DISSOCIATION DYNAMICS OF INNER-SHELL EXCITED MOLECULES BY MEANS OF PRECISE MEASUREMENTS OF RECOIL MOMENTA OF FRAGMENT IONS

When one of the inner-shell electrons of an atom in a molecule is promoted to a vacant valence molecular orbital or to a Rydberg orbital, either an Auger process or a series of Auger processes generally occur in the femtoseconds time scale and multiply charged ions are produced. These parent ions normally dissociate rapidly into fragments due to Coulomb repulsion among several positively charged centers. Recent research has demonstrated that nuclear motion can proceed in the core-hole state before the Auger decay occurs. This nuclear motion should be reflected in the angular correlation among products of dissociation that occurs following subsequent Auger decay.

To probe such nuclear motion in the study of dissociation dynamics, we have installed an apparatus at beamline **BL27SU** which enables us to take direct measurements of momentum distribution of all the fragment ions. This technique consists of a time-of-flight measurement using position-sensitive two-dimensional detectors with delay-line anodes. Combining this apparatus with the source of very high resolution linearly polarized soft X-rays [1], we have been able to study the dissociation dynamics of the linear triatomic molecule CO_2 following the excitation of either the C1*s* [2] or O1*s* [3] electron into $2\pi_u$ or σ^* molecular orbital in unprecedented detail. We focused on the three-body breakup of the triply charged molecular ion, $CO_2^{3+} \rightarrow C^+ + O^+ + O^+$, following the C1*s* $\rightarrow 2\pi_u$ excitation. The results of the measurements are best represented by so-called Newton diagrams as shown in Fig. 1. In these diagrams, the magnitude of the linear momentum of the first O^+ is normalized to unity and the vector is placed on the x-axis in the negative direction. The respective linear momentum of C^+ and the second O^+ are then plotted relative to this unit vector in the positive and negative y directions, respectively, so as to satisfy the momentum conservation requirements.

The separate observation of the two Renner-Teller split states claims for a salient feature in the present study. The C1$s^{-1}2\pi_u$ core-hole state is predicted to be split into two states via vibronic coupling with the bending vibration; one in which the π orbital lies in the bending plane (panel **a**, in-plane) and the other in which it extrudes perpendicularly from the bending plane (panel **b**, out-of-plane). However, the separate observation of these states has never been achieved. The present technique enables us to obtain this separation successfully. If only the events of which the vector product of the linear momenta of two O^+ fragments is parallel to the *E* vector and the linear momentum of the C^+ fragment is perpendicular to the *E* vector are selected from the recorded data, the selected events form an ensemble of the dissociation events from the core-hole state whose transition moment is perpendicular to the plane of the bending motion (panel **a**). In contrast, if the events of which the vector product of linear momenta of the two O^+ fragments is perpendicular to the *E* vector and the linear momentum of the C^+ fragment is parallel to the *E* vector are selected, then the obtained ensemble is that of the dissociation events from the core-hole state whose transition moment is parallel to the plane of the bending motion (panel **b**). For in-plane excitation, the islands of C^+ and second O^+ have clearly shown to possess considerably long tails, whereas those for out-of-plane excitation do not, indicating that the molecules are bent considerably in the former excitation just before

dissociation, whereas the latter is not. We can interpret this as reflection of the nuclear motion in the core-excited states toward the equilibrium geometry, representing the first direct verification of the occurrence of linear and bent structures for the C1$s^{-1}2\pi_u$ core-hole states (Renner-Teller split pair).

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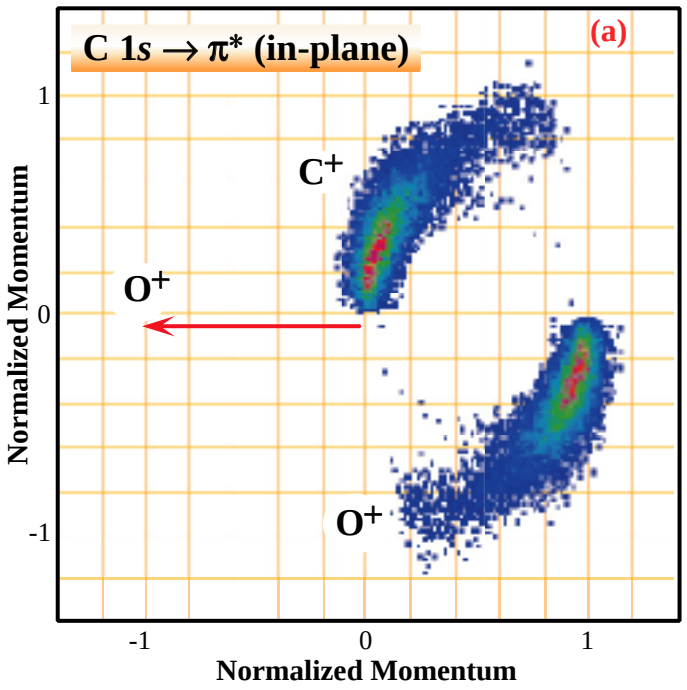

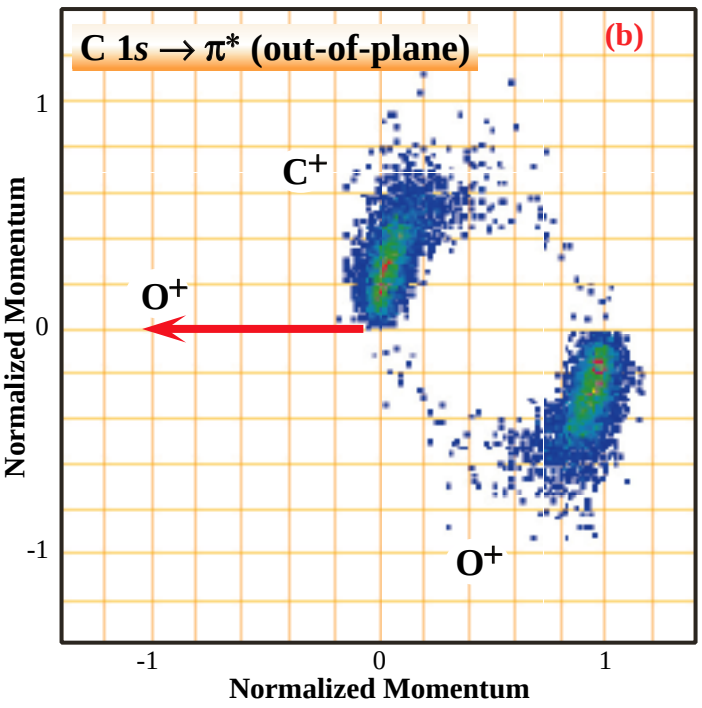

*Fig. 1. Newton diagrams for the three fragment ions, formed by three-body breakup of the triply charged molecular ion CO_2^{3+}. **(a)** for C1$s^{-1}2\pi_u$ (in-plane) excitation, **(b)** for C1$s^{-1}2\pi_u$ (out-of-plane) excitation.*

References

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