Infrared spectroscopy of carbo-ions. V. Classical vs nonclassical structure of protonated acetylene \( \text{C}_2\text{H}_3^+ \)

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The problem of classical vs nonclassical structure of protonated acetylene (vinyl cation) \( \text{C}_2\text{H}_3^+ \) has been studied using high resolution infrared spectroscopy. The spectrum has been observed in the 3.2 \( \mu \)m region in air-cooled and water-cooled plasmas using \( \text{C}_2\text{H}_3\text{H}_2\text{He} \) mixtures and in liquid nitrogen-cooled plasmas using \( \text{CH}_4\text{H}_2\text{He} \) mixtures. The difference frequency spectrometer with the velocity modulation method has been used to conduct the Doppler-limited, high sensitivity spectroscopy. The observed vibration–rotation pattern with the band origin at 3142.2 \( \text{cm}^{-1} \) has been identified as due to the antisymmetric CH stretching \( \nu_c \) band of the \( \text{C}_2\text{H}_3^+ \) ion with the nonclassical (bridged) structure. The observed spectral pattern was anomalous, but definitive assignments could be made for a part of the spectrum using the ground state combination differences which fit to the usual asymmetric rotor pattern. The discrimination between the classical and nonclassical structures is based on the observed spectral intensity pattern due to spin statistical weights. Agreement of vibrational band patterns and the rotational constants with \textit{ab initio} values gives supporting evidence. The anomaly of the spectrum is at least partly ascribed to the small energy difference between the classical and nonclassical structures and possible rearrangement between them, the idea used by organic chemists over the years in wet chemistry. Systematic splittings with the intensity ratio of 2:1 have been noticed in some parts of the spectrum indicating that the protons tunnel between the apex and the two end equilibrium positions of the bridged structure. Using a simplified internal rotation model proposed by Hougen, the barrier height of the tunneling has been estimated. Chemical kinetics in plasmas related to \( \text{C}_2\text{H}_3^+ \) is also discussed. We conclude that (1) the nonclassical structure is lower in energy than the classical structure, and (2) the apex proton and the two end protons exchange their positions with a measurable time scale.

I. INTRODUCTION

Among the carbo-ions studied in this series of papers,\(^1\)–\(^4\) protonated acetylene, or vinyl cation, \( \text{C}_2\text{H}_3^+ \) is of special interest in quantum chemistry because of its two isomers with nearly equal stability. The classical and the nonclassical (bridged) structures are shown in Fig. 1. In this paper we report our observation of an infrared vibration–rotation spectrum of this molecular ion and address the following two specific questions: (a) the structural problem; which of the two structures is more stable? and (b) the dynamical problem; whether or not the ion rearranges between the two structures on a measurable time scale.

The first experimental study of this protonated ion appears to be its mass spectroscopic detection in the decomposition of various hydrocarbons in a positive ray tube reported by Stewart and Olson in 1931.\(^5\) Since then a great many papers have been published on gas phase ion–molecule reactions involving this species. Readers are referred to Albritton’s summary on ion–neutral reaction rate constants\(^6\) and to Huntress’ summary of kinetic cross sections for chemical reactions of astrophysical interest.\(^7\) Some important works will be quoted later in this paper when we discuss plasma chemistry. The importance of protonated acetylene in interstellar chemistry, in particular, in producing the long chain polyacetylenic compounds observed by radio astronomers has been noted (see Smith’s review on interstellar molecules\(^8\)). Quite independent of these studies on free protonated acetylene, organic chemists postulated vinyl cations in understanding the mechanism of electrophilic addition reactions to acetylenic compounds.\(^9\) Readers are referred to Stang’s review on vinyl and allenyl cations.\(^10\) The problem of the classical vs nonclassical structure has been a great controversial issue especially in this field, as vividly pictured in Brown’s monograph.\(^11\)

With the advent of modern computers many theoretical studies of protonated acetylene have been reported. We find 35 theoretical papers beginning with Hoffmann’s extended Hückel theory treatment in 1964.\(^12\) The relative stability of the classical vs nonclassical ion has been the main issue. In general, earlier calculations using the SCF method predicted the classical structure to be more stable\(^13\) while more recent calculations taking into account configuration interactions reversed this conclusion. While many papers treat protonated acetylene as one of many carbocations, there are papers from five theoretical groups which focus on the discussion of the two structures of protonated acetylene. Żurawski, Ahl-
The classical and nonclassical $C_2H_3^+$ can be used to differentiate the two forms. We will use this argument later in this paper.

There have been very few experimental studies of the structure of $C_2H_3^+$ . Kanter, Vager, Both, and Zajfman conducted a Coulomb explosion experiment and stated "Although our results are still in the preliminary stage, the data clearly show the nonclassical structure to dominate our sample of molecules". More recently Berkowitz, Mayhew, and Rušičić conducted a photoionization study of the vinyl radical and discussed the relation between their observed autoionization structure and the structure of vinyl cation. A recent paper by Yeh, Price, and Lee on the classical and nonclassical $C_2H_3^+$ ion is also noteworthy.

Our spectrum of $C_2H_3^+$ was first observed in March 1985. A great many lines were observed in the region between 3250 and 2950 cm$^{-1}$, and initially the identity of the carrier of the spectrum was not certain. The spectra of $CH_3^+$ (papers I and III) and $C_2H_3^+$ (paper II) reported in this series of papers emerged more or less as by-products of our work on $C_2H_3^+$. The progress of experiments and our understanding of the spectrum of $C_2H_3^+$ has been reported in four Ohio symposia on molecular spectroscopy. We refrained from publishing a paper because the observed spectrum did not accurately fit the expected asymmetric rotor pattern. Three theoretical papers have appeared in attempts to shed light on this special problem. Houten proposed a model calculation in which he assumed that the three protons of $C_2H_3^+$ are fixed in an equilateral triangle and rotate around the $C_2$ frame thus covering the six equivalent classical and nonclassical structures. This model is discussed later in this paper. Escibano, Bunker, and Gomez have proposed a similar model using the ab initio potential of Lindh, Roos, and Kraemer.

While accurate fitting of the observed spectrum is still not possible, our continuous experimental and analytical effort has brought us to a plateau so that we can give some conclusive results especially for the ground vibrational state of $C_2H_3^+$. These results together with the remaining difficulties are reported in this paper. Part of the results have been published in the Royal Society Meeting of Molecular Ions. It is our hope that the results presented in this paper will be of interest to those who would join us in the endeavor to study this fascinating molecular ion.

II. EXPERIMENT

The experimental method used for the spectroscopy of $C_2H_3^+$ is essentially the same as that used for the other carbo-ions $CH_3^+$, $C_2H_3^+$, and $C_2^-$ described earlier in this series of papers. The molecular ions are produced in A.C. plasmas using mixtures of (hydrocarbon):H$_2$:He with a typical mixing ratio of 1:10:1000 with the total pressure of ~7 Torr. Three generations of multiple-inlet-outlet discharge tubes (1 m long and 1.2 cm in diameter) have been used. The first spectrum was obtained using an air-cooled discharge tube (nicknamed "spider") and a mixture of $C_2H_2$:H$_2$:He 1:20:700. This produced many lines of
C$_2$H$_5^+$ and C$_2$H$_3^+$, with CH$_3^+$ lines only weakly present. The intensities of the CH$_3^+$ lines were greatly enhanced when CH$_4$ was used instead of C$_2$H$_2$ thus allowing us to discriminate the CH$_3^+$ spectrum from those of C$_2$H$_5^+$ and C$_2$H$_3^+$. The second generation of scans was done using a water-cooled discharge tube ("tarantula") which was described in some detail in paper III. They produced stronger lines of C$_2$H$_5^+$ and C$_2$H$_3^+$. The third generation of scans was done using a liquid N$_2$-cooled discharge tube ("black widow"). A sketch of the discharge tube is shown in Fig. 2. Since acetylene froze in this discharge tube, a mixture of CH$_4$He was necessary. This produced extremely strong lines of CH$_3^+$ (signal to noise ratio 100) and fortunately also produced the best spectra of C$_2$H$_3^+$ and C$_2$H$_5^+$. The chemical discrimination between the C$_2$H$_5^+$ and the C$_2$H$_3^+$ spectral lines was done by observing their intensity dependences on the H$_2$ concentration. In general the intensities of the C$_2$H$_3^+$ lines depend rather critically on the mixture and the discharge conditions, while the C$_2$H$_5^+$ spectral lines were observed in almost any discharge containing hydrocarbon, H$_2$, and He. We obtained similar spectra when we used C$_2$H$_4$, C$_2$H$_6$, C$_2$H$_5$Br, and CH$_2$CCH$_2$ as when we used C$_2$H$_2$. We have used various mixtures of H$_2$ and D$_2$ to determine the number of protons from intensity variations. We have also used $^{13}$C species of C$_2$H$_2$ and CH$_4$ to observe $^{13}$C isotopic species of C$_2$H$_3^+$. All of these points will be discussed in more detail in Sec. III B.

A difference frequency laser system developed by Pine has been used as the tunable infrared radiation source. Mixing single-mode ring dye laser radiation of $\sim 0.5$ W and single mode Ar ion laser radiation of $\sim 1$ W in a temperature-controlled LiNbO$_3$ crystal, we obtain continuously tunable infrared radiation with power on the order of a few tenths of mW. Using InSb infrared detectors with $D^* \sim 10^{-11}$ cm Hz$^{1/2}$/W and a detector area of $10^{-7}$ cm$^2$, the rms noise of the detector with the detection bandwidth $\Delta f \sim 1$ Hz is on the order of $10^{-8}$ of the infrared power. The method of velocity modulation developed by Gudeman, Begemann, Pfaff, and Saykally, combined with noise subtraction and unidirectional multiple reflection, makes the overall sensitivity of detection on the order of $\sim 1 \times 10^{-9}$ cm$^{-1}$ in terms of the minimum detectable absorption coefficient. Using the intensity of the antisymmetric C-H stretching vibrations of $\sim 400$ km/mol predicted by Lee and Schaefer and the observed signal to noise ratio of $\sim 30$ for stronger lines, the number concentration of C$_2$H$_5^+$ in the plasma is estimated to be on the order of $5 \times 10^{10}$ cm$^{-3}$.

III. OBSERVED SPECTRUM AND IDENTIFICATION

We first observed an extremely rich spectrum in the region between 3200 and 3100 cm$^{-1}$ using the mixture of C$_2$H$_3$:H$_2$:He in the air-cooled discharge tube and measured $\sim 500$ lines. Some of the lines were identified to be due to the methyl cation CH$_3^+$ from their width (which is mass dependent $\sim 1/\sqrt{m}$), chemical conditions, and finally spectral analysis. 165 lines have been measured and assigned in paper III. A special effort has been made to identify weak high rotational transitions in order to exclude them from the C$_2$H$_3^+$ spectrum. The simple extrapolation using computers does not solve the problem completely because perturbations from other vibrational levels cause shifts of the spectral lines. Since the submission of paper III, an additional 35 lines have been assigned to high J, K transitions based on the method combination differences. This leaves about 20 lines which are due to CH$_3^+$ or other ions containing one carbon atom, judging from their linewidths and chemical behavior. They are most likely hot bands of CH$_3^+$. They are excluded from the C$_2$H$_5^+$ spectrum.

The second group of spectral lines to emerge from the bush of lines were those for C$_2$H$_4^+$. They appear very similar to those of C$_2$H$_2^+$. Both band origins (3136 vs 3142 cm$^{-1}$) and rotational constants [$B_0 = 1.1046$ cm$^{-1}$ vs (B + C)/2 = 1.0940 cm$^{-1}$] are very close to each other, suggesting the nonclassical structure of C$_2$H$_4^+$. According to structural calculations by Raine and Schaefer and Lee and Schaefer, the proton attaches to acetylene to form a nonclassical ion without much change of the acetylene structure. Initially we were tempted to assign this group of lines to C$_2$H$_3^+$ with the classical structure but the spectral pattern for low J lines clearly indicated that they belonged to the $\Pi \rightarrow \Pi$ v$_3$ band of C$_2$H$_4^+$. A preliminary analysis of this spectrum has been published as paper II of this series. We noted that the spectral line intensities of C$_2$H$_3^+$ are very sensitive to discharge conditions. This fact was used for identifying C$_2$H$_4^+$ lines up to $J = 25$; for levels higher than $J = 10$, a perturbation causes the energy levels of the v$_3$ state to deviate significantly from the usual $^2\Pi$ patterns.

After assigning these two groups of lines, we are left with a great many lines which are due to C$_2$H$_5^+$ and possibly a few other carbocations. The strongest of these which we assign to the nonclassical C$_2$H$_5^+$ have the general pattern of the a-type parallel band of a slightly asymmetric rotor, that is, distinct R and P branches spaced at about 2.2 cm$^{-1}$ intervals from the band origin with an increasing number of components as J increases, and a dense Q branch. However, we could not find any series of lines with regular spacings as we find in the spectra of similar ordinary molecules such as
H₂CO and H₂CCH₂. We identify the carrier of this spectrum as C₂H₃⁺ based on the following observations.

A. Spectral patterns

The observed line shapes and widths of the group of lines indicate that they are due to cations containing more than one carbon. The slightly asymmetric rotor pattern with the R and P branch spacings of ~2.2 cm⁻¹ shows that the carrier has two carbon atoms. With the help of ab initio structural predictions by Pople and his colleagues, we can exclude cations with less than two hydrogen atoms such as C₂H⁺ and more than three hydrogen atoms such as C₄H₆⁺; they give too large and too small spacings, respectively. The possibility that the spectrum is due to some unknown electronic transitions of C₂⁺ or C₂⁺ like the 2Π → 2Σ⁺ of C₂⁺ (paper IV) has been negated by the spectrum using a C₂D₂:He mixture. These considerations leave C₂H₂⁺ as the only candidate other than C₂H₃⁺ for the spectrum. The spectral lines of the ν₂-band have been well characterized as mentioned earlier. This leaves two possibilities.

First, the ν₁ + ν₁ → ν₂ hot band of C₂H₂⁺ will give a spectrum with the right spacings; the spectrum will be complicated and unusual because of the Renner–Teller effect. This possibility was negated because of the observed comparable intensities of the spectrum in question and that for the fundamental band of C₂H₂⁺. The value of ν₁ for C₂H₂⁺ has been determined to be 1830 cm⁻¹ by photoelectron spectroscopy. The vibrational temperature must be extremely high (T ~ 3000 K) to account for the relative intensities. While such high vibrational temperatures have been realized for special plasma conditions, it is highly unlikely that the temperature is so high for all the diverse plasma conditions used to take the spectrum. Absence of other bands of comparable intensity supports this conclusion. The second possible spectrum of C₂H₂⁺ is an electronic transition which happens to fall in the infrared region. Being isoelectronic to C₂H and C₂⁺, C₂H₂⁺ may have a low lying 2Σ⁺ electronic state and the 2Σ⁺ → 2Π electronic transition might occur in the infrared region. The case of the extremely complicated C₂H spectrum studied by Curl and his colleagues is well known. We believe that the observed spectrum is due to an excited electronic state in the infrared region. The transitions from the ground state to excited states may occur in the infrared region. The transitions from the ground state to excited states may occur in the infrared region. The transitions from the ground state to excited states may occur in the infrared region.

B. Plasma chemistry

The spectral lines have been observed under different plasma conditions. In general, we found that the C₂H₂⁺ spectrum is always observable while the other coexisting spectra of CH⁺ and C₂H⁺ vary their intensity greatly depending on the plasma condition. When a C₂H₂:He mixture is used, a strong C₂H₂⁺ spectrum is observed if the concentration of H₂ is low, while its intensity decreases drastically when the H₂ concentration is increased (Fig. 3). This is obviously due to the equilibrium of the hydrogen abstraction reaction

$$\text{C}_2\text{H}_2^+ + \text{H}_2 \leftrightarrow \text{C}_2\text{H}_3^+ + \text{H}$$

(1)

which is slightly endothermic ($\Delta H \sim 0.02 \text{ eV}$) for reactants in the ground vibrational state. The rate constant for this reaction, $1.00 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, reported by Smith and Adams is much lower than the Langlevin rate, but is sufficiently fast to shift the equilibrium of Eq. (1) to the right when the H₂ concentration is high. It is critical dependence on plasma conditions of the C₂H₂⁺ spectrum intensity which allowed us to exclude experimentally the possibility that the observed spectrum may be due to some other C₂H₂⁺ transitions. The production of C₂H₂⁺ may occur through various reaction channels. In the He-dominated C₂H₂:He mixtures (~1:20:700), the C₂H₂⁺ ions are produced through the dissociative charge transfer reactions studied by Kim and Huntress.

$$\text{He}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2^+ + \text{H} + \text{He} \quad 7\%$$

$$\rightarrow \text{C}_2\text{H}^+ + \text{H} + \text{He} \quad 25\%$$

$$\rightarrow \text{C}_2^+ + \text{H}_2 + \text{He} \quad 46\%$$

$$\rightarrow \text{CH}^+ + \text{CH} + \text{He} \quad 22\%$$

(2)

with the total rate coefficient of $3.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, followed by the sequence of hydrogen abstraction reactions

$$\text{C}_2^+ \rightarrow \text{C}_2\text{H}^+ \rightarrow \text{C}_2\text{H}_2^+ \rightarrow \text{C}_2\text{H}_3^+,$$

(3)
which all have a large Langevin rate,\(^{46}\) and which stop at C\(_2\)H\(_5\)+. The special stability of C\(_2\)H\(_3\)+ results from the fact that C\(_2\)H\(_3\)+ does not react further with H\(_2\). (The rate constant for this reaction is reported to be less than 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \) by Herbst, Adams, and Smith.\(^{37}\) Although not reported, the metastable He\(^+\) and HeH\(^+\) will cause similar ionization dissociation reactions as those in Eq. (2) and will produce C\(_2\)H\(_3\)+ efficiently. In more H\(_2\)-abundant discharges, C\(_2\)H\(_3\)+ will be produced from ionic hydrogenic species following

\[
\text{C}_2\text{H}_2 + \text{H}^+ \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \quad 9\% \\
\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2 \quad 91\% \tag{4}
\]

with the rate constant of 5.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \(^{45}\) and

\[
\text{C}_2\text{H}_2 + \text{H}^+ \rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2 \quad (5)
\]

with the rate constant of 3.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}.\(^{44}\) We saw the C\(_2\)H\(_3\)+ spectrum in an H\(_2\)-C\(_2\)H\(_2\) mixture without He. In such a case C\(_2\)H\(_3\)+ must be produced by Eq. (5) or by (4) followed by Eq. (1). Recently, Amano\(^{48}\) observed the spectrum of C\(_2\)H\(_3\)+ in a hollow cathode discharge. His C\(_2\)H\(_3\)+ spectrum is free of C\(_2\)H\(_2\)+ absorptions and indicates that C\(_2\)H\(_3\)+ is produced solely from the reaction of Eq. (5). The destruction of C\(_2\)H\(_3\)+ will proceed via electron recombination, ambipolar diffusion, and polymerization reaction with neutral hydrocarbons such as

\[
\text{C}_2\text{H}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_4^+ + \text{H}_2 \tag{6}
\]

The rate constant for this reaction has been measured by Schiff and Bohme\(^{49}\) to be 7.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}. A crude estimate gives a combined destruction rate of \approx 5 \times 10^{-5} \text{ s}^{-1} which leads to the estimated steady state concentration of C\(_2\)H\(_3\)+ of \approx 5 \times 10^{-10} \text{ cm}^3 which, together with the observed intensity, give a transition intensity in rough agreement with the \textit{ab initio} prediction.\(^{16,17}\)

Many other hydrocarbons were used in our effort to maximize the spectral intensities. When other hydrocarbons such as C\(_2\)H\(_4\), C\(_2\)H\(_6\), and C\(_2\)H\(_2\)Br were used instead of C\(_2\)H\(_2\), we obtained spectra with similar intensity and pattern. The reactions similar to those in Eqs. (2) and (3) produce C\(_2\)H\(_3\)+ equally efficiently from these hydrocarbons. For example, according to Kim and Huntress,\(^{45}\)

\[
\begin{align*}
\text{He}^+ + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{He} \quad 7\% \\
\rightarrow \text{C}_2\text{H}_3^+ + \text{H} + \text{He} & \quad 5\% \\
\rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2 + \text{He} & \quad 64\% \\
\rightarrow \text{C}_2\text{H}_3^+ + \text{H} + \text{H} + \text{He} & \quad 13\% \\
\rightarrow \text{CH}^+ + \text{CH}_2 + \text{He} & \quad 12\% \tag{7}
\end{align*}
\]

with the total rate constant of 3.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}. The detailed values of the branching ratio may depend on discharge conditions, but as long as the majority of ions are produced as C\(_2\)H\(_3\)+ (0 \leq n \leq 3), they will end up in C\(_2\)H\(_3\)+ through the reactions in Eq. (3).

For the liquid N\(_2\)-cooled plasmas we used CH\(_4\)-H\(_2\)-H\(_2\) mixtures. The reaction here is perhaps much more complicated. Diatomic or polyatomic hydrocarbon species are produced in the discharge and some are frozen on the wall. Such hydrocarbons react with He\(^+\), He\(^*\), HeH\(^+\) to produce C\(_2\)H\(_4\)+. The spectrum could also be observed with no hydrocarbon parent compound at all so long as the cell was coated with carbon-type deposit produced by running the discharge for sometime with hydrocarbon parent compounds.

When equal amounts of H\(_2\) and D\(_2\) are used instead of H\(_2\), the CH\(_3\)+ spectrum showed a statistical decrease by a factor of 8, while the decrease of intensity in the C\(_2\)H\(_3\)+ is less, about a factor of 4. This is understandable because the deuterium exchange reaction

\[
\text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2 \tag{8}
\]

proceeds with the Langevin rate,\(^{50}\) while the corresponding reaction

\[
\text{C}_2\text{H}_3^+ + \text{HD} \rightarrow \text{C}_2\text{H}_2\text{D}^+ + \text{H}_2 \tag{9}
\]

has a much lower rate.\(^{51}\) A similar lower rate of isotope exchange has been observed for C\(_2\)H\(_4\)+.\(^{52}\) When C\(_2\)D\(_2\) was substituted for C\(_2\)H\(_2\), no spectral lines were found in the region of 3000−2900 cm\(^{-1}\) eliminating the possibility that the spectrum is due to a pure carbon ion.

All these chemical observations are consistent in supporting our assignment of the spectrum to C\(_2\)H\(_3\)+.

IV. ASSIGNMENT AND THE EVIDENCE FOR THE BRIDGED STRUCTURE

Although the observed spectrum has no regular series of lines, a preliminary assignment of the spectrum was made by using the general resemblance of the observed spectrum with a parallel band spectrum of a slightly asymmetric prolate rotor. After several attempts we arrived at an assignment with numerous uncertainties and diverse possibilities of alternative assignments. If the spectrum was of the perpendicular type, strong Q branch lines would have assisted the assignment through the four-line combination differences of the type

\[
\nu_{P(J)} + \nu_{R(J+1)} = \nu_{Q(J)} + \nu_{Q(J+1)} \tag{10}
\]

but the observed weak, highly congested Q branch lines shown in Fig. 5 did not allow us to use this relation to help assignment. Only after a definitive assignment was made did we pick up some such relations.

We arrived at a more definitive assignment in March 1987 when we realized the simple fact that the ground state combination differences, that is,

\[
\nu_{P(J+1)} - \nu_{R(J+1)} = \nu_{P(J)} - \nu_{R(J)} - E_{J+1} - E_{J-1} \tag{11}
\]

fit well to the asymmetric rotor pattern. The fitting was particularly good for K-doublet transitions with K = 1 and allowed us to assign these transitions with confidence. This enabled us also to assign some K = 0 and K = 2 transitions. However, transitions with K > 2 have not been assigned with confidence. The spectral lines ascribed to C\(_2\)H\(_3\)+ are listed in Table I. Only a fraction of the lines (marked \(\star\) in the Table) have been rotationally assigned with certainty, but they exhaust most of the stronger lines. The ground state combination differences of Eq. (14) and their fitting to the asymmetric rotor pattern are given in Table II. It is noted that the ground state combination differences fit well for K = 0 and K = 1. We interpret this result as indicating that at least for
low $K$ values, C$_2$H$_3^+$ behaves like a usual nearly rigid rotor in the ground vibrational state and the observed anomalous spectral pattern results mainly from the excited state. The assignment thus obtained has enabled us to conclude that the C$_2$H$_3^+$ ions producing these spectral lines have the nonclassical structure. The three characteristics of the spectrum used to derive this conclusion are summarized in the following subsections.

A. Spin statistics and $K$ doublets

The clearest evidence for the nonclassical structure is the intensity alternation of the $K$-doublet pattern for $K = 1$. If rigid structures are assumed, both the classical and the nonclassical structures have two equivalent protons and thus have the ortho and the para species with a spin statistical weight of 3 to 1. How the statistical weight appears as intensity alternation of spectral lines depends on the direc-
TABLE I. Observed spectral lines of the antisymmetric C–H stretching band of the nonclassical C$_2$H$_4^+$ (in cm$^{-1}$). Only assigned lines are listed. Those with an asterisk are firm assignments. Others are tentative.

<table>
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<th>Transition$^*$</th>
<th>Frequency</th>
<th>Transition$^*$</th>
<th>Frequency</th>
<th>Transition$^*$</th>
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</tbody>
</table>

$^*$ The symmetry of rotational levels in the ground state is shown.

ition of the $C_3$ symmetry axis which permutes the equivalent protons. It is seen in Fig. 1 that for the classical structure such an axis lies along the $a$ axis (with the smallest moment of inertia) while for the nonclassical structure it is along the $b$ axis. Therefore when the asymmetric rotor energy level is specified by the conventional $J, K_a, K_c$ notation, the ortho and the para spin modifications are combined with rotational levels with $K_a = 0$ and even, respectively, for the classical structure, but with $K_a + K_c = 0$ and even, respectively, for the nonclassical structure. In the former case, both of the components of the $K = 1 K$ doublet (transitions starting from $J_{1, J = 1}$ have stronger intensity than the corresponding transitions starting from $J_{1, J = 1}$ if $J$ is odd and weaker intensity of $J$ is even. This clearly indicates that the C$_2$H$_4^+$ molecules producing the spectrum have the $C_3$ symmetry axis along the $b$ axis, i.e., the nonclassical (bridged) structure. It is observed that the intensity components belong to different species and have different spin weights. Since other factors determining the relative intensities for the $K$ doublet are nearly equal for a slightly asymmetric rotor, this qualitative difference of the intensity pattern distinguishes the spectra of the classical and nonclassical species. A computer-generated stick diagram of observed low $J, P$, and $R$ branch lines is shown in Fig. 5. It is seen that the transitions starting from $J_{1, J = 1}$ have stronger intensity than the corresponding transitions starting from $J_{1, J = 1}$. If $J$ is odd and weaker intensity of $J$ is even. This clearly indicates that the C$_2$H$_4^+$ molecules producing the spectrum have the $C_3$ symmetry axis along the $b$ axis, i.e., the nonclassical (bridged) structure.
TABLE II. Ground state combination differences and rotational constants (in cm⁻¹).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Combination Difference</th>
<th>Rotational Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>3₁₋₁₁</td>
<td>10.698 (3)*</td>
<td>3₂₁₋₁₀₁</td>
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<tr>
<td>3₂₋₁₂</td>
<td>11.176 (3)</td>
<td>5₂₀₋₃₀₃</td>
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<td>4₁₋₂₋₂₂</td>
<td>14.981 (1)</td>
<td>6₀₀₋₄₀₄</td>
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<td>19.261 (1)</td>
<td>7₀₀₋₅₀₅</td>
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<td>20.118 (0)</td>
<td>3₂₁₋₁₁₀</td>
</tr>
<tr>
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<td>23.538 (3)</td>
<td>3₂₁₋₁₁₀</td>
</tr>
<tr>
<td>7₋₃₋₃₂</td>
<td>27.808 (1)</td>
<td>3₂₁₋₁₁₀</td>
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<td>29.053 (2)</td>
<td>3₂₁₋₁₁₀</td>
</tr>
<tr>
<td>8₋₅₋₅₁</td>
<td>32.081 (4)</td>
<td>3₂₁₋₁₁₀</td>
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<td>9₋₆₋₆₁</td>
<td>33.516 (2)</td>
<td>3₂₁₋₁₁₀</td>
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<td>37.957 (1)</td>
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<td>1₃₋₁₁₋₁₀</td>
<td>64.650 (5)</td>
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</tr>
<tr>
<td>1₆₋₁₆₋₁₆</td>
<td>66.153 (2)</td>
<td>3₂₁₋₁₁₀</td>
</tr>
</tbody>
</table>

\[ B = 1.14195 (21)* \]
\[ D_{J} = 1.61(44) \times 10^{-6} \]
\[ D_{K} = 1.63(68) \times 10^{-4} \]

*The numbers in parentheses are calculated minus observed values.
*The two independent values are obtained from \( R(J - 1) - Q(J) \) and \( Q(J) - P(J + 1) \).
*The numbers in parentheses are 3σ.

The ratio of the two components is actually closer to 2:1 rather than 3:1. This is related to the tunneling motion of the three protons which we will discuss in Sec. V A.

B. The ground state rotational constants

The rotational constants of C₂H₂⁺⁺ in the ground state are determined from the fitting given in Table II. Since the observed transition is of parallel (ΔKₕ = 0) α-type, the largest rotational constant \( A \) was not obtained. The pure rotational transition is of β-type and the \( A \) constant is needed for its prediction for future laboratory experiments and for astronomical observation. The best we can do at this stage is to calculate \( A \) based on an estimated inertial defect. Assuming the inertial defect of C₂H₄⁺⁺ to be the same as that of vinyl radical recently studied by Hirota and his colleagues, \( D_{0} = 0.0738 \text{ amu Å}^{2} \), \( D_{0} = 0.056 \text{ amu Å}^{2} \) for H₂CO \( 20 \) and \( D_{0} = 0.049 \text{ amu Å}^{2} \) for C₂H₄ \( 20 \) we obtain

\[ A = 13.24 \text{ cm}^{-1}, \quad B = 1.14195 (21) \text{ cm}^{-1}, \quad C = 1.04645 (21) \text{ cm}^{-1} \]

which agree well with the rotational constants of the nonclassical structure theoretically predicted by Lee and Schaefer \( 17 \):

\[ A = 13.79 \text{ cm}^{-1}, \quad B = 1.13 \text{ cm}^{-1}, \quad C = 1.04 \text{ cm}^{-1}, \]

and \( A = 13.41 \text{ cm}^{-1} \) by Lindh, Roos, and Kraemer. \( 20 \) The predicted constants for the classical structure are

\[ A = 9.29 \text{ cm}^{-1}, \quad B = 1.08 \text{ cm}^{-1}, \quad C = 0.97 \text{ cm}^{-1}, \]

which differs significantly from our experimental value.

These results give the second evidence that the carrier of the spectrum is C₂H₂⁺⁺ with the nonclassical structure.

C. Other vibrational bands

In doing the spectroscopy of carbo-ions we have thoroughly searched for spectral lines in the region between 3300 and 2700 cm⁻¹. The spectral band discussed in this paper which has its band origin at 3141 cm⁻¹ has been the only one which can be assigned to C₂H₂⁺⁺. This is consistent with our conclusion that C₂H₂⁺⁺ has the nonclassical structure in light of Lee and Schaefer’s theory. \( 17 \). For the nonclassical structure there are only two singly bonded C–H bonds. The antisymmetric stretching vibration which has a large vibration-induced dipole moment is the observed band. The symmetric stretching has a very small dipole moment because it corresponds to the infrared inactive symmetric stretching vibration of acetylene; the attached proton scarcely bends the molecule as shown in Fig. 1. The nonclassically bound proton at the apex of the triangle has much longer C–H bonds and a much lower vibrational frequency than the isolated C–H bond. On the contrary, the classical structure has three isolated C–H bonds and each remains strongly infrared active. Lee and Schaefer’s theory predicts three infrared active bands at 3179 cm⁻¹ (end C–H), 2954 cm⁻¹ (sym. C–H) and 3040 cm⁻¹ (asym. C–H) with intensities 125.4, 234.8, and 171.1 (km/mol), respectively, for the classical structure. The observed spectrum matches their prediction for the nonclassical structure and gives the third evidence for our conclusion.

V. SPLIT LINES AND EVIDENCE FOR TUNNELING

After the analysis given so far, the question remains as to what is causing the observed anomaly of the spectrum. Is it because of perturbations by other vibrational states? (It has been observed that even for simpler molecular ions CH⁺ and C₂H⁺⁺, some spectral anomaly results from perturbation for high J levels. \( 20 \).) Since C₂H₂⁺⁺ is more complicated with nine modes of vibration, the probability of perturbation is higher.) Or is it because of the tunneling exchange of the apex proton and the end protons in the nonclassical structures (organic chemist’s rearrangement)? In this sec-

![Fig. 5. Conjected Q'branch transitions typical for a parallel bond of a slightly asymmetric rotor. Only a small fraction of them are assigned: d(1, -1, 0), d(4, -4, 0), e(3, -3, 0), d(2, -2, 0), e(3, -3, 1). 1 and 2 are CH⁺⁺ lines Q(5, 4) and Q(6, 4), respectively. The upper trace shows the reference spectrum of C₂H₂ and frequency markers from a spectrum analyzer.](image-url)
tion we present what we believe is observational evidence for such tunneling in the excited state. Again, it is a qualitative feature of the observed spectrum which gives the most definitive evidence for the tunneling. We first review a symmetry argument applied to this problem. 26, 27

A. Tunneling and the spin statistical weight

As discussed in Sec. IV A, if a rigid molecular structure is assumed, the nonclassical structure has two equivalent protons and the levels are classified into ortho (I = 1) and para (I = 0) spin modifications, which have the spin weight of 3 and 1, respectively. Here I is the total spin quantum number corresponding to \( I = I_1 + I_2 \). However, if the proton at the apex of the triangle of the bridge may interchanging with one of the other two protons by some mechanism, and if the effect of this tunneling motion is spectroscopically resolved (Longuet-Higgins’ feasibility \(^{27} \)), then we have to treat all three protons as equivalent particles; the two proton problem now becomes a three proton problem. For a three proton problem, the ortho and the para species correspond to the total spin quantum number of \( I = 3/2 \) and \( 1/2 \) and the spin statistical weight of 4 and 2, respectively, as for \( H_2^+ \) and \( CH_3^+ \). Thus, if we can determine experimentally whether the relative intensities of the two components of the \( K = 1 \) doublet are 2:1 instead of 3:1, we have the evidence for tunneling. As mentioned earlier in Sec. IV A this indeed seems to be the case although the relative intensity of two lines separated by several tenths of a cm\(^{-1} \) is not easy to measure accurately especially in a congested spectral region. More convincing evidence is given by our observation of the splitting of spectral lines into two components with the intensity ratio of 2:1. This is based on the following simple group theoretical argument given earlier in Refs. 26 and 27.

For the rigid nonclassical \( C_2H_7^+ \), the symmetry of vibrational levels is classified according to a group composed of four permutation–inversion operations \(^5 \) \{ \( E, \ (12) \ (ab), \ E^*, \ (12) (ab)^* \) \} where the operation \( (12) \) represents the permutation of the two equivalent protons while \( (ab) \) that of the carbon nuclei; the operation \( E^* \) represents the space inversion. This group is isomorphic to the \( C_{2v} \) point group and has the four irreducible representations \( A_g, A_u, B_1, \) and \( B_2 \). The symmetry of the asymmetric rotor wave function corresponding to the \( J_{K,K} \) level is classified according to whether \( K_g \) and \( K_u \) are even or odd. The relations are

\[
(e,e) \rightarrow A_1, \ (a,a) \rightarrow A_2, \ (e,a) \rightarrow B_1, \ (e,a) \rightarrow B_2.
\]

Here we use the convention that \( B_2 \) corresponds to the representation which is antisymmetric with respect to \( E^* \). Now, if an interchange of protons, which are inequivalent in the rigid structure, is allowed, we must invoke the full permutation–inversion group

\[
G_{24} = S_3 \times S_3 \times E^*, \quad (12)
\]

where \( S_n \) is the symmetry group for \( n \) particles and \( E^* = \{ E, E^* \} \). This group is composed of 24 permutation–inversion operations \( \{ E, 2(123), 3(12), \ (ab), 2(123), 3(ab)(12), E^*, 2(123)^*, 3(12)^*, \ (ab)^*, 2(ab)(123)^*, 3(ab)(12)^* \} \). The group is isomorphic to the \( D_{3h} \) point group and has 12 irreducible representations,

\[ A_1, A_2, E^*, A_1^+, A_2^+, E^+, A_1^+ \ , A_2^+ , E^+ \text{ where } \pm , \ \sqrt{2} , (g,u) , (1,2) \text{ and } (A,E) \text{ discriminate symmetry with respect to the parity operation } E^* , \text{ the carbon permutation } (ab) , \text{ the proton exchange } (12) \text{, and permutation } (123) \text{, respectively. The correlation between the symmetry of rotational wave functions using the two groups is worked out as}^{58} (\text{Table IV, Ref. 26}) \]

\[
K_a \quad K_c \quad \text{Rigid} \quad \text{Nonrigid}
\]

\[
e \ e \ A_1 \ A_1^+ \ + \ A_2^+ \ + \ E^+ \ + \ E^+
\]

\[
o \ o \ A_2 \ A_1^+ \ + \ A_2^+ \ + \ E^+ \ + \ E^-
\]

\[
o \ e \ B_1 \ A_1^+ \ + \ A_2^+ \ + \ E^+ \ + \ E^-
\]

\[
o \ e \ B_2 \ A_1^+ \ + \ A_2^+ \ + \ E^+ \ + \ E^-
\]

The usual symmetry arguments \(^{57,59,60} \) show that, for \( C_2H_3^+ \), the symmetry of the total wave function should be either \( A_1^+ \) or \( A_2^+ \) and that of the spin wave function is \( 4A_1^+ + 2E^+ \). Multiplying the symmetry of the rotational wave function and that of the spin wave function, and imposing the symmetry requirement of the total wave function, we note that only rotational species belonging to \( A_1^+ \) and \( E^+ \) are allowed. None of the ungerade species is allowed for the obvious reason that the carbon nuclei, being a boson with \( I = 0 \), require only the symmetric state. We thus obtain the correlation with the statistical weight listed in Table III. We note that the para, \( (ee) \) and \( (oo) \), levels do not split further as a result of the tunneling, but the ortho, \( (oe) \) and \( (eo) \), levels which have the statistical weight of 3 for a rigid species split into two levels \( A \) and \( E \) with the statistical weights of 2:1. It is the observation of this splitting which convinces us of the presence of tunneling.

For the isotopically substituted \(^{13}C_2H_3^+ \), the situation is more complicated because the \(^{13}C \) nucleus is a fermion with \( I = 1/2 \) and both \( gerade \) and \( ungerade \) states are allowed. The total wave function must be of symmetry of either \( A_1^+ \) or \( A_2^+ \) and the spin wave function \( 12A_1^+ \ + \ 4A_2^+ \ + \ 6E^+ \ + \ 2E^-. \) The correlations of the symmetry and the statistical weight are given in Table III. It is noted that this species should show many more split lines. This is indeed the case as given below.

B. Observed splittings

Some examples of the observed \( A-E \) splittings are shown in Fig. 6. Because of the crowded spectrum, it would

---

**TABLE III. Symmetry and statistical weight correlations between rigid and nonrigid \( C_2H_3^+ \) and \( ^{13}C_2H_3^+ \)**

<table>
<thead>
<tr>
<th>( K_a )</th>
<th>( K_c )</th>
<th>( \text{Rigid} )</th>
<th>( \text{Nonrigid} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e \ e )</td>
<td>( 2A_1 )</td>
<td>( 2E^+ )</td>
<td></td>
</tr>
<tr>
<td>( o \ o )</td>
<td>( 2A_2 )</td>
<td>( 2E^- )</td>
<td></td>
</tr>
<tr>
<td>( e \ o )</td>
<td>( 6B_1 )</td>
<td>( 4A_1^+ + 2E^+ )</td>
<td></td>
</tr>
<tr>
<td>( e \ o )</td>
<td>( 6B_2 )</td>
<td>( 4A_2^+ + 2E^+ )</td>
<td></td>
</tr>
<tr>
<td>( e \ e )</td>
<td>( 20A_1 )</td>
<td>( 12A_1^+ + 2E^+ + 6E^- )</td>
<td></td>
</tr>
<tr>
<td>( o \ o )</td>
<td>( 20A_2 )</td>
<td>( 12A_2^+ + 2E^+ + 6E^- )</td>
<td></td>
</tr>
<tr>
<td>( e \ o )</td>
<td>( 12B_1 )</td>
<td>( 4A_1^+ + 2E^+ + 6E^- )</td>
<td></td>
</tr>
<tr>
<td>( e \ e )</td>
<td>( 12B_2 )</td>
<td>( 4A_2^+ + 2E^- + 6E^- )</td>
<td></td>
</tr>
</tbody>
</table>

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not be easy to recognize the splittings simply from the spectral pattern without additional evidence. Here again the ground state combination differences are utilized to identify splitting pairs. As observed in Fig. 6, we see a pair of splittings in the $R(J - 1)$ transition and in the $P(J + 1)$ transition which have both equal spacings and corresponding 2:1 intensity ratios. This indicates that the $A-E$ splittings in the ground state are negligible compared with our spectral resolution, and the observed spectral splitting results solely from the $A-E$ splittings of levels in the excited state. This situation is shown schematically in Fig. 7. The observed $A-E$ splittings are summarized in Table IV. Some satellite lines are not definitely identified because of overlapping transitions, but at least for upper components of the $K = 1$ $K$ doublets (related to $J_{1,0}$ with $J$ even in the excited state), the agreement between the $R$ and $P$ transitions and the intensity ratios of 2:1 are observed generally and consistently to convince us that the splitting is due to the tunneling.

In the spectrum of $^{13}$C$_3$H$_4^+$, we have observed more splittings as was expected from the symmetry argument. A comparison of the spectrum of the normal species and that of the isotopic species is shown in Fig. 8. While the detailed study of the $^{13}$C$_3$H$_4^+$ spectrum is outside the scope of this paper, the increase in the number of the spectral components is obvious, thus supporting the tunneling picture.

VI. ESTIMATE OF THE BARRIER HEIGHT

While the observational evidence and the analysis given in Sec. IV show that the nonclassical structure is lower in energy than the classical structure, we have no experimental information on the classical structure. Does it have a potential minimum? If it does, how deep is it? The only conclusion we can draw from our observation is that it cannot have a potential minimum comparable to that for the nonclassical structure as predicted by some theory. As we discussed in Sec. V, however, there is an evidence that the three protons exchange their equilibrium positions. If we can assume planarity of the molecule during this tunneling, as organic chemists usually do (and also theoretically predicted by Weber, Yoshimine, and McLean), the configuration must pass through the classical structure during the proton tunneling process as shown on the left in Fig. 9. Thus if we can estimate the barrier height for tunneling, the value would give the upper limit for the energy difference between the classical and the nonclassical structures. One such estimate is given in this section using the internal rotation model proposed by Hougen.

A. The internal rotation model

If we treat the problem of proton tunneling in general, we have at hand a nine-dimensional dynamical problem even for a fixed C–C frame. We assume the planarity of the proton rearrangement as shown on the left in Fig. 9. In this model, the rearrangement of protons goes through the classical structure regardless of whether there is a potential minimum or not. Even in this simplified case, however, we still have a six-dimensional dynamical problem. Hougen's model reduces this to a tractable one-dimensional problem by assuming a rigid equilateral triangle configuration for the three protons and the coplanarity of the triangle and the C–C
bond. In this model, the tunneling motion can be depicted as
on the right in Fig. 9. This model makes the calculation simple
because the three rotational constants $A$, $B$, and $C$ do not
depend on the internal rotation angle $\alpha$. This is obviously a
very crude approximation but we adopt it here for our esti-
mate of the tunneling barrier height. The semirigid bender
model by Escribano and Bunker26,28 and other more so-
plicated models may be needed for a more accurate
description of this problem.

Once Hougen's model is adopted, the problem becomes
mathematically equivalent to the internal rotation dynamics
studied by microwave spectroscopists over many years.51-67
The case in hand is similar to the sixfold barrier problem of
CH$_3$BF$_2$62 or CH$_3$NO$_2$63 except that C$_2$H$_3^+$ is planar. The
tunneling motion shown in Fig. 9 is only a portion of the
whole potential which consists of six equivalent nonclassical
structures. The Hamiltonian for the rotation–internal-rota-
tion problem (in cm$^{-1}$) can be written as

\[ H = AJ_x^2 + BJ_y^2 + C'J_z^2 \]

\[ + F^2 + V_6(1 - \cos 6\alpha)/2 \]

\[ + V_{12}(1 - \cos 12\alpha)/2, \]

where $J_x$, $J_y$, and $J_z$ are the components of the dimension-
less rotational angular momentum $J$ along the principal axes of inertia for the nonclassical structure, and $J$ is the angular
momentum of the internal rotation defined in terms of the
kinetic energy and the internal rotation angle $\alpha$ as $\hbar J$

---

**TABLE IV.** Observed splittings ($v_{4} - v_{E}$ in cm$^{-1}$) and relative intensities ($I_{4}/I_{E}$) of the antisymmetric

<table>
<thead>
<tr>
<th>$R$</th>
<th>$v_{4} - v_{E}$</th>
<th>$I_{4}/I_{E}$</th>
<th>$P$</th>
<th>$v_{4} - v_{E}$</th>
<th>$I_{4}/I_{E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2_{10} - 1_{10}$</td>
<td>0.2070</td>
<td>2.1</td>
<td>$2_{11} - 3_{12}$</td>
<td>0.2074</td>
<td>1.7</td>
</tr>
<tr>
<td>$2_{00} - 1_{01}$</td>
<td>0.3421</td>
<td>2.3</td>
<td>$2_{01} - 3_{03}$</td>
<td>0.3397</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$4_{11} - 5_{14}$</td>
<td>0.0561</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>$4_{01} - 5_{03}$</td>
<td></td>
<td>$4_{03} - 5_{03}$</td>
<td>0.0630</td>
<td>2.1</td>
</tr>
<tr>
<td>$8_{15} - 7_{14}$</td>
<td>-0.0579</td>
<td>2.2</td>
<td>$6_{14} - 7_{16}$</td>
<td>-0.0604</td>
<td>2.2</td>
</tr>
<tr>
<td>$8_{16} - 7_{16}$</td>
<td>0.0220</td>
<td>3.3</td>
<td>$7_{17} - 8_{18}$</td>
<td>0.1006</td>
<td>2.2</td>
</tr>
<tr>
<td>$10_{8} - 9_{8}$</td>
<td>0.0529</td>
<td>2.2</td>
<td>$9_{18} - 9_{18}$</td>
<td>0.0225</td>
<td>2.6</td>
</tr>
<tr>
<td>$11_{11} - 10_{10}$</td>
<td>0.1472</td>
<td>4.7</td>
<td>$11_{11} - 12_{12}$</td>
<td>0.1479</td>
<td>2.5</td>
</tr>
<tr>
<td>$12_{13} - 11_{10}$</td>
<td>0.0791</td>
<td>2.3</td>
<td>$12_{11} - 13_{12}$</td>
<td>0.0791</td>
<td>2.0</td>
</tr>
<tr>
<td>$14_{13} - 13_{12}$</td>
<td>0.0427</td>
<td>2.1</td>
<td>$14_{13} - 15_{14}$</td>
<td>0.0421</td>
<td>1.7</td>
</tr>
<tr>
<td>$15_{15} - 14_{14}$</td>
<td>-0.1044</td>
<td>3.4</td>
<td>$15_{15} - 16_{16}$</td>
<td>-0.1036</td>
<td>2.9</td>
</tr>
</tbody>
</table>

---

**FIG. 8.** A comparison of the R(6) transitions of C$_2$H$_3^+$ and $^{13}$C$_2$H$_3^+$. The latter transitions split into more components because of the symmetry argument summarized in Table III.

**FIG. 9.** Rearrangement of the nonclassical and classical structure (left) and the simplified internal rotation model of Hougen. The pictures show one-sixth of the total rearrangement/internal rotation cycle.
\[ \frac{\partial T}{\partial \alpha} \]. The rotational constants in Eq. (13) are expressed in terms of the moment of inertia \( I \) of the C–C frame and the moment of inertia \( I_a \) of the proton triangle around the \( C_2 \) axis as

\[
A = \frac{h}{8\pi^2 c(I_a/2)}, \quad B = \frac{h}{8\pi^2 c(I + I_a/2)}, \quad C' = \frac{h}{8\pi^2 c I}, \quad \text{and} \quad F = \frac{h}{8\pi^2 c I I_a/(I + I_a)}. \tag{14}
\]

Note that the \( C' \) constant defined here is the rotational constant for the carbon frame and is larger than the rotational constant given earlier in Table II by \( C'^{1/2}/F \). We use the numerical values of \( C' = 1.845 \text{ cm}^{-1} \) and \( F = 4.237 \text{ cm}^{-1} \) calculated from the \textit{ab initio} structure predicted by Lee and Schaefer.\textsuperscript{17} The \( V_{12} \) term in Eq. (13) represents the deviation of the potential from the sixfold symmetry due to the possible stability of the classical structure. Two possible cases are shown in Fig. 10.

The cases of molecules with the sixfold barrier so far studied by microwave spectroscopists always corresponded to low barrier cases\textsuperscript{62,63} in which the barrier height \( V_0 \) is much lower than the vibrational frequencies. For such a case quantum states corresponding to high \( J \) values appear in the spectrum. Hougen's computer program also handles such cases. The approximate asymmetric rotor patterns observed in our case, however, indicate that what is at hand is closer to the high barrier case. We thus can estimate the barrier height from the observed splitting using the classical procedure developed by Wilson\textsuperscript{62,64} and Herschbach.\textsuperscript{65} For the ground state we can set an upper limit for the splitting and thus give the lower limit of the barrier. Thus we treat the coupling term \(-2C'J_c J_c\) as the perturbation for a high barrier case. The set of torsional wave functions which diagonalize the Hamiltonian

\[
H_{tr} = FJ^2 + V_\phi(1 - \cos 6\alpha)/2
\]

are used for the perturbation. The \( V_{12} \) term in Eq. (13) is neglected in the present treatment because it is not possible to separate the effect of \( V_0 \) and \( V_{12} \) from the observed splitting.\textsuperscript{63} \textit{Ab initio} calculations\textsuperscript{18,19} predict that this assumption is not unreasonable. After the perturbation treatment, the effective Hamiltonian is

\[
H = H_0 + H'
\]

with the asymmetric rotor Hamiltonian

\[
H_0 = AJ_a^2 + BJ_b^2 + CJ_c^2
\]

and the additional term

\[
H' = -2C' \langle \sigma | J \| \sigma \rangle J_c + 4C'^{1/2} \sum_\sigma \frac{\langle \sigma | J \| \sigma' \rangle^2}{E_{\sigma \sigma} - E_{\sigma' \sigma}} J_c^2,
\]

where the quantum numbers \( \sigma \) and \( \sigma' \) specify vibrational and torsional sublevels, respectively, and \( E_{\sigma \sigma} \) is the eigenvalue.

Equation (16) can be rewritten in Herschbach's form:

\[
H_{\sigma \sigma'} = AJ_a^2 + BJ_b^2 + CJ_c^2 + F \left( W_{\sigma \sigma'}^{(1)} \frac{C'}{F} J_c + W_{\sigma \sigma'}^{(2)} \frac{C'^{1/2}}{F} J_c^2 \right),
\]

where \( C = C' + C'^{1/2}/F \) is now the usual rotational constant and

\[
W_{\sigma \sigma'}^{(1)} = -2 \langle \sigma | J \| \sigma \rangle J_c
\]

and

\[
W_{\sigma \sigma'}^{(2)} = 1 + 4F \sum_\sigma \frac{\langle \sigma | J \| \sigma' \rangle^2}{E_{\sigma \sigma} - E_{\sigma' \sigma}}.
\]

**B. Application to \( C_2H^+ \)**

The values of \( W_{\sigma \sigma'}^{(1)} \) and \( W_{\sigma \sigma'}^{(2)} \) in Eq. (18) as functions of barrier height are listed for the case of the threefold barrier in the table of internal rotation problem.\textsuperscript{66} Herschbach's general relation

\[
W_{\sigma \sigma'}^{(n)} = f^{n-2} W_{\sigma \sigma'}^{(n)}
\]

is conveniently used to relate the eigenvalues for the threefold barrier and those for the sixfold barrier case. The allowed \( A_{2g} \) and \( E_g \) states correspond to \( \sigma = 0 \) and \( \sigma = \pm 2 \), respectively, for the sixfold barrier.

When the \( W_{\sigma \sigma'}^{(1)} \) term in Eq. (18) is treated as an off-diagonal perturbation (\( \Delta K_c = \pm 1 \)) for the asymmetric rotor Hamiltonian and its magnitude examined, we note that its effect is negligible compared with that for \( W_{\sigma \sigma'}^{(2)} \). We thus find that the splittings between the \( A_{2g} \) and \( E_g \) levels are ascribed to the difference between the effective \( C \) constants due to the different \( W_{\sigma \sigma'} \) values for the two levels. For the upper \( K \) doubling component of \( K = 1 \), where the splittings are most systematically noted, we have
\[ \Delta \nu = (C_A - C_E) \left[ J(J + 1) - 2 \right]/4, \]

where

\[ C_A - C_E = \frac{C^{2}}{F} \left[ W^{(2)}_{\nu_0,0} - W^{(2)}_{\nu_{0}, \pm 2} \right]. \]

The observed splittings listed in Table IV do not follow this simple relation. The simple \( J(J + 1) \) dependence is not obvious and low \( J \) levels show large splittings. The observed values of \( \Delta \nu \) even changes sign with \( J \). In order to explain such complicated behavior, a much more sophisticated theory appears to be necessary. The best we can do at this stage is to estimate the approximate barrier height using the order of magnitude of the splitting. If we take \( \Delta \nu \sim 0.06 \text{ cm}^{-1} \) (0.5 ns) for \( J = 10 \) as a typical value, we obtain the barrier height of \( V_0 \sim 1400 \text{ cm}^{-1} \) (4.0 kcal/mol) for the \( \nu_0 \) state and this gives the approximate energy difference between the classical and nonclassical structures in the \( \nu_0 \) state. The tunneling splitting is a very sensitive function of the barrier height and, conversely, the barrier height is rather insensitive to the values of splitting. If we use the double or half value of the splitting used above we obtain approximate barrier heights of \( V_0 \sim 1200 \) and \( 1600 \text{ cm}^{-1} \), respectively. The anomalously large values of splittings for low \( J \) values listed in Table IV cannot be explained with the present model. For those we need some effective coupling terms of the form

\[ \alpha J_a \text{ or } \beta (J_b J_c + J_c J_b). \]

For the ground vibrational state the splitting was not measurable, and we can estimate only the lower limit of the barrier height. Setting the upper limit of the observed level splitting as \( \Delta \nu < 0.005 \text{ cm}^{-1} \) and using the internal rotation model, we obtain the lower limit \( V_0 > 2100 \text{ cm}^{-1} \) (6.0 kcal/mol) which is also the lower limit for the energy difference between the classical and nonclassical structure.

**VII. SUMMARY**

The dynamical problem of the proton tunneling encountered in the analysis of the observed spectrum of \( \text{C}_2\text{H}_3^+ \) seems to be unique among the large amplitude problems studied so far in high resolution spectroscopy. It is similar to the cases of the inversion motion in \( \text{NH}_3 \) and \( \text{H}_2\text{O}^+ \) or the internal rotation in \( \text{CH}_2\text{OH} \) and \( \text{CH}_2\text{CHO} \) in that protons tunnel between separate equilibrium positions, but is conceptually different in that the chemical bonds are broken in the process. Unlike the cases of large amplitude motions in hydrogen bonded molecules such as the HF dimer \(^{72-74}\) and the \( \text{H}_2\text{O} \) dimer \(^{75,76}\) van der Waals molecules, \(^77\) and ion clusters such as \( \text{ArH}_3^+ \) \(^{78,79}\) where the system is composed of two weakly bound parts, the three protons in \( \text{C}_2\text{H}_3^+ \) are strongly bound to the \( \text{C}_2 \) frame (the proton affinity of \( \text{C}_2\text{H}_3 \) is \( 6.5 \text{ eV}, -150 \text{ kcal/mol} \(^{80}\)). Such motions have been considered for very high vibrationally excited states of \( \text{C}_2\text{H}_3 \), but for \( \text{C}_2\text{H}_3^+ \) the effect of the motion is visible in the fundamental band. This seems to be a unique problem for some molecular cations with "one proton too many." It is fortunate that \( \text{C}_2\text{H}_3^+ \) introduces us to this type of problem because here we have a "moderate" case in that the effect of tunneling complicates the spectrum but does not totally wipe out the asymmetric rotor pattern. Similar cases will be observed for other carbocations. Some cases, for example, the spectrum of protonated methane, \( \text{CH}_4^+ \), may be much more complex because of the rearrangement of five protons and the lower barrier.

From the analysis given in this paper the following conclusions are made.

(A) Identification: We have observed the \( \nu_0 \) fundamental band (antisymmetric \( \text{C}-\text{H} \) stretching mode) of \( \text{C}_2\text{H}_3^+ \) with the band origin at \( 3142.2 \text{ cm}^{-1} \). This is based on the spectral pattern and the spectral intensity response to plasma chemistry.

(B) Structure: The spectrum is due to \( \text{C}_2\text{H}_3^+ \) with nonclassical (bridged) structure. This is based on (a) the spin statistical weight of the observed \( K = 1 \) doublets, (b) the values of the ground state constants, and (c) absence of other equally strong vibrational bands in the region between 3300 and 2700 \text{ cm}^{-1} \).

(C) Dynamics: The two equivalent end protons and the apex proton exchange their equilibrium positions and the effect of this tunneling is spectroscopically resolved in the excited state.

While this study establishes that the nonclassical structure is more stable than the classical structure, it does not give any direct experimental evidence as to the stability of the latter. We used Hougen's simplified model of one-dimensional internal rotation and estimated the effective barrier height to be \( V_0 \sim 1400 \text{ cm}^{-1} \) for the \( \nu_0 \) state and \( V_0 \geq 2100 \text{ cm}^{-1} \) for the ground state. These values also give the estimates of energy difference between classical and nonclassical structures if planarity of arrangement between the two structures may be assumed. The barrier being so low, it is not likely that the classical structure has a sufficient potential minimum to accommodate zero point motion of the protons, but a definitive conclusion should await more theoretical and experimental work. It is highly desirable that this dynamical problem of proton tunneling be dealt with using a more sophisticated approach such as the method of discrete variable representation.\(^{82,83}\)

The order of magnitude increase in the tunneling splittings for the \( \nu_0 \) state compared with those for the ground state is somewhat puzzling in view of the fact that an excitation of a vibrational mode affect the tunneling splitting only by a factor of less than 3 in the inversion motion of \( \text{NH}_3 \) and \( \text{H}_2\text{O}^+ \) and the internal rotation of \( \text{CH}_2\text{OH} \) unless the mode is directly related to the motion. A possible explanation for this may be that the \( \nu_0 \) state, being so high in energy, may couple through vibration-rotation interaction with other vibrational states which involve a few quanta of anti-symmetric bending vibration and thus expected to show larger tunneling splitting. One such example has been noted for the \( \nu_3 \) band (CH rocking) of \( \text{C}_2\text{H}_6 \) and has been ascribed to the Coriolis interaction with the \( 3\nu_4 \) state (\( \nu_4 \) : \( \text{CH} \) torsion).\(^{88,89}\) (We are grateful to J. T. Hougen for bringing this case to our attention.) If this is the case, the barrier height and thus the energy difference between the nonclassical and the classical structures might be higher than estimated above.

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The spectroscopic analysis given in this paper is far from complete in the usual standard of high resolution vibration-rotation spectroscopy. Only spectral lines corresponding to $K_v = 1$ have been assigned with confidence. Even lines with $K_v = 0$ and 2 are not assigned with confidence when $J$ exceeds 6–7. The $Q$ branch lines, relatively weak and highly congested, are poorly assigned. The usual asymmetric rotor energy pattern is noted only in the ground state but the pattern is unusual in the excited state even for $K_v = 1$ lines. More studies on high $J$ lines as well as isotopic species are in progress. These studies are particularly important for studies of more complicated carbo-ions such as $C_2H_4^+$, $C_2H_5^+$, and many others because the ubiquitous $C_2H_5^+$ ions are likely to coexist with other carbo-ions.

The protonated acetylene $C_2H_4^+$ and the acetylene ion $C_2H_5^-$ are predicted to play a crucial role in interstellar chemistry for carbon containing polyatomic molecules such as cyanopolyacetylene. For a radioastronomical search for $C_2H_5^-$, it is imperative to have an accurate $A_g$ constant. The present work does not provide this crucial number experimentally. A search for the $v_\nu$ perpendicular band of $C_2H_5^-$ predicted at $\sim 13 \mu m$ is planned. Such a low-lying vibrational state may also have an advantage of less complication from vibration-rotation perturbation. If such an observation leads to successful observation of microwave spectrum, the higher resolution might allow us to resolve the tunneling splitting in the ground state and thus to determine more reliable energy difference between the nonclassical and the classical structures.

Note added in proof: Watson has pointed out to us that, in order to be consistent with the symmetry labels of homonuclear diatomic molecules, $(s,a)$ should be used to specify the symmetry with respect to the carbon permutation $(ab)$ rather than $(g,u)$ which should be used for $(ab)$. While we fully agree with this, we keep the $(g,u)$ notation here in view of the consistency with the earlier theoretical work and the need of rather extensive corrections. The rovibrational symmetry labeling for planar $C_2H_4$ molecules used in this paper is according to Herzberg's old convention and contrary to Mulliken's recommendation. We find the former more convenient in sorting out vibrations and correlating groups.

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T. Amano (private communication).
D. Smith and N. G. Adams (private communication).
D. G. Burkhard and D. M. Dennison, Phys. Rev. 84, 408 (1951).