Site-Selective Photochemistry of Core Excited Molecules: Role of the Internal Energy

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A further insight into the photochemistry of a core excited polyatomic molecule has been obtained using a new electron-ion coincidence setup. Selecting the kinetic energy of Auger electrons in coincidence with fragment ions we observed a strong site selective fragmentation for the lowest states of the $ClCH_2Br^{2+}$ ion, following selective Br $3d$ or Cl $2p$ core photoionization. At higher energy the selectivity diminishes and is completely lost for the highest states. The pure photoselective effect has been emphasized by subtracting the thermodynamical, naturally selective, fragmentation pattern. [S0031-9007(98)07582-6]

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The idea of site-selective photofragmentation of a core excited molecule naturally merged up several years ago in relation with the very localized character of the core orbitals [1]. Indeed, by tuning the photon energy to the appropriate transition, one is able to excite a well defined site in a complex molecule and expects to selectively break the surrounding chemical bonds. Such studies, referred to as site-selective photochemistry, have not only a fundamental motivation related to the general topic of the specific damages induced by monochromatic radiation on complex systems but are also highly interesting in several related fields such as photodesorption, photoreactivity, and photochemistry in general, which explain the numerous review papers [2–5] (and references therein) and articles [6–12] devoted to this subject.

When looking at site-selective fragmentation, the first crucial point is the "degree of localization" of the primary Auger process following core excitation or ionization. Apart from special cases (e.g., an ultrafast neutral dissociation preceding the Auger decay [13]), the electronic relaxation process can be treated sequentially: photoelectron emission followed by a normal Auger process leading to a doubly charged ion. One can expect a site specific dissociation process of this doubly charged ion only if the location of the two positive charges in the final two hole state of the Auger process shows a memory of the initial photoexcitation site. Indeed, for most of the known systems, a "localized" Auger process takes place following core ionization because the Auger decay rate depends on the overlap between the core-hole orbital and the molecular orbitals involved in the Auger process. However, exceptions where the dicationic final states of the Auger process completely loose the memory of the initial ionization site have been demonstrated, as in the case of the silicon Auger spectrum of the highly ionic SiF_4 molecule, where strong localization effects of the two holes on the same or distinct fluorine atoms take place [14,15]. On the other hand, even if the two holes are localized on or close to the initially excited site, a fragmentation process around this site is expected to occur only if other possible electronic relaxation channels are not faster than dissociation, as will be discussed later. These other relaxation channels are also expected to become more efficient with an increase in the molecular ion size.

With respect to the specific photofragmentation process, the halogenated alkanes represent a particular class of molecules to which several studies have been dedicated [6,12,16,17]. The particular interest on the di-halogenated alkanes comes from the possibility of selectively exciting the one or the other among the two halogen atoms which are placed in identical or similar geometrical and chemical environments. For instance, after bromine $3d$ ionization of $ClCH_2Br$, Schmelz *et al.* showed that the molecule preferentially dissociates along the C-Br chemical bond whereas after chlorine $2p$ ionization it is the C-Cl chemical bond which is preferentially broken [3,12]. However, in this study the observed fragmentation is summed up over all open electronic channels and the origin of the selective effect is hidden.

In this Letter we report new evidence of strong site-selective photofragmentation processes in the core ionized bromochloromethane molecule and disentangle its origin. We used the energy selected Auger electron photoion coincidence (ES-AEPICO) technique in order to gain deeper insight into the dissociation mechanism of doubly charged $ClCH_2Br^{2+}$ ions created through Auger decay. The main advantage of this technique is that the detection of only one electron simultaneously determines the binding energy of the doubly charged ion and the hole which was initially created.

The experiment has been performed at the SA22 bending-magnet beam line of SuperACO storage ring. A plane-grating monochromator provides photons in the 100–920 eV energy range with a resolving power $(E/\Delta E)$ up to 5000. The photon energy was set at $h\nu = 219$ eV to isolate the $Br3d^{-1}$ and $Cl2p^{-1}$ photoelectron lines from the $Br(3d)VV$ or $Cl(2p)VV$ Auger bands.

The experimental setup combines a new high luminosity (acceptance angle of 5% of 4π) electron analyzer with a conventional time of flight mass spectrometer. The electron analyzer is a double toroidal type, which combines the advantages of the cylindrical mirror analyzer (high acceptance angle) and the hemispherical analyzer (multichannel analysis within a wide energy range). Full details of its design and operation are described elsewhere [18] and only a brief description is given here. A four element conical retarding lens system focuses the electron beam on the entrance slit of the analyzer. The electrons are then dispersed and focused, by two pairs of toroidal deflecting plates, on the detection plane perpendicular to the analyzer symmetry axis, where they are collected on a position sensitive detector. The measurements have been performed at a pass energy of 80 eV, for which the electron kinetic energy resolution is better than 1 eV. When an electron is detected, a 1 kV pulsed extraction field is applied to the ionization chamber in order to extract the ions towards the drift tube, which allows differentiation of the fragments based on their m/q ratio.

Figure 1a shows a global view of the electron emission spectra of the $ClCH_2Br$ molecule recorded with a pass energy of 80 eV at $h\nu = 219$ eV. This is about 10 eV above the chlorine $2p_{3/2,1/2}$ and about 140 eV above the bromine $3d_{5/2,3/2}$ ionization thresholds. The four main bands correspond to the chlorine $2p$ photoelectrons (below 18 eV), the Br($3d$)VV Auger bands (in the range 20–70 eV), the bromine $3d$ photoelectrons (in the range 137–144 eV), and to the Cl($2p$)VV Auger bands (above 151 eV), respectively. Figure 1b is an enlargement of the Br($3d$)VV and Cl($2p$)VV Auger bands plotted on a binding energy scale. Obviously our resolution is not sufficient to resolve the different final electronic states of the Auger processes in neither case. However, a shift of about 3 eV between the onsets (low binding energy side) of the two Auger bands can be clearly identified. This is due to the different localizations of the two valence holes in the final state: in the present case these lowest states originate from two vacancies in the lone pairs of the bromine or of the chlorine atoms, respectively. Indeed, using the binding energies of these lone pairs in $ClCH_2Br^+$ measured by Novak *et al.* to be 10.77 and 11.81 eV [19], an empirical rule of thumb [20] allows one to estimate an energy shift of 2.9 eV between these states, in agreement with our data.

We have performed ES-AEPICO coincidence experiments with binding energies of the $ClCH_2Br^{2+}$ ion ranging from ~27 to ~57 eV by steps of ~5 eV. Figure 2 illustrates selected ES-AEPICO coincidence spectra for

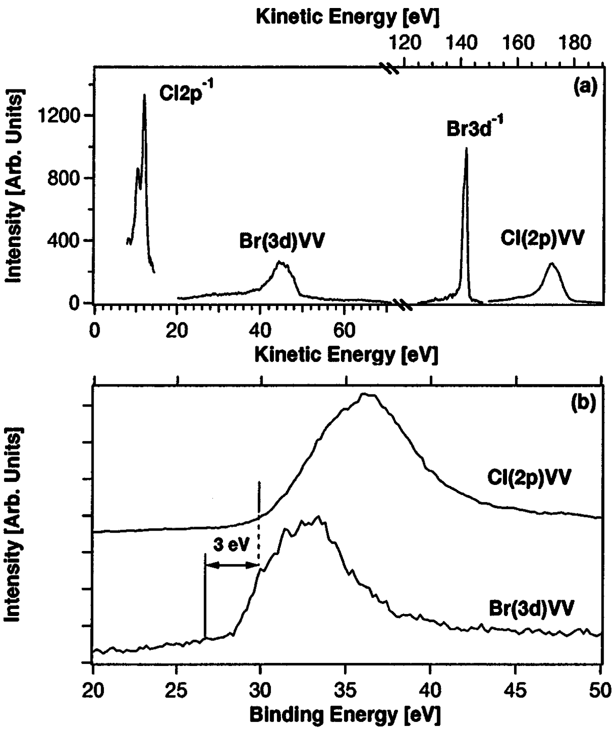

FIG. 1. (a) Electron emission spectra of $ClCH_2Br$ recorded at $h\nu = 219$ eV and a pass energy $E_p = 80$ eV. The origins of the four bands are also indicated on the figure. (b) Br($3d$)VV and Cl($2p$)VV Auger bands plotted together on the same binding energy scale. A shift of about 3 eV between the onsets of the Auger bands is to be noticed.

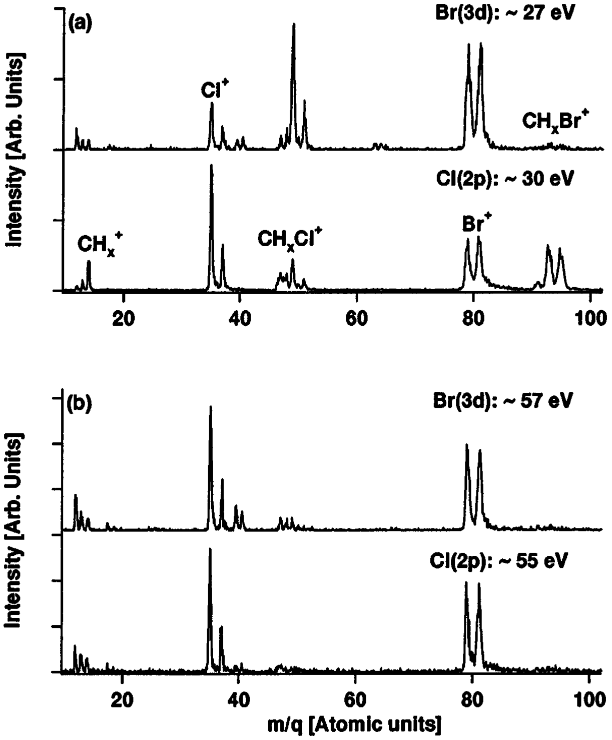

FIG. 2. $ClCH_2Br$ ES-AEPICO coincidence spectra for low (a) and the high (b) binding energy states of $ClCH_2Br^{2+}$. At low binding energy one can note a strong site-selective fragmentation of the doubly charged ion (top panel), whereas at high binding energy atomization processes are dominant (bottom panel).

binding energies of ~27 and ~30 eV (a) and, respectively, ~57 and ~55 eV (b). The top spectra correspond to the creation of the initial core hole in the bromine $3d$ shell whereas the bottom spectra correspond to the creation of the initial core hole in the chlorine $2p$ shell. Comparing the spectra in Fig. 2a, it is obvious that the dissociation patterns of the lowest electronic states created via Auger processes following Br $3d$ or Cl $2p$ ionization are very different. In the light of the previous discussion, a different location of the two valence holes in the doubly charged ion is indicated, due to an Auger process preserving the memory of the initial excitation site. Moreover the observed site selectivity is very strong: Br$(3d)VV$ Auger processes lead to a coincidence spectrum which is strongly dominated by the Br^+ and $\mathrm{CH}_x\mathrm{Cl}^+$ ions (signature of a C-Br bond breaking) whereas Cl$(2p)VV$ Auger processes lead to one which is dominated by the Cl^+ and $\mathrm{CH}_x\mathrm{Br}^+$ ions (signature of a C-Cl bond breaking). Let us concentrate now on the spectra in Fig. 2b corresponding to high binding energies (55 and 57 eV) of the dissociating ion. The two spectra are practically the same and the components due to the molecular fragment ions are negligible compared to those associated with the atomic fragment ions. The photoselectivity is completely lost for high binding energies of the doubly charged ion and the fragmentation seems to be independent of the ionization path and leads to atomization patterns.

In order to quantitatively describe the selectivity as a function of the binding energy of the dissociating $\mathrm{ClCH_2Br}^{2+}$ ion, let us define two experimental selectivity coefficients C^s_{Br} (C^s_{Cl}) derived from the branching ratio for preservation of the C-Br (C-Cl) chemical bonds after excitation at the Br $3d$ (Cl $2p$) edge. These coefficients are given by

$$\begin{aligned} C^s_{\mathrm{Br}} &= 1 - \frac{N_{\text{C-Br}}}{N_{\text{C-Br}} + N_{\text{C-Cl}}} \quad \text{and} \\ C^s_{\mathrm{Cl}} &= 1 - \frac{N_{\text{C-Cl}}}{N_{\text{C-Br}} + N_{\text{C-Cl}}}, \end{aligned} \tag{1}$$

where $N_{\text{C-Br}}$ and $N_{\text{C-Cl}}$ represent the integrated area of the coincidence peaks corresponding to $\mathrm{CH}_x\mathrm{Br}^+$ and $\mathrm{CH}_x\mathrm{Cl}^+$, respectively. Thus C^s_X increases as the probability of breaking a C-X bond increases.

Figure 3a illustrates the variation of the selectivity coefficients C^s_{Br} and C^s_{Cl} as a function of the binding energy of the doubly charged ion. The graph indicates that for the creation of an initial $\mathrm{Br}3d^{-1}$ hole or a $\mathrm{Cl}2p^{-1}$ hole the site selectivity for the first accessible electronic states of the $\mathrm{ClCH_2Br}^{2+}$ ion is indeed very strong. The site selectivity and the differences observed in the Br$(3d)VV$ and Cl$(2p)VV$ Auger spectra (Fig. 1b) reflect noticeable differences in the topologies of the corresponding potential surfaces in the neighborhood of the C-Br and C-Cl bonds for these electronic states. Notice that the time scales of the relaxation processes must also be considered at this stage, because the system behavior indicates that the dissociation occurs before other relaxation processes (e.g., internal conversion of the electronic into vibrational energy) which would probably take place over larger characteristic time scales. According to the previous discussion concerning the "local" character of the Auger process, we conclude that this pronounced site-selective fragmentation is probably induced by a very rapid and direct C-X bond breaking between the halogen atom and the rest of the molecular ion.

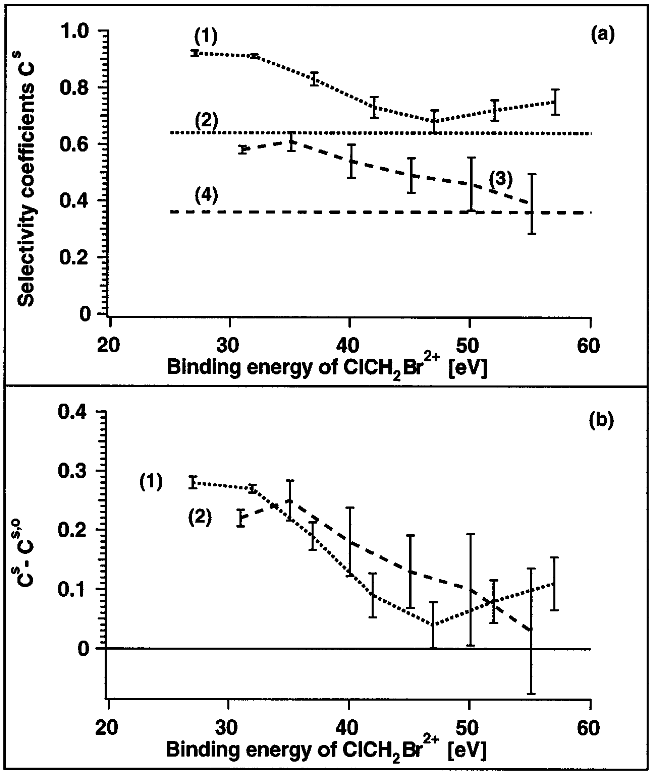

FIG. 3. (a) The dependence of the selectivity coefficients on the binding energy of the doubly charged ion: (1) C^s_{Br}, (2) $C^{s,0}_{\mathrm{Br}}$, (3) C^s_{Cl}, and (4) $C^{s,0}_{\mathrm{Cl}}$. (b) The pure photoselectivity coefficients: (1) $C^s_{\mathrm{Br}} - C^{s,0}_{\mathrm{Br}}$; (2) $C^s_{\mathrm{Cl}} - C^{s,0}_{\mathrm{Cl}}$.

Notice the clear distinction between the observed photoinduced site-selective fragmentation and a naturally selective bond breaking solely due to a possible difference in the thermodynamical dissociation energies of the C-Br and C-Cl chemical bonds in $\mathrm{ClCH_2Br}^{2+}$: the weaker the bond, the more efficiently the bond is broken. As soon as the total energy stored in the system is high enough, there is a basic fragmentation pattern in which the branching ratios of the $\mathrm{CH}_x\mathrm{Br}^+$ and $\mathrm{CH}_x\mathrm{Cl}^+$ fragment ions can be slightly different. Thus, before comparing the magnitudes of the two site-selective photofragmentation processes, this basic fragmentation pattern has to be evaluated. To determine the basic selectivity coefficients $C^{s,0}_{\mathrm{Br}}$, $C^{s,0}_{\mathrm{Cl}}$, similarly to (1), we further performed coincidence experiments between energy selected C$1s$ *photoelectrons* and fragment ions (ES-PEPICO) at $h\nu = 330$ eV.

Indeed, because $ClCH_2Br$ is not a highly ionic molecule, there is no particular reason for the $C(1s)VV$ Auger processes to populate two hole valence states with any localized character on one or both halogen atoms. Thus, after ionization of the central atom ($C1s^{-1}$) one can expect to reach the so called basic fragmentation pattern. As ES-PEPICO-type experiments contain an average information about the fragmentation of all final electronic states of the doubly charged ion, they are the most appropriate to give an estimation of the basic $C_{\mathrm{Br}}^{s,0}$, $C_{\mathrm{Cl}}^{s,0}$ selectivity coefficients (0.64 and 0.36, respectively), which are represented together with the energy dependent C_{Br}^{s}, C_{Cl}^{s} selectivity coefficients in Fig. 3a.

In order to emphasize the pure photoselective effect, the differences $C_X^s - C_X^{s,0}$ ($X = \mathrm{Br}, \mathrm{Cl}$) are represented in Fig. 3b. Two points are of interest: their magnitude is the highest at the lowest binding energy and the variation of the two curves with increasing binding energy is the same. The similarity for the lowest binding energies shows that the localized character of the lone pair orbitals is the same in Br and Cl, leading to the same selective fragmentation. The monotonously decreasing selectivity tends to the basic selectivity coefficients. There are two possible ways of explaining this loss of selectivity. The first one involves the direct formation of high binding energy electronic states *via* nonlocal Auger processes. The second possibility is to invoke a fast internal conversion process where the electronic energy is converted into vibrational energy of a lower electronic state of the ion. The rate of these energy redistribution processes is known to strongly depend on the actual density of states, which is likely to dramatically increase with binding energy. In such a statistical energy redistribution, the initial localization is lost and the fragmentation pattern is governed only by thermodynamical properties. Such a process has been already invoked in other systems, like hexamethyldisilane [21] and very recently in *n*- and iso-propanol [22]. Furthermore, as the available energy in the system increases, a more efficient explosion of the molecule is observed. Knowledge of the topology of the potential surfaces of the $ClCH_2Br^{2+}$ ion and of its spectroscopy make it possible to distinguish between the two explanations and would be very useful in elucidating the mechanism of the selectivity.

In summary, we have observed a strong site-selective photofragmentation of the first excited states of the $ClCH_2Br^{2+}$ ion, following $Br3d^{-1}$ or $Cl2p^{-1}$ core ionization, emphasized after removal of the "natural" selectivity. Furthermore, the evolution of the observed selectivity has been studied as a function of the binding energy of the dissociating doubly charged ion, showing a rapid disappearing of the photoselective effect with increasing binding energy. A coincidence experiment between two threshold electrons and ions after valence double ionization, to study the influence on dissociation of the decay path forming the doubly charged ion, would give more insight into the dissociation dynamics of the system. Moreover, the higher "differentiation" attainable by this technique would allow a better understanding of the fragmentation mechanism by the selection of the precise electronic state of the dissociating ion.

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