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" (*1*, 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$_4$D$^+$ and CD$_4$H$^+$ are not rearranging but are stable. That these ions are relatively stable complexes of [CH$_3$···HD]$^+$ and [CD$_3$···HD]$^+$ was inferred from quenching reactions with NH$_3$.

Assuming that the lifetime in 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 isomeric C$_S$ structures (*1, 2*) with energies close to that of the (3c-2e) entity must be considered questionable.

George M. Kramer
36 Arden Court,
Berkeley Heights, NJ 07922, USA

References
1. E. T. White, J. Tang, T. Oka, *Science* **284**, 135 (1999).
2. D. Marx and M. Parrinello, *Science* **284**, 59 (1999).
3. P. R. Schreiner, S.-J. Kim, H. F. Schaefer III, P. von Ragué Schleyer, *J. Chem. Phys.* **99**, 3716 (1993).
4. A. J. R. Heck, L. J. de Koning, N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.* **2**, 453 (1991).

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 two (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$_4$D$^+$ and CD$_4$H$^+$ that were uncontaminated with other ions with the same nominal mass. They then examined results of the proton (deuteron) transfer reaction

$$CH_5^+ + NH_3 \rightarrow CH_4 + NH_4^+ \qquad (1)$$

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$_4$D$^+$ and CD$_4$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$_4^+$/NH$_3$D$^+$ ratio approached to statistical values of 4/1 for CH$_4$D$^+$ and 1/4 for CD$_4$H$^+$.

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

$$CH_4 + CD_4^+ \rightarrow CH_4D^+ + CD_3$$
$$(CD_4 + CH_4^+ \rightarrow CD_4H^+ + CH_3) \qquad (2)$$
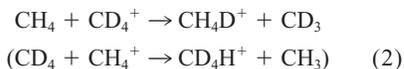
In order to accept the conclusion made by Heck *et al.*, it is necessary to assume that (i), CH$_4$D$^+$ (CD$_4$H$^+$) is produced by deuteron (proton) transfer and that the transferred deuteron (proton) ends up in one of the (3c-2e) bonds and not in the other three C–H bonds, without causing scrambling, and (ii) subsequent CH$_4$D$^+$ (CD$_4$H$^+$) collisions with CH$_4$ or CD$_4$ scramble isotopes. The collisions are weak, without exchange of proton and deuterons, because Heck *et al.* did not observe CH$_3$D$_2^+$ or CH$_2$D$_3^+$. We find it difficult to accept these two results together in view of the fact that reaction (*2*) is exothermic by approximately 5 to 8 kcal/mol and that the collisions are "weak interactions between the protonated methane and methane" with energies of perhaps much less than 1 kcal/mol (*4*).

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 stated that "our results are not inconsistent 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.

Takeshi Oka
Edmund T. White
Department of Chemistry and
Department of Astronomy and Astrophysics
and *Enrico Fermi Institute*
University of Chicago
Chicago, IL 60637, USA

References
1. E. T. White, J. Tang, T. Oka, *Science* **284**, 135 (1999).
2. M. D. Sefcik, J. M. S. Henis, P. P. Gaspar, *J. Chem. Phys.* **61**, 4321 (1974).
3. R. D. Smith and J. H. Futrell, *Chem. Phys. Lett.* **36**, 545 (1975).
4. A. J. R. Heck, L. J. de Koning, N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.* **2**, 453 (1991).
5. K. Hiraoka and T. Mori, *Chem. Phys. Lett.* **161**, 111 (1989); K. Hiraoka, I. Kudata, S. Yamabe, *Chem. Phys. Lett.* **184**, 271 (1991).
6. D. W. Boo and Y. T. Lee, *Chem. Phys. Lett.* **211**, 358 (1993); *J. Chem. Phys.* **103**, 520 (1995).
7. P. R. Schreiner, S.-J. Kim, H. F. Schaefer III, P. von Ragué Schleyer, *J. Chem. Phys.* **99**, 3716 (1993).
8. H. Müller, W. Kutzelnigg, J. Noga, W. Klopper, *J. Chem. Phys.* **106**, 1863 (1997).

Response by Marx and Parinello: Various evidence, particularly from theory, seems to suggest that protonated methane, CH$_5^+$, is a fluxional molecule [see (*1*)]. Contrary to this, mass spectroscopic reactivity experiments (*2*) on deuteronated methane CH$_4$D$^+$ and protonated per-deuteromethane CD$_4$H$^+$ are interpreted to show scrambling only if it is induced by intermolecular interactions, that is, each isotopomer "exhibits chemically distinguishable hydrogens" (*2*) without external perturbations. As recently stressed by Kramer, this implies that "in the absence of intermolecular collisions CH$_4$D$^+$ and CD$_4$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$_5^+$ (*6*). In particular, we have studied the isotopomer CH$_4$D$^+$, where the initial configuration was the optimized C$_s$ ground-state structure of CH$_5^+$ (which may be pictured as

consisting of a H_2 moiety attached to a CH_3 tripod by means of a three-center two-electron bond [see figure 1, left panel (*1*)], with one proton of the H_2 moiety being substituted by a deuteron, that is, symbolically $[CH_3 \cdot HD]^+$. As for CH_5^+ (*6*), C_s-like configurations contribute most to the overall appearance of CH_4D^+ 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 CH_2D tripod, thus leaving two protons in the three-center bond forming a H_2 moiety, symbolically $[CH_2D \cdot H_2]^+$. The onset of scrambling was also observed in a much shorter run for a similarly prepared CD_4H^+ molecule. In conclusion, our calculations show hydrogen scrambling in CH_5^+, CH_4D^+, and CD_4H^+. We cannot infer the time-scale of this process from our path integral calculations. We also point out other limitations of these calculations: the approximate nature of the density-functional-based potential energy surface; the neglect of quantum statistics (the Fermi-Dirac and Bose-Einstein exchange statistics for H and D); and the use of the Born-Oppenheimer approximation.

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 C_s structure (*7*). In the case of CH_4D^+, substitution of one proton by a deuteron in the CH_3 tripod of CH_5^+ leads to isotopomers that have a lower ZPE in the range of $\approx$0.25 to 0.45 kcal/mol than those where substitution takes place in the three-center bonded H_2 moiety. Exactly the reverse is true for isotope labelling in CD_5^+. 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 CH_2H tripod.

These energy differences, although very small, are nonnegligible on the energy scale set by the Born-Oppenheimer energy barrier of only $\approx$0.6 kcal/mol (*6*)—the best literature value being $\approx$0.8 kcal/mol (*8*)—to the closest transition state of C_{2v} 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 CH_5^+ isotopomers will lead to crucial novel insights into this fascinating molecular ion. As we concluded in our per-spective (*1*), "CH_5^+ will certainly continue to challenge many groups in various fields of expertise for some time to come."

Dominik Marx
Michele Parrinello
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1
70569 Stuttgart
Germany

References and Notes
1. D. Marx and M. Parrinello, *Science* **284**, 59 (1999).
2. A. J. R. Heck, L. J. de Koning, N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.* **2**, 453 (1991).
3. See the comment by G. M. Kramer on the report by E. T. White, J. Tang, and T. Oka [*Science* **284**, 135 (1999)].
4. Response by T. Oka and E. White to Technical Comment by G. M. Kramer on their report [E. T. White, J. Tang, T. Oka, *Science* **284**, 135 (1999)].
5. D. W. Boo and Y. T. Lee, *Chem. Phys. Lett.* **211**, 358 (1993); D. W. Boo, Z. F. Liu, A. G. Suits, J. S. Tse, Y. T. Lee, *Science* **269**, 57 (1995); D. W. Boo and Y. T. Lee, *J. Chem. Phys.* **103**, 520 (1995).
6. D. Marx and M. Parrinello, *Nature* **375**, 216 (1995).
7. On the basis of the unscaled harmonic frequencies, we obtain for CH_5^+ 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*).
8. H. Müller, W. Kutzelnigg, J. Noga, W. Klopper, *J. Chem. Phys.* **106**, 1863 (1997).
9. We thank D. Schröder (Technische Universität Berlin) and R. Saykally (University of California Berkeley) for comments.