CH$_5^+$ Stability and Mass Spectrometry

The report by E. T. White et al. (1) and the accompanying Perspective by D. Marx and M. Parrinello (2) both refer extensively to theoretical papers (3) which “indicate that the five protons in CH$_5^+$ are well bound to the central carbon . . . so that the C–H stretching potential is well defined but the angles between the five C–H bonds can change freely. The five equivalent protons are effectively swarming around the central carbon atom” (I, p. 136). The complexity of the system led White et al. to present the infrared spectrum of CH$_5^+$ (near 2939 cm$^{-1}$) without any specific assignments.

The theoretical models in these papers, however, appear to be in conflict with the Mass Spectral study of Heck, de Koning, and Nibbering (4), which showed that in the absence of intermolecular collisions, CH$_3^+$D$^+$ and CD$_2$H$^+$ are not rearranging but are stable. That these ions are relatively stable complexes of [CH$_5^+$-HD$^+$] and [CD$_5^+$-HD$^+$] was inferred from quenching reactions with NH$_3$.

Assuming that the lifetime of the mass spectrometry experiments is of the order of milliseconds implies a significant activation energy, possibly exceeding 10 kcal/mol for the intramolecular scrambling process. Thus, CH$_5^+$ appears to be a particularly stable van der Waals complex of a methyl cation and a hydrogen molecule. It may well be described as a (3c-2e) system, but it is not scrambling.

It may be a classic example of an ion-molecule interaction, but the existence of static isotopic Cs structures (I, 2) with energies close to that of the (3c-2e) entity must be considered questionable.

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Response: We regret not to have sufficiently discussed in our report (1) earlier experimental results on the structure of CH$_5^+$, especially of the proton/deuteron transfer experiments (2, 3, 4), the cluster stability measurements by Hiraoka and his colleagues (5), and the predissociation spectroscopy of clusters by Boo and Lee (6). In particular, the paper by Heck, de Koning, and Nibbering (4) gives definitive experimental results indicating that the three (3c-2e) C–H bonds are isolated from the other three C–H bonds and do not scramble, a conclusion incompatible with the most recent ab initio theory (7, 8).

The high resolution of their mass spectrometer allowed Heck et al. (4) to extract CH$_3^+$D$^+$ and CD$_2$H$^+$ that were uncontaminated with other ions with the same nominal mass. They then examined results of the proton (deuteron) transfer reaction

CH$_3^+$ + NH$_3$ → CH$_4$ + NH$_4^+$ (1)

With the use of a low-pressure CH$_5^+$ plasma source, they observed a 1:1 ratio of NH$_4^+$/NH$_3$D$^+$ for both CH$_3^+$D$^+$ and CD$_2$H$^+$, and concluded that the two (3c-2e) C–H bonds were isolated from the rest and that all chemical reactions occurred via those two bonds. When the pressure of the CH$_5^+$ source was increased, the NH$_3^+$/NH$_4^+$ ratio approached statistical values of 4/1 for CH$_3$D$^+$ and 1/4 for CD$_2$H$^+$.

The CH$_3$D$^+$ (CD$_2$H$^+$) was produced (4) from a 1:1 mixture of CH$_4$ and CD$_4$ through the ion-neutral reactions

CH$_4$ + CD$_3$ + → CH$_3$D$^+$ + CD$_3$

In order to accept the conclusion made by Heck et al., it is necessary to assume that (i), CH$_3$D$^+$ (CD$_2$H$^+$) is produced by deuteron (proton) transfer and that the transferred deuteron (proton) ends up in one of the (3c-2e) bonds and not in the other three C–H bonds, without causing scrambling, and (ii) subsequent CH$_3$D$^+$ (CD$_2$H$^+$) collisions with CH$_4$ or CD$_4$ scramble isotopes. The collisions are weak, without exchange of proton and deuteron, because Heck et al. did not observe CH$_3$D$_2^+$ or CH$_3$D$_2^+$.

In view of our lack of knowledge of their experimental method and the limited space for text and references in our report (1), we chose not to go into the discussion given above. The same applies to discussions on works by Hiraoka and his colleagues (5), and Boo and Lee (6).

We state that “our results are not consistent with the theoretical predictions of Schreiner et al. [7] and Müller et al. [8].” If the conclusion of Heck et al. is correct, the spectrum will be composed of five C–H stretch vibration bands with vibration-rotation interaction between them. Such a spectrum will also be complicated. The definitive spectroscopic conclusion will have to wait until we understand the reported CH$_5^+$ spectrum.

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Response by Marx and Parrinello: Various evidence, particularly from theory, seems to suggest that protonated methane, CH$_3^+$, is a fluxional molecule [see (I)]. Contrary to this, mass spectroscopic reactivity experiments (2) on deuteronated methane CH$_3$D$^+$ and protonated per-deuteronmethane CD$_2$H$^+$ are interpreted to show scrambling only if it is induced by intermolecular interactions, that is, each isolopomer “exhibits chemically distinguishable hydrogens” (2) without external perturbations. As recently stressed by Kramer, this implies that “in the absence of intermolecular collisions CH$_3$D$^+$ and CD$_2$H$^+$ are not rearranging but are stable” (3). As for some of the assumptions underlying the interpretation of these measurements, we draw attention to the objections put forward by Oka and White (4). In addition, the details of the reaction dynamics of both the formation and detection processes (such as preferred collision geometries and dipole locking) might yield crucial clues toward an understanding of the experimental data (2). Even weakly interacting ligands, such as several additional H$_2$ molecules leading to CH$_5^+$ (H$_2$)$_n$ complexes, can freeze the hydrogen scrambling motion in CH$_5^+$ (5).

In an effort to shed light on this puzzle through theoretical means, we have undertaken further ab initio path integral simulations similar to the previous one performed for CH$_3^+$ (6). In particular, we have studied the isolopomer CH$_3$D$^+$, where the initial configuration was the optimized C$_g$ ground-state structure of CH$_5^+$ (which may be pictured as

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**References**


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consisting of a H₂ moiety attached to a CH₃ tripod by means of a three-center two-electron bond [see figure 1, left panel (1)], with one proton of the H₂ moiety being substituted by a deuteron, that is, symbolically [CH₂H-D⁺]. As for CH₅⁺ (6), C₅-like configurations contribute most to the overall appearance of CH₅⁻ in its ground state. Most important, the protons, and in particular the deuteron, undergo scrambling (although the run was not long enough to lead to complete scrambling). These rearrangements lead to configurations—contributions to the nuclear density matrix in the sense of statistical sampling—where the deuteron is found in the CH₅₁D₂ tripod, thus leaving two protons in the three-center bond forming a H₂ moiety, symbolically [CH₂D₁H₂]⁺. The onset of scrambling was also observed in a much shorter run for a similarly prepared CD₄H⁺ molecule. In conclusion, our calculations show hydrogen scrambling was also observed in a much shorter run for a similarly prepared CD₄H⁺ molecule. In a fluxional molecule, harmonic analysis is a severely limited tool. Nevertheless, it is instructive to compare—within the Born-Oppenheimer approximation—the harmonic zero-point vibrational energies (ZPE) of various isotopomers in the ground-state C₄ symmetry (7). In the case of CH₃D⁺, substitution of one proton by a deuteron in the CH₃ tripod of CH₃⁺ leads to isotopomers that have a lower ZPE in the range of ~0.25 to 0.45 kcal/mol than those where substitution takes place in the three-center bonded H₂ moiety. Exactly the reverse is true for isotope labeling in CD₅⁺. Here the two isotopomers that possess a mixed HD moiety are preferred by about 0.25 to 0.45 kcal/mol over the other two, where the single proton is located in the CH₅₁H₂ tripod.

These energy differences, although very small, are nonnegligible on the energy scale set by the Born-Oppenheimer energy barrier of only ~0.6 kcal/mol (6)—the best literature value being ~0.8 kcal/mol (8)—to the closest transition state of C₅₀ symmetry [see figure 1, right panel in (1)] leading to hydrogen scrambling. Anharmonicities, tunneling, thermal excitations, and rotational contributions will alter the reported ZPE differences. Nevertheless, it is to be expected that these differences will affect the probability distribution of the various isotopomers by biasing the ZPE-favored substitution sites.

In view of these arguments, it is likely that experiments performed systematically for a family of CH₅⁺ isotopomers will lead to crucial novel insights into this fascinating molecular ion. As we concluded in our perspective (1), “CH₅⁺ will certainly continue to challenge many groups in various fields of expertise for some time to come.”

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References and Notes
3. See the comment by G. M. Kramer on the report by E. T. White, J. Tang, and T. Oka [Science 284, 135 (1999)].
7. On the basis of the unscaled harmonic frequencies, we obtain for CH₅⁺ a ZPE of 32.45 kcal/mol versus the best literature value of 32.71 kcal/mol based on a CCSD/TZ2P + f calculation by P. R. Schreiner, S.-J. Kim, H. F. Schaefer III, and P. V. Ragué Schleyer [J. Chem. Phys. 99, 3716 (1993)]. For details concerning the underlying electronic structure method (Kohn-Sham density functional theory using the local density approximation with Becke’s exchange-gradient correction, pseudopotentials, and a plane wave expansion of the valence electrons), see (6).
9. We thank D. Schröder (Technische Universität Berlin) and R. Saykally (University of California Berkeley) for comments.
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