Photodissociation of state selected BrCl$^+$ cations: branching ratios and angular anisotropies of the Br$^+$ product forming channels

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High resolution velocity map ion imaging methods have been used to explore the photofragmentation dynamics of state-selected BrCl$^+$ ($X^2\Sigma_g^+, v = 0$) cations following excitation in the wavelength range 370–420 nm. The parent ions are formed by $2\rightarrow 1$ resonance enhanced multiphoton ionization (REMPI) via the $[{2\Pi}_1/2, 5s]^{5s}$ Rydberg level. Experimental measurables include the wavelength dependent branching ratios and recoil anisotropies of the various Br$^+({3\Pi}_j)$+Cl(${2\Pi}_j$) product channels. Ground state Br$^+({3\Pi}_j)$ fragments dominate the fragment ion yield throughout the photolysis wavelength range investigated, with spin–orbit excited Cl(${2\Pi}_j/2$) atoms the preferred co-fragment whenever energetically allowed. All fragmentation channels show a predominantly parallel recoil anisotropy, consistent with an initial $A^2\Pi\rightarrow X^2\Pi (\Delta\Omega = 0)$ excitation in the parent cation, but the best-fit description of the fragment angular distributions requires use of higher terms in the Legendre expansion than is traditionally the case for a one-photon dissociation process. The additional angular modulation is rationalised by recognizing that the REMPI preparation laser induces unwanted (but unavoidable) parent ion fragmentation, leaving a spatially aligned distribution of ions for the intended photolysis study. Interpretation of the measured product branching ratios and recoil anisotropies is guided by complementary ab initio calculations of spin–orbit free potential energy curves for many of the lower lying electronic states of BrCl$^+$ and subsequent semi-empirical inclusion of spin–orbit effects. The adiabatic potentials so derived exhibit a plethora of avoided crossings. Preliminary wavepacket propagations following excitation to the $A^2\Pi$ state show rapid flux redistribution to adiabatic potentials that correlate with the lower dissociation asymptotes, but are unable to reproduce the details of the experimentally determined product branching ratios.

1. Introduction

Although less extensive than the database of knowledge relating to neutral molecular fragmentation dynamics, the literature reporting innovative experimental investigations of cation fragmentation, and the results therefrom, are nonetheless impressive. Most such studies have involved excitation of the precursor neutral molecule of interest with photons of sufficiently short wavelength to exceed the threshold energy for one (or more) of the available dissociative photoionization channels. One fruitful route to such insights employs tuneable vacuum ultraviolet (VUV) light – e.g. from a synchrotron – to measure ‘action’ spectra, and thus provide estimates of branching ratios, for forming particular charged (or neutral) products as a function of the parent excitation energy [1]. An obvious limitation of this type of study is the lack of knowledge regarding the nature of the parent cation state from which the fragmentation occurred – an uncertainty which can be reduced by coincidence measurements of, for example, the fragment cation and the photoelectron arising from the same dissociative ionization event [2, 3]. Nonetheless, many factors conspire to limit the resolution of such experiments. Most restrictive, generally, is the fact that the photoexcitation process starts from the ground state neutral molecule. The number and nature of the parent cation states prepared at any given excitation wavelength will be influenced by a variety of considerations – e.g. the relative efficiencies of direct ionization and autoionization processes, and the various Franck–Condon factors associated with each [4]. Such details can be unravelled, at least in principle, by appropriate coincidence measurements, but the inherent richness of the photoionization process usually precludes preparation of a single cation state by one photon excitation from the ground state neutral.
Any internal energy spread in the parent ions formed in this way (which in many cases will itself be excitation wavelength dependent) will imprint itself upon the action spectrum for forming the fragment of interest – thereby greatly complicating spectral interpretation and limiting the achievable resolution.

The advent of resonance enhanced multiphoton ionization (REMPI) methods has provided a route to preparing molecular ions with a much higher degree of quantum state selectivity. Typically, tuneable dye laser radiation is used to populate a Rydberg state of the molecule of interest by, for example, a coherent two-photon excitation process. These excited molecules are then ionised by absorption of one further photon. Many Rydberg states are well described by a model involving a cation core, about which the Rydberg electron orbits – almost as a spectator – in a large, spatially diffuse, orbital [5]. In such cases, photoelectron kinetic energy measurements reveal a (not unexpected) propensity for the characteristics of the resonance enhancing Rydberg state (notably its spin–orbit and vibrational quantum numbers) to be conserved upon ionization. Quantum state selection in the parent cation can thus be obtained by judicious selection of resonance enhancing Rydberg state; this, in turn, can be determined by the appropriate choice of excitation wavelength. Such a strategy has already found quite widespread use as a means of preparing state-selected molecular ions for subsequent spectroscopic and/or photofragmentation studies [6, 7], and for exploring the influence of internal (vibrational) in ion–molecule reactions [8].

Several recent studies have demonstrated the potential of velocity map imaging methods [9–11] for investigating the quantum state resolved photodissociation of molecular cations like Br⁺[12, 13], BrCl⁺[14] and CF₃I⁺[15]. The precursor in such experiments is a state-selected molecular ion – here BrCl⁺ – that is created in a defined electronic, spin–orbit and vibrational state by REMPI. Photodissociation of the resulting molecular ion yields an ionic fragment, which can be imaged directly. BrCl⁺ has an inverted 2Π ground state, derived from the electronic configuration (12σ)²(5π)⁴(6π)⁴(13σ)⁰ which, hereafter, we shall write simply in terms of the respective orbital occupancies, i.e. 243o. Prior to our recent ion imaging study [14], the best available thermochemical and spectroscopic information for this ion derived from analysis of the ‘traditional’ He I photoelectron spectrum by Dyke and coworkers [16]. Our recent measurements enabled refinement of the adiabatic ionization potentials for forming [79Br]⁺ ions in their 2Π₃/2 and 2Π₁/2 spin–orbit states (IE = 88 292 ± 6 cm⁻¹ and 90 362 ± 4 cm⁻¹, respectively), the spin–orbit splitting constant in the 2Π ground state (A = –2070 ± 4 cm⁻¹) and the respective bond dissociation energies D₀([79Br]⁺BrCl⁺(2Π₁/2)) = 25 019 ± 4 cm⁻¹ and D₀([79Br]⁺BrCl⁺(2Π₃/2)) = 22 949 ± 2 cm⁻¹. The present work reports wavelength dependent branching ratios and recoil anisotropies of the various Br⁺ fragment ion forming channels following photolysis of BrCl⁺ ions prepared in the ν = 0 levels of both the 2Π₃/2 and 2Π₁/2 spin–orbit states. It also serves to illustrate some of the potential pitfalls – in the detailed interpretation of recoil anisotropy parameters, for example – when, as here, the REMPI preparation laser causes substantial parent ion photolysis. As in our recent studies of Br⁺ photolysis [13], our interpretation of the experimental measurements is guided by complementary spin–orbit free ab initio calculations of the potential energy curves for the ground and first few excited states of BrCl⁺ associated with the . . .(12σ)(5π)(6π)(13σ) valence space, with subsequent incorporation of spin–orbit effects semi-empirically and then wavepacket propagation following excitation to the A'Π(2340) state. These model calculations provide some rationale for the observed preference for forming spin–orbit excited Cl⁺ co-fragments whenever the relevant product channel(s) are accessible energetically.

2. Experimental

Both the apparatus and the experimental procedures have been described previously [17], so only essential details are repeated here. A pulsed, skinned, supersonic molecular beam containing BrCl molecules (in equilibrium in a mixture comprising typically 25 Torr Br₂ and 150 Torr Cl₂, made up to a total pressure of 1 atm. in Ar), directed towards the centre of the detector (i.e. along the Z axis), was crossed at right angles by the outputs of two pulsed tuneable dye lasers which counter-propagate along the X axis. Laser 1, an Nd:YAG pumped frequency doubled dye laser (Spectra-Physics GCR-250 plus Sirah Cobra Stretch, output bandwidth <0.1 cm⁻¹ in the visible), was used to prepare the state-selected BrCl⁺ ions. For all experiments reported here, laser 1 was tuned to a wavelength λprep = 324.51 nm (defined in air, with a corresponding vacuum wavenumber νprep = 30807.6 cm⁻¹), with its electric vector εprep perpendicular to the molecular beam axis and parallel to the plane of the detector (i.e. εprep // Y). Two photon excitation at this wavelength populates the ν = 0 level of the [2Π₁/2]5s5p Rydberg state of BrCl. The two [2Π₁/2]5s5p → X¹Σ⁺ transitions are the only Rydberg transitions of BrCl yet identified that show resolved vibronic structure [18]. Our previous imaging study [14] showed that this particular vibronic excitation gave the highest parent to fragment ion
yield ratio. The same study also showed that ~84% of the BrCl\(^{+}\) ions formed by absorption of one more photon at this particular wavelength are in their \(^2\Pi_{1/2}\), \(v^+ = 0\) state, with most of the remainder in the corresponding \(^2\Pi_{3/2}\), \(v^+ = 0\) level. The resulting BrCl\(^{+}\) parent ions were then photodissociated with the output of a second tunable laser system (laser 2, Spectra-Physics GCR-170 plus PDL-2 dye laser, output bandwidth ~0.2 cm\(^{-1}\)), which provided linearly polarized radiation (\(\epsilon_{\text{phot}}/\gamma\)) in the wavelength range 370 < \(\lambda_{\text{phot}}\) < 436 nm. Typical pulse energies were 250–400 \(\mu\)J and 150–400 \(\mu\)J for lasers 1 and 2, respectively. Both pulses were focussed (20 cm f.l. lenses) into the interaction region, monitored by a fast photodiode, and timed so that the photolysis laser pulse followed the BrCl\(^{+}\) ion preparation pulse by ~5 ns. The resulting ions were extracted along \(Z\) under velocity map imaging conditions, and arranged to impinge on the front face of a position sensitive detector (a pair of microchannel plates and a phosphor screen) positioned 860 mm downstream from the interaction volume. This detector is read by a CCD camera equipped with a fast intensifier (Photic Science) gated to the time-of-flight (TOF) of \(79\)Br\(^{+}\) ions [12–14]. The image resulting from each 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\(^4\) laser shots. Analysis of the accumulated ion images involved reconstruction of the 3D velocity distribution as described previously [19] using an algorithm based on the filtered back-projection method of Sato et al. [20].

3. Results and discussion

3.1. Product branching ratios

Figure 1 shows 2D slices through the reconstructed 3D velocity distributions derived by back projecting images of the \(79\)Br\(^{+}\) fragment ions resulting from BrCl\(^{+}\) parent ions prepared by 2 + 1 REMPI at \(\tilde{\nu}_{\text{prep}} = 30807.6\) cm\(^{-1}\) and photolysed at \(\tilde{\nu}_{\text{phot}} = 23200\), 24390, 25700 and 26500 cm\(^{-1}\), respectively. These complement the selection of raw images, recorded at neighbouring excitation wavenumbers, shown in an earlier publication [14]. The 26500 cm\(^{-1}\) data were actually shown in the earlier work – as a raw image rather than a 2D slice through the reconstructed 3D velocity distribution – but incorrectly labelled as having been recorded at 26150 cm\(^{-1}\). As in the earlier work, the fact that ion preparation at the chosen \(\tilde{\nu}_{\text{prep}}\) involves two photon resonance enhancement by a state with \(\nu^+ = 0\) means that these fragment ion images necessarily contain contributions from photolysis of both \(79\)Br\(^{-}\)Cl\(^{+}\) and \(79\)Br\(^{+}\)Cl\(^{+}\) parent ions. Also as previously, each image contains a ‘one-colour’ contribution, from BrCl\(^{+}\) photolysis at the REMPI preparation wavelength; these features all appear at larger radius than the ‘two-colour’ signals of current interest. The right-hand panels in figure 1 show the speed distributions of the \(79\)Br\(^{+}\) fragments resulting from photolysis at the specified \(\tilde{\nu}_{\text{phot}}\), i.e. after subtracting the attendant one-colour contribution. This was achieved by intensity scaling the speed distribution of a reference one-colour image (by least squares fitting to that part of the measured distribution at sufficiently large radius to be unambiguously associated with one-colour dissociation only) and subtracting it from the measured one-plus two-colour distribution. The image recorded at \(\tilde{\nu}_{\text{phot}} = 23200\) cm\(^{-1}\) shows just one two-colour ring, arising from BrCl\(^{+}\)(\(^2\Pi_{1/2}\), \(v^+ = 0\) ions dissociating via channel (1). The radius of this ring expands as \(\tilde{\nu}_{\text{phot}}\) is increased, and additional peaks appear. By \(\tilde{\nu}_{\text{phot}} = 26500\) cm\(^{-1}\), peaks attributable to the following fragmentation processes

\[
\begin{align*}
\text{BrCl}^+ (^2\Pi_{1/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^+ (^3P_2) + \text{Cl}(^2P_{3/2}) \\
\tilde{D}_1 &= 22949 \text{ cm}^{-1} \\
\text{BrCl}^+ (^2\Pi_{1/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^+ (^3P_2) + \text{Cl}(^2P_{1/2}) \\
\tilde{D}_2 &= 23831 \text{ cm}^{-1} \\
\text{BrCl}^+ (^2\Pi_{3/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^+ (^3P_2) + \text{Cl}(^2P_{3/2}) \\
\tilde{D}_3 &= 25019 \text{ cm}^{-1} \\
\text{BrCl}^+ (^2\Pi_{3/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^+ (^3P_2) + \text{Cl}(^2P_{1/2}) \\
\tilde{D}_4 &= 25901 \text{ cm}^{-1} \\
\text{BrCl}^+ (^2\Pi_{1/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^{++^+} (^3P_1) + \text{Cl}(^2P_{3/2}) \\
\tilde{D}_5 &= 26085 \text{ cm}^{-1}
\end{align*}
\]

are all clearly identifiable. The listed threshold wavenumbers \(\tilde{D}_i\) are all defined relative to the \(v^+ = 0\) level of the appropriate spin–orbit state of the parent ion. Two further fragmentation channels

\[
\begin{align*}
\text{BrCl}^+ (^2\Pi_{1/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^{++^+} (^3P_0) + \text{Cl}(^2P_{3/2}) \\
\tilde{D}_6 &= 26787 \text{ cm}^{-1} \\
\text{BrCl}^+ (^2\Pi_{1/2}) + \nu_{\text{phot}} &\rightarrow \text{Br}^{++^+} (^3P_1) + \text{Cl}(^2P_{1/2}) \\
\tilde{D}_7 &= 26968 \text{ cm}^{-1}
\end{align*}
\]

are energetically allowed at the highest two-colour photolysis wavenumber studied in this work (\(\tilde{\nu}_{\text{phot}} = 27000\) cm\(^{-1}\)). We see no signal attributable to either of these channels in images recorded at this photon energy. One, or other, or both are active in the
one-colour photolysis at 30807.6 cm\(^{-1}\), however. Weak features attributable to photolysis of parent ions with \(v^+ > 0\) are evident in these images (e.g. the peak centred at a recoil velocity of \(\approx 320\) m s\(^{-1}\)) in the 24390 cm\(^{-1}\) data, which is attributable to BrCl\(^+\)\((2\Pi_{1/2}, v^+ = 1)\) ions dissociating via channel (2). Analysis of all reasonably resolved features in the velocity distributions derived from all measured images analysed yields a value of 504 cm\(^{-1}\) for the \(v^+ = 1 - v^+ = 0\) separation in the \(2\Pi_{1/2}\) state of the parent ion.

A non-linear Levenberg–Marquardt method [21] was used to fit the measured velocity distributions to a function of the form

\[
S(r) = \sqrt{\frac{8\ln 2}{\pi}} \left\{ \sum_{i=1}^{5} \left( \frac{S_i}{w_{1/2}} \exp[-4 \ln 2((r - r_i)/w_{1/2})^2] \right) \right\},
\]

(8)

where \(i\) labels the contributing BrCl\(^+\)\((2\Pi_{1/2}) \rightarrow \text{Br}^+\)\((3P_j) + \text{Cl}(2P_j)\) channels (as defined above), \(S_i\) is the corresponding peak intensity, \(r_i\) is the radius in pixels, and \(w_{1/2}\) is the width (FWHM) of the Gaussian function used to describe the radial distribution of each product pair. \(r_i\) is related to the \(^{79}\text{Br}^+\) fragment recoil velocity by

\[
r_i(\alpha; D_i) = \frac{1}{\alpha} \left[ \frac{2m_{\text{Cl}}(hv - D_i)}{m_{\text{Br}}m_T} \right]^{1/2},
\]

(9)

where \(\alpha\) is a proportionality constant, \(m_{\text{Br}} = 78.918\) amu, \(m_{\text{Cl}} = 35.534\) amu, \(m_T = (m_{\text{Br}} + m_{\text{Cl}})\) and \(D_i\) is the dissociation energy of the particular parent \(\rightarrow\) product fragmentation process.

Figure 2(a) shows plots of the wavelength dependent branching fractions

\[
\Gamma(\tilde{2}\Pi_{1/2}; \text{Cl}^+) = \frac{\sigma_2}{\sigma_1 + \sigma_2}
\]

(10)

\[
\Gamma(\tilde{2}\Pi_{3/2}; \text{Cl}^+) = \frac{\sigma_4}{\sigma_3 + \sigma_4}
\]

(11)
and (7). Interestingly, however, $\Gamma(\tilde{2}\Pi_{1/2};\text{Br}^{+})$ is only $\sim 0.27$ at $\tilde{v} = 30807.6 \text{cm}^{-1}$. Spin–orbit excited Br$^+$ atoms also appear as soon as the relevant threshold ($\tilde{D}_5$) is exceeded, but are only a small fraction of the total Br$^+$ fragment yield ($\Gamma(\tilde{2}\Pi_{1/2};\text{Br}^+) \sim 0.1$) at all $\tilde{v}_{\text{phot}}$ in the range $26085$–$27000 \text{cm}^{-1}$, and at $30807.6 \text{cm}^{-1}$.

Figure 2(b) shows the $\tilde{v}_{\text{phot}}$ dependence of the ratio

$$\Gamma(\text{BrCl}^{+}) = \frac{\sigma_1 + \sigma_2 + \sigma_5}{\sum_{i=1}^{5} \sigma_i}.$$  \hspace{2cm} (13)

Our previous analysis of the photoelectron image recorded at the same $\tilde{v}_{\text{prep}}$ showed that $\sim 84\%$ of the accompanying BrCl$^+$ parent ions were formed in the $\tilde{2}\Pi_{1/2}$ excited spin–orbit state [14]. The similarity between that value, and the mean value of the $\Gamma(\text{BrCl}^{+})$ ratio represented by equation (13), implies similar absorption and fragmentation efficiencies for both spin–orbit states of the ion over the range of $\tilde{v}_{\text{phot}}$ displayed in figure 2(b). Analysis of the one-colour image implies $\Gamma(\text{BrCl}^{+}) \sim 0.8$ at $\tilde{v} = 30807.6 \text{cm}^{-1}$ also.

### 3.2. Product recoil anisotropies

Figure 3 shows 2D slices through reconstructed 3D velocity distributions obtained by back projecting images of the $^{79}\text{Br}^+$ fragment ions that result when BrCl$^+$ parent ions prepared by $2+1$ REMPI at $\tilde{v}_{\text{prep}} = 30807.6 \text{cm}^{-1}$ are exposed to photolysis laser radiation at, respectively, $\tilde{v}_{\text{phot}} = 24770$, 24896 and 25200 cm$^{-1}$. Once again, each image contains a ‘one-colour’ contribution due to $^{79}\text{Br}^+$ fragment ions that arise as a result of BrCl$^+$ photolysis at the REMPI preparation wavelength; the assignment of these contributions, which are responsible for the four outermost rings that appear in all three images, were discussed in an earlier publication [14]. All show a preference for recoil parallel to $\epsilon_{\text{phot}}$. Angular distributions of the various one- and two-colour contributions have been fitted using the following Legendre expansion:

$$I(\theta) \propto \left[1 + \sum_{n=2}^{n} \beta_n P_n(\cos \theta)\right]$$  \hspace{2cm} (14)

where $\theta$ is the angle between $\epsilon_{\text{phot}}$ and the direction of photofragment recoil, and the $\beta_n$ are coefficients weighting the contributions from the various ($n = \text{even}$) Legendre polynomials. This expression reduces to the ‘classical’ expression

$$I(\theta) \propto \left[1 + \beta_2 P_2(\cos \theta)\right]$$  \hspace{2cm} (15)
that is normally used to describe the angular distribution of fragments arising in the case of a one-photon excitation and dissociation from an isotropic sample of parent molecules [22]. $\beta$ in equation (15) is termed the anisotropy parameter, which takes limiting values of +2 and −1 in the case of prompt dissociations following, respectively, a pure parallel (i.e. $\Delta \Omega = 0$) or pure perpendicular (i.e. $\Delta \Omega = \pm 1$) excitation of a diatomic molecule.

Not surprisingly, the more flexible function (equation (14) with $n \leq 6$) provides the better fit to the angular distributions of the various one-colour signals, particularly near the poles. As shown previously [14], the one-colour ring of largest $r$ is mainly attributable to dissociation channel (2). Best-fit parameters for this ring in the image displayed in figure 4 of [14] are $\beta_2 = 1.23 \pm 0.02$, $\beta_4 = -0.08 \pm 0.04$ and $\beta_6 = -0.08 \pm 0.04$ when using equation (14), or $\beta = +1.28 \pm 0.02$ if equation (15) is used. These best-fit values show some variation from ring to ring (e.g. the smallest of the obvious one-colour rings, which is noticeably more isotropic but can involve contributions from two near-degenerate fragmentation channels), and from image to image, but a number of common features are evident. The best-fits to all rings in the one-colour image return positive $\beta_2$ values (typically $\sim +1$) and small negative $\beta_4$ values; $\beta_6$ is generally not defined by the fitting. Additionally, the $\beta_2$ value obtained using equation (14) is always within ±0.1 of the $\beta$ value obtained by fitting the same ring in terms of equation (15). All channels show a preference for fragment recoil along an axis parallel to $\epsilon_{\text{phot}}$ but the negative $\beta_4$ term has the effect of reducing the intensity near the poles relative to that which would be observed in the case that $\beta_4 = 0$.

Equation (14) is also found to be superior in describing the angular anisotropy of the various two-colour signals. This is illustrated by the right-hand panels in figure 3, which show the angular distributions of the two-colour Br$^+$ + Cl$^*$ products (channel (2)) formed at each $\nu_{\text{phot}}$. This particular fragmentation channel is responsible for the innermost ring in images (a) and (b), and the innermost but one ring in image (c). Given the centre line noise in the back-projected images, we limit the data fitting to the range $10 \leq \theta \leq 90^\circ$. Clearly, equation (14) (with $n \leq 6$, solid line) provides

*Figure 3. Left-hand panels: 2D slices through the reconstructed 3D velocity distributions derived by back projecting images of the $^{79}$Br$^+$ fragment ions resulting from BrCl$^+$ parent ions prepared by 2+1 REMPI at $\nu_{\text{prep}} = 30807.6 \text{ cm}^{-1}$ and photolysed at $\nu_{\text{phot}} = 24770$, 24896 and 25200 cm$^{-1}$, respectively. $\epsilon_{\text{prep}}$ and $\epsilon_{\text{phot}}$ were both perpendicular to the molecular beam axis and parallel to the front face of the detector (i.e. parallel to $Y$ and vertical in the plane of the displayed images). Each image contains one-colour contributions at larger radius. The right-hand panels display the angular distribution associated with the two-colour Br$^+$ + Cl$^*$ product channel (2). This fragmentation is responsible for the innermost ring in images (a) and (b), and the smallest but one ring in image (c). Best-fits to data points in the range $10 \leq \theta \leq 90^\circ$ in terms of equations (13) (with $n \leq 6$) and (14) are shown by the solid and dashed lines, respectively. The associated coefficients returned by the fitting are ($\beta_2 = 1.61 \pm 0.08$, $\beta_4 = -0.06 \pm 0.11$, $\beta_6 = 0.19 \pm 0.13$; $\beta = 1.64 \pm 0.08$; (b) $\beta_2 = 1.39 \pm 0.03$, $\beta_4 = -0.67 \pm 0.05$, $\beta_6 = 0.06 \pm 0.05$; $\beta = 1.66 \pm 0.04$; (c) $\beta_2 = 1.51 \pm 0.03$, $\beta_4 = -0.72 \pm 0.01$, $\beta_6 = -0.15 \pm 0.06$; $\beta = 1.74 \pm 0.04$; where the quoted uncertainties are the 1σ (statistical) errors on the fits.*
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a much better fit of the angular distributions in (b) and (c) – which show a maximum at \(\theta \neq 0\) – than the dashed curve obtained using equation (15). Figure 4 shows the \(\nu_{\text{phot}}\) dependence of the \(\beta_2\) parameters for each of Br\(^+\) product forming channels (1)–(5). The two-colour signals associated with channels (1) and (2) are overlapped by the (generally more isotropic) one-colour signal at \(\nu_{\text{phot}} > 25400\ \text{cm}^{-1}\) and with channel (2) data at \(\nu_{\text{phot}} > 26100\ \text{cm}^{-1}\) reflects the respective thresholds at which the signal of interest becomes significantly overlapped by the (generally more isotropic) one-colour signal.

Figure 4. Plot showing the \(\nu_{\text{phot}}\) dependence of the \(\beta_2\) parameters for product channels (1)–(5) determined by fitting the appropriate rings in back-projected \(^{79}\)Br\(^+\) fragment ion images in terms of equation (14). The larger error bars associated with channel (1) data at \(\nu_{\text{phot}} > 25400\ \text{cm}^{-1}\) and with channel (2) data at \(\nu_{\text{phot}} > 26100\ \text{cm}^{-1}\) reflects the respective thresholds at which the signal of interest becomes significantly overlapped by the (generally more isotropic) one-colour signal.

Non-zero values for higher order anisotropy contributions in the present images are not unreasonable. The parent ions are formed by a three photon ionization process, resonance enhanced at the two photon energy by a predissociated state with \(\Omega = 1\). Dixon [23] has derived expressions for the photofragment recoil anisotropies expected in a range of resonance enhanced multiphoton dissociation processes. Broadly similar considerations should apply in the case of parent ions prepared by \(m + 1\) REMPI. The detailed spatial distribution of their molecular frames will be determined by a number of factors. Firstly, the symmetry of the initial \(m\) photon excitation – which, in the present case, is carried by the \(T_2^0(\mu\mu)\) component of the two photon transition tensor and should thus maximise at \(\theta = \pm 45^\circ\). As in the multiphoton dissociation case [23], the spatial anisotropy of the parent ions formed by the subsequent one photon ionization step may be influenced by the lifetime (and thus the extent of rotation) of molecules in the resonance enhancing level, and by the symmetry of the final ionising transition – which we assume to be a Rydberg (5s\(\sigma\) \(\rightarrow\) continuum (mainly \(p\)-wave) excitation. Given the comparatively high light intensities needed to drive the initial \(m\) photon absorption in an \(m + 1\) REMPI transition, it is likely that this ionization step will generally be at least partially saturated; in the limit of high intensities all \(m\) photon excited molecules would be ionised and the spatial anisotropy of the parent ions should mirror that of the excited Rydberg molecules save for any (small) effects due to electron recoil.

The observables in the present experiments are fragment ions, formed by interaction of a further (linearly polarized) photon with the anisotropic spatial distribution of BrCl\(^+\) parent ions; the Br\(^+\) photofragment angular distribution will thus reflect some convolution of the anisotropies associated with the preparation and photolysis steps. Interpreting the detailed form of such distributions is non-trivial, for several reasons. The two-colour images shown in figures 1 and 3 illustrate the efficiency of the competing one-colour dissociation process. This, too, should come as no surprise given the likely magnitude of the \(\pi^\pm \leftarrow \pi\) excitation in the parent ion, the intensity of the REMPI laser pulses employed and, particularly, the fact that in the one-colour experiment the parent ion preparation and photolysis laser photons are (inevitably) optimally overlapped in both space and time. At this stage it is probably worth reiterating our previous observation that the one-colour ion TOF spectra obtained following REMPI via the \(^2\Pi_{1/2}\) \(5\sigma\) \(\rightarrow\) 0 level of BrCl show the highest parent (BrCl\(^+)\) to fragment (Br\(^+\)) ion ratio [14] REMPI via all higher \(\nu\) levels results, almost exclusively, in fragment ion formation. In an effort to maximize reproducibility in the present work, a ‘standard’ operating procedure was adopted whereby the intensity of the REMPI laser at \(\nu_{\text{prep}} = 30807.6\ \text{cm}^{-1}\) was adjusted so as to ensure roughly equal BrCl\(^+\) and Br\(^+\) peak sizes in the ion TOF spectrum. Introduction of pulses from laser 2, overlapped in space and
delayed by $\sim 5$ ns, led to an increase in $\text{Br}^+$ signal and concomitant decrease in $\text{BrCl}^+$ signal, but never caused total extinction of the parent ion signal.

3.3. Accounting for the two-colour recoil anisotropy

The foregoing introduces a rationale for many of the experimental observations. Excitation to the $^2\Pi_{1/2, 3/2}$ $5\sigma$ Rydberg state in the $\text{BrCl}^+$ ion preparation stage is carried by the $T_{1g}^2(\mu\mu)$ component of the two-photon transition tensor which, if not degraded by rotation, would produce a $\sin^2\theta\cos^2\theta$ distribution of Rydberg molecule axes or, in terms of a Legendre expansion, $\beta_2 \sim 0.714$ and $\beta_4 \sim -1.714$, as shown in figure 5(a). The subsequent transition to the ionization continuum involves ejection of the $5\sigma$ electron. This can be promoted with essentially equal probability to any of the three $\pi^+, \pi^-$ or $\pi^-$ outgoing waves. Thus the probability of ionization will be independent of the molecular orientation, and the anisotropy of this step will be carried away with the outgoing electron, in keeping with the observation of a predominantly parallel ($\beta \sim 1$) photoelectron image [14]. However, the earlier study of the REMPI spectrum also indicated that the two photon transition to the Rydberg state exhibits residual rotational structure, with a profile that was simulated with a $3 \text{cm}^{-1}$ rovibronic linewidth and a parent rotational temperature $T_{\text{rot}} = 8 K$. Rotational dephasing will thus degrade the anisotropy of excitation through this intermediate resonant state. Application of theory developed elsewhere [23] reveals that this dephasing will lead to $\beta_2 \sim 0.34$ and $\beta_4 \sim -0.58$ at the peak of the action spectrum (see figure 5(b)). This provides our best estimate of the anisotropy of the nascent distribution of ground state ions following ejection of the electron. But these ground state ions will, on average, live for nanoseconds (corresponding to hundreds of rotational periods) before further photon absorption and dissociation, by which time the rotational super-position of states will have become completely dephased. In consequence, $\beta_2$ and $\beta_4$ will have reduced to, respectively, 1/4 and 9/64 of their nascent values, leading to $\beta_2 \sim 0.086$ and $\beta_4 \sim -0.081$, i.e. the nascent anisotropy will be further degraded by rotation, and have evolved to an almost isotropic distribution in the time interval between creation and photolysis of the parent ion (see figure 5(c)). Even this is probably an overestimate of the true spatial anisotropy, since we have not attempted to include ($J$-dependent) nuclear hyperfine depolarization effects in this analysis.

Unavoidable one-colour photolysis (at $\nu_{\text{prep}}$) occurred in competition with the desired two-colour photolysis at $\nu_{\text{phot}}$ in all of the present experiments. The $\beta_2$ values measured for all of the $\text{Br}^+$ product channels indicate that parallel transitions dominate the $\text{BrCl}^+$ parent photolysis step, but the observed recoil anisotropy is different in the one- and two-colour processes. The unavoidable one-colour photolysis is seen to cause a substantial depletion of the total parent ion population. The observed value of $\beta_2 = 1.23$ for the one-colour photolysis of the $^2\Pi_{1/2}$ parent ions [14] corresponds to $\sim 74\%$ parallel and $\sim 26\%$ perpendicular excitation overall, i.e. one colour photolysis will preferentially deplete the parent ion population near the poles of its spatial distribution. As discussed in more detail below, the $^2\Pi(2340) \leftrightarrow ^2\Pi(2430)$ parallel transition is the dominant contributor to the parent ion absorption at the longer wavelengths investigated in the present two-colour studies. The outputs of lasers 1 and 2 are polarised parallel to one another, but laser 2 is time delayed relative to laser 1. Laser 2 will thus also seek to dissociate $\text{BrCl}^+$ parent ions whose bond axes (and thus transition dipoles) are aligned parallel to $\varepsilon_{\text{phot}}$, but – in a manner reminiscent of other ‘hole burning’ experiments – this part of the spatial ensemble will already have been preferentially depleted by interaction with laser 1 photons. Thus we might anticipate that the two-colour images should show greater modulation at the poles. Experiment lends support to this conjecture.
Table 1. The effect of the \((1 - \lambda \cos^2 \theta)\) one-colour hole-burning function on the calculated two-colour anisotropy.

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(\beta_2)</th>
<th>(\beta_4)</th>
<th>(\beta_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.019</td>
<td>-0.034</td>
<td>-0.071</td>
</tr>
<tr>
<td>0.2</td>
<td>1.905</td>
<td>-0.189</td>
<td>-0.071</td>
</tr>
<tr>
<td>0.4</td>
<td>1.755</td>
<td>-0.392</td>
<td>-0.070</td>
</tr>
<tr>
<td>0.6</td>
<td>1.548</td>
<td>-0.673</td>
<td>-0.068</td>
</tr>
<tr>
<td>0.8</td>
<td>1.245</td>
<td>-1.085</td>
<td>-0.066</td>
</tr>
<tr>
<td>1.0</td>
<td>0.758</td>
<td>-1.746</td>
<td>-0.063</td>
</tr>
</tbody>
</table>

We therefore model the two-colour photolysis step by multiplying the (rotationally dephased, but still anisotropic) spatial distribution of parent ions discussed above by, first, a \((1 - \lambda \cos^2 \theta)\) function (where \(\lambda\) is a parameter between 0 and 1 – see figures 5(d) and 5(e)) to accommodate the effects of hole-burning by laser 1, and then by a \(\cos^2 \theta\) excitation function to describe the subsequent photolysis step (see figures 5(f), 5(g) and 5(h)). The fragment recoil anisotropy values so derived, for various \(\lambda\), are shown in table 1. The values for \(\lambda = 0.4\) and \(\lambda = 0.6\) are close to those derived from the two-colour images of figures 3(b) and 3(c), respectively. Note particularly, that increasing \(\lambda\) leads to a decrease in \(\beta_2\) but an increase in the magnitude of the negative \(\beta_4\) values, as observed. The small (negative) values of \(\beta_4\) and \(\beta_6\) for \(\lambda = 0\) accord with the values for these parameters found when analysing the one-colour image; that \(\beta_2 \neq 2\) for any of the channels contributing to that image presumably indicates that perpendicular transitions gain in importance as the excitation wavenumber is increased [14].

However, we also note the apparently large \(\tilde{\nu}_{\text{phot}}\) dependence of the best-fit \(\beta_6\) values for the two-colour images. Though not investigated systematically, the values of the \(\beta_4\) parameters (particularly \(\beta_4\) and \(\beta_6\)) obtained by analysing two-colour images recorded on different days at the same (or similar) photolysis wavelengths are found to vary by amounts that significantly exceed the statistical uncertainties associated with fitting any one image. Given the discussion above, we suspect this to be primarily due to inevitable day-to-day variations in the spatial distribution of the BrCl\(^{+}\) ions prepared by laser 1 and in their sampling by laser 2, such that the extent of the hole-burning will be very sensitive to the respective beam profiles, their spatial overlap and time delay.

This discussion has been based on a spatial description of the hole-burning process, rather than that of the \(J, M_J\) distribution. In the collision-free environment of a skimmed supersonic molecular beam, hole-burning will deplete the populations of specific \(J, M_J\) states, and this depletion will not be re-filled in the interval between creation and photolysis.

In concluding this discussion of the experimental findings relating to BrCl\(^{+}\) photolysis it is worth contrasting the present results with our earlier studies of the photodissociation of state selected Br\(^{2+}\) ions [13]. The Br\(^{2+}\) study provided what, in many senses, was an optimal illustration of the present technique: The parent ions in that case were again prepared by 2 + 1 REMPI, but via a state with \(\Omega = 0\) and an excitation that was dominated by the (spherically symmetric) \(T_0^0(\mu \mu)\) component of the two-photon transition tensor. Additionally, the ion preparation wavelength caused little unwanted photolysis of the resulting Br\(^{2+}\) ions. Equation (14) was found to provide a perfectly adequate description of the angular distributions of the Br\(^{+}\) fragment ions formed in the subsequent two-colour photolysis studies. The present BrCl\(^{+}\) studies benefit from none of these advantages and, given the complications discussed above, it would be unwise to attempt to over-interpret the Br\(^{+}\) fragment ion recoil anisotropy data. Nonetheless, a number of firm conclusions emerge from this experimental programme: Contributions from each of channels (1)–(5) are evident as soon as their respective dissociation thresholds are exceeded, though such is not the case for either channel (6) or (7). All of the active fragmentation channels are accessed by (predominantly) parallel excitations of the parent BrCl\(^{+}\) ion. The plot of \(\beta_2\) versus \(\tilde{\nu}_{\text{phot}}\) for channel (1) appears to exhibit a local minimum at the threshold for channel (2). The \(\beta_2\) values for channel (3) also minimize at the energy corresponding to the onset of channel (4). Apart from these, we have found no evidence of resonance structure in the plots of \(\beta_2\) versus \(\tilde{\nu}_{\text{phot}}\) such as was found in the case of Br\(^{2+}\).

### 3.4. Potential energy curves for the valence states of BrCl\(^{+}\)

As in the earlier Br\(^{2+}\) study [13], a series of high-level \textit{ab initio} calculations were performed using the MOLPRO 2002 [24] electronic structure package running on a Beowulf cluster of networked PCs in an effort to gain further insight into the experimental measurements. These calculations were performed in the abelian C\(_{2v}\) sub-group of the full C\(_{3v}\) point group, in which the symmetry species \(\Sigma^+, \Sigma^-, \Pi\) and \(\Delta\) are represented by \(A_1, A_2, B_1 + B_2\) and \(A_1 + A_2\), respectively. A spin restricted Hartree–Fock calculation was first performed on the \(1\Sigma^+\) ground state of BrCl. The Hartree–Fock orbitals so derived were then used as the starting point for a complete active space self-consistent field (CASSCF) [25, 26] calculation on
the $^{2}\Pi$ ground state of BrCl$^+$. A further CASSCF calculation, was then performed for internuclear separations between 1.7 and 5 Å, using an active space comprising the \([\text{core}]10\sigma_{1s}^2\sigma_{2s}^2\sigma_{2p}^6\pi_{1s}^*13\pi^*\) valence space and occupied by 13 electrons. The core orbitals, although constrained to be doubly occupied in all configurations, were fully optimised. An internally contracted multi-reference configuration interaction (MRCI) \([27, 28]\) calculation was then performed to include the effects of dynamical electron correlation, thereby allowing determination of accurate adiabatic potential energy curves. The Davidson correction \([29]\) was applied to the MRCI energies in order to account for the contribution that quadrupole excitations make to the correlation energy, and scalar relativistic corrections to the two-electron integrals were included using the Douglas–Kroll approximation \([30]\). These calculations were all performed using the contracted correlation-consistent polarised valence quadruple zeta (cc-pVQZ) basis set developed by Dunning and co-workers \([31–33]\).

As mentioned above, the requirement within MOLPRO that \(C_2\nu\) symmetry be used to represent the non-Abelian \(C_{2\nu\nu}\) group means that some states of different symmetry will be represented by the same irreducible representation – e.g. \(\Delta\) and \(\Sigma^+\) share the same \(A_1\) symmetry in \(C_{2\nu}\). Such care was exercised when labelling states in \(C_{\infty\nu}\). \(\Pi(\Delta)\) states were assigned on the basis of degenerate CASSCF energies in both \(B_1\) and \(B_2\) \((A_1\) and \(A_2\)) symmetries. In the CI calculations, however, the two components of the \(\Delta\) states were generally found not to be exactly degenerate, due to state-averaging over non-symmetrical density matrices. In such cases, calculation of additional identifying properties – e.g. the dipole moments – and comparison with the \(C_{2\nu}\) results allowed confirmation of the assignment of a state.

Figure 6(a) shows potential energy curves for the ground and first nine doublet excited states (in the vertical Franck–Condon region). Potential energy curves for the corresponding quartet spin states are shown in figure 6(b). The calculated equilibrium bond length for the ground electronic state, \(R_e = 2.050\) Å, and its \((\text{spin–orbit averaged})\) well depth \(D_e = 24127\) cm$^{-1}$. This \(R_e\) value is in excellent accord with that derived by Dyke and co-workers on the basis of Franck–Condon modelling of the first band of the photoelectron spectrum of BrCl \([16]\). As before \([13]\), to compare the calculated well depth with the experimentally determined ground state bond dissociation energy, it is necessary to remove the effects of the spin–orbit averaging. The minimum of the \(X^2\Pi_{3/2}\) state will lie below that of the spin–orbit averaged potential by an energy equal to half of the spin–orbit splitting \((A = -2070\) cm$^{-1}$ \([14]\). The asymptotic energy also needs to be corrected, since the calculated asymptote lies at the average energy of the Br$^+ (^3P_J) +$ Cl$(^3P_J)$ atomic limit. This correction factor \((C)\) is given by

$$
C = \frac{5E(^3P_J) + 3E(^3\Pi_J) + E(^3\Pi_0)}{9} + \frac{4E(^3\Pi_{5/2}) + 2E(^3\Pi_{1/2})}{6} = 1755\text{ cm}^{-1}, \quad (16)
$$

where the term energies \(E\) are taken from the NIST Atomic Spectra Database \([34]\) and the premultipliers are the appropriate \((2J + 1)\) electronic degeneracies. The calculated ground state dissociation energy \(D_g[\text{BrCl}^+ (^2\Pi_{3/2})]\) is thus

$$
D_g[\text{BrCl}^+ (^2\Pi_{3/2})] = D_g[\text{BrCl}^+ (^2\Pi)_{s-o\text{ averaged}}] + \frac{A}{2} - C = 23936\text{ cm}^{-1}. \quad (17)
$$

Given the sole reported value for the wavenumber of the ground state fundamental vibration, \(\omega_e \approx 486\) cm$^{-1}$ \([14]\) we arrive at a calculated value for \(D_g[\text{BrCl}^+ (^2\Pi_{3/2})] \approx 23153\) cm$^{-1}$, \(\sim 7.5\%\) lower than the experimental value: 25019 ± 4 cm$^{-1}$ \([14]\).

Diagonal spin–orbit matrix elements were also calculated for the \(X^2\Pi\) ground state around its equilibrium geometry, using MRCI wavefunctions. The full Breit–Pauli spin–orbit Hamiltonian was used to calculate matrix elements between configuration state functions in which no external (virtual) orbitals were occupied. For external configurations, a mean field analogue was employed. The generally contracted basis set employed in the earlier spin–orbit averaged MOLPRO calculations could not be used to evaluate the spin–orbit integrals; the segmented cc-pVTZ basis set obtained from the EMSL basis set library \([35]\) was used instead. The calculated spin–orbit splitting at 2.05 Å is \(-1860\) cm$^{-1}$ (cf. the experimentally derived value \(A = -2070 \pm 4\) cm$^{-1}$).

We have also calculated transition dipole moments from the ground state to various of the excited states, as a function of internuclear separation \(R\), at the same level of theory. Absorption to the \(A^2\Pi\) state is dominant, with a calculated transition dipole moment of \(\sim 1.96\) D at the ground state equilibrium geometry. By way of comparison, the corresponding transition dipole moments to the neighbouring \(^3\Delta, ^2\Sigma^-\) and \(^2\Sigma^+\) excited states at the same value of \(R\) are calculated to be, respectively, 0.03, 0.04 and 0.04 D – i.e. all less that 2.5% that of the \(A^2\Pi – X^2\Pi\) transition.
3.5. *Inclusion of spin–orbit effects using a semi-empirical approach*

An understanding of the observed branching between open dissociation channels following excitation via the $\Lambda^2\Pi(2340)$ state requires knowledge of the asymptotic behaviour of many of the molecular states at long range. The combinations of $\text{Br}^+(\ldots4p^5) + \text{Cl}^+$ ($\ldots3p^6$) and of $\text{Br}^+(\ldots4p^4) + \text{Cl}^+(\ldots3p^5)$ each lead to a total of 90 spin–orbit substates of $\text{BrCl}^+$. Inclusion of all of these for the full range of internuclear separation was not possible with the available *ab initio* software. However, the spin–orbit matrix elements will be dominated by one-centre integrals that can be taken semi-empirically from the known atomic term values. A model Hamiltonian was therefore constructed, using the same approximations as in our earlier paper on the dissociation of $\text{Br}_2^+$. The *ab initio* spin–orbit averaged potential energy curves of section 3.4 were first simulated using empirical matrix elements.

---

**Figure 6.** Spin–orbit averaged MRCI adiabatic potential energy curves for (a) the ground $\text{X}^2\Pi$ state and first nine excited doublet states of $\text{BrCl}^+$ and (b) the first 10 quartet states arising from a one-electron excitation within the defined valence space. The spin–orbit averaged energy of the $\text{X}^2\Pi$ ground state is set at 0 cm$^{-1}$ in these plots.
as functions of $R$, in a basis of coupled products of atomic wavefunctions with spin–orbit averaged term values, using the ZDO (zero differential overlap) approximation. The calculations were then repeated with the inclusion of the atomic splittings. Note that in this and the following section, the energies are expressed relative to that for the lowest dissociation limit $[\text{Br}^+(2\Pi) + \text{Cl}(^3\Sigma)]$.

The substates for Br(4p) 2P can be represented using a Russell–Saunders coupling scheme with a spin–orbit splitting of $-3685\text{ cm}^{-1}$ between $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ ($\xi = -2457\text{ cm}^{-1}$). However, for Br(3p) the term values of $E(^3\Pi_2) = 0\text{ cm}^{-1}$, $E(^3\Pi_1) = 3136.4\text{ cm}^{-1}$ and $E(^3\Pi_0) = 3837.5\text{ cm}^{-1}$ depart significantly from the Landé interval rule, requiring an intermediate coupling basis [36] for $^3\Pi$, $^1\Delta$ and $^1\Sigma$ with $\xi = -2806\text{ cm}^{-1}$ and $F_2 = 1581\text{ cm}^{-1}$. The corresponding values for Cl(3p) 2P are $-881\text{ cm}^{-1}$ ($\xi = -587\text{ cm}^{-1}$), and for Cl(3p) 2P, $^1\Delta$ and $^1\Sigma$: $\xi = -675\text{ cm}^{-1}$ and $F_2 = 1878\text{ cm}^{-1}$. The molecular basis can be partitioned into 42 functions for $\Omega = \pm 1/2$, 30 functions for $\Omega = \pm 3/2$, 14 functions for $\Omega = \pm 5/2$ and 4 functions for $\Omega = \pm 7/2$, each consisting of from 2 to 20 orbital products. The molecular Hamiltonian matrix made use of a ZDO approximation in a hybrid LCAO model. The sums of the Br, Cl, $^1\Sigma^+$ and $^1\Pi^+$ atomic term values contributed to the diagonal elements in the coupled basis, whereas all molecular terms were expressed in terms of eight functions of $R$ in the primitive basis of coupled orbital products. Coulomb integrals $a(R)$ for each $\sigma r$ or $\pi r$ electron were represented by Rydberg functions [37] with three parameters. Valence bond exchange integrals $A(R)$ for each sigma or pi electron pair, and molecular two-centre $\sigma r$, $\pi r$ and $\sigma r$, $\pi r$ exchange integrals, were represented by simple exponential functions (two parameters each). Finally, resonance integrals $\beta(R)$ for single uncoupled $\sigma r$ or $\pi r$ electrons were also represented by simple exponential functions (two parameters each).

The 19 parameters in this model were optimized by least squares fitting to the ab initio spin–orbit averaged potential energy curves for the lowest two $^2\Sigma^+$ states, two $^4\Sigma^+$ states, two $^2\Xi^-$ states, three $^4\Xi^-$ states, five $^2\Pi$ states, one $^4\Pi$ state, two $^2\Delta$ states and one $^4\Delta$ state. Any portion of a potential curve lying higher than 0.07 hartrees above the lowest dissociation asymptote was excluded from the fit, which gave a standard deviation of 0.003 hartrees (700 cm$^{-1}$). These semi-empirical potential curves repeat the pattern of figure 6 for the relative energies and crossing points of states of differing $\Delta, \Sigma$ symmetry.

As the two panels in figure 7 show, inclusion of atomic spin–orbit coupling results in a large number of avoided crossings in the adiabatic potential curves. These have been investigated further by re-calculating the spin–orbit coupling matrix in a basis of eigenfunctions of the spin–orbit averaged Hamiltonian. The diagonal splitting so derived for the $^2\Pi^*$ ground state of BrCl$^+$ is $-1720\text{ cm}^{-1}$, which can be compared with a first order splitting of $-1860\text{ cm}^{-1}$ calculated ab initio using the full Breit–Pauli Hamiltonian, thus giving an indication of the validity of the method. The semi-empirical calculation also yields an estimate of the spin–orbit splitting of the $^4\Pi$ state ($-1480\text{ cm}^{-1}$) at its minimum energy configuration ($R = 2.40\text{ Å}$).

The spin–orbit averaged $^4\Pi(2340)$ state is asymptotic at long range to the products Br(2P) + Cl($^3\Pi$), which lie $>9000\text{ cm}^{-1}$ above the lowest energy asymptote Br$^+(3\Pi) + \text{Cl}(2\Pi)$ – see figure 7. The coupling matrix elements and crossing points that directly mediate dissociation to the first six limits (denoted $(a)–(f)$ and defined in the caption to figure 7) are listed in table 2. Note that the lack of a centre of symmetry in BrCl$^+$ tends to double the number of avoided crossings compared with the centro-symmetric Br$^+_2$. From this table it is clear that the lower dissociation limits are open channels from $^4\Pi(2340)$, with branching ratios that will depend on the relative probabilities of surface hopping at these multiple avoided crossings. The branching ratios have been explored by running wavepackets representing the $^4\Pi(2340) \leftrightarrow ^2\Pi(2430)$ $v = 0$ excitation. The use of the full set of potential surfaces for each value of $\Omega$ would have been excessive but, given the large number of open channels, it was important that their relative energies should be correct. This was achieved by using the lowest 11 spin–orbit free potential functions for $\Omega = 3/2$, and 16 for $\Omega = 1/2$, as diabatic states, and contracting the spin–orbit coupling matrix to second-order using a Van Vleck transformation over the full basis [38].

3.6. Wavepacket propagations on the spin–orbit resolved potentials

Flux evaluations show that, following excitation to the $^4\Pi(2340)$ state, the outgoing wavepacket becomes distributed over most of the lower adiabatic potentials at the first passage through the various avoided crossings. Propagation was continued for 2000 time steps to $\tau = 4.24\text{ ps}$. After this time interval there remained an oscillating wave associated, in part, with the fully bound vibrational states below the lowest dissociation limit, but also in part with quasi-bound states trapped within higher adiabatic minima. The absorption spectra calculated from the auto-correlation functions (figure 8) reflect this, and only become truly continuous above the uppermost accessible limit – i.e. limit (f) for $\Omega = 1/2$, and limit (e) for $\Omega = 3/2$. 

...
This structure is also reflected in the action spectra for each of the lower energy dissociation products. It has many parallels with that reported previously for \( \text{Br}^+ \text{Br} \), although without the obvious regularity evident in the earlier study. Such structure has not been detected in the current experiments, but these did not carry out a systematic high resolution variation of the two-colour excitation frequency. It is worth noting in this respect that the structure for \( \text{Br}^+ \text{Br} \) only became apparent in the frequency dependence of the recoil anisotropy because of quantum interference between structured parallel transitions and a continuous perpendicular background.

One consequence of this structure is that the branching ratios for the various channels show rapid variations with the excitation energy, with the lowest three channels being dominant once open. For clarity, figure 9 shows the branching fractions for \( \Omega = 3/2 \) and 1/2 after smoothing with a box width of 160 cm\(^{-1}\). The branching fractions for most of the channels peak upon opening and, for \( \Omega = 3/2 \), dissociation to limit (b) \([\text{Br}^+ (3P_2) + \text{Cl}(2P_{3/2})]\) becomes dominant at threshold.
Table 2. Spin–orbit coupling matrix elements at the first crossing points between the diabatic $\text{A}_2\Pi(2340)$ state and other states with the same value of $\Omega$.

<table>
<thead>
<tr>
<th>$\Omega$</th>
<th>Coupled state</th>
<th>$R/\text{Å}$</th>
<th>$(V_i+H_{ii})/\text{cm}^{-1}$</th>
<th>$H_{ij}/\text{cm}^{-1}$</th>
<th>Asymptotic products</th>
<th>Limit/\text{cm}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>$^4\Sigma^+$</td>
<td>2.60</td>
<td>-4190</td>
<td>187</td>
<td>(a) $\text{Br}^+(3\text{P}_2)+\text{Cl}(2\text{P}_3/2)$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$^2\Delta$</td>
<td>2.64</td>
<td>-3790</td>
<td>89</td>
<td>(b) $\text{Br}^+(3\text{P}<em>2)+\text{Cl}^+(3\text{P}</em>{1/2})$</td>
<td>881</td>
</tr>
<tr>
<td></td>
<td>$^4\Delta$</td>
<td>2.66</td>
<td>-3570</td>
<td>-154</td>
<td>(b) $\text{Br}^+(3\text{P}<em>2)+\text{Cl}^+(3\text{P}</em>{1/2})$</td>
<td>881</td>
</tr>
<tr>
<td></td>
<td>$^4\Sigma^-$</td>
<td>3.05</td>
<td>1230</td>
<td>190</td>
<td>(c) $\text{Br}^+(3\text{P}_1)+\text{Cl}(2\text{P}_3/2)$</td>
<td>3139</td>
</tr>
<tr>
<td></td>
<td>$^2\Pi$</td>
<td>3.06</td>
<td>1320</td>
<td>-174</td>
<td>(c) $\text{Br}^+(3\text{P}_1)+\text{Cl}(2\text{P}_3/2)$</td>
<td>3139</td>
</tr>
<tr>
<td></td>
<td>$^2\Pi$</td>
<td>3.13</td>
<td>2310</td>
<td>813</td>
<td>(d) $\text{Br}^+(3\text{P}_0)+\text{Cl}(2\text{P}_3/2)$</td>
<td>3840</td>
</tr>
<tr>
<td>1/2</td>
<td>$^4\Sigma^+$</td>
<td>2.51</td>
<td>-3440</td>
<td>82</td>
<td>(a) $\text{Br}^+(3\text{P}_2)+\text{Cl}(2\text{P}_3/2)$</td>
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<td>$^2\Sigma^+$</td>
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<td>$^4\Delta$</td>
<td>2.65</td>
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<td>268</td>
<td>(b) $\text{Br}^+(3\text{P}<em>2)+\text{Cl}^+(3\text{P}</em>{1/2})$</td>
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<td>$^2\Sigma^-$</td>
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<td>(b) $\text{Br}^+(3\text{P}<em>2)+\text{Cl}^+(3\text{P}</em>{1/2})$</td>
<td>881</td>
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<tr>
<td></td>
<td>$^4\Sigma^-$</td>
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<td>1230</td>
<td>-66</td>
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<td>$^2\Sigma^-$</td>
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<td>342</td>
<td>(c) $\text{Br}^+(3\text{P}_1)+\text{Cl}(2\text{P}_3/2)$</td>
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</tr>
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</table>

Figure 8. Absorption spectra, computed from wavepacket auto-correlation functions, for excitation from the $v'=0$ level of the $X^2\Pi$ state of $\text{BrCl}^+$ to the $A^2\Pi(2340)$ state, with $\Omega = 3/2$ (top) and $\Omega = 1/2$ (below).

Figure 9. Computed branching fractions to dissociation limits (a)–(f) [(a)–(e)] only for $\Omega = 3/2$ as defined in figure 7 following excitation via the $A^2\Pi \leftrightarrow X^2\Pi$ transition, starting from $\Omega = 3/2$ (top) and $\Omega = 1/2$ (below), plotted as a function of excess energy over the lowest limit. The various curves have been smoothed with a box width of 160 cm$^{-1}$. 

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as is observed experimentally. Even so, the experimentally observed yields are not reproduced particularly well by the model calculations, which predict excessive branching to products (c) and underestimate the extent of dissociation to limit (b). At the highest energies, the calculated pattern tends towards that for a statistical distribution over the open channels, whereas limits (d), (e) and (f) have not been detected experimentally. This, and the non-observation of the predicted rapid variation of branching ratio with increasing energy, may indicate that the calculated predissociation rates are too slow. Note in this regard that any dynamic coupling with an electronic (rather than purely spin–orbit) origin, such as is evident between the two $^2\Sigma^-$ states near 2.5 Å in the ab initio potentials shown in figure 6(a) for example, has been neglected in the present modelling.

Table 2 and figure 7 indicate, that for both $\Omega = 1/2$ and $3/2$, the strongest avoided crossings are those at around $R = 3.1$ Å between the $A^2\Pi$ state and a repulsive $^2\Sigma^-$ state. Their coupling matrix elements are sufficiently large that, were these the only spin–orbit induced avoided crossings, excitation via $A^2\Pi$ would result in a single vibrational progression followed by adiabatic dissociation to products (c). Predissociative branching to the lower limits (a) and (b) is brought about through the weaker avoided crossings at shorter range, the rates of which are highly sensitive to the magnitudes of the coupling matrix elements. The early peaks in the calculated flux profiles for $R = 2.8$, 3.0 and 3.4 Å, following excitation to $A^2\Pi$, show a progressive branching to curves asymptotic first to limits (a) and (b), and then later to (d). Table 2 provides a graphic illustration of the complexity of this problem, with a close proximity of many couplings exhibiting a wide range of coupling matrix elements. The model calculations indicate that many of these matrix elements are themselves strongly varying function of $R$. Thus the failure to reproduce the experimental branching ratios derives most probably from errors in the spin–orbit coupling model, rather than in the under-lying spin–orbit free ab initio potentials. These errors could be remedied by the use of a fully ab initio spin–orbit calculation when an appropriate code becomes available.

4. Conclusions

This paper describes complementary experimental and theoretical studies of the photodissociation of state selected BrCl$^+$ ($X^2\Pi_{1/2}$, $v = 0$) cations. Mesures of particular interest include the wavelength dependent branching ratios and recoil anisotropies of the various Br$^+(3\Pi_J) +$ Cl($2\Pi_J$) product channels. Ground state Br$^+(3\Pi_2)$ fragments are found to dominate the fragment ion yield throughout the photolysis wavelength range (370 $\leq$ $\lambda_{phot} \leq$ 436 nm) investigated, with spin–orbit excited Cl($2\Pi_{1/2}$) atoms the preferred co-fragment whenever energetically allowed. All fragmentation channels exhibit recoil anisotropies that are predominantly parallel, consistent with initial $\Delta\Omega=0$ excitation to the $A^2\Pi_{1/2}$ state of the parent cation, but the detailed angular distributions show contributions from higher ($n > 2$) terms in the Legendre expansion than is traditionally the case for a one-photon dissociation process. The additional angular modulation can be explained once it is recognised that the REMPI preparation laser induces unwanted (but unavoidable) parent ion fragmentation, leaving a spatially aligned distribution of ions for the intended photolysis study. Such alignment effects are likely to be an issue in any experiment of this kind, if the target parent cations happen to absorb strongly at the wavelength used in their REMPI preparation step. Interpretation of the measured product branching ratios and recoil anisotropies has been aided by complementary ab initio calculations of spin–orbit free potential energy curves for many of the lower lying electronic states of BrCl$^+$, and subsequent inclusion of spin–orbit effects semi-empirically. The adiabatic potentials so derived exhibit a multitude of avoided crossings. Preliminary wavepacket propagations following excitation to each spin–orbit component of the $A^2\Pi_{1/2}$ state indicate rapid flux redistribution to adiabatic potentials that correlate with the lower dissociation asymptotes, but are not able to reproduce the details of the experimentally determined product branching ratios.

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References

[2] T. Baer, J. Booze, K.-M. Weitzel. In Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and


[35] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 6/19/03, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, PO Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.


