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MULTIPHOTON IONIZATION OF NO-RARE GAS VAN DER WAALS SPECIES

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Multiphoton Ionization of NO-Rare Gas van der Waals Species

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To date, most spectroscopic studies of electronic states of clusters involving small molecules and rare gas (RG) atoms have employed laser-induced fluorescence techniques. Consequently, such studies (e.g., Levy and co-workers on I_2-RG species [1]) have been limited to the lowest lying electronic states, which are usually valence in character. Furthermore, the identification of the cluster often must be inferred from spectral shifts, pressure dependence, etc.

We have applied the technique of multiphoton ionization (MPI) to the study of electronic spectroscopy of NO-RG van der Waals species and extended the previous experiments of SATO et al. [2]. These works show several of the advantages of the MPI technique relative to the LIF method. Specifically, mass analysis can provide identification of the new species formed as well as allowing discrimination against other species (the parent monomer or higher clusters) while recording spectra. Furthermore, the use of MPI photoelectron spectroscopy can provide data on the states of the cluster ion as well [2].

The MPI technique has another advantage which is particularly important in the study of van der Waals molecules. This is the ability to study Rydberg states much more easily than LIF or other techniques. Because most excited states are highly polarizable, van der Waals forces are enhanced. Furthermore, for high Rydberg states, the influence of the positively charged core allows the stronger dipole forces to become more important contributors to the binding energy. Thus, the binding energy of molecule-RG complexes should increase in the order: ground state < valence state < Rydberg state < ionic ground state. Nitric oxide is the "alkali atom" of molecules, having one unpaired electron outside of filled molecular orbitals. Consequently, its spectroscopy is dominated by Rydberg transitions which have been very well characterized.

The apparatus is a modified version of that used previously for MPI mass analysis [3] and MPI photoelectron spectroscopy [4]. The apparatus consists of a pulsed supersonic nozzle, a short, low-resolution time-of-flight mass spectrometer and an excimer pumped dye laser. Typically, the laser (1-5 mJ) is focused by a 38-mm lens into the gas pulse (5% NO in Ar at a total backing pressure of 2 atm) after a variable delay relative to the nozzle opening. The time (and hence mass) gated ion signal is averaged with a boxcar integrator and recorded as a function of wavelength. Mass spectra showing the production of $NeNO^+$, $ArNO^+$ and $KrNO^+$ are shown in Fig. 1.

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MPI spectra are presented for several NO-RG van der Waals molecules. Structured excitation spectra of the ArNO cluster associated with the $B^2\pi$ ($v=0$), $C^2\pi$ ($v=0,1,2,3$), and $D^2\Sigma^+$ ($v=0$) states of NO are observed as well as an unstructured, presumably dissociative, spectrum near the $A^2\Sigma^+$ ($v=0$) state. The C state was also observed for NeNO and KrNO. The B state represents a valence transition and the A, C, and D states are Rydberg states. Details of these studies may be found in a recent paper [5].

From the observed spectral shifts and analysis of the spectra, excited state vibrational constants and bond dissociation energies can be extracted. These parameters are summarized in Fig. 2 for ArNO.

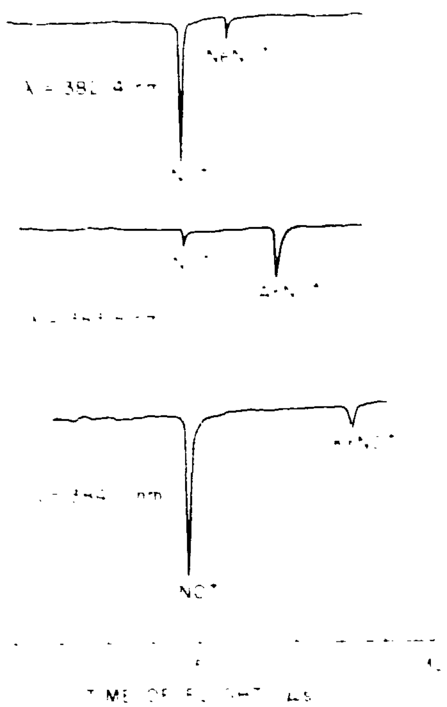

Fig. 1. Time-of-flight mass spectra showing the MPI detection of NeNO, ArNO, and KrNO van der Waals molecules. The figure is traced from photographs of the oscilloscope image.

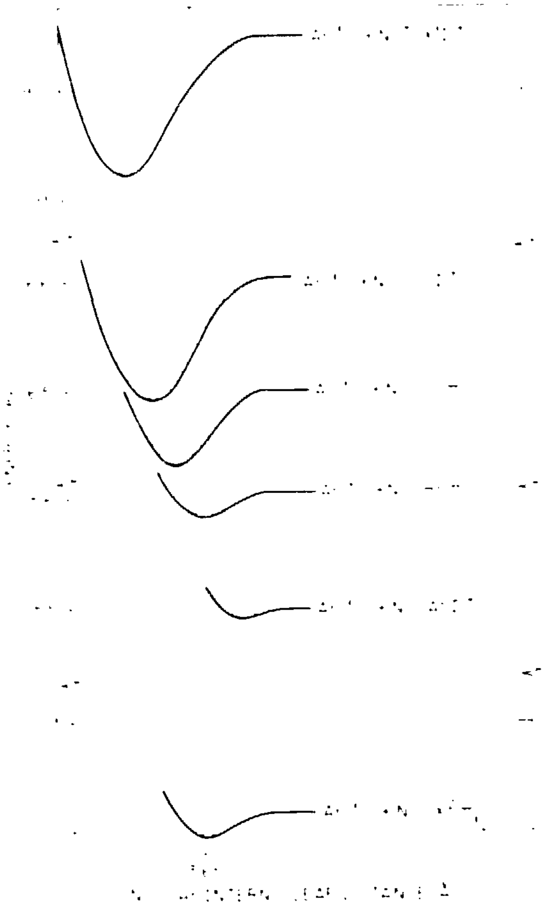

Fig. 2. Schematic representation of the potential energy curves for ArNO.

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