A combination of velocity map imaging and slicing techniques have been used to measure the product recoil anisotropy and angular momentum polarization for the photodissociation process $I_2 \rightarrow I(2P_{3/2}) + I(2P_{3/2})$ and $I_2 \rightarrow I(2P_{3/2}) + I(2P_{1/2})$ in the 450–510 nm laser wavelength region using linearly polarized photolysis and probe laser light. The former channel is produced predominantly via perpendicular excitation to the $^1\Sigma_u^+$ state, and the latter is predominantly parallel, via the $B^3\Pi(0_u^+)$ state. In both cases we observe mostly adiabatic dissociation, which produces electronically aligned iodine atoms in the $|m|=1/2$ states with respect to the recoil direction.


I. INTRODUCTION

Vector correlations in photodissociation, particularly the $[e,v,J]$ three-vector correlation where $e$ is the photodissociation laser polarization direction, $v$ the product recoil velocity, and $J$ the product angular momentum vector, have attracted the interest of molecular physicists for many years. Recently, they have been studied with renewed vigor since the complete quantum-mechanical description of Siebbeles et al., and due to the experimental advances in imaging techniques. Important information about the dissociation dynamics, the shape of the potential curves, the symmetries of the excited states, and the role of nonadiabatic interactions can be obtained from a detailed analysis of the photofragment recoil anisotropy and angular momentum polarization.

Photofragment vector correlations have been measured using velocity map ion imaging, Doppler profiles, and ion time-of-flight profiles. The most recent and robust technique is the direct measurement of the photofragment polarization using slice imaging, where a narrow “slice” through the middle of the sphere of recoiling ionized photofragments is detected, allowing the direct measurement of the angular distribution of this sphere without the need for any deconvolution procedure. The power of the method is demonstrated in this paper on molecular iodine, which plays an active role in atmospheric photochemistry because of its chemical and spectroscopic properties.

Mulliken conducted the first detailed theoretical studies of the $I_2$ molecule and summarized the results of previous works in his seminal paper. Since then, many experimental papers have been published on the topic. Tellinghuisen made some of the most significant contributions to the $I_2$ spectroscopic studies. The vacuum-ultraviolet absorption spectrum of $I_2$, Rydberg states, ion-pair states, and autoionizing Rydberg states of $I_2$ have inspired recent research. While $[e,v,J]$ measurements have provided information on nonadiabatic processes in the photodissociation of the $Cl_2$ and $Br_2$ molecules and the interhalogens IBr, ICl, and BrCl, similar data is not yet available for $I_2$. Asano and Yabushita have recently presented theoretical predictions for $I_2$ which are examined in this paper.

We present here the measurements of alignment and orientation of ground-state $I(2P_{3/2})$ atoms following dissociation of the $I_2$ molecule to the first and second dissociation limits. The I-atom laboratory-frame polarization data is converted to the molecular-frame polarization parameters $a_q^{(k)}(p)$, where the index $p$ distinguishes between contributions to the photofragment polarization from parallel ($||$) or perpendicular ($\perp$), or mixed transitions ($||,\perp$).

Some of the known potential-energy surfaces of $I_2$ are shown schematically in Fig. 1. The ground state of $I_2$ is of $^1\Sigma_g^+(0^+_g)$ symmetry, where the value of $\Omega$ is given in parentheses. Many of the low-lying excited states of $I_2$ can be...
accessed via fully allowed (ΔΩ=0, ±1, g→u, +→+) one-photon transitions from the ground state in the visible-infrared range. The purely continuum absorption spectrum of molecular iodine ranges from 400 to 499 nm, mainly due to transitions to the $^1\Pi_g(1_u)$ and $B^1\Pi(0_u)^+$ states. The continuous region is followed by bound transitions to the $B^1\Pi(0_u)^+$ state and continuous absorption to the $^1\Pi_g$ state between 499 and 840 nm. Absorption to the $A^3\Pi_{1/2}(1_u)$ state starts at 540 nm and becomes dominant above 650 nm. Our studies cover photodissociation in the 510–450 nm region.

II. EXPERIMENT

A brief overview of our velocity map imaging setup, which has been described in detail elsewhere, is given here. A pulsed valve creates a molecular beam of I$_2$ vapor (0.2 Torr) in argon (2 bars). The molecular beam passes a 2 mm skimmer into the ion lens system where the first dye laser (0.1–0.2 mJ/pulse, collimation diameter ~2 mm, and pulse duration ~6 ns) dissociates the iodine molecules, and the iodine atoms recoil with a fixed amount of excess energy. After about 10–20 ns, a second dye laser pulse (0.3 mJ/pulse, focused by an f=25 cm lens, and pulse duration ~6 ns) ionizes the iodine atoms from the ground $^2P_{3/2}$ state through the $^4P_{1/2}$ intermediate state by (2+1) resonantly enhanced multiphonon ionization (REMPI) at 303.68 nm (vacuum wavelength). The polarization of both lasers can be chosen to be either linear or circular. The recoiling ions fly apart, forming an ion sphere. After 1500 ns the electric field of the ion lens is switched on in the velocity mapping mode and the ions are accelerated towards a two-dimensional (2D) position-sensitive multichannel plate (MCP) detector able to detect single ions. The MCP detector is gated by a homebuilt high-voltage pulse supply with τ$_{\text{pulse}}$ ~25 ns. This short-time gate of the detector allows selective detection of only the middle slice of the ion sphere. The MCP detector, combined with a phosphor screen, converts each single ion event into a light spot. A charge-coupled device (CCD) camera records the ion image from the phosphor screen, and a personal computer (PC) accumulates and stores the image for further analysis. The image contains information about the product recoil anisotropy and polarization from the angular distribution and the product kinetic energy from the radial distribution.

For the image analysis, we follow Rakitzis and Zare and write (in the molecular frame) the relative probability $I$ to ionize iodine atoms after dissociation of the I$_2$ molecule,

\begin{equation}
I(\Theta, \Phi, \theta_r, \beta, a_0^{(k)}(p)) = 1 + \beta P_2(\cos \theta_r) + s_1 G_1 \sqrt{2} \sin \theta_r \cos \theta_r \sin \Theta \sin \Phi \text{Im}[a_1^{(1)}(\|, \perp)] + s_2 G_2((1 + \beta)\cos^2 \theta_r P_2(\cos \Theta) a_0^{(2)}(\|) + (1 - \beta/2)\sin^2 \theta_r P_2(\cos \Theta) a_0^{(2)}(\perp)) + \sqrt{3}/2 \sin \theta_r \cos \theta_r \sin 2\Theta \cos \Phi \Re{|a_1^{(2)}(\|, \perp)|} + \sqrt{3}/2(1 - \beta/2)\sin^2 \Theta \cos 2\Phi a_2^{(2)}(\perp)),
\end{equation}

where $\Theta$ is the angle between the recoil direction and polarization axis $e_\text{probe}$ of detection laser, $\Phi$ is the angle between the projections of $e_\text{probe}$ and $e_\text{phot}$ onto the plane perpendicular to the detection axis, $\theta_r$ is the angle between photolysis laser polarization and recoil direction, and $P_2(x)$ is the Legendre polynomial of second order. Sensitivity factors $s_1$ and $s_2$ depend explicitly on the ellipticity of the detection laser polarization and recoil direction, and $P_2(x)$ is the Legendre polynomial of second order. Using Eqs. (9a)–(9d) from Rakitzis et al. we can transform Eq. (1) to the laboratory frame for all experimental geometries. The result of such transformation can in general be represented in the following form:

\begin{equation}
I^{XY}(\theta) = b_0^{(XY)} + b_1^{(XY)} P_1(\cos \theta) + b_2^{(XY)} P_2(\cos \theta) + b_3^{(XY)} P_3(\cos \theta) + b_4^{(XY)} P_4(\cos \theta),
\end{equation}

where $b_k$ are the coefficients that depend on the polarization parameters, $XY$ denotes the polarization directions of the dissociation and detection lasers, respectively, and $P_k(x)$ is a Legendre polynomial of $k$ order. Numerical values of $b_k$ can be found by fitting the experimental angular distributions by using Eq. (2). In our experiment, only even $k$-member parameters were measured, thus $b_0$, $b_2$, and $b_4$. General expressions for these $b_k$ in the case of $J=3/2$ for some geometries of $XY$ are

\begin{equation}
b_0^{(VV)} = 1 - \frac{G_2 s_2}{15}(2 - \beta)a_0^{(2)}(\perp) - 2(1 + \beta)a_0^{(2)}(\|),
\end{equation}

\begin{equation}
b_2^{(VV)} = \beta + \frac{G_2 s_2}{21}(2 - \beta)[5a_0^{(2)}(\perp) - 4\sqrt{6}a_2^{(2)}(\perp)] + 11(1 + \beta)a_0^{(2)}(\|) + 2\sqrt{6}\Re{|a_1^{(2)}(\|, \perp)|},
\end{equation}

\begin{equation}
b_4^{(VV)} = \frac{2G_2 s_2}{35}(-2 - \beta)[\sqrt{6}a_0^{(2)}(\perp) + 3a_2^{(2)}(\perp)] + 6(1 + \beta)a_0^{(2)}(\|) - 4\sqrt{6}\Re{|a_1^{(2)}(\|, \perp)|},
\end{equation}

\begin{equation}
b_0^{(VH)} = 1 - \frac{G_2 s_2}{6}(2 - \beta)[a_0^{(2)}(\perp) + \sqrt{6}a_2^{(2)}(\perp)] + (1 + \beta)a_0^{(2)}(\|),
\end{equation}

\begin{equation}
In addition, the polarization of both lasers can be chosen to be either linear or circular. The recoiling ions fly apart, forming an ion sphere. After 1500 ns the electric field of the ion lens is switched on in the velocity mapping mode and the ions are accelerated towards a two-dimensional (2D) position-sensitive multichannel plate (MCP) detector able to detect single ions. The MCP detector is gated by a homebuilt high-voltage pulse supply with $\tau_{\text{pulse}}$ ~25 ns. This short-time gate of the detector allows selective detection of only the middle slice of the ion sphere. The MCP detector, combined with a phosphor screen, converts each single ion event into a light spot. A charge-coupled device (CCD) camera records the ion image from the phosphor screen, and a personal computer (PC) accumulates and stores the image for further analysis. The image contains information about the product recoil anisotropy and polarization from the angular distribution and the product kinetic energy from the radial distribution.

For the image analysis, we follow Rakitzis and Zare and write (in the molecular frame) the relative probability $I$ to ionize iodine atoms after dissociation of the I$_2$ molecule,
TABLE I. Polarization parameters for I(2P_{3/2}) products of I$_2$ photodissociation to the I(2P_{3/2})+I(2P_{3/2}) channel.

<table>
<thead>
<tr>
<th>Wave length</th>
<th>β</th>
<th>$a^{2P}_{0}(\perp)$</th>
<th>$a^{2P}_{0}(\perp)$</th>
<th>Ref[a$^{2P}_{0}(\perp)$]</th>
<th>$P(J=3/2, m_J=\pm 1/2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>510 nm</td>
<td>-0.88±0.03</td>
<td>-0.93±0.02</td>
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dequation

$P(v=0,1,2,3,\ldots) \rightarrow I(2P_{3/2})+I(2P_{3/2})$ from the different vibrational states of I$_2$(X) ground state in the molecular beam. Our method resolves the small vibrational energy spacing of 214.5 cm$^{-1}$ for dissociation near threshold. By comparing the relative intensities of these channels and accounting for the Franck-Condon factors for transitions from each particular I$_2$(X) vibrational state to the B state, we find a vibrational temperature of I$_2$ in the molecular beam of 240±10 K, which is typical for vibrational cooling in a supersonic beam. The rotational temperature is estimated to be much lower; a value of ~5 K is typical for our conditions.

For the perpendicular channels the signals from different vibrational states are not resolved because the kinetic-energy resolution reduces with increasing fragment energy in velocity space. The smaller-radius perpendicular channel arises from I$_2[X(v=0,1,2,3,\ldots)] \rightarrow I(2P_{3/2})+I(2P_{3/2})$. The sharpness of the outer channels of the image shown in Fig. 2 is reduced by distortion due to the finite size of the ion lens system. This distortion is easily avoided by making the image smaller, using a higher electrostatic lens voltage, as shown in the inset in Fig. 2. Table I contains the extracted polarization parameters for the (1$^2P_{3/2}$+1$^2P_{3/2}$) channel following photodissociation at 450–510 nm, using VV and VH laser geometries. Selected data from Tables I and II are shown graphically in Fig. 3.

The excited electronic states that participate in the dissociation, the $^1$II$_2$(1$^2$A), $B^1II(0_u^+)$, and $A^1II$_2$(1_u)$ states, correlate asymptotically to the atomic m states ($m_A, m_B$) as

$
|\pm 1/2\rangle_A \rightarrow \frac{1}{\sqrt{2}}(\pm 1/2, \pm 1/2),$

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III. RESULTS AND DISCUSSION

A typical raw experimental image is shown in Fig. 2, where two (large radius) perpendicular and several (small radius) parallel channels are clearly resolved. The parallel dissociation channels are formed by the dissociation process $I_2[X(v=0,1,2,3,\ldots)] \rightarrow I(2P_{3/2})+I(2P_{3/2})$ from the different vibrational states of I$_2$(X) ground state in the molecular beam. Our method resolves the small vibrational energy spacing of 214.5 cm$^{-1}$ for dissociation near threshold. By comparing the relative intensities of these channels and accounting for the Franck-Condon factors for transitions from each particular I$_2$(X) vibrational state to the B state, we find a vibrational temperature of I$_2$ in the molecular beam of 240±10 K, which is typical for vibrational cooling in a supersonic beam. The rotational temperature is estimated to be much lower; a value of ~5 K is typical for our conditions.

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$^a$Vibrational resolusion was possible here.
The values of the $a_0^{(2)}$ parameter (for $J=3/2$) can be written in terms of the difference between the $m$-state populations $p(m)$ of the $|m|=3/2$ and $|m|=1/2$ states,

$$a_0^{(2)} = \frac{4}{5} \left( p(|m|=3/2) - p(|m|=1/2) \right),$$

so that the $a_0^{(2)}$ parameter ranges from $+4/5$ (for all the population in the $|m|=3/2$ states) to $-4/5$ (for all the population in the $|m|=1/2$ states), and is 0 for equal population of the $|m|=3/2$ and $|m|=1/2$ states.

We consider the first dissociation channel (Table I and Fig. 3), which yields two ground-state iodine atoms,

$$I_2 \rightarrow I^2P_{3/2} + I^2P_{3/2}.$$  

This channel is produced predominantly by perpendicular excitation (notice that $\beta$ is close to $-1$) from the ground state to the $^1\Pi_u$ state. In this case, for adiabatic dissociation described by Eq. (4), we see that the $I^2P_{3/2}$ photofragments are populated in the $|m|=1/2$ states only, and are described by $a_0^{(2)}(\perp)=-0.8$ [see Eq. (7)], which, to a first approximation, agrees well at all wavelengths with the measured $a_0^{(2)}(\perp)$. The small deviation from $\beta=-1$ likely originates from about 3% excitation to the $B^3\Pi_u(0^+)$ state via a parallel transition. This state also produces $|m|=1/2$ only, therefore there is no deviation from $a_0^{(2)}(\perp)=-0.8$ from excitation to this state. In contrast, excitation or nonadiabatic transfer to the $A^3\Pi_u(1_u)$ state produces iodine atoms with equal population in the $|m|=3/2$ and $|m|=1/2$ states [Eq. (4)], giving an alignment of $a_0^{(2)}(\perp)=0$ for that state. Therefore, the average value of the $a_0^{(2)}(\perp)$ parameter will range between 0 and $-0.8$, and can be expressed in terms of the nonadiabatic transfer probability to the $A^3\Pi_u(1_u)$ state $p$ by

$$a_0^{(2)}(\perp) = -\frac{4}{5} \left( 1 - p \right).$$

where $\Delta \varphi$ is the phase difference between the asymptotic wave functions associated with the $^1\Pi_u(1_u)$ and $A^3\Pi_u(1_u)$ states. The value of the $a_0^{(2)}(\perp)$ parameter is, however, measured to be zero (within the error limits) and the upper limit of $p$ is only about 2% [as determined from the $a_0^{(2)}(\perp)$ parameter].
Therefore, we conclude that to a good approximation (\(>95\%\)) the first dissociation channel can be described by perpendicular excitation to the \(^{3}\Pi_{u}(1_u)\) state, followed by adiabatic dissociation to yield \(I^{2}\left(P_{3/2}\right)\) photofragments characterized by \(|m|=1/2\) with respect to the recoil direction. Any interference between the parallel and perpendicular transitions becomes evident in the \(\text{Re}[a^{(2)}_1]\) and \(\text{Im}[a^{(1)}_1]\) parameters; this interference is small because the magnitude of the parallel transition to the \(B^{3}\Pi_{u}(0_u)^{\mp}\) state is about 3\%, and therefore the \(\text{Re}[a^{(2)}_1]\) and \(\text{Im}[a^{(1)}_1]\) parameters are limited to about a third of their maximal value. The \(\text{Im}[a^{(1)}_1]\) parameter [proportional to \(\sin\Delta\psi_{ll}\), where \(\Delta\psi_{ll}\) is the asymptotic phase difference between the wave functions associated with the \(B^{3}\Pi_{u}(0_u)^{\mp}\) and \(^{3}\Pi_{u}\) states] is measured to be zero. In comparison, the \(\text{Re}[a^{(2)}_2]\) parameter (proportional to \(\cos\Delta\psi_{ll}\)) is measured to be at most a third of its maximal value. We conclude that \(\Delta\psi_{ll}\) is approximately 0 or \(\pi\).

We next consider the second dissociation channel (Table II), which yields a ground-state and spin-orbit excited iodine atoms,

\[
\text{I}_2 \rightarrow I^{2}\left(P_{3/2}\right) + I^{2}\left(P_{1/2}\right). \tag{11}
\]

This channel is produced predominantly by parallel excitation (notice that \(\beta\) is close to +2 in Table II and Fig. 3) from the ground state to the \(B^{3}\Pi_{u}(0_u)^{\mp}\) state. As mentioned above, this state correlates to atoms in the \(|m|=1/2\) states only, producing \(a^{(2)}_2(\perp)=-4/5\). The experimental data agrees, within error, with this value over all the photodissociation wavelengths and parent vibrational states (Table II), indicating that dissociation from this state is also adiabatic. The small contribution from a perpendicular transition (between about 2\% and 5\%), that causes the \(\beta\) parameter to be less than 2, originates from excitation to the \(^{3}\Pi_{u}(1_u)\) state followed by nonadiabatic transfer to one of the \(1/2\sum_{ud}(1_u)\) states at large internuclear separation. During this process, the \(m\)-state distribution does not change, and thus we expect \(a^{(2)}_0(\perp)=4/5\) and \(a^{(2)}_2(\perp)=0\), as for adiabatic dissociation from the \(^{3}\Pi_{u}(1_u)\) state. It should be noted that despite the small contribution of the perpendicular component, the polarization of this channel can be observed because slice imaging [with the photolysis linear polarization parallel to the time-of-flight (TOF) axis] completely removes the contribution of the parallel transition in this geometry (in the limit of perfect slice imaging). The obtained values of \(a^{(2)}_0(\perp)\) and \(a^{(2)}_2(\perp)\) are within error of the expected ones.

Both dissociation pathways of \(I_2\) were observed to proceed adiabatically, following excitation to the \(B^{3}\Pi_{u}(0_u)^{\mp}\) and \(^{3}\Pi_{u}(1_u)\) states. This adiabatic behavior extends to at least 10 000 cm\(^{-1}\) above the first dissociation limit and was followed to more than 2000 cm\(^{-1}\) above the second dissociation limit. Adiabatic behavior was also observed (at one dissociation energy) for \(\text{Br}_2\).\(^{30}\) In contrast, the dissociation of \(\text{Cl}_2\) via the \(C^{1}\Pi_{u}(1_u)\) state includes an additional nonadiabatic transfer to the \(A^{3}\Pi_{u}(1_u)\) state (approximately 40\%).\(^{4,30}\) The situation is more complex for heteronuclear systems due to their lower symmetry, as was shown previously by Wouters et al.\(^8\) for \(\text{BrCl}\). For the simpler dihalogens we see that, as expected, the heavier systems dissociate adiabatically, whereas the lighter \(\text{Cl}_2\) system shows significant nonadiabatic dissociation dynamics.

In a theoretical paper by Asano and Yabushita, it was concluded that the nonadiabatic transition probability between the dominant potential-energy surfaces of a molecule is influenced mainly by the spin-orbit splitting energy, the size of the atomic orbitals, and the relative nuclear velocity. According to their results, dihalogens with bigger spin-orbit splitting energy show more adiabatic behavior. This is consistent with the sequence \(\text{Cl}_2\), \(\text{Br}_2\), and our present experimental results on \(I_2\). Our results could also be used to probe the dependence on the nuclear velocity (i.e., initial vibrational energy). We observe no distinct differences in polarization parameters for the vibrational states \(v=0–3\), but this range of quantum numbers may be too small to expect a measurable effect.

**ACKNOWLEDGMENTS**

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\(^{1}\)R. N. Zare and D. R. Herschbach, Proc. IEEE. \(^{51}\), 173 (1963).
34 R. N. Zare, Angular Momentum (Wiley, New York, 1988).
37 Reference 30. Notice the sign error in this equation.