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Rotationally Resolved Spectrum of the Degenerate Antisymmetric C−H Stretching Band of c-$C_3H_3^+$

Published as part of ACS Earth and Space Chemistry special issue "Harold Linnartz Festschrift".

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Cite This: *ACS Earth Space Chem.* 2025, 9, 952−958
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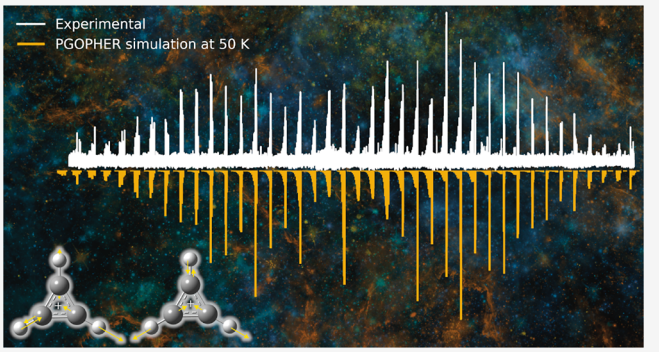
ABSTRACT: The rotationally resolved spectrum of the degenerate ν_4 antisymmetric C−H stretching band of the cyclopropenyl cation, c-$C_3H_3^+$, the smallest aromatic hydrocarbon cation, has been recorded employing leak-out-spectroscopy (LOS) in a cryogenic 22-pole ion trap instrument operated at T = 42 K. About 370 lines were measured in the region 3110−3150 cm^{-1} and assigned to rovibrational transitions of the fundamental antisymmetric C−H stretching band. Spectroscopic parameters have been refined compared to the previous experimental work from the group of Harold Linnartz [Zhao et al., *Astrophys. J. Lett.* 2014, 791, L28] and previous high-level theoretical predictions [Huang et al., *J. Phys. Chem. A* 2011, 115, 5005−5016]. Details of the spectral signatures allow for a thorough comparison of action spectroscopy in low-temperature ion traps to cavity ring down spectroscopy in a free-jet cooled discharge.



KEYWORDS: *action spectroscopy, rovibrational, infrared, symmetric oblate top, ions*

INTRODUCTION

Ions in space form an essential part of astrochemical networks as ion-neutral reactions remain fast down to cold temperatures and are believed to be pivotal for the gas-phase synthesis of complex molecules in the interstellar medium (ISM).[1−4] Small hydrocarbons in UV-rich environments like diffuse molecular clouds and photodissociation regions (PDRs), have also been proposed as tracers of the interplay between polycyclic aromatic hydrocarbon (PAH) formation and their photodestruction.[5] Only five pure hydrocarbon cations have been detected so far in the interstellar and circumstellar medium, namely CH^+, l-C_3H^+, C_5H^+, $H_2C_3H^+$, and CH_3^+.[6−12] The latter three have only been detected in the past three years. While the former four were detected using their rotational spectrum, CH_3^+ could only be detected in the infrared region using the James Webb Space Telescope (JWST),[12] as it possesses no permanent dipole moment. To evaluate which ions play an important role in space, laboratory spectra of many more species are required to detect them.

The propargyl cation mentioned above, $H_2C_3H^+$, has a sizable dipole moment (0.55 D) and was detected recently based on its rotational spectrum in the cold molecular cloud TMC-1.[11] It is one of two isomers of the $C_3H_3^+$ family, of which c-$C_3H_3^+$, the cyclopropenyl cation, is the lower energy isomer. Astrochemical models propose that both $C_3H_3^+$ cation isomers play an important role in the chemical evolution of the ISM.[11,13] Vibrational signatures for both isomers have been determined theoretically[14−16] and experimentally.[17−19] Marimuthu et al.[17] measured the broadband vibrational gas-phase spectra of both isomers and reported the band centers for their IR-active modes down to 600 cm^{-1}. The cyclic isomer, c-$C_3H_3^+$, is believed to exist in space because it is thought to be the parent of c-C_3H_2, which is ubiquitous in space[20] and expected to be formed in the gas phase by the dissociative recombination of the cyclopropenyl cation with an electron.[21] Unfortunately, it is not possible to test this hypothesis, because c-$C_3H_3^+$ does not possess a permanent electric dipole moment and can not be detected using radio astronomy. Therefore, rovibrational and in particular rotational spectra of the singly deuterated cyclopropenyl cation, c-$C_3H_2D^+$ (dipole moment = 0.23 D), were measured in the laboratory, but the deuterated cation could not be detected in TMC-1 under the current detection limits.[22]

The cyclic isomer, c-$C_3H_3^+$, constitutes the smallest aromatic ring and therefore, its properties and spectroscopic quantities

Received: January 30, 2025
Revised: March 9, 2025
Accepted: March 10, 2025
Published: April 2, 2025

are of general interest. The group of Harold Linnartz pioneered its spectroscopic investigation by measuring the rotationally resolved spectrum of the degenerate fundamental ν_4 C−H antisymmetric stretching vibration.[18] Figure 1 illustrates the set of two normal mode displacement vectors contributing to the degenerate ν_4 vibrational mode. Thanks to the high sensitivity of the Leiden cavity ring-down spectroscopy (CRDS) instrument, it became possible to record 129 spectral lines of c-$C_3H_3^+$ in a jet-cooled discharge of propyne (C_3H_4) in He employing a commercial infrared cw-OPO system. The analysis of the spectrum revealed the band origin, the rotational constants (B, C), centrifugal distortion constants (D_J, D_K, and D_{JK}) for both the ground and vibrationally excited state, as well as a Coriolis coupling constant (ζ_4) and *l*-type doubling constant (q_4). These results agreed very favorably with the theoretical predictions by Huang et al.[14]

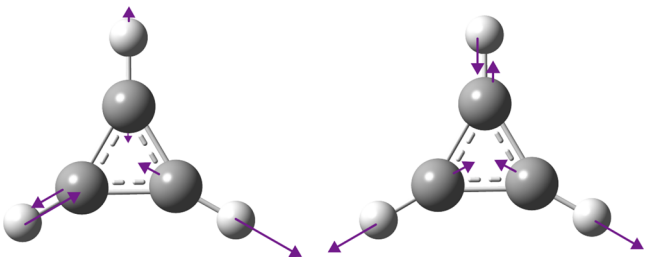


Figure 1. Schematic of the displacement vectors belonging to the ν_4 doubly degenerate C−H stretching mode of c-$C_3H_3^+$.

With the advancement of action spectroscopy in cryogenic ion traps, it has become possible to investigate a large set of small hydrocarbons[22−27] in great detail with the propargyl cation $H_2C_3H^+$[17,26,28] and c-$C_3H_3^+$[17] being two astrophysically important examples. In the current work, we revisit the fundamental ν_4 C−H antisymmetric stretch of c-$C_3H_3^+$ employing the recently developed leak-out spectroscopy (LOS) method,[29] where a cryogenic 22-pole ion trap is coupled with a commercial narrow line width cw-OPO infrared light source. Details of the apparatus and measurement procedure will be given in the experimental section. Refined and new spectral parameters are derived from the measured spectrum and presented in the results section. Finally, a comparison of the highly sensitive CRDS method with LOS will be drawn in the discussion section and implications of this work, such as a further search for c-$C_3H_3^+$ in space using the JWST, will be given in the conclusion section.

EXPERIMENTAL METHODOLOGY

The rovibrational transitions of this work were measured in the 22-pole trap instrument, LIRtrap. Details of this setup are well documented[29−31] and will be described only briefly here. Ions were generated in a storage ion source (SIS) by electron impact ionization of allene, C_3H_4. Here, primary ions are trapped upon ionization and are thus subject to potential secondary reactions with the precursor gas. Several times per

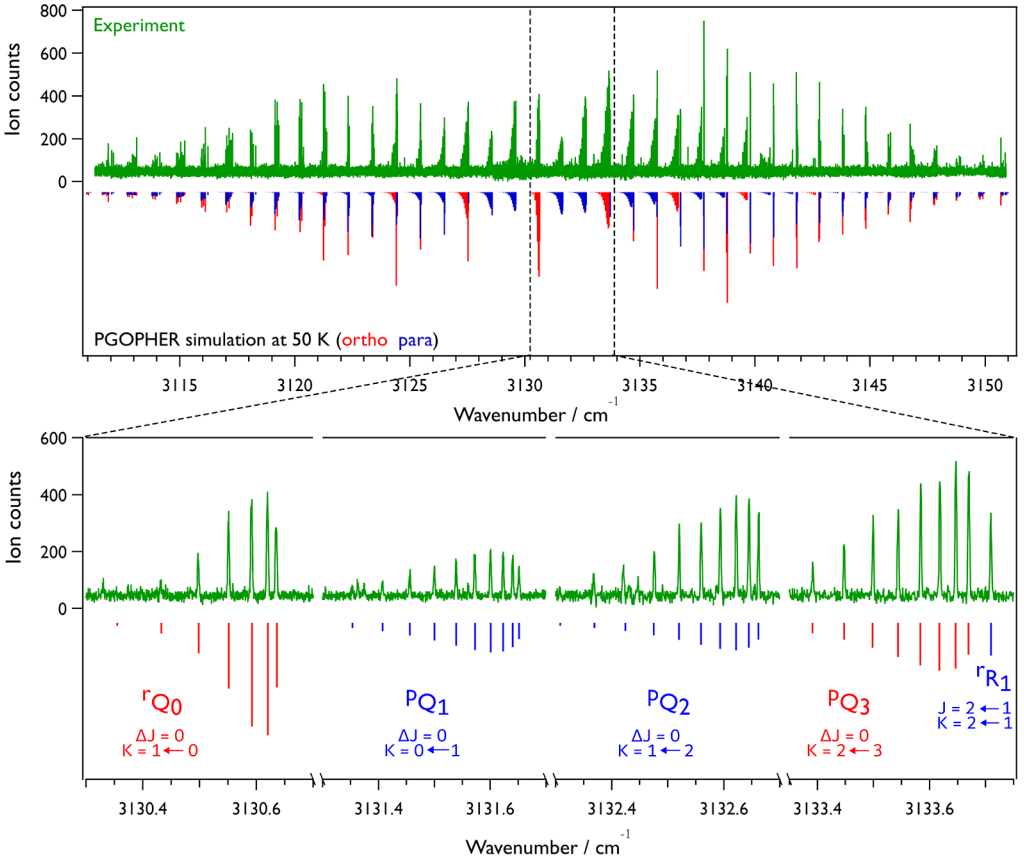


Figure 2. Overview spectrum of the $\nu_4 = 1 \leftarrow 0$ band of c-$C_3H_3^+$ measured at 42 K. Upper part: Experimental data of this work (green) and PGOPHER simulation at a rotational temperature of $T = 50$ K with red and blue sticks corresponding to the ortho and para nuclear spin species, respectively. Lower part: The zoom gives a detailed view of a selection of sub-bands.

https://doi.org/10.1021/acsearthspacechem.5c00032
ACS Earth Space Chem. 2025, 9, 952−958

Table 1. Spectroscopic Constants (in cm^{-1}) of c-$C_3H_3^+$[a]

	ground state			$\nu_4 = 1$		
constants	this work	prev. exp.[18]	theory[14]	this work	prev. exp.[18]	theory[14]
ν				3131.14344(14)	3131.1447(5)	3131.7
B	1.0256963(75)	1.02584(6)	1.02610	1.0228465(41)	1.02298(7)	1.02324
C	0.51158	0.51165	0.51178	0.5103404(30)	0.51040(2)	0.51037
D_J ($\times 10^6$)	2.340(57)	4.3(6)	2.44	2.298(26)	3.7(6)	2.44[b]
D_{JK} ($\times 10^6$)	−3.81(12)	−6.9(6)	−4.07	−3.753(55)	−6.3(8)	−4.07[b]
D_K ($\times 10^6$)	1.69	1.8	1.83	2.023(40)	2.2(4)	1.83[b]
q ($\times 10^3$)				2.5518(77)	0.19(7)	
ζ ($\times 10^3$)				−8.136(22)	−7.9(1)	−9.2
η_J ($\times 10^6$)				1.63(28)		
η_K ($\times 10^7$)				3.0(29)		

[a] ζ is dimensionless. Numbers in parentheses are one standard deviation in units of the last significant digit. The rotational constant, C, of the ground state is adjusted according to the theoretically predicted value of inertial defect.[14] The D_K of the ground vibrational state is estimated based on the planarity condition. Details on the fit are given in the text. The value of the theoretical ζ_4 is reported by Zhao et al.[18] provided to them by Huang et al.[14] from their QFF results [b] Same values as the ground vibrational state.

second, a pulse of ions is extracted from the SIS into a first quadrupole mass analyzer. A train of several thousand mass-selected ions with $m/z = 39$, including the $C_3H_3^+$ species, was injected into a cryogenically cooled 22-pole ion trap. The trap was filled constantly with the collision gas for employing the action spectroscopy, N_2 in this case ($n \approx 10^{12}$ cm^{-3}), and it was held at a nominal temperature of 42 K to avoid excessive freeze-out of N_2. Additionally, a high-density pulse of cold He gas was injected into the trap through a piezo-valve at the beginning of each trapping cycle. The pulse of He is used to thermalize the ions close to the cryogenic temperature of the trap through sufficient collisions within the first ≈ 75 ms of the trap time before the ions interact with infrared light.

Once trapped, the rovibrational transitions of c-$C_3H_3^+$ were detected using the sensitive action spectroscopic method of leak-out-spectroscopy (LOS).[29] This method relies on collision-induced transfer of the vibrational energy of the ions into kinetic energy. The trapped cooled ions were irradiated for 200 ms by a narrow- line width infrared beam entering the vacuum environment via a CaF_2 window and traversing the trap along its longitudinal axis. The IR beam is produced by a continuous wave optical parametric oscillator (cw-OPO, Toptica Topo) and its frequency is measured by a wavemeter. A secondary calibration procedure was performed by comparing the reported frequencies of the HCO^+ rovibrational spectrum using a frequency comb[32] to those measured in our setup. As a result, the reported frequencies in our work are accurate to the quoted value of the wavemeter (Bristol Instruments, model 621 A IR; 0.001 cm^{-1} accuracy).

During the irradiation time, the vibrational excitation of the c-$C_3H_3^+$ ions is eventually quenched via collisions with the N_2 molecules, leaving a fraction of ions with higher kinetic energy ready to escape the trap. The potential difference between the DC potential of the trap and the exit electrode was kept sufficiently low during the irradiation period such that these ions could indeed leave the trap and enter a second mass filter set for $m/z = 39$ to finally reach the ion detector where they are counted. Before a new train of ions is filled into the trap, remaining ions are removed and the process starts over again. The resulting trapping cycles were repeated at a rate of ∼3/s with the OPO frequency being stepped nominally by 0.0005 cm^{-1} per cycle, and the escaping c-$C_3H_3^+$ ions being counted as a function of the resulting OPO wavenumber.

RESULTS AND SPECTRAL ANALYSIS

c-$C_3H_3^+$ is a planar closed-shell oblate symmetric top molecule with a $^1A_1'$ electronic ground state. The spectroscopic properties of such a molecule have been discussed, e.g., by Crofton et al.[33] (for CH_3^+) and Zhao et al.,[18] and are explained here in more detail in the Supporting Information for the particular case of c-$C_3H_3^+$ with D_{3h} symmetry. c-$C_3H_3^+$ has eight fundamental vibrational modes, four of which are infrared-active. This work investigates the degenerate fundamental ν_4 C−H antisymmetric stretch (vibrational symmetry E'), as illustrated in Figure 1.

The leak-out measurements were performed in high spectral resolution over the 3.2 μm region which was covered through multiple consecutive scans, each ranging over 2−5 cm^{-1}. The recorded rovibrational spectrum, after applying the baseline correction routine from PGOPHER,[34] is displayed in Figure 2. The total collection time of this measurement amounted to roughly 10 h. The observed spectrum is typical for a perpendicular band of an oblate symmetric top and shows a clear structure consisting of a number of Q-branches which are separated by about 1 cm^{-1}, which roughly corresponds to $2(C - B)$. A zoom-in into several of these Q-branches is shown in the lower part of Figure 2. Also, some R-branch transitions with seemingly similar spacing become clearly discernible in the overview spectrum for higher energy transitions of the ν_4 band where the number of Q-branches becomes rarer. Even at the low temperature of the trap experiment, many Q-branches populate the center of this vibrational band such that it is a challenge to identify the band center in this rich spectrum. However, the position of a number of isolated lines in the spectrum, e.g. the $^rR_1(1)$ line in the lower part of Figure 2, help in finding the unique assignment. As a result, the band center is found at 3131.143 cm^{-1}.

In total, 369 lines were assigned to this ν_4 fundamental band of c-$C_3H_3^+$, covering a range of ∼40 cm^{-1}. Not all lines can be identified in the upper part of Figure 2 due to the display resolution, but the zoom in the lower part shows that the spectral resolution is good enough for an accurate determination of each line position if they were not blended occasionally. All 129 spectral line assignments by Zhao et al.[18] could be identified in this spectrum as well, and a comparison of the line positions is provided in the Supporting Information (Table S1).

https://doi.org/10.1021/acsearthspacechem.5c00032
ACS Earth Space Chem. 2025, 9, 952−958

An effective Hamiltonian for a symmetric top rotor, as implemented in PGOPHER, was used for a fitting procedure. As is known from previous studies, the rotational constants C of the two vibrational states C_0 and C_4 are correlated and so are C_4 and $C_4\zeta_4$, and hence they cannot be determined unambiguously via a global fit where all rotational parameters of the two states can be determined at the same time. Furthermore, the centrifugal distortion constant $D_{K,0}$ and Coriolis centrifugal distortion constant, η_K, suffer from the same problem. Therefore, to arrive at a unique fit, which will be presented here, additional information has to be used to lift the ambiguity described above.

As a consequence, a fit of ground state combination differences was performed as the first step of the fitting procedure using 168 possible combination differences (CDs). The complete list of CDs is given in the Supporting Information (Table S2). Based on the selection rules (ΔJ = 0, ±1; ΔK = ±1) this allowed us to determine values for ground state B, D_J and D_{JK} accurately. Even though c-$C_3H_3^+$ is planar, it exhibits an inertial defect ($\Delta_0 = 1/C_0 - 2/B_0$). We use the value of this inertial defect as predicted by the quartic force field (QFF) calculations[14] to obtain C_0 based on our accurate value of B_0. Then, the planarity relation for the quartic distortion constants,[35] $2D_J + 3D_{JK} + 4D_K = 0$, was used to determine $D_{K,0}$. While this expression is only true for the equilibrium geometry, it can be used as a good estimate when an experimental determination of this parameter is not possible, as shown by former examples.[33,36,37] By keeping the ground state constants fixed to these values, a least-squares fit of the observed rovibrational transitions was performed to obtain the rotational parameters of the excited vibrational state as well. For the fit, blended lines were assigned a standard deviation three times that of well-separated lines. The resulting spectroscopic constants are given in Table 1 along with a summary of those reported by Zhao et al.[18] and theoretical predictions of Huang et al.[14] The observed and calculated line positions along with the fit residuals ($obs - calc$) are given in the Supporting Information (Table S1).

The result of this fit is shown as a stick spectrum in Figure 2, pointing downward in order to compare to the measured spectrum pointing upward. Visual inspection of Figure 2 reveals a very good agreement between the experiment and the model. Even all the detailed Q-branches are fit with high accuracy as seen in the details of Figure 2. The RMS error of the fit obtained is 0.001 cm^{-1} which agrees with the experimental accuracy thus showing that the spectrum is indeed nicely approximated by the model. The energy level diagram associated with this model describing the ground and vibrationally excited state is detailed in the Supporting Information (Figure S1).

Molecular rotation of the ground and vibrationally excited molecule are well described by the rotational constants B and C, and the corresponding centrifugal distortion constants for the oblate top molecule. In fact, these constants do not change much for the ground and vibrationally excited state as the constant 2B spacing of the R-branch lines already indicates. Including the computed higher order sextic terms from Huang et al.[14] did not significantly affect the fit. So, these higher-order constants were not included in the fit. The degenerate vibrational mode observed here involves a vibrational angular momentum, l. The coupling of this vibrational angular momentum with the molecular rotation (J,K) gives rise to the Coriolis interaction parameters, ζ_4, and l-type doubling parameter, q_4, for ν_4 = 1. Their values as well as Coriolis centrifugal distortion constants, η_J and η_K, could be derived in this fit.

In summary, with only one vibrational band being observed, i.e., only one set of selection rules applying, not all spectroscopic constants can be determined just from a global fit. Instead, the values for C_0 and $D_{K,0}$ are derived from the inertial defect and planarity conditions. Therefore, no uncertainties are associated with their values in Table 1, and since these are kept fixed in the fit, likely the uncertainties in the rotational constants of the vibrational excited state are slightly higher than just one standard deviation as provided there. But with this additional information, all other spectroscopic parameters are determined with very high accuracy.

DISCUSSION

In addition to the spectral analysis presented above, the overall band profile in the measured spectrum corresponds to a rotational temperature of ∼50 K, as shown by the nice resemblance of the measured spectrum with the corresponding fit at this temperature. Here it should be noted that the LOS signal intensity is associated with the absorption probability of the infrared photon but it also involves the likelihood of a vibration to translation (V-T) energy transfer. Based on the fact that the vibrational energy in the excited state is much higher than the rotational energy, it seems likely that the probability of a V-T transfer is very similar for all rotational states and thus the spectrum can be compared in intensity to a conventional absorption spectrum with an effective rotational temperature. The similarity between the experimental spectrum and the model spectrum in PGOPHER supports this reasoning.

The Doppler width of the spectral lines is measured to be of the order ∼0.003 cm^{-1}, which corresponds to a kinetic temperature of ∼70 K. This value is significantly higher than the wall temperature of the cryogenic 22-pole trap of 42 K. Such a heating effect is typically found for buffer gas cooled trapped ions, in particular when the buffer gas (here N_2) is not much lighter than the ion ($C_3H_3^+$). The rotational temperature of the ions is given by the average collision energy between the ions and the buffer gas. Taking the line width as a measure for the kinetic temperature of the ions, T_{kin} ∼ 70 K, and the temperature of the buffer gas (T ∼ 42 K), the effective collision temperature which should be the rotational temperature amounts to ∼ 50 K which agrees with the fitted temperature as shown above (see Schmid et al.[29] for more details).

These findings shall be compared to the results of Zhao et al.[18] who measured their spectrum in a free jet expansion. They report a rotational temperature of ∼35 K which is lower than in the current trap experiment. As a result, higher (J,K) rotational states are populated and thus more lines have been observed in the present study which results in more accurate values for the distortion constants. Both works show very good agreement with the previous quantum chemical calculations, demonstrating the extremely high quality of the predictions from the group of Timothy Lee.[14]

Thanks to the seminal work of Zhao et al.[18] who succeeded in recording the spectrum of the transient ion c-$C_3H_3^+$ by cavity ring-down spectroscopy, it is now possible to compare LOS, a new technique of action spectroscopy, to one of the most sensitive methods of absorption spectroscopy. A fraction of both spectra is shown in Figure 3. The CRDS spectrum is

https://doi.org/10.1021/acsearthspacechem.5c00032
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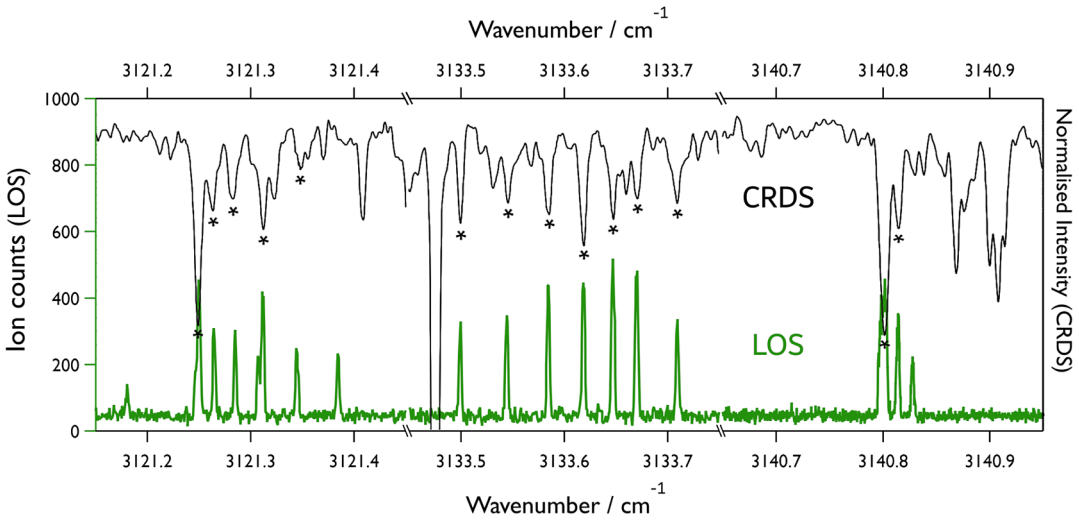

Figure 3. Rovibrational spectrum of c-$C_3H_3^+$ in three regions as measured by the LOS method (in green) and by CRDS (Zhao et al.,[18] inverted in black) with the asterisks marking the spectral features corresponding to c-$C_3H_3^+$. The experimental spectrum from Zhao et al.[18] has been reproduced by permission. Copyright AAS, 2014.

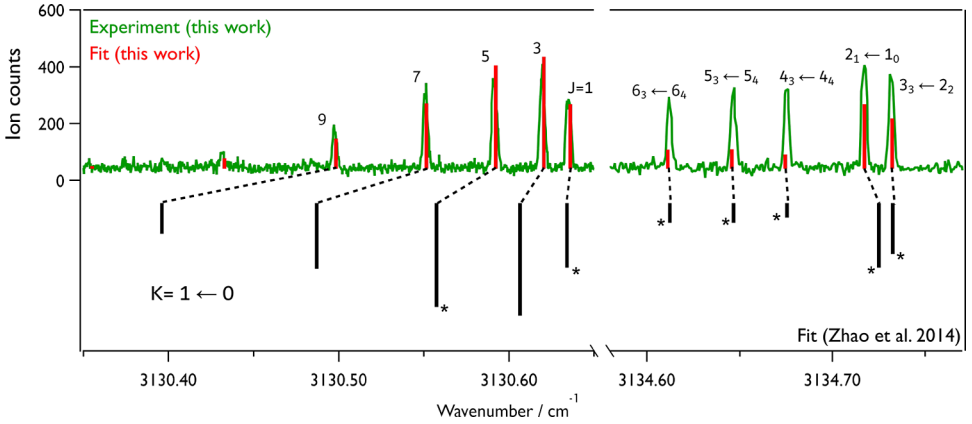

Figure 4. Details of the experimental spectrum in two selected regions shown as a green trace displaying the $^rQ_0$ branch around 3130.5 cm^{-1} and part of the $^pQ_4$ branch as well as the $2_1 \leftarrow 1_0$ ($^rR_0$ (1)) and $3_3 \leftarrow 2_2$ ($^rR_2$ (2)) transitions. The red stick spectrum represents the final fit of this work. The black solid lines show the transitions assigned (indicated by asterisks) and modeled by Zhao et al.[18]

mainly comprised of lines from the target ion (assigned by an asterisk) but it contains a number of additional lines which are transitions of other species generated in the discharge. In contrast, this part of the LOS spectrum only contains lines from c-$C_3H_3^+$ because by mass selection only species with a m/z = 39 can contribute. Despite this considerable advantage of LOS, we also have to consider other isomers of $C_3H_3^+$ and other species of the same mass which are created from allene in the ion source. This part of the spectrum is free from any other contributions as seen in the lower trace of Figure 3. However, a closer inspection of the LOS overview spectrum (Figure 2) reveals that it exhibits a few weak linales of the $\nu_3 + \nu_7$ combination band of the $H_2C_3H^+$ isomer.[28] The proper assignment by Zhao et al.[18] has been achieved by the comparison of different discharge conditions. This shows that even without the advantage of mass selection, a clear analysis of these spectra is possible.

Another difference in the spectra is the line width, which is narrower for LOS than for CRDS even though the temperature of the jet expansion is lower than the conditions chosen for the trap experiment. This indicates that the width in the CRDS experiment is dominated by the angular spread of the jet which leads to velocity components perpendicular to the jet propagation. This behavior then results in a symmetric broadening. As a consequence, the spectral resolution of the LOS measurements is somewhat better and several blended lines of the CRDS study could be resolved in the present work. Zhao et al.[18] reported a frequency accuracy of the measured positions of absorption lines to be better than 0.003 cm^{-1} compared to ours of 0.001 cm^{-1}. The frequencies of the line centers of both works are given in the Supporting Information (Table S1). The average deviation of lines reported by Zhao et al.[18] and in this work is 0.001 cm^{-1}, which is within the accuracy limit of the wavemeters used in both experiments.

Due to the narrow line width in the LOS data, some close-lying Q-branch transitions are nicely resolved, as shown in Figure 4. These more accurate line positions did not change the spectral parameters by a lot as seen in Table 1. Both the B and C constants in the $\nu_4 = 1$ state change from the respective ground rotational constants by less than 0.3% which is similar to what was reported by Zhao et al.[18] As can be seen in Table 1, the uncertainty in the rotational constants determined in this work could be improved by an order of magnitude compared to the previous experimental work,[18] except for C_0 and $D_{K,0}$.

https://doi.org/10.1021/acsearthspacechem.5c00032
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The higher number of assigned lines and high (J, K) accessed in this work also allows us to provide first values of the Coriolis quartic distortion constants, η_J and η_K. The higher value of η_J compared to η_K is typical of what would be expected for an oblate symmetric top, and the opposite of what is found for prolate top molecules. The order of magnitude of the uncertainty on both these values is the same, however, for η_K it is close to its magnitude and thus not determined with high significance.

The only value which is significantly different in our fit is that of the l-type doubling constant, q_4, which is an order of magnitude higher than reported in Zhao et al.[18] We assume this is due to an incorrect assignment in their $^rQ_0$ branch. Zhao et al.[18] only assigned two features in the $^rQ_0$ branch, corresponding to J = 1 and 5, shown in Figure 4 (marked with an asterisk in the lower model spectrum). Zhao et al.[18] overestimated the spacing between the transitions in this branch and also other transitions with K = 1 in the upper state, which are affected by q_4. However, overall the comparison of the two spectra underpins the high quality of the original work by the Linnartz group.

CONCLUSIONS

Leak-out action spectroscopy has been used to record a high-resolution spectrum of the degenerate ν_4 vibrational band of c-$C_3H_3^+$ at cryogenic temperatures. The unambiguous assignment and higher rotational temperature achieved in this work allowed for a refinement of the spectroscopic parameters for this planar ion and confirmed the high-quality CRDS measurements of the Linnartz group.[18] This ion lacks a permanent dipole moment which prohibits its radio detection in space. However, JWST might find it through its rovibrational spectrum as it was envisioned by Harold Linnartz already 10 years ago. This could provide crucial abundance estimates for this ion which is thought to have significant relevance in astrochemical networks.

In the future, other infrared active bands in the mid-infrared region at 7 μm (in-plane wagging), 11 μm (in-plane scissoring), and 13 μm (symmetric out-of-plane bending) found in recent studies[17] could also be measured with LOS in high-resolution for the bare ion using suitable light sources. Measuring these along with some combination bands could also allow for better estimates for the ground state C and D_K. The LOS method has been shown to work efficiently at lower frequencies, e.g., the C−C stretch vibrations of C_3H^+ and HC_3O^+ were measured in the 5 μm range in high-resolution.[23] The lowest lying vibration detected with LOS has been the bending vibration of $C_2D_2^+$ in the infrared regime at 520 cm^{-1}/20 μm.[24] For H_5^+, we have found signals even below 400 cm^{-1}/25 μm.

Different isobaric species, structural isomers and nuclear spin conformers may be present within the mass-selected ion ensemble in the trap as seen in the present case. This can complicate a proper assignment but in most cases, the respective bands can be disentangled because of the subtle spectral details of the respective species, even if the bands are overlapping significantly. Zhao et al.[18] showed how the source conditions can be varied in a systematic fashion such that the spectra of the target ion can be determined with high confidence. Such an approach is also easy to apply in trap experiments by choosing different precursor molecules which will lead to largely different signals of the respective bands.

However, LOS allows a more elegant way to isolate the spectra of different species. Since the LOS technique ejects one species out of the trap, it is possible to expel all ions of one sort and to be left with only one species as already described in Schmid et al.[29] This unique way of analyzing and/or preparing isomer-specific ensembles in cryogenic ion traps will allow the study of isomer-specific reactions which opens new routes in understanding low-temperature ion chemistry. Finally, the LOS technique is highly selective, highly sensitive and universal. This has been already applied to many species and the much-increased scanning speeds will allow to record many more (high-resolution) spectra of otherwise rather elusive molecular ions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.5c00032.

Energy level diagram for c-$C_3H_3^+$, complete list of assigned spectral lines in this work, and CDs obtained in the GSCD fit (PDF)

Experimental data files (raw and baseline corrected versions) with wavenumber (in cm^{-1}) and corresponding ion counts (dat); list of assigned spectral lines, transition details, and fit residuals in this work (dat) (ZIP)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is dedicated to Harold Linnartz who pioneered many aspects of laboratory astrophysics and spectroscopy in particular. His previous work on c-$C_3H_3^+$ demonstrates his experimental skills and scientific determination which remains an inspiration for all of us. We thank Dongfeng Zhao for allowing the reproduction of their spectrum from reference 18 for a comparison of CRDS and LOS. This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) via Collaborative Research Center 1601 (Project No. 500700252, subprojects B8 and C4) and "Schmid

514067452". The Cologne group acknowledges the ERC advanced grant (MissIons: 101020583) for funding. D.G. acknowledges funding from the Marie Skłodowska-Curie grant agreement 101109890-IONTRAP. D.G. thanks Dr. Holger Müller for extremely useful discussions regarding inertial defect and *l*-type doubling. The authors would like to acknowledge Michael Mies for participating in some of the experimental measurements.

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https://doi.org/10.1021/acsearthspacechem.5c00032
ACS Earth Space Chem. 2025, 9, 952−958