H_3^+ Formation from Methyl Halogens and Pseudohalogens: Experiment, Theory, and Governing Factors

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The formation of H_3^+ following the double ionization of small organic compounds via a roaming mechanism that involves the generation of a neutral H_2 molecule and a subsequent proton abstraction has gained significant attention in recent years. In our recent study [1], which is the subject of this lecture, we developed a cohesive microscopic model that explains the observed trends in the yield of H_3^+ from these important unimolecular reactions. To do this, we performed a series of yield and femtosecond time-resolved measurements following the strong-field double ionization of several CH_3X molecules, where X = OD, Cl, NCS, CN, SCN, and I, which were accompanied by high-level double-ionization-potential (DIP) equation-of-motion (EOM) coupled-cluster (CC) *ab initio* computations with up to 3-hole–1-particle and 4-hole–2-particle correlations on top of the CC treatment with singles and doubles of the parent CH_3X species that allowed us to obtain detailed information about the low-lying electronic states and geometries of the CH_3X^{2+} dications and the associated reaction pathways leading to H_3^+ formation. We also carried out *ab initio* molecular dynamics simulations employing the complete-active-space self-consistent-field approach calibrated to the DIP-EOMCC data to gain insights into the mechanism, yields, and timescales of H_3^+ formation from the CH_3X molecules. The combination of the state-of-the-art experimental measurements and *ab initio* electronic structure and dynamics computations discussed in this presentation and Ref. [1] allowed us to obtain detailed understanding of the key factors that govern the formation of H_3^+ by some doubly ionized CH_3X species and its absence in the others and develop useful guidelines for examining alternative sources of the H_3^+ cation in the universe.

[1] J. Stamm, S.S. Priyadarsini, S. Sandhu, A. Chakraborty, J. Shen, S. Kwon, J. Sandhu, C. Wicka, A. Mehmood, B.G. Levine, P. Piecuch, and M. Dantus, *Nat. Commun.* **16**, 410 (2025).