0, 1, and 2 are reported in Fig. 3, showing the oscillations as well as the parity effect for odd resonances. The period is reproduced with $D = 0.292$ K and $E = 0.046$ K as in (23), but with a different C value of -2.9×10^{-5} K. The calculated tunneling splitting is, however, about three times smaller than the observed one. These small discrepancies are not surprising. In fact, with the C parameter, we took into account the effects of the neglected higher order terms in S_x and S_y of the spin Hamiltonian, which, even if very small, can make an important contribution to the period of oscillation and markedly affect Δ, as first pointed out by Prokof'ev and Stamp (22). In addition, the nuclear spins could affect the value of Δ (24). Finally, the total quantum spin phase is built up from all magnetic spins of the system. For Fe_8, the total spin $S = 10$ results from a complex antiferromagnetic exchange topology and can be schematized by eight spins with spin values of $s = 5/2$ where six spins are aligned parallel and antiparallel to the other two spins (25). It should also be mentioned that internal dipolar and hyperfine fields hinder a quench of Δ (26).

Our measurement technique is opening up a way of directly measuring very small tunnel splittings on the order of 10^{-8} K that are not accessible by resonance techniques. We have found a very clear oscillation in the tunnel splittings Δ, which is direct evidence of the role of the topological spin phase in the spin dynamics of these molecules (14). We have also observed an "Aharonov-Bohm" type of oscillation in a magnetic system, analogous to the oscillations as a function of external flux in a SQUID ring (1). A great deal of information is contained in these oscillations, both about the form of the molecular spin Hamiltonian and about the dephasing effect of the environment. We expect that these oscillations should thus become a very useful tool for studying systems of nanomagnets.

References and Notes

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CH$_5$$^+$: The Infrared Spectrum Observed

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Protonated methane, CH_5^+, 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 CH_5^+ 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 CH_5^+.

Since its discovery by Tal'roze and Lyubimova (1), protonated methane or methonium ion, CH_5^+, 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 CH_5^+ 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 CH_3^+ and H_2 are well separated, but as the theory was more refined, the separation between CH_3^+ and H_2 was reduced. An additional structure with C_{2V} symmetry, in which three protons are in a plane bisecting the H_2 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

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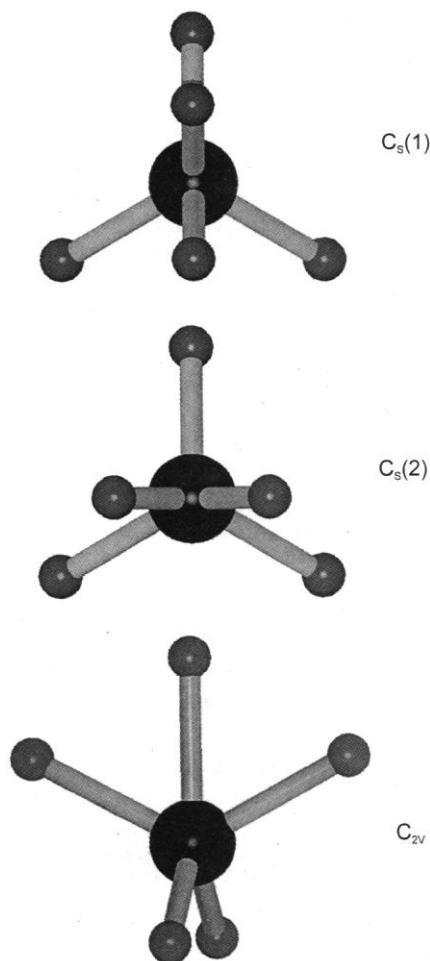
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0.09 and 0.90 kcal/mol, respectively, and Müller *et al.* (*6*) report values of 0.1 and 0.8 kcal/mol, respectively. Both groups agree that, if the zero point vibrations are taken into account, the energies of the three structures become practically 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

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (1)$$

$$H_3^+ + CH_4 \rightarrow CH_5^+ + H_2 \qquad (2)$$
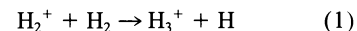
The H_2-CH_4 mixing ratio of 50:1 with the total gas pressure of ~1 torr produced the optimum conditions for observing the CH_5^+ spectrum. Notably, the minimum discharge current within stable plasma conditions (~80 mA) gave the best results, in sharp contrast to the optimum conditions for other carbocations (150 to 200 mA). About 900 spectral lines were measured as CH_5^+ lines in the 3-μm region from 3150

Fig. 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.

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 ● 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.
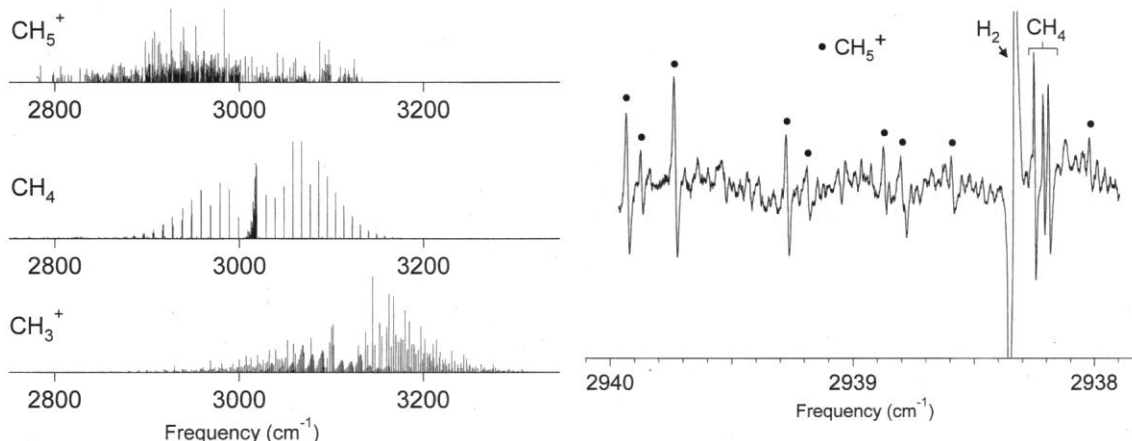
cm^{-1} to 2770 cm^{-1} (Fig. 2). Known spectral lines of H$_3^+$, CH$_3^+$, and C$_2$H$_3^+$ together with those of impurity ions HCO$^+$ and HCNH$^+$ weakly appeared in the region, as well as the Rydberg spectrum of H$_2$, but these lines were easily identified. The ν_3 triply degenerate C–H stretch band of CH$_4$, whose spectral lines are stronger than those of CH$_5^+$ 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 CH$_5^+$ lines are weak, if they happen to overlap with those other lines, they would be lost. The observed scarcity of CH$_5^+$ 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 $\Delta\nu \sim 0.003$ cm^{-1} for stronger lines and $\Delta\nu \sim 0.006$ 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 CH$_3^+$ and CH$_4$ spectra also shown in Fig. 2. The center of the band is at about 2950 cm^{-1}, lower than that of CH$_3^+$ (3108.4 cm^{-1}) and CH$_4$ (3019.5 cm^{-1}), and agrees approximately with the band origin of the CH$_5^+$ group in the spectrum of cluster ions CH$_5^+$(H$_2$)$_n$ reported by Boo and Lee (21) and with ab initio predictions (5, 22). The spread of the band is comparable to those of CH$_3^+$ and CH$_4$, suggesting a similar rotational constant. Although we do not have any rotational assignment, we believe that the spectral lines are due to CH$_5^+$ 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 $\Delta\nu \sim (M)^{-1/2}$ relation between the Doppler broadened line width $\Delta\nu$ and mass M. (iii) Spectra of CH$_3^+$, CH$_2^+$,

CH$^+$, and C$^+$ are well known. (iv) CH$_4^+$ is not abundant in the hydrogen-dominated H$_2$-CH$_4$ plasmas. The last of these statements is the weakest, and we cannot completely exclude the possibility that some stronger lines of CH$_4^+$, 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 CH$_5^+$ lines.

The sensitivity of our spectrometer is estimated to be $(\Delta I/I)_{\min} \sim 4 \times 10^{-6}$, where I is intensity, corresponding to the minimum detectable absorption coefficient of $\gamma_{\min} \sim 5 \times 10^{-9}$ cm^{-1}. The strongest line has a signal-to-noise ratio of ~20, corresponding to $\gamma \sim 10^{-7}$ cm^{-1}. This value is about 1/20 of the strongest lines of CH$_3^+$. Because the number of the CH$_5^+$ lines is an order of magnitude more than that of the CH$_3^+$ lines, reflecting the higher partition functions due to tunneling, the band intensities are comparable. The number density of CH$_5^+$ is estimated to be [CH$_5^+$] $\sim 2 \times 10^{10}$ cm^{-3} from plasma chemical considerations.

The complexity of the observed CH$_5^+$ 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 $I = \Sigma_{i=1}^{5} I_i$. 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 CH$_4$, 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 CH$_3^+$ and H$_2$ are considered as separate units. Whether such treatment is useful remains to be seen.

The problem of the intramolecular dynamics of CH$_5^+$ 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 H$_3^+$ 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-

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