The visible photoabsorption spectrum of Ar_3^+

Nancy E. Levinger, Douglas Ray, Kermit K. Murray, Amy S. Mullin, C. P. Schulz, and W. C. Lineberger

Department of Chemistry and Biochemistry and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

(Received 12 January 1988; accepted 18 March 1988)

The photodissociation cross section of Ar_3^+ was measured at a number of wavelengths between 1064 and 320 nm. A single broad and featureless band was observed peaking near 520 nm with a width of $\approx 2600\ cm^{-1}$ and a peak cross section of $\approx 10^{-16}\ cm^2$. Consideration of the electronic structure of Ar_3^+ indicates that the measured spectrum is equivalent to the photoabsorption spectrum. Two ionic products, Ar^+ and Ar_2^+, were observed in the photodissociation of Ar_3^+, indicative of at least two exit pathways and suggestive of two electronic transitions.

I. INTRODUCTION

Recently, heightened interest in the photophysics of the Ar_3^+ ion has developed. Part of this interest is a result of investigations on the $A \leftarrow C$ band of XeF.[1,2] Models developed by Nachson *et al.*[1] and Nighan *et al.*[2] show that formation of Ar_3^+ is likely in the intense, high pressure discharges required by XeF lasers; the models suggest that Ar_3^+ may be the transient absorber identified[1,2] in XeF laser plasmas. Indeed, if the Ar_3^+ absorption cross section were $\geqslant 10^{-17}\ cm^2$ near 500 nm, Ar_3^+ would significantly reduce the output energy of a XeF laser oscillating on the $A \leftarrow C$ transition. Additional interest in Ar_3^+ stems from a general interest in the characterization of small cluster ions.

In the process of studying the photodissociation and photofragmentation of Ar_n^+ ($n = 3$–60) cluster ions[3] we observed a striking difference in the photodissociation cross sections of the dimer and trimer ions. For the reasons indicated above, we have pursued a more detailed measurement of the Ar_3^+ photodissociation cross section.

There have been numerous studies of Ar_3^+, including thermochemical experiments,[4–6] theoretical calculations,[7–12] and one recent experimental measurement[13] of the Ar_3^+ photodissociation cross section. Turner and Conway,[4] employing high pressure mass spectrometry techniques, have measured the temperature dependence of the equilibrium constant for the reaction $Ar_2^+ + 2Ar \rightleftarrows Ar_3^+ + Ar$, from which they deduced an Ar_2^+–Ar dissociation energy of 0.219 ± 0.05 eV. This is substantially smaller than the dissociation energy of Ar_2^+, 1.3 eV.[14] The derived entropy change for the reaction above implies a linear geometry for Ar_3^+. Using photoionization techniques, Dehmer and Pratt[5] determined the dissociation energy of Ar_3^+ to be 0.18 ± 0.05 eV, while Fehsenfeld *et al.*,[6] using a variable temperature flow reactor, report $D_0 = 0.217$ eV.

Several different theoretical investigations[7–11] of Ar_3^+ have been presented. Although the details differ, all are in agreement about the magnitude of the Ar_3^+ binding energy, ≈ 0.2 eV, in consonance with the thermochemical data. A configuration interaction (CI) calculation,[10] a combination CI and diatomics-in-molecules (DIM) calculation,[8] and purely DIM calculations[9,11] all predict a linear, symmetric geometry for the Ar_3^+ molecule. In their first calculation, Michels *et al.*[7] predicted a slightly bent geometry for the ground state of Ar_3^+. A recent, more extensive calculation by Michels[12] using a large basis set and extensive CI predicts Ar_3^+ to be linear and asymmetric. The salient feature,[12] however, is that near the Ar_3^+ equilibrium geometry, the Ar_2^+–Ar potential is very flat, allowing large amplitude Ar motion. Theoretical estimates for Ar_3^+ photoabsorption[7,8] predict a strong ($\approx 10^{-16}\ cm^2$), broad transition to a repulsive surface with the maximum cross section near 500 nm. These calculations and the small dissociation energy of Ar_3^+ indicate that the quantum yield for photodissociation is near unity, and thus measurement of the photodissociation cross section is equivalent to measurement of the photoabsorption cross section.

Recently Albertoni *et al.*[13] have measured the photodissociation cross section of Ar_3^+ from 620 to 539 nm. They report a band approximately 300 cm^{-1} wide with a peak cross section of $\approx 5 \times 10^{-19}\ cm^2$ at 544 nm. These results will be discussed in detail later, in conjunction with our results.

II. EXPERIMENTAL

Two separate instruments were used to obtain the data presented here. The absolute photodissociation cross section and the photofragmentation data were obtained with a pulsed laser crossed ion beam instrument. The relative photodissociation cross section was also measured with a cw laser coaxial ion beam apparatus from 574 to 525 nm. Each apparatus is discussed briefly below.

A. Pulsed laser crossed ion beam apparatus

The pulsed laser crossed ion beam apparatus has been described in detail elsewhere.[15,16] Briefly, a pulsed supersonic expansion of neat Ar gas is crossed by a continuous 1000 eV, 200 μA beam of electrons. Ar_3^+ cluster ions are generated via ion–molecule association reactions. The ions drift 20 cm and cool to an estimated 20–50 K before pulse extraction into a tandem time-of-flight (TOF) mass spectrometer. Mass selected ions are intersected by laser pulses from a Nd:YAG pumped dye laser (Quanta Ray

 0021-9606/88/130071-04$02.10

DCR-3 and PDL-1) at the spatial focus of the primary TOF. After laser interaction, parent and fragment ion trajectories are reversed in a reflectron-type[17] secondary TOF mass analyzer and refocused onto a particle multiplier. Neutral fragments arising from the photodissociation of Ar_3^+ are not affected by the reflectron, and traverse it, striking a separate particle multiplier.

The data required to obtain the cross section for photodissociation of Ar_3^+ were taken with a multichannel, current integrating, gated integrator (LeCroy 2249SG) which simultaneously collected the Ar_3^+ parent ion signal, the neutral fragment signal, and a photodiode signal monitoring the laser flux. Data were taken for 200 valve openings with the laser striking the Ar_3^+ ions and 200 with the laser blocked, providing a background correction. This procedure was repeated at least ten times to reduce statistical fluctuations and systematic effects. The neutral fragment signal was normalized on every valve opening to the Ar_3^+ parent ion signal and the laser energy fluctuations. The normalized neutral fragment signal was then corrected for the absolute number of photons per pulse (determined with a Scientech model 3600 power meter) to yield a relative photodissociation cross section measurement. The relative cross section was made absolute by comparison with the known Ar_2^+ absolute photodissociation cross section[18,19] at two wavelengths. Minor further corrections due to the momentum dependent detection efficiency of the particle multiplier were also performed. An estimate of the absolute cross section was also obtained from direct observation of the depletion of the Ar_3^+ signal by the laser pulse.

All photodissociation measurements were made with the dye laser pumped by the near Gaussian second or third harmonic output of the YAG laser. The final amplification stage was collinearly pumped to improve the spatial intensity distribution of the beam. The laser beam was collimated and apertured to a diameter of 7 mm, much larger than the 1–2 mm diameter ion beam, ensuring good spatial and temporal overlap. Laser fluences were 0.03–1.0 mJ/pulse, chosen to limit depletion of the parent ion signal to $\leqslant 10\%$, thus avoiding possible multiphoton effects.

Ionic photofragmentation products were also investigated. The mass analyzed fragment ion signals were digitized and averaged with a transient digitizer/signal averager, then stored and analyzed on a computer. These data, which were consistent with the neutral product data described above, were mainly employed to provide Ar^+/Ar_2^+ branching ratios as a function of wavelength.

B. Coaxial cw laser ion beam apparatus

The coaxial cw laser ion beam apparatus has been described in detail elsewhere.[20,21] The ion source is similar to that described in Sec. II A above. Near Ar gas expands through a pulsed valve with a 400 μm aperture and is crossed by a 1000 eV, 200 μA continuous beam of electrons. Ar_3^+ ions created in the expansion drift through a 5 mm diameter skimmer located 3 cm downstream of the nozzle before being accelerated to 2 keV and mass selected in a 90° sector magnet. The collimated ion beam is merged with the cw laser beam by an electrostatic quadrupole deflector. The ion and laser beams are coaxial over a 30 cm path before the ion beam is deflected by a second quadrupole deflector into a Faraday cup. Neutral species produced by dissociation of Ar_3^+ are unaffected by the second deflector and strike a CaF_2 plate; secondary electrons ejected from the plate are detected by a ceramic electron multiplier operating in a pulse counting mode.

The laser used in this experiment was a home built cw dye laser using Coumarin 540 dye pumped by the 488 nm line of an argon ion laser. The laser was configured as a standing wave cavity with a single plate birefringent filter as the sole tuning element. The laser linewidth in this configuration was approximately 0.2 nm. The laser wavelength was measured with a monochromator to an accuracy of approximately 1 nm. Output powers of 400 mW were obtained with 4 W of pump power from the argon ion laser. The data collection system consisted of a gated pulse counter which accumulated neutral detector pulses for a fixed number of valve openings. Ion current from the Faraday cup was converted to a voltage by a low noise preamplifier and sent to a gated integrator. The laser power was monitored with a photodiode. The ion signal and laser power were measured every valve opening, averaged over the total number of valve openings, and used to normalize the neutral signal to relative laser flux and ion current. Data were taken in this manner for 100 to 200 valve openings per point, with data points spaced by 0.3 nm. Spurious signals due to collision induced dissociation with background gas in the interaction region and to detector dark current were negligible.

III. RESULTS AND DISCUSSION

The photodissociation spectrum of Ar_3^+ obtained with the pulsed laser apparatus from 670 to 476.2 nm is shown in Fig. 1. Additional measurements made at 700, 355, and 320 nm yielded photodissociation cross sections of similar magnitude to that at 670 nm. Photodissociation of Ar_3^+ is detectable at 820 nm but the cross section is significantly smaller than that at 670 nm; at 1064 nm no photodissociation was detected. The observed photodissociation band is ≈ 2600

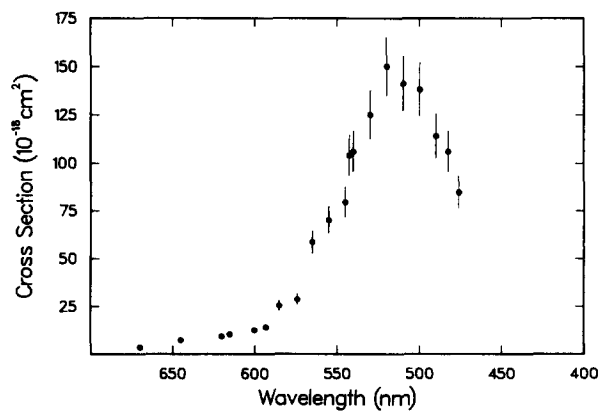

FIG. 1. The absolute photodissociation cross section of Ar_3^+ obtained with the pulsed laser crossed ion beam apparatus. The error bars indicate one standard deviation statistical uncertainty. The uncertainty in the absolute cross section is a factor of 2.

cm^{-1} wide (FWHM). The error bars represent only statistical errors and indicate one standard deviation. To obtain the absolute magnitude of the Ar_3^+ photodissociation cross section, the data were normalized to reported values of the Ar_2^+ photodissociation cross section[18,19] at selected wavelengths where photodissociation of both Ar_2^+ and Ar_3^+ was observed and where there are reported absolute values for Ar_2^+. Normalization of the Ar_3^+ relative photodissociation cross section to the Ar_2^+ absolute measurement by Lee *et al.*[18] at 700 nm ($1.8 \pm 0.3 \times 10^{-19}$ cm^2) yields a photodissociation cross section of $2.8 \pm 0.7 \times 10^{-18}$ cm^2 at 700 nm and, based upon our relative photodissociation cross section, $2.0 \pm 0.5 \times 10^{-16}$ cm^2 at the 520 nm peak for Ar_3^+. Normalization ot Lee *et al.*'s measurements at 620 nm, where the Ar_2^+ photodissociation cross section has diminished to $8 \pm 3 \times 10^{-20}$ cm^2, results in an Ar_3^+ photodissociation cross section of $5.5 \pm 2.1 \times 10^{-18}$ cm^2 at 620 nm and $1.2 \pm 0.5 \times 10^{-16}$ cm^2 at the 520 nm peak. Finally, normalization to the Ar_2^+ photodissociation cross section measured by Lee and Smith[19] at 476.2 nm ($3.5 \pm 1.5 \times 10^{-20}$ cm^2) yields a photodissociation cross section for Ar_3^+ of $1.3 \pm 0.6 \times 10^{-18}$ cm^2 at 476.2 nm and $2.3 \pm 1.0 \times 10^{-17}$ cm^2 at the 520 nm peak. The normalization at 620 nm is more reliable than either of the other wavelengths, since the Ar_2^+ photodissociation cross sections at 476.2 and 700 nm are highly temperature dependent while the Ar_2^+ photodissociation cross section at 620 nm is relatively insensitive to temperature,[22,23] The normalization at 476.2 nm is unreliable in our judgement, given the small signal levels observed for Ar_2^+ photodissociation at this wavelength, and therefore is not used in the absolute cross section determination.

An *independent* estimate of the absolute photodissociation cross section of Ar_3^+ can be obtained from the measured depletion of the Ar_3^+ absorber in the pulsed laser experiment. This estimate of the absolute photodissociation cross section is not likely to be in error by more than an order of magnitude. Use of the formula

$$\frac{I_{\text{final}}}{I_{\text{initial}}} = e^{-\sigma\Phi},$$

where I_{initial} and I_{final} are the Ar_3^+ absorber signal intensity before and after laser interaction, σ is the photodissociation cross section in cm^2, and Φ is the photon flux in photons/cm^2/pulse, allows the use of depletion measurements to obtain an estimate of the absolute photodissociation cross section. At 520 nm, 15% depletion was observed with 0.25 mJ/cm^2/pulse (6.5×10^{14} photons/cm^2/pulse) which yields a cross section of 2.5×10^{-16} cm^2. Under the same conditions, with the laser timing set for Ar_2^+, depletion was not detectable, i.e., $< 1\%$; hence the photodissociation cross section of Ar_2^+ must be $< 10^{-17}$ cm^2 at this wavelength, consistent with the measurements by Lee and Smith.[18] Thus, three determinations indicate an absolute photodissociation cross secton of $0.8\text{–}3 \times 10^{-16}$ cm^2 for Ar_3^+ at 520 nm.

The relative photodissociation cross section of Ar_3^+ obtained with the coaxial cw laser ion beam apparatus from 574 to 525 nm is shown in Fig. 2. The results shown in Fig. 2 are an average of nine data sets. The error bars represent one standard deviation of the mean. The increased uncertainty at shorter wavelengths in Fig. 2 is due to decreased laser power. It is clear from Fig. 2 that the photodissociation spectrum is featureless in this region, as expected for a transition from a bound to a repulsive surface. The data from the pulsed laser experiment between 575 and 520 nm are also shown in Fig. 2. The cw laser data have been normalized to the pulsed laser data at 545 nm. This normalization point was chosen since we expect the photodissociation cross section at the half-maximum points of the band to be relatively insensitive to temperature, in analogy with other bound–free transitions,[22,23] and hence insensitive to possibly different ion formation conditions in the two instruments. This comparison shows that the two data sets are in good agreement concerning the shape of the Ar_3^+ photodissociation cross section over the wavelength range of overlap.

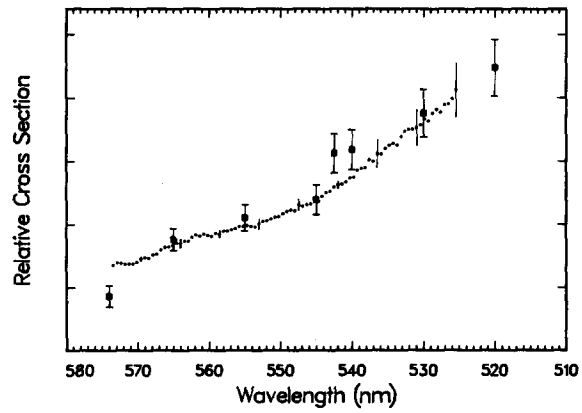

FIG. 2. The photodissociation cross section of Ar_3^+ obtained with the cw laser coaxial ion beam apparatus (circles) and the pulsed laser crossed ion beam apparatus (squares). The two data sets have been normalized at 545 nm. The error bars indicate one standard deviation statistical uncertainty.

The Ar_3^+ photodissociation data presented here differ from the results of Albertoni *et al.*[13] There are two major differences: first, the absolute magnitude of their reported photodissociation cross section is ≈ 200 times less than our measured cross section from 620 to 544 nm, and second, their reported photodissociation band in one-tenth as wide, with the maximum cross section occurring near 545 nm. Their data[13] would lead to the conclusion that Ar_3^+ is not an important absorber in the high pressure XeF laser. Very recently, Albertoni *et al.*[24] have reinvestigated the photodissociation of Ar_3^+, measuring *depletion* of the Ar_3^+ absorber. This measurement yields an absolute photodissociation cross section in qualitative agreement with the values reported here from 620 to 544 nm.

There remains, however, substantial disagreement in the energy dependence of the photodissociation cross sections for wavelengths shorter than 544 nm. The feature we find is broad, 2600 cm^{-1} (FWHM), similar to the Ar_2^+ photodissociation spectrum,[18,19] while that reported by Albertoni *et al.*[13] has a width of ≈ 300 cm^{-1} (FWHM). Both bands have similar shapes from 620 to 544 nm, but diverge at shorter wavelengths, beginning at the 544 nm maximum reported by Albertoni *et al.*[13] The cross sections presented here (obtained with two *different* apparatus from 574 to 525 nm)

continue to increase to 520 nm, while the band reported by Albertoni *et al.*[13] decreases sharply from 543 to 539 nm. In our pulsed laser experiment, a single laser dye, Coumarin 500, was used from 545 to 490 nm. A single laser dye, Coumarin 540, was also used from 574 to 525 nm in the cw experiment presented here and data were taken only for wavelengths where the laser power was at least 13% of the peak power. Albertoni *et al.*[13] utilized the intracavity radiation of an argon ion pumped cw dye laser and normalized the relative cross section to photon flux by measurement of the light transmitted through a high reflectivity mirror. The gain curve (and intracavity power) of Rhodamine 560, the dye used by Albertoni *et al.*[13] from 570 to 539 nm, drops sharply over the wavelength range (543–539 nm) where they observe the decrease in photodissociation cross section. Whether this effect is responsible for the disagreement can be tested in further experiments.

In addition to measuring the photodissociation cross section of Ar_3^+, we have also investigated the ionic photofragmentation products. Data in Table I show the branching ratios of Ar^+ and Ar_2^+ fragments via the reactions

$$Ar_3^+ + h\nu \rightarrow Ar^+ + 2Ar$$
$$\rightarrow Ar_2^+ + Ar.$$

The primary fragment ion at all wavelengths was Ar^+; a small amount of the Ar_2^+ fragment ion was observed at wavelengths longer than 600 nm. The relative Ar_2^+ production increases with decreasing photon energy.

The appearance of both Ar^+ and Ar_2^+ photofragments indicates the existence of more than one pathway for photodissociation of Ar_3^+. There are two possible explanations for the multiple pathways: the existence of two different electronic transitions from the ground state of Ar_3^+ present within the one measured band or two different exit channels from one excited state. If Ar_3^+ were a linear, symmetric molecule, as some theoretical predictions indicate,[8–11] it would display the same allowed transitions as Ar_2^+: $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$, $^2\Pi_g$. In Ar_2^+, the $^2\Sigma_u^+ \leftarrow {}^2\Pi_g$ transition is approximately 100 times weaker than the $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ transition. If the two transitions in Ar_2^+ were close to each other in energy, the $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ transition would dominate the absorption spectrum masking any features due to the $^2\Sigma_u^+ \leftarrow {}^2\Pi_g$ band. Similarly, a $\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ transition masking a $^2\Sigma_u^+ \leftarrow {}^2\Pi_g$ transition in Ar_3^+ might result in two photofragmentation pathways for Ar_3^+, while the photodissociation spectrum displays only one apparent band.

TABLE I. Ratio of Ar^+ and Ar_2^+ photofragments to total ionic photofragments from the photodissociation of Ar_3^+ as a function of wavelength.

λ(nm)	Ar^+	Ar_2^+
820	0.64	0.36
700	0.86	0.14
670	0.95	0.05
620	0.98	0.02
532	1.00	0.0

In summary, the photodissociation cross section of Ar_3^+ has been measured continuously from 670 to 476.2 nm and at 1064, 820, 700, 355, and 320 nm. The cross section displays a single peak, $\approx 2600\ cm^{-1}$ wide, centered at 520 nm. The absolute cross section at this peak is found to be

$$1.5\begin{pmatrix}+1.5\\-0.7\end{pmatrix}\times 10^{-16}\ cm^2.$$

Two pathways for photofragmentation were observed, yielding Ar^+ and Ar_2^+ as products. The magnitude of the photodissociation cross section measured implies that Ar_3^+ ions can represent an important loss mechanism for the $A \leftarrow C$ transition of XeF in high pressure excimer lasers.

ACKNOWLEDGMENTS

This research was supported by NSF Grant Nos. CHE 83-16628 and PHY 86-04504. We are pleased to acknowledge very useful and stimulating discussions with H. H. Michels, W. L. Nighan, A. W. Castleman, Jr., and C. R. Albertoni. One of us (C.P.S.) thanks the Deutsche Forschungsgemeinschaft for support during his stay in JILA.

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