

Experiment and Theory Elucidate the Pathways for H_3^+ Formation in the Ultrafast Double Ionization of Methanol

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Abstract

This Research Highlight provides context for the report of Gope et al. on experimental and computational probes of the decay of doubly-ionized methanol to H_3^+ and $\text{HCO}^+/\text{COH}^+$. The formation of the H_3^+ ionic product is shown to occur through the agency of a roaming H_2 molecule generated from the carboxyl moiety that undergoes prompt proton transfer from the carbon atom, or, delayed proton transfer from the oxygen atom. This novel method for H_3^+ formation is contrasted with the conventional ion-molecule pathway, known for over a century, that forms the basis for interstellar molecule formation.

HIGHLIGHT

Experiment and Theory Elucidate the Pathways for H_3^+ Formation in the Ultrafast Double Ionization in Methanol

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The H_3^+ molecular ion has been well-known in chemistry for over a century. The ion is the simplest member of a class of protonated closed-shell molecules including H_3O^+ , NH_4^+ , and CH_5^+ that can be formed by ion-molecule reactions in high-pressure ion sources.[1] Such species have been employed extensively in chemical ionization mass spectrometry [2-4] as a means of soft ionization. The H_3^+ ion has played a central role in atomic and molecular physics dating back to the earliest days of mass spectrometry. At the beginning of the 20th century, J. J Thomson’s pioneering parabolic ray experiments with hydrogen gas [5] confirmed the presence of ions with mass to charge (m/e) ratios of 1 and 2, but also an unexpected peak corresponding to m/e of 3. Thomson correctly identified this peak as H_3 , a result that was later confirmed by Hogness and Lunn,[6] who employed mass spectrometry with a high-pressure ion source. Their results showed unequivocally that this species was produced by reaction between the primary ionization product H_2^+ and molecular hydrogen.

More recently, H_3^+ produced by a fast ion-molecule reaction between molecular hydrogen and H_2^+ formed by cosmic ray ionization has been established as the central ion that initiates chemistry in the interstellar medium. In a seminal paper, Herbst and Klemperer [7] proposed a detailed chemical kinetic scheme to account for the presence of the large number of molecules detected by radioastronomy in the 1960s and early 1970s.[8] Proton transfer reactions of H_3^+ to abundant atomic and molecular species CO, O, N, O_2 , and N_2 initiate this scheme. The formyl cation, HCO^+ , speculated to be “X-ogen”, [9-11] the carrier of a prominent line observed in radioastronomy, is a particularly important reaction product. Protonation of CO on the

oxygen end to form the isoformyl cation, COH^+ , was shown to lead to significant concentrations of this species as well.[12]

Laboratory studies of the high-resolution spectroscopy of H_3^+ , [13, 14] supported by measurements of reaction rates of this species with numerous small molecules,[15] provided excellent context to the report by Geballe and Oka in 1996 [16] of the direct detection of H_3^+ in interstellar space. The preeminence of H_3^+ in astrochemistry and astrobiology has been summarized recently in important publications.[17, 18]

The original mass spectrometric findings of Hogness and Lunn have withstood the test of time as the “standard model” to produce H_3^+ in ionized gases, especially interstellar space. In light of the extensive literature that highlights both the terrestrial and interstellar chemistry of H_3^+ , it is remarkable to discover new motifs for its production. The emerging field of multiply-charged ions has provided the context for several studies of alcohols and hydrocarbons in which electron impact and strong field laser ionization have produced H_3^+ by Coulomb explosion. The paper by Gope, Livshits, Bittner, Baer, and Strasser,[19] the subject of the present Highlight, represents the state of the art of such studies, reporting time-resolved ultrafast pump-probe experiments on CH_3OD with 3D coincidence imaging of the products of Coulomb explosion. The experimental work is complemented with *ab initio* molecular dynamics (AIMD) computations that characterize the timescales and kinetic energy releases for the two distinct pathways for product formation: $\text{H}_3^+ + \text{COD}^+$, and $\text{H}_2\text{D}^+ + \text{HCO}^+$.

The work of Gope *et al.* was preceded by a number of studies, notably the one-color multiphoton double ionization (MPDI) experiments conducted on CH_3OD by Dantus and co-workers, [20, 21] in which near IR (NIR) laser pulses both ionized CH_3OD and initiated the H^+/D^+ transfers leading to chemical reaction. The experiments revealed that H_2D^+ product formation was delayed relative to the appearance of H_3^+ , leading to a proposal that reaction was controlled by the formation of a nascent roaming H_2 molecule [22] on the carboxyl (CH_3CO) moiety of methanol that could undergo rapid *geminal* proton transfer from carbon to form the early H_3^+ product, or the roaming molecule could react with the deuterium ion on the *vicinal* oxygen to form H_2D^+ after a measurable delay. Similar experiments with longer chain alcohols led to the expected result that the longer the distance between the proton-donating carbon atom and the OD group, the longer the delay time between H_3^+ and H_2D^+ formation.

Gope *et al.* have performed single photon double ionization (SPDI) experiments with low field ultrafast extreme-ultraviolet (EUV) pump pulses, followed by NIR probe spectroscopy to overcome the strong sensitivity of MPDI experiments to laser parameters. Three-dimensional coincidence imaging provides reliable product detection with a determination of the kinetic energy release. Complementary AIMD calculations on both the CH_3OD and CH_3OH systems play a critical role in revealing important dynamical signatures of prompt and delayed H_3^+ formation. Specifically, monitoring the time evolution of the $\text{H}_3 - \text{COH}$ distance shows that delayed proton transfer (from oxygen) occurs approximately 110 fs after the prompt proton transfer from carbon. Of special interest is a comparison of the computed kinetic energy releases for the prompt and delayed proton transfers in CH_3OH with the same processes in CH_3OD . As expected, the kinetic energy releases for prompt reactions (proton transfer from carbon) in CH_3OH and CH_3OD are not affected by deuteration. However, the kinetic energy release for delayed proton transfer (from oxygen) in CH_3OH to form $\text{H}_3^+ + \text{HCO}^+$ is shifted to *lower* energies relative to delayed proton transfer (from oxygen) in CH_3OD to form $\text{H}_2\text{D}^+ + \text{COH}^+$. The authors attribute this surprising result to a subtle kinetic isotope effect rather than an energetic effect arising from the greater total energy available to the HCO^+ product.

Throughout the history of elementary reaction dynamics, the symbiosis of experiment and theory has been a recurring theme. As experiments have become more sophisticated, advancing from the specification and measurement of asymptotic reactant and product quantum states to time-resolved probes of detailed atomic motions, so also has theory responded with advanced methodologies to probe ever-increasing detail. The work of Gope *et al.* is an outstanding exemplar of the synergy between theory and experiment, and illuminates the way to additional advances in both disciplines.

The author declares that he has no conflict of interest associated with this manuscript.

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