Multiphoton dissociation dynamics of BrCl and the BrCl$^+$ cation

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Ion imaging methods have enabled identification of three mechanisms by which $^{79}$Br$^+$ and $^{35}$Cl$^+$ fragment ions are formed following one-color multiphoton excitation of BrCl molecules in the wavelength range $324.6 > \lambda > 311.7$ nm. Two-photon excitation within this range populates selected vibrational levels ($\nu' = 0$) of the [$X^2\Pi_{1/2}]5\sigma$ Rydberg state. Absorption of a third photon results in branching between (i) photoionization (i.e. removal of the Rydberg electron—a traditional 2 + 1 REMPI process) and (ii) $\pi^+ \leftrightarrow \pi$ excitation within the core, resulting in formation of one or more super-excited states with $\Omega = 1$ and configuration [$A^2\Pi_{1/2}]5\sigma$. The fate of the latter states involves a further branching. They can autoionize (yielding BrCl$^+$($X^2\Pi$) ions in a wider range of $\nu'^+$ states than formed by direct 2 + 1 REMPI). Further, one-photon absorption by the parent ions resulting from direct ionization or autoionization leads to formation of Br$^+$ and (energy permitting) Cl$^+$ fragment ions. Alternatively, the super-excited molecules can fragment to neutral atoms, one of which is in a Rydberg state. Complementary ab initio calculations lead to the conclusion that the observed [Cl$^{**}$[$^3P$]4s + Br/Br$^+$] products result from direct dissociation of the photo-prepared super-excited states, whereas [Br$^{**}$[$^3P$]5p + Cl/Cl$^+$] product formation involves interaction between the [$A^2\Pi_{1/2}]5\sigma$ and [$X^2\Pi_{1/2}]5\sigma$ Rydberg potentials at extended Br–Cl bond lengths. Absorption of one further photon by the resulting Br$^{**}$ and Cl$^{**}$ Rydberg atoms leads to their ionization, and thus their appearance in the Br$^+$ and Cl$^+$ fragment ion images.

1. Introduction

The potential of velocity map imaging methods for high resolution studies of the photodissociation dynamics of neutral molecules is becoming ever more widely recognized, but application of these methods to studies of molecular cations remains relatively rare. Examples include our own detailed studies of the photofragmentation of vibrational and spin–orbit state-selected Br$_2$, BrCl$^+$, and DCl$^+$ cations, investigations of OCS$^+$ photofragmentation by Liu and coworkers, of the photolysis of C$_2$H$_4^+$ by Suits’ group and of CF$_3$I$^+$ by Aguirre and Pratt.

The present paper describes detailed investigations of the speed and angular distributions of the Br$^+$ and Cl$^+$ products formed following one-color multiphoton excitation of BrCl; the ensuing analysis will serve to highlight the rich variety of fragment ion formation mechanisms. The parent excitation wavelengths were chosen so as to be two photon resonant with successive vibrational levels of the first ($n = 5$) member of the $n\sigma - 6\sigma$ Rydberg series of BrCl. This Rydberg excitation takes the form of two short vibronic progressions, separated by the spin–orbit splitting of the $^3\Pi$ ion core ($\sim 2070$ cm$^{-1}$). It proves convenient to persist with the previously introduced labelling scheme for these progressions, viz. $a_\delta(\nu', 0)$ (i.e. $[^3\Pi_{1/2}]5\sigma$, $\nu' \leftarrow X^1\Sigma^+$, $\nu' = 0$) and $b_\delta(\nu', 0)$ ($[^2\Pi_{1/2}]5\sigma$, $\nu' \leftarrow X^1\Sigma^+$, $\nu' = 0$).

Such a dominance of fragment (rather than parent) ions following one-color REMPI of diatomic molecules is not without precedent. Related observations have been reported for the cases of H$_2$, NO, O$_2$ and Cl$_2$, and a range of fragment ion formation mechanisms proposed. These include: (i) dissociation of super-excited states of the parent molecule (formed, in the present case, at the energy of three absorbed photons), followed by photoionization of one of the resulting neutral fragments; (ii) photodissociation of the parent ions that are formed by autoionization of such super-excited states; and (iii) generally unintended) photodissociation of parent ions formed by the direct REMPI process. These various routes to forming fragment ions are illustrated in Fig. 1, to aid the ensuing discussion.
leading to formation of these super-excited state(s), and the mechanisms of their subsequent fragmentation. The study serves to provide a particularly clear illustration of both the advantages, and of the potential complications, associated with the use of REMPI as a means of preparing state-selected molecular ions.

2. Experimental method and \textit{ab initio} calculations

The velocity map ion imaging experiment in Bristol has been described previously.\textsuperscript{7,8,22} A skinned, pulsed molecular beam containing BrCl (in a Br\textsubscript{2}/Cl\textsubscript{2} mixture) seeded in Ar was directed at the centre of the detector (\textit{i.e.} along the \(z\) axis). The skinned beam was crossed at right angles by the frequency doubled output of a pulsed dye laser (Spectra-Physics GCR-250 Nd:YAG laser plus Sirah Cobra Stretch dye laser, yielding an output bandwidth <0.1 cm\(^{-1}\) in the visible) which propagated along the \(x\) axis and was focused into the interaction volume with a 20 cm focal length plano-convex lens. Ultraviolet (UV) excitation frequencies were chosen so as to be resonant, at the two-photon energy, with the \(b_3(v' = 0–5)\) levels of BrCl; wavelengths (in air) and the corresponding vacuum wavenumbers were measured using a wavemeter (Coherent, Wave-Master). The polarization vector, \(\varepsilon\), of the UV radiation was usually arranged to be perpendicular to the molecular beam axis and parallel to the front face of the detector (\textit{i.e.} \(\varepsilon // y\)), but the radiation could also be circularly polarized by application of an appropriate voltage to a Pockels’s cell inserted in the UV beam path. Excitation \textit{via} the \(b_3(v' = 3)\) level was investigated using both linearly and circularly polarized radiation. The resulting ions were extracted, along \(z\), under velocity map imaging conditions. The ion cloud impinged on the front face of a position sensitive detector (a pair of microchannel plates and a phosphor screen) mounted 860 mm downstream from the interaction volume. This was read out by a CCD camera equipped with a fast intensifier (Photonic Science) that was gated to the time-of-flight (TOF) apparatus appropriate for \(^7\)BrCl or \(^35\)Cl\(^+\) ions. Each ion image resulting from a single laser shot was processed with an event counting, centroiding algorithm provided with the commercial camera software DaVis (LaVision) running on a PC, and the resulting counts accumulated for, typically, \(10^8\) laser shots. The accumulated fragment ion images were analysed by reconstructing the 3-D velocity distribution as described previously\textsuperscript{23} using an algorithm based on the filtered back projection method of Sato \textit{et al.}\textsuperscript{24} High-level \textit{ab initio} calculations for the various singlet valence and Rydberg states of BrCl deemed most relevant to the current investigation were performed using the MOLPRO 2002 electronic structure package.\textsuperscript{25} As in our previous studies on BrCl\textsuperscript{+},\textsuperscript{8} these calculations were carried out in the abelian \(C_{2h}\) sub-group of the full \(C_{\infty v}\) point group at the CASSCF/MRCI level. The extended molecular orbitals of the Rydberg states required use of the aug-cc-pVTZ basis set.\textsuperscript{26,27} The active space consisted of 14 electrons occupying the usual valence orbitals, (10\(\sigma\)(11\(\sigma\))(12\(\sigma\))(5\(\pi\))(6\(\pi\))(13\(\sigma\)), to which 2 extra \(\sigma\) orbitals were added in order to describe the lowest Rydberg orbitals of interest.
3. Results

3.1 $^{35}$Cl$^+$ fragment imaging

$^{35}$Cl$^+$ ion images were recorded at six different wavelengths, chosen to be resonant (at the two photon energy) with the $b_2(v' = 0–5, v'' = 0)$ transitions. Fig. 2 shows an illustrative image, obtained following excitation via the $b_2(3, 0)$ transition ($\bar{\nu} = 31 568.4$ cm$^{-1}$). Cl$^+$ velocity distributions were obtained by integrating the reconstructed 3-D speed distribution over all angles. These were then converted into total kinetic energy release (TKER) distributions, assuming an (isotope averaged) mass $m_{Br} = 79.904$ amu for the neutral partner fragment. Also shown in Fig. 2 are the TKER distributions derived from such images for the Cl$^+$ + Br products formed when exciting at $\bar{\nu} = 30 807.0, 31 066.4, 31 318.5, 31 568.4, 31 818.3$ cm$^{-1}$ and $32 075.3$ cm$^{-1}$, i.e. via the $b_2(v' = 0–5)$ levels. All of the major features evident in these spectra can be assigned in terms of dissociation mechanisms (i) and (iii). These are now considered in turn.

3.1.1 Dissociation of super-excited states. Super-excited states are here defined as electronically excited states of the neutral molecule lying at energies above the ionization potential of BrCl. As discussed more fully below, generation of the super-excited states relevant to the present work is best envisaged in terms of two-photon excitation to the [2$^3\Pi_{1/2}$]5s$\sigma$ Rydberg state, followed by a further one-photon $\pi^* \rightarrow \pi$ excitation within the $^2\Pi_{1/2}$ core.

In the case of $^{35}$Cl$^+$ images formed by absorbing three photons of wavenumber $\bar{\nu}$, the TKER (in cm$^{-1}$) associated with any given products from dissociation of a super-excited state will be generated by the energy conserving relation:

$$\text{TKER} = 3\bar{\nu} - D_0(\text{Br} - \text{Cl}) - E(\text{Cl}^{**}) - E(\text{Br}/\text{Br}^*),$$

where $D_0(\text{Br} - \text{Cl})$ is the dissociation energy of BrCl [18 027 cm$^{-1}$ (ref. 28)]. Table 1 lists TKERs (in cm$^{-1}$) calculated for all combinations of [Br + Cl$^{**}$] and [Br$^*$ + Cl$^{**}$] products for which TKER $> 0$ at the various $3\bar{\nu}$ energies used here, i.e. combinations for which

$$3\bar{\nu} - D_0(\text{Br} - \text{Cl}) > E(\text{Cl}^{**}) + E(\text{Br}/\text{Br}^*).$$

Cl$^{**}$ denotes a Rydberg state of atomic chlorine, with term value $E(\text{Cl}^{**})$, that can be ionized by absorption of one further photon with wavenumber $\bar{\nu}$. All Cl$^{**}$ states identified in the present study have electronic configuration [Ne]3s$^2$3p$^4$(3P)$4s^1$. Energy conservation requires that the partner bromine atom is formed in its ground ($^2P_{3/2}$, henceforth Br) or spin–orbit excited ($^2P_{1/2}$, Br$^*$) state. The TKER spectra in Fig. 2 have been arranged so that a given [Br/Br$^*$ + Cl$^{**}$] product channel aligns vertically; assignments of the various active channels are indicated above the uppermost TKER spectrum.

3.1.2 Dissociation of BrCl$^+$ molecular ions. The heteronuclear BrCl$^+$ cation can dissociate via either channel (3) or (4), yielding distinguishable cation products:

$$\text{BrCl}^+ + hv \rightarrow \text{Br}^+ + \text{Cl}$$

(3)

$$\rightarrow \text{Br} + \text{Cl}^+. $$

(4)

Our previous multiphoton imaging studies of BrCl focused on Br$^+$ product formation. Since the ionization potential (IP) of Cl (104 591 cm$^{-1}$) is greater than that of Br (95 284.8 cm$^{-1}$), process (4) requires use of shorter photon wavelengths than are needed for products (3). The TKERs (in cm$^{-1}$) associated with Cl$^+$ ion formation following one-photon dissociation of BrCl$^+$ at an excitation wavenumber $\bar{\nu}$ are given by:

$$\text{TKER} = \bar{\nu} - D_1(\text{Br}^+ - \text{Cl}) - E(\text{Cl}^+) - E(\text{Br}/\text{Br}^*) - 9306.2$$

(5)

Fig. 2  Cl$^+$ ion image obtained following excitation via the $b_2(3, 0)$ transition ($\bar{\nu} = 31 568.4$ cm$^{-1}$) of BrCl with $s$ aligned vertically (double headed white arrow), together with TKER distributions of the Cl$^+$ + Br/Br$^*$ fragments derived from images such as that shown in (a) following excitation via $b_2(v')$ levels with $v' = 0 \ (\bar{\nu} = 30 807.0$ cm$^{-1}$), 1 ($\bar{\nu} = 31 066.4$ cm$^{-1}$), 2 ($\bar{\nu} = 31 318.5$ cm$^{-1}$), 3 ($\bar{\nu} = 31 568.4$ cm$^{-1}$), 4 ($\bar{\nu} = 31 818.3$ cm$^{-1}$) and 5 ($\bar{\nu} = 32 075.3$ cm$^{-1}$). The TKER spectra are plotted on a common dispersion and positioned so that a given product channel aligns vertically, but the <2000 cm$^{-1}$ part of the $v' = 4$ spectrum is plotted on a ×3 expanded vertical scale. Assignments of the various [Cl$^{**}$ + Br/Br$^*$] product channels are indicated by the comb festooned above the spectra. Selected peaks at low TKER due to one photon dissociation of BrCl$^+$($^2\Pi_{1/2}$, $v'$) parent ions yielding [Cl$^+(^3P_s)$ + Br($^3P_{3/2}$)] fragments are indicated by their associated ($v' : J$) values on the relevant spectra.

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Table 1. List of energetically accessible dissociation channels from super-excited states of BrCl following absorption of three photons with wavenumber $\tilde{\nu}$. Br$^+$ and Cl$^+$ represent atoms with ground state electronic configurations in, respectively, their ground $^3P_0$, spin–orbit excited $^3P_1$, or $^3P_2$ states. Br$^\ast$ and Cl$^\ast$ indicate Rydberg states, with configurations $\cdots 4s^2 4p ^3S_{1/2} L_J 3s^1$ or $\cdots 4s^2 4p ^3S_{1/2} L_J 3p^1$, and $\cdots 3s^2 3p ^3S_{1/2} L_J 4s^1$, respectively. For compactness, only the term symbol of the core and the outer electron are listed in the first two columns. Columns 3–5 give the term values of the respective atomic products, and their sum. Bold characters indicate all those production combinations that are accessible, energetically, following absorption of three $\tilde{\nu}$ photons, i.e., which satisfy the inequality shown in eqn (2) using the particular resonance enhancing $b_{ij}(\tilde{\nu}, 0)$ transition indicated in column 6. Fragmentation channels observed as being open in the present work are shown in bold font.

<table>
<thead>
<tr>
<th>Br term</th>
<th>Cl term</th>
<th>$E(\text{Br})$/cm$^{-1}$</th>
<th>$E(\text{Cl})$/cm$^{-1}$</th>
<th>$E(\text{total})$/cm$^{-1}$</th>
<th>$b_{ij}(\tilde{\nu}, 0)$</th>
<th>$3\tilde{\nu} - D_i(\text{Br} - \text{Cl})$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^+$</td>
<td>Cl$^+$</td>
<td>0</td>
<td>882.4</td>
<td>882.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Br$^\ast$</td>
<td>Cl$^\ast$</td>
<td>3685.2</td>
<td>882.4</td>
<td>4567.6</td>
<td></td>
<td></td>
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<tr>
<td>$[{}^3P_0]5s; {}^2P_{1/2}$ Cl$^\ast$</td>
<td>63 436.5</td>
<td>0</td>
<td>63 436.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[{}^3P_0]5s; {}^2P_{1/2}$ Cl</td>
<td>63 436.5</td>
<td>882.4</td>
<td>64 318.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[{}^3P_1]5s; {}^2P_{3/2}$ Cl$^\ast$</td>
<td>68 970.2</td>
<td>0</td>
<td>68 970.2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$[{}^3P_1]5s; {}^2P_{3/2}$ Cl</td>
<td>68 970.2</td>
<td>882.4</td>
<td>69 852.6</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$[{}^3P_2]5s; {}^4P_{3/2}$ Cl$^\ast$</td>
<td>95 284.2</td>
<td>$- 29 151.9$</td>
<td>66 132.3</td>
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<tr>
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<tr>
<td>$[{}^3P_2]5p; {}^4P_{1/2}$ Cl$^\ast$</td>
<td>67 183.6</td>
<td>882.4</td>
<td>68 066.9</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$[{}^3P_2]5p; {}^4P_{1/2}$ Cl</td>
<td>67 183.6</td>
<td>0</td>
<td>67 183.6</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$[{}^3P_2]5p; {}^4P_{3/2}$ Cl$^\ast$</td>
<td>68 970.2</td>
<td>882.4</td>
<td>69 852.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[{}^3P_2]5p; {}^4P_{3/2}$ Cl</td>
<td>69 268.7</td>
<td>0</td>
<td>69 268.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[{}^1D]5s; {}^2D_{3/2}$ Cl$^\ast$</td>
<td>75 908.5</td>
<td>882.4</td>
<td>75 891.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[{}^1D]5s; {}^2D_{3/2}$ Cl</td>
<td>76 403.9</td>
<td>0</td>
<td>76 403.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The wavenumber of the photon used to induce BrCl$^+$ dissociation in the present one-color experiments is dictated by the energy of the state of neutral BrCl resonant at the two photon energy. Given the propensity for preserving both the vibrational and core spin–orbit quantum numbers during the third photon ionization step, it follows that $\tilde{\nu}$ in eqn (6) will be correlated with $E_i$ and thus $D_i$. From the six excitation wavenumbers used here, the lowest $\tilde{\nu}$ for which we should expect $^{35}\text{Cl}^+$ fragment ion formation via dissociation of the
REMPI-generated BrCl$^+$ molecular ions is $\tilde{\nu} = 31318.5 \text{ cm}^{-1}$, exciting the $b_3(2, 0)$ band and thus favoring formation of BrCl$^+$($^2\Pi_{1/2}$, $v^+ = 2$) parent ions.

Consistent with such expectations, the TKER distribution measured at $\tilde{\nu} = 31318.5 \text{ cm}^{-1}$ shows two slow peaks at TKER values that match none of those predicted for the dissociation of the super-excited BrCl$^+$ molecules. These peaks are assignable to Cl$^+$($^3P_2$) ions formed via dissociation process (4), from BrCl$^+$ cations in their $^2\Pi_{1/2}$, $v^+ = 2$ and $v^+ = 3$ states, respectively, and are labeled as such in Fig. 2 using the convention ($v^+ : J$). The peak-to-peak separation (485 cm$^{-1}$) is reasonable for successive $v^+$ levels of BrCl$^+$, matching well with the reported spacing between $v' = 2$ and $v' = 3$ levels of the resonance enhancing $b_5$ Rydberg state ($\sim 500 \text{ cm}^{-1}$, ref. 13). Four slow peaks are evident in the TKER spectrum measured at $\tilde{\nu} = 31568.4 \text{ cm}^{-1}$ ($b_3(3, 0)$ transition). The more intense peaks derive from ions with $v^+ = 3$ (as expected on Franck–Condon grounds), and reveal formation of Cl$^+$ ions in both the ground ($J = 2$) and first excited spin–orbit ($J = 1$) states, while the two weaker features are attributable to formation of ground state products following dissociation from $^2\Pi_{1/2}$ parent cations with $v^+ = 4$ and 2. Weak peaks attributable to dissociation of $^2\Pi_{1/2}$ parent cations with $v^+ = 4$ and 3 were observed following excitation at $\tilde{\nu} = 31818.3 \text{ cm}^{-1}$ ($b_3(4, 0)$ transition), but no features attributable to parent ion photolysis were identifiable in images recorded at $\tilde{\nu} = 32075.3 \text{ cm}^{-1}$ ($b_3(5, 0)$ transition).

No features attributable to Cl$^+$ products from the photo-dissociation of BrCl$^+$($^2\Pi_{3/2}$) cations are identified, nor do we see any peaks consistent with Cl$^+$ + Br$^-$ ion-pair formation.

### 3.1.3 Recoil angular anisotropy

As the illustrative image in Fig. 2 shows, the various Cl$^+$ product velocity sub-groups exhibit anisotropic angular distributions, some of which show an unusual degree of modulation. The angular distribution of each well-resolved product channel in this and all other images recorded with linearly polarized laser radiation were fitted in terms of expression (7)

$$P(\theta) = \frac{1}{4\pi} \left[ 1 + \sum_{n=2,4,6} \beta_n P_n(\cos(\theta)) \right]. \tag{7}$$

where $\theta$ is the angle between the laser polarization and the fragment recoil velocity vector, $\beta_n$ are anisotropy parameters and $P_n$ are $n$th order Legendre polynomials. Fig. 3 shows angular distributions of $^{35}\text{Cl}^+$ products arising in the multi-photon excitation and dissociation of BrCl at $\tilde{\nu} = 31568.3 \text{ cm}^{-1}$ ($b_3(3, 0)$ transition). The distributions shown in Fig. 3a and 3b are for Cl$^+$ ions arising as a result of one photon ionization of Cl$^{**}(^3P_{3/2})$ fragments formed by three-photon excitation to, and dissociation of, a super-excited state using (a) linearly (i.e. as in the image shown in Fig. 2) and (b) circularly polarized laser radiation. By energy conservation arguments, the partner fragment is known to be a ground ($^3P_{3/2}$) state Br atom. The former image, in particular, is noteworthy, showing maximum intensity at $\theta \sim 33$ and $147^\circ$.

The product recoil anisotropy will be determined by three-photon excitation to the super-excited state. In the language of ref. 21, the $b_3(3, 0)$ transition is a two photon $\Pi \leftrightarrow \Sigma$ excitation. The super-excited state(s) of BrCl populated at the three-photon energy could thus have $\Sigma$, $\Pi$ or $\Delta$ symmetry. The general forms of the recoil anisotropy observed under both linear and circular excitations follow curves B in Fig. 4 and 5 of ref. 21, showing that the dissociating super-excited state(s) populated at the three photon energy have $\Pi$ symmetry (i.e. $\Omega = 1$). $P(\theta)$ in such a case varies as $\sin^2 \theta \cos^2 \theta$ (for linearly polarized excitation), or $\sin^2 \theta (1 + \cos^2 \theta)$ when using circularly polarized light. The best-fit values of the anisotropy parameters (eqn (7)) used to fit the angular distributions in Fig. 3a and 3b are, respectively: $\beta_2 = 1.77 \pm 0.01$, $\beta_4 = -0.82 \pm 0.01$ and $\beta_0 = -0.87 \pm 0.01$, and $\beta_2 = -1.15 \pm 0.07$, $\beta_4 =$
0.13 ± 0.09 and \( \beta_0 = 0.05 \pm 0.10 \), where the quoted uncertainties are 1σ values from fitting the 10° ≤ θ ≤ 170° data in terms of eqn (7) with \( n \leq 6 \). Similar recoil anisotropies, characterized by a \( \beta_2 > +1 \) and negative \( \beta_4 \) and \( \beta_6 \) values are found for all \( \text{Cl}^{-} + \text{Br}^+ \) products formed following linearly polarized excitation via \( b_0(v') \) transitions with \( 1 ≤ v' ≤ 4 \). \([\text{Cl}^{-} + \text{Br}^+]\) products formed when exciting at the lowest and highest wavenumbers (resonant with the \( b_0(0,0) \) and \( b_0(5,0) \) transitions) display recoil anisotropies with \( \beta_4 \) and \( \beta_6 \) values closer to zero, however, and \( \beta_2 \) values close to +1 and +2, respectively.\(^{30}\) All show some deviation from the limiting values calculated\(^{21}\) for such a \( \Pi \leftrightarrow \Pi \leftrightarrow \Sigma \) excitation; these almost certainly reflect the breakdown of one or more of the assumptions implicit in deriving the limiting anisotropy values. For example, the resonance enhancing \( b_0(v') \) levels are predissociated (i.e. have a finite lifetime). The \( b_0(v',0) \) bands thus have a rotational contour and, as shown by Dixon,\(^{21}\) the choice of \( \nu \) will determine the mix of \( J' \) in the coherent superposition state created by the initial two-photon absorption and the degree to which rotation degrades their spatial anisotropy prior to absorption of the third photon.

The angular distribution shown in Fig. 3c is for the \([\text{Cl}^{-}(\text{P}_2) + \text{Br}^+(\text{P}_{3/2})]\) products from linearly polarized, one photon dissociation of \( \text{BrCl}^{-}(\Pi_{1/2},v^+ = 3) \) parent cations at \( \bar{\nu} = 31 \, 568.4 \, \text{cm}^{-1} \) (the innermost bar one of the more intense rings evident in the image shown in Fig. 2). The best-fit to this distribution in terms of eqn (7) yields: \( \beta_2 = 1.65 \pm 0.01 \), \( \beta_4 = -0.20 \pm 0.01 \) and \( \beta_6 = -0.11 \pm 0.01 \). Similar anisotropy parameter values were measured for the \([\text{Cl}^{-}(\text{P}_1) + \text{Br}^+(\text{P}_{3/2})]\) spin–orbit excited products arising in this same dissociation, and for the \([\text{Cl}^{-}(\text{P}_2) + \text{Br}^+(\text{P}_{3/2})]\) products formed from \( \text{BrCl}^{-}(\Pi_{1/2},v^+ = 3) \) parent cations formed when exciting at \( \bar{\nu} = 31 \, 318.5 \, \text{cm}^{-1} \). These anisotropy parameter values are broadly reminiscent of those we have reported previously for the case of \( \text{Br}^+ \) fragments arising from photolysis of \( \text{BrCl}^{-}(X^2\Pi_{1/2},v^0 = 0) \) cations\(^{2} \) and, as in that case, we attribute the non-limiting value of \( \beta_2 \) and the non-zero best-fit values of \( \beta_4 \) and \( \beta_6 \) to the effects of (i) some residual alignment of the parent cation introduced by the multiphoton preparation step at the instant of the final \( \Lambda^2 \Pi \leftrightarrow X^2\Pi \) excitation, and (ii) partial saturation of this latter transition at the intensities required to drive the initial multiphoton excitation.

3.2 \(^{79}\)Br\(^+\) fragment imaging

\(^{79}\)Br\(^+\) ion images were also recorded at wavenumbers appropriate for two-photon excitation via each of the \( b_0(v',0) \) \( (0 \leq v' \leq 5) \) bands. Fig. 4 shows the \(^{79}\)Br\(^+\) image measured at \( \bar{\nu} = 31 \, 568.4 \, \text{cm}^{-1} \) (\( b_0(3,0) \) transition). Image analysis reveals contributions from all three of the fragment ion formation mechanisms depicted in Fig. 1. As for the \( \text{Cl}^{-} \) products, velocity distributions obtained from the reconstructed 3-D \(^{79}\)Br\(^+\) recoil distributions were converted into TKER distributions (assuming \( m_q = 35.453 \, \text{amu} \)). Fig. 4 also provides an overview of the TKER distributions obtained when exciting via each of the \( b_0(v') \) \( (0 \leq v' \leq 5) \) levels. It proves convenient to consider the various \( \text{Br}^+ \) forming channels in a different order to those yielding \( \text{Cl}^+ \) (above).

3.2.1 Dissociation of \( \text{BrCl}^{-}\) molecular ions. The TKERs (in cm\(^{-1}\)) of products arising through channel (3) are given by:

\[
\text{TKER} = \bar{\nu} - D_0(\text{Br}^- - \text{Cl}^-) - E(\text{Br}^+) - E(\text{Cl}/\text{Cl}^+) \tag{8}
\]

where \( E(\text{Br}^+) \) and \( E(\text{Cl}/\text{Cl}^+) \) are the respective term values of the \( \text{Br}^+ \) and \( \text{Cl}^- \) fragments. Analysis of the image obtained by imaging \(^{79}\)Br\(^+\) fragments following excitation at \( \bar{\nu} = 30 \, 807 \, \text{cm}^{-1} \) (\( b_0(0,0) \) transition) has been reported previously.\(^{7} \) Most of the resolved structure was rationalized in terms of one photon dissociation of \( \text{BrCl}^{-}(X^2\Pi_{1/2},v^+ = 0) \) cations to a range of \([\text{Br}^+(\text{P}_3) + \text{Cl}^+(\text{P}_3)]\) limits. In contrast to the \( \text{Cl}^- \) image analysis above, some \( \text{Br}^+ \) products clearly derive from photolysis of parent ions with \( \Omega = 3/2 \). Measurement and analysis of the complementary photoelectron image recorded at this same wavenumber served to reinforce the conclusion that a fraction (~16%) of the parent ions are formed in the \( X^2\Pi_{1/2} \) spin–orbit state.\(^{7} \)

The earlier analysis failed to account fully for the signal at higher velocities, however. As the lower panels in Fig. 4 show, the velocity distributions derived from images recorded when exciting via higher \( b_0(v',0) \) transitions are less well-resolved, but have a qualitatively similar appearance. The peaks of the respective distributions shift to higher TKER, and maximize at TKER values appropriate for \([\text{Br}^+(\text{P}_3) + \text{Cl}^+(\text{P}_3)]\) product formation following dissociation of \( \text{BrCl}^{-}(X^2\Pi_{1/2}) \) cations with \( v^+ = v' \). However, the detailed form of the distributions, especially at high TKER, requires that \( \text{BrCl}^{-} \) cations with \( v^+ \neq v' \) contribute as well. Analysis of the \( \text{Cl}^- \) images provided term values for the \( v^0 = 0 \)–3 levels of \( \text{BrCl}^{-} \) with sufficient accuracy to allow estimation of the term values for higher \( v^+ \) levels of the parent ion. The combs superposed above the various spectra in Fig. 4 indicate predicted TKERs for the \([\text{Br}^+(\text{P}_3) + \text{Cl}^-/\text{Cl}^+]\) products arising from dissociation of \( \text{BrCl}^{-}(X^2\Pi) \) cations with \( \Omega = 1/2 \) and 3/2. Peaks appearing at the low TKER end of the main feature (e.g. the peaks at ~3300 and 4900 cm\(^{-1}\) in the case of excitation via the \( b_0(3) \) level) are attributable to dissociations with \( v^0 = v' \) yielding \( \text{Br}^+(\text{P}_3) \) products with \( J = 1 \) or 0.

3.2.2 Dissociation of super-excited states. As Fig. 4 showed, TKER spectra obtained by monitoring \(^{79}\)Br\(^+\) ions formed by excitation via all \( b_0(v' > 0) \) levels show additional sharp features at low TKER. Three of these, with \( 1 ≤ v' ≤ 3 \), are illustrated in greater detail in Fig. 5. As in the case of \( \text{Cl}^- \), many of these can be unambiguously associated with one photon ionization of Rydberg atoms (\( \text{Br}^+ * \) in this case) formed by dissociation of super-excited states at the energy of three absorbed photons. As before, to appear in the TKER spectrum a given \( \text{Br}^+ * \) product state must satisfy the relations

\[
3\bar{\nu} - D_0(\text{Br}^- - \text{Cl}^-) > E(\text{Br}^+) > E(\text{Cl}/\text{Cl}^+) \tag{9}
\]

Table 1 also lists term values for the possible \( \text{Br}^+ * \) product limits, ordered in terms of increasing wavenumber. The dashed vertical lines in Fig. 5 indicate the active product channels. The populated \( \text{Br}^+ * \) Rydberg states all have the (dominant) configuration [Ar]4s3d\(^{10}\)4p\(^{6}\)\((^{3}\text{P}_3)\)\(^{5}\)p. Most converge to the ground \( \text{P}_3 \) state of \( \text{Br}^+ \), but excitation at \( \bar{\nu} = 32 \, 076.4 \, \text{cm}^{-1} \) (via the \( b_0(5) \) level) provides just sufficient energy to form, and to observe, a \( ^5 \)p Rydberg state converging.
to the first spin–orbit excited core \([\text{Ar}]4s^23d^{10}4p^4(3P_1)\). Dissociation channels leading to Br** states with configuration \([\text{Ar}]4s^23d^{10}4p^4(3P_J)5s\) are open at all \(\nu\) wavenumbers investigated, as are one or more states with configuration \([\text{Ar}]4s^23d^{10}4p^4(1D)5s\) when exciting via \(b_3(\nu')\) levels with \(\nu' \geq 2\), but no such products have been identified in any of the measured images. Neither are any peaks consistent with \(\text{Br}^+ + \text{Cl}^-\) ion-pair formation.

3.2.3 Recoil angular anisotropy. Anisotropy parameters for the most intense part of the outer ring (arising via process (3)) in \(^{79}\text{Br}^+\) images obtained when exciting via the \(b_3(\nu')\) levels with \(1 \leq \nu' \leq 3\), plotted on a common dispersion and arranged so that a given \([\text{Br}^{**} + \text{Cl}/\text{Cl}^*]\) product channel aligns vertically. Br** products formed in association with Cl and Cl* products are distinguished by long (---) and short (-----) dashed vertical lines, respectively.

4. Discussion

The resonance enhancing \(b_3\) levels of \(\text{BrCl}\) have dominant configuration \(\pi^*\pi^+\pi^\pi^\pi\). Direct \(2 + 1\) REMPI via this state leads to loss of the Rydberg electron and formation of ground \((X^2\Pi)\) state \(\text{BrCl}^+\) cations. The present data reveal significant probability for an alternative electron excitation.
forming one (or more) super-excited states of BrCl at the energy of three absorbed photons. The most likely candidate for this excitation is a $\pi^* \leftarrow \pi$ promotion within the core, with the outer electron remaining in the same Rydberg orbital. This particular core excitation was found to be dominant in transition dipole moment calculations performed from the ground state to various excited states of the BrCl$^-$ molecular ion,

and the discussion that follows is based on such an assignment. We note that the analogous one-photon $\pi^* \leftarrow \pi$ core promotion has been invoked to explain the formation of core-excited autoionization following excitation to one or both of the 1,3$\sigma$ levels (see Fig. 2), consistent with three photon induced dissociation following excitation to the repulsive inner limb of the 1,3$\sigma$ state. Nonetheless, we can be confident that the 1,3$\sigma$ super-excited state(s) correlate diabatically with the corresponding Br** Rydberg atom products (i.e., $[\text{Br}^{(3P)5p} + \text{Cl}^{(3P)}]$ in this case). It should be noted that the curve shown in Fig. 6a for the ($X^2\Pi_{1/2}$)5$\sigma$ Rydberg state is simply the ab initio potential for the ($X^2\Pi_{1/2}$)5$\sigma$ state, uplifted in energy to match the experimentally reported $^1\Sigma_g^+$ origin for the 1$\Sigma_g^+$ state. Nonetheless, we can be confident that the ($A^2\Pi_{1/2}$)5$\sigma$ and ($X^2\Pi_{1/2}$)5$\sigma$ potentials cross, given that the asymptotic limits associated with the former lie below those of the latter (Table 1). The Br** fragments observed in the Br$^+$ images can thus be understood in terms of two photon resonance enhanced three photon excitations to the same ($^3\Pi(\cdot\pi \pi^55\sigma)$) super-excited state(s) as implicated in Cl$^{**}$ atom formation, followed by Rydberg–Rydberg interaction in the crossing region between the ($X^2\Pi_{1/2}$)5$\sigma$ and ($X^2\Pi_{1/2}$)5$\sigma$ potentials.

**4.1 Dissociation of super-excited states**

The super-excited state(s) populated at the three photon energy are deduced to have $\Omega = 1$ (from the measured recoil anisotropies) and assumed to have dominant electronic configurations $^1\Pi(\cdot\pi \pi^55\sigma)$ and to be members of Rydberg series converging to the $\Lambda^2\Pi(\cdot\pi \pi)$ state of BrCl$^+$. Ab initio calculations show that the $A^2\Pi$ state of the ion correlates with the asymptotic products $[\text{Br}^{(3P)} + \text{Cl}^{(3P)}]$. In a diabatic picture, the parent $\rightarrow$ product correlation accompanying Rydberg state dissociation should follow that of the corresponding ion. On this basis, we assume that the $^1\Pi(\cdot\pi \pi^55\sigma)$ super-excited state(s) correlate diabatically to the products $[\text{Br}^{(3P)} + \text{Cl}^{**}(3P)4s]$. Readers should be aware of the potential ambiguity introduced by the Rydberg numbering scheme; the orbital labelled as 5$\sigma$ in BrCl, the 5s orbital in atomic Br and the 4s atomic orbital in atomic Cl are the lowest s Rydberg orbitals in the respective species. $[\text{Br}^{(3P)} + \text{Cl}^{**}(3P)4s; 4P]$ and $[\text{Br}^{(3P)} + \text{Cl}^{**}(3P)4s; 4P]$ atomic products are indeed identified following excitation via all $b_3(v')$ levels (see Fig. 2), consistent with three photon induced dissociation following excitation to the repulsive inner limb of the $^1\Pi(\cdot\pi \pi^55\sigma)$ super-excited state potential(s).

The Br$^+$ images (Fig. 3) reveal selective formation of Br$^{**}(3P)5p$ Rydberg atoms. Ab initio calculations for the singlet Rydberg states of BrCl provide a rationale for this observation as well. Specifically, as Fig. 6a shows, the potential curves for the $^1\Pi(\cdot\pi \pi^55\sigma)$ super-excited states are crossed, near their minima, by the long range part of Rydberg state potentials with configuration $\cdot\pi \pi^55\sigma$—that converge to the $X^2\Pi$ ground state ion. BrCl$^+$(X$^2\Pi$) correlates with the ground state atomic products $[\text{Br}^{(3P)} + \text{Cl}^{(3P)}]$. Using the same logic as previously, Rydberg states built on this core (e.g., states with configuration $\cdot\pi \pi^55\sigma$) should correlate diabatically with the corresponding Br** Rydberg atom products (i.e., $[\text{Br}^{(3P)5p} + \text{Cl}^{(3P)}]$ in this case). It should be noted that the curve shown in Fig. 6a for the ($X^2\Pi_{1/2}$)5$\sigma$ Rydberg state is simply the ab initio potential for the ($X^2\Pi_{1/2}$)5$\sigma$ state, uplifted in energy to match the experimentally reported $^1\Sigma_g^+$ origin for the 1$\Sigma_g^+$ state. Nonetheless, we can be confident that the ($A^2\Pi_{1/2}$)5$\sigma$ and ($X^2\Pi_{1/2}$)5$\sigma$ potentials cross, given that the asymptotic limits associated with the former lie below those of the latter (Table 1). The Br** fragments observed in the Br$^+$ images can thus be understood in terms of two photon resonance enhanced three photon excitations to the same ($^3\Pi(\cdot\pi \pi^55\sigma)$) super-excited state(s) as implicated in Cl$^{**}$ atom formation, followed by Rydberg–Rydberg interaction in the crossing region between the ($A^2\Pi_{1/2}$)5$\sigma$ and ($X^2\Pi_{1/2}$)5$\sigma$ potentials.

**4.2 Dissociation of molecular ions**

Our previous photodissociation studies of Br$^j$ and BrCl$^+$ cations5,6 relied on direct ionization of the resonance enhancing Rydberg state level to generate the required state-selected parent molecular ions. However, as the previous sub-section shows, two photon resonance enhanced, three photon excitation of BrCl also results in population of super-excited $^1\Pi(\cdot\pi \pi^55\sigma)$ Rydberg states. These states lie at energies above the threshold for forming ground state BrCl$^+$ cations. Autoionization of these super-excited states thus offers

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**Fig. 6** (a) Ab initio potential energy curves (spin–orbit averaged) relevant to the present one-color multiphoton excitation studies of BrCl, resonance enhanced at the two photon energy by levels of the $b_3([X^2\Pi_{1/2}]5\sigma)$ state. (The curve shown for the ($X^2\Pi_{1/2}$)5$\sigma$ Rydberg state is simply the ($X^2\Pi_{1/2}$)5$\sigma$ potential, raised in energy to match the experimentally reported origin for the ($X^2\Pi_{1/2}$)5$\sigma$ state.) The asymptotic limits are as follows: (a) Br + Cl; (b) Br$^{**}(5s) + \text{Cl}$; (c) Br$^{**}(5p) + \text{Cl}$; (d) Br + Cl$^{**}(4s)$ and (e) Br$^+$ + Cl, and the shaded bar illustrates the energy range sampled by three-photon absorption in the present work. (b) Schematic illustration of the competition between dissociation and electronic autoionization following excitation to one or both of the $^1\Pi(\cdot\pi \pi^55\sigma)$ super-excited state(s).

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The TKERs of the $[^{79}\text{Br}]^+$ and [Br $+^{35}\text{Cl}$] fragments resulting from one photon dissociation of BrCl$^+$ (eqns (5) and (8)) depend not just on the respective product term values but also on the vibrational energy content of the parent ion (through the value of $D(\text{Br}^+-\text{Cl})$). Image analysis allows estimation of the relative contributions from different parent $v^+$ levels; the distribution of $v^+$ state populations so derived can give insights into the parent ion formation mechanism(s). The ionization step in a direct 2 + 1 REMPI process will normally show a strong propensity for $\Delta v = v^+-v' = 0$ transitions, because of the very similar equilibrium geometries of the intermediate Rydberg state and the corresponding ionic state. The excitation wavenumbers used in this work have been chosen to enable resonance enhanced excitation via successive $b_2(v')$ levels. If all BrCl$^+$ cations were formed by direct 2 + 1 REMPI, the choice of $v'$ should dictate their $v^+$ quantum number, and thus $D(\text{Br}^+-\text{Cl})$. One photon dissociation should then yield a comparatively simple TKER spectrum, with just a single peak for each active [Br$^+$(\text{Cl}($^3P$)) + Cl(\text{Br}($^3P$))] product channel. Such expectations are reasonably satisfied in TKER spectra obtained by monitoring Br$^+$ ions when exciting $v_0$ the $b_2(0)$ level but, as Fig. 4 showed, TKER spectra recorded at higher wavenumbers (i.e. via $b_2(v' > 0)$ levels) indicate population of (and dissociation from) a wider spread of $v^+$ levels, stretching up to the highest $v^+$ quantum numbers permitted by energy conservation (assuming three photon absorption).

Electronic autoionization offers a route to forming BrCl$^+$ cations in a range of $v^+$ levels. It can occur when, as here, a Rydberg state belonging to a series converging to an excited state of the ion (i.e. the 1,3 super-excited states) couples with the continuum of a lower electronic state of the same ion (i.e. one, or other, or both spin–orbit components of the X$^2\Pi$ state in this case). The case of a molecule autoionizing along the repulsive part of a potential curve during bond extension has been investigated, both experimentally and theoretically, for the cases of H$_2$ and NO. A key signature of the process is that autoionization can occur over a time interval that is long enough to allow significant movement of the nuclei—giving rise to a non-Frank–Condon vibrational population distribution within the ground state cation. Weak features attributable to such $\Delta v \neq 0$ transitions are identifiable in the previously reported 2 + 1 REMPI-photoelectron image of BrCl recorded at 30 807.6 cm$^{-1}$ (i.e. when exciting via the $b_2(0, 0)$ transition).

Fig. 6b illustrates the possible competition between dissociation and autoionization following three photon excitation to the 1,3 super-excited states. We assume that autoionization of this state can occur at any internuclear separation up to the stabilization point (i.e. the point at which the potential curves for the super-excited state and the ground state ion cross). The classical model of Hazi then predicts that the resulting BrCl$^+$ (X) ions should be formed with a smoothly varying vibrational state population distribution, ranging from $v^+ = v'$ up to the maximum value of $v^+$ allowed energetically. Such predictions are wholly consistent with the experimental observations, whereby we deduce maximal population of parent ion levels with $v^+ = v'$ (from direct REMPI), supplemented by a broader $v^+$ population distribution from autoionization.

$^{35}\text{Cl}^+$ fragments from dissociation of BrCl$^+$(2$^3\Pi_{3/2}$) cations are observed when exciting via $b_2$ levels with $2 \leq v' \leq 4$, but not $v' = 5$. The $v' \geq 2$ onset is understandable in terms of energy and Franck–Condon arguments (see section 3.1.2), as is the non-observation of $^{35}\text{Cl}^+$ fragments from dissociation of BrCl$^+$(2$^3\Pi_{1/2}$) cations. Neither do we observe any obvious indication of $^{35}\text{Cl}^+$ fragments attributable to dissociation from a spread of parent $v^+$ states, such as might be formed by autoionization of the super-excited state, at any of the excitation energies for which the [Br($^3P$) + Cl($^3P_2$)] dissociation channel is energetically open. The previously reported ab initio potential curves for BrCl$^+$ provide a possible explanation for these observations. Within the energy range investigated, the dominant transition moment from low $v^+$ levels of the ground state ion is to the A$^2\Pi$ state. Diabatically, this state correlates with [Cl$^+$(\text{P}) + (Br$^3P$)] products, but the calculations predict strong avoided crossings, for both spin–orbit components, with a repulsive $^3\Pi$ state. A diabatically, therefore, the calculations predict that much of the flux excited to the A$^2\Pi$ state will dissociate to the [Br$^+(^3P_1)$ + Cl($^3P_2$)] limit. We note, however, that wavepacket calculations using these same potentials and couplings failed to replicate the observed [(Br$^3P$) + Cl($^3P_2$)] spin–orbit branching fractions, so there must be some remaining uncertainty as to the validity of this rationale.

A few peaks remain unidentified in the lower energy part of some of the TKER spectra measured monitoring Br$^+$ ions. These might arise via one photon excitation of BrCl$^+$ (X) cations to an excited state [e.g. $^2\Sigma^+(-\cdots^1\Pi^+\pi^*\pi\pi^*)$ state] which the ab initio calculations suggest should correlate with the dissociation limit [Br$^+(^3\Delta_2) + \text{Cl}(^3P)$]. This limit lies 12530.3 cm$^{-1}$ above that for the ground state products, and could only be reached by higher $v^+$ parent ions such as are formed via the autoionization mechanism. Unfortunately, the term values of such higher $v^+$ levels are not known to sufficient accuracy to be able to validate (or refute) this suggestion.

5. Conclusions

Analysis of the TKER and angular distributions of the $^{79}\text{Br}^+$ and $^{35}\text{Cl}^+$ fragments resulting from one-color multiphoton excitation of BrCl molecules, resonance enhanced at the two photon energies by the $v' = 0$–5 vibrational levels of the [X$^2\Pi_{3/2}$]5s$\sigma$ Rydberg state, has enabled identification of three distinct fragment ion formation mechanisms. Absorption of a third photon by [X$^2\Pi_{3/2}$]5s$\sigma$ Rydberg molecules is shown to yield two distinct outcomes: (i) photoionization (i.e. removal of the Rydberg electron—a traditional 2 + 1 REMPI process) and (ii) $\pi^* \leftrightarrow \pi$ excitation within the core, resulting in formation of one or more super-excited states with $\Omega = 1$ and configuration [A$^2\Pi_{1/2}$]5s$\pi$. These latter state(s) lie above the first ionization limit and can autoionize (yielding BrCl$^+$(X$^2\Pi$) ions in a wider range of $v^+$ states than would be expected by direct 2 + 1 REMPI), and/or fragment to
neutral atoms. Further one-photon absorption by the parent ions formed by \(2 + 1\) REMPI or by autoionization results in formation of \(\text{Br}^+\) and (energy permitting) \(\text{Cl}^-\) fragment ions. One or other atom formed when the super-excited molecule fragments will itself be in a Rydberg state. Guided by \textit{ab initio} potentials, we deduce that \([\text{Cl}^*]^3\text{P}_{1/2} + \text{Br}^+/\text{Br}^+\) products arise from direct dissociation of the super-excited state(s), whereas \([\text{Br}^*]^3\text{P}_{3/2} + \text{Cl}/\text{Cl}^-\) product formation occurs as a result of interaction between the \([\text{A}^2\text{I}_1\text{S}]\sigma\) and \([\text{X}^2\text{II}_1\text{S}]\sigma\) Rydberg potentials at extended Br–Cl bond lengths. Absorption of one further photon by the resulting \(\text{Br}^{**}\) and \(\text{Cl}^{**}\) Rydberg atoms leads to their ionization, and thus their appearance in the resulting \(\text{Br}^+\) and \(\text{Cl}^-\) fragment ion images.

The present results, taken together with those reported previously from similar multiphoton excitation and ionization studies of \(\text{Br}_2\) and \(\text{Cl}_2\), serve to illustrate both the advantages, and the potential complications, associated with REMPI as a means of preparing state-selected molecular ions. In favorable cases, \(n + 1\) REMPI via an appropriate Rydberg state can serve as a clean and efficient route to forming quantum-state selected molecular ions for subsequent use in, for example, photodissociation or reaction dynamics experiments. Such will apply in those cases where the cross-section for ionizing the Rydberg electron, by one-photon absorption at the chosen excitation wavelength, far exceeds that for any alternative photo-excitation process. Multiphoton excitations can drive multi-electron promotions, however—as illustrated by the present results. Thus, particularly in cases where the parent ion shows strong absorption at the chosen excitation wavelength, the corresponding core excitation may have a greater cross-section than that for promoting the Rydberg electron into the continuum. The super-excited states that result can decay by autoionizing and/or by (pre)dissociating. The (pre)dissociation products may include Rydberg species, lying at energies within one photon of their ionization limit. These will be very susceptible to ionization at the intensities prevailing in most REMPI experiments. Such a multiplicity of possible ion (and electron) formation channels is unlikely to be revealed through the traditional parent REMPI spectrum (in which some selected (or the total) ion yield is measured as a function of excitation wavelength) but can, at least in the case of small molecules, be unraveled by kinetic energy resolving the resulting ions and/or photoelectrons.

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