RESEARCH ARTICLE

On the use of photoelectron spectroscopy to probe the dynamics of a dissociative intermediate state

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An in-depth experimental investigation into the use of photoelectron spectroscopy to probe the dynamics of a dissociative intermediate state is reported here. More than 70 velocity-mapped photoelectron images were acquired from either one-colour or two-colour two-photon ionization processes, covering the energy range from the ionization limit of CH₃I to about 3600 cm⁻¹ above the IP. Numerous autoionizing states, both vibrationless and vibrationally excited, were observed and spectroscopically assigned. The final ion state distributions, derived from the photoelectron kinetic energy analysis, are highly selective both in vibrational modes and in quantum numbers, as well as exhibit sensitive dependences on photon energy. These findings were interpreted as a manifestation of vibronic autoionization processes rather than a direct reflection of the dissociation dynamics of the resonant intermediate state in the (1+1) resonance-enhanced multiphoton ionization of CH₃I as suggested in previous studies.

Keywords: photoelectron imaging; autoionization; REMPI

1. Introduction

Photodissociation dynamics is a relatively matured, yet fascinating subfield in physical chemistry. A host of modern experimental techniques, both in time- and frequency-domain, are now available for obtaining detailed information about bond breaking processes. Using the pump-and-probe laser spectroscopic approach, complete state-resolved distributions of the photofragments have been routinely measured for numerous systems [1, 2]. With the advent of femtosecond laser technologies, the temporal evolution of the bond breaking process can also be followed in a snapshot manner [3]. The connection of the information obtained from the two types of experimental approach (in frequency- and time-domains), however, often is not that straightforward because of the different time-scales of the dynamics being probed and the complexity of molecular energy level structures.

In 1982, Kinsey and coworkers pioneered a nanosecond (ns) Raman technique [4] to acquire the state-resolved information while a molecule is dissociating, thus getting around the loophole of the uncertainty principle. The basic idea of this innovative approach [5, 6] can be briefly outlined as follows. When a parent molecule is photoexcited to a repulsive excited state, the molecule undergoes a rapid bond rupture (within a picosecond, ps) with near unity of dissociation yield. Nonetheless, a tiny fraction (typically 10⁻⁵–10⁻⁶) of dissociating molecules can emit photons back to the electronic ground state of the parent molecule, giving rise to the so-called Raman emission. The resulting resonance Raman emission spectrum thus carries unique imprints of short-time dynamics of the dissociation process. Since then, this powerful approach has been adopted by several groups, [7–11] and a number of molecular systems have been investigated in this manner. Among them, the prototypical system of methyl iodide photodissociation, CH₃I+hv→CH₃+I, has been studied most extensively [12–18].

Raman scattering process is governed by the dipole selection rules. On the other hand, the photoelectron spectroscopy in general has less restricted selection rules, thereby offering the opportunity to probe more vibrational modes that are active while the photofragments are flying apart. In 1993, Bondybey and coworkers implemented exactly such a probe, in an effort to explore the effect of a purely dissociative
intermediate resonant state on the competing ionization process, by acquiring the one-colour two-photon (1C2P) zero kinetic energy (ZEKE) spectra of CH$_3$I via the intermediate A-band using a tunable ns-laser [19]. The molecule is excited into the dissociative A-state continuum, which situates approximately half way to the ionization limit, by the first photon absorption. While dissociating, the molecule can absorb a second photon, producing the CH$_3$I$^+$ ion excited along the dissociation coordinate, the $v_3^+$ (C–I stretch) mode. In other words, the short-time dissociation dynamics is manifested as a series of vibrationally assignable peaks of the molecular ion CH$_3$I$^+$, which can be interpreted as the projection of the dissociating wavepacket onto the ionization continuum by the second ionizing photon in this (1+1) REMPI process. The ZEKE spectra revealed, in addition to an extensive and dominant progression corresponding to the $v_3^+$ excitation, significant deformed-rocking $v_2^+$ excitation as a result of the diabatic coupling between the optically active state $^2Q_0$ that correlates with $^1P^+_1(Q_1)$ and the higher-lying $^1Q_1$ state (correlating to I ($^3P_{3/2}$)) as the molecule dissociates [19-21].

Shapiro and coworkers subsequently performed theoretical treatment of the two-photon ionization of CH$_3$I through the A-band [22, 23]. Contrary to the experimental observations, the calculation predicted predominant excitation of the combination bands of $v_3^+$ and $v_2^+$ (the CH$_3$ umbrella bend of CH$_3$I$^+$) modes. This discrepancy was later under detailed scrutiny in two photoelectron spectroscopic studies [24, 25]. Both studies employed ps-laser systems owing to the weak signals when using the ns-laser. Exploiting a conventional photoelectron time-of-flight spectroscopy at laser wavelength of 252.5 nm, Schultz and Fisher found reasonable agreements in both peak positions and intensities with those of the earlier ZEKE spectrum [24]. On the other hand, a very different spectral pattern was recorded using a slightly different laser wavelength at 251 nm. Such a dramatic dependence on small variation of the dissociation wave-lengths was attributed to very subtle changes in the intermediate repulsive potential energy surfaces, which consequently resulted in an extreme sensitivity on the observed photoelectron time-of-flight spectrum [24].

To verify that, Samartzis et al. performed a photoelectron velocity imaging experiment, using a 5 ps and a 0.5 ps laser at 248.6 nm [25]. Both photoelectron kinetic energy spectra are dominated by the origin band, followed by a series of regularly spaced peaks. Further data analysis indicated that all possible CH$_3$I$^+$ vibrational states and their combinations were needed in order to fit the spectra. Since the best-fitted CH$_3$I$^+$ vibrational populations compare favourably with those observed for CH$_3$ fragment produced at the same dissociation wavelength, it was concluded that the CH$_3$I$^+$ vibrational propensities obtained by photoelectron spectroscopy are mainly determined at the absorption step of the dissociation process rather than by the topological details of repulsive surfaces reached later in the photodissociation event [25]. This conclusion is somewhat at variance with that drawn by Schultz and Fisher; nonetheless, both interpretations focused on the influences of the intermediate dissociative states on the photoelectron kinetic energy distributions.

To shed light onto the nature of the observed photoelectron spectrum and to expand its possible application in probing the dynamics of wavepacket evolution over the intermediate dissociative state, we carried out an extensive two-colour two-photon (2C2P) photoelectron imaging experiment. Through systematic investigations and careful analysis of the photoelectron spectroscopic results, a very different interpretation emerges. Reported here are our findings.

2. Experiment

The apparatus and experimental details for this investigation have been given elsewhere [26, 27]. Briefly, a molecular beam of about 9.5% CH$_3$I in He at total pressure of 30 psi was pulsed at 20 Hz. To minimize the cluster formation and to ensure the signals from the CH$_3$I monomer, we used a fast opening pulsed valve (Even-Lavie valve) and interrogated the early part of the beam. The well-resolved and energetically assignable peaks in photoelectron kinetic energy (eKE) distribution confirmed that assertion. After being skimmed and collimated to ~1 mm diameter along the ion time-of-flight axis, it was intersected at right angles by two counter-propagated UV laser beams, which were frequency-doubled from two dye lasers. The wavelengths of the dye lasers were read off from a wavemeter. Both lasers were vertically polarized (i.e. parallel to the detector face) and focused by two independent f = 50 cm spherical lens to the centre between the repeller and extractor electrodes. Electrons produced in the interaction region were velocity-imaged onto the micro-channel plates (MCP), and the subsequent 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. The details of the imaging calibrations, both in speed and angle, of the present setup have been given recently [27], thus, will not be repeated here.
3. Results and discussion

3.1. Two-colour photoelectron images

Presented in Figure 1 are the 1C2P spectra obtained by probing the photoelectron (a) and the parent ion CH$_3$I$^+$ (b). The abscissa corresponds to the two-photon energy of the UV laser. The two spectra are nearly identical except for a number of sharp lines marked by ‘*’ in (a), which appear in (b) as negative-going signals. As shown previously [27], the sharp lines originate from two types of resonance-enhanced multiphoton (REMPI) processes of the I-fragments. The negative-going CH$_3$I$^+$ signal in (b) is the experimental artefact from the electronic ringing of the huge I$^+$ signal when gating the CH$_3$I$^+$ signal in ion time-of-flight spectrum. Also mentioned previously, the spectral features other than the I-fragments can not be assigned as the CH$_3$I(X$^1A_1$) → CH$_3$I$^+$ (X$^2E_3/2$) resonant transitions [27]. The nature of these features will be discussed in section 3.2.

The A-band absorption of CH$_3$I arises from a $n \rightarrow \sigma^*$ transition in which an iodine nonbonding $p$-electron is promoted to the lowest available antibonding molecular orbital [28]. The resulting electron configuration, $\cdot \cdot \cdot (a_1^2)(e_1^2)(a_1^*)^1$, (where $a_1^*$ is the $\sigma^*$ antibonding orbital along the C–I bond, $e_1$ is a nonbonding orbital, and $a_1$ is a bonding orbital situated on the C–I bond) gives rise to five electronic states due to the strong spin-orbit coupling induced by the iodine atom. The two-photon ionization process, mediated through the intermediate A-bond, corresponds to removal the $a_1^*$-electron to the ionization continuum by the second photon absorption, which yields CH$_3$I$^+$ with an electron configuration, $\cdot \cdot \cdot (a_1^2)(e_1^2)$, i.e. two electronic states $^2E_{1/2}$ and $^2E_{3/2}$. To explore the potential of using photoelectron spectroscopy to gain deeper insights into the CH$_3$I dissociation dynamics over the A-band, the two-colour two-photon (2C2P) photoelectron images were acquired. Over most of the wavelength region shown in Figure 1, two-photon energy is sufficient to ionize parent molecule CH$_3$I (ionization potential, IP = 76932 ± 5 cm$^{-1}$) [21]. In order to ensure that the observed signals indeed come from a two-colour two-photon process, each set of measurements consists of three UV laser frequencies that were chosen such that $2\nu_3 = \nu_1 + \nu_2$, as illustrated in Figure 1(a).

Exemplified in Figure 2 are five raw images taken from one set of such two-colour measurements. Three are one-colour images, (A), (C), and (E), acquired at three different frequencies; two are two-colour images, (B) and (D), labelled as on-time (i.e. $\nu_1$ and $\nu_2$ were temporally overlapped) and off-time (i.e., $\nu_1$ and $\nu_2$ were time-delayed by ~20 ns). The last one shown in (F), $S_{\text{on}}$–$S_{\text{off}}$, is the difference-image between the (two-colour) on-time and

![Figure 1](image-url)  
**Figure 1.** A portion of the photoionization spectrum with electron detection (a) and the two-photon ionization spectrum of CH$_3$I$^+$ (b). The peaks marked with ‘*’ on the top are from the iodine-fragments. For two-colour investigations, three laser frequencies were invoked in each set of measurements. Illustrated by $2\nu_3 = \nu_1 + \nu_2$ are the respective two-photon energies for one of such sets (see text for details). The two-photon frequencies from the previous photoelectron spectroscopy studies are also indicated in (a). The insert in (b) is the expanded view of a narrow energy range of photoelectron spectrum, and the numbers label the positions at which photoelectron images were acquired to elucidate the nature of the spectral features.
off-time images. Thus, the image of $S_{\text{on}}-S_{\text{off}}$ originates from a true 2C2P process. An immediate question is then posed: Does it provide additional information about the dissociation dynamics that could not have been obtained from the 1C2P images? Compared it to the one labelled $2\nu_3$ in Figure 2, the two images (E) and (F) are nearly identical, thus suggestive of a negative answer.

Figure 2. Five raw images, (A)–(E), acquired to decipher the true two-colour, two-photon signal (F). The three laser frequencies used in the measurements are indicated in Figure 1(a). The two images of (E) and (F) are nearly identical, which suggests that the final ion state distributions are dominated by the ionization dynamics.
We used the basis-set expansion method BASEX [29] to reconstruct the photoelectron images for quantitative analysis. The resulting eKE distributions for the images shown in Figure 2 are displayed in Figure 3. Several comments are worth noting. First, the photoelectron images are clearly dominated by the two-photon ionization of the CH₃I monomer under the experimental conditions of this study since all major peaks in eKE distributions are well resolved and can energetically be ascribed to the known CH₃I⁺ vibrational states [19–21] based on that assumption. Second, as anticipated, the two-colour off-time distribution appears to be the simple sum (D), aside from a normalization factor, of the two one-colour distributions for 2hv₁ (A) and 2hv₂ (C). On the other hand, additional features are noticeable in the on-time two-colour distribution, which are accentuated in the (Son–Soff) difference distribution. As alluded to early, however, this true two-colour difference distribution turns out to be virtually identical to that of an one-colour distribution when the laser frequency was set at v₃ = (v₁ + v₂)/2. [Note: Some small peaks are seen in Son–Soff, but are absent in 2hv₃. These residual differences depend sensitively on the exact normalization factor between the on-time and off-time distributions, and they were not reproducible from several repeated runs, thus, should not be of concern.]

More than 20 sets of such 2C2P measurements, including some with the same v₃ but different combinations of v₁ and v₂, and the others for which 2v₂ are below the IP, were performed. They all showed nearly identical photoelectron kinetic energy distributions of the two images, Son–Soff and 2hv₃, as exemplified in Figure 3. Should the 2C2P processes really probe the wavepacket evolution over the intermediate dissociative state, one would have expected to observe a different final ion state distribution of Son–Soff from that of 2hv₃. Experimental result is completely opposite to this expectation. In addition, the frequency v₃ was chosen so that its two-photon excitation reaches the same ionization continuum in energy as that by v₁ + v₂, yet the two cases proceed through different energies in the intermediate A-states. We therefore concluded that the photoelectron kinetic

Figure 3. Quantitative comparisons of photoelectron kinetic energy distributions for the six images shown in Figure 2. By conservation of energy, all peaks can be ascribed to the parent ion CH₃I⁺ states, as indicated, from the two-photon ionization processes.
energy distribution is essentially determined by the ionization dynamics, at variance with the ZEKE probe [19–21] that clearly reveals the short-time dynamics of the neutral dissociation process. This conclusion is also in sharp contrast, as aforementioned earlier, to those drawn from earlier photoelectron spectroscopic approaches [24, 25].

3.2. Spectral assignment of the Rydberg series
Having argued that the photoelectron kinetic energy release, either by 1C2P or 2C2P process, is dominated by the ionization dynamics, then what is the underlying mechanism that gives rise to the observed distribution? To shed light onto it, the photoionization spectrum (with electron detection) shown in Figure 1 is reproduced in Figure 4, along with our spectral assignments as the CH3I electronic Rydberg series (i.e. for vibrational ground states). In Figure 4, those photoelectron peaks marked by * are from the I-fragments, whose ionization mechanisms have recently been discussed [27]. The remaining features are all above the IP (76932 cm\(^{-1}\)) of CH3I [21]. As can be seen, most of the major features can be successfully assigned by the Rydberg formula

\[
E_n = E_I - \frac{R}{(n - \delta)^2}
\]

as the superexcited Rydberg states (or the autoionizing states) converging to the spin–orbit excited state of CH3I\(^+\) (\(^{2}E_{1/2}\)). Here, R is the Rydberg constant (109737 cm\(^{-1}\)), E\(_I\) is the ionization energy of the \(^{2}E_{1/2}\) state (81985 cm\(^{-1}\)) [21], n and \(\delta\) are the principal quantum number and the quantum defect, respectively. The assignments of ns, np, and nd series are consistent with the previous reports based on the lower resolution one-photon photoionization spectra of CH3I [30–34]. The derived quantum defects based on Equation (1) for the ns, np, and the two nd series are 3.939 ± 0.014, and 3.459 ± 0.025, and 2.177 ± 0.013 and 2.073 ± 0.007, respectively. [Note: the “±” uncertainty reflects the systematic variations of \(\delta\) values for different n states.] Splitting of the nd series into two peaks have barely been observed in previous studies [30–34], which was attributed to the anisotropic interaction of the Rydberg electron with the quadrupole moment and polarization of the ionic core [29]. Observation of the three series identified here as nf series is for the first time, since the \(p \rightarrow f\) transition is dipole-forbidden in the one-photon process but allowed in the present two-photon excitation. The fitted quantum defects for the three nf series in order of higher energies are 1.009 ± 0.005, 0.983 ± 0.010 and 0.826 ± 0.010, respectively. It is gratifying to note that almost all major spectral peaks, besides those for the I-atom, can be accounted for in this manner.

3.3. Evidence for vibronic autoionization states by one-colour images
We have shown above that most of the major features in the ionization spectrum can be ascribed to the origin

Figure 4. CH3I Rydberg series assignments of the photoionization spectrum (with electron detection). As in Figure 1, the peaks marked with * are from the iodine atom. Almost all major features are accounted for by the present spectroscopic assignment.
bands of a number of CH$_3$I superexcited Rydberg series. The autoionization mechanism of those Rydberg states must invoke the spin-orbit couplings of the $^{2}\!\!E_{1/2}$-core Rydberg states to the $^{2}\!\!E_{3/2}$ ion-continuum. Some minor peaks as indicated by the shaded areas in Figure 4, however, remain unassigned.

We chose a narrow frequency range, 78000–78400 cm$^{-1}$, for detailed investigation into the nature of those spectral peaks. Displayed in Figure 1 is the expanded view of that range, and the numbers 1–21 label the one-colour, two-photon frequencies at which the photoelectron images were acquired.

Figure 5 illustrates a few raw images in the top row, accompanied by the inverted images in the middle, and the bottom row displays the corresponding photoelectron kinetic energy distributions. It is clear from the peak assignment that the final ion state distributions are highly mode-selective – predominantly the $v_1+$ mode excitation followed by $v_2^+$ and $v_6^+$, and are sensitively dependent on the laser frequencies. A closer inspection of the images also reveals different angular distributions for the different final ion states. Expressing the angular distribution in terms of the Legendre polynomials

$$I(\theta) \propto \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta).$$

Figure 6 presents the photoelectron angular distributions in the polar representation for the two dominant CH$_3$I$^+$ ion states, $0_{0}^+$ and $3_{2}^+$. As is seen, while the angular distributions for forming the CH$_3$I$^+$(2$E_{1/2,0_{0}^+}$) product state are dominated by a positive $\beta_2$ value, those for CH$_3$I$^+$(2$E_{1/2,3_{2}^+}$) exhibit clearly a negative $\beta_2$ and show a significant contribution from $\beta_4$ for image numbers 9, 18, and 20.

The resulting vibrational branching ratios and the $\beta$ values of the CH$_3$I$^+$ products over this frequency range are summarized in Figure 7. An intriguing dependence of the vibrational branching on laser frequencies is vividly displayed. The formation of CH$_3$I$^+$ ion state $3_{2}^+$ appears quite significant, with the branching fraction reaching about 50% near 78164 cm$^{-1}$, where both CH$_3$I$^+$ REMPI spectrum and photoionization spectrum (by detecting electron) also exhibit a peak. The formation of the $3_{1}^+$ product state indicates enhanced branching at $\sim$78082 cm$^{-1}$ and 78325 cm$^{-1}$. The corresponding features in photoionization yield spectra can also be readily identified.

In terms of the anisotropy parameter $\beta_2$, while that for the ground-state ion $0_{0}^+$ shows little dependence on photon energy, those for both $3_{2}^+$ and $3_{1}^+$ states clearly display a negative-going trend (i.e. window-like behavior) near their respective peaks in ion yields.

Figure 5. A few representative photoelectron image data. The numbers correspond to those indicated in the insert of Figure 1. The top row are the raw images, the middle row show the inverted ones, and the bottom row display the corresponding photoelectron kinetic energy distributions with the assignments of the final ion states. Note that the product state distributions are highly selective and depend sensitively on the two-photon frequencies.
We interpret these observations as manifestations of the vibronic autoionization process. Here, we assume that the 1C2P process excites CH$_3$I into a superexcited Rydberg state whose ion-core is not only spin–orbit excited (i.e. the $^2E_1$ state) but also vibrationally excited. Hence, the autoionizing mechanism invokes a vibronic coupling between the Rydberg electrons with the vibronic-excited core. It is well known that when energetically allowed, the propensity of $\Delta v = -1$ often dominates the vibrational autoionization routes [35–37]. This vibrational propensity is in contrast to that for a purely electronic autoionization, where the electronic state of the ion core changes and the vibrational state distribution in the ion is usually governed by the Franck–Condon (F-C) factors between the autoionization state and the ionization continuum. Assuming the same $\Delta v = -1$ vibrational propensity rule holds for the present vibronic coupling and using $E_n = 76592 \text{cm}^{-1}$ for the vibrationless $8p$ Rydberg state (from equation (1) and $\delta = 3.489$ extrapolated from the quantum defects of the higher $np$ series), we tentatively assigned the spectral feature at which $3^+_2$ ion state peaks as the $[1/2]8p3^2\ell_0^0$ transition, i.e., to a combination-band excited $8p$ Rydberg state (vide infra). Here, the notation $[\omega_c]\ell nl\nu$ denotes the ion-core total angular momentum $\omega_c$, Rydberg electron orbit $nl$, and vibrational mode $\nu$ of the ion-core making an optical transition from $i$ quantum state to $j$ state. Similarly, the two features, from low to higher energies, with significant $3^+_1$ populations are $[1/2]8p3^2\ell_0^0$ and $[1/2]8p3^2\ell_0^1$, respectively. With these assignments, the corresponding...
vibrational frequencies in the $[1/2]8p$ Rydberg state can be estimated by the differences between the (two-photon) peak centres and the origin of the $[1/2]8p$ state (76592 cm$^{-1}$): $v(3_1^+2_i) = 1490$ cm$^{-1}$, $v(3_2^+2_i) = 1572$ cm$^{-1}$, and $v(3_5^+2_i) = 1733$ cm$^{-1}$. It is also interesting to note that all three vibronically excited autoionization states display a spectral width of FWHM $\sim 65$ cm$^{-1}$, which corresponds to a lifetime of about 85 femtoseconds (fs) for all possible decay routes (autoionization and predissociation). This value can be compared to other Rydberg states in the literature. The lifetime of the 6$s$ Rydberg state was found to be about 500 fs from a linewidth measurement [38] and the 6$p$ Rydberg state was determined as 175 fs in a real-time study [39].

### 3.4. Vibronic autoionization up to 3600 cm$^{-1}$ above IP

As presented above, a detailed analysis of photoelectron images strongly suggests that some minor spectral features could be ascribed to the vibronically excited autoionization states. Are the other unassigned features (the shaded parts) shown in Figure 4 of the same nature? To address this question and to confirm the combination-band assignments given in Section 3.3., we then examined the photoelectron images over a much wider spectral range. As alluded to earlier, over the spectral range shown in Figure 1 more than 70 photoelectron images were acquired. Analysing the photoelectron kinetic energy distribution of those images then yields a comprehensive set of data on product state branching ratios, ranging from the IP of CH$_3$I to about 3600 cm$^{-1}$ of excess energy. Figure 8 summarizes the results, and for ready reference the photoionization spectrum (with electron detection) is repeated in the top panel. The final ion states are grouped into four panels roughly by the magnitudes of their branching fractions. As it turns out, this grouping also conveniently partitions the vibrational excitations of product ions as the ground state, the $v_J^+$-excitations, other single-mode excitations, and the combination modes.

Besides the ground state CH$_3$I$^+$, the 1C2P ionization process preferentially yields more C–I stretching excited ($v_J^+$) ions than any other modes. Also apparent from the third panel, the quantum state preferences of the $v_J^+$ mode show oscillatory structures in energy. A closer inspection of the branching ratios for the $3^+_m$ states ($m = 1, 2, \ldots, 7$) reveals an intriguing trend that every product ion state has a very low yield near the energetic threshold (marked as the vertical arrow), followed by series of peaks with the first one peaking at $\sim 270$ cm$^{-1}$ above the threshold. In addition, for each $3^+_m$ state the series of peaks show rather regular pattern in that their energy spacing are more or less replicated from one final ion state to the other. For example, the relative spacing between peaks of $a_2^+, b_2^+, \ldots, f_2^+$ for the $3^+_2$ state are nearly the same as those between $a_3^+, b_3^+, \ldots, f_3^+$ for the $3^+_3$ state, and similarly for the other ion states. It is also interesting to note that the positions of those structural peaks in branching ratios with those in

![Figure 8. Summary of the vibrational branching ratios of the observed CH$_3$I$^+$ ion states in this study, covering the energy range from the IP of CH$_3$I to about 3600 cm$^{-1}$ above. For reference, the photoionization spectrum (with electron detection) is repeated in the top panel. The final ion states are grouped into four panels for display.](image-url)
the photoionization spectrum (the top panel, the shaded areas), there is one-to-one correspondence. We therefore ascribed those minor unassigned spectral features (the shaded areas) to the vibrationally excited Rydberg states. Guided by the above observations, we analyzed in Figure 9 the regularities among the branching ratio peaks, where the abscissa 'm' denotes the quantum number of the final ion state $3_m^+$. Quite remarkably, almost all branching peaks follow closely a linear equation expression:

$$(2hv - IP)_m = S_i m + I_i$$

with $S_i$ and $I_i$ being the slope and the intercept of the $i$th (i.e. a, b, c, etc.) progression, respectively. The best-fitted $S_i$ and $I_i$ are summarized in Table 1. Also apparent from Figure 9, all seven progressions display nearly identical slope $\sim 440 \text{cm}^{-1}$. We interpreted the results as an indication of combination-band excitations of Rydberg states with a vibrational frequency of $\sim 440 \text{cm}^{-1}$ in forming the progression. We further assigned this frequency as the $v_3$ (the C–I stretch) mode. The vibrational frequency for the other mode of excitation for each progression can then be deduced from the respective $I_i$ value. Based on the vibrational autoionization propensity rule of $\Delta v_i = -1$, we tentatively assigned those vibrationally excited autoionizing states as listed in Table 1. Since there are numerous possible Rydberg series below this energy window, as can be gleaned from Figure 4, and none of their vibrational frequencies (except for the lowest 6s Rydberg state) are known, the assignments are not entirely unambiguous. Other possibilities, as given by alternative assignments in Table 1, can't be completely ruled out. We prefer the assignments to the $8p$, $9p$, $9s$ etc [40]. Rydberg states for they are of the 'penetrating' Rydberg orbitals that in general tend to have faster autoionizing rates [36] thus, more likely to be observed. The deduced fundamental frequencies from the present assignments are summarized in Table 2, along with the vibrational frequencies of the other relevant electronic states for comparisons [20, 41, 42]. It is interesting to note that the $v_6^*$ and $v_2$-modes for the $8p$ and $9s$ Rydberg states show significant deviations from the frequencies of the corresponding ion modes. Since only the combination bands were observed in this study, the vibrational frequencies thus deduced include the intermode anharmonicities, which may account for part of the discrepancies. Nonetheless, it may also suggest that the potential curves of the Rydberg states along those particular normal-mode coordinates are not quite parallel to those of the ion, signifying the effect of the Rydberg electron on the potential of the nuclei.

3.5. Dynamical implications and some general comments

In light of the above findings, a few comments are in order. First, since the geometric structures of the ground-state CH$_3$I and the ground-state ion CH$_3$I$^+$ are quite similar, the F–C factors will then strongly favor the $\Delta v_i = 0$ optical transition. The supersonically expanded CH$_3$I is mostly populated in the vibrational ground state; the F–C transition should then yield mainly the vibrational ground-state CH$_3$I$^+$ ion. The conventional one-photon photoelectron spectrum of Karlsson et al. [43], confirmed this expectation. Figure 8 displays instead a significant and long progression of the C-I excitation of CH$_3$I$^+$ in the final ion yield, clearly indicative of non-F–C type of transitions for the present $(1 + 1)$ REMPI process. We assert the origin of such an extensive non-F–C progression being the manifestation of the wavepacket evolution of the dissociative intermediate state upon the second photon absorption in the ionization step, as originally suggested by Bondybey and coworkers in their ZEKE probe [19–21]. However, unlike the ZEKE probe that projects the dissociating wavepacket directly onto the vibrational manifolds of the parent ion, the photoelectron spectroscopy reflects the projection onto the superexcited Rydberg states that subsequently eject the electron by autoionization.

![Figure 9](https://example.com/figure9.png)

Figure 9. Analysis of the perplexing patterns of the $3_m^+$ vibrational branching ratios shown in Figure 8. The abscissa 'm' denotes the quantum number of the final ion state $3_m^+$. The data points are the peak positions in $(2hv-IP)$ from Figure 8 and the line is the best fit to the respective progression. Due to the sparsity of data points, the peak positions for $a_i$ and $b_i$ are uncertain or missed, thus absent in the plot. Nearly all noticeable structural peaks can be accounted for by such linear progressions, which strongly suggest combination-band excitations of autoionization states.
Due to the sparse data points in locating the peak positions, the uncertainties of the deduced vibrational frequencies are estimated to be \( \pm 15 \text{ cm}^{-1} \). The numbers in parenthesis for A and B are their peak positions (Figure 8) in \( \text{cm}^{-1} \).

The dynamical implication of this finding is that although the appearance of the non-F–C progression closely corroborates the picture of wavepacket evolution, the intensities of the final ion state distribution are predominantly governed by the vibronic autoionization process, rendering the quantitative interpretation of the observed distribution in terms of photodissociation dynamics subtle and dubious.

Second, nearly all structural features in the vibrational branching plot can be assigned as combination bands, i.e. an autoionizing Rydberg series converging to an ionic limit in which two different vibrational modes are simultaneously excited. This is in sharp contrast to that from the ZEKE probe [19–21] where the dominant features are the overtone transitions \( \left( \text{3}_0^m \right)^{\pm} \). The absence of any assignable features in photoelectron spectrum to the \( \nu_3 \)-overtone transition is intriguing. It implies either an unfavorable F–C factor for the transition from the A-state to a super-excited Rydberg state (yet, a favourable one for the ZEKE probe) or less efficient nonadiabatic couplings between the \( \nu_3 \)-mode and Rydberg electron for autoionization to effectively compete with predissociation or other nonradiative processes. Further works are needed to clarify the origin of this observation. In any event, as pointed out and convincingly demonstrated for a few small molecules by Pratt [36, 44–47], the application of photoelectron spectroscopy to interrogate the combination-band excited Rydberg states can provide valuable information about the mode-specific behaviours in vibrational autoionization process. Those autoionizing states can in principle decay via a \( \Delta \nu_1 = -1 \) process for either normal mode; thus, the relative intensities of the corresponding photoelectron peaks reflect the relative rates of the two vibrationally induced autoionization pathways. Following this viewpoint, we note that mainly three types of combination-band excitations, \( \text{3}_0^m \text{6}^m \text{0}^m \), \( \text{3}_0^m \text{2}^m \text{1}^m \), and \( \text{3}_0^m \text{5}^m \text{0}^m \), are invoked. Yet, the final ion states autoionized from these vibronically excited neutral state are always the \( \text{3}_0^m \) states; the corresponding peaks for the alternative decay pathway, for example forming...
the \((3^1\ell_0)^+\) ion from the \(8p^2\ell_0^6\) Rydberg state, are nearly absent. A simple energetic argument suffices to explain this mode-selective autoionization process, as illustrated in Figure 10 for the \([1/2]8p^2\ell_0^6\) Rydberg states. Similar energetic arguments apply to the other combination-band excited Rydberg states.

Lastly, for a given ion state \(3^1m\), the relative intensities of the vibrational branching ratios from the three combination-mode excitations show an interesting pattern. For example, the branching ratios for forming the \(3^12\) state from the \(8p\) Rydberg state indicate that peaks \(a_2 > c_2 \approx d_2\), i.e., the transitions \(3^12^6_0^0 > 3^12^1_0^1 \approx 3^12^1_0^1\); similarly, for the other \(3^1m\) product state. However, for the \(9s\) Rydberg state one observes \(3^12^1_0^1 > 3^12^1_0^1 > 3^12^1_0^1\), e.g., \(f_1 > g_1 > e_1\) for the \(3^12\) state and \(f_2 > g_2 > c_2\) for the \(3^13\) state, etc. One might be tempted to interpret these findings as the dependence of mode-specific autoionization on the Rydberg electron orbital. Namely, the nonadiabatic coupling of the \(v_6\) mode (the C–I bend) to the \(p\)-orbital Rydberg electron is considerably stronger than those for the \(v_3\) (the CH3 umbrella) and \(v_5\) (the CH3 d-deformation) modes, whereas the coupling of the \(s\)-orbital Rydberg electron to the \(v_5\) mode is more efficient than to the \(v_6\) and \(v_5\) modes. Recalling however, that autoionization is not necessarily the only decaying route of a superexcited Rydberg state; other radiationless processes such as predissociation may be in competition. In other words, the observed mode-specific branching ratios could also

be interpreted as a consequence of the mode-specific competing processes. Further works, both experimental and theoretical, are needed to gain deeper insights into the observed mode-specific behaviours and their underlying mechanisms.

4. Conclusions

We report an in-depth experimental study, using velocity-mapped imaging technique, on the nature of photoelectrons produced from \((1+1)\) REMPI of CH3I through the dissociative intermediate A-band. Despite the uncertainties in assigning some of the minor features in the photoionization spectrum, several conclusions can be drawn.

1. Comparisons of the 1C2P and 2C2P images clearly demonstrate that the observed final ion state distribution is predominantly governed by the ionization step, rather than the dissociation dynamics of the resonant intermediate state in the \((1+1)\) REMPI process.

2. The main factor in the ionization step appears to be the autoionization process, as evidenced by the successful assignments of almost all major spectral features to the origin bands of the \(ns, np, nd\), and \(nf\) Rydberg series (Figure 4).

3. Through the vibrational branching determination, the remaining minor spectral features are tentatively ascribed to vibrationally excited Rydberg states converging to \(\text{CH}_3I^+\)\((^{3}E_{1/2})\). Here, the propensity rule of \(\Delta v = -1\) was assumed. Violations of this propensity rule are known, but all of the examples can be understood in terms of concurrent electronic autoionization or predissociation processes [48–50].

4. Since the nature of ZEKE spectroscopy excludes the fast moving electrons (i.e. those with finite kinetic energy), its spectrum reflects mainly the final ion state distribution. Hence, the observed \(\text{non F–C behaviour could reveal the information about the wavepacket dynamics of the intermediate dissociative state in a more direct manner. It should be noted that ZEKE spectra are not always free from the effects of channel couplings; such couplings between the Rydberg states and field-ionized continuum are closely related to the bound-continuum couplings observed here [51]. On the other hand, the photoelectron spectrum, either by the conventional time-of-flight measurement or via imaging technique, comprises mostly
finite KE electrons, which by and large originate from numerous autoionizing states. Hence, the information on the dissociation dynamics of the intermediate repulsive state is contaminated and lost in the final state distribution, which is mostly dictated by the autoionization process. Since autoionizing phenomenon is ubiquitous for excitation energies of a few eV above IP, this conclusion is not just limited to the present case of CH$_3$I and probably holds true for all molecular systems.

(5) Finally, as demonstrated in this study, while the photoelectron imaging technique does not seem to be an appropriate approach to probe the dissociation dynamics of the intermediate resonant state in a REMPI process, it is a powerful tool to elucidate the dynamics of molecular autoionization processes. The study of the vibrational autoionization of polyatomic molecules, especially the mode-specific behaviours, has been proven particularly insightful to understand the nonadiabatic couplings induced by different types of nuclear motions in photoionization dynamics [36, 37]. The photoelectron imaging technique may find a wide range of applications in this fruitful area.

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References