Infrared Spectroscopy of CH_5^+ Cations in Helium Nanodroplets

Amandeep Singh[1], *Sofia H. Allison*[1,2], *Andrew Abishek A. Azhagesan*[3], *Deepak Verma*[1,#], *Andrey F. Vilesov*[1,4]*

[1]Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

[2]Department of Chemistry, Mount St. Mary's University, Emmitsburg, Maryland, USA, 21727

[3]Department of Computer Science, University of Southern California, Los Angeles, California 90089, United States

[4]Department of Physics, University of Southern California, Los Angeles, California 90089, United States

*Author to whom correspondence should be addressed.

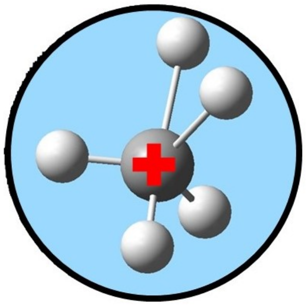
Electronic address: vilesov@usc.edu.

#Present address: Intel Corporation, Ronler Acres, 2501 NE Century Blvd, Hillsboro, OR 97124, USA.

Abstract

The methanium CH_5^+ is a prototypical fluxional ion whose infrared spectra remain unassigned. Here we report on the infrared spectra of CH_5^+ cations and its deuterated isotopomer, CH_4D^+ in helium droplets at a low temperature of 0.38 K. The ions were produced upon protonation of CH_4 molecules, a technique that was developed in this work. The spectra of CH_5^+ around 3000 cm^{-1} show two strong and broad infrared bands and a weak shoulder reflecting its highly fluxional nature. The spectrum of CH_4D^+ shows a much sharper infrared band indicating a partial quenching of the exchange of H/D atoms. This work also reports on the infrared spectrum of the methane dimer radical cations $(CH_4)_2^+$.

TOC Graphic



The structure of the methanium ion remains one of the most fascinating puzzles in physical chemistry. The CH_5^+ cation is a primitive model for the penta-coordinated carbon, fluxional molecules, and 3 center 2 electron (3c2e) bonds. [1] The CH_5^+ ion has 120 equivalent minima on its potential energy surface related to the permutation of hydrogen atoms.[2] Quantum chemical calculations show that the energy minima structure has the H_2 moiety presiding over a tripod made of the CH_3^+ ion in eclipsed C_s (e-C_s) configuration.[2-10] The e-C_s state could pass to an equivalent state through a saddle point of either C_{2v} geometry or staggered C_s (s-C_s) geometry, which have potential energies of 341 cm^{-1} and 29 cm^{-1}, respectively.[4] Small activation barriers between equivalent structures facilitate quantum mechanical tunneling and scrambling of hydrogen atoms. Therefore CH_5^+ ions have attracted the attention of spectroscopists as well as of the theoretical chemists. [2-4, 7, 11-26]

Early spectroscopic studies of the CH_5^+ were performed on complexes with hydrogen molecules and other adducts. [15-17] High-resolution infrared spectra of the bare CH_5^+ in the C-H stretching range have previously been demonstrated in electric discharge [19] and ions traps.[24] Even at cryogenic temperatures, the spectra have numerous rovibrational-tunneling lines that until date remain unassigned. [19, 24] Attaining low-resolution spectra at a low temperature may help identify the vibrational structure of the bands providing a reference point for the assignment of the high-resolution spectra. A spectrum obtained with the help of a free electron laser using the laser-induced reaction technique at a temperature of ~100 K has a single broad infrared band (($\delta\upsilon$~200 cm^{-1}) around 3000 cm^{-1} beside several other weaker broad bands at the lower frequency region. [20] The spectra of the isotopologues show no dramatic narrowing or simplification with respect to the CH_5^+, which is likely related to the high temperature of the ions of ~110 K. [27] The spectra of the CH_5^+ and deuterated isotopologues were also computed from the Fourier transform of the classical autocorrelation function of the total dipole momentum at temperatures of 300 K and 110 K,[28] and 50 K.[3] Recently, the spectrum of CH_5^+ was obtained in small He clusters containing less than about 100 He atoms at low temperature of the order of ~5K. [29] However, the spectrum may still sustain some broadening due to the cluster size distribution and higher temperature of helium clusters compared to larger helium droplets. [30]

Here, we obtained CH_5^+ ions in helium nanodroplets containing ~10^4 He atoms and having temperature of 0.4 K. CH_5^+ ions were produced via protonation of CH_4 molecules in the droplets, a technique that is introduced in this work. The ions were studied by infrared spectroscopy in the C-H stretching range. The spectrum of CH_5^+ has two partially resolved bands centered at 2935 and 2985 cm^{-1}. The spectrum deviates significantly from the predictions of the calculations. Replacing some or all the hydrogen atoms of the CH_5^+ with deuterium atoms is expected to influence the exchange of the hydrogen atoms. Here we report the spectra of the CH_4D^+ in helium droplets which shows a factor of ~10 narrower bandwidth consistent with the quenching of the exchange of atoms in the ion.

A detailed description of the experimental setup is provided elsewhere.[31] Helium nanodroplets are produced by a pulsed expansion of helium gas at 23 K at a stagnation pressure of 23 bar through a 1 mm diameter nozzle. The helium droplet beam is formed by a 2 mm wide skimmer placed about 10 cm downstream from the nozzle and enters a 44 cm long pickup chamber filled with either methane, hydrogen, or deuterium. The doped droplets are ionized by electron impact and pass through a 22 cm long RF octupole collision cell filled with room-temperature helium gas at a nominal pressure of 2×10^{-5} mbar. Collisions with He atoms reduce the droplet size which increases the laser-induced signal.[32] Further downstream, the droplets containing molecular ions enter the ion region of the quadrupole mass spectrometer (QMS) where they are irradiated by the focused beam of the pulsed infrared laser. Upon excitation, the vibrational energy is transferred to the droplet leading to its complete evaporation and release of the free ions. The free ions are mass-selected by the QMS and detected by a Channeltron electron multiplier. The signals from the multiplier are then recorded by a boxcar integrator with a gate of 5 μs.

The experiments employed a mid-IR OPO/OPA laser system (LaserVision) with a nominal line width of 1 cm^{-1} and pulse energy of 8-10 mJ. The laser pulses are 7 ns long with a repetition rate of 20 Hz. The absolute frequency is calibrated by measuring a photoacoustic spectrum of the ν_3 band of methane.

Before the laser spectroscopic experiments, mass spectra of the droplets doped with methane molecules were recorded upon ionization of the droplets by the electron impact in the ion region of the QMS, i.e., standard QMS operation, which are shown in Fig. SI 1 in Supporting Information (SI). The mass spectra show that free CH_5^+ ions belong to the main products of the ionization of the droplets doped with methane dimers. Our previous measurements indicated that such ions are also found embedded in the droplets. [33-37] Therefore, we started with the study of the infrared spectra of the CH_5^+ originated from the dissociative ionization of the methane dimers in helium droplets. The results of corresponding measurements are summarized in Section S2 of the SI, which contains the spectra recorded at mass channels m/z=17 and 32 in Fig. SI 2 as well as the pickup pressure dependence of the signal in Fig. SI 3 and the laser-induced mass spectrum in Fig. SI 4. The results show that the spectrum of CH_5^+ is contaminated by the signal originating from the laser-induced dissociation of the $(CH_4)_2^+$ ionic clusters whose absorption contributes to both mass channels m/z=17 and m/z=32. This indicates that $(CH_4)_2^+$ ions consist of relatively weakly bound CH_5^+ and CH_3 units. Although the observation of the CH_5^+-CH_3 radical cations is interesting by itself, the fragmentation complicates the assignment of the CH_5^+ bands.

Hence, we developed a different method for producing CH_5^+ based on the protonation of the methane molecules in helium nanodroplets. Accordingly, the droplets were first doped with H_2 (or D_2 to produce CH_4D^+) followed by electron impact ionization. The charge transfer reaction of He^+ ions and H_2 in the gas phase at low temperatures mainly produces H^+ ions with a small yield of H_2^+ ions. [38] The ionization of the hydrogen clusters will also produce H_3^+ and H_5^+ ions. Nonetheless, at the low hydrogen pickup pressure, the droplets are mostly doped with single hydrogen molecules and protons are expected to be the primary ionization products. Methane gas was added to the octupole cell at a small pressure in addition to the helium gas. The droplets containing H^+ (D^+) ions capture methane molecules leading to the formation of the embedded CH_5^+ (CH_4D^+) ions by addition reaction. The CH_5^+ formation follows the first-order kinetics for the CH_4 pressure as well as the H_2 pressure. Therefore, at sufficiently small pressure of methane, the formation of the $(CH_4)_2^+$ and CH_5^+-CH_4 ions, which follow the second-order kinetics with respect to CH_4, could be minimized.

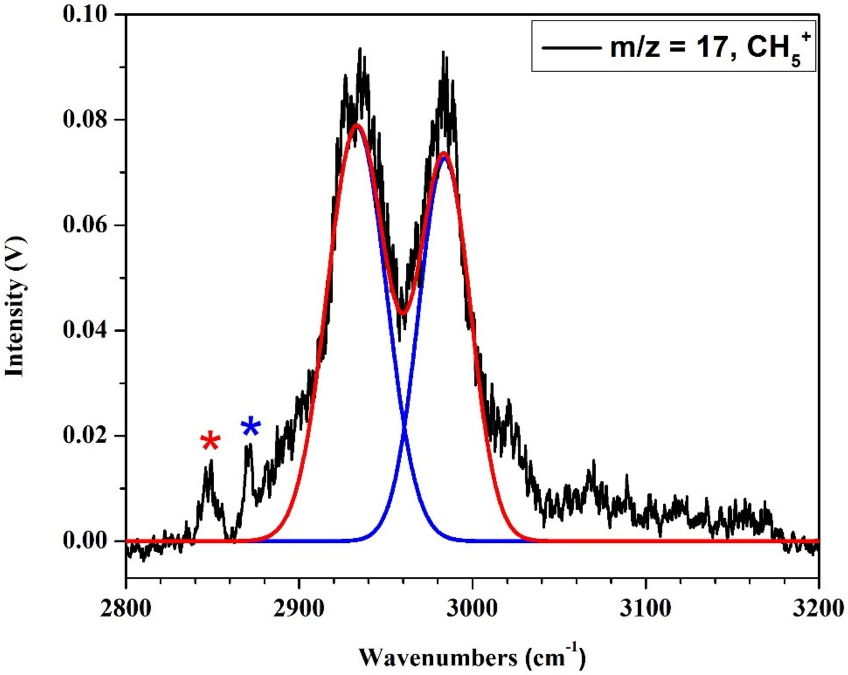


Figure 1: The infrared spectrum recorded at m/z = 17 for CH_5^+ cations (black trace). The H_2 gas is filled in the pickup chamber at 1.2×10^{-7} mbar. CH_4 gas was added in the octupole ion guide at 1.5×10^{-7} mbar in addition to He gas. The red curve is a fit by two Gaussian shapes. The blue traces show the individual Gaussian functions used in the fit. The daughter ions band originating from the fragmentation of $(CH_4)_2^+$ is marked by a red asterisk and the band coming from CH_5^+-CH_4 is marked by a blue asterisk.

Figure 1 shows the infrared spectrum recorded at m/z = 17 for CH_5^+. The spectrum shows two bands centered at 2935 cm^{-1} and 2985 cm^{-1}, weak narrow bands at 2848 cm^{-1} and 2871 cm^{-1}, and a broad shoulder extending in the range of 3050-3180 cm^{-1}. The experimental spectrum is fitted by two Gaussian functions centered at 2933 cm^{-1} and 2984 cm^{-1} having a width (FWHM) of ~40 cm^{-1}. The narrower bands marked by asterisks are due to CH_5^+-CH_3 and CH_5^+-CH_4 clusters which fragment upon laser excitation and yield CH_5^+ ions. In comparison to the spectrum obtained upon ionization of the methane dimers in Fig. SI 2, the spectrum in Fig. 1 contains similar main CH_5^+ bands but the intensity of the spurious bands due to $(CH_4)_2^+$ and CH_5^+-CH_4 is negligible. To elucidate the CH_5^+ formation mechanism, we measured the intensity of the CH_5^+ signal versus the pickup pressure of H_2 and CH_4.

Figures 2 (a) and (b) show the dependence of the intensity of the signal with the laser parked at 2988 cm^{-1} vs the nominal pickup pressure of H_2 and CH_4, respectively. The results are fitted with the Poisson equation for the pickup of *k* molecules: [32, 39]

$$I_k(P) = \frac{C * e^{(-\frac{P}{A})}}{(k!)} * \left(\frac{P}{A}\right)^k \qquad (1)$$

Where *P* is the pickup pressure and '*A*' and '*C*' are fitting parameters. The constant '*A*' gives the pickup pressure required for the doping of the droplets with on average a single molecule. The fit with *k*=1 shows good agreement with the experimental results consistent with the production of H^+ ions upon ionization of the droplets containing single hydrogen molecules.

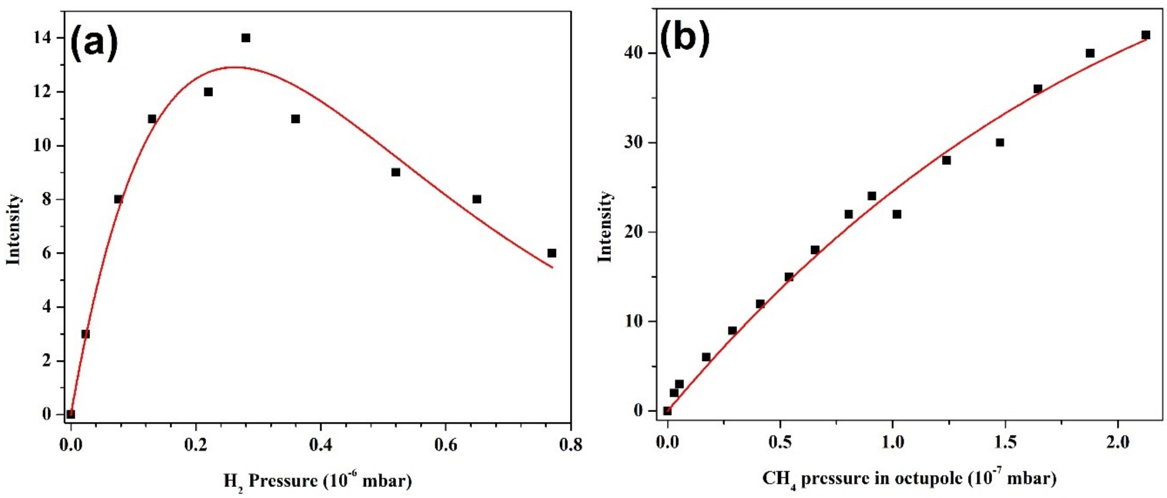


Figure 2: The dependence of signal recorded at m/z = 17 with the laser parked at 2988 cm^{-1} *on the pressure of* H_2 *in the pickup chamber (a) and* CH_4 *in the octupole collision cell (b). The octupole cell was additionally filled with He up to a total nominal pressure of* 2.5×10^{-5} *mbar. In (a) the pickup pressure of* CH_4 *was* 4.5×10^{-7} *mbar. In (b) the* H_2 *pressure was* 3.5×10^{-7} *mbar. Red traces are the fits with eq. (1) with k = 1.*

Similarly, Fig. 2 (b) shows that at lower CH_4 pressure, the intensity rises linearly, which is consistent with the production of CH_5^+ by protonation. In addition to protons, the electron impact also produces droplets containing He^+ ions and He* metastable species which cause the ionization of the methane molecules and clusters. Therefore, at higher CH_4 pressure the yield of $(CH_4)_2^+$ and CH_5^+-CH_4 clusters becomes noticeable, which produce CH_5^+ ions upon laser-induced fragmentation. Thus, the spectrum of CH_5^+ in Fig. 1 was obtained at the smallest practical pressure of methane.

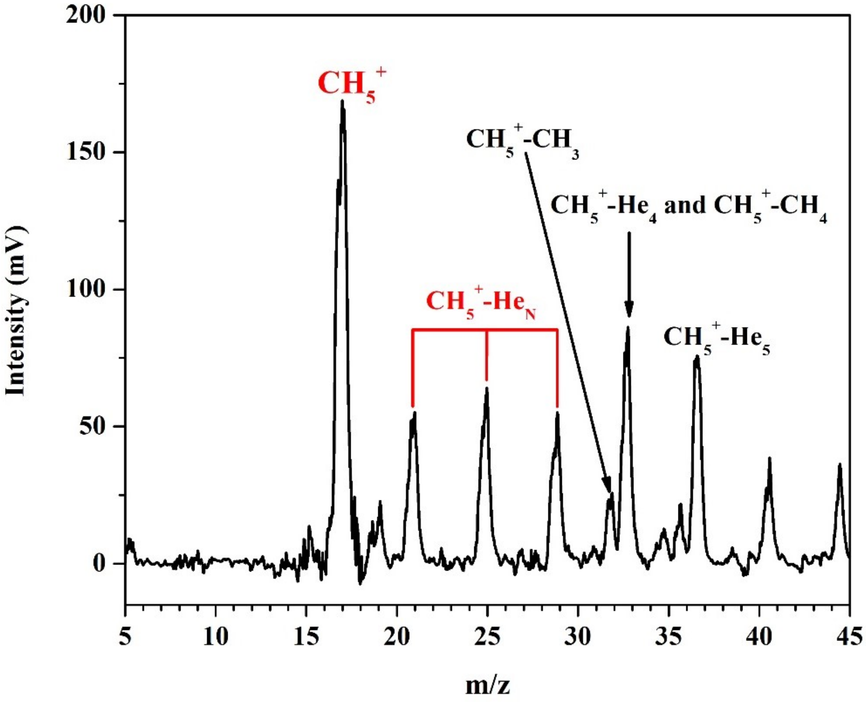


Figure 3: The mass spectrum recorded by parking the laser frequency at 2936.9 cm^{-1}. The H_2 pressure in the pickup cell is kept constant at 1.2×10^{-7} mbar and the pressure of the CH_4 in the octupole collision cell is 1.5×10^{-7} mbar. The total nominal pressure in the octupole cell is maintained at 2.7×10^{-5} mbar.

Figure 3 shows the mass spectrum recorded with the laser parked at 2936.9 cm^{-1}. It shows a strong peak at m/z = 17 due to CH_5^+ cations, followed by a progression of peaks due to CH_5^+-He_N complexes. The mass spectrum has a peak at m/z = 33 which corresponds to protonated methane dimer cation $CH_5^+CH_4$ and CH_5^+-He_4 complexes. A small peak at m/z = 19 corresponds to the CH_5^+-H_2 complex. The comparison of the mass spectra in Fig. 3 and Fig. SI 4 shows that the here-introduced protonation technique enables a higher yield of CH_5^+ feature in the spectrum in comparison to the $(CH_4)_2^+$ and CH_5^+-CH_4 bands by about a factor of 10.

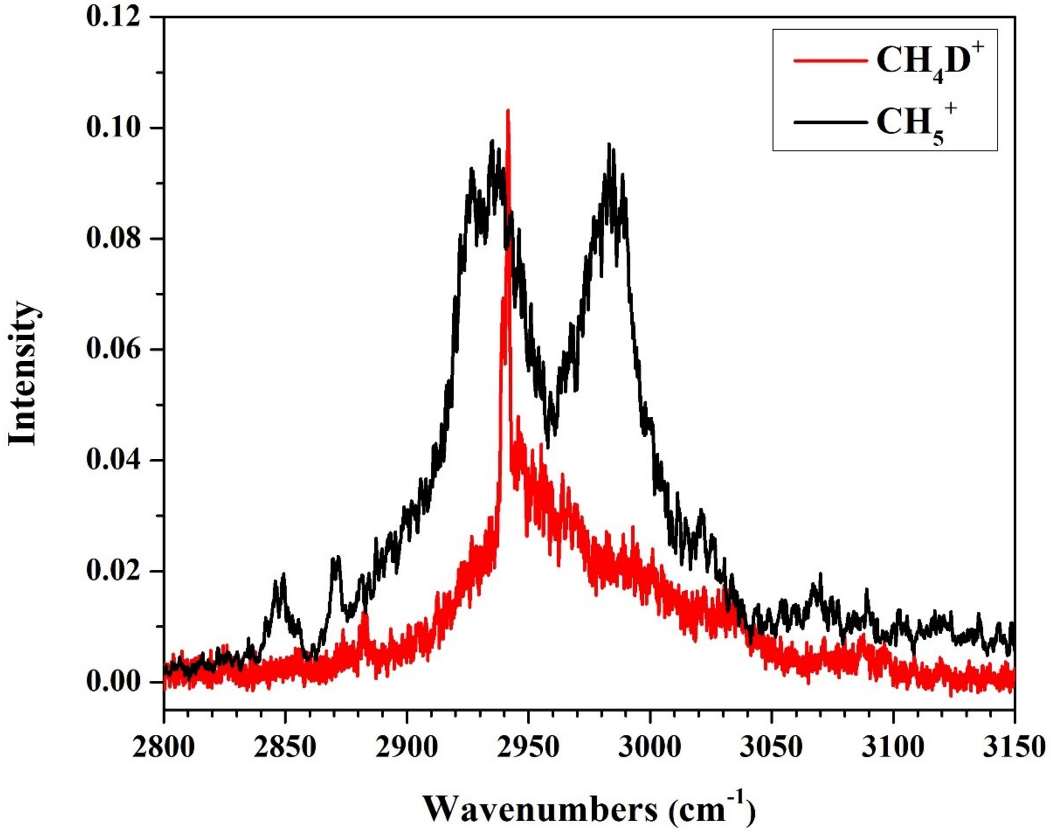


Figure 4: The infrared spectrum measured at m/z = 18 for CH_4D^+ cations (red trace). The D_2 gas is filled in the pickup chamber at 1.5×10^{-7} mbar of nominal pressure. CH_4 gas was added in the octupole ion guide at 1.0×10^{-7} mbar pressures in addition to He gas. The black trace shows the spectrum of CH_5^+ ions (from Figure 1).

Figure 4 shows the infrared spectrum of CH_4D^+ cations measured in the CH stretching range at m/z = 18 mass channel. The spectrum was obtained similarly to that for CH_5^+ in Fig. 1, but instead of H_2, the droplets were first doped with D_2 molecules. The spectrum of the CH_4D^+ ions shows a sharp band at 2942 cm^{-1} ($\delta\nu$ = 2 cm^{-1}) which is superimposed on a broader band covering the range of 2900- 3050 cm^{-1}.

Infrared spectra of CH_5^+ have been investigated by several groups over the past three decades. [15-17, 19, 20] The high-resolution spectra contained numerous rovibrational lines which remain unassigned. [19, 24] Here we limit our discussion to the low-resolution spectra which could be directly compared with the spectra obtained in this work. In early works, Boo et al. obtained spectra of CH_5^+ ions tagged with H_2 molecules.[15] The spectrum shows a broad band centered at 2965 cm^{-1}, which was further fitted with three Gaussians centered at 2907 ($\delta\upsilon \sim 200$ cm^{-1}), 2965 ($\delta\upsilon \sim 80$ cm^{-1}), and 3070 cm^{-1} ($\delta\upsilon \sim 60$cm^{-1}). The bands were assigned to the excitation of the vibrational modes of the CH_3^+ moiety. The bands become about a factor of two narrower in complexes with a larger number of H_2 molecules, or in clusters with Ar, N_2, and CH_4. The effect is assigned to some quenching of the tunneling motion in CH_5^+. [15, 16, 17] The spectrum of CH_5^+ obtained by Laser Induced Reaction (LIR) at ~100 K has a strong broad band ($\delta\upsilon \sim 200$ cm^{-1}) centered at ~2980 cm^{-1}. [20] The spectrum of CH_5^+ solvated in small helium clusters appears to have a broad band centered at 2966 cm^{-1} ($\delta\nu \sim 100$ cm^{-1}) and a weaker wing extending up to ~3200 cm^{-1}. [29] The spectrum of the CH_5^+ ions in large helium droplets in Fig. 1 shows two partially resolved bands centered at ~2935 cm^{-1} and 2985 cm^{-1}. The band of CH_5^+ obtained in this work is narrower than in the previous study in small He clusters,[29] which likely relates to lower temperature in He droplets and smaller effect of the droplet size distribution. Nevertheless, the bands in Fig. 1 have FWHM ~40 cm^{-1} and are about a factor of ten broader compared to the bands of CH_5^+-CH_3 in Fig. SI 2 of SI and those in the spectra of other carbo-cations in helium droplets. [33, 34, 40] The large width of the CH_5^+ bands was assigned to the fluxional character of the ions, whose spectra have some extended rotation-tunneling structure that remains unresolved in this work. [3, 4, 13, 18, 20] The spectrum of CH_5^+ in Fig. 1 also has a weak wing in the region of 3050-3180 cm^{-1}.

The CH_5^+ bands in the range of 2900-3000 cm^{-1} observed in previous works[20, 29] and in this work are in broad agreement with the high density of the lines of CH_5^+ in this spectral range obtained in the high-resolution study in the discharge.[19] The most recent study in the cold ion trap at 4 K using a laser-induced inhibition of complex growth (LIICG) shows that the strongest lines gather around 3030 cm^{-1} to 3070 cm^{-1}. [24] The authors concluded that this is one of the CH-stretching band centers. However, this frequency is well outside the range of maximum intensity obtained in different low-resolution studies, [20, 29] including the current one at 0.4 K. The origin of this discrepancy is yet unclear.

Quantum chemical calculations show that the CH_5^+ structure corresponding to the minimum potential energy has the H_2 moiety presiding over a tripod made of the CH_3^+ ion in eclipsed C_s (e-C_s) configuration.[2-10 13-15, 22, 41, 42] The e-C_s state could pass to an equivalent state through a saddle point of either staggered C_s (s-C_s) geometry or C_{2v} geometry which correspond to the internal rotation of the H_2 unit relative to the CH_3^+ unit and the exchange of hydrogen atoms between the H_2 and CH_3 moieties, respectively. Several works reported the calculated vibrational spectra of the CH_5^+ in the global minimum e-C_s geometry. [14, 28, 6, 22] Recent CCSD(T)/cc-pVTZ calculations give the scaled (0.9748) frequencies of the C-H stretches at 3218, 3120 and 2988 cm^{-1} with comparable infrared intensities. [22] The bands correspond to an antisymmetric (A'') and a symmetric (A') vibration of the two out-of-plane H atoms of the CH_3^+ moiety and the symmetric breath of C-H bonds (A'), respectively. The vibration frequencies were also calculated for the C_{2v} and s-C_s saddle point structures. [6, 14, 15] In Ref. [4] the CH_5^+ spectrum was approximated by the sum of the spectra at each stationary point weighted by the corresponding probability from DMC calculations. [6, 8-10] The calculated spectrum has three prominent peaks with scaled frequencies of

~3020, ~2950, and ~2870 cm^{-1}, and several other weaker peaks in the C-H stretching region which is at variance with the spectrum in Fig. 1.

The CH_5^+ spectrum was also computed from the Fourier transform of the classical autocorrelation function of the total dipole momentum with quantum corrections at temperatures of 300 K and 110 K,[28] and 50 K.[3] Calculated spectra at 300 K were found to be in good agreement with the measured low-resolution spectrum showing a broad band in the C-H stretching range. [20]

However, at T=50 K and 110 K, the hydrogen scrambling is frozen and the internal rotation of the H_2 moiety is partially frozen, which is an artifact of the classical molecular dynamic's calculations. The calculated spectra[28] have three high-frequency bands due to CH_3^+ moiety at 3309, 3218, and 3080 cm^{-1} having comparable intensities, similar to that found in the quantum chemical calculations for the e-C_s potential minimum structure.[3] This is in disagreement with the results in this work in Fig. 1 which shows only two prominent bands separated by 50 cm^{-1}.

The infrared spectra of the deuterated isotopologues of CH_5^+ may provide insights into the quenching of the tunneling exchange. In the minimum energy structure of CH_4D^+ the deuterium atom resides in the tripod unit - CH_2D^+. [2, 21, 27, 43] The calculated harmonic frequencies of the asymmetric and symmetric stretching modes of the CH_2 unit in the tripod were found to be at 3178 cm^{-1} and 3018 cm^{-1}, respectively. The CD stretching frequency was calculated at 2299 cm^{-1}, [43] and is likely out of the spectral range of the current laser system. Based on the results of the calculations, the spectrum of the CH_4D^+ should have two C-H stretching bands around 3000 cm^{-1}. However, the spectrum in Fig. 4 shows one sharp band at 2942 cm^{-1} besides a broad spectral feature extending from 2920 to 3040 cm^{-1}. However, the vibrational frequencies calculated for the minimum energy configuration may not reflect the true nature of the CH_4D^+. The Diffusion Monte Carlo calculations show that the CH_4D^+ remains fluxional. [10] The probabilities of finding the deuterium in all three sites of the tripod are comparable, indicating that the internal rotation of the H_2 unit relative to the CH_3^+ unit remains active. The probability of finding the deuterium with the dimer moiety was found to be about 10%, indicating the exchange of the deuterium between the dimer and the tripod locations. [10] The sharpening of the spectrum agrees with the partial quenching of the exchange of H atoms in CH_4D^+ as compared with CH_5^+. On the other hand, the broad band agrees with unresolved tunneling splitting of the transitions akin that in the CH_5^+ ions. The assignment of the spectrum calls for a better molecular spectroscopic picture of the vibrational-rotational transitions in the CH_5^+ and its isotopologues which considers the tunneling motion.

In this work, CH_5^+ and CH_4D^+ ions are produced in superfluid helium droplets at 0.4 K and studied by laser infrared spectroscopy in the range of C-H stretching vibrations. We demonstrated that the ions could be produced via protonation of CH_4 molecules in He droplets, a technique that enables the reduction of the intensity of spectral bands resulting from the fragmentation of larger ions. The infrared spectra of CH_5^+ show two partially resolved bands ($\delta\nu \sim 50$ cm^{-1}) separated by $\delta\nu \sim 50$ cm^{-1}. The spectrum of CH_4D^+ shows a sharp band ($\delta\nu \sim 2$ cm^{-1}) along with a broader band in the same range as observed for CH_5^+. This shows that the replacement of a hydrogen atom by deuterium partially quenches the exchange, leading to the narrowing of the spectrum.

Previous calculations of the spectra of the CH_5^+ and CH_4D^+ [2, 10, 21, 27, 43, 44] in the C-H stretching range yielded a much larger number of bands of comparable intensity. It is not immediately clear that the spectra calculated as the weighted average of the spectra for the stationary point structures[4] or obtained from the classical molecular dynamics calculations[3] is a fair approximation for the fluxional CH_5^+ (CH_4D^+) where atoms partake in quantum mechanical tunneling motion. [2, 10, 21, 27, 43, 44]

The discrepancy between the measured and calculated spectra calls for more work toward the understanding of the spectra involving vibrational- rotational-tunneling transitions in the CH_5^+ and its isotopologues. Future work could be extended toward the measurement of the infrared spectra of the rest of the isotopically substituted cations such as $CH_3D_2^+$, $CH_2D_3^+$, CHD_4^+, and CD_5^+, as well as towards the broader spectral range.

Supporting Information:

SI 1: Mass spectrum of methane-doped He droplets upon electron impact.

SI 2: Comparison of the infrared spectra of CH_5^+ and $(CH_4)_2^+$.

SI 3: The dependence of laser-induced intensity recorded at m/z=17 on methane pickup pressure at ν =2936.90 cm^{-1}.

SI 4: Laser-induced mass spectrum measured at ν=2936.90 cm^{-1}.

Supporting Information section also contains the following references: [33], [34] and [40].

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