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Postcollision-interaction effects in HCl following photofragmentation near the chlorine *K* edge

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Ion time-of-flight mass spectroscopy was used to study the relaxation dynamics of HCl following photoexcitation in the vicinity of the Cl *K* threshold (≈ 2.8 keV). Detailed observations of molecular fragmentation mediated by postcollision interaction between a photoelectron and an Auger electron are presented, evidenced by the recapture of Cl *K* photoelectrons by either Cl^{n+} or H^+ dissociation fragments. [S1050-2947(98)51206-1]

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Following photoionization of an inner-shell electron in the energy region just above threshold, the photoion is left in a highly excited state and, in most cases, relaxes by means of radiationless decay. In this context, the slow-moving photoelectron, having an energy E_{exc} equal to the difference between the photon energy and the ionization potential, interacts with the more energetic Auger electron and exchanges energy in the continuum. This postcollision interaction (PCI) manifests itself through changes in the Auger line shape and energy shifts in the electron spectra, as well as through trends in ion-yield spectra.

In atoms, PCI is a relatively well understood effect. Experimental [1–7] as well as semiclassical [8–11] and quantum-mechanical theoretical work [12–15] has been done for both shallow and deep core levels. In contrast, PCI effects in molecules are less well understood. Electron-spectroscopy measurements have been obtained following shallow core-shell excitation [16–18], and some qualitative results have been presented regarding PCI following deep core photoexcitation in molecules [19,20]. In this work, we present a detailed quantitative analysis describing PCI-moderated dissociation of molecules. We find that recapture effects observed in the ion yields of Cl^{n+} following photodissociation of HCl are related to *K*-shell Auger emission, and that these effects in molecules can be described with a hydrogenic PCI model. In addition, we also find that the H^+ yield increases in the first few eV immediately above threshold, suggesting that this fragment sometimes captures the Cl *1s* photoelectron; an effect that cannot be described using conventional atomic-PCI models.

The experiments were performed using x-ray synchrotron radiation (SR) from beamline 9.3.1 at the Advanced Light Source (ALS) [21,22], and beamline X-24A at the National Synchrotron Light Source (NSLS) [23,24], both of which have a photon-energy resolution $E/\Delta E \approx 7000$. An ion time-of-flight (TOF) mass spectrometer, comprised of five cylin-

dric regions of differing length and electric field strength and oriented with its axis parallel to the polarization vector of the incident SR, was used to measure relative ion yields following x-ray absorption. In the first (extraction) region, a grounded needle serves as an effusive source of the gas through which the x-ray beam is focused. Voltages on all regions are selected to achieve maximum time resolution by satisfying space-focusing conditions [25]. Ions formed in the extraction region of the analyzer are accelerated by a 2-kV/cm field toward a dual microchannel plate assembly that provides an electron cascade with a gain of 10^6 . The signal from an individual ion is further amplified and used as the start pulse for a timing circuit in which the storage-ring timing pulse, related to the periodic pulsing of the SR (328 ns at the ALS, 567 ns at the NSLS), provides the stop signal. The resultant timing information is used to produce a TOF spectrum in which peaks for all ions are accumulated simultaneously. Acceleration voltages and discriminator settings were selected to ensure uniform detection efficiency for all ions and charge states. In addition, measurements were taken with the analyzer parallel or perpendicular to the polarization vector of the SR as well as at several different extraction voltages to ascertain if ions escape the extraction fields of the TOF analyzer. The full extent of these tests, which demonstrated that the extraction efficiency is unaffected by angular distributions, is described elsewhere [26]. Photon-energy calibration [26] is checked periodically over the course of an experiment by scanning the monochromator through the Cl *1s* threshold region while monitoring total-ion yield (TIY) and comparing subthreshold resonances in these absorption-like spectra [27].

Ion-TOF spectra were collected at a number of different photon energies in the Cl *1s* threshold region in the “singles” mode, where spectra are collected with only one or two electron bunches in the storage ring. Peaks in these spectra, representing individual photofragments (i.e., H^+ ,

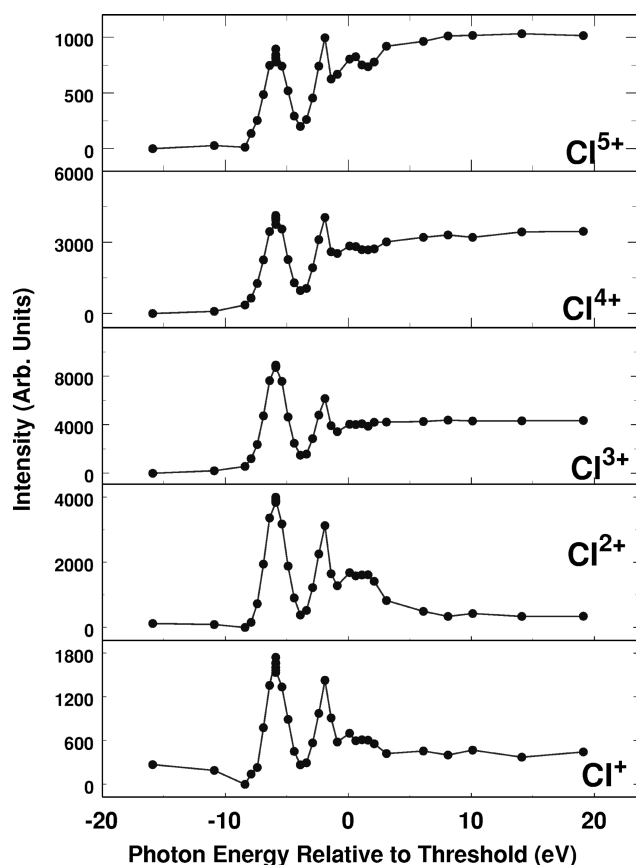


FIG. 1. Partial ion yields for different Cl charge states formed after photoexcitation of HCl. Valence and L -shell background subtracted.

Cl^{n+}), were integrated and fractional ion yields as a function of energy were determined. Then, by multiplying the TIY curve by the fractional ion yields for each ion, it was possible to determine partial ion yield (PIY), or the intensity of each ion-TOF peak as a function of energy. The relative contributions of the interaction of incident photons with L -shell and valence electrons were determined by the magnitude of the PIY intensity below resonance, and were subtracted from the PIY to give the results shown in Fig. 1.

It is interesting to compare the present results with a previous study [6] where Ar photoion spectra were measured in coincidence with K - LL and K - LM Auger electrons in order to ensure that primary vacancies were in the K shell. These challenging electron-ion-coincidence measurements permitted a detailed view of PCI effects on individual charge states in Ar. In the present experiment, the data-analysis procedure outlined below permits isolation of PCI effects in the Cl K shell of HCl using simpler noncoincidence measurements. Because HCl is isoelectronic with Ar, it is not unreasonable to expect that when the molecule fragments into H^+ and Cl^{n+} the relaxation processes may be similar to those that lead to $\text{Ar}^{(n+1)+}$. We see this upon examination of the Cl^{2+} PIY (Fig. 1); one can observe that this charge state essentially appears only due to resonant enhancement below threshold and photoelectron recapture by Cl^{3+} just above threshold. Outside of this narrow energy region, and particularly at higher energies, little or no Cl^{2+} yield is apparent. This result is similar both qualitatively and quantitatively to

the Auger electron-ion-yield measurements of the Ar^{3+} charge state in the Ar K -shell threshold region [6].

In the region just above the K -shell threshold at 2829.8 eV, each Cl^{n+} PIY is affected by two PCI-induced electron-recapture effects: a decrease resulting from the loss of Cl^{n+} ions to the $\text{Cl}^{(n-1)+}$ charge state, and an increase arising from $\text{Cl}^{(n+1)+}$ ions recapturing electrons to become Cl^{n+} . For example, the yield of Cl^{4+} will be reduced by Cl^{4+} ions that recapture electrons and become Cl^{3+} , but will be augmented by Cl^{5+} ions that recapture and become Cl^{4+} . In order to isolate the recapture effect on each charge state, we first assume that because the Cl^{6+} yield is negligible, PCI trends in the Cl^{5+} PIY [Fig. 2(a)] reflect only the loss of Cl^{5+} ions through electron recapture. Thus, an estimate of the Cl^{5+} relative recapture cross section at energies just above threshold is obtained from the Cl^{5+} PIY by subtracting the near-threshold PIY values from the asymptotic Cl^{5+} yield. The asymptotic yield was taken as the average of the data points around 7 eV, above the energy regime where PCI effects are most prevalent, but below the energy where double-ionization effects begin. This recapture cross section for Cl^{5+} is then subtracted from the Cl^{4+} PIY to give an adjusted PIY curve with the contribution of Cl^{5+} recapture removed [Fig. 2(b), circles]. The procedure is then repeated using each adjusted PIY curve, in turn, to isolate the recapture effect on each Cl^{n+} charge state.

In order to interpret the results in Fig. 2, we have attempted to reproduce the modified PIY curves using electron escape probabilities calculated with a hydrogenic model using a core-hole width $\Gamma = 0.6$ eV [28]. The hydrogenic model is based on the assumption that once a K -shell hole localized around the Cl atom is created, the intermediate states are localized far from the molecule (i.e., $\langle r \rangle \geq 50$ a.u.). Thus the structure of the core is unimportant, and the electron in the excited state “sees” an HCl^+ ion. The escape probabilities plotted in Fig. 2 were normalized to the PIY curves above threshold. Within the experimental uncertainties for Cl^{3+} , Cl^{4+} , and Cl^{5+} charge states, the data agree with the K -shell PCI curves, indicating that PCI recapture occurs in conjunction with K -shell Auger decay, and that the process of PCI recapture for the Cl^{n+} ions in HCl is similar to that observed in ions formed following relaxation of excited atomic species. The disagreement between the model and the data for the first two eV above threshold is at least partially explained by the excitation of the Cl K electron to Rydberg orbitals, and the photon and natural linewidths. It is also clear from the modified PIYs for Cl^{2+} and Cl^+ (not shown) that, within our uncertainties, the Cl^{2+} ion does not typically recapture an electron to become Cl^+ . The same can be said for the recapture of an electron by Cl^+ to become a neutral. Our inability to observe electron recapture by the lower charge states is in part a result of the low K -shell-related intensity for these charge states above threshold and in part a result of the fact that Cl^+ and Cl^{2+} are formed primarily through x-ray emission, and, as a result, cannot show a K -shell PCI-recapture effect because the system does not relax through a Cl K -shell Auger decay.

Figure 3 shows the PIY for H^+ (circles) following K -shell photoexcitation and the TIY (diamonds) normalized to

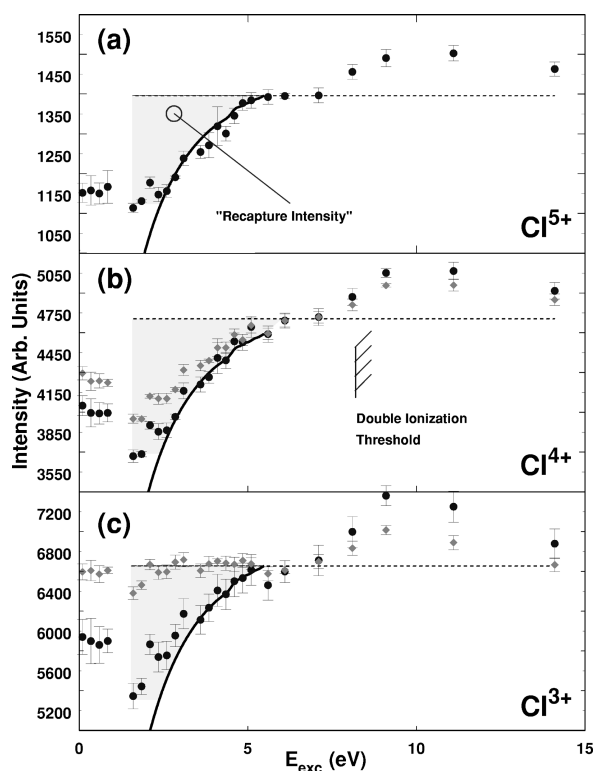


FIG. 2. (a) Partial ion yield (circles) for Cl^{5+} . (b) Partial ion yield (diamonds) and partial ion yield modified for PCI recapture (circles) for Cl^{4+} . (c) Partial ion yield (diamonds) and partial ion yield modified for PCI recapture (circles) for Cl^{3+} . The solid line represents the hydrogenic model for PCI following K -shell Auger electron ejection. No modifications were made to the Cl^{5+} yield because the Cl^{6+} yield was negligible. The dashed line represents the asymptotic limit for single electron ionization. The shaded region represents the loss in intensity as a result of PCI recapture.

the H^+ PIY. The yield for H^+ increases with energy just above threshold similar to, but over a shorter energy range than, the yields for the Cl^{n+} ($n \geq 3$) charge states. Comparison to the TIY for HCl indicates that this is not merely a result of a change in cross section for K -shell excitation of the HCl molecule. Because of the atomiclike PCI behavior for the Cl^{n+} ions it seems that a likely explanation for the data is recapture of the photoelectron by H^+ following dissociation of the molecule, suggesting that the H^+ fragment also is involved in PCI, occasionally recapturing the Cl $1s$ photoelectron. This marks an observation of PCI-mediated fragmentation, where the photoelectron is recaptured by an ion around which the initially excited orbital is not localized.

Comparison of the H^+ yield to the hydrogenic model, as well as to a semiclassical model [13] for PCI shows a clear deviation of the data from PCI theory. This is hardly surprising because the empirical formula is based on the assumption that the electrons are receding in a spherical Coulombic potential. This is not the situation at the time of Auger decay due to perturbations in the potential well resulting from the close proximity of the H^+ ion, and the fact that recapture by H^+ is a molecular effect, and is not included in the current models; an entirely different physical effect is being observed.

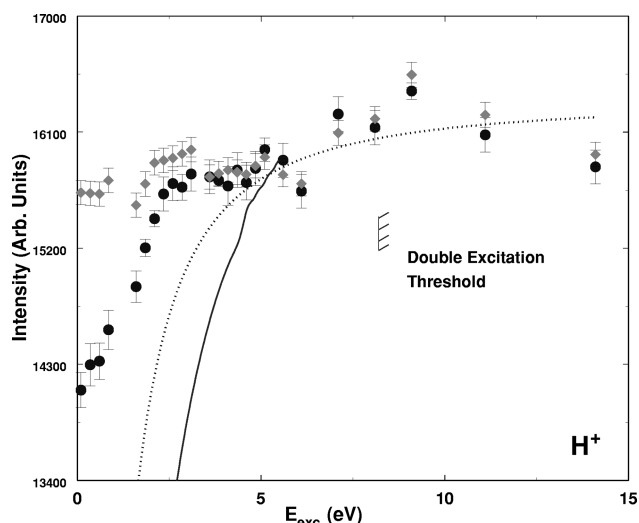


FIG. 3. Partial ion yield for hydrogen (circles), and total ion yield for HCl (diamonds). The TIY has been normalized to the H^+ PIY in order to facilitate comparison. The solid line represents the hydrogenic model for PCI following K -shell Auger electron ejection, the dotted line represents a semiclassical model.

The possibility that the photoelectron is recaptured while the hydrogen atom is still part of the molecule is worthy of mention. The H^+ PIY shows the greatest deviation from the TIY in the first 2.5 eV above resonance. We previously noted that the PIYs for the Cl^{n+} ions did not follow the PCI curves in this energy regime and attributed it to excitations to Rydberg orbitals, coupled with photon and natural linewidths. In most cases, if the photoelectron is recaptured in a molecular orbital, the molecule will still dissociate, and because of its higher electronegativity, the Cl^{n+} ion would most likely retain the electron instead of the hydrogen. This process produces an identical result to the case where recapture by $\text{Cl}^{(n+1)+}$ follows fragmentation. An exception to this may arise if the electron is recaptured in an antibonding orbital, leading sometimes to neutral dissociation, as observed previously following resonant excitation to the $6\sigma^*$ orbital [26]. In addition, in cases where the photoelectron is ejected in the direction of the H^+ ion, it is possible for recapture by H^+ to occur whether or not an Auger electron is emitted. Regardless of the explanation(s) for the PCI effect on the H^+ PIY, it is clear that a different physical effect, unexplainable by conventional models of PCI, has been observed.

In conclusion, time-of-flight mass spectroscopy was used to study the relaxation dynamics of HCl following photoexcitation of the Cl K shell. Following a straightforward analysis of the data, partial ion yields for Cl^{3+} , Cl^{4+} , and Cl^{5+} were found to agree with a hydrogenic model of PCI, while for H^+ it did not. This indicates that while this PCI model was developed for recapture of a photoelectron following core-shell excitation in atoms, the model also can be extended to apply to photoexcitation of molecules at deep core levels when the orbital is localized on the ionic fragment under study. However, for fragments around which the orbital is not localized, current PCI models are inapplicable.

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