Inner-Shell Photoionization of Molecules using a Two-Dimensional Imaging Technique

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Abstract. Angle resolved two-dimensional photoelectron spectroscopy has been used to study resonances corresponding to inner-shell excitation in hydrogen halide molecules. In HBr $3d \rightarrow \sigma^*$ excitations have been studied, whilst in HCl and DCl $2p \rightarrow \sigma^*$ resonances have been explored. In HBr the photon energy positions of the two $3d_{5/2,3/2} \rightarrow \sigma^*$ resonances have been measured directly. Atomic Br is produced following dissociation of the $\sigma^*$ state and the asymmetric photon energy profile of Br atomic Auger lines is discussed. Angular distribution parameters of Br Auger lines have also been measured. In HCl and DCl the comprehensive nature of the analogous 2DPES reveal unexpected spectral features, the origin of which is considered.

1. Introduction

Synchrotron radiation has been used extensively to investigate the behaviour of atomic and molecular systems upon the excitation of a core electron to a vacant orbital. In molecules, the excited state can be either bound or dissociative, and in the latter case the molecule may fragment on the same femtosecond time scale as Auger decay. The two-step process of fast dissociation followed by autoionization in the fragment limit is known as atomic decay and gives rise to sharp Auger decay lines, at energies corresponding to transitions within the fragment. These were first observed for inner shell excitation in HBr [1]. It is however important to note that these sharp peaks may also contain contributions from resonant Auger decay before the fragmentation is complete, in cases where the energy separation between the two potential curves becomes constant before the dissociation limit is reached. Alternatively, broader spectral features are associated with electron emission before or during fragmentation, when there is not a constant separation between the potential curves involved. This is typically referred to as molecular decay. These processes are illustrated in figure 1. Following the first observation of atomic decay lines, many small molecules were studied to explore the competition between these two extremes of Auger decay [2]. In this article different aspects of resonant decay processes in HCl, DCl and HBr are re-examined with the benefit of the comprehensive technique of

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angle-resolved two-dimensional photoelectron spectroscopy. This technique can be used to look at the competition between atomic and molecular decay, the degree to which different final states are populated and the angular behaviour of various spectral features.

**Figure** 1. (Colour online) Schematic representation of relevant inner-shell excitation processes and photoelectron spectrum indicating the appearance of so called molecular and atomic Auger decay features.

1.1 Interpretation of two-dimensional photoelectron spectra (2DPES)

Extensive 2DPES, in which photoelectron yield is measured as a function of both electron and photon energy, have been collected in HCl and HBr and their deuterated isotopes. The electronic configuration of HBr in its ground state is $1s^22s^22p^63s^23p^63d^104s^24p^2\pi^4$ and the next available orbital is $4p^\sigma^*$. It is useful to consider three different regions of the spectrum associated with 3d excitation in HBr. The three regions correspond to (i) 3d excitation to the unoccupied $4p^\sigma^*$ orbital, (ii) 3d excitation to Rydberg orbitals which lie at higher photon energies and (iii) 3d ionization. There are close parallels between the HBr and HCl systems, the HCl ground state configuration is similar to that of HBr with $n=3$ orbitals forming the valence orbitals, as opposed to $n=4$ for HBr, and 2p excitation being analogous to 3d excitation in HBr.

The three 3d excitation regions are clearly shown in figure 2, which is a 2DPES in the vicinity of the 3d ionization thresholds of HBr. In the 2DPES the photoelectron yield (denoted by different colours as illustrated to the right of the 2DPES) is shown as a function of electron kinetic and photon energy. 2DPES are collected by obtaining a number of conventional photoelectron spectra at photon energies that differ by small increments [3]. The main panel of the 2DPES shows the Auger and photoelectrons emitted in the photon energy regions corresponding to the three distinct processes: the resonant (i) $3d_{5/2,3/2} \rightarrow \sigma^*$, dissociative and (ii) $3d_{5/2,3/2} \rightarrow n\lambda\lambda$, Rydberg excitations and (iii) ionization. These regions are marked in the panel to the right of the 2DPES where the total electron yield has been projected onto the photon energy axis.

There are four distinct types of feature in the 2DPES.

(i) Diagonal lines of constant binding energy correspond to direct ionization features. The kinetic energy of the emitted electron increases in step with the incident photon energy. The kinetic energy width of the feature will depend on the experimental resolution and the nature of the final ion state. If the final ion state is bound the band will exhibit vibrational structure in each photoelectron spectrum, the exact appearance depending on the overlap of the wave-functions of the states involved. Direct population of a dissociative final ion state also gives rise to a diagonal band of constant binding energy. In this case, the line profile is determined by the projection of the wave-function of the initial state onto the potential energy curve of the ion state; this projection does not vary quickly with photon energy. Direct population of both dissociative and bound ion states therefore shows up as diagonal
bands, of constant binding energy, with intensities that vary slowly with photon energy. The two diagonal lines in the lower right hand corner of the 2DPES correspond to ionization caused by second harmonic photons and hence have slopes that correspond to a doubled increase in electron kinetic energy with first harmonic photon energy.

\[\text{Kinetic Energy /eV} \]

\[\begin{array}{cccc}
30 & 40 & 50 & 60 \\
\end{array}\]

**Figure 2.** (Colour online) Two-dimensional photoelectron spectrum of HBr in the vicinity of the 3d resonances and 3d ionization thresholds. The calibration of this spectrum was done by comparison with literature values for various spectral features [2]. The spectrum was recorded at an angle of 0° relative to the electric field vector of the photon beam. The colour bar to the top right shows the colours that represent the different electron intensities. The spectrum above the 2DPES is a conventional photoelectron spectrum corresponding to the last photon energy of the 2DPES, whilst the spectrum to the right is a pseudo-photoabsorption spectrum formed by summing the electron yield as a function of photon energy. A more detailed explanation of the spectrum is given in the text.

(ii) *Narrow lines of constant kinetic energy* superimposed on an underlying background in the photon energy range 69.5 eV to 73.5 eV. These are Auger lines produced from so called *atomic decays* that occur when excited Br*(3d⁻¹4p⁶) atoms emit electrons after dissociation of the HBr molecules. Since the kinetic energy of these Auger electrons depends only on the energy difference between the initial excited Br* state and the singly charged Br⁺ ion state, the atomic lines appear on the 2DPES as vertical lines of constant kinetic energy. The background underlying these atomic Auger lines is formed by electrons emitted before dissociation is complete.
(iii) **Horizontal lines** above 73.5 eV arise from *molecular* Auger decay following excitation of various 3d Rydberg resonances [4-7]. A particular resonance may decay to different final states. All of these Auger electrons occur at the photon energy of the Rydberg resonance, and hence these features appear as horizontal lines in the 2DPES.

(iv) **Vertical lines** above a photon energy of 77 eV, which correspond to normal Auger decay following the photoionization of 3d electrons [8-10]. For a given Auger transition the electrons have a constant kinetic energy, the energy difference between the intermediate core-hole state and the doubly charged final-state of HBr++. However, as the 3d ionization thresholds are approached from above these lines shift towards higher kinetic energies, demonstrating the effect of post-collision interaction.

### 2. Experimental Details

The measurements were carried out at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory on the undulator beamline 10.0.1, which is used for high-resolution atomic, molecular and optical physics and photoemission studies of highly correlated materials. The two-dimensional photoelectron spectra (2DPES) were acquired using two time-of-flight energy analyzers in a rotatable chamber [11]. Measurements were made by recording data simultaneously in the two analyzers in two positions; with the analyzers at $0^\circ$ and at $54.7^\circ$, close to the pseudo magic angle (where the electron yield is proportional to the partial cross-section), with respect to the axis of polarization of the photons; and at $35.3^\circ$ and $90^\circ$. To optimize the spectra within the region of particular interest potentials were applied to the time-of flight tubes. Final 2DPES were obtained by combining individual data sets, after each had been corrected for variations in the incident light intensity. The time-of-flight spectra were converted to a kinetic energy scale using conversion points obtained from neon spectra taken under the same analyzer conditions [12]. Since the Ne 2s intensity is zero at $90^\circ$, time–to–kinetic-energy conversion points for $90^\circ$ were obtained from equivalent data recorded with the same analyzer at a slightly different angle. For the HBr data, the transmission efficiency for each of the analyzers and their relative detection efficiencies were obtained using the 2s and 2p lines of Ne, whose cross-sections [13] and angular distribution parameters [14] are well known. To calibrate the HBr data at $90^\circ$, Ne data recorded at $75^\circ$ were used. This angle was chosen as a compromise between sufficiently strong Ne 2s intensity and an angle as close to $90^\circ$ as possible.

### 3. Results and Discussion

The 2DPES of figure 2 indicates how comprehensive 2DPES are and this technique coupled with angular measurements frequently yields a large amount of interesting information about the target species. For example, as evidenced in the higher photon energy region of figure 2, the evolution of a line profile as a result of post-collision interaction as an ionization threshold is approached. The focus here will be on the broad $\sigma^*$ dissociative resonances, which for HBr occur at photon energies between approximately 69.5 and 73.5 eV. The peak of the analogous feature formed by 2p excitation in HCl occurs at 201 eV [15].

#### 3.1 Hydrogen Bromide

An inspection of the 2DPES of figure 2 corresponding to the 3d$\rightarrow\sigma^*$ excitation reveals a number of sharp constant kinetic energy lines that can be assigned to Auger transitions in atomic bromine once the molecule has dissociated. The lines fall into two groups according to their maxima on the photon energy scale, one group of lines has a maximum at 70.89 eV and the other at 54.7°, these maxima corresponding to the two 3d$^5/2\rightarrow\sigma^*$ resonances [2]. In the majority of cases these lines form pairs, corresponding to decays to the same final Br$^+$ state but via 3d$^5/2$ or 3d$^3/2$ excitation to the $\sigma^*$ orbital. The separation of these line pairs on the kinetic energy axis is approximately 1.03 eV, which corresponds to the spin-orbit splitting for the Br 3d orbital. The identification of the atomic Auger lines was facilitated by 2DPES recorded at $90^\circ$, due to the suppression of the 4s$\sigma^{-1}$ and 4p$\sigma^{-1}$ photo-lines, which appear in the same region of the spectrum as the *atomic decay* lines, at this angle. These photo-lines have positive values of the angular asymmetry parameter, $\beta$, and hence are relatively weak.
in the $90^\circ$ spectrum. The $\beta$ parameter describes the variation in electron yield as a function of emission angle with respect to the axis of polarization of the incident radiation \([2]\).

In addition to identifying atomic Auger lines, the profile, as a function of photon energy, of these features can be readily determined from 2DPES. This has permitted the determination of the photon energy positions of the two spin-orbit components of the $3d \rightarrow \sigma^* \sigma^*$ resonance for the first time and provided new information on the dependence of the significance of \textit{atomic Auger decay} with photon energy. The dependence of the dissociation rate, which directly influences the \textit{atomic decay} rates, has been investigated in both HBr \([16]\) and HCl \([17,18]\) by comparing \textit{atomic} and \textit{molecular decay} rates. The 2DPES indicate that atomic line profiles are asymmetric, implying that the \textit{atomic decay} becomes more significant as the photon energy increases. This asymmetry is related to the profile of the potential energy curve of the $\sigma^*$ excited state. The wave-function of the HBr molecule in its vibrational ground state can be approximated by that of an harmonic oscillator, which has a Gaussian profile with a maximum at the equilibrium inter-nuclear separation. The projection of this distribution onto the dissociative curve of the $\sigma^*$ state may result in an asymmetric absorption spectrum. Additionally, the dissociation rate increases with photon energy, the two effects leading to the observed asymmetric profiles. The 2DPES therefore contain information that would be helpful in the determination of the potential energy curves of the two intermediate resonance states.

### 3.2 Angular Distributions

Although \textit{molecular Auger decay} lines usually show little or no anisotropy, surprisingly large anisotropy has been measured for \textit{atomic decay} lines in Cl following the dissociation of core-hole excited HCl molecules \([17,19]\). Analysis of the four 2DPES obtained for HBr show that the same is true for this molecule \([2]\). This analysis provides the asymmetry parameter, $\beta$, for the various atomic lines and indicates that the $\beta$ values for line pairs (corresponding to decays to the same final ion state from the two spin-orbit components of the $\sigma^*$ resonance) are very similar, there are only two pairs for which the difference in $\beta$ is larger than 0.1.

The two step nature of the process resulting in the \textit{atomic Auger decay} lines is reflected by expressing the angular asymmetry parameter, $\beta$, as a product of two factors $\alpha_\sigma$, the intrinsic anisotropy parameter for the Auger transition, and a second parameter which characterizes the anisotropy of the decaying state \([20]\). The similarity in $\beta$ values for the atomic line pairs is perhaps surprising as the alignment parameters for the two resonance states are different.

### 3.3 Hydrogen Chloride

Following the analogous $2p \rightarrow \sigma^*$ excitation in HCl, there is a similar competition between \textit{atomic} and \textit{molecular Auger decay}. Figure 3 shows a 2DPES recorded in the vicinity of this resonance, measured at an electron emission angle of $0^\circ$. Again constant kinetic energy lines which may be identified as Auger transitions in atomic Cl are clearly evident in the spectrum \([21]\). In this case there are two sets of five constant kinetic energy lines, separated by the spin-orbit splitting between the Cl $2p_{3/2}$ and $2p_{1/2}$ orbitals \([22]\). There are also weaker, broader spectral features associated with Auger emission when there is not a constant energy separation between the molecular potential curves involved. Generally these features are towards the lower kinetic energy side of the sharp atomic lines, as illustrated in figure 1 for a conventional photoelectron spectrum.

If \textit{molecular Auger decays} produce electrons with kinetic energies that match those produced in decays following fragmentation and a common final, atomic, ion state is populated via both routes, it is possible that interference effects may be observed. A negative spectral contribution or \textit{hole} that has been identified in an atomic Auger line following dissociation of the $\sigma^*$ resonance in HCl has been ascribed to this kind of interference \([23]\). This feature is where the dashed lines cross in the 2DPES of figure 3. However due to the presence of similar spectral features, labelled as resonant enhancements, in a region of the spectrum where the atomic and molecular Auger electrons have different energies, so that this type of interference cannot occur, alternative explanations for the data are required. It is
evident from the 2DPES that the dashed lines cross between the upper two elliptical resonant enhancements. The atomic line coincident with the vertical dashed line has been assigned to the Cl$^+$ ($^1S$) final state which correlates with the third molecular ion state of $^3\Sigma^+$ symmetry [24] and this dissociative state has been associated with a peak in the photoelectron spectrum which corresponds to a binding energy of 25.85 eV [25]. The broad diagonal band appearing at approximately 172.5 eV at the bottom of figure 3 corresponds to a binding energy consistent with direct population of this $(3)^3\Sigma^+$ state. It is clear from the 2DPES that the resonant enhancements occur in a similar binding energy range. The two sets of resonant enhancements are displaced in photon energy and kinetic energy by amounts corresponding to the relevant spin–orbit splittings. The two pairs of features occur in essentially the same photon energy ranges as the two sets of constant kinetic energy lines and the 2DPES therefore suggests that the hole is associated with population of the dissociative state from the $2p_{\frac{1}{2}}$ orbital and that the similar set of spectral features occurring at a lower photon energy corresponds to resonant Auger contributions arising from $2p_{\frac{3}{2}}$ excitation.

Figure 3. (Colour online) 2DPES recorded in the vicinity of the $2p\rightarrow\sigma^*$ resonance in HCl, taken at an emission angle of $0^\circ$ with respect to the photon polarization direction. The calibration of this spectrum was done by comparison with literature values for various spectral features [21].

However, there is another kind of interference that could be considered. The simulations of Pahl et al [26] show that interference effects can be observed when the energies of the electrons associated with the molecular and atomic contributions are significantly different. These authors studied the $^1\Sigma^-$-$^4\Pi$ transition in HF. It is possible that all of the resonant Auger contributions arising from $2p\rightarrow\sigma^*$ excitation in the HCl 2DPES can be explained using their interpretation. This sort of interference takes place between parts of the wave-packet created earlier in time and parts added later, removing the requirement for the energy of electrons emitted before and after fragmentation to be the same. The narrow bandwidth of the exciting radiation corresponds to a pulse duration that is comparable to the time scale of the nuclear dynamics in the excited state. Depending on the Franck–Condon overlap between the initial state and the dissociative excited state, these interferences are mainly constructive on resonance and become increasingly destructive as the photon energy is detuned further from resonance. The detuning effectively reduces the lifetime of the dissociating neutral state so that the spectrum is more dominated by the molecular contributions and the atomic, constant kinetic energy
peak is suppressed. This is consistent with experimental evidence showing that the molecular decay fraction is minimized on top of the resonance and increases with both positive and negative detunings [18].

Although the features in the 2DPES can be ascribed to interference effects, it is also possible to account for them more straightforwardly. The simplest explanation for the two-dimensional resonance decay patterns in the region of the \((3)^5\Sigma^+\) line is that final ion states in this spectral region are accessed indirectly via Auger decay from the resonance state. The existence of multiple final ion states in this binding energy region, due to electron correlation, has been predicted theoretically [24, 25 and 27] and has been confirmed experimentally [28, 29]. The binding energy at which the enhancements occur might indicate that the \((3)^5\Pi\) state could be among those populated, since calculations suggest that this state lies closest to the \((3)^5\Sigma^+\) state [24]. However, interactions between the various ion states in this spectral region make definite identification difficult. The appearance of two enhancements per spin–orbit component might suggest that two different final ion states are involved. When spectra extracted from equivalent 2DPES in DCI and HCl are compared there is a general increase in intensity in the DCI spectra in the vicinity of the resonant enhancements in comparison to the atomic, constant kinetic energy, lines. This supports the association of the two-dimensional enhancements with a process that occurs in the molecular regime, before the system completely fragments, as DCI dissociation will be slower than the equivalent HCl process.

4. Conclusions
Detailed angle resolved investigations of the production and decay of the 3d→\(\sigma^*\) resonances in HBr and the 2p→\(\sigma^*\) resonances in HCl and DCI have been carried out using two-dimensional photoelectron spectroscopy. The two-dimensional data sets reveal a more complete picture of the decay processes than that provided by single photoelectron spectra recorded at selected photon energies.

For HBr all of the 3d resonances have been studied, with the focus being on the dissociative \(\sigma^*\) resonances. Once these excited states are populated, the molecules begin to fragment and therefore produce excited atomic bromine fragments that autoionize to give Br\(^+\) ions. The photon energy positions of the two 3d\(_{5/2,3/2}\)→\(\sigma^*\) resonances in HBr have been measured directly from photon energy profiles of atomic Auger lines and the asymmetric nature of these profiles has been discussed. The angular distribution parameters of these Br Auger lines have also been measured.

In HCl and DCI the comprehensive nature of the 2DPES reveal unexpected spectral features, the origin of which is considered. These resonant enhancements are consistent with interferences between parts of the wave-packet excited at different times during a pulse whose duration is governed by the bandwidth of the incident photon beam. It is also possible that the resonant enhancements are due to simple resonant Auger decay to multiple final ion states, occurring before the dissociating molecule has fragmented completely.

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