Selective Fragmentation of Valence and Core Electron Excited CD$_4$ and SF$_6$ Molecules


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Electron-ion coincidence measurements with energy resolved electrons are a powerful tool in studies of molecular fragmentation processes. By detecting events correlated with the electrons of defined kinetic energy only fragmentations from a specific doorway state are monitored while the remaining channels are discriminated [1]. Presently, we have applied this technique in measurements of coincidence spectra of the CD$_4$ and SF$_6$ molecules following valence and core electron excitation. Our experiment has been implemented using an electron-ion coincidence set up installed at the undulator beam line 411 in MAX Laboratory in Lund, Sweden. It comprises a 125 mm hemispherical electron energy analyser and 110 mm ion time-of-flight analyser mounted collinearly. An inbuilt gas cell provides a target pressure 10-100 times above the chamber pressure. The measurements are performed at the magic angle with respect the synchrotron light polarization’s plane.

Our results show that the CD$_4^+$ molecule in the 1t$_2^{-1}$ state is stable or breaks up into CD$_3^+$ + D only. None of these reactions occur from the 2a$_1^{-1}$ state for which the D$^+$, CD$^+$ and CD$_2^+$ fragments were observed only. CI computations [2] reveal that the CD$_4^+$ fragments into CD$_3^+$ + D in a process,
where the initially excited $^2B_1$ state of the $C_{2v}$ geometry undergoes the transition to the state of the $C_{3v}$ geometry which instantaneously fragments to $\text{CD}_3^+ + \text{D}$. Dissociations from the $2a_{1}^{-1}$ state are governed by the $2^2A_1$ states of $C_{2v}$ and $C_{3v}$ geometries. Molecular fragmentation of $\text{CD}_4$ was also studied following core excitations of the C 1s electrons. Autoionization of the excited state to the $1t_2^{-1}$ state significantly alters the $\text{CD}_4^+/\text{CD}_3^+$ fragments ratio, which is the first demonstration of a correlation between nuclear motion and molecular dissociation in the $\text{CD}_4$ molecule. In addition, strong spectator Auger transitions that create double-hole ionic states result in a drastically different fragmentation pattern. Molecular fragments $\text{D}^+$, $\text{C}^+$, $\text{CD}^+$ and $\text{CD}_2^+$ are detected in coincidence with the Auger electrons, indicating a more complete breakdown of the molecule.

The coincidence measurements of the $\text{SF}_6$ molecule show that after ionisation to the $1t_{1g}^{-1}$ state the $\text{SF}_6^+$ ion is unstable and fully dissociates into the $\text{SF}_5^+ + \text{F}$ channel. Also unstable is the $4t_{1u}^{-1}$ state which fragments into $\text{SF}_3^+ + 3\text{F}$ in full agreement with predictions of Hitchcock et al [3]. Also, the mass spectra acquired in coincidence with the $5t_{1u}$, $3e_{g}$, $1t_{2u}$, $1t_{2g}$, and $5a_{1g}$ electrons reveal strong selectivity in dissociation from these states, which reflects the bonding properties of the potential surfaces involved in the studied processes.

References

