry of Sc_4 is tetrahedral. For a tetrahedral (T_d) tetramer, we expect to observe three fundamentals: a singly degenerate totally symmetric stretch $\nu_1(a_1)$, a triply degenerate mode $\nu_2(t)$ and a doubly degenerate $\nu_3(e)$ mode, and we may assign these to the 222, 166, and 103 cm^{-1} frequencies respectively. Further evidence for this assignment may be obtained by comparison with the modes observed¹¹¹ in Ta_4 . In that molecule, we observed many more than three lines, which provided further evidence that the molecule was tetrahedral. The most important evidence was the observation of a weak Jahn-Teller effect in the $\nu_3(e)$ mode. Any other reasonable

geometry would not have an electronically degenerate (E) ground state as is required by the Jahn-Teller coupling. Furthermore, the ratios ω_2/ω_1 and ω_3/ω_1 observed in Ta_4 were quite close to those expected for tetrahedral geometry from a valence (central) force approximation¹¹² (i.e. $\omega_2/\omega_1 = 0.71$ and $\omega_3/\omega_1 = 0.5$). For Sc_4 we have no additional confirmation (such as a Jahn-Teller effect), but we may compare the ratios of observed frequencies to those obtained in Ta_4 . For Ta_4 the ratio ω_2/ω_1 is 0.69 while for Sc_4 it is 0.75. For Ta_4 the ratio ω_3/ω_1 is 0.48 while for Sc_4 it is 0.46. We take this as confirmation of the tetrahedral geometry for Sc_4 . There is not sufficient data on Sc_4 to justify a more sophisticated force field calculation.

Of course these considerations cannot completely rule out other possible geometries, the most likely of which is the planar rhomboid. For that geometry we would expect to observe six distinct fundamentals, but it is risky to draw conclusions from the *absence* of spectral lines, which may, after all, be too weak to be observed. For a rhomboidal tetramer, at least in the central force approximation, the predicted ratios of the higher frequency lines are $\omega_2/\omega_1 \approx 0.85$ and $\omega_3/\omega_1 \approx 0.70$. Thus on existing evidence we conclude the most likely geometry for Sc_4 is tetrahedral.

Since we now have good ground state vibrational frequencies for Sc_2 , Sc_3 , and Sc_4 , it would be of considerable value to compare the variation of force constant with cluster size in scandium clusters. Using the central force approximation¹¹³ ($k_e = (m/4) \omega_{a_1}^2$, where ω_a is the frequency of the totally symmetric a_1 vibration, and the conversion factor is 5.8919×10^{-7} mdyne/Å-amu-cm⁻²) we obtain a value for the bond stretching constant $k_e = 0.318$ mdyne/Å. In order to determine how good this approximation is, we may compare the results, which would be obtained with the central force approximation, with more complete force field determinations for other tetrahedral tetramers. Such determinations exist for Mg_4 ¹¹⁴, Be_4 ¹¹⁵ and P_4 ¹¹⁶. The resulting bond stretch force constants from these calculations are 0.130, 0.58, and 1.69 mdyne/Å, respectively. The bond stretch force constants obtained from the observed $\omega_1(a_1)$ frequencies by central forces are 0.149, 0.58, and 1.74 mdyne/Å, respectively. A somewhat better value for the force constants may be obtained for Sc_4 if we adopt the tetrahedral force field of Pistorius¹¹⁷ who used the FG matrix method of Wilson¹¹⁸. This force field involves a bond-stretch force constant k_r , and two stretch-stretch interaction constants k_{rr} and k'_{rr} . It may be shown that

$$\omega_a^2 = 4/m(k_r + 4k_{rr} + k'_{rr}),$$

$$\omega_t^2 = 2/m(k_r - k'_{rr}),$$

$$\omega_e^2 = 1/m(k_r - 2k_{rr} + k'_{rr}),$$

Using the observed frequencies, we obtain $k_r=0.331$ mdyne/Å; $k_{rr}=0.0076$ mdyne/Å, and $k'_{rr}=-0.0344$ mdyne/Å.

We have now determined the stretching force constants for all three of the lowest clusters of scandium. These calculations are collected in table 5.1.2. The only other transition metal for which force constants are known for dimer, trimer and tetramer is tantalum^{110, 119, 111} and in the table we compare the observed force constants (in mdyne/Å) for small Sc and Ta clusters. Note the force constants for the tantalum clusters are uniformly much larger than those for the corresponding scandium clusters, reflecting the increased participation of d electrons in bonding in all clusters.

The overall decrease in magnitude of force constant with cluster size is consistent with expectations of the effect of increasing coordination number. This idea was formalized by Ozin and McIntosh¹²⁰, who devised a method by which the force constants of larger clusters ($k^{(n)}$) could be estimated from that of the dimer ($k^{(2)}$). Their procedure involved calculation of a parameter β_n such that:

$$k^{(n)} = \beta_n k^{(2)}$$

where $\beta_n = 2/\alpha_n$, and α_n for each bond (between two chosen atoms) is the sum of the coordination number of each atom in the bond. For an equilateral triangle $\beta_3 = 1/2$ while for a tetrahedral tetramer $\beta_4 = 1/3$. The rules of Ozin and McIntosh have found considerable utility in cluster science, aiding in the assignment of spectra as well as providing a benchmark for theoretical calculations. Underlying these rules is the implicit assumption that in forming larger clusters from smaller ones, the type of bonding remains unchanged. This is the same as saying that the bond order (or electron density) inherent in a dimer bond is spread out evenly among the added bonds.

In a recent review (see table 7 of that article), the observed ratios of trimer force constants to dimer force constants were compared in all the transition metals for which observations have been made. If the above relationship were to hold, the values listed in the table should all be close to 0.5 (β_3). For a large majority of the species this is true. One exception is Mn for which the ratio is 4. This large deviation is explained by the fact that for the dimer of Mn, bonding is van der Waals in nature, while for the trimer there is covalent bonding. Other deviations include Au (0.59), Pt (0.68), Rh (0.86) and Sc (0.71). In table 5.1.2 we list the observed ratios

for the Sc and Ta clusters. Note that for Ta the ratios are close to those predicted by Ozin and McIntosh, while for Sc the deviations are considerable. It is therefore worthwhile examining the bonding in the small clusters of Sc more closely to search for an explanation of these deviations.

For the dimer of Sc considerable work exists. Knight, Van Zee and Weltner observed the ESR spectrum of Sc_2 and established that the ground state is $^5\Sigma_u^-$. Walch and Bauschlicher used a CASSCF multi-reference calculation to confirm this assignment and showed that the dominant configuration is $4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^1 3d\pi^2$, arising from the $^2D(4s^2 3d^1) + ^4F(4s^1 3d^2)$ atomic states. Gingerich, using third law techniques, determined the dissociation energy (to two ^2D atoms) to be $D_0 = 1.65$ eV. Later, in a density functional study, Papai and Castro¹²¹ confirmed the previous calculation. Their calculated dissociation energy is $D_e = 0.92$ eV. Recognizing that there are five bonding electrons and one antibonding (σ_u) electron, the formal bond order for Sc_2 is 2.

The trimer of Sc was shown by Knight, Van Zee and Weltner to be of $^2A_1'$ (D_{3h}) symmetry, and the density functional calculations of Papai and Castro confirm this. They show that the ground state configuration is $(1a_1')^2 (1t')^4 (1a_2'')^2 (2a_1')^1$, and that the likely dissociation is

$\text{Sc}_3 \rightarrow \text{Sc}(^1\text{D}) + 2 \text{Sc}(^4\text{F})$ leading to a predicted diabatic energy of atomization of 2.49 eV/atom. Note that all the electrons in the ground state configuration are essentially bonding electrons, resulting in a formal bond order of 4.5 or formal bond order per bond of $4.5/3 = 1.5$.

Clearly, the information on the tetramer is scarcer. The spectra indicate that the tetramer is tetrahedral (T_d) in geometry. Dai and Balasubramanian¹²² have carried out CASSCF plus MRSDCI multi-reference calculations on Y_4 , and indicate that from the configuration $(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^2$, three states can arise: $^3T_1$, $^1A_1$, and $^1T_1$, of which the triplet is the lowest. These orbitals are all bonding in character. If the same configuration holds for the ground state of Sc_4 , then the formal bond order is 6, and since for a tetrahedral molecule there are six equivalent bonds, the formal bond order per bond is 1.

If we now compare the ratios of formal bond order per bond for the clusters of Sc, we find that the trimer/dimer ratio is 0.75 and the tetramer/dimer ratio is 0.5. These values are much closer to the observed ratios of force constants shown in table 5.2.2 than those predicted by the rules of Ozin and McIntosh (0.5 and 0.33 respectively). This may be seen to be due to the fact that the dimer of Sc has an anti-bonding electron, which considerably weakens

the bond relative to the trimer and likely tetramer, which have only bonding electrons. This shows up in the relative values of the dissociation energies (regardless of whether we use the experimental or calculated numbers) as well. Thus we attribute the deviation of the force constant ratios in Sc clusters from those predicted by Ozin and McIntosh to a somewhat weaker dimer bond, stemming from an anti-bonding electron, in comparison to the next larger clusters, which have only bonding electrons in their ground state configuration.

A similar analysis for the clusters of Ta is difficult due to the lack of good calculations on these clusters. However, if the bonding in Ta_2 is the same as that in V_2 and Nb_2 ¹²³ the ground state is a $^3\Sigma_g^-$ arising from a $1\pi_u^4 1\sigma_g^2 2\sigma_g^2 1\delta_g^2$ configuration. All of the electrons are bonding, and if that pattern holds for the ground state of the trimer and tetramer, either the rules of Ozin and McIntosh or a calculation of the formal bond order per bond will give the same result, as observed experimentally.

V. Acknowledgements

This work was supported by the National Science Foundation under Cooperative Agreement No. RII-9353488 and

Grant No. CHE-0091362 and by the City University of New York PSC-BHE Faculty Research Award Program.

M/C ^{a,b} =45	Atom ^c	M/C ^b =90	Dimer ^c	M/C ^b =135	Assignment ^d
		309 (M)			A
315 (S)	319	313 (M)			A
	326	327 (S)		323 (S)	T/A
		334 (S)	335		D
		350 (M)			T
387 (S)	388	385 (S)		384 (S)	A
394 (S)	395	393 (S)		393 (S)	A
399 (S)	400	399 (S)		399 (S)	A
408 (S)		405 (S)		406 (S)	A
412 (S)		411 (S)		414 (M)	A
417 (S)		417 (S)			A
436 (M)				437 (W)	A
444 (M)		443 (VS)		441 (W)	A
	450				A
		451 (VS)		451 (M)	T
459 (W)				459 (W)	A
		466 (M)	470		D
482 (W)					A
487 (VW)				485 (VW)	A
		497 (W)			T/D
		538 (VW)			T
		563 (VW)			T
594 (VW)	596	593 (M)		590 (VW)	A
		614 (S)		610 (W)	T/D
		624 (S)		620 (VW)	T/D
		679 (VW)	662		D

VS, very strong; S, strong; M, middle; W, weak; VW, very weak.

Table 5.1.1 The SDS absorption peaks position and relative intensity of various scandium clusters deposits.

a: Scandium cluster mass-charge ratio;

b: This work;

c: From reference (100)

d: A = atom, D = dimer and T = tetramer.;

Cluster	Scandium	$k^{(n)}/k^{(2)}$	Tantalum	$k^{(n)}/k^{(2)}$
Dimer	0.756		4.80	
Trimer	0.539	0.71	2.25	0.47
Tetramer	0.318	0.42	1.89	0.39

Table 5.2.2: Force constants (mdyne/Å) for small clusters of Sc and Ta.

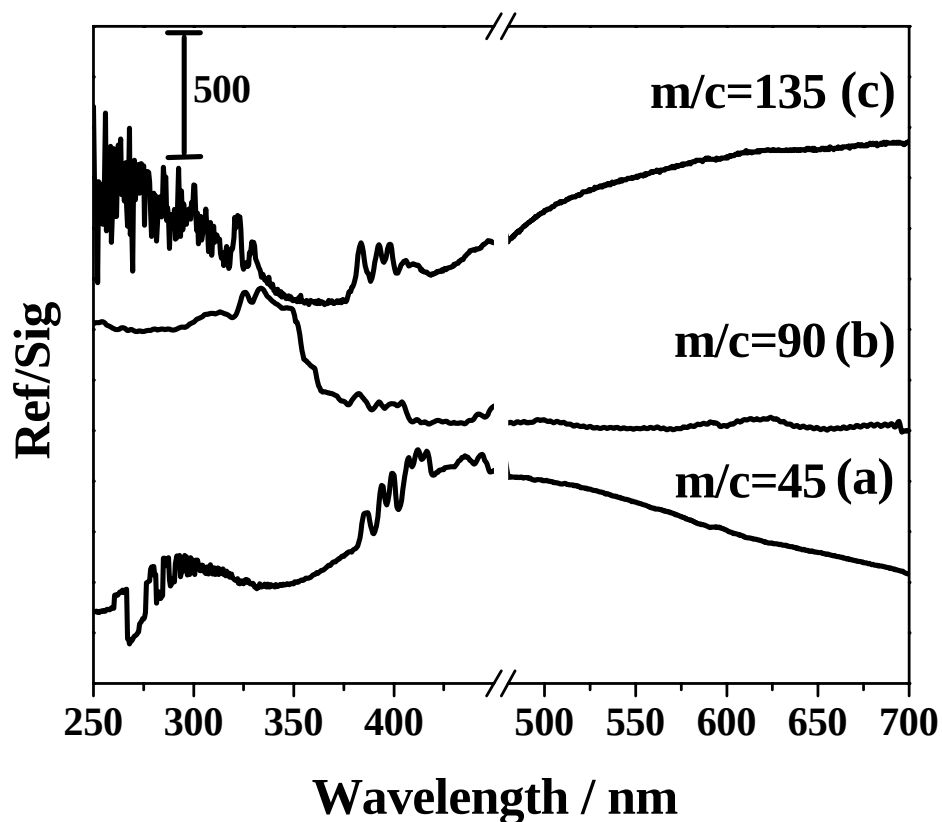


Figure 5.1.1. Scattering depletion spectra (SDS) of scandium clusters deposited at mass/charge ratios of a) 45, b) 90 and c) 135 respectively. Arrows indicate the positions of new bands at 350, 451, 538, and 563 nm attributed to the tetramer. Note also the large amount of atomic intensity in the M/C = 135 deposit.

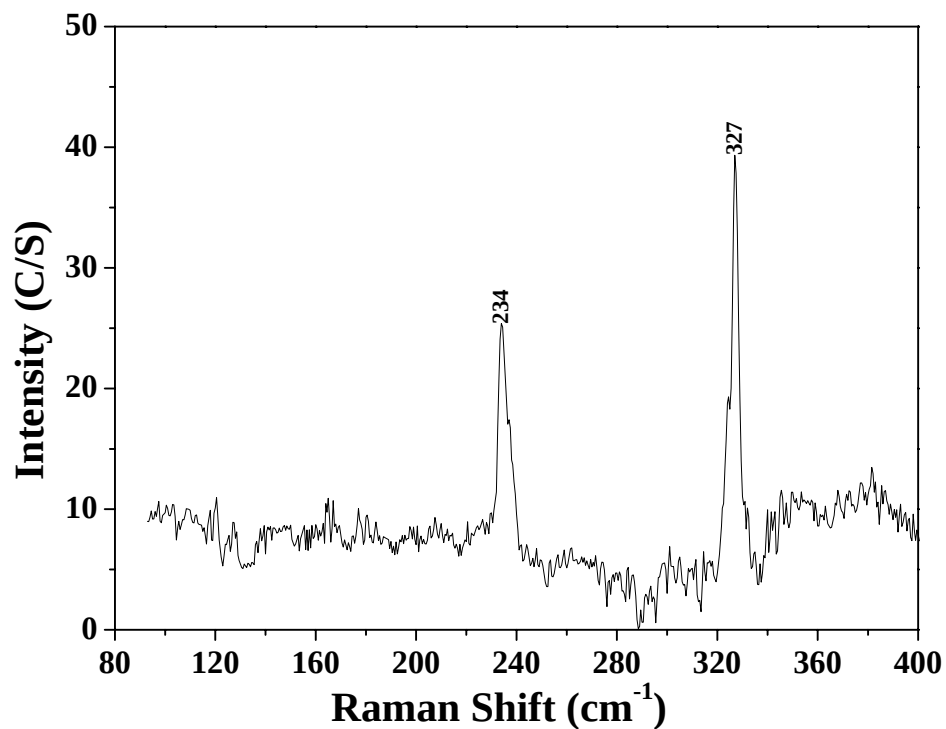


Figure 5.2.2. Resonance Raman spectrum of scandium deposited at a mass-to-charge ratio of 90 in an argon matrix at 16K. The excitation wavelength is the 676.5 nm line of the krypton ion laser at a power of 10 mW. The line at 327 cm^{-1} is due to the CaF_2 substrate and is used as a calibration mark.

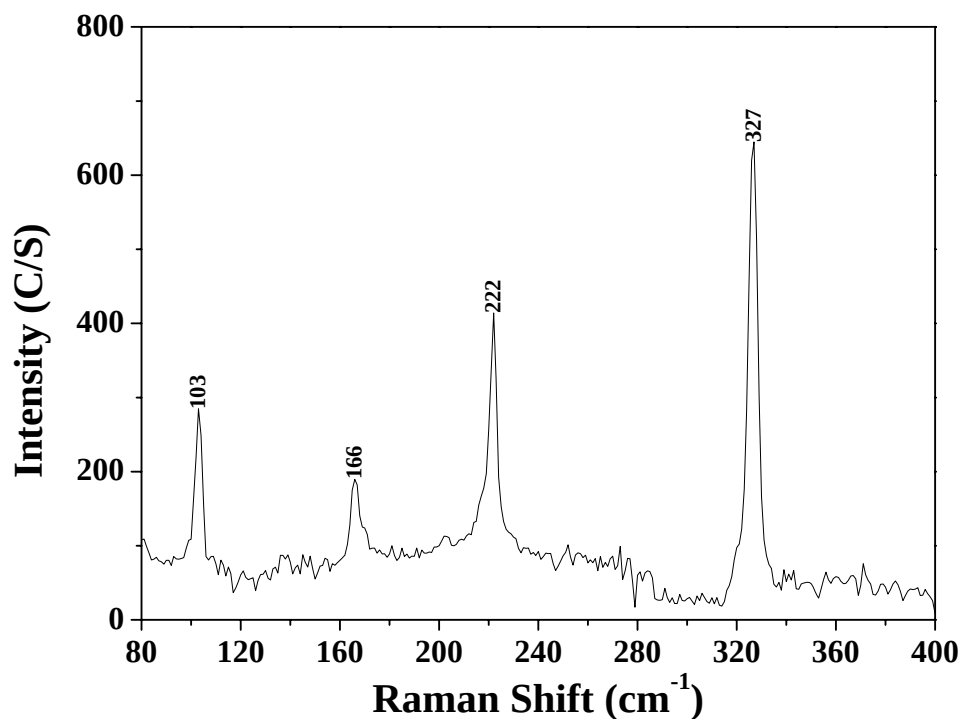


Figure5.1.3. Resonance Raman spectrum of scandium deposited at a mass-to-charge ratio of 90 in an argon matrix at 16K. The excitation wavelength is the 488 nm line of the argon ion laser at a power of 80 mW. The line at 327 cm⁻¹ is due to the CaF₂ substrate and is used as a calibration mark.

Chapter VI Heteroclear Transition Metal Dimers

6.1 Spectroscopy of mass-selected VCo and VFe in argon matrices

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Abstract

We examine the resonance Raman spectroscopy of the heteronuclear dimers VCo and VFe, using a mass-selected cluster source. Cluster cations are produced in a sputtering source and mass filtered with a Wien filter, then neutralized and deposited in an Ar matrix at low temperatures. For VCo we obtain the resonance Raman spectra in Ar matrix excited with 457.9, 488.0, 496.5, 501.7, and 514.5 nm laser lines. We observe Raman shifts of 459 and 916 cm^{-1} , and we assign these lines to the fundamental and first overtone of the ground state. The resulting force constant is $k_e = 3.42 \text{ mdyne/\AA}$. Resonance Raman spectra of VFe, obtained at the same five excitation wavelengths, display Raman shifts at 423 and 836 cm^{-1} , and we assign

these to the fundamental and first overtone of the ground state vibration. The resulting force constant is $k_e = 2.94$ mdyne/Å. We compare these observed force constants and configurations with those of other V-X dimers ($X = \text{Ti-Ni}$), as well as related isoelectronic species. The value for VFe, with thirteen valence electrons, is considerably lower than its neighbors. This molecule most likely has a $^2\Sigma^+$ ground state, stemming from a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2(4s\sigma^*)^1$ configuration. The higher force constant for VCo with 14 valence electrons indicates either a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta)^2(4s\sigma)^2$ configuration with a Σ^3 state, or a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta)^1(4s\sigma)^2(4s\sigma^*)^1$ configuration with a $^3\Delta$ state.

INTRODUCTION

The electronic, physical, and chemical properties of metal clusters are crucial to understanding the chemical bonding and electronic structure of metal atoms in the bulk, on metal surfaces, and in binuclear organometallic compounds. As a result, many studies have been undertaken to investigate the chemical bonding and structure of metal dimers and small clusters^{124,125,126}. In the past decade, this laboratory and others have accumulated and interpreted a considerable amount of spectroscopic data for the homonuclear transition metal clusters, such as dimers, trimers, and tetramers. Such studies have provided

considerable insight as to the relative contributions of s and d electrons to metallic bonding in small, homonuclear metal clusters. It is worthwhile to investigate whether similar studies of the properties of heteronuclear clusters will be of comparable value. Should we expect, for example, added stability to result from bimetallic compounds as is found in bulk metallic alloys? Consideration of valence-bond theory led Engel¹²⁷ and Brewer¹²⁸ to a model of intermetallic bonding in which augmented stability could be obtained through partial charge transfer of d-electron density for certain bimetallic combinations.

In this paper, we turn our attention to the spectroscopy of the heteronuclear dimer molecules vanadium-cobalt (VCo) and vanadium-iron (VFe)¹²⁹. Our intention is to examine the extent to which intermetallic clusters affect the strength of chemical bonding through comparison of the magnitude of force constants observed for various related clusters.

The homonuclear dimer molecules of cobalt, iron, and vanadium have been thoroughly studied. Several calculations^{130, 131, 132} have identified the ground state of cobalt dimer (Co_2) as either $^5\Delta_g$ or $^5\Sigma_g^+$. In a mass-selected resonance Raman study in matrix isolation, Dong et al.¹³³ obtained values of $\omega_e = 296.8(54) \text{ cm}^{-1}$ and $\omega_e x_e = 2.2(8) \text{ cm}^{-1}$. These

results indicate a rather small force constant (1.53 mdyne/Å), which implies little or no d-electron contribution to bonding, and an experimental bond order of 1.15. (The experimental bond order is the ratio of the measured force constant to that of a single bond. We take this to be that of the dimer formed from the noble metal of the same row of the periodic table, in this case, Cu₂ for which $k_e = 1.33$ mdyne/Å). The ground state configuration is most likely $3d^{15}4s\sigma_g^2\sigma_u^1$, with a formal bond order of 1/2. Using effusion and mass spectrometric techniques, Kant and Strauss¹³⁴ found $D_e = 1.72 \pm 0.29$ eV, while using collision induced dissociation (CID) a value of ≤ 1.32 eV was obtained¹³⁵.

In a density functional calculation, Harris and Jones¹³⁶ suggest that the ground state of iron dimer (Fe₂) is $^7\Delta_u$ from a configuration $(3d\sigma_g)^{1.57}(3d\pi_u)^{3.06}(3d\delta_g)^{2.53}(3d\sigma_u)^{2.47}(3d\pi_g)^{2.89}(3d\sigma_u)^{1.49}(4s\sigma_g)^{2.00}$ with a formal bond order of 1. These results are similar to a MCSCF calculation by Noro et al.¹³⁷ Using EXAFS on matrix isolated Fe₂, Purdam et al.¹³⁸ determined the equilibrium internuclear distance to be $r_e = 2.02$ Å. In matrix isolation Raman studies, Moskovits¹³⁹ found $\omega_e = 299.6$ cm⁻¹ with $\omega_e x_e = 1.4$ cm⁻¹. The experimental bond order from the force constant (1.48 mdyne/Å) is 1.11.

Considerable variation has been observed in dissociation energies. Lin and Kant¹⁴⁰ used third law methods to determine a value of 0.78(17) eV. In a later analysis Haslett, Moskovits, and Weitzman¹⁴¹ found values in the range of 1.25-1.75 eV. Lian, Su, and Armentrout¹⁴² found a value of 1.14 eV using collision induced dissociation, and it seems this is the more reliable. Leopold, *et al.*¹⁴³ indicate that dissociation is to $4s^23d^6 + 4s^13d^7$ atomic configurations. This is confirmed by a CASSCF/MRCI calculation by Hübner and Sauer¹⁴⁴, who find a $^9\Sigma_g^-$ ground state.

Several measurements of the ground state vibrational frequency of divanadium (V_2) have been made. In the gas phase Langridge-Smith *et al.*¹⁴⁵ obtained a value of $G_{1/2} = 529.5(10) \text{ cm}^{-1}$ while Cosse *et al.*¹⁴⁶ obtained $\omega_e = 537.5 \text{ cm}^{-1}$ and $\omega_e x_e = 4.2 \text{ cm}^{-1}$ in matrix isolation Raman spectra. With mass-selection techniques, the resonance Raman spectrum¹⁴⁷ yielded the values of $\omega_e = 536.9(11) \text{ cm}^{-1}$ and $\omega_e x_e = 4.1(1) \text{ cm}^{-1}$. Density functional calculations¹⁴⁸ confirm the result of Langridge-Smith *et al.*, that the ground state is most likely a $^3\Sigma_g^-$, deriving from a $4s\sigma_g^2 3d\sigma_g^2 3d\pi_u 3d\delta_g^2$ configuration, with a formal bond order of 5. The experimental bond order, however, at 3.25 is somewhat smaller. Still this represents the largest bond order of

all the first row homonuclear transition metal dimers. Spain, Behm and Morse¹⁴⁹ obtained $r_e = 1.77 \text{ \AA}$ for the equilibrium internuclear distance and a dissociation energy of 2.75 eV, while Spain and Morse¹⁵⁰ indicate dissociation to two $3d^34s^2$ atoms. The s-d promotion energy is only 0.26 eV so that the resulting diabatic dissociation energy $D_0^d = 3.27 \text{ eV}$.

In the next section we briefly describe our mass-selected cluster apparatus, and following that we present the absorption and resonance Raman spectra of VCo and VFe. In the last section we discuss the implications of our results for intermetallic bond strengths in these and related compounds.

Experiment

The absorption and resonance Raman spectrum of mass-selected VFe and VCo clusters were acquired using the CCNY metal cluster deposition source. The design of this apparatus has been discussed in detail in other publications^{151, 152} but will be described briefly here. An argon ion beam of 10 mA (at 25 keV) sputters a water-cooled alloy (VFe or VCo) metal target. Metal targets about 2.0 cm in diameter and 0.3 cm thick were prepared by heating a mixture of the pure elements, the molar ratio of iron or

cobalt to vanadium is chosen to be 2:1, because the dissociation energy of V_2 is considerably larger than that of Fe_2 and Co_2 . It was felt that this would compensate for the tendency of V to form strongly bound dimers, possibly precluding production of the mixed dimers. In fact, in all our spectra we see evidence of V_2 , but relatively little of Co_2 or Fe_2 . Pure elements were purchased in the powder form from Alfa Aesar at 99.9% (REO).

In the beam, the metal target was maintained at about 300V. A series of einzel lenses collects the sputtered metal cluster ions from the metal sputtering region, and a Wien filter mass selects the focussed cluster ions. Any neutral atoms or clusters produced during the sputtering process that pass through the mass selector are removed by a 10^0 bend in the path following the Wien filter. A second set of einzel lenses focuses the mass-selected cations into the deposition region, which are then codeposited with argon gas and electrons, for neutralization, onto a CaF_2 substrate. A cryostat cools the substrate to ~ 16 K. To prevent degradation upon impact with the CaF_2 substrate, focussed ions are slowed to ~ 10 eV to ensure a soft landing on the substrate. The metal cluster/Ar matrix had a growth rate of ~ 6 /h. The argon: cluster ratio was $\sim 10^4:1$. Several deposits were carried out for each alloy, during

which the current for a particular mass-to-charge (M/C in amu/electron charge) ratio was optimized. For $M/C = 51$ the optimized current was 190 and 170 nA for Fe^+/V^+ and Co^+/V^+ , for $M/C = 108$, the current was 70 and 60 nA for $VFe^+/Fe_2^+/V_2^+$ and $VCo^+/Co_2^+/V_2^+$, respectively. Since the resolving power of our Wien filter is relatively low (around 6-7) in order to attain high throughput, we cannot adequately separate the homonuclear dimers V_2 , Co_2 , or Fe_2 from the mixed dimer of interest (VCo or VFe). However, the spectra of the former are well known, and in any case, except for V_2 , relatively weak, so that we have no trouble obtaining unambiguous Raman spectra desired. We may then use the Raman excitation profile obtained to confirm at least partially, the assignment of the absorption spectrum.

Resonance Raman spectroscopy was carried out *in situ* on the matrix sample. An absorption spectrum, in the form of a "scattering depletion spectrum" (SDS) was also obtained. The "SDS" absorption is a ratio between scattered light from the edge and center, where most of the sample is deposited, to that of the CaF_2 substrate. The scattered light is collected at a 90° angle from the incident radiant.

The visible lines of a Spectra Physics 2045 argon ion laser, as well as laser lines from a Coherent model CR599

dye laser, employing the dyes R6G, R110, and DCM were used to observe resonance Raman features of the mass-selected species. The laser power incident on the sample was typically about 50 mW. Plasma lines were removed by predispersing the laser beam with a diffraction grating. The 327 cm^{-1} line of the CaF_2 substrate was used to calibrate all Raman shifts. The Raman detection system consists of a Spex 1877E 0.6m Triplemate Spectrometer coupled with a liquid nitrogen cooled CCD system (Spectrum One and CCD30). The detector resolution is about 2 cm^{-1} . The computer software DM3000R acquired, interpreted, and displayed spectral information from the CCD.

The extent of dimer fragmentation on deposition may be estimated by comparing the intensities of atomic excitation features in a dimer deposition with those obtained from depositions of the atom under similar conditions. By this measure we estimate the fragmentation of VFe and VCo to be 20 % and 25 %, respectively.

RESULTS

VFe dimer

The SDS spectra of VFe, Fe_2 , and V_2 are shown in Figure 6.1.1. Since there is no evidence to support the existence of much iron dimer from the Raman spectra, we conclude that the SDS spectra of the VFe deposit represents contribution

from the VFe dimer, vanadium dimer, and to a lesser extent iron and vanadium atom produced by fragmentation of dimers on deposition. A relatively intense band appears in the region of 250-400 nm, which can be assigned to the VFe dimer. Comparing with the SDS spectrum of vanadium dimer (Figure 6.1.1b), the spectrum in the region of 400-700 nm of Figure 6.1.1(a) clearly differs in intensity and fine structure, and most likely comes from both the vanadium dimer and VFe. The Raman excitation profile of the 423 cm^{-1} line in the 460-515 nm region shows that much of the intensity of the sharp feature of the SDS in that region is due to VFe.

We have observed the resonance Raman spectrum of VFe at five excitation wavelengths (457.9, 488.0, 496.5, 501.7, and 514.5 nm). The spectrum for excitation at 488 nm is shown in Figure 6.2.2. Two spectral lines are clearly observed. The average of all the observed lines gives Raman shifts at $423(1)$ and $836(1)\text{ cm}^{-1}$, and we assign these to the fundamental and first overtone of the ground state vibration. From these we obtain $\omega_e = 433.0\text{ cm}^{-1}$ and $\omega_e x_e = 5.0\text{ cm}^{-1}$. The peaks at 327 and 527 cm^{-1} are due to the CaF_2 substrate and vanadium dimer¹⁴⁷ respectively. Note the value for the V_2 frequency differs slightly from that reported

previously due to an improved value of the CaF_2 line used for calibration (previously 330 cm^{-1}).

The detailed Raman spectrum of VFe dimer (Figure 6.1.3) shows a weak shoulder at 428 cm^{-1} , which may arise from: isotopic structure, site effects, or possibly some excited state. No isotopes of either Fe or V are sufficiently abundant to account for this peak. The Raman spectrum of VFe dimer after annealing the sample to 70 K shows no relative intensity change of two peaks, 423 and 428 cm^{-1} , and thus if the peak is caused by site effects, both sites are sufficiently stable to persist after annealing. This is the most likely explanation, although we cannot rule out a low-lying state. This latter, however, is quite unlikely.

VCo dimer

The SDS spectra of VCo, V_2 , and Co_2 are shown in Figure 6.1.4. There is no evidence to support the existence of cobalt dimer from the Raman spectra, we conclude that the SDS spectra of VCo (a) is composed of contributions from the VCo dimer, vanadium dimer, and to a lesser extent, cobalt and vanadium atoms from fragmentation. An intense, broad band appears in the 250-500 nm region, centered at 370 nm. It is clearly the sum of the absorbance of vanadium dimer and the VCo dimer. The latter can be seen as a non-

structured broad absorbance peak shown (curve d) in Figure 6.1.4. The Raman excitation profile (Figure 6.1.4e) of the 459 cm^{-1} line provides clear evidence that most of the intensity of this band is due to VCo.

We have observed resonance Raman spectra of VCo dimer in Ar matrix excited with 457.9, 488.0, 496.5, 501.7, and 514.5 nm laser lines. The spectrum excited at 457.9 nm is shown in Figure 6.1.5. The average of these measurements gives Raman shifts of $459(1)$ and 916 cm^{-1} , and we assign these lines to the fundamental and first overtone of the ground state vibration of VCo. From these we obtain $\omega_e = 461.0\text{ cm}^{-1}$ and $\omega_e x_e = 1.0\text{ cm}^{-1}$.

DISCUSSION

We have shown that force constants can provide a valuable tool for examining the strengths of chemical bonds in homonuclear transition metal dimers, and by comparing periodic variation of these parameters, the extent of contribution of d-electrons to bonding can often be extracted. From the observed vibrational frequencies, we may calculate the force constants for each dimer. The results are $k_e = 2.94\text{ mdyne/\AA}$ for VFe and $3.42\text{ mdyne/\AA}$ for VCo. Here it is convenient to extend to heteronuclear dimers, the method of obtaining an experimental value of

the bond order using the suggestion of Johnston¹⁵³, which utilizes Pauling's rule¹⁵⁴. This involves taking the ratio of observed force constant to that of a dimer with a single bond, in this case Cu_2 . The experimental bond orders obtained by this method are 2.21 for VFe and 2.57 for VCo.

First it is worthwhile examining the extent to which the force constants deviate significantly from what might be expected from simple considerations of heteronuclear bonding. For alloys of the coinage metals, we expect that due to the filled d-orbitals, only s electrons can contribute to the bonding, and that therefore no Engel-Brewer effects will be seen. For coinage metals, observed force constants of mixed dimers (such as CuAg ^{155, 156}; $k_e = 1.24$ mdyne/Å) are found to be almost exactly equal to the average of the component homonuclear dimers (e.g. Cu_2 ; $k_e = 1.33$ mdyne/Å and Ag_2 ; $k_e = 1.18$ mdyne/Å). With that in mind, we compare the force constants of VCo and VFe with those of each corresponding homonuclear dimer in table 6.1.1.

Note that both Fe_2 and Co_2 have almost the same force constant and that V_2 has a much larger force constant than either Fe_2 or Co_2 . For VFe, the force constant is close to the average of Fe_2 and V_2 (2.91) while in VCo the force constant is somewhat larger than the average of Co_2 and V_2

(2.93). The implication is that Engel-Brewer d-electron contributions to intermetallic bonding are of some importance in VCo but not so in VFe.

VFe has thirteen valence electrons and is isoelectronic with several dimers, which have been studied, namely ScNi, TiCo¹⁵⁷. These have been shown by ESR to have a $^2\Sigma^+$ ground state, stemming from a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2(4s\sigma^*)^1$ configuration, and this is a reasonable assignment for VFe as well. This configuration has a formal bond order of 5.5, and since the promotion energy of Fe ($4s \rightarrow 3d$) is rather large (0.87eV), this most likely correlates with $V(3d^4 4s^1) + Fe(3d^6 4s^2)$ in dissociation. Furthermore, the $4s\sigma^*$ orbital is quite antibonding in character, and this is consistent with the relatively low force constant observed for VFe. In table 6.1.2, we compare the force constants, as determined from the harmonic frequencies, and configurations of several vanadium dimers VX with X = Ti - Ni.

In determining the ground configuration for VCo with 14 valence electrons it would seem reasonable on the basis of nearby configurations with less electrons to assign VCo to the $[(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2(4s\sigma^*)^2]$ implying a $^1\Sigma^+$ state. This, however, is unlikely since the presence of two

electrons in the $4s\sigma^*$ orbital should result in even further lowering of the force constant compared to VFe, which is not the case. We turn instead to an argument suggested by Morse¹⁵⁸. The $(4s \rightarrow 3d)$ promotion energies for V and Co are not too high (0.26 and 0.43 eV respectively), so that the ground state VCo could easily correlate to $V(3d^4 4s^1)$ and either $Co(3d^7 4s^2)$ or $Co(3d^8 4s^1)$. We might then expect that instead of two electrons in the $4s^*$ orbital that the more likely configuration would be $(3d\sigma)^2 (3d\pi)^4 (3d\delta)^4 (3d\delta^*)^2 (4s\sigma)^2$. Here two electrons are placed in the relatively non-bonding $3d\delta^*$ orbital, which is considerably less antibonding than the $4s\sigma^*$ orbital. In this case we would then expect the ground state to be $^3\Delta$, with dissociation to $V(3d^4 4s^1) + Co(3d^8 4s^1)$. Another possibility is a $(3d\sigma)^2 (3d\pi)^4 (3d\delta)^4 (3d\delta)^1 (4s\sigma)^2 (4s\sigma^*)^1$ configuration with a Δ^3 state and dissociation to $V(3d^4 4s^1) + Co(3d^7 4s^2)$. This is less likely, since we would expect somewhat weaker bonding due to the $4s\sigma^*$ electron, but it has a reasonable dissociation pathway, and could be the correct ground state configuration if there were still larger Engel-Brewer contributions to the bonding.

A few other features of table 6.1.2 are worth examining. First note that the dimers with an odd number of valence

electrons have lower force constants than either of their even-numbered neighbors. Also note the rather large value of force constant for VMn (5.1 mdyne/Å). In fact, this is the largest observed value so far for a dimer of the first transition metal series. At first it might seem surprising, given the extremely small value observed in the (essentially van der Waals) Mn₂ molecule. However, VMn is isoelectronic with Cr₂, which has a force constant of 3.54 mdyne/Å¹⁵⁹ and a ¹Σ⁺ ground state. Furthermore, the second row transition metal dimer Mo₂ (also ¹Σ⁺), which has the same number of valence electrons as Cr₂, has the highest force constant (6.33 mdyne/Å)¹⁶⁰ of all the homonuclear dimers. The fact that the value of the force constant in VMn is even larger than that of Cr₂ indicates that Engel-Brewer bonding is clearly an important contribution for this molecule, despite the proximity of V and Mn in the periodic table. VMn has the largest force constant in table 6.1.2 since at the point where the number of valence electrons is 12; this is enough to just fill all the bonding orbitals. The formal bond order is 6, and the experimental bond order is 3.8. As more electrons are added, as in VFe and VCo, they go into anti-bonding orbitals, considerably weakening the bonds, leading to the much smaller force constants observed.

Conclusions

We have obtained absorption (SDS) and resonance Raman spectra for the two species VCo and VFe using mass-selection. For VCo we obtain Raman shifts of 459 and 916 cm^{-1} , and we assign these lines to the fundamental and first overtone of the ground state. The resulting force constant is $k_e = 3.42 \text{ mdyne/\AA}$. Resonance Raman spectra of VFe are obtained at 423 and 836 cm^{-1} , and we assign these to the fundamental and first overtone of the ground state vibration. The resulting force constant is $k_e = 2.94 \text{ mdyne/\AA}$. We then compare these observed force constants and configurations with those of other V-X dimers ($X = \text{Ti-Ni}$), as well as related isoelectronic species. The value for VFe is considerably lower than its neighbors, and most likely has a $^2\Sigma^+$ ground state, stemming from a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2(4s\sigma^*)^1$ configuration. The higher force constant for VCo with 14 valence electrons indicates either a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta^*)^2(4s\sigma)^2$ configuration with a $^3\Sigma$ state, or a $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta)^1(4s\sigma)^2(4s\sigma^*)^1$ Configuration with a $^3\Delta$ state.

Acknowledgements

This work was supported by the National Science Foundation under Cooperative Agreement No. RII-9353488 and

Grant No. CHE-0091362 and by the City University of New York PSC-BHE Faculty Research Award Program. We are also indebted to Professors Michael Morse and Doreen Leopold for helpful comments on the manuscript.

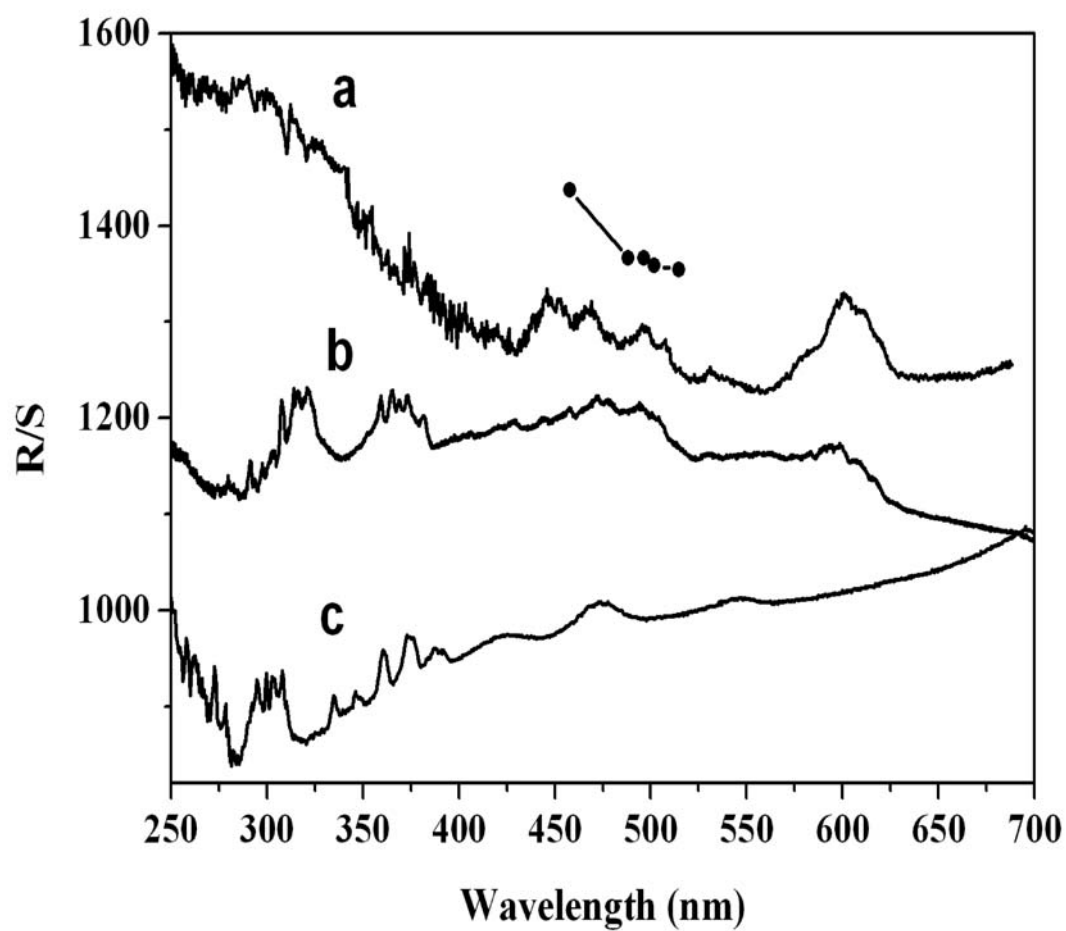


FIGURE 6.1.1 Scattering Depletion Spectra (SDS) of dimer of VFe(a), V₂ (b), and Fe₂ (c). Dotted curve is the Raman excitation profile for the 423 cm⁻¹ line.

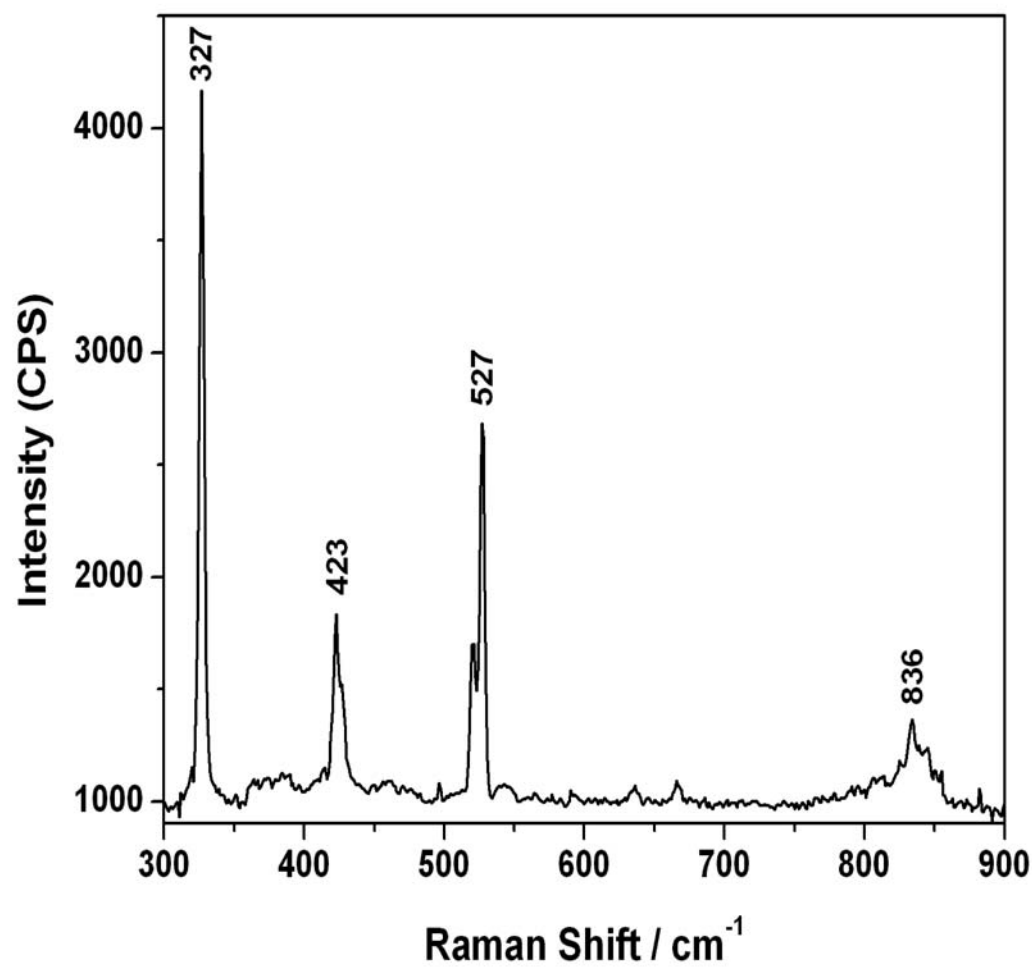


FIGURE 6.1.2 The resonance Raman spectrum of VFe dimer in Ar matrix excited at 488 nm.

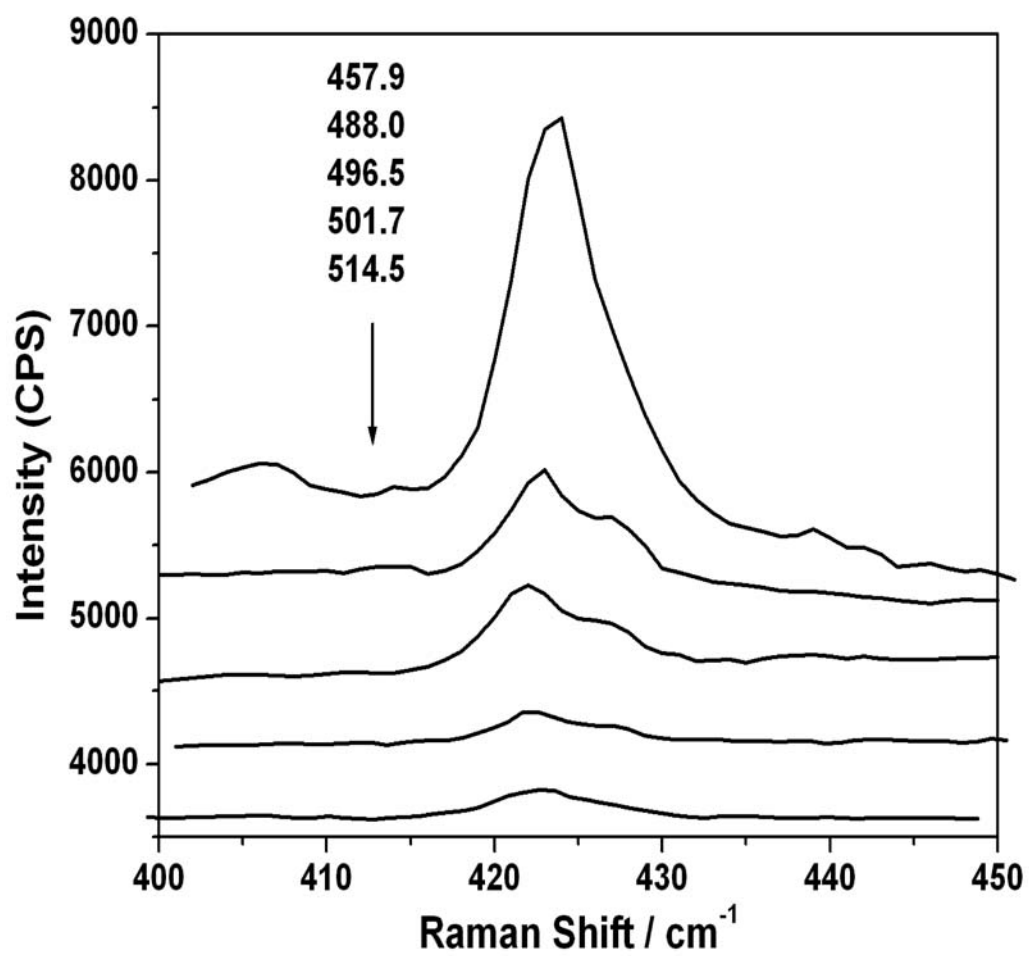


FIGURE 6.1.3. Detail of the resonance Raman spectrum of VFe dimer for the 423 cm^{-1} line.

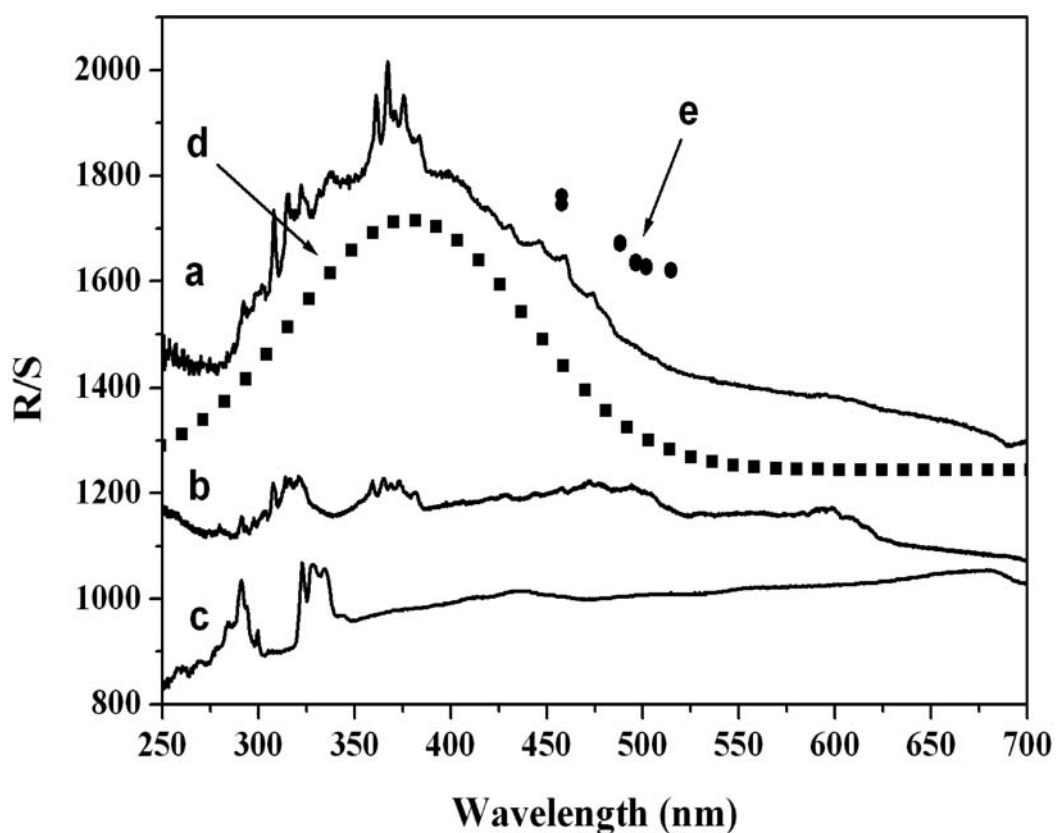


FIGURE 6.1.4. Scattering Depletion Spectra (SDS) of dimer of VCo (a), and pure elemental V_2 (b), Co_2 (c). The broad peak centered at 370 nm is attributed to VCo, and is shown in curve (d). Dotted curve (e) is the Raman excitation profile for the 459 cm^{-1} line.

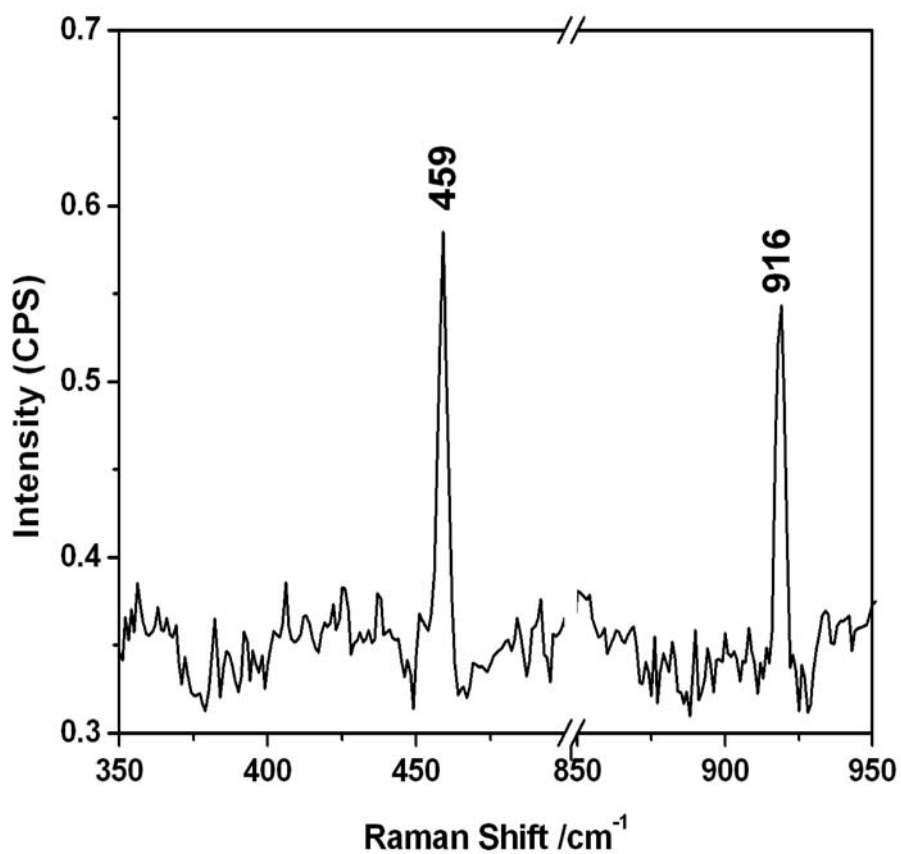


FIGURE 6.1.5. The resonance Raman spectrum of VCo dimer in Ar matrix excited at 457.9 nm.

Fe_2	VFe	V_2
1.48	2.94 (2.91)	4.33
Co_2	VCo	V_2
1.53	3.42 (2.93)	4.33

Table 6.1.1. Comparison of experimental force constants (in mdyne/Å) for VFe and VCo with their homonuclear component counterparts. Values in parentheses are the average of the component homonuclear force constants (first and last columns).

#	X (V-X)	k_e	Configuration	Term	Ref
9	Ti		$(3d\sigma)^1(3d\pi)^4(3d\delta)^2(4s\sigma)^2$	$^4\Sigma$	161
10	V	4.33	$(3d\sigma)^2(3d\pi)^4(3d\delta)^2(4s\sigma)^2$	$^3\Sigma_g$ -	147
11	Cr	4.1	$(3d\sigma)^2(3d\pi)^4(3d\delta)^3(4s\sigma)^2$	$^2\Delta$	¹⁶² , ¹⁶³
12	Mn	5.1	$(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2$	$^1\Sigma$	¹⁶⁴
13	Fe	2.94	$(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2(4s\sigma^*)^1$	$^2\Sigma^+$	(a)
14	Co	3.42	$(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta^*)^2(4s\sigma)^2$ $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta^*)^1(4s\sigma)^2(4s\sigma^*)^1$	$^3\Sigma^+$ $^3\Delta$	(a)
15	Ni		$(3d\sigma)^2(3d\pi)^4(3d\delta)^4(4s\sigma)^2(4s\sigma^*)^1(3d\delta^*)^2$	$^4\Sigma$	161

(a) This work

Table 6.1.2. Force constants (mdyne/Å), configurations, ground state term symbols of various V-X dimers with X = Ti - Ni. The first column indicates the number of valence electrons.

6.2 Luminescence of Mass-Selected CuAg in Argon Matrices

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Abstract

We report on an observation of the luminescence spectrum of mass-selected CuAg in an argon matrix. Although no Raman spectrum is obtained, an emission progression up to $v''=5$ is observed, corresponding to the $A0^+-X^1\Sigma^+$ transition observed in the gas phase. The origin of the transition is determined to be $20,262(10) \text{ cm}^{-1}$. We obtain a value of $\omega_e = 226.1(4.9) \text{ cm}^{-1}$, which is consistent with the gas-phase observations.

INTRODUCTION

In this paper, we examine the spectroscopy of the heteronuclear dimer molecule copper-silver. Much of our previous work concentrated on homonuclear clusters¹⁶⁵. The heteronuclear molecule CuAg is one of the simplest transition metal dimers, since it is formed from atoms with filled d subshells. Several spectroscopic experiments on gas phase CuAg^{166, 167} have been carried out. Bishea, Marak,

and Morse used resonant two-photon ionization spectra to analyze jet-cooled diatomic CuAg and obtained $\Delta G''_{1/2} = 229.17 \text{ cm}^{-1}$. This was based on observation of only one hot band in the ground state, although transitions to numerous excited states were both vibrationally and rotationally resolved. They assigned the ground state to $X^1\Sigma^+$, corresponding to a molecular configuration of $3d_{\text{Cu}}^{10} 4d_{\text{Ag}}^{10} \sigma^2$, with an observed bond length of $r_e'' = 2.3735 \text{ \AA}$. From the emission spectrum of CuAg in the visible region, Joshi and Majumdar found a ground-state vibrational frequency of $\omega_e = 231.8 \text{ cm}^{-1}$ and $\omega_e x_e = 0.80 \text{ cm}^{-1}$.

In this paper we report on an observation of the luminescence spectrum of mass-selected CuAg in an argon matrix. Although no Raman spectrum is obtained, a fluorescence progression up to $v'' = 5$ is observed, corresponding to the $A0^+-X^1\Sigma^+$ transition observed in the gas phase. We obtain values of $\omega_e = 226.1 (4.9) \text{ cm}^{-1}$, which is consistent with the gas-phase observations.

Experiment

The absorption and resonance Raman spectrum of mass-selected CuAg clusters were acquired using the CCNY metal cluster deposition source. The design of this apparatus has been discussed in detail in other publications^{168,169} but will

be described briefly here. An argon ion beam of 10 mA (at 25 keV) sputters a water-cooled CuAg target (Goodfellow, 72:28 % in molar ratio Ag:Cu. The melting point is of the sample 779 °C).

In the beam, the metal target was maintained at about 300V. A series of einzel lenses collects the sputtered metal cluster ions from the metal sputtering region, and a Wien filter mass selects the focussed cluster ions. Any neutral atoms or clusters produced during the sputtering process that pass through the mass selector are removed by a 10^0 bend in the path following the Wien filter. A second set of einzel lenses focuses the mass-selected cations into the deposition region, which are then codeposited with argon gas and electrons, for neutralization, onto a CaF_2 substrate. A cryostat cools the substrate to ~ 16 K. To prevent degradation upon impact with the CaF_2 substrate, focussed ions are slowed to ~ 10 eV to ensure a soft landing on the substrate. The metal cluster/Ar matrix had a growth rate of ~ 6 $\mu\text{m/h}$. The argon: cluster ratio was $\sim 10^4:1$. Several deposits were carried out, during which the current for a particular mass-to-charge (M/C in amu/electron charge) ratio was optimized. For M/C = 170 the optimized current was 35 nA for CuAg^+ . Since the resolving power of our Wien filter is relatively low (around 6-7) in order to attain

high throughput, we cannot adequately separate the homonuclear dimers Cu_2 (130 amu) and Ag_2 (215 amu) from the mixed dimer. However, the spectra of the former are well known, and in any case, the spectra of both Cu_2 and Ag_2 are relatively weak, so that we have had no trouble obtaining unambiguous emission spectra desired. We may then use the luminescence excitation profile obtained to confirm at least partially, the assignment of the absorption spectrum.

Optical emission spectroscopy was carried out *in situ* on the matrix sample. An absorption spectrum, in the form of a "scattering depletion spectrum" (SDS) was also obtained. The "SDS" absorption is a ratio between scattered light from the edge and center, where most of the sample is deposited, to that of the CaF_2 substrate. The scattered light is collected at a 90° angle from the incident radiant.

The visible lines of a Spectra Physics 2045 argon ion laser, as well as laser emission from a Coherent model CR599 dye laser, employing the dyes R6G and R110 were used to observe emission features of the mass-selected species. The laser power incident on the sample was typically about 50 mW. Plasma lines from the laser were removed by predispersing the laser beam with a diffraction grating. The 327 cm^{-1} line of the CaF_2 substrate was used to calibrate all spectral shifts. The detection system

consists of a Spex 1877E 0.6m Triplemate Spectrometer coupled with a liquid nitrogen cooled CCD system (Spectrum One and CCD30). The computer software DM3000R was utilized to acquire, interpret and display spectral information from the CCD.

Results and Discussion

The SDS (absorption) spectrum of CuAg is shown in Figure 6.2.1. Since there is no spectroscopic evidence to support the existence of much copper dimer, copper trimer and silver dimer from the Raman spectra, we conclude that the SDS spectra of the CuAg deposit represents contributions from the CuAg dimer, and to a lesser extent atomic copper and silver produced by fragmentation of dimers on deposition. The weak absorption between 300-330 nm are mainly due to the contribution of Cu and/or silver atoms^{170, 171}, and we infer that the fragmentation of CuAg is about 25 %. The extent of fragmentation on deposition may be estimated by comparing the intensities of atomic excitation features in a dimer deposition with those obtained from depositions of the atom under similar conditions. Figure 1 also shows, for comparison, a bar graph illustrating the results of Bishea et al. in the gas phase. We can see that despite the considerably lower resolution afforded in this experiment, there is general

agreement between the results of both experiments. The dotted curve in Figure 6.2.1 shows the luminescence excitation profile of the line at $19,813\text{ cm}^{-1}$, and this further confirms our assignment of the band to CuAg.

No Raman signal was observed because a much stronger luminescence is obtained when exciting with an argon ion laser. Figure 6.2.2 shows the laser excited fluorescence spectra of CuAg excited at 457.9nm. A vibrational progression with spacing approximately 224 cm^{-1} can clearly be discerned. The data represents averaged emission frequencies from four different excitation wavelengths (457.9, 465.8, 472.8, and 476.5 nm). The average emission frequencies are listed in the table 6.2.1. These frequencies were obtained by using a least-squares fitting routine, with a set of four or five Gaussian functions, and the uncertainties listed represent half-width of the function used in the optimized fit. The Franck-Condon envelope of intensity of the progression indicates that there is a considerable change in internuclear distance between the two electronic states involved in the transition. The location of the transition and the approximate vibrational spacing indicates that it most likely corresponds to the $A^0-X^1\Sigma^+$ transition observed in the

gas phase by Bishea et al. They found a spectroscopic origin at $20,807 \text{ cm}^{-1}$ for this transition, and were able to observe only the first hot band from the ground state, with $\Delta G''_{1/2} = 229.17(28) \text{ cm}^{-1}$. From a rotational analysis they found that the equilibrium internuclear distances in the two states were $r_e' = 2.522(2) \text{ \AA}$ and $r_e'' = 2.3732(8) \text{ \AA}$ respectively. Utilizing this information, and assuming that matrix effects are small, we may assign the observed emission spectrum. The most intense band in our spectrum (at $19,813 \text{ cm}^{-1}$) is expected to be that vibration for which the ground state potential curve lies directly below the potential minimum of the excited state. Thus we solve the equation $(\nu + \frac{1}{2}) \hbar \omega_e = \frac{1}{2} k_e (r_e' - r_e'')^2$ for the unknown ν . Using $\hbar \omega_e = 229 \text{ cm}^{-1}$ and $k_e = 1.24 \text{ mdyne/\AA}$ we obtain $\nu = 2.5$. Using a more sophisticated method, assuming a Morse potential function: $V(r - r_e'') = D_e (1 - e^{-\beta(r - r_e'')})^2$ for which $\beta = 1.2177 \times 10^7 \omega_e \sqrt{\frac{\mu}{D_e}}$, we obtain graphically $\nu = 2.0$, and we assign this to the most intense peak observed. The resulting assignments are shown in Figure 6.2.2, and listed in the table. The origin of the transition is determined to be $20,262 (10) \text{ cm}^{-1}$, in reasonable agreement with that of Bishea et al.. Note also that our observed value of the

spectral origin is shifted about 545 cm^{-1} to the red of the gas phase values. Since there are so few examples of transition metal diatomic emission spectra, it is difficult to know if this is typical. However, for Pt_2 we obtained a blue shift¹⁷² of 503 cm^{-1} .

This assignment enables us to fit the observed values of $\Delta G(v''+1/2)$ by standard techniques to obtain $\omega_e = 226.1$ (4.9) cm^{-1} . (We have excluded the $v'' = 5$ line from this fit, since it is so poorly determined, and only observed in one spectrum.) This value can be seen to be in excellent agreement with that observed in the gas phase, and this may be taken as further confirmation of our assignment. From the observed value of the vibrational frequency we may determine the force constant to be $1.20\text{ mdyne/\AA}$. This is also in good agreement with previous determinations. The observed force constants of the mixed dimer CuAg ($k_e = 1.20\text{ mdyne/\AA}$ in Ar matrix, $1.24\text{ mdyne/\AA}$ in gas phase) is found to lie between those of the component homonuclear dimers Cu_2 ; $k_e = 1.33\text{ mdyne/\AA}$ and Ag_2 ; $k_e = 1.18\text{ mdyne/\AA}$.

We can obtain further confirmation of our assignment by obtaining a Franck-Condon analysis of the observed spectra. We utilize a potential function with terms up to fourth power in the internuclear distance, and include the values of ω_e and $\omega_e x_e$ for the excited state obtained from

the gas phase results. We took the value of r_e to be an adjustable parameter, and obtained an optimum fit to the intensity envelope shown in figure 3 by the horizontal lines. The value of $r_e = 0.156 \text{ \AA}$ is quite close to the gas phase value of $0.149 \text{ \AA}$ obtained by Bishea et al.

In summary, we have obtained an emission spectrum of mass-selected CuAg in argon matrices. A progression was observed up to $v'' = 5$, corresponding to the $A0^+-X^1\Sigma^+$ transition observed in the gas phase. The origin of the transition is determined to be $20,262 (10) \text{ cm}^{-1}$. We obtain the value of $\omega_e = 226.1 (4.9) \text{ cm}^{-1}$, which is consistent with the gas-phase observations.

Acknowledgements

This work was supported by the National Science Foundation under Cooperative Agreement No. RII-9353488 and Grant No. CHE-0091362 and by the City University of New York PSC-BHE Faculty Research Award Program.

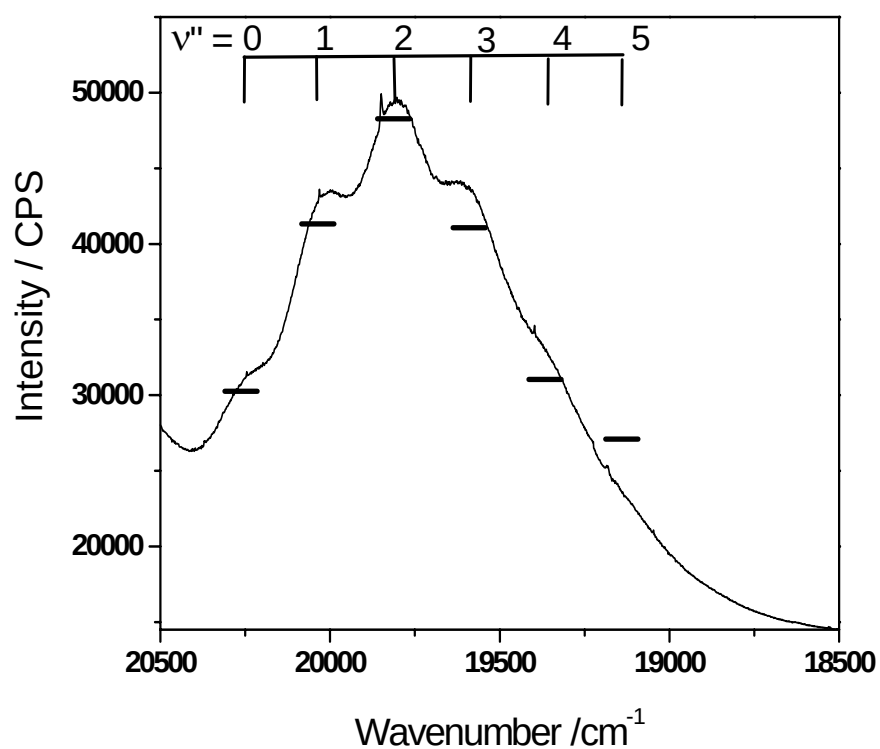


FIGURE 6.2.1. Scattering Depletion Spectrum (SDS) of CuAg. Also shown is the gas-phase data from Bishea, Marak and Morse (ref 166). Insert curve (squares) is the luminescence excitation profile for the 19,813 cm⁻¹ emission line.

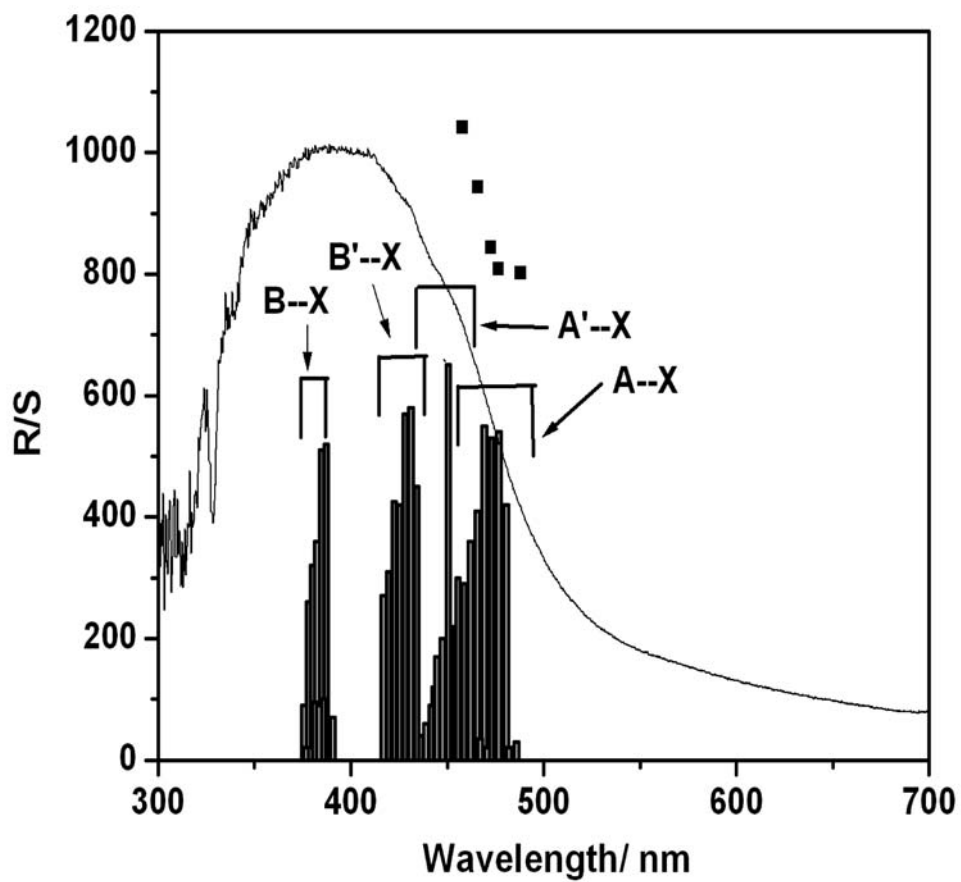


FIGURE 6.2.2. Laser excited fluorescence spectra of CuAg in an argon matrix excited with the 457.9 nm argon ion laser line. The horizontal lines represent the calculated Franck-Condon factors.

Assignment ($\nu' - \nu''$)	Frequency (cm^{-1})	$\Delta G(\nu''+1/2)$
0-0	20,262 (22)	226
0-1	20,036 (25)	223
0-2	19,813 (27)	223
0-3	19,590 (27)	223
0-4	19,367 (25)	227
0-5	19,140 (30)	

TABLE 6.2.1 Observed emission frequencies of CuAg.

6.3 Raman Spectroscopy of Mass-Selected CrFe

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Abstract

We report on the resonance Raman spectroscopy of mass-selected CrFe. The molecule is isolated by sputtering a CrFe metal target, followed by mass-separation through a Wien filter under ultra-high vacuum. Samples are deposited on a CaF₂ plate in an argon matrix at 14K. Raman spectra are obtained at several exciting wavelengths (476.5, 488.0, 496.5, 501.7, 514.5nm) and a clear progression up to $v'' = 6$ is obtained. Analysis results in values of $\omega_e = 166.6 \pm 0.8$ cm⁻¹ and $\omega_e x_e = 1.1 \pm 0.1$ cm⁻¹. This rather low frequency gives a force constant of 0.44 mdyne/Å, indicating considerably weaker bonding than observed in either Cr₂ or Fe₂. The results imply a $(4d_{Cr})^5(4d_{Fe})^6(4s)^2(4s^*)^1$ configuration with little or no participation of d-electrons in bonding, and are discussed in terms of the Engel-Brewer model for bonding in mixed metals, as well as bulk property calculations.

INTRODUCTION

Chromium (Cr) metal is often added to iron (Fe) in bulk metal in order to harden steel¹⁷³. It would be of interest to determine if the results of such effects are anticipated in small metal clusters of Cr and Fe. This was certainly the case in observations of homonuclear transition metal clusters, for which it was shown that the variation in dimer and trimer force constants¹⁷⁴ across the periodic table almost exactly parallels the variation in the bulk moduli. An important advance was made in understanding the bonding in bulk transition metal alloys by Engel¹⁷⁵ and Brewer^{176,177}. They showed that the relative stability of certain alloys could be predicted by consideration of the number of *s*- and/or *p*- electrons available for bonding from each contributing atomic species. The role of *d*- electrons, however, is more indirect, influencing the *s*- electrons through promotion energies as well as providing an additional number of unpaired electrons for bonding. In Fe ($3d^64s^2$) the $4s \rightarrow 3d$ promotion energy (to $3d^74s^1$) is large and this, combined with the relative ineffectiveness of *d*- electron bonding in the first transition metal row, results in a preferred body-centered cubic (bcc) crystal structure for pure Fe. Addition of Cr ($3d^54s^1$) to the bulk can go as high as 100%

without changing the crystal structure, since the number of s -electrons remains low. In order to form the more stable face-centered cubic (fcc) structure, a larger average number of s - and/or p -electrons are required, and the maximum concentration of Cr in Fe which maintains the fcc structure is only 13%. These considerations indicate that the role of Cr in strengthening Fe is limited to low concentrations. In fact, as we shall see below, detailed application of the Engel-Brewer theory to small transition metal clusters indicates that we might expect a weakening of the CrFe bond compared to the homonuclear dimers Cr_2 and Fe_2 . More recent work has been presented by Herper *et al.*¹⁷⁸ who carried out an *ab initio* calculation of Fe and Cr/Fe(001) bcc crystals. They found that the mixing energy of CrFe alloys is positive at all concentrations, which they interpreted to mean that no stable cubic compounds of Cr-Fe exist at $T = 0\text{K}$. Moroni and Jarlborg¹⁷⁹, in an LMTO study of CrFe alloys showed that the bulk modulus of non-magnetic CrFe is lower than that of either Cr or Fe, but that for the ferro-magnetic phase, the bulk modulus of CrFe is higher.

In this work we obtain the absorption, and resonance Raman spectrum of mass-selected CrFe molecules. Little previous work on this molecule exists. Nagarathna, Montano,

and Naik¹⁸⁰ determined the Mössbauer spectrum in matrix isolated CrFe and carried out SCF-X-SW calculations, in which they predict a $\sigma^2\sigma^2\pi^3\delta^2\delta^{*2}\pi^{*3}$.configuration with a Δ^7 ground state. The formal bond order suggested by this calculation is 2, which indicates a relatively large force constant should be obtained experimentally. Baumann, Van Zee, and Weltner¹⁸¹ reported the inability to observe an ESR signal, despite indications that the molecule should be stable under their conditions. This was taken as indirect support for the Δ^7 ground state, since this would be unlikely to be observed in an ESR experiment.

There are several studies of Cr₂ and Fe₂. Through pulsed YAG laser vaporization of chromium metal, Bondybey and English¹⁸² observed fluorescence excitation spectrum for Cr₂. From their observed high-resolution gas phase emission spectrum, they derived $\Delta G_{1/2} = 452.34 \text{ cm}^{-1}$ and a ground state vibrational frequency for the dimer to be $\omega_e \sim 470 \text{ cm}^{-1}$. They also determined $r_e = 1.679 \text{ \AA}$. The value for ω_e was confirmed in the negative ion photoelectron spectroscopy of Casey and Leopold.¹⁸³ Their extensive study resulted in the conclusion that the ground state of Cr₂ has a potential curve that deviates strongly from a Morse potential. In order to explain the observed vibrational spectrum, they

had to assume a "shelf" like addition to the curve and required terms up to order $(v + \frac{1}{2})^6$ to obtain an adequate fit. Their value of $\omega_e = 474.3 \text{ cm}^{-1}$ is in excellent agreement with that of Bondybey and English.

Using EXAFS on matrix isolated Fe_2 , Purdam *et al.*¹⁸⁴ determined the equilibrium internuclear distance to be $r_e = 2.02 \text{ \AA}$. In matrix isolation Raman studies, Moskovits¹⁸⁵ found $\omega_e = 299.6 \text{ cm}^{-1}$ with $\omega_e x_e = 1.4 \text{ cm}^{-1}$. Considerable variation has been observed in dissociation energies. Lin and Kant¹⁸⁶ used third law methods to determine a value of $0.78(17) \text{ eV}$. In a later analysis Haslett, Moskovits, and Weitzman¹⁸⁷ found values in the range of $1.25\text{--}1.75 \text{ eV}$. Lian, Su, and Armentrout¹⁸⁸ found a value of 1.14 eV using collision induced dissociation, and it seems this is the more reliable. Leopold, *et al.*¹⁸⁹ indicates that dissociation is to $4s^2 3d^6 + 4s^1 3d^7$ atomic configurations. This is confirmed by a CASSCF/MRCI calculation by Hübner and Sauer¹⁹⁰, who find a ${}^9\Sigma_g^-$ ground state.

In this study we observe the resonance Raman spectrum of CrFe using mass-selection techniques to isolate the species of interest. Samples are deposited with Ar at liquid helium temperatures, and both absorption and Raman spectra are obtained. Exciting at five different laser

wavelengths (476.5, 488.0, 496.5, 501.7, 514.5nm), we obtain a fundamental and four of the overtones, and from the analysis are able to obtain accurate values of the harmonic frequency and force constant.

EXPERIMENT

The CCNY cluster deposition source has been described in detail elsewhere ¹⁹¹. Briefly, an argon ion beam (typically 15mA at 25keV) sputters a water-cooled CrFe target. The metal target is about 2.0 cm in diameter and 0.3 cm thickness, prepared by heating a mixture of the pure Cr and Fe powders (Alfa Aesar 99.9%). The molar ratio between Cr and Fe is chosen to be 3:4. This is in order to account for the fact that the dissociation energy of Cr₂ is somewhat larger than that of Fe₂. It has been found that this procedure optimizes the production of a mixed dimer. The sputtered products are extracted by electrostatic lenses, mass-selected using a Wien filter, bent by 10° to eliminate neutrals and then guided into the deposition region. To prevent degradation upon impact with the CaF₂ substrate, focussed ions are slowed to ~10 eV to ensure a soft landing on the substrate.

Dimer (or atomic) ions were then co-deposited with argon gas and electrons (for neutralization) from a tungsten filament, onto a ~14K CaF₂ substrate. Ion currents

under soft landing conditions could be measured on a Faraday plate in the deposition region.

The deposited samples could be probed *in situ* via resonance Raman and absorption spectroscopy. The absorption measuring technique in which a ratio between scattered light from the center of the CaF_2 substrate, where a majority of the sample is deposited, and scattered light from the edge of the substrate is obtained 90° from the incident radiation. This is called scattering depletion spectroscopy (SDS) and we have found it to be more sensitive than absorption through our optically thin samples. The absorption spectrum (SDS) of CrFe in an argon matrix was acquired after a five hour deposition of the molecule at an average current of 24 nA, giving a total concentration of ~ 140 nA-h. As a check on our results, we re-deposited CrFe with a total concentration of 130 nA-h.

Resonance Raman experiments were performed employing the visible lines of a Spectra Physics 2045 argon ion laser, as well as dye lasers utilizing R6G (spectral range ~ 575 to 622nm), and DCM (spectral range ~ 630 to 685 nm) dyes. All Raman lines were detected with a Spex 1877E 0.6m Triplemate Spectrometer coupled to liquid nitrogen cooled CCD (Spectrum One and CCD30). All collected data was

interpreted and displayed by DM3000R software interfaced with a computer.

RESULTS

In Figure 6.3.1, we present a mass scan of one of our deposits. The ion current is plotted against the mass/charge (m/c) ratio. Due to the relatively low resolution of our Wien filter, it is impossible to completely separate various Cr and Fe ionic species. Our deposits were both at m/c of 109, and it can be seen that we expect some Cr_2^+ and Fe_2^+ to be transmitted by the filter. However, the Raman spectra of Cr_2 and Fe_2 are well known and indicate negligible amounts of Cr_2 and small amounts of Fe_2 .

The absorption (SDS) spectra of CrFe, Cr_2 and Fe_2 are shown in Figure 6.3.2. It is likely that the SDS spectra of the CrFe deposit represents contributions which are observed from the CrFe dimer (487nm) as well as Cr_2 (415 and 646 nm), and Fe_2 (440, 454 and 466 nm), and to some extent Fe (367, 404 and 454nm) and Cr (367 and 466 nm) atom produced by fragmentation of dimers on deposition. The Raman excitation profile for the five exciting wavelengths is shown in squares in the vicinity of 475-515 nm, which confirm the assignment of the 487nm line to CrFe.

We have observed the resonance Raman spectrum of CrFe at five excitation wavelengths (476.5, 488.0, 496.5, 501.7, 514.5nm). The spectrum for excitation at 488.0 nm, 496.5 nm, 501.7 nm are shown in Figure 6.3.3. Five spectral lines are clearly observed, and we list the measurements in Table 6.3.1. The average of all the observed lines gives Raman shifts at 164, 485, 644, 800 and 952 cm^{-1} . We assign these to the fundamental and second through fifth overtones of the ground state vibration. The first overtone peak, expected at 326 cm^{-1} , is masked by the more intense line, which is due to the CaF_2 substrate.

By using standard fitting techniques, we were able to determine the harmonic frequency to be $\omega_e = 166.6 \pm 0.8 \text{ cm}^{-1}$ and the anharmonic correction is $\omega_e x_e = 1.1 \pm 0.1 \text{ cm}^{-1}$. From these measurements we obtain a force constant of $k_e = 0.44 \text{ mdyne/\AA}$ and a spectroscopic dissociation energy of $D_e = \omega_e^2 / 4\omega_e x_e = 0.76 \text{ eV}$. With knowledge of the force constant, we may obtain an experimental measure of the bond order, using a procedure recommended by Johnston¹⁹². The experimental bond order (n) is related to the force constant by $n = k_e / k_e^{(1)}$, where $k_e^{(1)}$ is the force constant for a single bond. We have shown that for the first row of the transition metals, this may be taken to be that for Cu_2 ($k_e = 1.33$

mdyne/Å) ¹⁹³ since the $3d^{10}4s^1$ configuration of atomic Cu precludes the participation of d electrons in bonding. The resulting bond order for CrFe is 0.33.

DISCUSSION

As mentioned in the introduction, due to the ability of alloys of Cr to strengthen Fe metal, we initially expected a reasonably high force constant to be obtained from the dimer CrFe. However, after detailed consideration of the Engel-Brewer theory, as well as examination of various calculations, we concluded that this is only true for low concentrations of Cr. At concentrations of Cr higher than 13%, it is difficult for CrFe alloys to maintain the more stable fcc structure. Engel and Brewer showed that for average sp -electron configurations of up to 1.5, only bcc crystals could be stable, while for configurations between 1.7 and 2.1, hcp crystals are formed. In order to achieve the most stable fcc crystal structure, there must be at least 2.5 sp -electrons. Thus, we were led to expect a smaller force constant for the dimer. In table 6.3.2 we list the observed force constants for several related transition metal dimers from the third row of the periodic table. The observed result of 0.44 mdyne/Å for CrFe is considerably lower than obtained for other transition metal dimers, except for the van der Waals

bonded Mn_2 . It is especially telling that the value for CrFe is much lower than that of either Cr_2 or Fe_2 . The bulk property most closely associated with the force constant is the bulk modulus. Several calculations exist for the bulk modulus of CrFe alloys. Herper et al. carried out an *ab initio* calculation of Fe and Cr/Fe(001) bcc crystals. They found that the mixing energy of CrFe alloys is positive at all concentrations, which indicates that no stable cubic compounds of Cr-Fe exist at $T = 0\text{K}$. This suggests that CrFe compounds should have weaker bonding, and therefore lower force constants and bulk moduli than the pure substances. In a LMTO study, Moroni and Jarlborg showed that the bulk modulus of non-magnetic (bcc) CrFe ($B = 2.46$ Mbar) is lower than that of either Cr (2.83 Mbar) or Fe (3.00 Mbar), but that for the ferro-magnetic phase, the bulk modulus of CrFe (2.69 Mbar) is higher than that of either Cr (2.36 Mbar) or Fe (2.51 Mbar). This calculation on CrFe is consistent with the calculation of Qiu, Marcus and Moruzzi¹⁹⁴, who found a value of 2.73 Mbar for the magnetic phase of CrFe. It thus appears that the relative value of the dimer force constant is more comparable with the non-magnetic phase bulk modulus.

The last three entries of table 6.3.2 are isoelectronic, each with a total of 14 valence electrons. As a result, we might expect them to have similar bonding.

Note, however, the wide disparity in observed force constants. The force constant for CrFe is over four times larger than that for Mn₂, and that for VCo is almost a factor of 10 larger than that of CrFe. We have previously argued that for VCo the most likely configuration would be $(3d\sigma)^2(3d\pi)^4(3d\delta)^4(3d\delta^*)^2(4s\sigma)^2$. Since the force constant measured for VCo was somewhat higher than the average of V₂ and Co₂ it was argued that Engel-Brewer considerations were of at least some importance in strengthening the bonding. In this case we would then expect the ground state to be Σ^3 , with dissociation to $V(3d^44s^1) + Co(3d^84s^1)$. On the other hand, the bonding in Mn₂ is extremely weak. This is due to the $3d^54s^2$ ground state configuration of Mn coupled with a relatively high (4s→3d) promotion energy, making it impossible to form a good bond with the s electrons. Thus the bonding is considered to be of the van der Waals type, augmented by anti-ferromagnetic coupling. The resulting force constant is 0.094 mdyne/Å. In CrFe, with atomic configurations for Cr of $3d^54s^1$ and for Fe of $3d^64s^2$, strong bonding will be prevented by the somewhat large 4s→3d promotion energy of Fe (0.87 eV). As in Mn₂ we would expect weak bonding, and inhibition of d-electron contributions to bonding. Engel-Brewer theory predicts the strongest bonding for species somewhat distant from each other in the

periodic table, e.g. between groups 4 and 9/10, such as Zr and Pt¹⁹⁵, while for atoms as close as Cr and Fe, the predicted bonding is considerably weaker. We might then expect a $(4d_{Cr})^5(4d_{Fe})^6(4s\sigma)^2(4s\sigma^*)^1$ configuration for CrFe with essentially no contribution from the 3d electrons. This results in a formal bond order of $\frac{1}{2}$, in keeping with the experimental bond order of 0.33 (see section III).

This analysis is at odds with the SCF-X-SW calculation of Nagarathna, Montano, and Naik, which predicts a $\sigma^2\sigma^2\pi^3\delta^2\delta^{*2}\pi^{*3}$ configuration with a ${}^7\Delta$ ground state. They felt that this was the most likely result because it gave the best value of the experimental quadrupole splitting (2.9 mm/s), which they observed in the Mössbauer spectrum. The formal bond order of their configuration is 2, and their internuclear distance was chosen to be the average of Cr₂ and Fe₂, which was 2.0 Å. This result was supported indirectly by the inability of Baumann, Van Zee, and Weltner to observe an ESR spectrum in CrFe. They suggest that a ${}^7\Delta$ state will be unobservable due to the rather large anisotropy of the g-tensor. However, the rather low force constant observed here indicates a much lower bond order, and a much larger internuclear distance for CrFe. Using Pauling's relationship¹⁹⁶ $[r_e = r_e^{(1)} - 1.02 \log(n)]$, where $r_e^{(1)}$ is taken to be the internuclear distance

for a single bond, in this case that of Cu_2 , which is 2.22 Å, and n , from above is 0.33] we estimate $r_e = 2.71$ Å. At this distance, participation of d -electrons in bonding is expected to be slight, and a configuration with only s -electrons, as suggested above, is more likely.

In summary, we have obtained the resonance Raman spectrum of CrFe. The rather low value of the observed harmonic frequency, and resulting force constant indicate a relatively weak chemical bond. It is unlikely that such a low value is a result of d -electron participation in bonding and we recommend that the ground state configuration of $(4d_{\text{Cr}})^5 (4d_{\text{Fe}})^6 (4s\sigma)^2 (4s\sigma^*)^1$ is most consistent with the observed force constant.

Acknowledgements

This work was supported by the National Science Foundation under Cooperative Agreement No. RII-9353488 and Grant No. CHE-0091362 and by the City University of New York PSC-BHE Faculty Research Award Program. We are also indebted to Professors Michael Morse and Doreen Leopold for helpful suggestions.

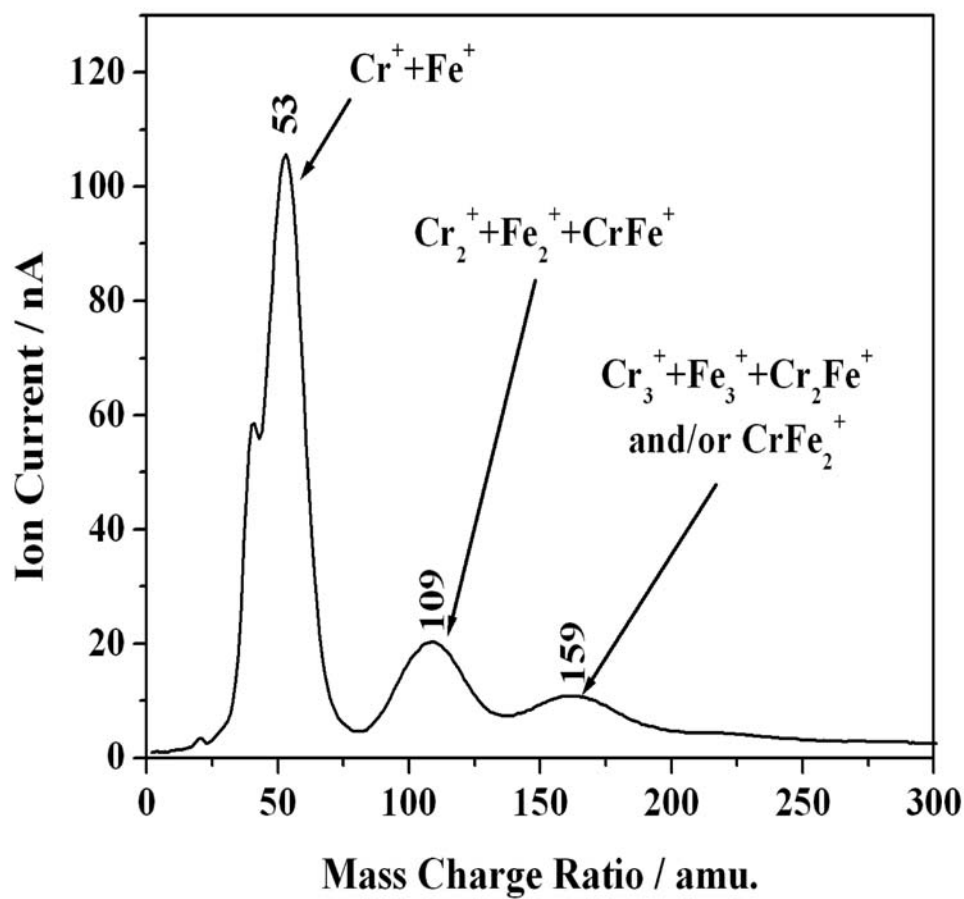


Figure 6.3.1. The sputtering mass-spectrum of a CrFe target. Ion current is plotted against mass/charge ratio. Peaks at 53, 109 and 159 indicate ionic atoms, dimers, and trimers.

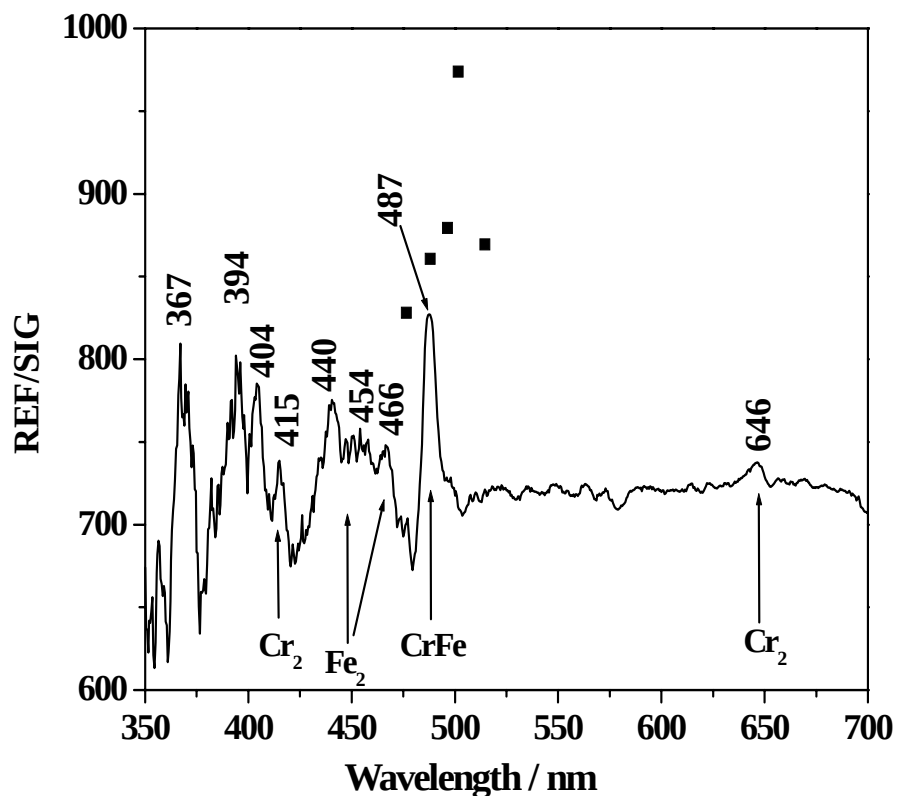


Figure.6.3.2. The absorption (SDS) spectrum of CrFe in an argon matrix at 14K. Contributions are observed from the CrFe dimer (487nm) as well as Cr₂ (415 and 646 nm), and Fe₂ (440, 454 and 466 nm), and to some extent Fe (367, 404 and 454nm) and Cr (367 and 466 nm) atom produced by fragmentation of dimers on deposition. The Raman excitation profile for the five exciting wavelengths is shown in squares.

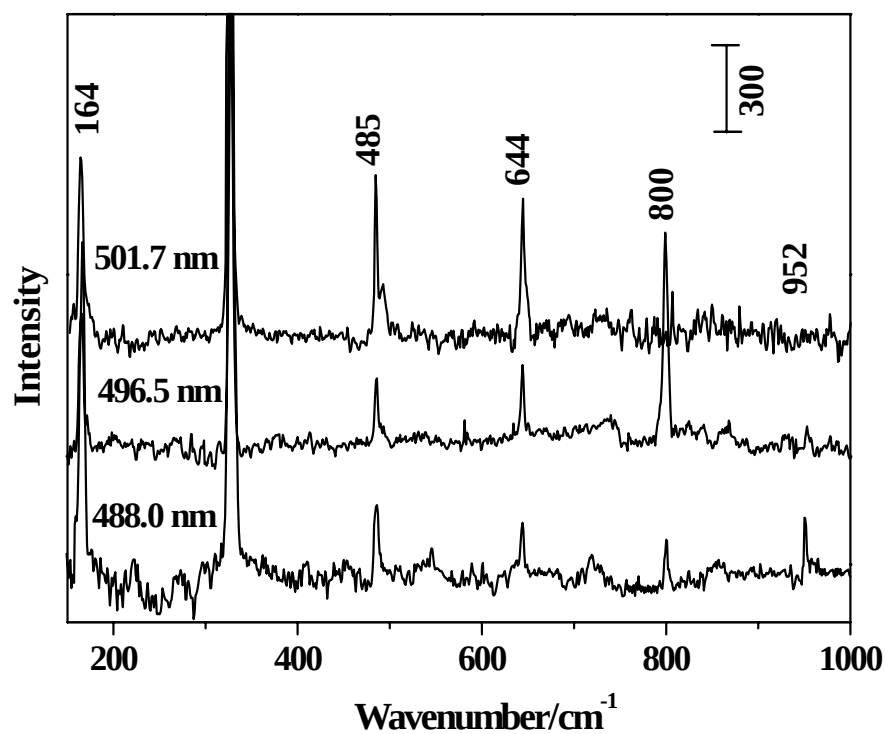


Figure 6.3.3. Resonance Raman spectra of mass-selected CrFe in argon matrices at 14K. Excitation wavelengths shown are 501.7 nm, 496.5 nm and 488.0 nm. The substrate (CaF_2) line at 327 cm^{-1} obscures a presumed spectral line at 326 cm^{-1} .

λ_{ex} (nm)	$\nu''=1$	$\nu''=2$	$\nu''=3$	$\nu''=4$	$\nu''=5$	$\nu''=6$
476.5	164					
488.0	166		486	644	800	951
496.5	164		486	644	799	953
501.7	164		485	644	801	
514.5	162		485	644	800	
Mean (σ)	164 (0.6)	326*	485.5 (0.3)	644 (0)	800 (0.4)	952 (1)

*Overlapped by the 327 cm^{-1} peak from the substrate.

TABLE 6.3.1. Observed resonance Raman frequency shifts (cm^{-1})
for CrFe in an argon matrix

Dimer	k_e (mdyne/Å)	Reference
Cr ₂	3.54	72, 73
Fe ₂	1.48	185
V ₂	4.33	¹⁹⁷
VFe	2.94	¹⁹⁸
VCr	4.1	^{199, 200} /
VMn	5.1	²⁰¹
Mn ₂	0.094	²⁰²
CrFe	0.44	This work
VCo	3.42	198

TABLE 6.3.2. Force constants of selected transition metal dimers

Chapetr VII Heteronuclear Transition Metal tetramer**7.1 Spectroscopy of mass-selected TiCu_3 in argon matrices*****Bing Zhao, Haiyan Lu, Ija Likhtina and John R. Lombardi******Department of Chemistry and Center for Analysis of Structures and Interfaces (CASI)******The City College of New York Convent Ave. at 138th Street New York, N.Y.
10031*****Abstract**

We have examined the absorption and resonance Raman spectrum of mass-selected transition metal tetramers sputtered from a Ti-Cu alloy and deposited in an Ar matrix at 10 K. For the tetramers $\text{Ti}_{4-n}\text{Cu}_n$, we observed only a single Raman progression in approximately 300 cm^{-1} . This progression is most likely the totally symmetric stretch. The resolution of our mass-selection filter is insufficient to separate the tetramers, but from the isotopic Raman intensities we infer that the species observed in the Raman spectrum is TiCu_3 . Since only one progression was observed, sufficient information to determine the structure was not obtained.

Introduction

There now exists a considerable body of work on the spectroscopy of almost all the homonuclear transition metal dimers as well as a large number of homonuclear trimers^{203, 204}. The heteronuclear dimer molecules, CrFe²⁰⁵, CuAg²⁰⁶, VCo and VFe²⁰⁷ have recently been studied by Raman spectroscopy. However, among the transition metals, only two homonuclear tetramers, Ta₄ and Sc₄ have been examined by Raman spectroscopy^{208, 209}. In this Letter, we present the first description of the Raman spectroscopy of a heteronuclear tetramer molecule TiCu₃.

Heteronuclear clusters are of special interest in regard to the study of bulk alloys, for it is worthwhile to examine whether understanding of the structure and stability of small clusters sheds any light on the properties of corresponding alloy. Engel²¹⁰ and Brewer^{211, 212} have made important advances in the understanding of bonding in bulk transition metal alloys. They showed that the relative stability of certain alloys could be predicted by consideration of the number of s- and/or p-electrons available for bonding from each contributing atomic species. The role of d-electrons, however, is more indirect, influencing the s-electrons through promotion energies as

well as providing an additional number of unpaired electrons or holes for bonding. Engel-Brewer showed that as the total number of s and p electrons increases, the crystal structure goes from bcc to hcp and finally the most stable fcc crystal structure. Applying these ideas to small heteronuclear clusters, Engel-Brewer theory predicts the strongest bonding for species somewhat distant from each other in the periodic table, e.g. between groups 4 and 9/10, such as Ti or Zr and Pt²¹³. However, since Cu has a filled d-shell, and Ti in any case is not a good sink for d-electrons²¹² we might expect considerably less Engel-Brewer strengthening of a Ti-Cu bond, despite their distance in the periodic table.

Nevertheless, bulk intermetallic Ti-Cu compounds have been found to possess special properties, including increased hardness, as well as displaying enhanced sound absorption and electrical conductivity²¹⁴. Furthermore, with the addition of small amounts of Ni, they display shape memory. It is found by XPS that addition of Ti to a Cu lattice reduces the width of the 3d-density of states. This implies that the interaction of copper 3d-electons is weaker in TiCu than in a pure Cu lattice²¹⁴. Karlsson²¹⁵ carried out an X-ray study of the Cu-Ti phases. He showed the β -phase had an orthorhombic (hcp) structure with a

composition of TiCu_3 . Chanda and De^{216, 217} examined the high strength spinodal decomposition products of Ti-Cu alloys by X-ray diffraction. They found microstructural precipitates of both $\alpha\text{-TiCu}$ and $\beta\text{-TiCu}_3$. Micro-hardness measurements indicated that the $\beta\text{-TiCu}_3$ phase aged at 673 K for 2 h had an abrupt increase in hardness, giving it additional strength with an fcc structure. Precipitation hardening experiments²¹⁸ using transmission electron microscopy also confirmed the relative stability and strength of the $\beta\text{-TiCu}_3$ phase. The tendency of structures with TiCu_3 stoichiometry to form either hcp or fcc structures and show increased hardness implies stronger bonds in bulk than expected from simple consideration of Engel-Brewer theory.

With these results in mind, we initiated a mass-selected study of the small mixed clusters of Ti and Cu. Previous Raman and fluorescence research has been carried out in various laboratories on the homonuclear clusters of Ti_2 , Cu_2 and Cu_3 ^{203, 204}. Under the conditions of our experiments, higher homonuclear clusters of either Ti or Cu have not shown sufficient sputtering intensity to obtain a reasonable deposition concentration. Although we did find a large sputtering current for the mixed dimer TiCu and the trimers $\text{Ti}_{3-n}\text{Cu}_n$, no Raman or fluorescence intensity could be observed despite extensive searches. However, for the

tetramers $\text{Ti}_{4-n}\text{Cu}_n$, we were able to obtain a single Raman progression with intervals of approximately 300 cm^{-1} . Observation of the isotopic intensities allows us to infer that the species observed is TiCu_3 . This progression is most likely the totally symmetric stretch. However, since we observed only a single progression, there is insufficient information to determine the structure of the tetramer.

Experiment

The absorption and resonance Raman spectrum of mass-selected $\text{Ti}_{4-n}\text{Cu}_n$ clusters were acquired using the CCNY metal cluster deposition source. The design of this apparatus has been discussed in detail in other publications^{219,220} but will be described briefly here. An argon ion beam of 10 mA (at 25 keV) sputters a water-cooled TiCu alloy metal target. Metal targets about 2.0 cm in diameter and 0.3 cm thick were prepared by heating a mixture of the pure elements, the molar ratio of titanium to copper are chosen to be 1:1. Pure elements were purchased in the powder form from Alfa Aesar at 99.9% (REO).

In the beam, the metal target was maintained at about 300 V. A series of einzel lenses collects the sputtered metal cluster ions from the metal sputtering region, and a Wien filter mass selects the focussed cluster ions. Any

neutral atoms or clusters produced during the sputtering process that pass through the mass selector are removed by a 10° bend in the path following the Wien filter. A second set of einzel lenses focuses the mass-selected cations into the deposition region, which are then codeposited with argon gas and electrons, for neutralization, onto a CaF_2 substrate. A cryostat cools the substrate to ~ 16 K. To prevent degradation upon impact with the CaF_2 substrate, focussed ions are slowed to ~ 10 eV to ensure a soft landing on the substrate. The metal cluster/Ar matrix had a growth rate of ~ 6 $\mu\text{m/h}$. The argon:cluster ratio was $\sim 10^4:1$. Several deposits were carried out for each alloy, during which the current for a particular mass-to-charge (m/c in amu/electron charge) ratio was optimized. For $m/c = 49.0$ the optimized current was 105 nA for Ti^+/Cu^+ , for $m/c = 103$, the current was 75 nA for $\text{TiCu}^+/\text{Ti}_2^+/\text{Cu}_2^+$, for $m/c = 173$, the current was 28 nA for $\text{Ti}_3^+/\text{Ti}_2\text{Cu}^+/\text{TiCu}_2^+/\text{Cu}_3^+$, for $m/c = 217$, the current was 45 nA for $\text{Cu}_3^+/\text{Ti}_4^+/\text{Ti}_3\text{Cu}^+/\text{Ti}_2\text{Cu}_2^+/\text{TiCu}_3^+/\text{Cu}_4^+$, respectively. Since the resolving power of our Wien filter is relatively low (around 6-7) in order to attain high throughput, we cannot adequately separate the homonuclear molecules from the mixed ones. We may then use the Raman excitation profile obtained to confirm at least partially, the assignment of the absorption spectrum.

Resonance Raman spectroscopy was carried out in situ on the matrix sample. An absorption spectrum, in the form of a "scattering depletion spectrum" (SDS) was also obtained. The "SDS" absorption is a ratio between scattered light from the center of the sample, where most of the metal is deposited, to that of the edge, where only argon has been deposited. The scattered light is collected at a 90° angle from the incident.

The visible lines of a Spectra Physics 2045 argon ion laser, as well as laser lines from a Coherent model CR599 dye laser, employing the dyes R6G were used to observe resonance Raman features of the mass-selected species. The laser power incident on the sample was typically about 50 mW. Plasma lines were removed by predispersing the laser beam with a diffraction grating. The 327 cm^{-1} line of the CaF_2 substrate was used to calibrate all Raman shifts. The Raman detection system consists of a Spex 1877E 0.6 m Triplemate Spectrometer coupled with a liquid nitrogen cooled CCD system (Spectrum One and CCD30). The detector resolution is approximately 2 cm^{-1} . The computer software DM3000R acquired, interpreted, and displayed spectral information from the CCD.

Results

In Fig.7.1.1, we present a mass scan of one of our deposits, and for comparison the mass scan of pure titanium and copper targets are also shown. The ion current is plotted against the mass/charge (m/c) ratio. It can be seen from the plots that there is almost no Ti_3 or Ti_4 obtained from a pure Ti target, and thus we expect little of either in our deposit from TiCu alloy. Pure Cu scans reveal measurable currents due to Cu_2 ($m/c = 127.5$) and Cu_3 ($m/c = 192.0$), but previous extensive searches of such deposits provided no observable Raman signals. Consequently, these species are unlikely to be responsible for our Raman observations from deposition from the alloy target. Due to the relatively low resolution of our Wien filter, it is impossible to completely separate various mixed cluster species. Our deposits were carried out at m/c of 103, 173 and 217 for hetero-dimer, trimer and tetramer, respectively. Only for the deposit at $m/c = 217$ were we able to observe a Raman signal. Note also that the mass scan peak of tetramer species ($m/c = 217$) is more intense than that of the trimer species ($m/c = 173$), which indicates that under the conditions of our experiment, the tetramers are more readily formed than the trimers.

The SDS spectra obtained with separate $\text{Ti}_{4-n}\text{Cu}_n$, TiCu , Ti_2 , and Cu_2 deposits are shown in Fig.7.1.2. The spectrum obtained from the $m/c = 103$ (Fig.7.1.2c) deposit differs considerably from that obtained from for Ti_2 or Cu_2 molecules. Since these are the only impurities likely to be deposited from the mixed metal target at $m/c = 103$, the SDS spectrum in the range 525-625 nm is assigned to TiCu . Peaks further to the blue (400-475 nm) are assigned to atomic absorptions of Ti and Cu, which are produced in the deposition process. Deposition of a sample at $m/c = 217$ (Fig.7.1.2d) leads to weak features between 575 and 625 nm. These features are different from the peaks assigned to diatomic TiCu , and are not observed in deposits from either pure metal target. There is no evidence of fragmentation of the tetramer deposited at $m/c = 217$ to either atomic fragments or to diatomic TiCu , so these weak absorptions are assigned to a tetramer of the formula $\text{Ti}_{4-n}\text{Cu}_n$. The Raman excitation profile of the 300 cm^{-1} line in the 575-625 nm regions (Fig.7.1.2e) supports the contention that much of the intensity of the sharp feature of the SDS in that region is due to $\text{Ti}_{4-n}\text{Cu}_n$.

We have observed the resonance Raman spectrum of $\text{Ti}_{4-n}\text{Cu}_n$ at a series of eighteen excitation wavelengths (570-625 nm). The spectrum for excitation at 609.7 nm is

shown in Fig.7.1.3. The peak at 327 cm^{-1} is due to the CaF_2 substrate and is used as a calibration line. Four members of a progression are evident, and we assign these to the fundamental and three overtones of the ground state vibration. The average of all the observed spectra gives Raman shifts at 300, 596, 893 and 1190 cm^{-1} . From these we obtain $\omega_e = 299.5(11)$ and $\omega_e x_e = 0.5(5)\text{ cm}^{-1}$ (see Table.7.1.1).

The detailed Raman spectrum of $\text{Ti}_{4-n}\text{Cu}_n$ tetramer (Fig.7.1.3) shows in the overtones clear triplet peaks, which arise from isotopic structure. We list individual observed frequencies of these lines in the table, along with observed triplet splittings. The possibility that these lines come from site splittings can be eliminated since they persist on annealing. In any case the observed splittings increase in rough proportionality to quantum number, an indicator that they are due to isotope effects, and can not come from site effects.

The observation of the relative intensities of the isotopic lines enables us to determine the nature of the tetramer from which the Raman spectrum is obtained. Copper has two relatively abundant isotopes at 63 amu (69%) and 65 amu (31%), while titanium has only one at 48 amu (74%). All

other Ti isotopes are less than 8% in abundance, and unlikely to contribute significantly to the spectrum. Using these natural abundances, we can calculate the number of lines and relative intensities expected for Ti_3Cu , Ti_2Cu_2 and TiCu_3 . (By examining the pure metals separately, we have eliminated the possibility that we are observing either Ti_4 or Cu_4 .) Retaining only tetramer isotopes with more than 10% net abundance, for Ti_3Cu and Ti_2Cu_2 we expect to observe only a doublet structure. For TiCu_3 , by contrast we expect a triplet with relative abundances of 33%, 44% and 20% for the $\text{Ti } ^{63}\text{Cu}_3$, $\text{Ti } ^{63}\text{Cu}_2^{65}\text{Cu}$, and $\text{Ti } ^{63}\text{Cu } ^{65}\text{Cu}_2$, respectively. (The $\text{Ti } ^{65}\text{Cu}_3$ isotope is less than 4% in abundance.) Remembering that the lightest isotope should be of highest frequency, we can see that the calculated relative abundances almost exactly match the relative intensities of the observed triplets. We conclude that the species responsible for the observed spectrum is TiCu_3 .

Discussion

Unfortunately, since only one progression is observed, there is not sufficient information to determine the structure of TiCu_3 . Previous studies of the transition metal tetramers Ta_4 ⁶ and Sc_4 ⁷ showed more than one progression, enabling the determination that their structures are

tetrahedral (T_d). Additional experimental evidence is needed in order to establish a definitive geometry for $TiCu_3$.

The clear observation of $TiCu_3$ as a stable tetramer is at least consistent with the bulk phase studies mentioned in the introduction^{214, 215,217,218}, which indicate that the β - $TiCu_3$ phase has special stability and hardness in the Ti-Cu alloy. Of course we cannot rule out the production and deposition of other tetramers in our experiment, since it may be that they just do not have a Raman spectrum in the region that we have examined. However, we have at least shown that $TiCu_3$ is stable.

Acknowledgements

This work was supported by the National Science Foundation under Cooperative Agreement No. RII-9353488 and Grant No. CHE-0091362 and CHE-0345987 and by the City University of New York PSC-BHE Faculty Research Award Program.

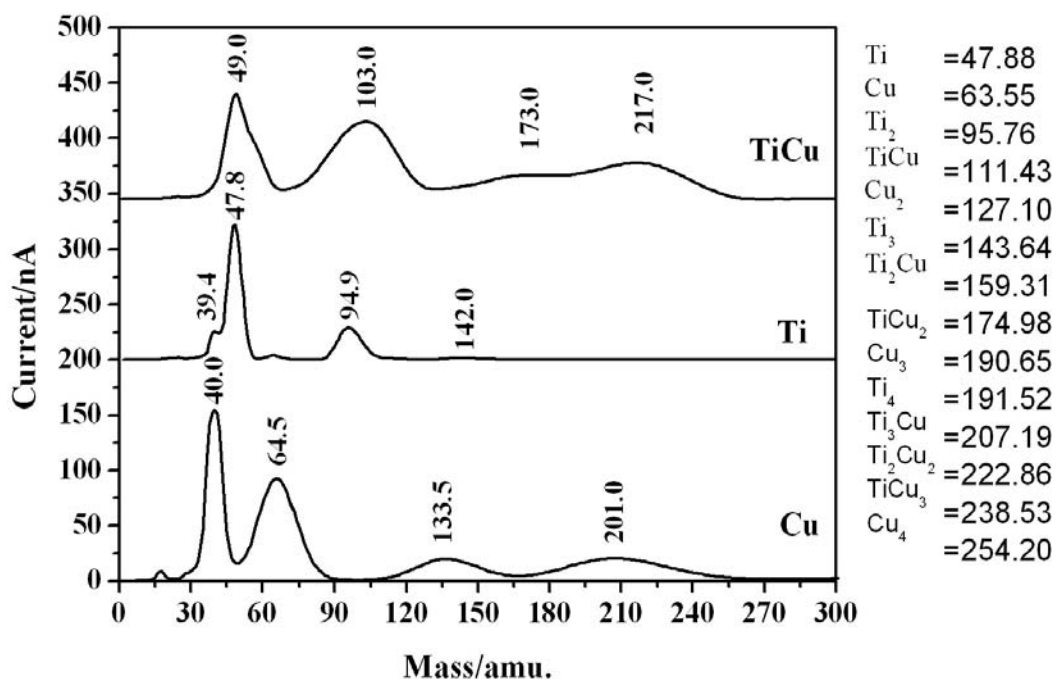


Fig.7.1.1. Mass spectra of sputtered titanium, copper pure metal and titanium/copper alloy clusters obtained by scanning the Wien filter magnetic field.

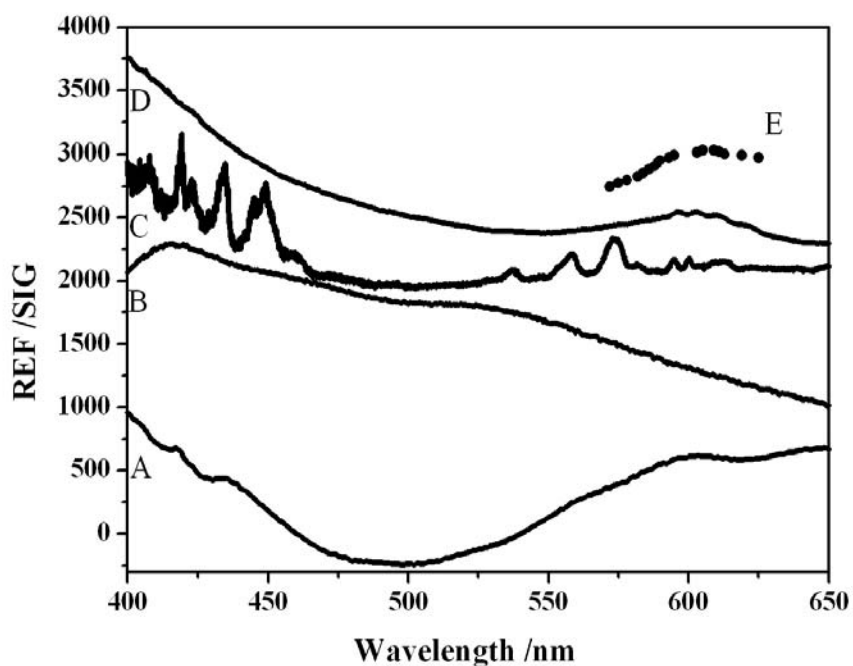


Fig.7.1.2. The Scattering Depletion Spectra (SDS) of Ti_2 (a); Cu_2 (b); TiCu (c); $\text{Ti}_{4-n}\text{Cu}_n$ (d) in an Ar matrix. The Raman excitation profile of the 300 cm^{-1} line is shown in dotted curve (e).

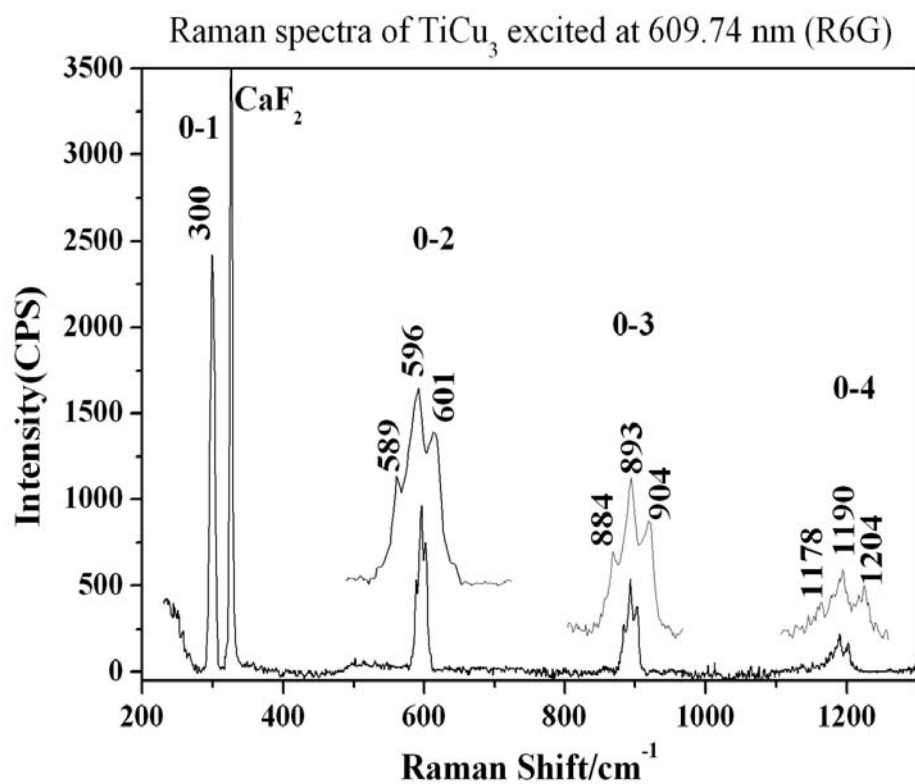


Fig.7.1.3. Raman spectrum of TiCu_3 excited at 609.74 nm dye laser (R6G).

Assignment	Lowest	Middle	Highest	Splittings
0-1	300			Unresolved
0-2	589	596	601	7;12
0-3	884	893	904	9;20
0-4	1178	1190	1204	12;26

Table 7.1.1 Observed Raman lines from sample excited at 609.74 nm. In the second column we present the lowest frequency (in cm^{-1}) line of each triplet. In the fifth column we present the observed separation of each line in the triplet from the lowest line

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