Photodissociation dynamics of bromoiodomethane from the first and second absorption bands. A combined velocity map and slice imaging study†

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The photodissociation dynamics of bromoiodomethane (CH₂BrI) have been investigated at the maximum of the first A and second A’ absorption bands, at 266 and 210 nm excitation wavelengths, respectively, using velocity map and slice imaging techniques in combination with a probe detection of both iodine and bromine fragments, I(2P₃/2), I*(2P₁/2), Br(2P₃/2) and Br*(2P₁/2) via (2 + 1) resonance enhanced multiphoton ionization. Experimental results, i.e. translational energy and angular distributions, are reported and discussed in conjunction with high level ab initio calculations of potential energy curves and absorption spectra. The results indicate that in the A-band, direct dissociation through the 5A’ excited state leads to the I(2P₃/2) channel while I*(2P₁/2) atoms are produced via the 5A’ → 4A*/4A” nonadiabatic crossing. The presence of Br and Br* fragments upon excitation to the A-band is attributed to indirect dissociation via a curve crossing between the 5A’ with upper excited states such as the 9A’. The A’-band is characterized by a strong photoselectivity leading exclusively to the Br(2P₃/2) and Br*(2P₁/2) channels, which are likely produced by dissociation through the 9A’ excited state. Avoided crossings between several excited states from both the A and A’ bands entangle however the possible reaction pathways.

1 Introduction

Photochemistry of halomethanes has attracted significant attention due to their role in atmospheric chemistry and most notably to their adverse impact on the ozone depletion in the Earth’s ozone layer.1,2 Furthermore, the intricate excited state structure involved in the photochemistry of these species provides them with additional academic interest. In particular, bromoiodomethane (CH₂BrI) can be considered as a prototype for bond-selective electronic excitation and photochemistry. Bromoiodomethane constitutes, in addition, a suitable candidate for the investigation of optical control of chemical bond cleavage due to the presence of two distinct carbon–halogen bonds.

Early investigations3,4 on the photodissociation of CH₂BrI already proved the ability to control photoproduct branching ratios with an appropriate selection of the excitation wavelength.

The UV absorption spectrum5 of dihalomethanes consists typically of two bands, associated each one of them almost exclusively to one of the two C–X chromophores. In the case of CH₂BrI, the first absorption band, named A-band, lies between 320 and 240 nm and has been assigned to the σ*(C–I) ← n(I) transition while the second absorption band, labelled here A’-band, covers the 240–200 nm range, has a maximum around 210 nm and has been attributed to the σ*(C–Br) ← n(Br) transition.

Lee and Bersohn3 published a first investigation on the photodissociation of CH₂BrI at 258 nm using photofragment translational spectroscopy. Butler et al.4 reported later a more detailed study at 248 nm, 210 nm and at 193 nm using the same photofragment translational spectroscopy technique. It was found that C–I bond fission results to be the dominant channel in the A-band (258 and 248 nm) with minor Br(2P₃/2) formation, while in the A’-band (210 nm) the C–Br cleavage is the unique pathway, with no contribution of the C–I bond cleavage channel. At higher excitation energies (193 nm) corresponding to excitation to the B-band, IBr produced by concerted elimination was also observed.4

† Electronic supplementary information (ESI) available: Energy at the Franck–Condon (FC) geometry, symmetry in C₃, as well as total dipole moment (TDM) and for each axis of the computed electronic states of CH₂BrI. See DOI: 10.1039/c7cp07077b
From a theoretical point of view, Liu et al.\textsuperscript{6} computed vertical excited energies and oscillator strengths for excited states in the A and A’ bands using unrestricted Hartree–Fock, complete active space self-consistent field (CASSCF) and configuration-interaction-singles methods, though the spin–orbit interaction was not taken into account. The reported results predicted a significant bond selectivity in the A and A’ bands, in particular in terms of differences in bond charge densities. A deeper theoretical study was performed by Lindh and co-workers\textsuperscript{7} employing multistate second-order multi-configurational perturbation theory in conjunction with spin–orbit interaction CASSCF method. The reported potential energy curves (PECs) as a function of both the C–Br and C–I distances underline the relevant role of the spin–orbit interaction in halomethanes, especially for those containing an iodine atom. Lindh and co-workers\textsuperscript{7} confirmed the dominant C–I cleavage in the A-band through direct dissociation in repulsive states and predicted minor dissociation in the A’-band induced by relaxation to lower excited states via internal conversion or intersystem crossing. In addition, the isomerization reaction to iso-CH\textsubscript{3}Br–I and iso-CH\textsubscript{2}I–Br was extensively discussed by these authors. Such isomerization processes have been largely reported in experimental photoexcitation studies of bromiodomethane in solution (see, for instance, ref. 8–10). Investigation using different solvents and matrices demonstrated the solvent-induced character of the isomerization process as well as the observed coupling between the \( \sigma^*(C-I) \rightarrow \pi(I) \) and the \( \sigma^*(C-Br) \rightarrow \pi(\text{Br}) \) transitions at specific wavelengths.

Bromiodomethane photodissociation in the gas phase, however, has never been investigated using imaging techniques and/or selective detection of photofragments such as that provided by resonance enhance multiphoton ionization (REMPI) schemes. Besides, several questions remain open related to the photodynamics of bromiodomethane in both the A and A’-bands concerning, in particular, the symmetry of the excited states and the role of the curve crossings leading to the final products.

The photodissociation dynamics of other methyl halides, especially of monohalomethanes, has been largely investigated. Among them, methyl iodide has indeed served as a benching test for different imaging techniques and fragment detection schemes.\textsuperscript{11,12} The first absorption band of CH\textsubscript{3}I, the A-band, consists in a broad featureless continuum between 220 and 350 nm assigned to the \( \sigma^*(C-I) \rightarrow \pi(I) \) excitation.\textsuperscript{13} Three transitions contribute to the absorption: a strong parallel transition to the \( ^3Q_0 \) state – in Mulliken’s notation for C\textsubscript{3v} symmetry – and to a lesser extent, the perpendicular transitions to the \( ^1Q_1 \) and \( ^3Q_1 \) states which play a relevant role mainly in the red and blue wings,\textsuperscript{14,15} respectively. Those three excited states present a repulsive shape and lead to prompt dissociation along the C–I coordinate. In the diabatic representation, the \( ^3Q_0 \) state is correlated to the CH\textsubscript{3}I + I\textsuperscript*(P\textsubscript{1/2}) channel while both the \( ^3Q_1 \) and \( ^3Q_2 \) states correlate with the CH\textsubscript{3}I + I\textsuperscript*(P\textsubscript{3/2}) dissociation limit (henceforth, I* and I channels, respectively).\textsuperscript{16,17} Around the maximum absorption of the band, the dissociation process occurs mainly in the \( ^3Q_0 \) state although a small amount of iodine atoms in their ground state are formed via a non-adiabatic curve crossing between the \( ^3Q_0 \) and \( ^1Q_1 \) states. The radial derivative coupling between the \( ^3Q_0(A_1) \) and the \( ^1Q_1(E) \) surfaces is necessarily zero as the states are of different symmetry,\textsuperscript{18} and, therefore, if the CH\textsubscript{3}I molecule maintained a perfect C\textsubscript{3v} geometry there should be no branching to the I channel. The observed branching requires amplitude at C\textsubscript{3v} geometries, where the C\textsubscript{3v} \( ^3Q_0 \) state transforms to 4A' in C\textsubscript{v} and the doubly degenerated \( ^3Q_1 \) and \( ^1Q_1 \) states split into two components each one of them, \( [3\text{A}', 2\text{A}'] \) and \( [5\text{A}', 4\text{A}'] \), respectively. Being of the same symmetry, the A’ components can couple via the radial derivative terms in the Hamiltonian and the intersection between the dissociative surfaces becomes a conical intersection in C\textsubscript{v} geometry.\textsuperscript{19} A dissociative wave function with significant amplitude in regions of the \( ^3Q_0 \) with reduced C\textsubscript{3v} symmetry will show branching to the I channel,\textsuperscript{20,21} such as is the case for the methyl iodide, where the reduction of symmetry is produced by large zero-point motion in the \( \nu_6 \) bend and other e-symmetry vibrations.\textsuperscript{22} In the red and blue wings, diabatic dissociation via the \( ^3Q_1 \) and \( ^1Q_1 \) states is produced, leading to a significant amount of iodine in its ground spin–orbit state. The energy partitioning, photofragment angular distributions and \( \Phi^* \) quantum yield \( (\Phi^* = [I^*/[I^*] + [I]]) \) have been reported and extensively discussed in terms of the dynamics described above (see, for instance, ref. 14, 15 and 23–25).

In dihalomethanes, the introduction of the second halogen atom produces the reduction of symmetry from C\textsubscript{3v} to C\textsubscript{v}. As a consequence, the electronic structure becomes more complex through all the absorption band, especially considering the spin–orbit interactions. The reduction of symmetry implies an additional change regarding the nature of the transitions involved. From a general point of view, transitions to A” states are characterized by a transition dipole moment perpendicular to the X–C–Y plane (X and Y = halogen atom) while transitions to A’ states can be either parallel or perpendicular to the C–X bond but in the X–C–Y plane. As we have recently reported,\textsuperscript{26} the transition dipole moment for such 4A’ and 5A’ states (the \( ^3Q_0 \) and one component of the \( ^1Q_1 \) states in C\textsubscript{3v}) in CH\textsubscript{2}BrCl are in fact oriented at an intermediated angle with respect to the C–X bond instead of being completely parallel or perpendicular to that bond as it was suggested before.\textsuperscript{28} In opposition to the case of methyl iodide, the [5A’, 4A’] states in CH\textsubscript{2}BrCl (the \( ^1Q_1 \) state in C\textsubscript{3v} symmetry) were found to be the main responsible of the absorption in the A-band, while the 4A’ [\( ^3Q_0 \)] and [3A’, 2A’] \( (^1Q_1) \) states contribute slightly at the red edge. For CH\textsubscript{2}BrCl photodissociation,\textsuperscript{26} the formation of Br\textsuperscript{*}(P\textsubscript{1/2}) atoms was attributed to direct dissociation through the 6A’ state as well as dissociation through the 5A’ state requiring a 5A’ → 4A’ reverse non-adiabatic crossing. The Br\textsuperscript{*}(P\textsubscript{1/2}) channel showed two different features: a fast contribution characterized by a similar energy partitioning and anisotropy than those for the Br\textsuperscript{*}(P\textsubscript{1/2}) channel, which was assigned to direct dissociation through the 5A’ state, and a slower component assigned to direct dissociation on the 4A’ state. Despite the work carried out, some aspects remain unclear concerning the effect of the observed avoided crossing between the 5A’ and 4A’ states and the dynamics involved in the second mechanism producing the slower contribution of the ground halogen atom.
With regard to the photodissociation dynamics of bromiodo-methane in the A-band, a similar scenario to the one described above for the CH$_2$BrCl and which would lead here to the C–I cleavage is expected. The dissociation dynamics in the A’-band, associated to the production of Br and Br* atoms, may however become more complex, due to the interference of the overlapping A-band.

The aim of the present study is to investigate the photodissociation dynamics of CH$_2$BrI around the maximum absorption wavelength of both A and A’ bands, located at 266 and 210 nm, respectively, using imaging techniques in combination with probe detection of iodine-atom, I($^2P_{3/2}$) and I($^2P_{1/2}$), and bromine-atom, Br($^2P_{3/2}$) and Br($^2P_{1/2}$), fragments via appropriate (2 + 1) resonance enhanced multiphoton ionization (REMPI) schemes. The A band is studied in one colour experiments where the same pulse, set at the REMPI resonance (≈266 nm) serves as pump and probe, i.e., excites the parent CH$_2$BrI and ionizes the corresponding fragment. The A’ band is studied in a two colour experiment, where a first pulse of 210 nm excites the parent molecule and a second pulse, set at the corresponding REMPI resonance, ionizes the selected product. The experimental results, i.e. translational energy distributions and angular distributions, are interpreted with the aid of high-level ab initio calculations consisting mainly of absorption spectra and potential energy curves in the C–I and C–Br coordinates. The paper is organized as follows: in Section 2, the experimental and theoretical approaches are presented. The most relevant experimental and theoretical results are presented in Sections 3 and 4, respectively. In Section 5, the results are discussed jointly and, finally, Section 4 is dedicated to the most important conclusions of the work.

2 Methods

2.1 Experimental

The main characteristics of the experimental setup have been described in detail previously. The whole experiment runs at a repetition rate of 10 Hz. A molecular beam is created by expanding a gas mixture of CH$_2$BrI in He (10%, 1.5 atm backing pressure) into vacuum using a pulsed nozzle (General Valve Series 9, 0.5 mm orifice). The gas pulse passes through a skimmer (Beam Dynamics, Standard Model 2, 0.5 mm diameter orifice) and reach 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 photolysis and the probe laser pulses, which are focused (f = 25 cm) and counter propagated to each other.

A sum-frequency mixing nonlinear crystal is used to combine the fundamental and second harmonic radiation of a Nd:YAG (Quanta Ray Pro 230) pumped frequency doubled dye laser (Sirah Cobra-Stretch) in order to generate the excitation radiation at 210 nm used in the two-colour experiment in the second absorption A’-band. The resulting radiation, of typically 0.15 mJ per pulse, was focused into the reaction chamber with a lens of 25 cm focal length.

The Br($^2P_{3/2}$) and Br*($^2P_{1/2}$) fragments produced in the photodissociation are detected 10 ns later via the $^2P_{3/2} \rightarrow 5P_{1/2}^{0}$ and $^2P_{3/2} \rightarrow 5P_{3/2}^{0}$ (2 + 1) REMPI schemes, respectively, at 266.62 nm and 266.68 nm (≈0.8 mJ) using a Nd:YAG (Quanta Ray Pro 190) pumped frequency doubled dye laser (Sirah Cobra-Stretch). Similarly, the I($^2P_{3/2}$) and I($^2P_{1/2}$) fragments are detected using the $^2P_{3/2} \rightarrow 7P_{3/2}^{0}$ and $^2P_{1/2} \rightarrow 7P_{1/2}^{0}$ (2 + 1) REMPI schemes at 265.8 nm and 267.3 nm, respectively.

One-colour experiments are performed using this laser at the wavelengths for (2 + 1) REMPI detection of the four atomic fragments for the study of the photodissociation at around the maximum of the first absorption A-band. In the experiments shown here, images are recorded using a parallel polarization configuration with respect to the detector plane of both the photolysis and detections lasers. However, images have also been recorded using a perpendicular polarization setup of both lasers in order to check the detector response as well as the alignment.

The I$^+$ and Br$^+$ ions are recorded using our velocity map imaging (VMI) apparatus in the single-field configuration. Briefly, only two electrodes are used and the focusing condition is achieved by translating the laser position along the time-of-flight (TOF) axis, i.e. the interaction between the laser and the molecular beam takes place at a specific distance from either the repeller or the extractor. The generated $^{81}$Br$^+$ and I$^+$ 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 microchannel plates (MCPs, Chevron configuration, 40 mm diameter). The resulting electron avalanche strikes a phosphor screen (P47), thereby creating the ion image, which is recorded by a CCD camera (SONY 1024 × 768 pixel) controlled using National Instruments (NI) LabView 7.1 and IMAQ VISION software. The final image is obtained as the sum of around 20000 laser shots, depending on the quality of the signal.

All the I$^+$ images as well the Br$^+$ images for the Br*($^2P_{1/2}$) channel in the two-colour experiments are recorded using the delayed pulsed extraction slicing. This extraction allows the ion cloud to spread in velocities so that the arrival time of the ion packet at the detector has a width of several hundreds of nanoseconds. By using a narrow detector time gate of a few tens of nanoseconds, we are able to image only the central slice of the ion packet. As Br presents two isotopes $^{79}$Br and $^{81}$Br with similar abundance, it is necessary to select an extraction delay allowing a complete separation of the ion clouds from both isotopes such that the imaged slice correspond to a single isotope. The slicing technique is employed for the Br*($^2P_{1/2}$) fragment in the two-color experiment as well as for the iodine fragment. For the other experiments, i.e. all the one-color experiments detecting Br fragments as well as for the detection or Br*($^2P_{1/2}$) fragment in the two-color experiment, the slicing technique cannot be employed due to the low signal. In the present experiment, slice images of the I$^+$ and $^{81}$Br$^+$ ions are recorded using a 400 ns extraction delay applied on the repeller plate and an effective 10 ns detector gate on the front micro-channel plate (MCP).
The velocity map Br⁺ images are quadrant symmetrised and Abel inverted using the Hankel transform, while the I⁺ and Br⁺ sliced recorded images are only quadrant symmetrised, prior to extracting the translational energy and angular distributions. We note that for all the Br⁺ images measured, the two-colour pump–probe signal represents 10–15 times the probe signal alone while the pump signal is almost non-existent.

Independent velocity-radius calibration of the apparatus is done by measuring I⁺(2P₁/₂) fragments produced after the photodissociation of CH₃I at 267.3 nm using the 3P₁/₂ → 7P₃/₂ (2 + 1) REMPI scheme (one colour pump probe experiment) taking advantage of the well known cold vibrational distribution for the CH₃ + I⁺(2P₁/₂) channel at this photolysis wavelength.⁷⁹

2.2 Theoretical

Multireference calculations were performed to simulate the absorption spectrum of CH₂BrI using a semiclassical methodology. A harmonic Wigner distribution of trajectories was employed to describe the zero point energy of the system. Geometries and frequencies were optimized using the MP2 method with the Sapporo relativistic basis set contracted to triple zeta,⁴⁶ whereas the electronic excitation energy was calculated using SA-CASSCF corrected by perturbation theory in its spin–orbit multiconfigurational quasi degenerate perturbation theory (SO-MCQDPT)⁵¹,³² form with level shifts of 0.02 and 0.01 H. Form these calculations were performed by selecting an active space that contains 12 electrons in 8 orbitals (bonding and antibonding for C–I and C–Br, and 2 lone pairs on each halogen atom). The number of states included in the state average was 18 states where all multiplicities were averaged. Since SO-MCQDPT cannot be used to calculate relaxed densities,⁴⁴ the dipoles, that require a large number of configurations to be included in the wavefunction similar to CH₃I,¹⁷ were obtained with a configuration interaction method including single excitation (CIS) considering 20 singlet and 20 triplet states. This procedure has been already checked for CH₄ and CH₂ICl.³⁵ These calculations were performed with the GAMESS-US suite with relativistic integrals until 3rd order Douglas–Kroll-Hess,³⁸-⁴⁰ with quadruple precision, taking into account explicitly the spin–orbit coupling as a two electron operator.³¹-⁴⁴

Potential energy curve calculations were performed with MOLCAS⁴⁵,⁴⁶ using the ANO-RCC basis set with a similar protocol, using a regular Douglas–Kroll Hamiltonian₄⁸-⁵⁰ and the AMFI approximation⁵¹ to take into account relativistic effects. The active space included in the calculations was the same as in the previous case, but the state averaging was done independently for singlet and triplet states. The optimizations were performed at CASSCF⁵² whereas the final potential energy curves was calculated at MS-CASPT²⁵³ with a level shift of 0.2⁵⁴ and including the spin–orbit coupling in a modified perturbation frame.

3 Experimental results

The slice images measured for the I⁺(2P₁/₂) and I⁺(2P₁/₂) species – I and I⁺ from now, respectively – obtained in one-colour experiments around 266 nm are shown in Fig. 1a and c. The same laser is employed to dissociate the molecule and to detect the 1 atoms via the corresponding (2 + 1) REMPI scheme. A single ring for each I and I⁺ photofragment is observed in the images and is attributed to the one-photon dissociation process in the A-band leading to prompt C–I bond cleavage. The center-of-mass fragment translational energy distributions (TEDs) are obtained by angular integration of the images and presented in the figures. The distributions exist in both cases in a single broad peak, centred at 0.82 eV (FWHM ≈ 0.5 eV) and at 0.42 eV (FWHM ≈ 0.3 eV) for I and I⁺, respectively, in qualitative agreement with previous results reported by Butler et al.³⁸ at 248.5 nm. The vertical bars represent the maximum translational energy $E_T(0)$ for the I⁺ and I channels, given by:

$$E_T(0) = \frac{m_{\text{CH}_2\text{Br}}}{m_{\text{CH}_2\text{Br}I}} [h
u - D_0 - E_{\text{SO}} + E_i(\text{CH}_2\text{Br})]$$ (1)

where $h\nu$ is the excitation photon energy, $E_i(\text{CH}_2\text{Br})$ is the internal energy of the bromoiodomethane molecule in the molecular beam – which is considered negligible in the present experiments – $D_0$ corresponds here to the dissociation energy of the C–I bond, 2.389 eV and $E_{\text{SO}}$ is the spin–orbit splitting of I(2P) (0.943 eV for I⁺). Finally, $m_{\text{CH}_2\text{Br}}$ and $m_{\text{CH}_2\text{Br}I}$ represent the masses for the co-fragment and the parent molecule, respectively. Since I and I⁺ are atomic species, the significant shift observed between the rise of the distributions and the maximum total available energy should be attributed to internal (ro-vibrational) energy of the CH₂Br co-fragment.

Fig. 1b and d show the inverted VMI images for 8¹Br⁺(2P₁/₂) and 8¹Br⁺(2P₁/₂) – from now Br and Br⁺, respectively – obtained in a similar one-colour experiment at around 266 nm. A careful inspection of the images brings to light three contributions in this case. The intense unstructured blot at the center obscures a weaker anisotropic ring, barely distinguishable at intermediate radii; a feeble and broad less anisotropic feature constitutes the contribution at higher radii. For both fragments the three contributions are recovered in the corresponding center-of-mass fragment translational energy distributions, also presented in Fig. 1b and d. The distributions are dominated by the broad feature located at high energies (centred at 1.25 eV), clearly differentiated from the narrow Boltzmann-like distributions at low energies; between them, a shoulder centred at 0.5 and 0.4 eV for Br and Br⁺, respectively, is perceptible. The high energy contributions have been fitted to Gaussian functions (blue and cyan lines) while the low energy contribution has been fitted using the following function:

$$I(E_T) = AE_T^2(1 - E_T)^j$$ (2)

described firstly by Muckerman⁵⁵ and lately used by Suits and coworkers.⁵⁶ This function, where $E_T$ is the translational energy, is generally used to reproduce easily Boltzmann type distributions although the fitting parameters ($A$, $i$ and $j$) do not contain physical meaning. The result of the fit is represented by the magenta line. For the sake of clarity, these three contributions are labelled a, b and c in Fig. 1b and d. Although these three contributions are not well resolved, in particular the Gaussian
distribution b, three main arguments justify this analysis. Firstly, the results presented in Fig. 1b and d are well reproducible for varying experimental conditions such as the power of the laser and the molecular beam. Secondly, these three contributions have been previously reported by Butler and co-workers, following excitation at 248 nm. Finally, the measured angular distributions discussed below and summarized by the anisotropy parameters in Table 1 support the existence of three contributions.

As previously, vertical bars represent the maximum fragment translational energy \( E_T \) for the \( \text{Br}^* \) and \( \text{Br} \) channels, given by eqn (1), where now \( D_0 \) corresponds to the dissociation energy of the C–Br bond, 2.936 eV, \( E_{SO} \) to the spin–orbit splitting of \( \text{Br}(2P) \), 0.46 eV for \( \text{Br}^* \) and \( m_{\text{CH}_2\text{I}} \) is employed as the mass of the co-fragment. We observe that the broad contribution c lies partially at translational energies above the maximum reference, suggesting that it might be attributed to a different process. The available energy is calculated without taking into consideration the internal energy of the parent molecule, which in certain cases is known to play a relevant role in the photodissociation process. To investigate such possibility images of both fragments were taken in different temporal regions of the pulsed molecular beam with respect to the laser pulses, where different degrees of internal relaxation of the parent molecule are expected. In general terms, it is expected that rotational and vibrational relaxation increases when inner parts of the gas pulse are interrogated. Since no significant dependence of the TEDs was found with the relative position of the laser and gas pulses, any contribution from initially excited

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<th>Channel</th>
<th>( f_{\text{int}} )</th>
<th>( \beta_2 )</th>
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<th>( f_{\text{int}} )</th>
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<td>( \text{Br}(2P_{3/2}) )</td>
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<td>0.25</td>
<td>—</td>
<td>0.46</td>
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<td>Process b</td>
<td>0.7</td>
<td>0.73</td>
<td>−0.15</td>
<td>0.73</td>
<td>0.55</td>
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<td>Process c</td>
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<td>0.77</td>
<td>−0.32</td>
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<td>( \text{Br}^*(2P_{3/2}) )</td>
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<td>Process a</td>
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<td>0.21</td>
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<td>0.53</td>
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<tr>
<td>Process b</td>
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<td>0.75</td>
<td>—</td>
<td>0.7</td>
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<td>−0.24</td>
<td>1.21</td>
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(mainly vibrationally) parent molecules was ruled out in the current experiments. Secondary dissociation of the CH₂Br radicals produced in the first one-photon C–I bond cleavage of the molecule – such as shown in Fig. 1a and c – has been considered as a possible source of the broad c contribution, i.e.: 

\[ \text{CH}_2\text{Br} + h\nu \rightarrow \text{CH}_2\text{Br} + 1/1^* \]
\[ \text{CH}_2\text{Br} + h\nu \rightarrow \text{CH}_2 + \text{Br}/\text{Br}^* \]  

(3)

The Br/Br* species formed in the photodissociation of the CH₂Br radical would then be ionized via the corresponding (2 + 1) REMPI scheme. This kind of secondary photodissociation processes have been evoked previously in dihalomethanes photodissociation© and, in particular, for Br/Br* formation from CH₂BrI at 248.5 nm.© Taking into account the available energy after the first step and the C–Br bond dissociation energy of the CH₂Br radical, \( D_0 = 3.84 \text{ eV,}^{60} \) such process is indeed energetically allowed. Nevertheless, the maximum translational energy expected for the Br/Br* fragments becomes complicated to determine since it depends on the mechanism, e.g. sequential, synchronous or asynchronous, on the emission angles of each fragment as well as on the internal energy of the intermediate CH₂Br radical.© The broad translational energy distribution associated to the process c would reflect the partitioning in energy between internal – ro-vibrational – and translational modes. Further investigations are required in order to get a deeper understanding of the mechanisms and dynamics leading to process c.

According to the maximum \( E_T(\text{Br}) \) reference for the one-photon dissociation process, the middle contribution b can be assigned to a one-photon absorption and dissociation process at around 266.6 nm leading to C–Br bond cleavage. To clarify the source of the c and b contributions, Br and Br* images as a function of the power of the pump laser have been recorded. The results support the former assignments, i.e. the one-photon process assignment for b and the two-photon assumption for process c.

The low-energy contribution (process a) can be attributed to either relaxation and statistical dissociation in the ground state or, more probably, to multiphoton dissociative ionization processes. The fact that the low energy contribution does not appear in the I/I* images indicate that the multiphoton absorption step for the Br/Br* channels should involve excited-state resonances in the C–Br coordinate. The possible photodissociation of dimers present in the molecular beam could explain contribution a, as evoked by Butler et al.© In a former work on the photodissociation of nitromethane at 193 nm carried out in our group,© such low energy contributions in the TEDs, attributed to dimers photodissociation, strongly depended on the region of the molecular beam investigated. The same experiment described above to interrogate the source of contribution c, in which Br and Br* images were recorded in different temporal regions of the pulsed molecular beam – where the concentration of clusters varies due to the different degrees of ro-vibrational cooling of the parent molecule – served us to rule out dimer photodissociation as a source for contribution a. In any case, in this study we will focus mainly on contribution b, associated to the photodynamics occurring in the A and A' bands.

As pointed out previously, since Br and Br* are atomic species, the energy shift between the observed peak (blue line) for this process b and the maximum available energy reflects the internal (ro-vibrational) energy of the CH₂I co-fragment. The internal energy distributions of the CH₂I and CH₂Br species can be deduced from the corresponding TEDs by energy conservation according to the following equation:

\[
E_{\text{int}}(\text{co-fragment}) = E_{\text{av}} - E_{\text{tot}}
\]
\[
= h\nu + E_i(\text{CH}_2\text{Br}) - D_0 - E_{\text{SO}} - E_{\text{tot}}
\]
\[
= h\nu + E_i(\text{CH}_2\text{Br}) - D_0 - E_{\text{SO}} - m_{\text{CH}_2\text{Br}}(E_T(\text{fragment})/m_{\text{co-fragment}})
\]  

(4)

where \( E_{\text{av}} \) represents the total available energy and \( E_{\text{tot}} \) the total translational energy, \( m_{\text{co-fragment}} \) represents the corresponding mass for CH₂Br or CH₂I, and \( E_i(\text{fragment}) \) the fragment translational energy for the I or Br fragment, respectively. The CH₂Br and CH₂I internal energy distributions derived from the corresponding TEDs are shown in Fig. 2a and b, respectively. For both Br and Br* channels (see Fig. 2b), the CH₂I internal energy distribution is plotted for process b (blue line in the TED shown in Fig. 1b and d) exclusively using the Gaussian function employed in the fit.

Significant internal energy in both CH₂Br and CH₂I species is observed for all channels, as expected from the TEDs. For both C–Br and C–I bond cleavage pathways, the ground spin–orbit (Br and I) channels are characterized by a higher ro-vibrational excitation of the co-fragment, as reflected by both the full-width-half-maximum (FWHM) of the distributions and the position of their maxima. Similar results have been reported for the photodissociation of other dihalomethanes, such as CH₂I₂,© CHBrCl,© CH₂ClI,© and CH₂BrCl.© The fractions of the available energy released into internal energy of the co-fragment, \( f_{\text{int}} \), are summarized in Table 1. The obtained values vary between \( f_{\text{int}} = 0.63 \) and 0.73 in qualitative agreement with previous results reported by Butler et al. at 248.5 nm.© Strikingly, the \( f_{\text{int}} \) is slightly higher for the excited spin–orbit I* channel than for the ground state, in contrast to the Br/Br* case and to almost all previous reports on dihalomethanes (see, for instance, Fig. 7 of ref. 64).

In a first attempt to assign the possible populated vibrational modes of the CH₂Br and CH₂I co-fragments, the CH₂ s-stretch mode \( \nu_1 = 3050 \) and 3049 cm⁻¹, for CH₂Br and CH₂I, respectively© and the CH₂ scissors mode \( \nu_2 = 1330 \) and 1355 cm⁻¹, respectively© have been represented by combs in Fig. 2a and b. These two modes have been selected considering previous reports where their role in the photodissociation of other methyl halides is particularly highlighted.© These models predict a significant
vibrational and rotational excitation imparted to the polyatomic fragment with no thermal distribution of rotational states. Bearing this in mind and if no further considerations concerning the rotational distributions are made, the results of Fig. 2 suggest that photodissociation of CH$_2$BrI produces CH$_2$Br and CH$_2$I products with major vibrational excitation in $n_1$ (with quanta between 2 and 4) and some excitation in $n_2$.

In the two-colour experiments with excitation at 210 nm, no I or I* species were detected, in agreement with the previous report by Butler and co-workers.$^4$ As expected, excitation around the maximum of the A$_0^0$-band appears to lead mainly to C–Br bond cleavage while the C–I bond fission seems unfavoured. The images recorded for the Br and Br* channels following excitation at 210 nm are presented in Fig. 3a and b, respectively, as well as the corresponding fragment translational energy distributions. The three contributions observed in Fig. 1 are recovered here although significant differences in their relative intensity are observed. For both channels, an almost isotropic ring characterizes the images and the corresponding TEDs are dominated – especially for the Br* channel – by the matching sharp peak. The ring is assigned to prompt dissociation along the C–Br coordinate, the process b observed at 266 nm (see Fig. 1b and b). The broad structure observed at higher energies, process c, is significantly weaker at this excitation wavelength and almost non existent for the Br channel; finally contribution a at low energies is the major contribution for the Br ground spin–orbit state channel.

To disentangle the three contributions, a similar fitting procedure to the one employed in the one-colour experiments is used here. The overall profile is fitted to two Gaussian functions to reproduce contributions b and c (blue and cyan lines, respectively) and a Muckerman function (eqn (2)) for the Boltzmann-type contribution a (magenta line). The weaker contribution of process c at this wavelength supports indeed the possible two-photon secondary dissociation, described by eqn (3). The first step of this reaction mechanism consisting on the C–I cleavage leading to CH$_2$I formation, is not favoured in the A$^0$-band and therefore this process c would be unattainable.

Fig. 4 displays the CH$_2$I internal energy distribution deduced from eqn (4) corresponding to process b using the blue Gaussian function (shown in Fig. 3). Similarly to the photodissociation at 266 nm, the process is characterized by a significant internal energy of the co-fragment, slightly higher for the ground state Br channel than for the excited spin–orbit Br* channel. Similar attempt to characterize the internal energy of the co-product suggests that the CH$_2$I species is formed with vibrational excitation in the $n_1$ s-stretch mode between 4 and 6, although the same considerations should be done in this case.

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**Fig. 2** (a) CH$_2$Br and (b) CH$_2$I internal energy energy distributions obtained from the corresponding I(3P$_{3/2}$), I*(3P$_{1/2}$) and Br(3P$_{3/2}$), Br*(3P$_{1/2}$) co-fragment translational energy distributions depicted in Fig. 1 using eqn (4). The combs indicate possible populated vibrational levels of the representative CH$_2$ s-stretch ($v_1$) and CH$_2$ scissors ($v_2$) modes of the CH$_2$Br and CH$_2$I fragments. In the case of the Br(3P$_{3/2}$) and Br*(3P$_{1/2}$) channels, the Gaussian functions employed in the fits are plotted (blue curves in Fig. 1b and d).

**Fig. 3** (a) Inverted velocity map image for the Br fragment and (b) symmetrized slice image for the Br* fragments, both detected by (2 + 1) REMPI at around 266.6 nm from the CH$_2$BrI photodissociation at 210 nm (two-colour experiment). The double arrow indicates the direction of the polarization of both laser pulses. The corresponding translational energy distributions obtained from the angular integration of the images are included in the figures. The vertical bars indicate the maximum translational energy for the corresponding dissociation limits: CH$_2$I + Br(3P$_{3/2}$) (a) and CH$_2$I + Br*(3P$_{1/2}$) (b). The colour lines represent the fit to the different contributions that can be distinguished in the distributions. Low energy contribution (process a, magenta line); direct dissociation (process b, dark blue line); secondary dissociation (process c, cyan line). The red line represents the overall fit.
The corresponding \( f_{\text{int}} \) fractions, also summarized in Table 1, present values around 0.7, reflecting a similar partitioning of the available energy between the internal excitation and translational energy in both A and A'

bands.

The inverted velocity map or the raw slice images recorded for all channels (Br and Br* as well as I and I*) in both A and A' bands are radially integrated to obtain the corresponding angular distributions, depicted in Fig. 5. For the Br and Br* channels at 266 nm three specific ranges of pixels were carefully selected in order to extract the angular information for each contribution as separately as possible although the three contributions partially overlap in the TED. The obtained angular distributions for the I and I* species formed at 266 nm are shown in Fig. 5a and d, respectively; the Br and Br* distributions assigned to prompt C-Br bond cleavage (contribution b in the corresponding TEDs) obtained at 266 nm and 210 nm are shown in Fig. 5b and e and in Fig. 5c and f, respectively.

The anisotropy parameters \( \beta_{2k} \) are obtained by fitting the experimental angular distributions to

\[
I(\theta) \approx 1 + \sum_{k=0}^{N} \beta_{2k} P_{2k}(\cos \theta)
\]

where \( \theta \) represents the angle between the photolysis laser polarization and the fragment recoil velocity and \( P_{2k}(\cos \theta) \) is the 2\( k \)th order Legendre polynomial. The number of parameters needed to characterize the angular distribution depends both on the number of photons involved in the process and the total angular momenta of the species detected. For a one photon dissociation process and a (2 + 1) REMPI detection scheme through a single intermediate \( J \)-level, \( n \) is constrained by the maximum allowed integers of \( 2 + 1 \) or \( J + 1 \), which ever is smallest. For excited state spin–orbit I* and Br* fragments, \( J = 1/2 \) and only one anisotropy parameter \( \beta_2 \) is necessary to characterize the angular distribution. For ground state I and Br fragments, \( J = 3/2 \) and up to \( \beta_6 \) could be necessary.

The anisotropy parameters obtained from the fitting are summarized in Table 1. For the Br and Br* channels at 266 nm the values for processes a and c are also reported. The values extracted for process b are, however, contaminated by the two other contributions due to the overlap between the three distributions as observed in the TEDs (see Fig. 1). An almost isotropic distribution characterizes contribution a, which is consistent with a statistical dissociation mechanism. In addition, two anisotropy parameters characterize contribution c, which

Fig. 4 CH₂I internal energy distributions obtained from the corresponding Br and Br* co-fragments translational energy distributions using eqn (4). The combs indicate possible populated vibrational levels of the CH₂I \( v_1 \) and \( v_2 \) modes (see the text for details).

Fig. 5 Angular distributions corresponding to the I and I* species formed at 266 nm, (a and d), respectively, and for the direct dissociation mechanism leading to the formation of Br and Br* (contribution b) at 266 nm, (b and e), and 210 nm, (c and f), respectively. The red curves represent the fit of the data to eqn (5).
supports the two-photon process assumption. Besides, following Dixon’s model of angular distributions produced by multiphoton dissociation processes for a linear molecule, a positive $\beta_2$ parameter and a negative $\beta_1$ parameter are usually associated with a two-photon absorption step involving both parallel and perpendicular transitions. A more realistic interpretation of our case should be carried out on the base of theoretical modelization taking into account the geometry of the CH$_3$BrI molecule and the possible rotation of the molecule.

In the one-colour experiments at 266 nm, two anisotropy parameters are needed to fit the angular distributions corresponding to contribution b for both ground-state Br and I channels. This fact reflects certain angular momentum polarization, although a deeper analysis would require supplementary measurements in order to understand such effects, which are out of the scope of the present study.

All the reported $\beta_2$ values are rather positive although significantly lower compared to the limiting value for a parallel transition ($\beta_2 = 2$). Intermediate $\beta$ values in between the extreme values of 2 and $-1$ can have several origins: a mixed transition, depolarization due to an excited state lifetime comparable to the rotational period of the molecule, a breakdown of the axial recoil approximation and/or, in polyatomic molecules, to a recoil axis which is neither parallel nor perpendicular to the transition dipole moment.

The C–I bond cleavage process at 266 nm yielding I and I$^*$ atoms is characterized by $\beta_2$ values of 1.38 and 1.08, respectively, which are lower in comparison with those obtained for CH$_3$I$^{23}$ and ICH$_2$Cl.$^{35}$ Besides, the higher $\beta_2$ value is obtained for the I channel compared to the excited spin–orbit channel in contrast to the case of CH$_3$I and CH$_2$I, highlighting the occurrence of a different photodynamics in CH$_3$BrI.

A similar value of $\beta_2$ characterizes both Br and Br$^*$ channels at 266 nm, while at 210 nm the angular distributions become more isotropic especially for the Br$^*$ channel.

4 Theoretical results

The CH$_3$BrI electronic states resulting from $ab$ initio calculations are listed in Table 2 in terms of the energy at the Franck–Condon geometry – from the SA-CASSCF calculation – and the electronic notation in C$_2$v symmetry. For the sake of clarity, the correspondence with Mulliken’s notation in C$_2$v symmetry is indicated only for the excited states corresponding to the A-band. The symmetry obtained for these electronic states is consistent with the results obtained in our recent study on the photodissociation of CH$_3$BrCl.$^{26}$ The two first excited electronic states of CH$_3$Br correspond actually to the two C$_2$v $^3Q_2$ states, previously reported by Lepetit and coworkers,$^{74}$ for CH$_3$Br, lying here at 3.83 eV, which were not taken into account by North and coworkers.$^{20}$ The correlation between the notation employed here and North and coworkers’ notation is also specified in Table 2. The total transition dipole moment and the transition dipole moments (TDMs) calculated with respect to each axis were computed using the CIS method and are also summarized in Table 2. The XY plane is defined by the Br, C and I atoms (Br–C–I plane), where the Y axis lies along the C–I bond.

Electronic states with A$'$ symmetry are characterized by a transition dipole moment perpendicular to the Br–C–I plane, $i.e.$ along the Z axis, while TDMs for those with A$''$ symmetry are

Table 2  Energy at the Franck–Condon (FC) geometry, symmetry in C$_v$, as well as total dipole moment (TDM) and for each axis of the computed electronic states of CH$_3$BrI. X axis is located in the I–C–Br plane, perpendicular to the C–I bond, Y axis in the I–C–Br plane, along the C–I bond, and the Z axis is perpendicular to the I–C–Br plane. The correlated symmetry in C$_3$v, and the notation by North et al.$^{23}$ are also listed. The table has been truncated up to the 12A$'$ state. The complete list of states up to 1B$'$ is reported in Table S1 (see ES1).

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<th>State number</th>
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<th>Symmetry (C$_v$)</th>
<th>Correlated symmetry (C$_3$v)</th>
<th>North et al.'s notation$^{23}$</th>
<th>TDM</th>
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<th>Y</th>
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contained in the Br–C–I plane. In transitions corresponding to the A-band leading to the C–I bond cleavage, the TDMs could lie either along the Y axis or along the X axis, i.e. parallel or perpendicular to the C–I bond, respectively. TDMs appear, however, to be located at a certain angle with respect to the C–I bond, as observed in Table 2. In the A-band, total TDMs reflect the fact that the absorption is produced mainly to the 5A′ excited state (1Q1 in C3v symmetry) and in a less extent to the 3A′ (1Q1 in C3v symmetry), 4A′ (1Q0 in C3v symmetry) and 6A′ excited states. Absorption to the 4A′ excited state (1Q1 in C3v symmetry) appears to be minor in contrast with the role of this state in the absorption of CH2BrCl.\(^{26}\) We note that absorption to the 4A′ excited state (3Q0 in C3v symmetry) is rather secondary for CH2BrI in strong contrast to CH3I. The major role of this state in the photodissociation of CH3I is in fact pretty exceptional due to the coupling of the 1Q1 state, mainly characterized as a triplet state, with different singlet electronic states by the agency of the strong spin–orbit interaction which characterizes the iodine atom.\(^{17}\) Such strong coupling seems to be somehow unachievable in the presence of the second halogen atom.

Regarding the A′-band, which corresponds to the C–Br bond cleavage, a TDM parallel to the C–Br bond would in fact present components along both X and Y axis, since the computed Br–C–I angle is around 114°. Total TDMs show in this case the major contribution of the 9A′ excited state to the absorption spectrum and minor contributions of the 8A′, 9A′′, 10A′, 10A″ and 11A′ excited states.

The total computed absorption spectrum is depicted in Fig. 6a and compared to the experimental spectrum recorded by Mössinger et al.\(^{5}\) The first A absorption band is well reproduced, lying between 3.5 and 5.2 eV with a maximum around 4.6 eV (\(\approx 270\) nm) while the second A′ absorption band appears shifted to lower energies with respect to the experimental one. This shift may be due to the partial overlap between the A′-band and the B-band rising around 200 nm as observed in the experimental spectrum. Further calculations including the Rydberg states excited in the B-band may allow a better reproduction of the experimental spectrum. We note, nevertheless, that the good agreement obtained here using the SO-MCQDPT method is remarkable, considering the inherent difficulty in computing energies for halomethanes containing iodine.

The absorption spectrum is also represented as a function of the orientation of the transition dipole moment in Fig. 6a. In both the A and A′ bands, the absorption is mainly governed by a contribution contained in the Br–C–I plane while the contribution perpendicular to the plane (in the Z axis) is rather negligible. In the A-band, the contribution along the X axis (i.e. perpendicular to the C–I bond) represents around 30% at 266 nm with respect to the total absorption. A similar ratio was obtained and recently reported for CH3I in its A-band.\(^{35}\) In the A′-band the contribution perpendicular to the C–Br bond represents only a \(\approx 10\)% of the total absorption at the maximum absorption wavelength.

The decomposition of the absorption spectrum into the components associated to the different computed excited states has also been performed and represented in Fig. 6b, although this decomposition is tentative. While the CIS method used here permits to obtain a reasonable absorption spectrum as a function of the orientation of the TDMs, out-of-plane movements are allowed, the C3v symmetry is broken and, therefore, the assignment to A′ or A′′ electronic symmetries is somewhat speculative.

According to Fig. 6b the absorption spectrum in the A-band appears to be equally dominated by both the 5A′ and 4A′′ excited states (blue and cyan lines) (1Q1 in C3v symmetry) especially at the maximum absorption wavelength, close to the wavelength employed in the experiments, 266 nm. Considering the computed TDMs listed in Table 2, the contribution from the 4A′′ state seems to be, however, significantly overestimated. The absorption spectrum shows good agreement with the computed TDMs at the edges, where minor contributions from the 4A′ (3Q0 in C3v symmetry, magenta line) and the 6A′ and 6A″ states are obtained at the red and blue wings, respectively. In addition, the 2A′ excited state and to a lesser extent, the 3A′ contribute marginally to the absorption in the red edge.

In the A′-band, three excited states contribute mainly to the spectrum around the maximum absorption wavelength, namely the 9A′, the 8A″ and the 10A″ excited states. Minor contributions from the 10A′ and the 11A′ states in the blue edge, and from the 7A′ in the red edge, are also observed. Similarly to the A-band,
the contribution from both the 8A’’ and 10A’’ states is certainly overestimated since the perpendicular contribution along the Z axis is completely negligible according to Fig. 6a. This discrepancy reflects the limitations in the assignment of electronic states of A’ and A’’ symmetries performed in Fig. 6b.

The corresponding potential energy curves (PECs) have been computed as a function of the C-I distance and are shown in their adiabatic representation in Fig. 7. The bound ground state correlates to the first dissociation limit, CH$_2$Br + I($^3P_{3/2}$), and several purely repulsive states characterize the A-band, similarly to the case of other halomethanes.$^{16,26,35,74}$ Adiabatically, the [2A’, 3A’], 4A’ and 4A’’ states correlate as well with the I channel, while the 5A’ state correlates with the CH$_2$Br + I($^3P_{1/2}$) limit. The band is completed with the repulsive 6A’ and 6A’’ excited states which correlate with the I$^*$ channel. As expected in halomethanes, an avoided crossing is observed close to the Franck–Condor region involving the 4A’, 4A’’ and the 5A’ states. An expanded view of the curve crossing is shown in the inset of Fig. 7. In the corresponding diabatic representation, the 4A’ state can be expected to correlate to the I$^*$ channel while the 5A’ and 4A’’ states would lead to the I channel similarly to other methyl halides.$^{75-77}$ The present PECs are indeed consistent with those reported previously by Lindh and co-workers$^7$ although in their work the A’ and A’’ electronic symmetries of the excited states were not assigned. The authors performed, on the other hand, a diabatization of the electronic states involved in the curve crossing which is coherent with the picture proposed here based on our experimental and theoretical results.

At higher energies corresponding to the A’-band, several bound excited states correlating with an upper limit at around 6.2 eV are observed. In particular, transitions from the ground state to the 8A’, 9A’ and 10A’ states certainly correspond to this band.

Fig. 8 shows the potential energy curves as a function of the C–Br distance. The observed excited states generate now a heavily intricate picture. Taking into account that the A-band is associated to the C–I bond cleavage and the A’-band corresponds to the C–Br bond cleavage, the production of Br and Br$^*$ atoms at 266 nm is explained if an avoided crossing is produced between the excited states corresponding to both bands. The states involved in the crossing are, mainly, the A-band 2A’, 3A’, 4A’, 4A’’, 5A’ and 6A’’ states and the A’-band 8A’, 9A’ and 10A’ states. In a diabatic representation, the 2A’, 3A’, 4A’, 4A’’ and 5A’ states are in fact expected to be bound and to correlate with an upper limit around 6.2 eV while the 8A’, 9A’ and 10A’ states would be repulsive and lead to the C–Br bond cleavage. These latest states would be correlated to either the Br or the Br$^*$ channel.

We note that the potential energy curves presented here (Fig. 7 and 8) are in good agreement with those reported previously by Lindh and coworkers.$^7$ In their detailed study, an attempt of diabatization of the curves involved in the avoided crossing between the two bands as a function of C–Br distance was performed. Since the diabatization process did not change substantially the shape of the PECs, including the avoided crossing, the authors concluded that the excited states in the A’-band were bound along both the C–I and C–Br coordinates and that the dissociation could only occur through relaxation to nearby lower excited states involving e.g. internal conversion or intersystem crossing.

5 Discussion

The experimental and theoretical results presented here allow us to propose a coherent picture of the reaction pathways taking place around the maximum of the A and A’ bands.

5.1 One-colour experiments: A-band photodissociation

The angular and translational energy distributions of the I and I$^*$ products obtained from the photodissociation at 266 nm are
consistent with a prompt dissociation process along a repulsive surface, presumably the 5A' according to the ab initio calculations presented here. In comparison with monohalomethanes, the energy distributions in Fig. 1a and c show larger internal energy in the polyatomic co-fragment, which is a consequence of the different symmetry of the CH₂ and CH₂Br moieties in the respective ground and excited states. In monohalomethanes the 3Q₉₀ ← Xₐₐ₁ absorption step involves little change in the parent molecule geometry and most of the vibrational excitation shown in the CH₃ product is produced due to the 3Q₀ ← 3Q₁ curve crossing. In the dissociation of the CH₂BrI, however, the CH₂Br radical receives a substantial amount of internal energy in the dissociation process, in particular in rotational degrees of freedom, caused by the change in the internal angles of the molecule upon electronic excitation. While the C–H does not vary substantially, the computed H–C–H and H–C–Br angles change from 113° and 107.9° in CH₂BrI to 123.4° and 117.6° in CH₂Br, respectively. In addition, the I channel is characterized by a slightly lower fₘₐₜ with respect to the I* channel.

The reduced anisotropy parameters obtained for the I and I* channels in comparison with the limiting values for a parallel or perpendicular transition are related to the fact that the recoil axis lies not parallel nor perpendicular to the dipole transition moment. The TDM for the 5A' state is in the Br–C–I plane and is estimated to be at around 33° with respect to the C–I bond. On the other hand, the I channel is characterized by a higher β₂ value with respect to the I* channel (see Table 1). Indirect dissociation through the 5A' state involving the 5A' → 4A'/4A'' non adiabatic crossing would lead to the formation of I*. Such transfer of population at a non adiabatic crossing often involves vibrational selectivity and, therefore, to reduced measured anisotropy parameters. In particular, the 5A' → 4A'' crossing is forbidden by symmetry and therefore a breakdown of the symmetry due to some vibrational excitation of the molecule or a torsion of the C–I bond may be needed to allow this transfer of population.

It must be noted that, considering the decomposition into spectral components shown in Fig. 6b, a second dissociation mechanism should be taken into consideration. At 266 nm, the calculations predict a maximum absorption to the 4A' spectral components shown in Fig. 6b, a second dissociation of population. Symmetry due to some vibrational excitation of the molecule or is forbidden by symmetry and therefore a breakdown of the dynamics leading to process b is similar up to some extent to the one discussed above for the formation of I and I* species. At 266 nm, major excitation is produced to the 5A' excited state which, in a typical diabatic representation is likely to be bound in the C–Br coordinate. A curve crossing with an upper excited repulsive state of the proper symmetry, such as the 9A' would lead to the asymptotic Br and Br* channels. The experimental β₂ anisotropy parameters obtained for Br and Br* are markedly smaller than those obtained for I and I*, reflecting the adiabatic passing through the conical intersection. Similarly to what has been previously reported for CH₂I₂²,²³ and for CH₂BrCl,²⁶ such curve crossing may induce a certain selection of ro-vibrationally excited states leading to a distortion of the geometry – i.e. to reduced anisotropy parameters. The widths of contribution b of the Br and Br* TEDs are likewise broader than those of the corresponding I and I* TEDs. In the vicinity of the conical intersection, the sampling of different geometries that enables the excited CH₂BrI* to go through the passage, produces a transfer of energy from translational to internal degrees of freedom. If such effect is added to the change of geometry produced between the parent CH₂BrI and the CH₂I product radical (for Br/Br* co-products), the result would be the observed broadening in the TEDs. The analysis made of contribution b must, however, be considered carefully due to the overlapping with contributions a and c. In particular, a process presents a rather isotropic distribution, which could affect the β₂ extracted for process b. The anisotropy parameter values measured for contribution c are, nevertheless, safely measured without contamination from the other two processes. Bearing this in mind, and considering the β₂ values measured for process c, it can be conclude that the β₂ values presented in Table 1 for process b constitute lower limits for the dissociation anisotropy.

5.2 Two-colour experiments: A'-band photodissociation

The main fact to be noted at 210 nm excitation is the absence of the I and I* channels. In agreement with the computed absorption spectrum and the PECs shown in Fig. 7, absorption at 210 nm leads mainly to the 9A' state and, to a less extent, to the 8A'' and 10A'' states, which indeed appear to be bounded in the C–I coordinate. Besides, no avoided crossing is observed between these states and the lower repulsive states correlating to the I and I* channels. The Br and Br* channels are on the other hand characterized by a significant increase of process b with respect to processes a and c. In a diabatic representation, direct dissociation of the 9A' excited state is expected to lead to the Br or Br* channels. However, since the observed avoided crossing involves several excited states from both absorption bands, it is difficult to completely elucidate the reaction pathways. The TEDs for both channels are sensibly narrower than those obtained at 266 nm, while the β₂ parameters are smaller. The first fact points towards a minor participation of non adiabatic pathways, while the second points towards the contribution of different A' and A'' states to the process.

The diabatization of the PECs presented in Fig. 8 could shed some light on the dynamics involved in the curve crossing and could help to specify the populated excited states and reaction pathways involved in the Br and Br* dissociation channels.
Finding an accurate procedure for the diabatization seems, however, rather difficult, mainly due to the presence of two halogen atoms with a strong spin–orbit interaction. On the other hand, femtosecond time-resolved experiments following excitation at 210 nm as well as on-the-fly trajectories could be an asset in order to unravel the dynamics induced by the avoided crossing involving several states from both the A and A’ absorption bands.

6 Conclusions

The photodissociation dynamics of CH2BrI has been investigated by combining imaging pump–probe experiments at the maximum of the A and A’ bands, around 266 (in one-colour experiments) and 210 nm (in two-colour experiments), and high-level ab initio calculations. Translational energy distributions and angular distributions for the I, I*, Br and Br* photofragments detected by 2 + 1 REMPI schemes are presented and discussed. The absorption spectrum has been computed and decomposed as a function of the orientation of the transition dipole moment and as a function of the populated excited states. The potential energy curves as a function of the C–I and C–Br distances for the first thirty-six excited states have also been reported.

According to the experimental and theoretical results, in the A-band, a direct dissociation through the 5A’ excited state leads to the I channel, while I* atoms are produced via the 5A’ → 4A’/4A” non adiabatic crossing. The presence of Br and Br* fragments has been attributed to the indirect dissociation via a curve crossing between the 5A’ with upper excited states such as the 9A’ correlating to the Br and Br* channels.

A strong photoselectivity characterizes the dynamics in the A’-band since I and I* atoms in the two-colour experiments are attributed to the indirect dissociation.

There are no conflicts to declare.

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