

CH₅⁺: The Infrared Spectrum Observed

Edmund T. White, Jian Tang, Takeshi Oka*

Protonated methane, CH₅⁺, has unusual vibrational and rotational behavior because its three nonequivalent equilibrium structures have nearly identical energies and its five protons scramble freely. Although many theoretical papers have been published on the quantum mechanics of the system, a better understanding requires spectral data. A complex, high-resolution infrared spectrum of CH₅⁺ corresponding to the C–H stretching band in the 3.4-micrometer region is reported. Although no detailed assignment of the individual lines was made, comparison with other carbocation spectra strongly suggests that the transitions are due to CH₅⁺.

Since its discovery by Tal'roze and Lyubimova (1), protonated methane or methonium ion, CH₅⁺, has been well known among ion chemists. Its spectrum, however has not been reported in any spectral region. Here we present an observation of the spectrum of this fundamental molecular ion, a high-resolution infrared vibration-rotation-tunneling spectrum corresponding to the C–H stretching vibrations.

Because of the lack of spectroscopic data, the quantum chemical understanding of CH₅⁺ has been based almost exclusively on ab initio

theoretical calculations. Early calculations (2) showed that a configuration with C_s symmetry [shown in Fig. 1 as C_s(1)] has lower energy than the more intuitive and symmetric trigonal bipyramid (D_{3h}) or symmetric top (C_{4v}) configurations. Subsequent self-consistent field calculations by Pople and his colleagues (3) gave a structure in which CH₃⁺ and H₂ are well separated, but as the theory was more refined, the separation between CH₃⁺ and H₂ was reduced. An additional structure with C_{2v} symmetry, in which three protons are in a plane bisecting the H₂ unit (shown in Fig. 1 as C_{2v}), was shown to have low energy (4). The most recent calculations find that the three structures have nearly equal energy. Schreiner *et al.* (5) report that the energies of the C_s(2) and C_{2v} structures (shown in Fig. 1) are higher than that of C_s(1) by only

Department of Chemistry, Department of Astronomy and Astrophysics, and the Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, USA.

*To whom correspondence should be addressed.

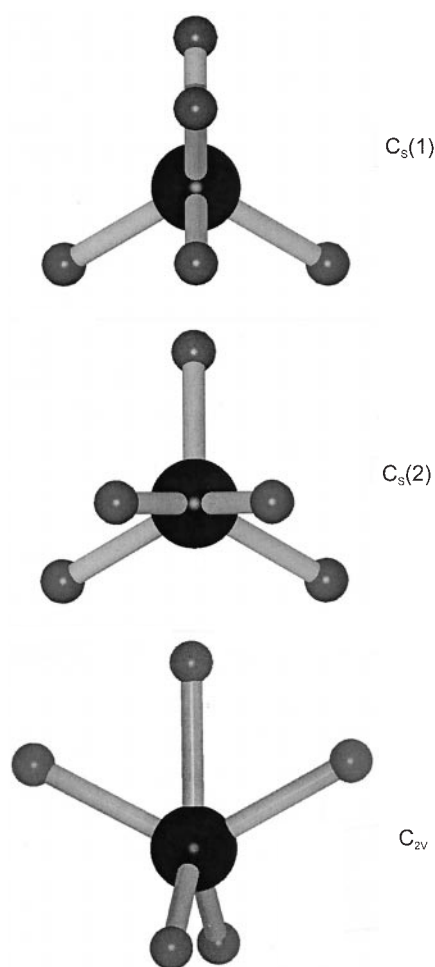


Fig. 1. Three low-energy structures of CH_5^+ . In the $C_s(1)$ and $C_s(2)$ structures, the three C–H bonds of the CH_3 radical have C_{3v} symmetry with H_2 either eclipsed [$C_s(1)$] or staggered [$C_s(2)$] with respect to the C–H bonds of the CH_3 subgroup. In the C_{2v} structure, three C–H bonds are in the plane of the figure. Ab initio theory gives minimum equilibrium energy for $C_s(1)$, whereas $C_s(2)$ and C_{2v} form saddle points with slightly higher energy. When zero point vibrations are taken into account, the energy differences almost vanish.

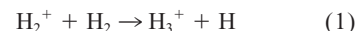
0.09 and 0.90 kcal/mol, respectively, and Müller *et al.* (6) report values of 0.1 and 0.8 kcal/mol, respectively. Both groups agree that, if the zero point vibrations are taken into account, the energies of the three structures become practically identical, in agreement with earlier work by von Ragué Schleyer and Carneiro (7). Schreiner *et al.* (5, p. 3176) state, “The differences in energies (of the three structures) decrease and essentially vanish at the most sophisticated levels . . . , there is essentially *no barrier* to complete hydrogen scrambling.” Müller *et al.* (6, p. 1863) state “the $C_s(2)$ and C_{2v} structures, which are both saddle points on the potential energy surface, are so little above the minimum that CH_5^+ is highly fluxional, to the extent that the very concept of molecular structure becomes problematic for this molecule.” The topological analysis on this system by Marx and collaborators (8) gives a perspective on this problem from a different angle.

These theoretical works indicate that the five protons in CH_5^+ are well bound to the central carbon (the proton affinity of CH_4 is 5.72 eV, or 132 kcal/mol) 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. We earlier faced a somewhat similar but much simpler problem in the spectroscopy of protonated acetylene, C_2H_3^+ , in which the three protons exchange their equilibrium positions (9–11). The case of CH_5^+ , however, is incomparably more complex (12) because of the practical absence of equilibrium positions and because of the larger number of protons. Here we present its spectrum as observed without assignment (or even qualitative understanding).

We first searched for the CH_5^+ spectrum in 1985 using air-cooled and water-cooled plasma tubes with helium-dominated He– H_2 – CH_4 gas mixtures. Because the sensitivity and discrimination of the velocity modulation method invented by Saykally’s group (13) allowed us to

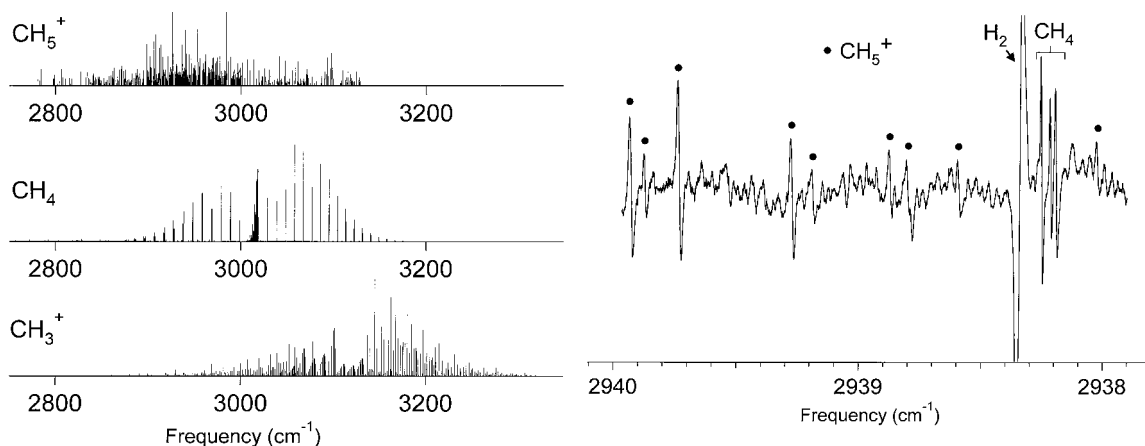
study spectra of NH_4^+ (14) and H_3O^+ (15), we believed that the spectrum of CH_5^+ would be identified readily. An extremely rich spectrum was obtained in the 3- μm region, but all of the strong lines were assigned to the C–H stretch bands of CH_3^+ (16), CH_2^+ (17), C_2H_2^+ (18), and C_2H_3^+ (9, 10). Subsequent searches for CH_5^+ were conducted in 1987 and 1993 with liquid nitrogen-cooled plasma tubes and H_2 -dominated H_2 – CH_4 gas mixtures, which provided a wealth of spectral lines. As all of the stronger lines were eventually “weeded out” by more thorough spectroscopic and plasma chemical studies of other carbocations (10, 19), many lines remained, suggesting that they are due to CH_5^+ . (In hindsight, we now realize that some CH_5^+ lines were observed in the experiments of 1987 and 1993 but could not be identified until after several more years of systematic study.)

We conducted a high-sensitivity scan in the 3- μm region using a liquid nitrogen-cooled positive column discharge tube of ~ 12 mm in diameter and ~ 1 m in length and a 6-kHz AC discharge for velocity modulation. Infrared radiation of ~ 200 μW generated by our difference frequency laser system was divided into two beams with equal energy, each traversing unidirectionally four times through the plasma in opposing directions to give a total path length of 8 m that results in effective noise subtraction (20). Hydrogen-dominated H_2 – CH_4 gas mixtures were used for the simplest CH_5^+ production through



The H_2 – CH_4 mixing ratio of 50:1 with the total gas pressure of ~ 1 torr produced the optimum conditions for observing the CH_5^+ spectrum. Notably, the minimum discharge current within stable plasma conditions (~ 80 mA) gave the best results, in sharp contrast to the optimum conditions for other carbocations (150 to 200 mA). About 900 spectral lines were measured as CH_5^+ lines in the 3- μm region from 3150

Fig. 2 (left). Observed overall infrared spectrum of CH_5^+ as compared with spectra of CH_4 and CH_3^+ . **Fig. 3 (right).** An example of a small portion of the CH_5^+ spectrum. Spectral lines marked with \bullet are due to CH_5^+ . The sharp lines are due to CH_4 caused by small asymmetry of the AC discharge. The strong line with negative slope is due to a Rydberg spectrum of H_2 . The line is velocity modulated by electron bombardment excitation to the excited state.



cm⁻¹ to 2770 cm⁻¹ (Fig. 2). Known spectral lines of H₃⁺, CH₃⁺, and C₂H₃⁺ together with those of impurity ions HCO⁺ and HCNH⁺ weakly appeared in the region, as well as the Rydberg spectrum of H₂, but these lines were easily identified. The ν₃ triply degenerate C–H stretch band of CH₄, whose spectral lines are stronger than those of CH₅⁺ by perhaps six orders of magnitude because of the higher abundance and lower partition function, is in the same region (Fig. 2). As these are spectral lines of a neutral molecule, they should escape the velocity modulation detection, but unavoidable slight asymmetry of the AC plasma operation can sometimes make them appear with sizable intensities. As the CH₅⁺ lines are weak, if they happen to overlap with those other lines, they would be lost. The observed scarcity of CH₅⁺ in some regions is due to such overlaps. An example of a portion of the spectrum is shown in Fig. 3. The peak-to-peak widths of the derivative shapes of the spectral lines are ~0.011 cm⁻¹. The spectral lines were measured with an uncertainty of Δν ~ 0.003 cm⁻¹ for stronger lines and Δν ~ 0.006 cm⁻¹ for weaker lines. (A list of frequencies and relative intensities is available at www.sciencemag.org/feature/data/987367.shl or from T.O. upon request).

The observed spectrum shown in Fig. 2 is extremely rich and complicated. There is no obvious regularity or symmetry, except that it is approximately symmetric with respect to the most congested central area, which perhaps forms the Q branch. The spectrum is in sharp contrast with the well-behaved CH₃⁺ and CH₄ spectra also shown in Fig. 2. The center of the band is at about 2950 cm⁻¹, lower than that of CH₃⁺ (3108.4 cm⁻¹) and CH₄ (3019.5 cm⁻¹), and agrees approximately with the band origin of the CH₅⁺ group in the spectrum of cluster ions CH₅^{+(H₂)_n} reported by Boo and Lee (21) and with ab initio predictions (5, 22). The spread of the band is comparable to those of CH₃⁺ and CH₄, suggesting a similar rotational constant. Although we do not have any rotational assignment, we believe that the spectral lines are due to CH₅⁺ for the following reasons: (i) The carrier of the spectrum is a cation because the spectrum was observed by velocity modulation with positive slope of the derivative shape. The spurious lines due to neutrals can be readily recognized from their response to plasma conditions and 2f detection (ions are velocity modulated through Doppler shifts at the AC frequency *f*, whereas neutrals are detected at two times the AC frequency because they are insensitive to the phase of the discharge). (ii) The carrier contains one carbon atom because spectral lines for heavier ions are observed to be narrower because of the Δν ~ (*M*)^{-1/2} relation between the Doppler broadened line width Δν and mass *M*. (iii) Spectra of CH₃⁺, CH₂⁺,

CH⁺, and C⁺ are well known. (iv) CH₄⁺ is not abundant in the hydrogen-dominated H₂-CH₄ plasmas. The last of these statements is the weakest, and we cannot completely exclude the possibility that some stronger lines of CH₄⁺, for which the spectrum is unknown, may be in the spectrum as weak lines. We are convinced, however, that the majority of the lines in Fig. 2 and listed in the supplementary table are CH₅⁺ lines.

The sensitivity of our spectrometer is estimated to be (Δ*I*/*I*)_{min} ~ 4 × 10⁻⁶, where *I* is intensity, corresponding to the minimum detectable absorption coefficient of γ_{min} ~ 5 × 10⁻⁹ cm⁻¹. The strongest line has a signal-to-noise ratio of ~20, corresponding to γ ~ 10⁻⁷ cm⁻¹. This value is about 1/20 of the strongest lines of CH₃⁺. Because the number of the CH₅⁺ lines is an order of magnitude more than that of the CH₃⁺ lines, reflecting the higher partition functions due to tunneling, the band intensities are comparable. The number density of CH₅⁺ is estimated to be [CH₅⁺] ~ 2 × 10¹⁰ cm⁻³ from plasma chemical considerations.

The complexity of the observed CH₅⁺ spectrum is not inconsistent with the theoretical predictions of Schreiner *et al.* (5) and Müller *et al.* (6). If their model of complete scrambling with no barrier is the case, we then have only three familiar quantum numbers, the rotational angular momentum *J*, the parity, and the total nuclear spin angular momentum *I* = Σ_{*i*=1}⁵ *I_i*. The angular momentum formula [D_{1/2}]⁵ = D_{5/2} + 4D_{3/2} + 5D_{1/2} shows that the spectral lines appear as a set of components with spin statistical weight of 6:4:2 each with the frequency of 1:4:5 just like in CH₄, where they appear with the weight of 5:3:2 (2 for the double parity) with frequency 1:3:1. Our search for such sets was unsuccessful because of inaccuracy of the intensity measurements and because of the effects of large splitting and the severe congestion of lines. The complete proton scrambling necessitates the use of *S*₅^{*} = *G*₂₄₀ (2 × 5!) to specify symmetry of the energy levels (23). Bunker and colleagues (23, 24) have developed an extensive quantitative theory by using a mechanical model in which the problem is projected to symmetry *G*₁₂, where CH₃⁺ and H₂ are considered as separate units. Whether such treatment is useful remains to be seen.

The problem of the intramolecular dynamics of CH₅⁺ will require use of the accurate full ab initio potential and the variational calculations of the dynamics of the five protons in the potential. Such calculations have been developed by Sutcliffe and Tennyson (25) and applied successfully to the three-particle problem of H₃⁺ by Miller *et al.* (26) and many others (27–29). However, application of such a method to the five-proton problem perhaps must await development of considerably more pow-

erful computers. Experimentally, the next step will be to observe the spectrum at low temperatures and to observe deuterated species.

References and Notes

- V. L. Tal'roze and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR* **86**, 909 (1952); G. C. Eltenton (Shell Development Company unpublished report, 1940) is quoted by D. P. Stevenson and D. O. Schissler [*J. Chem. Phys.* **23**, 1353 (1955)].
- A. Gamba, G. Morosi, M. Simonetta, *Chem. Phys. Lett.* **3**, 20 (1969); G. A. Olah, G. Klopman, R. H. Schlosberg, *J. Am. Chem. Soc.* **91**, 3261 (1969); W. T. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.* **4**, 389 (1969).
- W. A. Lathan, W. J. Hehre, J. A. Pople, *J. Am. Chem. Soc.* **93**, 808 (1971); J. A. Pople, in *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XVI Theoretical Chemistry*, M. O. Milligan, Ed. (Robert A. Welch Foundation, Houston, TX, 1973), pp. 10–57.
- V. Dyczmons, V. Staemmler, W. Kutzelnigg, *Chem. Phys. Lett.* **5**, 361 (1970); V. Dyczmons and W. Kutzelnigg, *Theor. Chim. Acta* **33**, 239 (1974).
- P. R. Schreiner, S.-J. Kim, H. F. Schaefer III, P. von Ragué Schleyer, *J. Chem. Phys.* **99**, 3716 (1993).
- H. Müller, W. Kutzelnigg, J. Noga, W. Klopper, *ibid.* **106**, 1863 (1997).
- P. von Ragué Schleyer and J. W. D. M. Carneiro, *J. Comput. Chem.* **13**, 997 (1992).
- D. Marx and M. Parrinello, *Nature* **375**, 216 (1995); D. Marx and A. Savin, *Angew. Chem. Int. Ed. Engl.* **36**, 2077 (1997).
- M. W. Crofton, M.-F. Jagod, B. D. Rehfuss, T. Oka, *J. Chem. Phys.* **91**, 5139 (1989).
- C. M. Gabrys, D. Uy, M.-F. Jagod, T. Oka, T. Amano, *J. Phys. Chem.* **99**, 15611 (1995).
- D. Marx and M. Parrinello, *Science* **271**, 179 (1996).
- G. E. Scuseria, *Nature* **366**, 512 (1993).
- C. S. Gudeman, M. H. Begemann, J. Pfaff, R. J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).
- M. W. Crofton and T. Oka, *J. Chem. Phys.* **79**, 3157 (1983).
- D. J. Liu and T. Oka, *Phys. Rev. Lett.* **54**, 1787 (1985).
- M. W. Crofton, M.-F. Jagod, B. D. Rehfuss, W. A. Kreiner, T. Oka, *J. Chem. Phys.* **88**, 666 (1988).
- M. Rösslein, C. M. Gabrys, M.-F. Jagod, T. Oka, *J. Mol. Spectrosc.* **153**, 1 (1992).
- M.-F. Jagod *et al.*, *J. Chem. Phys.* **97**, 7111 (1992).
- M.-F. Jagod, C. M. Gabrys, M. Rösslein, D. Uy, T. Oka, *Can. J. Phys.* **72**, 1192 (1994).
- M. G. Bawendi, B. D. Rehfuss, T. Oka, *J. Chem. Phys.* **93**, 6200 (1990).
- D. W. Boo and Y. T. Lee, *Chem. Phys. Lett.* **211**, 358 (1993); *J. Chem. Phys.* **103**, 520 (1995).
- D. J. DeFrees and A. D. McLean, *J. Chem. Phys.* **82**, 333 (1985).
- P. R. Bunker, *J. Mol. Spectrosc.* **176**, 297 (1996).
- M. Kolbuszewski and P. R. Bunker, *J. Chem. Phys.* **105**, 3649 (1996); A. L. L. East and P. R. Bunker, *J. Mol. Spectrosc.* **183**, 157 (1997); A. L. L. East, M. Kolbuszewski, P. R. Bunker, *J. Chem. Phys.* **A101**, 6746 (1997).
- B. T. Sutcliffe and J. Tennyson, in *Molecules in Physics, Chemistry, and Biology*, J. Maruani, Ed. (Kluwer Academic, Dordrecht, Netherlands, 1988), vol. II, pp. 313–333.
- S. Miller, J. Tennyson, B. T. Sutcliffe, *J. Mol. Spectrosc.* **141**, 104 (1990).
- L. Wolniewicz and J. Hinze, *J. Chem. Phys.* **101**, 9817 (1994).
- J. K. G. Watson, *Chem. Phys.* **190**, 291 (1995).
- R. Jaquet, W. Cencek, W. Kutzelnigg, J. Rychlewski, *J. Chem. Phys.* **108**, 2837 (1998).
- One of the authors (T.O.) wishes to thank G. A. Olah for his continuous plying for us to study this ion. The following students and postdoctoral fellows spent considerable time earlier on this experiment: M. W. Crofton, M.-F. Jagod, B. D. Rehfuss (1985), M. G. Bawendi, M. Okumura (1987), C. M. Gabrys, and D. Uy (1993). This work was supported by NSF grant PHY-9722691 and NASA grant NAG5-4234.

28 December 1998; accepted 17 February 1999