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 CD_3^+ + 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 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 CD_4^+/CD_3^+ fragments ratio, which is the first demonstration of a correlation between nuclear motion and molecular dissociation in the CD_4 molecule. In addition, strong spectator Auger transitions that create double-hole ionic states result in a drastically different fragmentation pattern. Molecular fragments D^+, C^+, CD^+ and CD_2^+ are detected in coincidence with the Auger electrons, indicating a more complete breakdown of the molecule.

The coincidence measurements of the SF_6 molecule show that after ionisation to the $1t_{1g}^{-1}$ state the SF_6^+ ion is unstable and fully dissociates into the $SF5^+$ + F channel. Also unstable is the $4t_{1u}^{-1}$ state which fragments into SF_3^+ + 3F 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

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