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I am submitting herewith a dissertation written by Sunil Ramesh Desai entitled "Multiphoton Ionization of Molecular Clusters." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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Multiphoton Ionization of Molecular Clusters

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Sunil Ramesh Desai

May 1995

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To my parents

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Abstract

Mixed clusters of the form $(\text{NO})_m^+ (\text{Ar})_n$ ($m \leq 4$, $n \leq 22$) were produced in a supersonic expansion and ionized by nonresonant two-photon absorption of 30 ps, 266 nm photons. The cluster distribution exhibited intensity anomalies for $\text{NO}^+(\text{Ar})_n$ ($n = 12, 18$ and 22) and $(\text{NO})_2^+ (\text{Ar})_n$ ($n = 17, 21$). These “magic numbers”, at $m + n = 13, 19, 23$ were compared with those observed in rare gas and other M^+Ar_n clusters and were assigned to symmetric and stable icosahedral structures. Four-photon ionization with 30 ps, 532 nm light yielded a cluster distribution in which only the $\text{NO}^+(\text{Ar})_n$ cluster series was observed. The known photodissociation of $(\text{NO})_2^+$ and $(\text{NO})_3^+$ and the cluster distributions obtained at 266, 355 and 532 nm light suggested that the dissociation of $(\text{NO})_m^+ (\text{Ar})_n$ ($m > 1$) was taking place in the ion.

A variety of binary heteroclusters of the form $(\text{NO})_m^+ (\text{Y})_n$, where $\text{Y} = \text{N}_2\text{O}$, CO_2 , NO_2 , H_2O , CS_2 , SO_2 and SF_6 were investigated by coexpanding nitric oxide, argon and the complexing agent. Cluster distributions of neat $(\text{NO})_m^+$ exhibited an odd-even intensity alternation which was explained by electron pairing effects and differences in the relative stabilities of the cluster ions which are enhanced by the kinetic effects in the evaporation process. The observation of the exceptionally stable $(\text{NO})_3^+ (\text{Y})_n$ cluster series is of particular interest and possible structures for these species are discussed.

The vibronic spectroscopy of NO, ArNO, CH₄NO and CD₄NO was investigated using mass resolved REMPI. Spectra for NO are presented for transitions associated with the A²Σ⁺ state (v = 2 and 3). Multiphoton ionization spectra are also presented for various van der Waals molecules, namely ArNO, CH₄NO and CD₄NO. The spectra were obtained via a two-photon electronic transition associated with the C²Π (v= 0) state of nitric oxide. Dissociation energies of the ground and excited states of the vdW molecules are discussed.

Laser induced polymerization was investigated in clusters of carbon disulfide. The observation of various ionic photoproducts such as (S)_m⁺, (CS)_m⁺, S_m⁺ (CS₂)_n, (CS₂)_m⁺ and CS_m⁺ (CS₂)_n is attributed to a cycle of ion-molecule reactions occurring entirely within an isolated cluster of carbon disulfide.

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Chapter I

Introduction

Multiphoton Processes: Historical

The theoretical aspects for the simultaneous absorption of two photons were first introduced by Göppert-Mayer^{1,2} by using second-order time-dependent perturbation theory. Experimental verification of this process was provided by Kaiser *et al.*³ when they observed fluorescence at 425 nm after irradiating $\text{CaF}_2:\text{Eu}^{2+}$ crystals with a ruby laser. Two-photon absorption was observed by Abella⁴ by exciting the $6\text{S}_{1/2}$ - $9\text{D}_{3/2}$ transition in cesium and observing the subsequent fluorescence decay from the $9\text{D}_{3/2}$ to the $6\text{P}_{3/2}$ state at 584.7 nm.

Multiphoton processes were not only observed in atomic species but also in diatomic and large molecular species. Two-photon spectroscopy was used to observe photodetachment from C_2^- by initially creating the anions in a CO- C_2H_2 discharge, mass analyzing them and then intersecting them with a tunable dye laser⁵. A two-photon detachment cross-section was obtained and the $^2\Sigma_g^+$ state was assigned as the ground state of C_2^- ⁵. Other experiments in gas-phase two-photon spectroscopy were carried out by Hochstrasser *et al.*⁶ on benzene and by Boesl *et al.*⁷ on naphthalene where, in both cases, vibrational frequencies of the ground and excited states were obtained by the

analysis of hot bands. The versatility of multiphoton spectroscopy was demonstrated by Bergman *et al.*⁸ who used the process to obtain absorption spectra for both crystalline and liquid anthracene and were able to identify the symmetry forbidden, $^3B_{3u}^-$ state and the symmetry allowed $^1B_{1g}^+$, $^1B_{1g}^-$ and $^1A_{1g}^-$ electronic states. Later, Hochstrasser *et al.*⁹ were able to obtain vibrationally resolved spectra for crystals of benzene, naphthalene and biphenyl¹⁰. Two-photon processes allow for transitions between states of even parity and furthermore, odd-parity transitions can be made accessible by Herzberg-Teller vibronic coupling¹¹.

A major obstacle in obtaining narrow spectral linewidths, in the gas phase, was the phenomenon of Doppler broadening. Molecules in the gas phase have an isotropic velocity distribution that produces difference frequency shifts in the observed transitions for those with different velocity components in the direction of light propagation¹². The average of these shifts results in the Doppler broadening of the transition¹². The theoretical construct for the elimination of Doppler broadening was laid down by Vasilenko *et al.*¹³ who demonstrated that if an atom absorbed two photons from counter-propagating light sources, the shifts in their Doppler shifts have opposite signs and, if the two light sources have the same frequency, the shifts cancel each other out. Experimental evidence for the elimination of Doppler broadening was provided by numerous experiments on the excited states of sodium^{14,15,16}. It was discovered, however, that despite the elimination of Doppler effects, lifetime broadening still

contributed to the width of spectral lines. Doppler-free two-photon spectroscopy was also employed in the study of molecules such as Na_2 ¹⁷, CO and N_2 ¹⁸ and NO¹⁹.

The polarization properties of light can be used in multiphoton processes to provide information not only about the symmetry of excited states that would otherwise be inaccessible by one-photon spectroscopy, but it is also possible to study the dependence of multiphoton cross-sections on the polarization of light. Polarization was used to determine excited state symmetries for two and three-photon processes²⁰ and was later extended to gas-phase molecules by Bray *et al.*²¹ and by Wunsch *et al.*²² for C_6H_6 and C_6D_6 who analyzed the rotational structure of the $\text{S}_1 \leftarrow \text{S}_0$ transition by using linear and circularly polarized light.

If a molecule is excited by an intense light field, it can absorb many photons and eventually ionize. The phenomenon of multiphoton ionization (MPI) has been used as a sensitive detector of many-photon processes. MPI was theoretically addressed in 1964 by Keldish²³ and was first observed, experimentally, in xenon by Voronov *et al.*²⁴ who observed an ion current following a seven-photon ionization process. A powerful feature of MPI is the ability to measure the spectrum of intermediate states and detect new ones, by observing the ionization signal, that would not be observable by one-photon methods. Furthermore, MPI makes the detection of ions relatively easy. Multiphoton spectroscopy can excite those states that are parity forbidden in one-photon spectroscopy, in atoms and molecules with a center of symmetry. This was demonstrated by Johnson²⁵ who used the technique to observe a low-lying and

previously unobserved excited state of benzene namely, $^1E_{2g}$ and the ^1B_g state in trans-1,3-butadiene. Dalby *et al.*²⁶ were able to detect a new Rydberg state of symmetry, 1_g of molecular iodine and were able to determine the ionization cross-section from that Rydberg level. New states have been observed and identified in many polyatomic molecules such as, ammonia^{27,28}.

When combined with mass spectrometry, MPI becomes a very sensitive technique not only for the detection of ionized molecules but also for both neutral and ion spectroscopy. Since the initial observation of H_2^+ in a mass spectrometer²⁹, there have been numerous experiments that have employed multiphoton ionization spectroscopy and spectrometry. In MPI the intermediate state can be investigated by using the ion signal as the confirmation of the resonant excitation. In this type of technique, the intermediate resonant state does not need to fluoresce or predissociate in order to be detected. Furthermore, the use of a supersonic gas expansion can greatly simplify vibronic spectra via the cooling of rotational and vibrational degrees of freedom. If fragmentation is not a desirable result, then it can be controlled by ionizing very close to threshold. It is possible to use multiphoton spectroscopy to perform isotope selective spectroscopy where isotope shifts are used to assign vibronic spectra of molecules. This vibronic shift is important in understanding the nature of bonding within the molecule and can be use to determine force fields and electronic origins. This has been used to investigate the vibronic bands of S_1-S_0 transition in benzene, p-xylene and toluene

together with their $^{13}\text{C}_1$ isotopomers³⁰. In the case of ion spectroscopy, emission and excitation can be used to study the ground and excited vibronic states of the ions³¹, respectively. These methods, however, are limited in their use and so photoelectron spectroscopy (PES) has been employed to study excited electronic states of ions. Conventional PES typically has limited resolution and therefore, zero kinetic energy photoelectron spectroscopy (ZEKE) has been developed to investigate ions and provide high resolution spectra ($\sim 1\text{cm}^{-1}$)³². Both PES and ZEKE can be used in conjunction of with a mass spectrometer to do photoion-photoelectron coincidence experiments. Linear time-of-flight mass spectrometers are most frequently used because of their simplicity of construction and they provide good mass resolution (in the range 100-1000). However, reflectron time-of-flight spectrometers provide a number of advantages. It is possible to obtain higher mass resolution (up to $m/\Delta m = 35000$)³³ and furthermore, reflectrons allow the study of decay processes in the 20 ns to 20 μs range³⁴.

Finally, one of the most important applications of multiphoton spectroscopy is harmonic generation. This was first demonstrated by Ward *et al.*³⁵ when they observed third harmonic generation (THG) in rare gases as well as molecular systems. The advent of efficient dye lasers made it possible to obtain tunable THG light³⁶ and to use it in high resolution spectroscopy of H_2 , HD, D_2 ^{37,38,39} and NO⁴⁰. Harmonic generation has been observed not only in the vacuum ultraviolet (VUV) but also in the infrared using four-wave mixing processes⁴¹.

Theoretical Considerations

It is possible to use second order perturbation theory to describe a multiphoton process and obtain an expression for an n-photon cross-section. One can consider a two-photon process in which the sum of the energy of the two-photons is equal to the energy separation of an initial and final state. The initial transition can be envisioned as an absorption from the ground state, $|g\rangle$, to a virtual level, $|k\rangle$. The second photon completes the process by undergoing a transition from the virtual level to a final state, $|f\rangle$. The two-photon absorption cross section can then be expressed as⁴²

$$\sigma^2 = 8\pi^3 \left(\frac{e}{\hbar c}\right)^2 (\hbar\omega)^2 \left| \sum_k \left\{ \frac{\langle f | \mathbf{r} \cdot \mathbf{E} | k \rangle \langle k | \mathbf{r} \cdot \mathbf{E} | g \rangle}{(\omega_{gk} - \hbar\omega_1)} + \frac{\langle f | \mathbf{r} \cdot \mathbf{E} | k \rangle \langle k | \mathbf{r} \cdot \mathbf{E} | g \rangle}{(\omega_{gk} - \hbar\omega_2)} \right\} \right|^2 \quad (\text{I-1})$$

where ω_1 and ω_2 are photons of different frequencies and $\omega_{gk} = E_g - E_k$. The selection rules for the net transition moment is a product of the single-photon matrix elements, and consequently, the process allows for the transitions such as $g \rightarrow g$, $u \rightarrow u$, and $+$ $\rightarrow$ $+$ and $- \rightarrow -$.

For ionization, the transition probability for multiphoton processes can be expressed as⁴².

$$W^{(N)} = \sigma^{(N)} I^N \quad (\text{I-2})$$

where I is the intensity of the laser, $\sigma^{(N)}$ is the generalized cross-section for an N-photon process. For a two-photon process, the cross-section can be expressed as⁴³

$$\sigma_{fi}^2 = \frac{m \cdot (2\pi\alpha F\omega)^2}{2\pi^2 \cdot \hbar} \int |M_{fi}^2|^2 d\Omega_k \quad (I-3)$$

where α is the fine structure constant, $\frac{e^2}{\hbar c}$, F is the photon flux, k is the wavevector of the outgoing electron, m is the electron mass and ω is the incident frequency. The integral is over all the possible directions of the emitted electron over the solid angle, $d\Omega_k$. If the incident frequencies, ω_1 and ω_2 , in equation I-1 are equal, the second order matrix element M_{fi}^2 can be written as⁴⁴

$$M_{fi}^2 = \left| \sum_l \frac{\langle f|V|l\rangle\langle l|V|i\rangle}{(E_f - E_i - 2\omega_L)(E_l - E_i - \omega_L)} \right|^2 \quad (I-4)$$

where “i” and “f” refer to the initial and final continuum of states, ω_L is the incident laser frequency, the number “l” refers to the intermediate quantum state and V refers to the Hamiltonian of the interaction between the molecule and the electric field. When the incident laser frequency is tuned to a resonance an enhancement of the ionization signal is observed. Including effects of the finite lifetime of the state introduces an imaginary part to the denominator and removes the singularity apparent in equation I-4.

Freejet Expansions

Freejet expansions serve a valuable role in the spectroscopy of molecules for a variety of reasons. The supersonic beam provides an intense source of molecules with a narrow velocity distribution which undergo vibrational and rotational cooling. This

phenomenon simplifies spectra because excited vibrational and rotational levels are not populated and therefore, transitions from these levels are not observed. An example of this was observed in the expansion of NO₂ in a supersonic beam of helium which showed that less than 2% of the NO₂ molecules were rotationally or vibrationally excited⁴⁵. Supersonic cooling has also been observed in larger molecules such as s-tetrazine⁴⁶ and phthalocyanine⁴⁷. Furthermore, the low temperatures obtained in the supersonic beam allows the formation of weakly bound species such as vdW molecules.

Molecular beams can be characterized by the number of collisions that take place within the beam as it passes through the nozzle. This quantity is called the Knudsen number and is written as⁴⁸

$$K = \frac{\lambda_0}{D} \quad (\text{I-5})$$

where λ_0 is the mean free path of the gas in the reservoir and D is the diameter of the nozzle. If $K > 10$ then the result is effusive flow and there are no collisions within the beam. If $K \ll 1$ then the result is a supersonic expansion which undergoes numerous bimolecular collisions as it exits the orifice. The sonic velocity can be expressed by⁶⁰

$$v = \left(\frac{\gamma RT}{m} \right)^{\frac{1}{2}} \quad (\text{I-6})$$

where γ is the ratio of heat capacities, C_p/C_v , R is the gas constant, T is the temperature and m is the mass. The temperature, T_b , of the supersonic beam, for an ideal gas, is⁴⁹

$$T_b = T_0 \left(1 + \frac{(\gamma - 1)M^2}{2} \right)^{-1} \quad (\text{I-7})$$

where M is the Mach number, which is the ratio of the mass-flow velocity to the velocity of sound in the particular gas. The Mach number can also be expressed in terms of the distance from the nozzle⁵⁰

$$M \equiv c \left(\frac{x}{D} \right)^{\gamma-1} \quad (\text{I-8})$$

where c is a constant that depends on γ , x is the distance from the nozzle and D is the diameter of the nozzle. As the beam gets further from the nozzle, collisions cease and the Mach number approaches a limiting value which is given by⁴⁸

$$M_t \equiv 1.17K^{-0.4} \approx (p_0 D)^{0.4} \quad (\text{I-9})$$

where p_0 is the pressure of the gas in the reservoir and M_t is referred to as the terminal Mach number. The degree of clustering can be increased by increasing the pressure, increasing the diameter of the nozzle or decreasing the temperature of the gas in the reservoir, T_0 . However, an increased nozzle diameter not only requires a higher pumping speed but it has been determined experimentally that for argon, the mole fraction of the argon dimer scales as $p_0^2 D$ and so it is better to increase the backing pressure than to increase the nozzle diameter⁵¹. Assuming a backing pressure of 5205 torr (100 psi), a nozzle diameter of 0.5 mm and a γ of 5/3, equations I-7 and I-9 yield a beam temperature of $\sim 1.6^\circ\text{K}$. This translates to a kT value of $\sim 1 \times 10^{-4}$ eV, at which a

vdW molecule, such as ArNO ($D_e = 1.5 \times 10^{-2}$ eV) can exist without dissociating. At room temperature, however, kT is $\sim 2.6 \times 10^{-2}$ eV and, therefore, ArNO would dissociate. Nozzle geometry also plays an important role in the degree of clustering, as was demonstrated by Hagena *et al.*⁵²

Clusters: Historical

Clusters have become the focus of intense study in the past decade and continue to provide exciting challenges in the areas of chemistry, physics and material science. Although the observation and investigation of clusters is relatively new, they fill an important gap in the study of the fundamental properties of matter. Clusters have been referred to as the “fifth state of matter”⁵³ because they provide researchers with an invaluable tool to study the change in properties (structure, bonding, thermochemical properties) of matter from the gas to the condensed phases. Furthermore, clusters have been utilized in various applications such as catalysis, microelectronics, plasma fuel injection and combustion processes⁵⁴.

Clusters can be classified by their average binding energies and consequently, they fall into two categories: (i) those that are weakly bound (van der Waals, homogeneous molecular clusters and hydrogen bonded clusters) and (ii) those that are strongly bound (ionic, valence and metallic clusters). A list of the types of clusters and their respective binding energies is given in table I-1⁵⁵. Clusters range in size from the dimer to an aggregate composed of 10^5 species. The first experimental observation of

Table I-1. Classification of Clusters according to their average binding energies⁴⁵

Cluster Type	Prototypical case	Binding forces	Average Binding energy (eV)	Average Binding Energy (kcal/mol)
Van der Waals clusters	(Rare gases) _n (N ₂) _n , (CO ₂) _n	Dispersive plus weak electrostatic	≤ 0.3	≤ 6.9
Molecular Clusters	(I ₂) _n , organics	Dispersive, electrostatic (weak valence)	~ 0.3 to 1	~ 6.9 to 23.1
Hydrogen-bonded clusters	(H ₂) _n , (NH ₃) _n	H-bonding, electrostatic	~ 0.3 to 0.5	~ 6.9 to 11.5
Ionic clusters	(NaCl) _n	Ionic bonding	~ 2 to 4	~ 46.1 to 92.2
Valence clusters	C _n , S ₈	Conventional chemical bonds	~ 1 to 4	~ 23.1 to 92.2
Metallic clusters	Na _n , Cu _n	Metallic bonds	~ 0.5 to 3	~ 11.5 to 69.2

cluster formation in free jets was made by Becker *et al.*⁵⁶ when they expanded molecular hydrogen, argon and nitrogen through a nozzle and into a vacuum.

Experiments have been performed on van der Waals (vdW) clusters to study their structures, ionization mechanisms and stability as a function of cluster size. Clusters of xenon up to $n = 150$ were observed⁵⁷. Stephens *et al.*⁵⁸ observed helium clusters up to $n = 36$ in their mass spectra and Ding *et al.*⁵⁹ have taken mass spectra in which they observed clusters of neon up to $n = 90$ and argon up to $n = 300$. In these spectra, certain sized cluster ions exhibited exceptional stability relative to other clusters in the distribution. These stable species, called magic numbers, occur at $n = 13, 19$ and 55 and are attributed to structural stability. Although magic numbers have been observed in metal clusters, the stability has been attributed to shell closings (Fermi gas model) which occur at $n = 2, 8, 20, 40, 58$ and 92 ⁶⁰. However, in neutral vdW clusters, the electrons are not delocalized, as in metal clusters, and so a structural argument must be used to explain the stability of these magic numbers. The stability of the magic number at $n = 13$ and 19 are attributed to the formation of very symmetric and hence, stable, icosahedral and double icosahedral structures. The magic number at $n = 55$ corresponds to the second complete shell closing. Magic numbers at intermediate sizes, $n = 16, 23, 25, 29$ etc, correspond to partial shell closings that provide some stability to the cluster species. Magic numbers, due to structural stability, have also been observed in vdW molecular clusters such as H_2 ⁶¹, water⁶² and $ArNO$ ⁶³. Weakly bound clusters (vdW) have also been utilized to study metastable decay rates and the kinetics of fragmentation. These

metastable species, with lifetimes up to 200 μ s, have been studied using a variety of experimental techniques including time-of-flight mass spectrometry, single and double focusing sector field mass spectrometer and quadrupole mass spectrometry. The goal, in these experiments, is to examine the dispersion and subsequent disposal of energy in a molecule or cluster, upon ionization. Using these techniques, metastable reaction rates have been obtained for various species^{64,65}.

More strongly bound clusters, with ionic bonds, have been studied by Pflaum *et al.*⁶⁶ They investigated sodium halide cluster distributions and discovered that the $\text{Na}_{14}\text{X}_{13}^+$ peak, where X = Cl, Br, F and I, was especially stable. This stability was attributed to the formation of a cubic structure. Similar results were obtained by Martin *et al.*⁶⁷ in examining copper halide clusters in where the (14,13) cluster ion was very stable due to the formation of a cubic, rock salt structure.

Developments in laser vaporization and molecular beam techniques has made it possible to study many metal cluster systems. Early spectroscopic work was limited to the dimers of coinage metals (copper, silver and gold)⁶⁸ and to Cr_2 and Mo_2 ⁶⁹. More detailed work was performed by Morse *et al.*⁷⁰ in which they studied various transition metal clusters and assigned ground and excited states for dimers and trimers. Since then, both theoretical and experimental work on metal clusters has been performed quite extensively and their role in catalysis and surface chemistry is being further investigated⁷¹.

The most exciting development, in recent years, has been the discovery of C_{60} , also known as Buckminsterfullerene. In studying the stability of various species in a carbon plasma, it was discovered that sixty carbon atoms formed an especially stable cluster ion. Upon further study, the stability was attributed to the formation of a cage structure which has twelve pentagons and twenty hexagons⁷². The carbons are bound to each other in a sp^2 network. Clusters of carbon with up to 600 atoms have been observed and are members of the fullerene family. Experiments showed that C_{60} was able to trap various metal atoms, such as Cs, La, K and Y, inside the cage⁷³. This encapsulation causes the endohedral species to donate electrons to the lowest unoccupied molecular orbital (LUMO) of C_{60} and increase the electron affinity of the cluster significantly⁷⁴. This, in turn, has led to the study of conductivity and superconductivity in endohedral C_{60} . The ability to make macroscopic quantities of fullerenes⁷⁵ enabled scientists to study the physical and chemical properties of fullerenes to an extent that had been impossible before. Other stable and novel cage-like species have been observed by Castleman *et al.*⁷⁶ in which metal atoms bind strongly to carbon atoms in particular combinations. These clusters, referred to as “metcars”, form stoichiometric clusters of the form, $M_8C_{12}^+$ ($M = \text{Zr, Hf, Ti and V}$) and are believed to possess a dodecahedral structure⁷⁷.

Thesis Overview

In this thesis, multiphoton ionization, in conjunction with mass spectrometry, was used to investigate cluster distributions and the stability of certain species within them. Chapter II discusses the experimental setup and describes the methods which were used to obtain the data in this thesis. Chapter III examines the appearance of magic numbers in $(\text{NO})_m^+ (\text{Ar})_n$ clusters using 30 ps, 266 nm light and investigates photodissociation processes in the same clusters for $m > 1$ using 30 ps, 532 nm light. Chapter IV deals with the non-resonant 266 nm, MPI of binary, heterogeneous clusters of nitric oxide and various ligands, and the appearance of magic cluster *series* of the form $(\text{NO})_3^+ (\text{Y})_n$ where Y refers to the complexing agent. Chapter V presents vibronic spectra, using REMPI, of NO, ArNO, CH_4NO and CD_4NO . Chapter VI presents some observations of intracuster ion-molecule chemistry in carbon disulfide clusters.

Chapter II

Experimental

A schematic of the experimental layout used to obtain mass spectra of cluster distributions and to obtain REMPI spectra is shown in figure II-1. The setup consisted of a Nd:YAG laser that could be operated in either nanosecond or picosecond modes, a YAG pumped dye laser, a multistaged vacuum system with a linear time-of-flight (TOF) mass spectrometer and a digital oscilloscope that was connected to an IBM PC. For the cluster distribution experiments, the fourth harmonic (266 nm) of a picosecond, mode-locked Nd:YAG laser (Quantel YG571C) was directed through a sapphire window into a vacuum chamber, containing the front end of a TOF mass spectrometer. The laser beam was then focused with a 75 mm FL quartz lens, which was mounted within the vacuum chamber, into the interaction region established by the extraction and backing plates of the TOF. The laser was intersected, at 90°, in the interaction region by a supersonic molecular beam produced by a pulsed valve (R. M. Jordan Co.) which is described in detail elsewhere⁷⁸. The resulting photoions were extracted into the time-of-flight tube and detected by a microchannel plate assembly. The mass spectrum was recorded by a digitizing oscilloscope (Tektronix 11402) which allowed the mass spectra to be averaged over a selected number of laser shots. The spectra were stored and manipulated using an IBM PC. The individual components of the apparatus are described in more detail below.

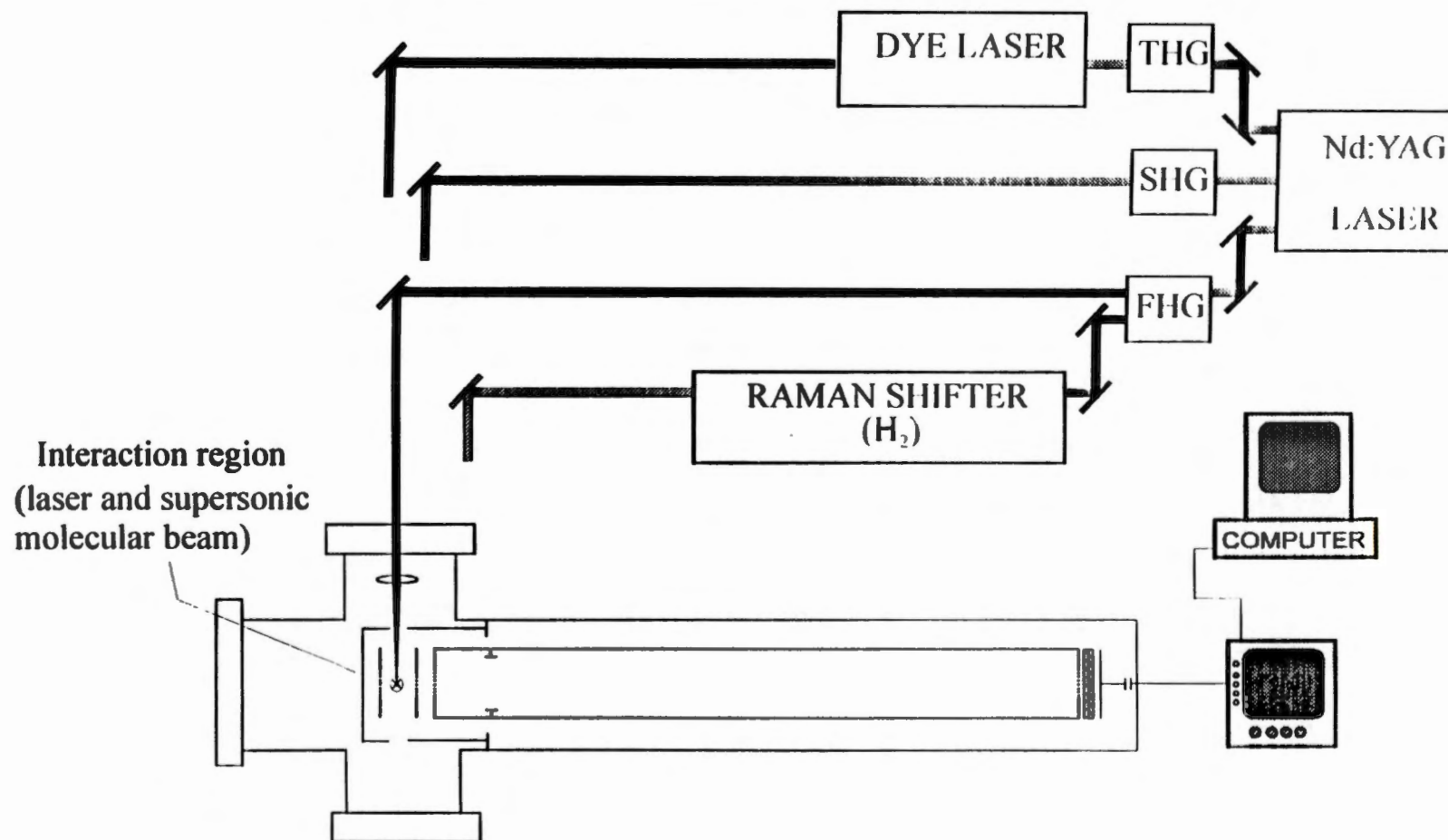


Figure II-1. Schematic of the experimental layout.

A schematic of the multistaged vacuum system incorporated in the apparatus is shown in figure II-2. The first stage consisted of a 6" six-way cross with entrance and exit windows, on two ports, for the laser light, a pulsed valve on the top port, a diffusion pump on the bottom port and a time-of-flight system on the other. The liquid nitrogen trap was attached to the 6" diffusion pump to minimize oil backstreaming and yielded a typical base pressure of $\sim 8 \times 10^{-8}$ torr. The TOF system was enclosed in a 4" stainless steel can which penetrated into the cross. The skimmer for the molecular beam was mounted on the outside of the can, directly above the interaction region. The discarded portion of the gas pulse was thus pumped away within the first stage. The stainless steel can had entrance and exit holes, which were 1 cm in diameter, for the laser light and 1 cm holes (perpendicular to the holes for the laser beam) for the molecular beam. The holes were designed to maximize the differential pumping between the diffusion pumped stage and the TOF assembly. The TOF assembly consisted of an interaction region, steering plates and a microchannel plate assembly. The TOF tube was 75 cm in length and 2.54 cm in diameter. The interaction region consisted of a backing plate (V_1), an extraction plate (V_2), and a plate at the front of the TOF (V_3), all of which were made of stainless steel and were 5.08 cm in diameter. All of the plates had a circular aperture with a diameter 0.953 cm and were covered with molybdenum mesh (150 lpi). The optimum experimental voltages for the backing plate, extraction plate and TOF tube were found to be 2360V, 1900V and ground, respectively. The deflection plate assembly, situated 10 cm from the interaction region, consisted of 4 square, stainless

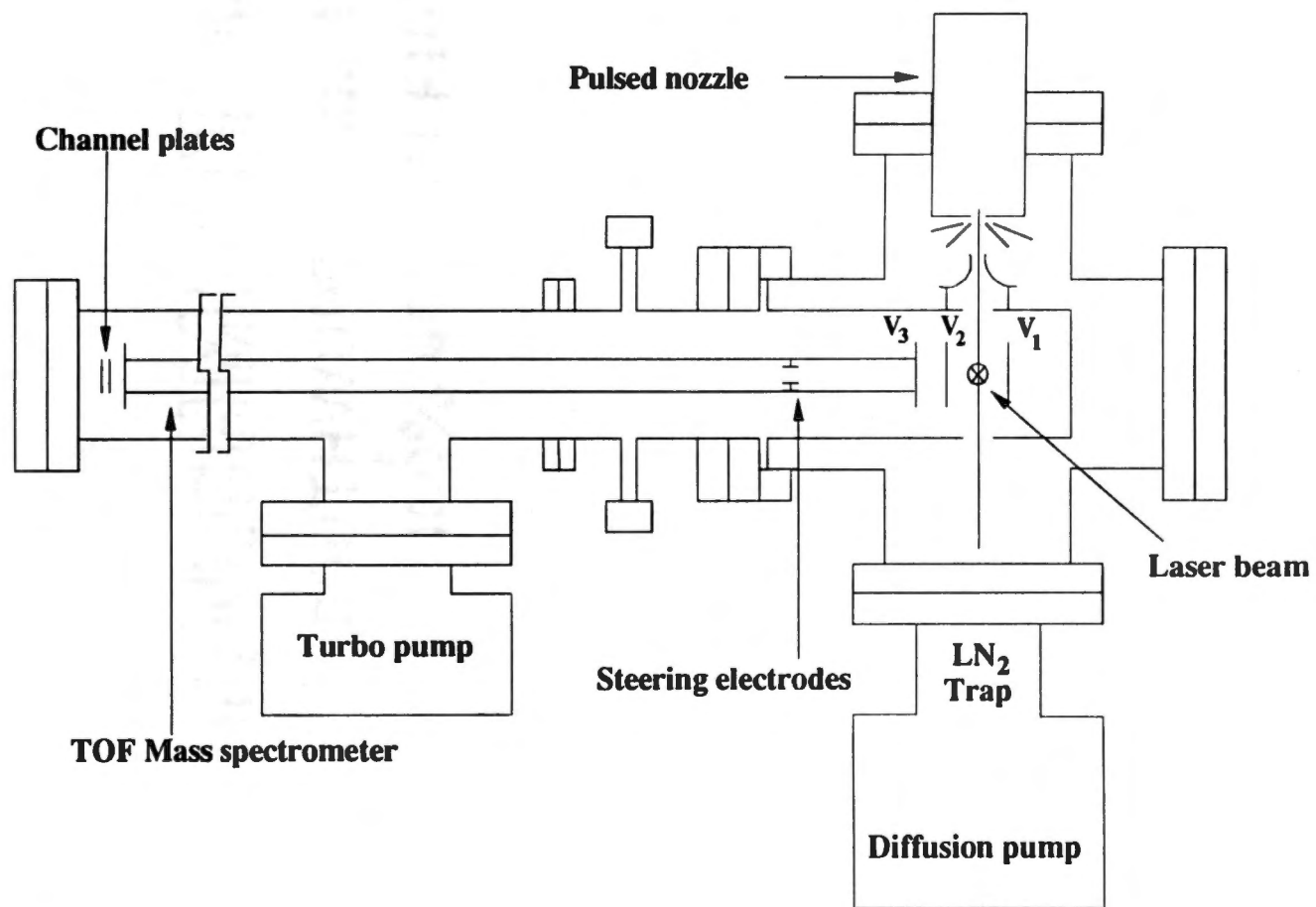


Figure V-2. Schematic of the vacuum chamber.

steel plates (designated top, bottom, left and right) which were 1cm on a side. The top, left and right plates were kept at ground potential while the bottom plate was kept at 100 V in order to compensate for the initial velocity of the molecular beam perpendicular to the TOF path. Approximately two-thirds of the way down the TOF tube, a six inch tee was connected to a 200 l/s turbomolecular pump (Varian V200) which was used to provide differential pumping for the system. This setup allowed the operating pressure in the TOF to be more than a factor of two smaller than in the diffusion pumped chamber. The operating pressure in the detector region was $\sim 3 \times 10^{-5}$ torr while that in the chamber was $\sim 1 \times 10^{-4}$ torr. The detector consisted of a secondary suppression grid, a dual microchannel plate assembly and an anode. The suppression grid was held at -2500 V while the front of the channel plates was biased to -2250 V. The design of the spectrometer is similar to that introduced by Wiley *et al.*⁷⁹. The mass spectrometer exhibited a mass resolution, $m/\Delta m = 300$, in the range of 1-2500 amu.

The pulsed valve had a nozzle of conical geometry and a diameter of 0.5 mm. The molecular beam passed through a 2 mm skimmer (Beam Dynamics) before arriving at the interaction region. The distance between the skimmer and the interaction region was fixed at 7.5 cm whereas the nozzle to interaction region distance could be varied between 10-17 cm. Backing pressures from a few hundred torr to 200 psi were employed depending on the gas composition and the degree of cooling desired.

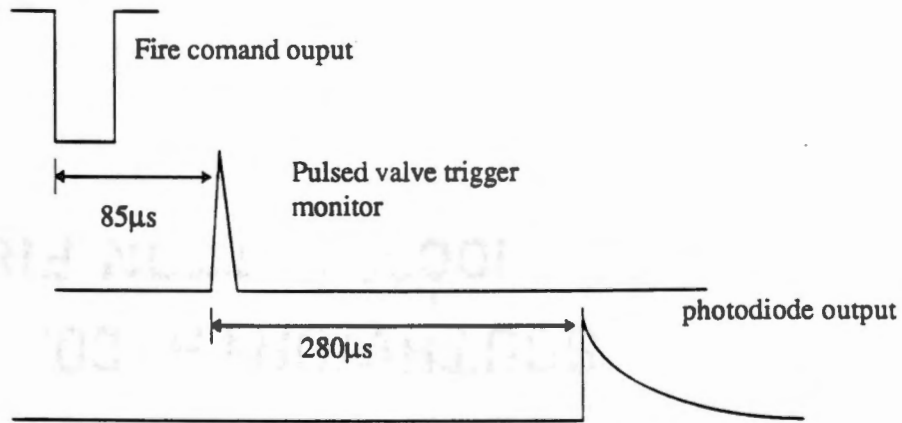
The laser system consisted of an Nd:YAG laser (Quantel YG571C), an H₂ Raman cell (Quanta Ray) and a dye laser (Lumonics HD 300). The Nd:YAG laser could

be operated in either nanosecond (Q-switched, 10 ns) or picosecond (mode-locked, 30 ps) modes. The pulse energies at 1064, 532, 355 and 266 nm, in the Q-switched mode were 1200 mJ, 500 mJ, 200 mJ and 90 mJ, respectively. In the mode-locked setup, the pulse energies at the same four wavelengths were 75 mJ, 30 mJ, 10 mJ and 4 mJ, respectively. In the picosecond mode, the peak powers, for 1064, 532, 355 and 266 nm, were 1×10^{14} , 6×10^{13} , 2×10^{13} and 8×10^{12} W/cm², respectively. These calculation assume a Gaussian, diffraction-limited beam and perfect focusing optics. The dye laser was of a commercial design and was used in conjunction with Exalite 384, Exalite 389, Exalite 416 and LD 390 dyes to obtain the vibronic spectra in chapter V.

The Raman cell was used to obtain the data in Chapter VI and consisted of a stainless steel cell with quartz windows on both ends. In order to perform the experiments, the cell was filled with hydrogen gas to a pressure of ~ 200 psi. The fourth harmonic of the YAG (266 nm) was directed into the cell and the various Stokes and Anti-Stokes lines were dispersed with a Pellin-Broca prism. The desired wavelength was then directed into the vacuum chamber. The wavelengths of choice were the first Anti-Stokes line at 239.53 nm (5.18 eV) and the first Stokes line at 299.05 nm (4.15 eV) which had pulse energies of 20 μ J and 60 μ J, respectively.

The timing events for the operation of the laser and the triggering of the nozzle with the laser operating in the nanosecond and picosecond modes are shown in figure II-3-3 (a) and (b). In the nanosecond mode, the timing sequence was initiated by the fire command from the laser control unit to the capacitor banks. This negative pulse was

(a) The timing diagram for the nanosecond mode (not drawn to scale)



(b). The timing diagram for the picosecond mode (not drawn to scale).

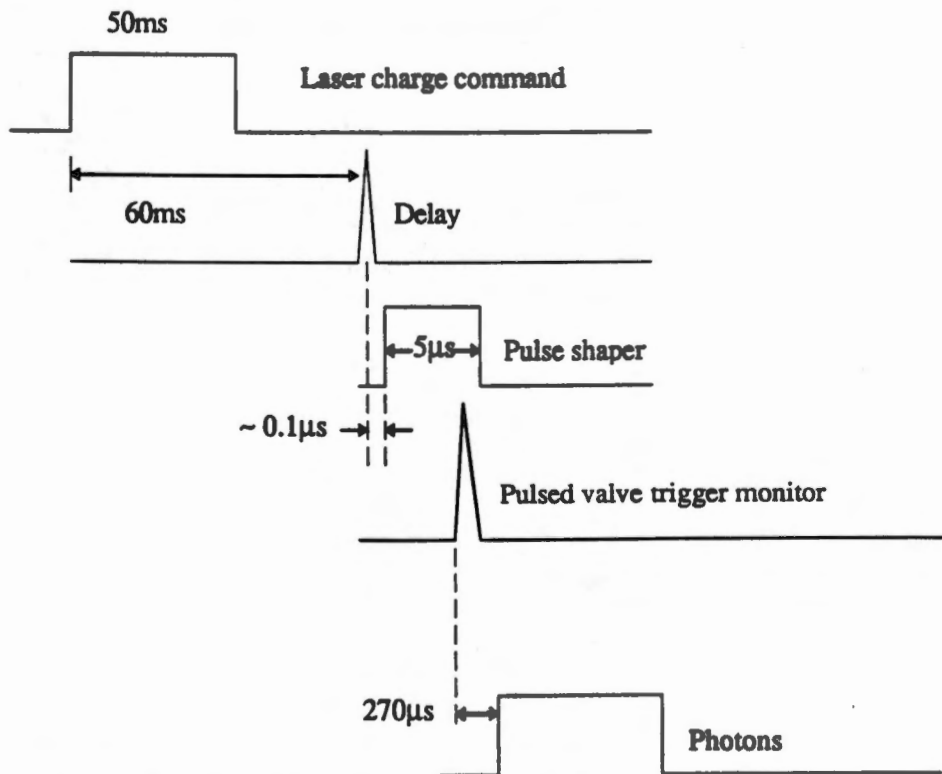


Figure II-3. Timing Diagram for both nanosecond and picosecond operation.

directed into a home-made voltage converter which produced a TTL pulse which was then used as an external trigger for the nozzle. The nozzle was further delayed ($\sim 85\mu\text{s}$) by the nozzle controller so that the arrival of the gas pulse at the interaction region coincided with the actual firing of the laser, which occurred $\sim 365\mu\text{s}$ after the fire command. The picosecond timing event is shown in figure II-3 (b) and was initiated by the charge command from the laser control unit to the capacitor banks. This 5V pulse was put through a delay generator and the resulting output was directed into a pulse shaper. The pulse shaper was necessary to create a 50% duty cycle pulse which was essential to run the laser properly. After the pulse shaper, the output was fed into the controller to externally trigger the pulsed valve. As in the nanosecond mode, the delay between the opening of the valve and firing of the laser could be varied through the nozzle controller.

Gases used in these experiments were either used without further purification (e.g. 1% NO/Ar) or a slush bath distilled or a liquid nitrogen controlled freeze-pump-thaw cycle was employed before making the mixed gas sample. Gas mixtures were prepared by condensing the individual components into a stainless steel mixing cylinder, which was immersed in liquid nitrogen. After all the components were trapped in the cylinder, the latter was valved off from the gas manifold and allowed to reach room temperature. The cylinder was then opened to the manifold and the gas mixture was allowed to expand through the pulsed valve.

Chapter III

MPI of $(\text{NO})_m(\text{Ar})_n$ Clusters

Introduction

The coupling of supersonic beams and mass spectrometry has enabled scientists to study many weakly-bound atomic and molecular clusters. Mass spectrometer based experiments have been used to provide information on the stability and fragmentation mechanisms of both neutral and ionic clusters. In studying cluster ion distributions, it was noted that certain-sized clusters exhibited enhancements in their intensities, with respect to neighboring peaks. These especially stable species were referred to as magic numbers and were first observed, experimentally, by Echt *et al.*^{80,81} in xenon clusters. Later experiments by Kriesle *et al.*⁸² investigated the dissociation rates of xenon clusters and found that local minima in these rates correlated with magic numbers in the distribution. Further evidence for magic numbers in rare gas systems was provided by Stephens *et al.*⁸³ who observed enhancements of certain peaks in cluster distributions of helium. Other rare gas systems such as Ar, Kr^{84,85,86} and Ne⁸⁷ also exhibit magic numbers in their cluster distributions. Magic numbers have been observed in metal cluster distributions⁸⁸ and have been explained by shell-closing arguments.

In the early stages of vdW cluster research, it was unknown whether the observed cluster ion distribution and magic numbers reflected neutral or ionic

characteristics. It was eventually determined that fragmentation processes played a major role during and after ionization. Furthermore, the geometrical configuration of the cluster was observed to change quite significantly, upon ionization, thereby releasing internal energy. This energy is then distributed into the vdW bonds causing the evaporation of weakly-bound species and leading to a time-dependent evolution of the cluster distribution⁸⁹. Therefore, the final ion distribution is a convolution of the neutral cluster distribution, size dependent ionization cross-sections and neutral and ion cluster fragmentation and decay rates. There have been attempts to relate neutral and ionic cluster distributions by modeling the direct ionization of the neutral and the subsequent evaporative decay of the cluster ions.^{90,91,92} The degree of fragmentation depends very strongly on the amount of excess energy that is deposited into the cluster. Magic cluster ions are formed by the fragmentation of larger cluster ions that remove the excess energy by the successive evaporation of monomers from the cluster. In certain cases, the dominant evaporative channel involves the ejection of a dimer. The apparent stability of a certain-sized cluster is a reflection of a barrier to further evaporation which may be derived from a variety of sources including, structural factors and electronic bonding patterns.

Clusters can provide important models for the study of the solvation of ions because they offer the unique capability of controlling the degree of solvation around an ionic core. In modeling solvation vdW clusters it was necessary to elucidate the structure of the cluster and the nature of bonding. Initial work focused on the solvation

of an atomic ion core by neutral species, such as Xe^+Ar_n ⁹³. Later experiments suggested that, in the case of certain clusters, the central specie was a dimer ion which led to the appearance of different magic numbers than those that satisfy the icosahedral model^{94,95,96,97}. Recently, it has been shown both theoretically^{98,99,100} and experimentally^{101,102,103,104} that, in the case of argon clusters, the core is a trimer ion for clusters with less than 15 units and a tetramer ion for clusters with greater than 15 units.

Magic numbers have also been observed in various molecular cluster ions such as $(\text{C}_6\text{H}_6)_m^+$ ¹⁰⁵ where magic numbers are observed with 14, 20, 24 etc units in the cluster. The core is considered to be a dimer ion of benzene. Other systems that exhibit magic numbers include dimethyl ether¹⁰⁶, cyclohexane and naphthalene¹⁰⁷, ammonia^{108,109}, various alcohols¹¹⁰ and clusters of argon ions solvated by various ligands^{111,112}.

This chapter describes the measurements of cluster ion distributions in which nitric oxide molecular ions were solvated by argon atoms to produce clusters of the form, $(\text{NO})_m^+(\text{Ar})_n$. The cluster ion distribution, produced by two-photon ionization with 266 nm light, was extensive, where $m \leq 4$ and $n \leq 22$. Intensity anomalies are observed at $m + n = 13$ and 19 for $m = 1$ and at $m + n = 19$ for $m = 2$. The reasons for this are explained later. The enhancements of the two cluster species (at 13 and 19) are explained in terms of magic numbers and the formation of exceptionally stable clusters with highly symmetric structures. Similar cluster distributions have been previously observed by Kung *et al.*¹¹³ who expanded mixtures of NO and argon through a nozzle

and irradiated the skimmed molecular beam with 381.5 nm light in order to ionize the sample (2+1) via the *C* state of NO. However, they did not discuss the intensity anomalies in their mass spectra. Magic numbers for $n = 13, 19$ and 55 have also been observed by Lezius *et al.*¹¹⁴ in $\text{NO}^+(\text{Ar})_n$ clusters. The authors produced the clusters by expanding neutral argon gas into a differentially pumped chamber which contained stagnant NO gas. The NO was ionized with an electron beam at varying energies. The magic numbers in the spectra were explained using icosahedral shell arguments. When clusters of NO/Ar were four-photon ionized using 532 nm light, the only cluster ions observed involved the solvation of a nitric oxide monomer ion by argon atoms. This distribution is discussed in terms of the photodissociation of larger clusters of nitric oxide. The same magic numbers were observed in this distribution as those obtained by ionizing with 266 nm light.

Results and Discussion

The time-of-flight (TOF) mass spectrum in fig III-1 was obtained by irradiating a supersonic molecular beam with 30 ps, 266 nm pulses. The molecular beam was obtained by expanding a 1% NO/Ar mixture at 100 psi backing pressure. The cluster ion distribution is quite extensive and is dominated by four cluster series, namely $(\text{NO})^+(\text{Ar})_n$, $(\text{NO})_2^+(\text{Ar})_n$, $(\text{NO})_3^+(\text{Ar})_n$ and $(\text{NO})_4^+(\text{Ar})_n$. The largest number of argon atoms solvating a nitric oxide (or a nitric oxide cluster ion) is 23. Experiments have

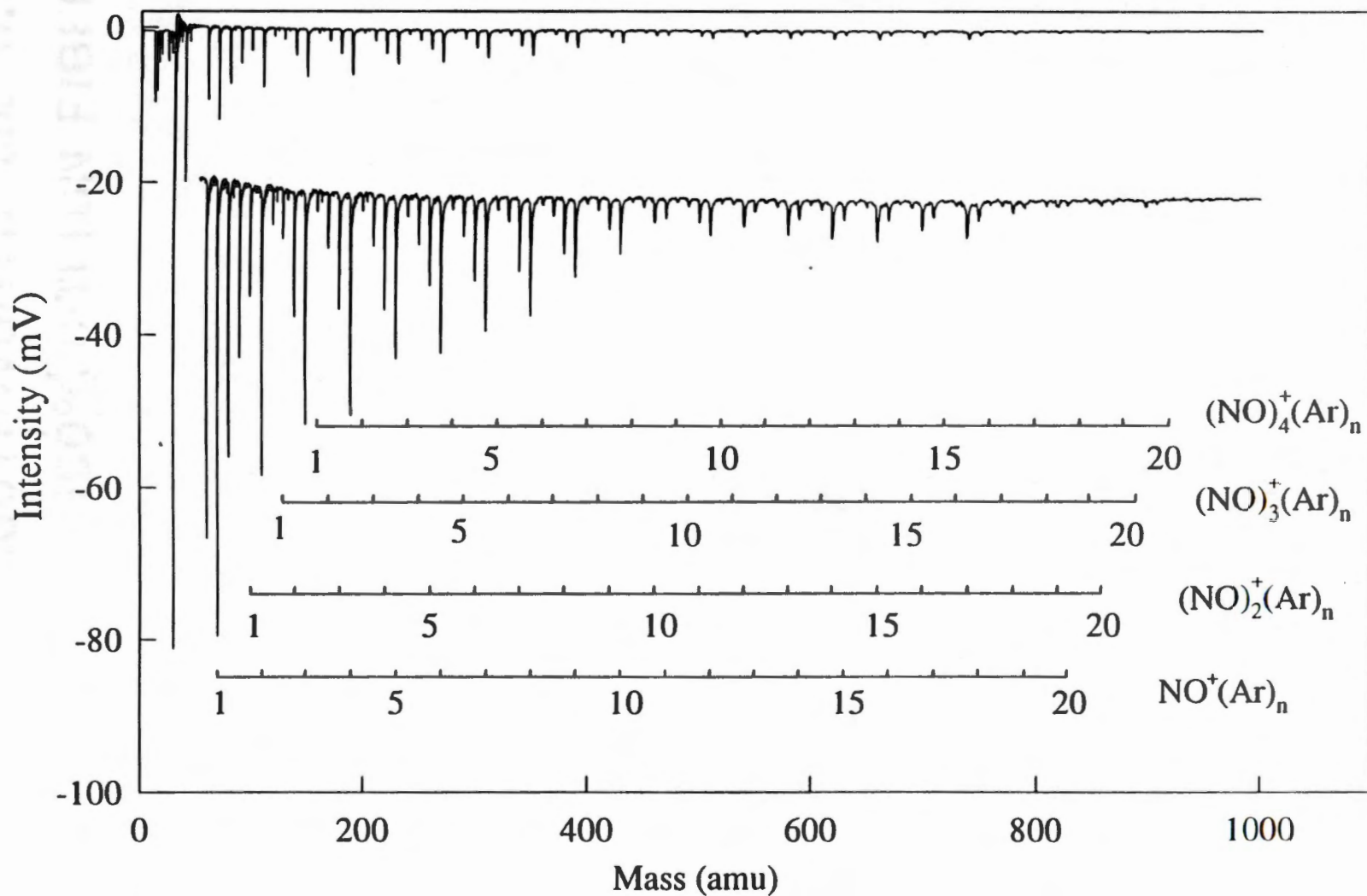


Figure III-1. The $(NO)_m^+(Ar)_n$ cluster distribution following two-photon ionization with 266 nm light.

been performed in which up to 45 argon atoms have been observed. The most intense peak in the spectrum is that of NO^+ which is followed by the Ar^+ ion, separated by 10 amu. The peak at 60 amu corresponds to the $(\text{NO})_2^+$ cluster after which the $(\text{NO})^+(\text{Ar})_n$ series begins with its first member, NO^+Ar , at 70 amu. The argon dimer, at 80 amu, is also observed in the mass spectrum. The tetramer, $(\text{NO})_4^+$ at 120 amu, is the largest pure nitric oxide cluster that is unambiguously observed. The four cluster series arrange themselves in a repeating pattern of quartets in which the total number of units within a cluster, of the form $(\text{NO})_m^+(\text{Ar})_n$, $m+n$ remains constant. The quartet begins with the smallest peak, corresponding to the cluster with the largest m , and progresses in 10 amu intervals to the largest peak which is due to $\text{NO}^+(\text{Ar})_n$. Figure III-2 shows an example of a particular quartet in which $m + n = 7$.

There are certain ambiguities that must be addressed in the assignment of clusters, containing four nitric oxide molecules. Since the mass of $(\text{NO})_4^+$ is very similar to that of $(\text{Ar})_3^+$ the two peaks would appear at the same time in the spectrum. The mass spectrometer that was used in these experiments did not have a sufficiently high resolution to distinguish the small mass difference between $(\text{NO})_4^+$ and $(\text{Ar})_3^+$. Experiments with ^{15}NO have shown that the nitric oxide tetramer and argon trimer are equal contributors to the peaks in question. However, at larger cluster sizes, the NO

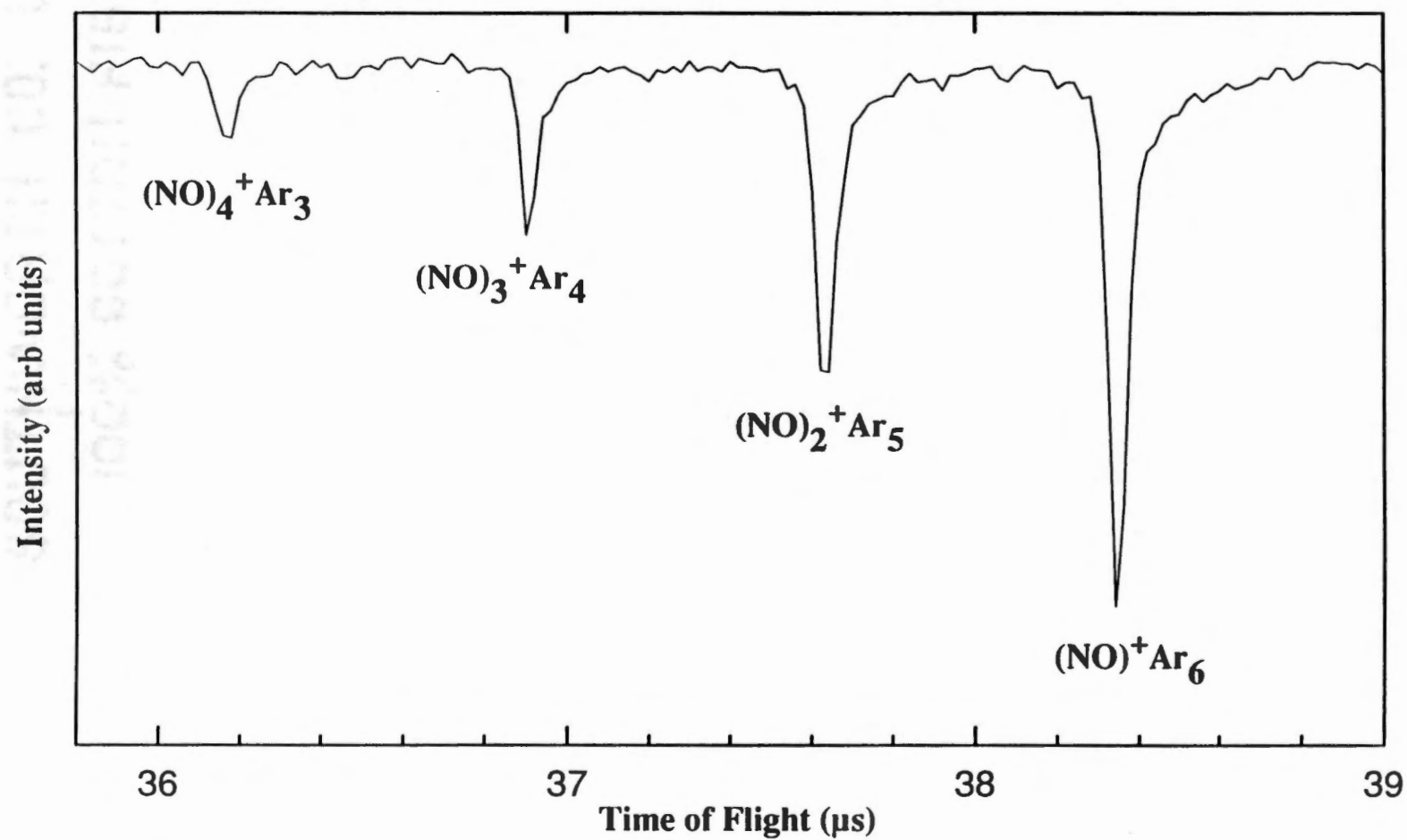


Figure III-2. Expanded portion of the spectrum in figure III-1 showing a particular quartet where the total number of species $m + n = 7$.

tetramer becomes the major fraction of the peaks. This is consistent with the ionization potential (IP) of NO, at 9.264 eV, being significantly lower than that of argon, at 15.759 eV. The IP's of both large argon and NO clusters are lower than the monomers. Therefore, the ionization of the NO tetramer would require only two photons, of 266 nm light (4.66 eV), as opposed to the argon trimer, which would require four photons. The TOF mass spectrum in figure III-3 shows a 1% $^{15}\text{NO}/\text{Ar}$ mixture that was ionized with a 30 ps, 266 nm pulse. The cluster distribution is very similar in extent and form to that in figure III-1. A vertically expanded section of a high mass region is shown in figure III-4 in which the $(\text{Ar})_{11}^+$ cluster ion is observed weakly. Furthermore, the mixed cluster peak, $(^{15}\text{NO})_4^+(\text{Ar})_8$ is shifted by four amu to higher mass. The $(^{15}\text{NO})_4^+(\text{Ar})_8$ peak is a factor of three more intense than the argon cluster ion peak. At even higher cluster sizes, the $(\text{NO})_4^+(\text{Ar})_n$ cluster ions are ten times more intense than the neighboring argon cluster ion. This proves that the larger cluster ions that had mass ambiguities in figure III-1. were due mainly to the $(\text{NO})_4^+(\text{Ar})_n$ series and not to the argon cluster ions. The mass spectra that are shown here were obtained by varying the voltages on steering plates at the front of the flight tube in order to optimize the observation of larger clusters while still allowing for the observation of lighter ones. The reason being that since all the clusters have a component of kinetic energy that is perpendicular to the TOF tube, the larger clusters require an additional "push" in the opposite direction to compensate for this kinetic energy. Failure to do so results in the observation of a severely curtailed

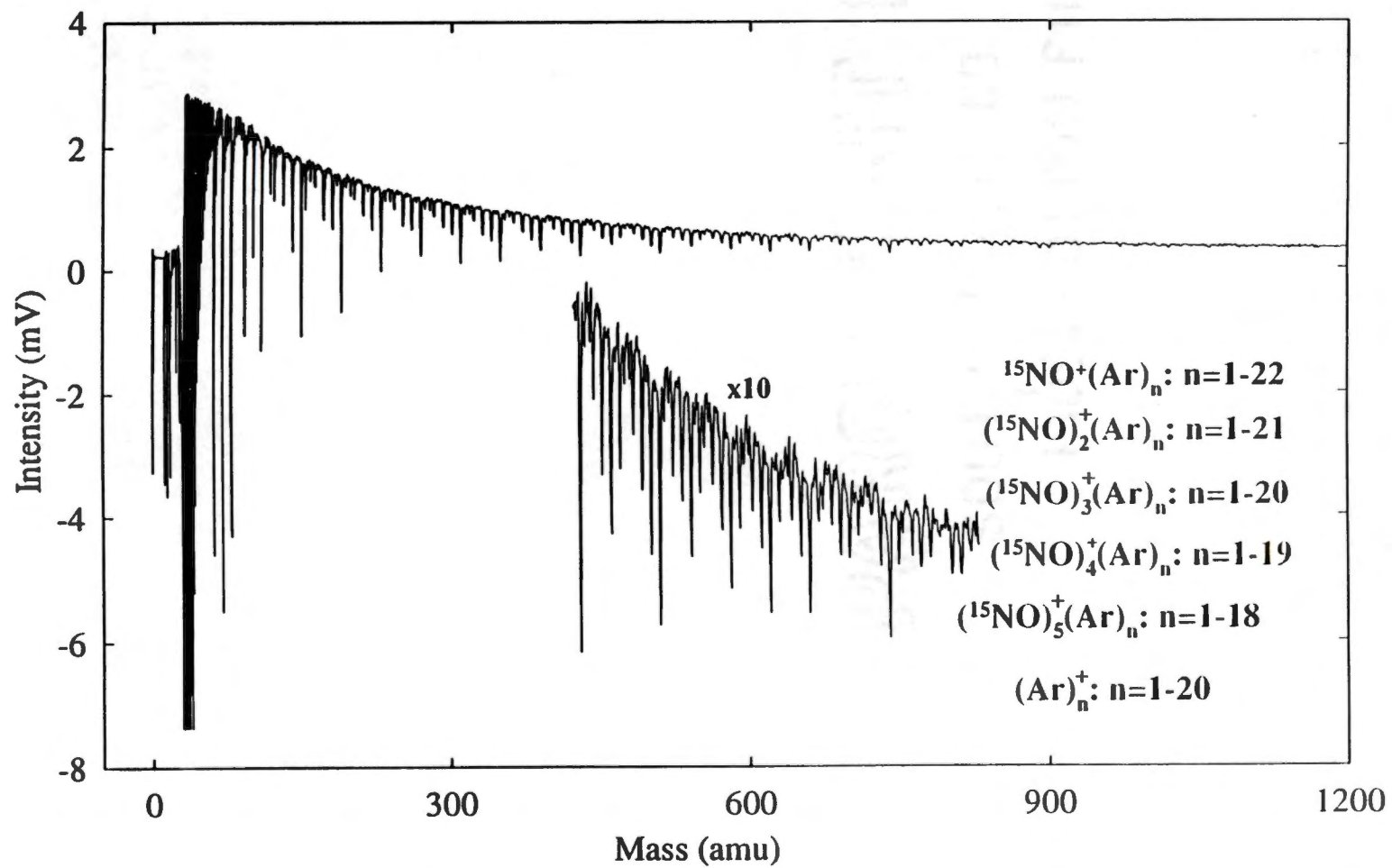


Figure III-3. The mass spectrum obtained by ionizing a 100 psi, 1% $^{15}\text{NO}/\text{Ar}$ expansion with 266 nm light.

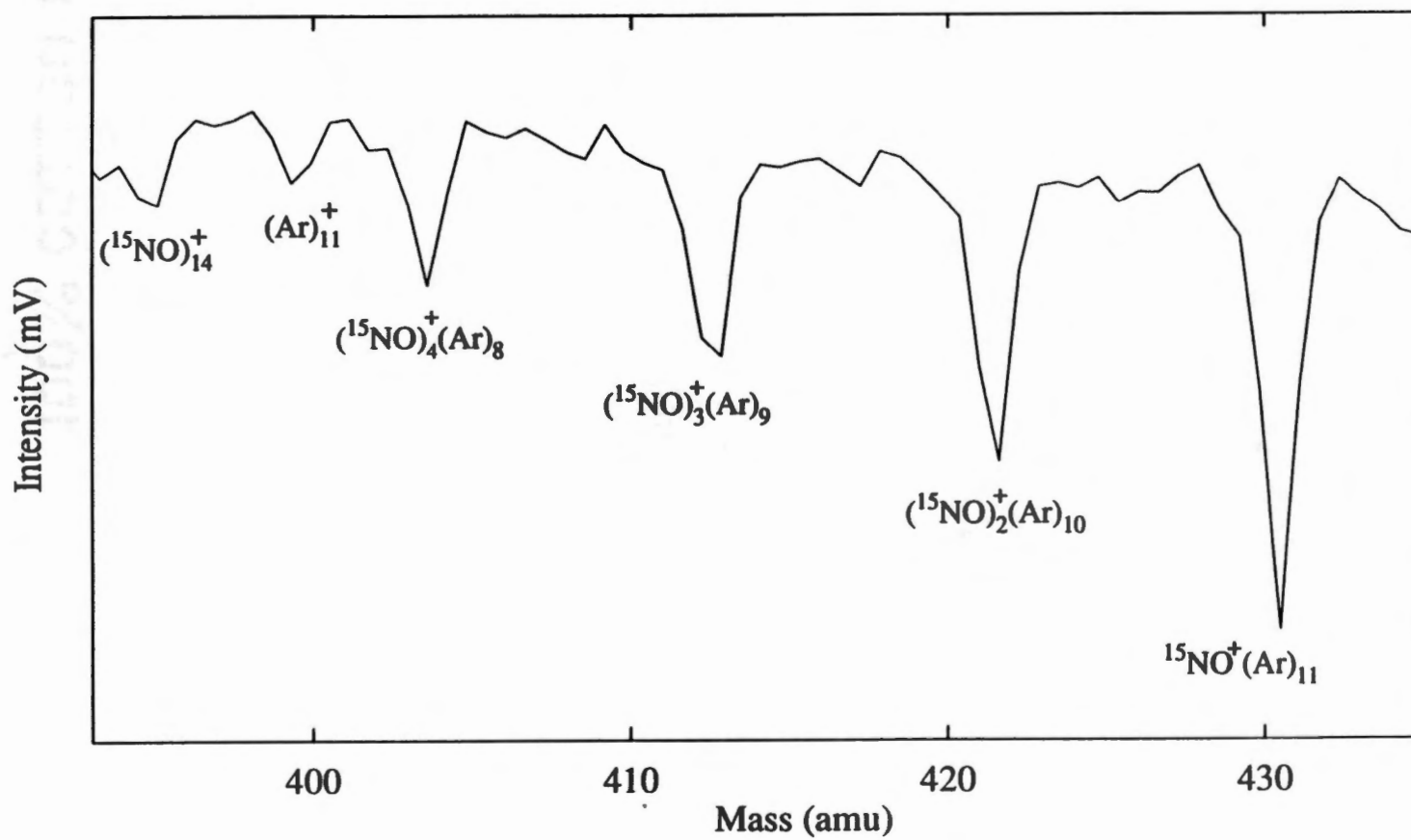


Figure III-4. Expanded portion of the high mass region of figure III-3.

cluster distribution in which the larger clusters are absent due to them hitting the sides of the TOF tube upon extraction.

The similarity in the mass of $(\text{NO})_4^+$ and $(\text{Ar})_3^+$ also causes ambiguities between mixed clusters e.g. $\text{NO}^+(\text{Ar})_5$ has the same mass as $(\text{NO})_5^+(\text{Ar})_2$ (at mass 230). However, within a particular quartet, the trend in intensity progresses from small to large as a function of m . That is, those peaks with greater numbers of nitric oxide molecules are lower in intensity than those with relatively fewer NO molecules. Therefore, any contributions from the $(\text{NO})_5^+(\text{Ar})_2$ to the peak at mass 230 are minor.

Excess Energy

The amount of excess energy that is deposited into a cluster, greatly affects the fragmentation rates and its final size. It was demonstrated that upon ionization, the formation of an ionic core, both atomic and polyatomic, releases a significant amount of internal energy⁹⁷. This energy is dissipated by the evaporation of neutral species which are bound to the core by vdW bonds. Furthermore, excess energy due to the interaction between the ion and induced dipoles is also released via evaporative processes. Table III-1 summarizes the known ionization potentials for nitric oxide¹¹⁵, nitric oxide clusters^{116,117,118} and ArNO ^{119,120}. Also given are the neutral and ion dissociation energies. It is evident, from the table, that the ion dissociation energies, for nitric oxide dimer, are significantly higher than their neutral counterparts. A consequence of this

TABLE III-1. Ionization and dissociation energies (eV) of nitric oxide clusters.

Species	Reference	IP	D_0^a	$D_0^{+ a}$	ΔE^b
NO	47	9.264	6.50	10.851	0.055
(NO) ₂	38,47	8.745	0.088	0.608	0.520
(NO) ₃	37	8.486	not known	----	----
(NO) ₄	37	8.39	not known	----	----
(NO) ₅	37	8.32	not known	----	----
(NO) ₆	37	8.28	not known	----	----
NOAr	40,41	9.159	0.0107	0.116	0.163

$$^a D_0^+ [(NO)_{n-1}^+ + NO] = IP[(NO)_{n-1}] - IP[(NO)_n] + D_0^0 [(NO)_{n-1} + NO]$$

$$^b \Delta E = 2 \times 4.66 - IP[(NO)_n].$$

phenomenon is that the two-dimensional potential well, along the N-N bond is much deeper in the case of the ion and hence, the internuclear distance is slightly shorter. Any transitions to this electronic state would then populate high vibrational levels which predissociate and cause the weakest bond within the cluster to break. The last column in table III-1 shows the excess energy that is left in the cluster after the absorption of two photons of 266 nm. This is graphically portrayed in figure III-5. From experimental studies it has been seen that the IP of nitric oxide clusters decreases as a function of increasing cluster size¹¹⁶. Furthermore, experiments to investigate fragmentation mechanisms as a function of electron energy, showed that for up to the pentamer, the preferred fragment is the nitric oxide monomer ion¹²¹. The fragmentation process in nitric oxide clusters occurs with the evaporation of neutral nitric oxide molecules, that are bound by purely vdW bonds. It is expected that the excess internal energy within NO/Ar clusters is dissipated by the evaporation of argon atoms because the NO⁺-NO bond is much stronger (0.598 eV) than the NO⁺-Ar bond (0.116 eV). The evaporation process proceeds until the remaining energy is insufficient to break the weakest bond in the cluster.

It is conceivable that most of the excess energy is carried off by the exiting electron but this is deemed highly unlikely as the Franck-Condon overlap leads to high vibrational excitation of the ion and hence, the excess energy is believed to reside in the ion. The dissociation process in the clusters is believed to be very rapid on the detection timescale as no broadening of cluster peaks is observed¹²².

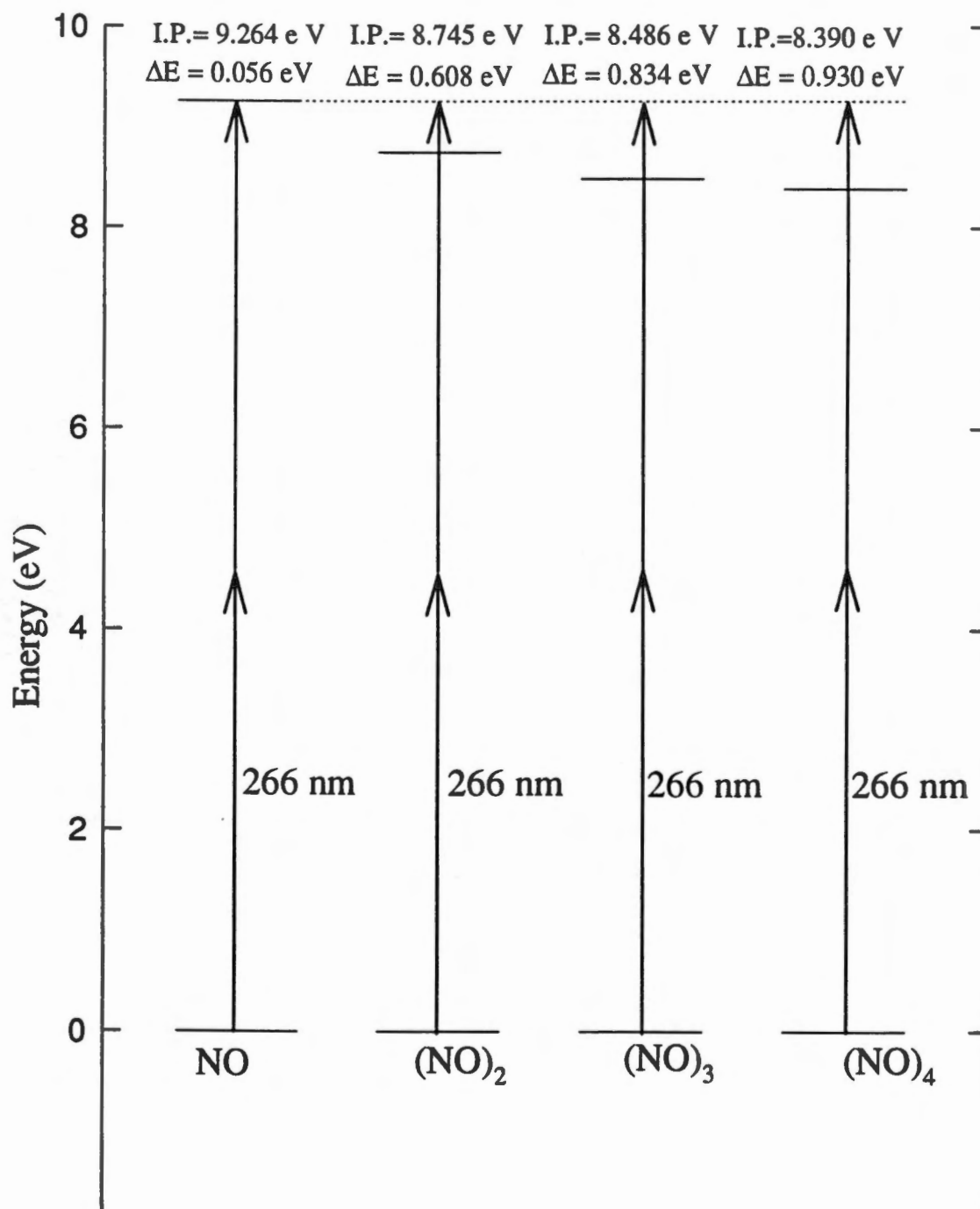


Figure III-5. Schematic energy level showing the two-photon ionization of $(\text{NO})_n$ ($n = 1-4$) clusters. The ionization potential and the maximum excess energy are also given.

Magic Numbers

Cluster ion distributions are known to reflect ion stabilities rather than neutral ones. Furthermore, the distribution is a convolution of neutral cluster number densities, size dependent ionization cross-sections, amount of excess energy deposited into the cluster and energy dependent evaporative processes. The appearance of magic numbers within a cluster distribution is largely due to the evaporation of neutral species from a cluster ion until a stable configuration is reached. This section will discuss the observation of these magic numbers in NO/Ar cluster distributions. Magic numbers are a result of the formation of especially stable structures and symmetric structures.

Figures III-6 (a) and III-6 (b) show expanded spectra of high mass regions of figure III-1. The magic number at $m + n = 13$ can be seen as an intensity enhancement of $\text{NO}^+(\text{Ar})_{12}$ relative to $\text{NO}^+(\text{Ar})_{11}$ and $\text{NO}^+(\text{Ar})_{13}$. Similar intensity enhancements are observed in figure III-6 (b), where the peaks corresponding to $\text{NO}^+(\text{Ar})_{18}$ and $(\text{NO})_2^+(\text{Ar})_{17}$ are especially stable relative to their $n-1$ or $n+1$ counterparts. In these clusters, the total number of units add up to 19. All of the magic numbers have been marked with an asterisk. Magic numbers are not observed for $(\text{NO})_2^+(\text{Ar})_{11}$ or for $(\text{NO})_3^+(\text{Ar})_{10}$ and $(\text{NO})_3^+(\text{Ar})_{16}$ or $(\text{NO})_4^+(\text{Ar})_9$ and for $(\text{NO})_4^+(\text{Ar})_{12}$ even though the total number of units within the cluster add up to a 13 and 19. As will be discussed in subsequent paragraphs, the absence of stable structures for these species is due to the large size of the ion core which distorts the icosahedral symmetry of the cluster. Figure III-7 shows

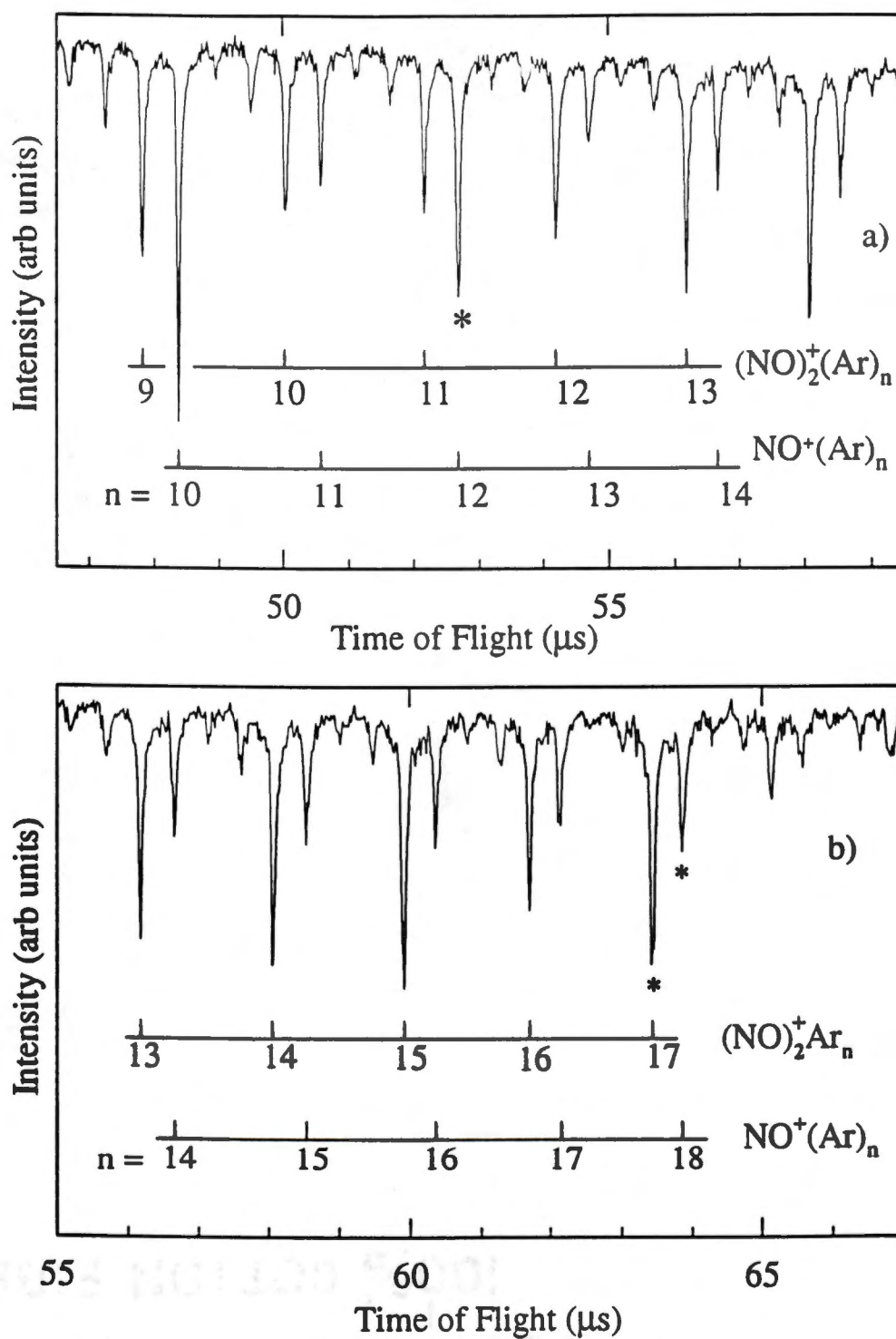


Figure III-6. Expanded portions of the mass spectrum in figure III-1 for the region surrounding the "magic" numbers with (a) $(m+n)=13$ and (b) $(m+n)=19$.

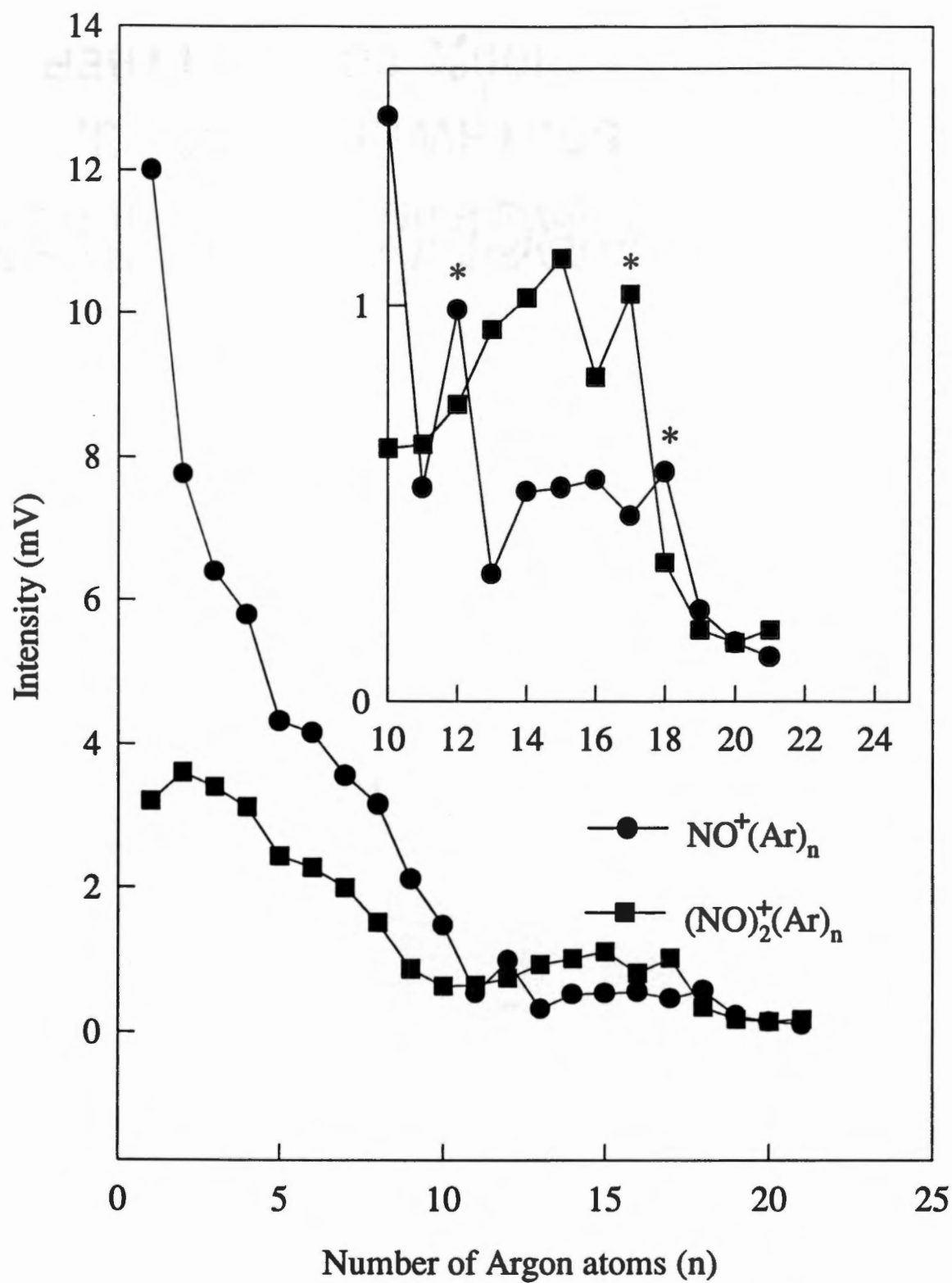
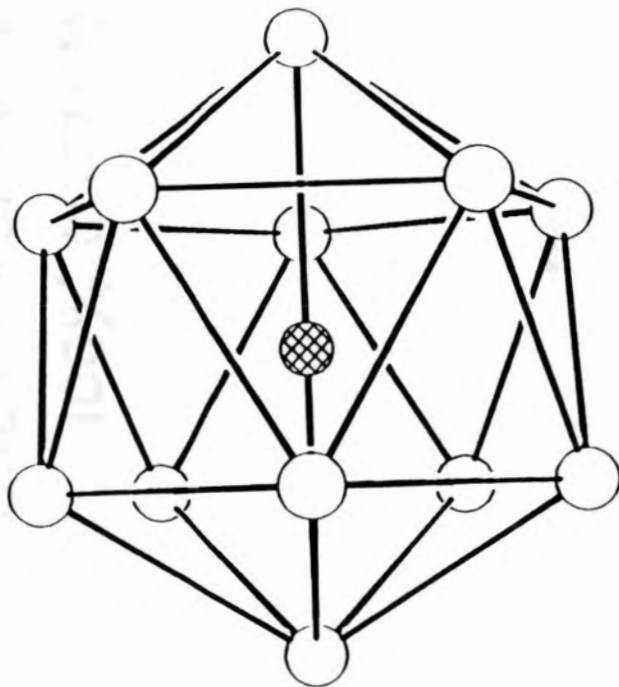


Fig III-7. The intensity distribution of $\text{NO}^+(\text{Ar})_n$ and $(\text{NO})_2^+(\text{Ar})_n$ ions as a function of n . In the insert the "magic" cluster ions are indicated with an asterisk.

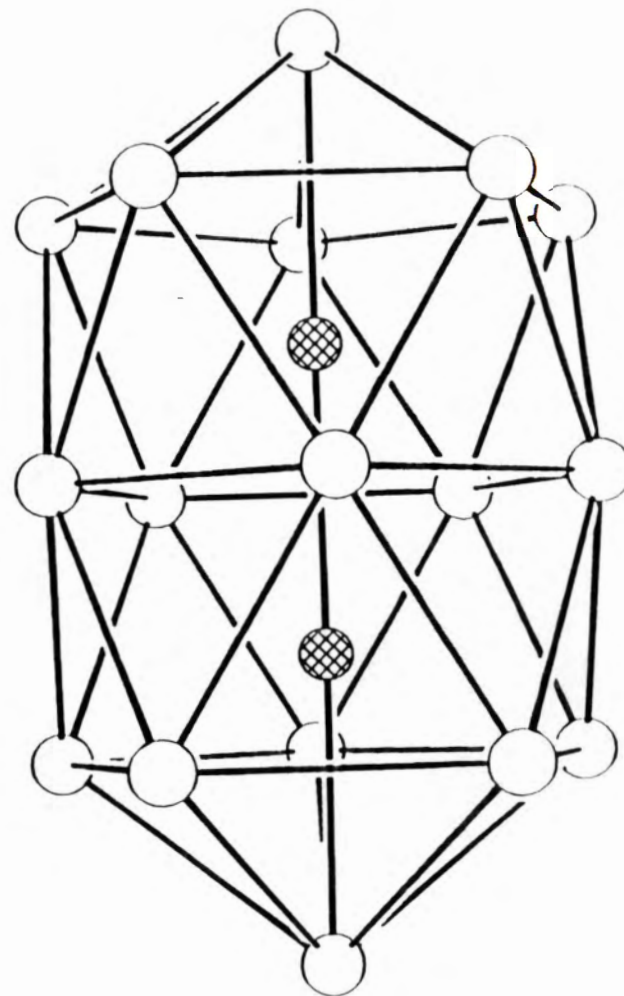
the intensity of the cluster distribution as a function of size. The inset focuses on the two regions that were discussed above. As was noted before, the spectrum in figure III-6 (a) shows the increasing intensity of a cluster, with decreasing m , in a particular quartet. However, this trend does not continue after $\text{NO}^+(\text{Ar})_{12}$. Instead, $(\text{NO})_2^+(\text{Ar})_n$ peaks are observed to dominate the rest of the spectrum. This is explained by the increasing stability of the dimer solvated cluster ions and to the stability of the $\text{NO}^+(\text{Ar})_{12}$ peak towards dissociation.

Magic numbers at $n = 13$ and 19 have been observed not only in homogeneous rare-gas clusters^{80,81,82,84,85,92} such as xenon and argon but also in mixed clusters^{89,93,94,111}. Experiments by numerous groups have shown that $n = 14$ is especially stable in cluster distributions of Ar and Kr⁸⁴, and Ne⁸⁷. This stability has been explained by assuming a dimeric core model for the cluster of the form $\text{Ar}_2^+(\text{Ar})_{12}$. Experiments where $n = 13$ was observed were rationalized by using a "trimeric core" model in which the diatomics-in-molecules method (DIM) was employed to obtain stable structures for a linear trimer ion core solvated by neutral species^{98,104}.

The magic numbers for $(\text{NO})_m^+(\text{Ar})_n$ clusters with $m + n = 13$ and 19 are attributed to geometrical factors, namely the formation of an icosahedron and double icosahedron structures. These structures which have been theoretically treated, maximize the number of ion-neutral and neutral-neutral interactions⁹³. The structures in figure III-8 show the structures responsible for the stability of the aforementioned cluster



ICOSAHEDRON



DOUBLE ICOSAHEDRON

Figure III-8. Potential "magic" structures for $(m + n = 13)$ (icosahedron) and $(m + n = 19)$ (double icosahedron)

species. The single site in the icosahedral structure could accommodate an NO^+ with the solvation shell consisting of argon atoms. The lack of a magic number for the $(\text{NO})_2^+$ $(\text{Ar})_{11}$ cluster is due to the size of the nitric oxide dimer ion which would destabilize the ion-induced dipole interactions and destroy the symmetric nature of the icosahedral structure. The double icosahedron, on the other hand, has two sites which could be occupied by the nitric oxide dimer ion or in the case of the $\text{NO}^+(\text{Ar})_{18}$ cluster, the two sites could be occupied by a nitric oxide ion and an argon atom. It has been suggested by Stace⁹⁴ that in the case of Ar_nI^+ clusters, the $n = 18$ species does not form an icosahedron but instead forms a face-centered-cubic structure. This is due to the ion core being atomic and not dimeric. The similarity in the polarizabilities of Ar and NO and in the internuclear distances, 3.76 Å and 3.71 Å, respectively, would suggest that there is no preference for either the argon or NO as the core species. Indeed, in the neutral cluster distribution, the magic number at $n = 19$ may be in the form, $\text{NO}\cdot\text{NOAr}_{17}$ with one or both of the nitric oxide molecules on the solvation shell. However, in the case of the ion, the charge is believed to be localized on the $(\text{NO})_2^+$ ion which is then solvated by argon atoms. The degree of localization is highly dependent on the IP of the moieties involved in the cluster. This was demonstrated by Ozaki *et al.*¹¹¹ who argued that the species with the lower IP would have the charge localized on it. In the case of $(\text{NO})_m^+$ $(\text{Ar})_n$ clusters, both the nitric oxide monomer and dimer have lower IP's than argon and

so are expected to reside at the core of the cluster as ions. The addition of non-spherical solvent molecules around an ion core, as in Ar_ℓX^+ , where $\text{X}^+ = \text{N}_2, \text{Xe}, \text{CO}_2$ and CH_3OH also produces magic numbers at $\ell=13, 19$ and 55^{111} . This is despite the fact that the difference in geometric shapes between the different ions cause the interaction potentials between these ions and argon to be different from one another.

The effect that the size of the core ion has on magic numbers is also observed by Stace¹⁰⁶ in clusters of argon and dimethyl ether. Intensity enhancements were observed for both $\text{Ar}_{12}\cdot\text{CHO}^+$ and $\text{Ar}_{18}\cdot\text{CHO}^+$ and these were attributed to the formation of an icosahedral structure in which an atomic oxygen cation sits at the center of the icosahedron and the hydrocarbon part, which is linear, juts out from the body of the cluster. In the case of $\text{Ar}_n\cdot(\text{CH}_3)_2\text{O}^+$ and $\text{Ar}_n\cdot\text{CH}_3\text{OCH}_2^+$, the large size of the methyl and methylene groups distort the symmetry of the icosahedron and double icosahedron structures and hence, magic numbers for $n = 18$ are not observed.

It is possible to compare the present results with those obtained by Kung *et al.*¹¹³ and Lezius *et al.*¹¹⁴, both of whom observed clusters of the form $(\text{NO})_m^+(\text{Ar})_n$ using the ion seed technique. In both cases the nitric oxide was ionized by electron impact and then mixed with argon to facilitate the formation of the mixed clusters. The magic numbers that are observed in their mass spectra are identical to those observed in our experiments. This suggests that the formation of these clusters is not dependent on the method of ionization. In contrast, different magic numbers are observed for pure argon

clusters depending on the type of ion core that is produced. An argon dimer ion core leads to extra stability for $n = 14, 16, 19, 21, 23$ and 27 while a trimeric ion core produces the $n = 13, 16, 19, 23$ and 27 magic numbers⁹⁹. Kung *et al.*¹¹³ observed a more extensive spectra than those displayed in this chapter in which they were able to make $(\text{NO})_m^+ (\text{Ar})_n$ clusters with larger numbers of nitric oxide partners ($m \leq 15$).

Photodissociation of $(\text{NO})_m^+ (\text{Ar})_n$ clusters

If a 1% NO/Ar mixture is irradiated with 532 nm light, a dramatically different cluster distribution is observed. Figure III-9 shows a mass spectrum taken under these conditions and the most striking feature is that only the $\text{NO}^+(\text{Ar})_n$ series is observed. The clusters that have more than one nitric oxide molecule have been photodissociated. However, those magic numbers observed in 266 nm case, for NO^+Ar_n , are also produced in figure III-9 and are labeled with an asterisk ($n = 13, 19$ and 23). Conditions have been found where the cluster corresponding to the formation of a second complete solvation shell, $\text{NO}^+(\text{Ar})_{54}$, has been observed to be magic. The process of photodissociation is an interesting one in spectroscopy because it provides information about the energy, shapes and symmetries of excited potential surfaces¹²³.

The clusters with more than one nitric oxide could be photodissociated by transitions in the neutral or ionic manifold of electronic states. The energy level diagram in figure III-10. shows that it would require at least four photons, at 532 nm, to ionize

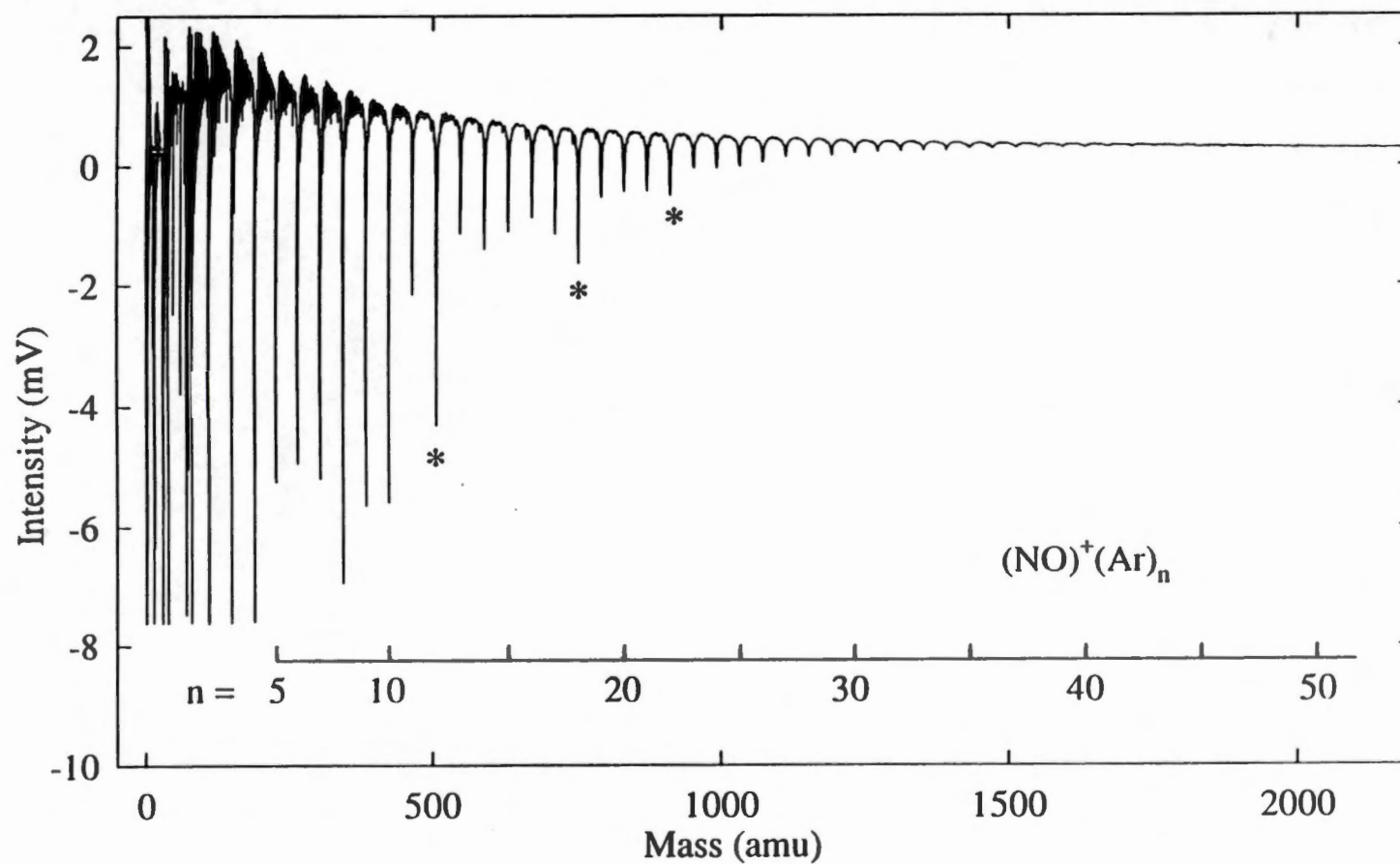


Figure III-9. Mass spectrum showing the $\text{NO}+(\text{Ar})_n$ cluster ion distribution produced by 532 nm MPI and the photodissociation of $(\text{NO})_m^+(\text{Ar})_n$ clusters with $m > 1$.

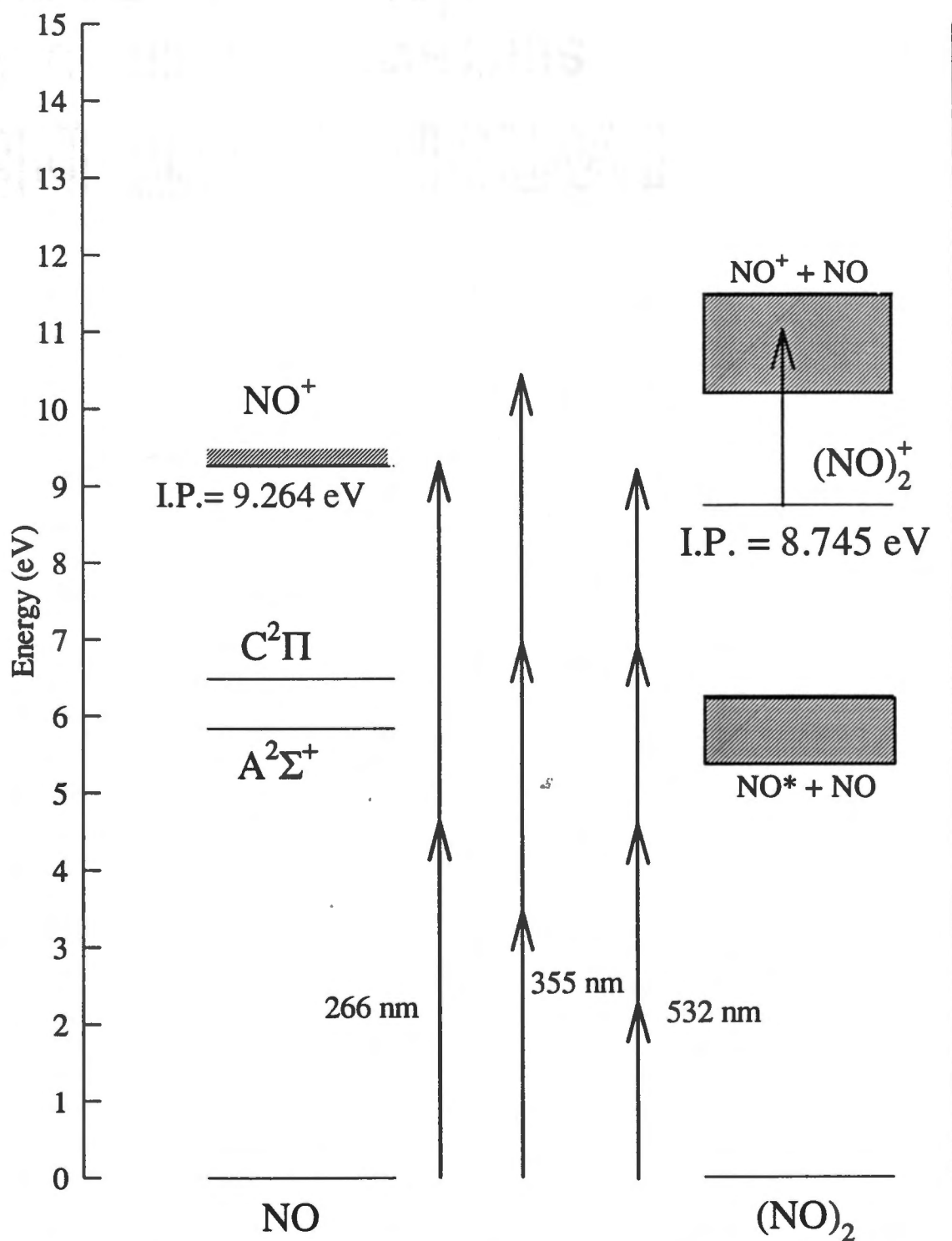


Figure III-10. Energy level diagram showing the MPI of NO and (NO)₂ with 266 nm, 355 nm and 532 nm light. Dissociative resonances of the dimer neutral and its ion are shown.

any $(\text{NO})_2$ clusters. The first and third photons access energies that are not probed by 266 nm while the second photon falls short of the known dissociative channel of NO dimer into $\text{NO}^* + \text{NO}$ ¹²⁴. The laser being used in these experiments has a 20 ps pulse width and even when it is specifically tuned to the dissociative resonance, at 217.8 nm, complete dissociation is not observed because the peak power of the short pulse is sufficient to cause the molecule to absorb an additional photon and become ionized¹²⁵. Therefore, the photodissociation of the NO dimer must be occurring in the ion where it absorbs four photons (see figure III-10) to ionize, leaving it with some excess energy. After the dimer ion relaxes to its ground state, a fifth photon is absorbed which then accesses the known ion dissociative state for $(\text{NO})_2^+$. Furthermore, two photons of 355 nm light and three photons of 532 nm light access the same absorption in the neutral manifold of the dimer and, therefore, if the dissociation was occurring in the neutral, the mass spectra obtained at these wavelengths should be identical. However, the 355 nm light produces a cluster distribution that is intermediate between those obtained by 266 nm and 532 nm.

Experiments performed by Jarrold *et al.*¹²⁶ have investigated the dynamics of photodissociation for both the $(\text{NO})_2^+$ and $(\text{NO})_3^+$ and have found that both species have dissociative absorptions over a wide wavelength range (488-660 nm). The dissociation process strongly depends on the amount of internal energy that the clusters possess upon ionization. Photoelectron spectroscopy¹²⁷ and ZEKE¹¹⁸ have shown that the Franck-

Condon factors limit the amount of vibrational excitation in the NO dimer ion to a few quanta in a low frequency torsional bend and the NO symmetric stretch. These data are consistent with our observation of mixed clusters with a large number of nitric oxide molecules with 266 nm light. The observation of intermediate cluster distributions, when using 355 nm, suggests that the dissociation process at this wavelength is less efficient than at 532 nm.

Chapter IV

Laser Ionization of Homogeneous and Binary Molecular Clusters of Nitric Oxide

Introduction

Nitric oxide (NO) is a simple molecule which is quite prevalent in nature. Together with other nitrogen oxides, N_yO_z , it plays an important role in atmospheric processes such as the formation of photochemical smog, acid rain and it is partly responsible for the depletion of the ozone layer in the upper atmosphere¹²⁸. Nitric oxide has also been discovered in various types of cells in the body including the liver, brain and pancreas¹²⁹ and is known to play an active role as a neurotransmitter, as a vasodilator and it is partly responsible for causing various neurodegenerative diseases¹³⁰. The importance of the molecule in a variety of areas led to its naming as the “Molecule of the Year” in Science magazine for 1992¹³¹.

In studying NO, it is important to recognize that it is rarely found in its isolated form, due to its relatively short lifetime in air (≤ 6 s). In the upper atmosphere, nitric oxide is thought to cluster with other atmospheric gases. Upon ionization these clusters are expected to be in the form of an NO^+ ion core around which various solvating atoms and molecules can arrange themselves in aggregates. In these clusters the nitric oxide molecule is expected to be preferentially ionized because it has a relatively lower IP (9.26 eV) than other atmospheric gases such as CO_2 (13.78 eV), NO_2 (9.75 eV) and

N_2O (12.87 eV). One of the most important application of this phenomenon is the hydration of the nitric oxide cation to form $\text{NO}^+(\text{H}_2\text{O})_n$ ions, hydronium ions and nitrous acid. These species are important in the understanding of chemical processes that occur in the ionosphere and also in the stratospheric depletion of ozone. The solvation of nitric oxide with various species can help to elucidate not only the more fundamental properties of $(\text{NO})_m(\text{Y})_n$ species but can also serve as a starting point for understanding the solution phase chemistry and biochemistry of nitric oxide and nitric oxide containing species.

Nitric oxide is a convenient molecule to study in the gas phase because it is simple, has a low ionization potential (IP) (9.264 eV) and yields a stable cation which is a useful core for solvation. The ability to study solvation processes with nitric oxide is made possible by the fact that when a heterogeneous cluster is ionized, the charge is usually localized on the species with the lower IP. Since all of the binary partners investigated in this chapter have higher IP's than NO, the presence of the latter eases the interpretation of the structures of the mixed cluster. Due to its relatively low IP, NO can be used as a spectroscopic tag for a variety of ionic clusters. In this chapter, data are presented that reveal particularly stable cluster configurations when nitric oxide is solvated by a variety of molecules namely, CO_2 , N_2O , NO_2 , SO_2 , H_2O , CS_2 and SF_6 .

In this chapter, the use of 266 nm light to ionize $(\text{NO})_n$ and $(\text{NO})_m(\text{Y})_n$ clusters proves to be fortuitous because two-photon ionization of nitric oxide at this wavelength

exceeds its IP by only 55 meV. This greatly reduces the amount of excess energy that must be dissipated by the cluster. It is expected, however, that the IP's of $(\text{NO})_m(\text{Y})_n$ clusters are lower than that of NO.

Results and Discussion

Pure Nitric Oxide Clusters

It has been previously observed¹³² that nitric oxide readily clusters with most rare gases. Experiments performed in this lab, where NO is coexpanded with argon, have produced clusters of the form $(\text{NO})_m^+$ and $(\text{NO})_m^+(\text{Ar})_n$ where $m \leq 8$ and $n \leq 54$. Argon is seen to be the most efficient carrier gas in producing cold supersonic expansions of NO because of its mass similarity. In general, clustering releases energy in the form of the heat of condensation which greatly affects the temperature of the cluster, the rates of further condensation and evaporation and consequently, the observed cluster distribution. This can be observed in the evaporation processes from weakly bound clusters such as NO-Ar ($D_0^\circ = 89 \text{ cm}^{-1}$)¹³³ and $(\text{NO})_2$ ($D_0^\circ = 710 \text{ cm}^{-1}$)¹³⁴. One needs to be careful in choosing the concentration of the dopant because the greater the concentration of nitric oxide, the greater the collision frequency between two molecules and the higher the terminal beam temperature.

In chapter III, it was demonstrated that a relatively dilute mixture of NO and argon (~1% NO/Ar) resulted in a cluster distribution that was dominated by the $(\text{NO})_m^+$ $(\text{Ar})_n$ species. In this chapter, experiments performed at a higher concentration of nitric oxide lead to a dramatically different cluster distribution composed almost entirely of pure nitric oxide clusters, $(\text{NO})_m^+$. Peaks identified as due to $(\text{NO})_m^+$ $(\text{NO}_2)_n$ and $(\text{NO})_m^+$ $(\text{N}_2\text{O})_n$ are also observed in the mass spectrum and are attributed to naturally occurring impurities in the gas cylinder. These impurities could be reduced by passing the gas mixture through a cold trap that was immersed in a slush bath of isopentane and liquid nitrogen (~ -135 °C). Such binary clusters are interesting in their own right and will be discussed later in the chapter.

Figure IV-1 shows the low mass region of the time-of-flight mass spectrum produced by ionizing an expansion of a 100 psi, 5% NO/Ar mixture with 30 ps pulses of 266 nm light. There are two striking features in this mass spectrum that must be addressed. First, the odd $(\text{NO})_m^+$ ions are more intense than their even counterparts. This odd-even effect is seen weakly for $m < 8$ but becomes stronger thereafter. Second, after $m = 19$ *only* the odd $(\text{NO})_m^+$ cluster ions are observed, as is seen in figure IV-2. The intensity of $(\text{NO})_m^+$, as a function of m , is displayed in figure IV-3. Similar odd-even alternations have been observed in $(\text{NO})_m^+$ clusters by Kung *et al.*¹³⁵ who

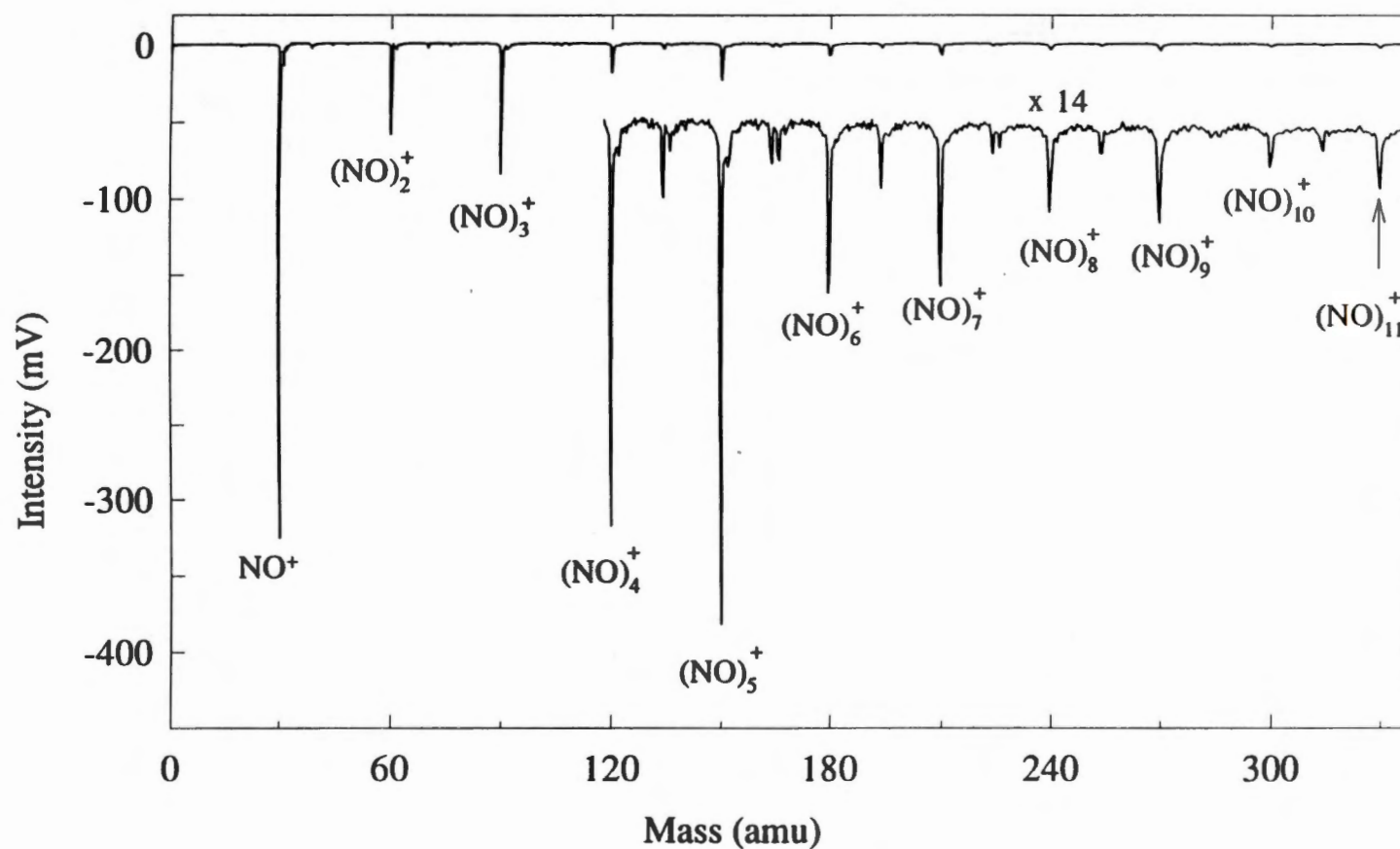


Figure IV-1. The low mass region of a 266 nm MPI mass spectrum produced by a 5% NO in argon expansion showing odd-even alternation in the $(\text{NO})_m^+$ cluster distribution.

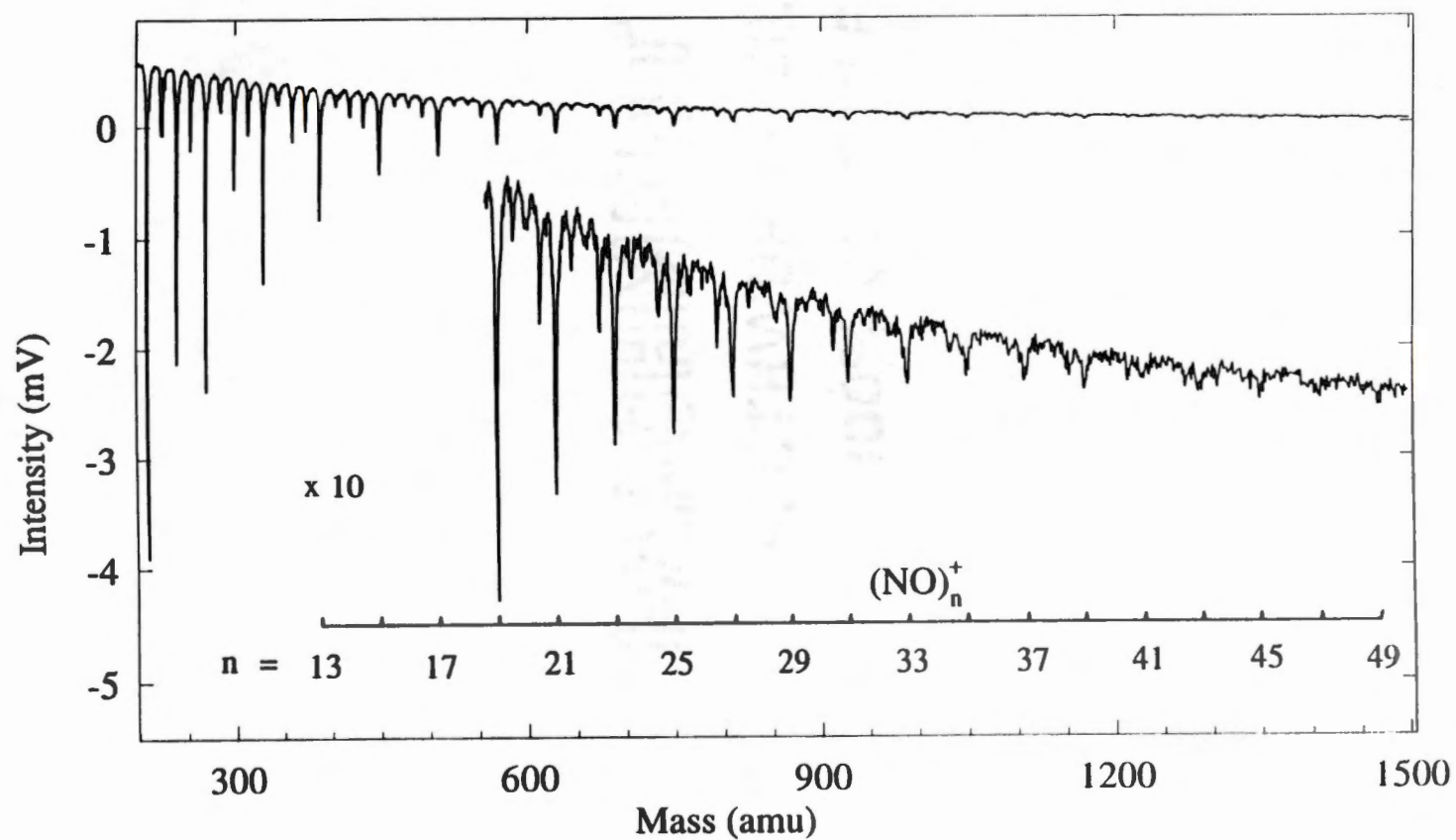


Figure IV-2. Extension of figure IV-1 showing the high mass region. Note that only the odd $(\text{NO})_m^+$ clusters are observed after $n = 19$.

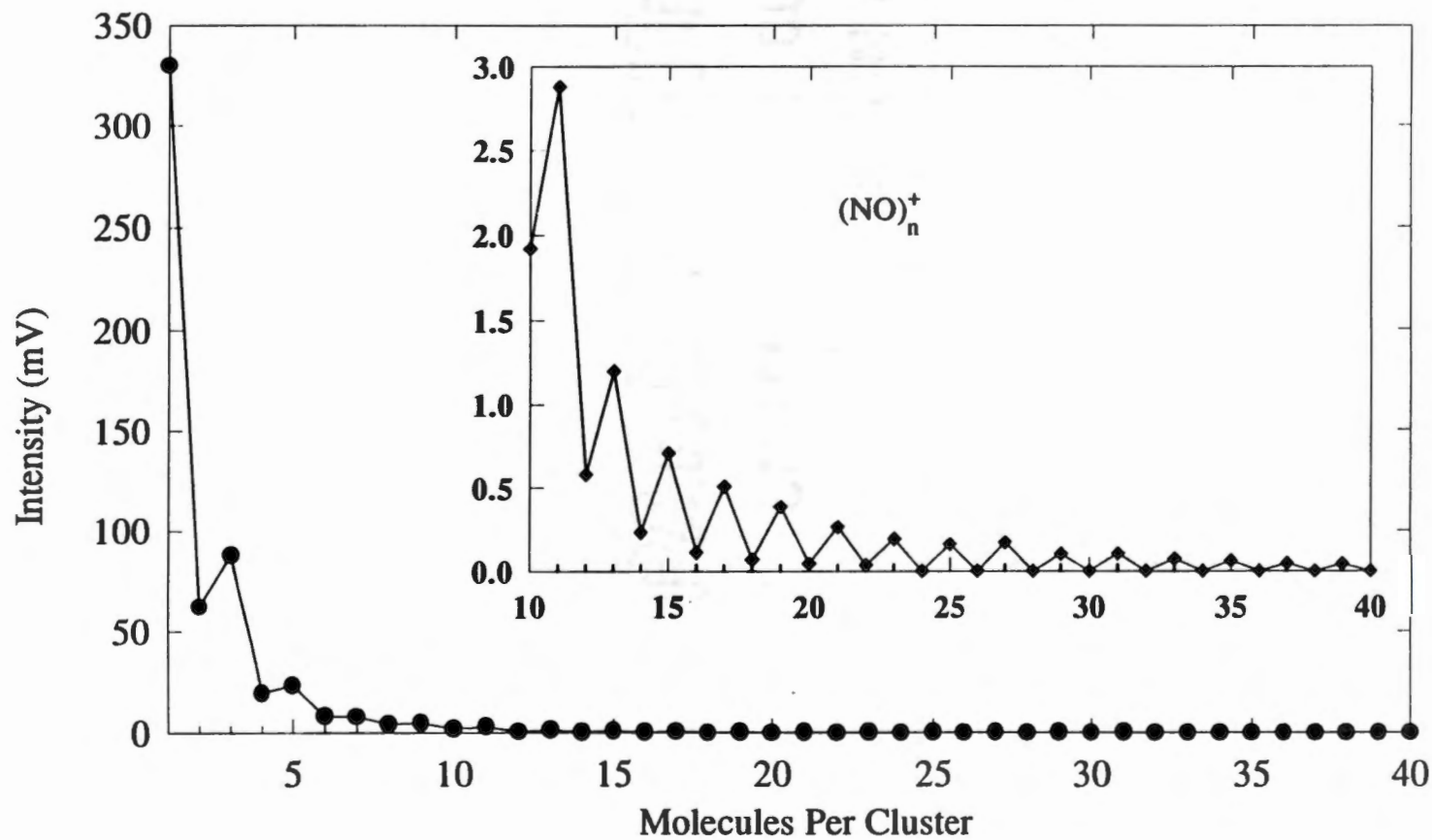
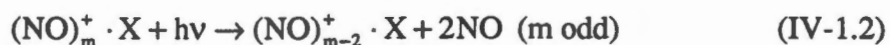


Figure IV-3. The relative intensity distribution of $(\text{NO})_m^+$ clusters as a function of m . The insert shows the distribution for $m > 10$ where the odd-even intensity alternation is fully developed.

investigated $(\text{NO})_m^+ (\text{Ar})_n$ and $(\text{NO})_m^+$ clusters grown around an NO^+ seed. The odd-even intensity effect was observed for up to $m = 15$. Woodward *et al.*¹³⁶ subsequently observed an odd-even intensity alternation when they investigated the infrared predissociation dynamics of $(\text{NO})_m^+ \cdot \text{X}$ (where $\text{X} = \text{SF}_6$ or C_2H_4). The odd-even effect, for m , was prevalent in both cases and furthermore, the fragmentation patterns for odd and even cluster ions were found to be different¹³⁶:



Carman¹³⁷ has also observed a strong intensity alternation (odd > even) in negative nitric oxide clusters, which were produced by the Rydberg charge exchange technique.

This odd-even intensity alternation reflects an enhanced stability due, not to structural factors as in the case of $(\text{NO})_m^+ (\text{Ar})_n$ clusters, but electron pairing effects.

Nitric oxide has a $^2\Pi_i$ ground state with an electron configuration in which there is one unpaired electron in a π^* orbital $[\text{KK} (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)]$. This leads to extensive dimerization of nitric oxide in the condensed phase as the two unpaired electrons become paired in a partially bonding orbital of the dimer¹³⁷. The dimerization of NO was first discovered when researchers were investigating its thermodynamic properties^{138,139}. Later, Raman spectroscopy of both solid and liquid NO confirmed this result¹⁴⁰. The energetically preferred structure of the NO dimer has been determined by

both x-ray diffraction¹⁴¹ and microwave spectroscopy^{142,143} to be cis-planar structure with a C_{2v} symmetry. Experimental measurements of the quadrupole coupling constants have shown that the unpaired electron on each monomer pair up in an orbital which lies in the plane of the NO dimer^{137,142}. *Ab initio* calculations have shown that this orbital is a σ -type bonding orbital between the two N-N atoms¹⁴⁴. The bond energy of the NO dimer has been determined by Hetzler *et al.*¹³⁴ to be $710 \pm 40 \text{ cm}^{-1}$ which is unusually large for a van der Waals molecule. This type of bonding has been referred to as “an incipient chemical bond”.

A consequence of this dimerization is that for neutral clusters, the even members are expected to be more stable than the odd ones because they have all of their electrons paired up. However, for the ion, either negative or positive, the argument is reversed and the odd clusters are more stable since all of their electrons are spin paired. Similar electron-pairing arguments have been observed in metals^{145,146} and cluster distributions of nitrogen dioxide^{147,148}. Polarity experiments using molecular beam electric deflection have established that the NO monomer and dimer ions are both polar while the trimer and tetramer are non-polar¹⁴⁹.

An important aspect of the cluster distribution in figure IV-2 is the *increase* in the odd-even effect as the cluster size increases. Electron-pairing arguments alone are insufficient to explain this phenomenon. This contrasts with what is observed in metal clusters where the odd-even effect decreases very rapidly with increasing cluster size. This decrease occurs because the heats of vaporization for odd and even cluster ions

approach the same value in the limit of very large clusters namely, the heat of atomization of the bulk metal¹³⁷. Nitric oxide is different because it is almost completely dimerized in the bulk and dimer formation plays a critical role in determining the cluster distribution of nitric oxide.

Carman¹³⁷ has suggested that dimerization within the cluster leads to a difference in the rates of evaporation of odd and even cluster ions. If one models the cluster ions as a NO^+ core (or possibly $(\text{NO})_3^+$), solvated by dimers and at most a single monomer, the activation energy for evaporation of an unpaired monomer will be lower than that for evaporation of a “dimerized” monomer. Within this model, an even cluster ion would lose a monomer to become odd, while an odd cluster ion would lose a dimer to remain odd. The odd ion is not expected to lose a monomer over a dimer because the dimer units in the solvation shell are held by typical, weak, vdW bonds while the energy to dissociate a dimer is substantially higher. This effect becomes greater as the heat capacity increases (i.e. the cluster size increases) and has been modeled by Klots¹⁵⁰. Further experimental verification of this effect has been obtained by Woodward *et al.*¹³⁶.

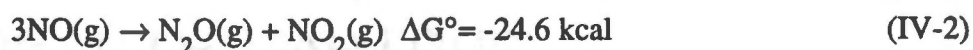
It is important to address the weak nature of the odd-even effect for clusters of $m < 8$. For cluster bigger than this the effect is very clear and is characterized by the arguments listed in the previous paragraph. A weak odd-even alternation was also observed by Kung *et al.*¹³⁵ for nitric oxide in $(\text{NO})_m^+$ and $(\text{NO})_m^+ (\text{Ar})_n$ clusters. There are two possible explanations. First, the stability of the clusters with $m < 8$ could be due

to structural factors rather than electron-pairing effects in whereby the $m = 7$ corresponds to the formation of a complete solvation shell. Second, the amount of excess energy greatly affects the evaporation process and hence, the appearance of magic numbers. Therefore, smaller clusters, which have very little excess energy, may not be able to dissipate their excess energy by evaporating neutral clusters thereby hindering the appearance of enhanced stability for odd cluster ions.

$(\text{NO})_m^+ (\text{N}_2\text{O})_n$ and $(\text{NO})_m^+ (\text{NO}_2)_n$ clusters

These species were observed initially observed in both the 1% NO/Ar and the 5% NO/Ar mixtures in the form of $(\text{NO})_m^+ \text{N}_2\text{O}$ and $(\text{NO})_m^+ \text{NO}_2$ clusters. The odd-even effect that was observed in the pure nitric oxide clusters is also observed for the aforementioned species in figure IV-1. For the peaks containing nitrous oxide, the odd cluster ions (m is odd) are more intense than the even ones while for peaks containing nitrogen dioxide, the even cluster ions are more intense (m is even) than their odd counterparts. In the case of $(\text{NO})_m^+ \text{N}_2\text{O}$ clusters, both nitrous oxide and odd $(\text{NO})_m^+$ species have an even number of electrons and since the total number of electrons within these binary clusters is even, they exhibit enhanced stability. In $(\text{NO})_m^+ \text{NO}_2$ clusters the nitrogen dioxide molecule has an odd number of electrons and so enhanced stability for these peaks can only occur if it is complexed to an odd electron containing $(\text{NO})_m^+$

species to make the total number of electrons in the binary cluster even. Hence, even m species in $(\text{NO})_m^+ \text{NO}_2$ clusters are stable relative to the odd ones. These data suggest that, for $(\text{NO})_m^+ \text{NO}_2$ clusters, the electron pairing might lead to a form of chemical bonding between the nitric oxide cluster and the nitrogen dioxide. The first member of the series, $\text{NO} \cdot \text{NO}_2$ is a well known molecule (also known as N_2O_3)^{151,152}. The existence of nitrous oxide and nitrogen dioxide impurities in samples of NO was investigated by a number of groups who found that the latter decomposes into nitrogen, oxygen, nitrous oxide and nitrogen dioxide¹⁵³. The decomposition reaction



is believed to occur readily at elevated pressures¹⁵³.

These decomposition reactions could also occur within neutral or ionic clusters of nitric oxide. Any impurities formed this way, and later ionized, would be indistinguishable in a mass spectrometer from those formed in the gas cylinder. However, it is highly unlikely that a photoinduced reaction is taking place because first, the intensity of the $(\text{NO})_m^+ \text{NO}_2$ and $(\text{NO})_m^+ \text{N}_2\text{O}$ clusters did not exhibit a power dependence. Second, when a new ^{15}NO sample was used, no mixed clusters were observed. Furthermore, it was possible to eliminate most of these impurities from the sample by passing the gas through a cold trap before expanding it through the supersonic

nozzle. These impurities, in the form of mixed clusters, have been observed in many experiments¹⁵⁴ with both positive¹⁵⁵ and negative^{137, 156} nitric oxide clusters.

When nitrous oxide is intentionally doped into a mixture containing NO and argon, the cluster distribution that is observed depends on the relative concentrations of NO, N₂O or Ar. The mass spectrum resulting from ionizing the expansion of a 10% N₂O/ 1% NO/ 89% Ar mixture with 30 ps pulses of 266 nm light is shown in figure IV-4. Two cluster series, NO⁺(N₂O)_n and (N₂O)_m⁺, characteristic of an expansion rich in N₂O, are seen to dominate the spectrum. The pure nitric oxide clusters are formed by the absorption of additional photons by NO⁺(N₂O)_n clusters which then undergo dissociation and charge transfer to form (N₂O)_m⁺. This type of process has been previously observed by Miller *et al.*¹³² who produced Ar⁺, Kr⁺ and Xe⁺ after the ionization of the NO·X (where X = Ar, Kr or Xe). Although (N₂O)_m⁺ are not completely dissociated by 266 nm light, their fragmentation dynamics have been studied by Kamke *et al.*¹⁵⁷ who used synchrotron radiation (55-110 nm) to irradiate nitrous oxide clusters and observed the loss of a neutral N₂O molecule for clusters up to the hexamer. Large positively charged nitrous oxide clusters have been produced in electron impact experiments and magic numbers in their cluster distributions have been observed¹⁵⁸. In the present experiment, however, (N₂O)_m⁺ cluster were not observed when nitrous oxide was expanded only with argon. This implies that either nitrous oxide clusters are

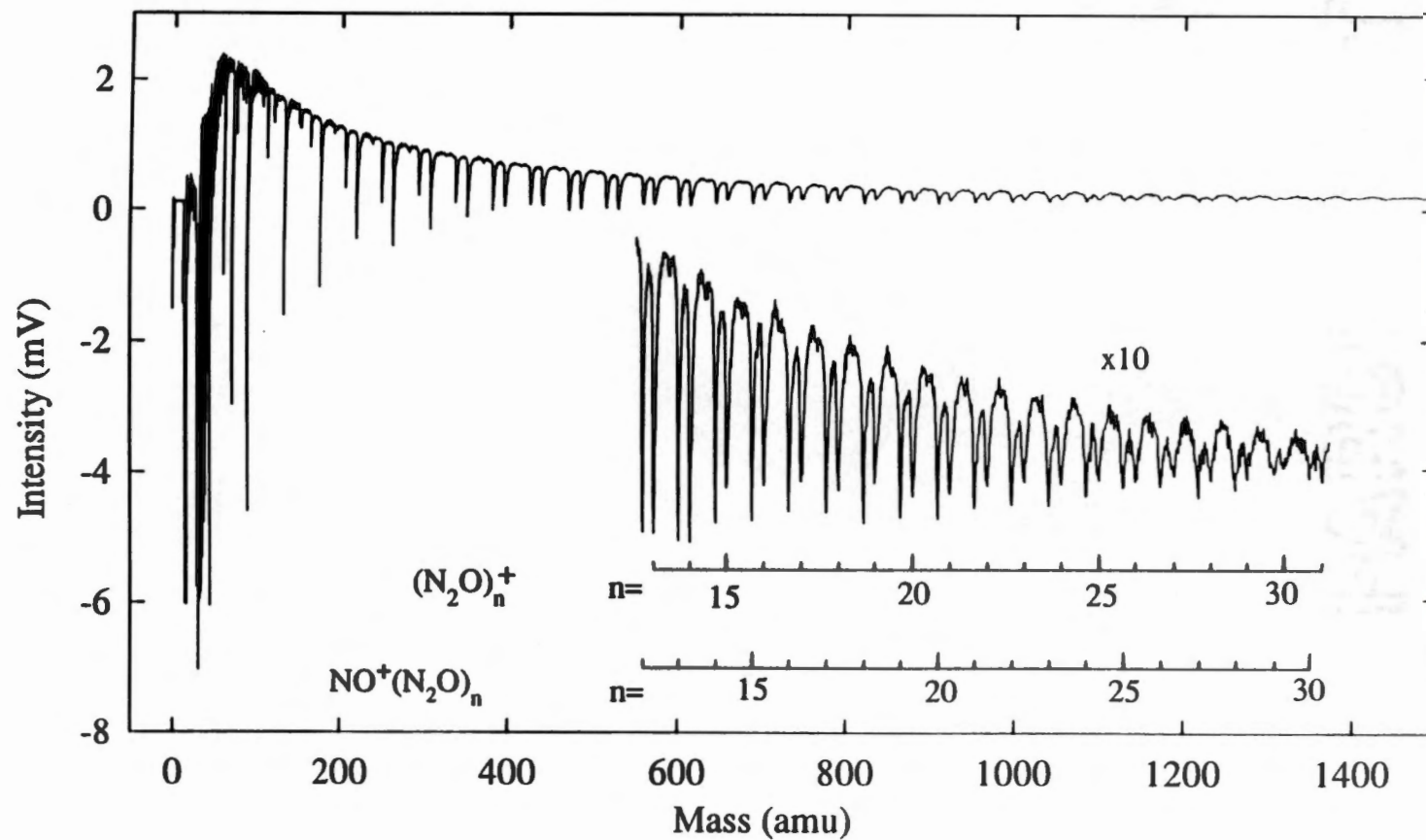


Figure IV-4. The 266 nm MPI mass spectrum produced by a 10% N_2O /1% NO /89% Ar expansion showing the $(\text{N}_2\text{O})_n^+$ and the $\text{NO}^+(\text{N}_2\text{O})_n$ cluster series.

not easily ionized by 266 nm light (three photons are required) or, that they undergo complete dissociation in the neutral or ionic manifold of electronic states. It is more likely that they are dissociated as neutrals because other clusters, such as Xe_n and $(\text{CO}_2)_n$, have been successfully observed following three-photon ionization.

There are studies that have investigated both the homogeneous molecular clusters and the binary molecular clusters of N_2O and NO_2 . There are two reviews that have examined N_yO_z species quite extensively^{151,152}. The energetically favored structure for $(\text{NO})_2$ has been determined by microwave spectroscopy to be a cis-planar structure with a C_{2v} symmetry¹⁵⁹. Infrared spectroscopy has been used to determine the structures of both $(\text{NO}_2)_2$ ^{151,152} and $(\text{N}_2\text{O})_2$ ¹⁶⁰. The molecule $\text{NO}\cdot\text{NO}_2$ (or N_2O_3) has been extensively studied in matrix isolation experiments^{151,153}. Photoionization studies of $(\text{N}_2\text{O})_2^+$ ions were performed by Linn *et al.*¹⁶¹ in the 600-1200 Å range. Later, high pressure mass spectrometry was used to determine the bond strength of $\text{NO}^+\text{N}_2\text{O}$ as 0.33 eV¹⁶² which is lower than that of $(\text{NO})_2^+$ (0.598 eV) or $(\text{N}_2\text{O})_2^+$ (0.80 eV).¹⁶². Recently, Hiraoka *et al.*¹⁶³ used electron-beam high pressure mass spectrometry to obtain bond energies and structures for $\text{NO}^+(\text{N}_2\text{O})_n$ ($n \leq 7$). Their estimate for the bond energy of $\text{NO}^+\text{N}_2\text{O}$ (0.38 eV) is slightly higher than those obtained by Illies¹⁶². Photoelectron spectroscopy¹⁶⁴ and electron-beam high pressure mass spectrometry¹⁶³

have yielded bond strengths, structures and solvation energies for $(\text{N}_2\text{O})_n^-$ and NO^- $(\text{N}_2\text{O})_n$.

The previous paragraphs showed that when the concentration of nitrous oxide was much lower than nitric oxide, the $(\text{NO})_m^+ \text{N}_2\text{O}$ clusters were observed but when the concentration of nitrous oxide was much greater than NO, both $\text{NO}^+(\text{N}_2\text{O})_n$ and $(\text{N}_2\text{O})_m^+$ were produced. The intermediate case, where the concentration of nitrous oxide was approximately equal to that of NO, produced a dramatically different cluster distribution in which $(\text{NO})_m^+ (\text{N}_2\text{O})_n$ clusters were observed (where $m \leq 9$, $n \leq 20$). Figure IV-5 shows the low mass region of a $(\text{NO})_m^+ (\text{N}_2\text{O})_n$ mass spectrum in which the $(\text{NO})_3^+ \text{N}_2\text{O}$ peak is significantly larger than its dimer or tetramer counterparts. In fact, in figure IV-6, which shows the entire mass spectrum, the $(\text{NO})_3^+ (\text{N}_2\text{O})_n$ cluster *series* ($n \leq 20$) dominates the spectrum and is 5-10 times larger than any other cluster series. This is a different type of "magic" than the $(\text{NO})_m^+ (\text{Ar})_n$ where only *specific* sized clusters exhibited enhanced stability ($m + n = 13, 19$ and 55). These data suggest a stable configuration is produced when nitrous oxide clusters are complexed to the $(\text{NO})_3^+$ unit. It must be noted that in the 1% NO/Ar expansion the intensity of the NO trimer ion decreased monotonically while in the 5% NO/Ar the NO trimer only had minor increased intensity relative to such a monotonic decay. In the case of $(\text{NO})_3^+ (\text{N}_2\text{O})_n$, the $(\text{NO})_3^+$

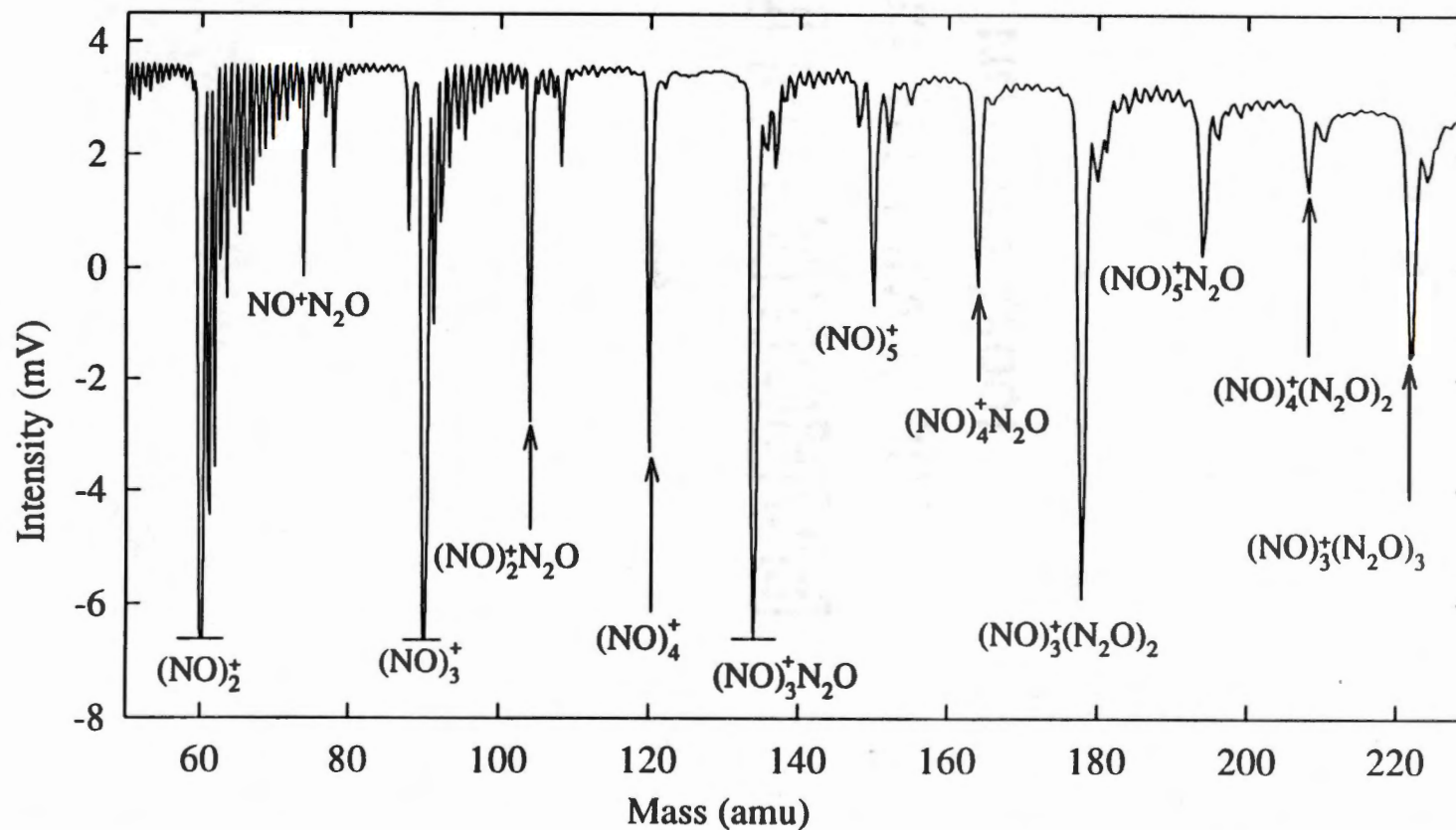


Figure IV-5. The low mass region of a 266 nm MPI mass spectrum produced by a 1% N_2O /10% NO /89% Ar expansion showing the dominance of the $(\text{NO})_3^+(\text{N}_2\text{O})_n$ peaks over those of the $(\text{NO})_2^+(\text{N}_2\text{O})_n$ and the $\text{NO}^+(\text{N}_2\text{O})_n$. The ringing observed at the high mass side of the largest peaks is an experimental artifact.

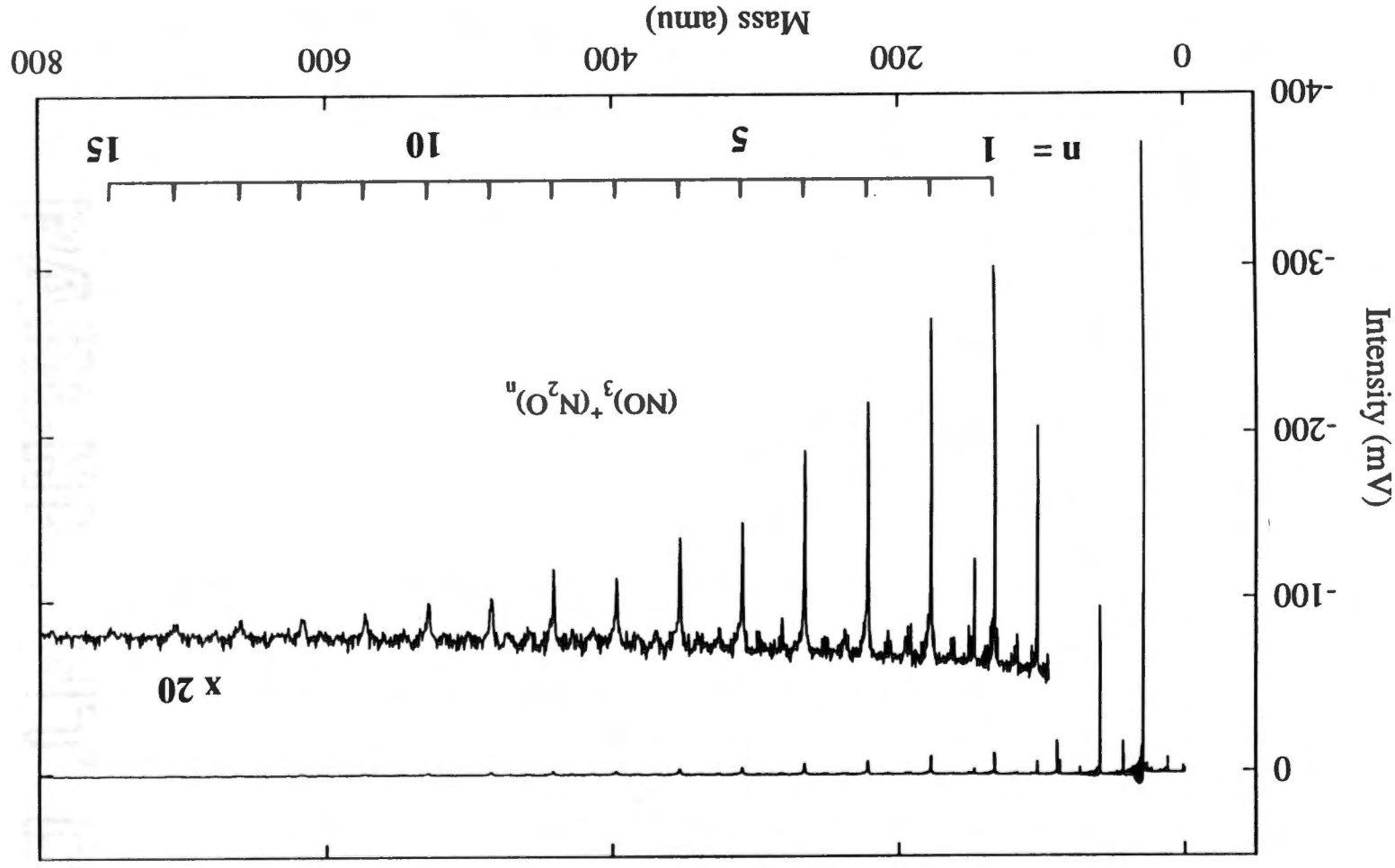
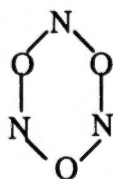


Figure IV-6. The 266 nm MPI mass spectrum produced by a 1% $\text{N}_2\text{O}/5\%$ $\text{NO}/94\%$ Ar expansion showing the dominance of the $(\text{NO})_3+(\text{N}_2\text{O})_n$ series.

unit provides a core around which neutral solvent molecules can aggregate. The data suggest that the stability is brought to the cluster by the complexing agent and not by the $(\text{NO})_3^+$ unit.

Recently, calculations were performed to elucidate the structure of clusters of the form $(\text{NO})_3^+ (\text{N}_2\text{O})_n$ and it was postulated that the nitrous oxide molecules added exothermically to a stable, cyclic $(\text{NO})_3^+$ ion¹⁶⁵. In our case, the binary cluster would be formed as a neutral. A stable, cyclic structure for $(\text{NO})_3^+$ would explain the dominance of the $(\text{NO})_3^+ (\text{N}_2\text{O})_n$ over the dimer and tetramer mixed clusters. The structure proposed by Jones¹⁶⁵ would have the cyclic trimer arranged so that the nitrogen and oxygen atoms alternate in the following manner.



This would result in the formation of a nonpolar moiety which agrees with the experimental work of Novick *et al.*¹⁴⁷. A less likely arrangement would have the nitric oxide trimer as a linear string of three nitric oxide molecules solvated by nitrous oxide molecules. This configuration, however, does not explain why a linear arrangement of three NO's would be favored over any other number. Another possibility could involve the rearrangement of the NO trimer to $\text{N}_2\text{O} \cdot \text{NO}_2$ and then the cluster series would have

the form $\text{NO}_2^+ (\text{N}_2\text{O})_{n+1}^+$. In fact reaction IV-2 could account for this result. Attempts at producing $(\text{NO})_3^+ (\text{N}_2\text{O})_n^+$ from expansions of NO_2 and N_2O were unsuccessful, indicating that cluster disproportionation is unlikely.

$(\text{NO})_m^+ (\text{CO}_2)_n$ and $(\text{NO})_m^+ (\text{CS}_2)_n$ clusters

It was expected that both carbon dioxide and carbon disulfide would exhibit the same behavior as nitrous oxide because they are not only isovalent (have the same number of outer electrons) with the latter but they are all linear molecules in their ground states.

Figure IV-7a, IV-7b and IV-8 show the cluster distributions that were obtained in three carbon dioxide concentration regimes. Figure 7a shows a mass spectrum resulting from a 100 psi, neat CO_2 expansion following three-photon ionization where clusters are observed out to $n = 20$. This is in contrast to the nitrous oxide case where the $(\text{N}_2\text{O})_m^+$ cluster aren't observed with 266 nm light. Similar positive cluster ion distributions have been observed following electron impact¹⁶⁶ while negative carbon dioxide clusters have been observed with both electron beams¹⁶⁶ and Rydberg charge exchange¹⁶⁷. The negative cluster ion distributions, with both of the above techniques, produce various magic numbers. Figure 7b shows a mass spectrum of a 5% CO_2 /1% NO /94% Ar following two-photon ionization where both $\text{NO}^+ (\text{CO}_2)_n$ and $(\text{CO}_2)_m^+$

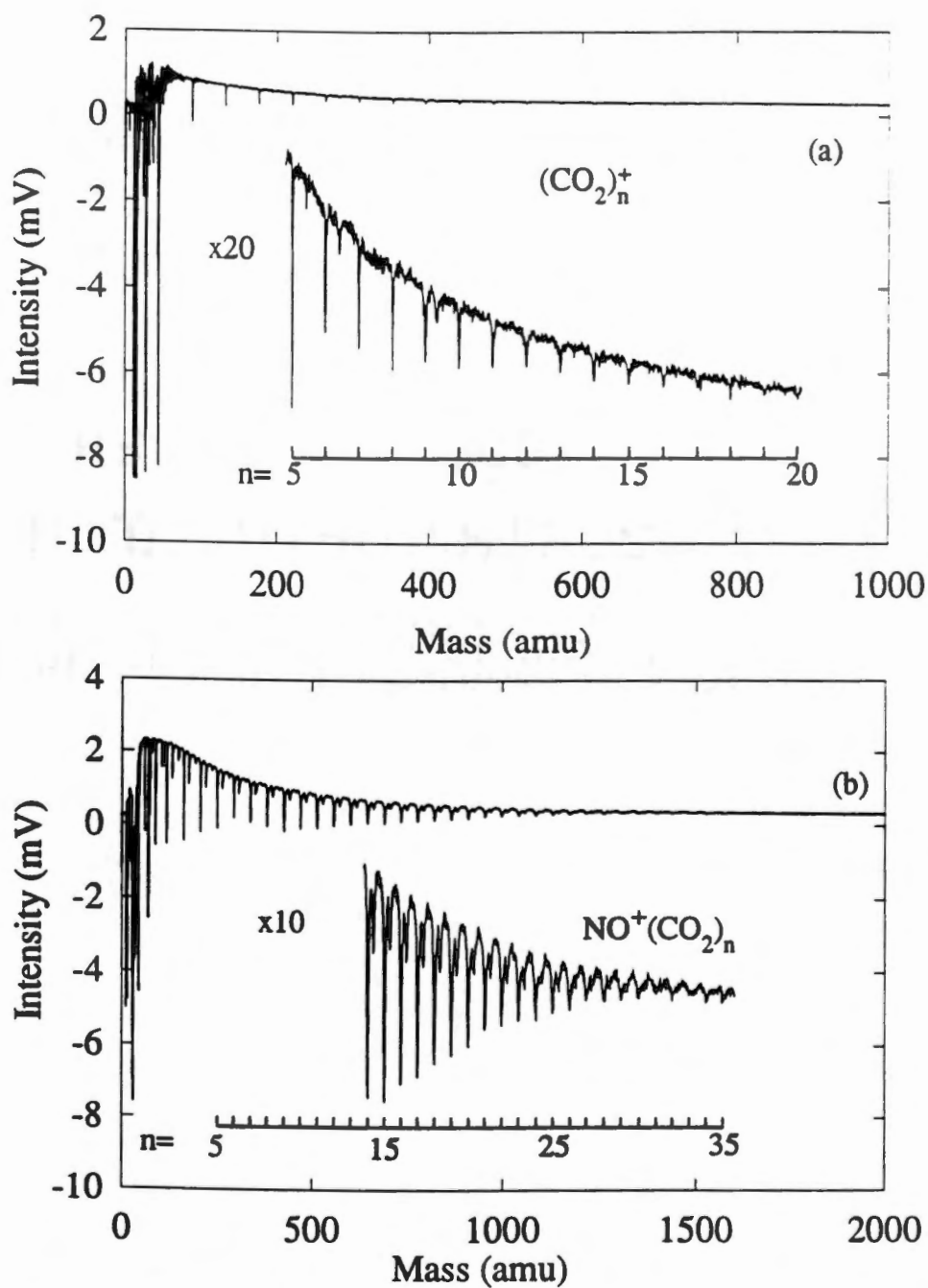


Figure IV-7. The 266 nm MPI mass spectrum of (a) a neat CO_2 expansion and (b) a 5% CO_2 /1% NO /94% Ar mixture where the concentration of the CO_2 is much greater than that of NO .

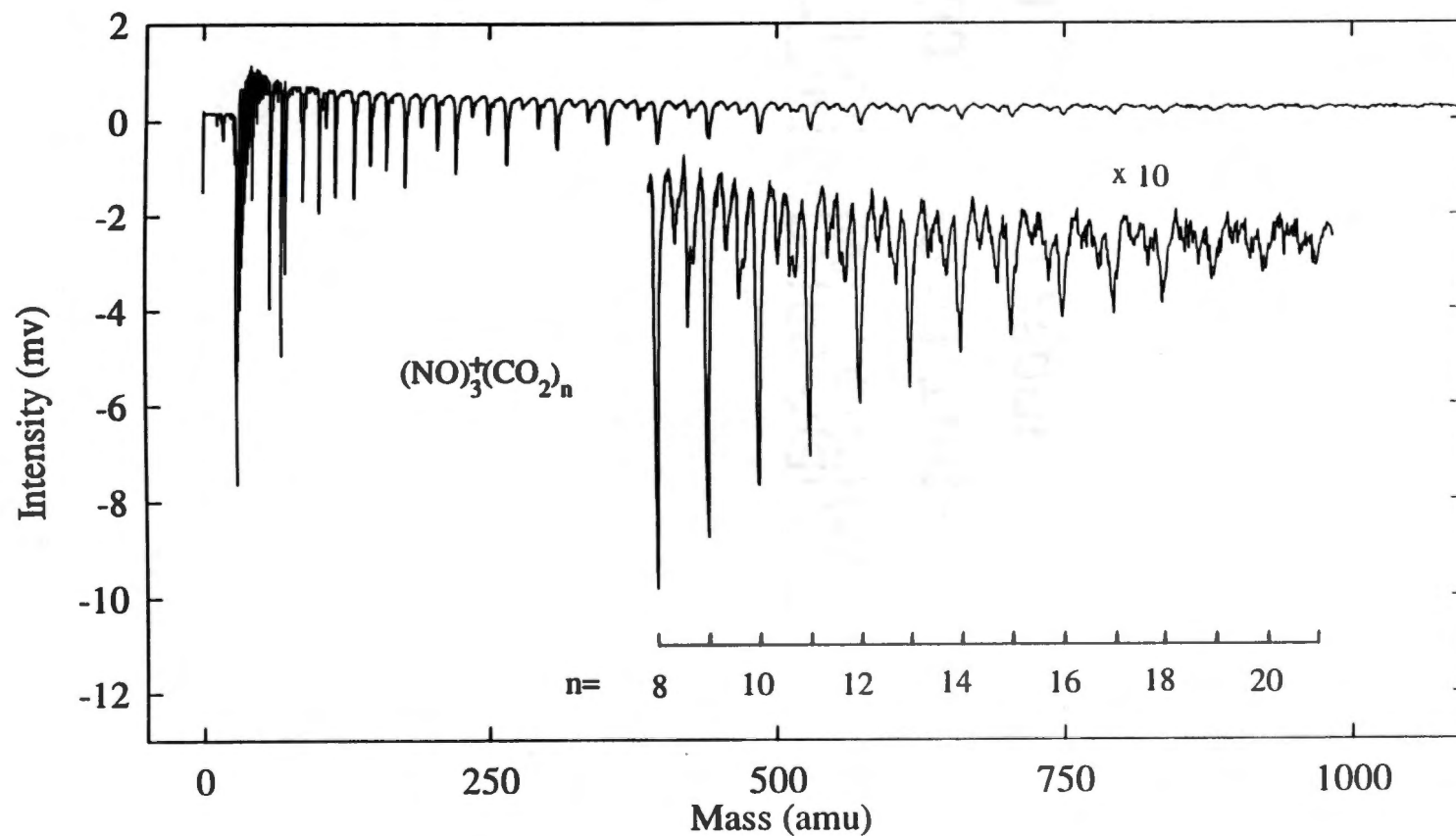


Figure IV-8. The 266 nm MPI mass spectrum produced by a 1% CO_2 /1% NO /98% Ar expansion where the concentration of the CO_2 is approximately equal to that of NO . Note the dominance of the $(\text{NO})_3^+(\text{CO}_2)_n$ series.

series were observed. This relatively high concentration of carbon dioxide produced a similar mass spectrum as what was obtained from a 10% N₂O/1% NO/89% Ar mixture. In figure IV-8 the concentrations of both CO₂ and NO are approximately equal which leads to a distribution in which the (NO)₃⁺(CO₂)_n is the dominant series, which is similar to the nitrous oxide case.

Experiments have been performed on a few of the homogeneous and mixed clusters to elucidate their structures and thermodynamic stabilities. The bond strengths of (CO₂)₂⁺ and NO⁺CO₂ have been determined by Illies¹⁶² to be 0.69 eV and 0.37 eV respectively. High pressure mass spectrometry has been used to obtain the bond dissociation energies for NO⁺(CO₂)_n (n ≤ 5) while *ab initio* calculations have yielded structural information¹⁶⁸. Hiraoka *et al.*¹⁶⁸ have argued that NO⁺CO₂ is responsible for the observation of hydronium ions in the D region of the Earth's atmosphere.

Mass spectra have also been obtained for NO/CS₂/Ar expansions using 266 nm light. A 1%/5% NO/94% Ar mixture produces a cluster distribution that is dominated by (NO)₃⁺(CS₂)_n cluster series, similar to those obtained for carbon dioxide and nitrous oxide (see figure IV-9). It is expected that the structures of (NO)₃⁺(CS₂)_n clusters are very similar to those involving nitrous oxide and carbon dioxide, since they are all linear and isovalent.

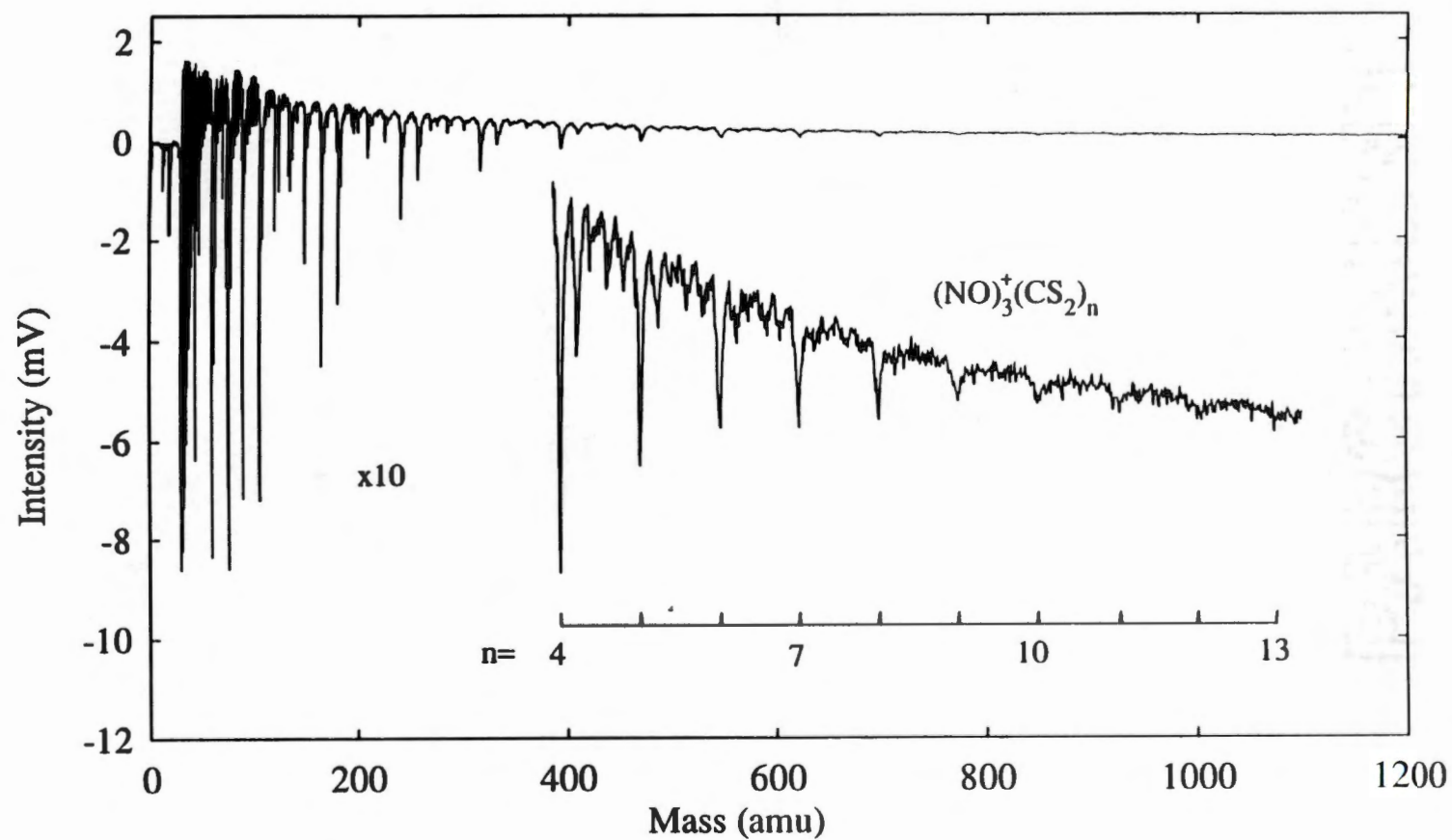


Figure IV-9. The 266 nm MPI mass spectrum produced by a 1% CS_2 /5% NO /94% Ar expansion showing the dominance of the $(\text{NO})_3^+(\text{CS}_2)_n$ series.

$(\text{NO})_m^+ (\text{SF}_6)_n$ clusters

Figure IV-10 shows the time-of-flight mass spectrum produced by ionizing an expansion of a 100 psi, 1% SF_6 /5% NO /94% Ar mixture with 30 ps pulses of 266 nm light. Three series of the form, $(\text{NO})_m^+ (\text{SF}_6)_n$, where $m \leq 3$ and $n \leq 15$, can be identified. Clusters of sulfur hexafluoride are not observed, however and SF_5^+ was observed as a fragmentation product. In addition to the series identified above, figure IV-11b shows the $\text{SF}_5^+ (\text{SF}_6)_n$ distribution, built upon the SF_5^+ fragmentation product. This was also the case when a neat expansion of SF_6 was irradiated. In figure IV-11b, an expanded portion of the low mass region of figure IV-10 is shown which extends out to $n = 12$. Those peaks with an asterisk are believed to correspond to the ternary cluster series, $(\text{NO})_3^+ \text{N}_2\text{O}(\text{SF}_6)_n$.

A striking aspect of the distribution in figure IV-10 is that in mixed clusters of $(\text{NO})_m^+ (\text{SF}_6)_n$, no members are observed for $m > 3$. This is in marked contrast with the nitrous oxide case where $(\text{NO})_m^+ (\text{N}_2\text{O})_n$ with $m > 3$ were observed. The SF_6 data can be explained by considering that for clusters with $m > 3$ the $\text{NO} \cdot \text{SF}_6$ bond is much weaker than the $\text{SF}_6 \cdot \text{SF}_6$ bond. Therefore, in order to dissipate excess energy, this leads to a preferential evaporation of NO molecules upon ionization. A similar process has been observed by Stace *et al.*¹⁶⁹ where they investigated the fragmentation patterns of

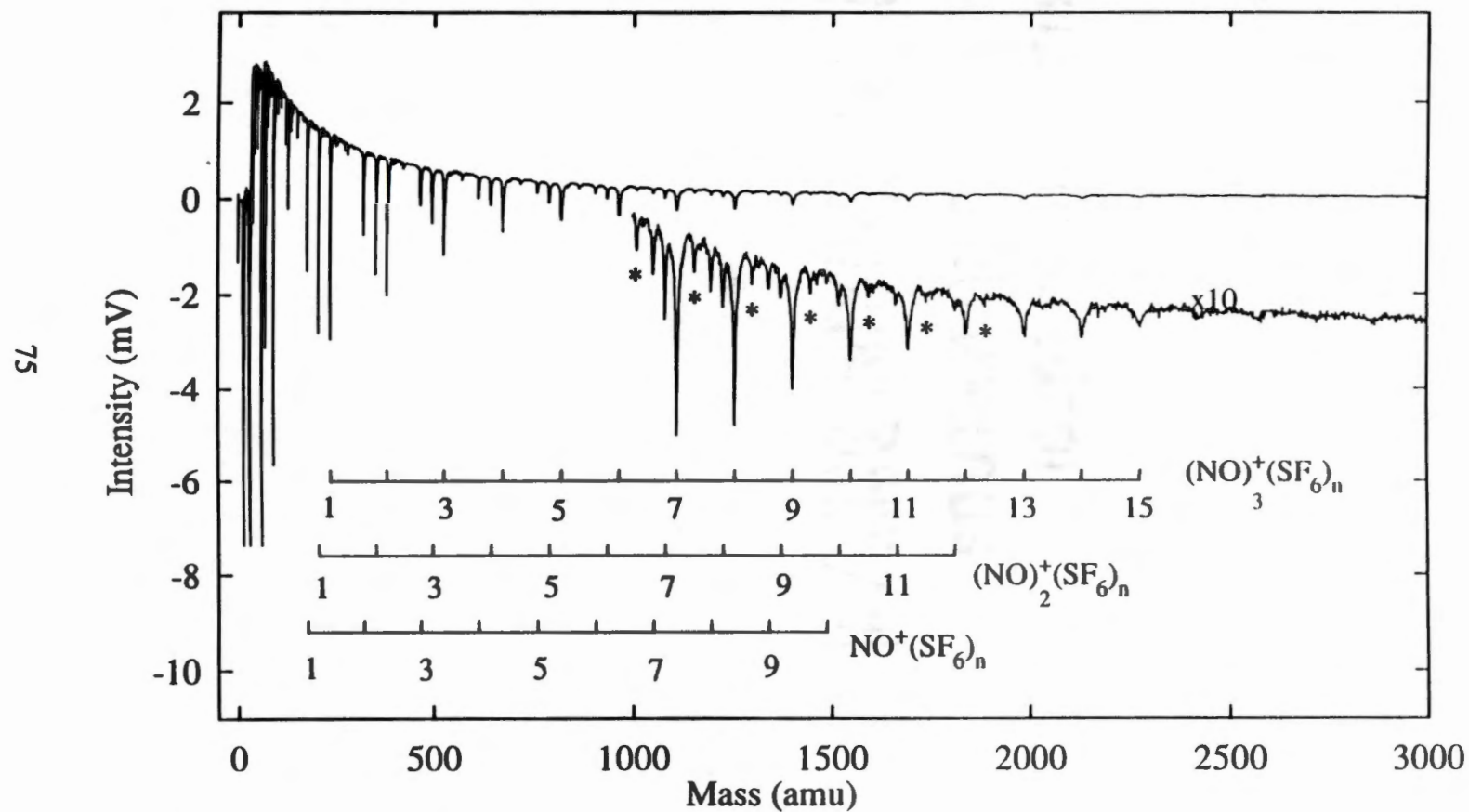


Figure IV-10. The 266 nm MPI mass spectrum produced by a 1% SF_6 /5% NO /94% Ar expansion showing the dominance of the $(\text{NO})_3^+(\text{SF}_6)_n$ series. Peaks with an asterisk are members of the $(\text{NO})_3^+(\text{N}_2\text{O})(\text{SF}_6)_n$ ternary cluster peaks.

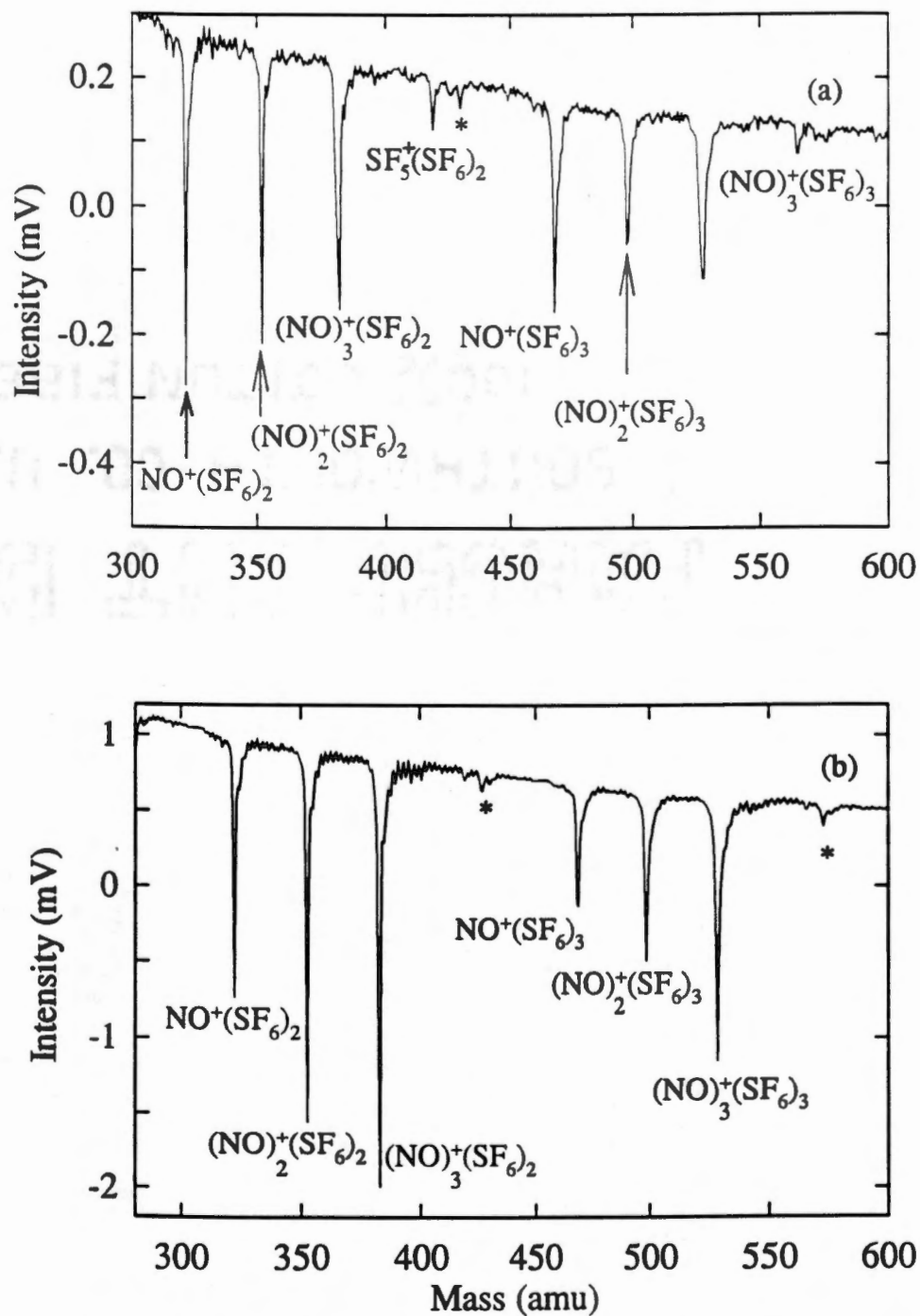


Figure IV-11. The low mass region of a 266 nm MPI mass spectrum produced by (a) a 1% SF₆/1% NO/98% Ar expansion with (b) a 1% SF₆/5% NO/98% Ar expansion.

$(\text{NO})_m^+ (\text{SF}_6)_n$, by exciting the ν_1 vibrational mode of SF_6 and monitoring the migration of that energy into the weak vdW bond. They observed that large mixed clusters preferentially lost NO molecules while smaller mixed clusters lost SF_6 molecules. It is believed that for $(\text{NO})_m^+ (\text{N}_2\text{O})_n$ the bond strength of NO·NO bond is similar in strength to the NO· N_2O bond which leads to a more varied fragmentation pattern.

As in the case of the molecules discussed previously, figure IV-10 shows the dominance of the $(\text{NO})_3^+ (\text{SF}_6)_n$ cluster series over the $\text{NO}^+ (\text{SF}_6)_n$ and $(\text{NO})_2^+ (\text{SF}_6)_n$. The same arguments that were used to explain the dominance of the $(\text{NO})_3^+ (\text{X})_n$ in previous chapter are not as easily applied to the SF_6 case. Sulfur hexafluoride is not linear like N_2O , CO_2 or CS_2 and is not isovalent with them. However, sulfur hexafluoride does have a relatively large polarizability which might help to stabilize the $(\text{NO})_3^+$ unit.

Two reasons can be provided for the non-observation of pure sulfur hexafluoride clusters. First, they have a large ionization potential, 13.42 eV¹⁷⁰ requiring three photons of 266 nm light, which would result in low ionization probabilities. This is, however, a less likely occurrence because other three-photon ionization processes, in carbon dioxide and xenon, have been observed with the present apparatus. A more plausible explanation would be that pure SF_6 clusters are dissociated by 266 nm light,

either in the neutral or the ionic manifold of electronic states. The SF_5^+ (SF_6)_n clusters are produced as a result of fragmentation and charge transfer processes within (NO)_m⁺ (SF_6)_n clusters. Electron impact experiments have produced SF_5^+ and SF_5^+ (SF_6)_n clusters¹⁵⁵ while collision induced dissociation experiments have yielded bond dissociation energies for SF_5^+ , SF_4^+ , SF_3^+ , SF_2^+ and SF^+ and ionization potential for their neutral analogs¹⁷⁰. The same study concluded that sulfur hexafluoride ion is highly susceptible to dissociation because the bond dissociation energy of $\text{F}_5\text{S}^+-\text{S}$ is much lower than the weakest S-F bond in the neutral cluster and, in fact, the researchers compare this bond to an ion-induced dipole bond¹⁷⁰.

(NO)_m⁺ (H_2O)_n clusters

One of the most important motivations for studying the solvation dynamics of nitric oxide with various partners is to try and understand their behavior on a larger scale and in more complex systems. No solvent partner for nitric oxide provides us with a better opportunity to do this than water. It is now known that nitric oxide is solvated by water in atmospheric and cellular environments and so it is important to study the way in which the two molecules interact. Clusters of water and NO have been observed with the present apparatus and by Kennedy *et al.*¹⁷¹ who solvated about a preformed NO^+ seed ion. The hydration of NO^+ at room temperature has been investigated by the

flowing afterglow method and rate constants for clustering and proton transfer reactions were obtained^{172,173,174,175}. Negative-ion water clusters have been studied by Posey *et al.*¹⁷⁶ in order to study the phenomenon of the hydrated electron and to investigate charge transfer to various reactant molecules, including NO. Photoelectron spectroscopy¹⁷⁷ was employed to determine vertical detachment energies, adiabatic electron affinities and dissociation energies of $\text{NO}^-(\text{H}_2\text{O})_n$ clusters. Measurements have shown that both $\text{NO}^+\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+\text{H}_2\text{O}$ are resistant to dissociation in the 350-799 nm wavelength range^{178,179,180}. The observation of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $\text{NO}^+\text{H}_2\text{O}$ and NO^+CO_2 in the D region of the atmosphere has led to the conclusion that the NO containing species are intermediates that undergo ligand switching and proton transfer reactions to produce the hydronium cluster ions¹⁸¹. The entire chain of reactions is started off by the ionization of nitric oxide with solar Lyman- α radiation¹⁸².

Figure IV-12 shows the time-of-flight mass spectrum produced by ionizing an expansion of a 100 psi, 0.4% D_2O /1% NO/98.6% Ar mixture with 30 ps pulses of 266 nm light. Three series can be identified, $\text{NO}^+(\text{D}_2\text{O})_n$, $\text{D}_3\text{O}^+(\text{D}_2\text{O})_n$ and $\text{NO}^+(\text{Ar})_n$. Both protonated and deuterated water were used in order to distinguish mass ambiguities. For example, $\text{NO}^+(\text{H}_2\text{O})_n$ clusters, with $n > 5$ cannot be distinguished from $(\text{NO})_4^+(\text{H}_2\text{O})_{n-5}$ clusters. Also, $\text{NO}^+(\text{D}_2\text{O})_{2n}$ is indistinguishable from $\text{NO}^+(\text{Ar})_n$. The corresponding NO/ H_2O /Ar spectrum is similar in form but not as extensive as the

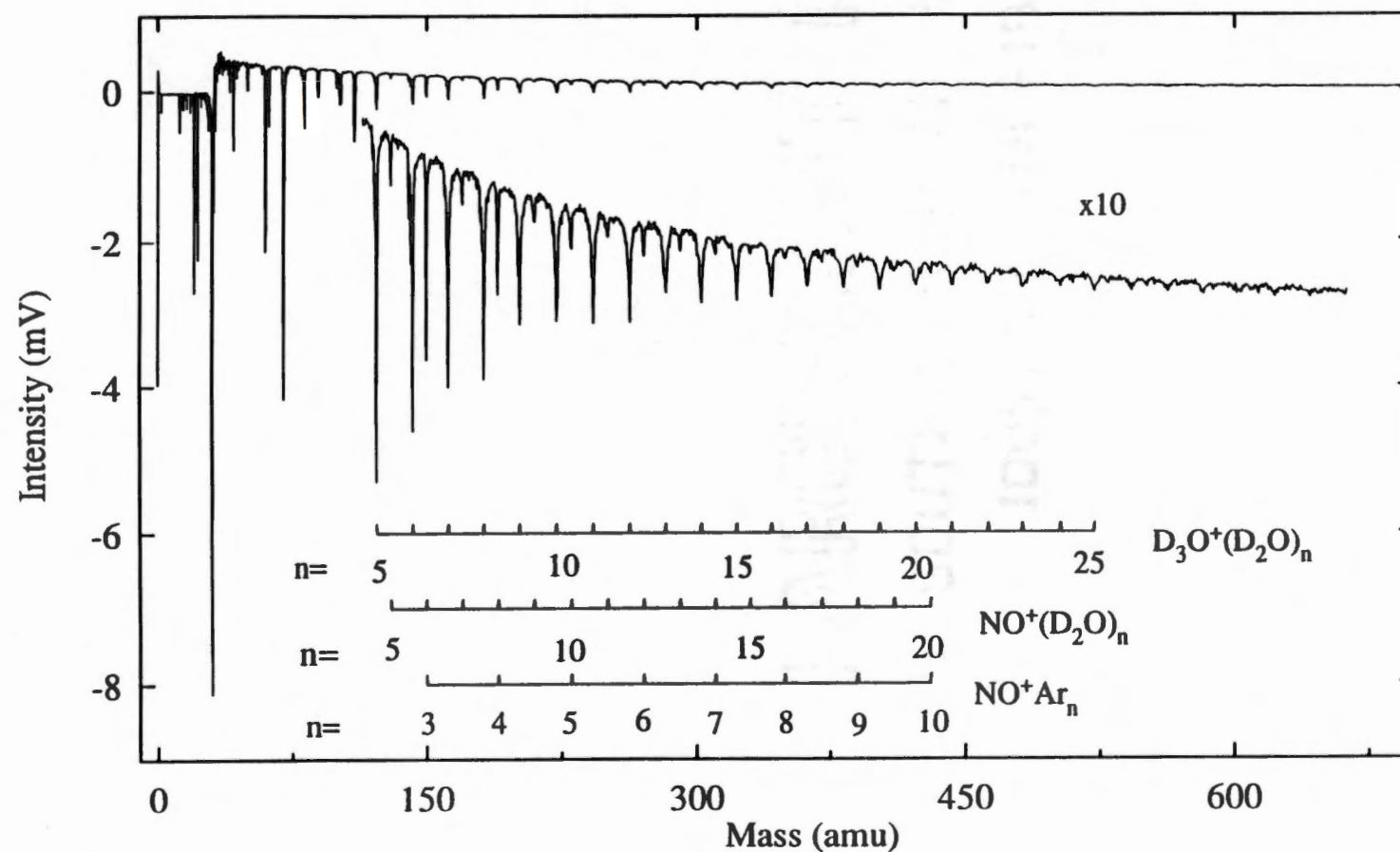
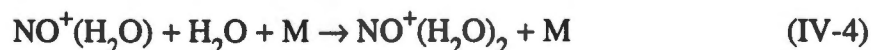
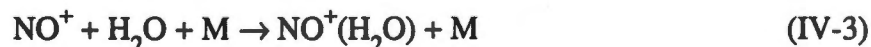


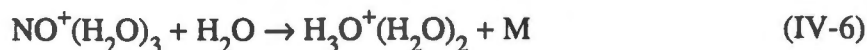
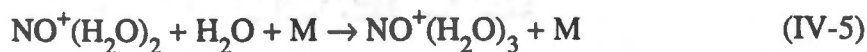
Figure IV-12. The 266 nm MPI mass spectrum produced by a 0.4% H_2O /1% NO /98.6% Ar expansion showing the $D_3O^+(D_2O)_n$, $NO^+(D_2O)_n$ and the $NO^+(Ar)_n$ series.

deuterated expansion. Similar results have been obtained by Kennedy *et al.*¹⁷¹ who observed $(\text{NO})_m^+ (\text{H}_2\text{O})_n$ ($m \leq 3$ and $n \leq 5$) and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters by solvating water molecules around a NO^+ ion seed. The present apparatus, using deuterated water, was able to produce $\text{NO}^+(\text{D}_2\text{O})_n$ clusters with up to 20 water molecules (as seen in figure IV-12). The intensity alternation in the $\text{NO}^+(\text{D}_2\text{O})_n$ peaks correspond to the contribution of the $\text{NO}^+(\text{Ar})_n$ series.

The mass spectrum in figure IV-12 shows an extensive $\text{D}_3\text{O}^+(\text{D}_2\text{O})_n$ cluster distribution which is observed out to $n = 40$. Similar distributions, produced without NO, have been observed by many groups using both beam and sputtering techniques¹⁸³. Although magic numbers at $n = 12$ and 21 were not observed in figure IV-12, they have been observed in numerous studies and their stability was attributed to the formation of a pentagonal dodecahedral clathrate structure¹⁸³.

As noted previously, the $\text{NO}^+(\text{D}_2\text{O})_n$ clusters are believed to be intermediates that undergo dissociation and charge transfer reactions to ultimately produce the hydronium cluster ions that are observed in the upper atmosphere^{184,185}. It has been proposed that the nitric oxide ion undergoes two and three body ion-molecule switching reactions which can be expressed as^{172,173,175,184}





Therefore, large water clusters are formed by additional collisions of the $\text{NO}^+(\text{H}_2\text{O})_n$ ions with water molecules. When these reactions were studied by the flowing afterglow method, $\text{NO}^+(\text{H}_2\text{O})_n$ clusters with $n > 3$ were not observed^{173,184}. These studies also yielded rate constants for the above reactions and bond strengths between the nitric oxide ion and varying numbers of water molecules. However, the observation of $\text{NO}^+(\text{H}_2\text{O})_4$ by Kennedy *et al.*¹⁷¹ and $\text{NO}^+(\text{D}_2\text{O})_n$, with n up to 20, in the present experiments may require a reassessment of these values. Specifically, reaction IV-7 must be slightly endothermic in order to proceed readily at room temperature but be less probable in colder, supersonic expansions. Experiments by Stace *et al.*¹⁸⁵, where water molecules were allowed to solvate a NO^+ ion seed, have yielded the same results and they, too, come to the same conclusions. The $\text{NO}^+(\text{H}_2\text{O})_n$ clusters have been treated theoretically by Pullman *et al.*¹⁸⁶ who have determined hydration energies and structures for up to $n = 4$.

$(\text{NO})_m^+(\text{SO}_2)_n$ clusters

Figure IV-13 shows the time-of-flight mass spectrum produced by ionizing an expansion of a 100 psi, 5% SO_2 /5% NO /90% Ar mixture with 30 ps pulses of 266 nm

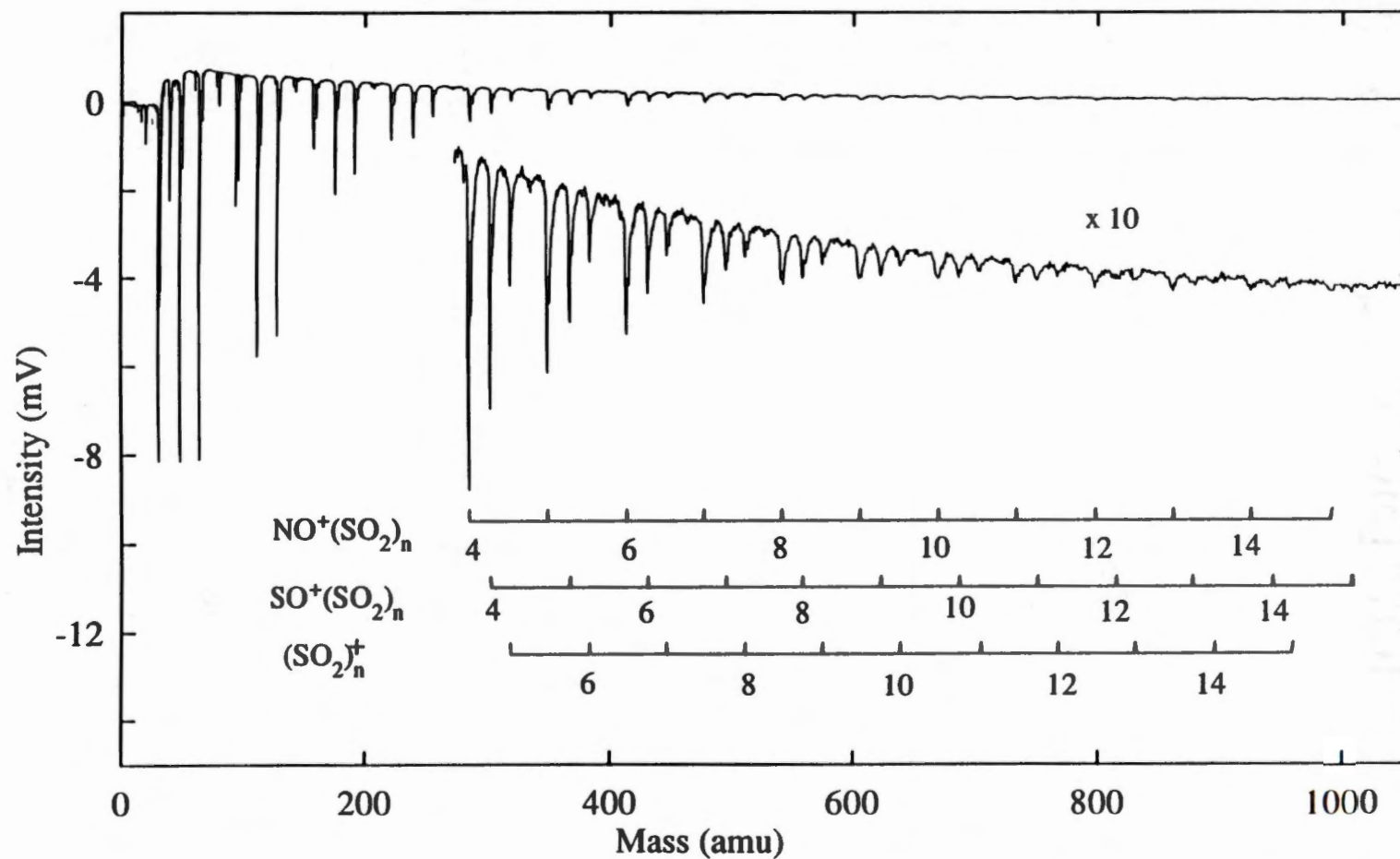


Figure IV-13. The 266 nm MPI mass spectrum produced by a 5% SO_2 /5% NO /90% Ar expansion showing the $\text{NO}^+(\text{SO}_2)_n$, $\text{SO}^+(\text{SO}_2)_n$ and the $(\text{SO}_2)_n^+$ series.

light. Three cluster series are observed, $\text{NO}^+(\text{SO}_2)_n$, $\text{SO}^+(\text{SO}_2)_n$ and $(\text{SO}_2)_m^+$. The $\text{S}^+(\text{SO}_2)_n$ series is observed weakly. The $(\text{SO}_2)_2^+$ and $\text{SO}^+ \text{SO}_2$ species have also been observed by Erickson *et al.*¹⁸⁷ in a molecular beam experiment using a VUV lamp. Using measured appearance energies, they were able to determine the binding energies for $(\text{SO}_2)_2^+$ and $\text{SO}^+ \text{SO}_2$ as 0.66 eV and 0.60 eV, respectively¹⁸⁷. High-pressure mass spectrometric studies gave a higher binding energy for $\text{SO}_2^+ \text{SO}_2$ (0.9 eV)¹⁸⁸. Three-photon REMPI, in the 252-263 nm range, showed that upon ionization, SO_2^+ fragments into S^+ and SO^+ exclusively. This is consistent with the observation of mixed clusters containing these fragments in the present experiments and with REMPI studies¹⁸⁹. Photodissociation of the $(\text{SO}_2)_2^+$ cluster ion, in the 458-590 nm, showed that the only fragment produced was SO_2^+ after the dimer underwent vibrational predissociation¹⁹⁰. Photodetachment studies of the $(\text{SO}_2)_2^-$ have yielded electron affinities and electron binding energies¹⁹¹. The lack of $(\text{NO})_m^+ (\text{SO}_2)_n$ with $m > 1$ is attributed to the relatively stronger bond of $\text{NO} \cdot \text{SO}_2$ species compared to $\text{NO} \cdot \text{NO}$ thus causing the preferential evaporation of nitric oxide molecules in the process of dissipating excess energy.

Chapter V

Tunable Spectroscopy of NO and X-NO (X = Ar, CH₄ and CD₄)

Introduction

The development of high-power, narrow bandwidth, tunable dye lasers has led to the study of both atoms and molecules with two- and three-photon spectroscopy. This method can be used to induce vibrationally and rotationally resolved electronic transitions which can be used to investigate highly excited states and obtain structural information about them. Various atomic and molecular systems have been studied in this manner^{192,193,194}. Nitric oxide is an excellent candidate for tunable spectroscopy because many of its excited states are readily accessible with available dyes and frequency doubling in either one or two photons. Furthermore, its simplicity makes it ideal to study kinetic processes of excited states such as predissociation¹⁹⁵. The ground state of NO has an electronic configuration of $KK (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$ which gives rise to a ${}^2\Pi$ term with two spin-orbit components, ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ ¹⁹⁶. They are split by 121.1 cm⁻¹ with the ${}^2\Pi_{1/2}$ state being the lowest in energy¹⁹⁷. The potential energy curves for nitric oxide are shown in figure V-1 including the ground $X^2\Pi_{1/2}$ state and the two excited states that were probed in this study, namely, the $A^2\Sigma^+$ and $C^2\Pi$ states¹⁹⁸. The $X^2\Pi$ ground state belongs to Hund's case (a) at low rotational levels while at high

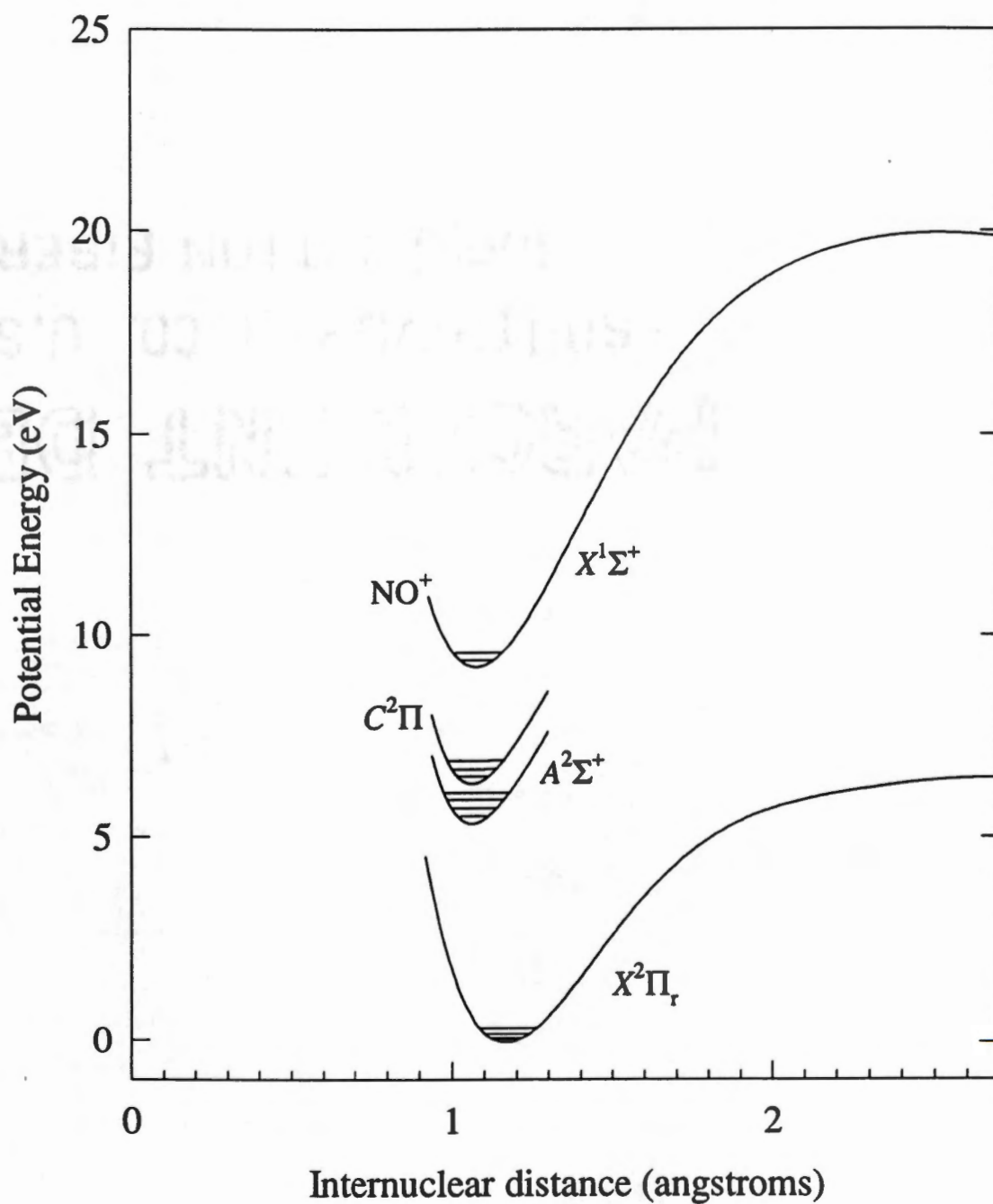


Figure V-1. Potential energy curves for nitric oxide. The spin-orbit splitting of the $X^2\Pi_r$ and the $C^2\Pi$ state is too small to be resolved in this figure.

rotational levels it switches to Hund's case (b). This intermediate coupling case was treated theoretically by Hill *et al.*¹⁹⁹ The two excited states studied in this chapter belong to Hund's case (b). Halpern *et al.*¹⁹² have determined the rotational line intensity factors for two-photon excitation of NO. Several studies of excited states of NO, detected by ionization^{200,201,202,203,204} and fluorescence^{205,206,207,208,209}, have appeared in the literature.

Results and Discussion

Nitric Oxide

Figure V-2 shows the nitric oxide ion signal as a function of two-photon excitation energy for the (2+2) REMPI of NO through the $A^2\Sigma^+ v' = 2 \leftarrow X^2\Pi v'' = 0$ transition. The spectrum consists of five bands where the peak at 48865 cm⁻¹ corresponds to the S₂₁ band, the peak at 48854 cm⁻¹ corresponds to the S₁₁+R₂₁ bands and the peak at 48846 cm⁻¹ corresponds to the Q₂₁+R₁₁ bands. These transitions originate from the $X^2\Pi_{1/2}$ state. The subscripts that are placed after the branch-type designation refer to the initial and final rotational term series, F₁ and F₂ involved in the transition. The splitting between these two rotational terms is determined by the spin-orbit coupling constant A. The F₁ and F₂ terms are each further split into two levels, F_{1e} and F_{1d} due to Λ -type doubling in which the rotation of the nuclei and the total orbital angular momentum of the electrons are strongly coupled for high *J* values¹⁹⁶. This

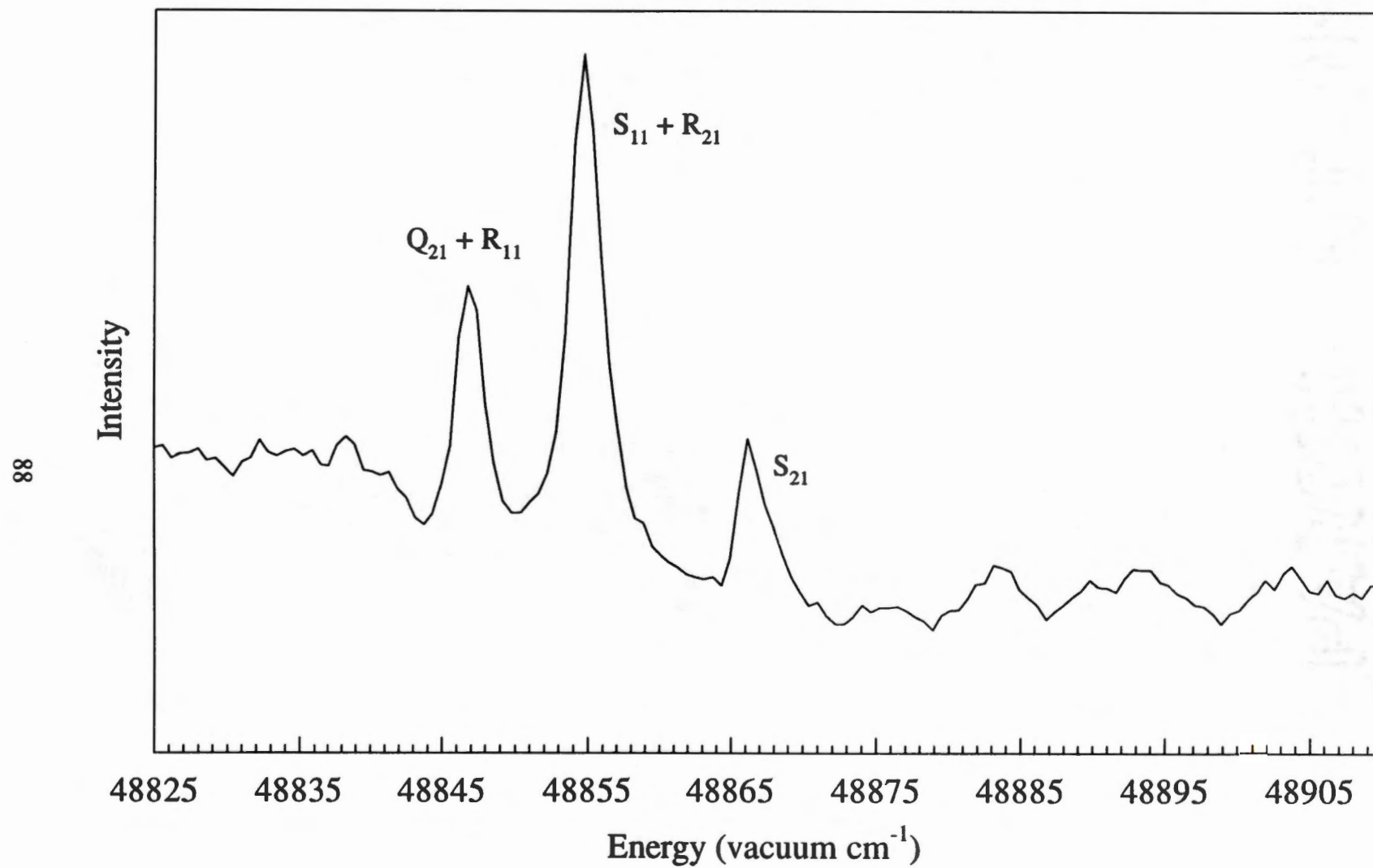


Figure V-2. Multiphoton ionization (2+2) spectrum of the $A^2\Sigma^+ (v = 2) \leftarrow X^2\Pi_{1/2} (v = 0)$ transition of NO.

causes a splitting in the each J value which increases with increasing rotation (or J). The rotational terms for Λ -type doubling in NO were first derived by Mulliken *et al.*²¹⁰ If one neglects the Λ -type doubling in the ground state, which is smaller than the resolution of the peaks in the spectra, the rotational terms for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are given by¹⁹⁶

$$F_1''(J) = B_{\text{eff}}^{(1)} J(J+1) \quad \text{and} \quad (V-1)$$

$$F_2''(J) = B_{\text{eff}}^{(2)} J(J+1) \quad (V-2)$$

where $J = 1/2, 3/2 \dots$ etc for $^2\Pi_{1/2}$ and $J = 3/2, 5/2 \dots$ etc for $^2\Pi_{3/2}$.

$B_{\text{eff}}^{(1,2)}$ are, in the limit of large A , given by¹⁹⁶

$$B_{\text{eff}}^{(1)} = B_v''(1 - B_v''/A) \quad \text{and} \quad (V-3)$$

$$B_{\text{eff}}^{(2)} = B_v''(1 + B_v''/A), \quad (V-4)$$

where A refers to the spin-orbit coupling constant. The rotational terms for the $A^2\Sigma^+$ (neglecting the spin rotation splitting) can be expressed as¹⁹⁶

$$F_1'(J) = B_v'(J-1/2)(J+1/2) \quad \text{and} \quad (V-5)$$

$$F_2'(J) = B_v'(J+1/2)(J+3/2) \quad (V-6)$$

where $J = 1/2, 3/2 \dots$ etc. The result is that 10 branches, from each spin-orbit component (for a total of 20), are expected. However, if the spin-doubling in the excited state is neglected (it is usually smaller than the bandwidth of the laser) only six of the possible ten bands, from each Ω , are observed since some of the branches merge together due to their rather small splitting. In the colder, supersonic expansions even fewer bands are observed due to the effective cooling of rotational modes.

Spectroscopic measurements of the A state have been carried by a number of groups with a number of different techniques. Zacharias *et al.*²⁰³ used two-photon ionization to determine the ionization cross-section from $v' = 0$ of the $A^2\Sigma^+$ state to be $7.0 \times 10^{-19} \text{ cm}^2$ with the ionizing wavelength being 266 nm. Extensive work was performed by Miller *et al.*²⁰⁰ who used resonantly enhanced multiphoton ionization (REMPI)-photoelectron electron spectroscopy (PES) to investigate transitions through various vibrational levels of the $A^2\Sigma^+$ state ($v' = 0-2$). Using a (2+2) photoionization scheme, they were able to determine that the high energy electrons that they observed were due to direct ionization from the excited state. The photoelectron spectra were dominated by Franck-Condon factors which led to the ion being formed in the same vibrational state as the excited state, i. e., $\Delta v = 0$. The majority of the excess energy was being carried off by the exiting electron²⁰⁰. Internal conversion and autoionization arguments were used to explain the presence of near zero kinetic energy electrons in their spectra²⁰⁰. The two-photon absorption cross-section for the $A^2\Sigma^+ v' = 2 \leftarrow X^2\Pi v'' = 0$ transition was determined by Gross *et al.*²¹¹, using a fluorescence technique, to be $1.2 \times 10^{-48} \text{ cm}^4 \text{ s}$ while Hochstrasser *et al.*²¹² and Burris *et al.*²¹³. Both arrived at a value of $2.9 \times 10^{-49} \text{ cm}^4 \text{ s}$. Multiphoton ionization of vibrationally hot nitric oxide was investigated using a (1+1) scheme via the $A^2\Sigma^+$ state and bandheads were assigned²¹⁴.

The spectrum in figure V-3 shows the ion signal of NO again as a function of two-photon excitation energy for resonantly enhanced (2+1) MPI through the $A^2\Sigma^+ v' = 3 \leftarrow X^2\Pi v'' = 0$ transition. The peak at 51142 cm^{-1} corresponds to the S_{21} band, while

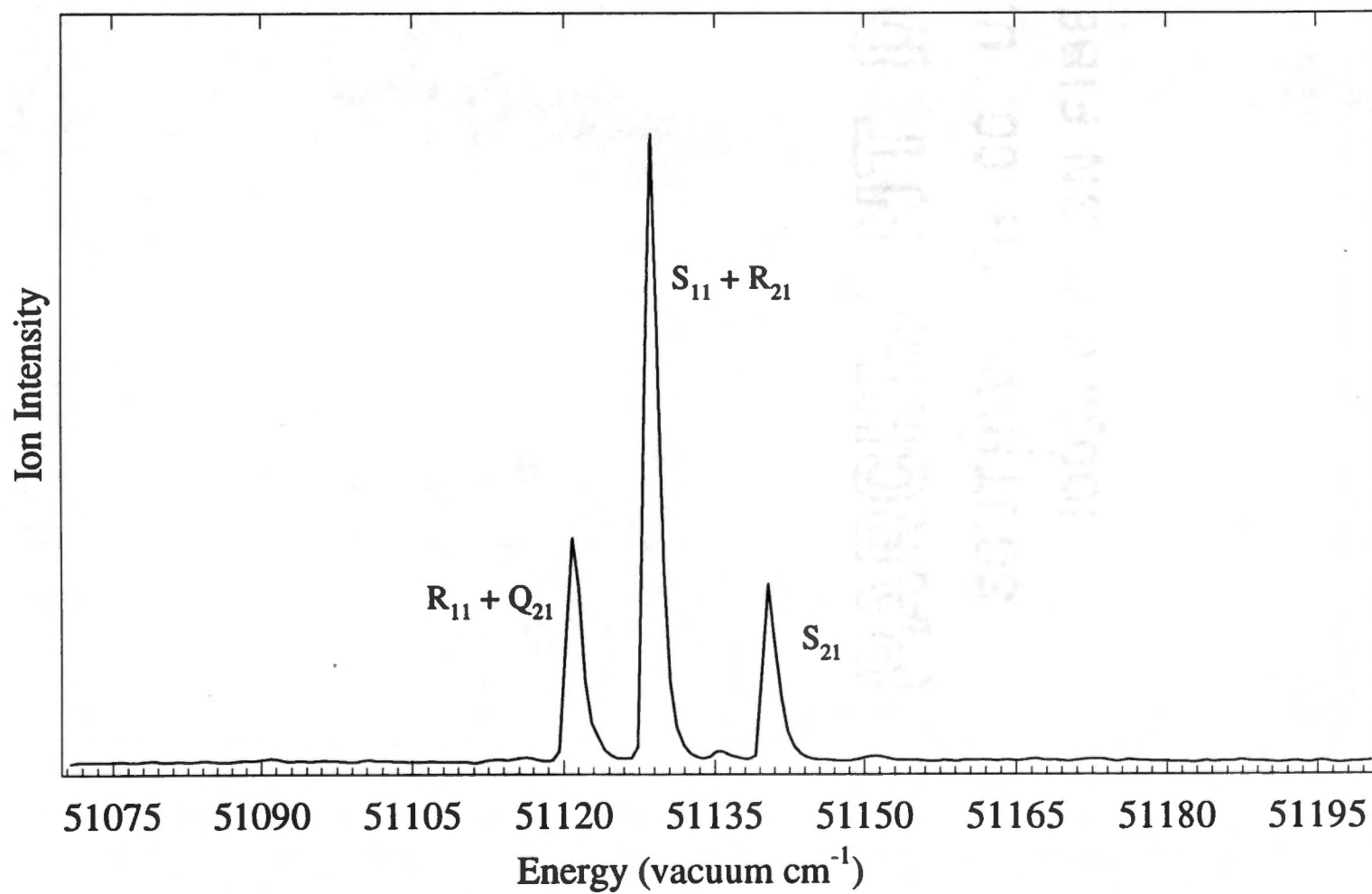


Figure. V-3. Multiphoton ionization (2+1) spectrum of the $A^2\Sigma^+ (v = 3) \leftarrow X^2\Pi_{1/2} (v = 0)$ transition of NO.

the peaks at 51129 cm^{-1} and 51121 cm^{-1} correspond to the $S_{11}+R_{21}$ and $R_{11}+Q_{21}$ bands, respectively. In studying the REMPI-PES of NO via various vibrational levels in the $A^2\Sigma^+$ state, Miller *et al.*²⁰⁰ discovered that when the ionization process proceeded through the $v' = 3$ level of the $A^2\Sigma^+$ state there was a trade-off in the formation of the ion between direct ionization and vibrational autoionization. The former process involved the absorption of two photons, of 3.17 eV each, into the $v' = 3$ level of the $A^2\Sigma^+$ state and the subsequent absorption of another 3.17 eV photon into the $v'' = 0$ of the ground state of the ion (with the exiting electron carrying off most of the energy). The latter process had the same absorption step into the excited state but involved the absorption of an additional two 3.17 eV photon into the continuum, leaving the ion in the $v'' = 3$ level. The trade-off occurred due to the fact that the Franck-Condon factors for the electron to be in the $v'' = 0$ level were very small ($\sim 10^{-7}$) but the ionization probability with three photons was higher than the four photon process. In the four-photon scheme, the Franck-Condon factors, that left the ion in the $v'' = 3$ level, were much higher because it obeyed the $\Delta v = 0$ propensity rule for ionization from a Rydberg state, however, the ionization probability was much lower than in the three photon case. The multiphoton ionization of NO via the $v' = 3$ level was carried out by Zakheim *et al.*²⁰¹ who observed predissociative processes. Table V-1 summarizes the transition energies measured in these experiments on the A state.

Table V-1. Transition Energies for $A^2\Sigma^+ v' = 2 \leftarrow X^2\Pi_{1/2} v'' = 0$ and $A^2\Sigma^+ v' = 3 \leftarrow X^2\Pi v'' = 0$ transitions.

	Transition Energy (in vacuum)
$A^2\Sigma^+ v' = 2 \leftarrow X^2\Pi_{1/2} v'' = 0$	
$Q_{21}+R_{11}$	48846 cm^{-1}
$S_{11}+R_{21}$	48854 cm^{-1}
S_{21}	48865 cm^{-1}
$A^2\Sigma^+ v' = 3 \leftarrow X^2\Pi_{1/2} v'' = 0$	
$Q_{21}+R_{11}$	51121 cm^{-1}
$S_{11}+R_{21}$	51129 cm^{-1}
S_{21}	51142 cm^{-1}

ArNO

The van der Waals complex, ArNO, was investigated with a (2+1) resonant ionization scheme. The only accessible transition was via the $C^2\Pi$ state of the complex which was formed by the conjunction of the ground state of Ar and the $C^2\Pi$ ($v' = 0$) state of NO. The $C^2\Pi$ ($v' = 0$) $\leftarrow X^2\Pi_{1/2}$ transition of NO have been extensively studied by absorption²¹⁵ and emission²¹⁶ spectroscopy and by subjecting NO to external magnetic fields²¹⁷. The 2+1 ionization spectrum of ArNO is shown in figure V-4 and four Ar-NO vibrations were observed. The peaks correspond to the progression of the NO-Ar stretch. The spectrum is obtained by gating the TOF mass spectrum to the ArNO^+ peak with a gated integrator and boxcar averager and recording the output as a function of laser wavelength. The ground state of ArNO has a T-shaped geometry with the 3p Rydberg orbital oriented perpendicular to the molecular axis of NO, an N-Ar distance of 3.711 Å and an O-N-Ar angle of 80.483°^{218,219}. The complex has a ground state well-depth²²⁰ (D_e) of 118 cm^{-1} which leads to a dissociation energy (D_e) of 472 cm^{-1} for the excited C state^{219,221}. The two-photon resonance frequencies associated with the $C^2\Pi \leftarrow X^2\Pi_{1/2}$ transition of NO are shown in table V-2. The 0-0 transition at 52039 cm^{-1} represents a shift of $\sim 334 \text{ cm}^{-1}$ from the corresponding transition in the uncomplexed NO. The shift represents the difference between the ground state and excited state well-depths²²¹. Therefore, by using 118 cm^{-1} as the ground state well-depth, the dissociation energy of the ArNO C state is estimated to be $\sim 452 \text{ cm}^{-1}$ which is in agreement with the value obtained by Miller *et al.*²²¹. The latter authors also determined the force constant

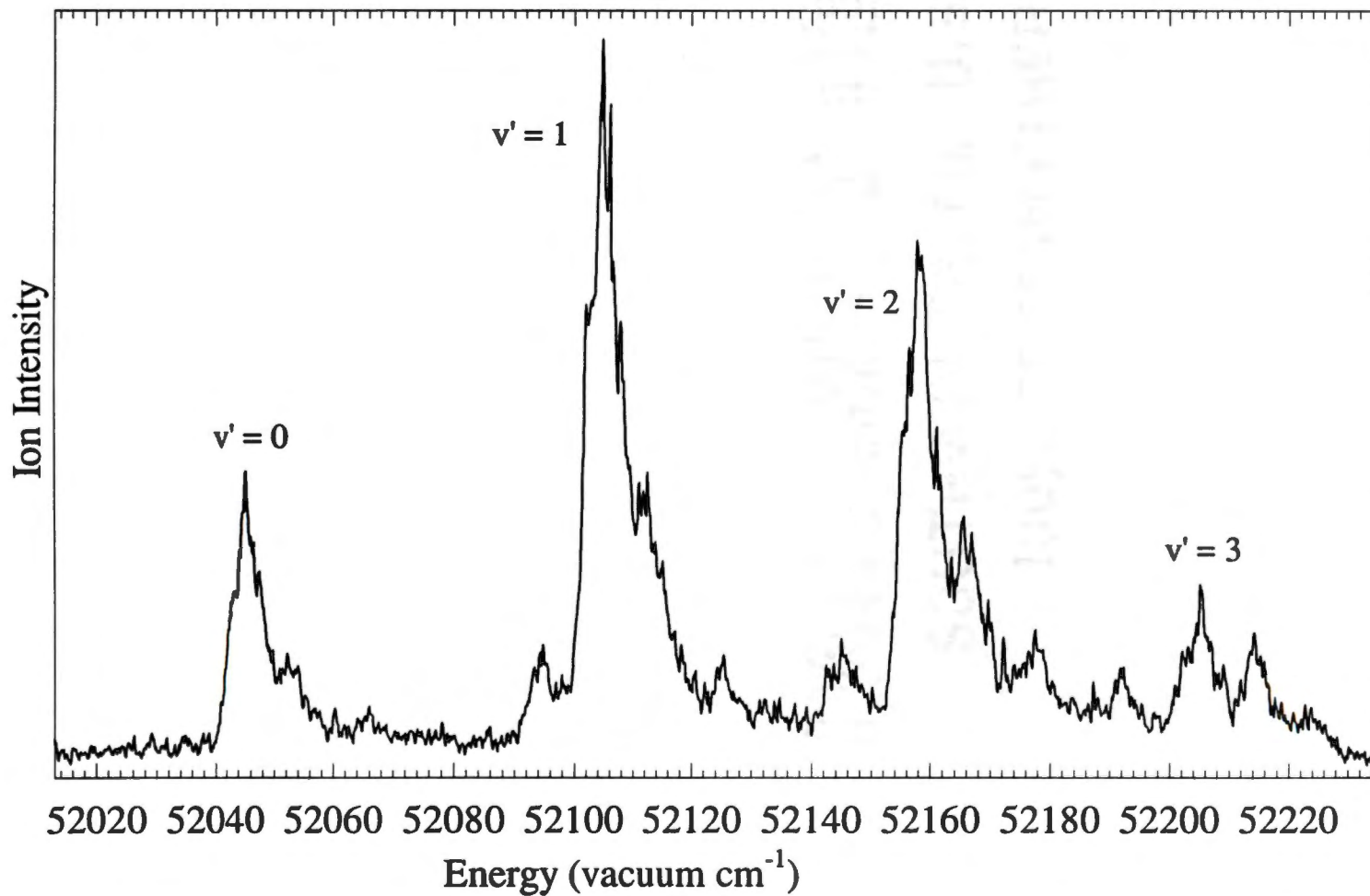


Figure V-4. Multiphoton ionization (2+1) ionization of ArNO associated with the $C^2\Pi(v=0) \leftarrow X^2\Pi_{1/2}(v=0)$ transition of NO. The v' refers to progressions in the Ar-NO stretch.

Table V-2. Transition Energies for $C^2\Pi\ v' = 0 \leftarrow X^2\Pi_{1/2}\ v'' = 0$ transition.

	Laser wavelength	Transition energy (in vacuum)	vibrational spacing
NO($v' = 0$)	381.77 nm	52373 cm⁻¹	
ArNO($v' = 0$) ^a	384.21 nm	52039 cm ⁻¹	0
ArNO($v' = 1$)	383.79 nm	52096 cm ⁻¹	57 cm ⁻¹
ArNO($v' = 2$)	383.41 nm	52149 cm ⁻¹	53 cm ⁻¹
ArNO($v' = 3$)	383.08 nm	52193 cm ⁻¹	44 cm ⁻¹

^a v' refers to the vibrational progression in the NO-Ar stretch.

of the van der Waals bond to be 3.39×10^{-2} mdyne/Å²²¹. If the measured data in table V-2 is fit to a Morse potential, a vibrational frequency (ω_e) of 64.3 cm⁻¹ and a constant $\omega_e x_e$ of 3.25 cm⁻¹ is obtained. The calculated vibrational frequency are similar to the value obtained by Miller *et al.*²²¹. Rotational fine structure in the peaks is unresolved in the experiment, consistent with a rotational constant of 0.08 cm⁻¹ as determined by scattering experiments²²². Takahashi²²³ used REMPI-PES to observe vibrational progressions of the Ar-NO⁺ cation and determined the dissociation energy of the ground state of the ion to be 951 cm⁻¹. Using mass resolved REMPI, McQuaid *et al.*²²⁴ have investigated the A-X vibronic transitions and have arrived at an upper limit of 43 cm⁻¹ for the dissociation energy of the A state of ArNO²²⁴.

CH₄NO and CD₄NO

The CH₄NO and CD₄NO van der Waals complexes can be produced when either or deuterated methane is coexpanded with nitric oxide and argon. The spectrum in figure V-5 shows six peaks which correspond to progressions of the CH₄ - NO stretch following a (2+1) REMPI processes involving the C state of NO. Figure V-6 shows a similar spectrum of CD₄NO. The measured transition energies for both species are summarized in table V-3. The protonated methane complex has a progression with an origin of 51604 cm⁻¹ which represents a shift of ~770 cm⁻¹ from the uncomplexed NO and is in agreement with the value obtained by Miller²²⁵. Fitting the data in table V-3 to a Morse potential yields an ω_e of 102 cm⁻¹ and a $\omega_e x_e$ of 3.3 cm⁻¹ for CH₄NO and an ω_e

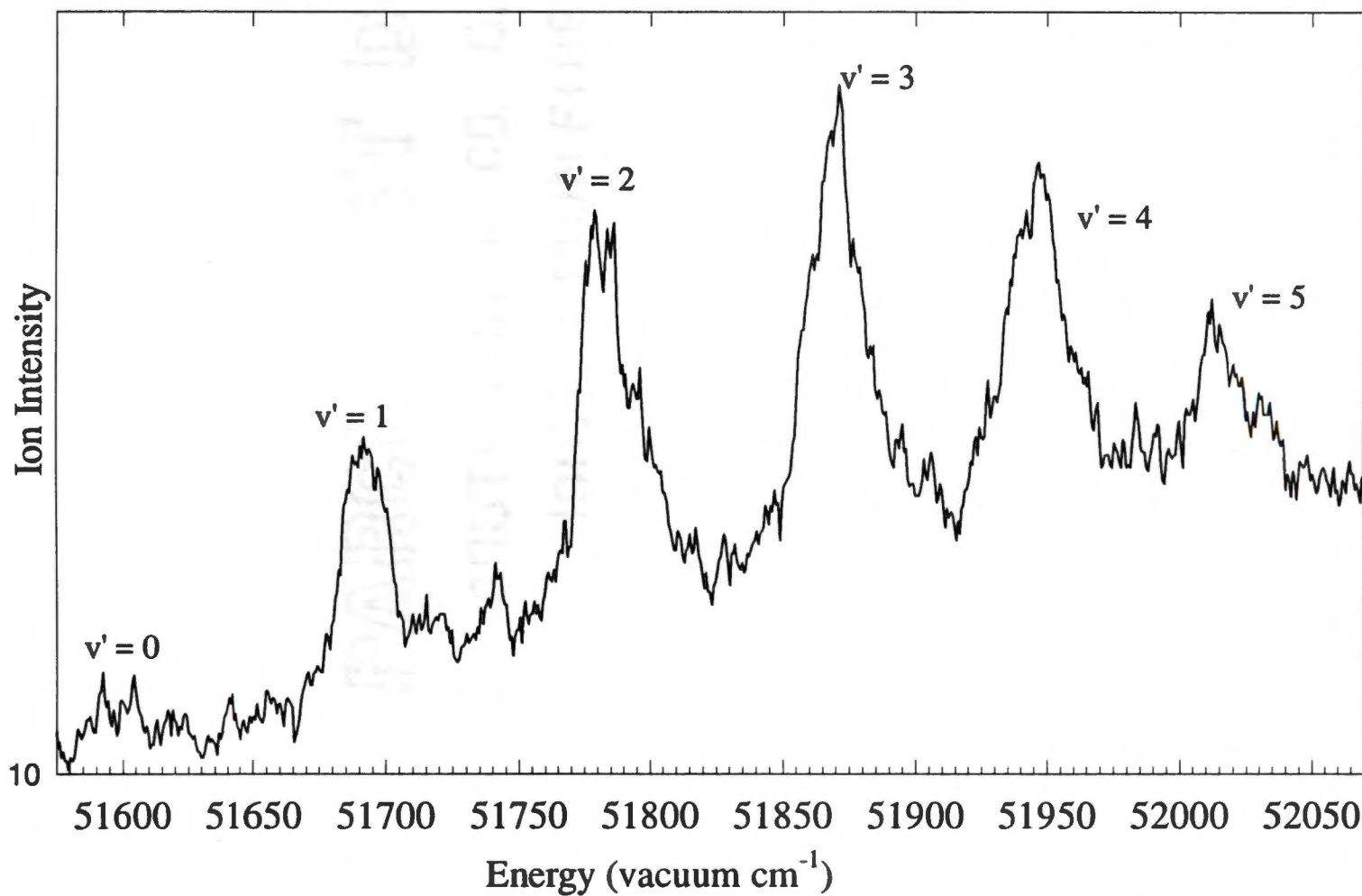


Figure V-5. Multiphoton ionization (2+1) ionization of CH_4NO associated with the $C^2\Pi (v = 0) \leftarrow X^2\Pi_{1/2} (v = 0)$ transition of NO. The v' refers to progressions in the $\text{CH}_4\text{-NO}$ stretch.

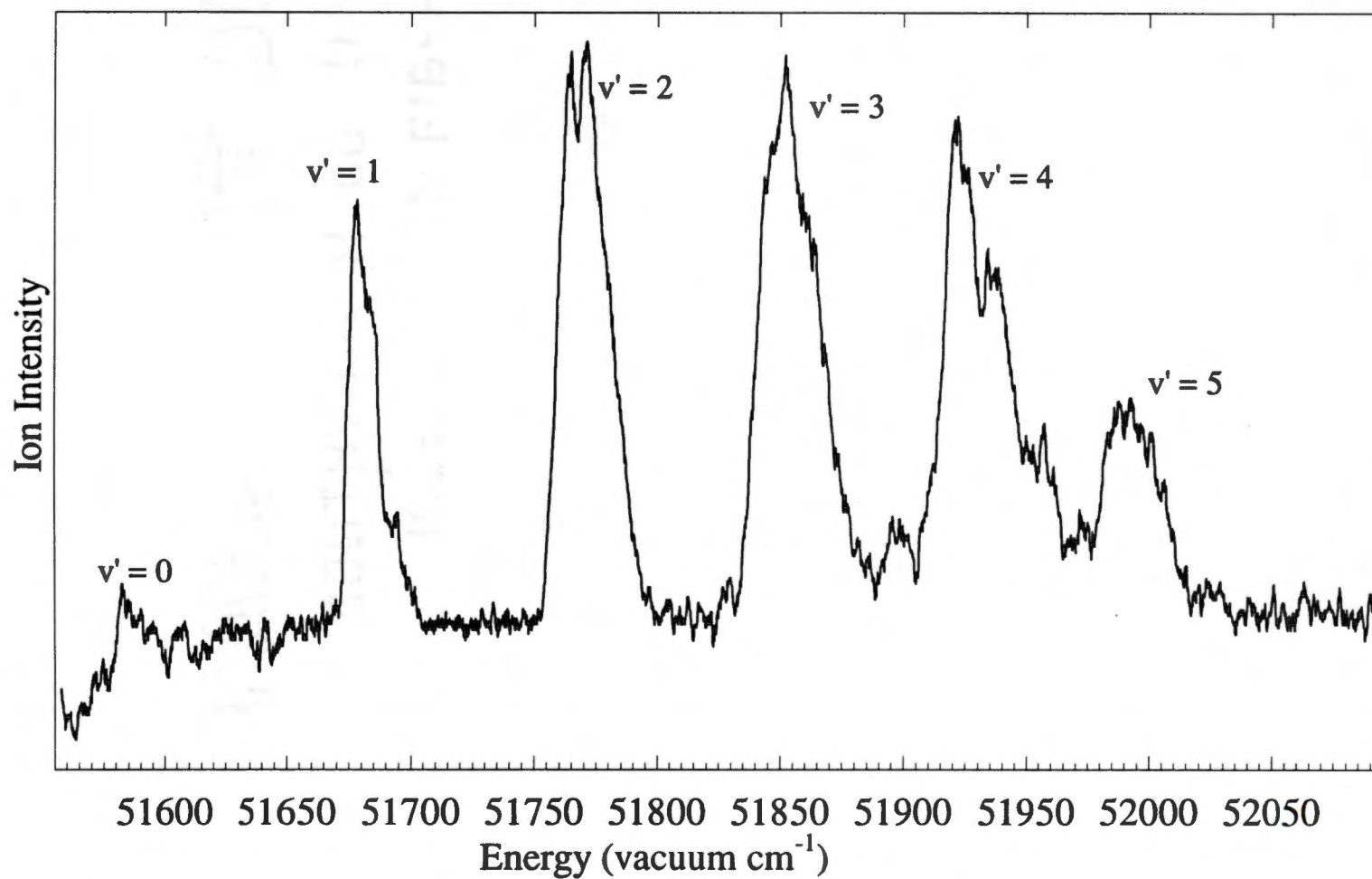


Figure V-6. Multiphoton ionization (2+1) ionization of CD_4NO associated with the $C^2\Pi (v=0) \leftarrow X^2\Pi_{1/2} (v=0)$ transition of NO. The v' refers to progressions in the $\text{CD}_4\text{-NO}$ stretch.

Table V-3. Transition Energies for ArNO associated with the $C^2\Pi\ v' = 0 \leftarrow X^2\Pi_{1/2}\ v'' = 0$ transition of NO.

Transition	Laser wavelength	Transition energy (in vacuum)	vibrational spacing
$\text{CH}_4\text{NO}(v' = 0)^a$	387.45 nm	51605 cm^{-1}	0
$\text{CH}_4\text{NO}(v' = 1)$	386.73 nm	51701 cm^{-1}	96 cm^{-1}
$\text{CH}_4\text{NO}(v' = 2)$	386.07 nm	51788 cm^{-1}	87 cm^{-1}
$\text{CH}_4\text{NO}(v' = 3)$	385.46 nm	51870 cm^{-1}	82 cm^{-1}
$\text{CH}_4\text{NO}(v' = 4)$	384.88 nm	51949 cm^{-1}	79 cm^{-1}
$\text{CH}_4\text{NO}(v' = 5)$	384.38 nm	52016 cm^{-1}	67 cm^{-1}
$\text{CD}_4\text{NO}(v' = 0)$	387.45 nm	51605 cm^{-1}	0
$\text{CD}_4\text{NO}(v' = 1)$	386.81 nm	51689 cm^{-1}	84 cm^{-1}
$\text{CD}_4\text{NO}(v' = 2)$	386.18 nm	51774 cm^{-1}	85 cm^{-1}
$\text{CD}_4\text{NO}(v' = 3)$	385.60 nm	51852 cm^{-1}	78 cm^{-1}
$\text{CD}_4\text{NO}(v' = 4)$	384.05 nm	51927 cm^{-1}	75 cm^{-1}
$\text{CD}_4\text{NO}(v' = 5)$	384.56 nm	51992 cm^{-1}	65 cm^{-1}

^a v' refers to the vibrational progression in the NO- CH_4 and the NO- CD_4 stretch.

of 91.8 cm^{-1} and a ω_{ex} of 2.4 cm^{-1} for CD_4NO . These values are in agreement with those obtained by Miller²²⁵.

Chapter VI

Laser Induced Polymerization in CS₂ clusters

Introduction

Carbon disulfide has been studied extensively by electron and photon excitation techniques to investigate its fragmentation dynamics^{226,227}, spectroscopy^{228,229,230,231}, photochemistry^{232,233} and nucleation^{234,235}. Recently, the phenomena of nucleation and laser induced-polymerization of small molecules such as CS₂ has generated great interest. These experiments fall into three main categories which are described separately below: those that are performed at low to moderate pressures, those that are performed at high pressures, and those in molecular beams.

At moderate pressures (1-75 torr) laser induced particle formation or "laser snow" can be observed in CS₂ vapor^{235,236,237,238}. This phenomenon was first seen in a mixture of cesium and hydrogen after excitation of the 7P state of cesium²³⁹. The laser-induced reaction was extensive enough to lead to the production of macroscopic particles of cesium hydride which were visible to the naked eye, hence the term laser snow. Laser snow studies in CS₂ vapor by Ernst *et al.*^{236,237,238} used 337 nm light from a nitrogen laser and the 351 nm and 357 nm lines of a krypton laser to induce clustering. A more detailed wavelength-dependence study of clustering in the 335 to 342 nm region²³⁵ indicated that the process was initiated following the absorption of photons to

produce electronically excited CS_2 molecules, which, in turn, collided with ground state molecules and underwent nucleation and dissociation. The entire reaction sequence was thought to proceed through the neutral manifold of electronic states. The rate of growth of $(\text{CS})_m$ and S_m was measured by collecting the light from a helium-neon laser that scattered from macroscopic particles. It is interesting to note that the scattered light signal exhibited oscillations as a function of time²³⁵. The scattering increased as a function of particle size but after a critical size was reached larger particles were removed from the vapor phase in the form of particulates and consequently, a decrease in the scattering was observed. This was followed by the regrowth of the smaller particles that remained in the vapor and the cycle resumed.

At higher total pressures (100-500 torr), nucleation can be photoinduced in supersaturated vapors^{234,240,241}. In experiments by Kalisky *et al.*²³⁴ a thermal diffusion cloud chamber (TDCC) was used to contain a supersaturated vapor of CS_2 and a xenon arc lamp was used to induce nucleation. S_n particles were deposited on the bottom of the chamber while CS molecules diffused to the wall and formed a brownish coating. The mechanism given for the production of S_n is highly dependent on the S_2 molecule which is produced by the collision of an excited CS_2 molecule with a molecule in the ground state. The S_2 molecule serves as a seed for the formation of an S_n cluster of critical size and once this size is reached the cluster itself becomes the nucleus for the formation of S_n droplets that are observed in the TDCC. That is, the S_2 molecule reacts with another S_2 molecule to produce S_4 which in turn reacts with an S_2 molecule to

produce S_6 and so on. The same group also investigated photoinduced nucleation involving small amounts of carbon disulfide in supersaturated host vapors, such as ethanol and helium.

In contrast to the phenomena described above, reactions within van der Waals (vdW) clusters in molecular beams at very low pressures is a relatively new area of study. There have been many reported instances of intracluster reactions^{242,243,244,245,246,247,248} which are initiated by the ionization of a cluster to form the cation. The excess energy that is deposited into the cluster can be dissipated by the successive evaporation of species that are weakly bound to the ion, by the fragmentation of the cluster ion where the fragment also carries off the excess energy, or by the initiation of reactions within the cluster to form new cationic species. A subset of this class of reactions involves polymerization processes within vdW clusters. They have been reported by two groups^{249,250} which have studied species that are also known to polymerize in bulk samples. In these reactions the fragmentation of the parent cluster is thought to be followed by a series of addition and elimination reactions that produce polymeric cations. As an example, El-Shall *et al.*²⁴⁹ have reported cationic polymerization in isoprene clusters. Clusters were generated by expanding isoprene and helium through a conical nozzle, ionized by electron impact and detected by a quadrupole mass spectrometer. The mass spectrum showed pure isoprene clusters and numerous fragment ions that were a result of a series of addition-elimination reactions.

The isoprene intracluster processes have a well known analog in ion-molecule chemistry as demonstrated by Kascheres *et al.*²⁵¹. In Kascheres' work an isoprene radical cation and its neutral counterpart were guided into an ion trap where they were allowed to react for 300 milliseconds. The resulting fragment ion distribution was very similar in extent and abundance when compared to the intracluster reactions.

In the present paper, we report the observation of S_m^+ and $(CS)_m^+$ ions and provide unambiguous evidence of their formation via a unique cycle of consecutive intracluster reactions within parent CS_2 clusters. The proposed reactions are supported not only by the observation of the cluster ions that initiate the cycles but also by the intermediates that are involved. Furthermore, the reactions are based on previously observed ion-molecule reactions involving excited CS_2^+ .

The excited states of the carbon disulfide ion have been studied and their respective dissociation limits and dissociative products have been characterized.¹ The photoelectron spectrum of CS_2 shows five prominent bands with four of the bands having resolved vibrational structure.²³⁰ The spectroscopy of neutral CS_2 has also been well studied and shows an extensive and complex absorption spectrum. Some of the stronger bands include the $\tilde{a}^3A_2 \leftarrow \tilde{X}^1\Sigma_g^+$ transition between 330 nm and 430 nm, the $\tilde{A}^1B_2 \leftarrow \tilde{X}^1\Sigma_g^+$ transition between 180 nm and 220 nm, the $\tilde{C} \leftarrow \tilde{X}$ transition between 162 nm and 172 nm and the $\tilde{E} \leftarrow \tilde{X}$ transition between 136 nm and 153.5 nm^{231,245,252}. The spectrum below 136 nm is dominated by a number of Rydberg transitions.

The present work is a continuation of previous cluster studies using picosecond laser ionization coupled with mass spectrometry. Earlier work by this group has involved the study of "magic numbers" in both homonuclear and heteronuclear cluster distributions^{253,254,255}.

Results and Discussion

The TOF mass spectrum produced by two-photon ionization (239.53 nm) of a low pressure (125 torr) expansion of a CS₂/Ar mixture is shown in figure VI-1. This expansion produced no clusters and the only ions observed are S⁺ and CS₂⁺. In the mass spectrum the small peak that is separated by one amu from CS₂⁺ is due to HCS₂⁺ which is a result of reactions with trace quantities of water while the peak that is separated by two amu is due to CS₂⁺ with one ³⁴S isotope. Figure VI-2 presents an energy level diagram of CS₂ showing the excited states of both the neutral and the ion. The excited states of the ion are shown with their respective dissociation limits and products while the arrows indicate the number of photons needed to ionize CS₂ at 239.53 nm and the energy corresponding to one- and two-photon absorption in the neutral and ionic manifolds. The CS₂⁺ that is observed in figure VI-1 arises from direct two-photon MPI of the neutral. The formation of the sulfur ion occurs by two-photon ionization of CS₂ with subsequent absorption of a third 239.53 nm (5.17 eV) photon by

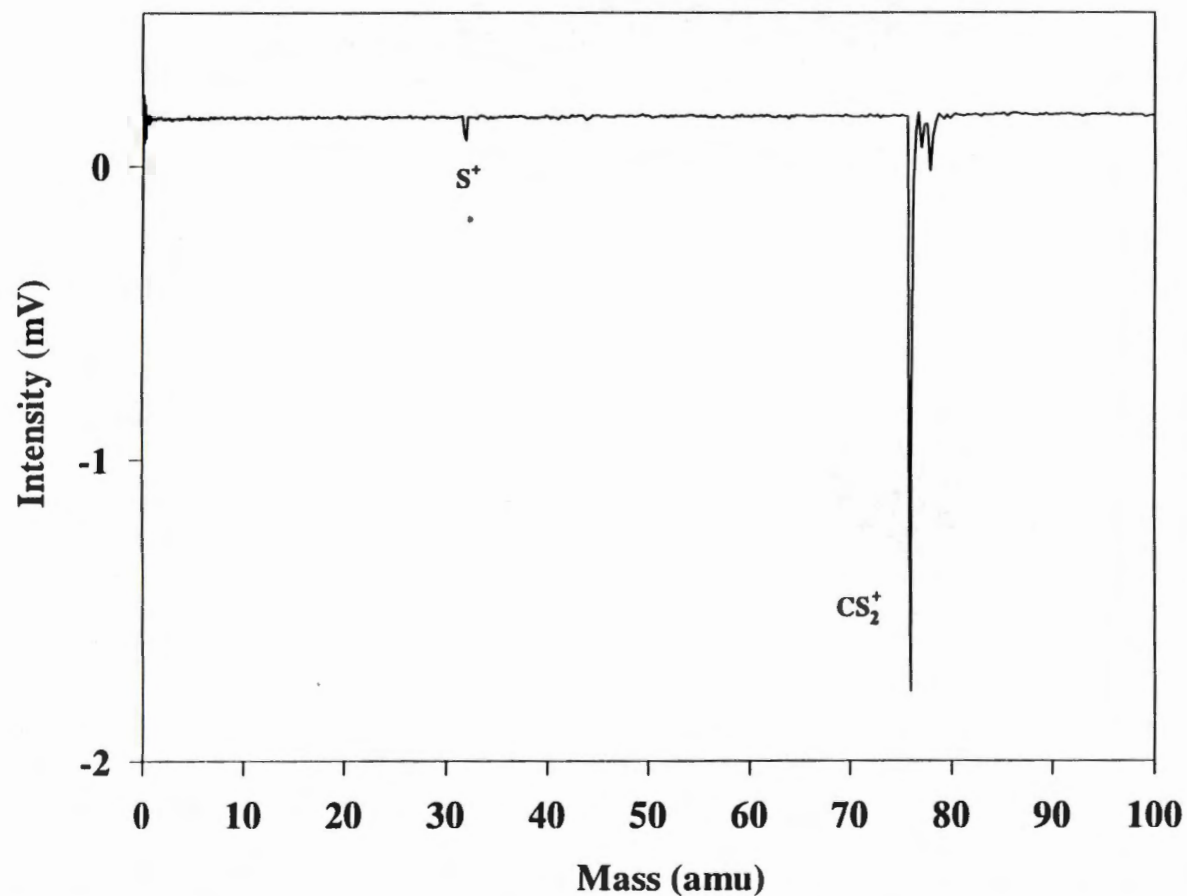


Figure VI-1. The 239.53 nm MPI mass spectrum produced by a 125 torr expansion of CS_2 showing the S^+ and the CS_2^+ ions. The small peak that is separated by one amu from the CS_2^+ peak is due to HCS_2^+ while the peak that is separated by two amu is due to one ^{34}S isotope on CS_2^+ .

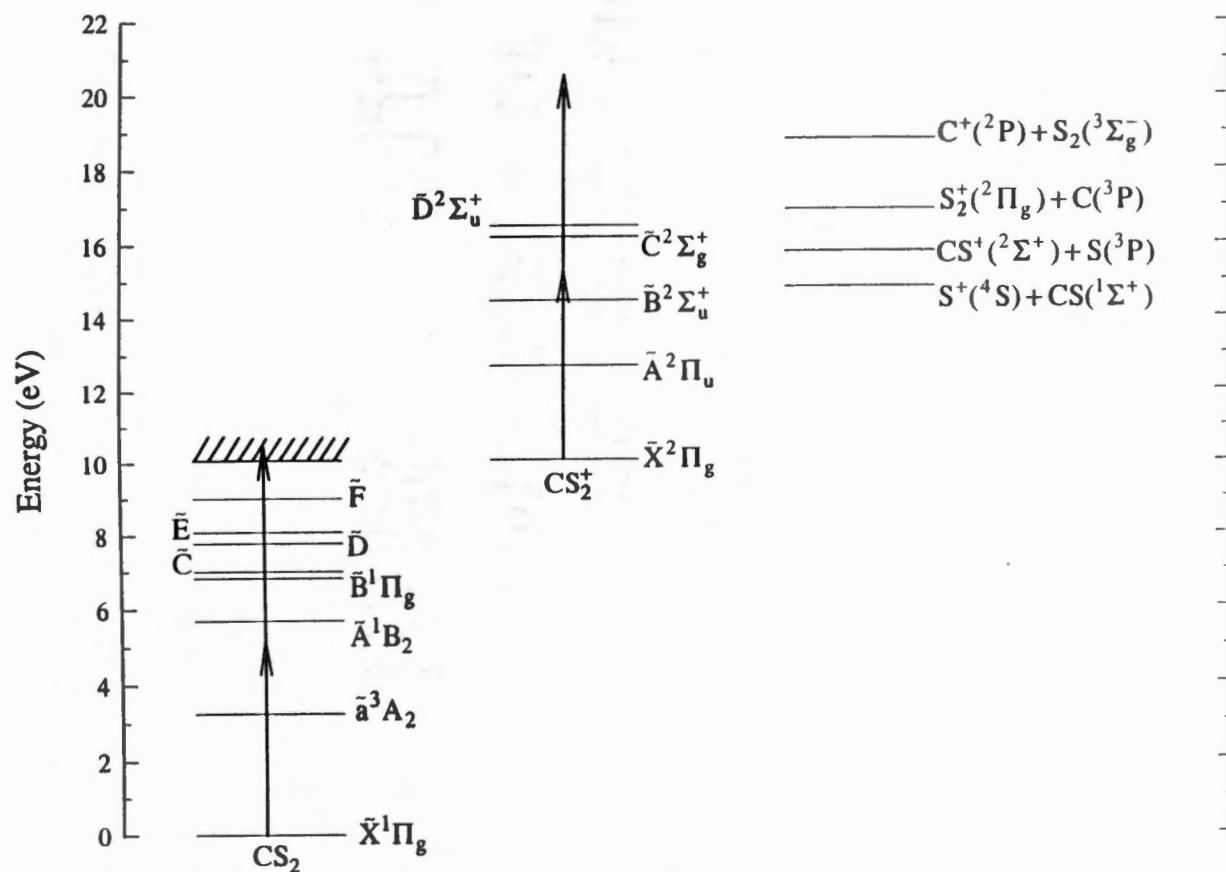
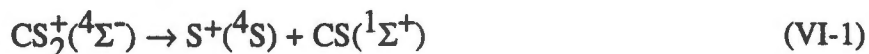


Figure VI-2. Schematic of the energy level diagram for CS_2 and CS_2^+ . Also, shown, in the CS_2^+ manifold are the dissociation products and their respective dissociation limits. The arrows represent the number of photons needed to ionize CS_2 at 239.53 nm and the energy corresponding to one and two-photon absorption in the neutral and ionic manifolds.

CS_2^+ into the $\tilde{\text{B}}^2\Sigma_u^+$ state which can predissociate via the $^4\Sigma^-$ repulsive state.⁴ The threshold for this process is 14.81 eV with respect to the ground state of CS_2 . The last step in the formation of S^+ can therefore be described as follows:



This process has been previously observed at 240 nm by Fischer *et al.*²⁵⁶ who also see only CS_2^+ and S^+ in their mass spectrum.

Figure VI-3 shows the low mass region of the time-of-flight mass spectrum obtained by ionizing a 5% CS_2/Ar mixture using focused 239.53 nm light. In this case the backing pressure has been increased to 100 psi in order to enhance cluster formation. In contrast to the mass spectrum obtained at the low backing pressure (figure VI-1) the spectrum in figure VI-3 shows numerous ions with masses up to 300 amu. In addition to the S^+ and CS_2^+ ions seen previously in figure VI-1 we observe two main classes of cluster ions in the mass spectrum. The first includes homogeneous clusters of the form $(\text{CS}_2)_m^+$, $(\text{S})_m^+$, or $(\text{CS})_m^+$ while the second category includes sulfur and carbon monosulfide cluster ions solvated by additional CS_2 molecules [i.e., $\text{S}_m^+(\text{CS}_2)_n$ or $\text{CS}_m^+(\text{CS}_2)_n$]. Again, the small peaks that are separated by one amu from the S^+ and CS^+ ions in figure VI-4 are due to HS^+ and HCS^+ ions, respectively, and clusters with one

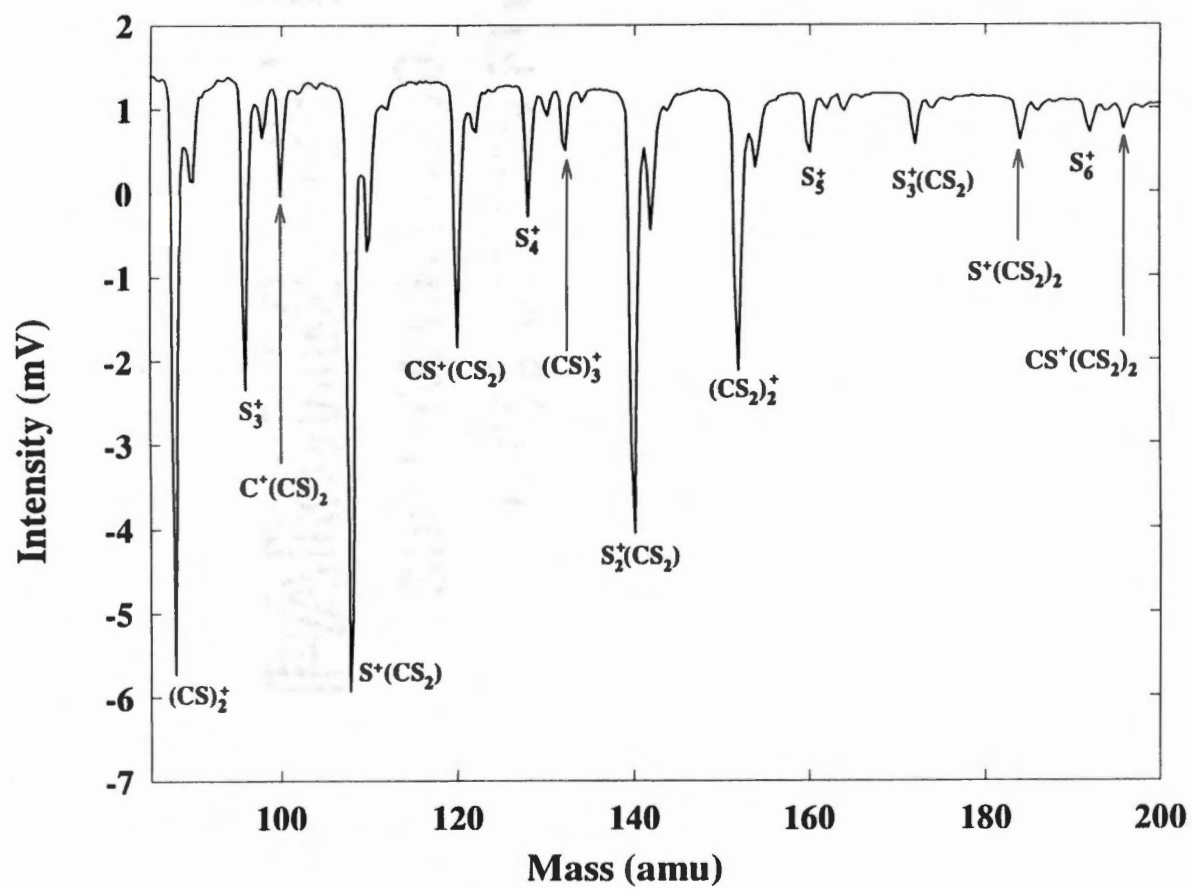


Figure VI-3. The low mass region of a 239.53 nm MPI mass spectrum produced by a 100 psi 5% CS_2 /Ar expansion showing the fragments resulting from the parent and cluster ions.

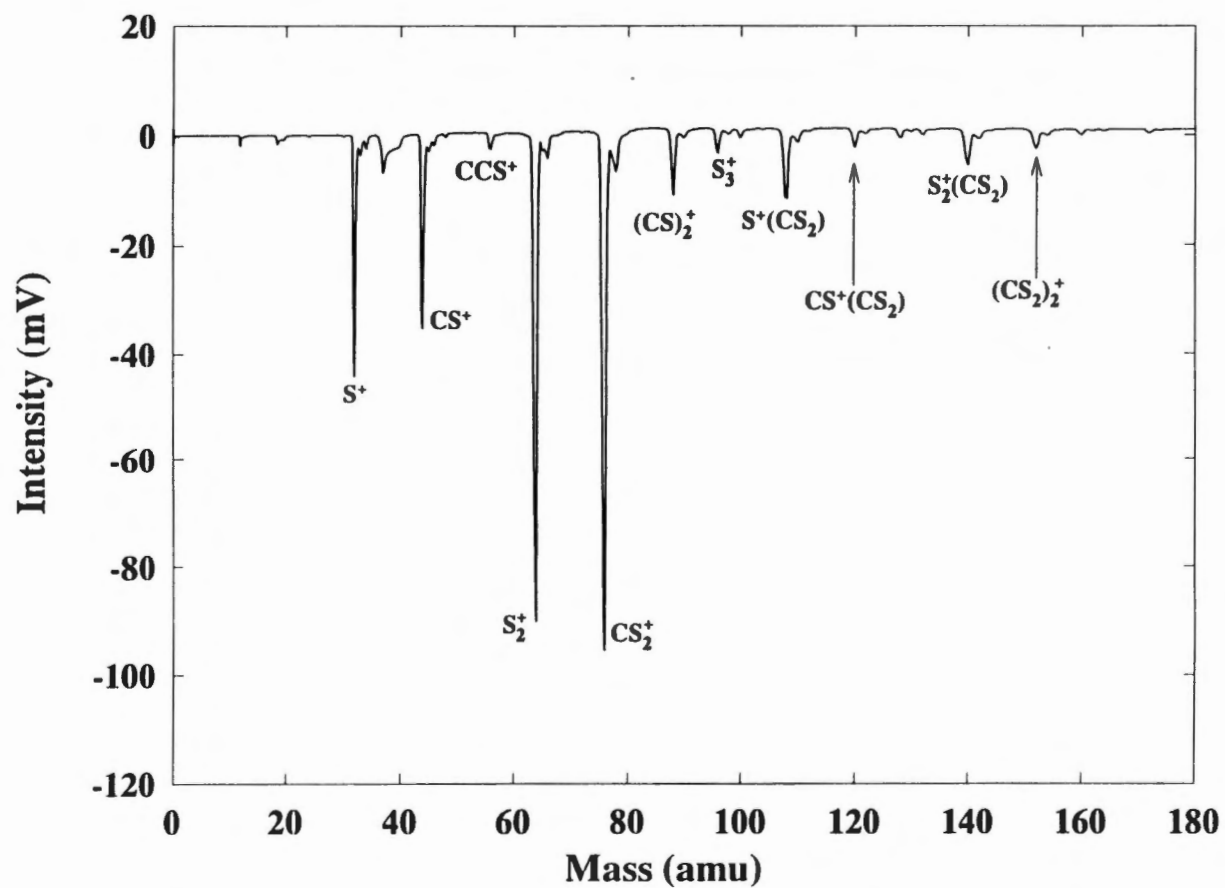


Figure VI-4. The extension of figure VI-3 showing the higher mass region. The $(S)_2^+$ and $(CS)_2^+$ peaks are a result of intracuster polymerization reactions while the other ions come from purely fragmentation and dissociation processes.

^{34}S are observed two amu from most of the peaks. The presence of CS^+ and S_2^+ in this mass spectrum (figure VI-3) and their absence in figure VI-1 indicates that these ions are produced from the dissociation of carbon disulfide cluster ions rather than from the monomer. Although CS_2 has a number of *neutral* dissociation channels which could give rise to both CS and S species which could, in turn, be ionized, we believe that the formation of the sulfur and carbon monosulfide ions occurs from the dissociation of CS_2^+ and $(\text{CS}_2)_m^+$, respectively. The dissociation channel producing CS+S in the $^1\Sigma^+$ and ^3P states, respectively, has a threshold of 4.46 eV (278 nm)²³⁵. Thus absorption into the $^1\text{B}_2 \leftarrow ^1\Sigma_g^+$ transition which extends from 189 nm to 220 nm can result in neutral fragments. Another broad absorption band extends from 290 nm to approximately 350 nm which cannot lead to dissociation with one photon²³¹. However, the absorption cross-section at 239.53 nm appears to be very small²³¹. Consequently, we expect two-photon ionization to dominate over any possible one-photon dissociation processes.

Figure VI-4 shows the higher mass region of figure VI-3 on an expanded and amplified scale and we observe pure sulfur clusters up to the hexamer, carbon monosulfide clusters up to the trimer, and various heterogenous cluster ions. The observed ions in figures VI-1 and VI-2 are summarized in table VI-1. The largest cluster of CS_2 observed (but not shown) under the conditions of figures VI-3 and VI-4 is the $(\text{CS}_2)_5^+$ species. However, experimental conditions of backing pressure and laser

Table VI-1. Summary of ions observed in Figs. 3 and 4.
($\lambda = 239.53$ nm)

ION	m	n
$(S)_m^+$	1-11	
$(CS)_m^+$	1-5	
$(CS_2)_m^+$	1-5	
CCS^+	1	
$S_m^+(CS_2)_n$	1-9	1-4
$CS_m^+(CS_2)_n$	1-3	1-3

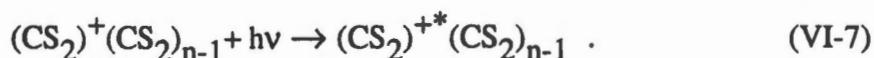
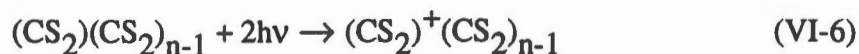
power can be varied such that clusters up to $(\text{CS}_2)_{13}^+$ are observed. The formation of the fragment ions in figures VI-3 and VI-4 (except for S^+ and CS_2^+) is attributed to intracluster photochemistry occurring entirely within individual clusters. Since the CS_2 clusters are ionized approximately six inches downstream from the supersonic nozzle it can be safely assumed that all collisions have ceased. It is well known that species such as $(\text{CS})_m^+$, $\text{CS}^+(\text{CS}_2)_m$ and $(\text{S})_m^+(\text{CS}_2)$ can be created as a result of ion-molecule reactions which are given below and were proposed by Henglein²⁵⁷ to explain his observations in electron impact high-pressure mass spectrometry studies:



Ionization efficiency (IE) curves were also reported and all the secondary ions were observed to have the same appearance potential (13.3 eV). The IE curve for $(\text{CS})_2^+$ didn't rise as steeply as the other ions at threshold while above 16 eV it increased dramatically. Henglein concluded that $(\text{CS})_2^+$ is formed by the two separate processes shown above. Reaction (VI-3) accounted for the $(\text{CS})_2^+$ ions that were observed up to

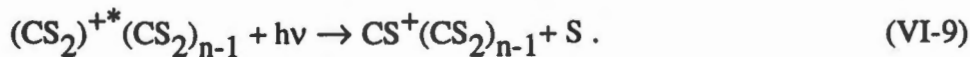
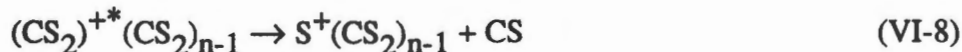
16 eV while those $(\text{CS})_2^+$ ions observed at higher energies had contributions from both reactions (VI-3) and (VI-5) since the threshold for reaction (VI-5) is 16 eV.

The initial steps in the mechanisms that we propose for the formation of $(\text{S})_m^+$, $(\text{CS})_m^+$ and their respective intermediates are given below:



The formation of carbon disulfide clusters is followed by their two-photon ionization and subsequent absorption of an additional 5.17 eV photon to an excited state. All clusters of carbon disulfide can be ionized by two photons of 5.17 eV energy since their I.P's decrease from that of the monomer (10.068 eV) as a function of increasing cluster size²⁵⁸. The extra photon is necessary to reach the fragmentation appearance potentials measured by Henglein²⁵⁷.

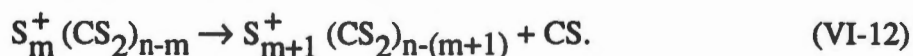
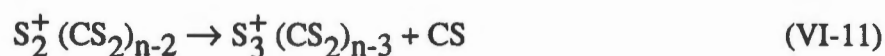
The following two reactions are proposed for the creation of sulfur and carbon monosulfide ions that are solvated by carbon disulfide molecules:



Note that reactions (VI-8) and (VI-9) are cluster analogs of the ion-molecule reactions (VI-2) and (VI-4). Reaction (VI-9) requires an additional 5.17 eV photon because the

reaction is slightly endothermic (see table VI-2). The enthalpies of reaction for a few of the cluster reactions and for the analogous ion-molecule reactions are given in tables VI-2 and VI-3 respectively and are discussed later. The enthalpies of formation were obtained from various references^{258,259,260,261}.

We propose the following cycle of intracuster ion-molecule reactions to account for the creation of pure sulfur cluster ions:



Likewise, the following reactions are proposed for the formation of carbon monosulfide cluster ions:

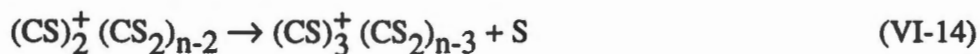


TABLE VI-2. ENTHALPIES FOR CLUSTER REACTIONS^{a,b}

CLUSTER REACTIONS	ΔH_r (kcal/mol)
$\text{CS}_2^{+*}(\text{CS}_2) \rightarrow \text{S}^+(\text{CS}_2) + \text{CS}$	-26.6
$\text{CS}_2^{+*}(\text{CS}_2) \rightarrow \text{CS}^+(\text{CS}_2) + \text{S}$	1.9
$\text{S}^+(\text{CS}_2) \rightarrow \text{S}_2^+ + \text{CS}$	18.8
$\text{S}_2^+(\text{CS}_2) \rightarrow \text{S}_3^+ + \text{CS}$	77.4
$\text{CS}^+(\text{CS}_2) \rightarrow \text{CS}^+ + \text{CS}_2$	37

^a Enthalpies of formation obtained from refs 36-39

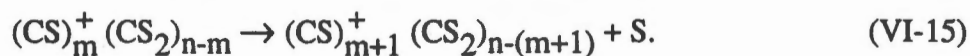
^b CS_2^{+*} denotes an excited ion following absorption of a 5.17 eV photon by the ground state ion.

TABLE VI-3. ENTHALPIES FOR KNOWN ION-MOLECULE
REACTIONS^{a,b}

ION-MOLECULE REACTIONS	ΔH_r (kcal/mol)
$\text{CS}_2^{+*} + \text{CS}_2 \rightarrow \text{S}^+(\text{CS}_2) + \text{CS}$	-51.5
$\text{CS}_2^{+*} + \text{CS}_2 \rightarrow \text{CS}^+(\text{CS}_2) + \text{S}$	-23.0
$\text{S}^+ + \text{CS}_2 \rightarrow \text{S}_2^+ + \text{CS}$	-22.5
$\text{S}_2^+ + \text{CS}_2 \rightarrow \text{S}_3^+ + \text{CS}$	46.5
$\text{S}_3^+ + \text{CS}_2 \rightarrow \text{S}_4^+ + \text{CS}$	49.0
$\text{S}_4^+ + \text{CS}_2 \rightarrow \text{S}_5^+ + \text{CS}$	-10.0
$\text{S}_5^+ + \text{CS}_2 \rightarrow \text{S}_6^+ + \text{CS}$	44.0
$\text{S}_6^+ + \text{CS}_2 \rightarrow \text{S}_7^+ + \text{CS}$	31.0
$\text{S}_7^+ + \text{CS}_2 \rightarrow \text{S}_8^+ + \text{CS}$	41.0

^a Enthalpies of formation obtained from refs 36-39 (also see text)

^b CS_2^{+*} denotes an excited ion following absorption of a 5.17eV photon by the ground state ion.



Again, note that reaction (VI-15) is analogous to the ion-molecule reaction given previously. The ion-molecule analog of reaction (VI-10) has been previously reported by Hiraoka *et al.*²⁶⁰ who observed the following addition reaction:



Related ion-molecule reactions that cycle to produce sulfur cluster ions have also been observed in the isoelectronic OCS molecule by Dzidic *et al.*²⁶²



In both of our sulfur and carbon monosulfide polymerization mechanisms, the respective intermediates cycle through intracuster ion-molecule reactions and terminate with the formation of a homogeneous cluster ion. For example, the production of S_5^+ proceeds as follows:





Likewise, S_m^+ and $(CS)_m^+$ arise from $(CS_2)_m^+$ or larger clusters. The reactions above show that the production of a given S_m^+ ion needs a $CS_2^{+*}(CS_2)_{m-1}$ cluster as the initiating species. Therefore, the termination step, and hence, the formation of resulting pure sulfur ion is dependent upon the size of the carbon disulfide cluster that initiates the cycle of reactions. Since the molecular beam has a distribution of CS_2 cluster sizes, a similar distribution of pure sulfur cluster ion results. In the case above, reaction VI-24 is the terminating step since there are no more CS_2 “reactant” molecules in the cluster. Alternatively, if the clusters have insufficient internal energy to proceed to completion then the intermediate heteronuclear ions are detected.

The formation of $S^+(CS_2)$ and $(CS)_2^+$ has been previously investigated by Patsilinakou *et al.*²⁶³ in a similar mass analyzed multiphoton ionization experiment. They observed CS_2^+ , CS^+ , $(CS)_2^+$, and $S^+(CS_2)$ ions. They concluded that both the $S^+(CS_2)$ and $(CS)_2^+$ fragment ions were created by either a dissociation of the carbon disulfide dimer ion or by the fragmentation of the neutral dimer and its subsequent ionization. The absence of carbon disulfide cluster ions in their mass spectra was attributed to the high efficiency of fragmentation processes. Their mechanism for the production of the

$S^+(CS_2)$ and $(CS)_2^+$ clusters of CS_2 was also supported by their pressure dependence studies. They observed a quadratic dependence of the $(CS)_2^+$ and $S^+(CS_2)$ signal on the CS_2 pressure and therefore, concluded that both these fragment ions were products of carbon disulfide clusters and not the monomer.

In our mechanisms the elimination reactions and the processes by which sulfur and carbon monosulfide are solvated by CS_2 are very similar to those proposed by El-Shall *et al.*²⁴⁹ and by the Garvey group²⁵⁰. Both suggest processes where the final size of an ion is dependent on the size of the parent ion and internal barriers to intracluster reactions coupled with the thermodynamics and rate kinetics of particular elimination reactions. However, we believe that we have provided unambiguous evidence for a unique cycle of consecutive intracluster reactions within CS_2 clusters that produces pure sulfur and carbon monosulfide cluster ions. Our proposed reactions are supported by the observation of the cluster ions that initiate the cycles and the respective intermediates that are involved. Our mechanisms are based on known ion-molecule reactions and CS_2 spectroscopy and are similar in this respect to the studies by El-Shall *et al.*²⁴⁹ and methyl halide reactions which were studied by Garvey *et al.*²⁵⁰

The heats of formation that were used to determine the values in tables VI-2 and VI-3 come from a variety of sources. Heats of formation for $S^+(CS_2)$ and $CS^+(CS_2)$ were obtained by Ono *et al.*²⁵⁹ who used a helium light source to ionize a CS_2/Ar mixture and subsequently detected the ions with a quadrupole mass spectrometer. They

determined the appearance potentials for these fragment ions which combined with the binding energies gave heats of formation for $S^+(CS_2)$ and $CS^+(CS_2)$ as 291.7 and 318 kcal/mol respectively²⁵⁹. The bond dissociation energies for $(CS_2)^+(CS_2)$ and $S_2^+(CS_2)$ were obtained by Hiraoka *et al.*²⁶⁰ using a pulsed electron-beam high pressure mass spectrometer and are given as 30.9 and 24.9 kcal/mol respectively²⁶⁰. Using these values and knowing the heats of formation for CS_2 , CS_2^+ and S_2^+ we can obtain the heat of formation for $(CS_2)^+(CS_2)$ and $S_2^+(CS_2)$ as 263.1 and 243.6 kcal/mol respectively. The heats of formation for S_m , S_m^+ , CS , CS^+ , CS_2 and CS_2^+ were obtained from tabulated values given by Lias *et al.*²⁶¹ Structures for $S_2^+(CS_2)_n$ and $CS_2^+(CS_2)_n$ have been calculated by Hiraoka *et al.*²⁶⁰ and energy differences between geometrical isomers are given. The discrepancies that arise between the different values may be due to the fact that some of the heats of formation have been obtained by ionization methods where unfavorable Franck-Condon factors near the ionization limit could make the determination of the true adiabatic energies difficult. In these cases, the appearance potential is the only value that can be extracted from the data.

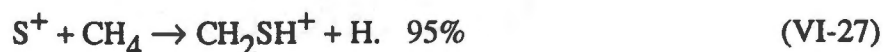
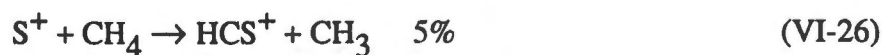
Other Carbon Disulfide Reactions

Having a ready source of excited CS_2^+ ions, it was of interest to identify other intracuster reactions suggested by known ion-molecule reactions. The first system to be

studied was a mixture of methane and carbon disulfide. Here, 260 torr of CS₂ was coexpanded with an equal amount of methane and 100 psi of argon and the resulting supersonic beam was photoionized with 239.53 nm light. Although extensive fragmentation of CS₂ was observed, the new ions of interest in the mass spectrum were CH₃S⁺, CHS⁺ and CS⁺CH₄. The formation of these ions is attributed to intracluster chemistry but they also have well known ion-molecule analogs. In the case of CHS⁺, a bimolecular reaction between the CS⁺ ion and a neutral methane molecule produces the product ion exclusively²⁶⁴:



The bimolecular reaction between the sulfur ion and neutral methane produces the CH₂SH⁺ and HCS⁺ ions.²⁶⁴



Experiments were also performed on mixtures of NO/Ar and carbon disulfide to investigate the possibility of intracluster chemistry. A 100 psi mixture of 5% NO/5% CS₂/90% Ar was irradiated with focused 239.53 nm light. Three new ions were observed that were of particular interest, NO⁺S, NO⁺S₂ and (NO)₂⁺S. The corresponding ion-molecule reactions have not been studied but the neutral species have been observed by Hawkins *et al.*²⁶⁵ in photolysis experiments of carbonyl sulfide with

NO monomer and dimer²⁶⁶. Calculations have been performed on SN_2O_2 where the geometric, electronic and vibrational characteristics were studied.^{266, 267}

Chapter VII

Conclusions

This thesis has shown that non-resonant multiphoton ionization can be used to observe intensity anomalies in cluster distributions and induce ion-molecule chemistry within clusters. In chapter III, nonresonant MPI, using 266 nm light, was used to investigate cluster distributions of $(\text{NO})_m^+ (\text{Ar})_n$ which resulted in the observation of magic numbers in the spectrum. The latter were attributed to the formation of very symmetric, and hence stable, icosahedral and double icosahedral structures. These magic numbers had been previously observed in rare gas cluster distributions. When a 100 psi 1% NO/Ar expansion was four-photon ionized with 532 nm light, the $(\text{NO})_m^+ (\text{Ar})_n$ clusters ($m > 1$) were dissociated leaving only the $\text{NO}^+(\text{Ar})_n$ series, which still exhibited intensity anomalies at $n = 12$ and 18. This is consistent with the nitric oxide dimer and trimer cluster ions having a large dissociative absorption at 532 nm^{268} . Even though nitric oxide clusters ($m \leq 3$) have well known dissociative resonances both in the neutral and ionic manifold of states, the data suggested that the dissociation of $(\text{NO})_m^+ (\text{Ar})_n$ occurred in the ionic manifold because the three photon level (which is the only possibility for photodissociation), lies outside the known dissociative absorption of nitric oxide dimer. Furthermore, even though the laser was tuned to the peak of the neutral

resonance, at 217.8 nm and with a 20 ps pulse, a substantial number of nitric oxide cluster ions were detected²⁶⁹.

In Chapter IV, picosecond, non-resonant MPI of a 5% NO/Ar expansion resulted in the detection of large nitric oxide clusters with an odd-even intensity alternation (odd > even). This odd-even effect increased until after $m > 19$, only the odd cluster ions were observed. The odd-even effect was explained in terms of electron pairing in the odd cluster ions, thus making them more stable than their even counterparts. The increase in the effect was attributed to the differences in the relative stabilities of the odd and even cluster ions which were magnified by kinetic effects during the evaporation process. When nitric oxide was coexpanded with various partners, the $(\text{NO})_3^+ (\text{Y})_n$ cluster series (where $\text{Y} = \text{N}_2\text{O}$, CO_2 , SF_6 and CS_2) dominated the mass spectra. Although more calculations are needed, the stability of these series is believed to be due to a cyclic $(\text{NO})_3^+$ ion solvated by various partners. The nitric oxide trimer ion was not observed to be especially stable on its own and so it is suggested that the stability is provided by the complexing agent.

In chapter V, REMPI was used to probe various excited states of NO and X·NO (where $\text{X} = \text{Ar}$, CH_4 and CD_4). The spectra showed vibrational progressions in the X-NO stretch and yielded excited state dissociation energies. In order to apply this technique to larger clusters, it is necessary to do mass-selected REMPI using a two-

color process where one laser would be used to ionize while the other would act as a probe. This method has the potential of yielding structural information.

Chapter VI dealt with the MPI of carbon disulfide clusters. This resulted in the observation of various fragment ions and, more importantly, pure sulfur and carbon monosulfide cluster ions. The formation of the latter was attributed to a cycle of ion-molecule reactions that occurred entirely within carbon disulfide clusters. The mechanisms that were proposed had collisional ion-molecule analogs. In order to further study this phenomenon, it would be desirable to use a reflectron time-of-flight mass spectrometer to monitor fragment production from mass-selected parent ions after a known amount of energy is deposited into the latter.

List of References

- ¹ M. Göppert-Mayer, *Naturwissenschaften*. **17**, 932 (1929).
- ² M. Göppert-Mayer, *Ann. Physik*. **9**, 273 (1931).
- ³ W. Kaiser and C. G. B. Garrett, *Phys. Rev. Lett.* **7**, 229 (1961).
- ⁴ I. D. Abella, *Phys. Rev. Lett.* **9**, 453 (1961).
- ⁵ W. C. Lineberger and T. A. Patterson, *Chem. Phys. Lett.* **13**, 40 (1972).
- ⁶ R. M. Hochstrasser, G. R. Meredith and H. P. Trommsdorff, *Chem. Phys. Lett.* **53**, 423 (1978).
- ⁷ U. Boesl, H. J. Neusser and E. W. Schlag, *Chem. Phys.* **15**, 167 (1976).
- ⁸ A. Bergman and J. Jortner, *Chem. Phys. Lett.* **15**, 309 (1972).
- ⁹ R. M. Hochstrasser, H. N. Sung and J. E. Wessel, *Chem. Phys. Lett.* **24**, 7 (1974); *Chem. Phys. Lett.* **24**, 168 (1974).
- ¹⁰ R. M. Hochstrasser, H. N. Sung and J. E. Wessel, *J. Chem. Phys.* **58**, 4694 (1973).
- ¹¹ J. M. Hollas, *High Resolution Spectroscopy* (Butterworths, London, 1982).
- ¹² S. H. Lin, Y. Fujimura, H. J. Neusser and E. W. Schlag, *Multiphoton Spectroscopy of Molecules* (Academic Press, Inc, New York, 1984).
- ¹³ L. S. Vasilenko, V. P. Chebotaev and A. V. Shishaev, *JETP Lett.* **12**, 133 (1970).
- ¹⁴ F. Biraben, B. Cagnac and G. Grynberg, *Phys. Rev. Lett.* **32**, 643 (1974).
- ¹⁵ M. D. Levenson and N. Bloembergen, *Phys. Rev. Lett.* **32**, 645 (1974).
- ¹⁶ T. W. Hänsch, K. C. Harvey, G. Meisel and A. L. Schawlow, *Opt. Commun.* **11**, 50 (1974).
- ¹⁷ J. P. Woerdman, *Chem. Phys. Lett.* **43**, 279 (1976).
- ¹⁸ S. V. Filseth, R. Wallenstein and H. Zacharias, *Opt. Commun.* **23**, 231 (1977).
- ¹⁹ A. Timmermann and R. Wallenstein, *Opt. Commun.* **39**, 211 (1981).

- ²⁰ W. M. McClain, *J. Chem. Phys.* **55**, 2789 (1971); *J. Chem. Phys.* **57**, 2264 (1972).
- ²¹ R. G. Bray and R. M. Hochstrasser, *Mol. Phys.* **31**, 1199 (1976).
- ²² L. Wunsch, F. Metz, H. J. Neusser and E. W. Schlag, *J. Chem. Phys.* **66**, 386 (1977).
- ²³ L. V. Keldish, *Sov. Phys. JETP*. **20**, 1307 (1964); translation of *Zh. Eksp. Teor. Fiz.* **47**, 1945 (1964) (Rus.).
- ²⁴ G. S. Voronov and N. B. Delone, *Sov. Phys. JETP*. **1**, 66 (1965); translation of *Zh. Eksp. Teor. Fiz.* **1**, 42 (1965) (Rus.).
- ²⁵ P. M. Johnson, *J. Chem. Phys.* **62**, 4562 (1975); *J. Chem. Phys.* **64**, 4638 (1976).
- ²⁶ F. W. Dalby, G. Petty-Sil, M. H. L. Pryce and C. Tai, *Can. J. Phys.* **55**, 1033 (1977).
- ²⁷ N. K. Berezhetskaya, G. V. Voronov, G. A. Delone, N. B. Delone and G. K. Pisskova, *JETP*. **31**, 403 (1970).
- ²⁸ G. C. Neiman and S. D. Colson, *J. Chem. Phys.* **68**, 5656 (1978).
- ²⁹ G. C. Neiman and S. D. Colson, *J. Chem. Phys.* **71**, 571 (1979).
- ³⁰ U. Boesl, *J. Phys. Chem.* **95**, 2949 (1991).
- ³¹ J. P. Maier, *J. El. Spectrosc. Rel. Phenom.* **40**, 203 (1986).
- ³² K. Müller-Detlefs, M. Sander and E. W. Schlag, *Chem. Phys. Lett.* **112**, 291 (1984).
- ³³ T. Bergmann, T. P. Martin and H. Schaber. *Rev. Sci. Instrum.* **60**, 348 (1989).
- ³⁴ U. Boesl, R. Weinkauff, R. Neusser and E. W. Schlag. *J. Phys. Chem.* **86**, 4857 (1982).
- ³⁵ G. H. C. New and J. F. Ward, *Phys. Rev. Lett.* **19**, 556 (1967); *Phys. Rev.* **185**, 57 (1969).
- ³⁶ R. T. Hodges, P. P. Sorokin and J. J. Wynne, *Phys. Rev. Lett.* **32**, 343 (1974).
- ³⁷ H. Egger, R. T. Hawkins, J. Bokar, H. Plummer, M. Rothschild and C. K. Rhodes, *Opt. Lett.* **5**, 282 (1980).

- ³⁸ M. Rothschild, H. Egger, R. T. Hawkins, H. Plummer, and C. K. Rhodes, *Chem. Phys. Lett.* **72**, 404 (1980).
- ³⁹ M. Rothschild, H. Egger, R. T. Hawkins, J. Bokov, H. Plummer, and C. K. Rhodes, *Phys. Rev. A* **23**, 206 (1981).
- ⁴⁰ P. J. Miller, P. Chen and W. A. Chupka, *Chem. Phys. Lett.* **120**, 217 (1985).
- ⁴¹ P. P. Sorokin, J. J. Wynn and J. R. Lankard, *Appl. Phys. Lett.* **22**, 342 (1973).
- ⁴² P. Lambropoulos, *Adv. At. Mol. Phys.* **12**, 87 (1976).
- ⁴³ H. B. Bebb, *Phys. Rev.* **149**, 25 (1966).
- ⁴⁴ V. S. Antonov and V. S. Letokhov, *Appl. Phys.* **24**, 89 (1981).
- ⁴⁵ R. E. Smalley, B. L. Ramakrishna, D. H. Levy and L. Wharton, *J. Chem. Phys.* **61**, 4363 (1974).
- ⁴⁶ R. E. Smalley, L. Wharton, D. H. Levy and D. W. Chandler, *J. Mol. Spectrosc.* **66**, 375 (1977).
- ⁴⁷ P. S. Fitch, L. Wharton and D. H. Levy, *J. Chem. Phys.* **69**, 3424 (1978).
- ⁴⁸ J. B. Anderson and J. B. Fenn, *Phys. Fluids.* **8**, 780 (1965).
- ⁴⁹ H. W. Liepman and A. Roshko, *Elements of Gas Dynamics*, (Wiley, New York 1957).
- ⁵⁰ H. Ashkenas and F. S. Sherman, Proceedings of the 4th Symposium on Rarefied Gas Dynamics. 2, 84 (1966).
- ⁵¹ T. A. Milne, A. E. Vandergrift and F. T. Greene, *J. Chem. Phys.* **52**, 1552 (1970).
- ⁵² O. F. Hagena and W. Obert, *J. Chem. Phys.* **56**, 1793 (1972).
- ⁵³ G. D. Stein, *Phys. Teacher.* 503 (1979).
- ⁵⁴ T. D. Märk and A. W. Castleman, Jr., *Adv. At. Mol. Phys.* **20**, 65 (1985).
- ⁵⁵ J. Jortner, *Ber. Bunsenges. Phys. Chem.* **88**, 188 (1984).
- ⁵⁶ E. W. Becker, K. Bier and W. Henkes, *Z. Phys.* **146**, 333 (1956).
- ⁵⁷ O. Echt, K. Sattler and E. Recknagel, *Phys. Rev. Lett.* **47**, 1121 (1981).

- ⁵⁸ P. W. Stephens and J. G. King, *Phys. Rev. Lett.* **51**, 1538 (1983).
- ⁵⁹ A. Ding and J. Hesslich, *Chem. Phys. Lett.* **94**, 54 (1983).
- ⁶⁰ T. D. Märk, *Int. J. Mass Spectrom. Ion Processes.* **79**, 1 (1987).
- ⁶¹ A. van Lumig and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **27**, 197 (1978).
- ⁶² D. Dreyfuss and H. Y. Wachman, *J. Chem. Phys.* **76**, 2033 (1982).
- ⁶³ S. R. Desai, C. S. Feigerle and J. C. Miller, *J. Chem. Phys.* **97**, 1793 (1992).
- ⁶⁴ T. D. Märk and P. Scheier, *Chem. Phys. Lett.* **137**, 245 (1987).
- ⁶⁵ D. Kreisle, O. Echt, M. Knapp and E. Recknagel, *Phys. Rev. A.* **33**, 768 (1982).
- ⁶⁶ R. Pflaum, P. Pfau, K. Sattler and E. Recknagel, *Surf. Sci.* **156**, 165 (1988).
- ⁶⁷ T. P. Martin and A. Kakizaki, *J. Chem. Phys.* **80**, 3956 (1984).
- ⁶⁸ K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ⁶⁹ Y. M. Efremov, A. N. Samoilova and L. V. Gurvich, *Opt. Spectrosc.* **36**, 381 (1974);
Y. M. Efremov, A. N. Samoilova, V. B. Kozhukhovskiy and L. V. Gurvich, *J. Mol. Spectrosc.* **73**, 430 (1978).
- ⁷⁰ M. D. Morse and R. E. Smalley, *Ber. Bunsenges. Phys. Chem.* **88**, 228 (1984).
- ⁷¹ See for example Proceedings of the International Meeting on Small Particles and Inorganic Clusters. *Z. Phys. D.* **1-4** (1988); *Z. Phys. D.* **20** (1991); *Z. Phys. D.* **26** (1992).
- ⁷² H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature.* **347**, 354 (1990).
- ⁷³ S. C. O'Brien, J. R. Heath, R. F. Curl and R. E. Smalley, *J. Chem. Phys.* **88**, 220 (1988).
- ⁷⁴ L. S. Wang, J. M. Alford, Y. Chai, M. Diener and R. E. Smalley, *Z. Phys. D.* **26**, 297 (1993).

- ⁷⁵ W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*. **347**, 354 (1990).
- ⁷⁶ B. C. Guo, K. P. Kerns and A. W. Castleman, *Science*. **255**, 1411 (1992).
- ⁷⁷ B. V. Reddy, S. N. Khanna and P. Jena, *Science*. **258**, 1640 (1992).
- ⁷⁸ R. J. Rorden and D. M. Lubman, *Rev. Sci. Instr.* **54**, 641 (1983).
- ⁷⁹ W. D. Wiley and I. H. McLaren, *Rev. Sci. Instr.* **26**, 1150 (1955).
- ⁸⁰ O. Echt, K. Sattler and E. Recknagel, *Phys. Rev. Lett.* **47**, 1121 (1981);
- ⁸¹ O. Echt, M. C. Cook and A. W. Castleman, *Chem. Phys. Lett.* **135**, 229 (1987).
- ⁸² D. Kriesle, O. Echt, M. Knapp and E. Recknagel, *Phys. Rev A*. **33**, 768 (1986).
- ⁸³ P. W. Stephens and J. G. King, *Phys. Rev. Lett.* **51**, 1538 (1983).
- ⁸⁴ A. Ding and J. Hesslich, *Chem. Phys. Lett.* **94**, 54 (1983).
- ⁸⁵ I. A. Harris, R. S. Kidwell and J. A. Northby, *Phys. Rev. Lett.* **53**, 2390 (1984).
- ⁸⁶ W. Miehe, O. Kandler, T. Leisner and O. Echt, *J. Chem. Phys.* **91**, 5940 (1989).
- ⁸⁷ T. D. Märk and P. Scheier, *Chem. Phys. Lett.* **137**, 245 (1987).
- ⁸⁸ W. D. Knight, W. A. de Heer, W. A. Saunders, K. Clemenger, M. Y. Chou and M. L. Cohen, *Chem. Phys. Lett.* **134**, 1 (1987).
- ⁸⁹ E. Holub-Krappe, G. Ganteför, G. Bröker and D. Ding, *Z. Phys. D*. **10**, 319 (1988).
- ⁹⁰ P. S. Bechthold, *Z. Phys. D*. **20**, 115 (1991).
- ⁹¹ C. E. Klotz, *Z. Phys. D*. **5**, 83 (1987); **20**, 1001 (1991).
- ⁹² S. Wei, Z. Shi and A. W. Castleman, *J. Chem. Phys.* **94**, 8604 (1991).
- ⁹³ H. -U. Böhmer and S. D. Peyerimhoff, *Z. Phys. D*. **8**, 91 (1988).
- ⁹⁴ A. J. Stace, *Chem. Phys. Lett.* **113**, 355 (1985).

- ⁹⁵ A. Ding, J. H. Futrell, R. A. Cassidy, L. Cordis and J. Hesslich, *Surf. Sci.* **156**, 282 (1985).
- ⁹⁶ H. Haberland, *Surf. Sci.* **156**, 305 (1985).
- ⁹⁷ J. J. Sáenz, J. M. Soler, N. García and O. Echt, *Chem. Phys. Lett.* **114**, 15 (1985); *Chem Phys. Lett.* **109**, 71 (1984).
- ⁹⁸ J. Hesslich and P. J. Kuntz, *Z. Phys. D.* **2**, 252 (1986); P. J. Kuntz and J. Valldorf, *Z. Phys. D.* **8**, 195 (1988).
- ⁹⁹ H. -U. Böhmer and S. D. Peyerimhoff, *Z. Phys. D.* **11**, 239 (1989);
- ¹⁰⁰ M. Amarouche, G. Durand and J. P. Malrieu, *J. Chem. Phys.* **88**, 1010 (1988).
- ¹⁰¹ P. G. Lethbridge and A. J. Stace, *J. Chem. Phys.* **89**, 4062 (1988).
- ¹⁰² G. Ganteför, G. Bröker, E. Holub-Krappe and A. Ding, *J. Chem. Phys.* **91**, 7972 (1989).
- ¹⁰³ N. E. Levinger, D. Ray, M. L. Alexander and W. C. Lineberger, *J. Chem. Phys.* **89**, 5654 (1988).
- ¹⁰⁴ F. Carnovale, J. B. Peel, R. G. Rothwell, J. Valldorf and P. Kuntz, *J. Chem. Phys.* **90**, 1452 (1989).
- ¹⁰⁵ K. E. Schriver, A. J. Paguia, M. Y. Hahn, E. C. Honea, A. M. Camarena and R. L. Whetten, *J. Phys. Chem.* **91**, 3131 (1987).
- ¹⁰⁶ A. J. Stace, *J. Am. Chem. Soc.* **106**, 4380, 1984.
- ¹⁰⁷ B. W. van de Waal, *J. Chem. Phys.* **79**, 3948 (1983).
- ¹⁰⁸ O. Echt, S. Morgan, P. D. Dao, R. J. Stanley and A. W. Castleman, Jr, *Ber. Bunsenges. Phys. Chem.* **88**, 217 (1984).
- ¹⁰⁹ W. R. Peifer, M. T. Coolbaugh and J. F. Garvey, *J. Chem. Phys.* **91**, 6684 (1989).
- ¹¹⁰ G. Vaidyanathan, W. J. Herron and J. F. Garvey, *J. Phys. Chem.* **97**, 7880 (1993).
- ¹¹¹ Y. Ozaki and T. Fukuyama, *Int. J. Mass. Spectrom. Ion. Process.* **88**, 227 (1989).

- ¹¹² G. Vaidyanathan, M. T. Coolbaugh, W. R. Peifer and J. F. Garvey, *J. Phys. Chem.* **95**, 4193 (1991).
- ¹¹³ C. -Y. Kung, R. A. Kennedy, D. A. Dolson and T. A. Miller, *Chem. Phys. Lett.* **145**, 455 (1988).
- ¹¹⁴ M. Lezius, P. Scheier and T. D. Märk, *Chem. Phys. Lett.* **196**, 118 (1992).
- ¹¹⁵ K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Rheinhold, New York, 1979).
- ¹¹⁶ S. H. Linn, Y. Ono and C. Y. Ng, *J. Chem. Phys.* **74**, 3342 (1981).
- ¹¹⁷ J. R. Hetzler, M. P. Casassa and D. S. King, *J. Phys. Chem.* **95**, 8086 (1991).
- ¹¹⁸ I. Fischer, A. Strobel, J. Staecker, G. Neidner-Schatteburg, K. Müller-Dethlefs and V. E. Bondybey, *J. Chem. Phys.* **96**, 7171 (1992); G. Reiser, W. Habenicht, K. Müller-Dethlefs and E. W. Schlag, *Chem. Phys. Lett.* **152**, 119 (1988).
- ¹¹⁹ M. Takahashi, *J. Chem. Phys.* **96**, 2592 (1992).
- ¹²⁰ K. Sato, Y. Achiba and K. Kimura, *J. Chem. Phys.* **81**, 57 (1984); K. Sato, Y. Achiba, N. Nakamura and K. Kimura, *J. Chem. Phys.* **85**, 1418 (1986).
- ¹²¹ U. Buck, G. Hoffman, J. Kesper, D. Otten and M. Winter, *Chem. Phys.* **126**, 159 (1988).
- ¹²² S. R. Desai, C. S. Feigerle and J. C. Miller, *J. Chem. Phys.* **97**, 1793 (1992).
- ¹²³ J. T. Mosely, R. P. Saxon, B. A. Huber, P. C. Cosby, R. Abouaf and M. Tadjeddine, *J. Chem. Phys.* **67**, 1659 (1977).
- ¹²⁴ J. Billingsley and A. B. Callear, *Trans. Faraday Soc.* **67**, 589 (1971).
- ¹²⁵ D. B. Smith and J. C. Miller, *J. Chem. Soc. Faraday Trans.* **86**, 2441 (1990); *J. Chem. Phys.* **90**, 5203 (1989).
- ¹²⁶ M. F. Jarrold, A. J. Illies and M. T. Bowers, *J. Chem. Phys.* **81**, 222 (1984); *J. Chem. Phys.* **79**, 6086 (1983).
- ¹²⁷ F. C. Carnovale, J. B. Peel and R. G. Rothwell, *J. Chem. Phys.* **84**, 6526 (1986).
- ¹²⁸ B. J. Finlayson-Pitts and J. N. Pitts, *Atmospheric Chemistry: Fundamentals and Experimental Techniques* (Wiley, Interscience, 1986).

- ¹²⁹ J. R. Lancaster, *Am. Sci.* **80**, 248 (1992).
- ¹³⁰ S. H. Snyder and D. S. Bredt, *Sci. Am.* **68** (1992).
- ¹³¹ J. S. Stamler, D. J. Singel and J. Loscalzo, *Science*. **258**, 1898 (1992).
- ¹³² J. C. Miller and W. C. Cheng, *J. Phys. Chem.* **89**, 1647 (1985); J. C. Miller, *J. Chem. Phys.* **86**, 3166 (1987); J. C. Miller, *J. Chem. Phys.* **90**, 4031 (1989).
- ¹³³ K. Sato, Y. Achiba, H. Nakamura and K. Kimura, *J. Chem. Phys.* **85**, 1418 (1986).
- ¹³⁴ J. R. Hetzler, M. P. Casassa and D. S. King, *J. Phys. Chem.* **95**, 8086 (1991).
- ¹³⁵ C. -Y. Kung, R. A. Kennedy, D. A. Dolson and T. A. Miller, *Chem. Phys. Lett.* **145**, 455 (1988).
- ¹³⁶ C. A. Woodward, J. F. Winkel, A. B. Jones and A. J. Stace, *Chem. Phys. Lett.* **206**, 49 (1993); J. F. Winkel, A. B. Jones, C. A. Woodward, D. A. Kirkwood and A. J. Stace, *J. Chem. Phys.* **101**, 9436 (1994).
- ¹³⁷ H. S. Carman, Jr., *J. Chem. Phys.* **100**, 2629 (1994).
- ¹³⁸ H. L. Johnston and W. F. Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929); H. L. Johnston and H. R. Wiemer, *J. Am. Chem. Soc.* **56**, 625 (1934).
- ¹³⁹ O. K. Rice, *J. Chem. Phys.* **4**, 367 (1936).
- ¹⁴⁰ A. L. Smith, W. E. Keller and H. L. Johnston, *J. Chem. Phys.* **19**, 189 (1951); A. Anderson and B. Lassier-Govers, *Chem. Phys. Lett.* **50**, 124 (1977).
- ¹⁴¹ W. J. Dulmage, E. A. Myers and W. N. Lipscomb, *Acta. Crystallogr.* **6**, 760 (1953); W. N. Lipscomb, F. E. Wang, W. R. May and E. L. Lippert, Jr., *Acta. Crystallogr.* **14**, 1100 (1961).
- ¹⁴² C. M. Western, P. R. R. Langridge-Smith, B. J. Howard and S. E. Novick, *Mol. Phys.* **44**, 145 (1981).
- ¹⁴³ S. G. Kukolich, *J. Am. Chem. Soc.* **104**, 4715 (1982).
- ¹⁴⁴ R. D. Harcourt, *J. Mol. Struct. (Theochem.)* **206**, 253 (1990).
- ¹⁴⁵ C. Brechignac, Ph. Cahuzac, F. Carlier, M. deFrutos and D. E. Powers, *J. Chem. Phys.* **93**, 7449 (1990).

- ¹⁴⁶ D. E. Powers, S. G. Hansen, M. E. Geusic, D. L. Michalopoulos and R. E. Smalley, *J. Chem. Phys.* **78**, 2866 (1983).
- ¹⁴⁷ S. E. Novick, B. J. Howard and W. K. Klemperer, *J. Chem. Phys.* **57**, 5619 (1972).
- ¹⁴⁸ N. Washida, H. Shinohara, U. Nagashima and N. Nishi, *Chem. Phys. Lett.* **121**, 223 (1985).
- ¹⁴⁹ S. E. Novick, P. B. Davies, T. R. Dyke and W. Klemperer, *J. Am. Chem. Soc.* **95**, 8547 (1973).
- ¹⁵⁰ C. E. Klotz, *Z. Phys. D.* **21**, 335 (1991).
- ¹⁵¹ J. Laane and J. R. Ohlsen, *Prog. Inorg. Chem.* **27**, 466 (1980).
- ¹⁵² F. Mélen and M. Herman, *J. Phys. Chem. Ref. Data.* **21**, 831 (1992).
- ¹⁵³ T. P. Melia, *J. Inorg. Nucl. Chem.* **27**, 95 (1965).
- ¹⁵⁴ L. Beneventi, P. Casavecchia, L. Yu and G. G. Volpi, *The Chemical Physics of Atomic and Molecular Clusters*, edited by G. Scoles (North Holland, Amsterdam, 1990), p. 579.
- ¹⁵⁵ D. Golomb and R. E. Good, *J. Chem. Phys.* **49**, 4176 (1968).
- ¹⁵⁶ T. Kondow, in *Electronic and Atomic Collisions*, edited by D. C. Lorents, W. E. Meyerhof, J. R. Peterson (Elsevier Science, Amsterdam, 1986), p. 517.
- ¹⁵⁷ W. Kamke, B. Kamke, H. U. Keifl and I. V. Hertel, *J. Chem. Phys.* **84**, 1325 (1986).
- ¹⁵⁸ M. Knapp, D. Kreisle, O. Echt, K. Sattler and E. Recknagel, *Surf. Sci.* **156**, 313 (1985).
- ¹⁵⁹ P. D. A. Mills, C. M. Western and B. J. Howard, *J. Phys. Chem.* **90**, 4961 (1986).
- ¹⁶⁰ M. Gauthier, *J. Chem. Phys.* **88**, 5439 (1988), and references therein.
- ¹⁶¹ S. H. Linn, Y. Ono and C. Y. Ng, *J. Chem. Phys.* **74**, 3342 (1981); S. H. Linn and C. Y. Ng, *J. Chem. Phys.* **75**, 4921 (1981).
- ¹⁶² A. J. Illies, *J. Phys. Chem.* **92**, 2889 (1988); D. Ying, S. E. Kenum and A. J. Illies, *Chem. Phys. Lett.* **187**, 245 (1991).

- ¹⁶³ K. Hiraoka, S. Fujimaki, K. Aruga and T. Sato, *J. Chem. Phys.* **101**, 4073 (1994); K. Hiraoka, S. Fujimaki, K. Aruga and S. Yamabe, *J. Phys. Chem.* **98**, 8295 (1994).
- ¹⁶⁴ J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh and K. H. Bowen, *Chem. Phys. Lett.* **124**, 274 (1986); *J. Chem. Phys.* **87**, 4302 (1987).
- ¹⁶⁵ W. H. Jones, *J. Phys. Chem.* **95**, 2588 (1991); *J. Phys. Chem.* **96**, 594 (1992); *J. Phys. Chem.* **96**, 5184 (1992); *J. Mol. Struct (Theochem)* **284**, 299 (1993); W. H. Jones and I. G. Csizmadia, *Z. Phys. D.* **32**, 145 (1994).
- ¹⁶⁶ M. Knapp, D. Kreisle, O. Echt, K. Sattler and E. Recknagel, *Surf. Sci.* **156**, 313 (1985); D. Kreisle, O. Echt, M. Knapp and E. Recknagel, *Surf. Sci.* **156**, 321 (1985).
- ¹⁶⁷ F. Misaizu, K. Mitsuka, T. Knodow and K. Kuchitsu, *J. Chem. Phys.* **94**, 243 (1991).
- ¹⁶⁸ K. Hiraoka and S. Yamabe, *J. Chem. Phys.* **95**, 6800 (1991).
- ¹⁶⁹ C. A. Woodward, J. F. Winkel, A. B. Jones and A. J. Stace, *Chem. Phys. Lett.* **206**, 49 (1993); J. F. Winkel, A. B. Jones, C. A. Woodward, D. A. Kirkwood and A. J. Stace, *J. Chem. Phys.* **101**, 9436 (1994).
- ¹⁷⁰ E. R. Fisher, B. Kickel and P. B. Armentrout, *J. Chem. Phys.* **97**, 4859 (1992).
- ¹⁷¹ R. A. Kennedy, C. Y. Kung and T. A. Miller, in *Ion and Cluster Ion Spectroscopy and Structure*, edited by J. P. Maier (Elsevier, Amsterdam, 1989), p. 213.
- ¹⁷² C. J. Howard, H. W. Rundle and F. Kaufman, *J. Chem. Phys.* **55**, 4772 (1971).
- ¹⁷³ F. C. Fehsenfeld, M. Mosesman and E. E. Ferguson, *J. Chem. Phys.* **55**, 2120 (1971).
- ¹⁷⁴ L. J. Puckett and M. W. Teague, *J. Chem. Phys.* **54**, 2564 (1971).
- ¹⁷⁵ W. C. Lineberger and L. J. Puckett, *Phys. Rev.* **187**, 286 (1969).
- ¹⁷⁶ L. A. Posey, M. J. Deluca, P. J. Campagnola and M. A. Johnson, *J. Phys. Chem.* **93**, 1178 (1989).
- ¹⁷⁷ J. G. Eaton, S. T. Arnold and K. H. Bowen, *Int. J. Mass Spectrom. Ion. Proc.* **102**, 303 (1990).
- ¹⁷⁸ J. A. Vanderhoff, *J. Chem. Phys.* **67**, 2332 (1977).
- ¹⁷⁹ R. R. Burke and R. P. wayne, *Int. J. Mass Spectrom. Ion. Phys.* **25**, 199 (1977).

- ¹⁸⁰ G. P. Smith, P. C. Cosby and J. T. Mosely, *J. Chem. Phys.* **69**, 5393, 1978; G. P. Smith and L. C. Lee. *J. Chem. Phys.* **67**, 3818 (1977).
- ¹⁸¹ F. Arnold and D. Krankowsky, *Proceedings of The International Symposium on Solar-Terrestrial Physics*, COSPAR, SaoPaulo (Maruzan Comapny, Tokyo, 1987).
- ¹⁸² E. E. Ferguson, F. C. Fehsenfeld and D. L. Albritton in, *Gas-Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979) p. 45.
- ¹⁸³ X. Yang and A. W. Castleman, Jr., *J. Am. Chem. Soc.* **111**, 6845 (1989) and references therein; Z. Shi, S. Wei, J. V. Ford and A. W. Castleman, *Chem. Phys. Lett.* **200**, 142 (1992).
- ¹⁸⁴ M. A. French, L. P. Hills and P. Kebarle, *Can. J. Chem.* **51**, 456 (1973).
- ¹⁸⁵ A. J. Stace, J. F. Winkel, R. B. Lopez Martens and J. E. Upham, *J. Phys. Chem.* **98**, 2012 (1994).
- ¹⁸⁶ A. Pullman and S. Ranganathan, *Chem. Phys. Lett.* **107**, 107 (1984).
- ¹⁸⁷ J. Erickson and C. Y. Ng, *J. Chem. Phys.* **75**, 1650 (1981).
- ¹⁸⁸ A. Illies, *Chem. Phys. Lett.* **162**, 99 (1989).
- ¹⁸⁹ J. R. Appling, M. R. Harbol, R. A. Edgington and A. C. Goren, *J. Chem. Phys.* **97**, 4041 (1992).
- ¹⁹⁰ M. F. Jarrold, A. J. Illies and M. T. Bowers, *J. Chem. Phys.* **82**, 1832 (1985).
- ¹⁹¹ J. T. Snodgrass, J. V. Coe, C. B. Freidhoff, K. M. Mchugh and K. H. Bowen, *J. Chem. Phys.* **88**, 8014 (1988).
- ¹⁹² J. B. Halpern, H. Zacharias and R. Wallenstein, *J. Mol. Spectros.* **79**, 1 (1980).
- ¹⁹³ R. M. Hochstrasser, J. E. Wessel and H. N. Sung, *J. Chem. Phys.* **60**, 317 (1974); R. G. Bray, R. M. Hochstrasser and J. E. Wessel, *Chem. Phys. Lett.* **27**, 167 (1974).
- ¹⁹⁴ F. H. M. Faisal, R. Wallenstein and H. Zacharias, *Phys. Rev. Lett.* **39**, 1138 (1977); R. Wallenstein and H. Zacharias, *Opt. Commun.* **25**, 363 (1978).
- ¹⁹⁵ J. E. Murphy, B. A. Bushaw and R. J. Miller, *J. Mol. Spectrosc.* **159**, 217 (1993).
- ¹⁹⁶ G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., (Van Nostrand Company Inc., New York, 1950).

- ¹⁹⁷ J. M. Hollas, *High Resolution Spectroscopy*, (Butterworths, Boston, 1982).
- ¹⁹⁸ F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer.* **5**, 369 (1965).
- ¹⁹⁹ E. Hill and J. H. van Vleck, *Phys. Rev.* **32**, 250 (1928).
- ²⁰⁰ J. C. Miller and R. N. Compton, *J. Chem. Phys.* **75**, 22 (1981).
- ²⁰¹ D. Zakheim and P. M. Johnson, *J. Chem. Phys.* **68**, 3644 (1978).
- ²⁰² P. M. Johnson, M. R. Berman and D. Zakheim, *J. Chem. Phys.* **62**, 2500 (1975).
- ²⁰³ H. Zacharias, R. Schmiedl and K. H. Welge, *Appl. Phys.* **21**, 127 (1980).
- ²⁰⁴ W. M. Jackson and C. S. Lin, *Int. J. Chem. Kinet.* **10**, 945 (1978).
- ²⁰⁵ R. G. Bray, R. M. Hochstrasser and J. E. Wessel, *Chem. Phys. Lett.* **27**, 167 (1974);
R. G. Bray, R. M. Hochstrasser and H. N. Sung, *Chem. Phys. Lett.* **33**, 1 (1975).
- ²⁰⁶ H. Zacharias, J. P. Hapler and K. H. Welge, *Chem. Phys. Lett.* **43**, 41 (1976).
- ²⁰⁷ P. A. Freedman, *Can. J. Phys.* **55**, 1387 (1977).
- ²⁰⁸ Y. Takubo, S. Hasegawa and M. Shimazu, *Jpn. J. Appl. Phys.* **16**, 1679 (1977).
- ²⁰⁹ M. Asscher and Y. Haas, *Chem. Phys. Lett.* **59**, 231 (1978).
- ²¹⁰ R. S. Mulliken and A. Christy, *Phys. Rev.* **38**, 87 (1931).
- ²¹¹ K. P. Gross and R. L. McKenzie, *J. Chem. Phys.* **76**, 5260 (1982).
- ²¹² R. J. Hochstrasser, G. R. Meredith and H. P. Trommsdorf, *Chem. Phys. Lett.* **53**, 423 (1978).
- ²¹³ J. Burris, T. J. McGee and T. J. McIlrath, *Chem. Phys. Lett.* **101**, 588 (1983).
- ²¹⁴ C. S. Feigerle and J. C. Miller, *J. Chem. Phys.* **90**, 2904 (1989).
- ²¹⁵ P. A. Freedman, *Can. J. Phys.* **55**, 1387 (1977).
- ²¹⁶ F. Ackerman and E. Miescher, *J. Mol. Spectrosc.* **31**, 400 (1969).

- ²¹⁷ S. Guizard, N. Shafizadeh, D. Chapoulard, M. Horani and D. Gauyacq, *Chem. Phys.* **156**, 509 (1991).
- ²¹⁸ B. J. Howard, C. M. Western and P. D. Mills, *Faraday. Discuss. Chem. Soc.* **73**, 129 (1982); P. D. A. Mills, C. M. Western and B. J. Howard, *J. Phys. Chem.* **90**, 3331 (1986); P. D. A. Mills, C. M. Western and B. J. Howard, *J. Phys. Chem.* **90**, 4961 (1986).
- ²¹⁹ K. Sato, Y. Achiba and K. Kimura, *J. Chem. Phys.* **81**, 57 (1984).
- ²²⁰ H. H. W. Thuis, S. Stolte, J. Reuss, J. J. H. van den Biesen and C. J. N. van den Meijdenberg, *Chem. Phys.* **52**, 211 (1980).
- ²²¹ J. C. Miller and W. -C. Cheng, *J. Phys. Chem.* **89**, 1649 (1985).
- ²²² P. Casavecchia, A. Lagen, and G. G. Volpi, *Chem. Phys. Lett.* **112**, 445 (1984).
- ²²³ M. Takahashi, *J. Chem. Phys.* **96**, 2594 (1992).
- ²²⁴ M. J. McQuaid, G. W. Lemire, R. C. Sausa, *Chem. Phys. Lett.* **227**, 54 (1994).
- ²²⁵ J. C. Miller, *J. Chem. Phys.* **86**, 3166 (1987).
- ²²⁶ B. Brehm, J. H. D. Eland, R. Frey and A. Küstler, *Int. J. Mass Spectrom. Ion. Phys.* **12**, 213 (1973).
- ²²⁷ I. M. Waller and J. W. Hepburn, *J. Chem. Phys.* **87**, 3261 (1987).
- ²²⁸ F. Greening and G. W. King, *J. Mol. Spec.* **59**, 312 (1976).
- ²²⁹ J. P. Maier, *J. Electron. Spec. Related Phenom.* **66**, 15 (1993).
- ²³⁰ C. R. Brundle and D. W. Turner, *Int. J. Mass Spectrom. Ion. Phys.* **2**, 195 (1969).
- ²³¹ J. W. Rabalais, J. M. McDonald, V. Scheer and S. P. McGlynn, *Chem. Rev.* **71**, 73 (1971) (and references therein).
- ²³² J. H. D. Eland and J. Berkowitz, *J. Chem. Phys.* **70**, 5151 (1979).
- ²³³ W. -B. Tzeng, H. -M. Yin, W. -Y. Leung, J. -Y. Luo, S. Nourbakhsh, G. D. Flesch and C. Y. Ng, *J. Chem. Phys.* **88**, 1658 (1988).
- ²³⁴ O. Kalisky and R. Heist, *J. Chem. Phys.* **83**, 3668 (1985).

- ²³⁵ Y. P. Vlahoyannis, E. Patsilinaou, C. Fotakis, J. A. D. Stockdale, *Radiat. Phys. Chem.* **36**, 523 (1999); E. Patsilinaou (Ph.D. Thesis).
- ²³⁶ K. Ernst and J. J. Hoffman, *Chem. Phys. Lett.* **68**, 40 (1979).
- ²³⁷ K. Ernst and J. J. Hoffman, *Chem. Phys. Lett.* **75**, 388 (1980).
- ²³⁸ K. Ernst and J. J. Hoffman, *Phys. Lett.* **87A**, 133 (1981).
- ²³⁹ A. Tam, G. Moe and W. Happer, *Phys. Rev. Lett.* **35**, 1630 (1975).
- ²⁴⁰ F. C. Wen, T. McLaughlin and J. L. Katz, *Phys. Rev. A* **26**, 2235 (1982).
- ²⁴¹ J. L. Katz, W. C. Fen, T. McLaughlin and R. J. Reusch, *Science*. **196**, 1203 (1977).
- ²⁴² J. Garvey, W. R. Peifer and M. T. Coolbaugh, *Acc. Chem. Res.* **24**, 48 (1991).
- ²⁴³ Y. Ono and C. Y. Ng, *J. Am. Chem. Soc.* **104**, 4752 (1982).
- ²⁴⁴ A. J. Stace, *J. Am. Chem. Soc.* **107**, 755 (1985).
- ²⁴⁵ J. E. Kenny, D. V. Brumbaugh and D. H. Levy, *J. Chem. Phys.* **71**, 4757 (1979).
- ²⁴⁶ A. J. Stace and A. K. Shukla, *J. Phys. Chem.* **86**, 865 (1982).
- ²⁴⁷ N. Nishi, K. Yamamoto, K. Shinohara, U. Nagashima and T. Okuyama, *Chem. Phys. Lett.* **122**, 599 (1985).
- ²⁴⁸ S. Wei, W. B. Tzeng and A. W. Castleman, *J. Phys. Chem.* **95**, 5080 (1991) (and refs therein); A. W. Castleman, W. B. Tzeng, S. Wei and S. J. Morgan, *J. Chem. Soc. Faraday. Trans.* **86**, 2417 (1990).
- ²⁴⁹ M. S. El-Shall and C. J. Marks, *J. Phys. Chem.* **95**, 4932 (1991); M. S. El-Shall and K. E. Scriven, *J. Chem. Phys.* **95**, 3001 (1991).
- ²⁵⁰ S. G. Whitney, M. T. Coolbaugh, G. Vaidyanathan and J. F. Garvey, *J. Phys. Chem.* **95**, 9625 (1991); M. T. Coolbaugh, G. Vaidyanathan, W. R. Peifer and J. F. Garvey, *J. Phys. Chem.* **95**, 8337 (1991).
- ²⁵¹ C. Kascheres and R. G. Cooks, *Anal. Chim. Acta.* **215**, 233 (1988).
- ²⁵² G. Herzberg in *Molecular Spectra and Molecular Structure III*, Van Nostrand Reinhold, New York, 1966).

- ²⁵³ S. Desai, C. S. Feigerle and J. C. Miller, *J. Chem. Phys.* **97**, 1793 (1992); *Z. Phys. D.* **26**, 220 (1993).
- ²⁵⁴ S. Desai, C. S. Feigerle and J. C. Miller, *Z. Phys. D.* **26**, S186 (1993).
- ²⁵⁵ S. Desai, C. S. Feigerle and J. C. Miller, *J. Chem. Phys.* **101**, 4526 (1994).
- ²⁵⁶ I. Fischer, A. Lochschmidt, A. Strobel, G. Neidner-Schatteburg, K. Müller-Dethlefs and V. E. Bondybey, *Chem. Phys. Lett.* **202**, 542 (1993).
- ²⁵⁷ A. Henglein, *Z. Naturforschg.* **17a**, 37 (1962).
- ²⁵⁸ Y. Ono, S. H. Linn, H. F. Prest, M. E. Gress and C. Y. Ng, *J. Chem. Phys.* **73**, 2523 (1980).
- ²⁵⁹ Y. Ono, S. H. Linn, H. F. Prest, M. E. Gress and C. Y. Ng, *J. Chem. Phys.* **74**, 1125 (1981).
- ²⁶⁰ K. Hiraoka, S. Fujimaki, K. Aruga and S. Yamabe, *J. Phys. Chem.* **98**, 1802 (1994).
- ²⁶¹ S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data.* **17**, Suppl. No. 1 (1988).
- ²⁶² I. Dzidic, A. Good and P. Kebarle, *Can. J. Chem.* **48**, 664 (1969).
- ²⁶³ E. Patsilinakou, D. Proch and C. Fotakis, *Chem. Phys.* **153**, 503 (1991); D. A. Prinslow and V. Vaida, *J. Phys. Chem.* **93**, 1836 (1989).
- ²⁶⁴ T. McAllister, *Int. J. Mass Spectrom. Ion. Phys.* **13**, 63 (1974).
- ²⁶⁵ M. Hawkins and A. J. Downs, *J. Phys. Chem.* **88**, 3042 (1984).
- ²⁶⁶ O. G. Stradella, S. A. Maluendes, E. A. Castro and A. H. Jubert, *J. Mol. Struct (Theochem)*. **210**, 169 (1990).
- ²⁶⁷ S. A. Maluendes, A. H. Jubert and E. A. Castro, *J. Mol. Struct (Theochem)*. **204**, 145 (1990).
- ²⁶⁸ M. F. Jarrold, A. J. Illies and M. T. Bowers, *J. Chem. Phys.* **79**, 6086 (1984); *J. Chem. Phys.* **81**, 222 (1983).
- ²⁶⁹ D. B. Smith and J. C. Miller, *J. Chem. Soc. Faraday. Trans.* **86**, 2441 (1990).

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