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Vibrational Spectroscopy and Dynamics of Ionic Complexes
of CH$_5^+$, CH$_5^+(A)_{x}(B)_{y}$ (A,B=Ar,N$_2$,CH$_4$;x,y=0-5)

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Abstract

The vibrational spectra for the ionic complexes of CH₃⁺, CH₃⁺(A)ₓ(B)ᵧ (A,B=Ar,N₂,CH₄; x,y=0-5) in the 2500-3200 cm⁻¹ frequency region are presented. The scrambling motions of the CH₃⁺ core slow considerably as the ion-solvent interactions increase (Ar<N₂<CH₄), and as the number of the solvent molecules in the complexes increase. The CH₃⁺ core of CH₃⁺(CH₄)ₓ (n≥3) was regarded as rigid. For CH₃⁺(N₂) and CH₃⁺(CH₄)ₓ (n=1,2,3), the H-H stretching bands of the CH₃⁺ core, which are direct evidence for three-center two-electron bonding in CH₅⁺, were found in the 2500 - 2700 cm⁻¹ region. The structures of the methane-solvated carbonium ions CH₃⁺(CH₄)ₓ (n=1-5) were predicted from the analysis of the vibrational spectra, improving on the previous theoretical and experimental predictions.

Keywords: Carbonium ions; Vibrational spectra; Ionic complexes; Solvent effects; Dynamics.
Introduction

Hydrocarbons are essential in our modern life not only as energy sources but also to produce commonly used products ranging from polymers to textiles to pharmaceuticals. Many of the chemical processes used in the transformation of hydrocarbons are acid-catalyzed electrophilic reactions involving carbocationic intermediates. Consequently, the knowledge of these intermediates and their chemistry is of substantial significance in both fundamental research and applied science [1,2]. Among these carbocations, the nonclassical carbonium ions, which are intermediates in the acid-catalyzed electrophilic reactions of saturated hydrocarbons, are known to form a three-center two-electron (3c2e) bond having pentacoordinated carbon atoms and bridged hydrogens, different from the trivalent classical carbenium ions [3].

CH$_3^+$ is the simplest carbonium ion. It is the intermediate in direct electrophilic conversion of methane (the major component of natural gas still abundant on Earth) to higher hydrocarbons, one of the most promising routes for future hydrocarbon synthesis [1]. This species exists only as a transient species in the solution phase but is quite stable in the gas phase, where unimolecular dissociation (CH$_3^+$ → CH$_3^+$ + H$_2$) requires at least ~40 kcal/mole. It is routinely used as a source in chemical ionization mass spectrometry [4], and is also of astrophysical interest, since it may be an intermediate in the formation of methane in galactic cold molecular clouds [5].

During the last two decades, much theoretical work has been performed to determine the structure of CH$_3^+$, but the structure has been very elusive [6-14]. The early theoretical
calculations consistently suggested that CH₅⁺ can be regarded as the complex between CH₃⁺ and H₂, and the global minimum energy structure is an eclipsed C₄ (e-C₄) symmetry structure [6-9]. However, recent ab initio calculations at the most sophisticated level predicted that the calculated energy differences between the e-C₄ structure and others, such as the staggered C₄ (s-C₄) or C₂ᵥ structures, were very small and became negligible when corrected for the zero point vibrational energies [10-12]. It was therefore suggested that CH₅⁺ does not have a unique, stable equilibrium structure, and the hydrogen atoms scramble almost freely among multiple equivalent minima [13]. However, the most recent quantum ab initio path integral simulations on CH₅⁺ at 5 K, with the incorporation of density functional electronic structure calculations, suggested that the ground state structure of CH₅⁺ can best be pictured as C₂-like with 3c2e bonding, in spite of prominent quantum mechanical effects on the structure, such as fluxionality, pseudo-rotations, and hydrogen scrambling [14].

In contrast to the numerous theoretical studies on CH₅⁺, only a few indirect mass spectrometric experiments have been performed to characterize the structure of CH₅⁺ [15-20]. Hiraoka and coworkers measured -ΔHⁿ⁻¹,n and -ΔSⁿ⁻¹,n for the formation of the CH₅⁺ ionic complexes, CH₅⁺(H₂)ₙ (n=1-4) [15] and CH₅⁺(CH₄)ₙ (n=1-9) [16,17] using pulsed electron beam high pressure mass spectrometry. They found that the positive charge of the CH₅⁺ core for the weakly bound clusters CH₅⁺(H₂)ₙ was more or less delocalized, indicated by the gradual decrease in -ΔHⁿ⁻¹,n with increasing n, but proposed that a large gap in the van’t Hoff plots between n=2 and 3 was suggestive of a C₄ structure [15]. In contrast, irregular decreases in the value -ΔHⁿ⁻¹,n and -ΔSⁿ⁻¹,n for CH₅⁺(CH₄)ₙ
were observed between n=2 and 3, and n=7 and 8 (shown in Table 1), suggesting a \( C_2 \)

symmetry structure for the \( \text{CH}_3^+ \) core and the formation of the first solvation shell at n=7

for \( \text{CH}_5^+(\text{CH}_4)_n \), respectively [16,17]. The observed differences between \( \text{CH}_5^+(\text{H}_2)_n \) and

\( \text{CH}_5^+(\text{CH}_4)_n \) suggested that the structure and dynamics of the \( \text{CH}_5^+ \) ions could be

significantly influenced by the solvent molecules in the ionic complexes. Experiments

using Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometry [18-20]

have also been performed on the collisionally-induced intramolecular randomization of

hydrogen and deuterium atoms in \( \text{CH}_4\text{D}^+ \) and \( \text{CD}_4\text{H}^+ \), but the conclusions on the structure

of \( \text{CH}_5^+ \) were inconsistent (see ref 23). Because of difficulties in the indirect

colorization of the \( \text{CH}_5^+ \) structures, much effort has been made to obtain high

resolution infrared (IR) spectra for \( \text{CH}_5^+ \), but has achieved little success, probably because

of the scrambling of \( \text{CH}_5^+ \) even at low temperatures, which caused significant spectral

congestion.

In an attempt to determine the structure and dynamics of \( \text{CH}_5^+ \) directly and to study

the solvent effects on the scrambling of \( \text{CH}_5^+ \), we have studied a series of the ionic

complexes of \( \text{CH}_5^+ \), \( \text{CH}_5^+(A)_x(B)_y \) (\( A,B=\text{H}_2,\text{Ar},\text{N}_2,\text{CI};x,y=0-6 \)) by measuring the IR

spectra for these complexes. Here the solvent \( \text{H}_2 \) and \( \text{CH}_4 \) molecules represented the

cases for the weakest and strongest solvent effects on \( \text{CH}_5^+ \), respectively. Recently the IR

spectra for \( \text{CH}_5^+(\text{H}_2)_n \) (n=1-6) have been reported in a series of papers [21-23], along with

the results of \textit{ab initio} molecular dynamics (MD) simulations on \( \text{CH}_5^+(\text{H}_2)_n \) (n=0-3) at

100 K [22]. The \textit{ab initio} MD simulations at 100 K provided better comparison with the

experimental observations since the average vibrational temperatures for the \( \text{CH}_5^+(\text{H}_2)_n \)
(n=1-3) ions produced in the corona discharge ion source were expected to be similar to the simulation temperature. Moreover, the simulations at 100 K, compared to that at 5 K, could be less subject to the possible inaccuracy of density functional theory in describing the fine features of electronic potential energy surfaces, which may be important for the simulations at 5 K, close to the zero-point energy level. As will be summarized later, the CH₅⁺ ions scramble extensively at 100 K, and the scrambling motions slow down considerably with increasing number of H₂ molecules in the complexes. The experimental details and the complete analysis of the IR spectra for CH₅⁺(H₂)ₙ (n=1-6) were addressed in ref. 23.

In this paper, we report a systematic study of the solvent effects on the structure and dynamics of CH₅⁺ by using various solvent molecules such as Ar, N₂, and CH₄, and by changing the number of the solvent molecules in the complexes. In addition, it will be shown that the structures of the methane-solvated carbonium ions CH₅⁺(CH₄)ₙ (n=1-5) can be precisely determined from the analysis of the vibrational spectra for these complexes, improving on the previous theoretical and experimental predictions on the structures of CH₅⁺(CH₄)ₙ.
Experimental Details

The experimental apparatus used in this work has been described previously [24-28]. Briefly, the solvated carbonium ions, \( \text{CH}_5^+(A)_x(B)_y \) (\( A,B=\text{Ar},\text{N}_2,\text{CH}_4; x,y=0-5 \)) were produced from a high pressure corona discharge source and subsequent supersonic expansion through a 75 \( \mu \)m nozzle. The corona discharge was maintained in 60-300 torr of a gas mixture with ultrahigh purity (UHP) \( \text{H}_2 \) and UHP \( \text{CH}_4 \), and with the addition of UHP \( \text{Ar} \) and \( \text{N}_2 \) for the corresponding clusters, flowing past a 1.0 kV potential from the discharge tip of the needle to the source body maintained at 350 V above ground. The discharge currents under these conditions were 20-40 \( \mu \)A. The temperature of the source body was maintained between -20 and -70 °C by heating the source body in contact with a liquid nitrogen trap. Typical pressures in the source chamber were \( 2\times10^{-5}-4\times10^{-5} \) torr during the experiment. To prevent the acceleration of ions in the higher pressure region which causes internal excitation and dissociation of the ion clusters via collisions with the background gas, the potential of the skimmer was maintained within 1 V of that of the source body.

After the skimmer, the ion beam entered a second differential pumping region containing collimating and focusing lenses. The pressure in this region was typically an order of magnitude lower than that of the source region. The beam was directed into a 60° sector magnet mass analyzer through a third differentially pumped region maintained at \( 2\times10^{-8} \) torr. The mass-selected beam was then bent 90° in a dc quadrupole field, decelerated to less than 0.5 eV, and focused into a rf octapole ion trap through an
entrance aperture lens. The ions were usually trapped here for ~2 msec before IR irradiation. The trapped, mass-selected clusters were then vibrationally excited by a pulsed, tunable infrared (IR) laser. A Quanta-Ray IR WEX was used as a tunable IR light source. The IR wavelength was produced in a LiNbO₃ crystal that generates the difference frequency between a Lambda Physics pulsed dye laser (Model FL3002E) and the 1.06 μm fundamental of a Continuum Nd-YAG laser. The IR resolution was 0.2 cm⁻¹. The pulse duration was 6 nsec with a 20 Hz repetition rate, and the laser power was 0.5-2 mJ/pulse in the 2500-3200 cm⁻¹ region scanned in this work.

If the ions absorb one or more IR photon(s) in the usual tuning range of 2500-3200 cm⁻¹, the CH₅⁺(A)ₓ(B)ᵧ ions vibrationally predissociate into the daughter ions CH₅⁺(A)ₓ-m(B)ᵧ-n and the solvent molecules mA + nB (m,n=0,1,2,...,but ≤ x,y). Roughly 0.5 msec after the laser pulse, the potential on the exit aperture was lowered to extract ions of all masses from the trap. These ions were filtered by a quadrupole mass spectrometer tuned to pass only one of the daugther ions CH₅⁺(A)ₓ-m(B)ᵧ-n. In this work, the quadrupole mass filter was fixed at the mass of a specific daughter ion which gave the maximum intensity among the CH₅⁺(A)ₓ-m(B)ᵧ-n daughter ions. The observation of the daughter ion signal as a function of laser frequency was a measure of the infrared absorption of the parent ion CH₅⁺(A)ₓ(B)ᵧ (A,B=Ar,N₂,CH₄;x,y=0-5). Daughter ions were counted with a Daly ion detector [29] for each laser shot. Background daughter ions resulting from the decay of metastable parent ions in the rF ion trap were monitored in a separate cycle with the laser off at each wavelength and subtracted from the laser on signal. The laser power
was monitored at each data point, and spectra were normalized for the power of the
tunable infrared laser assuming a simple linear power dependence.

In this experiment, it was seen that the composition of ions in the beam was strongly
dependent on the mixing ratio of gases, the discharge current, the source temperature and
the pressure inside the source. Practical rules used in the discharge for the carbonium ion
clusters are as follows: First, the concentration of CH\textsubscript{4} in the gas mixture was kept low to
reduce the formation of larger hydrocarbon ions such as C\textsubscript{2}H\textsubscript{3}\textsuperscript{+}, C\textsubscript{2}H\textsubscript{5}\textsuperscript{+}, C\textsubscript{3}H\textsubscript{7}\textsuperscript{+}, etc, via
CH\textsubscript{3}\textsuperscript{+} precursor ions (see ref. 28 for the details). When these larger hydrocarbon ions
were present as the major ions in the mass spectra, the intensities of the solvated
carbonium ions were observed to be considerably low. Second, the discharge current was
kept as low as possible to reduce the internal excitation of the ions at the expense of the
ion intensities. A slight increase of the discharge current resulted in an increase in the
background level. The source temperatures and source pressures were optimized to
maximize the intensity of each cluster ion, but they were preferred optimally to set at the
low and high values, respectively as long as no significant decrease in the ion intensity was
observed, in order to produce the ions as cold as possible.

For CH\textsubscript{5}\textsuperscript{+}(CH\textsubscript{4})\textsubscript{n} (n=1-5), the CH\textsubscript{4}/H\textsubscript{2} mixing ratio of 1:10,000 was found to be an
optimum ratio in the discharge. Usually, ~750 ions for CH\textsubscript{5}\textsuperscript{+}(CH\textsubscript{4})\textsubscript{n} with n=1 and 2, and
~300 ions for CH\textsubscript{5}\textsuperscript{+}(CH\textsubscript{4})\textsubscript{n} with n=3, 4, and 5 were trapped per cycle, which are not
enough to allow direct measurement of photon absorption. For a typical experiment,
signals were averaged for about 500 laser shots at each wavelength in the range of 2500-
3200 cm\textsuperscript{-1}. Fig. 1 shows the mass spectrum obtained with a 200 torr source pressure,
-50°C source temperature and 40 µA discharge current with a gas mixture of \( \text{CH}_4: \text{H}_2 = 1:10,000 \). As shown in Fig. 1, the \( \text{CH}_5^+ (\text{CH}_4)_x (\text{H}_2)_y \) \( (x, y = 0, 1, 2, \ldots) \) ions were observed as the major species in the mass spectrum.

For \( \text{CH}_5^+ (\text{Ar})_x (\text{CH}_4)_y \) \( (x=1,2; y=0,1) \), the Ar gas was mixed with the \( \text{CH}_4/\text{H}_2 \) mixture with the ratio of \( \text{CH}_4: \text{Ar}: \text{H}_2 = 1:1,000:10,000 \). Typically, ~200 ions were trapped per cycle, and the signals were averaged for about 500 shots at each wavelength in the 2500-3200 cm\(^{-1}\) region. For \( \text{CH}_5^+ (\text{N}_2) \), the \( \text{CH}_4/\text{H}_2 \) mixture was used in the discharge with an impurity amount of \( \text{N}_2 \) which was originally introduced by a small leak in the gas inlet line. The discharge of the gas mixture with UHP \( \text{N}_2 \) in an exact ratio identified the mass peak at \( m/e=45 \) to be \( \text{CH}_5^+ (\text{N}_2) \). Since \( \text{C}_3 \text{H}_9^+ \) has the same mass-to-charge ratio (\( m/e=45 \)), the isotope of methane, \( ^{13}\text{CH}_4 \) was used in the gas mixture to identify the \( \text{CH}_5^+ (\text{N}_2) \) by observing the mass peak shifting from \( m/e=45 \) to \( m/e=46 \).
Results and Analysis

A. Previous work

According to the previous experimental and theoretical studies on CH₅⁺(H₂)ₙ (n=1-6) [21-23], the five H atoms in the CH₅⁺ core scramble considerably via the CH₃ internal rotation and the in-plane wagging motion of the 3c2e bond. Consequently the observed C-H stretching features for the CH₅⁺ core were highly congested in the spectrum. An important observation was that such scrambling motions slowed substantially as the number of the solvent H₂ molecules in the complexes increased. Briefly, the results are summarized as follows: For CH₅⁺(H₂), the three CH₃ stretching modes of the CH₅⁺ core (predicted in the ab initio calculation to be well-separated in frequency [11,30]), were found as one broad feature with shoulders in the spectrum due to the scrambling via the two large amplitude motions. In particular, the extremely broad low frequency shoulder (2700-3100 cm⁻¹) was interpreted as the signature for the free in-plane wagging motion of the 3c2e bond (via a C₂ᵥ transition state) [22,23]. Ab initio MD simulation on CH₅⁺(H₂) at 100 K also supported these experimental findings [22].

For CH₅⁺(H₂)₂, one broad and one narrow vibrational feature were observed in the same frequency region, and were assigned to the two strongly-coupled CH₃ stretching modes and one less-coupled CH₃ stretching mode, respectively. The CH₃ internal rotation was predicted to be still free, responsible for the coupling of two CH₃ stretching modes, while the 3c2e in-plane wagging motion was expected to be hindered, as suggested by the absence of the low frequency shoulder. This result indicated that the coordination of two
H₂ molecules to the electron-deficient two 3c2e H atoms could stabilize the 3c2e bonding configuration of the CH₅⁺ core. For CH₅⁺(H₂)ₙ (n≥3), three vibrational features were found in the 2800-3100 cm⁻¹ region, and assigned to the symmetric CH₃ breathing, symmetric CH₃ degenerate stretching, and asymmetric CH₃ stretching modes of an e-C₃ CH₅⁺ core. The two large amplitude motions were suggested to be more or less hindered, and the CH₅⁺ core in CH₅⁺(H₂)₃ was thus regarded as semi-rigid. These solvent effects for stabilizing the floppy ion core would be much more significant for the CH₅⁺ ions solvated by the heavier and the more strongly bound solvents such as Ar atom, N₂, and CH₄ molecules. In particular, CH₄ was expected to have the strongest solvent effects since the core and solvent molecules have the same proton affinities. In the following sections (B-E) spectroscopic evidence will be given for the effects of solvents on the dynamics of the CH₅⁺ core in CH₅⁺(A)ₓ(B)ᵧ (A,B=Ar,N₂,CH₄;x,y=0-5).

B. Mono-solvated carbonium ions, CH₅⁺(A) (A=Ar,N₂,CH₄)

Fig. 2 shows the vibrational spectra for the mono-solvated carbonium ions, CH₅⁺(A) (A=Ar, N₂, CH₄), obtained by monitoring the CH₅⁺ signal (m/e=17) in the frequency region of 2700-3200 cm⁻¹. The vibrational features in this frequency region were attributed to the C-H stretching modes of the core ion CH₅⁺ and the solvent CH₄ molecules [11,23,31]. The vibrational frequencies and the tentative vibrational assignments are listed in Table 2.
Two vibrational features, centered at 2974 and 3081 cm\(^{-1}\), were found in the spectrum for the frequency region of 2820-3120 cm\(^{-1}\) as shown in Fig. 2A. By comparison with the previous results on CH\(_5\)^+(H\(_2\))\(_n\) (n=1-6), these vibrational features were assigned to the two strongly-coupled CH\(_3\) stretching modes, and one less-coupled CH\(_3\) stretching mode of the CH\(_5\)^+ core, respectively (see refs. 21-23). The observation of two vibrational features, in contrast to the single extremely broad feature for CH\(_5\)^+(H\(_2\)), suggested that the coupling of the C-H stretching modes due to the scrambling of the CH\(_5\)^+ core (via the CH\(_3\) internal rotation and the \(3c2e\) in-plane wagging motion) decreased somewhat. The broad low frequency shoulder (2700-3100 cm\(^{-1}\)) observed for CH\(_5\)^+(H\(_2\)), signature for the free \(3c2e\) in-plane wagging motion, was not observed in the spectrum (see Fig. 2A). These results suggested that the heavy Ar atom in CH\(_5\)^+(Ar) could better stabilize the floppy CH\(_5\)^+ core than the H\(_2\) molecule in CH\(_5\)^+(H\(_2\)). This could arise from the fact that the heavy Ar atom has a large average electric dipole polarizability (\(\alpha\)), almost twice that of H\(_2\) (\(\alpha\)(Ar)=1.64x10\(^{-24}\), \(\alpha\)(H\(_2\))=0.80x10\(^{-24}\) cm\(^3\)) [32], so that the increased charge-induced dipole interaction in CH\(_5\)^+(Ar) would slow the scrambling motions, in spite of the absence of the charge-quadrupole interaction predicted for CH\(_5\)^+(H\(_2\)) (the electric quadrupole moment \(\Theta=2.12x10^{-40}\) Cm\(^2\) for H\(_2\)) [32]. Besides, the Ar solvent atom was expected to be more efficient in decoupling the mixed C-H stretching modes of the core ion than the H\(_2\) molecule due to the heavy mass effect. It is also interesting to notice that the spectral pattern for CH\(_5\)^+(Ar) is closer to that for CH\(_5\)^+(H\(_2\))\(_2\) than for CH\(_5\)^+(H\(_2\)), except for the narrow bandwidth of the 2974 cm\(^{-1}\) feature (see refs. 22,23). Therefore, the CH\(_3\) internal
rotation in the \( \text{CH}_3^+ \) core of \( \text{CH}_5^+(\text{Ar}) \) was expected to still be free, as evidenced by the single feature for the two strongly-coupled \( \text{CH}_3 \) stretching modes (2974 cm\(^{-1}\)), while the in-plane wagging motion was more or less frozen.

2. \( \text{CH}_5^+ (\text{N}_2) \)

Since the mass-to-charge ratio of \( \text{CH}_5^+ (\text{N}_2) \) (m/e=45) was the same as that of \( \text{C}_3\text{H}_9^+ \) (consisting of \( \text{C}_2\text{H}_5^+ \) and \( \text{CH}_4 \), a probable ion species which could be formed in a discharge of methane and hydrogen gases), another experiment using the \(^{13}\text{C}\)-isotope of methane was performed to confirm the mass assignment. In a discharge with a \(^{13}\text{CH}_4 \cdot \text{H}_2 \) gas mixture, the mass peak at m/e=45 was shifted to m/e=46, indicating the presence of only a single C atom in this molecule, and the vibrational spectrum for the m/e=46 ions was similar to that for the m/e=45 ions, except for the slight frequency shifts due to the isotope effect. This confirmed the assignment of the m/e=45 peak to \( \text{CH}_5^+ (\text{N}_2) \).

Two vibrational features, centered at 2983 and 3077 cm\(^{-1}\), were found in the spectrum (shown in Fig. 2B) for the frequency range of 2800-3200 cm\(^{-1}\) and were assigned to the two strongly-coupled \( \text{CH}_3 \) stretching modes and one less-coupled \( \text{CH}_3 \) stretching mode of the \( \text{CH}_5^+ \) core, respectively, based on their similarity to those for \( \text{CH}_5^+ (\text{Ar}) \). The slightly narrower bandwidths of the observed features, compared to those for \( \text{CH}_5^+ (\text{H}_2) \) and \( \text{CH}_5^+ (\text{Ar}) \), were suggestive of the decreased scrambling of the \( \text{CH}_5^+ \) core due to the increased ion-solvent interactions in \( \text{CH}_5^+ (\text{N}_2) \) vs. \( \text{CH}_5^+ (\text{H}_2) \), \( \text{CH}_5^+ (\text{Ar}) \). The major interactions in \( \text{CH}_5^+ (\text{N}_2) \) would be the charge-induced dipole and charge-quadrupole interactions, which are similar to, but much stronger than those in \( \text{CH}_5^+ (\text{H}_2) \) (\( \alpha=1.74\times10^{-24} \))
cm³, Θ=-5x10⁻⁴⁰ Cm² for N₂) [32-34]. The negative sign of the quadrupole moment of N₂ suggested that the N₂ molecule in CH₅⁺(N₂) was oriented linearly toward the charge center, according to the expression of the electrostatic interactions for a positive point charge interacting with the diatomic molecule(s) (different from the T-shaped configuration for H₂ in CH₅⁺(H₂)) [23,33,34]. The CH₃ internal rotation was expected to still be free, while the 3c2e in-plane wagging motion was hindered, as indicated by the absence of the broad low frequency shoulder (2700-3100 cm⁻¹). Such hindered 3c2e in-plane wagging motion was also suggested by the observed vibrational feature centered at 2623 cm⁻¹ (Fig. 6A), which could be assigned to the 3c2e H-H stretching mode (see the Discussion). The 3c2e H-H stretching mode could have such high vibrational frequency only when the 3c2e bond is highly localized in CH₅⁺ [11].

3. CH₅⁺(CH₄)

Three vibrational features, centered at 2869, 2982, and 3063 cm⁻¹, were found in the 2800-3100 cm⁻¹ region of the spectrum as shown in Fig. 2C. Among these vibrational features, the 2869 cm⁻¹ feature was assigned to the C-H stretching mode of the solvent CH₄ molecule in CH₅⁺(CH₄), because this peak was not observed in the spectra for the other mono-solvated carbonium ions CH₅⁺(A) (A=H₂,Ar,N₂). It was 45 cm⁻¹ red-shifted from the totally symmetric ν₁ C-H stretching mode of free CH₄ (2914 cm⁻¹) [31], indicating some weakening of the C-H bonds of the CH₄ molecule upon coordination to the CH₅⁺ core. Since the solvent CH₄ molecule was predicted to coordinate via the 3-fold face according to the ab initio calculation [35], the C-H stretching mode responsible for
the 2869 cm\(^{-1}\) feature could be more or less localized in the three C-H bonds bonded directly to the CH\(_3^+\) core (subsequently referred to as the bound CH\(_3\) stretching mode).

The 2982 and 3063 cm\(^{-1}\) features, on the other hand, were assigned to the two strongly-coupled CH\(_3\) stretching modes and one less-coupled CH\(_3\) stretching mode of the CH\(_3^+\) core, respectively, as in the cases of CH\(_3^+(\text{Ar})\) and CH\(_3^+(\text{N}_2)\). These peaks were much narrower than those for CH\(_3^+(\text{Ar})\) and CH\(_3^+(\text{N}_2)\), suggesting that the floppy core CH\(_3^+\) was more stabilized by the strong interaction between CH\(_3^+\) and CH\(_4\). Such strong interaction has also been predicted in previous experimental and theoretical work on CH\(_3^+(\text{Ar})_n\) [16,17,38]. Experimentally, the measured -\(\Delta H^\circ\) for the reaction CH\(_3^+ + \text{CH}_4 = \text{CH}_3^+(\text{CH}_4)\) was 6.87 kcal/mole (also listed in Table 1), somewhat higher than the predicted value for the pure electrostatic interactions between CH\(_3^+\) and CH\(_4\) (\(\alpha=2.59\times10^{-24}\) cm\(^3\) for CH\(_4\)) [16,32,34]. Theoretically, \textit{ab initio} MO calculations on CH\(_3^+(\text{CH}_4)\) predicted that the covalent interaction between the highly occupied molecular orbital (HOMO) of CH\(_4\) and the lowest unoccupied molecular orbital (LUMO) of CH\(_3^+\) was responsible for about half of the total binding energy (comparable to the charge-induced dipole interaction) [38].

The 2982 cm\(^{-1}\) feature possesses a high frequency shoulder centered at 3010 cm\(^{-1}\), determined from a least squares fit, as shown in Fig. 3. The shoulder feature was assigned to another C-H stretching mode of the solvent CH\(_4\) (one C-H bond not directly involved in the coordination), since it was only \(\sim10\) cm\(^{-1}\) shifted from the triply degenerate \(v_3\) C-H stretching modes of free CH\(_4\) (3020 cm\(^{-1}\)) (subsequently referred to as the free CH\(_4\) stretching mode). The spectral pattern for the two C-H stretching bands of CH\(_4\)
(2869,3010 cm⁻¹) was different from that for free CH₄, where the $v₁$ C-H stretching mode is IR inactive and the $v₃$ mode is IR active [31]. The difference could arise from the fact that the whole ion complex would have a $C₄$ symmetry, different from the $T₄$ symmetry for free CH₄, and the bound CH₄ stretching mode involving the C-H bonds close to the charge center could have higher oscillator strength. Such spectral patterns (similar vibrational frequency shifts and IR intensities) have been observed previously in the infrared spectra for CH₄ polarized by an external electric field, such as the CH₄ molecule adsorbed on NaCl film [36] and also on cationic forms of high-silica zeolites [37]. Another vibrational feature, centered at 2608 cm⁻¹, was observed in the frequency region of 2500-2700 cm⁻¹ as shown in Fig. 6B. As in the case of CH₅⁺(N₂), this vibrational feature was assigned to the $3c2e$ H-H stretching mode of the CH₅⁺ core (see the Discussion).

The $3c2e$ in-plane wagging motion of the CH₅⁺ core in CH₅⁺(CH₄) was likely to be frozen, as indicated by absence of the broad low frequency shoulder in the spectrum and also by the observed $3c2e$ H-H stretching band, while the CH₃ internal rotation of the CH₅⁺ core would be still free. Finally, the complex CH₅⁺(CH₄) (a proton bound symmetric dimer), would be an interesting system for studying the proton transfer between two identical neutral molecules. The proton in the ground state CH₅⁺(CH₄) is expected to be highly localized in one CH₄ unit as evidenced by the observed high $3c2e$ H-H stretching frequency and the observed C-H stretching features assigned exclusively to the core CH₅⁺ or the solvent CH₄. Therefore, the proton transfer in CH₅⁺(CH₄) would occur in a double well potential energy surface (PES) with certain barrier, somewhat different from the cases
of H$_3$O$^+$ (H$_2$O) [39] and NH$_4^+$ (NH$_3$) [40] (The results on the proton transfer in CH$_5^+$ (CH$_4$) will be reported elsewhere.).

C. Di-solvated carbonium ions, CH$_5^+$(A)(B) (A,B=Ar,CH$_4$)

Fig. 4 shows the vibrational spectra for di-solvated carbonium ions, CH$_5^+$(A)(B) (A,B=Ar,CH$_4$) obtained in the frequency region 2700-3200 cm$^{-1}$. The vibrational features in this frequency region were again attributed to the C-H stretching modes of the core CH$_5^+$ and the solvent CH$_4$. The observed frequencies and the tentative vibrational assignments are listed in Table 2. As mentioned above for CH$_5^+$ (H$_2$)$_2$, two solvent H$_2$. molecules were expected to coordinate to the electron deficient H atoms of the 3c2e bond, respectively. The CH$_3$ internal rotation was predicted to be free while the 3c2e in-plane wagging motion was hindered due to the stabilization of the 3c2e bonding configuration by two solvent molecules. The scrambling of the CH$_5^+$ core in CH$_5^+$(A)(B) (A,B=Ar,CH$_4$) would slow down more due to stronger interaction between the core ion and the solvents Ar and CH$_4$ vs. H$_2$. Consequently the vibrational modes of the core ion would be much less coupled, compared to the cases of CH$_5^+$ (H$_2$)$_2$ and the mono-solvated carbonium ions.

1. CH$_5^+$(Ar)$_2$

The vibrational spectrum shown in Fig. 4A was obtained by monitoring the CH$_5^+$ signal in the frequency region of 2820-3120 cm$^{-1}$. One broad and one sharp feature, centered at 2957 and 3072 cm$^{-1}$, respectively, were observed in the spectrum, similar to the case for CH$_5^+$ (H$_2$)$_2$, and thus assigned to the two strongly-coupled CH$_3$ stretching
modes, and one less-coupled CH₃ stretching mode of the CH₅⁺ core, respectively. The 2957 cm⁻¹ feature was much broader and red-shifted, compared to the corresponding feature for CH₅⁺(Ar) (2974 cm⁻¹), and its top was slightly flatter than the 2957 cm⁻¹ feature for CH₅⁺(H₂)₂ (see Fig. 2A, 4A, and refs. 22,23). The 3072 cm⁻¹ feature, on the other hand, was much sharper and better resolved than the corresponding features for CH₅⁺(Ar) and CH₅⁺(H₂)₂. These results suggested that the two strongly-coupled CH₃ stretching modes could start to decouple and separate in frequency, due to the increased solvent effect of two Ar atoms for stabilizing the floppy core, but yet insufficient to be resolved, and simultaneously, the less-coupled CH₃ stretching mode (3072 cm⁻¹) was much more decoupled. Since the free CH₃ internal rotation was the primary cause for mixing the two CH₃ stretching modes of CH₅⁺(H₂)ₙ (n=1,2) [22,23], the CH₃ internal rotation in CH₅⁺(Ar)₂ was predicted to be slower due to coordination of two bulky Ar atoms to the 3c2e H atoms of the CH₅⁺ core. The 3c2e in-plane wagging motion of the CH₅⁺ core was more or less frozen as indicated by the absence of the broad low frequency shoulder observed for CH₅⁺(H₂).

2. CH₅⁺(Ar)(CH₄)

The vibrational spectrum for CH₅⁺(Ar)(CH₄) shown in Fig. 4B was obtained by monitoring the CH₅⁺(CH₄) signal (m/e=33) in the frequency region of 2800-3100 cm⁻¹. Three vibrational features, centered at 2874, 2974, and 3072 cm⁻¹, were found in the spectrum along with a broad background at ~2900 cm⁻¹. The 2874 cm⁻¹ feature, assigned to the bound CH₄ stretching mode, was 40 cm⁻¹ red-shifted from the v₁ C-H stretching
frequency of free CH$_4$ (2914 cm$^{-1}$), and 5 cm$^{-1}$ blue-shifted from the corresponding feature for CH$_3^+$CH$_4$, suggesting that the interaction of the CH$_3^+$ core with CH$_4$ was slightly weaker than that for CH$_3^+$CH$_4$, due to the delocalization of charge density in the core by the coordination of the second solvent Ar atom. The 2974, ~2900 cm$^{-1}$ features were assigned to the two coupled CH$_3$ stretching modes, respectively, and the 3072 cm$^{-1}$ feature was assigned to the less-coupled CH$_3$ stretching mode as in the case of CH$_3^+$Ar$_2$. The separation of the two coupled CH$_3$ stretching modes (2974 and ~2900 cm$^{-1}$) would be a consequence of the slowing down of the CH$_3$ internal rotation due to the increased ion-solvent interactions in CH$_3^+$CH$_4$Ar. The 3072 cm$^{-1}$ feature (assigned to the less-coupled CH$_3$ stretching mode), on the other hand, was not shifted from the corresponding feature for CH$_3^+$Ar$_2$. These results were consistent with the prediction that the floppiness of the CH$_3^+$ core decreases as the ion-solvent interactions increase.

3. CH$_3^+$CH$_4$_2

The vibrational spectrum for CH$_3^+$CH$_4$_2 (Fig. 4C) was obtained by monitoring the CH$_3^+$CH$_4$ signal (m/e=33) in the frequency range of 2700-3150 cm$^{-1}$. Three vibrational features, centered at 2879, 2974, and 3082 cm$^{-1}$, were found in the spectrum along with the broad feature at ~2900 cm$^{-1}$ and one shoulder feature at ~3000 cm$^{-1}$. The 2879, ~3000 cm$^{-1}$ features were assigned to the bound CH$_4$ and free CH$_4$ stretching modes, respectively, as in the case of CH$_3^+$CH$_4$. The single feature for the bound CH$_4$ stretching modes suggested that the two CH$_4$ molecules in CH$_3^+$CH$_4$_2 coordinated symmetrically to the CH$_3^+$ core with almost equal strength, consistent with the previous prediction that the
two equivalent acidic H atoms of the $3c2e$ bond in CH$_5^+$ core would be the preferential coordination sites for the first two solvent molecules [16,17]. It was 10 and 5 cm$^{-1}$ blue-shifted from the corresponding features for CH$_5^+(CH_4)$ and CH$_5^+(Ar)(CH_4)$, respectively, suggesting that the interaction between the CH$_5^+$ core and one CH$_4$ molecule in CH$_5^+(CH_4)_{2}$ was weaker than those in CH$_5^+(CH_4)$ and CH$_5^+(Ar)(CH_4)$, due to the equal partitioning of the charge densities of the core ion by the two solvent CH$_4$ molecules.

The 2974, $\sim$2900 cm$^{-1}$ features, on the other hand, were assigned to the two coupled CH$_3$ stretching modes of the CH$_5^+$ core, as in the case of CH$_5^+(Ar)(CH_4)$. The relative intensity for the $\sim$2900 cm$^{-1}$ feature was somewhat higher, compared to the case for CH$_5^+(Ar)(CH_4)$, suggesting that the two coupled CH$_3$ stretching modes were more decoupled due to the increased ion-solvent interactions in CH$_5^+(CH_4)_{2}$ in slowing down of the CH$_3$ internal rotation. The unresolved features, however, indicated that the solvent effects were still insufficient to completely freeze the scrambling motion and decouple the two coupled CH$_3$ stretching modes. The 3082 cm$^{-1}$ feature, assigned to the less-coupled CH$_3$ stretching mode of the CH$_5^+$ core, was 10 cm$^{-1}$ blue-shifted and slightly narrower, compared to the corresponding feature of CH$_5^+(Ar)(CH_4)$ (3072 cm$^{-1}$) and CH$_5^+(Ar)_{2}$ (3072 cm$^{-1}$). Considering the fact that the less-coupled CH$_3$ stretching frequencies for CH$_5^+(Ar)_{2}$ and CH$_5^+(Ar)(CH_4)$ were identical, the 10 cm$^{-1}$ frequency shift suggested that the CH$_5^+(CH_4)_{2}$ ions could form a tightly bound cluster, possibly involving some geometrical changes in the CH$_5^+$ core in order to accommodate two CH$_4$ solvent molecules close to the core ion.
Fig. 6C shows the vibrational spectrum for CH$_3^+$(CH$_4$)$_2$, obtained in the frequency region of 2500-2700 cm$^{-1}$. One broad feature, centered at 2577 cm$^{-1}$, was found and assigned to the $3e$ H-H stretching mode of the CH$_3^+$ core, as in the cases for CH$_5^+(N_2)$ and CH$_5^+(CH_4)$. Therefore, the $3e$ in-plane wagging motion was likely to be frozen, while the CH$_3$ internal rotation was somewhat hindered but still insufficient to completely decouple the two coupled CH$_3$ stretching modes.

D. Tri-solvated carbonium ions, CH$_5^+$(A)$_2$(B) (A,B=Ar,CH$_4$)

Fig. 5 shows the vibrational spectra for tri-solvated carbonium ions, CH$_5^+$(A)$_2$(B) (A,B=Ar,CH$_4$), obtained in the frequency region of 2700-3200 cm$^{-1}$. The vibrational features in this frequency region were again attributed to the C-H stretching modes of the core CH$_3^+$ and the solvent CH$_4$ molecules. The observed frequencies and the vibrational assignments are listed in Table 2. The CH$_3^+$ core in CH$_5^+$(H$_2$)$_3$, as mentioned previously, was regarded as semi-rigid having an $e-C_4$ structure, a consequence of the frozen scrambling motions of CH$_5^+$ (as indicated by the three resolved vibrational features for this frequency range). For the Ar, CH$_4$ solvated carbonium ions CH$_5^+$(A)$_2$(B) (A,B=Ar,CH$_4$), the CH$_3^+$ cores would be even more rigid than that of CH$_5^+$(H$_2$)$_3$, due to the strong ion-solvent interactions for these complexes. In particular, the CH$_3^+$ core in CH$_5^+$(CH$_4$)$_3$ (where the CH$_3^+$ core was expected to be the most strongly perturbed by the solvent molecules) would be regarded as rigid having a somewhat different geometry from that of free CH$_3^+$. 
1. $\text{CH}_5^+(\text{Ar})_2(\text{CH}_4)$

The vibrational spectrum for $\text{CH}_5^+(\text{Ar})_2(\text{CH}_4)$ (Fig. 5A) was obtained by monitoring the $\text{CH}_5^+(\text{CH}_4)$ signal ($m/e=33$) in the frequency range of 2800-3100 cm$^{-1}$. Three vibrational features, centered at 2877, 2980, and 3066 cm$^{-1}$, were found in the spectrum along with the broad feature at $\approx$2900 cm$^{-1}$. The 2877 cm$^{-1}$ feature, assigned to the bound CH$_4$ stretching mode, was 3 cm$^{-1}$ blue-shifted from that for $\text{CH}_5^+(\text{Ar})(\text{CH}_4)$, indicating increased delocalization of the positive charge of the core ion by the additional Ar atom. In addition, the 2 cm$^{-1}$ red-shift from the corresponding feature for $\text{CH}_5^+(\text{Ar})(\text{CH}_4)$ suggested that the coordination of two Ar atoms to the CH$_5^+$(CH$_4$) unit was less perturbative than that of one CH$_4$ molecule. The 2980, $\approx$2900 cm$^{-1}$ features were assigned to the two coupled CH$_3$ stretching modes, and the 3066 cm$^{-1}$ feature to the less-coupled CH$_3$ stretching mode, analogous to the assignments for the mono- and di-solvated carbonium ions. The scrambling of the CH$_5^+$ core was expected to be more frozen than those of the mono- and di-solvated carbonium ions due to the increased solvation.

2. $\text{CH}_5^+(\text{Ar})(\text{CH}_4)_2$

The vibrational spectrum for $\text{CH}_5^+(\text{Ar})(\text{CH}_4)_2$ (Fig. 5B) was obtained by monitoring the $\text{CH}_5^+(\text{CH}_4)$ signal ($m/e=33$) in the frequency range of 2800-3100 cm$^{-1}$. Three vibrational features, centered at 2881, 2978, and 3079 cm$^{-1}$, were found in the spectrum along with the $\approx$2900 cm$^{-1}$ feature, as in the case of $\text{CH}_5^+(\text{Ar})_2(\text{CH}_4)$. The 2881 cm$^{-1}$ feature, assigned to the bound CH$_4$ stretching modes, was 4 and 2 cm$^{-1}$ blue-shifted from the corresponding features for $\text{CH}_5^+(\text{Ar})_2(\text{CH}_4)$ and $\text{CH}_5^+(\text{CH}_4)_2$, respectively, due to the
increased perturbation on the CH₅⁺(CH₄) unit from the stronger solvent effect of CH₄ vs. Ar, and from the coordination of the additional Ar atom, respectively. The single feature for the bound CH₄ stretching modes of two CH₄ solvent molecules in CH₅⁺(Ar)(CH₄)₂, suggested that the equal interactions between the core ion and two CH₄ molecules observed for CH₅⁺(CH₄)₂ were not perturbed by the coordination of the third solvent Ar atom. This was suggestive of the tight coordination of two CH₄ molecules to the electron deficient two 3c2e H atoms of the CH₅⁺ core. The 2978, ~2900 cm⁻¹ features were assigned to the two coupled CH₃ stretching modes, and the 3079 cm⁻¹ feature to the less-coupled CH₃ stretching mode of the CH₅⁺ core, similar to the case for CH₅⁺(Ar)(CH₄)₂.

3. CH₅⁺(CH₄)₃

Fig. 5C shows the vibrational spectrum for CH₅⁺(CH₄)₃, obtained by detecting the CH₅⁺(CH₄)₂ signal (m/e=49) in the frequency range of 2700-3100 cm⁻¹. Several spectral differences, compared to the cases of the previous solvated carbonium ions, were found in the spectrum: First, the vibrational features for the 2900-3100 cm⁻¹ region were much sharper and more intense. Second, one new broad and intense feature centered at ~2823 cm⁻¹ was present in the spectrum, instead of the broad ~2900 cm⁻¹ feature observed for CH₅⁺(CH₄)₂, CH₅⁺(Ar)(CH₄)₂, and CH₅⁺(Ar)₂(CH₄) (see Fig. 4C and 5). Third, a doublet feature for the bound CH₄ stretching modes, centered at 2880 and 2890 cm⁻¹, was different from the single feature for other solvated carbonium ions containing no more than two CH₄ solvent molecules CH₅⁺(CH₄)ₓ(Ar)ᵧ (x=1,2; y=0-2). Finally, fine structure was observed around 3010 cm⁻¹.
The broad $\sim2823$ cm$^{-1}$ feature, red-shifted considerably from the $\sim2900$ cm$^{-1}$ feature for other tri-solvated carbonium ions, was assigned to the bound CH$_3$ stretching mode of the CH$_3^+$ core, localized somewhat in one C-H bond (of the CH$_3$ group in CH$_3^+$) coordinated directly by the third CH$_4$ molecule. In this case, such a significant frequency shift and band broadening could be due to the fact that the C-H bond strength became weaker upon direct coordination of the third CH$_4$ molecule, with accompanying band broadening for the vibrational transitions. Similar results have been previously observed in the cases of the hydrated hydronium ion complexes H$_3$O$^+(H_2O)_n$ ($n=1$-8) [27,39] and the ammoniated ammonium ion complexes NH$_4^+(NH_3)_n$ ($n=1$-10) [40], and such information was used as evidence for the binding sites (on the core ion) for the solvent molecules. Two sharp features at 2989, 3077 cm$^{-1}$, on the other hand, were assigned to the symmetric and asymmetric CH$_3$ stretching modes, respectively, localized more or less in the remaining two C-H bonds of the CH$_3$ group (subsequently referred to as the symmetric and asymmetric free CH$_2$ stretching modes, respectively). The narrow bandwidths for these features were suggestive of the rigid CH$_3^+$ core, where the vibrational coupling between the CH$_3$ stretching modes (via the scrambling motions of CH$_3^+$) were completely decoupled.

The doublet feature (2880, 2890 cm$^{-1}$) assigned to the bound CH$_4$ stretching modes (of the three CH$_4$ molecules in CH$_3^+$-$(CH_4)_3$), suggested that the three CH$_4$ molecules coordinated differently to the core ion. The former (2880 cm$^{-1}$) was only 1 cm$^{-1}$ blue-shifted from the bound CH$_4$ stretching mode of CH$_3^+$-$(CH_4)_2$, and the latter (2890 cm$^{-1}$) was absent in the spectra for the tri-solvated carbonium ions containing no third CH$_4$.
Thus, the 2880 and 2890 cm$^{-1}$ features could be assigned to the bound CH$_4$ stretching modes for the first two CH$_4$ molecules, and to for the third CH$_4$ molecule in CH$_5^+(\text{CH}_4)_3$, respectively. In this case, the coordination of the third CH$_4$ molecule was predicted to be much less strongly bound than the first and second CH$_4$ molecules, inducing only slight perturbation to the CH$_5^+(\text{CH}_4)_2$ unit, as indicated by the 1 cm$^{-1}$ frequency shift of the 2880 cm$^{-1}$ feature from that of CH$_5^+(\text{CH}_4)_2$. The fine features at $\sim$3010 cm$^{-1}$ (including the sharp features at 3002 and 3022 cm$^{-1}$) were attributed to the free C-H stretching modes of the solvent CH$_4$ molecules as in the other methane solvated carbonium ions.

Fig. 6D shows the vibrational spectrum for CH$_5^+(\text{CH}_4)_3$ obtained in the frequency range of 2525-2675 cm$^{-1}$. One broad feature, centered at $\sim$2578 cm$^{-1}$, was found in the spectrum, and again assigned to the 3c2e H-H stretching mode of the CH$_5^+$ core. The center of the vibrational feature was only slightly shifted from the corresponding feature for CH$_5^+(\text{CH}_4)_2$ (2577 cm$^{-1}$), suggesting little or no perturbation of the 3c2e bond by the third CH$_4$ molecule. In summary, the CH$_5^+$ core in CH$_5^+(\text{CH}_4)_3$ was regarded as rigid, evidenced by the sharp and intense CH$_3$ stretching features, and consequently the structure would be distinct from those of free CH$_5^+$ and its weakly bound complexes.

E. Tetra- and penta-solvated carbonium ions, CH$_5^+(\text{A})_{4,5}$ (A=CH$_4$)

The vibrational spectrum for CH$_5^+(\text{CH}_4)_4$ (Fig. 7D) was obtained by monitoring the CH$_5^+(\text{CH}_4)_2$ signal (m/e=49) in the frequency range of 2700-3100 cm$^{-1}$. The observed vibrational features were very similar to those for CH$_5^+(\text{CH}_4)_3$ (see Fig. 7C, D), with the
exception of the seemingly single feature at 2890 cm⁻¹. The broad ~2840 cm⁻¹ feature and the 2989, 3079 cm⁻¹ features were assigned to the bound CH₃ stretching mode, symmetric and asymmetric free CH₂ stretching modes of the CH₃ group, respectively, as in the case of CH₅⁺(CH₄)₃. Notice that these vibrational frequencies were very close to the frequencies for CH₅⁺(CH₄)₃ (~2823, 2989, 3077 cm⁻¹). The 2890 cm⁻¹ feature could have a shoulder feature centered at 2881.5 cm⁻¹ as shown in Fig. 8, and both of the features were assigned to the bound CH₄ stretching modes (see the Discussion). The fine structure at ~3010 cm⁻¹ was again assigned to the free C-H stretching modes of the solvent CH₄ molecules in CH₅⁺(CH₄)₄ as in the case for CH₅⁺(CH₄)₃.

Fig. 7E shows the vibrational spectrum for CH₅⁺(CH₄)₅, obtained by monitoring the CH₅⁺(CH₄)₃ ions (m/e=65) in the frequency range of 2850-2950 cm⁻¹. Two sharp features at 2886, 2896 cm⁻¹ were found in the spectrum along with one possible peak at 2892 cm⁻¹, in spite of the low signal-to-noise ratio, and assigned to the bound CH₄ stretching modes (of the five CH₄ molecules in CH₅⁺(CH₄)₅). Notice that the multiple features for the bound CH₄ stretching modes were different from the case for CH₅⁺(CH₄)₄, but similar to the case for CH₅⁺(CH₄)₃.
Discussion

A. Vibrational assignment of the feature in 2500-2700 cm\(^{-1}\)

Additional vibrational features for \(\text{CH}_5^+ (\text{N}_2)\) and \(\text{CH}_5^+ (\text{CH}_4)_n\) \((n=1,2,3)\) were found in the frequency region of 2500-2700 cm\(^{-1}\) as shown in Fig. 6. The low signal-to-noise ratio for the observed features was due to the combined effect of the low IR laser intensity for this frequency region (2-3 times lower than that for the 2800-3200 cm\(^{-1}\) region), the broad vibrational features, and the relatively small oscillator strength for this vibrational transition. Nevertheless, the centers of the vibrational features were determined to be 2623, 2608, 2577, and \(\sim 2578\) cm\(^{-1}\) for \(\text{CH}_5^+ (\text{N}_2)\) and \(\text{CH}_5^+ (\text{CH}_4)_n\) \((n=1,2,3)\), respectively (see Fig. 6 and Table 2). Since these vibrational features were seen for both of the \(\text{CH}_4\) and \(\text{N}_2\)-solvated carbonium ions, they could be attributed exclusively to the vibrational transitions of the core \(\text{CH}_5^+\), rather than the solvent molecules. In this case, the possible assignment for the vibrational features would be either the H-H stretching mode of the \(3c2e\) bond in the \(\text{CH}_5^+\) core (the \(3c2e\) H-H stretching mode), the overtones, or the combination bands involving the low frequency modes of the \(\text{CH}_5^+\) core and/or the van der Waals (vdW) modes of the complexes.

According to the vibrational analysis on \(\text{CH}_5^+\) (at TZ2P+f CCSD level [11]), the \(3c2e\) H-H stretching frequencies for \(\text{e-C}_4\) and \(\text{e-C}_4\) \(\text{CH}_5^+\) were predicted to be 2633 and 2650 cm\(^{-1}\), respectively, after appropriate anharmonicity corrections. These vibrational frequencies are expected to be red-shifted somewhat when the \(\text{CH}_5^+\) ions are complexed by one or two solvent molecules (as in the mono- or di-solvated carbonium ions), since the first two solvent molecules would bind preferentially to the electron deficient H atoms of the \(3c2e\) bond causing
some decrease in the $3c2e$ H-H bond strength and an increase in the effective reduced mass for the vibration. In fact, the calculated $3c2e$ H-H stretching frequency for the $e-C_4$ CH$_3^+$ core in CH$_5^+(H_2)$ (where the H$_2$ was bound to one of the two $3c2e$ H atoms) was 2600 cm$^{-1}$ (at TZ2P CCSD level [30]), 33 cm$^{-1}$ red-shifted from the corresponding frequency for $e-C_4$ CH$_5^+$ (2633 cm$^{-1}$). The $3c2e$ H-H stretching frequency for $e-C_4$ CH$_5^+(H_2)_2$ (where the two H$_2$ molecules were bound to the two $3c2e$ H atoms) was further red-shifted from that for CH$_5^+(H_2)_2$, according to ab initio calculation at MP2/6-311G(D,P) level (2737, 2687 cm$^{-1}$ for CH$_5^+(H_2)$ and CH$_5^+(H_2)_2$, respectively) [41]. On the other hand, the calculated $3c2e$ H-H stretching frequency for CH$_5^+(H_2)_3$ (where the third H$_2$ molecule was bound to the in-plane H atom to the $3c2e$ bond) was 2689 cm$^{-1}$, only slightly shifted from that for CH$_5^+(H_2)_2$ (at MP2/6-311G(D,P) level [41]). This result suggested that the $3c2e$ H-H stretching frequency is strongly perturbed by the first two solvent molecules bonded directly to the $3c2e$ bond, and only slightly perturbed by the third solvent molecule bonded to one (non $3c2e$ bonded) H atom of the CH$_5^+$ core. Thus, if the observed vibrational features for the 2500-2700 cm$^{-1}$ region were due to the $3c2e$ H-H stretching mode of the CH$_5^+$ core, the observed frequencies for CH$_5^+(CH_4)_n$ (n=1,2,3) should show the same trend of frequency shifts as in the above prediction for CH$_5^+(H_2)_n$ (n=1,2,3).

As shown in Fig. 6 and also listed in Table 2, the center of the vibrational features for CH$_5^+(CH_4)_n$ (n=1,2,3) were 2608, 2577, and ~2578 cm$^{-1}$, respectively. The observed frequency for CH$_5^+(CH_4)_2$ was 31 cm$^{-1}$ red-shifted from that for CH$_5^+(CH_4)$, while that for CH$_5^+(CH_4)_3$, only 1 cm$^{-1}$ red-shifted from that for CH$_5^+(CH_4)_2$. This result showed indeed the same trend of frequency shifts as in the prediction for the $3c2e$ H-H stretching modes. In
addition, the observed frequency for CH$_5^+$ (N$_2$) (2623 cm$^{-1}$), 15 cm$^{-1}$ higher than that for CH$_5^+$ (CH$_4$), also supported this vibrational assignment, since the stronger ion-solvent interactions in CH$_5^+$ (CH$_4$) vs CH$_5^+$ (N$_2$) would give more perturbation to the 3c2e H-H bond strength.

Neither the overtones nor the combination bands of the CH$_5^+$ core, on the other hand, could explain the observed intensities or the trend of frequency shifts. According to the *ab initio* calculations on CH$_5^+$ (H$_2$)$_n$ (n=1,2,3) [11,30,41], the vibrational modes around 1300 cm$^{-1}$ (which could give the first overtones in this frequency region) had low IR intensities, and showed no evidence for such frequency shifts. Similarly, no combination bands involving the low frequency modes of the CH$_5^+$ core were found which could explain the observed intensities and the trend of frequency shifts. The other combination bands involving the vdW stretching mode(s) of the complexes were also ruled out from the fact that such a combination frequency for CH$_5^+$ (CH$_4$) would be higher than that for CH$_5^+$ (N$_2$), due to the expected higher vdW stretching frequency for the strongly bound complex CH$_5^+$ (CH$_4$). Therefore, it is reasonable to assign the observed features for CH$_5^+$ (H$_2$)$_n$ (n=1,2,3) and CH$_5^+$ (N$_2$) in the 2500-2700 cm$^{-1}$ region to the 3c2e H-H stretching mode for the CH$_5^+$ core. Obviously, the *ab initio* frequencies and IR intensities for these complexes (not yet available) could provide better comparison with the experimental observations than those for CH$_5^+$ (H$_2$)$_n$ (n=1,2,3) used in this analysis. Multidimensional vibrational dynamics calculation [42] for these complexes, though it may be quite challenging, would provide the most convincing theoretical evidence for this vibrational assignment.
B. Structures of \( \text{CH}_5^+(\text{CH}_4)_n \) (n=1-5)

Vibrational spectroscopy of the mass-selected ions has been a powerful tool for the determination of the structures for some large ionic complexes, for which individual rotational transitions cannot be resolved due to the small rotational constants. In this method one monitors the spectral changes of the vibrational modes of the core ion and solvent molecule(s) (such as frequency shifts, changes in intensity and bandwidth, etc.) due to the coordination of solvent molecules. This technique has been previously used in our laboratory to determine successfully the structures for the hydrated hydronium ions \( \text{H}_3\text{O}^+(\text{H}_2\text{O})_n \) (n=1-8) \[27,39\] and the ammoniated ammonium ions \( \text{NH}_4^+(\text{NH}_3)_n \) (n=1-10) \[40\]. The same approach was adopted in this section to determine the structures for the methane-solvated carbonium ions \( \text{CH}_5^+(\text{CH}_4)_n \) (n=1-5). The vibrational spectra for \( \text{CH}_5^+(\text{CH}_4)_n \) (n=1-5) are gathered together in Fig. 7, in order to demonstrate clearly the spectral changes in the vibrational spectra as the number of solvent molecules increase. Note that the corresponding vibrational features for \( \text{CH}_5^+(\text{CH}_4)_n \) (n=1-5) are connected by dashed lines (---) as shown in Fig. 7.

Previous experimental and theoretical results \[16,17,35,38\] on the methane-solvated carbonium ions \( \text{CH}_5^+(\text{CH}_4)_n \) (n=1-9) showed consistently that the first two \( \text{CH}_4 \) molecules in \( \text{CH}_5^+(\text{CH}_4)_n \) would bind preferentially to the two H atoms of the \( 3c2e \) bond in the \( \text{CH}_5^+ \) core, respectively. The results of this work also suggested the same binding sites (the \( 3c2e \) H atoms) for the first and second \( \text{CH}_4 \) molecules as discussed in the previous section. Such preferential coordination to the \( 3c2e \) H atoms of the \( \text{CH}_5^+ \) core can be regarded as a general feature for the ionic complexes of \( \text{CH}_5^+ \), since the same was true for other solvent atoms and molecules such
as H₂, Ar, and N₂. The solvent CH₄ molecules in CH₃⁺(CH₄)ₙ on the other hand, were predicted to coordinate via the 3-fold face from the fact that the observed spectral pattern for the CH₄ vibrations (the C-H stretching frequencies and intensity pattern) was quite similar to the case for the methane molecule perturbed by an external electric field where the direction of the field was along the 3-fold face of CH₄ molecule [43]. The proposed structures for CH₃⁺(CH₄) and CH₃⁺(CH₄)₂ are sketched in Fig. 9A and 9B, respectively.

As mentioned previously, however, the CH₃⁺ core in CH₃⁺(CH₄) and CH₃⁺(CH₄)₂ was still floppy in that the three CH₃ stretching modes were strongly coupled via the CH₃ internal rotation as indicated by only two observed vibrational features for CH₃⁺(CH₄) (2982, 3063 cm⁻¹) and the unresolved vibrational features for CH₃⁺(CH₄)₂ (~2900, 2974, 3082 cm⁻¹) (see Fig. 7A, 7B). The vibrational coupling for CH₃⁺(CH₄)₂ would be less significant than that for CH₃⁺(CH₄) due to the increased stabilization of the floppy core by the two CH₄ molecules. The 3c2e bond of the CH₃⁺ core in CH₃⁺(CH₄) and CH₃⁺(CH₄)₂, nevertheless, was expected to be highly localized as evidenced by the observed 3c2e H-H stretching features.

For CH₃⁺(CH₄)₃, the previous experimental and theoretical predictions on the coordination site for the third CH₄ molecule have been inconsistent. Ab initio calculations predicted that it could bind to the in-plane H atom to the 3c2e bond in e-C₄ CH₃⁺ core [35,38], while the experimental results (by Hiraoka et al. [16]) showed that it would bind out-of-plane to the 3c2e bond of the CH₃⁺ core. Nonetheless, they predicted consistently that the third CH₄ molecule coordinates to the CH₃⁺ core much less strongly than the first two CH₄ molecules as listed in Table 1 (except for the CNDO/2 result by Simonetta et al.). The results of this work also supported the weaker interaction of the CH₃⁺ core with the third CH₄ (vs. the first and second
molecules) as indicated by the two bound CH₄ stretching features (2880, 2890 cm⁻¹) for the first two CH₄ and the third CH₄ molecules, respectively. The controversy on the binding site for the third CH₄ molecule was more or less resolved by the observation of the ~2823 cm⁻¹ feature assigned to the bound CH₃ stretching mode of the CH₅⁺ core, as mentioned previously. Such broadening and strong red-shift of the vibrational feature(s) were regarded as the signatures for the strongly perturbed vibrational mode(s) of the core ion upon direct coordination of the solvent molecule(s) [39,40]. Therefore, the in-plane H atom to the 3c2e bond in e-C₂H₅⁺ core would be the coordination site for the third CH₄ molecule in CH₅⁺(CH₄)₃, since the out-of-plane coordination to the 3c2e bond was unlikely to explain such spectral changes. As mentioned previously, the CH₅⁺ core in CH₅⁺(CH₄)₃ was regarded as rigid, with all the scrambling motions of the core ion frozen completely. The proposed structure for CH₅⁺(CH₄)₃ is shown in Fig. 9C.

For CH₅⁺(CH₄)₄, the three possible structures have been proposed in the previous experimental and theoretical studies. The first, predicted by Hiraoka and coworkers, was the structure where the third and fourth CH₄ molecules coordinate to the 3c2e bond in the out-of-plane fashion [16]. The second, predicted by Yamabe et al. [38] and Simonetta et al. [35], was the structure where the fourth CH₄ molecule coordinates to one of two free C-H bonds in the CH₅⁺ core, following coordination of the third CH₄ molecule to the in-plane H atom as shown in Fig. 9C. The third was the structure where the third and fourth CH₄ molecules coordinate to the first two CH₄ molecules already bound to the 3c2e H atoms of the core ion, as predicted by Kebarle and coworkers [17]. In this structure, the electron deficient 3c2e H atoms of the core ion interacted with the electron pair of one C-H bond in the first two CH₄ molecules forming
another $3c2e$ bond, respectively. The resulting electron deficient two $3c2e$ H atoms (in the first CH$_4$ molecules) were responsible for the coordination of the third and fourth CH$_4$ molecules. In addition, one could imagine other possible structures such as a combination of the three predicted structures, and the structures involving other CH$_3^+$ isomers ($s$-$C_3$, $C_2$, $C_4$, etc).

The observed vibrational features for CH$_3^+$(CH$_4$)$_4$ (Fig. 7D) were quite similar to those for CH$_3^+$(CH$_4$)$_3$ (Fig. 7C), with the exception of the single feature for the bound CH$_4$ stretching modes (of the four solvent CH$_4$ molecules). In particular, the observed three CH$_3$ stretching frequencies (~2840, 2989, 3079 cm$^{-1}$) were very close to those for CH$_3^+$(CH$_4$)$_3$ (~2823, 2989, 3077 cm$^{-1}$), assigned to the bound CH$_3$ stretching, symmetric and asymmetric free CH$_2$ stretching modes of the CH$_3$ group, respectively (refer to the previous section). The results suggested strongly that the CH$_3^+$(CH$_4$)$_3$ unit of this complex has more or less the same structure as that of CH$_3^+$(CH$_4$)$_3$ (shown in Fig. 9C), excluding all of the previously proposed structures for CH$_3^+$(CH$_4$)$_4$ described above. In this case, the possible structure for CH$_3^+$(CH$_4$)$_4$ would be the structure where the fourth CH$_4$ molecule coordinates either out-of-plane to the $3c2e$ bond of the CH$_3^+$ core or to the first two CH$_4$ molecules already bound to the $3c2e$ H atoms of the core ion (similar to the case for the third proposed structure), with restriction that the CH$_3^+$(CH$_4$)$_3$ structure be more or less the same as the structure shown in Fig. 9C. *Ab initio* calculation by Yamabe and coworkers, however, showed that the latter coordination does not provide enough energetic stability, compared to the former case. Moreover, the latter requires some structural changes in the coordination of the first two CH$_4$ molecules (via from the 3-fold face to single C-H bond), in order to form another $3c2e$ bond, but no evidence for such changes was found yet. The former structure (where the fourth CH$_4$ molecule coordinates out-
of-plane to the $3c2e$ bond) would therefore be the most probable structure for CH$_5^+$-(CH$_4$)$_4$ as shown in Fig. 9D.

The remaining question is how this structure with three inequivalent CH$_4$ molecules (i.e. the first two CH$_4$ molecules, the third and the fourth CH$_4$ molecules) can explain the seemingly single feature for the bound CH$_4$ stretching modes (2890 cm$^{-1}$). The experimental binding energies for the third and fourth CH$_4$ molecules, as listed in Table 1, were very similar ($\Delta H^\circ_{23}=3.14$, $\Delta H^\circ_{34}=3.02$ kcal/mole), so the bound CH$_4$ stretching frequencies for the third and fourth CH$_4$ molecules would be close to that for the third CH$_4$ molecule in CH$_5^+$-(CH$_4$)$_3$ (2890 cm$^{-1}$). Therefore, the intense 2890 cm$^{-1}$ feature (Fig. 7D) could be mostly due to the bound CH$_4$ stretching modes for the third and fourth CH$_4$ molecules. The bound CH$_4$ stretching frequencies for the first two CH$_4$ molecules were expected to be in-between 2880 cm$^{-1}$ (the bound CH$_4$ stretching frequency for the first two CH$_4$ molecules in CH$_5^+$-(CH$_4$)$_3$) and 2890 cm$^{-1}$, since such solvent vibrational frequencies would increase slowly (approaches that for free CH$_4$) as the coordination number increases. As mentioned previously, a close examination of the 2890 cm$^{-1}$ feature revealed that it could possess a low frequency shoulder, in spite of interference from the broad ~2840 cm$^{-1}$ feature. In a least squares fit with three gaussian functions (as shown in Fig. 8) for the 2770-2920 cm$^{-1}$ region, one gaussian peak centered at 2881.5 cm$^{-1}$ (but with low intensity), was able to fit the shoulder feature, and assigned to the bound CH$_4$ stretching features for the first two CH$_4$ molecules.

The reason for such dramatic changes in IR intensity for CH$_5^+$-(CH$_4$)$_4$, compared to the case for CH$_5^+$-(CH$_4$)$_3$, are still uncertain, but it could be related to the change in the symmetry of the complex upon coordination of the fourth CH$_4$ molecule. The plane-symmetry of the
complex will be broken when the fourth CH₄ molecule coordinates out-of-plane to the 3c2e bond of the core ion. This role of symmetry on the solvent vibrations was supported by the observed multiple vibrational features for CH₅⁺(CH₄)₃, where the plane-symmetry of the complex would be recovered (this will be discussed shortly). On the other hand, one could imagine that the seemingly single feature for the bound CH₄ stretching modes in CH₅⁺(CH₄)₄ could be better explained by assuming a C₄ᵥ CH₅⁺ core for the CH₅⁺(CH₄)₄ ions where the four equivalent C-H bonds of the C₄ᵥ CH₅⁺ core interact with the four CH₄ solvent molecules. Such a CH₅⁺(CH₄)₄ structure was, however, unlikely to explain the similar CH₃ stretching features as those for CH₅⁺(CH₄)₃, containing the e-C₄ᵥ CH₅⁺ core. Therefore, it is reasonable to predict that the fourth CH₄ molecule coordinates to the 3c2e bond of the CH₅⁺ core in an out-of-plane fashion, with the CH₅⁺(CH₄)₃ unit having a similar structure to CH₅⁺(CH₄)₄, with broken plane-symmetry as shown in Fig. 9D. Further spectroscopic and theoretical work will be necessary in order to provide more convincing evidence for the structure of CH₅⁺(CH₄)₄, and to reveal the exact mechanism for the symmetry effect on the solvent vibrations.

For CH₅⁺(CH₄)₅, the fifth CH₄ molecule would coordinate to the other out-of-plane side of the 3c2e bond, recovering the plane-symmetry of the complex, as shown in Fig. 9E. In this structure are three inequivalent CH₄ solvent molecules (i.e. the first two CH₄ molecules, the third CH₄, and the fourth, fifth CH₄ molecules). The solvent vibrational frequencies in the ionic complexes would increase slowly, as mentioned previously, as the number of the solvent molecules in the complexes increases, due to the increased charge delocalization in the core ion [23,39,40]. Thus, the 2886 cm⁻¹ feature can be correlated with the 2880 cm⁻¹ feature for CH₅⁺(CH₄)₃ and the 2881.5 cm⁻¹ feature for CH₅⁺(CH₄)₄, which were assigned to the bound
CH₄ stretching modes for the first and second CH₄ molecules. Similarly, the 2896 cm⁻¹ feature could be assigned to the bound CH₄ stretching modes for the fourth and fifth CH₄ molecules, and the possible feature at 2892 cm⁻¹ to that for the third CH₄ molecules. As mentioned previously, the multiple bound CH₄ stretching features, different from the case of CH₃⁺(CH₄)₄, but similar to the case of CH₃⁺(CH₄)₃, were suggestive of the possible role of symmetry on the vibrational transitions of the solvent CH₄ molecules in CH₃⁺(CH₄)ₙ (n=4,5).
Conclusions

The vibrational spectra for the ionic complexes of \( \text{CH}_3^+ \), \( \text{CH}_3^+(\text{A})_x(\text{B})_y \) (\( \text{A,B}=\text{Ar},\text{N}_2,\text{CH}_4;x,y=0-5 \)) have been presented and suggest an important role for the solvent effects on the dynamics of \( \text{CH}_3^+ \). The scrambling motions of the \( \text{CH}_3^+ \) core slowed considerably as the ion-solvent interactions increased (\( \text{Ar}<\text{N}_2<\text{CH}_4 \)), and as the number of the solvent molecules in the complexes increased. The \( \text{CH}_3^+ \) core of \( \text{CH}_3^+(\text{CH}_4)_n \) (\( n\geq3 \)) was regarded as rigid. For \( \text{CH}_3^+(\text{N}_2) \) and \( \text{CH}_3^+(\text{CH}_4)_n \) (\( n=1,2,3 \)), the H-H stretching bands of the \( \text{CH}_3^+ \) core were found in the 2500-2700 cm\(^{-1} \) region, direct evidence for \( 3c2e \) bonding in \( \text{CH}_3^+ \). The structures of the methane-solvated carbonium ions \( \text{CH}_3^+(\text{CH}_4)_n \) (\( n=1-5 \)) were predicted accurately from the analysis of the vibrational spectra, improving on the previous theoretical and experimental predictions: The first two \( \text{CH}_4 \) molecules coordinated to the two \( 3c2e \) H atoms, and the third \( \text{CH}_4 \) molecule to the in-plane H atom of an \( e-C_2 \) \( \text{CH}_3^+ \) core. The fourth and fifth \( \text{CH}_4 \) molecules were predicted to coordinate out-of-plane to the \( 3c2e \) bond of the core ion.
Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
References


Table 1. Experimental and theoretical dissociation energies and enthalpies for \( \text{CH}_3^+(\text{CH}_4)_n \). Units are in kcal/mole.

<table>
<thead>
<tr>
<th>Reference</th>
<th>( n = 1 )</th>
<th>2</th>
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<th>4</th>
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<th>6</th>
<th>7</th>
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<td>Hiraoka and Mori(^a) ( -\Delta H^\circ_T )</td>
<td>6.87</td>
<td>5.34</td>
<td>3.14</td>
<td>3.02</td>
<td>2.79</td>
<td>2.71</td>
<td>2.67</td>
<td>2.04</td>
<td>1.54</td>
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<td>Hiraoka and Kebarle(^b) ( -\Delta H^\circ_T )</td>
<td>7.4</td>
<td>5.9</td>
<td>4.1</td>
<td>3.9</td>
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<td>Simonetta et al.,(^c) ( D_e )</td>
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<td>3.01</td>
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<td>CNDO/2</td>
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<td>HF/4-31G</td>
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\(^a\)Error is ±0.3 kcal/mole for \( n = 1-2 \) and ±0.2 kcal/mole for \( n = 3-8 \) (ref. 16). \(^b\)Error is ±0.1 kcal/mole (ref. 17). \(^c\)Ref. 35. \(^d\)Ref. 38.
Table 2. Observed vibrational frequencies and assignments for the ionic complexes of CH$_5^+$, CH$_5^+$/(A)$_x$(B)$_y$ (A,B=Ar,N$_2$,CH$_4$;x,y=0-5).

<table>
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<th>Mono-solvated carbonium ions, CH$_5^+$/(A)</th>
<th>Frequencies (cm$^{-1}$)</th>
<th>Vibrational assignment</th>
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<td>CH$_5^+$/(Ar)</td>
<td>2974</td>
<td>two coupled CH$_3$ stretches, CH$_5^+$</td>
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<td>3081</td>
<td>one less-coupled CH$_3$ stretch, CH$_5^+$</td>
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<tr>
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<td>2623</td>
<td>3c2e H-H stretch, CH$_5^+$</td>
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<td></td>
<td>2983</td>
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<td>3077</td>
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<tr>
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<td>3010</td>
<td>free C-H stretch, CH$_4$</td>
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<td>Stretch</td>
<td>Description</td>
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<td>3c2e H-H stretch, CH$_5^+$</td>
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<th>( \text{CH}_3^+(\text{CH}_4)_5 )</th>
<th>2886</th>
<th>bound CH\textsubscript{4} stretches, CH\textsubscript{4} (1,2)⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>2892</td>
<td>&quot;</td>
<td>CH\textsubscript{4} (3)⁺</td>
</tr>
<tr>
<td>2896</td>
<td>&quot;</td>
<td>CH\textsubscript{4} (4,5)⁺</td>
</tr>
</tbody>
</table>

*The numbers in parentheses indicate no. of the solvent CH\textsubscript{4} molecules in the complexes.*
Figure Captions

Fig. 1 Mass spectrum showing the methane and hydrogen solvated carbonium ions, \( \text{CH}_5^+(\text{CH}_4)_x\text{H}_2)_y \) \( (x,y=0,1,2,...) \). The mixing ratio \( \text{CH}_4\text{H}_2 \) was 1:10,000, and source pressure, the source temperature, and the discharge current were 200 torr, -50° C, and 40 \( \mu \text{A} \), respectively.

Fig. 2 Vibrational spectra for the mono-solvated carbonium ions: (A) \( \text{CH}_5^+(\text{Ar}) \); (B) \( \text{CH}_5^+(\text{N}_2) \); and (C) \( \text{CH}_5^+(\text{CH}_4) \).

Fig. 3 Deconvolution of the 2982 cm\(^{-1}\) peak of \( \text{CH}_5^+(\text{CH}_4) \) into two gaussian peaks representing the coupled CH\(_3\) stretching bands of the core \( \text{CH}_5^+ \) (2982 cm\(^{-1}\)), and one free C-H stretching band of the solvent \( \text{CH}_4 \) (3010 cm\(^{-1}\)).

Fig. 4 Vibrational spectra for the di-solvated carbonium ions: (A) \( \text{CH}_5^+(\text{Ar})_2 \); (B) \( \text{CH}_5^+(\text{Ar})(\text{CH}_4) \); and (C) \( \text{CH}_5^+(\text{CH}_4)_2 \).

Fig. 5 Vibrational spectra for the tri-solvated carbonium ions: (A) \( \text{CH}_5^+(\text{Ar})_2(\text{CH}_4) \); (B) \( \text{CH}_5^+(\text{Ar})(\text{CH}_4)_2 \); and (C) \( \text{CH}_5^+(\text{CH}_4)_3 \).

Fig. 6 Vibrational spectra for the H-H stretching mode of the \( 3e2e \) bond in the \( \text{CH}_5^+ \) core of (A) \( \text{CH}_5^+(\text{N}_2) \); (B) \( \text{CH}_5^+(\text{CH}_4) \); (C) \( \text{CH}_5^+(\text{CH}_4)_2 \); and (D) \( \text{CH}_5^+(\text{CH}_4)_3 \).
Fig. 7  Vibrational spectra for the methane-solvated carbonium ions, CH$_3^+$(CH$_4$)$_n$ (n=1-5).

Fig. 8  A least squares fit for the vibrational features of CH$_3^+$(CH$_4$)$_4$ in the 2770-2920 cm$^{-1}$ region, with three gaussian functions centered at ~2840, 2881.5, 2890 cm$^{-1}$.

Fig. 9  Proposed structures of the methane-solvated carbonium ions, CH$_3^+$(CH$_4$)$_n$ (n=1-5).
$\text{CH}_5^+(\text{CH}_4)_n(\text{H}_2)_m$

$n = 1, 2, 3$

$m = 0, 1, 2, 3$

Mass (m/e)