Role of bending in the dissociation of selective resonant inner-shell excitation as observed in CO_2

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Combining high-resolution electron spectroscopy with electron-ion coincidence data, we have been able to show the role of bending excitation in the dissociation of CO_2 after C $1s \rightarrow \Pi_u$ resonant excitation. We demonstrate that the predissociation of the dominating A state created through participator decay is not constant along the resonance profile. The interpretation is based on a preferential excitation of high levels of the bending mode at low-photon-energy side of the resonance, which favors the $O^+ + CO$ decay channel.

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Core excitation of simple molecules in the soft-x-ray regime offers the possibility of inducing electronic transitions into resonant states with selected vibrational energy. Special efforts both theoretically [1–4] and experimentally [5–7] have been done recently to emphasize the role of nuclear motion in that situation and its interplay with the electronic core hole relaxation. Indeed, with the dramatic improvement of both excitation sources and electron analyzer performances, it is now possible to perform experiments where the total bandwidth (excitation and analysis) is lower than the natural width of the excited core hole. In this regime the usual two-step picture (hole creation followed by Auger decay) cannot be used, as shown by the experimental sharpening of the Auger lines, and the process has to be treated as a single-step one, according to the resonant inelastic x-ray scattering formalism, often referred to as the Raman Auger process [3] . It has been shown, for instance, that coherent excitation of bound states or dissociative states leads to interference effects that can be controlled by energy detuning within a resonance [4]. One can easily understand the new opportunities this tool offers to catch the time evolution of a system in a very short time scale (sublifetime) [8]. Up to now, most of these studies have focused on atomic or diatomic systems. However, despite their increased complexity, the case of polyatomic systems represents in this context a more general situation, as shown in a previous study on BF_3 [9].

In this Rapid Communication we demonstrate how such dynamical effects can be seen directly in the case of a dissociative polyatomic system. Moreover, we show that the final fragmentation pattern at a state-selected internal energy is dependent on the intermediate vibrational state. To perform such an experiment, it is essential to measure in coincidence the emitted electron (and its kinetic energy) and the corresponding ionic fragments.

The experiment has been performed on CO_2, where the dissociative ionization has been studied in great detail both experimentally [10,11] and theoretically [12,13] in the valence region. Previous studies on dissociation dynamics have already been reported on CO_2 after carbon K-shell excitation [14], but without analysis of the electron energy. In this pre-vious work, mostly devoted to dissociative double ionization, it has been shown that the C $1s \rightarrow \Pi_u$ resonance was inducing a change of geometry from linear to bent. As a consequence, the central atom (carbon in that case) was emitted with a significant kinetic energy. A similar observation and interpretation were done also for N_2O [15] after $N_{term.}$ $1s \rightarrow \Pi^*$ excitation. In both cases the same ''core equivalent'' molecule was invoked, i.e., NO_2, which is bent in the ground state (see below). In this study, we focus on the single ionization process, with the aim of emphasizing the role of the ion internal energy.

The coincidence experiment has been done at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, on a high-resolution–low-flux beam line (SA22), whereas the high-resolution electron spectra have been obtained at the undulator beam line 9.0.1 of the Advanced Light Source (ALS) using an end station based on a Scienta SES-200 hemispherical electron energy analyzer. This experimental setup, described elsewhere [16], combines high brightness and photon-energy resolution achievable at a third generation synchrotron light source with high-energy resolution of electron detection.. The coincidence setup has been described elsewhere [17] . Briefly, it consists in a double toroidal electron analyzer optimized for a very high transmission, facing a short (12-cm) time-of-flight spectrometer. In order to keep a good electron resolution, the ion extraction field (1 kV/cm) is applied only after electron detection. During the coincidence experiment, a range of 4-eV electron energy can be simultaneously recorded. For each electron the corresponding ion time of flight is stored. The data are analyzed afterwards, with an electron energy filtering adapted to the actual resolution.

The total ion yield spectrum is shown in Fig. 1, as obtained with a 75-meV photon bandpass, in the region of the C $1s \rightarrow {}^2\Pi_u$ resonance. The resonance located at 291 eV is much wider (0.69 eV) than the natural width of the C $1s$ vacancy and the actual photon bandwidth. This broadening is due to the excitation of vibrational modes of the resonant state, as already seen in previous studies [18].

Electron spectra have been recorded off resonance (OR), on the left (L), on top (T), and on the right side (R) of the
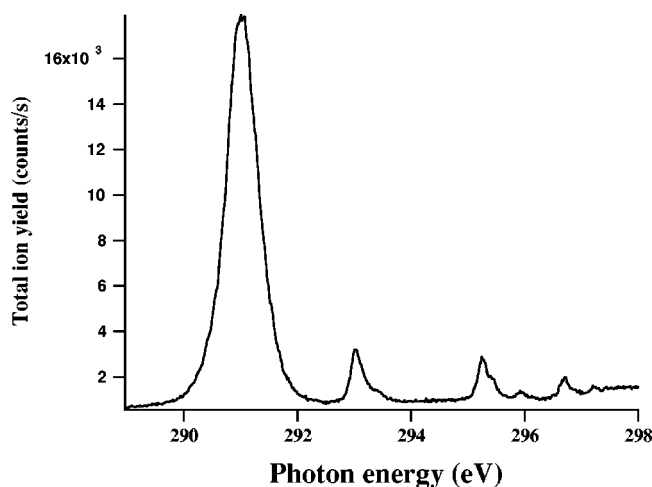
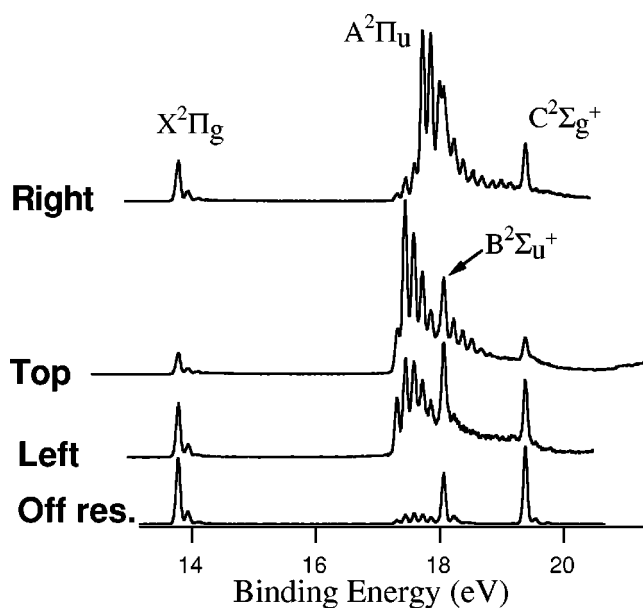FIG. 1. Total ion yield spectrum obtained with a 75-meV photon bandwidth.

FIG. 2. Electron spectra (ALS results) recorded along the $^2\Pi_u$ resonance, with a 75-meV photon-energy resolution and a 40-meV electron bandwidth. Out of resonance (OR), 280 eV; left (L), 290.6 eV; top (T), 291 eV; and right (R), 291.4 eV.

resonance, at high resolution (ALS results). We show in Fig. 2, a set of photoelectron spectra covering the X, A, B, and C state region of CO_2^+. The first striking observation is that the only resonating state is the A $^2\Pi_u$ state. This point will simplify the following discussion. The second point is the observed change in the vibrational population of the A state and the third point concerns the appearance of a background underlying this vibrational progression, specially clear in the spectrum (L). This background is obviously not due to a lack of resolution, as it is for instance totally absent from the (OR) spectrum. The detailed discussion of the spectra, especially the change in the vibrational distribution will be discussed in a separate publication [19]. In the three cases the key point is the role of the intermediate resonant state. Indeed, the core equivalent model indicates that a change of geometry (linear to bent) is expected, as the core equivalent molecule (NO_2) is known to be bent at 144°. This change in geometry is rationalized as a Renner-Teller effect in this case, as already mentioned by Adachi *et al.* [18]. It gives rise to a broad resonance (0.69 eV in this case) due to a large envelope of unresolved vibrational modes. The Π_u ($D_{\infty h}$) resonant state is split into an A_1 and B_1 component in the C_{2v} symmetry group. When exciting at low energy, one preferentially excites the A_1 configuration in the high vibrational bending mode, whereas at higher photon energy, both A_1 and B_1 are excited. Moreover, because the B_1 configuration has a minimum at 180° as the CO_2 ground state, only the stretching mode is likely to be populated in that case. These statements are clearly corroborated by the comparison of the spectra shown in Fig. 2.

Indeed, the spectrum (R) shows an extended vibrational progression mostly corresponding to the excitation of symmetric stretching quanta (ν_1), with a maximum in the distribution towards $\nu_1 = 3-4$, whereas the spectrum (T) shows a maximum around $\nu_1 = 1$, as due to different Franck-Condon factors. The excitation of bending quanta ν_2 is also present but more difficult to extract, because in CO_2 there is a coincidental energy degeneracy between ν_2 and ν_1: $2\nu_2 = 1\nu_1$. However, the existence of odd quanta can be seen in the

apparent change in resolution between OR and the other spectra. For instance, the minimum height between $\nu_1 = 1$ and $\nu_1 = 2$ is very low in OR as compared to T or L, where it is found to be the strongest. The precise assignment of the band is impossible at this level of resolution where (ν_1, ν_2, x) cannot be distinguished from $(\nu_1 - n, \nu_2 + 2n, x)$. Interestingly, Praet *et al.* [12] and more recently Polak *et al.* [13] have shown in a theoretical work on the relevant potential curves of the ion that a strong perturbation was induced along the ν_2 coordinate due to an avoid crossing between the A $^2\Pi_u$ and the $(3)^2\Pi_u$ state. This means that for high ν_2 quanta, a congestion of states is likely to be observed rather than a regular vibrational progression, leading to the appearance of a background, as observed in the spectra. Notice that the effect is stronger on L, where higher bending levels are excited.

Figure 3 shows the mass spectra recorded at the three reported photon energies (L, T, and R) in coincidence with electrons of the same binding energy: 19.1 eV, i.e., in the region where the lowest dissociation limits are open. From the above photoelectron study, this region corresponds to a highly vibrationally excited level of the A state. The three O^+, CO^+, and CO_2^+ ions are observed, and the most striking feature is the observed change in the resulting branching ratio of the ionic fragments. Indeed, at low and medium photon energy, a higher O^+ production is observed, whereas it drops down at high photon energy where the CO_2^+ parent ion is preferentially produced. This clearly shows the role of the vibrational excitation of the intermediate state on the subsequent fragmentation of the final ion. The lowest dissociation limits available are the following (calculated from the thermodynamical data of Locht and Davister [11]):
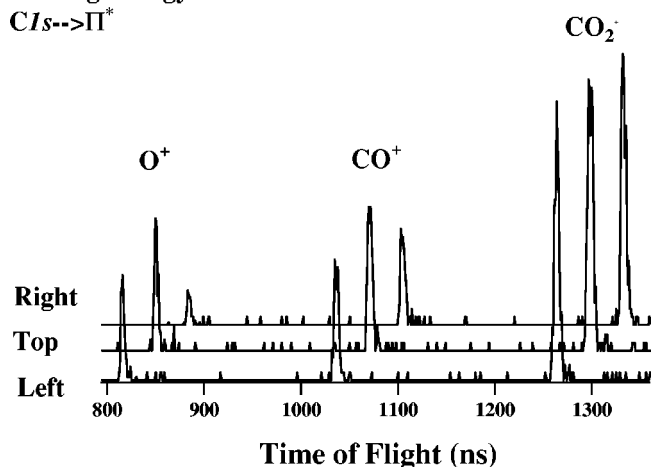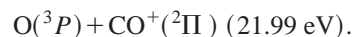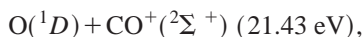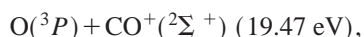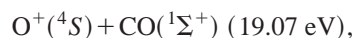
Binding Energy: 19.1 eV

$C1s\text{-->}\Pi^*$

FIG. 3. Coincidence mass spectra recorded at 19.1-eV electron binding energy, along the Π_u resonance (left, top, and right as in Fig 2).

$$O^+(^4S) + CO(^1\Sigma^+) \ (19.07 \text{ eV}),$$

$$O(^3P) + CO^+(^2\Sigma^{\ +}) \ (19.47 \text{ eV}),$$

$$O(^1D) + CO^+(^2\Sigma^{\ +}) \ (21.43 \text{ eV}),$$

$$O(^3P) + CO^+(^2\Pi\ ) \ (21.99 \text{ eV}).$$

In the coincidence experiment the binding energy (19.1 eV) of the ion is defined at an overall resolution of only 1.2 eV. Indeed, in a coincidence experiment one has to minimize the difference between electron and ion counting rates. Thus, we had to operate the analyzer at high pass energy and the monochromator at a still good resolution (150 meV photon bandwidth).

At this energy, the ionization process can only form $O^+(^4S)$, $CO^+(^2\Sigma^{\ +})$, or $CO_2^{\ +}$ $(^2\Pi_g)$. Because of the moderate resolution, and because it has been stated before that the A state is the only resonating state, we had to subtract the C state contribution (BE: 19.36 eV) from the coincidence mass spectra (the B state at 18.1 eV can be neglected). The C state contribution has been estimated from the high-resolution electron spectra. Assuming an instrumental Gaussian function of 1.2 eV full width at half maximum, it has been found at 17%, 7% and 15%, respectively, corresponding to the L, T, and R photon energies. The high-resolution spectra show in addition that the C state is formed at 80% in the (0,0,0) state. From the work of Richard-Viard et al. [10], this state dissociates quasiexclusively into $O^+ + CO$. The corresponding amount of O^+ has thus been subtracted, resulting in the following $O^+/CO^+/CO_2^{\ +}$ branching ratio: 18(2)/25(3)/57(6) (L), 18(2)/27(3)/55(6) (T), and 7(1)/24(3)/69(6) (R).

In the linear geometry, the only accessible limit from the $A^2\Pi_u$ state is $O(^1D) + CO^+(^2\Sigma^+)$, which is too high in energy to explain the observed CO^+ production. However, because of spin-orbit coupling, the dissociative $^4\Pi_u$ state, known to predissociate the C state [12], explains the formation of CO^+. Indeed, Polak et al. [13] calculated the spin-orbit coupling in C_{2v} geometry between the corresponding $^4B_1$ dissociative state and the A state. They found a coupling of about 40 cm^{-1}, quasi-independent of the angle. In a first approximation, this predissociation should not be strongly influenced by the bending of the molecule. Following the previous theoretical studies by Praet et al. and Polak et al., it has also been shown that a $^4\Sigma^-$ dissociative state is responsible for the production of O^+ in the lowest dissociation limit. In that case, the predissociation mechanism implies both spin-orbit coupling and lowering of symmetry. Indeed, in linear geometry the $^4\Sigma$ state crosses the $^4\Pi$ at $R_{CO} = 1.35$Å, but they do not interact. However, in the bent geometry and including asymmetric stretching (vibronic coupling), the symmetry lowering reduces these states into ^4A components that therefore interact. Such a conical intersection induced by the dissociative $^4\Sigma$ state is responsible for the $O^+(^4S) + CO(^1\Sigma^+)$ dissociation process. The dissociation is indirectly induced by the bending coordinate, which leads to an enhanced O^+ production when the molecule is bent. The effect is maximum when comparing L and R spectra, the T spectrum combining in principle both effects.

In conclusion, we have shown that resonant core excitation is able to produce dramatic changes in the geometry of the intermediate state, which allows the analysis of a still unexplored region of potential surfaces of polyatomic systems. In the case of the well-documented CO_2 molecule, the vibrationally selective excitation of the resonant state allows us to modify the final dissociation pattern. We have pointed out, especially, that the preferential excitation of the bending mode was responsible for an enhanced O^+ production. It is interesting to note the importance of combining high-resolution photoelectron data with coincidence data to achieve this level of understanding in the dissociation mechanism of small molecules. More generally, we have pointed out within the CO_2 case that the final fragmentation pattern of the ion is not only governed by its internal energy, but by the way the ion has been produced. We believe this kind of behavior could be observed in numerous species, as long as nuclear dynamics is fast enough compared to pure electronic relaxation or internal energy conversion processes, for instance.

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