Femtosecond Dissociation of Core-Excited HCl Monitored by Frequency Detuning

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Core excitation of gaseous HCl to the dissociative σ^* state leads to a deexcitation spectrum with two qualitatively different contributions—a broad molecular background and narrow atomic lines. The experiment demonstrates that the ratio of integrated intensities from these two contributions depends crucially on the excitation frequency; the molecular background is enhanced with increased detuning of the photon frequency. This is discussed in a time-dependent model, using the concept of an effective duration time for the resonant x-ray scattering process. [S0031-9007(97)04296-8]

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The development in synchrotron instrumentation has recently enabled Auger electron and x-ray emission studies with selective, resonant excitation using tunable narrow bandpass radiation [1–5]. Despite this progress, truly time-resolved measurements, which now are standard in optical laser spectroscopy, are not possible to carry out for the resonant x-ray scattering (RXS) processes owing to the very short lifetimes of core excited states and to the—for this purpose—still insufficient intensity. However, the uncertainty relation indicates a principal possibility to obtain indirect information on the time-dependent dynamics of the RXS process even by a stationary measurement, namely, at a time scale set by the inverse of the detuning frequency (Ω), that is, the frequency difference between the excitation and the x-ray absorption resonance maximum. This idea has recently been realized by introducing the concept of a duration time of the RXS process [6,7] expressed as $\tau_c = (\Omega^2 + \Gamma^2)^{-1/2}$, where Γ is the lifetime of the core-excited state. According to this relation the RXS duration time can be varied with help of the excitation frequency. This concept has recently been used to understand the suppression of the slow nonadiabatic symmetry-breaking process (symmetry restoration) in CO_2 [6,7] and the suppression of the rearrangement of the nuclear wave packet on the core-excited potential surface (collapse effect) in CO [8,9].

In the present work we demonstrate another experiment which makes it possible to test the concept of a *duration time* of the RXS process in an intuitively appealing way, namely, by using a species with a repulsive intermediate core-excited state. This leads to an interplay between the time scales of RXS duration versus dissociation which is possible to study experimentally. Core excitation of small molecules with repulsive intermediate states, such as HBr, HCl, or H_2S, has been shown to lead to dissociation of the molecule on the same time scale as the core hole state lifetime, i.e., a few femtoseconds [10,11]. This is manifested in two contributions to the Auger spectra: sharp lines from "slow" decays taking place when the influence of the outgoing neutral fragment is negligible, and broad features from "fast" decays taking place in intermediate geometries during the dissociation [11–14]. The concept of duration time has been used to theoretically predict [15] that the experimental Auger spectra involving such dissociative core-excited states showing molecularlike and atomiclike transitions will be highly dependent on the detuning frequency as schematically indicated in Fig. 1. In this Letter we present an experimental verification of this theory and thus a direct evidence of the validity of the concept of a duration time for the RXS process.

The experiments were performed at beam line 51 of MAX-LAB, the Swedish synchrotron radiation facility [16,17]. All the Auger spectra were recorded with an electron kinetic energy resolution of ≈0.3 eV, and a photon energy resolution of ≈85 meV, except for the spectrum with 2.0 eV detuning, for which a photon energy resolution of ≈170 meV was used due to intensity reasons. The HCl gas was produced by a reaction between solid NaCl

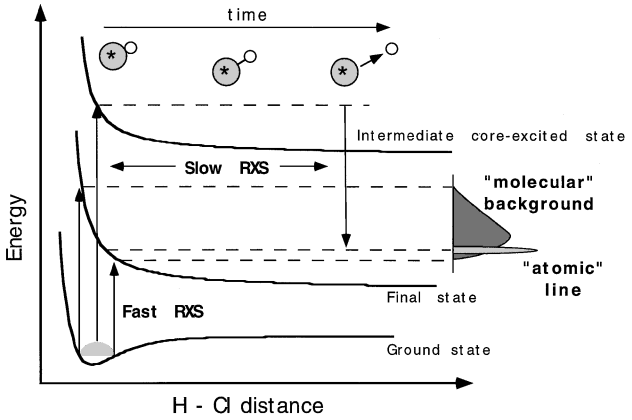

FIG. 1. A simple picture of the formation of the atomic and molecular line profiles in resonant x-ray scattering spectra involving a dissociative core-excited state.

and hydrochloric acid, and was found free of contaminants by on-line valence photoelectron spectroscopy.

Resonant Auger spectra were recorded for excitation to the $2p^{-1}\sigma^*$ state. The corresponding x-ray absorption spectral feature is a broad structure due to the dissociative nature of the state, and the existence of the partly overlapping $2p_{3/2}$ and $2p_{1/2}$ spin-orbit components [18]. As the energy width of the exciting radiation was $\approx$85 meV, i.e., substantially smaller than the $\approx$1 eV width of each spin-orbit component, this allowed selective excitation on top of the resonance as well as at various off-resonance energies, corresponding to detunings Ω ranging from -2.0 to $+0.74$ eV relative to the resonance maximum. Because of the overlap between the $2p_{3/2}$ and $2p_{1/2}$ resonance components, the spectra for negative and positive Ω were recorded on the low energy flank of the $2p_{3/2}$ and high energy flank of the $2p_{1/2}$ component, respectively. The corresponding shift in kinetic energy, equaling the spin-orbit splitting of the Cl $2p$ level, has for the sake of simplicity been removed from the $\Omega = +0.74$ eV spectrum in Fig. 2.

The resulting Auger spectra are shown in Fig. 2. The on resonance, i.e., $\Omega = 0$ eV, spectrum is very similar to earlier broad band excited spectra [11,13]. The spectrum consists of two types of features: broad features resulting from decay in intermediate geometries of the dissociating "molecular" H-Cl* species and three sharp spectral lines from decay in the dissociated "atomic" Cl* species. Apart from the final states of the Auger decay the spectra also include lines produced by off-resonance photoemission ($5\sigma^{-1}$ and a $^2\Sigma^+$ satellite [19]), which become more prominent with increasing detuning. Neither any contributions in the region of the Auger final states from photoemission nor any enhancement of the photoemission final states on resonance could be detected. For the present purpose, it is thus sufficient to treat the resonant Auger and direct photoemission channels as separate, with no appreciable interference between them. The narrow atomic lines can be assigned to the following final states of the Cl$^+$ ion: $A = {}^1S$, $B = {}^1D$, and $C = {}^3P$, Fig. 2. These atomic states correspond to the following final molecular states of the HCl$^+$ ion, ^1S: $^2\Sigma^+$, ^1D: $^2\Delta, {}^2\Sigma^+, {}^2\Pi$, and ^3P: $^4\Sigma^-, {}^2\Sigma^-, {}^4\Pi$ [18].

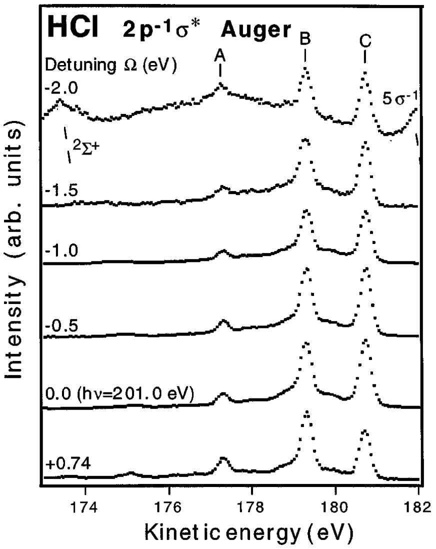

FIG. 2. Experimental resonant Auger spectra, showing the $2p_{3/2}^3 3p^6 \rightarrow 3p^4$, $2p_{1/2}^1 3p^6 \rightarrow 3p^4$ region of the atomic Auger decay transitions in HCl as function of detuning.

As seen in Fig. 2 the Auger spectra are markedly altered as the photon energy is detuned from the resonance energy: the broad molecular features resulting from decay in the dissociating H-Cl* species are enhanced relative to the sharp spectral lines from decay in the dissociated atomic species. While the kinetic energies of the atomic Cl* lines remain fixed, the broad molecular background shifts with the photon energy.

In order to quantify the intensity variations, the spectra were fitted using sharp lines for the atomic decays and broad bands for the molecular background. The position, shape, and intensity ratios of the atomic lines were kept fixed in order to perform the fitting as consistently as possible. The result presented in Fig. 3 shows that the molecular fraction increases with increased detuning, both in the negative and positive directions.

The observed behavior can be viewed as due to an interplay between two time-dependent processes: the RXS process, governed by the duration time, and the dissociation process, governed by the effective mass of the system and the slope of the dissociative potential energy surfaces. Auger decay of the core-excited state takes place at all internuclear distances R. However, the analysis in Ref. [15] shows that two regions are mainly responsible for the spectral shape: the molecular region with R close to the equilibrium ground state geometry R_o, where the neutral fragment strongly interacts with the core-excited fragment ($R \sim R_o$, fast RXS), and the atomic region with large R, for which the interaction is negligible ($R = \infty$, slow RXS). In the case of the dissociative core-excited state $|c\rangle$ (or core

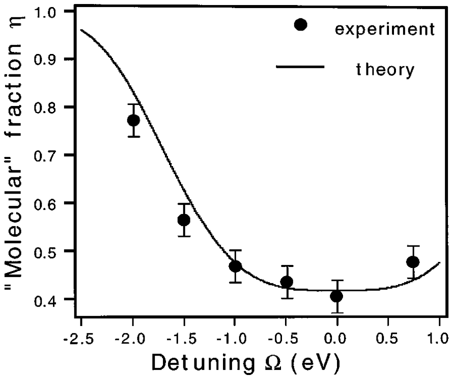

FIG. 3. Comparison of the experimental and theoretical fraction η of the molecular background to the total Auger intensity.

excitation above dissociation threshold) the nonradiative (Auger) RXS cross section consists of two qualitatively different parts

$$\sigma(\varepsilon,\omega) = \sum_f |F_f|^2 = \sum_f [\sigma^f_{\mathrm{at}}(\varepsilon,\omega) + \sigma^f_{\mathrm{mol}}(\varepsilon,\omega)]. \tag{1}$$

The first contribution is caused by the decay transition with energy ε to the final state $|f\rangle$ in the dissociated region and corresponds to the slow RXS [15]. The spectral shape of this cross section is close to a Lorentzian [5,15]

$$\sigma^f_{\mathrm{at}}(\varepsilon,\omega) = \frac{\sigma}{[\varepsilon - \omega_{cf}(\infty)]^2 + \Gamma^2} e^{-(\Omega/\gamma_c)^2} \tag{2}$$

if the lifetime width Γ of the core-excited state is smaller than the width of the absorption Franck-Condon distribution, γ_c. Here $\Omega = \omega - \omega_{co}(R_o) + \mathcal{F}_c a_c$ is the detuning from the vertical photoabsorption transition, $\mathcal{F}_c a_c$. $\omega_{co}(R_o) = U_c(R_o) - E_o$ and $\omega_{cf}(R) = U_c(R) - U_f(R)$. $\mathcal{F}_i = -[dU_i(R)/dR]_{R_o}$ is the interatomic force at the equilibrium point R_o of the ground state. $\gamma_i = \mathcal{F}_i a$, where $a = (\mu\omega_o)^{-1/2}$ is the size of the ground state vibrational wave function with ω_o as vibrational frequency and $a_i = (2\mu\mathcal{F}_i)^{-1/3}$. All unessential quantities are collected in the constant σ.

The spectral profile of the broad molecular background $\sigma^f_{\mathrm{mol}}(\varepsilon,\omega)$ is formed by Auger decays occurring in the molecular region. The main features of this background can be understood in the limiting case; $\tau_c \ll \tau$, where $\tau \sim \gamma_c^{-1} \sim \Delta^{-1}$ has the meaning of the time of the rearrangement of the nuclear wave packet on the core-excited potential surface $U_c(R)$ with Δ as the effective width of the corresponding x-ray absorption spin-orbit component. When the RXS process is fast the RXS amplitude is proportional to the Franck-Condon amplitude [7,8,15] $F_f \propto \langle \varphi_{E_f} \mid \varphi_o\rangle/(\Omega - \imath\Gamma)$ between the nuclear wave functions of ground $|\varphi_o\rangle$ and final $|\varphi_{E_f}\rangle$ states, where $E_f = \omega + E_o - \varepsilon$. This means that the RXS process can be considered as "vertical" or "sudden." The spectral shape of the molecular background can in the fast limit approximately be written as [15]

$$\sigma^f_{\mathrm{mol}}(\varepsilon,\omega) = \exp\left[-\left(\frac{\varepsilon - \omega_{cf}(R_o) - \Omega + \delta}{\gamma_f}\right)^2\right] \times \frac{\sigma\,\beta_f}{(\Omega - \mathcal{F}_c a_c)^2 + \Delta^2}, \tag{3}$$

where $\delta = \mathcal{F}_c a_c - \mathcal{F}_f a_f$. We here used a harmonic approximation for $\varphi_o(R)$ and a linear approximation of the core-excited state potential $U_c(R)$ near the point of the vertical transition R_o. It can be shown (see Fig. 1) that the spectral profile (3) is essentially asymmetric if the nonlinearity of $U_o(R)$ is taken into account. The dimensionless constant β_f is of the order of 1, and is here considered as a fitting parameter. For a dissociative final state the spectral shape of $\sigma^f_{\mathrm{mol}}(\varepsilon,\omega)$ is in the limit of fast RXS ($\tau_c \ll \tau$) given by a Gaussian with the width γ_f.

There are important differences between the molecular and the atomic parts of the RXS cross section. The energy positions of the atomic lines (2) do not depend on the excitation energy, while the energy position of the center of gravity of the molecular background (3) approximately follows the Raman-Stokes dispersion law [15,20], exhibiting a linear photoemissionlike dependence on the excitation energy as experimentally observed. Another striking peculiarity of RXS through dissociative states is the increase of the contribution in the molecular region to the RXS cross section as the excitation energy is tuned from the resonant frequency of the vertical photoabsorption transition [8,15]. This means that the relative intensity of the atomic lines (2) decreases if $|\Omega| \gg \Delta$. This result follows directly from the strict expression for the amplitude for fast scattering, where the atomic contribution is exactly equal to zero [15]. Qualitatively, this can be described as being due to the shortening of the duration time with increased detuning, giving the molecule less time to dissociate before the Auger decay.

To give a quantitative description of the experimental Auger spectra a simplified model with only three final molecular states i with relative weights κ_i were used for the simulation. The molecular and atomic parts of the RXS cross section were approximated by the asymptotic formulas (3) and (2), respectively. The following values of fitting parameters were used: $\kappa_A = 0.24$, $\kappa_B = 0.9$, $\kappa_C = 1$, $\beta_f = 0.86$; $\bar{\gamma}_f = \Delta = 0.9$ eV, and the energy distance between the molecular and atomic contributions $\omega_{cf}(\infty) - \omega_{cf}(R_o) + \delta = 0.5$ eV.

The result of the simulations, depicted in Fig. 4, shows the total RXS profile as the sum of the three bands, each band consisting of the narrow atomic contribution with the lifetime width $\Gamma = 70$ meV and the molecular background with the full width at half maximum (FWHM) $2\bar{\gamma}_f = 2\gamma_f\sqrt{\ln 2} \approx 2$ eV. The relative strength of the

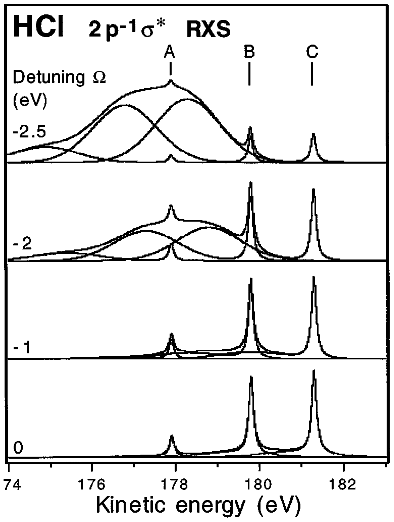

FIG. 4. Simulated RXS profiles as a function of detuning Ω.

molecular background increases with the absolute value of the detuning Ω, corresponding to a shortening of the RXS duration time $\tau_c \sim 1/|\Omega|$.

The simulations exhibit a striking qualitative correspondence to the experimental spectra; see Fig. 2. To make this comparison more quantitative, the relative contribution of the molecular part was calculated. This is defined as the ratio η of integral cross section $\sigma_{\mathrm{mol}}(\omega) = \sum_f \int d\varepsilon\, \sigma^f_{\mathrm{mol}}(\varepsilon, \omega)$ and $\sigma(\omega) = \sum_f \int d\varepsilon \times \sigma^f(\varepsilon, \omega)$. When γ_f, β_f, and ζ_f do not depend on f this ratio reads $\eta = z/(1 + z)$ with

$$z = \frac{\sigma_{\mathrm{mol}}(\omega)}{\sigma_{\mathrm{at}}(\omega)} = \frac{\gamma_f \Gamma}{\beta_f \Delta^2 \sqrt{\pi}} \xi(\Omega)\,, \qquad \xi(\Omega) = \frac{\Delta^2}{(\Omega - \mathcal{F}_c a_c)^2 + \Delta^2} e^{(\Omega/\gamma_c)^2}. \tag{4}$$

Such a comparison for the molecular fraction is given in Fig. 3. The correspondence between the theoretically derived and experimentally obtained values is very good.

In summary, using HCl we have presented direct experimental evidence of the double feature of resonant Raman scattering involving dissociative potentials, with a resonant Auger spectrum consisting of atomic lines on top of a molecular broad background. It is shown that the latter is greatly enhanced by detuning of the excitation frequency, and that, in contrast to the atomic lines, this behaves photoemissionlike, following a Raman-Stokes dispersion law. The enhancement of the molecular part of the experimental spectra is qualitatively and quantitatively explained using the concept of a shortened duration time for the RXS process upon frequency detuning. This points at interesting new possibilities to set time scales and obtain temporal information concerning femtosecond or even subfemtosecond dynamic processes by changing the duration time. Pending the realization of truly femtosecond-resolved measurements in the soft x-ray region, this method could be used to obtain otherwise inaccessible information.

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