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FRAGMENTATION OF SMALL MOLECULES FOLLOWING SOFT X-RAY EXCITATION*

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ABSTRACT

Soft x-ray excitation involving C 1s electrons in CO and acetone, (CH₃)₂CO, is found to result in ionic fragmentation of the original molecule. The fragmentation pattern changes whether the C 1s electron gets ionized, excited into a Rydberg-line orbital or into an antibonding π^* molecular orbital. Also the fragmentation occurs specifically around the site of the carbon atom where the optical excitation takes place. Based on these observations one might consider the use of tunable soft x-rays to stimulate chemical reactions.

Valence excitations by ultraviolet absorption in small molecules and the subsequent fragmentation has been studied extensively. However very little is known about the processes following core (C 1s) excitations in these molecules. Carlson and Krause¹ have shown for a variety of small molecules that core ionization by x-ray line sources results in an abundance of ionic fragments. In light elements like C, N, O a core hole created in the initial optical absorption process decays preferentially via an Auger KLL transition rather than by x-ray emission resulting in a highly charged molecule that is unstable and falls apart in a Coulombic explosion.

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We here report the first studies of these fragmentation processes using continuously variable synchrotron radiation at the National Synchrotron Light Source (NSLS) Brookhaven. We find that in the region of the C 1s absorption threshold organic molecules decompose into ionic fragments not only after direct core ionization but also following core to bound state (π^* or Rydberg) transitions. The fragmentation pattern however changes completely between these various types of excitation or ionization. Even more important we will demonstrate that in larger molecules like acetone $(\text{CH}_3)_2\text{CO}$ site specific core to π^* excitations cause a break in the molecular structure at the site where the optical excitation occurred. Both the site specific behavior and the modulation with photon energy of the fragmentation process could become important for a new area of x-ray induced chemical reactions.

The ion branching ratio of CO changes radically with photon energy (see table I). The C 1s $\rightarrow 2\pi^*$ transition causes the molecule to predominantly break apart into $\text{C}^+ + \text{O}$, whereas other channels dominate at different photon energies.

The fragmentation pattern of acetone $[(\text{CH}_3)_2\text{CO}]$ on the other hand indicates that the local C 1s $\rightarrow \pi^*$ excitation in the CO group causes a local fragmentation in the same group within the molecule. This observation could have important applications with respect to fragmentation of larger molecules containing inequivalent C, N or O atoms.

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*Meanwhile this work has been published in Phys. Rev. Lett. 50, 1038 (1983).

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Table I
Branching Ratio of Singly Charged Species of CO

h ν	280 eV	287.3 eV (C 1s $\rightarrow 2\pi^*$)	293 eV (C 1s $\rightarrow 3p$)	310 eV
C^+	19.7%	65%	18.5%	23%
O^+	7%	3.9%	7.7%	8.9%
$(\text{CO})^+$	71.8%	28%	70.6%	63%
Total ion yield	100	390.5	151.2	136.6

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