Atomic Autoionization Following Very Fast Dissociation of Core-Excited HBr

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Photoelectron spectroscopy excited by monochromatic synchrotron radiation (68–80 eV range) is used to study the Br $3d$ excitation in HBr. The transition to an antibonding orbital is shown to produce a resonant state whose repulsive nature has been observed directly. A two-step relaxation process involving a fast neutral dissociation followed by the autoionization of the excited fragment has been shown for the first time.

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Inner-shell excitation of molecules has been the subject of recent investigations by electron-energy-loss spectroscopy (EELS) and photoabsorption. As shown in the review by King and Read,[1] the high-resolution EELS results reveal two kinds of resonances: the usual Rydberg series converging to inner-shell ionization thresholds and, at lower energy, resonances assigned to the excitation of atomiclike inner-shell electrons into the first empty molecular orbital (MO). This is a typical molecular effect which is not found in the isoelectronic rare-gas absorption spectrum. For example, the first resonance observed in the $3d$ excitation spectrum of Kr is assigned[2] to the $3d \rightarrow 5p$ transition, in contrast to the case[3] of HBr for which it is a $3d \rightarrow 4\sigma^*$ transition. These molecular resonances manifest themselves as intense features with vibrational structure[1] (N_2, CO) or as a broad absorption band[3,4] (HBr, CH_3Br, CH_3I, . . .) whose width is interpreted as due to autoionization[5] or to their dissociative nature.[3,4]

In this Letter we present, for the HBr molecule, direct experimental evidence of the repulsive character of the $3d \rightarrow 4p\sigma^*$ resonance, and determine its very specific decay channel. Moreover, we give evidence, for the first time, of a new relaxation process of an excited molecule, involving a two-step scheme, namely a fast neutral dissociation followed by the autoionization of the excited fragment.

We have used the technique of angle-resolved photoelectron spectroscopy in association with monochromatic synchrotron radiation in the energy range 68–80 eV, in order to study the HBr excitation near the $3d_{5/2,3/2}$ edge of bromine (77.12, 78.23 eV).[3] The experimental procedure is described in detail elsewhere.[6] Photoelectron spectra (PES) allow us to distinguish the partial decay into various electronic states, while constant-ionic-state (CIS) spectra give directly the variation of the partial photoionization cross section with photon energy. The grazing-incidence monochromator and the electron analyzer were operated with 550- and 750-meV energy resolution, respectively. Both kinds of spectra were obtained at the magic angle which eliminates angular effects.

The electronic configuration of HBr in its ground state is

$$\underset{\text{(core Br orbitals)}}{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}} \quad \underset{\text{(valence MO's)}}{4s\sigma^2 4p\sigma^2 4p\pi^4 4p\sigma^{*0}}$$

in the separated-atom terminology. Figure 1(a) shows a PES recorded at 68.2 eV, i.e., below the $3d \rightarrow 4p\sigma^*$ resonance. The peaks X, A, and B correspond to the ionization of the $4p\pi$, $4p\sigma$, and $4s\sigma$ MO's, respectively, in agreement with previous PES[7,8] and dipole $(e,2e)$ results.[9] Note that the $4s\sigma$ line is distributed over a large set of satellite lines which reflects the breakdown of the one-electron picture.[9] In Fig. 1(a)

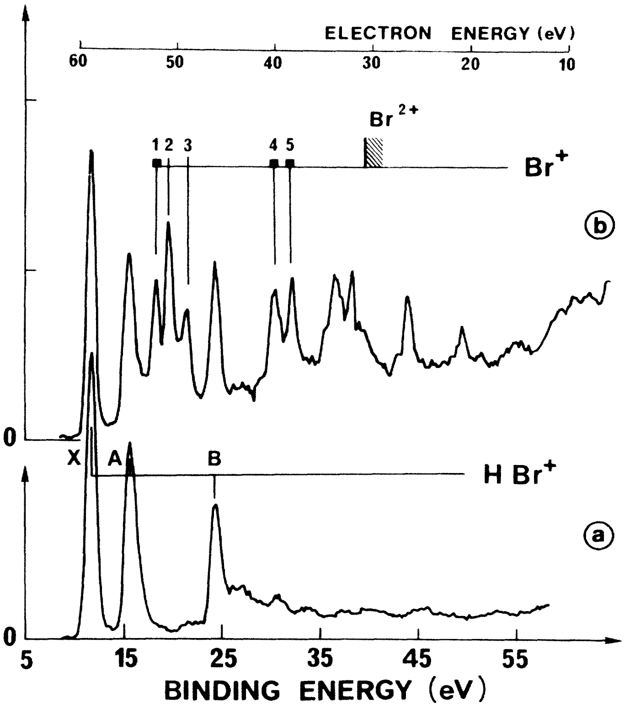

FIG. 1. PES recorded (a) "off" ($h\nu = 68.2$ eV) and (b) "on" the resonance ($h\nu = 70.6$ eV). The Br autoionization lines are positioned on a kinetic-energy scale (see Table I for assignment).

we distinguish at least five additional satellite bands as compared to previous observations[9] (this point will be discussed elsewhere). Figure 1(b) represents a PES taken on resonance at 70.6 eV. The most striking observations are (i) the numerous sharp lines that appear along the spectrum, the intensity of which represents about 75% of the spectrum, and (ii) some lines that appear at considerably low binding energy (18.4 eV), below the $4s\sigma$ main peak (24.4 eV). In our previous work on $Si(CH_3)_4$,[10] we have shown that the silicon $2p$ excitation, which is resonant just below the edge, was followed by autoionization into an inner-valence single-hole ionic state as well as multiexcited-configuration ones. In the present work the same processes do not occur because (i) no correspondence is found between the lines observed in Figs. 1(a) and 1(b), and (ii) the inner-valence $4s\sigma$ state is only very weakly resonant, as also indicated in Fig. 2, curve *c*. The upper part of this figure reproduces the EEL spectrum from Shaw *et al.*[3] and exhibits the strong $3d \rightarrow 4p\sigma^*$ resonance around 71 eV. As shown from our CIS curves *a*, *b*, and *c* (Fig. 2), autoionization of this resonance into the valence-state continua is weak. This contrasts with the 19.5-eV-band CIS curve which resonates strongly and uniquely around 71 eV as discussed in detail below. Our photon resolution was not good enough to resolve Rydberg resonances, but they are undoubtly present in curve *c*.

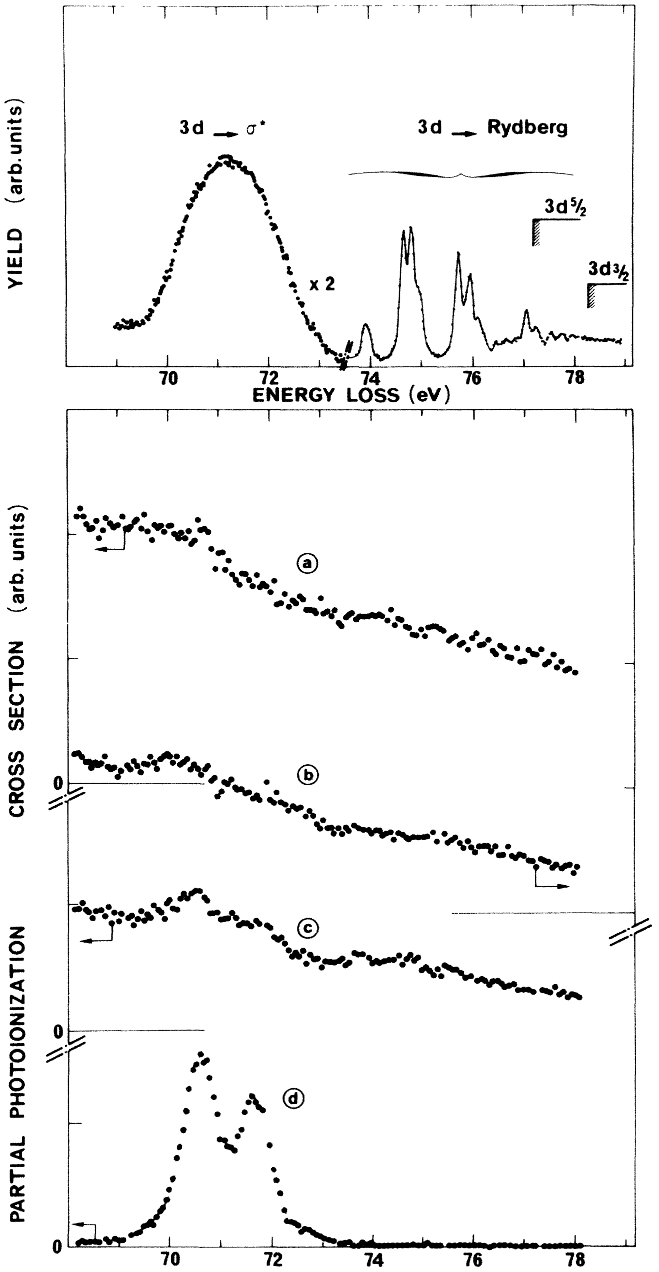

FIG. 2. Upper part, EEL spectrum from Ref. 3 (by courtesy of F. Read). Lower part, CIS curves *a*, *b*, and *c* corresponding to partial ionization of $X(4p\pi)$, $A(4p\sigma)$, and $B(4s\sigma)$ states of HBr, respectively. Curve *d* is a CIS curve of a hypothetical state of 19.5-eV binding energy.

At this point, assume the $3d \rightarrow 4p\sigma^*$ resonance to be a strongly repulsive state. If we consider the lifetime of the $3d$ hole to be long enough, we can imagine the neutral dissociation of the resonance, to be achieved before any electronic relaxation processes occur. Figure 3 is a schematic of this two-step process: The first step is the excitation of the resonance along its repulsive potential curve which is split into the two components $3d_{5/2}, 3d_{3/2}$ of the initial hole [separated by $\Delta E = 1.05$ eV (Ref. 3)], and correlated with the disciation limit into $H(^2S) + Br(\ldots 3d^9 4s^2 4p^6 \, ^2D_{5/2}$ or $^2D_{3/2})$. The second step is the atomic autoionization of the excited $Br^*(^2D)$ atom, which takes place at a very large internuclear distance (R). Let us now evaluate the kinetic energy of the ejected electron, in the case of the $3d_{5/2}$ excitation. We know from the absorption spectrum of the bromine atom[11] that the transition $3d^{10}4s^2 4p^5 \, ^2P_{3/2} \rightarrow 3d^9 4s^2 4p^6 \, ^2D_{5/2}$ occurs at $E(Br^*) = 64.38$ eV. In addition, Ruscic, Greene, and

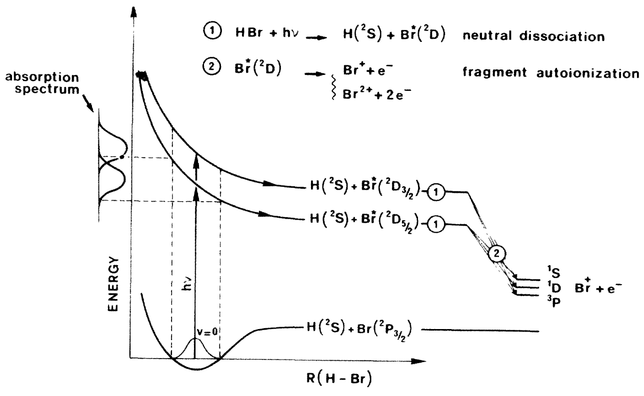

FIG. 3. Potential-energy curves of HBr describing the two- step relaxation process.

Berkowitz[12] determined accurately the ionization potentials (V_I) of bromine in its ground configuration $4s^2 4p^4\,{}^3P_{2,4,0}, {}^1D_2, {}^1S$; higher excited-state energies, involving multiple excitations, are extracted from Moore's table.[13] If we assume that the autoionization takes place at large R ($\geqslant 3$ Å), the kinetic energy is obtained (see Fig. 3) as $E(\mathrm{Br}^*) - V_I(\mathrm{Br})$. The corresponding lines with their assignments are reported in Fig. 1 and also in Table I. The agreement between the calculated and observed line positions is extremely good and rules out any other explanation. It is interesting to note that sharp structures persist well above the double-ionization threshold of Br, despite the quasicontinuum resulting from excited states of Br^+. This means that the $\mathrm{Br}^*({}^2D)$ autoionization is selective and proceeds via a multielectron process.

Let us now analyze this phenomenon on a real time scale. The lifetime τ of the $3d$ hole can be estimated, in the atomic case, from the width of the $3d \to 4p$ resonance observed in the bromine absorption spectrum.[11] The 90-meV measured value corresponds to $\tau > 7 \times 10^{-15}$ s. In a first approximation, we can assume this lifetime to be the same in the molecular case, which implies that the neutral dissociation occurs on a femtosecond time scale. This is indeed the case for a direct dissociation process. The kinetic energy E_R released in the dissociation is given by the difference between the photon energy (70.6 eV) and the dissociation limit

$$\begin{aligned} D(\mathrm{H}+\mathrm{Br}({}^2D_{5/2})) &= D(\mathrm{H}+\mathrm{Br}({}^2P_{3/2})) + E(\mathrm{Br}^*) \\ &= 3.75 + 64.38, \end{aligned}$$

where the value 3.75 is from Herzberg.[14] We obtain $E_R = 2.47$ eV which is entirely transferred to the H atom because of the high Br/H mass ratio of 80. In the simplest model where E is immediately converted into kinetic energy, we can estimate the internuclear distance d at which the Br* inner hole relaxes, after the time τ. We obtain

$$d = R_e + (2E_R/m_{\mathrm{H}})^{1/2}\tau,$$

where the equilibrium internuclear distance $R_e = 1.41$ Å is obtained from Ref. 14 and m_{H} is the hydrogen mass. The 3-Å value thus estimated is large enough to justify, *a posteriori*, the description of the relaxation process as two independent steps.

Further experimental evidence of the validity of our model is obtained by comparison of two PES taken at 70.00- and 70.6-eV photon energy [Figs. 4(a) and 4(b)], corresponding to the low-energy side and to the maximum of the $3d \to {}_{5/2}4p\sigma^*$ resonance. The PES of Fig. 4 have been plotted on a kinetic-energy scale; the A and B states of HBr give rise to peaks which are correctly shifted by $70.6 - 70 = 0.6$ eV, but the autoionization lines of Br* appear exactly at the same kinetic energy. This observation fully confirms our two-step description where the energy of the autoionization electron does not depend upon the photon energy. In other words, when one scans the resonance, the excess energy is carried away by the atoms, and not by the electron, in close analogy with an Auger process where excess energy is carried away by the primary electron and not by the Auger electron.

Let us now consider the $3d_{3/2}$ excitation; the same description holds, with the only difference being that

TABLE I. Peak positions (kinetic energy) as observed in Fig. 1(b) and the corresponding Br^+ autoionization lines.

Peak number	Electron energy (E_e) (eV) Expt.	Calc.[a]	Assignment
1	52.2	52.53, 52.14, 52.05[b]	$4s^1 4p^4\,{}^3P_{2,1,0}$
2	50.8	51.06[b]	$4s^2 4p^4\,{}^1D_2$
3	49.0	49.11[b]	$4s^2 4p^4\,{}^1S_0$
4	40.2	40.58, 40.29[c] 40.33[c]	$4s4p^5\,{}^3P_{2,4}{}^\circ$ $4p^3({}^4S^\circ)5s\,{}^3S^\circ$
5	38.4	38.97, 38.94, 38.85[c] 38.6, 38.49, 38.61[c] 38.54[c] 38.1[c]	$4p^3({}^2D^\circ)5s\,{}^3D_{1,2,3}{}^\circ$ $4p^3({}^4S^\circ)4d\,{}^3D_{1,2,3}{}^\circ$ $4p^3({}^2D^\circ)5s\,{}^1D^\circ$ $4p^3({}^2P^\circ)5s\,{}^1P^\circ$

[a] $E_e = 64.38\ \mathrm{eV} - E_b$; 64.38 eV is the Br ${}^2P_{3/2} \to {}^2D_{5/2}$ transition energy.

[b] E_b, the binding energy, from Ref. 12.

[c] E_b, the binding energy, from Ref. 13.

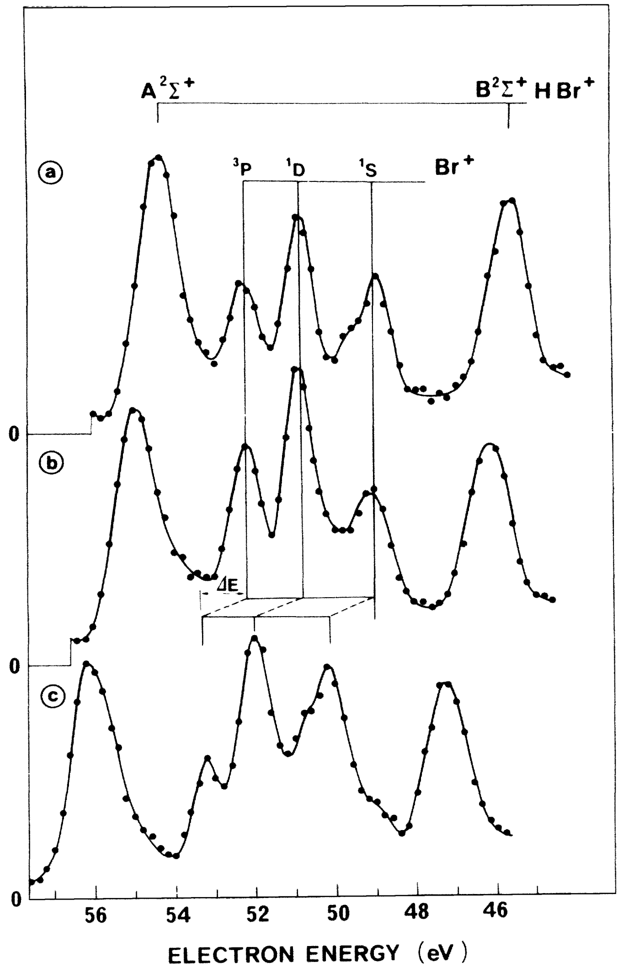

FIG. 4. PES recorded at (a) 70, (b) 70.6, and (c) 71.6 photon energy, plotted on a kinetic-energy scale.

the Br*($^2D_{3/2}$) autoionization lines are expected to be shifted by an amount 1.05 eV (3d spin-orbit splitting) on a kinetic-energy scale, as illustrated in Fig. 3. We indeed observe this effect in a PES taken at 71.6-eV photon energy which corresponds to the $3d_{3/2} \to 4p\sigma^*$ excitation. The three lowest Br$^+$ lines (and also higher ones not reported in the figure) are shifted by $\Delta E \approx 1$ eV. Note that the lines are observed at the same "binding energy" ($h\nu - E_{\text{kinetic}}$) because the 3$d$ spin-orbit splitting is the same in the atom and the molecule. This is the reason why CIS curve d of Fig. 2 has a shape rather different from the absorption line. Even though such CIS measurement (of a band of constant kinetic energy) does not provide a correct partial cross section, the two observed peaks in Fig. 2, curve d, give the position of the maxima for the $3d_{5/2}, 3d_{3/2} \to 4p\sigma^*$ transitions. These two resonances have a wide Franck-Condon envelope and are strongly overlapping as seen from the lack of spin-orbit structure in the absorption spectrum (Fig. 2); this explains the different branching ratios of the Br$^+$ lines in Figs. 4(a)–4(c) [two shoulders are observed in Fig. 4(c) which correspond to $^1D_2$ and $^1S_0$ lines of Br$^+$ originating from the $3d_{5/2} \to 4p\sigma^*$ resonance].

In conclusion, we have given evidence, for the first time, of a new relaxation process of a core-excited molecule: a very fast neutral dissociation followed by autoionization of the excited fragment. The repulsive nature of the $3d^{-1}4p\sigma^*$ state has been characterized directly; it confirms the antibonding character of the empty $4p\sigma^*$ orbital and emphasizes the molecular specificity of the phenomenon. We expect that similar effects should be observable in other systems for which the inner-hole lifetime is larger than the dissociation time. Extension of this work to polyatomic molecules as well as other halogen compounds is in progress.

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