

# Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

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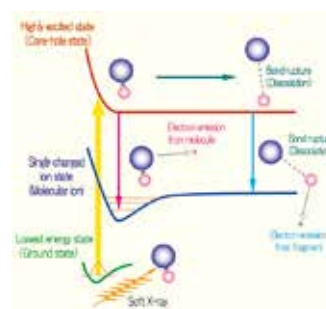
The detailed comprehension of the electronic structure of molecules is an important step toward understanding the chemical and physical properties of matter, and also provides a link between atomic and solid-state physics. Information on photoexcitation, photoionization, and photodissociation processes derived from molecular spectroscopy is of fundamental importance, and also useful in various scientific disciplines, including astrophysics, planetary sciences, radiation chemistry, and biology.

Synchrotron radiation combined with a suitable monochromator is a powerful research tool for systematic investigations of outer- and inner-shell excitation and ionization processes in molecules, because the spectral range matches the binding energies of the valence and core electrons of the elements which form molecules of physical and chemical interest, namely low-Z molecules. In order to promote inner-shell electrons of low-Z molecules efficiently, it is indispensable to utilize monochromatized synchrotron radiation in the soft X-ray region.

Inner-shell excited states of low-Z molecules relax mainly through Auger decay, leading to the formation of highly excited singly or multiply charged molecular ions with outer-shell holes. These molecular ions are in general quite unstable, and immediately break apart into fragment ions and neutrals.

The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

The major aim for investigating molecular inner-shell excitation is to determine what happens to molecules following the excitation and ionization of an inner-shell electron by using various spectroscopic techniques to define the initial photoexcitation process itself, and to characterize and correlate the electrons, ions, neutrals, and metastables that are produced as a result.



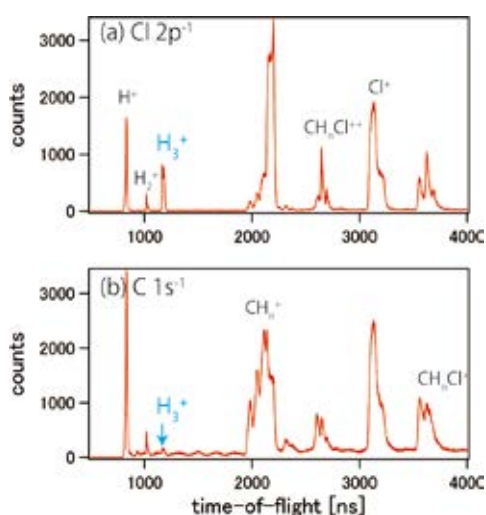
**Figure 1.** Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

### Selected Publications

- E. Shigemasa and N. Kosugi, "Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications," in *Advances in Chemical Physics*, S. A. Rice and A. Dinner, Eds., Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- H. Iwayama, T. Kaneyasu, Y. Hikosaka and E. Shigemasa, "Stability and Dissociation Dynamics of  $N_2^{2+}$  Ions Following Core Ionization Studied by an Auger-Electron-Photoion Coincidence Method," *J. Chem. Phys.* **145**, 034305 (8 pages) (2016).

## 1. Site-Specific Production of $\text{H}_3^+$ Ions Following Core Ionization of $\text{CH}_3\text{Cl}$

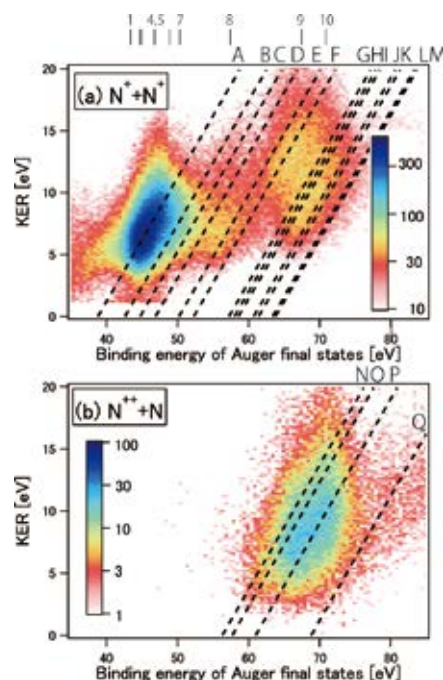
Trihydrogen cation  $\text{H}_3^+$  is one of the most interesting molecules in diverse fields from chemistry to astronomy because it is the simplest triatomic molecule and plays an important role in the interstellar. While the  $\text{H}_3^+$  ions can be mainly generated from the proton transfer reactant ( $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ ), it was shown that unimolecular reactions of soft x-ray irradiated  $\text{CH}_3\text{X}$  molecules ( $\text{X} = \text{Cl}, \text{OH}, \text{CN}, \text{etc.}$ ) also have a contribution of  $\text{H}_3^+$  formation in the interstellar.<sup>1)</sup>



**Figure 2.** Time-of-flight spectra of ions taken in coincidence with (a) Cl 2p and (b) C 1s photoelectrons.

In this work, we investigate the  $\text{H}_3^+$  production mechanism of soft x-ray irradiated  $\text{CH}_3\text{Cl}$  molecules with using an Auger-electron–ion coincidence technique, which allows us to correlate Auger final dicationic states with product ions. From coincidence Auger spectra, we reveal dicationic states which form the  $\text{H}_3^+$  ions.

Figure 2 shows total ion TOF spectra following the Cl 2p and C 1s photoionization. Main fragment ions are  $\text{H}_n^+$  ( $n = 1, 2, 3$ ),  $\text{CH}_n^+$  ( $n = 0-3$ ),  $\text{Cl}^+$  and  $\text{CH}_n\text{Cl}^+$  ( $n = 0, 1, 2$ ).  $\text{CH}_3\text{Cl}^+$  ions were not observed since the parent molecules following the Auger decay are doubly charged. Doubly charged ions such as  $\text{Cl}^{2+}$  and  $\text{CH}_n\text{Cl}^{2+}$  ( $n = 0-3$ ) were also observed. The most remarkable difference in fragmentation between the Cl 2p and C 1s photoionization is the relative abundance of  $\text{H}_3^+$  ions. The relative intensity of  $\text{H}_3^+$  ions for the Cl 2p photoionization is ten times larger than that for the C 1s photoionization. In order to correlate the production of  $\text{H}_n^+$  ( $n = 1, 2, 3$ ) ions with the Auger final states, we have measured the coincidence Auger spectra. It is clearly seen that the formation of the  $\text{H}_3^+$  ions is related to only the lowest band around the binding energy of 32 eV for both the Cl 2p and C 1s photoionization. In order to understand the mechanism of such a site-specific production of the  $\text{H}_3^+$  ions, theoretical calculations for the Auger final states of the  $\text{CH}_3\text{Cl}$  molecule are highly desired.



**Figure 3.** Two-dimensional Auger-electron–photoion coincidence maps for (a)  $\text{N}_2^{2+} \rightarrow \text{N}^+ + \text{N}^+$  and (b)  $\text{N}^{2+} + \text{N}$  dissociation pathways.

## 2. Photoionization of Helium Atoms by Higher Harmonic Radiation from a Helical Undulator

A core shell electron in a molecule can be promoted to unoccupied orbitals when a photon energy is tuned to resonances. For light elements ( $Z < 26$ ), the Auger decay is the dominant process after the core excitation, and various ionic states are formed through the Auger electron emissions. The stability and dissociation dynamics of the Auger final states depend on their charge states and electronic states, which can be investigated by using an Auger-electron–photoion coincidence technique. In this work, we investigate the stability and dissociation dynamics of core excited  $\text{N}_2$  molecules.<sup>2)</sup>

Two-dimensional Auger-electron–photoion coincidence maps are shown in Figure 3. The maps reveal diagonal structures, indicating correlations between Auger-electron binding energies and ion KERs. These correlations come from the fact that the KER is equal to the difference between the binding energy of the Auger final state and the dissociation limit energy. The dissociation limit energy corresponds to the binding energy at the dissociation asymptote, and depends on the electronic states of atomic fragments in addition to charge states. From the correlations in Figure 3, we have derived the dissociation limits of dissociative Auger final states. It is also found that the  $X^1\Sigma_g^+$ ,  $A^1\Pi_u$ , and  $c^3\Sigma_u^+$  states are associated with the formation of metastable dicationic states.

### References

- 1) S. Pilling *et al.*, *Mon. Not. R. Astron. Soc.* **375**, 1488 (2007).
- 2) H. Iwayama *et al.*, *J. Chem. Phys.* **145**, 034305 (2016).