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Infrared spectroscopy of the molecular hydrogen solvated carbonium ions, \( \text{CH}_5^+ (\text{H}_2)_n \) (\( n=1–6 \))

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The infrared spectra for the molecular hydrogen-solvated carbonium ions, \( \text{CH}_5^+ (\text{H}_2)_n \) (\( n=1–6 \)) in the frequency range of 2700–4200 cm\(^{-1} \) are presented. Spectroscopic evidence was found in support of the scrambling of \( \text{CH}_5^+ \) through the large amplitude motions such as the \( \text{CH}_3 \) internal rotation and the in-plane wagging motion of three-center two-electron bond. More importantly, the scrambling motions of \( \text{CH}_5^+ \) cores were slowed down considerably by attaching the solvent \( \text{H}_2 \) molecules to the core ion. The complete freezing of the scrambling motions was found when the first three \( \text{H}_2 \) molecules were bound to the \( \text{CH}_5^+ \) core. A good agreement between the experimental and the theoretical predictions was found in the dynamics of \( \text{CH}_5^+ \). © 1995 American Institute of Physics.

I. INTRODUCTION

Protonated alkanes are highly reactive intermediates in the acid-catalyzed transformations of hydrocarbons. These nonclassical carbonium ions are known to form a three-center two-electron (3c2e) bond having pentacoordinated carbon atoms and bridged hydrogens. \( \text{CH}_5^+ \) is the simplest carbonium ion.

The existence of \( \text{CH}_5^+ \) was first reported by Tal’roze and Lyubinova in mass spectrometric studies on the protonation of alkenes and alcanes in 1952. \(^3\) Olah and co-workers later reported that \( \text{CH}_5^+ \) played an important role as a reactive intermediate in super acid solution reactions. \( \text{CH}_5^+ \) is now used as a common reagent for protonation of gas phase molecules in the chemical ionization mass spectrometry. \(^5\) It is also of astrophysical interest in that it may play an intermediate for generation of methane and formaldehyde in the cold galactic molecular clouds. \(^6\)

A number of the early theoretical calculations on the structures of \( \text{CH}_5^+ \) consistently suggested that the eclipsed \( C_s \) (\( e-C_s \)) symmetry structure was the global minimum energy structure. \(^7\)–\(^10\) However, recent ab initio calculations at the most sophisticated level, performed by Schleyer and co-workers, found that the energy differences between the \( e-C_s \) structure and other structures such as staggered \( C_s \) (\( s-C_s \)) or \( C_{2v} \) were very small and became negligible when corrected for zero point energies (see Fig. 1 for the \( \text{CH}_5^+ \) structures). \(^11\),\(^12\) The \( C_{4v} \) and \( D_{3h} \) structures were predicted to be higher in energy than the \( e-C_s \) structure by 1 kcal/mol and 9 kcal/mol, respectively. As pointed out by Schleyer, Schaefer, and S., by Scu, the early prediction that \( \text{CH}_5^+ \) is regarded as a complex between \( \text{CH}_3^+ \) and \( \text{H}_2 \) with a localized 3c2e bond is not valid, but \( \text{CH}_5^+ \) is likely to scramble constantly through the low lying \( s-C_s \) and \( C_{2v} \) transition states, without possessing a definite equilibrium structure.

In contrast to the numerous theoretical works on \( \text{CH}_5^+ \), only a few experiments have been performed previously to characterize indirectly the structure of \( \text{CH}_5^+ \) using mass spectrometry. \(^14\)–\(^18\) Hiraoka and co-workers measured \( \Delta H_{n-1,n}^0 \) and \( \Delta S_{n-1,n}^0 \) for the clustering reactions \( \text{CH}_5^+ (\text{CH}_4)_n-1 + \text{CH}_4 = \text{CH}_5^+ (\text{CH}_4)_n \) for \( n=1–9 \) using a pulsed electron beam mass spectrometry. \(^14\) They showed an irregular decrease in the values of \( -\Delta H_{n-1,n}^0 \) and \( -\Delta S_{n-1,n}^0 \) between \( n=2 \) and 3, suggesting a \( C_s \) symmetry structure for \( \text{CH}_5^+ \) which contains a 3c2e bond, since the two acidic \( \text{H} \) atoms of the 3c2e bond would give the most favorable sites for the first two \( \text{CH}_4 \) ligands. However, this result only suggests the \( C_s \) structure for the core ion \( \text{CH}_5^+ \) of \( \text{CH}_5^+ (\text{CH}_4)_n \), not for free \( \text{CH}_5^+ \), because strong interaction between \( \text{CH}_5^+ \) and \( \text{CH}_4 \) could deform the structure of free \( \text{CH}_5^+ \) (\( \Delta H_{01}^0 = 6.87 \text{ kcal/mol} \)). In order to get more reliable information on the structure of \( \text{CH}_5^+ \), they also measured \( \Delta H_{n-1,n}^0 \) and \( \Delta S_{n-1,n}^0 \) for the cluster ions \( \text{CH}_5^+ (\text{H}_2)_n \) (\( n=1–4 \)), which were expected to have much weaker interactions between the core ion \( \text{CH}_5^+ \) and \( \text{H}_2 \) molecules. \(^15\) Unlike the case for \( \text{CH}_5^+ (\text{CH}_4)_n \), a gradual decrease of \( \Delta H_{n-1,n}^0 \) with \( n \) was observed for \( \text{CH}_5^+ (\text{H}_2)_n \), though a large gap in the van't Hoff plots was still seen between \( n=2 \) and 3. Based upon these observations, they proposed that \( \text{CH}_5^+ \) still has \( C_s \) structure but the positive charge is more delocalized in \( \text{CH}_5^+ \) when it is complexed by \( \text{H}_2 \).

Experiments using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometry have been performed on the collisionally induced intramolecular randomization of hydrogen and deuterium atoms in \( \text{CD}_3 \text{H}^+ \) and \( \text{CD}_4 \text{H}^+ \) by the groups of S. and S.,\(^16\) Smith’s,\(^17\) and H.\(^18\) In these works, the product ion branching ratio [\( \text{BH}^+ \)/[\( \text{BD}^+ \)] associated with the proton/deuteron transfer reaction from \( \text{CD}_3 \text{H}^+ \) and \( \text{CD}_4 \text{H}^+ \) to the base \( B \) was measured as a function of the average number (\( \langle n \rangle \)) of primary ion/molecule collisions (\( \text{CH}_3^+ / \text{CD}_3^+ \) or \( \text{CD}_4^+ / \text{CH}_4^+ \)). The idea of these studies was that if significant potential barriers exist for the scrambling motions of \( \text{CH}_5^+ \), the D atom in \( \text{CH}_3 \text{D}^+ \) and the H atom in \( \text{CD}_3 \text{H}^+ \) would be located at one of the two H atoms forming a 3c2e bond in the \( C_s \) structure, and the branching ratio will be 1:1 for both \( \text{CD}_3 \text{D}^+ \) and \( \text{CD}_3 \text{H}^+ \) cases (\( C_s \) model). If small or no barriers exist for the scrambling motions, the branching ratio will be 4:1 and 1:4 for \( \text{CH}_3 \text{D}^+ \) and \( \text{CD}_3 \text{H}^+ \) cases, respectively (randomized model). However, the results...
were inconsistent in that Sefcik's\textsuperscript{16} and Heck's results\textsuperscript{18} supported the $C_s$ model with a localized $3c2e$ bond whereas Smith's results\textsuperscript{17} suggested the randomized model.

Because of the difficulties in the indirect characterization of the structure of CH$_5^+$, much effort has been given to obtain high resolution infrared (IR) spectra for CH$_5^+$, but has achieved little success. One of the difficulties in the high resolution IR study is that CH$_5^+$ scrambles even at low temperatures, as predicted by the \textit{ab initio} calculations, causing significant spectral congestion. The spectral congestion would be more extensive for the CH$_5^+$ ions produced in the conventional ion sources since the ions tend to possess considerable internal energy.

In an attempt to overcome the difficulties of performing IR spectroscopy on CH$_5^+$, we have studied the molecular hydrogen solvated carbonium ions, CH$_5^+(H_2)_n$ ($n = 1–6$) where the H$_2$ molecules are weakly bound to the core ion. The motivation was the notion that the interactions between the core CH$_5^+$ ions and the H$_2$ molecules are weak enough to cause only a minor perturbation to CH$_5^+$, yet strong enough to slow down the scrambling motions. According to Hiraoka and co-workers, the binding energies ($\Delta H_{n-1,n}$) of the H$_2$ molecules to the CH$_5^+$ core were measured to be less than 2 kcal/mol.\textsuperscript{15} Schaefer and co-workers also calculated the dissociation energies and enthalpies for CH$_5^+(H_2)_n$ ($n = 1–6$), and performing \textit{ab initio} molecular dynamics (MD) simulations on CH$_5^+(H_2)_n$ ($n = 0–3$).\textsuperscript{21} The results provided considerable insight into the scrambling motion of CH$_5^+$, and revealed the slowdown of the scrambling of the CH$_5^+$ core by the solvent H$_2$ molecules in CH$_5^+(H_2)_n$ ($n = 1,2,3$).

In this paper, we present the complete IR spectra of the molecular hydrogen solvated carbonium ions, CH$_5^+(H_2)_n$ ($n = 1–6$) including the IR spectra for the H–H stretching modes of the solvent H$_2$ molecules, obtained in the frequency range of 2700–4200 cm$^{-1}$. It will be shown that correlation of the spectral features for the C–H stretching modes of the core CH$_5^+$ with the number of solvent H$_2$ molecules in CH$_5^+(H_2)_n$ ($n = 1–6$) can provide information on the structure and dynamics of CH$_5^+$. It will also be shown that the vibration–rotation transitions of the H–H stretching modes in CH$_5^+(H_2)_n$ ($n = 1–6$) can give additional information on the structure and dynamics of CH$_5^+$ as well as information about the interactions between the CH$_5^+$ core and the solvent H$_2$ molecules.

\section*{II. EXPERIMENTAL DETAILS}

The experimental apparatus used in this work has been described previously.\textsuperscript{22–26} A schematic of the machine is given in Fig. 2. Briefly, the molecular hydrogen solvated carbonium ions CH$_5^+(H_2)_n$ ($n = 1–6$) were produced from a high pressure corona discharge source and subsequent supersonic expansion through a 75 µm nozzle. A schematic of the corona discharge ion source is shown in Fig. 3. The corona discharge was maintained in 50–150 Torr of gas with ultrahigh purity (UHP) H$_2$ and UHP CH$_4$ in a 3 000 000:1 ratio, flowing past a 1.0 kV potential from the discharge tip of the needle to the source body maintained at approximately 350 V above ground. The discharge current under these conditions was 10–40 µA. The source was maintained at the optimum temperature for each kind of cluster ion in order to maximize the ion intensity, by heating up the source body cooled by contact with a liquid nitrogen reservoir. Typical source temperatures for the molecular hydrogen solvated carbonium ions CH$_5^+(H_2)_n$ ($n = 1–6$) were 10–40 µA.


\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Reference} & \textbf{$n = 1$} & \textbf{2} & \textbf{3} & \textbf{4} \\
\hline
Hiraoka et al.\textsuperscript{a} & $\Delta H^0$ & 1.88±0.10 & 1.78±0.10 & 1.61±0.10 & 1.57±0.10 \\
Hiraoka et al.\textsuperscript{b} & $D_1$ & 2.02 & 1.76 & 0.91 & 0.64 \\
MP2/6-31G** & $D_1(D_0)$ & 3.48(1.46) \\
TZ2P+d CCSD(T) & $D_1(D_0)$ & & & & \\
\hline
\end{tabular}
\caption{Experimental and theoretical dissociation energies and enthalpies for CH$_5^+(H_2)_n$ (units are kcal/mol).}
\end{table}

\textsuperscript{a}Reference 15.
\textsuperscript{b}Reference 19.
ions were usually trapped here for a rf octapole ion trap through an entrance aperture lens. The rupole field, decelerated to less than 0.5 eV, and focused into source; ions were between 1 and 10^20 and 10^31. Figure 2. Schematic of the experimental apparatus. (A) Corona discharge source; (B) skimmer and cone extractor; (C) electrostatic lenses; (D) plates separating two differential pumping regions; (E) quadrupole lens pair; (F) sector magnet; (G) quadrupole bending field; (H) deceleration field; (I) octapole ion trap; (J) quadrupole mass filter; (K) a Daly ion detector; (L) electron multiplier tube.

ions were between −20 and −70 °C. Pressures in the source chamber were between 1×10^−5 and 1×10^−4 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 10^−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 ms before IR irradiation. Usually, 100–500 ions were trapped per cycle, depending upon the stabilities of the cluster ions. These numbers are too small to allow direct measurement of photon absorption.

The trapped, mass-selected clusters were then vibrationally excited by a pulsed, tunable infrared 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 bandwidth was 0.2 cm⁻¹. The pulse duration was 6 ns with a 20 Hz repetition rate, and the laser power was 1–3 mJ/pulse in the 2700–4200 cm⁻¹ frequency region scanned in this work.

If the ions absorb one IR photon in the tuning range of 2700–4200 cm⁻¹, the CH5+(H2)n (n = 1–6) ions vibrationally predissociate into CH5+(H2)n−1 + yH2 (x + y = n). Large cluster ions are so weakly bound that the vibrational predissociation of these ions can produce two or more daughter ions which differ by the mass of H2. Roughly 0.5 ms 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 the daughter ions CH5+(H2)n−1. The observation of the CH5+(H2)n signal as a function of laser frequency was a measure of the IR absorption of CH5+(H2)n (n = 1–6).

Daughter ions were counted with a Daly ion detector 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 IR laser assuming a simple linear power dependence. For a typical experiment, signals were averaged for about 500 laser shots for CH5+(H2)n (n = 1–6) at each wavelength in the 2700–3200 cm⁻¹ and 4000–4150 cm⁻¹ frequency regions, where the IR absorptions were found for CH5+(H2)n (n = 1–6).

In this experiment, the composition of ions in the beam was strongly dependent on the H2/CH4 mixing ratios, source temperatures and source pressures. The experimental conditions used in this work were a H2:CH4 ratio of 3 000 000:1, a source temperature of −30 °C and a source pressure of 60–150 Torr. Figure 4 shows the mass spectrum for CH5+(H2)n (n = 1–6) obtained under these conditions. The mass spectrum shows a Gaussian distribution of the CH5+(H2)n ions with the cluster size ranging from n = 1 to n = 6. For the cluster ions with n ≥ 6, the mass peaks were overlapped with the intense peaks due to C2H5+(m/e = 29), C2H7+(m/e = 31), and CH5+(CH4) (m/e = 33). In this experiment, the maximum in the distribution of mass peaks was able to be easily shifted between n = 1 and n = 6 by changing the source pressures and source temperatures. The maximum ion intensities for large cluster ions were obtained when high source pressures and low source temperatures were used in the discharge.

As reported previously, the CH5+(H2)n ions were also produced using a H2:CH4 ratio of 2000:1, a −40 °C source temperature and 150 Torr source pressure. But, the IR spectra obtained with these two different conditions were similar to
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the superior signal-to-noise ratio.

each other. The IR spectra of CH$_3^+$ (H$_2$) obtained with the latter conditions is presented in this paper, simply because of the superior signal-to-noise ratio.

II. RESULTS AND ANALYSIS

A. Internally cold CH$_5^+$ (H$_2$)$_n$ ions

Since CH$_3^+$ is expected to scramble extensively even at the moderate temperatures, it is crucial to produce the ions in internally cold forms in order to obtain information about the structure and dynamics of the CH$_2^+$ cores in the molecular hydrogen solvated carbonium ions, CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6). Therefore, it seems appropriate to discuss the conditions of the carbonium ions [CH$_3^+$ and CH$_2^+$ (H$_2$)$_n$] produced in this experiment. As described in detail in the previous section, the carbonium ions were produced in a high pressure and low current corona discharge source and subsequent supersonic expansion. The ionization conditions were kept as soft as possible at the sacrifice of the ion intensity. Nevertheless, the carbonium ions were likely to be vibrationally excited by the discharge process, and were expected to cool down via collisions with cold neutral species in a small high pressure drift region and during supersonic expansion. It is well known that the collisional cooling strongly depends upon the efficiency of energy transfer from internally hot ions to the cold partners. If the cold partners (e.g., CH$_2^+$) possess similar vibrational frequencies as the internally hot ions, the ions would be cooled much more efficiently by the mechanism of resonant energy transfer. However, this mechanism may not be significant in the cooling process of the ions produced in this work, since the concentration of methane in the gas mixture was kept low in order to avoid the formation of larger hydrocarbon ions. Large hydrocarbon ions such as C$_2$H$_5^+$, C$_3$H$_5^+$, C$_4$H$_5^+$, and C$_5$H$_5^+$, instead of the carbonium ions, were found to be dominant in the mass spectrum when the concentration of methane was high (see Ref. 26 for the de-
tails). Therefore, the primary mechanism for the cooling of the carbonium ions in this work would be nonresonant energy transfer, efficient only when the molecules possess low frequency vibrational modes.

According to the ab initio calculations on CH$_3^+$ and CH$_4^+$ (H$_2$)$_n$$^{11,19}$ the lowest vibrational frequency for e–C$_3$H$_2^+$ was predicted to be quite high (856 cm$^{-1}$) since the CH$_3$–H$_2$ torsional mode (145 cm$^{-1}$) would be a free internal rotation. On the other hand, the molecular hydrogen solvated carbonium ions, CH$_5^+$ (H$_2$)$_n$ were predicted to possess several low frequency modes involving the core-ligand bonds. As a result, the CH$_5^+$ ions were expected to possess significant internal energy due to the inefficient cooling whereas the CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6) ions were expected to be internally cold. Besides, if CH$_5^+$ (H$_2$)$_n$ ions contain more internal energy than the solvation energy, it will dissociate and produce cooler ions.

Internally cold small clusters of CH$_5^+$ (H$_2$)$_n$ could also be formed during the flight before the mass selection in the magnetic sector, by releasing some H$_2$ molecules from the large clusters of CH$_5^+$ (H$_2$)$_n$. The CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6) ions were further cooled down by storing them in an ion trap for ~2 ms, during which some radiative cooling took place. Metastable ions, if they exist, would dissociate during the trapping time, and their contributions to the observed IR spectra were eliminated by doing a background substraction with the experimental scheme of laser on and off. In this experiment, the background level with laser off was found to be less than 0.1% of the parent ions, indicating the cold nature of the molecular hydrogen solvated carbonium ions, CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6).

B. Infrared spectra

Figure 5 shows the IR spectra for the molecular hydrogen solvated carbonium ions, CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–5) obtained in the frequency range of 2700–3200 cm$^{-1}$. The spectral features in this frequency region are due to the C–H stretching modes of the CH$_5^+$ cores in CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–5). Three C–H stretching bands were predicted by ab initio calculations in this frequency range, and the solid lines in Fig. 5 are the result of a least squares fit with three Gaussian peaks shown as dashed lines. But, one should note that each of the three fitted Gaussian peaks for CH$_5^+$ (H$_2$) and CH$_5^+$ (H$_2$)$_2$ [Figs. 5(A)–5(C)] does not necessarily represent a single vibrational mode of one CH$_5^+$ isomer, due to the expected scrambling of the CH$_5^+$ cores. The positions of the fitted Gaussian peaks are listed in Table III.

Figure 6 shows the IR spectra for the molecular hydrogen solvated carbonium ions CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6) obtained in the frequency range of 4050–4150 cm$^{-1}$. The observed features are due to the H–H stretching modes of the solvent H$_2$ molecules in CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6).

In this work, the signal to noise ratios of the IR spectra for the large clusters were found to be considerably lower than those for the small clusters, since the absolute number densities of the large clusters were found to be lower than the small clusters due to the weaker binding of the large clusters, and several vibrational predissociation channels available for

FIG. 4. Mass spectrum showing the carbonium ion CH$_5^+$ and the molecular hydrogen solvated carbonium ions CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–6). The mixing ratio of CH$_4$:H$_2$ was 1:3 000 000, and the source temperature and the discharge current were ~30 °C and 20 μA, respectively.

FIG. 5. Infrared spectra for the molecular hydrogen solvated carbonium ions, CH$_5^+$ (H$_2$)$_n$ ($n$ = 1–5). Three C–H stretching bands were predicted by ab initio calculations in this frequency range, and the solid lines in Fig. 5 are the result of a least squares fit with three Gaussian peaks as dashed lines. But, one should note that each of the three fitted Gaussian peaks for CH$_5^+$ (H$_2$) and CH$_5^+$ (H$_2$)$_2$ [Figs. 5(A)–5(C)] does not necessarily represent a single vibrational mode of one CH$_5^+$ isomer, due to the expected scrambling of the CH$_5^+$ cores. The positions of the fitted Gaussian peaks are listed in Table III.
the large clusters would compete each other, resulting in the smaller number of daughter ions at each channel.

1. \textit{CH}_3^+(\text{H}_2)

The IR spectra for the C–H stretching modes of \textit{CH}_3^+(\text{H}_2), shown in Figs. 5(A) and 5(B), were obtained by monitoring the \textit{CH}_3^+ signal \((m/e = 17)\). As reported previously, the two IR spectra [Figs. 5(A) and 5(B)] were obtained with hot ion conditions and cold ion conditions, respectively (see Ref. 20 for the details of the source conditions). One broad feature with shoulders, centered at 2964 cm\(^{-1}\), was observed in the IR spectrum with cold ion conditions [Fig. 5(B)], indicating the floppy nature of \textit{CH}_3^+. The shoulder features observed in the cold ion spectrum almost disappeared in the hot ion spectrum [Fig. 5(A)], revealing increased scrambling of the core \textit{CH}_3^+. The lowest frequency peak among three Gaussian peaks fitted into the observed IR spectrum with cold ion conditions was quite broad, extending from 2700 to 3100 cm\(^{-1}\), centered at 2907 cm\(^{-1}\) [see Fig. 5(B) and Table III].

According to the recent \textit{ab initio} calculation on \textit{CH}_3^+(\text{H}_2), three C–H stretching frequencies for \textit{e}-\textit{C}_\textit{s} \textit{CH}_3^+ core, the global minimum energy structure, were predicted to be 2898, 2998, and 3081 cm\(^{-1}\), corresponding to the symmetric CH\(_3\) breathing, symmetric CH\(_3\) degenerate stretching, and asymmetric CH\(_3\) stretching modes, as shown in Table II. These vibrational modes were also predicted to have more or less similar IR intensities. The C–H stretching frequencies for the low lying transition state structures such as \textit{s}-\textit{C}_\text{i} and \textit{C}_{2\text{v}} \textit{CH}_3^+ were predicted to be 2914, 2968, and 3085 cm\(^{-1}\) for the former, and 2732, 2987, and 3094 cm\(^{-1}\) for the latter (Table II). The two structures were regarded as the transition states along the CH\(_3\) internal rotation, and along the in-plane wagging of the H2 between H1 and H3 in the CH\(_3\) core, respectively (see Fig. 1). The latter motion will be referred to subsequently as the in-plane wagging motion. It is interesting to notice that the vibrational assignments for the two high C–H stretching frequencies of \textit{s}-\textit{C}_\text{i} \textit{CH}_3^+ core (2968 and 3085 cm\(^{-1}\)) were the asymmetric CH\(_3\) stretching and symmetric CH\(_3\) degenerate stretching modes, respectively, which were switched in order, compared to the case for \textit{e}-\textit{C}_\text{i} \textit{CH}_3^+. This could be the result of the substantial geometrical changes in the CH\(_3\) group during the internal rotation, as expected from the differences in the optimized C–H bond lengths and angles\(^{11,12}\) between \textit{e}-\textit{C}_\text{i} \textit{CH}_3^+ and \textit{s}-\textit{C}_\text{i} \textit{CH}_3^+. This suggests that the vibrational modes involving the three C–H bonds could be strongly coupled to each other via the CH\(_3\) internal rotation.

On the other hand, the \textit{C}_{2\text{v}} \textit{CH}_3^+ transition state consisted of two strong C–H bonds and three weak C–H bonds forming a four-center three-electron (4c3e) bond. Correspondingly, the three C–H stretching frequencies (2732, 2987, and 3094 cm\(^{-1}\)) were assigned to the asymmetric C–H stretching mode involving two weak C–H bonds, symmetric and asymmetric C–H stretching modes involving two strong C–H bonds, respectively (Table II). The 2732 cm\(^{-1}\) mode, strongly red-shifted from the other two C–H stretching
modes of the C2v structure, were distinct from the C–H stretching modes of the C1 (e–C1 and s–C1) structures, and could serve as an indicator of the scrambling of CH5 via the in-plane wagging motion involving the C2v transition state.

Based on the trend in the ab initio CH3 stretching frequencies for different CH5 structures, it can be predicted that if the CH3 internal rotation (via s–C1 transition state) and the in-plane wagging motion (via C2v transition state) are unhindered, the observed spectrum for the CH3 stretching vibrations will broaden considerably due to contributions from all the possible CH5 structures along the two internal coordinates, which are expected to have different CH3 stretching frequencies. Furthermore, the lowest CH3 stretching vibration of e–C1 CH5 structure will be strongly coupled to the vibrational modes of the 3e2 bond by the in-plane wagging motion, and could have frequencies ranging from 2898 cm−1 (e–C1 CH5 core) to 2732 cm−1 (C2v CH5 core) if the in-plane wagging motion is unhindered. Therefore, only appropriate statistical averages of the CH3 stretching frequencies over the coordinates of the two scrambling motions will describe the observed spectral features properly.

The observation of one broad feature with shoulders in the IR spectrum [Fig. 5(B)] and the result of the broad Gaussian peak fitted into the low frequency shoulder, instead of three distinct CH3 stretching bands as predicted by the ab initio calculation on e–C1 CH5, clearly suggested that the CH5 core in CH5(H2) scrambles considerably via large amplitude motions such as the CH3 internal rotation involving the s–C1 transition state, and the in-plane wagging motion involving the C2v transition state. Nonetheless, the center of the observed feature at 2965 cm−1 was only 27 cm−1 red-shifted from the average C–H stretching frequency of CH4 (2992 cm−1),28 reflecting the fact that when a hydrogen atom in CH5 does not participate in the scrambling motions, its corresponding C–H bond is similar to the C–H bond in CH4.

Figure 6(A) shows the IR spectrum for the H–H stretching mode of the H2 in CH5(H2), obtained by monitoring the CH5 signal (m/e = 17) with 0.2 cm−1 laser resolution. The vibration-rotational spectrum shows clear P, Q, and R branches, indicating the A-type transition of a near symmetric top. The band origin was 4077.4 cm−1, 82.6 cm−1 red-shifted from free H2 (4160 cm−1), which suggests that the interaction between the CH5 core and the H2 molecule in CH5(H2) is dominated by the electrostatic charge-induced dipole interaction. The dipole moment of H2 induced by the ion core allowed the H–H stretching mode to be IR active. The spacing of adjacent rotational lines ranged from 1.4 cm−1 to 1.6 cm−1. The rotational lines were found to possess some fine structures, as shown in Fig. 6(A). Two anomalously intense peaks were observed in the R-branch side, as indicated by asterisks in Fig. 6(A), and they could be assigned to the Q branches of two hot band transitions. The rotational progressions of the hot band transitions may contribute to the wide spread of rotational lines with a high

| TABLE II. Vibrational frequencies of the C–H and H–H stretching modes for CH5(CH3)n (n = 1–3) predicted by the ab initio calculations. Units are in cm−1. |
|---------------------------------|-----------------|-----------------|-----------------|
|                                | Asymmetric CH3 stretch | Symmetric CH3 deg stretch | Symmetric CH3 breath | H2 stretch |
|--------------------------------|---------------------|---------------------|---------------------|-----------|
| CH5, e–C1                        | 3079(3063)          | 2972(2956)          | 2706(2692)          | 4104(4082) |
| T2P+f CCSDb                       |                     |                     |                     |           |
| CH5, s–C1                        | 3079(3063)          | 2972(2956)          | 2706(2692)          | 4104(4082) |
| T2P+f CCSDb                       |                     |                     |                     |           |
| CH5, e–C1                        | 3079(3063)          | 2972(2956)          | 2706(2692)          | 4104(4082) |
| T2P CCSD                         |                     |                     |                     |           |
| CH5, e–C1                        | 3278(3069)          | 3183(2980)          | 3068(2872)          | 4446(4162) |
| MP2/6-311G(D,P)                  |                     |                     |                     |           |
| CH5, e–C1                        | 3280(3071)          | 3180(2977)          | 3043(2849)          | 4448(4164) |
| MP2/6-311G(D,P)                  |                     |                     |                     |           |
| CH5, e–C1                        | 3280(3071)          | 3180(2977)          | 3043(2849)          | 4448(4164) |
| MP2/6-311G(D,P)                  |                     |                     |                     |           |

aThe numbers in parentheses are the frequencies scaled by the ratio of 2977 cm−1, one of the observed peaks for CH3, and the corresponding ab initio C–H stretching frequency for the eclipsed C1 CH5 core at the level of theory. For example, the ratio was 2977/2993 = 0.995 at T2P+f CCSD; 2977/2998 = 0.993 at T2P CCSD; 2977/2993 = 0.995 at T2P SCF; 2977/3180 = 0.936 at MP2/6-311G(D,P).
bReference 11.
cReference 19.
dReference 29.

*Note that the vibrational assignments for C2v CH5 should be changed to the CH3 asymmetric, CH3 symmetric, and CH5 asymmetric stretching modes, respectively (CH5 indicates the two of three C–H bonds forming the 4e3e bond).
The observed spectrum showed clear vibrational frequencies of the molecular hydrogen solvated carbonium ions. Units are in cm$^{-1}$.

| Ions | C–H stretching modes$^a$ | Band origins of H–H stretching modes |
|------|--------------------------|-------------------------------------|
| CH$_5^+$ (H$_2$) | 2964(2907, 2965, 3070)$^b$ | 4077.4$^c$ |
| CH$_5^+$ (H$_2$)$_2$ | 2957(2930, 2983)$^b$, 3078 | 4088.2$^c$ |
| CH$_5^+$ (H$_2$)$_3$ | 2892, 2977, 3062 | 4099$^d$ |
| CH$_5^+$ (H$_2$)$_4$ | 2878, 2979, 3067 | 4106$^d$ |
| CH$_5^+$ (H$_2$)$_5$ | 2879, 2972, 3043 | 4109$^d$ |
| CH$_5^+$ (H$_2$)$_6$ | N.O.$^e$ | 4111$^d$ |

$^a$ These C–H stretching frequencies were determined by a least squares fit with three Gaussian peaks.

$^b$ These frequencies in parentheses for $n=1$ and $n=2$ were obtained by fitting with three Gaussian peaks and two equal Gaussian peaks, respectively, even though they were not resolved in the observed spectra [see Figs. 5(B) and 5(C)].

$^c$ These frequencies were measured at the center of the observed features.

$^d$ Not observed.

TABLE III. Vibrational frequencies of the molecular hydrogen solvated carbonium ions.

background, observed in the R-branch side [see Fig. 6(A)]. The full analysis of the vibration–rotational spectrum will be reported elsewhere.

2. CH$_5^+$ (H$_2$)$_2$

Figure 5(C) shows the IR spectrum for the C–H stretching modes of CH$_5^+$ (H$_2$)$_2$, obtained by monitoring the CH$_5^+$ signal ($n_{le}=17$). Two spectral features, centered at 2957 cm$^{-1}$ and 3078 cm$^{-1}$, were observed in the frequency range of 2700–3200 cm$^{-1}$. The broad and intense feature at 2957 cm$^{-1}$ was fitted with two equal Gaussian peaks centered at 2930 and 2983 cm$^{-1}$, respectively, as shown in Fig. 5(C) and Table III, and the narrow feature at 3078 cm$^{-1}$ was fitted with one Gaussian peak. The $ab$ initio C–H stretching frequencies for e-C$_2$, CH$_5^+$ (H$_2$)$_3$, shown in Table II, were more or less similar to those for e-C$_2$, CH$_5^+$ (H$_2$) after appropriate scaling. The $ab$ initio C–H stretching frequencies for s-C$_2$ and C$_2$H$_4$, CH$_5^+$ (H$_2$)$_2$ were also expected to be similar to the corresponding frequencies for CH$_5^+$ (H$_2$).

The low frequency shoulder feature observed in the IR spectrum for CH$_5^+$ (H$_2$) was not present in the spectrum for CH$_5^+$ (H$_2$)$_2$. This suggested that the scrambling motion through the in-plane wagging motion (via C$_2$H$_4$ transition state) may be frozen out by the two H$_2$ molecules in CH$_5^+$ (H$_2$)$_2$, unlike the case for CH$_5^+$ (H$_2$). However, the scrambling of the CH$_5^+$ core through the CH$_5$ internal rotation was still extensive, indicated by the broad feature at 2957 cm$^{-1}$, and strong anharmonic couplings for the vibrational modes involving these three C–H bonds were also expected.

Figure 6(B) shows the IR spectrum for the H–H stretching modes for the two H$_2$ molecules in CH$_5^+$ (H$_2$)$_2$, obtained by monitoring the CH$_5^+$ signal in the frequency range of 4050–4150 cm$^{-1}$. The IR spectrum was taken with 0.2 cm$^{-1}$ laser resolution and 1 cm$^{-1}$ scan step. In spite of the large scan step, the observed spectrum showed clear P, Q, and R branches, indicating the A-type transition of a near symmetric top. The presence of a single rotational progression suggested that the two H$_2$ molecules were bound to the two H atoms forming a 3c2e bond, with almost equal strength. In this case, the in-phase H–H stretching vibration of the two H$_2$ molecules would be responsible for the observed feature since the change of dipole moment due to the in-phase vibration would be along the A-axis of CH$_5^+$ (H$_2$)$_2$.

The band origin was $\sim$4088 cm$^{-1}$, 72 cm$^{-1}$ red-shifted from free H$_2$, but 10 cm$^{-1}$ blue-shifted from CH$_5^+$ (H$_2$). This indicated that the interactions between CH$_5^+$ core and two H$_2$ molecules in CH$_5^+$ (H$_2$)$_2$ were also the charge-induced dipole interactions, and the interactions were weaker for CH$_5^+$ (H$_2$)$_2$ since the positive charge of the core CH$_5^+$ was more delocalized in CH$_5^+$ (H$_2$)$_2$.

3. CH$_5^+$ (H$_2$)$_3$

Figure 5(D) shows the IR spectrum for the C–H stretching modes of CH$_5^+$ (H$_2$)$_3$, obtained by monitoring the CH$_5^+$ signal in the frequency range of 2800–3100 cm$^{-1}$. Three partially resolved peaks, centered at 2892, 2977, and 3062 cm$^{-1}$, were found in the IR spectrum. The presence of the three well-separated peaks suggested that the scrambling motions of the CH$_5^+$ core were almost frozen out by the three H$_2$ molecules in CH$_5^+$ (H$_2$)$_3$, and the CH$_5^+$ core could be considered as semirigid. It is interesting to notice that the observed frequencies (2892, 2977, 3062 cm$^{-1}$) match well with the three $ab$ initio CH$_5^+$ stretching frequencies for e-C$_3$, CH$_5^+$ (2891, 2993, 3079 cm$^{-1}$) and e-C$_4$, CH$_5^+$ (H$_2$) (2898, 2998, 3081 cm$^{-1}$), calculated at TZ2P (+f) CASSD level,$^{19}$ as shown in Table II. The $ab$ initio CH$_5^+$ stretching frequencies of e-C$_4$, CH$_5^+$ (H$_2$)$_3$, calculated at MP2/6-311G(D,P) level,$^{29}$ also match well with the observed frequencies after appropriate scaling (see Table II). It suggests that the CH$_5^+$ core in CH$_5^+$ (H$_2$)$_3$ possesses an e-C$_4$ structure. Since the adiabatic approximations made in the normal mode analysis on the C–H stretching frequencies are expected to be valid due to the semirigidity of the CH$_5^+$ core, the three observed features could be assigned to the symmetric CH$_3$ breathing, symmetric CH$_3$ degenerate stretching, and asymmetric CH$_3$ stretching modes, according to the $ab$ initio normal mode analysis.$^{19}$ Furthermore, the new scaling factors for the anharmonic corrections were calculated by the ratio of 2977 cm$^{-1}$, one of the observed frequencies, to the corresponding $ab$ initio frequency for the e-C$_4$, CH$_5^+$ core at the level of theory. The rescaled frequencies are listed in the parentheses of Table II.

Figure 6(C) shows the IR spectrum for the H–H stretching modes of the three H$_2$ molecules in CH$_5^+$ (H$_2$)$_3$, obtained by monitoring the CH$_5^+$ signal in the frequency range of 4050–4140 cm$^{-1}$. Unlike the cases for CH$_5^+$ (H$_2$) and CH$_5^+$ (H$_2$)$_2$, one broad feature was observed in the spectrum. One of the reasons for the spectral congestion was that the third H$_2$ molecule in CH$_5^+$ (H$_2$)$_3$ was bound to the CH$_5^+$ core in a different environment from the first two H$_2$ molecules, indicating the presence of a 3c2e bond in the CH$_5^+$ core in CH$_5^+$ (H$_2$)$_3$. The center of the broad feature was located at $\sim$4099 cm$^{-1}$, 61 cm$^{-1}$ red-shifted from free H$_2$, but 11 cm$^{-1}$ blue-shifted from that of CH$_5^+$ (H$_2$)$_2$. This also suggested that the interactions of the CH$_5^+$ core with the H$_2$ molecules be-
came weaker due to the increased charge delocalization in CH$_5^-$ (H$_2$)$_3$.

4. CH$_5^+$ (H$_2$)$_4$

Figure 5(E) shows the IR spectrum for the C–H stretching modes of CH$_5^+$ (H$_2$)$_4$, obtained by monitoring the CH$_5^+$ signal. Three peaks, centered at 2878, 2977, and 3067 cm$^{-1}$, were found in the IR spectrum. These three frequencies were similar to those for CH$_5^+$ (H$_2$)$_3$ (2892, 2977, and 3062 cm$^{-1}$), which were assigned to the symmetric CH$_3$ breathing, symmetric CH$_3$ degenerate stretching, and asymmetric CH$_3$ stretching modes, respectively. This result indicated an $e$-C$_s$ structure for the CH$_5^+$ core in CH$_5^+$ (H$_2$)$_4$, but also no significant solvation effect by the fourth H$_2$ molecule.

Figure 6(D) shows the IR spectrum for the H–H stretching modes of the H$_2$ molecules in CH$_5^+$ (H$_2$)$_4$. The spectrum was also obtained by monitoring the CH$_5^+$ signal in the frequency range of 4050–4140 cm$^{-1}$. One broad feature was again found, centered at ~4106 cm$^{-1}$, 54 cm$^{-1}$ red-shifted from free H$_2$, but 7 cm$^{-1}$ blue-shifted from CH$_5^+$ (H$_2$)$_3$, indicating the weaker interaction due to the increased charge delocalization in CH$_5^+$ (H$_2$)$_4$. In addition, the slight decrease in the frequency shift from the adjacent smaller cluster (7 cm$^{-1}$ vs 11 cm$^{-1}$) suggested that the solvent effect on the charge-induced dipole interaction between the hydrogen molecules and the CH$_5^+$ core started to decrease at $n = 4$, which was consistent with the trend in the C–H stretching bands described above.

5. CH$_5^+$ (H$_2$)$_n$ (n=5,6)

Figure 5(F) shows the IR spectrum for the C–H stretching modes of CH$_5^+$ (H$_2$)$_5$. The IR spectrum was obtained by monitoring the CH$_5^+$ signal ($m/e = 19$) instead of the CH$_5^+$ signal, since the CH$_5^+$ (H$_2$)$_5$ channel was found to be the major channel for the vibrational prescission dissociation of CH$_5^+$ (H$_2$)$_5$ in the frequency range of 2700–3200 cm$^{-1}$. Three features, centered at 2879, 2972, and 3043 cm$^{-1}$, were found in the spectrum, in spite of the low signal to noise ratio. These three frequencies are similar to those for CH$_5^+$ (H$_2$)$_3$ and CH$_5^+$ (H$_2$)$_4$, which were assigned to the symmetric CH$_3$ breathing, symmetric CH$_3$ degenerate stretching, and asymmetric CH$_3$ stretching modes of the $e$-C$_s$ CH$_5^+$ core, respectively. This suggested that the structure of the CH$_5^+$ core in CH$_5^+$ (H$_2$)$_5$ was not changed by the fifth H$_2$ molecule, but was still an $e$-C$_s$ structure.

Figures 6(E) and 6(F) show the IR spectra for the H–H stretching modes of CH$_5^+$ (H$_2$)$_5$ and CH$_5^+$ (H$_2$)$_6$, respectively. These IR spectra were obtained by monitoring the CH$_5^+$ signal, the major channel in this frequency region, which was different from the case for the C–H stretching bands. The additional photon energy in this frequency range was responsible for the complete dissociation. In both spectra, one broad feature was found, centered at 4109 and 4111 cm$^{-1}$, 51 and 49 cm$^{-1}$ red-shifted from free H$_2$, respectively. These features were only 3 and 2 cm$^{-1}$ blue-shifted from the adjacent smaller clusters, respectively. This result suggested that

the charge-induced dipole interactions between the H$_2$ molecules and the CH$_5^+$ core were almost in saturation for CH$_5^+$ (H$_2$)$_5$ and CH$_5^+$ (H$_2$)$_6$.

IV. DISCUSSION

A. Dynamics of CH$_5^+$ in CH$_5^+$ (H$_2$)$_n$ (n=0–6)

Since the IR spectra for CH$_5^+$ (H$_2$)$_n$ (n=1–5) provided information about the scrambling motions of CH$_5^+$ cores, it seems appropriate to discuss the details of the dynamics of CH$_5^+$ by combining the results of this work and the previous theoretical works. Two crucial theoretical works have been performed previously by Schleyer and co-workers, and by us in collaboration with Liu and Tse. The first was the high level ab initio calculation at TZ2P+f CCSD level, and the second was the ab initio molecular dynamics (MD) simulation. The two theoretical methods seem to be complementary to each other such that the first provides very accurate electronic energies and harmonic frequencies of CH$_5^+$, but only for a few optimized nuclear configurations, while the second can simulate all of the classical trajectories of CH$_5^+$, allowed at the finite temperatures on the ground electronic potential surface, calculated by the density functional method which may not be as accurate as the first.

Both methods predicted the complete scrambling of CH$_5^+$, according to the high level ab initio calculation, the scrambling was predicted to occur through $s$-$C_4$ and $C_{2v}$ structures, which were regarded as the transition states for the CH$_3$ internal rotation and the in-plane wagging motion. The two internal motions were expected to be strongly coupled to each other such that the CH$_3$ internal rotation would be free only when the 3c2e bond involved in the in-plane wagging motion is localized, like in the $C_4$ CH$_5^+$ structure. The same high level ab initio calculation on CH$_5^+$ (H$_2$) predicted almost the same results for the CH$_5^+$ core in CH$_5^+$ (H$_2$). At present, no high level ab initio calculation has yet been reported on CH$_5^+$ (H$_2$)$_n$ (n $\geq$ 2).

Ab initio MD simulations have been performed on CH$_5^+$ (H$_2$)$_n$ (n=0–3) as reported previously. During the simulation of ~3 ps at a temperature of ~100 K, the 3c2e bond representing a $C_4^*$ structure for CH$_5^+$ could be formed among any pair of H atoms in CH$_5^+$, for CH$_5^+$ (H$_2$), the 3c2e bond was more or less localized around the H atom of the CH$_5^+$ core which was complexed by the H$_2$ molecule. Scrambling through the two internal motions (via $s$-$C_4$ and $C_{2v}$ transition states) were still expected to be significant. For CH$_5^+$ (H$_2$)$_2$, the 3c2e bond was localized to the two H atoms which were bound by the two H$_2$ molecules. It was explained by the electron deficiency in the 3c2e bond which attracts the two H$_2$ molecules. Preference for the localized 3c2e bond was also predicted in the ab initio calculation at MP2/6-31G**, from the decrease in the angle of the 3c2e bond ($\pm$H1CH2) from 48.4° for CH$_5^+$ (H$_2$) to 47.7° for CH$_5^+$ (H$_2$)$_2$ [see Figs. 9(A) and 9(B)]. But, the scrambling through the CH$_3$ internal rotation was still extensive. For CH$_5^+$ (H$_2$)$_3$, the CH$_5^+$ core was semirigid with the CH$_3$ internal rotation considerably hindered, but the in-plane wagging motion unhindered.

In the IR spectrum for the C–H stretching modes of
CH$_5^+$ (H$_2$)$_4$ [Fig. 5(B)], as mentioned previously, the center of the observed feature (2965 cm$^{-1}$) was only 23 and 27 cm$^{-1}$ red-shifted from the average (2988 cm$^{-1}$) of the three highest \textit{ab initio} C–H stretching frequencies of a C$_4$ CH$_3^+$ ($e$-C$_4^+$ and s-C$_4$), as shown in Table II, and the average C–H stretching frequency (2992 cm$^{-1}$) of CH$_4$. This result suggested that most of the structures possessed by the CH$_5^+$ core during the scrambling still contain a CH$_3$ unit with strong C–H bonds like those in the optimized $C_s$ CH$_3^+$ structures or the C–H bonds in CH$_4$. The overall broad feature and the broad low frequency shoulder observed in the IR spectrum were suggestive of the scrambling through the CH$_3$ internal rotation (via $s$-$C_s$ transition state) and the in-plane wagging motion (via $C_2v$ transition state).

Therefore, the CH$_5^+$ core in CH$_3^+$(H$_2$)$_2$ continues to scramble through the CH$_3$ internal rotation and the in-plane wagging motion, but the C–H bonds which are not directly involved in the nonclassical bond (3$c$2$e$ or 4$c$3$e$ bond), are expected to be strong like the C–H's in CH$_4$. The $A$-type vibration–rotational transitions observed in the IR spectrum for the H–H stretching mode [Fig. 6(A)], suggested the structure of CH$_3^+$(H$_2$)$_2$ with the H$_2$ molecule weakly bound to one of the two H atoms forming the 3$c$2$e$ bond, in good agreement with the theoretical predictions. The anomalously intense peaks and the rotational fine features observed in the spectrum could be due to the scrambling motions involving the CH$_3$ internal rotation and in-plane wagging motion.

For CH$_5^+$ (H$_2$)$_2$, one broad and intense peak at 2957 cm$^{-1}$ and one narrow peak at 3078 cm$^{-1}$ were observed. While the broad low frequency shoulder observed for CH$_5^+$ (H$_2$) was no longer present in the IR spectrum [Fig. 5(C)]. This result was consistent with the theoretical prediction that the CH$_5^+$ core has a $C_s$ structure with the 3$c$2$e$ bond localized. The scrambling through the in-plane wagging motion was expected to be considerably hindered. The broad feature at 2957 cm$^{-1}$ suggested that the scrambling through the CH$_3$ internal rotation was still significant. Strong anharmonic couplings for the vibrational modes involving the CH$_3$ group were also expected. The broad and intense peak at 2957 cm$^{-1}$ could be assigned to the two strongly coupled C–H stretching modes, while the narrow feature at 3078 cm$^{-1}$ could be due to the other less coupled C–H stretching mode. The $A$-type vibration-rotational transitions observed in the IR spectrum for the H–H stretching modes [Fig. 6(B)], were suggestive of the CH$_3^+$ (H$_2$)$_2$ structure with the two H$_2$ molecules bound to the two H atoms forming the 3$c$2$e$ bond in the CH$_5^+$ core. The in-phase vibration of the two H–H stretching modes would be exactly along the $A$ axis of the ion when the CH$_3$ internal rotation is free.

For CH$_5^+$ (H$_2$)$_3$, three partially resolved features, centered at 2892, 2977, 3062 cm$^{-1}$ were observed in the IR spectrum [Fig. 5(D)], indicating the semirigid nature of the CH$_5^+$ core. Only scrambling would occur through quantum tunneling, causing the broad bandwidths. It is interesting to notice that the observed frequencies (2892, 2977, 3062 cm$^{-1}$) match well with the three \textit{ab initio} CH$_3^+$ stretching frequencies, for $e$-C$_4^+$ CH$_3^+$ (2891, 2993, 3079 cm$^{-1}$) (Ref. 11) and $e$-C$_4$, CH$_4^+$ (2898, 2998, 3081 cm$^{-1}$). It suggests that the CH$_5^+$ core in CH$_5^+$ (H$_2$)$_3$ possesses an $e$-C$_4$ structure. Correspondingly, the three C–H stretching frequencies could be assigned to the symmetric CH$_3$ breathing, symmetric CH$_3$ degenerate stretching, and asymmetric CH$_3$ stretching modes of $e$-C$_4$, CH$_3^+$ core in CH$_5^+$ (H$_2$)$_3$. The \textit{ab initio} MD simulation also predicted the semirigid nature of the CH$_5^+$ core, but predicted the scrambling through the in-plane wagging motion, different from the experimental result. The difference was attributed to the underestimation of the potential barrier for the in-plane wagging motion. In addition, other isomers of CH$_5^+$ (H$_2$)$_3$ such as the structure with the third H$_2$ located out of plane to the 3$c$2$e$ bond, may contribute to the observed IR spectrum.

For CH$_5^+$ (H$_2$)$_4$, three resolved features, centered at 2878, 2979, and 3067 cm$^{-1}$, were observed in the IR spectrum [Fig. 5(E)], similar to the spectral features observed for CH$_5^+$ (H$_2$)$_3$ [Fig. 5(D)]. This result suggested that the scrambling of CH$_5^+$ core was more or less frozen out by the first three H$_2$ molecules, and the addition of the fourth H$_2$ molecule resulted in only a minor change in the structure of the CH$_5^+$ core. It was consistent with the results of Hiraoka and co-workers’ measurements on CH$_5^+$ (H$_2$)$_n$ (see Table I), in that the stabilization of the cluster ions by the fourth H$_2$ molecule was small, compared to the stabilization by the third H$_2$ (0.17 vs 0.04 kcal/mol). In the IR spectrum for the H–H stretching modes of CH$_5^+$ (H$_2$)$_4$ [Fig. 6(D)], the frequency shift of the observed feature from the adjacent smaller cluster decreased from that for CH$_5^+$ (H$_2$)$_3$, which was consistent with the trend for the C–H stretching modes as described above. For CH$_5^+$ (H$_2$)$_n$ ($n = 5, 6$), the trend of the spectral features observed in the IR spectrum [Figs. 5(F), 6(E), 6(F)], were similar to the case for CH$_5^+$ (H$_2$)$_4$. The structures of the CH$_5^+$ cores were expected to be unchanged by the fifth and sixth H$_2$ molecules.

B. Stabilities and structures of CH$_5^+$ (H$_2$)$_n$ ($n = 1–6$)

In this section, the stabilities of the solvated complexes, CH$_5^+$ (H$_2$)$_n$ ($n = 1–6$) are discussed from the correlation between the H–H stretching frequencies and the strength of the interactions. Possible solvation structures are also presented.

As described previously, the interactions between CH$_5^+$ core and the H$_2$ molecules are dominated by the electrostatic charge-induced dipole interactions, where the strengths are proportional to the charge densities at the H atoms of CH$_5^+$ core, the binding sites for the H$_2$ molecules in CH$_5^+$ (H$_2$)$_n$ ($n = 1–6$). The effect of the electrostatic interaction on the vibrational frequency of the solvent H$_2$ molecules has been addressed previously in the calculation of the Stark shifts of the H–H stretching modes as a function of the distance from the charge to H$_2$ molecule by Hunt and Poll. The frequency shifts of the H–H stretching modes from free H$_2$ could be a measure of the strength of the electrostatic interactions. Figure 7 shows a plot of the peak positions of the H–H stretching modes as a function of the size of the clusters. The frequency shifts from free H$_2$ (4160 cm$^{-1}$) decreased as the number of H$_2$ molecules increased, and reached a limit at $n = 4$. This result clearly indicated that the positive charge of
the CH$_5^+$ core was gradually delocalized as the size of the clusters increased.

Figure 8 shows a plot of the correlation between the H–H stretching frequencies and the $-\Delta H_2^0$'s of the clustering reactions, CH$_5^+$ (H$_2$)$_{n-1}$ + H$_2$ = CH$_5^+$ (H$_2$)$_n$ ($n=1-6$), measured by Hiraoka and co-workers (see Table I). The correlation followed the idea of the previous work by Hunt and Poll as described above. A good correlation was found between the H–H stretching frequencies and the $-\Delta H_2^0$'s of the clustering reactions, as shown in Fig. 8. From the correlation, the $-\Delta H_2^0$'s for the formation of CH$_5^+$ (H$_2$)$_5$ and CH$_5^+$ (H$_2$)$_6$, which were not measured in the previous work by Hiraoka and co-workers, were calculated to be 1.52 and 1.49 kcal/mol, respectively. Furthermore, one could correlate the H–H stretching frequencies with the theoretical binding energies to test the consistency of the calculations.

Finally, it is appropriate to address the possible structures of the solvated complexes, CH$_5^+$ (H$_2$)$_n$ ($n=1-6$) by combining the results of this work and the results of the theoretical work. Figure 9 shows the possible structures of CH$_5^+$ (H$_2$)$_n$ ($n=1-6$). Both experimental and theoretical results consistently suggested the structures shown in Figs. 9(A) and 9(B) for CH$_5^+$ (H$_2$) and CH$_5^+$ (H$_2$)$_2$, where the H$_2$ molecules were bound to the H atoms forming the 3c2e bond in the CH$_5^+$ core. For CH$_5^+$ (H$_2$)$_3$, the most stable structure was predicted to be the structure shown in Fig. 9(C), but other structures such as the structure shown in Fig. 9(D), where the third H$_2$ was located out of plane to the 3c2e bond, could be formed in internally hot ions. Due to the weak interactions between the CH$_5^+$ core and the H$_2$ molecules in CH$_5^+$ (H$_2$)$_n$ ($n \geq 4$), the structures of the ions are better described as the mixture of several structures undergoing rapid isomerizations on the very shallow potential energy surfaces. But, it is still instructive to consider the local minimum energy structures for CH$_5^+$ (H$_2$)$_n$ ($n \geq 4$). For CH$_5^+$ (H$_2$)$_4$, the fourth H$_2$ could bind to either the H4 (or H5) of the CH$_5^+$ core [Fig. 9(E)] or the 3c2e bond in the out-of-plane fashion [Fig. 9(F)]. For CH$_5^+$ (H$_2$)$_5$, the fifth H$_2$ molecule could bind to the H5 (or H4) of the CH$_5^+$ core, completing the first solvation shell around the CH$_5^+$ core [Fig. 9(G)]. In addition, the CH$_5^+$ (H$_2$)$_5$ ions could form the structures with one or two H$_2$ molecules binding to the 3c2e bond in the out-of-plane fashion [Fig. 9(H)]. For CH$_5^+$ (H$_2$)$_6$, the sixth H$_2$ molecule can bind to the 3c2e bond of the CH$_5^+$ core in the out-of-plane fashion [Fig. 9(I)] after the first solvation shell is complete at $n=5$. Other structures involving the isomers of CH$_5^+$ (H$_2$)$_4$ and CH$_5^+$ (H$_2$)$_5$ are also possible for CH$_5^+$ (H$_2$)$_6$.

V. SUMMARY

The infrared spectra for the molecular hydrogen solvated carbonium ions, CH$_5^+$ (H$_2$)$_n$ ($n=1-6$) have been presented. Spectroscopic evidence has been presented in support of the scrambling of CH$_5^+$ through the large amplitude motions such as the CH$_3$ internal rotation and the in-plane wagging motion. More importantly, the scrambling motions of CH$_5^+$ cores were slowed down by attaching the solvent H$_2$ molecules to the core ion. The complete freezing of the scram-
bling motions was found when the first three H$_2$ molecules were bound to the CH$_5^+$ core. A good agreement between the experimental results and the theoretical predictions was found in the dynamics of CH$_5^+$.

A clear extension of this work would be to improve the resolution of the IR spectra for the H–H stretching modes of CH$_5^+$ (H$_2$) and CH$_5^+$ (H$_2$)$_2$, which would provide additional information on the structures and the rotational and tunneling dynamics of both the CH$_5^+$ cores and the entire clusters. High order overtone transitions of free CH$_5^+$ can be measured by improving the schemes for vibrational excitation and probe with the use of high power IR and CO$_2$ lasers. In addition, significant efforts for the generation of internally cold CH$_5^+$ ions should be made, so that the IR spectra are not smeared out due to spectral congestion by the scrambling of CH$_5^+$.

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