Photodissociation of rare gas cluster ions: Ar+ 3

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NOTES

Photodissociation of rare gas cluster ions: Ar₃⁺

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The study of cluster ions is currently an area of intense research in view of expectations that the results will provide a bridge between the gas and the condensed phase.[1] Rare gas clusters are of particular interest because their simplicity allows comparison of experiment with theory. They are also of importance due to their possible role in power loss phenomena in excimer lasers[2] and in elucidation of the origin of magic numbers[3] which arise in cluster distributions studied in molecular beams.

The dimer cation of argon has been the subject of extensive experimental and theoretical studies, but to the best of our knowledge no experimental information on the photodissociation of the trimer cation has been reported in the literature. The purpose of this communication is to report the first such data for Ar_3^+ which has been the subject of several conflicting theoretical studies.[4-7] Interest in this system has also been prompted by observations[8] that large cluster ions of argon readily photodissociate and indications that the trimer may be the chromophore.

The apparatus has been described in detail elsewhere.[9] Briefly it consists of a source chamber, a system of ion optics that provides a beam of well defined geometry and energy, a Wien velocity filter, a tunable dye laser pumped with an argon ion laser, and a quadrupole mass spectrometer. For these experiments the thermal ion source employed in previous work was replaced with a supersonic expansion. Approximately 1 atm of argon is expanded through a 25 μ orifice which is surrounded by a cooling coil. Air, cooled by passage through a tube submerged in liquid nitrogen, is flowed through the cooling coil. Ionization is induced by impact of a well collimated electron beam (~ 200 eV, 2–3 mA).[10] A Wien velocity filter selects the ion of interest, Ar_3^+, which is then focused into the laser–ion interaction region. Following interaction of the ions with the light, the fragment ions and the remaining parent ions are accelerated

into a quadrupole mass spectrometer. The laser beam is chopped to allow monitoring of fragment and parent intensities with and without the laser light.

It should be noted that the use of a tightly focused electron beam was crucial to this experiment. In order to avoid large metastable signals, it was necessary to ionize the expanded gas close to the orifice. Furthermore, the ions had to be created in a field free region to allow for sufficient collisions to take place. If an attractive potential was applied to the skimmer a large metastable signal was immediately observed. These findings suggest that cluster ions are produced by growth rather than by fragmentation of larger species or by direct ionization of the neutral precursor. Hence the cluster ions are expected to be cold since their generation takes place very early in the adiabatic expansion.

The experiments carried out to date have been made in the emission region of rhodamine 560 chloride and rhodamine 6G (539–620 nm), for a mass selected beam of Ar_3^+ corresponding to picoampere currents focused onto the Faraday probe which defines the region of the ion–laser beam overlap. The location of the probe enables the number densities to be determined from which absolute cross sections are deduced; details of the procedure are discussed elsewhere.[9] The photodissociation spectrum obtained is shown in Fig. 1. The cross section is found to increase with photon energy from 620 through a peak at 545 nm and then decrease rapidly. The value of the absolute cross section at the peak is about 5×10^{-19} cm². Power studies showed that the dissociation is a single photon process. The quadrupole mass spectrometer enables the product ions to be continuously monitored throughout the study. Ar^+ was the only photoproduct detected at all wavelengths investigated in the present work. No channel corresponding to Ar_2^+ was found within the limit of detection.[11]

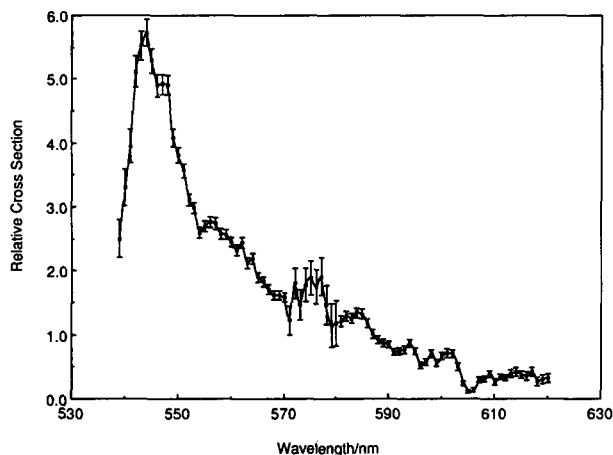Experimental studies of the bond energy of the dimer

FIG. 1. Photodissociation cross section of Ar_3^+ into Ar^+ in the emission region of rhodamine 560 chloride and rhodamine 6G. The error bars represent one standard deviation.

and trimer ions of argon establish[12] the respective bond energies as 1.3 and 0.22 eV. Based on considerations of the requisite frequencies to account for the experimental entropy of formation of Ar_3^+, Turner and Conway[13] suggested the structure to be linear. Until the present work there has been no experimental evidence for the absorption of light by Ar_3^+. However, the trimer ion has been the subject of four recent theoretical studies at various levels of approximation. Using a density functional method, Michels et al.[4] predicted the ground state cluster ion to have $^2E\,'$ symmetry with a trigonal structure; they further predicted the spectrum of the trimer to be red shifted from the dimer and to display a smaller cross section peaking at about 560 nm. Based on their considerations, photodissociation should lead solely to Ar^+ as the product ion. By contrast, a very recent configuration interaction calculation,[7] a diatomics-in-molecules calculation,[6] and a combination POL-CI (ground state) and diatomics-in-molecules (excited state) calculation[5] predicted the structure to be linear with a $^2\Sigma_u^+$ ground state. The calculations of Wadt[5] indicate that the strongest vertical transition should be at 557 nm and that the cross section of the trimer would be greater than that of the dimer cation.

The results of this work indicate that the photodissociation cross section of Ar_3^+ is less than the corresponding $^2\Sigma_u^+ \to {}^2\Sigma_g^+$ transition in Ar_2^+.[14] Perhaps only by coincidence, the findings of the present study are in agreement with the predictions of Michels[4] and co-workers that the trimer cation transition will have a smaller cross section than the corresponding one in the dimer ion. The measured wavelength of the maximum cross section is in good agreement with the predictions of both theoretical studies.[4,6] Work is currently in progress to extend the measurements and to investigate the dissociation dynamics.

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Energy differences from electrostatic potentials at nuclei

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There have been derived a number of formulas relating atomic and molecular total energies to the electrostatic potential $V_{0,A}$ created at each nucleus A by the electrons and other nuclei[1-11]:

$$V_{0,A} = \sum_{B \neq A} \frac{Z_B}{|R_B - R_A|} - \int \frac{\rho(r')dr'}{|r' - R_A|}, \qquad (1)$$

Z_A is the charge on nucleus A, located at R_A.