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Communications: Infrared spectroscopy of gas phase $C_3H_3^+$ ions: The cyclopropenyl and propargyl cations

Allen M. Ricks, Gary E. Douberly, Paul v. R. Schleyer, and Michael A. Duncan[a)]
Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556, USA

$C_3H_3^+$ ions produced with a pulsed discharge source and cooled in a supersonic beam are studied with infrared laser photodissociation spectroscopy in the $800-4000$ cm^{-1} region using the rare gas tagging method. Vibrational bands in the C–H stretching and fingerprint regions confirm the presence of both the cyclopropenyl and propargyl cations. Because there is a high barrier separating these two structures, they are presumed to be produced by different routes in the plasma chemistry; their relative abundance can be adjusted by varying the ion source conditions. Prominent features for the cyclopropenyl species include the asymmetric carbon stretch (ν_5) at 1293 cm^{-1} and the asymmetric C–H stretch (ν_4) at 3182 cm^{-1}, whereas propargyl has the CH_2 scissors (ν_4) at 1445, the C–C triple bond stretch (ν_3) at 2077 and three C–H stretches (ν_2, ν_9, and ν_1) at 3004, 3093, and 3238 cm^{-1}. Density functional theory computations of vibrational spectra for the two isomeric ions with and without the argon tag reproduce the experimental features qualitatively; according to theory the tag atom only perturbs the spectra slightly. Although these data confirm the accepted structural pictures of the cyclopropenyl and propargyl cations, close agreement between theoretical predictions and the measured vibrational band positions and intensities cannot be obtained. Band intensities are influenced by the energy dependence and dynamics of photodissociation, but there appear to be fundamental problems in computed band positions independent of the level of theory employed. These new data provide infrared signatures in the fingerprint region for these prototypical carbocations that may aid in their astrophysical detection. © *2010 American Institute of Physics.*
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As first recognized by Stieglitz 110 years ago,[1] carbocations are important reaction intermediates in organic chemistry.[2–4] Their isolation in superacid media provided the first measurements of spectroscopic and structural properties.[2–6] These ions are also well known in the gas phase, occurring often as fragments or reaction products in mass spectrometry.[7] Some carbocations are known or suspected to be abundant in the interstellar medium (ISM).[8] Recent advances in infrared lasers allow the vibrational spectroscopy of mass-selected carbocations to be studied in the gas phase, providing insights into their structure and bonding.[9–15] As in the present study, isomeric structures have been detected and characterized.[9,13] $C_3H_3^+$ is a prototypical ion present in many ionized hydrocarbon gases known to have two viable structural isomers, the cyclopropenyl and propargyl cations.[2–4,6,16–25] We now investigate these $C_3H_3^+$ isomers with new gas phase infrared spectra in the $800-4000$ cm^{-1} region.

With its two π electrons, cyclic c-$C_3H_3^+$ is the smallest aromatic hydrocarbon ion.[2–4,7,17,18] First prepared by Breslow *et al.*[17] in acid solutions and as stable salts, its IR (bands at 736, 908, 1276, and 3105 cm^{-1}) and NMR spectra confirmed the expected planar, D_{3h} symmetry.[18] Despite the ring strain, the CCC asymmetric stretch force constant was found to be larger than the analogous value for benzene,[18] demonstrating the large contribution of delocalized π electrons to the bonding. The linear $HCCCH_2^+$ propargyl cation, the

other $C_3H_3^+$ isomer, is less stable and is not observed in condensed phases. Both experiments[19] and high levels of theory[20–25] place its energy ~ 25 kcal/mol higher than that of the cyclic species. A ZEKE photoelectron spectrum of propargyl radical provided vibrations for the ground state $HCCCH_2^+$ cation.[26] However, this paper has been withdrawn from the literature and is therefore not discussed further. Both $C_3H_3^+$ isomers were studied by Maier and co-workers[27] with electronic and IR spectroscopy in a neon matrix. In gas phase experiments, Dopfer and co-workers[9] reported infrared photodissociation (IRPD) spectra in the C–H stretch region for $C_3H_3^+$ ions in complexes with various ligands. Although limited in sensitivity and spectral range, the results were consistent with the presence of both the propargyl and cyclopropenyl isomers.

The known ion-molecule chemistry of c-$C_3H_3^+$ strongly suggests its presence in the ISM.[28] c-$C_3H_3^+$ recombines with electrons six times faster than $HCCCH_2^+$ (Ref. 29) and this dissociative recombination has been proposed to yield the neutral c-C_3H_2 molecule ubiquitous in the ISM.[28] c-$C_3H_3^+$ is also unreactive with prevalent interstellar atomic and small-molecule species.[30,31] $C_3H_3^+$ has been detected by cation mass spectrometry in the tail of Halley's Comet.[32] Because of its D_{3h} symmetry, c-$C_3H_3^+$ has no pure rotational spectrum. Infrared spectra may aid in the detection of $C_3H_3^+$ ions in the ISM, as well as provide important information about relative isomeric abundances.

$C_3H_3^+$ ions are generated in a pulsed discharge/supersonic expansion from the vapor of propargyl bromide
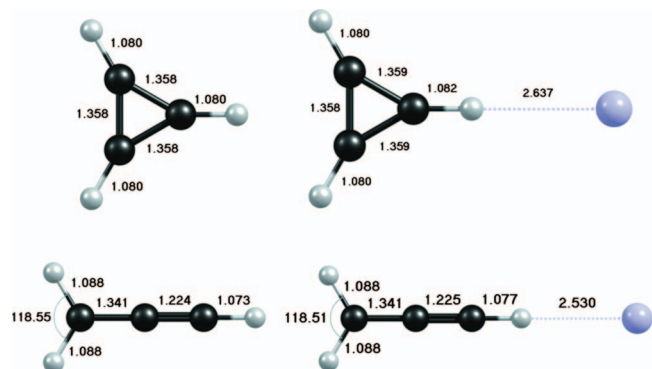
a)Electronic mail: maduncan@uga.edu.

FIG. 1. Structures computed at the DFT/B3LYP/cc-pVTZ level for the cyclopropenyl (c-$C_3H_3^+$) and propargyl (HCCCH$_2^+$) cations and their complexes with Ar.

FIG. 2. The IRPD spectrum of the $C_3H_3^+$−Ar ions along with the calculated harmonic spectra for the c-$C_3H_3^+$−Ar (red) and HCCCH$_2^+$−Ar (blue) ions. The inset experimental spectrum was obtained under "hotter" discharge conditions, while the lower spectrum was obtained under "colder" conditions. The theoretical spectra were given a 10 cm^{-1} FWHM Lorentzian line shape for comparison with the experiment. The doublet indicated with center at 3093 cm^{-1} has rotational branches at 3075 and 3107 cm^{-1}.

(80% in xylene, Aldrich) at 0 °C seeded in 20 atm of argon. The ions are mass-selected in a specially designed reflectron time-of-flight spectrometer and studied with infrared photodissociation (IRPD) spectroscopy.[12–15] IR excitation cannot break the strong covalent bonds, and therefore we employ the rare gas tagging technique.[12–15,33,34] In this method, $C_3H_3^+$−Ar ions are produced and selected, and IR absorption eliminates argon. The spectrum is recorded as the $C_3H_3^+$ fragment yield versus the frequency of an IR-optical parametric oscillator (OPO) laser (LaserVision).

The structures and harmonic frequencies of the c-$C_3H_3^+$ and HCCCH$_2^+$ ions, as well as their argon tagged analogs, were computed using density functional theory (DFT) and the GAMESS program package[35,36] at the B3LYP/cc-pVTZ level.[37,38] The optimized structures (Fig. 1) are consistent with the results of previous work,[9,20–25] and show that complexation with argon does little to perturb the structures. In both isomers, the argon binds to a hydrogen with an energy of roughly 600 cm^{-1}, giving each complex C_{2v} symmetry. Argon shifts the C–H vibrations most noticeably at its binding site, but the core C–C stretches are nearly unaffected. The energetics of the c-$C_3H_3^+$ and HCCCH$_2^+$ ions were explored with higher level CCSD(T)/cc-pVTZ calculations, which find the c-$C_3H_3^+$ isomer to be 23.4 kcal/mol lower in energy than HCCCH$_2^+$, in agreement with the experimental difference of 25 kcal/mol.[19] Prior computational studies have identified three pathways for interconversion of c-$C_3H_3^+$ to HCCCH$_2^+$ on the singlet potential surface.[25] Although direct, two of these have high barriers. The lowest energy two-step isomerization pathway involves a planar H shift in the end H to the central C and then the insertion of the resulting bare C of H$_2$CC(H)C: into a methylene C–H bond. The first, rate determining step has a ~49 kcal/mol barrier at the highest levels of theory [RCISD(T)].[25] (Our B3LYP/6-311+G** +ZPE energy is 51.3 kcal/mol.) While the high-lying carbene intermediate has nearly the same energy as the second transition structure and may not be viable, a large barrier clearly inhibits the isomerization of the propargyl into the more stable cyclopropenyl cation. This explains our difficulties in observing c-$C_3H_3^+$ starting from propargyl bromide.

The IRPD spectrum of $C_3H_3^+$−Ar is shown at the top of Fig. 2 and vibrational bands are compared with the results of theory and previous experiments in Table I. The computed
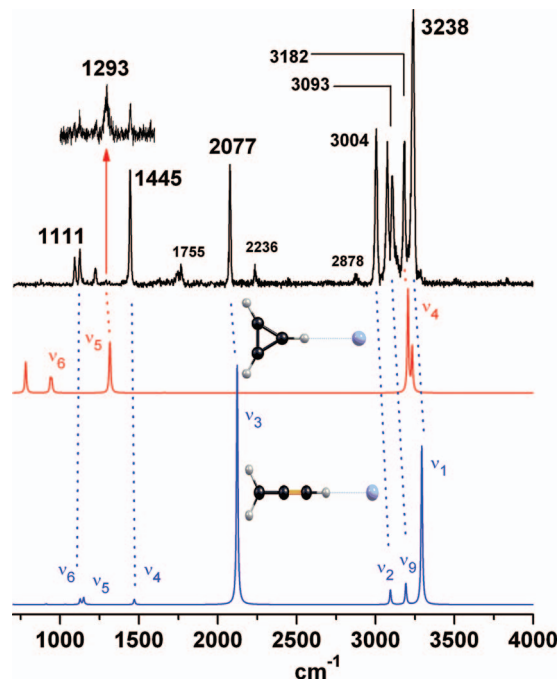
frequencies presented are unscaled. Trial scaling of the spectra with factors in the typical 0.95–0.98 range produced much poorer agreement with the experiment. This is true with the reported DFT data and it is even worse at the MP2(full)/cc-PVTZ level (not shown here). Bartlett and co-workers[39] recently performed anharmonic calculations on c-$C_3H_3^+$ (without argon) using the Vibrational Configuration Interaction (VCI) method and a potential surface generated at the CCSD(T)/aug-cc-PVTZ level of theory. Their frequencies are also reported in Table I.

The spectrum contains prominent bands in the C–H stretching region and weaker features at lower energy with an overall intensity pattern quite different from that predicted for either isomer. The main source of this difference is variation in the IR laser power across the spectrum; it is greatest in the 3500–2700 cm^{-1} region, drops off from 2200 to 2000 cm^{-1} before rising sharply below 2000 cm^{-1} and declines steadily to 800 cm^{-1}. Signal normalization to this is precluded by concomitant changes in the laser spot shape and intensity distribution, which changes its overlap with the ion beam in a way impossible to quantify. Therefore, band intensities in different regions of the spectrum are not expected to match computed ratios. Another factor is the photodissociation yield, which may be depressed when the photon energy approaches the argon binding energy. Lower excess energy slows the dissociation rate, reducing the intensity detected by the experiment on its microsecond timescale. Previous work has also found that band intensities detected by IRPD deviate from computed absorption intensities.[9–15]

TABLE I. Summary of the experimental and computed band positions (cm^{-1}) for the two C$_3$H$_3^+$ isomers. Calculations were performed at the B3LYP/cc-pVTZ level; the harmonic frequencies listed were not scaled. Intensities in parentheses are in km/mol.

IRPD (this work)	Calc.(int) c-C$_3$H$_3^+$	Calc.(int) HCCCH$_2^+$	Acid matrix[a]	IRPD[b]	Neon matrix[c]	Assignment
...	939 (27.2), 948 (23.6)		908			ν_6 (e′)
1111		1127 (11.3)				ν_6 (b$_1$) CH$_2$ out of plane wag with rotational structure
1222		1150 (14.5)				ν_5 (a$_1$) C–C single bond stretch
1293	1315 (46.1), 1318 (64.9),[d] 1290[e]		1276			ν_5 (e′) asym CCC ring stretch
1445		1471 (11.0)				ν_4 (a$_1$) CH$_2$ in plane scissors
1755						ν_{12} (b$_2$) in combination with ν_4
2077		2124 (490.2)			2080	ν_3 (a$_1$) C–C triple bond stretch
2236						ν_3 in combination with argon-ion intermolecular stretch
2878				3001		2ν_4
3004		3095 (30.0)				ν_2 (a$_1$) CH$_2$ sym stretch
3093		3193 (43.1)		3113		ν_9 (b$_2$) asym stretch with rotational structure
3182	3206 (210.9),[d] 3233 (91.3),[d] 3138[e]		3105	3094,[d] 3129[d]	3130	ν_4 (e′) CH asym stretch
3238		3294 (324.9)		3139		ν_1 (a$_1$) CH stretch

[a]Reference 17.
[b]Reference 9.
[c]Reference 27.

[d]The addition of argon to c-C$_3$H$_3^+$ splits the degenerate e′ modes into two nondegenerate modes.
[e]Reference 39.

The C–H stretching region is dominated by five intense peaks at 3004, 3075, 3107, 3182, and 3238 cm^{-1}. Neither C$_3$H$_3^+$ isomer alone can have this many fundamentals here and therefore more than one isomer must be present. Assignments are made on the basis of computed band positions and intensities as well as their dependence on the ion source conditions. The band at 3238 cm^{-1} is assigned to the ν_1 (a$_1$) CH stretch of HCCCH$_2^+$–Ar, although it occurs 115 cm^{-1} to the red from the value computed for the bare ion and 56 cm^{-1} to the red of that for the argon tagged ion. However, this assignment is consistent with the prediction that this band has the highest frequency and greatest intensity of the C–H stretches. The 3182 cm^{-1} band is assigned to the ν_3 (e′) CH stretch mode of the c-C$_3$H$_3^+$–Ar ion based on its position, its predicted intensity and its behavior with ion source conditions. More extreme discharge conditions cause this band and the one at 1293 cm^{-1} (also assigned to the cyclic species) to increase in relative intensity. The Auxiliary Information for this article shows the C–H stretching region measured under "hot" and "cold" conditions (Fig. S13).[40] The ν_3 vibration of c-C$_3$H$_3^+$ is predicted as two bands at 3206 and 3233 cm^{-1} as argon splits the doubly degenerate e′ C–H stretch into nondegenerate a$_1$ and b$_2$ vibrations. Dopfer and co-workers observed a splitting of 35 cm^{-1} here with N$_2$ tagging but we do not see this, although the higher member of a doublet may be obscured by the 3238 cm^{-1} band. The anharmonic calculations of Bartlett for the untagged species predict this band at 3138 cm^{-1} (Ref. 39) and 44 cm^{-1} to the red of our 3182 cm^{-1} band. This vibration has been reported previously in a neon matrix at 3130 cm^{-1},[26] at 3105 cm^{-1} in a polycrystalline salt,[17] and as two bands at 3094/3129 cm^{-1} in the gas phase with N$_2$ tagging.[9]

The peaks at 3075 and 3107 cm^{-1} are attributed to rotational branches (ΔK = $\pm$1 subbands) of a single vibration with a perpendicular-type band contour centered at 3093 cm^{-1}. The ν_9 (b$_2$) asymmetric CH$_2$ stretch of HCCCH$_2^+$–Ar is the only C–H stretch expected to have this kind of contour, and its frequency (computed at 3193 cm^{-1})

and intensity fit into the predicted trends. This band was not assigned in the work of Dopfer and co-workers.[9] A simulation of this band using an asymmetric top expression, the computed rotational constants, and appropriate nuclear spin statistics leads to a nice match to the contour and a rotational temperature of 25(5) K. The final C–H stretch at 3004 cm^{-1} is assigned to the symmetric ν_2 (a$_1$) CH$_2$ stretch of propargyl cation, which is 91 cm^{-1} lower than the value computed. No rotational contour is observed at our resolution for this or other bands with a$_1$ symmetry, consistent with their parallel band types and the low rotational temperature.

Similar comparisons to theory and dependence on ion source conditions allow assignment of bands in the lower frequency region. The 2077 cm^{-1} band is the ν_3 (a$_1$) C–C triple bond stretch of the HCCCH$_2^+$ isomer, seen previously at 2080 cm^{-1} in a neon matrix and computed at 2124 cm^{-1} (Table I). The lower-than-expected intensity is due to the fivefold lower OPO power between 2000 and 2200 cm^{-1} compared with that in the CH stretching region. Three bands predicted for the HCCCH$_2^+$–Ar ion between 1000 and 2000 cm^{-1} are assigned to the ν_4 (a$_1$) CH$_2$ scissors vibration, the ν_6 (b$_1$) out-of-plane CH$_2$ wag, and the ν_5 (a$_1$) CC single bond stretch. The strong peak at 1445 cm^{-1} is assigned to the ν_4 vibration. The peak at 1222 cm^{-1} is assigned to the ν_5 C–C single bond stretch predicted at 1150 cm^{-1}. The doublet at 1111 cm^{-1} is assigned to the perpendicular band contour of the ν_6 CH$_2$ out-of-plane wag, predicted at 1127 cm^{-1}. The subband spacing here is virtually the same as that for the ν_9 band above. The band at 1293 cm^{-1} shown in the inset of Fig. 2 is assigned to the ν_4 asymmetric C–C ring stretch of the c-C$_3$H$_3^+$ ion, which was predicted by Bartlett at 1290 cm^{-1},[39] and observed in a polycrystalline salt at 1276 cm^{-1}.[17] Like the C–H stretch at 3182 cm^{-1}, this peak is only seen with good intensity under hot discharge conditions and was not observed in the lower spectrum obtained using colder discharge conditions. This band is also more pronounced when allene is used as a precursor instead of

propargyl bromide, as shown in the Auxiliary Information file (Fig. S14).[40] The ν_6 (e′) band of c-$C_3H_3^+$ was seen previously in a polycrystalline salt at 926 cm^{-1}.[17] However, the IR laser power drops off precipitously below 1000 cm^{-1} and we could not observe this weaker band under conditions where c-$C_3H_3^+$ is detected. Several minor bands at 1755, 2236, and 2878 cm^{-1} are likely overtones, combination bands or other transitions with weak oscillator strengths; the most reasonable assignments are listed in Table I.

These data provide extensive new gas phase IR spectra for both the linear and cyclic isomers of $C_3H_3^+$. The D_{3h} symmetry of the cyclic isomer allows only two IR active fundamentals in the spectral region investigated, both of which are observed (at 1293 and 3182 cm^{-1}). The remaining bands are attributed to the propargyl cation. In both cases, the bands detected in our experiment are in good agreement with those from previous work. However, the unscaled harmonic frequencies computed are generally higher than those observed. Surprisingly, the effects of anharmonicity are quite variable and no single scaling factor works well across the spectrum nor even in localized regions. Thus, Bartlett's anharmonic computations for c-$C_3H_3^+$ ion are in excellent agreement with the 1293 cm^{-1} band, but were 44 cm^{-1} *lower* than the 3182 cm^{-1} band.[39] Inclusion of the argon should make this agreement even worse. The difficulties of theory for these ions require significant further investigation.

The ratio of the two isomers produced is a fascinating aspect of this experiment. By varying the ion source conditions we were able to influence the ratio of c-$C_3H_3^+$ to HCCCH$_2^+$ ions to help to confirm our band assignments. However, the present conditions produce more propargyl and less cyclopropenyl cation even though the latter is much more stable. This is understandable, given the noncyclic precursor employed and the high activation energy for isomer rearrangement.[25] Higher energy conditions permitting rearrangements are inconsistent with retention of the argon tag. Future experiments employing cyclic precursors (not presently available to us) should enhance the yield of c-$C_3H_3^+$. Now that vibrational fundamentals are established, higher resolution spectroscopy, deuteration, or two-laser double resonance techniques can be used to confirm these assignments and to provide more detailed structural probes. These spectra provide the first gas phase IR signatures for these ions in the fingerprint region, which may also be useful in identifying $C_3H_3^+$ isomers in the interstellar medium.

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