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## New insights in the photodissociation of methyl iodide at 193 nm: Stereodynamics and product branching ratios

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The stereodynamics of methyl iodide photodissociation after excitation at 193 nm has been studied using a combination of slice imaging and resonance enhanced multiphoton ionization (REMPI) detection of the methyl and iodine products. A weak anisotropic ring appearing in the image corresponding to vibrationally excited CH<sub>3</sub>(*v*<sub>1</sub>=1) confirms the production of ground state I(<sup>2</sup>P<sub>3/2</sub>) atoms at this excitation wavelength as a signature of the predissociation channel reported previously [M. G. González *et al.*, *J. Chem. Phys.*, 2011, **135**, 021102] tentatively assigned to the coupling between the *B*-band <sup>3</sup>R<sub>1</sub> Rydberg state and the *A*-band <sup>1</sup>Q<sub>1</sub> repulsive state. Direct REMPI detection of ground state iodine atoms indicate that most of the I(<sup>2</sup>P<sub>3/2</sub>) species are produced in correlation with highly internally excited methyl radicals, in excellent agreement with the recent results of Xu and Pratt [Xu *et al.*, *J. Chem. Phys.*, 2013, **139**, 214310; Xu *et al.*, *J. Phys. Chem. A*, 2015, **119**, 7548]. From comparison between the CH<sub>3</sub>(*v*) second order Dixon's bipolar moments β<sub>0</sub><sup>2</sup>(20), β<sub>0</sub><sup>0</sup>(22), β<sub>0</sub><sup>2</sup>(02) and β<sub>0</sub><sup>2</sup>(22) measured in this work with those reported previously for the *B*-band origin and the *A*-band, a general picture of the CH<sub>3</sub>I photodissociation stereodynamics in terms of different effects, such as the breakdown of the unique recoil direction (URD) approximation, the non-adiabatic curve crossings and the depolarization induced by the parent molecule rotation, is drawn.

### 1 Introduction

Angular distributions extracted from sliced images are easily fitted to the known expression for a one-photon dissociation process and (n+m) resonance enhanced multiphoton ionization (REMPI) detection:<sup>1-4</sup>

$$I(\theta) = \frac{\sigma}{4\pi} \sum_{i=0}^{2n+2} \beta_i P_i(\cos \theta) \quad (1)$$

where  $\theta$  is the angle between the photofragment recoil velocity and the photolysis laser polarization directions,  $\sigma$  is the absorption cross section,  $\beta_i$  are anisotropy parameters which reflect the dissociation dynamics and the photofragment polarization,  $P_i$  are the Legendre polynomials of *i*-th order and *n* is the number of photons of the resonant step of the REMPI process. As a result of the different forces and torques exerted on the parent molecule during the dissociation process, the rotational angular momen-

tum of the fragments, *J*, can be oriented or aligned along a preferential spatial direction, the effect known as photofragment polarization. The fragment recoil velocity *v* and transition dipole moment  $\mu$  directions are the natural laboratory frame references for the photofragment angular momenta. In a semiclassical picture, the β<sub>0</sub><sup>K</sup>(*k*<sub>1</sub>*k*<sub>2</sub>) Dixon's bipolar moments (BM)<sup>2</sup> quantify such vector correlations. When linearly polarized pump and probe laser pulses are used, the experiment is not sensitive to photofragment orientation<sup>4</sup> and, therefore, the index *K* takes only even values. The β<sub>0</sub><sup>2</sup>(20), β<sub>0</sub><sup>0</sup>(22) and β<sub>0</sub><sup>2</sup>(02) moments represent respectively, the  $\mu - v$ ,  $v - J$  and  $\mu - J$  first order alignment correlations while the β<sub>0</sub><sup>2</sup>(22) moment represent the triple  $\mu - J - v$  correlation. High order terms are obtained for values of  $J \geq 2$ .<sup>2</sup> With the exception of the analysis of the dissociation anisotropy, characterized by the β anisotropy parameter, vector correlations on methyl iodide (CH<sub>3</sub>I) photodissociation are scarcely reported in the literature due, in part, to the low sensitivity of the REMPI technique to polarization effects in the methyl product. Neutral CH<sub>3</sub> fragments are efficiently detected through the *Q* branch of the 3*p*<sub>z</sub> and 4*p*<sub>z</sub> transitions through two photon processes. The CH<sub>3</sub> *Q* branch is, however, spectrally congested and cannot be resolved for individually rotational states. In addition, the expressions reported

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in the literature for the  $s_k$  sensitivity factors are not valid in the case of  $\Delta J=0$  because they incorporate  $P_k$  line strength factors incompatible with the concomitance of linearly polarized light and  $\Delta J=0$ .<sup>5-7</sup>

The rotational spectra of the CH<sub>3</sub> and CD<sub>3</sub> radicals produced in the 266 nm photodissociation of CH<sub>3</sub>I and CD<sub>3</sub>I, respectively, were measured through different  $3p_z$  and  $4p_z$  (2+1) REMPI transitions by Loo and coworkers using time-of-flight (TOF) detection.<sup>8</sup> The rotational branching ratios indicated that the CH<sub>3</sub>/CD<sub>3</sub> total angular momentum,  $N$ , lies perpendicular to the C<sub>3</sub> axis ( $K=0$ ). The first quantitative analysis on fragment rotational alignment was carried out by Janssen and co-workers, although restricted to the CD<sub>3</sub>I molecule.<sup>9</sup> Using the ion imaging technique, the authors described the CD<sub>3</sub> rotational alignment in terms of an axial impulsive dissociation model, where the CD<sub>3</sub> product presents a tendency to inherit the  $K$  quantum number of the parent molecule.<sup>9</sup> Kim and co-workers proposed a minor  $\Delta K=\pm 3$  propensity in addition to the proposed  $\Delta K=0$ .<sup>10</sup> Up-to-date there is only one report on vector correlations in the  $A$ -band photodissociation of CH<sub>3</sub>I, but as in the previous publications, the study was limited to excitation at the center of the absorption band.<sup>11</sup> In addition to the  $A_0^k$  polarization parameters, Dixon's BMs were reported based on TOF profiles measured at different polarization geometries for the CH<sub>3</sub>I and CD<sub>3</sub>I. The CH<sub>3</sub>I data was presented as a demonstration of a practical approach for the determination of  $\mu$ - $v$ - $J$  vector correlations in (2+ $n$ ) REMPI and TOF experiments.<sup>11</sup>

In a recent work, we presented the first stereodynamical study of the CH<sub>3</sub>I photodissociation in the  $B$ -band.<sup>12</sup> The four  $k=2$ -order BMs determined for the band origin and for the overlapping  $^3A_1(E)$  state of the  $A$ -band were interpreted in terms of the vibrational couplings that take place in the absorption process.

The dissociation anisotropy parameter  $\beta$  has deserved special attention, in particular in the  $A$ -band, due to the different transitions involved. Briefly, the first absorption band of CH<sub>3</sub>I consists of a broad featureless continuum ranging from 210 to 350 nm, with a maximum at about 260 nm.<sup>13</sup> Three states are accessible through dipole allowed transitions from the ground state: the  $^3Q_1$  and  $^1Q_1$  states (in Mulliken's notation)<sup>14</sup> through weak perpendicular transitions, and the  $^3Q_0$  state through a strong parallel transition.<sup>15</sup> Only the  $^3Q_0$  state correlates adiabatically with CH<sub>3</sub>( $\tilde{X}^2A_2$ )+I\*( $^2P_{1/2}$ ) products, while the  $^3Q_1$  and  $^1Q_1$  states correlate with CH<sub>3</sub>( $\tilde{X}^2A_2$ )+I( $^2P_{3/2}$ ). From now on we will use I\* and I to refer to I\*( $^2P_{1/2}$ ) and I( $^2P_{3/2}$ ), respectively, and CH<sub>3</sub> to refer to CH<sub>3</sub>( $\tilde{X}^2A_2$ ). Due to the rotational alignment of the CH<sub>3</sub> fragment, the  $\beta$  parameter has been traditionally measured from I\* data.<sup>16</sup> In our previous experiments on the photodissociation of CH<sub>3</sub>I in the  $A$ -band, the CH<sub>3</sub> angular distributions were fitted to the Legendre expansion given by eqn (1). A wavelength-dependent tendency was proposed for the dissociation anisotropy although the exact  $\beta$  values could not be extracted.<sup>17,18</sup> Such approach had been widely employed in the literature for methyl halides.<sup>19,20</sup> The anisotropy parameter associated to photodissociation in the  $B$ -band has attracted far less attention due to the fact that only one electronic transition takes place. The quantum yield for production of ground state iodine atoms,  $\Phi$ , defined

as  $[I]/[I^*]+[I]$ , constitutes a different issue, specially at 193 nm. The  $B$ -band covers the spectral interval ranging from 190 to 205 nm and, contrary to the  $A$ -band, which is purely composed of dissociative valence states, it exhibits clear vibrational structure, which denotes its bound nature.<sup>21</sup> The three first vibronic transitions from the ground state,  $0_0^0$ ,  $2_0^1$  and  $3_0^1$ , were studied by our group using femtosecond<sup>22,23</sup> and nanosecond<sup>24</sup> laser pulses. In those works, it was assumed that the two first vibronic levels,  $0_0^0$  and  $2_0^1$  are predissociated through the  $A$ -band  $^3A_1(E)$  state, which correlates asymptotically with CH<sub>3</sub> and I\* products, implying a  $\Phi=0$ . However, the CH<sub>3</sub>+I channel was observed at 199.11 nm, corresponding to the  $3_0^1$  vibronic transition, and was tentatively assigned to the non-adiabatic curve crossing between the  $^3R_1$  Rydberg state and the  $A$ -band  $^1Q_1$  state, which takes place at such high energies.<sup>24,25</sup> At 193 nm there is sensibly more data – due to the availability of excimer lasers – which has been thoroughly reviewed by Xu and Pratt.<sup>26</sup> In particular, Xu and Pratt<sup>26</sup> studied the 193 nm photodissociation of CH<sub>3</sub>I using velocity map imaging and one-photon ionization (in the VUV) of the I, I\* and CH<sub>3</sub> fragments. They carefully characterized the relative photoionization cross sections for I and I\* and found that the absolute photoionization cross sections for I is quite large at the wavelength used (118 nm), making of this an extremely sensitive detection method for ground state iodine atoms. Using this detection method, they found that the  $\Phi$  quantum yield was nonzero, but  $\Phi=0.07\pm 0.01$  at this excitation wavelength. Furthermore, they found that the observed I atoms were only compatible with production of highly internally excited CH<sub>3</sub> cofragments. In a more recent work, Xu and Pratt<sup>27</sup> carried out similar experiments but using a narrow-band tunable UV light between 201.2 and 192.7 nm to cover all vibronic transitions in the  $B$ -band. They found that for most excited vibronic levels,  $\Phi$  quantum yield was nonzero, but small ( $\Phi\leq 0.07$ ), and that the I channel is always associated with production of internally excited CH<sub>3</sub> radicals. Interestingly, the case of the  $3_0^1$  vibronic level was a clear exception, showing a considerably higher quantum yield,  $\Phi=0.13\pm 0.02$ , and not highly internally excited CH<sub>3</sub> fragments.

The main goal of the stereodynamical study carried out in this work using slice imaging and REMPI techniques is to present a unified picture of the photodissociation dynamics of CH<sub>3</sub>I at 193 nm – including  $\Phi$ , fragment internal states and dissociation anisotropy – through the information provided by the  $\beta_0^2(20)$ ,  $\beta_0^0(22)$ ,  $\beta_0^2(02)$  and  $\beta_0^0(22)$  Dixon's bipolar moments. The paper is organized as follows. In Sec. II the experimental approach is presented. Section III describes the experimental results which are discussed in Sec. IV. Finally, Sec. V is dedicated to present the most important conclusions of the work.

## 2 Experimental

The set up employed in the slice imaging experiments has been described in detail previously<sup>7,28,29</sup> and only a brief description is presented here. A molecular beam is created by expanding a gas mixture of CH<sub>3</sub>I in He (10%, 1 atm backing pressure) into vacuum using a piezoelectronic pulsed valve. The beam is skimmed and collimated to a diameter of 2 mm prior to intersecting a focused laser beam at right angles. CH<sub>3</sub>I excitation is carried out

at 193 nm using an excimer laser (Lambda Physik COMPEX, operating with ArF), linearly polarized using Brewster reflection, and the detection of the  $\text{CH}_3(v=0)$  products at 333.45 nm –  $Q$  branch of the  $3p_z$  transition for a two-photon process – by a MOPO laser (Spectra-Physics 730D10) pumped by a Nd:YAG laser (Spectra-Physics Pro Series 450), delayed 10 ns with respect to the pump pulse. Detection of  $\text{CH}_3(v_1=1)$  and  $\text{CH}_3(v_2=1)$  is carried out at 333.9 and 329.4 nm, respectively. For the detection of  $\text{I}^2(\text{P}_{3/2})$  and  $\text{I}^*(\text{P}_{1/2})$  products, the probe laser was set to 304.64 and 305.57 nm, respectively, at the  $6p^4D_{1/2}$  and  $6p^4P_{3/2}$  transitions for two-photon processes. The generated  $\text{CH}_3^+$  or  $\text{I}^+$  ions are projected onto the position-sensitive detector system (two MCPs coupled to a phosphor screen). Slice images of  $\text{CH}_3^+$  or  $\text{I}^+$  are recorded using a 500 ns pulsed extraction delay applied on the repeller plate and an effective 10 ns detector gate on the front MCP. The images for  $\text{CH}_3(v=0)$ ,  $\text{CH}_3(v_1=1)$  and  $\text{I}^2(\text{P}_{3/2})$  have been recorded using four laser polarization configurations:  $X(\text{pump})X(\text{probe})$ ,  $XZ$ ,  $ZX$ , and  $ZZ$ , where  $X$  is perpendicular to the laser propagation axis ( $Y$ ) and  $Z$  is parallel to the molecular beam.

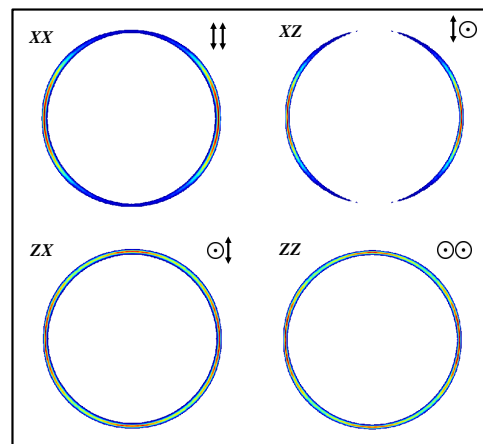
The  $XX$  images comprise alone all the information regarding the dissociation anisotropy and the orientation and/or alignment of the products. In the  $XZ$  images, the probe polarization vector lies perpendicular to the detection plane and, therefore, all the information related to the products angular momenta is lost. Similarly, the  $ZX$  images have lost the information related to the anisotropy of the dissociation process. The  $ZZ$  images do not contain any dynamical information and are used as a reference to avoid systematic errors, such as detector inhomogeneities. Thus, non-zero  $\beta_i^{ZZ}$  parameters extracted from the fit of the  $ZZ$  images to eqn (1) are taken as the instrumental function. In this work, we have followed the formalism described by North and co-workers to find the connection between the phenomenological  $\beta_i$  parameters and the Dixon's bipolar moments developed for the case of a  $(1+1')$  REMPI detection scheme.<sup>30,31</sup> For a  $(1+1')$  REMPI scheme, eqn (1) is truncated at  $i=4$ . In addition, since the  $XX$  images are the only ones which gather all the dynamical information of the one-photon absorption process, for the  $XZ$  and  $ZX$  polarization geometries, eqn (1) is truncated at  $i=2$ . Accordingly, the total number of  $\beta_i$  parameters is reduced to four, as required to determine the four Dixon's second-order bipolar moments in the high- $J$  limit.<sup>30</sup> For a  $(2+1)$  REMPI detection scheme, as the one used in the present work, the number of  $\beta_i$  parameters is increased to six. This is so because the  $\beta_4^{XZ}$ ,  $\beta_6^{XZ}$  and  $\beta_6^{ZX}$  coefficients are identically zero for a one-photon absorption process independently of the REMPI scheme employed, but, in principle,  $\beta_6^{XX}$  and  $\beta_4^{XZ}$  can take non-negligible values. In a previous publication,<sup>7</sup> we have proven that the formalism developed by North and co-workers for a  $(1+1')$  REMPI detection scheme is constrained only by the number of non-zero  $\beta_i$  parameters and, therefore, in some particular cases, it can be applied to higher order REMPI schemes, as in the present case. In the same publication, a detection sensitivity factor  $s_2=1.88$  for  $\text{CH}_3$  detection through the  $3p_z$  transition was calculated.<sup>7</sup> The recorded slice images of  $\text{CH}_3^+$  are quadrant symmetrized prior to extracting the kinetic energy and angular distributions. The kinetic energy distribution is calibrated using

the translational energy distributions of the  $\text{CH}_3$  products of the  $\text{CH}_3\text{I}$  photodissociation at 333.45 nm.

## 3 Results and discussion

### 3.1 Methyl images

Fig. 1 shows a series of sliced images for  $\text{CH}_3(v=0)$  recorded at the four different polarization configurations employed in this work. The images consist in a single high-recoiled ring, the characteristic feature of a fast photodissociation processes – either direct dissociation, or fast predissociation through a repulsive surface – with a polarization-dependent anisotropy.



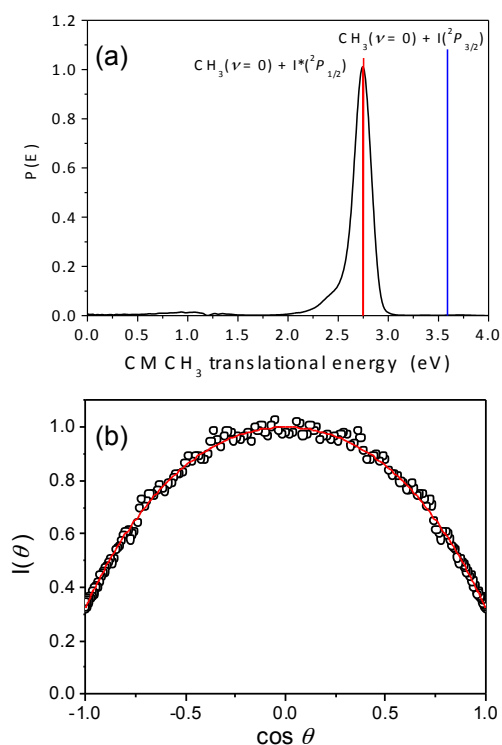
**Fig. 1** Sliced images for  $\text{CH}_3(v=0)$  fragments produced in the photodissociation of  $\text{CH}_3\text{I}$  at 193 nm taken at the different pump-probe polarization configurations  $XX$ ,  $XZ$ ,  $ZX$  and  $ZZ$ . The contribution from the probe laser alone (one-color pump-probe) has been carefully subtracted. At the top right side of each image the pump (left) and probe (right) polarizations are outlined. The  $Z$  axis is parallel to the molecular beam.

The  $XX$  image, which gathers all the possible dynamical effects involved in the process, shows a bias in the intensity distribution towards the equator suggesting an absorption step prior dissociation of perpendicular character. Such conclusion is confirmed by the  $XZ$  image distribution, which is insensitive to the photofragment polarization and reflects mostly the photodissociation anisotropy. In the  $XZ$  image the probe pulse is set perpendicular to the detector and, therefore, the angular momenta of the photofragments,  $J$ , are detected with equal probability independently of the recoil direction. The absence of signal at the poles of the  $XZ$  image, with respect to the same region in the  $XX$  image, indicates that the photofragment polarization effects are not irrelevant. The  $ZX$  image is insensitive to the photodissociation anisotropy and reflects primarily the photofragment polarization, but due to the variety of vector correlations and their effect on the product image, does not render usually significant information from visual inspection, and detailed quantitative analysis is needed. The  $ZZ$  image is insensitive to the intensity distribution generated in the photodissociation and detection processes, and, therefore, any variation from a perfect isotropic distribution is used to calibrate the intensity distribution of the  $XX$ ,  $XZ$  and  $ZX$

images. Angular integration of the  $XX$  image shown in Fig. 1 results in the translational energy distribution (TED) depicted in Fig. 2a. The vertical lines in the TED indicate the maximum available translational energy for the  $\text{CH}_3(v=0)+\text{I}({}^2P_{3/2})$  (blue) and  $\text{CH}_3(v=0)+\text{I}^*({}^2P_{1/2})$  (red) channels, given by:

$$E_{av}[\text{CH}_3] = \frac{m_{\text{I}}}{m_{\text{CH}_3}} [h\nu - D_0 - E_{SO}(\text{I}) + E_i(\text{CH}_3\text{I})] \quad (2)$$

where  $h\nu$  is the excitation photon energy,  $D_0$  the dissociation energy of  $\text{CH}_3\text{I}$ ,  $2.41 \pm 0.03$  eV<sup>16</sup>,  $E_{SO}$  the spin-orbit splitting of  $\text{I}({}^2P)$ ,  $0.943$  eV<sup>16</sup>,  $E_i$  the internal energy of the parent molecule (assumed to be zero) and  $m_{\text{I}}$  and  $m_{\text{CH}_3\text{I}}$  are the masses of  $\text{I}$  and  $\text{CH}_3\text{I}$ , respectively.



**Fig. 2** Center-of-mass  $\text{CH}_3(v=0)$  translational energy (a) and angular (b) distributions obtained by integration of the  $XX$  image shown in Fig. 1. The vertical lines in the TED indicate the maximum available energy for the  $\text{CH}_3(v=0)+\text{I}({}^2P_{3/2})$  (blue) and  $\text{CH}_3(v=0)+\text{I}^*({}^2P_{1/2})$  (red) channels. Clearly, no methyl radicals in correlation with ground state iodine atoms are observed (*i.e.*  $\Phi=0$ ). The red line superimposed to the angular distribution is the best fit to eqn (3) using  $\beta_2 = -0.552 \pm 0.003$ ,  $\beta_4 = -0.038 \pm 0.004$  and  $\beta_6 = 0$ .

The portion of distribution at the left of the maximum available energy corresponds to the internal energy transferred to the fragments in the process, while the portion at the right side indicates contribution from dissociation of vibrationally excited  $\text{CH}_3\text{I}$  present in the molecular beam,<sup>12,17</sup> which seems to be unimportant in the present case; furthermore, since we are detecting vibrational ground state  $\text{CH}_3$  fragments and given that the

$\text{I}({}^2P)$  spin-orbit term is included in eqn (2), the width of the TED only reflects  $\text{CH}_3(v=0)$  rotational excitation. The most relevant fact in Fig. 2a is the absence of methyl radicals produced in correlation with ground state iodine atoms, indicating that the  $\text{CH}_3(v=0)+\text{I}({}^2P_{3/2})$  channel, although energetically allowed, does not take place at 193 nm. This result is compatible with the  $\Phi$  value of  $0.07 \pm 0.02$  found by Xu and Pratt<sup>26</sup> for the 193 nm excimer photodissociation of  $\text{CH}_3\text{I}$  because in that case they were detecting all vibrational states of  $\text{CH}_3$  and this fragment appears internally excited.<sup>26</sup> The  $\text{CH}_3$  angular distribution shown in Fig. 2b is obtained by radial integration of the  $XX$  image shown in Fig. 1. The red line represents the best fit to the truncated form of eqn (1):

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) + \beta_6 P_6(\cos \theta)] \quad (3)$$

The  $i=0$  term in eqn (1) corresponds to the population of the studied species and given that the experimental setup has not been calibrated for total intensities, the quotient  $\sigma/4\pi$  in eqn (3) is treated as a normalization fitting parameter. The bipolar moments obtained from the experimental  $\beta_i$  parameters are shown in Table 1, along with the values reported in the literature for the photodissociation of  $\text{CH}_3\text{I}$  in different dynamical regions.

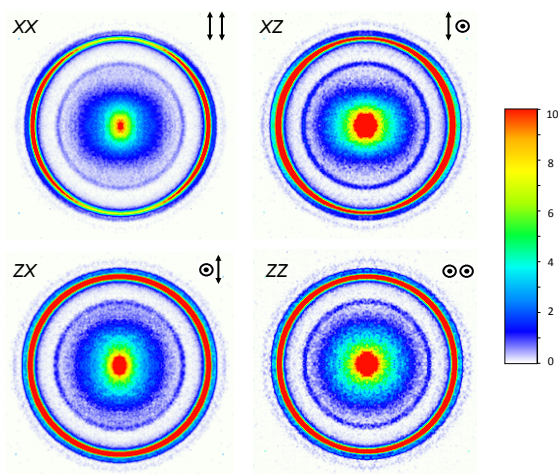
**Table 1** Dixon's second-order  $\beta_0^k(k_1 k_2)$  bipolar moments for the photodissociation of methyl iodide in different dynamical regions: a) Ref. <sup>11</sup>; b) Ref. <sup>12</sup>; c) Present work. The limiting values for the BM presented here are  $[-1/2, +1]$  for  $\beta_0^2(20)$ ,  $\beta_0^0(22)$  and  $\beta_0^2(02)$  and  $[-1, +1/2]$  for  $\beta_0^2(22)$ .

	$\beta_0^2(20)$	$\beta_0^0(22)$	$\beta_0^2(02)$	$\beta_0^2(22)$
266 nm - A-band ( ${}^3Q_0$ ) <sup>a</sup>	-	-0.3	-0.4	0.29
200.25 nm - A-band ( ${}^3A_1$ ) <sup>b</sup>	-0.48	0.18	-0.05	-0.09
201.11 nm - B-band (band origin) <sup>b</sup>	-0.17	0.11	-0.08	-0.07
193 nm - B-band [ $\text{CH}_3(v=0)+\text{I}^*$ ] <sup>c</sup>	-0.31	0.02	0.02	0.01
193 nm - B-band [ $\text{CH}_3(v_1=1)+\text{I}^*$ ] <sup>c</sup>	-0.26	0.05	-0.03	-0.01
193 nm - B-band [ $\text{CH}_3(v_1=1)+\text{I}$ ] <sup>c</sup>	-0.14	-0.05	-0.01	-0.02

### 3.1.1 Vibrationally excited $\text{CH}_3(v_1=1)$ and $\text{CH}_3(v_2=1)$ products

Fig. 3 shows color-saturated  $XX$ ,  $XZ$ ,  $ZX$  and  $ZZ$  sliced images obtained for the  $\text{CH}_3(v_1=1)$  products measured at the probe wavelength of 333.9 nm. The images consist in three main features: a low-recoiled anisotropic contribution associated most probably with  $\text{CH}_3\text{I}^+$  dissociative ionization; an intense anisotropic ring corresponding to  $\text{CH}_3(v_1=1)$  in correlation with  $\text{I}^*$ ; and a higher-recoiled, much weaker ring only visible in the saturated-color scale, assigned to the  $\text{CH}_3(v_1=1)+\text{I}$  channel. In this case, the contribution from the one-color pump-probe experiment at 333.9 nm that appears as a weak inner ring has not been subtracted from the images. The TED obtained by angular integration of the  $XX$  image of Fig. 3 is shown in Fig. 4a. The  $\text{CH}_3(v_1=1)+\text{I}^*$  peak appears in the TED with a shoulder peaking at 3.1 eV, which is attributed to non-resonant multiphoton ionization (MPI) of  $\text{CH}_3(v=0)$  products.<sup>24</sup> The inset in Fig. 4a depicts an enlargement of the TED that clearly displays a very weak peak at 3.7 eV

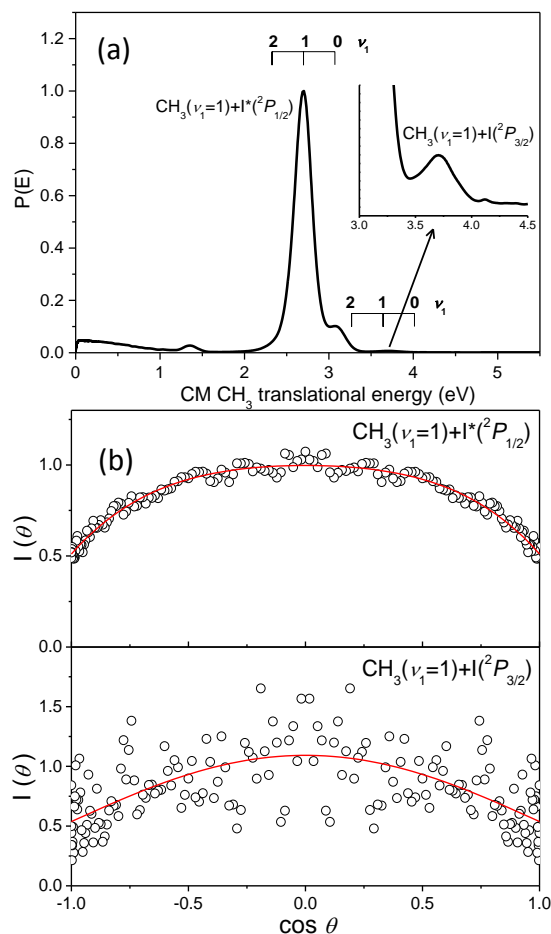
assigned to the  $\text{CH}_3(\nu_1=1)+\text{I}$  channel. From this TED, a quantum yield  $\Phi$  of 0.01 for the production of  $\text{CH}_3(\nu_1=1)$  at 193 nm is estimated. The angular distributions for the main and weak peaks attributed to the  $\text{CH}_3(\nu_1=1)+\text{I}^*$  and  $\text{CH}_3(\nu_1=1)+\text{I}$  channels, respectively, are shown in Fig. 4b. The anisotropy of these rings have been analyzed using eqn (3) and the corresponding BM are collected in Table 1.



**Fig. 3** Sliced images (color saturated) corresponding to  $\text{CH}_3(\nu_1=1)$  fragments produced in the photodissociation of  $\text{CH}_3\text{I}$  at 193 nm taken at the different pump-probe polarization configurations  $XX$ ,  $XZ$ ,  $ZX$  and  $ZZ$ . In this case, the contribution due to the one-color pump-probe experiment at 333.9 nm (inner ring) has not been subtracted. At the top right side of each image the pump (left) and probe (right) polarizations are outlined. The color scale is shown at the right. The  $Z$  axis is parallel to the molecular beam.

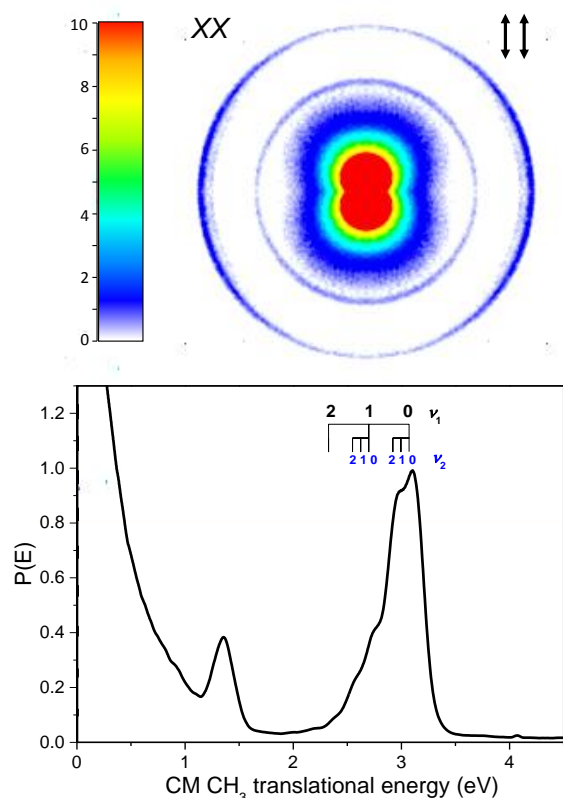
The  $XX$  image obtained when the probe laser is tuned to the  $\text{CH}_3(\nu_2=1)$  resonance at 329.4 nm shown in Fig. 5 displays a single ring (of perpendicular character) and the low recoiled contribution. The inner ring contribution (of parallel character) is due to the one-color pump-probe experiment at 329.4 nm that has not been subtracted from the image. The corresponding TED is depicted in the bottom panel of Fig. 5. As can be seen, the main peak centered at 3 eV shows a clear vibrational structure. Surprisingly, as indicated by the combs, the main contribution in this peak is assigned to non-resonant MPI of  $\text{CH}_3(\nu_2=0)$  followed by the shoulder assigned to REMPI detection of  $\text{CH}_3(\nu_2=1)$ . In addition, contributions from MPI of  $\text{CH}_3(\nu_1=1, \nu_2=0, 1)$  are clearly observed at lower translational energies. Similar MPI detection of different  $\text{CH}_3$  vibrational states other than the one initially detected by REMPI has been observed previously<sup>24</sup> and also in this work (MPI detection of  $\text{CH}_3(\nu=0)$  in Fig. 4 or, even, the shoulder observed in Fig. 2 at the left of the main peak and corresponding to MPI detection of  $\text{CH}_3(\nu_1=1)$ ). The effective MPI detection of  $\text{CH}_3$  fragments in comparison with the REMPI detection of the selected vibrational state of  $\text{CH}_3$  is due to the relative high abundance of other vibrational states of  $\text{CH}_3$  produced in the photodissociation of  $\text{CH}_3\text{I}$  at 193 nm. In this case, no feature attributable

to the production of ground state  $\text{I}({}^2P_{3/2})$  is observed.



**Fig. 4** Center-of-mass  $\text{CH}_3(\nu_1=1)$  translational energy (a) and angular (b) distributions obtained by integration of the  $XX$   $\text{CH}_3(\nu_1=1)$  image shown in Fig. 3. The peak at about 1.35 eV corresponds to the contribution of the one-color pump-probe experiment at 333.9 nm. The combs in the TED indicate the available energy for the production of the vibrational progression in the  $\nu_1$  mode of methyl,  $\text{CH}_3(\nu_1)$ , in correlation with  $\text{I}^*({}^2P_{1/2})$  and  $\text{I}({}^2P_{3/2})$ . The inset enlarges the peak at 3.7 eV that corresponds to  $\text{CH}_3(\nu_1=1)$  fragments in correlation with  $\text{I}({}^2P_{3/2})$ . The red lines superimposed to the angular distributions are the best fit to eqn (3), using  $\beta_2=-0.347\pm 0.006$  and  $\beta_4=-0.064\pm 0.007$  for the  $\text{CH}_3(\nu=0)+\text{I}^*({}^2P_{1/2})$  channel and  $\beta_2=-0.43\pm 0.05$  and  $\beta_4=-0.03\pm 0.06$  for the  $\text{CH}_3(\nu=0)+\text{I}({}^2P_{3/2})$  channel.

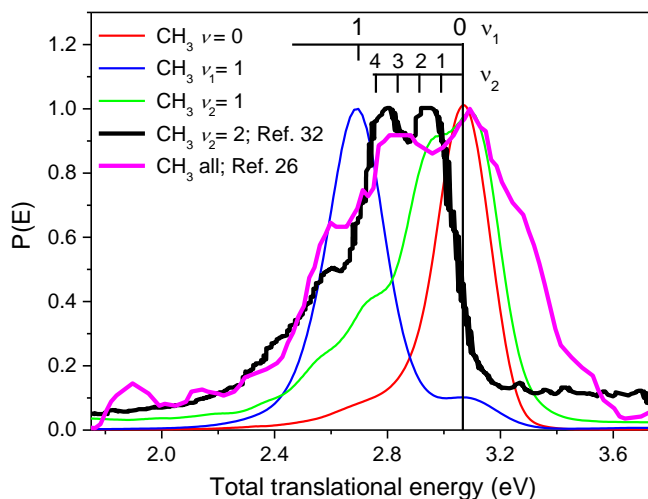
In Fig. 6, the  $\text{CH}_3(\nu=0)$ ,  $\text{CH}_3(\nu_1=1)$  and  $\text{CH}_3(\nu_2=1)$  TEDs (in this case, total translational energy) obtained in this work are superimposed with the  $\text{CH}_3(\nu)$  distribution measured by one-photon VUV ionization by Xu and Pratt,<sup>26</sup> and the previously reported  $\text{CH}_3(\nu_2=2)$  TED by Kitsopoulos and coworkers.<sup>32</sup> From the comparison between the different sets of experiments, it becomes clear that the resonant and nonresonant curves reproduce the one-photon VUV ionization distribution, with the exception of a high-energy shoulder, probably assignable to photodissociation of vibrationally excited  $\text{CH}_3\text{I}$  present in the molecular beam expansion in the experiments of ref.<sup>26</sup>. Vibrational branching ratios are not straightforwardly extracted from the  $\text{CH}_3$  fragment images, in part due to the fact that Franck-Condon factors for vibrationally excited methyl radicals depend strongly on the ex-



**Fig. 5** (Top) Sliced  $XX$  image corresponding to  $\text{CH}_3(v_2=1)$  fragments produced in the photodissociation of  $\text{CH}_3\text{I}$  at 193 nm and (Bottom) the corresponding translational energy distribution. The contribution due to the one-color pump-probe photodissociation (inner ring in the image and peak at about 1.2 eV in the TED) has not been subtracted. As previously, the polarizations and color scale are outlined. The combs represent the vibrational progression in the  $v_1$  and  $v_2$  modes of the  $\text{CH}_3$  fragment.

cited mode and the degree of excitation.<sup>26,33</sup> The curves in Fig. 6 have been arbitrarily normalized to the maximum intensity for a better comparison. However, some information about the vibrational state distribution of the methyl fragment can be obtained. Xu and Pratt assigned the one-photon ionization profile of the  $\text{CH}_3$  fragment to a non-inverted double progression of the  $v_1$  C–H stretching and  $v_2$   $\text{CH}_3$  umbrella modes.<sup>26</sup> Strikingly, similar selective vibrational activity in the  $\text{CH}_3$  product has been reported to happen after dissociation in very different spectroscopic regions, such as the  $B$ -band  $0_0^0$ ,  $2_0^1$  and  $3_0^1$  vibronic transitions,<sup>12,22–24</sup> and in the blue edge of the  $A$ -band.<sup>34</sup> In order to understand the apparent lack of correlation between the absorption step and the  $\text{CH}_3$  vibrational state distribution, it is necessary to analyze the  $\text{CH}_3(v)$  formation dynamics in both absorption bands.

In a high resolution time-of-flight (TOF) experiment, Hu and co-workers<sup>34</sup> studied the photodissociation of  $\text{CH}_3\text{I}$  at 225 nm (blue edge of the  $A$ -band) through REMPI detection of  $\text{I}$  and  $\text{I}^*$  products and found that vibrationally excited  $\text{CH}_3$  up to  $v_1=2$  and  $v_2=3$  is produced at this excitation wavelength. In addition, the TOF spectra measured at different pump and probe laser polarization configurations showed that the  $\text{CH}_3$  fragments pro-



**Fig. 6** Comparison between the  $\text{CH}_3(v)$  translational energy distributions obtained in the present work with those reported in ref.<sup>26</sup> for one-photon VUV ionization of  $\text{CH}_3$ . For completeness the  $\text{CH}_3(v_1=2)$  distribution of ref.<sup>32</sup> is presented as well. All TEDs have been normalized to unity at the maximum.

duced in correlation with ground state  $\text{I}$  atoms are generated significantly hotter than those produced in the  $\text{CH}_3(v) + \text{I}^*$  channel. The authors concluded that the direct  ${}^1Q_1 \leftarrow {}^3Q_0$  curve crossing induces larger vibrational activity in the  $\text{CH}_3$  fragment than the inverse  ${}^3Q_0 \leftarrow {}^1Q_1$  curve crossing. The effect of the initial vibrational excitation in the parent  $\text{CH}_3\text{I}$  molecule was studied by the same authors<sup>35</sup> in a vibrationally mediated photodissociation experiment at 277.5 nm, where the  $\text{CH}_3$  vibrational distribution produced in the photodissociation of  $\text{CH}_3\text{I}(v=0)$  and  $\text{CH}_3\text{I}(v_1=1)$  molecules were compared. The results showed that more than 90% of the C–H symmetric stretch vibration of the parent  $\text{CH}_3\text{I}$  is retained in the  $\text{CH}_3$  fragment.

In the  $B$ -band, the predissociation mechanism is considered to occur through potential energy surface crossings between the  $B$ -band  ${}^3R_1$  Rydberg state and the  $A$ -band  ${}^3A_1(E)$  state and, tentatively, the  ${}^1Q_1$  state,<sup>22,24,25</sup> which correlate adiabatically with the  $\text{CH}_3(v) + \text{I}^*$  and  $\text{CH}_3(v) + \text{I}$  channels, respectively. Using femtosecond lasers,  $\text{CH}_3$  vibrational population distributions after dissociation through the  $B$ -band  $0_0^0$ ,  $2_0^1$  and  $3_0^1$  vibronic levels were studied.<sup>12,22–24,36,37</sup> At the band origin ( $0_0^0$  transition), 11% of  $\text{CH}_3(v_1=1)$  excitation was found; the percentage increases up to 36% and 44% for the  $2_0^1$  and  $3_0^1$  transitions, respectively. These results correspond to the  $\text{CH}_3(v) + \text{I}^*$  channel, and therefore, to the  ${}^3A_1(E) \leftarrow {}^3R_1$  crossing. Minor production of ground state  $\text{I}({}^2P_{3/2})$  atoms were found only after excitation of the  $3_0^1$  transition and mainly in correlation with  $\text{CH}_3(v_1=1)$  – a quantum yield  $\Phi=0.07$  was estimated.

To the best of our knowledge no dynamical calculations on the photodissociation of  $\text{CH}_3\text{I}$  in the  $B$ -band have been reported, but there is quite enough literature regarding the  $A$ -band photodissociation to set up the issue. A thorough wave packet dynamical calculation of  $\text{CH}_3\text{I}$  photodissociation in the maximum of the  $A$ -band at 266 nm consisted in a reduced dimensionality model including three degrees of freedom (3D).<sup>38</sup> While there was a reasonable

quantitative agreement between the experimental and theoretical  $I(^2P_{3/2})/I(^2P_{1/2})$  branching ratios for  $v_2=0$ , an increasing divergence for  $v_2 \geq 1$  appeared. A possible explanation for these discrepancies was suggested in the sense that the reduced dimensionality model would be missing some couplings between the  $\text{CH}_3$  umbrella bending mode and some of the neglected modes (mainly the symmetric stretch mode of the  $\text{CH}_3$  moiety). In addition, the model failed in predicting the clocking times for the internally excited methyl fragments in the  $v_2$  umbrella mode in correlation with ground state iodine atoms.<sup>38</sup> The model was upgraded to a 4D version, which included specifically the C–H symmetric stretch mode.<sup>39</sup> Very small differences were found between the results of the 4D and 3D models, both in reaction times and product fragment state distributions. The reduced dimensionality issue was addressed more broadly in a full-dimensional (9D) quantum dynamics study, where no significant improvement was found.<sup>40</sup> If the limitations of dynamical approaches do not cause the discrepancies with the experimental data, the failure of theory must be sought in deficiencies of the *ab initio* potential energy surfaces (PES) employed and, in particular, of the  $^1Q_1$  PES.

Theoretical and experimental  $\text{CH}_3(v_2)/\text{CH}_3(v_1)$  branching ratios at the center of the A-band ( $\sim 270$  nm) and at the B-band origin do not differ dramatically. In the center of the A-band, the absorption is produced mainly to the  $^3Q_0$  state, which due to the similar  $\text{CH}_3\text{I}$  equilibrium geometry with the ground state, preserves adiabatically the vibrational content of the parent molecule.<sup>34,35</sup> The  $\text{CH}_3(v_2)$  activity in the  $\text{CH}_3+\text{I}$  channel has been traditionally assigned to the change in the equilibrium geometry of the umbrella bending angle occurring in the  $^1Q_1 \leftarrow ^3Q_0$  curve crossing. A similar argument stands for the dissociation at the B-band origin: the  $^3R_1$  Rydberg and ground  $\tilde{X}^1A_1$  states present similar equilibrium geometries in the Franck-Condon region and, since the crossing with the A-band  $^3A_1(E)$  state is produced near the equilibrium distance, the initial vibrational excitation is preserved in the dissociation process. However, in molecular beam experiments, such as those discussed here, the vibrational excitation content in the parent molecule is mild and only a small percentage of  $\text{CH}_3\text{I}(v_1)$  molecules is expected.<sup>17,41</sup>

If the origin of the  $\text{CH}_3(v_1)$  excitation cannot be assigned to vibrational adiabaticity, it must be sought in the geometry changes produced in the absorption and dissociation processes. The  $\text{CH}_3$  moiety in the  $\tilde{X}^1A_1$ ,  $^3Q_0$  and  $^3R_1$  states is pyramidal while is quasi-planar in the  $^1Q_1$  state,<sup>42</sup> so both the absorption and the different curve crossings involve geometrical changes. Even at 277 nm, non-negligible contribution from absorption to the  $^1Q_1$  state is expected,<sup>17</sup> which should account for the small proportion of  $\text{CH}_3(v_1)$  products, either through adiabatic dissociation in the  $\text{CH}_3(v)+\text{I}$  channel or via the  $^3Q_0 \leftarrow ^1Q_1$  inverse curve crossing in the  $\text{CH}_3(v)+\text{I}^*$  channel. The influence of the  $^1Q_1$  is amplified when the dissociation wavelength is decreased in the A-band, due to an increase of direct absorption probability to the  $^1Q_1$  state,<sup>24,34</sup> and in the B-band, due to the possible  $^1Q_1 \leftarrow ^3R_1$  crossing, which is not produced in the  $0_0^0$  and  $2_0^1$  vibronic transitions.<sup>24,25</sup>

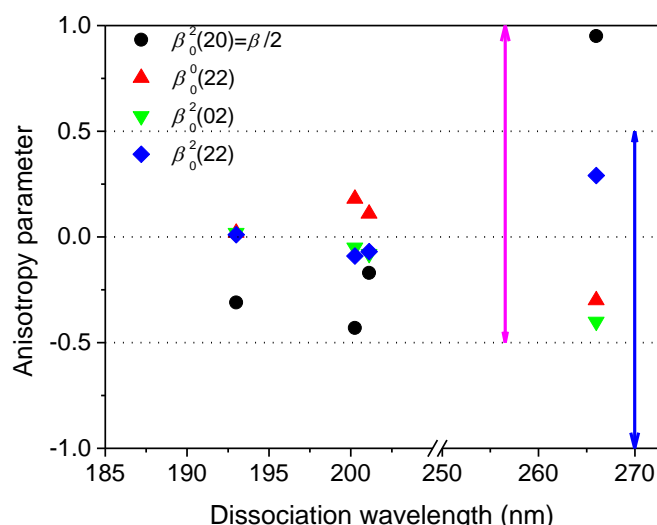
### 3.1.2 Bipolar moments

Vector correlations determined by Dixon's bipolar moments arise as the result of the forces and torques experienced by the parent molecule during the dissociation process. Such interactions are generated by the differences in the equilibrium geometries and vibrational activity in the ground and excited states involved. The absorption step plays, in this sense, a similar role than that of the curve crossings and, therefore the BM should allow us to extract the relevant information related to the different dynamics involved: absorption, adiabatic dissociation, predissociation and curve crossings.

The BM listed in Table 1 are plotted versus excitation wavelength in Fig. 7 (for clarity, at  $\lambda=193$  nm only the values for the  $\text{CH}_3(v=0)+\text{I}^*$  channel have been included). No correction for predissociation depolarization has been applied in this case. The lifetimes of the  $0_0^0$  and  $3_0^1$  vibronic levels of the B-band are 1.52 and 4.34 ps, respectively,<sup>23</sup> which implies that the BMs measured in this work suffered a depolarization effect due to the rotation of the parent molecule during the dissociation process.<sup>43–45</sup> The long lifetime limit – independent on the excited state lifetime – of the depolarization of the BMs, predicts a factor of 1/5 for the  $\beta_0^2(20)$ ,  $\beta_0^2(02)$  and  $\beta_0^2(22)$  moments, while the  $\beta_0^0(22)$  is not affected.<sup>46,47</sup> The depolarization factor must be applied, however, with caution when the BMs take values close to zero. At 201.11 and 193 nm the uncertainty associated to  $\beta_0^2(02)$  and  $\beta_0^2(22)$  advises that even a qualitative prediction of the spatial orientation (parallel or perpendicular) of the magnitudes involved is unsafe. Furthermore, if a factor of 1/5 should be applied to the  $\beta_0^2(20)$  moment obtained at 193 nm, a  $\beta$  parameter of  $-3$  would be obtained – tripling the fast dissociation limit for a perpendicular transition – what suggests that the approximations made to obtain the long lifetime depolarization factors<sup>43</sup> are not suitable for the  $\text{CH}_3\text{I}$  case. Bearing in mind such considerations, the most striking fact is that only in the center of the A-band, the BMs take near limiting values.<sup>11</sup> At 266 nm, the process proceeds through absorption to the  $^3Q_0$  state followed by adiabatic ( $\text{CH}_3 + \text{I}^*$ ) or curve crossing mediated ( $\text{CH}_3 + \text{I}$ ) dissociation. The K-conservation model predicts both the large BMs reported and the little  $\text{CH}_3$  vibrational activity discussed in the previous section. With the exception of  $\beta_0^2(20)$  – related to the anisotropy of the dissociation process itself – the BMs take slightly larger values at the onset of the B-band and at 200.25 nm – direct absorption to the A-band  $^3A_1(E)$  state – than at 193 nm, where they are virtually zero (see Fig. 7).

In a previous publication on the stereodynamics of photodissociation of  $\text{CH}_3\text{I}$  in the onset of the B-band, the small values for the BMs obtained after direct absorption to the  $^3A_1(E)$  state were assigned to a breakdown of the unique recoil direction (URD) approximation generated by a preferential contribution to the absorption process of in-plane vibrational modes provided by vibrationally excited  $\text{CH}_3\text{I}$ .<sup>12</sup> At the origin of the B-band no contribution from parent initial vibration is needed and little change in the  $\text{CH}_3\text{I}^*$  geometry is expected in the curve-crossing, which altogether suggests that relative high BMs should be expected. The small BM values measured must be, therefore, related to depolar-





**Fig. 7** Dixon's second order bipolar moments (shown in Table 1) for the  $\text{CH}_3+\text{I}^*$  dissociation channel plotted as a function of dissociation wavelength. The colored vertical double arrows show the argument range for the expectation values (magenta:  $\beta_0^2(20)$ ,  $\beta_0^0(22)$  and  $\beta_0^2(02)$ ; blue:  $\beta_0^2(22)$ ).

ization effects caused by parent rotation, as discussed above. At 193 nm, we might be seated in a mixed situation. At the equilibrium geometry of the  $\text{CH}_3\text{I}$  ground state, the overlap with the  $3_0^1$  wavefunction is poor and hence, some vibrational activity in the parent  $\text{CH}_3\text{I}$  could enhance the absorption step. On the other hand, the possible crossing between the  $^3R_1$  and  $^1Q_1$  states should involve significant geometrical changes. If the depolarization effect is added, the near-zero BMs obtained are not troublesome.

### 3.2 $\text{I}^*(^2P_{1/2})$ and $\text{I}(^2P_{3/2})$ images

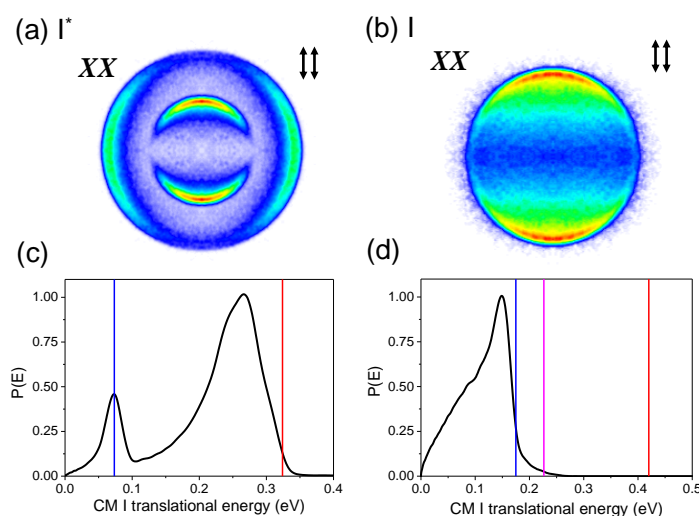
Fig. 8 shows the iodine images and TEDs for both spin-orbit electronic states. The  $\text{I}^*$  image consists of two anisotropic features: an outer ring corresponding to the two-color signal, where the 193 nm pulse excites  $\text{CH}_3\text{I}$  and the iodine (2+1) REMPI detection is carried out by the 305.57 nm pulse, and an inner ring corresponding to the one-color pump-probe process, where the 305.57 nm pulse carries out the dissociation and the fragment detection. The  $\text{I}$  image is taken by using a probe laser centered at 304.64 nm. In both cases, the one-color contribution has not been removed from the  $\text{I}$  and  $\text{I}^*$  images in order to set a reference for the identification of the possible elusive two-color  $\text{I}(^2P_{3/2})$  signal.<sup>26</sup>

The vertical lines in Fig. 8 represent the maximum available energies for the one-color (blue) and two-color (red) processes according to:

$$E_{av}[\text{I}] = \frac{m_{\text{CH}_3}}{m_{\text{CH}_3\text{I}}} [h\nu - D_0 - E_{SO}(\text{I}) - E_i(\text{CH}_3) + E_i(\text{CH}_3\text{I})] \quad (4)$$

where the internal energies  $E_i$  of  $\text{CH}_3$  and  $\text{CH}_3\text{I}$  are assumed to be zero.

As can be seen in Figs. 8c and 8d, the one-color contributions are readily identified for both  $\text{I}^*$  and  $\text{I}$  species as well as the  $\text{I}^*$  two-color formation process, while the  $\text{CH}_3 + \text{I}$  channel seems to



**Fig. 8**  $\text{I}^*(^2P_{1/2})$  (a) and  $\text{I}(^2P_{3/2})$  (b)  $XX$  slice images, and the corresponding center-of-mass iodine TEDs (c and d), obtained in the photodissociation of  $\text{CH}_3\text{I}$  at 193 nm. At the top right side of each image the pump (left) and probe (right) polarizations are outlined. The vertical bars in the TEDs denote the maximum available energy for the two-color (red) and one-color (blue) contributions. The magenta vertical bar has been shifted to lower translational energies with respect to the red one according to the estimated internal energy content of the  $\text{CH}_3$  fragment by Xu and Pratt<sup>26</sup> (1.86 eV). See the text for more details.

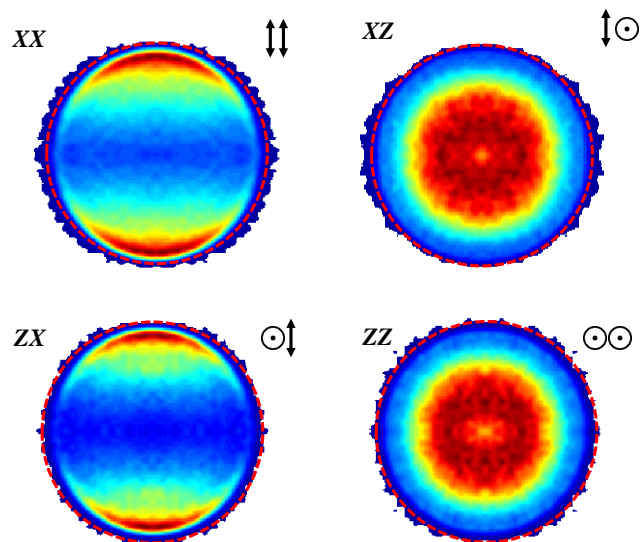
be closed at 193 nm. As commented on in the introduction section, Xu and Pratt<sup>26</sup> reported a small but measurable  $\Phi$  quantum yield of  $0.07 \pm 0.01$  where  $\text{I}(^2P_{3/2})$  is produced in correlation with highly internally excited ( $\sim 1.86$  eV)  $\text{CH}_3(\nu)$  cofragment. The magenta vertical line in Fig. 8d shows the corrected  $\text{CH}_3(\nu=0)+\text{I}$  available energy in agreement with Xu and Pratt's estimation. Apparently, if present, such  $\text{I}(^2P_{3/2})$  signal would overlap with the one-color contribution. To clarify this point, a thorough analysis of the distribution profile in Fig. 8d has been carried out. Particularly, the curve portion at the right side of the available energy line, which is assigned to photodissociation of vibrationally excited  $\text{CH}_3\text{I}$  molecules present in the molecular beam. Contribution from vibrationally excited  $\text{CH}_3\text{I}$  to the whole photodissociation process both in the  $A$ - and  $B$ -bands has been evidenced by our group in previous publications<sup>12,17</sup>. In our work on the photodissociation of  $\text{CH}_3\text{I}$  in the red edge of the  $A$ -band, it was shown that the vibrational content in the parent  $\text{CH}_3\text{I}$  enabled the crossing between the  $^3Q_0$  and  $^1Q_1$  surfaces;<sup>17</sup> in a recent work, on the other hand, the role of the  $\text{CH}_3\text{I}$  promoting vibrational modes was stated in the excitation to the  $^3A_1$  repulsive state in the vicinity of the  $0_0^0$  transition of the  $B$ -band.<sup>12</sup>

Being atomic species, the widths of the  $\text{I}$  and  $\text{I}^*$  peaks correlate with the internal energy – rotational and vibrational – of the dissociation co-product, the  $\text{CH}_3$  fragment, and of the parent molecule. The two-color  $\text{I}^*$  distribution in Fig. 8c shows negligible contribution from parent internal energy, in agreement with the measurements of the methyl fragment discussed above. The

available energy vertical line corresponding to the one-color signal, however, sits on top of the corresponding peak. In Fig. 3 of ref.<sup>17</sup>, it was shown that at 305 nm photolysis wavelength, the  $\text{CH}_3\text{I}(v_3)$  vibrational states contributing most to the observed  $\text{CH}_3(v=0)$  product are  $v_3=1$  and  $v_3=0$  for the  $\text{CH}_3(v=0)+\text{I}^*$  and  $\text{CH}_3(v=0)+\text{I}$  channels, respectively. That result is in agreement with the current observations, where the one-color distribution reveals some contribution from vibrationally excited  $\text{CH}_3\text{I}$  for the  $\text{CH}_3(v=0)+\text{I}^*$  channel and, conversely, little contribution for the  $\text{CH}_3(v=0)+\text{I}$  channel. In a previous work carried out by our group on the role of the conical intersection between the  $^3Q_0$  and  $^1Q_1$  surfaces in the photodissociation of  $\text{CH}_3\text{I}$  at 304 nm<sup>48</sup>, the contribution from vibrationally excited parent  $\text{CH}_3\text{I}$  was minimized in order to clarify the nature – inverted or statistical – of the methyl fragment vibrational distribution.<sup>48</sup> Li and coworkers<sup>49</sup>, in an earlier work employing hotter molecular beams, found out a statistical contribution from vibrationally excited  $\text{CH}_3\text{I}$  in the  $\text{CH}_3(v)+\text{I}$  channel. The shape of the  $\text{CH}_3(v)$  distribution in correlation with ground state iodine atoms (Fig. 3 top in ref.<sup>49</sup>) does not differ significantly from that one in Fig. 8d. There is a significant difference, however. The anisotropy of the one-color photodissociation from vibrationally excited  $\text{CH}_3\text{I}$  would be highly parallel ( $\beta=2$ )<sup>17,49</sup>, while any contribution from photodissociation at 193 nm would be perpendicular ( $\beta=-1$ ).

In order to check the polarization dependence of the iodine signal in Fig. 8,  $\text{I}(^2P_{3/2})$  velocity map images (VMI) were measured at the four pump-probe polarization configurations  $XX$ ,  $XZ$ ,  $ZX$  and  $ZZ$ <sup>50</sup>, an approach that has rendered successful results in the past to discriminate contributions from independent processes.<sup>51</sup> As expected, the anisotropic ring becomes a circle when the probe laser polarization rotates from  $X$  to  $Z$  while it does not depend on the pump laser polarization. As can be seen in the color saturated raw VMI images depicted in Fig. 9, there is a weak, "aura"-like contribution surrounding the intense one-color feature. Furthermore, this "aura"-like signal displays a polarization dependence. To better distinguish the polarization dependence of this signal, a dashed circle has been drawn around each image as a visual guide (see Fig. 9). The size of the circle has been chosen to fit the  $ZZ$  image, which is free from any anisotropy effect. Clearly, the circle fits perfectly the  $ZX$  "aura" but does not those of the  $XX$  and  $XZ$  images. The divergence is produced at the poles, where the "aura" does not reach the circle and in the equator, where the "aura" stands out of it. In summary, the "aura" corresponds to a perpendicular signal coming from the pump laser. Such conclusion rules out photodissociation of vibrationally excited  $\text{CH}_3\text{I}$  as the source of this signal and stands for the 193 nm induced  $\text{I}(^2P_{3/2})$  signal, in agreement with Xu and Pratt.<sup>26</sup>

The feeble proof we have just presented needs of further checks if we aim to present it as evidence. The visual analysis carried out in the previous paragraph cannot be translated into more quantitative translational energy distributions since the  $ZX$  and  $XZ$  images are not Abel-invertible. An alternative analysis can be carried out, though. First, the Abel-inverted  $XX$  image can be angularly integrated in a chosen angle interval. The resulting TEDs after integrating the inverted  $XX$  image (by  $\pm 15^\circ$ ) around the poles (blue curve) and the equator (red curve) are presented in

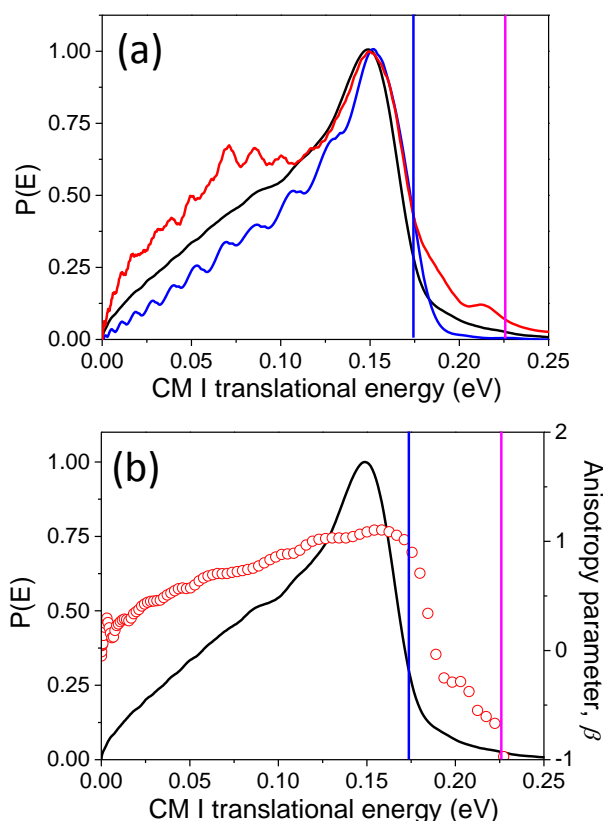


**Fig. 9** Colour saturated  $\text{I}(^2P_{3/2})$  velocity map raw images measured at the different pump-probe polarization configurations  $XX$ ,  $XZ$ ,  $ZX$  and  $ZZ$ . At the top right side of each image, the pump (left) and probe (right) polarizations are outlined. The  $Z$  axis is parallel to the molecular beam.

Fig. 10a and compared with the TED after full  $360^\circ$  integration (black curve). The partial angular integration confirms the perpendicular character of the weak two-color contribution: the blue curve is clearly narrower than the other two, in particular in the right side (high translational energies), where the signal above the maximum available energy bar for the one-color experiment is much reduced. The opposite case is for the red curve, which is the wider one.

A second test has been carried out by determining the speed-dependent (or center-of-mass iodine translational energy dependent) anisotropy  $\beta$  parameter. The Abel-inverted  $XX$  image was radially integrated pixel-by-pixel using homemade software, and the resulting angular distribution fitted to eqn. (3). Only a  $\beta$  parameter was needed, which suggests that no significant photofragment polarization effects are found for the  $\text{I}(^2P_{3/2})$  fragment. The obtained  $\beta$  parameter is plotted in Fig. 10b as a function of the center-of-mass  $\text{I}(^2P_{3/2})$  translational energy. Clearly, the  $\beta$  parameter takes positive values – which indicates a parallel process – until the high energy tail, where it drops fast to values near zero. The fact that no negative values (corresponding to a perpendicular transition) are reached can be attributed to the binning of  $\sim 60 \text{ ms}^{-1}$  employed in the fitting procedure. Therefore, Fig. 10 provides the confirmation needed to assign the high energy tail in the  $\text{I}(^2P_{3/2})$  TED to the production of  $\text{I}(^2P_{3/2})$  atoms at 193 nm, which, as suggested by Xu and Pratt<sup>26</sup>, correlates with highly internally excited  $\text{CH}_3$  fragments. However, the small signal does not allow us to determine a proper value for  $\Phi$ .

In the previous work on the photodissociation of  $\text{CH}_3\text{I}$  after



**Fig. 10** (a)  $I(^2P_{3/2})$  TEDs obtained after partial and total angular integration of the Abel-inverted  $XX$  image in Fig. 8. Blue curve: integration by  $\pm 15^\circ$  around the poles. Red line: integration by  $\pm 15^\circ$  around the equator. Black line: full  $360^\circ$  angular integration. (b) Energy-dependent  $\beta$  anisotropy parameter obtained from eqn. (3) (circles) and full angular integrated TED (black line). The vertical bars in the TEDs are as in Fig. 8. See the text for more details.

excitation of the  $3_0^1$  transition,<sup>24</sup> it was observed that the predissociation mechanism yielding  $\text{CH}_3$  fragments in correlation with ground-state  $I(^2P_{3/2})$  atoms, through the tentative coupling between the  $^3R_1$   $B$ -band Rydberg state and the  $^1Q_1$   $A$ -band repulsive state, provided a measurable  $\Phi$  quantum yield of 0.07 for the  $\text{CH}_3(v_1=1)$  fragments. For the ground state  $\text{CH}_3(v=0)$  products, the slicing technique provides visual evidence of tiny formation of ground-state iodine atoms (see Fig. 1c in ref.<sup>24</sup>) although the quantification of  $\Phi$  was not conclusive. In the current experiments, we have observed ground state iodine atoms in correlation with  $\text{CH}_3(v_1=1)$  fragments, with a  $\Phi \approx 0.01$ , while the formation of  $\text{CH}_3(v=0)$  and  $\text{CH}_3(v_2=1)$  radicals occurred exclusively in correlation with  $I^*$  atoms ( $\Phi=0$ ). In the experiments by Xu and Pratt<sup>26</sup>, only methyl radicals in correlation with spin-orbit excited state iodine atoms were observed by one-photon VUV ionization. The high internal excitation ( $\sim 1.86$  eV) estimated for the  $\text{CH}_3$  fragments in correlation with ground state iodine atoms would reduce drastically the associated Frank-Condon transition factors and, hence, the corresponding signal.<sup>26</sup>

## Conclusions

The results presented in this work consolidate the role of the curve crossing between the  $B$ -band  $^3R_1$  Rydberg state and the  $A$ -band  $^1Q_1$  repulsive state as a relevant predissociation mechanism of  $\text{CH}_3\text{I}$  in the  $B$ -band. The main conclusions that can be extracted from this work are the following: (a) The high sensitivity of the slice imaging technique employed in this work, with REMPI detection of  $\text{CH}_3(v_1=1)$  fragments, confirms the production of  $I(^2P_{3/2})$  atoms in correlation with methyl fragments with one quantum of excitation in the  $v_1$  symmetric stretch mode. (b) The direct observation of ground state iodine atoms by REMPI detection of this species confirms that  $I(^2P_{3/2})$  is produced in correlation with highly excited  $\text{CH}_3$ , in agreement with the work of Xu and Pratt.<sup>26</sup> (c) The vibrational activity in the symmetric stretch mode  $v_1$  of the produced methyl fragment is related to geometrical changes produced in the absorption step to the  $^1Q_1$  state and through the  $^1Q_1 \leftarrow ^3R_1$  and  $^1Q_1 \leftarrow ^3Q_0$  non-adiabatic curve crossings, suggesting that the  $\text{CH}_3\text{I}$  geometry in the  $^1Q_1$  state is not well described by the current *ab initio* theory. (d) The  $\beta_0^2(02)$ ,  $\beta_0^2(22)$  and  $\beta_0^0(22)$  second order Dixon's bipolar moments, measured for the  $\text{CH}_3(v=0)$  and  $\text{CH}_3(v_1=1)$  fragments, take near zero values at 193 nm excitation due to the confluence of various effects, such as the breakdown of the URD approximation, the effect of the  $^1Q_1 \leftarrow ^3R_1$  curve crossing and the depolarization induced by the parent molecule rotation. The experiments carried out in the present work let some questions unanswered. First, the  $\text{CH}_3(v_1)$  vibrational activity. Unfortunately, the  $\text{CH}_3(v)+\text{I}$  channel, when observed, does not present the necessary signal for a quantitative stereodynamics study. Second, if the role of conical intersections can be specifically traced back through stereodynamical measurements. And third, how the *real* bipolar moments, *i.e.* the bipolar moments free from depolarization effects due to parent rotation, can be measured in the  $B$ -band. To solve such questions new experiments must be carried out. The stereodynamics of the photodissociation of  $\text{CH}_3\text{I}$  in the  $A$ -band studied at different wavelengths should provide information concerning the first and second issues. The slice imaging technique has allowed us to determine with high accuracy the contribution to the overall process of the adiabatic and non-adiabatic pathways, including the anisotropy and the quantum yields,<sup>17,24,48</sup> in the  $A$ -band. A similar study would shed light to the unresolved issues. To solve the third question, a femtosecond time-resolved stereodynamical study is needed but, to the best of our knowledge, there is no literature on slice imaging – or equivalent – technique applied to time-resolved photodissociation experiments.

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