

Competition between atomic and molecular Auger decays: Study of the resonant Auger decay of HBr after the Br $3d \rightarrow \sigma^*$ transition

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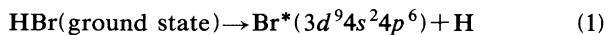
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High-resolution (width ~ 0.12 eV) resonant Auger spectra of HBr and DBr after the Br $3d \rightarrow \sigma^*$ transition are reported. Besides the atomic decay of $\text{Br}^*(3d^9 4s^2 4p^6)$ produced by dissociation of HBr after the antibonding transition, the molecular decay of $\text{HBr}^*(3d^9 \sigma^*)$ is also observed in this high-resolution study. Competition between the atomic and molecular decay is influenced by varying the photon energy and by isotopic substitution.

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Resonant Auger decay, which takes place after an electron is excited to an unoccupied orbital (antibonding or Rydberg) can be used to probe the dynamics of the decay of a core hole [1–4]. For molecules, there is an added dimension for this process, the dissociation of a molecule after the core excitation [5–7]. HBr was the first example of such dissociation effects on the subsequent Auger decay. Extra peaks were found in the valence photoelectron spectrum of HBr between the $4p\sigma^{-1}$ and the $4s\sigma^{-1}$ peaks when the photon energy falls into the energy region of the Br $3d \rightarrow \sigma^*$ transition. These peaks were assigned to the Auger decay of atomic $\text{Br}^*(3d^9 4s^2 4p^6)$, which was produced by the dissociation of $\text{HBr}^*(3d^9 \sigma^*)$ after the Br $3d \rightarrow \sigma^*$ excitation [6]. A similar atomic decay for $\text{Cl}^*(2p^5 3s^2 3p^6)$ was also observed in HCl after the Cl $2p \rightarrow \sigma^*$ transition [8]. However, in addition to relatively sharp (~ 0.3 eV) atomic features, weak and broad features were observed in the HCl spectrum, and were tentatively assigned to the molecular Auger decay of $\text{HCl}^*(2p^5 \sigma^*)$, although the resolution (~ 0.3 eV width) was not high enough to reach a definitive conclusion [8].

The lifetime of a core hole is usually in the femtosecond range [9,10]. For the Br $3d$ hole of HBr, the lifetime width is about 90 meV [11], translating to a lifetime (τ) of about 7×10^{-15} s. One vibrational period for the HBr stretching mode ($\nu \sim 0.3$ eV [12]) takes about 1.3×10^{-14} s. Using related spectroscopic data, Morin and Nenner calculated the excitation and dissociation energy needed for



to be $E_d = 68.31$ eV for the $3d_{5/2}$ transition [6]. The kinetic energy transferred to H, which is much lighter than Br and takes most of the kinetic energy \mathcal{E}_H in the dissociation, is

$$\mathcal{E}_H = h\nu - E_d, \quad (2)$$

where $h\nu$ is the photon energy used for the Br $3d \rightarrow \sigma^*$

excitation. Using a simplified model, the distance traveled by the H atom during the lifetime of the core hole is

$$\Delta R = \sqrt{2\mathcal{E}_H/m_H\tau}, \quad (3)$$

and the distance between Br and H can then be estimated by

$$d = R_e + \Delta R, \quad (4)$$

with $R_e = 1.41$ Å, the equilibrium bond length of H—Br [6]. As shown by Morin and Nenner, following this model, at the photon energy of 70.6 eV, ΔR is ~ 1.6 Å, and the H—Br distance d is then ~ 3 Å, which is long enough to justify an atomic treatment [6].

Although the above reasoning does indicate the extent of HBr dissociation to a certain degree, the actual situation can be more complicated, even without considering the details of the potential surface of $\text{HBr}^*(3d^9 \sigma^*)$. Taking a more dynamic viewpoint, the HBr molecule is constantly vibrating in the electronic and vibrational ground state. In other words, if we take Br as fixed at a point for discussion's sake, then the H atom is constantly moving away or towards the Br atom. Since the potential function is at a minimum at the equilibrium point, the velocity of the H atom is largest at this point, while the direction of the velocity can point towards or away from Br. According to the Franck-Condon principle [13], the direction of the H-atom velocity will not change upon electronic excitation. Thus if the H atom is moving away from the Br, after the excitation, the H atom will be accelerated away from the Br atom, and will move more than 1.6 Å (ΔR) away from the equilibrium point in 7×10^{-15} s (i.e., the H—Br distance around 3 Å), and atomic Auger decay is observed. But if the H atom is moving towards Br, after the electronic excitation the H atom will continue to move towards Br. It will then slow down, stop, and reverse its direction of motion (i.e., moving away from Br), due to the repulsive nature of the $\text{HBr}^*(3d^9 \sigma^*)$ potential surface. In this case, the H atom will not move very far away from the equilibrium point in such a short time span, and the two atoms can still be treated as a molecule of HBr. Thus the value 3 Å derived from Eq. (4) is only an average. What is pro-

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duced after the $\text{Br } 3d \rightarrow \sigma^*$ excitation is a mixture of atomic $\text{Br}^*(3d^9 4s^2 4p^6)$ and molecular $\text{HBr}^*(3d^9 \sigma^* 1)$ (and everything in between), and what should be observed in the resonant Auger spectrum is a competition between atomic and molecular processes. The atomic process, being free from molecular effects such as vibronic coupling or ligand-field splitting, should give sharp peaks in the spectrum, easily distinguishable from the broad molecular peaks (broadened mainly by dissociation). However, the experimental width reported in Ref. [6] was almost 1 eV, and thus was not able to distinguish these processes. In this Rapid Communication, we report a high-resolution study (~ 0.12 eV) as an effort to fully resolve both atomic and molecular decays in HBr and to sort out the competition between these two processes.

Two separate experiments were performed at the Aladdin ring of the University of Wisconsin, one using a Grasshopper monochromator with an 1800 grooves/mm grating [14] and the other using a 3M TGM monochromator with a high-energy grating [15]. In the 65–75-eV photon energy region the photon width for our Grasshopper beamline was around 0.1 eV with a slit width of $100 \mu\text{m}$, while the photon width for the 3M TGM beamline was estimated to be around 0.2 eV, both narrower than the ground-state vibrational frequency of HBr (~ 0.3 eV [12]). High-purity sample gas (HBr from Aldrich and DBr from Cambridge Isotope) was leaked into the gas cell and was ionized by synchrotron radiation. The electron signal was kinetically analyzed by a McPherson ESCA 36-cm mean radius electron energy analyzer [16], and detected by a position-sensitive detector [17]. The linewidth measured by the HBr $4p\pi^{-1}$ peak at a kinetic energy around 60 eV in the Grasshopper experiment was 0.16 eV, due to both the analyzer width

and the photon width. Taking the photon width as 0.1 eV, the analyzer width is estimated to be around 0.12 eV. Details of the calibration for both the photon energy and the peak position will be reported in another publication [18].

The resonant Auger spectra of HBr and DBr after the $\text{Br } 3d \rightarrow \sigma^*$ transition with $h\nu = 70.62$ and 72.49 eV are shown in Fig. 1. The narrowest linewidth obtained in these spectra is about 0.18 eV. These spectra contain both sharp and broad features. The sharp features, labeled as $A1$ – $A4$, are due to the atomic decay of $\text{Br}^*(3d^9 4s^2 4p^6)$ and are in reasonable agreement with previously reported results [6], except that the doublet $A1$ and $A2$, due to the $\text{Br}^*(3d^9 4s^2 4p^6)$ decay to 3P_2 and $^3P_{0,1}$ states of $\text{Br}^+(3d^{10} 4s^2 4p^4)$, are resolved for the first time in our high-resolution study. In addition, two weak and broad features, $M1$ and $M2$ are also resolved for the first time, and are due to molecular decay of $\text{HBr}^*(3d^9 \sigma^* 1)$. The widths of the atomic peaks are larger than the instrumental width (~ 0.12 eV), probably due to overlap with the broad molecular peaks whose widths are more than 0.5 eV. Thus in agreement with previous analysis, there exists a competition between the atomic and the molecular Auger decays after the HBr $\text{Br } 3d \rightarrow \sigma^*$ transition, and both processes can be observed in the HBr and DBr resonant Auger spectra.

By changing experimental conditions, the competition can be tilted towards either the molecular or the atomic process. The first way to do so is by varying the photon energy. A high-resolution study on the $\text{Br } 3d$ pre-edge excitation was previously reported by Shaw *et al.* [11] and the $\text{Br } 3d \rightarrow \sigma^*$ transition is a broad feature with a half width of around 2 eV, broadened by the dissociation after the transition and containing both the $3d_{5/2}$ and

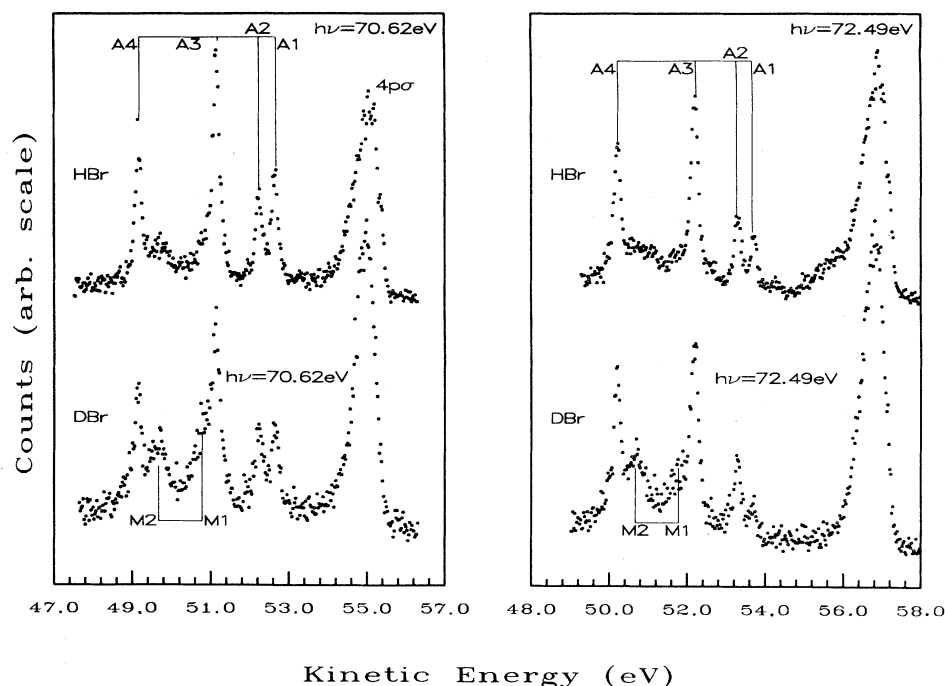


FIG. 1. The resonant Auger spectra of HBr and DBr with $h\nu = 70.62$ and 72.49 eV.

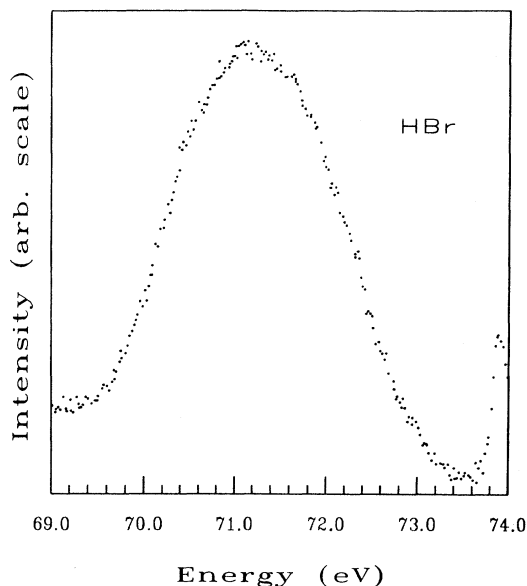


FIG. 2. Br $3d \rightarrow \sigma^*$ pre-edge transition measured by electron-energy-loss spectroscopy (digitized from Ref. [11]).

$3d_{3/2}$ components, as shown in Fig. 2. The $3d_{5/2} \rightarrow \sigma^*$ transition starts at around 69.7 eV, and taking the spin-orbit splitting of Br $3d$ as 1.1 eV, the $3d_{3/2} \rightarrow \sigma^*$ transition should start at around 70.8 eV. By increasing the photon energy within the 69.7–70.8-eV range, more energy is pumped into the kinetic energy of the dissociating H atom, based on Eq. (2), and thus the atomic decay should be enhanced. Shown in Fig. 3 are two resonant Auger

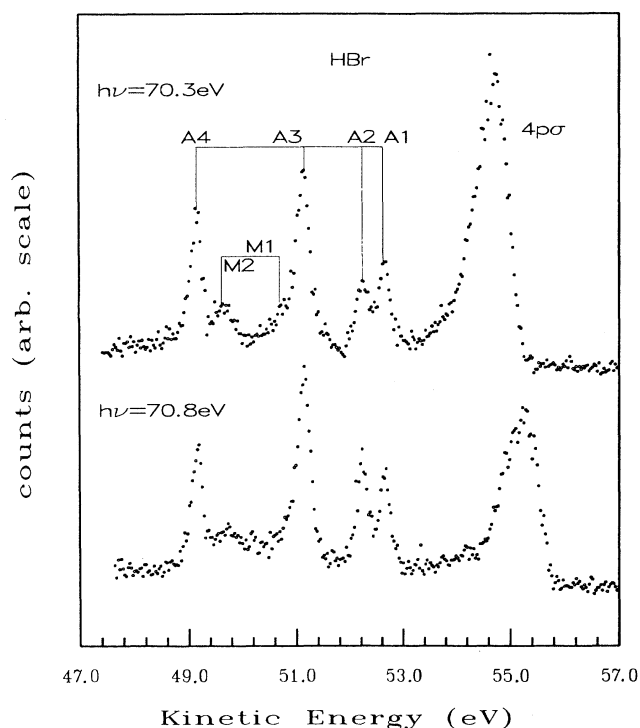


FIG. 3. The resonant Auger spectra of HBr with $h\nu=70.3$ and 70.8 eV.

spectra, taken separately with $h\nu=70.3$ and 70.8 eV, using the 3M TGM monochromator. Comparing the two spectra, the relative intensities of the resonant Auger features to the $4p\sigma$ peak increase when going to higher photon energy, since the $3d_{5/2}$ transition is more intense at $h\nu=70.8$ eV than at $h\nu=70.3$ eV. On the other hand, the molecular peaks $M1$ and $M2$ are smaller and less well resolved at $h\nu=70.8$ eV than at $h\nu=70.3$ eV (Fig. 3), since the increase in photon energy favors the atomic decay, not the molecular decay. More quantitatively, according to Eqs. (2) and (3), the ratio between the average distance traveled by the H atom at these two different photon energies can be estimated to be

$$\begin{aligned} \Delta R_{h\nu=70.8 \text{ eV}} : \Delta R_{h\nu=70.3 \text{ eV}} \\ = \sqrt{70.8 - 68.31} : \sqrt{70.3 - 68.31} \approx 1.0 : 0.9 \end{aligned} \quad (5)$$

Although this is only a small change, the effect is visible when comparing the two spectra in Fig. 3. For better comparison, it would be desirable to compare two spectra with a larger separation in photon energy. However, the choice is limited by the fact that above $h\nu=70.8$ eV the onset of $3d_{3/2}$ excitation can complicate the spectrum, while below 70.3 eV the $3d_{5/2} \rightarrow \sigma^*$ transition is too weak and the intensity of the resonant Auger peaks is too low.

Another way to tilt the competition between the atomic and molecular decay is by replacing the H atom with a D atom. Again according to Eqs. (2) and (3), and assuming the electronic excitation is the same for HBr and for DBr at the same photon energy, the ratio should be

$$\Delta R_{\text{DBr}} : \Delta R_{\text{HBr}} = \sqrt{m_{\text{H}}} : \sqrt{m_{\text{D}}} \approx 0.7 : 1.0, \quad (6)$$

and the change is larger in this case than by changing photon energy. Thus, going from HBr to DBr, the molecular decay will be enhanced significantly.

This is indeed the case, as shown in Fig. 1. For both $3d_{5/2}$ ($h\nu=70.62$ eV) excitation and $3d_{3/2}$ ($h\nu=72.49$ eV) excitation, the molecular peaks $M1$ and $M2$ are more intense in DBr than in HBr. By fitting these resonant Auger peaks to Voigt functions, we found that the ratio between the area of peak $M2$ and $A4$ is 0.78 for HBr at $h\nu=70.62$ eV, but increased to 1.17 for DBr. At $h\nu=72.49$ eV, this ratio is 0.41 for HBr, and 1.11 for DBr. A similar isotope substitution effect on the resonant Auger decay of (D)HCl after the Cl $2p \rightarrow \sigma^*$ also has been observed very recently [19].

The decay after $3d_{5/2}$ excitation ($h\nu=70.62$ eV) is similar to the decay after $3d_{3/2}$ excitation ($h\nu=72.49$ eV), as shown in Fig. 1, except for two minor differences. First, the intensity ratio between $M2$ and $A4$ is higher for the spectra taken at $h\nu=70.62$ eV than for the spectra taken at $h\nu=72.49$ eV for both HBr and DBr, i.e., the molecular features are stronger at $h\nu=70.62$ eV than at $h\nu=72.49$ eV. This can be understood by the fact that E_d defined in Eq. (1) is 68.31 eV for the $3d_{5/2}$ transition, and \mathcal{E}_{H} as defined in Eq. (2) is 2.31 eV for $h\nu=70.62$ eV, while E_d for the $3d_{3/2}$ transition is 69.41 eV (using the spin-orbit splitting of 1.1 eV for Br $3d$), and \mathcal{E}_{H} is 3.08 eV for $h\nu=72.49$ eV. So comparison between the spectra taken at these two photon energies again shows the effect

TABLE I. Kinetic energy (eV) and assignment for peaks observed in Fig. 1.

Peak label	Calculation ^a ($3d_{5/2}$)	$3d_{5/2}$ decay $h\nu=70.62$ eV	$3d_{3/2}$ decay $h\nu=72.49$ eV	Assignment
A1	52.57	52.58	53.70	$\text{Br}^+ 4s^2 4p^4 \ ^3P_2$
A2	52.18	51.16	52.30	$\text{Br}^+ 4s^2 4p^4 \ ^3P_{0,1}$
A3	51.07	51.08	52.19	$\text{Br}^+ 4s^2 4p^4 \ ^1D_2$
A4	49.11	49.09	50.21	$\text{Br}^+ 4s^2 4p^4 \ ^1S_0$
M1		50.8	51.7	$\text{HBr}^+ (4p\pi^2 \ ^1\Delta)\sigma^*1$
M2		49.7	50.8	$\text{HBr}^+ (4p\pi^2 \ ^1\Sigma^+)\sigma^*1$

^a $E = 64.38 - E_b$: 64.38 eV ($\text{Br}^2 P_{3/2} \rightarrow ^2 D_{5/2}$) from Ref. [21] and E_b from Ref. [22].

of a larger \mathcal{E}_H enhancing the atomic decay. The other difference observed was that the relative intensity of A1 versus A2 reversed going from $h\nu=70.62$ eV to $h\nu=72.49$ eV, which is due to the fact that the dissociation tail of the $4p\sigma$ peak [20] is underneath A1 and A2 at $h\nu=70.62$ eV, and it moves out of the resonant Auger region at $h\nu=72.49$ eV.

The assignment for the atomic peaks A1–A4 listed in Table I is the same as Morin and Nenner's previous assignment [6], except that the peak positions are now determined with an accuracy of 20 meV. An independent check for these positions is to use the excitation energy of $\text{Br } 3d^{10} 4s^2 4p^5 \ ^2P_{3/2} \rightarrow \text{Br}^* 3d^9 4s^2 4p^6 \ ^2D_{5/2}$ (64.38 eV) [21] and the binding energy for $\text{Br}^+ 3d^{10} 4s^2 4p^4$ states determined by van der Meulen, Krause, and Lange [22] to calculate the expected kinetic energy for these atomic decay peaks. These values are also listed in Table I and are in excellent agreement with our experiment. The

molecular features (M1 and M2) are due to the resonant Auger decay with a spectator electron in the σ^* orbital. Atomic features are also observed in a lower kinetic energy region, and a complete assignment of these features will be presented in another paper [18].

In summary, our high-resolution study on the resonant Auger decay of HBr and DBr resolved both atomic and molecular decay processes, and the competition between these two processes can be influenced by changing the photon energy and by isotopic substitution.

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