

# MULTIPHOTON IONIZATION OF $(Xe)_n$ and $(NO)_n$ CLUSTERS USING A PICOSECOND LASER\*

D. Barton Smith<sup>†</sup> and John C. Miller

*Chemical Physics Section, Health and Safety Research Division,  
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6125*

Presented to the Ninth International Conference on Laser Spectroscopy  
Bretton Woods, New Hampshire, June 18-23, 1989

<sup>†</sup>Postdoctoral Research Associate, The University of Tennessee,  
Knoxville, Tennessee 37996-1600

\*Research sponsored by the Office of Health and Environmental Research,  
U.S. Department of Energy under contract DE-AC05-84OR21400  
with Martin Marietta Energy Systems, Inc.

The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

**MASTER**

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

48

# Multiphoton Ionization of $(\text{Xe})_n$ and $(\text{NO})_n$ Clusters Using a Picosecond Laser

D. Barton Smith\* and John C. Miller

Chemical Physics Section, Oak Ridge National Laboratory,  
P.O. Box 2008, Oak Ridge, TN 37831-6125, USA

Mass-resolved multiphoton ionization (MPI) spectroscopy is an established technique for detecting and analyzing van der Waals molecules and larger clusters. MPI spectroscopy provides excellent detection sensitivity, moderately high resolution, and selectivity among cluster species. In addition to information provided by the analysis of photoions following MPI, photoelectron spectroscopy can reveal details regarding the structure of ionic states (1). Unfortunately, the technique is limited by its tendency to produce extensive fragmentation. Fragmentation is also a problem with other ionization techniques (e.g., electron impact ionization), but the intense laser beams required for MPI cause additional dissociation channels to become available. These channels include absorption of additional photons by parent ions ("ion ladder" mechanism), absorption of additional photons by fragment ions ("ladder switching" mechanism), and resonances with dissociative states in the neutral manifold. The existence of these dissociation channels can preclude the use of MPI spectroscopy in many situations.

Recently, MPI studies of stable molecules using picosecond lasers (pulse length = 1 - 10 ps) have indicated that limitations due to fragmentation might be subdued. With picosecond lasers, dissociation mechanisms can be altered and in some cases fragmentation can be eliminated or reduced. Additional photon absorption competes effectively with dissociation channels when a very short laser pulse or, perhaps more importantly, a sufficiently high peak-power is used. In the case where ionic absorption and fragmentation occurs, it has been shown that picosecond MPI might favor the ion ladder mechanism rather than the ladder switching mechanism (2). Larciprete and Stuke (3) have presented the argument that ionic fragmentation can be greatly reduced or even eliminated with the use of short laser pulses. Finally, two-color pump-probe experiments using picosecond lasers can, in principal, provide direct measurements of dissociation rates.

In an effort to extend the application of MPI spectroscopy to the study of weakly bound systems, we have begun a systematic investigation of picosecond MPI in van der Waals molecules and clusters. To our knowledge no previous picosecond MPI studies of weakly bound systems have been reported. We present here results of picosecond MPI of  $\text{Xe}_n$  ( $n = 1 - 20$ ) and  $(\text{NO})_n$  ( $n = 1 - 4$ ) clusters. Previous MPI studies using nanosecond lasers have not detected the NO cluster series, presumably because of fast dissociation channels. The use of high peak-power allows resonant and non-resonant photon absorption to the ionization limit to compete effectively with fast dissociative processes.

The apparatus and method used for our picosecond MPI studies is similar to that used for previous MPI experiments in our laboratory (4). In brief, we produce atomic or molecular clusters in a supersonic jet expansion from a pulsed nozzle and ionize clusters with tightly focused laser light. The photoions are detected and analyzed with a time-of-flight (TOF) mass spectrometer. The laser system consists of a dual-operational-mode Nd:YAG laser, an  $\text{H}_2$  Raman cell, and a short-cavity dye laser. The Nd:YAG delivers 1.2 J in a 10-ns pulse (Q-switched operation) or

\*Postdoctoral Research Associate, The University of Tennessee, Knoxville

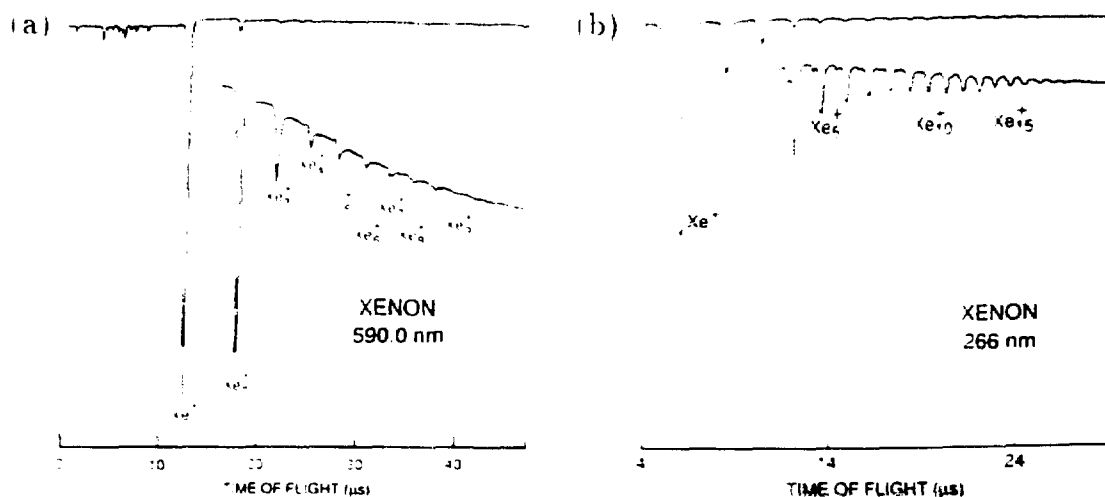


Fig. 1. MPI mass spectra of  $\text{Xe}_n^+$  at (a) 590 nm and (b) 266 nm.

75 mJ in a 20-ps pulse (mode-locked operation) at the 1064 nm fundamental wavelength. The second, third or fourth harmonic (532, 355 or 266 nm) of the fundamental and corresponding Raman-shifted wavelengths are available in either operational mode. The dye laser provides 10-ps pulses of red or blue light (580-710 or 440-590 nm), and these wavelength regions can be extended by frequency doubling or frequency mixing.

Electron impact ionization studies of rare-gas clusters have detected large cluster series, but resonant MPI using nanosecond lasers has yielded only rare-gas monomers and dimers. [Nonresonant MPI at 266 nm, however, has yielded an extended series of clusters (5).] In contrast to the results of the nanosecond MPI studies, we have observed  $\text{Ar}_n^+$  ( $n = 1, 2$ ),  $\text{Kr}_n^+$  ( $n = 1-4$ ) and  $\text{Xe}_n^+$  ( $n = 1-20$ ) ions using nonresonant MPI with our picosecond laser. For example, we have observed cluster ions as large as  $\text{Xe}_9^+$  or  $\text{Xe}_{20}^+$  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  $5d[3/2]_0^1$  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.

Nitric oxide and  $(\text{NO})_n$  van der Waals molecules have been the subjects of numerous spectroscopic studies because NO plays a prominent role in the chemistry of the upper atmosphere. Although NO dimers and rare gas-NO clusters are readily formed in a free jet expansion, nanosecond MPI experiments with these species have failed to detect the  $(\text{NO})_2^+$  parent ion (6-7). This failure to detect the dimer ion can be attributed to the presence of dissociative states in the  $(\text{NO})_2$  and  $(\text{NO})_2^+$  manifolds: the only known excited state of the neutral dimer very rapidly dissociates (8) and the dimer ion is readily photodissociated by visible light (9). Likewise, we do not observe the dimer ion (or larger polymers) when we use visible light (532 nm or 585-605 nm). However, when either nanosecond or picosecond UV light (355 nm, 266 nm, or frequency-doubled 585-605 nm) is used,  $(\text{NO})_n^+$  ( $n = 1-5$ ) ions are

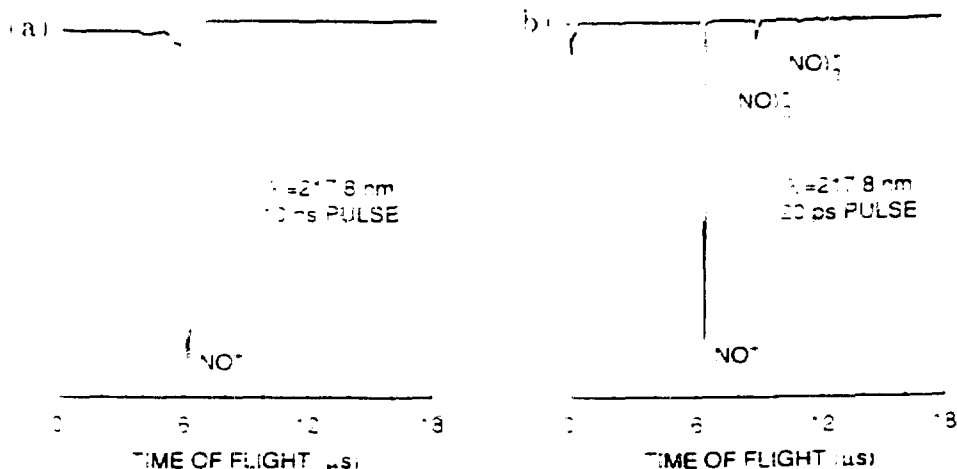


Fig. 2. MPI mass spectra of  $(NO)_n^+$  with (a) nanosecond and (b) picosecond pulses.

readily observed. Figures 2a and 2b show TOF spectra following MPI with 217 nm light (the second anti-Stokes Raman-shifted wavelength from the 266-nm output). In this case the two-photon ionization is resonant with the dissociative excited state in the neutral manifold. Only  $NO^+$  ions are observed with nanosecond pulses, while  $(NO)_n^+$  ( $n = 1 - 4$ ) ions are observed with picosecond pulses. Clearly, the higher peak-power available in the picosecond pulses enables MPI to compete effectively with the fast dissociation channel.

In conclusion, resonant or nonresonant MPI with a high peak-power picosecond laser is a versatile and rather general means of detecting and studying cluster distributions. Additional details on the present work are available elsewhere (10). Work in progress incorporates pump-probe techniques and photoelectron spectroscopy with picosecond MPI experiments.

Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

## References

1. R. N. Compton and J. C. Miller, in *Laser Applications in Physical Chemistry*, edited by K. Evans (Dekker, New York, 1989).
2. J. J. Yang, D. A. Gobeli, and M. A. El-Sayed, *J. Phys. Chem.* **89**, 3426 (1985); and references therein.
3. R. Larciprete and M. Stuke, *J. Crystal Growth* **77**, 235 (1986).
4. J. C. Miller and R. N. Compton, *J. Chem. Phys.* **84**, 675 (1986); J. C. Miller, *Anal. Chem.* **58**, 1702 (1986).
5. O. Echt, M. C. Cook, and A. W. Castleman, *Chem. Phys. Lett.* **135**, 229 (1987); *J. Chem. Phys.* **87**, 3276 (1987); and references therein.
6. 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).
7. K. Sato, Y. Achiba, and K. Kimura, *J. Chem. Phys.* **81**, 57 (1984); *Chem Phys. Lett.* **126**, 306 (1986); K. Sato, Y. Achiba, H. Nakamura, and K. Kimura, *ibid.* **85**, 1418 (1986).
8. J. Billingsly and A. B. Callear, *Trans. Faraday Soc.* **67**, 589 (1971).
9. G. P. Smith and L. C. Lee, *J. Chem. Phys.* **64**, 5395 (1978).
10. D. B. Smith and J. C. Miller, *J. Chem. Phys.* **90**, 5203 (1989); *Trans Faraday Soc. II* (to be published).