Photodissociation of the linear \( \text{Ar} - \text{I}_2 \) van der Waals complex: Velocity-map imaging of the \( \text{I}_2 \) fragment

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Photodissociation of the \( \text{Ar} - \text{I}_2 \) 1:1 linear van der Waals complex is studied over the 490–520 nm region using the velocity-map imaging technique. Molecular iodine, and both the T-shaped and linear \( \text{Ar} - \text{I}_2(X, v''=0) \) ground-state complexes absorb strongly in this range, and these transitions access both the bound and dissociative regions of the \( \text{I}_2(B) \) state. We measure the angle-speed distribution of vibrationally excited \( \text{I}_2(B, v') \) state products by resonant 1 + 1 ionization via the \( E \) and \( f \) ion-pair states, forming \( \text{I}_2^* \), which is imaged under velocity-mapping conditions. The images show a strong angular anisotropy, which is the same for all excitation energies, spanning from the bound region to above the molecular dissociation limit. The observed angular anisotropy of the \( \text{I}_2 \) fragments is consistent with a direct dissociation of linear \( \text{Ar} - \text{I}_2 \) complexes promoted to the inner repulsive potential wall of the \( \text{Ar} + \text{I}_2(B, v') \) potential energy surface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3075561]

I. INTRODUCTION

The stabilization of atomic and molecular species in weakly bound van der Waals complexes coupled with numerous spectroscopic methods has enabled intermolecular interactions to be systematically interrogated for a broad range of systems. The influence of the proximity and orientation of the partners within the complexes on the photoinitiated dynamics has subsequently become a topic of much interest. The \( \text{Ar} - \text{I}_2 \) van der Waals complex is a benchmark system for both of these research directions. The photoexcitation of \( \text{Ar} - \text{I}_2 \) in this region leads to very rich dynamics, with processes including vibrational predissociation (VP), intramolecular vibrational relaxation (IVR), electronic predissociation (EP), and the one-atom cage effect.\(^1,2\) The relative contributions of these dissociation mechanisms on the excited-state dynamics varying with the excitation energy and with the regions of the excited-state multidimensional potential energy surface (PES) that are sampled. The excitation spectrum of \( \text{Ar} - \text{I}_2 \) near the \( \text{I}_2(B-X) \) electronic region contains discrete bands superimposed on a broad continuum, and there are contributions from transitions of ground-state \( \text{Ar} - \text{I}_2(X, v''=0) \) complexes with T-shaped and linear equilibrium geometries.\(^3-7\)

For the \( \text{Ar} - \text{I}_2 \) complexes, the VP mechanism traditionally refers to promotion of the complexes to metastable intermolecular vibrational levels bound within the potential associated with an electronically excited state of the \( \text{I}_2 \) molecule. For clarity, the VP of complexes within the \( B \) electronic state is

\[
\text{Ar} - \text{I}_2(X, v''=0) + h\nu \rightarrow \text{Ar} - \text{I}_2(B, v') \rightarrow \text{Ar} + \text{I}_2(B, v)
\]

with \( v < v' \).

There is a general propensity for forming those \( \text{I}_2(B, v) \) VP fragments that lie energetically just below the intermolecular vibrational level, \( v = v' - 3 \), thereby minimizing the translational energy release to the fragments.\(^8,9\) Complexes prepared in discrete excited-state levels may also undergo IVR, resulting in the formation of \( \text{I}_2(B, v) \) fragments. The EP mechanism occurs because of the presence of repulsive electronic states that can be accessed in the \( \text{I}_2(B-X) \) spectroscopic region. Here, the electronically excited \( \text{I}_2 \) molecule dissociates, forming three different atomic fragments according to

\[
\text{Ar} - \text{I}_2(X, v''=0) + h\nu \rightarrow \text{Ar} - \text{I}_2^* \rightarrow \text{Ar} + 1(^2P_{3/2}) + 1(^2P_{3/2}).
\]

The excited \( \text{Ar} - \text{I}_2^* \) complexes in this energy region may be associated with one of the purely dissociative electronic states, \( B^+ 3\Pi_0^o \) or \( B^+ 3\Pi_0^e \), or the repulsive walls lying above the \( A^\pm 3\Pi_0^o \) or \( A^\pm 3\Pi_0^e \) states. Nonadiabatic coupling between the \( B \) state and any of these four states may also give rise to EP of the metastable \( \text{Ar} - \text{I}_2(B, v') \) intermolecular vibrational levels. Since the EP mechanism results in ground-state atomic fragments, fluorescence signals are not observed for this pathway. Recently, Kautzman et al.\(^10\) investigated the competition between VP and EP in the energy regime lying predominantly below the \( B \) state. These experiments utilized electron photodetachment of the T-shaped \( \text{Ar} - \text{I}_2^- \) anionic complex to interrogate the dynamics of the neutral complexes, predominantly with a T-shaped geometry.

The excited-state \( \text{Ar} - \text{I}_2 \) complexes having a linear geometry may also dissociate via the one-atom cage effect when promoted above the dissociation threshold of the \( B 0^+_u \)
state of I$_2$, 20 043.22 ± 0.01 cm$^{-1}$, as shown in Fig. 1. In contrast to free I$_2$ molecules, where this excitation results in prompt dissociation into I$^2P_{3/2}$ + I$^2P_{3/2}$ atomic fragments with a quantum yield of unity, the photoexcitation of complexes to this energy region results in the formation of I$_2$ dissociation fragments in the B $0_{u}^{+}$ electronic state with widely varying amounts of vibrational excitation, $v'$.

\[
\text{Ar} - \text{I}_2(X,v''=0) + h\nu \rightarrow \text{Ar} + \text{I}_2(B,v')
\]

with $h\nu > 20 043.22$ cm$^{-1}$.  

This one-atom caging was first observed experimentally by Saenger et al.\cite{saenger2006} and then by Valentini and Cross.\cite{valentini2006} These initial reports led to numerous experimental\cite{schuring1995, schuring1996, schuring1997, schuring1998, valentini2006} and theoretical\cite{valentini2006, janda2007, janda2008} efforts aimed at characterizing these continuum fluorescence signals and the dynamics incurred. Seemingly contradicting the one-atom cage-effect mechanism, similar signals were also observed following excitation of the Ar-I$_2$ complex to energies lying below the I$_2$($B_0^{+}$) state dissociation limit.\cite{schuring1995, schuring1996, schuring1997, schuring1998, valentini2006} Significantly, emission was observed from a broad range of I$_2$(B,$v'$) levels when exciting to regions lying to energies above these levels but still below the I$_2$(B) dissociation limit.

Two-laser action spectroscopy experiments were undertaken by Darr et al.\cite{darr2007} to identify the origin of the Ar-I$_2$ continuum signals that span from below to well above the I$_2$(B) dissociation limit. Specifically, they monitored the formation of several different I$_2$(B,$v'$) vibrational levels while scanning the excitation laser across the bound and dissociative regions of the I$_2$(B) potential. A continuum signal was observed to start at 250 ± 2 cm$^{-1}$ above each I$_2$ B-X, $v'$=0 monomer band origin that spanned an energy of at least 700 cm$^{-1}$. The intensity of the continuum signal did not track with the intensity of the discrete features associated with transitions of the ground-state T-shaped Ar-I$_2$(X,$v''$=0) as the expansion conditions and the downstream distance along the expansion was varied. They concluded that the continuum signals could not be from transitions of the T-shaped complex, instead they attributed the signals to transitions of the linear ground-state conformer. The results of these experiments led them to propose a variant of the one-atom cage-effect mechanism that is more appropriately termed direct dissociation. The continuum signals are attributed to bound-free transitions of the linear Ar-I$_2$(X,$v''$=0) conformer to the inner, repulsive walls of numerous Ar $+\text{I}_2(B,v'')$ intermolecular potentials, leading to fast dissociation of the complex along the Ar-I$_2$ bond. Comparable results were reported by Loomis and co-workers for other rare gas-dihalogen systems, including He-I$_2$, Ne-I$_2$, He-I$_2$, Ne-B$_2$, and He-B$_2$, in addition to the H$_2$I$_2$ (Ref. 29) and D$_2$I$_2$ (Ref. 30) four-atom complexes.

Recently, Janda et al.\cite{janda2007} reported a systematic investigation of the He-B$_2$, Ne-B$_2$, and Ar-B$_2$ family of complexes to interrogate the role of the rare gas atom on the propensity for accessing these bound-free transitions of the linear conformers. While experimentally verifying the mechanism for the promotion of the linear conformers to the inner repulsive regions of the excited-state van der Waals potentials, accompanying calculations also indicate the role that the dihalogen bond length plays during the dissociation process. Because of the nature of the electronic excitation in the B-X region, the Franck-Condon excitation of the halogen coordinate accesses the highly repulsive portion of the B-state potential.\cite{janda2007} Considering the Ar-B$_2$ complex, the wave function of the ground-state linear Ar-B$_2$(X,$v''$=0) conformer is projected onto the excited-state PES creating a wavepacket, which is localized on the repulsive wall of the B$_2$(B) potential. In contrast, the wavepacket samples only a mildly repulsive region of the Ar+B$_2$(B,$v'$) potential. The wavepacket then accelerates primarily along the Br–Br coordinate before colliding with the Ar–Br$_2$ repulsive wall.\cite{janda2007} The role of the dihalogen distance coordinate in transferring the requisite momentum to the Ar atom increases with higher excitation energies that access even more strongly repulsive regions of the B$_2$ potential. Similar momentum-transfer and direct-dissociation mechanisms most likely occur for Ar-I$_2$.

Most of the previous experimental works characterizing the one-atom caging and bound-free dissociation mechanisms were based on registration of I$_2$(B,$v'$) fluorescence. In the present study I$_2$(B,$v'$) molecules formed in the direct dissociation of the linear Ar-I$_2$ complexes are detected by means of the velocity-map imaging (VMI) technique,\cite{darr2007} which provides information about the kinetic energy of the products and about the angular anisotropy of the I$_2$(B,$v'$) recoil with respect to the linearly polarized excitation laser light. Our results on Ar-I$_2$ provide direct insight into the general stereodynamics of the dissociation mechanism and into the kinetic energy redistribution during the dissociation process. The wavelength of the excitation laser was scanned in the range of 490–520 nm (20 408–19 231 cm$^{-1}$), thus spanning from energies above the dissociation limit of I$_2$(B $0_{u}^{+}$) to those below this limit, 20 043.22 ± 0.01 cm$^{-1}$. In so doing, we were able to observe that there are no sudden changes in the dissociation dynamics when crossing the dissociation threshold. All of the results are consistent with bound-free transitions of the linear Ar-I$_2$ conformer, followed by a direct-dissociation mechanism giving rise to the continuum fluorescence signals observed throughout and above the I$_2$ B-X spectral region.
II. EXPERIMENT

The VMI setup was described in detail in a previous article on the photodissociation of (CH₃I)₂ van der Waals complexes,³³ and only a brief overview is given here. Ground-state Ar–I₂(X, v"=0) complexes are stabilized by flowing argon at a pressure of 1 bar through a sample of iodine crystals held at room temperature, providing a vapor pressure of I₂ of ≈0.2 Torr. The mixture is slowly flowed through the reservoir of a pulsed valve with a 0.2 mm orifice in order to form a supersonic free-jet expansion, which is directed parallel to the time-of-flight axis of the imaging apparatus. The expansion passes through a 2 mm skimmer mounted 20 mm downstream from the nozzle and is collimated 100 mm downstream from the nozzle by a 2 mm hole at the center of the repeller electrode plate. Excitation of the Ar–I₂(X, v"=0) complexes within and above the I₂(B) region and ionization of nascent I₂(B, v') products takes place in the region between the repeller and extractor electrodes using two counterpropagating pulsed tunable laser beams, which were linearly polarized with the same direction of polarization, set parallel to the imaging detector face.

The Ar–I₂(X, v"=0) complexes were excited using a tunable dye laser (Quanta Ray, PDL-2, coumarin 500), pumped by the third harmonic of a neodymium doped yttrium aluminum garnet (Nd:YAG) laser (Continuum Surelite). The wavelength of the excitation laser was tuned in the range of 490–520 nm. The excitation laser beam was unfocused, with a beam size of ≈2 mm. The energy and the duration of the pulse were 5 mJ and 5 ns, respectively. The nascent I₂(B,v') products were ionized with the frequency-doubled output of a second, tunable pulsed dye laser (Quanta Ray, PDL-2, sulforodamine B+rhodamine 640) pumped by the second harmonic of a Nd:YAG laser (Quanta Ray, GCR series, 532 nm). Three probe wavelengths were used: 315.67, 315.94, and 304.67 nm (all wavelengths are in vacuum). The pulse energy, duration, and bandwidth of the probe laser were 1–10 mJ, 5 ns, and ≈1 cm⁻¹, respectively. The probe laser was focused by a 33 cm focal length lens, and the probe wavelength was delayed by 50 ns from the excitation laser.

The I₂(B,v') products are ionized using (1+1) resonance enhanced multiphoton ionization (REMPI) by accessing the high vibrational levels of the E 0_u⁺ and f 0_u⁺ ion-pair states. Because of the high density of vibrational levels in the region of the E 0_u⁺ and f 0_u⁺ states accessed and the frequency bandwidth of the probe laser, it was difficult to access probe transitions that would ionize only molecules in single I₂(B,v') levels. As a result, several I₂(B,v') vibrational levels were often ionized at one probe laser wavelength. Details concerning the determination of the different levels accessed in the ionization step are provided in Sec. III. The ensuing ions were directed by the VMI lens to a position sensitive microchannel plate detector, which was gated for detection at the I₂⁺ arrival time. Images were recorded for 2000 laser shots and later analyzed using the BaseX inversion program.³⁴ The pulsed valve, both laser systems, and the detection equipment were operated with a 10 Hz repetition rate.

In order to calibrate the kinetic energies of the images, individual I₂ molecules were photodissociated at 498 nm. At this wavelength, I₂ molecules are known to dissociate to the first and second dissociation limits.³⁵ The I(²P₃/₂) atoms were ionized using (2+1) REMPI with the probe laser at 304.67 nm.³⁶ The ring formed by I(²P₃/₂) atoms produced in the dissociation to the first limit, which has a dissociation energy of 12 440.243 cm⁻¹,¹¹ was used for energy calibration.

III. DATA ANALYSIS

A. (1+1) ionization of nascent I₂(B, v')

The excitation of the linear Ar–I₂(X, v"=0) conformer in the wavelength region near 500 nm is known to lead to the formation of I₂(B,v') products spanning a broad distribution of v'.³³,¹⁴,¹⁶ The photoexcitation of the linear complexes at 496.5 nm resulted in the formation of I₂(B,v') products with 23 < v' < 49. In the present study, we fixed the probe laser at three different wavelengths: 304.67, 315.67, and 315.94 nm. Each wavelength is convenient for (1+1) REMPI of I₂(B,v') molecules with 15 < v' < 50 via the high vibrational levels of the E 0_v⁺ and f 0_u⁺ ion-pair states.³⁷ Absorption of the first probe photon by I₂(B,v') leads to the total excitation in the energy range of 49 000–53 000 cm⁻¹, relative to the I₂(X,v"=0) ground-state level. The breadth in the energy range results from the accidental overlap of the probe bandwidth with transitions from different I₂(B,v') levels to high-lying vibrational levels within the E 0_v⁺ and f 0_u⁺ ion-pair states. The breadth of the rotational profiles for the I₂(B,v') levels, spanning from 2 to 4 cm⁻¹, increase the overlap of the transitions. The subsequent absorption of a second probe laser photon by any of these ion-pair levels results in ionization.

Using the Dunham coefficients for the I₂(E), I₂(f), and I₂(B) states,³⁸ it is possible to identify the different I₂(B,v') levels that contribute to the ion signals at each probe laser wavelength. The total experimental and calculated transition energies that could be observed when using the (1+1) ionization at wavelengths of 315.94, 315.67, and 304.67 nm are compared in Table 1 along with the proposed vibrational level assignments for the lower-energy I₂(B) state, v', and higher-energy I₂(E) and I₂(f) states, v". In all cases, the experimental and calculated values agree within ≈3 cm⁻¹, which is quite satisfactory especially considering that rotational excitation in the states is not included, and that the laser is tuned to achieve relatively balanced signals from all the observed channels.

B. Kinetic energy of I₂(B, v') and energy partitioning

Following the photoexcitation of linear Ar–I₂(X, v"=0) complexes, the I₂(B,v') and Ar photoproducts recoil with a kinetic energy determined by the conservation of energy,

\[ hν = D_0^B + E_{\text{kin}}[I₂(B,v')] + E_{\text{kinetic}}. \]  

As shown schematically in Fig. 2, E_{\text{kinetic}} is the total kinetic energy release (TKER) of the dissociation fragments, hν is the excitation photon energy, D_0^B is the binding energy of the linear Ar–I₂(X, v"=0) ground-state conformer, and...
TABLE I. Assignments for (1 + 1) REMPI of I₂(B, v') at the wavelengths of 315.94, 315.67, and 304.67 nm.

Channels observed in the I₂ images shown in Figs. 3–5 are listed along with the product I₂(B, v') vibrational level and the resonant I₂(E, v) or I₂(f, v) level utilized in the ionization.

<table>
<thead>
<tr>
<th>No. of channel</th>
<th>I₂(B, v') vibrational level</th>
<th>Observed energy (cm⁻¹)</th>
<th>Resonance vibrational level</th>
<th>Calculated energy (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>43</td>
<td>51 085.2</td>
<td>f, v=42</td>
<td>51 087.4</td>
</tr>
<tr>
<td>1.2a</td>
<td>37</td>
<td>50 789.2</td>
<td>E, v=116</td>
<td>50 787.2</td>
</tr>
<tr>
<td>1.3</td>
<td>30</td>
<td>50 349.2</td>
<td>E, v=109</td>
<td>50 346.2</td>
</tr>
<tr>
<td>1.4b</td>
<td>24</td>
<td>49 452.9</td>
<td>f, v=24</td>
<td>49 454.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>40</td>
<td>50 973.9</td>
<td>E, v=119</td>
<td>50 972.1</td>
</tr>
<tr>
<td>2.2</td>
<td>30</td>
<td>50 376.7</td>
<td>f, v=34</td>
<td>50 376.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>43</td>
<td>52 256.1</td>
<td>E, v=141</td>
<td>52 256.7</td>
</tr>
<tr>
<td>3.2</td>
<td>30</td>
<td>51 520.1</td>
<td>f, v=47</td>
<td>51 519.9</td>
</tr>
</tbody>
</table>

1 For this channel the transitions starting from v'=36 and v'=37 were found to be equally possible. The observed ring probably corresponds to the superposition of two unresolved rings.
2 For this channel the transitions starting from v'=19 and v'=24 were found to be equally possible. The observed ring probably corresponds to the superposition of two unresolved rings.

$E_{\text{int}}[I₂(B, v')]$ is the internal energy of the I₂(B, v') fragment, which is the sum of electronic, vibrational, and rotational energies with an energy of zero corresponding to the energy of the ground-state molecule, I₂(X, v"=0). This TKER is shared between the I₂(B, v') and Ar products according to the conservation of the energy and momentum,

$$T_{I₂} = \left( \frac{m_{Ar}}{m_{Ar}+m_{I₂}} \right) E_{\text{kinetic}},$$

where $T_{I₂}$ and $T_{Ar}$ are the kinetic energies of the I₂(B, v') molecule and Ar atom, respectively. The masses of I₂ and Ar are $m_{I₂}=253.809$ amu and $m_{Ar}=39.948$ amu, respectively. The combination of Eqs. (4) and (5) gives the dependence of the kinetic energy of the nascent I₂(B, v') molecules on the photoexcitation energy,

$$h\nu = D_l^0 + E_{\text{int}}[I₂(B, v')] + T_{I₂} \left( \frac{m_{Ar}+m_{I₂}}{m_{Ar}} \right).$$

It is important to notice that Eq. (7) is associated with the dissociation of the 1:1 Ar–I₂ complex only and not Arₘ–I₂ higher-order complexes with m > 1. This equation offers a means for determining the van der Waals binding energy assuming a high-resolution excitation source, a definitive identification of the I₂(B, v') levels being probed, and an accurate measurement of the kinetic energy of these nascent I₂(B, v') product molecules.

FIG. 2. Schematic of the ground- and excited-state Ar+I₂ interactions along the linear Ar–I₂ orientation. The linear Ar–I₂(X, v"=0) conformers are photoexcited at $h\nu$ in the gray region, which includes energies above and below the I₂(B) dissociation limit (shown as a long-dashed line). The excited-state complexes may dissociate into different Ar+I₂(B, v') product channels. The binding energy of the linear conformer is $D_l^0$, the internal energy of the I₂(B, v') product is $E_{\text{int}}[I₂(B, v')]$, and the TKER of the Ar and I₂(B, v') fragments is $E_{\text{kinetic}}=h\nu-D_l^0-E_{\text{int}}[I₂(B, v')]$. The figure is adapted from Ref. 31 using the potential parameters from Ref. 45.

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IV. RESULTS AND DISCUSSION

A. Kinetic energy of $\text{I}_2(B, v')$ fragments

Raw velocity-mapped images of $\text{I}_2^+$ ions obtained from the photoexcitation of $\text{Ar}--\text{I}_2$ over the wavelength range from 490 to 520 nm (20 408–19 231 cm$^{-1}$) with subsequent ionization at 315.94, 315.67, and 304.67 nm are shown in Figs. 3–5, respectively. For each probe wavelength, several channels of the formation of $\text{I}_2(B, v')$ become visible. There are four $\text{I}_2^+$ ion channels observed when using a probe wavelength of 315.94 nm, and these are denoted as 1.1, 1.2, 1.3, and 1.4, as shown in Fig. 3. There are only two $\text{I}_2^+$ ion channels observed in the images acquired using probe wavelengths of 315.67 and 304.67 nm, and these channels are labeled as 2.1 and 2.2 in Fig. 3 and as 3.1 and 3.2 in Fig. 4. Each observed ion channel is associated with different $\text{I}_2(B, v')$ product vibrational levels, as listed in Table I.

The radii of the $\text{I}_2^+$ rings corresponding to each channel and the relative contributions to the total $\text{I}_2^+$ signal systematically depend on the excitation wavelength in Figs. 3–5. For example, the image in Fig. 3 obtained with photoexcitation at 490 nm is dominated by the 1.1 and 1.2 channels, which are associated with the detection of $\text{I}_2(B, v')$ products in the $v'=36$ or 37 and $v'=43$ levels, respectively. The radii of the 1.1 and 1.2 channel rings decrease in the images acquired with increasing excitation wavelengths due to the reduction in the available kinetic energy release to the $\text{Ar}$ and $\text{I}_2(B, v')$ products. The relative contribution of the 1.1 and 1.2 channels to the total $\text{I}_2^+$ ion signal also decreases with increasing excitation wavelength, especially as contributions from the 1.3 and 1.4 channels are detected. The image acquired using the longest excitation wavelength, 520 nm, is dominated by the 1.3 and 1.4 channel rings, which are associated with $\text{I}_2(B, v')$ fragments with $v'=19$ or $v'=24$ and $v'=30$, respectively (Fig. 6). These VMI data indicate that with lower photoexcitation energies (longer wavelengths), the $\text{I}_2(B, v')$ fragments are formed with less vibrational excitation. This trend is in agreement with the fluorescence-based results of Philippoz et al.$^{16}$ and Darr et al.$^3$

The photoexcitation energy, $h\nu$, is plotted in Fig. 7 versus the kinetic energies of each $\text{I}_2(B, v')$ product channel observed in Fig. 3. Considering the expected relation between the kinetic energy release of the $\text{I}_2(B, v')$ products, $T_{12}$, and the photoexcitation energy, $h\nu$, as described in Eq. (5), we fit the data for each channel in Fig. 7 to the linear function

$$h\nu = a + bT_{12}.$$  (8)

For each of the channels the linear function was found to provide an excellent fit of the experimental dependences, which indicates that the measured products arise from a one-photon dissociation process. The fits of the data in Figs. 4
The subtraction $8.20 \pm 0.20 - 212 \pm 4 = 19 589 \pm 15$

II. The distribution

$7.61 \pm 0.03 - 19281 \pm 8 = 150 \pm 15$

II. $19 439 \pm 5$

For all of the

$7.63 \pm 0.07 - 262 \pm 8 = 7.16 \pm 0.08$

There is some vari­

$7.39 \pm 0.20 - 18915 \pm 4 = 7.58 \pm 0.06$

tion in the estimated binding energies, but the average value

$139 \pm 5$

of $207 \pm 18 \text{ cm}^{-1}$. This value is slightly less than the value of

$252 \pm 31$

$D_0^b$ reported by Darr et al., $250 \pm 2 \text{ cm}^{-1}$. In order to im­

$19 638 \pm 7$

prove the consistency and accuracy of the measurement of

$167 \pm 8$

$D_0^b$ using this VMI scheme, it would be necessary to use a

$262 \pm 8$

narrow bandwidth probe laser to access distinct $(1+1)$ REMPI transi­tions that originate from specific $I_2(B,v')$ pro­duct levels. Such experiments are now in progress.

B. Angular distribution of the nascent $I_2(B,v')$

The product spatial angular distribution, or the recoil pattern of the products, for the single-photon photodissocia­

parameter is associated with $D_0^b + E_{MB}[I_2(B,v')]$, and the values obtained in the fits are given in Table II. The subtraction of the amount of internal energy of the nascent $I_2(B,v')$ from this value for each of the channels should yield an estimate of the binding energy of the linear Ar–I2(X,v"=0) conformer, $D_0^b$. The amount of rotational excitation in the $I_2(B,v')$ product channels is known to be very small; for instance, a rotational temperature of $7.5 \pm 0.3 \text{ K}$, which corresponds to an average rotational energy of $5.2 \pm 0.2 \text{ cm}^{-1}$, was measured for the $I_2(B,v' = 35)$ channel when photoex­citing the linear Ar–I2(X,v"=0) conformer at 495 nm. Therefore, we assume that the average internal energies of the $I_2(B,v')$ product channels are equal to the sum of the assumed rotational energy, $5 \text{ cm}^{-1}$, and the energy of the $I_2(B,v')$ level, which is relative to the energy of the $I_2(X,v"=0)$ level. The binding energies $D_0^b$ obtained for the different channels are listed in Table II. There is some vari­ance in the estimated binding energies, but the average value is $207 \pm 18 \text{ cm}^{-1}$. This value is slightly less than the value of $D_0^b$ reported by Darr et al., $250 \pm 2 \text{ cm}^{-1}$. In order to im­prove the consistency and accuracy of the measurement of $D_0^b$ using this VMI scheme, it would be necessary to use a narrow bandwidth probe laser to access distinct $(1+1)$ REMPI transitions that originate from specific $I_2(B,v')$ pro­duct levels. Such experiments are now in progress.

For this channel we assumed the vibrational energy to be equal to the average of the energies of $v' = 36$ and $v' = 37$.

For this channel we assumed the vibrational energy to be equal to the average of the energies of $v' = 19$ and $v' = 24$.

and 5 resulted in similar results, and the values of the $a$ and $b$ parameters obtained for each channel observed with the three probe wavelengths are given in Table II. For all of the channels the coefficient $b$ was found to be very close to the value of $(m_{Ar}+m_{I_2})/m_{Ar}=7.355$, as expected for the disso­ciation of the Ar–I2 1:1 complex. Contributions from the dissociation of Ar–I2 2:1 higher-order complexes are not de­tected since a value of $b=4.177$ would be expected.

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Photodissociation of Ar—I$_2$

The possible values of $\beta$ range from $-1$ to 2 with the limiting values of $\beta$ corresponding to the cases where the product recoil is parallel ($\beta=2$, so-called parallel transition) or perpendicular ($\beta=-1$, so-called perpendicular transition) to the vector $\vec{\mu}$.

The angular $I^+$ distributions associated with each channel were fit to Eq. (9) to obtain the $\beta$ values, as illustrated in Fig. 9. Although there were some fluctuations of the $\beta$ values measured at the varying excitation wavelengths, $< \pm 0.2$, no systematic dependence of $\beta$ on the wavelength was found. The excitation wavelength averaged values of $\beta$ for each of the channels were found to have a fluctuation of around 0.1, but again no systematic trend was found, so we assumed that all observed channels have identical angular anisotropy with the average value of $1.66 \pm 0.04$, where the error corresponds to the standard error of the values of $\beta$ obtained for different channels.

In this analysis, we assumed that the ionization probability was the same for all of the $I_2(2^1B, v')$ product channels, independent of the recoil direction. In so doing, we neglected the influence of the polarization of the probe laser on the angular distribution of the observed $I^+$ products. In order to test the validity of this assumption, we performed two series of experiments where the polarization of the probe laser was oriented parallel and perpendicular to the polarization axis of the excitation laser. We found no dependence of the polarization direction of the probe laser on the observed value of the angular anisotropy.

The fact that the observed anisotropy of $I_2$ recoil is close to 2 indicates that the direction of recoil of the nascent $I_2(2^1B, v')$ products is nearly parallel to the transition dipole moment of the transition of the linear Ar—I$_2$(X, $v''=0$) conformer within and above the $I_2(2^1B-X)$ region. Since the transition dipole moment $\vec{\mu}$ of this transition is known to be parallel to the $I-I$ internuclear axis, it is consistent with the initial orientation of the I—I axis, which would result in a negative value of $\beta$. If the dissociation process were slow in comparison to the rotational period of the complex or the motion of the $I_2$ atom about the $I_2$ moiety, we would expect to measure $\beta = 0$. We therefore conclude that the one-atom caging is a result of photoexcitation of linear Ar—I$_2$(X, $v''=0$) conformers to the inner repulsive walls of the Ar+I$_2$(2^1B, v') intermolecular PESs and prompt dissociation into the separate fragments occurs, as proposed previously.

Although the measured value of $\beta$, $1.66 \pm 0.04$, is close to 2, it is consistently lower than the maximum possible value. One of the possible reasons for the difference is some systematic error in measuring $\beta$ in our experiments. The small size of the observed rings and the existence of a background signal superimposed on the images are the factors that usually lead the observed value of $\beta$ away from the ultimate values. It is also possible that the measurement of $\beta=1.66 \pm 0.04$ indicates that either the structure of the conformer is slightly nonlinear or there is some force that generates a torque on the dissociating fragments.

In order to aid in distinguishing between these possibilities, we performed photodissociation experiments on bare Ar$_2$ molecules at an excitation wavelength of 494 nm. We used the subsequent (2+1) REMPI of $I^+(2^1P_{3/2})$ atoms to obtain $I^+$ images. The $I^+$ images contained rings associated with $I_2$ fragmentation at the second dissociation limit. At this excitation wavelength, the rings were nearly as small as the $I_2^+$ rings observed in Figs. 3–5. The angular anisotropy of the $I^+$ images were fit to Eq. (7), and a value of $\beta=1.80 \pm 0.04$ was obtained, not $\beta=2$ as expected for $I_2$ dissociation.

This deviation from $\beta=2$ is presumed to be a consequence of systematic error in measuring $\beta$ in the present experiments.
due to the background signal and the small diameter of the I$_2$ rings. We can, however, use $\beta = 1.80 \pm 0.04$ as the maximum possible value to scale Eq. (10) and estimate the actual $\beta$ parameter for the I$_2(B,v')$ product channel formed by photodissociation of the linear Ar--I$_2(X,v''=0)$ conformer using

$$\frac{\beta}{2} = \frac{1.66}{1.80} \times 0.92 \pm 0.03. \quad (11)$$

The scaled anisotropy parameter is then estimated to be $\beta = 1.84 \pm 0.06$, which is much closer to the maximum value. Using Eq. (10) with $\beta = 1.84 \pm 0.06$, we find $\langle \cos \chi \rangle = 0.973 \pm 0.012$. This corresponds to an angle of $\chi = 13 \pm 3^\circ$ between the recoil direction of the fragments and the orientation of I$_2$ molecule within the ground-state complex prior to photoexcitation.

The overall minimum in the ground-state Ar+I$_2(X,v''=0)$ PES is calculated to be in the linear orientation with an Ar to I$_2$ center-of-mass distance of 5.05 Å. The Ar+I$_2(B,v')$ intermolecular potentials are notably different than the ground-electronic state PES. The electronic excitation of I$_2$ to the B state corresponds to the promotion of an electron from a $\pi^*$ orbital to a $\sigma^*$ orbital. As a result, the electronic excitation increases the repulsion in the linear region of the excited-state potential, thereby lengthening the equilibrium intermolecular bond length for this orientation beyond that found in the ground state. Calculations of the Ar+I$_2(B,v')$ intermolecular PES quantitatively reproduce the major properties expected and experimentally measured. The minimum of the Ar+I$_2(B,v')$ PES is in the T-shaped geometry with nearly the same well depth and intermolecular bond length, as calculated for the ground state well in the T-shaped geometry. While there is a minimum along the internuclear coordinate at all orientations of the Ar atom about the I--I bond axis, defined using $\theta$, the minimum potential at the linear geometry, $\theta = 0^\circ$, in the excited state is calculated to be at significantly longer bond lengths, near 5.5 Å, than that for the linear ground-state conformer.

The calculations of the probability amplitude associated with the linear Ar--I$_2(X,v''=0)$ conformer indicate that the zero-point motion along the angular coordinate of the Ar atom about the I$_2$ molecule spans up to $\pm 10^\circ$ from the linear geometry, $\theta = 0^\circ$. Thus, the vertical excitation of the linear conformer promotes complexes with a small range of geometries about the linear structure on the inner repulsive wall of the Ar+I$_2(B,v')$ potentials. Because of the slight anisotropy of the excited-state potential, the dissociation of those complexes that sample angles near $\theta = 0^\circ$ will result in photoproduct recoil at larger values of $\chi$. This anisotropy is not expected to vary with excitation energy since the Ar--I$_2$ intermolecular distance is significantly longer in the excited state, and the region of the repulsive wall accessed lies energetically well above the associated Ar+I$_2(B,v')$ asymptote. The anisotropy of the I$_2^*$ images seem to be justified by the direct dissociation of linear Ar--I$_2$ complexes as proposed by Darr et al. Yet additional information about the probability of the ground-state linear Ar--I$_2(X,v''=0)$ conformer and possibly about the anisotropy of the repulsive potential region of the excited state is gleaned in these VMI experiments. Semiclassical trajectory calculations performed by projecting the wave function of the ground-state linear conformer onto the inner repulsive walls of the Ar +I$_2(B,v')$ PESs should provide further insights into the dissociation dynamics (see Fig. 9).

V. CONCLUSION

The formation of vibrationally excited I$_2$ in the electronic B $0^u_s$ state with kinetic energy resulting from the photodissociation of the linear conformer of the Ar--I$_2(X,v''=0)$ van der Waals complex is observed in the 490--520 nm wavelength region. The nascent I$_2(B,v')$ were ionized by a (1+1) REMPI process via the $E 0_g^+$ and $f 0_u^+$ ion-pair states, and were detected by means of the VMI technique. By changing the probe laser wavelength different I$_2(B,v')$ product channels with $v'=19, 24, 30, 36, 37, 40, \text{and } 43$ were imaged. For each of the channels the dependence of the kinetic energy and angular distribution of the recoil on the excitation wavelength were detected and analyzed. The kinetic energy release of the I$_2(B,v')$ products exhibit a linear dependence on the energy of the photoexcitation energy, which indicates a one-photon dissociation process.

The angular distributions of the nascent I$_2(B,v')$ products were found to be the same for the different $v'=19, 24, 30, 36, 37, 40, \text{and } 43$ vibrational levels. These distributions also do not depend on the excitation wavelength in the range of 490--520 nm. The average value of the anisotropy parameter $\beta$ for all channels was found to be 1.66 $\pm$ 0.04. This value may be as high as 1.84 $\pm$ 0.06 if we compensate for a measured reduction in the anisotropy that results from the small size of the rings in the images. From this adjusted $\beta$ parameter, we find that the Ar and I$_2(B,v')$ fragments dissociate at a nonzero angle, $13 \pm 3^\circ$, relative to the I$_2$ bond axis. These results support the impulsive one-atom caging model for photodissociation that better resembles a direct-dissociation mechanism of complexes prepared well above the Ar+I$_2(B,v')$ dissociation limits, as suggested by Darr et al. and further developed by Pio et al. Additional insights about the probability amplitude of the ground-state linear conformer are also gained in the VMI experiments.

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