Photoniation of the iodine atom following methyl iodide A-band photodissociation was studied over the wavelength range of 245.5–261.6 nm by photoelectron imaging technique. Final state-specific speed and angular distributions of the photoelectron were recorded. Two types of the photoelectron resulted from ionizing the I atom from the photodissociation of CH3I were identified: (a) (2 + 1) REMPI of the ground state I atom, and (b) two-photon excitation of spin–orbit excited 1P_{1/2} via autoionizing resonances converging to the 3P state of I+. In addition, some weaker signals were attributed to one-photon ionization of I atoms produced in some higher excited states from multiphoton ionization of CH3I followed by dissociation. Analysis of relative branching ratios to different levels of I+ (in case a) revealed that the final ion level distributions are generally dominated by the preservation of the ion-core configuration of the intermediate resonant state. A qualitative interpretation of the electron angular distribution from an autoionization process is also given.

I. Introduction

The A-band photolysis of methyl iodide (CH3I) is a prototypical system for studying molecular photodissociation dynamics, and has attracted much attention both experimentally and theoretically over the past decades. The well-known A-band of CH3I, lying in the range of 210–330 nm with the maximum near 260 nm and comprising three dissociative excited electronic states (designated as 3Q_b, 3Q_q, and 3Q_l by Mulliken), corresponds to the excitation of a nonbonding 5p orbit of iodine atom to the σ* antibonding C–I orbital. Photoexcitation to the A-band results in rapid direct dissociation producing CH3 and I(2P_{1/2} and 2P_{3/2}) on a timescale of ~150 fs from a real-time measurement. With the availability of high power pulsed lasers, the competition between the multiphoton ionization (MPI) and dissociation processes of CH3I in the wavelength region 266–307 nm has also been investigated and clarified, using a two-color, time-of-flight mass spectrometric technique. It was shown that the predominant ion is I+ from the MPI of the neutral I-atom. Recognizing that the fragmentation of CH3I can be an excellent source of both iodine atom and methyl radical for spectroscopic studies, numerous Rydberg states of iodine have been identified in this way by Pratt using photoelectron spectroscopy or from MPI spectrum of atomic iodine. From the pulsed-field extracted two-photon threshold photoionization spectrum of CH3I in the region from 255 to 230 nm, two other Rydberg series of atomic iodine, (3P_{1/2})np and (3P_{3/2})nf, have also been assigned to the autoionizing resonances by Zhu and Grant. In addition, Jung and co-workers have studied (2 + 1) REMPI of atomic iodine in the wavelength region 277–313 nm using photoelectron imaging technique. Both relative branching ratios to the final levels of I+ (in 3P_0, 3P_0.1, 4D_2 and 3S_0) and the angular distributions of outgoing photoelectrons were obtained. It was found that the final ion level distributions are dominated by the preservation of the ion-core configuration of resonant excited-state defined by the J, l coupling scheme.

Bondybey and co-workers proposed in a series of reports a new probe to watch how a photoexcited molecule dissociates using a nanosecond laser. The idea is analogous to the Raman emission probe pioneered by Kinsey and co-workers over two decades ago, and can be outlined as follows. When a molecule is photoexcited to a repulsive potential energy surface, the molecule undergoes a rapid bond rupture with a near unity dissociation yield. Nonetheless, a very tiny fraction of dissociating molecule can emit photon—the resonance Raman emission, which carries unique imprints of short-time dynamics of the photodissociation process. Since the photoelectron spectroscopy in general has less restricted selection rules than a Raman process, it potentially affords the opportunity to probe more vibrational modes that are active while the photofragments are flying part. Bondybey’s group carried out exactly such an experiment by acquiring the one-color, two-photon zero kinetic energy (ZEKE) spectra of CH3I via the intermediate A-band. The short-time dissociation dynamics is manifested as a series of vibrationally assignable peaks of the molecular ion CH3I+, which was interpreted as the projection of the dissociating wavepacket onto the ionization continuum—rather than back onto the neutral ground state in the Raman emission approach—by absorbing another photon from the repulsive surface.

Motivated by these reports, we recently engaged a project to explore the idea further by using the photoelectron imaging technique in a two-color, two-photon experiment. During the course of that study, many photoelectron images of the I-atom fragments were also taken, which served as a convenient reference system for rigorous calibration of the photoelectron imaging apparatus (in both speed and angle) due to the well-known energetics. In addition, this set of images revealed interesting photoionization dynamics, which is the main subject of this report.
II. Experimental Section

The experimental apparatus used in this study is similar in spirit to the time-sliced velocity-map imaging setup described elsewhere. However, several minor, yet crucial modifications were made to our original slice-imaging setup in order to achieve higher quality photoelectron image for the present experiment. Briefly, a cold molecular beam was produced by expanding a gas mixture, which was prepared by bubbling He through liquid CH3I at 274K (to suppress the I2 contamination) with typical about 9.5% CH3I in He at total pressure of 30 psi, into the source chamber via an Even-Lavie valve (pulse duration of 30 μs, and with 0.5 mm nozzle diameter). The molecular beam, which was skimmed and collimated to ~1 mm diameter along the ion-time-of-flight axis, was intersected at right angles by a frequency-doubled laser beam generated by a Nd:YAG pumped dye laser. The same laser was used for the A-band excitation of CH3I and subsequent ionization of either the parent molecule or the neutral photofragments (mainly I-atoms in this study) in a one-color experiment. The laser was vertically polarized (i.e., parallel to the detector face) and focused by a f = 50 cm spherical lens to the center between the repeller and extractor electrodes.

Electrons or ions produced in the interaction region were velocity-imaged by a suitable electric field and impacted onto the Chevron-type microchannel plate (MCP) after passing through a 45 cm field-free region. The fluorescence from a P46-phosphor was captured by a CCD camera and transferred to a computer on every-shot basis for event counting and for further data analysis. Two modifications of the apparatus were made to reduce the spurious photoelectron background. First, a turbo pump replaced the diffusion pump for the source chamber. Second, in view of the difficulty in time-slicing the photoelectron cloud, a simplified ion-optics assembly with significantly tighter focus and more restricted field-of-view than the original setup[17,18] was adapted for the conventional “crushed” velocity imaging.[1,2] The new setup consists of five thin electrodes (repeller, extractor, and three lenses) with the openings, in order of 10 mm, 10 mm, 20, 60, and 60 mm respectively. The spacing between the successive electrodes was kept at 19 mm. The voltage ratio for this arrangement was maintained, although the voltage employed for the repeller (Vrep) was changed over the range of 900–5000V, depending on the kinetic energy release of photoelectrons. A double-layered μ-metal shield (0.5 mm thickness each) was added to the whole ion optics assembly to minimize the effects from the earth’s magnetic field.

As mentioned in the Introduction, the present study also serves as a calibration, both in speed and angle, of photoelectron imaging detector. From the well-calibrated energy levels of I-atom and I+-ion, the speed calibration factor (i.e., km/sec per pixel) is readily obtained from the consistent assignments of the image features. The angular calibration is, on the other hand, more problematic and often neglected in literatures by simply symmetrizing the raw image prior to data analysis. Even with event-counting technique, we found that the residual nonuniformity of the detection sensitivity still manifests itself as slight asymmetry in angular distributions, which could lead to some errors in the reported β values. Hence, considerable efforts were devoted to finding a way to remedy the angular asymmetry problem.

An ideal source for calibrating the angular variations in detection sensitivity will be an isotropic and uniform distribution. We generated such a source by first choosing a nearly isotropic single-ring image at λ = 244.106 nm and then rotating the laser polarization 90° (i.e., along the TOF axis) to acquire the “calibration” image. Owing to the symmetry properties of the photoionization process, such a “calibration” image is necessarily uniform and thus serves the purpose for angular calibration of the detector sensitivity.

Figure 1 illustrates the effects of the nonuniform sensitivity on the measured angular distribution. The corresponding photoelectron image is the peak number 21, whose peak position is labeled in Figure 2 and the raw image shown in Figure 5 (vide infra). To perform quantitative analysis of the image asymmetry, we took the four quadrants of the photoelectron image and analyzed them independently. Thus, a raw image was converted to four symmetrized images prior to the inversion transformation. The resulted angular variations of the raw image data are presented in Figure 1a,b in the Cartesian and the polar representations, respectively. Noticeable angular asymmetry is vividly displayed. The same raw image was then corrected for the nonuniform sensitivity, using the “calibration” image, and analyzed similarly. The “corrected” results are shown in Figure 1c,d for comparisons. A significant improvement, through not perfect, can clearly be seen. The lines in Figure 1a,c are the best-fitted distributions for the data in each individual quadrant of Figure 1c,d; while the line in Figure 1b,d is the best fit after symmetrizing the “corrected” image (though the actual data points shown in panel d remained unsymmetrized). We found that after correcting the detector sensitivity variations, the best-fitted β-coefficients for a “corrected”, symmetrized image are well within the standard deviations of the β-coefficients obtained from the unsymmetrized four quadrants of the same “corrected” image. This is also clearly illustrated in panel d by comparing the goodness of the line-fit to the actual data point. Hence, for the results to be presented below, the data points are from the symmetrized, angular-corrected images and the best-fitted β coefficients are the averaged results from analyzing the four quadrants.

III. Results and Discussion

A. Spectral Assignment of MPI of Atomic Iodine. Presented in Figure 2 are the three (one-color) spectra over the two-photon energy range of 76 500–81 200 cm−1: the photoelectron spectrum (a), the photoionization yield spectrum of the parent molecular CH3I (b), and the I+ cation-detected photoionization following the photodissociation of CH3I (c). Over most of the wavelength region of this study, two-photon energy is sufficient to ionize the parent molecule CH3I (ionization potential, IP = 76 932 ± 5 cm−1).[10,11] Indeed, the onset of the photoionization of CH3I can be observed as a clear step in Figure 2a,b. But the spectral features in Figure 2b cannot be assigned as the CH3I(X1A1) → CH3I+(X+2E3)+ resonant transitions, which has been observed in threshold photoionization spectroscopy.[16] Instead, they are ascribed to the transitions from the ground state to the superexcited (or autoionizing) states of CH3I, as will be shown in the future. Interestingly, the I+ cation-detected photoionization spectrum, shown in Figure 2c, appears nearly identical to the ZEKE spectrum of Zhu and Grant[11] and can be assigned to the resonant photoionization of the fragmented iodine atoms. Since the photoelectron detection here did not differentiate the photoelectron produced from the ionization of either the parent molecule CH3I or the fragmented iodine atom, the features in the photoelectron spectrum, Figure 2a, comprise spectral features from both sources. Their relative intensities depend on the laser intensity used because of different numbers of photon involved: a two-photon process for CH3I → CH3I+ + e−, whereas at least three photons are required for CH3I → CH3 + 1 → I+ + e−.

In this study, we focused on the photoionization dynamics of the iodine atom by photoelectron imaging technique. A total
of twenty-one spectral features, which are labeled in Figure 2a,c in sequence, were imaged. The spectral positions and assignments, as well as the peak widths, are summarized in Table 1. Two different types of spectral features are classified in Table 1. One class shows narrow peaks with a typical width of \(<1 \text{ cm}^{-1}\); and its formation is ascribed to \((2S + 1)\) REMPI process of predominantly the ground state \(I(2P_{3/2})\). The observed widths are mainly due to the dye laser scan rate and the Doppler broadening of the \(I(2P_{3/2})\) fragments from photodissociation. Thus, the overall processes can be expressed as

\[
\text{CH}_3I + h\nu \rightarrow \text{CH}_3 + I(3P_{3/2})
\]

\[
I(3P_{3/2}) + 2h\nu \rightarrow \text{I}^* + h\nu \rightarrow \text{I}^+ + e^-
\]

(1)

The other type exhibits a broader wider peak with typical fwhm in the order of 2 to 15 cm\(^{-1}\). As will be shown later, those peaks are assigned to two-photon transitions originating from the spin–orbit excited state \(I(2P_{1/2})\) and terminating in superexcited Rydberg states converging to the \(I^+(3P)\) ionization threshold.\(^{11}\) In other words, the processes involved are

\[
\text{CH}_3I + h\nu \rightarrow \text{CH}_3 + I(3P_{1/2})
\]

\[
I(3P_{1/2}) + 2h\nu \rightarrow [I^{**}] \rightarrow I^+ (3P_2) + e^-
\]

(2)

where \([I^{**}]\) denotes a superexcited state that decays through autoionization process with a lifetime inversely proportional to its peak width. Two-photon excitation of a \(p\)-orbital electron dictates the superexcited Rydberg states being of the \(p\)- and \(f\)-series due to the optical selection rule \(\Delta l = 0\) and 2. Both the intermediate excited states in eq 1 and the superexcited states in eq 2 of neutral iodine are described as \(J, l\) coupling in Table 1, as originally suggested by Minnhagen.\(^{19}\) In this coupling scheme, the total angular momentum \(J_c\) of the \(I^+\) ion core is coupled to the orbital angular momentum \(l\) of the Rydberg electron to give the resultant \(K\). The spin, \(s\), of the Rydberg electron is then coupled to \(K\) to give the total angular momentum \(J\). The states are then labeled as \((^3P_l)nKJ\), where \((^3P_l)\) describes the ion core.

In general, the transition energies reported in Table 1 for the \((2 + 1)\) REMPI process 1 are about 1 cm\(^{-1}\) larger than the Minnhagen's values.\(^{19}\) Previously, two series of autoionizing states, \((^3P_l)np\) and \((^3P_l)nf\), have been identified by Zhu and Grant, using one-color two-photon ZEKE spectroscopic technique, with quantum defects of \(~0.45\) and \(~0.045\) respectively.\(^{11}\) Although the reported transition energies\(^{11}\) appear to be systematically smaller than this work for process 2 by about 4 to 6 cm\(^{-1}\), the spectral assignments are entirely consistent in view of the expected offset by the delayed field technique. A few points are, however, worth noting here.

First, it is known\(^9\) that effective principal quantum number \(n^*\) can be calculated directly from the expression

\[
n^* = [R_l(E(^3P_1) - E_0)]^{1/2}
\]

where \(R_l\) is the Rydberg constant for iodine (109736.85 \text{ cm}^{-1}), \(E(^3P_1)\) is the \(^3P_1\) ionization energy, and \(E_0\) the observed energy of the Rydberg state with respect to the ground state \(I(2P_{3/2})\). From eq 3, \(n^*\) is about 2.5 for \(5s^25p^6\) configuration, 3.5 for \(5s^25p^7p\), and 4.526 for the Rydberg states previously
TABLE 1: Assignments of the Ionizing Resonances of Atomic Iodine and Their Peak Widths

<table>
<thead>
<tr>
<th>transition mechanism</th>
<th>peak #</th>
<th>wavelength (Å)</th>
<th>transition energy (cm⁻¹)</th>
<th>assignment</th>
<th>peak width (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 + 1) REMPI</td>
<td>3</td>
<td>258.704</td>
<td>77308.4</td>
<td>2P₂1/2(6)</td>
<td>0.85 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>258.683</td>
<td>77311.9</td>
<td>2P₂1/2(5)</td>
<td>0.74 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>258.530</td>
<td>77360.6</td>
<td>2P₂1/2(4)</td>
<td>0.66 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>255.049</td>
<td>78416.3</td>
<td>2P₂1/2(2)</td>
<td>0.79 ± 0.04</td>
</tr>
<tr>
<td>autoionization</td>
<td>10</td>
<td>254.474</td>
<td>78593.6</td>
<td>2P₂1/2(1)</td>
<td>1.01 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>253.150</td>
<td>79004.7</td>
<td>2P₂1/2(1)</td>
<td>1.84 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>249.872</td>
<td>80004.1</td>
<td>2P₂1/2(1)</td>
<td>0.90 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>260.450</td>
<td>76790.3</td>
<td>2P₂1/2(1)</td>
<td>10.09 ± 11</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>260.166</td>
<td>76874.1</td>
<td>2P₂1/2(1)</td>
<td>4.07 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>255.747</td>
<td>78202.3</td>
<td>2P₂1/2(1)</td>
<td>12.87 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>255.392</td>
<td>78311.1</td>
<td>2P₂1/2(1)</td>
<td>15.41 ± 0.53</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>255.009</td>
<td>78428.8</td>
<td>2P₂1/2(1)</td>
<td>6.02 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>254.152</td>
<td>78693.2</td>
<td>2P₂1/2(1)</td>
<td>4.36 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>252.157</td>
<td>79315.8</td>
<td>2P₂1/2(1)</td>
<td>5.38 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>252.021</td>
<td>79358.5</td>
<td>2P₂1/2(1)</td>
<td>2.28 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>249.824</td>
<td>80056.5</td>
<td>2P₂1/2(1)</td>
<td>2.74 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>249.619</td>
<td>80122.1</td>
<td>2P₂1/2(1)</td>
<td>3.62 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>249.436</td>
<td>80180.9</td>
<td>2P₂1/2(1)</td>
<td>5.02 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>247.874</td>
<td>80686.2</td>
<td>2P₂1/2(1)</td>
<td>3.60 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>247.798</td>
<td>80710.9</td>
<td>2P₂1/2(1)</td>
<td>10.02 ± 0.20</td>
</tr>
</tbody>
</table>

a Ref 19. b Ref 11.

labeled as 5p[1]j/2 in ref 11. Following Minnhagen’s work, 19 5s5p6p and 5s5p7p are the only two np configurations where all levels based on 1s(3P) are below the 3P ionization limit. As such, we prefer to assign the l = 1 series as (3P)8p to 14p in Table 1, rather than as (3P)5p to 11p reported in ref 11.

Second, the transitions corresponding to peaks 8 and 10 were previously assigned as l = 1 series converging to 1s(3P), i.e., (3P)5p[1]j/2 and (3P)5p[0]j/2, respectively, on the basis of quantum defects and spin–orbit splitting patterns. 11 As will be shown later, the images acquired at these two peaks are energetically consistent with two-photon resonant, third photon ionization from I(2P3/2). Therefore, the two transitions are reassigned here as (3P)6p(3P)1/2 and (3P)6p(3P)3/2, respectively, on the basis of I(2P3/2) + 2 photons to the intermediate resonant state being the 6p Rydberg series converging to 1s level of I.
which are about the same magnitude as those of np Rydberg series converging to I+ (3 P1). So, they are tentatively assigned as (3 P1)np series, as indicated in Table 1.

It is instructive to take a closer look at the peak widths of the autoionizing states, which span from about 2 to 15 cm⁻¹; thus, the corresponding rates of autoionization lie over the range of 0.3–3 ps⁻¹. In addition, the data reveal a systematic trend. For a given autoionizing Rydberg series, i.e., those with the same designation l[K], the width decreases monotonically with the increase in n, the principal quantum number of the Rydberg electron. For example, the peak widths for the nf[2]3/2,5/2 series decrease from 10 cm⁻¹ for n = 4 to 5.4 cm⁻¹ for n = 5 and further down to 3.6 cm⁻¹ for n = 6, and these variations follow the relationship of (fwhm)ₙ ∝ n⁻³. Similar behaviors are also found for the nf[3]5/2, np[2]3/2, and np[1]1/2 series. This quantitative trend is anticipated and is in accord with the autoionization propensity rules documented by Berkowitz nearly 20 years ago.²⁰


Figure 3. Photoelectron images of the spectral features from the (2 + 1) REMPI processes of the I(3 P3/2) fragment. The number marked at the upper-left corner of each panel indicates the peak number, shown in Figure 2, at which the image was acquired. For each panel the left half displays the raw image and the right half shows the inverted one. Exemplified in the bottom are the two representative P(Ve) distributions of the photoelectrons for image numbers 4 and 8, respectively. The assignments of the final ion levels are indicated. The final product branching fractions from all seven images are given in Table 2.

The speed of photoelectron can be derived from the conservations of energy and momentum

\[ \nu_e = \sqrt{\frac{2(nhv + E_0 - E_i)}{m_e (m_e + m_i)/m_i}} \]  

(4)

where \( n \) stands for the numbers of photon involved in the ionization process, \( hv \) is the photon energy, \( E_0 \) the internal energy of photofragment iodine atom with respect to the ground state I(3 P3/2), \( E_i \) the internal energy of ionic iodine at the \( i \)th level, and \( m_e (m_i) \) the mass of the electron (ion). The lowest energy configuration of atomic iodine is [Kr]5s²5p² which splits into the 3 P3/2 ground state and the 3 P1/2 spin-orbital excited-state at 7603.15 cm⁻¹.¹⁹ The removal of an outer electron produces the [Kr]5s²5p⁶ configuration of I⁺, which yields five levels, 3 P₂, 3 P₁, 3 D₂, and 3 S₀ at 84295.1, 90743.0, 91382.1, 98022.3, and 113796.4 cm⁻¹, respectively, above the neutral ground state 3 P3/2.¹⁹,²² Given those energetics, the dominant peaks in the P(Ve) distributions can be assigned to the final iodine ion levels as indicated. On the other hand, the slow-speed
features, i.e., those <300 km/s, originate from the two-photon ionizations of the parent molecule CH₃I and the spin-orbit excited I(2P½), labeled as I*. The interpretations of those cases, which also confirms that the intermediate levels for peaks 8, 10, 12, and 15 converge to the I(2P½) level are indeed very large, >85% and even up to 98% for peak 12. Obviously, the core-level conserving propensity accounts for the final ion distribution in those cases, which also confirms that the intermediate levels can be well represented by the J, I coupling scheme proposed by Minnhagen.

As to the other three levels converging to I(3P2), however, a rather different behavior (see Table 2) was observed. Although high I(3P2) branching fractions (around 40%) are observed, they also show relatively high I(1D) branching fraction and some populations in I(3P0,1), indicating significant deviation from the simple core-conserving picture. In general, the violation of core-conserving ionization can arise from several factors, including the configuration interaction of the intermediate resonant state with other excited states of different ion cores and the autoionizing resonances in the continuum. From Table 2, the core-changing ionization occurs at the (3P2)4 level, typical branching fractions to the present work are reported. One-photon (2 + 1) REMPI experiments invoke the same intermediate resonant state but from different initial states, so the total ionization energies are different. Identical branching fractions among final ion states from the two studies, therefore, provide a strong support for the negligible autoionization effects on the observed core-changing behaviors.

2. Angular Distribution of Ejected Photoelectrons. The photoelectron angular distribution I(θ), as a function of the angle θ between the laser polarization direction and the direction of the ejected electron k-vector, reflects the detailed photoionization dynamics. It can be expressed by

$$I(\theta) \propto \sum_{k=0}^{k_{\text{max}}} \beta_{2k} P_{2k}(\cos \theta)$$

where $k_{\text{max}} = n + 1$ for a (n + 1) REMPI process, $P_{2k}(\cos \theta)$ are the Legendre polynomials of degree 2k, and $\beta_{2k}$s are the anisotropy coefficients.

Table 3 lists the fitted $\beta$ coefficients, up to the P₀(cos θ) terms, for the present (2 + 1) REMPI process. Two typical angular distributions and fitted results are displayed as polar plots in Figure 4. The others display similar patterns and the analyses are straightforward; thus, they are omitted here (but the $\beta$ coefficients are listed in Table 3). As can be seen from Table 3, in all cases the $\beta$s coefficients are negligibly small. In other words, the photoelectron angular distributions are well characterized by $P_{2}(\cos \theta)$ and $P_{4}(\cos \theta)$ terms only or $k_{\text{max}} = 2$ that is smaller than 3 for a three-photon process, suggesting additional angular momentum constraints. If only one intermediate J-level is involved in the (2 + 1) REMPI process, the $k_{\text{max}}$ will be constrained by the maximum allowed integers of 2 + 1, $J_{\text{mn}}$, or $l_{\text{max}}$, whichever is the smallest, where $l_{\text{max}}$ is the maximum orbital angular momentum of ejected photoelectrons. Since the $J$ values for all seven intermediate levels range from 3/2 to 7/2 (Table 3), the result (2 + 1)-restriction cannot account for the observed $l_{\text{max}} = 2$. Hence, the angular momentum constraint is likely limited by $l_{\text{max}}$. Treating process 1 as a direct one-electron ionization from an intermediate excited state, the character of outgoing electrons from $6p$ states (peak numbers 8, 10, 12, and 15) will be a mixture of s and d partial waves due to the selection rule $\Delta l = \pm 1$, which yields $l_{\text{max}} = 2$. And the observed photoelectron angular distribution reflects the interference pattern of the two partial waves. On the other hand, the ejected electrons will be characterized by the d and g

### Table 2: Product Branching Fractions among Final Ion Levels Resulting from the (2 + 1) REMPI Processes of the Fragment I(3P2) Atom

<table>
<thead>
<tr>
<th>peak #</th>
<th>2hν energy (cm⁻¹)</th>
<th>intermediate state</th>
<th>I(3P2) (%)</th>
<th>I(1D) (%)</th>
<th>I(1S) (%)</th>
<th>I(3P2) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>77308.4</td>
<td>(3P2)f[4]1/2</td>
<td>5.0 ± 1.3</td>
<td>0</td>
<td>57.3 ± 1.9</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>77314.9</td>
<td>(3P2)f[3]1/2</td>
<td>2.3 ± 0.4</td>
<td>0</td>
<td>35.9 ± 2.1</td>
<td>3.0 ± 1.5</td>
</tr>
<tr>
<td>5</td>
<td>77360.6</td>
<td>(3P2)f[2]1/2</td>
<td>5.1 ± 1.0</td>
<td>0</td>
<td>26.6 ± 1.6</td>
<td>3.0 ± 1.5</td>
</tr>
<tr>
<td>8</td>
<td>78416.3</td>
<td>(3P2)f[1]1/2</td>
<td>0.6 ± 0.1</td>
<td>2.3 ± 0.1</td>
<td>84.9 ± 4.6</td>
<td>3.0 ± 1.2</td>
</tr>
<tr>
<td>10</td>
<td>78593.6</td>
<td>(3P2)f[3]1/2</td>
<td>1.1 ± 0.3</td>
<td>0</td>
<td>96.3 ± 5.4</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>12</td>
<td>79004.7</td>
<td>(3P2)f[3]1/2</td>
<td>0</td>
<td>0.4 ± 0.1</td>
<td>98.0 ± 4.3</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>15</td>
<td>80041.0</td>
<td>(3P2)f[2]1/2</td>
<td>1.2 ± 0.2</td>
<td>0</td>
<td>93.2 ± 2.7</td>
<td>4.2 ± 0.3</td>
</tr>
</tbody>
</table>

*The numbers in parentheses for peaks 5, 8, and 10 are from ref 12.
from $P_1$ to $P_2$, the observed autoionization processes must account for the single-ring feature. Since the ion-core changes, the dots are the experimental results for the final ion states $I(P_1)$. Figure 4. Two representative photoelectron angular distributions showing in the polar representation. The laser polarization is vertical. The dots are the experimental results for the final ion states $I(P_1)$. The observation of $k_{\text{max}} = 2$ for those peaks suggests that the outgoing electrons via the $d$ intermediate state could be dominated by the $d$-wave character.

**C. Autoionization Following Two-Photon Excitation of I ($P_{12}$).** Photoelectron Images. As seen from Table 1, two-photon excitation of the spin–orbit excited state $I(P_{12})$ leads to autoionizing Rydberg series converging to the $P_1$ state of $I$. In contrast to the above $(2 + 1)$ REMPI of $I(P_{32})$, the photoelectron images here, shown in Figure 5, are all characterized by a predominant single-ring feature. Those autoionizing states lie from 84 393 cm$^{-1}$ to 88 676 cm$^{-1}$ above the neutral ground state $I(P_{32})$. The IP of the I-atom is 84 312 cm$^{-1}$; thus, $P_1$ is the only energetically accessible final state, which accounts for the single-ring feature. Since the ion-core changes from $P_1$ to $P_3$, the observed autoionization processes must invoke the spin–orbit couplings of the $(P_1)$ states with the $P_3$ continuum.

**2. Autoionizing Dynamics.** Since only the ion ground state $I(P_2)$ is energetically accessible, much of information on autoionization dynamics can only be retrieved from the photoelectron angular distribution. Listed in Table 4 are the Legendre coefficients $\beta_i$ obtained by the least-squares fits to observed distributions, and the corresponding angular distributions and the fits are shown as the polar representations in Figure 6. In contrast to the $(2 + 1)$ REMPI process (Figure 4), a rich variety of angular distributions are noted. In general, for excitation of $I(P_{12})$ to an autoionizing state, $k_{\text{max}}$ is equal to 2 due to the total number of photons involved in the process. From Table 4, $\beta_2$ ranges from $-0.45$ to $0.72$, and $\beta_4$ is either close to zero or negative. Since the $I(P_{12})$ initial state is of spherical symmetry, a finite value of $\beta_4$ coefficients may reflect the alignment induced by two-photon absorption or from autoionization processes. Despite the observed perplexing distributions, a closer inspection of their general patterns reveals an interesting systematic. There are two types of general patterns: one type features distinct four-lobes along the diagonal directions, such as peaks 1, 2, 7, 13, 14, 19, 20, and 21, and the other is characterized by a near zero $\beta_4$ coefficient, thus showing either a pair of lobes (e.g., peaks 11, 16, and 17) or an oval shape (peaks 6, 9, and 18). Examining the assignments listed in Table 4 indicates that all $f$-type autoionizing states belong to the $P_1$ state. The only two exceptions are peaks 7 and 21, which are assigned to the $p$-series yet exhibit four-lobes features. It is particularly interesting to note that the four-lobe pattern of the peak 21 is of the most distinct among all of this work.

To comprehend the observed intriguing angular distributions will undoubtedly required high-level theoretical studies in the future. Nonetheless, it is instructive to use a simple model to gain some qualitative insights into the main observations. As aforementioned, the autoionization processes reported here must invoke the spin–orbit couplings of the $(P_1)$-core Rydberg states to the $P_2$ ion-continuum. Physically, it can arise from either the spin-flip in the core to release the Rydberg electron or the ejection of the core electron. Assuming that the interaction matrix for autoionization is of the Coulomb repulsive form:

$$V = \langle \Psi_{\text{f}} |e^2/r_{jl}| \Psi_{\text{init}} \rangle$$

where $\Psi_{\text{init}}$ is the total wave function of the superexcited Rydberg state and $\Psi_{\text{f}}$ the corresponding total wave function of the final ion state and the continuum electron. Treating it as a two-electron problem, for simplicity, only one term ($1r_{12}$) is involved, which can be expanded as a sum over the spherical harmonics:

$$\frac{1}{r_{12}} = \sum_{m=0}^{\infty} r_{12}^m Y_{lm}(r_1)Y_{l-m}(r_2)$$

and $r_{12}^m$ ($r_{12}^{m+1}$) is for the core (Rydberg) electron.

The total wave functions can be expressed as products of core functions and outer electron functions:

$$\Psi_{\text{n}} = \psi_{\text{core}} \psi_{\text{R}}$$

with $\psi_{\text{core}}$ denoting the $P_1$-core; thus, $f = 1$ and

$$\Psi_{\text{f}} = \psi_{\text{f}}$$

with $\psi_{\text{f}}$ denoting the $P_2$ ion-continuum and $j = 2$.

**TABLE 3: Legendre Weighting Coefficients $\beta_k$ of Photoelectron Angular Distributions for the $(2 + 1)$ REMPI Processes of the Ground State $I(2P_{3/2})$.**

<table>
<thead>
<tr>
<th>peak #</th>
<th>intermediate state</th>
<th>$P_2$</th>
<th>$P_1$</th>
<th>$P_3$</th>
</tr>
</thead>
</table>
| 3      | ($)P_{3/2}$+l$(| $\beta_2$ | $\beta_4$ | $\beta_6$ | $\beta_2$ | $\beta_4$ | $\beta_6$ | $\beta_2$ | $\beta_4$ | $\beta_6$
| 4      | ($)P_{3/2}$+l$(| $0.80$ | $0.38$ | $0.03$ | $0.82$ | $0.24$ | $0.07$ | $0.88$ | $0.57$ | $0.17$
| 5      | ($)P_{3/2}$+l$(| $0.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 6      | ($)P_{3/2}$+l$(| $0.80$ | $0.38$ | $0.03$ | $0.82$ | $0.24$ | $0.07$ | $0.88$ | $0.57$ | $0.17$
| 7      | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 8      | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 9      | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 10     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 11     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 12     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 13     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 14     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 15     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 16     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 17     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$
| 18     | ($)P_{3/2}$+l$(| $1.00$ | $-0.20$ | $0.03$ | $1.15$ | $(0.20)$ | $0.07$ | $1.23$ | $0.30$ | $-0.14$

* The numbers in parentheses for peaks 5, 8, and 10 are from ref 12.
In the expansion of $1/r_{12}$, only three terms can couple $j = 1$ and 2, and they involve $l = 1, 2,$ or 3. Since the parity of the initial and final total wave functions, $\Psi_i$ and $\Psi_f$, should be the same (conservation of parity), the matrix elements invoke $l = 1$ and 3 (odd parity) must vanish. Hence, only the $l = 2$ term is at work, or

$$\frac{1}{r_{12}} = \frac{r_2^2}{r_>} Y_{2m}(r_1) Y_{2-m}(r_2)$$

(10)

And, eq 6 becomes

| Table 4: Legendre Weighting Coefficients $\beta_{2k}$ of Photoelectron Angular Distributions for Two-Photon Autoionizing Resonant Transitions from the Spin–Orbit Excited State $^1\text{P}(\text{I}_2)$

| Peak # | Total Energy (cm$^{-1}$) | Autoionization State | Legendre Coefficients $^a$
|--------|--------------------------|----------------------|-------------------------|
| 1      | 84393.45 $(^3\text{P})[2]_{2/2}$ | 0.28 ± 0.10 −0.52 ± 0.05 | $\beta_2$, $\beta_4$
| 2      | 84477.25 $(^3\text{P})[3]_{2/2}$ | 0.62 ± 0.06 −0.31 ± 0.06 |
| 3      | 85805.45 $(^3\text{P})[2]_{3/2}$ | −0.21 ± 0.03 0.08 ± 0.06 |
| 4      | 85914.25 $(^3\text{P})[1]_{1/2}$ | −0.28 ± 0.03 −0.32 ± 0.05 |
| 5      | 86031.95 $(^3\text{P})[2]_{3/2}$ | 0.17 ± 0.03 0.07 ± 0.03 |
| 6      | 86296.35 $(^3\text{P})[2]_{3/2}$ | 0.67 ± 0.03 −0.16 ± 0.05 |
| 7      | 86918.95 $(^3\text{P})[2]_{3/2}$ | 0.21 ± 0.04 −0.47 ± 0.03 |
| 8      | 86961.65 $(^3\text{P})[3]_{3/2}$ | 0.56 ± 0.04 −0.39 ± 0.03 |
| 9      | 87563.65 $(^3\text{P})[2]_{3/2}$ | 0.59 ± 0.06 −0.23 ± 0.05 |
| 10     | 87725.25 $(^3\text{P})[1]_{1/2}$ | −0.45 ± 0.03 0.06 ± 0.05 |
| 11     | 87784.05 $(^3\text{P})[1]_{1/2}$ | 0.15 ± 0.04 0.12 ± 0.03 |
| 12     | 88289.35 $(^3\text{P})[2]_{3/2}$ | 0.18 ± 0.05 −0.39 ± 0.04 |
| 13     | 88710.90 $(^3\text{P})[3]_{3/2}$ | 0.60 ± 0.04 −0.31 ± 0.04 |
| 14     | 88765.55 $(^3\text{P})[2]_{3/2}$ | 0.37 ± 0.03 −0.75 ± 0.06 |

$^a$ The final ion state is $^1\text{P}(\text{I}_2)$ for all peaks. $^b$ The uncertainty given here is ± one standard deviation from independent fittings of the four quadrants (see text for details).
The ejection of an autoionization electron is mediated by the Coulombic interaction between the Rydberg electron and core electrons. Within the two-electron approximation, it can be shown that the angular part of this electron interaction involves a sum of Gaunt integrals as

\[ \sum_{m=-l}^{l} (-1)^m \langle \psi_{lmn}| \psi_{lm'}| \psi_{lm''} \rangle \]

where the index \( m \) stands for the magnetic quantum number of the corresponding electron orbital angular momentum \( l \). The Gaunt integral can be expressed in terms of 3-f symbols

\[ (-1)^l \left( \frac{(2l_x + 1)(2l_y + 1)(2l_z + 1)}{4\pi} \right)^{1/2} \left( \frac{l_x}{m'} \frac{l_y}{m} \frac{l_z}{m''} \right) \sum_{j} \left( \begin{array}{ccc} l & l_x & l_z \\ m & m' & m'' \end{array} \right) \]

Thus, the Gaunt integral will be nonzero only under the following three conditions:

\[ |l_R + l_e| \geq l \geq |l_R - l_e| \]
\[ l_R + l_e + l = \text{even} \]
\[ m_R + m_e = m \]

As shown above, \( l = 2 \); hence, eq 14 leads to the propensity rule of \( \Delta l = 0, \pm 2 \) for autoionizing electrons. In the other words, for the \( p \)-like Rydberg states, \( l_R = 1 \); the allowed outgoing waves will be of the \( p \) and \( f \)-types. As to the \( f \)-like Rydberg states, \( l_R = 3 \), the dominant autoionizing electrons, are likely the \( p \) and \( f \)-waves again, though the contribution from the \( h \)-wave may not be neglected.

Examine the photoelectron angular distributions, as listed in Table 4 and shown in Figure 6, all six \( f \)-like autoionizing states display a “butterfly” shape, or a positive \( \beta_f \) with a sizable negative \( \beta_l \) value. The remaining eight \( p \)-series autoionizing states, except peaks 7 and 21, are characterized by near zero \( \beta_l \) values. For both cases, the dominance of the usual autoionization propensity \( \Delta l = 0 \) prevails, namely, \( l \)-unchanging Rydberg-continuum transitions are distinctly more probable than \( l \)-changing autoionization processes. The observed variations in shapes could be attributed to different contributions from the two outgoing waves and their interferences, as well as the possible alignments effects. As to peaks 7 and 21, either the spectroscopic assignments to predominant \( p \)-type Rydberg states are in question or the autoionization processes involve different mechanisms or couplings from the other \( p \)-series states to yield characteristic \( f \)-like outgoing electron waves. The above considerations are, of course, based on a single configuration in the \( J/J \) coupling scheme. This assumption is expected to hold reasonably well for the \( ^1P \) core configuration of the Rydberg state. On the other hand, the final ion state \(^2P_2\) might carry non-negligible \(^1D_2\) characters from configuration interactions, complicating the above simple arguments. Further theoretical studies are needed for a full account.

IV. Conclusions

A detailed study of the photoionization dynamics of the iodine atom was undertaken using photoelectron imaging technique. Two types of photoionization processes were identified and dynamics elucidated. For a \((2 + 1)\) REMPI process, the ionization dynamics can be viewed, to a good approximation, as one-electron ejection process from the intermediate excited state, provided that the ion-core configuration is properly accounted for. On the other hand, the photoelectron angular distributions from autoionizing states exhibit rich and remarkable variations. A simple model is proposed to lay the foundation for a qualitative, physical insight into the main observations. Much more theoretical studies will be needed for deeper understandings of autoionizing electron angular distributions.

Acknowledgment. National Science Council of Taiwan supported this work under NSC 95-2119-M-001-002. We are indebted to Dr. C. Chang for the help in the initial phase of this project.

References and Notes


