Molecular Auger Resonance Raman Effect: A High Resolution Study on the Resonance Auger Decay of HBr after the Br $3d \rightarrow 5p\pi$ Rydberg Transition

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High resolution resonance Auger spectra of HBr are recorded with the photon energy tuned to the HBr Br $3d \rightarrow 5p\pi$ resonance which is broadened by the molecular ligand-field splitting. The spectra show the characteristics of the Auger resonance Raman effect: The resonance Auger peak positions move linearly with the photon energy, and the lifetime broadening does not contribute to the widths of the resonance Auger peaks. Moreover, the ligand-field splitting effects are also absent from the resonance Auger spectra. The prospect for high resolution studies on molecular inner shell decays, using resonance Auger spectroscopy to eliminate both lifetime and ligand-field effects, is discussed.

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Spectator resonance Auger decay is usually explained as a two-step process [1,2]. First, a core electron is excited to an unoccupied orbital, creating a core hole. Then, with the excited electron remaining in the unoccupied orbital as a spectator, the core hole is filled with a valence electron and the energy released ionizes another valence electron. However, this process can also be treated as a two-electron excitation process which is usually called "shakeup" in photoelectron spectroscopy. In this picture, an atom or molecule absorbs an x-ray photon, which excites a valence electron to an unoccupied orbital (the spectator electron), and simultaneously ionizes another valence electron with the same kinetic energy as in the Auger decay. When the photon energy is tuned to the resonance between a core level and the unoccupied orbital, the cross section for such a two-electron process is enhanced by several orders of magnitude [3]. Thus, from this perspective, the spectator resonance Auger process is actually a one-step resonant two-electron excitation process. Its cross section is enhanced by the core to unoccupied resonance, but the core hole does not contribute to its width. As first shown by Crasemann and co-workers for the Auger decay of deep Xe $2p$ level ($E_{bin} \sim 4786$ eV), the peak width in such a process is determined by the photon width (~ 2.5 eV) and is narrower than the lifetime width of the Xe $2p$ hole (~ 3.0 eV) [4,5], and the phenomenon was termed the Auger analog of resonance Raman scattering [4] since these two processes are treated similarly in resonant scattering theory [3,6,7]. Thus the resolution of the resonance Auger study is not limited by the core hole inherent lifetime width.

The above resolution aspect of the resonance Auger decay has great significance for high resolution studies on inner shell processes. For example, the lifetime width for Xe $4d$ ($E_{bin} \sim 69$ eV) is 0.13 eV, and for I $4d$ of I_2 ($E_{bin} \sim 58$ eV) is ~ 0.20 eV [8]. Both the available electron analyzer resolution [9,10] and more recently the photon resolution from synchrotron radiation [11] can deliver widths narrower than the above lifetime width in the relevant energy range. However, the resolution in conventional photoelectron and normal Auger spectroscopy is ultimately limited by the lifetime width. This is a severe limit to our ability to elucidate the dynamics of inner shell processes, especially for molecules. For example, the vibrational frequency of I_2 is only ~ 0.03 eV [12] while the I $4d$ lifetime width of I_2 is ~ 0.2 eV [8], and such vibrational splitting can never be resolved in the photoelectron and Auger spectra. In contrast, resonance Auger spectroscopy, with its width limited only by instrument width (photon and analyzer width) and by the lifetime width of the valence shakeup state, is ideal for high resolution study on inner shell processes, since the lifetime widths of such states are very small, as shown recently by Baltzer *et al.* in their recent high resolution He II photoelectron study on the 20–30 eV binding energy region of N_2, which is dominated by valence shakeup states with a width of ~ 20 meV [13].

To date the potential of using such effects for high resolution studies (eliminating the core hole lifetime broadening) has been barely tapped. Little work has been done to study this effect on shallow, narrow core levels [14], and to our knowledge this effect has not been reported for molecules. In this communication, we report a high resolution study on the spectator resonance Auger decay and the observation of the Auger resonance Raman effect, with its special characteristics in a molecular environment, for HBr after the Br $3d \rightarrow 5p\pi$ transition. The widths obtained for the resonance Auger peaks were ~ 0.15 eV, an order of magnitude narrower than previous studies on deeper levels [4,5].

The experiment was performed at the Aladdin Ring of the University of Wisconsin, using a Grasshopper monochromator with an 1800 g/mm grating [15]. A high purity sample of gaseous HBr bought from Aldrich was leaked into the gas cell to interact with synchrotron radiation. The electron signal was kinetically analyzed by a

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McPherson ESCA 36 cm mean radius electron energy analyzer [10], and detected by a position sensitive detector [16]. Details of the calibration for both the photon energy and the peak position will be reported in another publication [17].

The Br $3d$ pre-edge excitation of HBr was previously studied by Shaw *et al.* [18]. The Br $3d \rightarrow \sigma^*$ transition is marked by a broad peak in the electron energy loss spectrum (EELS) due to the dissociation of HBr after the excitation, and the atomic decay of the Br* atom produced in the excitation has to be taken into consideration [19]. However, the Rydberg transitions are marked by sharp peaks in the 73–78 eV energy region, as shown in Fig. 1, and dissociation should not be a factor for these resonances. The resonance Auger decay of HBr corresponding to these Rydberg resonances is thus a molecular process. Because of spin-orbit interaction of the $3d$ hole, each pre-edge excitation is split into two components, $3d_{5/2}$ and $3d_{3/2}$. In the molecular environment of HBr, the deficiency of electron density along the H-Br bond (z axis) further splits the $3d_{5/2}$ into three components and the $3d_{3/2}$ into two components. Observation of such ligand-field splittings in the Br $3d$ photoelectron spectra of HBr was reported very recently [20]. Comparison between the Br $3d$ pre-edge EELS spectrum and the photoelectron spectrum of HBr proved that the pre-edge structure in Fig. 1 is dominated by ligand-field splitting. This conclusion was further supported by a scattered wave $x\alpha$ (SW-Xα) calculation which showed that the peaks in Fig. 1 are dominated by the ligand-field splitting components of the HBr Br $3d \rightarrow 5p\pi$ transition, mixed with much weaker $3d \rightarrow 5p\sigma$ and $3d \rightarrow 4d\pi$ transitions [20]. The resonance Auger decay with photon energy tuned to these ligand-field components of the Br $3d \rightarrow 5p\pi$ resonance shown in Fig. 1 is the subject of this Letter.

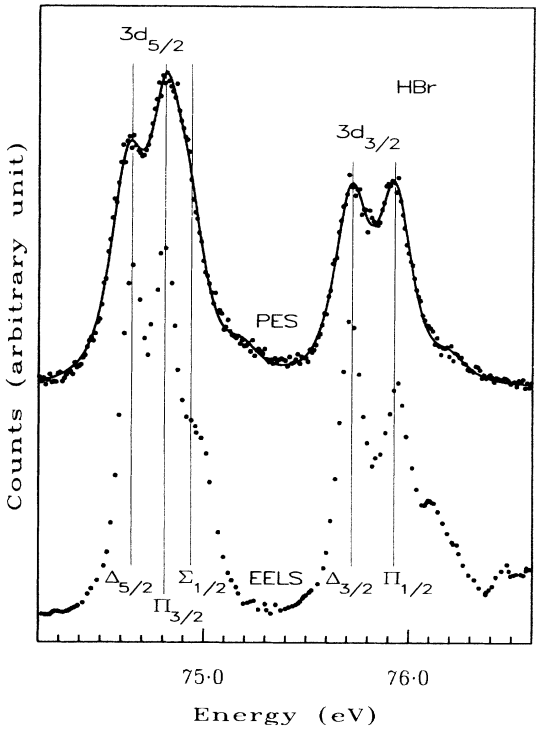

FIG. 1. The ligand-field splitting of the Br $3d \rightarrow 5p\pi$ transition in HBr (EELS) spectrum digitized from Ref. [18] as shown in the bottom curve, in comparison with the ligand-field splitting of Br $3d$ PES of HBr as shown in the top curve. The binding energy fo the PES spectrum is moved for better comparison with the EELS spectrum.

In Fig. 2, we compare part of our *MVV* normal Auger spectrum of HBr with the off resonance spectrum at $h\nu = 74.5$ eV, and the resonance Auger spectra. The normal Auger spectrum has been shifted by +4.6 eV kinetic energy so that a direct comparison of all these spectra can be easily made. At $h\nu = 74.5$ eV, only the valence $4s\sigma$ and inner valence photoelectron peaks are visible [21]. However, at $h\nu = 74.6$–74.9 eV, the spectra are dominated by three narrower resonance Auger peaks A, B, and C (overlapping with the weaker inner valence peaks). These peaks are all shifted by $\sim +5$ eV relative to the much broader (~ 0.5 eV) normal Auger peaks, and the energy separations among the three final states in the resonance Auger spectrum are almost the same as those in the normal Auger spectrum [22]. Such correspondence between resonance Auger and normal Auger peaks has been found before for Kr $3d$ resonances [23], with the $5p$

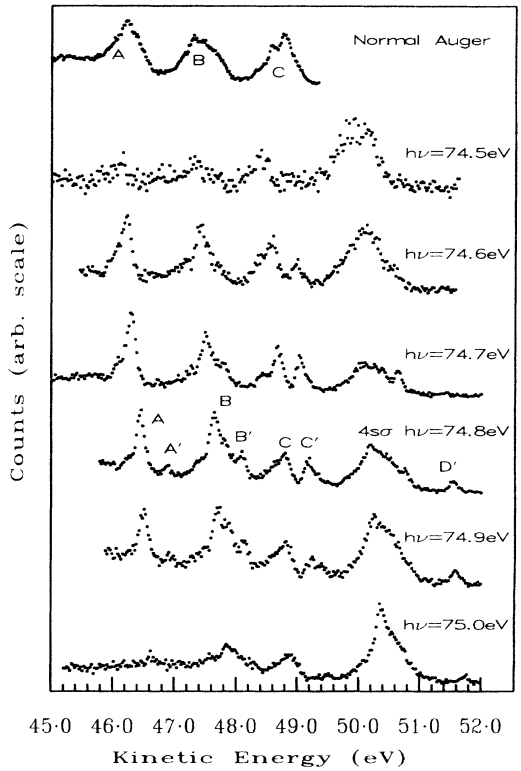

FIG. 2. The resonance Auger decay of HBr following the Br $3d_{5/2} \rightarrow 5p\pi$ resonance.

spectator resonance Auger peaks also being 5 eV higher in kinetic energy than their normal Auger counterparts.

These dominant resonance Auger peaks confirm our previous assignment, based on a SW-Xα calculation, that the pre-edge peaks in Fig. 1 are dominated by the ligand-field components of the Br $3d \rightarrow 5p\pi$ excitation [20], and peaks A, B, and C in Fig. 2 are thus due to the Auger decay with a spectator electron on the $5p\pi$ orbital. Peaks A'-D' are relatively weak and their intensity varies from $h\nu=74.7$ to $h\nu=74.9$ eV. These peaks are due to the spectator Auger decay following the Br $3d \rightarrow 5p\sigma$ and $4d\pi$ resonances, both of which are mixed with the $5p\pi$ transition but are much weaker [20].

There are several important features of the resonance Auger spectra which are best illustrated using peak A. First, the resonance Auger width of 0.15 eV is *much* narrower than the normal Auger peak width of 0.5 eV. The normal Auger decay $3d_{5/2} \rightarrow 4p\pi^{-2}\ ^1\Sigma^+$ is split into three peaks [21] due to ligand-field splitting, and its line shape resembles that of the Br $3d_{5/2}$ photoelectron peak [20] as shown in the left-hand side of Fig. 3. In contrast, peak A is narrow and sharp with a clearly defined weak peak on the low kinetic energy side (Fig. 3, top right). With a photon width of $\sim$0.1 eV used in our experiment at 74.72 eV, we could excite both the $\Delta_{5/2}$ and $\Pi_{3/2}$ components of the $3d_{5/2} \rightarrow 5p\pi$ transitions (Fig. 1). Could

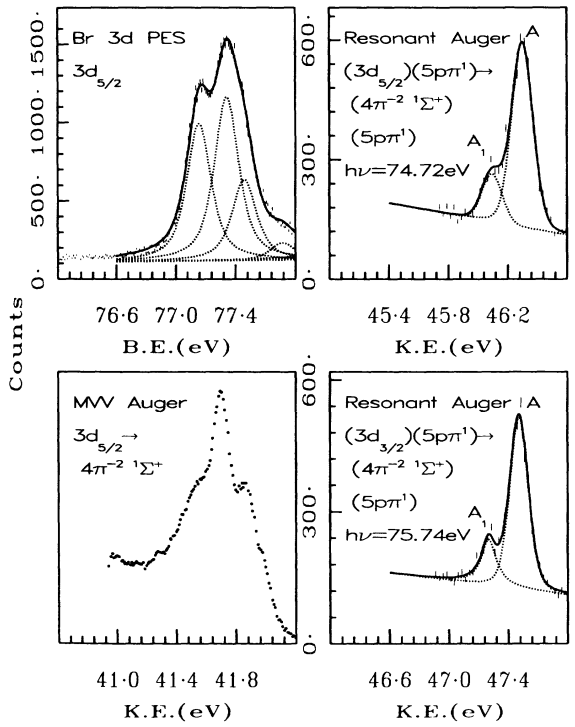

FIG. 3. Comparison among the HBr photoelectron spectrum (Br $3d_{5/2}$, top left), *MVV* normal Auger ($3d_{5/2} \rightarrow 4p\pi^{-2}\ ^1\Sigma^+$, bottom left, digitized from Ref. [22]), and resonance Auger spectra [$3d^{-1}5p\pi^1 \rightarrow (4p\pi^{-2}\ ^1\Sigma^+)(5p\pi^1)$ for both spin-orbit components, top right and bottom right].

$A1$ and A be due to the ligand-field splitting in the resonance Auger process, i.e., the splitting of the $3d$ $\Delta_{5/2}$ and $\Pi_{3/2}$ decay similar to the normal Auger peaks?

Detailed analysis rules out this possibility. As the photon energy sweeps across the $3d_{5/2} \rightarrow 5p\pi$ band in Fig. 1, different ligand-field components will be excited [20], and there should be a corresponding change in the line shape of peak $A1$ and A, if they are indeed due to ligand-field splitting. For example, at $h\nu=74.6$ and 74.7 eV, peak $A1$ should then be due to the $\Delta_{5/2}$ component and peak A to the $\Pi_{3/2}$ component of the $3d_{5/2} \rightarrow 5p\pi$ transition (see Fig. 1). For $h\nu=74.6$ eV, the transition is largely due to the $\Delta_{5/2}$ component, and peak $A1$ should be favored in intensity. For $h\nu=74.7$ eV, the transition is largely due to the $\Pi_{3/2}$ component, and the intensity of peak $A1$ (relative to peak A) should thus drop dramatically. Such a change is not observed in the experiment. Similarly at $h\nu=74.8$ and 74.9 eV, the component $3d_{5/2}\Sigma_{1/2} \rightarrow 5p\pi$ is excited and there should be a shoulder at the high kinetic energy side ($\sim$0.12 eV) of A. Such a change is again not observed in the experiment. Moreover, if peaks $A1$ and A are due to ligand-field splitting, the separation between them at $h\nu=74.72$ eV should reflect the separation between $\Delta_{5/2}$ and $\Pi_{3/2}$ of the $3d_{5/2}$ state ($\sim$0.19 eV) [20]. This separation should be increased at $h\nu=75.74$ eV (Fig. 1) to $\sim$0.23 eV [20], reflecting the separation between $\Delta_{3/2}$ and $\Pi_{1/2}$ of the $3d_{3/2}$ state. Such increase was observed in both *MVV* normal Auger spectrum [22] (comparing $3d_{5/2}$ and $3d_{3/2}$ decay) and Br $3d$ pre-edge excitation [18] (comparing $3d_{5/2}$ and $3d_{3/2} \rightarrow 5p\pi$ transitions; see Fig. 1). But the separation between $A1$ and A is 0.20 eV for *both* $h\nu=74.72$ eV ($3d_{5/2}$ spectator decay) and $h\nu=75.74$ eV ($3d_{3/2}$ spectator decay).

Indeed, as analyzed in the introduction, ligand-field splitting should disappear from the resonance Auger spectra. The final states of a spectator resonance Auger decay are valence double excitation states. The different ligand-field components of the $3d \rightarrow 5p\pi$ transition only serve to resonantly enhance the intensity of these states, while the energy and the linewidth of these states are determined by the photon energy and width [4]. The doublet $A1$ and A are probably due to the coupling between the spectator electron and the two valence electrons on $4p\pi$ [24]. They are definitely not due to ligand-field splitting based on the experimental results. Similar fine structures have also been observed in the resonance

TABLE I. Kinetic energy (eV) for *MVV* $5p\pi$ spectator Auger peaks in Fig. 2.

Photon energy (eV)	Peak A $(4p\pi^{-2}\ ^1\Sigma^+)(5p\pi^1)$	Peak B $(4p\pi^{-2}\ ^1\Delta)(5p\pi^1)$
$h\nu=74.6$	46.23	47.43
$h\nu=74.7$	46.30	47.50
$h\nu=74.8$	46.45	47.63
$h\nu=74.9$	46.51	47.69

Auger spectra of Kr after the Kr $3d \rightarrow 5p$ transition [23].

Second, the linewidth of 0.15 eV, although not narrower than the Br $3d$ lifetime linewidth of $\sim$0.1 eV [18], is significantly narrower than the linewidth of each component of the triplet in the normal Auger spectrum of 0.20 eV, or the photoelectron linewidth of 0.20 eV (Fig. 3). The latter two broad linewidths arise because of the significant contribution from the lifetime linewidth. The resonance Auger linewidth of 0.15 eV is due only to a photon width of 0.1 eV and an analyzer width of $\sim$0.1 eV, with no contribution from the lifetime linewidth.

The third effect is shown qualitatively in Fig. 2: The peak positions of the resonant Auger peaks move to higher kinetic energy with increasing photon energy. The positions for peaks A and B are detailed in Table I.

Thus for molecular resonance Auger decay, the ligand-field splitting does not contribute to the spectral structure, the lifetime width does not contribute to the linewidth, and the peak positions shift linearly with the photon energy. The latter two effects are expected from previous studies of the atomic resonance Auger Raman effects [4,5].

The elimination of the ligand-field effect from resonance Auger decay is quite significant for high resolution study of inner shell processes involving d and f levels. Recent high resolution studies have shown that ligand-field splitting can greatly complicate the elucidation of the photoelectron, normal Auger and pre-edge photoabsorption spectra of these levels [20,25]. By eliminating both lifetime broadening and ligand-field splitting, the resonance Auger spectroscopy offers an ideal way to study the electronic and vibronic effects in the inner shell process with a resolution limited only by instrument widths.

In summary, we have observed experimentally for the first time that the molecular ligand-field splitting effects are eliminated in the resonance Auger decay, in addition to the elimination of lifetime broadening.

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