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Ultrafast dynamics in C 1s core-excited CF₄ revealed by two-dimensional resonant Auger spectroscopy

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Following core excitation in an isolated molecule, ultrafast dissociation of one particular chemical bond can occur, where “ultrafast” is defined as taking place during the lifetime of the core hole, of the order of few femtoseconds. The signature of such phenomenon can be observed in resonant Auger spectra following core excitation. We present here an investigation of ultrafast dissociation following C 1s-to- σ^* core excitation in CF₄, with high-resolution resonant Auger spectroscopy. We are able to characterize final states of both the molecular ion and the CF₃⁺ fragment. We use two-dimensional (2D) maps to record resonant Auger spectra across the resonance as a function of photon energy and to characterize ultrafast dynamics. This method provides immediate visual evidence of one of the important characteristics of the study of spectral features related to molecular versus fragment ionic final states, and namely their dispersion law. In the 2D maps we are also able to identify the dissociation limit for one of the molecular final states. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4810871>]

I. INTRODUCTION

Core-electron resonant excitation in molecules provides a unique experimental and theoretical opportunity to investigate the interplay between Auger decay and nuclear motion of the molecule. Several phenomena can take place during the core-hole lifetime, such as nuclear motion, elongation of chemical bonds, and in some cases ultrafast dissociation of one particular chemical bond, where “ultrafast” is defined as taking place during the lifetime of the core hole. The relaxation via Auger electron emission occurs within the core-hole lifetime, which is of the order of 10^{-15} s for light atoms. Within this time scale, the nuclear motion of the molecule proceeds along the potential curve of the intermediate state, and, if such state is dissociative, can lead to ultrafast bond breaking. The signature of such phenomenon can be observed in resonant Auger spectra following core excitation, which then contain spectral features related to both molecular and fragment final states. Almost three decades ago, electron emission from the core-excited Br atom in the resonant Auger spectrum of the HBr molecule following Br 3d $\rightarrow$ σ^* excitation was observed in a pioneering paper.¹ Following this work, ultrafast dissociation followed by Auger decay of atomic or molecular fragment has been observed for several molecules.^{2–11} This body of work confirms that molecular Auger features coexist with fragment Auger lines, and therefore resonant Auger spectra provide a unique possibility to study the details of nuclear dynamics in core-excited molecular states.^{12–14} Other interesting phenomena such as the Doppler effect in electron emission following ultrafast dissociation have also been observed in

some cases.^{15–21} The CF₄ molecule, tetrafluoromethane, has been a benchmark for several photoemission and absorption studies, due to its high symmetry, same as methane, CH₄ (see, e.g., Ref. 22 and references therein). One of the most interesting observations deriving from the comparison between CH₄ and CF₄ is the relative intensity of below-threshold photoabsorption structures around the C 1s ionization threshold related to transitions to empty molecular orbitals versus Rydberg states: while the Rydberg series is dominant in methane, in tetrafluoromethane there are prominent broad structures at lower photon energy followed by a series of sharp peaks attributable to the Rydberg series. Such a striking difference in two structurally similar molecules has been attributed to a cage-like effect induced by the electronegative fluorine atoms, which creates a potential barrier that pushes the Rydberg states to a larger distance with respect to the antibonding orbitals. Therefore CF₄ is a good candidate to investigate the dynamical properties of core-excited states with an electron in the antibonding σ^* molecular orbital in a highly symmetric system. Another topic of interest is the extent of Jahn-Teller and quasi-Jahn-Teller coupling. The high symmetry of tetrahedral molecules implies that the dipole-allowed transitions are from the C 1s level with a_1 symmetry to the empty molecular orbitals of t_2 symmetry. However, the threefold degeneracy of the excited state can be removed by Jahn-Teller splitting, and this reduction in symmetry can allow transitions to the nominally symmetry forbidden a_1 state. Therefore, in CF₄, the lowest-energy region of the absorption spectrum below threshold contains a broad structured band which has been ascribed to transitions to the t_2 -Jahn-Teller-split states, plus quasi-Jahn-Teller coupling between the forbidden a_1 transition and the a_1 state resulting from the t_2 -Jahn-Teller splitting. In a previous work by some

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of us, partial positive and negative ion yield around both C 1s and F 1s ionization thresholds was used to characterize the dynamics following core-level excitation and ionization.²² Photoabsorption data have been reported around the C 1s ionization threshold.²³ Resonant Auger decay spectra were shown in Ref. 24. A study by electron-ion coincidence techniques has been reported, again following C 1s core excitation to the σ^* molecular orbital, showing that nuclear motion proceeds in the system during core-hole lifetime, possibly enhancing some of the fragmentation patterns.²⁵ This process has been labeled core-excitation-induced dissociation. Later on, ultrafast fragmentation in CF₄ has been described following F 1s core excitation to the σ^* .¹⁹ It has been demonstrated that strongly anisotropic dissociation occurs, which is direct evidence that the asymmetric nuclear motion proceeds in the F 1s-excited state, preferentially along the direction of the polarization vector, leading to the symmetry lowering from T_d to C_{3v} . While this process has been described in detail by resonant Auger spectroscopy upon core excitation below the F 1s threshold, core excitation from the C 1s level to the same dissociative intermediate state should lead to ultrafast dissociation as well, even more likely because of the longer core-hole lifetime of the C 1s hole. The C1s core-hole lifetime of CF₄ is 8.5 fs,²⁶ in the same order of magnitude as the periods of typical stretching vibrations. However, the situation below the C 1s threshold is rendered more complicated by the fact that while a C–F bond breaks following F 1s excitation, the fragment which leaves with the core hole is a F atom, while below the C 1s threshold the fragment is the tetra-atomic CF₃ neutral core-excited radical. Few examples are reported in the literature of ultrafast dissociation leading to a diatomic^{2,9,10} or triatomic²⁷ core-excited fragment. No examples of tetra-atomic fragments have been reported yet. We present here an investigation of ultrafast dissociation following C 1s to σ^* core excitation in CF₄, with high-resolution resonant Auger spectroscopy. The main novelty of our work is the use of two-dimensional (2D) maps to record resonant Auger spectra across the resonance as a function of photon energy with a small energy step and then to characterize ultrafast dynamics. This method allows us to follow in great details the evolution of the resonant enhancement of spectral features corresponding to final ionic states while scanning the energy across the resonance, and to fully exploit the so-called detuning effects (see, e.g., Ref. 28 and references therein). Furthermore, this method provides immediate visual evidence of one of the important characteristics of the study of molecular versus fragment ionic final states, and namely their dispersion law. Specifically, there are two different types of behaviors in the spectra, one set of structures which displays a linear kinetic-energy dispersion when the photon energy is changed, while another set of structures remains at constant kinetic energy. The structures dispersing linearly are identified as resonant Auger decay leading to the CF₄ molecular ion, while the non-dispersing peaks are assigned as originating from the CF₃ fragment ion. This trend is immediately evident in the 2D maps, together with the dissociation limit for one of the final states, which can be visually observed in the long tail of one of the spectral features related to decay to a molecular ionic state.

II. EXPERIMENTAL

The experiments were performed on the soft x-ray beamline BL6U at the Ultraviolet Synchrotron Orbital Radiation Facility (UVSOR), Okazaki, Japan. The radiation from an undulator was monochromatized by a variable-included-angle varied-line spacing plane-grazing monochromator. The photon energy resolution $E/\Delta E$ was set to 10 000 for total-ion yield, and 4000 for 2D map measurements. The monochromatized radiation was introduced into a cell with sample gases. Kinetic energies of the emitted electrons were measured by a hemispherical electron energy analyzer (MBS-A1) placed at a right angle with respect to the photon beam direction. The degree of the linear polarization of the incident light was essentially 100%, and the direction of the electric vector was set to be parallel to the axis of the electrostatic lens of the analyzer. The kinetic-energy resolution of the analyzer was set to 60 meV.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the total ion yield measured around the C 1s ionization threshold measured during the experiment in a gas cell installed on the beamline upstream to the electron analyzer. The photon energy was calibrated on the $3pt_2$ Rydberg transition at 299.442 eV.²³ The literature assignment is the following: the double feature with maxima at 297.7 and 298.4 eV is the Jahn-Teller-split transition to the σ^* of t_2 symmetry, followed by the Rydberg series.²³ In a theoretical paper²⁹ it was reported that the excitation from the C 1s orbital to the σ^* will trigger a bond-breaking molecular deformation, with the elongation of one of the C–F bonds, and the symmetry decreases from T_d to C_{3v} . This is consistent with our results (see discussion below). The following sharp peaks are attributed to the Rydberg series. Since the usual way of relaxation from Rydberg excitation is spectator decay, this spectral region is not investigated in the present work.

In Fig. 2 we show resonant Auger spectra taken at photon energies corresponding to the top of the resonance (298.4 eV) and off-resonance (296 eV). We can point out a series of changes between the resonant and non-resonant case. The first observation is that the three highest-kinetic-energy spectral features, labeled $1t_1$, $4t_2$, and $1e$,²² do not show a

FIG. 1. Total-ion yield spectrum measured in the C 1s excitation region of CF₄. The energy calibration is from Ref. 23.

FIG. 2. Resonant Auger spectra taken at photon energies corresponding to (a) the top of the $\sigma^*(t_2)$ resonance (298.4 eV) and (b) off-resonance (296 eV). The spectral assignment is from Ref. 23.

significant resonant enhancement. This is easily understood on the ground of the nature of the corresponding molecular orbitals: they are all mostly built of F 2*p* combinations with lone-pair character, and therefore they are not affected by the decay of the resonant state in which the core hole is located on the carbon atom. The main effect of the resonance is the enhancement of the spectral feature labeled $3t_2$, which corresponds to a molecular orbital mostly centered on the C–F bonds, and the appearance of a new feature around a kinetic energy of 279 eV. This broad structured peak is not present in the off-resonant spectrum, and it is therefore related to the decay dynamics of the core-excited state. One possible explanation would be that the decay of the neutral state with a C core hole leads to final states which are not populated in the direct photoionization process but gain intensity by coupling with the intermediate state. Such final states typically originate from spectator decay, and possess two valence holes and one electron (the “spectator”) in the excited state (antibonding or Rydberg orbitals). The distinction between participator decay, where the excited electron participates in the electron emission following core excitation, and the above described spectator decay is a “classical” one in resonant Auger work (see, e.g., Ref. 30), although in some cases its limits have been pointed out.³¹

However, in the present case a better explanation than spectator decay derives from the analysis of the dispersion law of such feature compared to the other peaks in the decay spectrum.

In Fig. 3 we report the 2D maps obtained by taking decay spectra at regular photon energy intervals of 100 meV across the resonance (bottom), together with the total-ion yield to visually show where in the resonance region the decay spectra are taken. It is immediately clear that some of the features show linear dispersion as a function of photon energy, while some other features stay at constant kinetic energy, in

FIG. 3. Total-ion yield (top) and 2D map obtained by taking decay spectra at regular photon energy intervals of 100 meV across the resonance (bottom). The decay spectra are taken across the photon energy range with an energy step of 0.1 eV.

particular the one discussed above, at 279 eV kinetic energy. This different trend has been observed in several cases, and it is the signature of ultrafast dissociation. Namely, it allows one to distinguish between spectral features related to molecular decay prior to dissociation and spectral features related to decay taking place after dissociation in the resulting fragment. This behavior can be understood simply on the ground of energy conservation: for decays to molecular final states the only energy dissipation channel is the kinetic energy of the ejected electron, and therefore this energy disperses linearly with the photon energy. In fragment decay there is an additional channel, and namely the nuclear coordinate along which dissociation takes place. Therefore, part of the energy put in the system by the primary excitation goes to the motion of the nuclei moving apart and the kinetic energy of the outgoing electron remains constant while the photon energy is changed. We assign this broad structure to the final state of the CF_3 fragment, on the ground of energy considerations, since it is unlikely that two (or more) strong C–F bonds are broken at the same time. Similar findings have been reported for ammonia, where the ultrafast dissociation has been shown to lead to the NH_2 core-excited fragment.²⁷ However, we do not exclude the possibility that in the upper limit of the explored photon energy range further fragmentation can occur (see discussion below about Fig. 4).

Another point to consider is that despite our very good experimental resolution (~ 90 meV) the feature is broad with no vibrational structure resolved. The CF_3 radical has been studied by theoretical methods.³² The main result connected to our findings is that the vibrational structure is complex with several vibrational modes active, due to the relatively

FIG. 4. Top: CIS spectra of the fragment final state, CF_3^+ , (1) and of the $3t_2$ (2) molecular final state, CF_4^+ . Bottom: resonant Auger 2D map showing only the resonant contributions: (1) the nondispersive state and (2) the $3t_2$ spectral line.

low symmetry, therefore what we observe is a superposition of several contributing closely spaced progressions.

To further clarify our findings, in Fig. 4 we report the 2D map after subtraction of the non-resonant contributions (bottom), and with on-top two pseudo-absorption curves obtained by the CIS (Constant Ionic State) method,³³ and namely plotting the integrated intensity of the two resonant features, the dispersive one related to the $3t_2$ molecular ionic state, CF_4^+ , and the non-dispersive one related to the fragment ionic state, CF_3^+ , as a function of photon energy. We notice that while the intensity of the molecular state closely mimics that of the absorption curve, the feature we assign to the fragment decreases in relative intensity across the resonance, and disappears in the photon energy region of the Rydberg states. Detailed calculations on the potential curves of the intermediate and final state would be needed to fully clarify this finding, which are beyond the scope of the present work. However, we can qualitatively hint at the fact that the intermediate state is Jahn-Teller-split, and possibly the two potential curves of the two electronic states do not have the same dissociative character. Alternatively, when the photon energy is scanned across the resonance, higher vibrational states in the final electronic states can be populated, up to a new dissociation limit which would lead to the breaking of another C–F bond and therefore the reduction in intensity of the spectral features related to the CF_3 fragment.

A similar result was reported in our previous work on CF_4 investigated by partial ion yield spectroscopy:²² the relative yield of the CF_3^+ fragment decreases across the reso-

nance. Although the time scale of Auger decay and ion yield collection are different, a similar explanation relating the observation to the slightly higher energy absorbed by the system as a function of photon energy which can enhance the probability of subsequent fragmentation for the CF_3^+ species was provided. Another very interesting finding which is evidenced in the 2D map in Fig. 4 is the very long tail of the spectral feature related to the $3t_2$ final state. Such tail is truncated for all photon energies at 270 eV kinetic energy. We interpret this finding as due to the dissociation limit of the CF_4^+ final state with a valence hole in the $3t_2$ orbital: vibrational states can be populated up to a limit, and above it the state dissociates. An interesting point can be noticed about the tail: it does not show linear dispersion, as the kinetic energy of the main peak does. This is due to the fact that above the dissociation limit the excess energy goes to the nuclear motion, and there is a new channel to disperse energy, while below the dissociation limit the energy is taken out only by the outgoing electron. This argument is somewhat similar to the above discussed explanation on why the spectral features related to fragments do not show linear dispersion. However, in the present case we find evidence of dissociation in one of the final states, in addition to the above discussed ultrafast dissociation in the intermediate state. This is another example of the power of the 2D maps in unraveling fine details of the decay dynamics following core excitation.

IV. CONCLUSION

The use of 2D maps to measure resonant Auger spectra is a powerful method which has allowed us to investigate in great detail the dynamics of ultrafast dissociation following C 1s-to- σ^* core excitation in the prototypical system CF_4 . The dispersion law of the spectral features is used to identify them as related to molecular or fragment final states, and such dispersion is immediately evident in the 2D maps. Furthermore, we show that such method provides information on the characteristics of final state, such as their dissociation limit.

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