Observation of a Continuum-Continuum Interference Hole in Ultrafast Dissociating Core-Excited Molecules

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(Received 7 March 2000)

The femtosecond dissociation of HCl after core excitation has been studied through the resonant Auger decay. The spectra contain contributions from decay occurring at both "molecular" and "atomic" internuclear distances. We have observed a new interference mechanism in these spectra: An atomic spectral line develops into a negative spectral contribution, a "hole," when detuning the excitation energy from the maximum of the Cl $2p^{-1}\sigma^*$ resonance. Resonant x-ray scattering theory quantitatively explains this behavior as due to a novel destructive continuum-continuum interference between molecular and atomic contributions to the Auger decay.

PACS numbers: 33.80.Eh, 33.70.Ca, 34.50.Gb

When exposing molecules to tunable synchrotron radiation, their electronic structure can be manipulated in different ways. Depending on the energy of the incoming photon an electron from either a valence or core level can be directly removed, or a core electron can be excited to an unoccupied valence orbital and subsequently undergo Auger decay. Many molecular core-excited states are dissociative or predissociative. In some cases the nuclear dynamics is so fast that dissociation occurs on the time scale of the Auger decay, i.e., a few femtoseconds, as first observed for HBr [1]. Such ultrafast dissociation of molecules can be thought of in a two-step picture: The first step is the excitation of a core electron from the ground state to a dissociative intermediate state whereby the molecule breaks apart, and the second step is an atomic autoionization via Auger decay [1]. It is statistically also possible that the Auger decay occurs before the molecule dissociates [2], and both possibilities are experimentally observed in the resonant Auger spectra [3,4]. The resonant Auger decay of ultrafast dissociating molecules exhibits a group of narrow atomiclike resonance lines from decay events in one of the dissociation products, and a smooth molecularlike background caused mainly by decay near the equilibrium distance of the molecule.

The two-step description, however, can be far too simple. It neglects the interplay between two time scales, the frequency-dependent duration time of the resonant x-ray Raman scattering (RXS) process and the dissociation time, which are both in the range of a few femtoseconds [4]. It also neglects any interference between the scattering channels. As predicted recently [5], the interference of the nondistinguishable channels in ultrafast dissociating molecules can drastically change the RXS spectral line shape and transform the narrow atomiclike peak into a narrow spectral hole for certain excitation energies. Although such interference processes subsequently have been supported by different theoretical approaches [6], experimental evidence has remained elusive.

Up to now several different interference phenomena have been described in core-level spectroscopy, for instance, Fano-type interference [7], i.e., the interference between a discrete state and a continuum, and lifetime-vibrational interference, i.e., interference between discrete states, in x-ray and Auger emission spectra [8,9]. The spectral hole considered here is caused by a fundamentally different type of interference effect, namely, by quantum interference of different continuum intermediate nuclear states [5].

We report in this Letter the first experimental observation of a continuum-continuum interference in resonant Auger decay spectra of ultrafast dissociating core-excited

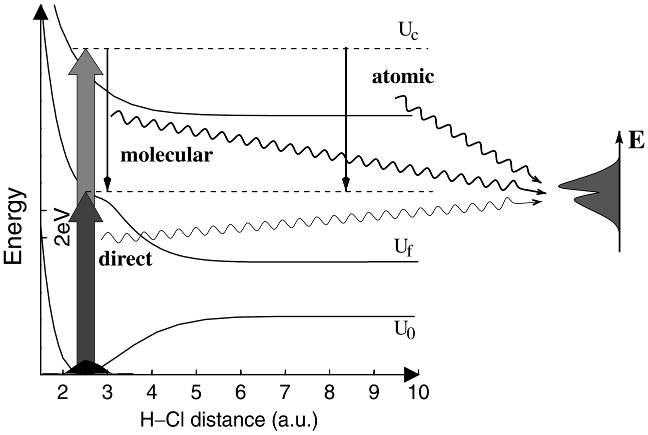

FIG. 1. Schematic figure illustrating interference of atomic-resonant, molecular-resonant, and molecular-direct term contributions to the total RXS cross section.

HCl. Although the direct photoemission channel is rather strong in the present case (see discussion below), it is sufficient for a qualitative description of this effect (Fig. 1) to consider only the resonant scattering channel. The incident x-ray photon excites a ground state nuclear wave packet to the repulsive intermediate state potential surface. During the propagation of this wave packet into the dissociation region, the core-excited system decays at different internuclear distances. These decay events cannot be strictly distinguished since they lead to the same final state, in this case an Auger electron and the H and Cl^+ fragments. We maintain, however, the nomenclature "molecular" and "atomic" features for the sake of simplicity, mainly on the ground of their different dispersion law (see discussion below). The molecular and atomiclike scattering channels interfere destructively for certain excitation energies and this gives rise to the observed spectral hole. In order to correctly describe this new phenomenon quantum mechanically one has to view the entire process as a one-step scattering event—with an incoming photon and an outgoing electron—and sum over all possible interfering scattering contributions. For dissociative core-excited and final states and monochromatic incident light, the RXS cross section is [5,9]

$$\sigma(E,\omega) \propto \left| S\langle \epsilon_f | 0 \rangle + \int d\epsilon_c \frac{\langle \epsilon_f | \epsilon_c \rangle \langle \epsilon_c | 0 \rangle}{E - \omega_{cf} + \imath\Gamma} \right|^2, \quad (1)$$

where S is the direct term strength parameter. S contains all the operators which have been factored out under the assumption that the transition matrix elements are independent of bond distance R. E and ω are the kinetic energy of the Auger electron and the frequency of the incident x-ray photon, respectively, Γ is the lifetime of the core-excited state, ϵ_c and ϵ_f are dissociation energies in core-excited and final states, respectively, and $\omega_{cf} = \epsilon_c + U_c(\infty) - \epsilon_f - U_f(\infty)$ (atomic units are used). Energy conservation implies $\epsilon_f = \omega + E_0 - U_f(\infty) - E$, where E_0 is the ground state molecular energy and $U_i(R)$ is the interatomic potential of electronic state i. The RXS cross section is here expressed in terms of Franck-Condon (FC) factors between final and core excited states, $\langle \epsilon_f | \epsilon_c \rangle$, and core-excited and ground states, $\langle \epsilon_c | 0 \rangle$. Contrary to the situation for transitions near the equilibrium geometry of the molecule, the kinetic energy of the Auger electrons will not change if the decay occurs in the dissociation region $\epsilon_f = \epsilon_c$ (Fig. 1). Indeed, the wave functions of the dissociation products are plane waves. Since the continuum-continuum FC factor $\langle \epsilon_f | \epsilon_c \rangle$ is singular, one can conclude that

$$\langle \epsilon_f | \epsilon_c \rangle \langle \epsilon_c | 0 \rangle = \mu + \alpha \delta(\epsilon_f - \epsilon_c) \quad (2)$$

consists of molecular (μ) and atomiclike or dissociated $[\alpha\delta(\epsilon_f - \epsilon_c)]$ contributions. Equations (1) and (2) imply that the scattering amplitude has a Fano-like [7] spectral shape, with F being the sum of smooth molecular, $\eta = \eta_1 + \imath\eta_2$, and singular atomiclike, $\alpha/(\Delta E + \imath\Gamma)$, contributions

$$F = \eta + \frac{\alpha}{\Delta E + \imath\Gamma}, \qquad \Delta E = E - [U_c(\infty) - U_f(\infty)]. \quad (3)$$

The functions η and α depend in general on the excitation energy [5]. The crucial point here is the interference between the molecular and the atomiclike contributions, σ_{int}, in the cross section (1)

$$\sigma(E,\omega) = |\eta|^2 + \frac{\alpha^2}{\Delta E^2 + \Gamma^2} + \sigma_{\text{int}}, \qquad \sigma_{\text{int}} = \frac{2\alpha(\eta_1 \Delta E - \eta_2 \Gamma)}{\Delta E^2 + \Gamma^2}. \quad (4)$$

Although there is a resemblance to the well-known Fano profile, there is a fundamental difference: For the atomiclike resonance no discrete state is present in either the core-excited state or in the final nuclear state.

The appearance of the discrete resonance in the RXS spectrum is due to the effective conservation of the kinetic energy under decay in the dissociation region, $\epsilon_c = \epsilon_f$, in Eq. (2). Apart from the evident asymmetry of the atomiclike profile, the interference leads to new striking spectral features: (i) The total suppression of the atomiclike resonance when $\eta_1 = 0$, $\eta_2 = \alpha/2\Gamma$ and (ii) a spectral hole akin to a "Fano window" emerges instead of the resonance peak when $|\eta_1| \ll |\eta_2|$ and $2\Gamma\eta_2\alpha > \alpha^2$.

The conditions for observing the hole are the following: (a) The photon energy must be chosen so that the molecular Auger electrons have the same kinetic energy as the Auger electrons emitted by the atomic fragments (i.e., the atomic peak is embedded in the molecular background); (b) the atomic contribution must be of the same order of magnitude as the molecular contribution; (c) the molecular and atomic contributions are out of phase.

The experiment was performed at beam line I 411 [10] connected to the third-generation synchrotron radiation storage ring MAX II at MAX-Lab in Lund, Sweden. This beam line is equipped with a modified Zeiss SX 700 PGM monochromator and with a rotatable hemispherical Scienta SES 200 high-resolution electron spectrometer. The monochromator resolution was varied from 20 meV down to 340 meV at a photon energy of 201 eV. The spectrometer resolution was 35 meV for all spectra. It is crucial for the present experiment that the electron spectrometer resolution be high. The main axis of the spectrometer lens was set at the magic angle (54.7°) with respect to the plane of polarization. HCl gas was obtained commercially from Air Liquide with a purity of >99.99%, and DCl gas of comparable purity was produced in our chemistry laboratory. The purity of both gases has been carefully checked by on-line valence photoelectron spectroscopy during measurements.

The HCl absorption spectrum near the Cl $2p^{-1}\sigma^*$ resonance consists of a broad structure due to the dissociative character of this state and to the two partly overlapping $2p$ spin-orbit components [11]. In Fig. 2 we show resonant Auger decay spectra of HCl and DCl measured after differently detuned excitations to the $2p^{-1}\sigma^*$ resonance. We denote the on-resonance spectrum as $\Omega = 0$, where Ω is the detuning from the maximum of the photoabsorption resonance. As discussed above, the spectrum consists of two types of features, namely, a broad "molecular background" and a sharp "atomic line." The narrow atomic line is assigned to following final state: $\mathrm{A} = \mathrm{Cl}^+(^1\mathrm{S})$. This atomic state is correlated to the following final molecular state [12]: $^1\mathrm{S}$: $\mathrm{HCl}^+(^2\Sigma^+)$. In the left panel of Fig. 2 we present how the "$4\sigma^{-1}$" molecular part and the A atomic line in HCl are developing for a series of excitation energies with $\Omega > 0$. Clearly, the center of gravity of the broad molecular background shifts with photon energy following approximately the Raman-Stokes dispersion law while the position of the A atomic line, being independent of the excitation energy, remains constant on the kinetic energy scale. Moreover, the molecular background increases in intensity relative to the atomic line according to the duration time concept of RXS theory for ultrafast dissociating molecules [2,4,9]. The sequence of spectra displays the remarkable feature that when the smooth molecular background moves across the narrow atomiclike resonance, the atomic peak (fixed in kinetic energy) develops into a negative spectral contribution, a hole [5].

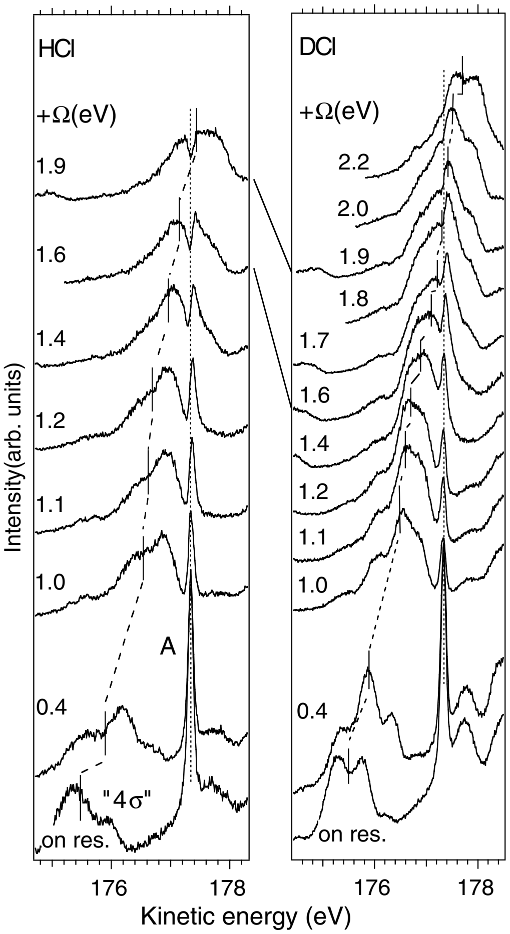

FIG. 2. Magnified $4\sigma^{-1}$ molecular part and the A atomic peak of resonant Auger decay spectra of HCl and DCl measured after differently detuned excitations. The spectral hole, which is clearly visible for HCl at $\Omega = 1.9$ eV, has completely disappeared for DCl for the same detuning value.

By comparing the valence spectrum measured at $\Omega = -13$ eV of HCl with the $2p_{3/2}^{-1}\sigma^*$ on-resonance spectrum ($\Omega = 0$ eV) we noticed that the strong contribution from direct photoionization processes to the $4\sigma^{-1}$ molecular background has to be considered. The present experiment and scattering K-matrix calculations [13] give roughly equal resonant and direct transition amplitudes. All spectra displayed in Fig. 2 have been recorded with a rather large photon bandwidth of 340 meV. One of the predictions of the RXS theory [5] is that the spectral width and position of the hole should be practically independent of the photon bandwidth. When decreasing the excitation bandwidth, γ, by more than 1 order of magnitude (from 340 to 20 meV), the hole is found to remain at a fixed kinetic energy of 177.32 eV and, to a very good approximation, the full width at half minimum (FWHM) of the hole does not change. The FWHM is in all cases found to be about 60 meV. This reflects the fact that the width of the atomiclike peak is independent of the photon bandwidth [3].

In the right part of Fig. 2 we present a series of DCl spectra for comparison. As shown there the spectral hole at $\Omega = 1.9$ eV has completely disappeared for DCl. With the almost doubled reduced mass for DCl the dissociation time is prolonged. This influences both the relative weight and the relative phase between atomic and molecular portions of the wave packet and thus the interference pattern. The spectral changes seen between HCl and DCl are clearly in accord with an interference picture where the observed interference pattern is extremely sensitive to the amplitudes and the relative phase of the interfering waves.

Simulations of the spectral region near peak A (Fig. 3) have been carried out for monochromatic excitation using the time-dependent formalism described in Ref. [5] (alternative time-dependent techniques are presented in [6,14]). The results shown in Fig. 3 are calculated with the same weights for the direct and resonant contributions, i.e., for the present case $S = 1/15$ in Eq. (1). The addition of the direct term together with the corresponding interference term to the resonant part of the RXS amplitude results in a slight shift of the energy of the spectral hole and the hole appears at a smaller detuning energy. The interference pattern does not disappear when $S = 0$.

We have used highly correlated quantum chemistry calculations to generate HCl potential surfaces of the HCl $^1\Sigma^+$ ground state, the $2p^{-1}\sigma^*$ core-excited state, and a set of final valence hole states (details are given in Ref. [13]). The atomic limits were used to identify the electronic state of interest. The spectral hole appears at a

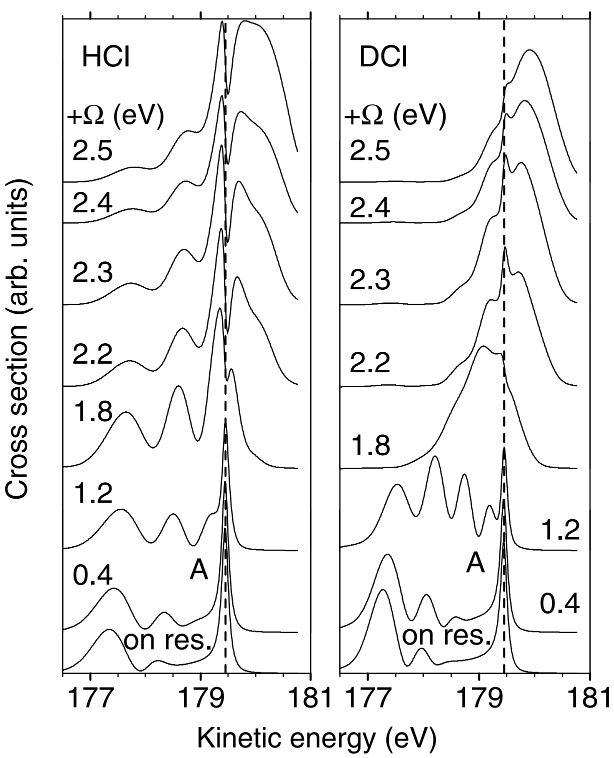

FIG. 3. The computed RXS cross sections. At resonance the direct contribution is given the same weight as the resonant term.

position corresponding to the $\mathrm{H}(^2\mathrm{S}) + \mathrm{Cl}^+(^1\mathrm{S})$ dissociation limit [15]. The 4σ level is split into several levels by static electron correlation [16], and the most intense state (the one of interest) corresponds to the third molecular state of $^2\Sigma^+$ symmetry. We find this state to have a weak avoided crossing near the ground state equilibrium internuclear distance (see also work of Pradhan *et al.* [15]), which enhances the excitation-energy dependent internal structure in the molecular part of the cross section [2]; see Fig. 2. The 2 eV exaggeration of the transition energies in Fig. 3 originates mostly from the fact that frozen Cl core orbitals were used for the core-excited state, though it has a completely negligible effect on the shape of the potentials. Overall, the cross section features are quite sensitive to the shape of the potential surfaces. This holds in particular for the spectral hole.

Such a continuum-continuum interference was predicted in the framework of a time-dependent formalism in Ref. [5] and was confirmed and elaborated upon in Ref. [6]. In Ref. [5] the interference was discovered for the $^4\Pi$ molecular state which, being effectively spin forbidden, possesses too low an electronic transition moment to be observable under present experimental conditions. Instead, the spectral hole is here found for the very high lying $4\sigma^{-1}(^2\Sigma^+)$ molecular final state as discussed above and which lies outside the energy range of the final states considered in the original theoretical paper [5].

In conclusion, we have observed a novel type of continuum-continuum interference effect associated with ultrafast dissociation of core-excited molecules. The effect shows up as a conversion of an atomic peak into a negative spectral contribution, a "hole," when detuning the excitation energy from the maximum of the resonance. It is shown that the properties of the observed phenomenon can be described using resonant x-ray scattering theory. The observation is compatible only with a unified one-step description of the RXS process.

The authors thank Professor D. Menzel for fruitful discussions. Support from the Swedish Natural Science Research Council (NFR), the Swedish Foundation for Strategic Research (SSF), the Swedish Research Council for the Engineering Sciences (TFR), and the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) is gratefully acknowledged. A. N. B. and C. M. thank the National Council for Scientific and Technological Development (CNPq-Brazil) and the Knut and Alice Wallenberg Foundation, respectively, for financial support. The collaboration of the staff of MAX-lab is gratefully acknowledged, as well as the NSC and PDC supercomputer centers for providing computing time.

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