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# PICOSECOND MULTIPHOTON IONIZATION OF ATOMIC AND MOLECULAR CLUSTERS

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## Abstract

High peak-power picosecond laser pulses have been used for the first time to effect nonresonant or resonant multiphoton ionization (MPI) of clusters generated in a supersonic nozzle expansion. The resulting ions are subsequently detected and characterized by time-of-flight mass spectroscopy. Specifically, we present results involving MPI of clusters of xenon and nitric oxide. Previous MPI studies of many molecular clusters using nanosecond lasers have not been successful in observing the parent ion, presumably due to fast dissociation channels. It is proposed that the present technique is a new and rather general ionization source for cluster studies which is complementary to electron impact but may, in addition, provide unique spectroscopic or dynamical information.

## Introduction

Multiphoton ionization (MPI) following irradiation of atoms in an intense laser field was first observed by Veronov and Delone in 1965. They tightly focused a ruby laser into xenon gas and observed seven-photon, nonresonant ionization.<sup>1</sup> This work paved the way for what is now a major field of atomic and molecular physics.

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The first studies of molecules appeared in 1972 and 1973.<sup>2,3</sup> Spurred on by the development and availability of widely-tunable, high-power lasers, studies of both atoms and molecules increased dramatically. Tunability allows the exploitation of resonances which both enhances the MPI cross section and allows spectroscopic studies.

Further advances followed the use of effusive and supersonic atomic and molecular beams and the development of mass-resolved ion detection and energy-resolved photoelectron spectroscopy. Comprehensive reviews of these latter two topics have recently appeared.<sup>4,5</sup> Although the first use of supersonic expansions for MPI in 1975 centered on the ability to rotationally cool the resonance spectra of nitric oxide,<sup>6</sup> the later combination of supersonic jets and mass-resolved MPI detection indicated the presence of weakly bound clusters of atoms and molecules. In the 1980s the use of both MPI and laser-induced fluorescence for the study of such van der Waals (vdW) molecules has increased exponentially. Finally, very recently the conjunction of high powered lasers and supersonic jets has led to the generation and use of coherent vacuum-ultraviolet and soft x-ray radiation.<sup>7</sup> A supersonic expansion of (usually) a rare gas serves as the nonlinear medium for the harmonic generation or n-wave mixing process and the necessity for windows (which absorb such light) is eliminated.

In the present paper, we will present results of studies which combine high peak power MPI with supersonic jets and mass-resolved detection to examine atomic and molecular clusters. Examples which will be discussed include clusters of rare gases, nitric oxide molecules, and mixed clusters involving vdW species such as ArNO. The advantages and disadvantages of nonresonant MPI detection of such clusters will be discussed, and the competition between ionization and dissociation will be demonstrated.

## Experimental

The pulsed supersonic nozzle (R. M. Jordan Co.), Wiley-McLaren-type time-of-flight (TOF) mass spectrometer and vacuum system used in the present studies are similar to those described elsewhere.<sup>8</sup> The laser system consists of a Nd:YAG laser (Quantel, YG571C Nano-Pico) which delivers 1.2 J in a 10 ns pulse (Q-switched) or 75 mJ in a 20 ps pulse (mode-locked) at the 1064 nm fundamental wavelength. In either operating mode, the second, third, or fourth harmonics (532, 355, or 266 nm) are available. Other wavelengths may be obtained by Raman shifting. In addition, a short-cavity dye laser (Quantel, PTL-10) provides tunable, picosecond pulses in the red (580-710 nm) which may be frequency-doubled or mixed. The laser beam is typically focused by a 50 mm lens into the expanding gas. The TOF spectrum is observed for each shot with a digitizing oscilloscope (Tektronix 11402). The signal-to-noise ratio is improved by averaging spectra from ~ 100 consecutive laser shots. The peak power as a function of wavelength was calculated to be approximately 214, 71, and 28 TW/cm<sup>2</sup> for the 532, 355, and 266 nm picosecond outputs, respectively, of the Nd:YAG laser. The calculated output for the dye laser at 590 and 295 nm was approximately 45 and 4.5 TW/cm<sup>2</sup>. These calculations were based on the assumption that the laser beam had a Gaussian spatial profile, was a diffraction-limited beam, and was focused with an aberration-free lens. The actual peak powers were unknown, but they were probably one order of magnitude less.

### Atomic Clusters

Electron impact ionization studies of rare-gas expansions have detected large cluster series, but resonant MPI using nanosecond lasers has, in general, yielded only rare-gas monomers and dimers. (Nonresonant MPI at 266 nm, however, has yielded an extended series of clusters.<sup>10</sup>) In contrast to the results of the nanosecond MPI studies, we have observed Ar<sub>n</sub><sup>+</sup> (n = 1, 2), Kr<sub>n</sub><sup>+</sup> (n = 1-4) and Xe<sub>n</sub><sup>+</sup> (n = 1-20) ions using nonresonant MPI with our picosecond laser. For example, cluster ions have been observed as large as Xe<sub>9</sub><sup>+</sup> or Xe<sub>20</sub><sup>+</sup> with picosecond light near 590 nm or

266 nm, respectively, as shown in Fig. 1. At least for uncomplexed Xe atoms, the six-photon process is nonresonant with 590-nm light, the nearest allowed resonance being with the  $5d[3/2]_1^0$  state at the five-photon level ( $\Delta = 856 \text{ cm}^{-1}$ ). Once formed, rare-gas cluster ions are known to be stable, but the relative ease of using high-order nonresonant MPI to observe clusters is rather remarkable since the high laser intensity ( $\sim 10^{12} \text{ W cm}^{-2}$ ) might be expected to completely dissociate the ions. (Indeed, the laser intensity was sufficient to produce a small amount of  $\text{Xe}^{+2}$  in some spectra, an ionization process requiring the absorption of 16 photons at 590 nm). These results belie the conventional wisdom that MPI of "fragile" species must be performed with the least possible number of photons and, if possible, by ionizing the molecule to just above the ionization threshold.

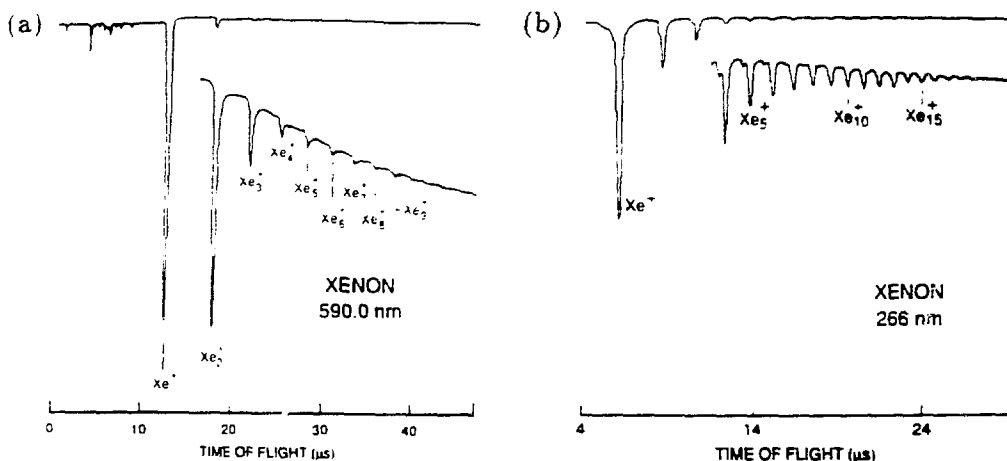


Fig. 1. MPI mass spectra of  $\text{Xe}_n^+$  at (a) 590 nm and (b) 266 nm.

Several interesting questions pertaining to frequency conversion in supersonic jets arise from the present observations. First, the presence of dimers has been shown in studies of third harmonic generation (THG) in high pressure experiments to effect the conversion efficiency via phase matching changes and reabsorption of the generated light.<sup>13-15</sup> The higher numbers of  $\text{Xe}_n$  species formed in a supersonic jet must have similar effects. A reasonable estimate of the percentage of xenon atoms

existing in complexed form is probably several percent. Secondly, as harmonic generation is a "collective effect" requiring an ensemble of atoms, one might ask what is the minimum-sized cluster which could yield observable THG in a single molecule. Back-of-the-envelope estimates indicate that  $n \cong 10^3$  would be required.<sup>16</sup>

### Molecular Clusters

For a number of years, we have been using resonantly-enhanced MPI in supersonic jets coupled with mass-resolved detection to study the spectroscopic and photophysical properties of vdW molecules composed of rare gas atoms and nitric oxide molecules.<sup>17,18</sup> We have extensively studied the electronic spectra of ArNO associated with the  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ , and  $D^2\Sigma^+$  states of uncomplexed NO using (2+1) and (1+1) resonantly enhanced MPI. For several of these states we have also studied the Ne, Kr, Xe, and  $CH_4$  analogues. Data on the ground neutral and ionic states of ArNO are known from other studies. Consequently, a rather complete picture of the spectroscopy, bonding, and photophysics of this weakly bound molecule has emerged.<sup>17,18</sup>

Similar MPI studies on other important vdW molecules have been impeded by the presence of dissociative neutral resonances or ion fragmentation. For instance, in none of the previously cited MPI studies of ArNO was the nitric oxide dimer ion,  $(NO)_2^+$ , observed, although the neutral dimers were known to exist in the molecular beam. Similarly, previous studies of iodine/rare gas expansions failed to detect the  $ArI_2^+$  ion.<sup>19</sup> In both of these cases efficient dissociative pathways prevented observation of the parent ion. Use of the present picosecond laser can ameliorate these problems in two ways. First, the high peak power allows nonresonant MPI to be observed, thus avoiding dissociative resonances of the neutral cluster. Furthermore, when such resonances are encountered, the short pulse (10-20 ps) and high ionization rate allow efficient competition with bond breaking. These points will be illustrated by the results of picosecond MPI of nitric oxide clusters at a number of fixed wavelengths.

The results of MPI of a 5% NO/Ar mixture by 10 ps dye laser pulses are shown in Fig. 2 for two different wavelengths, 590 nm and 295 nm. The results are seen to be quite different. Five-photon ionization with red light leads to observation of the  $\text{Ar}_n\text{NO}^+$  cluster ion series while three-photon MPI using the frequency doubled light at 295 clearly shows the  $(\text{NO})_n^+$  ions. The failure to observe nitric oxide clusters with red light and their dominance when using ultraviolet light may be understood with reference to the energy level diagram of Fig. 3. In this diagram, known energy levels of  $(\text{NO})_2$  are shown on the right and compared with those of the monomer on the left. The lowest state of neutral  $(\text{NO})_2$  is known to be dissociative,<sup>20</sup> and

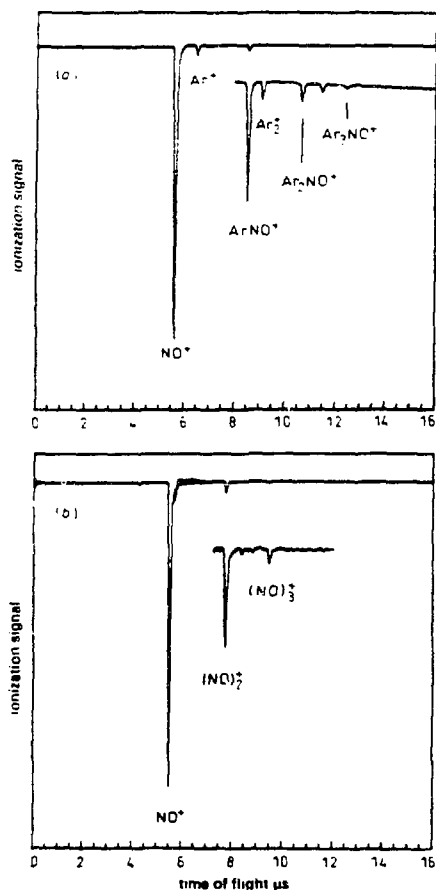


Fig. 2. Time-of-flight mass spectra of  $\text{Ar}_n\text{NO}^+$  and  $(\text{NO})_n^+$  following picosecond MPI with (a) 590-nm and (b) 295-nm light and under identical molecular beam conditions.

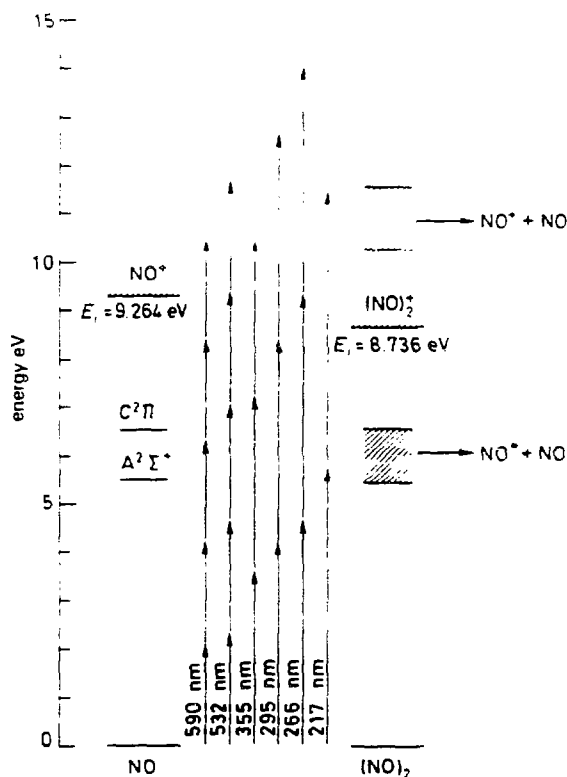


Fig. 3. Energy-level diagram for NO and  $(\text{NO})_n$  showing the various MPI schemes discussed in the text.

the dimer ion is readily photofragmented with visible light.<sup>21</sup> The absence of  $(\text{NO})_n^+$  for 590 nm (or other visible wavelengths) excitation is readily apparent. In this case, three-photon excitation leads to absorption into the dissociative state of the dimer which has been previously characterized by one-photon absorption spectroscopy.<sup>20</sup> It has been argued<sup>22</sup> that the lifetime for dissociation is  $\geq 10^{-13}$  s. Two-photon ionization cannot compete with such fast dissociation and so no  $(\text{NO})_n^+$  ions are expected. However, even if such ions were produced, they would be efficiently dissociated by further red photons. Studies<sup>21</sup> have shown that  $(\text{NO})_n^+$  ions have an absorption band extending from 400 to 800 nm and peaking around 650 nm. Photodissociation cross sections of  $\sim 1.6\text{-}1.8 \times 10^{-17}$  cm<sup>2</sup> are reported. Again, the upper state of this transition is thought to be purely repulsive. Small numbers of  $(\text{NO})_2^+$  ions are observed at the highest available laser powers indicating that these dissociations are not 100% complete.

In contrast, Fig. 2(b) shows the MPI spectrum of the same NO/Ar expansion after doubling the 590 nm light to 295 nm. In this experiment  $(\text{NO})_n^+$  ions are readily observed up to  $n = 4$  and  $\text{Ar}_n\text{NO}^+$  ions are observed only very weakly or not at all. Inspection of the energy level diagram shows that none of the virtual states of the three-photon MPI fall within the dissociative bands of the neutral or ionic dimer. Furthermore, 295 nm light does not photodissociate the  $(\text{NO})_2^+$  ion. The absence of  $\text{ArNO}$  at this wavelength is probably due to predissociation at the two-photon level. Although nothing is known of  $\text{ArNO}$  states at this energy, the lower-lying  $\text{D}^2\Sigma^+$  and  $\text{E}^2\Sigma^+$  states of the complex are thought to predissociate.<sup>17,18</sup>

Figures 4 and 5 compare the results of nanosecond and picosecond MPI for two different wavelengths. Again the results are readily interpreted with reference to the energy level diagram of Fig. 3. At 266 nm, both the neutral and ionic states of the nitric oxide dimer are avoided, and the ion is stable with regard to photofragmentation. Consequently, the  $(\text{NO})_2^+$  parent ion is observed irregardless

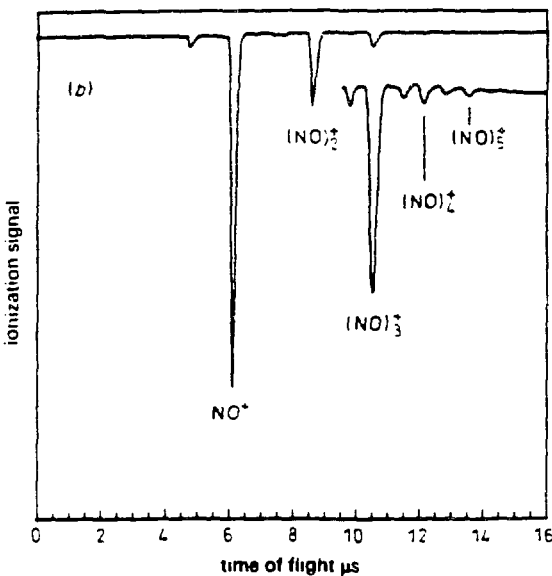
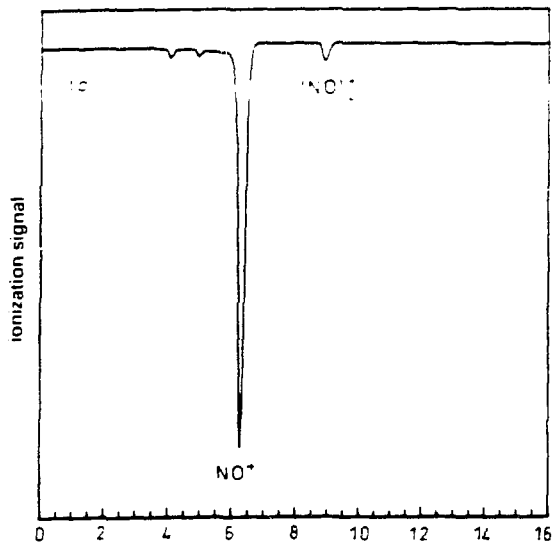


Fig. 4. Mass spectra following (a) 10 ns and (b) 20 ps MPI at 266 nm.

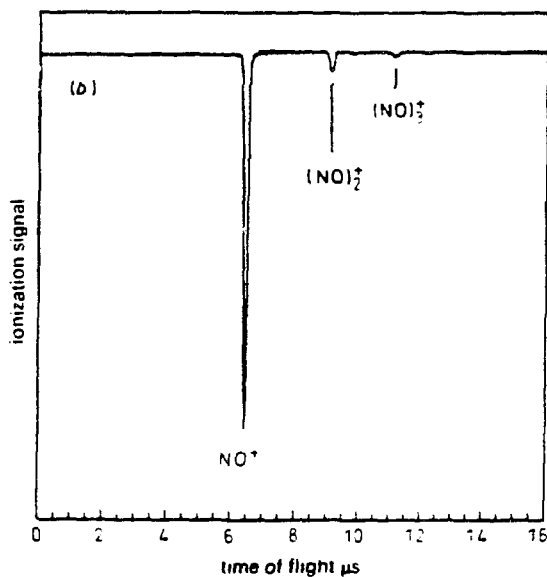
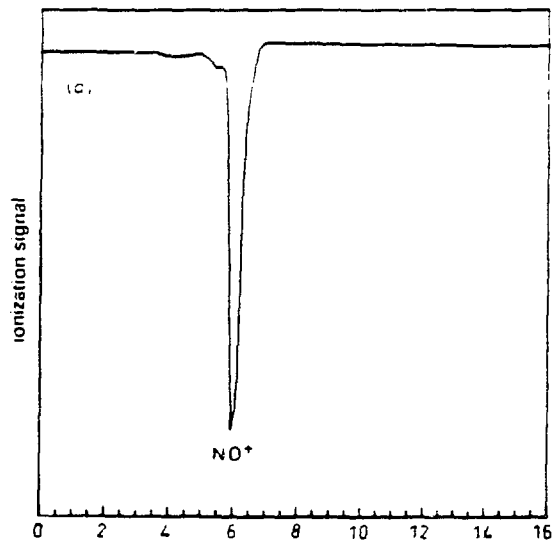


Fig. 5. Mass spectra following (a) 10 ns and (b) 20 ps MPI at 8 nm.

of the laser pulse length. In contrast, when 217 nm light is used (the second anti-Stokes component following Raman shifting of the 266-nm output) the excitation falls very near the peak of the continuous absorption, and the shortened photodissociation lifetime thus offsets the resonance effect. At this wavelength no



dimer signal is observed in the nanosecond experiments while  $(\text{NO})_2^+$  and  $(\text{NO})_3^+$  are clearly produced by picosecond laser MPI. These results dramatically illustrate the advantage of high-peak power MPI.

In principle, the lifetime of the excited dimer state might be determined from careful laser power dependence studies of the dimer ion intensity at 217.5 nm. A straightforward rate equation analysis for such a four-level system leads to a functional form of the power dependence from which the lifetime could be extracted if the excitation and ionization cross-sections were known. In fact, these quantities are not known for the dimer and, furthermore, power dependence studies are difficult to perform accurately in this wavelength region, so no such analysis is warranted at the present time.

Further details of the studies described above may be found in two recent publications.<sup>23</sup>

### Conclusions

We suggest that laser mass spectrometry using high-power lasers may constitute a near "universal" detector of atomic and molecular species. Unlike resonant MPI, no knowledge of intermediate states is required. Although more complex and more expensive than the traditional electron impact source, MPI has some unique advantages (and disadvantages) which have been outlined in the present study.

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