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VACUUM ULTRAVIOLET PHOTOIONIZATION OF COLD MOLECULAR BEAMS*

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VACUUM ULTRAVIOLET PHOTOIONIZATION OF COLD MOLECULAR BEAMS*

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ABSTRACT

Experiments will be described which combine nonlinear optics, mass- and energy-resolved ion detection, energy-resolved electron detection, and a supersonic nozzle to study vacuum ultraviolet photoionization and photoelectron spectroscopy of ultracold molecules.

INTRODUCTION

The vacuum ultraviolet (VUV) spectral region (≤ 200 nm) has traditionally been a difficult region in which to perform spectroscopic experiments on molecules and to interpret the resulting data. Experimental difficulties inherent in this region include low reflectivities, low window transmission (below 100 nm, no windows are available), and the need for a vacuum environment. Traditional monochromatic light sources for the VUV are weak, difficult to operate, and require vacuum monochromators which trade resolution for photon flux. Finally, the photophysics and photochemistry of high-lying states of molecules are complicated by their high density of states and distributed oscillator strengths as well as the numerous channels available to the molecule for the disposition of excess energy. Predissociation, ionization, and auto-ionization broaden spectral lines and complicate interpretation. Nevertheless, VUV spectroscopy has developed into a mature field over the last 50 years. A large body of reliable data has been acquired and an accompanying framework of theoretical explanations has been developed.

Very recently, a renaissance in the field of molecular spectroscopy in the VUV region has occurred. This resurgence has been driven by the technological advances provided by synchrotron light sources, tunable lasers, and supersonic molecular beams, each of which alleviates or eliminates some of the experimental and interpretational problems mentioned above. The synchrotron has made available an intense, broadly tunable, moderate resolution light source for the VUV and x-ray regions which also requires a monochromator. The well known attributes of tunable dye lasers such as high-intensity, very narrow bandwidth, spatial and temporal coherence, and short pulse times are being translated into the UV and VUV spectral regions. Coherent excitation in the VUV is now possible due to the development of new lasers in this spectral region and by the emergence of the complementary techniques of multiphoton excitation and nonlinear frequency conversion. Finally,

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supersonic molecular beam sources allow rotational and vibrational cooling which is imperative in order to simplify congested spectra. The renaissance of VUV spectroscopy was amply detailed in the first topical meeting on "Laser Techniques in the Extreme Ultraviolet" and will be expanded by the present meeting.

We have developed a versatile apparatus, based on the above cited technologies and techniques, for the study of VUV spectroscopy and photoionization of molecules. A pulsed, supersonic molecular beam is crossed with the focused beam of a pulsed dye laser or its doubled or tripled output. Ions are created by multiphoton ionization (MPI) with the fundamental beam (three to five photons), two-photon ionization using the doubled or tripled beam, or one-photon ionization with VUV light. Use of a second laser allows for two-color experiments.

The ionization event is monitored by time-of-flight mass spectrometry and by photoelectron energy analysis. This apparatus thus combines our previous work on VUV spectroscopy of high-pressure gases using nonlinear optical techniques¹ with fragment ion and photoelectron analysis extensively used for MPI experiments on effusive beams.²⁻⁴ The addition of the supersonic molecular beam allows examination of vibrationally and rotationally cold monomer beams as well as molecular clusters.

This paper will describe experiments designed to demonstrate and test the various capabilities of this new apparatus. These will include one-, two-, and four-photon ionization experiments on NO emphasizing photoelectron spectroscopy.

EXPERIMENTAL

The experimental arrangement is shown schematically in Fig. 1. The excitation source is an excimer-pumped dye laser (Lambda Physik EMG101/FL2000E) or its doubled or tripled output. Frequency conversion is achieved with an interactive frequency doubling system (Inrad) or by third-harmonic generation (THG) in rare gases. The THG cell is equipped with quartz and MgF₂ optics for the input and output, respectively, and contains a single electrode for monitoring MPI events in the tripling medium.⁵ A second, independent, nitrogen-pumped dye laser (Molelectron UV-400/DL400) provides two-color capability with the addition of a second lens to the chamber. The molecular beam/cluster source is a pulsed, supersonic nozzle (Quanta-Ray PSV-2) capable of delivering gas pulses of 60-100 μ s duration at backing pressures up to 10 atm and a nozzle temperature of 70°C. The nozzle is currently operated as a free jet expansion although a skimmer will be installed in the future. Translation in the x, y, and z directions are possible. The source is typically operated at ~10 Hz with a 0.5 mm aperture. The laser is triggered externally after a variable delay with respect to the valve opening. Following either single- or multiphoton ionization the ions and electrons are detected and characterized independently and simultaneously. Ions are extracted with a small electric field and mass-analyzed by time-of-flight techniques with a resolution (m/ Δ m)

Fig. 1. Schematic of experimental apparatus.

of about 50. The electron kinetic energy distribution (i.e., the photoelectron spectrum) is determined with a 160° spherical sector energy analyzer. Energy resolution ranges from 50 to 200 meV, depending on experimental conditions (ion intensity, analyzer pass energy, etc.). Photoelectron angular distributions may be determined by eliminating the extraction fields and rotating the polarization of the laser beam about the acceptance direction of the analyzer with a double Fresnel rhomb. Further details of the ion and electron analysis may be found in previous papers.²⁻⁴ Signal processing can be in either an analog mode using boxcar integrators or in digital mode using single pulse counting techniques and a multichannel analyzer.

BOUND STATE SPECTROSCOPY

We have used the MPI technique to investigate the ro-vibronic spectroscopy of a number of Rydberg states of NO in supersonic beams following the pioneering work of Johnson et al.^{6,7} The states studied thus far (with the MPI scheme used given in parenthesis) include the $A^2\pi$ ($v=0$) state, (2+2 and 1+1), $A^2\pi$ ($v=1$) state (2+2), the $C^2\pi$ ($v=0$) state (2+1), the $F^2\Delta$ ($v=3$) state (1+1), and the $N^2\Delta$ ($v=1$) state (1+1). Studies of the latter two states employed VUV light generated by THG in xenon as the first photon and the blue dye laser fundamental as the ionizing photon as described previously for high pressure studies.¹ Studies of the $A^2\pi$ ($v=0$) state by a (1+1) scheme employed frequency doubling in a KPB crystal.

As an example, the spectrum of the $F^2\Delta$ ($v=3$) state is shown in Fig. 2 for both a room temperature gas beam (trace a) and a supersonically cooled beam (trace b). Optimum phase-matching for the THG at these wavelengths occurred at about 50 torr of xenon. The beam is a 5% NO/He mixture expanded through a 0.5-mm hole at a backing pressure of ~2 atm. Because of rotational warming of the

Fig. 2. MPI spectra of the $\text{F}^2\Delta(v=3)$ state of NO for (a) a room temperature beam, and (b) rotationally cooled beam.

gas due to collisions with the extraction plates (see Fig. 1), the coldest spectra were obtained at laser delay times corresponding to the arrival of the earliest molecules from the gas pulse. At later delay times the temperature was considerably warmer or essentially room temperature. The rotational temperature of Fig. 2(b) corresponds to a temperature of about 3 K if only the $J=1/2$ and $3/2$ levels are used to characterize a Boltzmann distribution. The higher J levels occur with larger populations than expected from a 3 K Boltzmann distribution, however, and may have some contribution from the warm NO present as background gas in the chamber (average background pressure was typically 10^{-5} to 10^{-6} torr). For the more intense transitions to the $\text{A } 2\Pi$ and $\text{C } 2\Pi$ states temperatures below 1°K could be obtained. The assignments of the warm spectra of Fig. 2 are from Jungen⁸ and are confirmed by the rotationally cold spectra. Cooling of high vibrational levels ($\omega_e = 1904 \text{ cm}^{-1}$) is complete as is the electronic cooling of the $2\Pi_{3/2}$ state ($T_e = 120 \text{ cm}^{-1}$). At equivalent backing pressures, cooling of pure NO was less complete ($T \approx 10\text{--}25 \text{ K}$) than that for 5% NO/He and 1% NO/Ar mixtures which were essentially the same. AC Stark broadening was only observed for the $\text{A } 2\Pi(v=0)$ state as previously discussed by Otis and Johnson.⁷

PHOTOIONIZATION SPECTROSCOPY

The relatively low ionization potential of NO allows for the use of frequency tripling techniques to perform one-photon ionization experiments. The emphasis of these experiments thus shifts from bound states below the ionization threshold to autoionizing states coupled to the continuum. Figure 3 shows the spectrum of NO in the region of 380 to 386 nm obtained by frequency tripling the dye laser in xenon gas near its $6s'[1/2]^0J=1$ resonance.⁵ The rotational temperature of the gas is unknown but is probably in the range of 5-10 K based on rotationally resolved spectra taken under similar conditions. The positions of the absorption lines in this region and their assignment⁹ as listed by Ono et al.¹⁰ (including some calculated line positions) are given above the spectrum. This spectrum should represent the highest resolution spectrum (0.007 nm) obtained for the coldest NO sample (5-10 K) reported to date. The previous work of Ono et al.¹⁰ used conventional light sources with a resolution of 0.014 nm and obtained a gas temperature estimated to be 20 K. Although there is a general correspondence between the spectrum of Fig. 3 and the previous absorption⁹ and photoionization spectra¹⁰ a satisfactory line-by-line match is not obtained with either. The present spectrum should, however, be considered preliminary and work is continuing in this area. More careful calibration and systematic variation in the degree of rotational cooling are necessary to resolve the discrepancies. Studies of other spectral regions using THG near the 5s and 5s' resonances of Kr are also possible.

Fig. 3. One photon photoionization spectra of a rotationally cold beam of NO excited by VUV light produced by THG.

PHOTOELECTRON SPECTROSCOPY

We have extended our previous interest in MPI-PES^{3,4} by including the new capabilities of the present apparatus for studies of NO. For instance, studies of the photoelectron spectrum of ultracold NO ($\sim 1^\circ\text{K}$) following MPI (2+2) via the $A\ ^2\Sigma$ ($v=0, J=1/2$) state were performed under moderate resolution (see Fig. 4b). The appearance of the spectrum is independent of rotational temperature and initial and final state rotational quantum number. Similar spectra for NO have been described and discussed in detail previously.^{3,11-13} Briefly, a higher energy electron peak near 1.7 eV is due to direct two-photon ionization of the A state. Near zero-energy electrons are not yet completely understood but have been attributed to vibrational autoionization.³ Electrons due to electronic autoionization have also been observed.^{3,11} The new configuration of the apparatus allows several additional experiments to be performed which further clarify the photoelectron spectra.

The spectrum of Fig. 4(a) represents the MPI-PES via the same state as in trace (b) but following frequency doubling of the input laser; i.e., the two spectra represent (1+1) and (2+2) MPI-PES via the same state. We have argued previously that the (2+2) process allows near resonances in the third photon region which ultimately

may be responsible for the slow electrons via vibrational autoionization. The similarity of the spectra of Fig. 4(a) and (b) seems to rule out this possibility. However, other experiments involving accidental double resonances show varying intensity ratios of slow and fast electrons which may again implicate the higher resonances in production of slow electrons. Further work is necessary.

The measurement of angular distributions for photoelectrons provides a very sensitive probe of the ionization event, especially when the electrons result from autoionization. We have performed preliminary measurements of these angular distributions by rotation of the polarization of the incident laser about its propagation direction, thus varying the angle between the electric vector of the

Fig. 4. The photoelectron spectra of supersonically cooled NO following (a) UV MPI (1+1) and (b) visible MPI (2+2).

light and the acceptance direction of the analyzer. The angular dependence of the slow and fast electrons following MPI (2+2) via the $A^2\Sigma^+$ ($v=1$) state of NO are observed to be quite different. In general, the angular dependence can be expressed as

$$I(\theta) = \sum_{N=0}^K B(N) \cos^{2N}\theta, \quad (1)$$

where K is the order of the ionization process (i.e., $K = 2$ for a two-photon ionization).

For the distributions of the fast electrons, the following equation results from fitting the angular distribution to an N th order regression formula

$$I(\theta) = 1 + 7.0 \cos^2\theta - 10.2 \cos^4\theta - 7.6 \cos^6\theta - 3.3 \cos^8\theta. \quad (2)$$

The slow electrons exhibit a nearly isotropic distribution. Such a distribution implies that the molecule has "lost its memory" concerning the original orientation. The process of autoionization can lead to such a distribution. Although still considered preliminary, these distributions contain the most detailed clues so far available for understanding the origin of the slow electrons.

Finally, we have measured MPI-PES and angular distributions for the (1+1) MPI via the F and N states of NO using THG as described in a previous section. Only electrons from direct ionization are observed and their energy and angular dependences are similar to those measured for direct ionization in previous experiments.

TWO-COLOR EXPERIMENTS

Two-color MPI experiments (i.e., use of two independently tunable dye lasers) offer a number of significant advantages over those using a single laser. The major such advantage is the spectral simplification which arises from selecting a single ro-vibronic level with the first laser. The second laser will then only interact with these excited molecules and a simple PR or PQR structure will emerge in the probe laser spectrum. This simplification is complementary to but perhaps more versatile than that provided by supersonic cooling. Furthermore, by defining additional resonances in the MPI scheme (i.e., replacing virtual states with real states) the ionization cross section is increased and the experiment is better defined. Also, different selection rules may allow access to different states with sequential two-color excitation than with simultaneous multiphoton excitation. Finally, varying the relative polarization of the two lasers provides additional information about assignments. Several groups have previously published two-color spectra of NO.^{15,16} We have observed several additional two-color MPI pathways and plan to use this very powerful excitation technique to simplify and characterize photoelectron spectra. In addition, we hope to demonstrate two-color MPI where one excitation involves VUV light from THG.

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