Two-color studies of CH$_3$Br excitation dynamics with MPI and slice imaging†

Arnar Haflíðason, Pavle Glodíc, Greta Koumarianou, Peter C. Samartzis and Ágúst Kvaran

Two-color pump–probe experiments were performed to explore the multiphoton dynamics of CH$_3$Br at high excitation energies of 8–10 eV, involving two-photon resonant excitations to a number of np and nd Rydberg states (pump) followed by REMPI detection (probe) of the Br, Br* and CH$_3$(X) photoproducts. Slice images of Br$^+$ and CH$_3^+$ ions were recorded in pump-only, probe-only and pump and probe experiments. Kinetic-energy release spectra (KERS), as well as spatial anisotropy parameters, were extracted from the images to identify the processes and the dynamics involved. Predissociation channels, following the two-photon resonant excitations and non-resonant photodissociation forming CH$_3$(X) and Br/Br*, were identified and characterized. Furthermore, the probe excitations for CH$_3$(X) involved near-resonant excitations to lower energy 5s Rydberg states of CH$_3$Br. In three-photon excitation processes, a striking contrast is seen between excitations via the p/d and the s Rydberg states. Involvement of high-energy interactions between Rydberg and ion-pair states is identified.

I. Introduction

Significant emphasis has been placed on the photodissociation dynamics of the halo-carbons for decades; in particular for the methyl monohalides.$^{1-13}$ Whereas methyl iodide (CH$_3$I) has attracted most attention,$^{14-28}$ substantial work has also been done on methyl bromide (CH$_3$Br).$^{1-5,7,10-12,19,20,29-32}$ Most of those studies have explored the dynamics of repulsive valence states in the A-band spectral region.$^{3-9}$ Less is known about excitations to higher energies where Rydberg states dominate excitation dynamics. Laser excitations by the method of resonance enhanced multi-photon ionization (REMPI) are suitable to access Rydberg states conveniently by use of visible or near-UV radiation.$^{1,2,10,12,13,21,22,24,25,30,33-36}$ Furthermore, due to selection rules, more states may be accessed by multiphoton excitation than by single-photon absorption.$^{37-40}$ State interactions gradually increase with excitation energy as the density of states increases. This can cause spectral perturbations such as line shifts and/or line broadening.$^{41-46}$ Interactions between CH$_3$+Br Rydberg states and the ion-pair/valence state, CH$_3^+$Br$^-$, could be involved in photoion pair formation, analogous to observations for some halogen-containing diatomic molecules.$^{37-51}$ By further analogy with observations for the hydrogen halides there is reason to believe that Rydberg to ion-pair interactions are important in predissociation processes.$^{44,45,52-56}$

REMPI data of CH$_3$Br for one-, two- and three-photon resonant excitations to a series of Rydberg states have been reported.$^{2,10,13}$ In (2 + m) REMPI, formation of CH$_3^+$ ions is found to dominate whereas parent ion signals are negligible and Br$^+$ signals are very weak. Here, (2 + m) represents two-photon resonant excitation to intermediate (Rydberg) states followed by m-photon ionization to form M$^+$ for M = CH$_3$, CH$_3$, Br or CBr. The intensities of fragment ion signals typically vary as CH$_3^+$ > CH$_2^+$ > CH$^+$ > (Br$^+$,CBr$^+$).$^{2,10}$ Slice imaging experiments reveal different mechanisms for CH$_3^+$, CH$_3$Br$^+$ and Br$^+$ ion formation, depending on the excitation energy and resonant Rydberg states.$^{1,2}$ These are summarized in Fig. 1 and Table 1 in terms of the number of photons (1–4) required prior to fragmentation (1, 2, 3c, 3b and 4 in Fig. 1) or autoionization (3a in Fig. 1). Ion signals due to three-photon dissociation processes appear as sharp peaks in REMPI spectra (Fig. 2a) but as broad features peaking at low kinetic energies in images and KER distributions (KERS). The sharp REMPI peaks are due to the two-photon level-to-level resonant excitations (resonant contribution) to the CH$_3$Br Rydberg states (CH$_3$Br$^+$) and the broad KERS are due to energy redistribution among the molecule’s internal degrees of freedom prior to dissociation in metastable states. Ion signals due to one-photon dissociation non-resonant processes (non-resonant contributions), on the other hand, appear as a broad underlying continuum in the REMPI spectra (Fig. 2a) and as sharp peaks in KER distributions.

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Signals due to ionization of CH$_3$ Rydberg states (CH$_3$**) were found for all the measurements of the p/d Rydberg resonance states (a total of ten; channel 3b in Table 1), whereas, one-photon dissociation, non-resonant contributions were only observed for two, high energy excitations of these (channel 1 in Fig. 1 and Table 1). Furthermore, Br$^+$ signals due to ionization of bromine atoms formed by three-photon dissociation were only observed for the three highest energy excitations (channel 3c in Fig. 1 and Table 1). Surprisingly, no evidence was observed for two-photon dissociation channels, which would indicate predissociation of the p/d Rydberg states.

In this paper we present data and analysis of two-color (pump and probe) multiphoton excitations for CH$_3$Br. The pump laser was set at a wavelength corresponding to two-photon resonant excitation to a chosen vibrational level of a pump laser was set at a wavelength corresponding to high energy excitations of these (channel 1 in Fig. 1 and Table 1). This approach allows neutral photofragments produced by one-color (pump-only) excitations to be detected quantum-state-specifically and revealed additional processes and more details concerning fragmentation channels than the use of a one-color excitation scheme.

### II. Experimental

The VMI/slicing apparatus used in this work has been described in detail before$^{57,58}$ so only a brief description is given here. A molecular beam of 20% CH$_3$Br in He (around 1 bar total backing pressure) is formed by supersonic expansion through a home-made piezoelectrically-actuated nozzle valve ($\varnothing$ 1 mm diameter) and skimmed ($\varnothing$ 1.5 mm, Beam Dynamics) before it enters the detection chamber where the ion optics are positioned. The collimated molecular beam is intersected at right angles by the pump and probe lasers at the geometric focal point of a single-electrode repeller–extractor plate arrangement. The CH$_3$, Br and Br$^+$ photofragment images were recorded in two-color experiments where the pump laser was used for excitation of the parent molecule and the probe laser was used for (2 + 1) REMPI detection of the photofragments. The pump and the probe laser beams (typically 2–3 mJ per pulse) were generated by (pump) a pulsed Nd$^{3+}$:YAG laser (Spectra Physics Quanta Ray Pro 250) pumping a master oscillator–power oscillator system (Spectra Physics MOPO 730-D10), and (probe) by frequency doubling the output of an excimer-pumped (Lambda-Physik LPX300, operating with XeCl) dye laser (LPD3000) using the appropriate dyes. The CH$_3$ photofragments were probed via the $6_0^0$, $1_1^1$, $2_1^1$ and $2_2^1$ transitions from the ground electronic state CH$_3$(X) to the Rydberg state CH$_3$**(3p,$^2$A$_2$) (Table 2).$^{59}$ The probe laser transitions used for the detection of the Br and Br$^+$ photofragments were Br($^3$P$_{1/2}$) → Br$(^3$P$_{3/2}$) and Br$^+$($^3$P$_{1/2}$) → Br$^+$($^3$D$_{3/2}$) (see Table 2).$^{59}$ The probe laser pulses were delayed with respect to the photolysis pulse, in order to allow a sufficient density of photofragments to build up prior to REMPI detection.

### Table 1 Past and present work on MPI dynamics of CH$_3$Br involving two-photon resonance excitations to Rydberg states with reference to Fig. 1

<table>
<thead>
<tr>
<th>Two-photon (2hν) excitations/cm$^{-1}$</th>
<th>Molecular Rydberg state electron</th>
<th>Dissociation mechanisms$^a$</th>
<th>This work:Br/Br$^+$ probing</th>
<th>This work/CH$_3$(X) probing</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 139.6–59 952.0</td>
<td>5s</td>
<td>4,2 (2)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>66 019</td>
<td>5p</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>66 503</td>
<td>5p</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>67 275</td>
<td>5p</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>68 684</td>
<td>5p</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>72 977</td>
<td>4d</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>74 249</td>
<td>4d</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>75 905</td>
<td>6p, 4d</td>
<td>3b (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>77 165</td>
<td>6p</td>
<td>3b,3c,1 (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>78 370</td>
<td>6p, 5d</td>
<td>3b,3c (1)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>79 610</td>
<td>7p</td>
<td>3b,3c,1 (1)</td>
<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

$^a$ See Fig. 1.
Moreover, the time delay had to be carefully adjusted in order to avoid “fly-out” of the photofragments. Typically, the delay was set at ~5 ns, which ensured both these conditions for the 10 ns (FWHM) pump and the 20 ns (FWHM) probe lasers used. For the slicing experiments reported here, the repeller is pulsed ON at the appropriate time delay (~300 ns) following the photolysis/ionization. The photofragments traverse a field-free time-of-flight region (45 cm) and a gated, position-sensitive detector (dual, imaging-quality MCP array coupled to a phosphor screen) images the center slice of the photofragment sphere. The image frame is recorded asynchronously every second (~10 laser shots) by a CCD camera and several thousand frames are averaged to form images such as those shown in Fig. 3a. Each final image is integrated from its center over the angle to extract the speed and over the radius to extract the angular distributions of the corresponding fragments.

III. Results and analysis

A. Mass resolved MPI

The (2 + m) REMPI spectrum for CH$_3^+$ from ref. 10 for the two-photon resonant excitation region of 66 000–80 000 cm$^{-1}$ is reproduced in Fig. 2a. The relative ion intensities, $I(M^+)/I(CH_3^+)$, for $M^+ = CH_3^+$, CH$^+$ and Br$^+$ are found to vary with wavenumber and to reach maxima as the wavenumber values get closer to the ion-pair threshold (CH$_3^+$ + Br$^+$), whereas those for $M^+ = CBr^+$ remain unchanged (see Fig. 2b and ref. 61). This suggests some interaction between the Rydberg and ion-pair states and will be further discussed in Section IV.

B. Slice images and kinetic energy release spectra (KERs)

i. Br/Br*. Br$^+$ ion slice images (see examples in Fig. 3a) were recorded following multiphoton excitation of CH$_3$Br. Kinetic energy release spectra (KERs) were derived from the images. Three types of Br$^+$ images were recorded (Fig. 3a): First, pump-only images (Fig. 3a (left)), obtained by using one laser tuned to two-photon Rydberg state resonances of CH$_3$Br. Five such transitions were explored (Table 1). Br$^+$ is produced following multiphoton excitation of the molecule. We have already presented such results in ref. 1 and will briefly discuss them again here in relation to the two-color data (see below). Second, probe-only images (Fig. 3a (middle)) using one laser tuned to two-photon Rydberg state resonances of CH$_3$Br. For the slicing experiments reported here, the repeller is pulsed ON at the appropriate time delay (~5 ns) following the photolysis/ionization. The photofragments traverse a field-free time-of-flight region (45 cm) and a gated, position-sensitive detector (dual, imaging-quality MCP array coupled to a phosphor screen) images the center slice of the photofragment sphere. The image frame is recorded asynchronously every second (~10 laser shots) by a CCD camera and several thousand frames are averaged to form images such as those shown in Fig. 3a. Each final image is integrated from its center over the angle to extract the speed and over the radius to extract the angular distributions of the corresponding fragments.

Table 2 Probing of fragment species CH$_3$(X, $v_1$,$v_2$,$v_3$,$v_4$) and Br/Br*: states and transitions involved

<table>
<thead>
<tr>
<th>Fragments probed</th>
<th>Resonant state $^a$</th>
<th>$v^*$ vibrational transition $^b$</th>
<th>One-photon/ $^c$</th>
<th>Two-photon/ cm$^{-1}$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$(X;1000)</td>
<td>3p $^3$A$_{2g}$: 11$^b$</td>
<td>333.90</td>
<td>59 898</td>
<td></td>
</tr>
<tr>
<td>CH$_3$(X;0000)</td>
<td>3p $^3$A$_{2g}$: 0$^b$</td>
<td>333.49</td>
<td>59 972</td>
<td></td>
</tr>
<tr>
<td>CH$_3$(X;0100)</td>
<td>3p $^3$A$_{2g}$: 2$^b$</td>
<td>325.50</td>
<td>60 698</td>
<td></td>
</tr>
<tr>
<td>CH$_3$(X;0200)</td>
<td>3p $^3$A$_{2g}$: 2$^b$</td>
<td>325.80</td>
<td>61 387</td>
<td></td>
</tr>
<tr>
<td>Br*(1/2)</td>
<td>2D[3/2]</td>
<td>266.70</td>
<td>74 991</td>
<td></td>
</tr>
<tr>
<td>Br*(3/2)</td>
<td>2D[3/2]</td>
<td>266.63</td>
<td>75 009</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Resonant Rydberg states for probed fragments.$^{9,60}$ $^b$ Selected vibrational transition $v^*$ for $v_0$ (vibrational mode), $v^*$ (ground state vibrational level) and $v^*$ (excited state vibrational level).
CH$_3$Br to form CH$_3$Br$^+$ followed by one-photon photolysis is not followed by predissociation, but in that case the Br$^+$ KER would very likely either, as the Br KER in this case would be close in e.g. be higher (0.89 eV for the 68 684 cm$^{-1}$ excitation) but would not explain the whole range of energies (0.4 to nearly 0 eV) nor the structure observed. As discussed in ref. 1, threshold calculations and low Br$^+$ intensities point towards a three-photon excitation process leading to superexcited CH$_3$Br states, via the two-photon resonant excited Rydberg states, followed by dissociation to form Br/Br$^*$ along with Rydberg states of CH$_3$ (CH$_3$*) (i.e. channel 3b in Fig. 1). Br$^+$ is then produced by three-photon non-resonant ionization of Br/Br$^*$:

CH$_3$Br + 2$h\nu$ → CH$_3$Br**(p/d Ry; $v_1$,$v_2$,$v_3$); resonant transition (1a)

CH$_3$Br**(p/d Ry; $v_1$,$v_2$,$v_3$) + 1$h\nu$ → CH$_3$Br$^+$; photoexcitation (1b)

CH$_3$Br$^*$ → CH$_3$**(Ry; $v_1$,$v_2$,$v_3$); + Br/Br*$^*$; dissociation (1c)

Br/Br$^*$ + 3$h\nu$ → Br$^+$ + e$^-$; photoionization (1d)

where CH$_3$Br**($v_1$,$v_2$,$v_3$) represents vibrational modes $v_1$, $v_2$, and $v_3$ of the parent molecular Rydberg state and CH$_3$Br$^*$ represents one or more superexcited state. The vibrational structure observed corresponds to formation of vibrationally excited CH$_3$**($3p$ $^2A_2$) fragments in the umbrella/bending mode, $v_2$ (i.e. CH$_3$**($3p$ $^2A_2$; 0$\nu_2$00))$^{1,62}$

The images and KERS for the probe-only excitations show clear rings and peaks, respectively (Fig. 3a–c). The KERS peaks typically appear slightly below and slightly above 0.2 eV KER for Br$^+$ and Br, respectively. As seen in Fig. 2a (green bars), the probe excitations of Br and Br$^+$ correspond to non-resonant excitations within the CH$_3$Br molecule. Therefore, the KERS can be attributed to one-photon non-resonant transitions to repulsive valence states (A band) followed by dissociation (i.e. direct photodissociation) to form Br and Br$^+$ along with CH$_3$ (i.e. channel 1 in Fig. 1) prior to (2 + 1) REMPI of Br/Br$^*$, i.e.

CH$_3$Br + 1$h\nu$ → CH$_3$Br$^*$; non-resonant transition (2a)

CH$_3$Br$^*$ → CH$_3$(X, $v_1$,$v_2$,$v_3$,$v_4$) + Br/Br*$^*$; dissociation (2b)

Br/Br$^*$ + 2$h\nu$ → Br**$^*$; resonant transition (2c)

Br**$^*$ + 1$h\nu$ → Br$^+$ + e$^-$; photoionization (2d)

where CH$_3$Br$^*$ represents a repulsive valence state, CH$_3$(X, $v_1$,$v_2$,$v_3$,$v_4$) refers to the ground electronic state of CH$_3$(X) and vibrational modes $v_1$, $v_2$, $v_3$, and $v_4$ and Br**$^*$ refers to bromine atomic Rydberg states.

Images and KERS for the pump/probe excitations show the same features as observed in the pump and probe spectra as well as additional signal, which extends to higher KER (see Fig. 3a–c). Thus, the signals due to the three-photon excitation processes (eqn (1)) clearly appear in the pump/probe signal as shoulders at low KER. Signals formed by one-photon non-resonant photodissociation processes analogous to eqn (2) also appear in the pump/probe signal (near 0.2 eV). As an attempt to estimate the shape of the KERS contributions due to the probing after pumping the pump-only and probe-only contributions were subtracted manually from the pump/probe spectra (see Fig. 3b and c (gray broken curves) and ref. 61).
We, therefore, first, conclude that the lifetime of the 5p state with respect to formation of Br* is shorter than that of the 4d states and, second, that the lifetime of the 5p state with respect to formation of Br* is shorter than that with respect to formation of Br.

(ii) The relative signal intensity of the high KER/two-photon excitation components with respect to the pump/three-photon excitation component is significantly larger for Br* than for Br (see Fig. 3a–c and 4). Since the first step in both processes is two-photon absorption to a Rydberg state, the difference must be in the two secondary processes that follow: predissociation vs. one-photon absorption to the CH₃Br⁺ state (Fig. 1). This suggests that the formation of Br⁺ by predissociation is more favorable than by
three-photon excitation via CH₂Br², whereas the formation of Br by predissociation is less favorable than by three-photon excitation via CH₂Br⁶. This further indicates that the vibrational structure observed following three-photon excitation (see above) is more favorable for formation of the CH₃**(3p²A₂, 0ν₂00) fragments along with Br rather than Br*.

ii. CH₃+, CH₃⁺ ion slice images (Fig. 5a) were recorded for MPI of CH₃Br and kinetic energy release spectra (KERs) were derived from the images. Recordings were made for excitations corresponding to (2 + m) REMPI for resonant excitation to a total of three molecular Rydberg states in the two-photon excitation region of 66 000–80 000 cm⁻¹ (see Table 1 and Fig. 2a and 5a).

Analogous to the Br⁺ data described in the previous section (III, B, Br/Br*), images were recorded for pump-only excitations (see Section II and Table 2) (see Fig. 5a (middle)) and for pump/probe excitations (see Fig. 5a (right)).

The KERs for the pump-only excitations exhibit a broad spectral structure peaking at low kinetic energies in the region of about 0.2 eV (Fig. 5b). This structure has been attributed to the three-photon excitation process and dissociation according to eqn (1a)–(1c) above (i.e. channel 3b in Fig. 1) prior to one-photon ionization of CH₃**(Ry; ν₁ν₂ν₃ν₄).¹

![Figure 5](image_url)

**Figure 5** Slice images and KERs for CH₃⁺: (a) CH₃⁺ slice images and corresponding KERs obtained for pump laser only (left image), probe laser only (middle image) and pump and probe (pump/probe) lasers (right image). The images intensities have been adjusted to show all major features. The laser polarization is indicated by the double arrow. See also Tables 1 and 2. (b) CH₃⁺ kinetic energy release spectra (KERs) for the images in (a). The pump-only KER is in blue, probe-only in red and pump/probe in black. The energy thresholds (energy maxima) for the formation of CH₃(X, 0000) + Br/Br* after one-photon excitation of CH₃Br are indicated. The spectra are plotted as a function of the KER for the CH₃ fragment.

The images and KERs for the probe-only excitations show vibrational structure (Fig. 5a (middle), Fig. 5b and 6) of a frequency corresponding to an out of plane/umbrella vibrational mode (ν₂) for CH₃⁺ and CH₃ fragments.⁶¹ KERs recorded for different CH₃(X, ν₁ν₂ν₃ν₄) probe wavelengths (see Section II and Table 2) show vibrational peaks to line up reasonably well/within experimental error for spectra shifted by Δ(1ν₂) (where Δ(1ν₂) = |1ν₂| - 1ν₂0; see definitions in Section III, B, i) and plotted vertically as a function of the one-photon excitation wavenumber (y-axis to the left) and the total KER for the spectrum of 2ν₂ = 61 387 cm⁻¹(1/2²) (y-axis to the right) to guide the eye to identify matching spectral features. Common energy thresholds (energy maxima) for the formation of CH₃⁺(X, 0000) + Br/Br* after one-photon dissociation of CH₃Br** are indicated.

The KERs for the pump-only excitations exhibit a broad spectral structure peaking at low kinetic energies in the region of about 0.2 eV (Fig. 5b). This structure has been attributed to the three-photon excitation process and dissociation according to eqn (1a)–(1c) above (i.e. channel 3b in Fig. 1) prior to one-photon ionization of CH₃**(Ry; ν₁ν₂ν₃ν₄).¹

![Figure 6](image_url)

**Figure 6** CH₃⁺ kinetic energy release spectra (KERs) for probe-only excitations corresponding to the 1⁰ (furthest to the left), 0⁰ 2 and 2⁰ 2 (furthest to the right) CH₃ resonances (see Table 2). The KERs are normalized to the strongest peak in each spectrum. The spectra are shifted by Δ(1ν₂) (see the explanation in the main text, Section III, B, i) and plotted vertically as a function of the one-photon excitation wavenumber (y-axis to the left) and the total KER for the spectrum of 2ν₂ = 61 387 cm⁻¹(1/2²) (y-axis to the right) to guide the eye to identify matching spectral features. Common energy thresholds (energy maxima) for the formation of CH₃⁺(X, 0000) + Br/Br* after one-photon dissociation of CH₃Br** are indicated.

CH₃Br + 2hν → CH₃Br***(5s Ry; ν₁ν₂ν₃ν₄); near-resonant transition (4a)

CH₃Br***(5s Ry; ν₁ν₂ν₃ν₄) + 1hν → CH₃Br⁶; photoexcitation (4b)

CH₃Br⁶ → CH₃Br***(X3/2) + e--; autoionization (4c)

CH₃Br***(X3/2) + 1hν → CH₃Br**⁺; photoexcitation (4d)

CH₃Br**⁺ → CH₃⁺(X, 0ν₂00) + Br/Br⁺ dissociation (4e)

Analysis of the vibrational structure reveals a vibrational progression of frequency corresponding to ω₀ = 1382 ± 25 cm⁻¹ for the bending mode of CH₃⁺(X, 0ν₂00). This is to be compared...
with the vibrational value of $1359 \pm 7 \text{ cm}^{-1}$ reported for CH$_3^+(X)$. Observation of a single vibrational progression suggests that either one of the two formation channels (eqn (4e)) is dominant. By analogy with our observations concerning the Br images mentioned above (see Section III, B, i) and by considering the different energetics we believe that formation of CH$_3^+ (X, 0v_0,00)$ along with Br dominates over its formation along with Br$^*$. Images and KERs for the pump/probe excitations display structure corresponding to overlap of that observed in the pump-only and probe-only data as well as two sharp peaks at high KER (see Fig. 5a (left) and Fig. 5b) as inner rings of low intensity and outer rings of high intensity. KERs shifted by $\Delta(1h\nu)$ (where $\Delta(1h\nu) = [1h\nu_1 - 1h\nu_0]$; see definitions in Section III, B, Br/Br* for comparison) show the positions of these peaks to match common thresholds for CH$_3(X, v_1v_2v_3)$ + Br/Br$^*$ formation by one-photon dissociation. The sharp KER peaks are indicative of direct non-resonant photodissociation processes (see Section I and ref. 1). Based on these observations and analysis of angular distributions (see below) we conclude that these high KER peaks are due to direct one-photon dissociation (i.e. channel 1 in Fig. 1) followed by detection of CH$_3(X, v_1v_2v_3)$ by (2 + 1) REMPI, i.e.,

$$ \text{CH}_3\text{Br} + 1h\nu \rightarrow \text{CH}_3\text{Br}^*; \text{non-resonant transition (5a)} $$

$$ \text{CH}_3\text{Br}^* \rightarrow \text{CH}_3(X, v_1v_2v_3) + \text{Br}/\text{Br}^*; \text{dissociation (5b)} $$

$$ \text{CH}_3(X, v_1v_2v_3) + 2h\nu \rightarrow \text{CH}_3^{\dagger}(3p^2 2\Sigma^+_g; v_1v_2v_3); \text{resonant transition (5c)} $$

$$ \text{CH}_3^{\dagger}(3p^2 \Sigma^+_g; v_1v_2v_3) + 1h\nu \rightarrow \text{CH}_3^+ + e^-; \text{photoionization (5d)} $$

In all cases, the signals for CH$_3(X, v_1v_2v_3)$ + Br$^*$ formation are found to be noticeably less than those for CH$_3(X, v_1v_2v_3) +$ Br formation.

C. Angular distributions

Significant variations in angular distributions are observed for the Br$^*$ and CH$_3^+$ ions depending on the rings/ channels involved (see Fig. 3a and 5a). In an attempt to quantify the anisotropy of the rings, angular distributions, in the form of signal intensities as a function of the angle ($\theta$) from 0 to 180$^\circ$, derived from the images, were fitted by the expression corresponding to one-step, direct photodissociation

$$ P(\theta) = A \left[ 1 + \sum \beta_{2n} P_{2n}(\cos(\theta)) \right] $$

de to derive anisotropy parameters $\beta_{2n}$ ($n = 1$–3; see ref. 61). $n$ is the number of photons involved in the photolysis, $P_{2n}$ are the $2n$-th order Legendre polynomials and $A$ is a scaling factor. $\beta_{2n}$ are weighting coefficients of the corresponding $P_{2n}$ polynomials. The $\beta_{2n}$ parameter for $n = 1$ ($\beta_2$) is in the range between +2 (purely parallel transition) to −1 (purely perpendicular transition) for prompt dissociation. The $\beta_3$ and $\beta_6$ parameters are non-zero when the angular distribution contains $\cos^3(\theta)$ and $\cos^6(\theta)$ components respectively, indicative of alignment and orientation phenomena. In several cases (e.g. for the CH$_3$ angular distributions of the high KER rings corresponding to CH$_3$ + Br formation; see below) non-zero $\beta_2$ and $\beta_6$ parameters are observed (see ref. 61, Table S1 (ESI†)). Such values indicate the presence of alignment (in the case of $\beta_2$) and/or orientation (in the case of $\beta_6$) (see ref. 64 and references therein) or rotational alignment. The additional measurements needed to fully quantify such phenomena are beyond the scope of this paper.

i. Br/Br$^*$. The angular distribution shape of the Br$^*$ images for the pump-only excitations indicates dominant parallel transitions. Thus, positive values of $\beta_2$ in the range between about 1.1 and 1.4 for the broad low KER peaks were obtained, as shown before. These signals are due to three-photon excitation prior to dissociation (1a–c) as well as possible state mixing. The involvement of two-photon resonant parallel transitions corresponding to dominant halogen p-orbital to p/d Rydberg orbital transitions (see Fig. 2a) could be a controlling factor in determining the anisotropy observed.

The angular distribution shape of the images for the probe-only excitations implies purely parallel transitions for Br$^*$ detection ($\beta_2 \approx 2$) but virtually isotropic transitions for Br ($\beta_2 \approx 0$) (see Fig. 3a, 5b, Table 3 and ref. 61). The former observation is in agreement with formation of Br$^*$ along with CH$_3(X)$ by one-photon dissociation for a parallel transition from the ground state to the $^3\text{Q}_0$ state followed by dissociation on the same (i.e. the diabatic) potential curve. The latter observation could be due to a combination of one-photon parallel and perpendicular transitions to $^3\text{Q}_0$ and $^1\text{Q}_1^\prime\text{Q}_1$, respectively, followed by dissociation, involving curve crossing, to form Br and CH$_3$.$^4,8$

The angular distribution of the images for the pump/probe excitations (see Fig. 3a) at low KER is analogous to the observations for the pump-only excitations (see above) and the rings in the intermediate KER region resemble those observed for the probe-only excitations (see above). In addition, the broad structure at high KER corresponds to dominant perpendicular transitions (negative $\beta_2$ values in the range of about −0.3 to −1) for the two-photon resonant transitions to the p-orbital Rydberg states (i.e. for $2h\nu = 66$019, 67275 and 68684 cm$^{-1}$; see Table 1 and Fig. 2a) both for Br$^*$ and Br detection. On the other hand, the broad structure at high KER for the two-photon resonant transitions to the d-orbital Rydberg states (i.e. $2h\nu = 72$977 and 75905 cm$^{-1}$), both for Br$^*$ and Br detection, corresponds to dominant parallel transitions (positive $\beta_2$ values of about +0.5). Most likely the observed angular distribution difference is associated with the symmetry difference in the two-photon transitions to the p and d molecular Rydberg states, prior to predissociation.

ii. CH$_3$. The shape of the CH$_3^+$ image for the pump-only excitation $2h\nu = 72$977 cm$^{-1}$ (see Table 1 and Fig. 2a) indicates a dominant parallel transition for the broad low KER peak (a $\beta_2$ value of about +0.9) as shown before. This is similar to the observation for the corresponding Br$^*$ image (see above), as might be expected for fragments formed by the same channels (see eqn (1a)–(1c)), prior to ionization. The shapes of the corresponding CH$_3^+$ images for $2h\nu = 78$370 and
Table 3 | Anisotropy parameters, β2, derived from Br* and CH3+ for one-photon dissociation of CH3Br towards CH3(X) + Br/Br*

<table>
<thead>
<tr>
<th>One-photon excitations/cm(^{-1})</th>
<th>One-photon/ nm</th>
<th>β2 (Br*) for CH3 + Br</th>
<th>β2 (Br*) for CH3 + Br*</th>
<th>β2 (CH3+) for CH3 + Br</th>
<th>β2 (CH3+) for CH3 + Br*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>39 841</td>
<td>251.00</td>
<td>0.08</td>
<td>1.88</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39 805</td>
<td>251.00</td>
<td>0.20</td>
<td>1.90</td>
<td>8</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>39 805</td>
<td>251.22</td>
<td>0.24</td>
<td>1.90</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39 185</td>
<td>255.20</td>
<td>-0.93</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38 583</td>
<td>259.18</td>
<td>-0.47</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37 505</td>
<td>264.95</td>
<td>-0.15</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>37 494</td>
<td>266.70</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>37 494</td>
<td>266.71</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37 494</td>
<td>277.74</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) CH3(v2 = 0). \(^{b}\) CH3(v2 = 1). \(^{c}\) Pump/probe excitation. \(^{d}\) Probe excitation. \(^{e}\) Lower limit value, due to overlap of signals (see ref. 61).

79610 cm\(^{-1}\), on the other hand, imply virtually isotropic transitions (β2 ≈ 0).

The shapes of the images for the probe-only excitations, which show vibrational structure, imply dominant parallel transitions (Fig. 5a (middle)) (β2-values in the range of about +0.9 to +1.4). This is in close agreement with the observations made by Wang et al.,\(^{5}\) who attributed it to parallel transitions from CH3Br+ to the first excited electronic state of the ion (CH3Br+ (A)) followed by dissociation (see eqn (4d) and (4e)) by assuming C\(_3\)v symmetry for the dissociative molecular ion.\(^{71}\)

The shapes of the images for the pump/probe excitations (see Fig. 5a (right)) at low and intermediate KER are analogous to those observed for the pump-only and probe-only excitations (see above). In addition the shapes of the narrow rings (sharp peaks) at high KER correspond to dominant parallel transitions (β2 ≈ +1) (inner rings of low intensity) and to virtually isotropic or perpendicular transitions (β2 ≈ −0.4 to −0.9) (outer rings of high intensity). This is in close agreement with our observations based on the Br\(^+\) images for the probe-only excitations due to the one-photon dissociation processes. Thus, the former observation (β2 ≈ +1) suggests that CH3(X) is formed along with Br\(^+\) by a dominant parallel transition from the ground state to the \(^2\)Q\(_0\) state followed by dissociation on the same (i.e. the diabatic) potential curve,\(^8\) whereas the latter observation (β2 ≈ −0.4 to −0.9) could involve a combination of parallel and perpendicular transitions to \(^2\)Q\(_0\) and \(^4\)Q\(_1\),\(^2\)Q\(_1\), respectively, followed by dissociation to form CH3(X) and Br.\(^8\)

IV. Discussion

The detection of the Br/Br\(^+\) and CH3(X) fragments by REMPI allows detection of otherwise unnoticed channels in addition to those observed by a one-color scheme reported before.\(^1\) Thus, predissociation of Rydberg states following two-photon resonant excitation (eqn (3a) and (3b)/channel 2 in Fig. 1), as well as one-photon dissociation (eqn (2a) and (2b)/channel 1 in Fig. 1), not previously seen, is now evident in multiphoton excitation of CH3Br for selected p/d resonant molecular Rydberg states in addition to channels previously observed by one-color REMPI.\(^1\) This is summarized in Table 4.

The characteristic alteration in relative ion signals in the REMPI spectrum (see Section III. A., Fig. 2b and ref. 1 and 61) such as an increase in the \(I(\text{Br}^+)/I(\text{CH}_3^+)\) ratios with excitation wavenumber below the ion-pair threshold (CH3\(^+\) + Br\(^-\)) followed by a sudden drop above it is an indication of a Rydberg

Table 4 | Summary of observed multiphoton dynamic processes involving two-photon resonance excitations to p/d molecular Rydberg states with reference to Fig. 1

<table>
<thead>
<tr>
<th>Two-photon excitations/cm(^{-1})</th>
<th>One-photon/ nm</th>
<th>Molecular Rydberg state electron</th>
<th>Dissociation mechanisms(^{a}) (Ref.)</th>
<th>Dissociation mechanisms(^{a}) (This work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 139.6–59 952.0</td>
<td>344.00–333.60</td>
<td>[3/2]5s; 0, (100)/[1/2]5s; 0, (000), (003)</td>
<td>4,2 (2)</td>
<td>4(^{b})</td>
</tr>
<tr>
<td>66 019</td>
<td>302.94</td>
<td>[3/2]5p; 0, (000)</td>
<td>3b (1)</td>
<td>2(^{c})</td>
</tr>
<tr>
<td>67 275</td>
<td>297.29</td>
<td>[3/2]5p; 0, (010)</td>
<td>3b (1)</td>
<td>2(^{c})</td>
</tr>
<tr>
<td>68 684</td>
<td>291.19</td>
<td>[1/2]5p; 0, (000)</td>
<td>3b (1)</td>
<td>2(^{c})</td>
</tr>
<tr>
<td>72 977</td>
<td>274.06</td>
<td>[3/2]4d; 0, (000)</td>
<td>3b (1)</td>
<td>2(^{c})(^{d})</td>
</tr>
<tr>
<td>75 905</td>
<td>263.49</td>
<td>[3/2]4d; 0, (000)/</td>
<td>3b (1)</td>
<td>2(^{c})</td>
</tr>
<tr>
<td>78 370</td>
<td>255.20</td>
<td>[1/2]6p; 0, (000)/</td>
<td>3b,3c (1)</td>
<td>1(^{d})</td>
</tr>
<tr>
<td>79 610</td>
<td>251.22</td>
<td>[3/2]7p; 0, (000)</td>
<td>3b,3c,1 (1)</td>
<td>1(^{d})</td>
</tr>
</tbody>
</table>

\(^{a}\) See Fig. 1. \(^{b}\) Based on analysis of probe images/ KERs. \(^{c}\) Based on Br and Br\(^+\) probing. \(^{d}\) Based on CH3(X; v1v2v3v4v5) probing.
to ion-pair state interaction. The opening of a photodissociation channel forming CH$_3$(X) and Br/Br$^*$ at excitation energies higher than the ion-pair threshold is another indication of such interactions. Although we searched for Br$^-$ as well as for photoelectrons originating from its photodetachment, we did not detect any in our experiments. This might suggest that the interaction between the Rydberg and ion-pair states above the threshold energy does not end up in the ion-pair products (CH$_3$$^+ +$ Br$^-$). A lack of such evidence, however, does not exclude such interactions, but suggests that they do not affect significantly the exit channels giving rise to the photoproducts detected in our experiments. An interaction between a Rydberg state and an ion-pair state at energies lower than the ion-pair threshold corresponds to the bound energy region of the ion-pair state and will cause an effective enhancement in the bond distance of the mixed state. Furthermore, that bond distance will increase greatly as the energy approaches the ion-pair threshold. In the case of the higher energy excitations, on the other hand, an interaction will lead to dissociation in which case the ion-pair formation will compete with the photodissociation channel. Analogous Rydberg-to-ion-pair interactions are well known for diatomic molecules, but do not seem to be very important for the CH$_3$Br dynamics reported here.

Strikingly different photofragmentation channels resulting from three-photon excitation via s Rydberg states (probe-only excitations) and p/d Rydberg states (pump-only and pump/probe excitations) were observed (see also ref. 1 and 2). In the former case the superexcited states formed (CH$_3$Br$^*$) (pre)dissociate to form CH$_3$$^+$$^*$ Rydberg states (eqn (1)), whereas in the latter case CH$_3$Br$^*$ autoionizes to form CH$_3$Br$^*$ (X) (eqn (4)). This could be due to reasons such as:

(i) Formation of CH$_3$Br$^*$ at low vibrational energies by autoionization of CH$_3$Br$^*$ becomes more favorable (probable) as the energy difference between CH$_3$Br$^*$ and CH$_3$Br(X) decreases (see ref. 61).

(ii) Three-photon excitations to CH$_3$Br$^*$ via the 5s/5s$'$ Rydberg states are too low in energy to overcome barrier heights prior to dissociation to form CH$_3$$^+ +$ Br/Br$^*$ whereas excitations via the p/d state are of high enough energy. Whereas formation of CH$_3$(X) + Br/Br$^*$ is not detected by one-photon dissociation for excitations corresponding to two-photon excitation to the 5s/5s$'$ Rydberg states (Fig. 1 and ref. 2) it is clearly observed for those corresponding to resonant excitation to the p and d Rydberg states. This must be for energetic reasons. The transition probabilities and hence absorption cross section corresponding to one-photon excitations to the repulsive valence states (A band), although low, are high enough in the latter case for CH$_3$(X) formed along with Br/Br$^*$ to be detected as opposed to that in the former case. Whereas a large number of photodissociation studies have been performed on the first continuum absorption band (A band) of CH$_3$Br, only limited results are available for its red wing corresponding to one-photon wavenumber excitations below about 40 000 cm$^{-1}$ ($\lambda > 250$ nm). Our values for $\beta_2$ derived from relevant Br$^-$ and CH$_3$$^+$ images (see Sections III, C, i, ii and ref. 61) are in good qualitative agreement with those observed before for this excitation region (see Table 3).

Finally, predissociation following two-photon resonant excitation to the 5s/5s$'$ Rydberg states to form CH$_3$(X) and Br/Br$^*$, analogous to our observation for corresponding excitations to the p and d Rydberg states, has been observed by Wang et al. This channel is evident in the Br/Br$^*$ images and KERs, whereas the CH$_3$ co-fragment is too fast to be measured with our current extraction voltage/detector combination.

V. Summary and conclusions

Br$^-$ and CH$_3$$^+$ ion slice images were recorded for multiphoton excitation of CH$_3$Br followed by REMPI probing of the Br, Br$^*$ and CH$_3$(X, $\nu_2\nu_3\nu_4\nu_4$) photofragments (two-color experiments). Measurements were performed at seven wavelengths involving two-photon resonant transitions to vibrational levels of np and nd molecular Rydberg states (CH$_3$Br$^*$($^3$P$_1$)) (Table 4). The probing of Br, Br$^*$ and CH$_3$(X, $\nu_2\nu_3\nu_4\nu_4$) was done by (2 + 1) REMPI for resonant excitation to Rydberg states of bromine (Br$^*$) and CH$_3$(CH$_3$$^+$$^*$($^3$P$_1$) (Table 2). Slice images of Br$^-$ and CH$_3$ Br$^*$ photoproducts were recorded for the pump-only and the probe-only wavenumber, independently, as well as for the combination of pump followed by probe (pump/probe) excitations. Kinetic energy release spectra (KERs) as well as angular distributions and relevant fit parameters ($\beta_{2\omega}$; eqn (6)) were derived from the ion images.

For all the pump-only excitations the major channel was found to involve three-photon excitation of the molecule to a superexcited state(s) (CH$_3$Br$^*$) followed by dissociation to form Rydberg states of CH$_3$$^+$$^*$ along with Br/Br$^*$. For two of these ($2h\nu = 78 370, 79 610$ cm$^{-1}$; Table 4) the three-photon excitations were also found to form CH$_3$(X) along with Br/Br$^*$ and for one of these (79 610 cm$^{-1}$; Table 4) one-photon dissociation of CH$_3$(X) + Br/Br$^*$ was detected. The resonant detection of the fragment species (Br, Br$^*$ and CH$_3$(X, $\nu_2\nu_3\nu_4\nu_4$)) revealed predissociation of the np and nd molecular Rydberg states following the two-photon resonant excitations as well as one-photon dissociation in addition to that observed before as listed in Table 4. The channels observed by the two-color excitation scheme (this work) are shown in Fig. 7.

The comparison of results relevant to excitations involving REMPI via the p/d Rydberg states and those of the second color/probe-only excitations, which involved REMPI via the s Rydberg states, revealed a striking difference in the excitation dynamics following three-photon excitation. In the former case the superexcited states formed (CH$_3$Br$^*$) (pre)dissociate to produce CH$_3$$^+$$^*$ Rydberg states (eqn (1)), whereas in the latter case CH$_3$Br$^*$ autoionizes to form CH$_3$Br(3p $^3$A$_2$) (X) (eqn (4)).

Abrupt variations in relative ion signal intensities and dissociation channels associated with the ion-pair energy threshold strongly suggest that the dynamics of multiphoton dissociation and ionization via the molecular Rydberg states is affected by Rydberg to ion-pair state interactions.

Although, primarily, this paper deals with additional information relevant to fragmentation processes of the methyl halides we also feel that it is of importance to shed light on
the effect of various competing channels on the photoexcitation dynamics of molecules involving high energy Rydberg states in general. We sincerely hope that it will render further theoretical interpretation of the characteristic processes involved.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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60 NIST Atomic Spectra Database (ver. 5.3), [Online], http://physics.nist.gov/asd, accessed March 2016, National Institute of Standards and Technology, Gaithersburg, MD.
61 See ESI†.