The photoelectron spectra obtained following two-photon resonant, three-photon ionization of atomic iodine via a number of Rydberg states are presented. Photoelectron spectra obtained via the \( (^3P_2)np \) levels and via the \( (^3P_0)4f \) level demonstrate the production of state-selected \( 1^+ \) \( ^3P_2 \) and \( ^3P_0 \) ions, respectively, with \( \sim 85\% \) efficiency. Photoelectron spectra obtained via the \( (^3P_2)nf \) level show the effect of a perturbation by the \( (^3P_0)4f \) level, as both \( 1^+ \) \( ^3P_2 \) and \( ^3P_0 \) ions are observed. The relative magnitudes of the \( ^3P_2 \) and \( ^3P_0 \) photoelectron peaks are shown to be strongly dependent on the relative magnitudes of the \( (^3P_2)nf \) and \( (^3P_0)4f \) photoionization matrix elements. Two additional processes are observed in the photoelectron spectra. These correspond to fluorescence of the resonant intermediate level to lower-lying levels, followed by ionization of those levels, and to energy transfer from \( 1^+ \) \( ^3P_1/2 \) atoms to Rydberg atoms, resulting in ionization of the latter.

I. INTRODUCTION

Recent studies using resonantly enhanced multiphoton ionization—photoelectron spectroscopy (REMPI-PES) have shown that ionization into a structureless continuum via an unperturbed Rydberg state usually proceeds by the ejection of the Rydberg electron without a change in the electronic or vibrational state of the ion core. Thus, in many instances REMPI can be used as source of state-selected ions. However, the results can be quite different if the resonant intermediate level is perturbed, because the character of the unperturbed level will then be mixed with that of the perturbing level. If the two interacting levels have different ion cores, the perturbation is revealed in the photoelectron branching ratios following REMPI. Studies of perturbations using REMPI-PES have been reported for a number of atomic and molecular systems. In the present study, REMPI-PES is used to study a perturbation in the odd parity Rydberg series of atomic iodine and to determine the feasibility of producing state-selected \( 1^+ \) ions using REMPI. It is shown that, while state-selected ions can be produced in some cases, the state selecting capability of REMPI is dramatically reduced for perturbed levels, even when the perturbation is at the 2% level.

The \( np \) and \( nf \) Rydberg series converging to the \( ^3P_2 \) ground state of \( 1^+ \) have been investigated recently using two-photon resonant, three-photon ionization. Between 82.650 cm\(^{-1}\) and the \( ^3P_2 \) ionization threshold at 84.295.1 cm\(^{-1}\), the \( (^3P_2)np \) and \( (^3P_2)nf \) multiplets are relatively unperturbed; the only interfering level is based on the \( (^3P_0)4f \) configuration, where \( ^3P_0 \) is the first excited state of \( 1^+ \). This interloper causes perceptible shifts in the energies of only two \( (^3P_2)nf \) levels. This perturbation is now examined using REMPI-PES, which provides an alternative technique to determine the influence of the perturbation on neighboring levels. As in a number of earlier studies, atomic iodine is produced in both the \( ^2P_{3/2} \) ground state and in the \( ^2P_{1/2} \) excited state (7603.15 cm\(^{-1}\)) by photodissociation of methyl iodide. In the present work, the high-lying \( (^3P_2)np \) and \( (^3P_2)nf \) levels are accessed by two-photon transitions from the \( ^2P_{1/2} \) level rather than from the \( ^2P_{3/2} \) ground state.

In the absence of an interaction between the \( (^3P_0)4f \) level and the \( (^3P_2)nf \) levels, single-photon ionization of the \( (^3P_2)nf \) levels is expected to produce \( 1^+ \) \( ^3P_2 \), while single-photon ionization of the \( (^3P_0)4f \) level is expected to produce \( 1^+ \) \( ^3P_0 \). In the presence of an interaction, the wave function of the perturbed level becomes

\[
c^1\psi((^3P_2)nf) + c_2\psi((^3P_0)4f) \]

If it is assumed as a first approximation that the only nonzero photoionization matrix elements are

\[
\langle \psi((^3P_2)nf) | \mu \cdot E | \psi((^3P_2)1^+) + \epsilon l \rangle \]

and

\[
\langle \psi((^3P_0)4f) | \mu \cdot E | \psi((^3P_0)1^+) + \epsilon l \rangle ,
\]

then the photoelectron branching ratios are determined by

\[
c_1^2 | \langle \psi((^3P_2)nf) | \mu \cdot E | \psi((^3P_2)1^+) + \epsilon l \rangle |^2 + c_2^2 | \langle \psi((^3P_0)4f) | \mu \cdot E | \psi((^3P_0)1^+) + \epsilon l \rangle |^2 .
\]

Here, | \psi((^3P_0)1^+) + \epsilon l \rangle is the final state wave function of the electron-ion system and is assumed to contain contributions from all of the allowed partial waves. In this approximation, the photoelectron spectrum contains two peaks, with the branching ratios determined by the coefficients \( c_1 \) and \( c_2 \), and by the relative magnitudes of the matrix elements (1) and (2). As will be seen below, if matrix element (2) is significantly larger than matrix element (1), the effect of the perturbation on the photoelectron spectrum can be quite large, even if the coefficient \( c_2 \) is small.
II. EXPERIMENTAL

The apparatus has been described in detail in a previous publication.\textsuperscript{15} Briefly, it consists of a pulsed Nd:YAG (yttrium aluminum garnet) pumped dye laser, a time-of-flight mass spectrometer, and an electrostatic electron energy analyzer. The dye laser is of the modified Littman design described by Mahon and Tomkins.\textsuperscript{16} The laser beam was frequency doubled in a potassium dihydrogen phosphate (KDP) crystal using a commercial autotracking unit (INRAD 5—12). Approximately 50—100 μJ of the frequency doubled output was separated from the fundamental using dichroic mirrors and focused into the ionization region using a 125 mm lens. Methyl iodide was introduced into the ionization region via an effusive jet. In the present experiments, the background pressure in the chamber was approximately 5×10⁻⁶ Torr, with an estimated 10—100 times higher pressure in the laser focus. As in the earlier study,\textsuperscript{11} a single laser was used to photodissociate the methyl iodide and to resonantly ionize the atomic iodine fragment.

The experiments were performed in two steps. First, the REMPI spectrum was recorded in the region of interest by monitoring the I⁺ ion signal as the laser wavelength was scanned. The laser wavelength was then tuned to the feature of interest and the photoelectron spectrum was recorded. Unless it is stated otherwise, the polarization axis of the laser beam was parallel to the detection axis of the electron spectrometer. This was achieved by purifying the linear polarization of the frequency doubled beam with a Glan prism and rotating the polarization to the desired angle using a double Fresnel rhomb. The photoelectron spectra were corrected for the transmission function of the electron spectrometer in the manner described previously.\textsuperscript{15}

III. RESULTS AND DISCUSSION

A. General considerations

An energy level diagram of some of the atomic iodine states of interest is shown in Fig. 1.\textsuperscript{11,17} The lowest ener-
gy configuration of atomic iodine is \ldots 5s^25p^5, which produces the \(^5P_{3/2}\) ground state and the \(^5P_{1/2}\) state at 7603.15 cm\(^{-1}\) (Ref. 16). The removal of an outer electron produces the \ldots 5s^25p^4 configuration of \(^1P^+\), which yields five levels, \(^3P_2,\ ^3P_0,\ ^3P_1,\ ^1D_2,\) and \(^1S_0\) at 84295.1, 90743.0, 91382.1, 98022.3 and 113796.4 cm\(^{-1}\), respectively.\(^{17,18}\) The Rydberg states of atomic iodine are best described in \(J\ell\) coupling (also known as \(J\ell\,K\) coupling).\(^{17}\)

In this coupling scheme,\(^{19}\) the total angular momentum of the ion core, \(J_e\), is coupled to the orbital angular momentum, \(\ell\), to give \(K\). The spin of the Rydberg electron, \(s\), is then coupled to \(K\) to give the total angular momentum, \(J\). Specifying the ion core, the levels are then labeled, for example, \((\ell\ell\ell)\ell\{K\}J\). The present study is concerned with two-photon transitions from the \(^2P_{1/2}\) level to the \(^3P_2\)\(np\) and \(^3P_2\)\(nf\) Rydberg levels. Five electric dipole allowed two-photon transitions arise for both the \(np\) and \(nf\) configurations, with upper levels corresponding to \((\ell\ell\ell)\ell\{K\}J\), \((\ell\ell\ell)\ell\{K\}J\) and \((\ell\ell\ell)\ell\{K\}J\), \((\ell\ell\ell)\ell\{K\}J\) and \((\ell\ell\ell)\ell\{K\}J\). The allowed levels are shown for \((\ell\ell\ell)\ell\{K\}J\) in Fig. 1. The single allowed interloper in the energy region of interest corresponds to \((\ell\ell\ell)\ell\{K\}J\), and lies between the \((\ell\ell\ell)\ell\{K\}J\) and \((\ell\ell\ell)\ell\{K\}J\) multiplets. As discussed previously,\(^{11}\) the interloper interacts most strongly with the \((\ell\ell\ell)\ell\{K\}J\) levels, and appears to interact negligibly with the other \(J=\frac{1}{2}\) levels.

The determination of quantitative information about the mixing coefficients and photoionization matrix elements in Eq. (3) from the REMPI-photoelectron spectra requires a determination of the true photoelectron branching ratios. However, the photoelectron peak heights at a given angle between the polarization axis and the detector axis do not necessarily reflect these branching ratios, as different photoelectron peaks may have different angular distributions. In single-photon studies of unaligned samples, this can be overcome by recording the spectra at the magic angle, where the peak intensities are proportional to the branching ratios.\(^{20}\) Unfortunately, for multiphoton studies it generally not possible to find such a magic angle, and it is necessary to determine the complete angular distributions in order to determine the true branching ratios.\(^{21}\) In principle it is possible to determine the photoelectron angular distributions for each of the processes of interest, in order to obtain quantitative information about the perturbation and its effect on the photoelectron branching ratios. However, in the present experiments, the photoelectron spectra at a single angle are sufficient to give a qualitative understanding of the perturbation, and to demonstrate the feasibility of using REMPI to produce state-selected \(^1P^+\) ions.

The mass analyzed REMPI spectrum in the energy region of the present study has been discussed in detail previously,\(^{14}\) and will not be discussed here. In the next subsection, the REMPI-PES of the unperturbed \(^3P_2\)\(np\) and \(^3P_2\)\(nf\) levels is presented, followed by a discussion in Sec. III C of the REMPI-PES via the \(^3P_2\)\(nf\) and \(^3P_2\)\(nf\) levels.

B. REMPI-PES via the \(^3P_2\)\(np\) levels

The \(^3P_2\)\(np\) levels between 82650 cm\(^{-1}\) and the \(^3P_2\) ionization threshold are not visibly perturbed by any interlopers, and REMPI via these levels is expected to produce a relatively pure population of \(^1P^+\) \(^3P_2\) ions. Although, as was discussed above, it is not generally possible to find a magic angle for multiphoton processes, the \(J=\frac{1}{2}\) levels represent a special case for which a magic angle does exist. Because the methyl iodide is photodissociated with linearly polarized light and the atomic iodine is excited with the same, the excited state atoms can be aligned, but not oriented.\(^{22}\) In other words, levels with different values of \(|M_J|\) can be populated unequally, but levels with the same value of \(|M_J|\) must be populated equally. For the case of \(J=\frac{1}{2}\), the only values for \(M_J\) are \(M_J=\pm\frac{1}{2}\), and these levels must be equally populated. Thus, since ionization of the \(^3P_2\)\(np\) levels requires only a single photon, the angular distribution will be the same as that for single-photon ionization of an unaligned sample. The magic angle\(^{20}\) occurs at \(\theta=54.7^\circ\), where \(\theta\) is the angle between the polarization axis and the detection axis, and the relative photoelectron peak intensities recorded at the magic angle reflect the true branching ratios.

The REMPI photoelectron spectra of atomic iodine via the \(^3P_2\)\(13p\) and \(^3P_2\)\(18p\) levels were recorded at \(\theta=54.7^\circ\) and are shown in Fig. 2. As expected for unperturbed levels, the two spectra are nearly identical, and

![FIG. 2. The photoelectron spectra of atomic iodine obtained following two-photon resonant, three-photon ionization via the \(^3P_2\)\(18p\) and \(^3P_2\)\(13p\) levels.](image-url)
approximately 82—85% of the ions are left in the $^3P_2$ state. The $^1P_1$ and $^1D_2$ peaks are quite weak, and the $^1S_0$ and $^3P_0$ peaks are not observed. The small $^1D_2$ and $^3P_1$ peaks could be due to a weak interaction of the $np$ levels with other levels, or to effects in the ionization continuum. Single-photon ionization of the $13p$ and $18p$ levels gives a total energy (3hv + 7603.15 cm$^{-1}$) for the system of 120831.6 and 121861.4 cm$^{-1}$, respectively. In both cases this is well above the $^1S_0$ ionization threshold, and in a region where the single-photon ionization spectrum of ground state iodine is constant.\textsuperscript{23} Single-photon excitation from the $^2P_3/2$ ground state will access the same parity states as single-photon excitation from the $(^3P_1)np[3/2]$ levels, and, in addition, can access all of the same $J$ levels. The absence of structure in the single-photon spectrum between 120 800 and 121 900 cm$^{-1}$ indicates that the $^1D_2$ and $^3P_1$ photoelectron peaks in the spectra of Fig. 2 are not due to effects at the three-photon energy. Configuration interaction of the resonant intermediate level with other levels thus appears to be the source of the $^1D_2$ and $^3P_1$ peaks. The nearest levels\textsuperscript{17} with $^1D_2$ or $^3P_1$ ion cores and $J = 3/2$ are 400—1200 cm$^{-1}$ from the $(^3P_1)13p[1/2]$ and $(^3P_1)18[1/2]$ levels, and the interaction is expected to be quite weak. However, from Eq. (3) it is clear that even if the mixing coefficients are small, the photoelectron peak intensities also depend on the photoionization matrix elements, which may favor the production of $^1D_2$ or $^3P_1$. That this is possible is shown more clearly in the next subsection.

The photoelectron spectra of Fig. 2 show no signs of photoelectron peaks arising from the nonresonant ionization of methyl iodide, methyl radical, or any other species. Thus, the selectivity of REMPI allows the ionization of only the species of interest, and the photoelectron spectra are recorded without interference from other species. In addition, as a complement to HeI photoelectron spectroscopy of atomic iodine,\textsuperscript{24} REMPI allows one to choose a resonant intermediate level with the electronic character of interest and to selectively enhance or diminish a particular photoelectron peak.

C. REMPI-PES via the $(^3P_1)nf[3/2]$ and $(^3P_0)4f[3/2]$ levels

The photoelectron spectra obtained following REMPI via the $(^3P_0)4f[3/2]$, $(^3P_2)15f[3/2]$, $(^3P_2)14f[3/2]$, and $(^3P_2)11f[3/2]$ levels are shown in Fig. 3. The most striking features of these spectra are the complete dominance of the $^3P_0$ photoelectron peak in the $(^3P_2)15f[3/2]$ spectrum, and the similarity of this spectrum with the $(^3P_0)4f[3/2]$ spectrum. The $^3P_0$ peak is also reasonably strong in the $(^3P_2)14f[3/2]$ spectrum. As is expected for ionization via an unperturbed level, the $^3P_2$ peak is by far the largest in the $(^3P_2)11f[3/2]$ spectrum, and the $^3P_0$ peak is quite small. It should also be noted that the photoelectron spectrum obtained via the unperturbed (and unresolved) $(^3P_2)15f[2]$, $3f$, $5f$ levels shows no evidence of the $^3P_0$ peak. A number of additional features are observed in the spectra of Fig. 1 that cannot be assigned to direct photoionization of the resonant intermediate level into one of the five lowest-lying ionization continua.

These peaks will be discussed in more detail below. In order to understand the complete dominance of the $^3P_0$ peak in the $(^3P_2)15f[3/2]$ spectrum, it is necessary to determine the coefficients $c_1$ and $c_2$ in Eq. (3) above. Because the $(^3P_0)4f[3/2]$ level is the only observed member of the $nf$ series converging to the $^3P_0$ ionization limit, there is not enough information available to do a complete analysis using multichannel quantum defect theory. However, the coefficients can be obtained from the energy level shifts of the $(^3P_2)15f[3/2]$ and $(^3P_0)4f[3/2]$ levels. As a first approximation, it is assumed that only these two levels interact, which is reasonable as the energy level
shift of the \( ^3P_2 \) \( 14f[3]_{5/2} \) level is much smaller than that of the \( 15f \) level. The two-level interaction is treated in the usual manner.\(^{25}\) The deperturbed position of the \( 15f \) level \((E_1)\) is obtained by using the quantum defect of the unperturbed members of the same Rydberg series. This gives an effective principal quantum number \( n^* = 14.952 \), from which one obtains \( E_1 = 83804.2 \text{ cm}^{-1} \), as opposed to the observed energy, \( E_2 = 83809.3 \text{ cm}^{-1} \). In this approximation, the shift of the \( ^3P_0 4f[3]_{5/2} \) level must have the same magnitude, but opposite sign, yielding a deperturbed energy \( E_3 = 83791.2 \text{ cm}^{-1} \) from the observed energy \( E_b = 83786.1 \text{ cm}^{-1} \). Using the standard formulas,\(^{25}\) one obtains an interaction matrix element \( W_{12} = 9.6 \text{ cm}^{-1} \) and wave functions for the observed levels in terms of the deperturbed wave functions:

\[
\psi_a[(^3P_2)15f[3]_{5/2}] = 0.88 \psi[(^3P_2)15f[3]_{5/2}]
\]

\[
-0.47 \psi[0(^3P_0)4f[3]_{5/2}],
\]

\[
\psi_b[(^3P_0)4f[3]_{5/2}] = 0.47 \psi[(^3P_2)15f[3]_{5/2}]
\]

\[
+ 0.88 \psi[(^3P_0)4f[3]_{5/2}].
\]

Using Eq. (3), one then finds that the \( (^3P_2)15f[3]_{5/2} \) spectrum should show \( 22\% \) \( ^3P_0 \) character and \( 78\% \) \( ^3P_2 \) character. Thus, the large intensity of the \( ^3P_0 \) peak must be the result of a much larger value for the \( ^3P_0 4f \) photoionization matrix element than for the \( ^3P_2 15f \) matrix element (at least at \( \theta = 0^\circ \)). A similar calculation indicates that the \( ^3P_2 14f[3]_{5/2} \) photoelectron spectrum should contain approximately \( 2\% \) \( ^3P_0 \) character, leading to the same conclusion regarding the relative magnitudes of the photoionization matrix elements.

In the discussion above, the photoionizing transition from the Rydberg level has been treated as a single-electron transition, with no involvement of the ion core. Because the quantum defects of the \( n^f \) series are nearly zero, it is not unreasonable to expect that the photoionization matrix elements will have behavior similar to hydrogenic matrix elements, again in the single independent electron model. The latter are always a maximum at threshold and decrease monotonically with increasing energy above threshold.\(^{26}\) In addition, for a given Rydberg series the cross section at threshold increases with increasing \( n \), and the cross section falls faster with increasing energy above threshold, as most of the oscillator strength is concentrated in an energy region corresponding to a few times the binding energy of the Rydberg electron.\(^{26}\) In the present example, the \( ^3P_2 15f[3]_{5/2} \) level is only 485.8 \text{ cm}^{-1} \) from the \( ^3P_2 \) limit,\(^{11}\) and the photon energy is approximately 78 times the binding energy, at which point the photoionization matrix element should be quite small. The \( ^3P_0 4f[3]_{5/2} \) level is 6956.9 \text{ cm}^{-1} \) from the \( ^3P_0 \) limit, and in this case the photon energy is approximately only 5.5 times the binding energy. Therefore, it is completely reasonable that the \( ^3P_0 4f[3]_{5/2} \) matrix element in Eq. (3) is significantly larger than the \( ^3P_2 15f[3]_{5/2} \) matrix element, providing an explanation for the intense \( ^3P_2 \) photoelectron peak in the \( ^3P_2 15f[3]_{5/2} \) spectrum. A similar argument applies to the \( ^3P_2 14f[3]_{5/2} \) spectrum.

As was mentioned above, the spectra of Fig. 3 display a number of features that cannot be assigned to simple REMPI of atomic iodine. These features occur in two energy regions. Between 2.4 and 2.8 eV, one or two small photoelectron peaks are observed in all four spectra of Fig. 3. A second feature consisting of a single peak is observed between approximately 0.8 and 0.9 eV in the \( ^3P_2 14f[3]_{5/2} \) and \( ^3P_0 11f[3]_{5/2} \) spectra. An extremely weak peak can also be observed in the \( ^3P_2 11f[3]_{5/2} \) spectrum and in the \( ^3P_0 13p[1]_{1/2} \) spectrum of Fig. 2. The first possible explanation for these photoelectron peaks is that they are due to ionization of impurities in the sample or of the other species in the laser focus, i.e., CH\(_3\)I and CH\(_3\) radicals. This explanation is ruled out for two reasons. First, the peaks completely disappear if the laser is turned off the sharp atomic iodine resonance. It seems unlikely that the ionization of an impurity would have structure as sharp as that of atomic iodine and at exactly the same energies. Second, the structure persists even when ethyl iodide (CH\(_3\)CH\(_2\)I) or molecular iodine is used as the atomic iodide precursor. This indicates that the two-photon excitation of atomic iodine is an essential step in the production of these photoelectron peaks, and rules out the possibility that the structures are due to an impurity.

In a recent REMPI-PES study of methyl iodide, Chupka et al.\(^{25}\) present evidence for photodetachment of transient CH\(_3\)I\(^-\) and I\(^-\) ions that are formed by attachment of slow photoelectrons produced by REMPI of neutral CH\(_3\)I. This process gives rise to a new, fast photoelectron peak.\(^{27}\) The new peak is only observed with fairly high laser powers, at which the electron spectrometer resolution is significantly degraded by the Coulomb broadening that arises from high ionization rates.\(^{27}\) This type of process can be ruled out in the present studies for three reasons: (1) the laser power is quite low, (2) the photoelectron peaks are sharp and the electron spectrometer resolution is not observably degraded by Coulomb broadening, and (3) the observed photoelectron peaks do not occur at the correct energy for photodetachment of CH\(_3\)I\(^-\) (Ref. 28), I\(^-\) (Ref. 29), or CH\(_3\)I.\(^{30}\)

In fact, the two groups of photoelectron peaks in the present spectra arise from two different processes. The first group of photoelectron peaks, observed between 2.4 and 2.8 eV, arise from excitation of atomic iodine to the resonant intermediate level, which then fluoresces to lower-lying \( nd \) levels, which, in turn, are ionized by a single photon. For example, the photoelectron peak at 2.608 eV in the \( ^3P_0 4f[3]_{5/2} \) spectrum can be assigned to the process:

\[
1^+(^3P_0)4f[3]_{5/2} \rightarrow 1^+(^3P_0)5d[2]_{3/2,5/2} \rightarrow 1^+P_0 + e^-.
\]

The same process is observed at 2.608 eV in the \( ^3P_2 15f[3]_{5/2} \) spectrum due to the admixture of \( ^3P_0 4f[3]_{5/2} \) character in the \( ^3P_2 15f[3]_{5/2} \) wave function. The peak at 2.519 eV in the \( ^3P_0 4f[3]_{5/2} \) spectrum (2.525 eV in the \( ^3P_2 15f[3]_{5/2} \) spectrum) cannot be assigned, in the context of the above process, to any \( nd \) level, and all of the \( ng \) levels are at higher energy. However, the photoelectron peak is at the energy expected for ionization of the \( ^3P_0 5d[2]_{3/2,5/2} \) levels into the \( ^3P_1 \) continuum.\(^{17}\) The \( ^3P_1 \) continuum may obtain its strength...
through configuration mixing between the \((^3P_0)5d\) and \((^3P_1)5d\) levels. The peaks at approximately 2.467 and 2.608 eV in the \((^3P_2)14f[^3]3/2\) spectrum and 2.451 and 2.481 eV in the \((^3P_2)11f[^3]3/2\) spectrum must be assigned to fluorescence to a different set of levels. In this case, the photoelectron peaks occur at the energies expected for the processes\(^7\)

\[ \text{I}^*(^3P_2)\pi2[^3J3/2] \rightarrow \text{I}^*(^3P_2)5d[^3J3/2] \rightarrow \text{I}^*+^3P_2 + e^- \]  
(lower energy peak)

and

\[ \text{I}^*(^3P_2)\pi2[^3J3/2] \rightarrow \text{I}^*(^3P_2)5d[^1J1/2] \rightarrow \text{I}^*+^3P_2 + e^- \]  
(higher energy peak).

Although it may first seem surprising that fluorescence competes with ionization on the time scale of a 5—10 nsec laser pulse, two-photon laser-induced fluorescence of lower-lying levels of atomic iodine has been observed in a number of studies,\(^12,13\) under conditions similar to those employed here. In addition, Ties et al.\(^14\) have actually studied the competition between ionization and fluorescence for a number of levels. It was noted above that the ionization cross section for high-lying levels with the ultraviolet photons of the present study would be quite small. This would tend to increase the probability that fluorescence could compete with ionization. Using the same arguments, the photoionization cross sections for the low-lying \((^3P_2)5d\) and \((^3P_0)5d\) levels should be correspondingly larger, thus enhancing the probability for observation of this process in the photoelectron spectrum.

The single peak that appears at 0.870 eV in the \((^3P_2)14f[^3]3/2\) photoelectron spectrum and at 0.876 in the \((^3P_2)11f[^3]3/2\) spectrum cannot be assigned to fluorescence to and subsequent ionization of any known level of atomic iodine,\(^17\) and must therefore arise from another process. The photon energies necessary to ionize iodine in the \((^3P_2)14f[^3]3/2\) and \((^3P_2)11f[^3]3/2\) levels into the \(^3P_2\) continuum and to produce photoelectrons with the observed kinetic energies are 0.940 and 0.939 eV, respectively. Within the experimental uncertainty of the photoelectron peak positions (≈ 0.005 eV), these values are equal to the ground state \(^2P_{3/2}^1-^2P_{1/2}^1\) spin-orbit splitting of atomic iodine, 0.943 eV (7693.15 cm\(^{-1}\)).\(^17\) Thus, one explanation for the photoelectron peak which involves collisional energy transfer between the \(^1^2P_{1/2}^1\) atom and a \((^3P_2)\pi2[^3J3/2]\) Rydberg atom. A similar process has been observed in an earlier REMPI-PE study of high Rydberg states of Ba.\(^31\) A second related explanation involves the photoionization of the Rydberg atom by an infrared photon emitted by \(^1^2P_{1/2}^1\). Normally, one would expect the latter process to be quite weak; however, the same techniques of the present experiment (i.e., the production of I \(^2P_{3/2}\) and \(^1^2P_{1/2}^1\) by photodissociation of methyl iodide) can be used as the basis of the atomic iodine laser,\(^32\) which lases on the \(^2P_{1/2}^1-^2P_{3/2}^1\) transition. Thus, infrared photoionization cannot be ruled out. Both processes are expected to have large cross sections; in the former case, the collision cross section for an 11f or 14f Rydberg atom is quite large, and in the latter case, the photoionization of an 11f or 14f Rydberg atom by an infrared photon should have a much larger cross section than photoionization by an ultraviolet photon. In addition, photodissociation of methyl iodide is a single-photon process, thus a long column of I \(^2^2P_{1/2}^0\) atoms extending well outside of the laser focus will be produced. At present it is not possible to distinguish between the two possibilities, although they may show different pressure dependences. It should be noted that at higher pressures (≈ 5 X 10\(^{-5}\) Torr) the same mechanism can be observed in the \((^3P_2)13p[^3]1/2\) and \((^3P_0)14f[^3]3/2\) spectra.

IV. CONCLUSIONS

The photoelectron spectra of atomic iodine following REMPI via a number of Rydberg levels have been presented. It was shown that state-selected \(^1^2P_{0}^1\) and \(^3P_2\) ions can be prepared with > 85% purity by REMPI via selected intermediate levels. However, the spectra via other levels demonstrate that the ability to produce state-selected ions can be severely reduced by the influence of even weak perturbations. As is seen from Eq. (3), a small value of the coefficient of the perturbing level can be compensated for by a correspondingly large value of the photoionization matrix element, and the \((^3P_2)15f[^3]3/2\) and \((^3P_2)14f[^3]3/2\) spectra provide an excellent example of just this effect. As a general principle, it is worth remembering that most of the oscillator strength into the ionization continuum is concentrated near threshold in an energy region corresponding to a few multiples of the binding energy of the ionized level. Thus, in general, for high Rydberg levels, the ionization cross section with an ultraviolet photon will be quite small, and perturbations by a low-lying Rydberg level converging to a higher ionization potential (i.e., a level with a larger binding energy) can have dramatic effects on the photoelectron branching ratios. The small ionization cross sections with visible and ultraviolet photons has allowed a number of earlier experiments on high Rydberg states of Ba, in which the ion core is excited to produce doubly excited states without directly ionizing the initial Rydberg atom.\(^33,34\)

As a consequence of the small ionization cross sections of the Rydberg levels in the present experiments, two processes are observed that compete with REMPI. The first involves fluorescence of the resonant intermediate level to a lower-lying level, which is then ionized with greater efficiency, and the second involves energy transfer (either collisional or radiative) between \(^1^2P_{1/2}^1\) atoms and the Rydberg atoms. Although these two processes would be indistinguishable from direct REMPI using mass spectrometric techniques alone, the use of REMPI-PES allows one to separate the contributions of these different mechanisms and provides a more complete understanding of the overall process.

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1724  

S. T. PRATT


26See, for example, A. Burgess, Mem. R. Astron. Soc. 69, 1 (1964); A. Burgess and M. J. Seaton, Mon. Not. R. Astron. Soc. 120, 121 (1960).


