A velocity map imaging study of the photodissociation of the methyl iodide cation

S. Marggi Poullain, D. V. Chicharro, J. González-Vázquez, L. Rubio-Lago and L. Bañares*

The photodissociation dynamics of the methyl iodide cation has been studied using the velocity map imaging technique. A first laser pulse is used to ionize methyl iodide via a \(2+1\) REMPI scheme through the \(5\pi \sigma \rightarrow 6\) Rydberg state two-photon transition. The produced \(\text{CH}_3\text{I}^{+}(\tilde{X}^2E_{3/2})\) ions are subsequently excited at several wavelengths between 242 and 260 nm. The reported translational energy distributions for the methyl and iodine ions present a Boltzmann-type unstructured distribution at low excitation energies as well as a recoiled narrow structure at higher excitation energies highlighting two different dissociation processes. High level \(ab\) initio calculations have been performed in order to obtain a deeper understanding of the photodissociation dynamics of the \(\text{CH}_3\text{I}^+\) ion. Direct dissociation on a repulsive state from the manifold of states representing the \(\tilde{B}\) excited state leads to \(\text{CH}_3\text{I}^+ + \text{I}^*(2P_{3/2})\), while the \(\text{CH}_3 + \text{I}^*(2P_{3/2})\) channel is populated through an avoided crossing outside the Franck–Condon region. In contrast, an indirect process involving the transfer of energy from highly excited electronic states to the ground state of the ion is responsible for the observed Boltzmann-type distributions.

Introduction

Methyl iodide (\(\text{CH}_3\text{I}\)) has been a benchmark system for the study of photoinduced molecular dynamics for the past two decades. In particular, the photodissociation in the first and second absorption bands has been largely reported and revisited.\(^{1-5}\) This molecule has also proven to be an excellent system for the demonstration of new experimental techniques, such as ion imaging by Chandler and Houston\(^{6}\) or velocity map imaging (VMI) by Eppink and Parker.\(^{7}\) Studies on the methyl iodide cation (\(\text{CH}_3\text{I}^+\)) are, on the other hand, rather limited mostly from the 1980s. Published literature includes, in particular, photoelectron spectra recorded using first a helium lamp\(^{8,9}\) and lately synchrotron irradiation,\(^{10}\) studies using time-of-flight spectroscopy\(^{11-19}\) alone and in combination with the photoelectron photoion coincidence (PEPICO) technique\(^{20-22}\) for the \(\tilde{A}^2A_1 \leftrightarrow \tilde{X}^2E_{3/2}\) transition and photodissociation, and a detailed investigation of the Jahn–Teller effect in the \(\tilde{X}^2E\) ground state.\(^{23}\) The dissociation threshold for the formation of the methyl cation and the iodine cation as well as the vibrational frequencies were determined from a detailed analysis of the reported photodissociation spectra for the \(\tilde{A}^2A_1 \leftrightarrow \tilde{X}^2E_{3/2}\) transition.\(^{12,13}\) The ro-vibrational analysis was quite recently revisited using high resolution mass-analyzed threshold ionization by Kim and co-workers.\(^{17-19}\) Some theoretical work has also been reported regarding the position of different electronic states of the ion. The most recent work includes a schematic representation of the potential energy surfaces based on \(ab\) initio calculations by Locht et al.\(^{24}\)

The ground electronic state of the \(\text{CH}_3\text{I}^+\) ion is a bound state split into two spin–orbit compounds (\(\tilde{X}^2E_{3/2}\) and \(\tilde{X}^2E_{1/2}\)) lying at 9.53 eV and 10.15 eV,\(^{8,24}\) respectively, which correlates with the \(\text{CH}_3\text{I}^+(\tilde{X}^2A_1^+) + \text{I}^*(2P_{3/2})\) dissociation limit at 12.18 eV.\(^{25}\) The first excited state, \(\tilde{A}^2A_1\), is a slightly bound state located at around 12.5 eV with respect to the \(\text{CH}_3\text{I}\) ground state, while the second excited state, \(\tilde{B}^2E\), is a pure dissociative state located between 14 and 16 eV.\(^{10}\) The reported PEPICO studies on the photodissociation through the \(\tilde{A}^2A_1\) excited state indicated a statistical dissociation mechanism leading to the formation of the \(\text{CH}_3\) fragment with a small amount of translational energy.\(^{20-22}\) A long lifetime, around \(10^{-7}\) s, has indeed been estimated for the \(\tilde{A}^2A_1\) state.\(^{21}\) An internal conversion to the \(\tilde{X}^2E\) state at lower photon energy as well as to the \(\tilde{B}^2E\) state at higher photon energy has been evoked as part of the fragmentation pathway even though some questions remain unanswered. To the best of our knowledge, the photodissociation dynamics at higher energies through the \(\tilde{B}^2E\) state has, however, never been reported. Besides, a deeper theoretical study including the spin–orbit coupling appears to be necessary.
Some studies have been published on the photodissociation dynamics of other alkyl halide cations.26–30 Aguirre and Pratt26,27 reported a detailed velocity map imaging study of the one-photon dissociation of CF3I+ ions produced by resonance enhanced multiphoton ionization. Photoelectron spectra were measured to characterize the parent ion produced in the X2E3/2 ground state, while ion translational energy distributions for the CF3+ and I+ ions produced following excitation to the first excited state of the CF3I+ ion, the A2A1 state, were obtained as a function of the dissociation wavelength. For both CF3+ + I and CF3+ + I’ channels, two different mechanisms were observed. The first corresponds to the direct and fast dissociation of the A2A1 state resulting in high translational energies. The second mechanism, appearing at low translational energies, was described by the internal energy distribution of the nascent fragment. The CF3+ + I channel was found to be characterized by a high vibrational excitation in the ν2 umbrella mode of the molecular ion fragment, which can be understood by considering the Franck–Condon factors between the pyramidal CF3 moiety in CF3I+ and the planar CF3I+ cation.

In addition, Blanchet et al.28 and Wang et al.29 published almost simultaneously, studies on the competition between the one-photon dissociation in the second absorption band (ν2 = 2E) ions through a (2 + 1) REMPI scheme,29 followed by the two-photon dissociation in the second absorption band (ν2 = 2E state, in the C2v symmetry group). This process is characterized by vibrational progression in the ν2 umbrella mode of the methyl ion suggesting again that dissociation is controlled by the Franck–Condon factors between the CH3 moiety in CH3Br+ and the CH3+ fragment.

Recently, the photofragmentation dynamics of ethyl bromide and ethyl iodide cations were studied using velocity map imaging by Vallance and co-workers.30 The experimental results were interpreted with the aid of high-level ab initio potential energy surfaces. Regarding the C–I bond fission in the C2H5I+ photodissociation, translational energies for the ethyl ions were also found to be bimodal, where the low energy part was associated with near-threshold photodissociation, while the high translational energy region was attributed to the prompt dissociation in the second absorption band (σσ+).

The aim of this work is to study the photodynamics of the dissociation of the methyl iodide cation using velocity map imaging. A scheme of the experimental procedure is shown in Fig. 1. A first laser pulse is centred at 339.34 nm in order to produce CH3I+(X2E3/2) ions through a (2 + 1) REMPI scheme corresponding to the two-photon excitation of the 5pν → 6p[2]0 Rydberg state.31 A second laser pulse excited the methyl iodide ion into the first and second, A2A1 and B2E1, excited states. The methyl and iodine ions produced from the photodissociation of CH3I+ are then detected using velocity map imaging. The experimental results, i.e. translational energy distribution and angular distributions, are interpreted with the aid of high-level ab initio calculations.

The paper is organized as follows: in Section 2, the experimental and theoretical approaches are presented. In Section 3, the most relevant experimental and theoretical results are presented and discussed, respectively, and, finally, Section 4 is dedicated to the most important conclusions of the work.

Methods

Experimental

The main characteristics of the experimental setup have been described in detail previously.4 The whole experiment runs at a repetition rate of 10 Hz. Methyl iodide was seeded in helium (10%, 1 atm back pressure) and expanded into a vacuum using a pulsed nozzle (General Valve Series 9, 0.5 mm orifice) and reaches the ionization chamber where the molecular beam is intersected at right angles, in the middle of the electrical plates of a time-of-flight (TOF) mass spectrometer, by the ionization laser and the dissociation laser pulses, which are focused (f = 25 cm) and counter-propagated to each other.

The second harmonic of a Nd:YAG (Quanta Ray Pro 230) pumped dye laser (Sirah Cobra-Stretch) is used in order to ionize methyl iodide via a (2 + 1) REMPI scheme at 339.34 nm corresponding to the 5pν → 6p[2]0 Rydberg state two-photon transition.31 The CH3I+ ions produced are then excited at several wavelengths: 260, 250 and 242 nm using a Nd:YAG (Quanta Ray Pro 190) pumped frequency doubled dye laser (Sirah Cobra-Stretch).

CH3+ and I+ images are recorded using our velocity map imaging (VMI) apparatus in the single-field configuration.32,33 The generated ions are accelerated by an electric potential of 5 kV applied to the repeller plate and pass through a field-free TOF region (45 cm) before hitting the impedance matched micro-channel plates (MCPs, Chevron configuration, 40 mm diameter).
The recorded velocity map images of methyl or iodine ions are quadrant symmetrised and Abel inverted using the Hankel transform prior to extracting the kinetic energy spectrum and the angular distribution.

Independent velocity–radius calibration of the apparatus is done by measuring the resonantly ionized CH₃⁺(ν = 0) fragments produced after the photodissociation of CH₃I at 333.45 nm (one-colour pump–probe experiment) at different repeller potentials, taking advantage of the well-known kinetic energy release of the I(³Pₓ/₂) yielding channel at this photolysis wavelength.⁴

**Theoretical**

In order to characterize the methyl iodide cation, the energy of different electronic states was calculated along the C–I distance. This calculation was performed using multireference methods with relativistic corrections and a ANO-RCC³⁴,³⁵ basis set contracted to a TZP equivalent to a CASSCF wavefunction that was obtained using 6 electrons on 4 orbitals as depicted in Fig. 2. The set of orbitals considered in this study contains two lone pairs in the iodine atom, σ-bonding and σ-antibonding. These orbitals were optimized using the state average technique where the 12 doublets (7 of symmetry A₀⁰ and 5 of symmetry A₂⁰) and 3 quadruplets (1 of symmetry A⁰ and 2 of symmetry A₂⁰) were included. The spin–orbit (SO) was taken into account using the AMFI approximation,⁴⁶ resulting in a total of 36 electronic states. This number of states is required to describe different electronic states was calculated along the C–I distance.

The CASSCF energy was corrected by considering single and double excitations from the CASSCF wavefunctions (MRCISD). All the calculations were performed at C₆ symmetry using the MOLPRO package,⁴⁷,⁴⁸ using the modules SEWARD,³⁹ CASSCF,⁴⁰,⁴¹ the CI⁴²–⁴⁵ and geometry optimization⁴⁶ with analytical gradients for MP2⁷ and CASPT2.⁴⁸ In all cases relativistic effects were taken into account by using the Douglas–Kroll Hamiltonian⁴⁹–⁵¹ and calculating the SO coupling.⁵²

**Experimental results**

Fig. 3a and c present the VMI inverted images recorded for the CH₃⁺ and I⁺ ions, respectively, in a one-colour experiment using photon excitation at 339.34 nm. A highly anisotropic structure is observed in both cases that can be assigned to a two-step process. First, the ground state CH₃I parent molecule is ionized via a (2 + 1) REMPI scheme; second, the CH₃I⁺ cation thus formed is excited and dissociated through further absorption of one additional photon. The three-photon absorption step cannot lead to dissociation, since the total excitation energy (10.96 eV) is lower than the first dissociation limit of CH₃I⁺, which is 12.18 eV for the CH₃⁺(X³A₁⁺) + I(³Pₓ/₂) channel.

Angular integration of the images shown in Fig. 3a and c leads to the total translational energy distributions (TEDs) shown in Fig. 3b and d, respectively. For both ions, a Boltzmann-type distribution centred at around 0.15 eV is observed consistent with the previously reported TED for photon excitation energies in this region.⁵³ The vertical bars represent the maximum available energy for the CH₃⁺(X³A₁⁺) + I(³Pₓ/₂) (Fig. 3b) and CH₃⁺(X³A₁⁺) + I(³Pₓ/₂) (Fig. 3d) channels. If we consider photo-ionization into CH₃I⁺(X) in its ground ro-vibrational state, the available energy will be given by:

\[ E_{av} = (IP + h\nu) - E_D \]  

where hν is the excitation photon energy of \( \lambda_{exc} \) (here, \( \lambda_{exc} = \lambda_{ion} \)) and \( E_D \) is the dissociation energy of CH₃I⁺: 12.18 eV and 12.90 eV for the CH₃⁺(X³A₁⁺) + I(³Pₓ/₂) and CH₃⁺(X³A₁⁺) + I(³Pₓ/₂) channels, respectively. IP represents the ionization potential, here 9.54 and 10.16 eV for \( \lambda_{exc} \) and \( \lambda_{ion} \), respectively.⁵⁴,⁵⁵ We note, in addition, that the possible photodissociation of the 6p Rydberg state following two-photon absorption at 339.34 nm has been considered and would give rise to structures at higher energies that were not observed in all performed experiments.

The portion of the TED lying at values below the available energy in Fig. 3b and d corresponds to fragments produced

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**Fig. 2** Orbitals contained in the selected active space calculation CAS(5,4) in Frank–Condon geometry.

**Fig. 3** (a and c) Abel inverted velocity map images of CH₃⁺ (a) and I⁺ (c) ions from the methyl iodide photoexcitation in a one-colour experiment at 339.34 nm. (b and d) Corresponding translational energy distributions obtained from the angular integration of the inverted images (a and c).
with internal energy; on the other hand, the portion of the TED at higher energies is associated with fragments produced in the dissociation of internally excited CH₃I⁺ ions. Since the CH₃⁺ species is detected as it is produced, the observed Boltzmann distribution in Fig. 3b indicates the high ro-vibrational excitation of the nascent CH₃⁺ ion, a quite usual fact in dissociative multiphoton ionization (MPI) processes. In contrast, Fig. 3d indicates a significant contribution to the CH₃(X²A₂⁺) + I⁺(³P₂) channel from internally excited CH₃I⁺ ions.

Fig. 4a presents the VMI inverted image of the CH₃⁺ ion produced in a two-colour experiment where the CH₃I⁺ cation is firstly produced using three photons at 339.34 nm and the cation subsequently dissociated after excitation with a photon at 260 nm. One-colour contributions to the raw image coming from each laser have been carefully subtracted prior to inversion. The image presents a low-recoil highly anisotropic structure, similar to the one observed in Fig. 3a, which denotes a typical dissociative MPI process. However, a weak anisotropic ring with a clear parallel character is observed in this case, which can be attributed to the one-photon dissociation of CH₃I⁺ at 260 nm. The corresponding TED is obtained by angular integration of the inverted images (a and c). The I⁺ ion image recorded under the same conditions is presented in Fig. 4c. Clearly, the observed structure can be assigned to the formation of CH₃⁺ ions in correlation with the spin–orbit excited iodine atoms, I⁺(³P₁/₂), produced from the dissociation of ground state CH₃I⁺(X²E₃/₂). Since the observed peak represents ≈4% of the MPI signal located at the centre of the image, in order to investigate the peak profile, the energy region above 0.8 eV, which avoids the MPI feature, is represented separately in detail in Fig. 4b. The vertical solid line in Fig. 4b represents, therefore, the available energy for the CH₃I⁺(X²E₃/₂) + I⁺(³P₁/₂) channel. The narrow structure observed is developed towards energies above the channel reference, which indicates that the process involves some vibrational excitation of the CH₃I⁺(X²E₃/₂) parent ion. Although the photoelectron spectrum (PES) and thus the vibrational distribution in the CH₃I⁺(X) ion produced by the (2 + 1) REMPI scheme could not be measured in the present experiments, the PES for this transition was reported by Dobber et al. It clearly shows the main formation of CH₃I⁺(X²E₃/₂, all ν = 0) as expected taking into account the forecast Franck–Condon (FC) factors since the geometry of the CH₃⁺ cation is similar to that of the neutral CH₃I(X). The broadening characterizing the structure in Fig. 4b has been tentatively attributed to the C–I stretch mode (ν₃) which is the most plausible vibrational mode taking part in the C–I bond cleavage. The PES measured by Dobber et al. indeed presents a contribution assigned to the CH₃I⁺(X, ν₃ = 1) formation by the (2 + 1) REMPI scheme. The ro-vibrational distribution of the observed structure in Fig. 4b will, however, also depend on the FC factors between the ground CH₃I⁺(X²E₃/₂) and the excited state and thus cannot be deduced from the relative intensity of the different vibrational levels in the PES. The dashed lines in Fig. 4b represent the available energy for the CH₃⁺ fragment produced in the photodissociation of CH₃I⁺(X²E₃/₂, ν₃) cations. The observed broad peak corresponds to the photodissociation of vibrationally excited CH₃I⁺(X²E₃/₂,ν₃) cations between ν₃ = 0 and 3 with a maximum at ν₃ = 1. On the other hand, the rapid fall of the distribution towards the left side of the reference indicates that the CH₃⁺ fragment is produced in its ground vibrational state. The lack of vibrational excitation in the fragment together with the high anisotropy observed (discussed later), suggests that the narrow ring should be attributed a priori to a direct and rapid dissociation process.

The I⁺ ion image recorded under the same conditions is presented in Fig. 4c. Only a weak signal is observed at the centre of the image, which may be associated with a dissociative multiphoton ionization process. Although the pump and probe signal is significantly low in this case, the contribution of each laser alone has been carefully subtracted. The vertical bar represents the maximum available energy for one-photon dissociation at 260 nm of CH₃I⁺(X²E₃/₂) giving rise to CH₃(A²A₂⁺) + I⁺(³P₂) products. The TED is qualitatively similar to the one observed at 339.34 nm, involving an important ro-vibrational excitation of the CH₃ radical co-fragment. In contrast to the CH₃⁺ ion image (Fig. 4a) no other feature is observed, although from an energetic point of view, the photon energy would permit the excitation of CH₃I⁺ to the second B absorption band and then dissociation into CH₃(A²A₂⁺) + I⁺(³P₂). Thus, at this photon energy the I⁺ ion...
channel could require an energetic barrier to be overcome or an upper excited state to be populated.

The inverted images for CH\textsubscript{3}\textsuperscript{+} and I\textsuperscript{+} ions from the CH\textsubscript{3}I\textsuperscript{+} cation photodissociation at 250 nm are depicted in Fig. 5a and c, respectively. One-colour contributions to the raw image coming from each laser have been carefully subtracted prior to inversion. Similarly to Fig. 4a, the CH\textsubscript{3}\textsuperscript{+} image presents a strong anisotropic broad structure in the centre and weaker anisotropic rings with parallel character. Analogous structures are observed in this case in the I\textsuperscript{+} image (Fig. 5c) with an outer broad anisotropic ring with parallel character. The anisotropic structure in the centre is in both cases associated with a dissociative MPI process characterized by a strong ro-vibrational excitation of the fragment detected or, in the case of the I\textsuperscript{+} ion, the CH\textsubscript{3} co-fragment. Like in the one-colour 339.34 nm experiment, the Boltzmann distribution is measured for the MPI contribution from the two-colour experiments. Its characteristics do not vary indeed with the dissociation photon wavelength.

Fig. 5b and d show the TEDs corresponding to the CH\textsubscript{3}\textsuperscript{+} and I\textsuperscript{+} images. The corresponding energy regions where the observed rings appear are shown in detail. The patterns observed for the dissociation of CH\textsubscript{3}I\textsuperscript{+} into CH\textsubscript{3}\textsuperscript{+} at 260 nm (see Fig. 4b) are reproduced here at 250 nm. First, the anisotropic ring can be attributed to the formation of CH\textsubscript{3}\textsuperscript{+} ions in correlation with I*(2P\textsubscript{1/2}) atoms. Second, the CH\textsubscript{3}\textsuperscript{+} fragments are produced internally cold, but from vibrationally excited CH\textsubscript{3}I\textsuperscript{+}(X\textsubscript{\textit{3}}\textsubscript{E}/\textsubscript{3}) parent ions. According to the limits for vibrational excitation of CH\textsubscript{3}I\textsuperscript{+} in the \( \nu_3 \) mode (represented by dashed lines in Fig. 5b), the CH\textsubscript{3}\textsuperscript{+} ion TED shows a maximum for \( \nu_3 = 0 \) and 1 and a shoulder for \( \nu_3 = 2 \), similarly to the results obtained at 260 nm. In contrast to the results at 260 nm, the TED obtained for the I\textsuperscript{+} ion at 250 nm shows a broader and unstructured peak at around 1.6 eV (corresponding to the ring with parallel character observed in the image of Fig. 5c), which is characterized by a full-width-half-maximum (FWHM) of \( \approx 0.3 \) eV. As in the case of the CH\textsubscript{3}\textsuperscript{+} ion, the structure is associated with the dissociation of vibrationally excited CH\textsubscript{3}I\textsuperscript{+} ions, and is tentatively assigned to the vibrational activity in the \( \nu_3 \) mode.

Fig. 6a–d show the results of the photodissociation of the CH\textsubscript{3}I\textsuperscript{+} cation at 242 nm yielding CH\textsubscript{3}\textsuperscript{+} and I\textsuperscript{+} ions. Similar results to those obtained at 250 nm are found in this case for both photofragments: an unstructured strong anisotropic signal in the centre of the image and anisotropic rings with parallel character. Despite the lack of resolution in the associated TEDs (shown in Fig. 6b and d), the anisotropic rings can be attributed to the dissociation of internally excited CH\textsubscript{3}I\textsuperscript{+}(X\textsubscript{\textit{3}}\textsubscript{E}/\textsubscript{3}, \( \nu_3 \)) molecules is responsible for the production of CH\textsubscript{3}\textsuperscript{+} ions, while a small inversion around \( \nu_3 = 1–2 \) is expected for the I\textsuperscript{+} ion. In fact, at 250 and 242 nm – the wavelengths at which an anisotropic ring is observed for the I\textsuperscript{+} channel – the FWHM of the recoiled structures reflects a stronger vibrational excitation of the parent CH\textsubscript{3}I\textsuperscript{+} compared to that of the CH\textsubscript{3}\textsuperscript{+} ion channel ( \( \approx 0.5 \) eV for I\textsuperscript{+} and \( \approx 0.1 \) eV for CH\textsubscript{3}\textsuperscript{+}). For both dissociation channels, the FWHM does not show a dependence on the excitation energy.

The branching ratio of the recoiled peak with respect to the MPI signal at the centre of the image increases with the dissociation photon energy in both cases. For the CH\textsubscript{3}\textsuperscript{+} channel, the recoiled peak increases from 4% of the MPI signal at 260 nm to \( \approx 25\% \) at 242 nm; for the I\textsuperscript{+} channel, the recoiled contribution represents \( \approx 7\% \) of the MPI signal at 250 nm and 12% at 242 nm.
It is important to mention that the displacement in energy of the recoiled peak observed for both I$^+$ and CH$_3$I$^+$ ion channels as a function of the excitation photon wavelength confirms a one-photon dissociation process of the CH$_3$I$^+$(X$^2E$3/2) ion.

The angular distributions for the CH$_3$I$^+$ ion obtained by radial integration of the images depicted in Fig. 3a, 4a, 5a and 6a are presented in Fig. 7. The angular distribution shown in Fig. 7a corresponds to the broad low-recoiled anisotropic structure measured at 339.34 nm, while at 260, 250 and 242 nm, the angular distributions correspond to the anisotropic ring with parallel character. All angular distributions show a similar strong alignment along the laser polarization axis (parallel distributions) and are fitted using:

$$I(\theta) \propto \sum_{k=1}^{n} \beta_{2k} P_{2k}(\cos \theta)$$  \hspace{1cm} (6)

where $\theta$ is the angle between the photofragment recoil velocity and the photolysis laser polarization direction, $n$ is the number of absorbed photons, $\beta_{2k}$ is the anisotropy parameter and $P_{2k}$ represents the Legendre polynomial. We note that it is necessary to take into account all the absorbed photons from both the ionization laser and the dissociation laser, so that $n = 4$ for the main process studied here (3 for the one-colour experiment). Up to four anisotropy parameters could be needed, therefore, to characterize the angular distribution. The obtained $\beta$ anisotropy parameters are summarized in Table 1. For all wavelengths, the angular distributions for the CH$_3$I$^+$ ion are characterized by two anisotropy parameters, with values $\beta_2 \approx 1.6$ and $\beta_4 \approx -0.4$ for the narrow structure. The obtained parameters are in agreement with a first two-photon transition to the 6p Rydberg state characterized by a parallel orientation of the C–I bond with respect to the polarization axis. The first three-photon transition generates an ensemble of CH$_3$I$^+$ ions with the internuclear C–I axis aligned along the polarization axis, the $X$ axis. Since in the $XX$ polarization configuration, as used in this work, both pulses are polarized along the same axis, the dissociation pulse would, therefore, favour transitions along the C–I bond. In other words, if the dissociation takes place through a parallel transition, the process would be enhanced and high $\beta_2$ parameters are expected. A deeper interpretation of the angular distributions cannot be performed at this level. Considering $n$ photons, the ion angular distribution for a dissociation process results from the $n$ bound-to-bound transitions, while for a dissociative ionization process, such as those reported here, this angular distribution can be described as the result of the $(n - 1)$ bound-to-bound

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**Fig. 7** Angular distributions of CH$_3$I$^+$ ions from the methyl iodide photoexcitation at 339.34 nm (a) and in two-colour experiments at 339.34 nm and 260 nm (b), at 250 nm (c) and at 242 nm (d), obtained from the radial integration of the inverted images in Fig. 3a, 4a, 5a and 6a, respectively. Open circles: experimental points. Solid line: fit to eqn (6).

**Table 1** $\beta$ anisotropy parameters obtained from the fit of the angular distributions presented in Fig. 7 and 8

<table>
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<th>$\lambda_{dis}$ (nm)</th>
<th>CH$<em>3$I$^+$ + I$(^2P</em>{1/2})$</th>
<th>CH$_3$ + I$(^2P_3)$</th>
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<tr>
<td>339</td>
<td>1.84</td>
<td>1.50</td>
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<tr>
<td>260</td>
<td>1.53</td>
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<tr>
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</tr>
<tr>
<td>242</td>
<td>1.67</td>
<td>2.66</td>
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transitions between the valence states plus the effect of the photoionization reaction. Modelization of the angular distribution taking into account the 2-photon transition in the REMPI scheme as well as the photoionization reaction (through the dipole matrix elements) and the last bound-to-bound transition from CH$_3$I$^+$(X$^2$E$_{3/2}$) could help to extract the whole information on the reaction pathway.$^{54,55}$

Fig. 8 presents the angular distributions for the I$^+$ channel obtained through the angular radial integration of the images shown in Fig. 3c, 5c and 6c. The angular distribution shown in Fig. 8a corresponds to the broad, low-recoiled anisotropic structure measured at 339.34 nm, while at 250 and 242 nm, the angular distributions correspond to the anisotropic rings. We note that the angular distribution for the two-colour experiment at 260 nm is not presented here since the low pump–probe signal does not permit the angular information to be extracted properly. All distributions are strongly anisotropic, reflecting an important alignment of the molecule along the polarization axis of the ionizing pulse. Three $\beta$ asymmetry parameters are required to characterize these distributions using eqn (6). In particular, $\beta_3$ values above 2 have been found for the anisotropic ring at 250 and 242 nm.

### Theoretical results

Table 2 shows the energy of the electronic states of the CH$_3$I$^+$ cation at two different geometries: the minimum of the neutral molecule obtained at the MP2 level and in the dissociation limit referred to as the ground state energy of the neutral molecule. The active space at the equilibrium distance for the neutral molecule is depicted in Fig. 2, where the geometry corresponds to the $C_3v$ symmetry at a C–I distance of 2.133 Å, a C–H distance of 1.077 Å, and an I–C–H angle of 107.6 degrees. In order to calculate the ionization energy, the MRClSD using the same active space and including 4 singlets (3 of symmetry $A_1$ and 1 of symmetry $A_1''$) and 3 triplets (2 of symmetry $A_1$ and 1 of symmetry $A_2''$) was calculated for the neutral molecule. The dissociation limit was defined by a restricted optimization (C–I distance of 10 Å) at the CASPT2 level (considering only the first three doublets to describe correctly the first ionization limit) in the ground state of the cation, where the cation of the methyl fragment is planar at a C–H distance of 1.068 Å. Since the calculated ionization energy

<table>
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<th>State number</th>
<th>FC geometry</th>
<th>Dissociation energy, $E_D$ (eV)</th>
<th>Dissociation limit</th>
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<td>1</td>
<td>9.10</td>
<td>12.12</td>
<td>CH$<em>3$I$^+$ + I($^3$P$</em>{2/2}$)</td>
</tr>
<tr>
<td>2</td>
<td>9.10</td>
<td>12.12</td>
<td>I$^+$(3P$_2$) + CH$_3$</td>
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<td>CH$<em>3$I$^+$ + I($^3$P$</em>{1/2}$)</td>
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Fig. 8 Angular distributions of I$^+$ ions from the methyl iodide photoexcitation at 339.34 nm (a), and in a two-colour experiment at 339.34 nm and 250 nm (b) and at 242 nm (c), obtained from the radial integration of the inverted images in Fig. 3c, 5c and 6c, respectively. Open circles: experimental points. Solid line: fit to eqn (6).
is 9.10 eV and the first dissociation limit is at 12.12 eV, it is not possible to obtain ionization for the first electronic state of the cation. In fact, it is required to excite at least to the fifth electronic state (12.37 eV) to overpass the dissociation energy.

Potential energy surfaces (PESs) of the first electronic states of CH$_3$I$^+$ in the $C_3v$ symmetry group along the C–I dissociative coordinate were calculated, and are presented in Fig. 9 and 10. In Fig. 9, the methyl moiety is considered to have a rigid pyramidal geometry in all calculated states. The calculations performed without taking into account the spin–orbit coupling, shown in Fig. 9a, provide information about the symmetry of the electronic states involved. In agreement with the measured HeI photo-electron spectra previously reported, the CH$_3$I$^+$ cation presents a bound ground state and a slightly bound first excited state followed by a manifold of purely repulsive states associated with the second absorption $B\bar{g}$ band.

The $^2E$ ground electronic state in the $C_{3v}$ symmetry group corresponds to a combination of $^2\tilde{A}$ and $^2\tilde{A}'$ states in the $C_2$ symmetry group as it can be observed in the figure. Similarly, the first excited state $^3\tilde{A}_1$ in $C_{3v}$ becomes a $^2\tilde{A}$ state in $C_2$. In the literature, the second electronically excited state $B\bar{g}$ located between 4.5 and 6.5 eV with respect to the CH$_3$I$^+$($^X\tilde{E}$) ground state is identified as a $^3\tilde{E}$ state corresponding to $^2\tilde{A}$ + $^2\tilde{A}'$ states in the $C_2$ symmetry group. However, in the present calculations, the manifold of repulsive states accessible through vertical transitions from the ground state at $\approx$ 5 eV is composed of $^2\tilde{A}'$, $^1\tilde{A}'$ and $^2\tilde{A}'$ electronic states followed by several $^2\tilde{A}$ and $^2\tilde{A}'$ states at higher energies. The computed PESs shown here in Fig. 9a are in relatively good agreement with the ones reported recently by Vallance and co-workers for the ethyl iodide cation.

In contrast to the PESs shown in Fig. 9a, the computed PESS taking into account the spin–orbit coupling depicted in Fig. 9b do not allow us to identify the symmetry of the different electronic states but represent more accurate dissociation limits. The degeneracy of the electronic states disappears and a more complex picture arises. The ground electronic state is split into two spin–orbit compounds: $^2E_{1/2}$ and $^2E_{3/2}$. The slightly bound first electronic state is clearly identified around 2.75 eV in the Franck–Condon region associated with the ground state CH$_3$I$^+$($^X\tilde{E}$) and correlates with the CH$_3$ + I$^+$($^2P_3/2$) channel, which appears as the first dissociation limit. At higher energies, the complexity of the repulsive states manifold is considerably enhanced.

As mentioned above, the photodissociation of methyl halide cations is governed by the geometry change in the methyl moiety between the molecular ion (pyramidal) and the radical (planar). Fig. 10 presents, therefore, the PESs computed taking into account such relaxation of the methyl geometry, first without the spin–orbit coupling [Fig. 10a] and second including it [Fig. 10b]. The geometry relaxation does not alter the symmetry of the electronic states (Fig. 9a and 10a), but the order of the different states varies considerably, especially outside the Franck–Condon region. The most remarkable result is associated with the differences in the potential energy of the fragments at long C–I distances (dissociation limits) as summarized in Table 3. In particular, in Fig. 10b, the first dissociation limit associated with the adiabatic dissociation in the ground state of the ion is the CH$_3$ + I$^+$($^2P_{3/2}$) channel, while in the rigid case (Fig. 9b), the first dissociation limit was associated with the I$^+$ ion formation. Moreover, an interesting avoided crossing appears at $R_C$ around 3.8 Å in Fig. 10b. A similar avoided crossing was, in fact, predicted by Locht et al. as well as by our group in a femtosecond photodissociation study using non-resonant detection at 800 nm. The computed dissociation limits summarized in Table 3 are compared to the ones previously reported theoretically by Locht et al. and experimentally by Wang et al. The values obtained here for the calculation taking into account the relaxation of the methyl moiety are significantly higher than those from the literature. In the dissociation region, i.e. at long C–I distances, 36 electronic states (composed of 12 doublets and 4 quadruplets) are confined in around 4 eV, whereas the same number of states at the Frank–Condon region describes 12 eV. It is then expected that the averaging of the wavefunction will not affect both geometries in the same way.
way, which is reflected in the dissociation energy as shown in Table 3.

Although the symmetry of the electronic states cannot be deduced when we take into account the spin–orbit coupling in the calculations, the elements of the dipole moment matrix for the transition from CH₃⁺(^X̂₂E_{3/2}) to different electronic states have been computed in the C₃ᵥ symmetry with the C–I bond along the Z axis. Inspection of the absolute values of the dipole moment for the three defined axes allows us to determine the parallel or perpendicular character of each transition. A larger value for the Z axis reflects a favoured transition when the C–I bond is parallel to the light polarization axis and, therefore, a parallel distribution is expected experimentally. On the other hand, large values on the X and/or Y axes highlight an expected perpendicular distribution. The transition to the slightly bounded first excited state, the so-called Ã state, appears to be mostly perpendicular, as it was considered in previous reported work.¹⁰,²⁴,²⁶,²⁷ In contrast, the manifold of repulsive states constituting the so-called B̃ state is composed of electronic states with different symmetry, while in the literature the B ← X̂E transition is considered purely parallel. In particular, the transitions to the first repulsive states, represented by red dashed lines in Fig. 9b, are mostly characterized by a perpendicular orientation of the transition dipole moment while the transition to the repulsive state represented by an orange line is purely parallel.

**Discussion**

The measured angular and translational energy distributions can provide a picture of the dissociative ionization processes based on the PES scheme and the symmetries deduced. CH₃⁺ ions in the ^X̂₂E_{3/2} ground state are produced using a (2 + 1) REMPI scheme at 339.34 nm ³¹ through the 5p^p'[6p] Rydberg state two-photon transition, which is characterized by a transition dipole moment parallel to the polarization axis. In the one-colour experiment, the absorption of a fourth 339.34 nm photon would lead to the Ã₂A₁ ← X̂E excitation. Although this first state is slightly bound (see Fig. 9 and 10), the excess energy provided by the 339.34 nm photon should be enough to overcome the barrier. Fig. 3 clearly shows that the only contribution to the images for both fragments is the MPI dissociation process of the CH₃I⁺ ion. The Boltzmann shapes of the associated TEDs (for all wavelengths studied in this work) result as a consequence of the fact that the energy provided by the photons is relaxed through internal couplings towards the lower excited states, where a CH₃I⁺ ion that is highly ro-vibrationally excited is dissociated. The high anisotropy observed is a consequence of the strong molecular alignment produced by the four absorbed photons. The lack of a fast dissociation process through the Ã₂A₁ state is explained due to the alignment of the CH₃⁺ ion along the intermolecular axis produced by the ionizing step. Since the transition dipole moment of the two-photon transition lies parallel to the C–I bond (parallel transition), the REMPI scheme used to produce the CH₃⁺(^X̂₂E_{3/2}) ions generates, in turn, an ensemble of molecules with the C–I internuclear axis aligned along the light polarization direction. The Ã₂A₁ ← X̂E transition, on the other hand, possesses perpendicular character, which means that the

### Table 3

Calculated dissociation limits, considering the methyl moiety with a rigid pyramidal geometry or the relaxation of this radical to a planar geometry, with respect to the CH₃⁺(^X̂₂E_{3/2}) energy compared to those from the literature.

<table>
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<tr>
<th>Products</th>
<th>Dissociation energy, E_D (eV)</th>
<th>This work</th>
<th>Literature</th>
</tr>
</thead>
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<td></td>
<td>Without relax</td>
<td>Relax</td>
<td></td>
</tr>
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<td>3.00</td>
<td>2.45²⁴</td>
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<td>CH₃⁺ + I(1D₄)</td>
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<td>CH₃⁺ + I(1S)</td>
<td>7.43</td>
<td>7.09</td>
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Fig. 10 Computed MRCISD potential energy surfaces for the methyl iodide cation relaxing the methyl moiety in the ground cationic state, using CASPT2 (see text).
corresponding transition dipole moment is perpendicular to the C-I bond axis and, therefore, to the polarization vector of the fourth photon. The crossed orientation of both vectors reduces considerably – no signal is observed, actually – the probability of the absorption process leading to a fast photodissociation through the $A^2\Sigma^+$ state.

In the two-colour experiments, the origin of the dissociative MPI anisotropic signal appearing in the centre of the images does not differ from that of the one-colour experiment. Regarding the observed recoiled structures, the mechanism is clearer. The CH$_3$I$^+$($X^2E_{1/2}$) ions formed in the first step by the three-photon absorption at 339.34 nm are later excited by the dissociation pulse to the so-called $B$ manifold of states, a manifold of pure repulsive states, as observed in Fig. 10b, leading to the direct dissociation of CH$_3$I$^+$ into the CH$_3$($X^2A_1^+$) + I($2P_{1/2}$) or CH$_3$ + I($3P_2$) channels. Tentatively, and bearing in mind that the position of the computed electronic states of the ion at the Franck–Condon region is not highly accurate, the dissociation laser pulse could lead to the population of the excited state represented by the orange line in Fig. 10b. The transition to this state from the CH$_3$I$^+$($X^2E_{1/2}$) ion is characterized by a parallel dipole moment in agreement with the measured angular distributions. In addition, this excited state correlates adiabatically with the CH$_3$I$^+$($X^2E_{1/2}$) + I($2P_{1/2}$) channel and non-adiabatically with the CH$_3$ + I($3P_2$) channel through an avoided crossing, observed at $R_{C-I} = 3.8$ Å in Fig. 10b. Such a mechanism would explain the anisotropic structures observed in the images of the CH$_3$I$^+$ and I$^+$ ions. The experimental TEDs show a narrow structure located at the expected maximum available energy for these channels in agreement with a direct and rapid dissociation process. A possible vibrational excitation in the $\nu_3$ mode, the symmetric C-I stretch, of the CH$_3$I$^+$($X^2E_{1/2}$) ions may favour the dissociation process – without ruling out the participation of other less energetic modes – and in particular the CH$_3$ + I($3P_2$) channel through the crossing. The participation of CH$_3$I$^+$ hot bands would explain the broader structures observed for the I$^+$ ion compared to those obtained for the CH$_3$I$^+$ ion. At the lower dissociation energy corresponding to 260 nm, the CH$_3$ + I($3P_2$) channel is not observed experimentally, suggesting that the excitation energy might not be enough to allow the transfer of population in the avoided crossing.

Conclusions

The one-colour and two-colour photodissociation dynamics of the CH$_3$I$^+$ cation have been studied using the velocity map imaging technique and nanosecond laser pulses. A first laser pulse is used to ionize CH$_3$I via a (2 + 1) REMPI scheme through the 5$p_7$ $\leftrightarrow$ 6$p$ Rydberg state two-photon transition. The CH$_3$I$^+$($X^2E_{1/2}$) ions produced are subsequently excited at several wavelengths. The reported translational energy distributions for the CH$_3$I$^+$ and I$^+$ ions highlight two different dissociation processes, characterized by the Boltzmann-type unstructured distribution at low energies as well as a recoiled narrow structure at higher energies. In addition, the measured angular distributions show a large alignment of the C-I bond of the molecule along the light polarization axis associated with both processes.

High level ab initio calculations have been performed in order to obtain a deeper understanding of the photodissociation dynamics of the CH$_3$I$^+$ ion. Direct dissociation of a repulsive state from the manifold of excited states representing the $B$ excited state manifold leads to the formation of CH$_3$($X^2A_1^+$) + I($2P_{1/2}$), while the CH$_3$ + I($3P_2$) channel is populated through an avoided crossing outside the Franck–Condon region. The available energy is, therefore, totally converted into translational energy and, thus, a recoiled narrow structure characterizes this fast and direct dissociation process. In contrast, an indirect process involving energy relaxation from highly excited electronic states to the ground state is most probably responsible for the observed Boltzmann-type distributions.

Further experiments on the photodissociation of the CH$_3$I$^+$ cation using an electron–ion coincidence technique could allow a deeper understanding of the dissociation mechanisms to be obtained.

Acknowledgements

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Notes and references


