Velocity Map Ion Imaging Study of Ar_2^+ Photodissociation

J. A. Maner, D. T. Mauney, and M. A. Duncan*

Abstract

The argon dimer cation is produced in a plasma generated by a laser spark in a supersonic expansion. The cold ions are mass selected and investigated by photodissociation at 355 nm, with velocity map imaging of the Ar^+ photofragment. Using the radius of the image, we determine the kinetic energy release and derive the ground state dissociation energy of Ar_2^+ as $D_0'' = 1.32 \pm 0.03 / -0.02$ eV. Additionally, the angular distribution is described with $\beta = 1.71\text{--}1.95$, consistent with excitation of the parallel-type ${}^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$ transition.

Table of Contents Graphic:

1. Introduction

Photofragment imaging has been employed for nearly three decades to study the photodissociation dynamics of gas-phase molecules [1-11]. Imaging techniques allow the velocity and angular distributions of photofragments to be recorded simultaneously. Velocity and kinetic energy distributions may be used to study the partitioning of excess energy among the various internal degrees of freedom of the photofragments, and the nature of the electronic transition leading to photodissociation may be inferred from the angular distribution. While the field of photofragment imaging as applied to the photochemistry of neutral molecules has certainly come of age, very few ions have been studied in this way [12-19]. We have recently developed a new time-of-flight mass spectrometer for velocity-map imaging (VMI) [2] of the photofragments from mass-selected ions [19]. We employ this new selected-ion VMI (SI-VMI) instrument here to study the photodissociation of the well-known argon dimer cation.

Kinetic energy release in the unimolecular decomposition of ion-molecule complexes has been studied extensively using a variety of mass spectrometry-based techniques, including time-of-flight measurements, peak shape analysis, and translational energy spectroscopy [20-24]. The argon dimer cation is a prototypical system for these types of experiments. Its simple electronic structure and large absorption cross sections in the UV-visible region make Ar_2^+ tractable by both theory and experiment [20,25-41]. The binding energy of Ar_2^+ has been the subject of numerous studies [20,29,34-40] which have been summarized by Weitzel and Mähnert [40]. Moseley and coworkers studied the photodissociation of Ar_2^+ by measuring translational energy spectra of Ar^+ in a double focusing reverse geometry instrument, and reported a binding energy of 1.33 ± 0.02 eV [20]. Stace and coworkers employed a similar experiment using ultraviolet excitation, like that employed here [34]. Signorell and Merkt determined a binding energy of 1.3147 ± 0.0008 eV by PFI-ZEKE spectroscopy on Ar_2 and a potential fit of the many cation

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4 vibrational levels detected [38]. More recently, Weitzel and Mähner studied the dissociative
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6 ionization of Ar_3 in a TPEPICO experiment and generated a binding energy for Ar_2^+ of $1.29 \pm$
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8 0.05 eV [40]. Lepère and coworkers studied Ar_2^+ in an instrument developed for low-resolution
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10 photofragment imaging [41]. They reported an angular distribution corresponding to $\beta \approx 1$,
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12 indicating a parallel transition, and argued that their results were consistent with a theoretical
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14 binding energy of 1.38 eV. In this work, we investigate the kinetic energy release and
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16 photofragment angular distribution for the photodissociation of Ar_2^+ at 355 nm using the new SI-
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18 VMI spectrometer. We derive an independent value for the dissociation energy of this ion,
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20 which is consistent with previous results.
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28 29 **2. Experimental**

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31 The SI-VMI instrument has been described previously [19]. It is based on our reflectron
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33 time-of-flight (RTOF) mass spectrometer that has been used for many years to study the
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35 photodissociation products and spectroscopy of mass-selected ions [42]. Argon clusters are
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37 produced in a plasma generated by a pulsed Nd:YAG laser (355 nm; Spectra-Physics INDI)
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39 focused onto the surface of a tantalum rod in a supersonic expansion of argon (100 psi backing
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41 pressure; General Valve Series 9). The molecular beam is skimmed as it passes into a
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43 differentially-pumped chamber, and then ions are pulse-extracted into an orthogonal RTOF mass
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45 spectrometer. Different configurations of this device allow mass analysis of the cluster
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47 distribution and mass selection of specific ions for photodissociation measurements. For
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49 imaging experiments, the reflectron field is turned off to allow ions to be transmitted into the
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51 imaging flight tube, which is in line with the first flight tube of the RTOF. Ions are then
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53 decelerated prior to the laser excitation region, photodissociated (Nd:YAG laser; 355 nm;
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55 vertical polarization; Continuum SureLite SL-10), and reaccelerated using an assembly of
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electrostatic lenses configured for velocity map imaging [2]. For ion detection, we employ the DC-slice technique [43]. A dual MCP/P-47 phosphor detector (Beam Imaging Solutions BOS-75) is pulsed with a 140-ns gate (DEI PVX-4140), resulting in the detection of only the central ~90 ns of the Ar^+ arrival time distribution. Images are collected over 200,000 laser shots using a CCD camera (Edmund Optics) and processed using the NuACQ and BasisFit programs of Suits [44,45]. Images are also reconstructed using the BASEX algorithm of Reisler [46]. A photomultiplier tube coupled to a digital oscilloscope (LeCroy) views the phosphor screen to acquire time-of-flight data and monitor ion intensities.

3. Results and Discussion

A laser-generated plasma at the surface of a tantalum rod in an argon expansion produces a mass spectrum containing both Ar_n^+ and $\text{Ta}(\text{Ar}_n)^+$ cluster ions. This mass spectrum is presented in the Supporting Information for this paper. Ar_n^+ clusters have been produced with similar laser spark generation using many different metal rods in our lab, but tantalum was chosen to reduce mass spectral congestion in the range of the arrival time of Ar_2^+ and the Ar^+ fragment. Ar_n^+ cluster ions have also been produced in our lab using pulsed electrical discharges with needle or ring electrodes, but this leads to congestion in the lower mass range due to the presence of trace water and hydrocarbon masses. We have noted previously that ions produced by electrical discharges are somewhat warmer than those produced by the laser spark [47]. For example, in previous studies of protonated water clusters, mass spectra generated using the discharge were often skewed toward smaller cluster sizes compared to those produced by the laser spark under similar expansion conditions [48]. Ions generated with the spark tend to be cooler, giving sharper linewidths in measured infrared or UV-visible spectra, presumably because the focused output of the laser defines a relatively small ionization volume resulting in

minimal heating of the expansion gas. The discharge source has a larger excitation volume, resulting in more extensive ionization and gas heating.

A schematic of the ground and excited state potentials for Ar_2^+ is shown in Figure 1. The excited states of the Ar_2^+ cation have been investigated extensively in previous work [26-29]. Excitation at 355 nm is expected to cause the $^2\Sigma_g^+ \leftarrow ^2\Sigma_u^+$ transition, with dissociation in the excited state producing Ar^+ ($^2P_{1/2}$) and Ar (1S_0). The ground state binding energy can therefore be related to the kinetic energy release in the excited state via the following energetic cycle:

$$D_0'' = h\nu - KE - SO \quad (1)$$

where KE is the total energy in excess of the dissociation threshold and SO is the spin orbit splitting of Ar^+ (1431.58 cm^{-1} or 0.177 eV) [49]. Because we employ a supersonic expansion and the vibrational frequency of Ar_2^+ is small (315 cm^{-1}) [37], it is likely that our Ar_2^+ distribution has cooled efficiently to $v'' = 0$. Rotational cooling is usually more efficient than vibrational cooling, and therefore we also expect no contribution to our experiment from warm rotations. Additionally, since Ar and Ar^+ do not have low-lying electronic excited states, all of the excess energy must be associated with translation of the neutral and ionic Ar fragments in their ground states.

The photofragment image of Ar^+ obtained is shown in Figure 2, and the corresponding angular, velocity, and kinetic energy distributions are shown in Figure 3. In a typical VMI experiment studying neutral molecules, a velocity calibration is obtained using another system with well-known binding energy. However, there are very few ions with well-known binding energies and spectroscopy accessible under our current conditions. Therefore we use a time-of-flight/geometric approach to determine the fragment ion velocities. Using the radius of the Ar^+ image and the time of flight of the Ar^+ ions from the excitation point to the front surface of the imaging detector, we calculate the velocity of the Ar^+ fragment orthogonal to the path of the Ar_2^+

parent ion beam. This is then directly related to its kinetic energy by $\frac{1}{2}mv^2$. The diameter of the detector is 75 mm, which corresponds to 1690 pixels and a pixel width of 23 μm . The flight time of Ar^+ is 13.0 μs , which leads to a calibration factor of 3.41 m/s/pixel. Using this calibration, we plot the intensity profile of the image as a function of velocity as shown in the middle panel of Figure 3. From this velocity distribution, we determine the kinetic energy distribution in the lower panel of Figure 3. Because the edge of the image is noisy, we define the kinetic energy as the midway point between the onset of signal (1.02 eV) and its peak value (0.97 eV). The average of these two energies is 1.00 eV, corresponding to a velocity of 2196 m/s. Using equation 1, we calculate a binding energy of $1.32 \pm 0.03/-0.02$ eV. Within this uncertainty, our value for the dissociation energy agrees with other experimental values in the literature (see Table 1). Because of the supersonic expansion used in our source, it is likely that our Ar_2^+ ions are colder than those studied in some other experiments, which employed electron beam excitation on neutral argon clusters. Such excitation can produce some internally warm Ar_2^+ ions from the fragmentation of larger clusters. If other experiments had vibrationally or rotationally excited ions, photodissociation would produce a greater excess energy in the fragments, corresponding to lower derived binding energies than our value. The experiment of Signorell and Merkt was quantum-state resolved, and not sensitive to this issue [38]. However, the error in our measurement can also arise from the difficulty in defining the edge of the ion image. It is also possible that the gate on the detector is too wide, and that we have not effectively sliced the Ar^+ temporal distribution. The image was generated from the central 90-ns portion of the total 500-ns distribution, which corresponds to about 20%. This would not change the diameter of the image, but would lead to a widening of the Ar^+ ring, effectively skewing our results toward higher binding energies. More details about the image processing are provided in the Supporting Information for this paper.

Interestingly, the simple geometric method used here for kinetic energy determination usually cannot be used in VMI studies of neutral photodissociation [2]. Under conditions typically employed there, the VMI fields (1–3 kV) are much greater than the initial kinetic energies of the neutral photofragments (typically about 1 eV or less), producing an amplification in the observed image radius [2]. Calibration is then required to determine this amplification factor, which has typical values of 1.2–1.4. In the present work, the initial ion kinetic energy along the ion flight direction is set by deceleration to a value of about 1600 eV, whereas the VMI grids accelerate by an additional 800 eV. Because these two energies are much more similar, the image amplification factor should be much smaller. Because we obtained a binding energy in almost perfect agreement with other more accurate experiments, the amplification factor in this ion beam configuration must be very close to 1.

Figures 2 and 3 show the angular distribution of the photofragment signal, which has not been reported previously for this system except at very low resolution [41]. The intensity is clearly peaked at 0° and 180°. We fit this distribution to the following equation:

$$I = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)] \quad (2)$$

where $P_2(\cos \theta)$ is the second order Legendre polynomial and θ is the angle between the electric field vector of the linearly polarized laser and the velocity vector of the ionic fragment [50]. The β parameter falls between -1 and 2 , where -1 indicates a pure perpendicular transition and 2 indicates a pure parallel transition. For Ar_2^+ , we determined β values of 1.71 – 1.95 , depending on how the image is processed (see details about the distribution fitting in the Supporting Information). These values are consistent with the excitation of the $^2\Sigma_g^+ \leftarrow ^2\Sigma_u^+$ transition, as expected.

The data presented here show how the imaging of ion photodissociation can be used to derive dissociation energies and to reveal the polarization of the electronic transitions involved for the prototypical argon dimer cation. In the case of the dissociation energy, our imaging result cannot compete with the accuracy obtained with high resolution laser PFI-ZEKE experiments [38,39]. However, its uncertainty is perhaps comparable to values obtained by other measurements of kinetic energy release. As noted in other work, measurements of kinetic energy release can also avoid the threshold effects found in collision-induced dissociation measurements [23,24]. Because the ions in our experiment are produced in a cold supersonic expansion, uncertainties in their internal energy content are also significantly reduced. It is encouraging that our imaging results, even with their uncertainties, are consistent with the best data obtained for the dissociation energy by these other experiments. Because of this, similar imaging experiments may be useful in future studies to derive energetics for ions or ion-molecule complexes that cannot be studied by other methods.

4. Conclusion

The photodissociation of the argon dimer cation at 355 nm has been investigated with velocity map imaging. This provides a new and independent probe of the photodissociation dynamics in this system. The kinetic energy release following dissociation in the excited state is used in an energetic cycle to derive the ground state dissociation energy. Although the imaging method provides lower resolution than spectroscopic methods, the bond energy derived is consistent with previous high resolution results. Additionally, the angular distribution of the Ar^+ fragment indicates that excitation takes place via a parallel transition, consistent with the $^2\Sigma_g^+ \leftarrow ^2\Sigma_u^+$ transition expected at this energy. Imaging the products of selected-ion photodissociation

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4 provides another method in the toolbox of mass spectrometry applicable to a variety of ions and
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6 ion-molecule complexes.
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Table 1. Binding energies for Ar_2^+ from different experiments.

D_0'' (eV)	Method	Reference
1.33 ± 0.02	MIKES	20
1.27 ± 0.02	PI	30
1.24	TPEPICO	35
1.361	PI	36
1.32 ± 0.005	PI	37
1.3147 ± 0.0008	PFI-ZEKE	38
1.3130 ± 0.0007	PFI-ZEKE	39
1.29 ± 0.05	TPEPICO	40
$1.32 +0.03/-0.02$	SI-VMI	This work

Figure Captions

Figure 1. Schematic of the lowest-lying potentials of Ar_2^+ .

Figure 2. The photofragment image of Ar^+ from photodissociation of Ar_2^+ at 355 nm.

Figure 3. The angular distribution (top), velocity distribution (middle), and kinetic energy distribution (bottom) of the Ar^+ fragment from the image shown in Figure 2. The red trace in the top panel is the angular distribution fit to the experimental data in black, which corresponds to a β value of 1.95. The red bar in the kinetic energy distribution indicates the maximum translational energy of Ar^+ determined as described in the text. The width of the bar indicates the uncertainty in this value.

Figure 1

Figure 2

Figure 3