Isolation and Spectroscopy of C_2H^+ Ions in Helium Droplets

Alexandra J. Feinberg[1,&], Swetha Erukala[1,#], Cheol Joo Moon[1,2], Amandeep Singh[1], Myong Yong Choi[3] and Andrey F. Vilesov[1,4,*]

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

[2] Research Institute for Green Energy Convergence Technology, Gyeongsang National University, Jinju 52828, Republic of Korea

[3] Core-Facility Center for Photochemistry & Nanomaterials, Department of Chemistry (BK21 FOUR), Research Institute of Natural Sciences, Gyeongsang National University, Jinju, Republic of Korea

[4] Department of Physics and Astronomy, University of Southern California, Los Angeles, California 90089, USA

[&] Present address: Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, USA

[#] Present address: ASML, 17075 Thornmint rd, San Diego, 92127

[*]Author to whom correspondence should be addressed.

Electronic address: vilesov@usc.edu.

Abstract

Ethynylium (C_2H^+) may be an important intermediate in astrochemistry, however due to its high reactivity, C_2H^+ remains poorly studied by laboratory techniques. Immersion of single acetylene molecules in the droplets followed by electron impact ionization effectively generates and isolates C_2H^+ cations in an inert cryogenic environment, enabling spectroscopic measurements. We find that in the C-H stretching range, the C_2H^+ spectrum appears as a triplet with splitting of 33.6 cm^{-1} and 37.5 cm^{-1}. The splitting is temporarily assigned to the product of interactions between the C-H stretching mode and overtones of the bending mode.

1. Introduction

Ethynyl radicals, C_2H, exist in the environment of carbon rich stars[1] and in the atmosphere of Saturn's largest moon,Titan,[2] where it plays an important role as an intermediate for the formation of larger hydrocarbon molecules and possibly also polyaromatic compounds.[3] Reactions of ethynyl radicals with unsaturated hydrocarbons have been studied extensively.[4, 5] However, much less is known about reactions with ethynylium C_2H^+ cations, which may play an important role in astrochemistry. Quantum chemical calculations predict that C_2H^+ ions exist in a linear $^3\Pi$ ground state.[6, 7 8, 9, 10, 11] An experiment on translational energy spectroscopy of C_2H^+ supported the predicted $^3\Pi$ ground state.[12] Additionally, Coulomb explosion imaging of C_2H^+ has provided evidence for a low frequency bending vibration.[13] Ethynylium was identified in the Ar matrix experiments by its C-C vibration band at 1820 cm^{-1}.[6] On the other hand, recent photoelectron spectroscopic study of the C_2H radicals yields the C-C vibrational frequency to be at 1620 cm^{-1}.[7] It was also noticed that the infrared spectra of the C_2H^+ should be influenced by the Renner-Teller splitting of its linear $^3\Pi$ ground state upon excitation of the bending vibration.

It is known that C_2H^+ ions are produced upon electron impact of acetylene molecules.[14] Several groups studied the infrared spectra of argon-tagged carbocations that were generated in an acetylene discharge.[15, 16] However, no results for C_2H^+ have been reported. It is likely that in previous experiments, C_2H^+ ions were produced in the discharge, but rapidly reacted with acetylene to form larger carbocations. Recently, we found that ionizing acetylene dimers in helium nanodroplets (HNDs) leads to the formation of $C_4H_2^+$, $C_4H_3^+$ and $C_4H_4^+$ ions.[17] Isolating single ions in ultracold (0.4 K) HNDs is a promising matrix-assisted spectroscopic technique that may intrinsically help to eliminate any ultrafast secondary reactions. In this Letter, we report our results on HND matrix-assisted infrared (IR) spectroscopy of C_2H^+ ions, including the first observation of their C-H stretching band.

2. Experimental

The experimental apparatus used for production and spectroscopy of carbocations in HNDs has been described in our previous publications.[18,19] Briefly, HNDs are produced upon the expansion of helium gas into vacuum through a 0.5 mm diameter pulsed nozzle (General Valve series 99) attached to a Sumitomo RDK 408 cryostat. For this experiment, we employed a stagnation pressure of P_0 = 20 bar and a nozzle temperature of T_0 = 23 K.[20] At these conditions, our HNDs have average size of ~7000 He atoms.[19] Upon collimation of the HND beam by a 2 mm diameter skimmer, the droplets enter a pickup chamber where they collide with and capture acetylene molecules. Further downstream, the doped droplets pass through a differential pumping stage and enter the detection chamber that hosts a quadrupole mass spectrometer (QMS) (Extrel MAX 500) equipped with an electron beam ionizer. The setup has an additional external ionizer placed upstream from the ion region of the QMS. There are two modes of operation, namely the *probe* mode (standard mode) and *external* mode. In *probe* mode of operation, the doped droplets are ionized by the electron beam ionizer of the QMS to record their mass spectra. In *external* mode operation, the droplets are first ionized by the external ionizer such that they can be irradiated with a pulsed IR laser beam in the ion region of the QMS before being mass selected by the QMS. [18,19] The time of flight between the ionization and laser excitation amounts to about 0.5 ms; thus, we assume the cations relax to the ground state before being excited by laser. The infrared spectra were measured using an unseeded pulsed optical parametric oscillator-amplifier (LaserVision, spectral resolution: ~ 1 cm^{-1}, pulse duration ~ 7 ns, pulse energy ~ 5 - 8 mJ, repetition rate 20 Hz). The absolute frequency of the laser is calibrated using the photo-acoustic spectrum of ν_3 band of methane molecules.

3. Results

Like our previous works,[18, 21] prior to IR spectroscopic measurements, mass spectra of the acetylene-doped HNDs are recorded in the *probe* mode. Ionization of acetylene yields strong peaks at m/z = 25 and m/z = 26 from C_2H^+ and $C_2H_2^+$ ions as well as some peaks due to larger carbocations which are discussed elsewhere.[17] The free $C_2H_2^+$ intensity was found to be ~10x larger than that of the C_2H^+ ions. Figure 1 shows the dependence of the C_2H^+ (m/z = 25) peak intensity vs. the nominal acetylene pressure, *P*, in the pickup chamber. The absolute pressure was obtained by dividing the reading by the sensitivity coefficient for acetylene of 2.0. The data points were fitted by Poisson distribution equation:[22]

$$I_k(P) = C \cdot \frac{(P/A)^k}{k!} e^{-P/A} \qquad (1)$$

for the capture of *k*- acetylene molecules, with *A* and *C* fitting parameters. It is seen that a fit with $k = 1$ and an $A = 2.8\times10^{-6}$ mbar agrees with our collected data points at small pickup pressures. The *A* values in eq. (1) correspond to the pickup pressure at which the droplets are doped with (on average) single acetylene molecules. It follows that free C_2H^+ cations are predominantly produced upon the ionization of HNDs containing single acetylene molecules. At high pickup pressures of $P > 10^{-5}$ mbar, the C_2H^+ cation signal intensity does not approach zero as predicted by eq. (1), but remains finite and independent of *P*. This indicates that the ionization of dimers and larger clusters contributes to the production of free C_2H^+ cations.

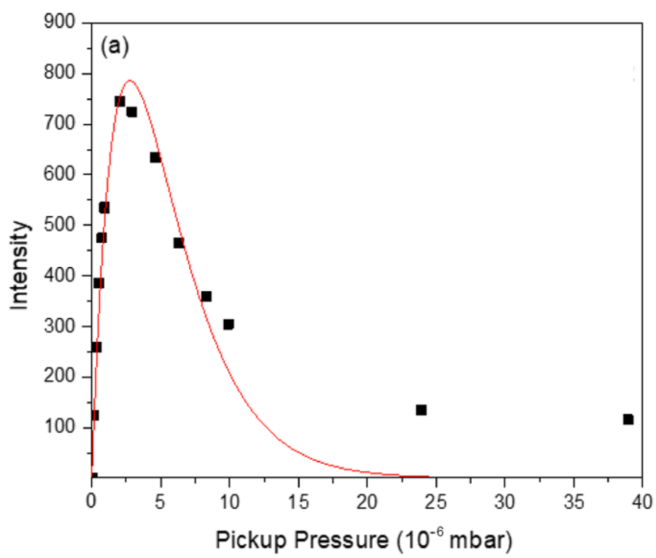

Figure 1. The intensity of C_2H^+ cations (m/z = 25, black squares) plotted against the nominal pickup pressure of acetylene. The data points are fitted with equation (1) at $k = 1$ (red trace). The fitting curve provides $A = 2.8\times10^{-6}$ mbar.

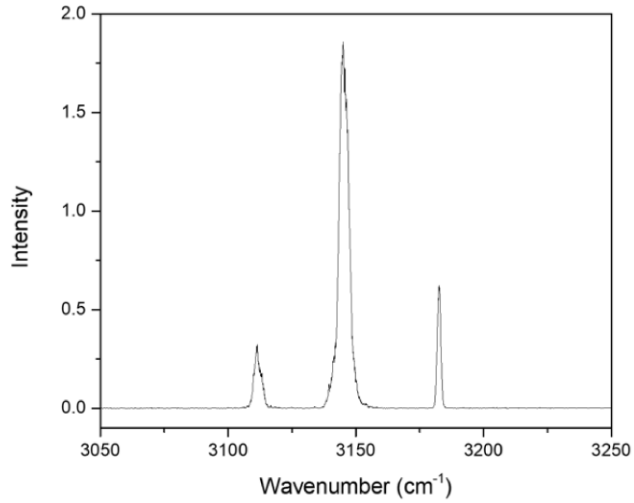

Figure 2. Infrared spectrum of C_2H^+ ions recorded at m/z = 25.

In spectroscopic experiments the acetylene-doped HNDs are ionized by the *external* ionizer and subsequently irradiated with a pulsed IR laser beam. Because there are many orders of magnitude more helium atoms in each droplet compared to number of acetylene molecules, electron impact initially produces He^+ ions which undergo charge transfer to the embedded acetylene molecules. Subsequently, dissociative ionization and formation of C_2H^+ and H products occurs within the HND. The ion-doped droplets continue traversing towards the QMS, whereas light ionic species are rejected by a high pass filter. The ion-doped droplets are irradiated by a focused infrared laser beam when they pass through the ion region of the QMS. Absorption of several IR quanta leads to the ejection of free cations, which are extracted, mass selected by the QMS, and detected by an electron multiplier.[19] The signal from the electron multiplier is amplified and measured by a SR250 boxcar integrator. Figure 2 shows the laser excitation spectrum of C_2H^+ ions recorded at m/z=25. The spectrum has three prominent peaks at 3111.4, 3145.0 and 3182.5 cm^{-1}. The C_2H^+ bands at 3111.4, 3145.3 and 3182.5 cm^{-1} have different width (FWHM) of 4.0, 3.4 and 1.5 cm^{-1}, respectively. In a broader scan at m/z = 25, no other spectral features were observed between 2700 to 3300 cm^{-1}.

Figure 3 shows the mass spectrometric identification of the spectral peaks found in Fig. 2. These mass spectra were recorded with the laser parked at the maxima of the corresponding peaks.

The peaks at m/z=18 correspond to the water background signal which is present without any laser irradiation. All traces in Fig. 3 show peaks at m/z=25 which correspond to C_2H^+ ions. Traces *a*) and *b*) show sequences of peaks at higher masses with increments of 4 amu, which are assigned to $C_2H^+He_N$ clusters. Trace *b*) has an additional sequence of peaks starting at M = 27 which belong to $C_2H_3^+$ ions. The $C_2H_3^+$ ions have a very strong band at 3144.4 cm^{-1} which was identified in our previous work.[18] It follows that the peaks at 3111.4, 3145.3 and 3182.5 cm^{-1} belong to C_2H^+ ions. The central peak has an overlap with the very strong $C_2H_3^+$ peak. However, does not contribute to the signal on the m/z = 25 channel in Fig. 2. Figure SM 1 in Supplementary Materials shows acetylene pickup pressure versus intensity of C_2H^+ group spectral peaks as measured at different wavenumbers and detection masses (M = 25 or M = 27).

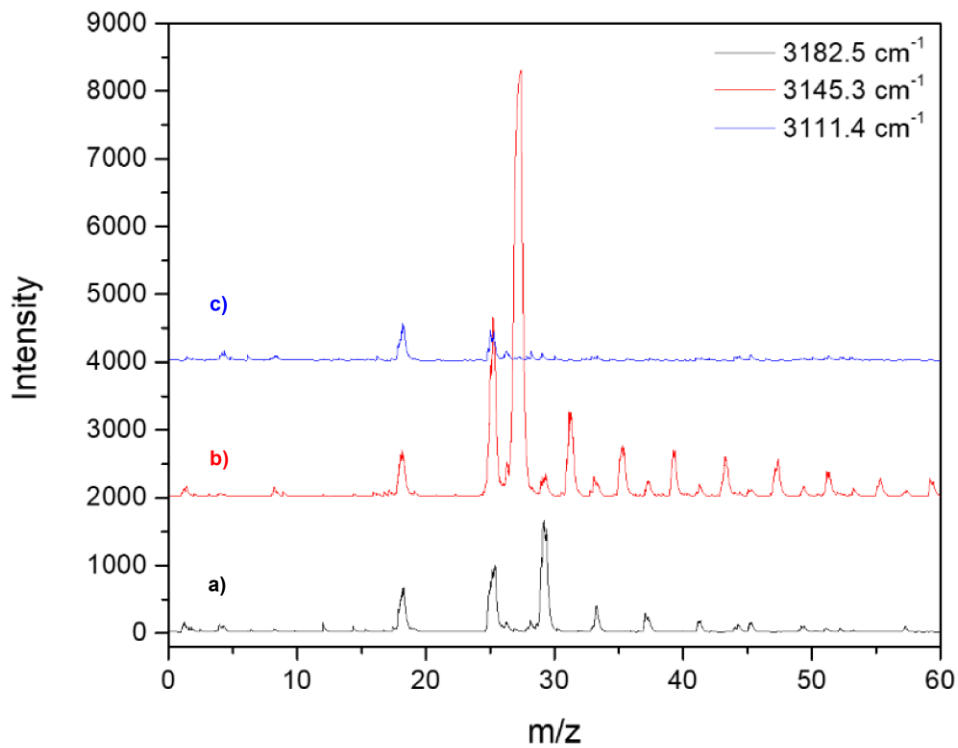

Figure 3. Mass spectra measured with IR irradiation at identified spectral bands of C_2H^+. Acetylene pickup pressure = 3.0×10^{-6} mbar. The peak at m/z = 18 is due to background water. Additionally, the tail of the peaks followed by the main peak at m/z = M+4*n* is due to *n*-helium atoms attached to the ion of mass M.

4. Discussion

Calculations show that ethynylium has a $^3\Pi$ linear ground electronic state and a low lying $^3\Sigma^-$ first excited state with energies of 0.1 eV,[8, 9] 0.9 eV,[10] and ~1 eV.[11] Recent calculations[11] have yielded the Renner–Teller parameter of $\varepsilon = 0.54$ and the value of the spin-orbit constant of $A_{SO} = -18$ cm^{-1} for the $^3\Pi$ ground electronic state. Thus, the lowest energy spin orbit component should be $^3\Pi_2$.

Andrews et al.[6] studied C_2H^+ in solid argon and neon matrices upon co-deposition of acetylene with the products of laser ablation of transition metals. The band at 1820.4 cm^{-1} in solid argon and at 1832.2 cm^{-1} in solid neon were assigned to the C-C stretching mode of C_2H^+ cations. Additionally, a broad feature at 549.5 cm^{-1} was assigned to the excitation of a higher frequency component of the Renner-Teller split C-C-H bending mode. In comparison, recent photoelectron spectroscopic measurements on C_2H radicals reported the frequency of the C-C stretch of C_2H^+ to be at 1620 cm^{-1}.[7] The magnitude of the Renner-Teller constants and the effect of the spin orbit splitting and the Renner-Teller interaction on the energy levels of the bending vibration of C_2H^+ are discussed in Ref. [7].

The spectrum in Fig. 2 shows three peaks with splitting of 33.6 cm^{-1} and 37.5 cm^{-1}. The central peak carries the largest intensity, whereas the high frequency peak has the narrowest width. Spectroscopy of C_2H^+ in He droplets should resemble that of NO molecules, which were previously studied in He droplets and have a $^2\Pi$ ground electronic state.[23] The Q(1/2) and R(1/2) rotational-vibrational lines found in Ref. [23] indicate relaxation of the upper $^2\Pi_{3/2}$ spin-orbit component to the lower $^2\Pi_{1/2}$ state. If a similar spin-orbit relaxation takes place in the case of C_2H^+, only the lowest $^3\Pi_2$ state would be expected to have a substantial population at the HND temperature of 0.38 K. If the cations have same rotational constant (as estimated from the calculated structure to be $B = 1.37$ cm^{-1} in the gas phase),[10, 11] the only substantially populated state would be $^3\Pi_2(J = 2)$. The IR spectrum would be represented by the P(2), Q(2) and R(2) lines with the distance between the P(2) and R(2) lines of $10B \approx 13.7$ cm^{-1}. Because the observed distance between the outermost peaks in Fig. 2 is a factor of ~ 4 larger, we conclude that the spectrum cannot be explained in terms of the rotational structure. The absence of the lines which could plausibly be assigned to P(2), Q(2) and R(2) triplet indicates that the rotational constant of C_2H^+

in HNDs is at least a factor of 10 smaller than in the gas phase, such that it agrees with the 5 cm^{-1} broad central feature. This conclusion agrees with our recent study of CH_3^+ and $C_2H_4^+$ ions, [18,24] for which the rotation perpendicular to the figure axis could not be resolved. The large splitting between the spin-orbit components of about 18 cm^{-1} is unlikely to contribute due to the strict $\Delta\Omega = 0$ selection rule for the vibrational transition involving low rotational levels. It seems that the only situation when the spin orbit interaction may give an appreciable splitting is if the observed transition is electronic, i.e., $^3\Pi$ <-- $^3\Sigma^-$, which will require the reversal of the currently accepted ordering of the electronic states of C_2H^+. Some different origins for the splitting should be considered, such as the interaction between the C-H stretching mode of C_2H^+ with some other vibrational states. Possible candidates could involve the low-laying first excited state $^3\Sigma$. Various quantum chemical calculations placed the energy of the $^3\Sigma$ state in the range of 0.1 to 1 eV. [8, 9, 10] Therefore we propose that the interaction with the overtones of the bending vibration (or their combination) with the C-C stretching modes is the most likely cause of the splitting, considering they make a dense manifold of levels due to the Renner-Teller interaction.[7]

More work is required for unambiguous identification of the origin of the band splitting. Future experiments may be extended towards isotopically substituted C_2D^+ ions in which the energy level pattern will be different, and the band may have some different pattern or appear as singlet. High level anharmonic frequency calculations may also be needed to corroborate the assignments. Previously we observed that the bandwidth of the different vibrations of molecular ions may span the range from 1 to 10 cm^{-1} and assigned to lifetime broadening in helium. The width of the spectral peaks in Fig. 2 is within the same range and likely related to different rates of relaxation of the corresponding energy levels.

5. Conclusions

In this work, we demonstrated isolation and IR spectroscopy of C_2H^+ ions in ultracold HNDs. Due to high reactivity, this cation has never been studied by IR spectroscopy and conventional molecular beam experiments. Ionization of single acetylene molecules in HNDs isolates C_2H^+ cations in an inert helium environment, enabling the IR spectroscopic measurements. We reported the first observation of the C_2H^+ IR spectrum C-H stretching range. The spectrum appears as a triplet (with splitting of 33.6 cm^{-1} and 37.5 cm^{-1}) which cannot be explained by rotational structure. It is temporarily assigned to the result of interaction between the C-H stretching mode and overtones of the bending mode which are make a dense manifold of levels due to Renner-Teller interaction. More work is required for an unambiguous assignment of the spectrum. It would be interesting to extend the measurements to the higher energy regime to pinpoint the energy of the $^3\Sigma^-$ first excited state, which according to recent calculations is around 1 eV, but was not detected.

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7. Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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