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Neutral dissociation of hydrogen following photoexcitation of HCl at the chlorine K edge

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Time-of-flight mass spectroscopy was used to study the relaxation dynamics of HCl following photoexcitation in the vicinity of the Cl K edge (~ 2.8 keV) using monochromatic synchrotron radiation. At the lowest resonant excitation to the $6\sigma^*$ antibonding orbital, almost half of the excited molecules decay by emission of a neutral H atom, mostly in coincidence with a highly charged Cl^{n+} ion. The present work demonstrates that neutral-atom emission can be a significant decay channel for excited states with very short lifetimes (1 fs). [S1050-2947(98)03604-X]

Application of mass spectroscopy and coincidence techniques to photoexcited atoms and molecules has begun to unravel some of the multitude of electronic and fragmentation decay pathways available to core-excited systems. Studies of Br M-shell excitation in HBr [1] gave evidence of the fast dissociation of a molecule into neutral fragments followed by atomic Auger decay. Subsequent studies found rapid neutral dissociation to be a decay mechanism in a number of other core-excited molecules [2–5] and, more recently, estimates of the branching ratios between ''molecular'' and ''atomic'' Auger decays have been made [6]. Essentially all of these measurements focus on shallow-core levels (e.g., Br $3d$ and Cl $2p$), defined herein as levels in which a core hole can decay electronically only through interactions with valence-shell electrons. In contrast, holes in deeper core levels (e.g., Cl $1s$) have shorter lifetimes and typically relax by means of a stepwise series of decays known as a vacancy cascade, where the initial decay step usually creates one or more shallow-core holes leading to highly charged residual ions [7].

As a simple diatomic with deep-core electrons, HCl was chosen for the present experiment because the core-level spectroscopy is well understood [8] and because of the relatively few ion fragments possible, facilitating interpretation of the subsequent mass spectra. Also, electron-spectroscopy measurements for the shallow-core Cl $2p$ level of HCl [3,6] as well as ion-spectroscopy measurements of the K shell of Ar [9,10], which is isoelectronic with HCl, are available for comparison. One conclusion from the shallow-core measurements on HCl was that excitation of a Cl $2p$ electron to the lowest antibonding molecular orbital ($6\sigma^*$) can lead to dissociation of neutral hydrogen in competition with electronic decay modes. Upon similar excitation of a Cl $1s$ electron we also find this to be a significant decay pathway. This result seems rather surprising considering the Cl K-hole lifetime is only 17% that of a Cl $L_{2,3}$ hole. Neutral dissociation occur-

ring competitively with Cl K Auger decay would be the fastest neutral-atom dissociation observed in photofragmentation to date.

The experiments were performed using x-ray synchrotron radiation (SR) from beamline 9.3.1 at the Advanced Light Source (ALS) in Berkeley, California [11,12] and beamline X-24A at the National Synchrotron Light Source (NSLS) in Brookhaven, New York [13,14]. An ion time-of-flight (TOF) mass spectrometer, comprised of five cylindrical regions of differing length and electric-field strength, was used to measure charge distributions of photoions produced following x-ray absorption. In the first (extraction) region, a grounded needle served as an effusive source for the gas through which the x-ray beam is focused. Voltages on all regions were selected to achieve maximum time resolution by satisfying space-focusing conditions [15]. Ions formed in the extraction region of the analyzer were accelerated toward a dual microchannel plate assembly, which provided an electron cascade with a gain of about 10^6. The signal was then further amplified and timing information, related to the pulsed SR, was extracted. Acceleration voltages and discriminator settings were selected to ensure uniform detection efficiency for all ions and charge states.

Photon-energy calibration is achieved by scanning the monochromator through the Cl $1s$ threshold region while monitoring total-ion yield (Fig. 1) with the TOF analyzer. Comparing features, particularly subthreshold resonances, in these absorptionlike spectra to previously measured photoabsorption results [8] determines the photon energy with an accuracy of 0.2 eV. The calibration is checked periodically over the course of the experiment to compensate for small drifts (<1 eV) primarily caused by heating of the first crystals of the monochromators [14].

The first peak (2823.9 eV) in Fig. 1 corresponds to the 1σ (Cl $1s$)$\rightarrow 6\sigma^*$ transition, where $6\sigma^*$ designates the lowest unoccupied molecular orbital, which in this case is antibond-
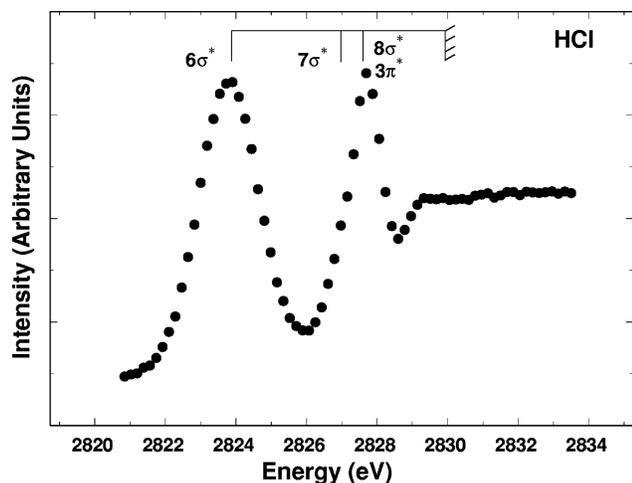
FIG. 1. Total-ion-yield spectrum for HCl.

ing. The second peak is the result of contributions from a number of Rydberg-like excitations. The Cl K threshold at 2829.8 eV is indicated in the figure.

Two modes of operation are used to collect ion-TOF data. In the "singles" mode, spectra (Fig. 2) are collected with the storage rings operating with only one or two electron bunches. The start pulse for the timing circuit is provided by the detection of an individual ion, while the ring timing pulse, produced by the periodic pulsing of the SR (328 ns for ALS 2-bunch, 567 ns at NSLS), provides the stop signal. Thus the ion-TOF spectra are inverted relative to actual flight times (i.e., slower ions appear to the left). In addition, because the ALS operates in 2-bunch mode, peaks due to the slowest ions "wrap around" in the narrower time window (Fig. 2).

In the second mode of operation, two ions from the same molecule provide the start and stop signals for the timing circuit (in this case, H^+ provides the start and Cl^{n+} provides the stop). Thus the difference in flight time between the two
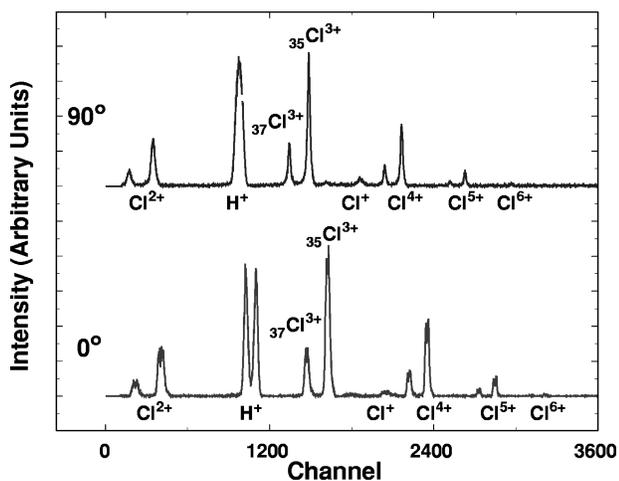

FIG. 2. TOF spectra of HCl taken on the $1\sigma \rightarrow 6\sigma^*$ resonance with the analyzer axis parallel (0°) and perpendicular (90°) to the polarization vector of the SR at the ALS. Two isotopes of chlorine are visible, as well as double peaking of hydrogen ions in the 0° orientation, which results from resonant alignment of the molecule. Different peak positions in the two spectra result from unimportant differences in the extraction conditions.
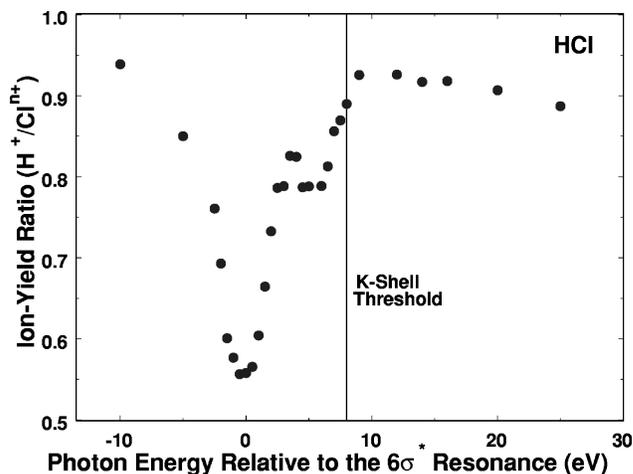

FIG. 3. Ratio of hydrogen ions detected to the sum of all chlorine ions detected in singles mode.

ions is measured and the operation mode of the storage ring is irrelevant. These photoion photoion coincidence (PIPICO) measurements inherently discriminate against decay processes where the molecule does not dissociate or where the molecule dissociates but one of the fragments is neutral.

Singles and PIPICO spectra were taken at a number of photon energies in the Cl K-shell region. Peaks in these spectra were integrated in order to calculate fractional yields as a function of energy. Results from the singles spectra are shown in Figs. 3 and 4, while the results for the PIPICO spectra are shown in Fig. 5.

The most prominent feature in Figs. 3 and 4 is the dip in the fraction of hydrogen produced on the $6\sigma^*$ resonance. Figure 3 shows a drop in the $I(H^+)/I(Cl^{n+})$ ratio of about 40% (Cl^{n+} denotes the sum of all chlorine charge states detected). All but one possible fate of the missing hydrogen ions can be ruled out. One possibility is that fewer H^+ ions appear on resonance because dissociation occurs less often. However, if hydrogen remains part of the HCl molecule and the molecule forms a molecular ion, then HCl^{n+} peaks would be seen in the singles spectra. Analysis shows that
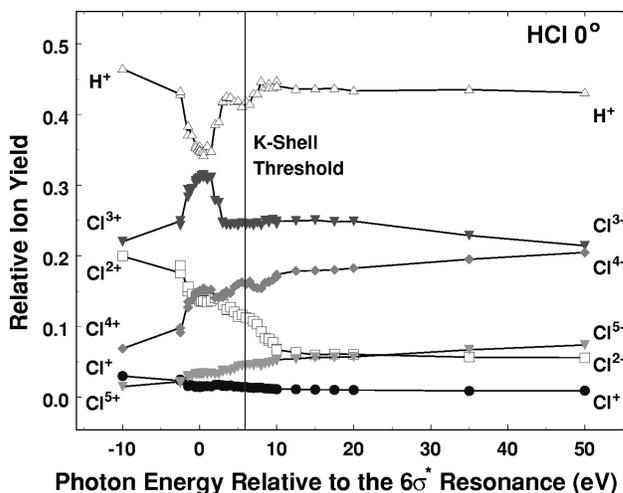

FIG. 4. Relative ion yields for HCl singles spectra with the analyzer oriented parallel to the polarization vector of the light (0° orientation).
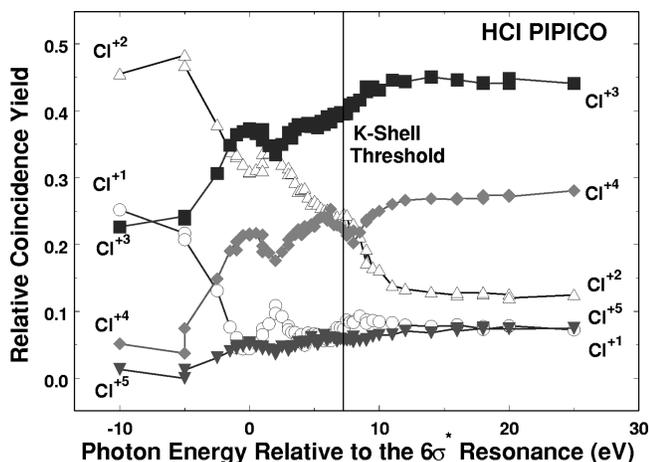
FIG. 5. Relative coincidence yields for HCl PIPICO spectra (0° orientation).

HCl$^+$ yields are consistently less than 1% of all ions detected, too small to explain the dip in H$^+$ yield. On the other hand, if the molecule remains intact and neutral, then it also would escape detection. Only radiative decay of the resonantly excited state could produce uncharged molecules and the radiative yields for such processes are known to constitute less than 1% of the possible decay processes of Cl K holes [16]. In addition, any process that leaves an intact HCl molecule would exhibit a matching decrease in Cl^{n+} yields, which is clearly not the case. So resonant excitation leads primarily to dissociation.
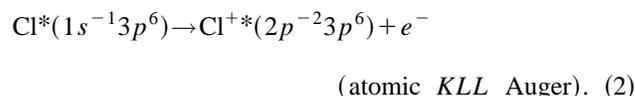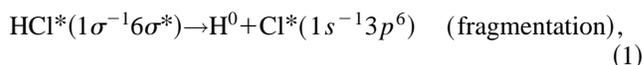
For resonant photofragmentation producing a H$^+$ ion, the 0° TOF spectra show a splitting in the H$^+$ peak (Fig. 2), which can be explained as follows. The molecules in the gas jet are randomly oriented, but because of the well-defined symmetry of the excited orbital (i.e., $6\sigma^*$), molecules that have their axes parallel to the polarization vector of the SR preferentially interact with the incident photons. Because decay and dissociation of the molecule occur rapidly compared to the rate of molecular rotation, fragments are ejected along the molecular axis, and the double peaks reflect orientation of the molecule following excitation. (This effect will be dealt with more completely in the future.)

It is possible that this angular-distribution effect is sufficient to enable H$^+$ ions to escape extraction and detection by the analyzer. Two tests were done to examine this possibility. First, the ratio of H$^+$ to Cl^{3+} was measured for extraction voltages in the interaction region as high as 2.2 kV/cm and as low as 1 kV/cm (data in Figs. 2–5 were collected at approximately 2 kV/cm) at photon energies both on resonance and just above threshold. In all cases, as the extraction voltage was changed, the $I(\text{H}^+)/I(\text{Cl}^{3+})$ ratio did not change significantly, strongly suggesting that extraction efficiency is unaffected by the on-resonant angular distrubutions. Second, the measurements were performed with the analyzer parallel and perpendicular to the polarization vector of the SR beam. For the parallel orientation, the two peaks that result from H$^+$ ions being ejected toward and away from the detector have identical intensities within experimental error, indicating that the collection efficiencies for ions ejected in either direction are equal. With the analyzer in the perpendicular orientation, H$^+$ ions are ejected perpendicular to the detector
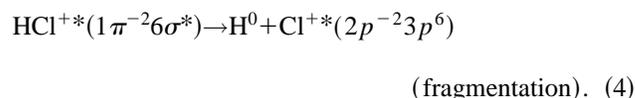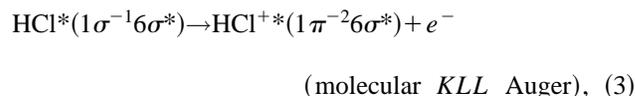
axis, presumably making it more likely that the extraction voltage would be insufficient to collect all the H$^+$ ions. However, the data show that the relative H$^+$ yields on resonance and above threshold are the same for both orientations of the analyzer. In addition, simulations indicate that at the nominal operating extraction voltages, there would be no angular discrimination against H$^+$ ions ejected with less than 50 eV kinetic energy. We conclude that H$^+$ ions are not escaping the extraction fields of the TOF analyzer. Thus the only plausible explanation of the dip in H$^+$ yield on the $6\sigma^*$ resonance is the dissociation of HCl, yielding neutral atomic hydrogen, which the analyzer cannot detect. The magnitude of this effect is particularly surprising considering the short lifetime of a Cl K-shell hole (1.1 fs) and that there is enough energy in the system to form highly charged chlorine ions (up to Cl^{6+}).

Corresponding to the decrease in the H$^+$ yield is an increase in the relative yields of Cl^{3+} and Cl^{4+} (Fig. 4), suggesting an association with formation of neutral hydrogen on resonance. This hypothesis is confirmed by the HCl PIPICO yields (Fig. 5). While for the singles spectra (Fig. 4) the yield of Cl^{3+} ions is greater on resonance than above threshold, the PIPICO spectra show that the coincidence yield between H$^+$ and Cl^{3+} on resonance is lower than the coincidence yield above threshold (Fig. 5). This is expected if the neutral hydrogen is being ejected in coincidence with Cl^{3+}; coincident detection of an ion pair is impossible, therefore reducing the coincidence yield on resonance.

These results suggest one or some combination of the following types of decay paths following resonant excitation of HCl:

$$\text{HCl}^*(1\sigma^{-1}6\sigma^*)\rightarrow\text{H}^0+\text{Cl}^*(1s^{-1}3p^6) \quad \text{(fragmentation)},$$
$$(1)$$

$$\text{Cl}^*(1s^{-1}3p^6)\rightarrow\text{Cl}^{+*}(2p^{-2}3p^6)+e^-$$

$$\text{(atomic } KLL \text{ Auger). } (2)$$

Auger decay of the two L-shell holes leads to the formation of a Cl^{3+} ion. Dissociation prior to relaxation of the K-shell hole is the key point in this mechanism. Another option is Auger decay of the Cl K-shell hole prior to dissociation of the molecule:

$$\text{HCl}^*(1\sigma^{-1}6\sigma^*)\rightarrow\text{HCl}^{+*}(1\pi^{-2}6\sigma^*)+e^-$$

$$\text{(molecular } KLL \text{ Auger), } (3)$$

$$\text{HCl}^{+*}(1\pi^{-2}6\sigma^*)\rightarrow\text{H}^0+\text{Cl}^{+*}(2p^{-2}3p^6)$$

$$\text{(fragmentation). } (4)$$

From the present experiments, it is impossible to determine which of these paths is more probable. The higher electron density around the H atom in the excited σ^* orbital, coupled with the fact that the H atom has very little time to move during the lifetime of the core hole, opens up the possibility that the excited electron in the σ^* orbital remains as a spectator electron, localized around the H atom. The spectator electron that is not ejected in the subsequent Auger decay thus allows the H atom to fragment as a neutral atom.

Electron spectroscopy of the *KLL* Auger electrons would reveal if the Auger decay takes place from an atomic or molecular species and in the case of molecular decay if the electron in the σ^* orbital is a spectator or participator in the Auger decay, thus determining if the dissociation of the molecule occurs on the same time scale as the Auger decay. Studies done at the Cl *L* edge of HCl [3] indicate that at the Cl $2p \rightarrow 6\sigma^*$ resonance, dissociation followed by Auger decay of the atomic Cl fragment is the dominant decay path. However, the fact that a Cl *K*-shell hole has a shorter lifetime than an *L*-shell hole by a factor of about 6 [for a *K*-shell hole, the lifetime $\Gamma = 0.6$ eV (1.1 fs); for an *L*-shell hole, $\Gamma = 0.1$ eV (6.6 fs) [16]] may allow Auger decay to compete more favorably as the first step in the decay process.

In conclusion, following photoexcitation of a Cl *K*-shell electron in HCl to the $6\sigma^*$ antibonding orbital, a significant decrease in the amount of H^+ observed is attributed to an increase in the amount of neutral hydrogen dissociation. The increase in neutral hydrogen corresponds to an increase in the amount of Cl^{3+} detected. Observation of a decrease in the amount of Cl^{3+} detected during PIPICO measurements confirms this interpretation. While electron spectroscopy is required to conclusively determine the decay mechanism, the present results suggest that the dissociation time for resonantly excited HCl may be competitive with the 1-fs electronic decay time of a Cl *K*-shell hole.

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