

The High-Resolution Infrared Spectroscopy of the Cyclopropenyl Cation

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1. Introduction

The cyclopropenyl cation ($c\text{-C}_3\text{H}_3^+$) has important applications in organic chemistry¹, combustion chemistry²⁻⁵, astrochemistry⁶, and theoretical chemistry^{7,8}. Central to its role in these diverse fields is its status as the simplest aromatic hydrocarbon. Despite the importance of this cation, its high-resolution gas-phase spectrum has not yet been recorded. In this prospectus, methods that should allow the high-resolution spectrum of the cyclopropenyl cation to be recorded are proposed and the theory needed to analyze this spectrum is reviewed.

Recording and analyzing the high-resolution spectrum of $c\text{-C}_3\text{H}_3^+$ is a natural continuation of the study of the C_nH_3^+ series of hydrocarbon cations; the first three members of this series— H_3^+ , CH_3^+ , C_2H_3^+ —have previously been studied by the Oka group⁹⁻¹². Because $c\text{-C}_3\text{H}_3^+$ is the smallest aromatic hydrocarbon, it is the best candidate for *ab initio* computational studies of aromaticity. However, without experimental structural data, it is difficult to evaluate the quality of such studies. Ultimately, we hope that analysis of this spectrum will help refine theory and lead to the astronomical detection of this ion.

2. Preliminaries

2.1. Background

Breslow and Groves were the first to synthesize salts of the cyclopropenyl ion in 1969¹³. These salts are quite stable, and can be stored indefinitely at $-20\text{ }^\circ\text{C}$. The stability of these cyclopropenyl salts is attributed to aromaticity. In the Hückel theory, a species is considered aromatic when a ring system has $4n + 2\pi$ electrons¹⁴. The cyclopropenyl cation ($n = 0$) is the simplest aromatic hydrocarbon given by this theory.

The cyclopropenyl cation is an astronomically important molecule. It has been proposed that this molecule plays a pivotal role in creating larger hydrocarbons in interstellar space through ion-neutral reactions with other carbon species⁶. The cyclopropenyl cation is thought to be the precursor of cyclopropenylidene ($c\text{-C}_3\text{H}_2$), which is ubiquitous in interstellar clouds. Cyclopropenylidene has been studied in the lab by Thaddeus *et al.*¹⁵. Astronomical studies of $c\text{-C}_3\text{H}_2$ reveal that it has an extraordinarily high deuterium fractionation¹⁶⁻¹⁸. The fraction of deuterated $c\text{-C}_3\text{H}_2$ is more than three orders of magnitude greater than the natural abundance of deuterium. It is possible that the high deuterium fractionation of $c\text{-C}_3\text{H}_2$ is due to an efficient production of deuterated $c\text{-C}_3\text{H}_3^+$.

2.2. Choice of Spectroscopy

It is difficult to search for electronic transitions of $c\text{-C}_3\text{H}_3^+$, because the search would need to be too expansive without an accurate calculation of transition frequencies. Since $c\text{-C}_3\text{H}_3^+$ does not have a

permanent dipole moment, it does not have a pure-rotational microwave spectrum. Thus, it is most promising to study the rovibrational infrared absorption spectrum. Rovibrational spectroscopy is particularly attractive because a low-resolution solid-phase spectrum has already been recorded for $c\text{-C}_3\text{H}_3^+$ and its deuterium isotopomers^{19,20}; thus, we already have rough approximations of the bandcenters.

2.3. Laser Source

A Burleigh FCL-20 color center laser will be used for the infrared radiation source. The FCL-20 is capable of lasing between 2900 and 4200 cm^{-1} , with an approximate bandwidth of 1 MHz and an average power of about 10 mW. Although other lasers cover this region, the color center laser is by far the most powerful tunable laser. Our Burleigh FCL-20 was recently computer automated by Lindsay²¹ and is now capable of continuous scanning at the speed of 10 cm^{-1}/hr . The active fundamental of $c\text{-C}_3\text{H}_3^+$ in this wavelength region is the degenerate CH-stretching mode (ν_4).

3. Theory

The quantum mechanical theory needed to describe rovibrational spectroscopy is well understood. In this section, this theory is outlined within the Born-Oppenheimer approximation²² and the neglect of relativistic effects. The ground electronic state of $c\text{-C}_3\text{H}_3^+$ is non-degenerate ($^1A'$), and the lowest excited electronic state lies above the vibrational levels of the ground electronic state; thus, the Born-Oppenheimer approximation is a good approximation for the rovibrational spectroscopy of $c\text{-C}_3\text{H}_3^+$. The ground state of $c\text{-C}_3\text{H}_3^+$ has no net electronic spin, and the magnetic effects of nuclear spin are negligible.

3.1. Normal Coordinates of Vibration

A non-linear molecule composed of N atoms has $f = 3N - 6$ vibrational fundamentals. The vibrational modes are usually described using the normal coordinates q_k , which are a linear transformation of the Cartesian displacement coordinates of the nuclei, chosen such that the Eckart conditions²³ are satisfied and the electronic energy calculated in the Born-Oppenheimer approximation has the diagonal form:

$$E_{elec} = \sum_k \lambda_k q_k^2 + \text{higher order terms} \quad (3.1)$$

If the higher order terms of (3.1) are ignored, then we have the harmonic oscillator approximation in which each fundamental vibration is a function of a single normal coordinate. The normal coordinates are

the best coordinates to describe the vibrational motion of molecules when the higher order terms of (3.1) are small enough to be handled by perturbation theory.

The normal modes of $c\text{-C}_3\text{H}_3^+$ have been calculated from *ab initio* electronic energy surfaces²⁴, as shown in Figure 1.

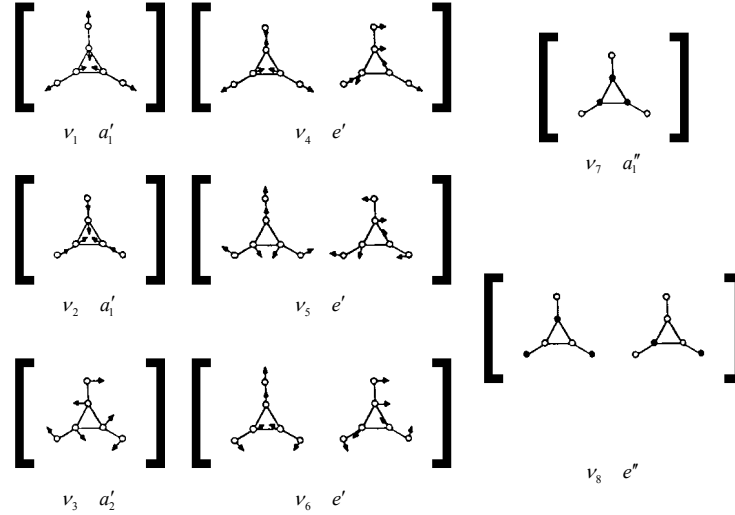


Figure 1. Normal Modes for $c\text{-C}_3\text{H}_3^+$.

3.2. Rigorous Nuclear Hamiltonian

In the Born-Oppenheimer approximation, the nuclear motion is described by the Schrödinger-like equation:

$$H_{nuc}\psi_{nuc} = (T_{nuc} + E_{elec})\psi_{nuc} = E\psi_{nuc} \quad (3.2)$$

The effective nuclear Hamiltonian H_{nuc} can be separated into rotational and vibrational components. First, a molecule-fixed coordinate frame must be defined using the Eckart conditions²³. Then, the method of Wilson and Howard^{25,26} is used to separate H_{nuc} :

$$H_{rot} = \frac{1}{2} \sum_{\alpha\beta} |\boldsymbol{\mu}|^{3/4} (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} |\boldsymbol{\mu}|^{-1/2} (J_\beta - \pi_\beta) |\boldsymbol{\mu}|^{1/4} \quad (3.3)$$

$$H_{vib} = -\frac{1}{2} \hbar^2 \sum_k |\boldsymbol{\mu}|^{3/4} \frac{\partial}{\partial q_k} |\boldsymbol{\mu}|^{-1/2} \frac{\partial}{\partial q_k} |\boldsymbol{\mu}|^{1/4} + E_{elec} \quad (3.4)$$

Watson showed rigorously that showed that (3.3) and (3.4) can be further simplified²⁷:

$$H_{rot} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} (J_\alpha - \pi_\alpha) (J_\beta - \pi_\beta) \quad (3.5)$$

$$H_{vib} = -\frac{1}{2} \hbar^2 \sum_k \frac{\partial^2}{\partial q_k^2} - \frac{1}{8} \hbar^2 \sum_\alpha \mu_{\alpha\alpha} + E_{elec} \quad (3.6)$$

The J_α of (3.3) are the components of nuclear rotational angular momentum along the molecule-fixed axes. The π_α of (3.3) are the components of vibrational angular momentum along the molecule-fixed axes:

$$\pi_\alpha = -i\hbar \sum_{k \neq l} \zeta_{kl}^{(\alpha)} q_l \frac{\partial}{\partial q_k} \quad (3.7)$$

where the $\zeta_{kl}^{(\alpha)}$ are Coriolis coupling constants. The matrix $\boldsymbol{\mu}$ referred to in (3.3) and (3.4) is closely related to the inverse of the inertia tensor:

$$\boldsymbol{\mu} = \mathbf{I}'^{-1} \quad (3.8)$$

$$I'_{\alpha\beta} = I_{\alpha\beta} + \sum_{k,l,m} \zeta_{km}^{(\alpha)} \zeta_{lm}^{(\beta)} q_k q_l \quad (3.9)$$

The components of the inertia tensor are:

$$I_{\alpha\beta} = I_{\alpha\beta}^e + \sum_k a_k^{(\alpha\beta)} q_k + \sum_{k,l} A_{kl}^{(\alpha\beta)} q_k q_l \quad (3.10)$$

Equations (3.3) through (3.10) are rigorous within the Born-Oppenheimer approximation and the neglect of relativistic effects, but the rotational motion and vibrational motion are still coupled. This rovibrational coupling occurs entirely in H_{rot} . Coupling enters H_{rot} in two ways: through the vibrational angular momentum π_α and through the dependence of $\boldsymbol{\mu}$ on the normal coordinates. The coupling with π_α arises from Coriolis effect and the coupling with $\boldsymbol{\mu}$ arises from centrifugal forces. We usually neglect H_{trans} because it is rigorously separable from the rest of the Hamiltonian in the absence of external fields.

3.3. Rovibrational Parameters

There are quite a few parameters involved in (3.7) through (3.10). The inertia tensor is symmetric, thus:

$$I_{\alpha\beta}^e = I_{\beta\alpha}^e \quad (3.11)$$

$$a_k^{(\alpha\beta)} = a_k^{(\beta\alpha)} \quad (3.12)$$

$$A_{kl}^{(\alpha\beta)} = A_{kl}^{(\beta\alpha)} \quad (3.13)$$

Similarly, the Coriolis constants are anti-symmetric with respect to the exchange of normal coordinates:

$$\zeta_{kl}^{(\alpha)} = -\zeta_{lk}^{(\alpha)} \quad (3.14)$$

Finally, we note that the inertia tensor can be diagonalized by rotating the coordinate frame. Thus, by properly choosing the reference frame, there are only 3 $I_{\alpha\alpha}^e$. Using (3.12) through (3.14), there are in general $6f$ $a_k^{(\alpha\beta)}$, $6f^2$ $A_{kl}^{(\alpha\beta)}$, and $\frac{3}{2}f(f-1)$ $\zeta_{kl}^{(\alpha)}$.

Obviously the $I_{\alpha\alpha}^e$, $a_k^{(\alpha\beta)}$, $A_{kl}^{(\alpha\beta)}$, and $\zeta_{kl}^{(\alpha)}$ are not independent of each other. Many authors have dealt with the relations between these parameters. We can evaluate the $I_{\alpha\alpha}^e$ and $A_{kl}^{(\alpha\beta)}$ in terms of $a_k^{(\alpha\beta)}$ and $\zeta_{kl}^{(\alpha)}$ using two of these relations²⁸:

$$I_{\alpha\alpha}^e = \frac{1}{4} \sum_k \left(a_k^{(\alpha\alpha)} \right)^2 \quad (3.15)$$

$$A_{kl}^{(\alpha\beta)} = \sum_m \zeta_{km}^{(\alpha)} \zeta_{lm}^{(\beta)} + \sum_{\xi} a_k^{(\alpha\xi)} a_l^{(\beta\xi)} \left(4I_{\xi\xi}^e \right)^{-1} \quad (3.16)$$

In addition, symmetry dictates that the $a_k^{(\alpha\beta)}$, $A_{kl}^{(\alpha\beta)}$, and $\zeta_{kl}^{(\alpha)}$ are nonvanishing only when $J_\alpha J_\beta q_k$, $J_\alpha J_\beta q_k q_l$, and $J_\alpha q_k q_l$, respectively, are totally symmetric for all symmetry operations of the molecule²⁸. The nonvanishing rotational parameters for an X_3Y_3 molecule with D_{3h} symmetry are given in Table 1.

Table 1. Nonvanishing Rovibrational Parameters for X_3Y_3 Molecule with D_{3h} Symmetry

$a_k^{(xx)} = a_k^{(yy)}$	$k = 1, 2$
$a_k^{(zz)}$	$k = 1, 2$
$a_{k_a}^{(yy)} = -a_{k_a}^{(xx)} = -a_{k_b}^{(xy)} = -a_{k_b}^{(yx)}$	$k = 4, 5, 6$
$\zeta_{k3}^{(z)} = -\zeta_{3k}^{(z)}$	$k = 1, 2$
$\zeta_{k8_a}^{(y)} = \zeta_{k8_b}^{(x)} = -\zeta_{8_a k}^{(y)} = -\zeta_{8_b k}^{(x)}$	$k = 1, 2, 3$
$\zeta_{k_a l_b}^{(z)} = -\zeta_{k_b l_a}^{(z)}$	$k, l = 4, 5, 6$
$\zeta_{k_a 7}^{(y)} = \zeta_{k_b 7}^{(x)} = -\zeta_{7 k_a}^{(y)} = -\zeta_{7 k_b}^{(x)}$	$k = 4, 5, 6$
$-\zeta_{k_a 8_a}^{(y)} = \zeta_{k_b 8_b}^{(y)} = \zeta_{k_a 8_b}^{(x)} = \zeta_{k_b 8_a}^{(x)} = \zeta_{8_a k_a}^{(y)} = -\zeta_{8_b k_b}^{(y)} = -\zeta_{8_b k_a}^{(x)} = -\zeta_{8_a k_b}^{(x)}$	$k = 4, 5, 6$

3.4. Approximate Rovibrational Hamiltonian

If we ignore the dependence of $\boldsymbol{\mu}$ on the normal coordinates, then (3.5) becomes:

$$H_{rot} \approx \frac{J_x^2}{2I_{xx}^e} + \frac{J_y^2}{2I_{yy}^e} + \frac{J_z^2}{2I_{zz}^e} - \frac{J_x \pi_x}{I_{xx}^e} - \frac{J_y \pi_y}{I_{yy}^e} - \frac{J_z \pi_z}{I_{zz}^e} + \frac{\pi_x^2}{2I_{xx}^e} + \frac{\pi_y^2}{2I_{yy}^e} + \frac{\pi_z^2}{2I_{zz}^e} \quad (3.17)$$

We can separate (3.17) into the rigid rotor Hamiltonian a Coriolis coupling operator, and a term to be added to the vibrational Hamiltonian. Furthermore, for a symmetric top like $c\text{-C}_3\text{H}_3^+$, $I_{xx}^e = I_{yy}^e$. Thus:

$$H_{rigid\ rot} = \frac{J_x^2}{2I_{xx}^e} + \frac{J_y^2}{2I_{yy}^e} + \frac{J_z^2}{2I_{zz}^e} = B\mathbf{J}^2 + (C - B)J_z^2 \quad (3.18)$$

$$H_{Coriolis} = -\frac{J_x \pi_x}{I_{xx}^e} - \frac{J_y \pi_y}{I_{yy}^e} - \frac{J_z \pi_z}{I_{zz}^e} = -2B\mathbf{J} \cdot \boldsymbol{\pi} - 2(C - B)J_z \pi_z \quad (3.19)$$

$$H_{vib} = -\frac{1}{2}\hbar^2 \sum_k \frac{\partial^2}{\partial q_k^2} + \frac{\pi_x^2}{2I_{xx}^e} + \frac{\pi_y^2}{2I_{yy}^e} + \frac{\pi_z^2}{2I_{zz}^e} - \frac{1}{8}\hbar^2 \sum_a \mu_{aa} + E_{elec} = -\frac{1}{2}\hbar^2 \sum_k \frac{\partial^2}{\partial q_k^2} + B\boldsymbol{\pi}^2 + (C - B)\pi_z^2 - \frac{1}{8}\hbar^2 \sum_a \mu_{aa} + E_{elec} \quad (3.20)$$

$$B \equiv \frac{\hbar^2}{2I_{xx}^e} \quad C \equiv \frac{\hbar^2}{2I_{zz}^e} \quad (3.21)$$

Hamiltonians (3.18) through (3.20) lead to the first order energy formulas for the ν_4 band of $c\text{-C}_3\text{H}_3^+$:

$$E'' = BJ''(J''+1) + (C-B)K''^2 \quad (3.22)$$

$$E' = BJ'(J'+1) + (C-B)K'^2 - 2\zeta_{4a4b}^{(z)} CK'\ell' + E_{vib} \quad (3.23)$$

where K is the unsigned projection on nuclear angular momentum on the symmetry axis.

3.5. Quantum Numbers

The isotropy of space dictates that the total angular momentum F is a good quantum number. Because the nuclear spin-rotation interaction is small, the total nuclear spin angular momentum I and $J = F - I$ are nearly good quantum numbers. The vibrational quantum numbers ν_1 through ν_8 are good approximate quantum numbers when the anharmonicity and centrifugal distortion are negligible. The component of vibrational angular momentum ℓ and the component of nuclear rotational angular momentum k on the symmetry axis of $c\text{-C}_3\text{H}_3^+$ are no longer good quantum numbers, due to the Coriolis interaction. However $g \equiv k - \ell$ is an approximate good quantum number, because:

$$[(J_z - \pi_z), H_{Coriolis}] = 0 \quad (3.24)$$

Because the energy is independent of the sign of g , we will more often use the unsigned $G \equiv |g|$.

3.6. Nuclear Spin Statistics and Selection Rules

The nuclear spin statistics for all C_nH_3^+ molecules are the same because ^{12}C has no spin. Thus, we must have $I = \frac{3}{2}$ (*ortho*) for $g = 3n$ and $I = \frac{1}{2}$ (*para*) for $g = 3n \pm 1$ ²⁹. Furthermore, in the vibrational ground state, nuclear spin statistics remove the g degeneracy for $g > 0$ and forbid the even J for $g = 0$. In the $\nu_4 = 1$ state the g degeneracy for $g = 3n$; $n > 0$ is removed.

In order for a transition from $|\Psi''\rangle$ to $|\Psi'\rangle$ to be allowed, we require that:

$$\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle \neq 0 \quad (3.25)$$

Where $\boldsymbol{\mu}$ is the dipole moment operator. The representation of $\boldsymbol{\mu}$ in the three-dimensional rotation group K is \mathcal{D}_1 , whereas the representations of $\langle \Psi' |$ and $|\Psi''\rangle$ are $\mathcal{D}_{J'}$ and $\mathcal{D}_{J''}$. In group theory, the condition of (3.25) becomes:

$$\mathcal{D}_{J'} \otimes \mathcal{D}_1 \otimes \mathcal{D}_{J''} \supseteq \mathcal{D}_0 \quad (3.26)$$

$$\left. \begin{array}{l} J'' \neq 0 \\ J'' = 0 \end{array} \right\} \left. \begin{array}{l} \mathcal{D}_{J'} (\mathcal{D}_{J'+1} + \mathcal{D}_{J'} + \mathcal{D}_{J'-1}) \\ \mathcal{D}_{J'} \mathcal{D}_1 \end{array} \right\} \supseteq \mathcal{D}_0 \quad (3.27)$$

$$\begin{aligned} J'' \neq 0 \quad \Delta J = 0, \pm 1 \\ J'' = 0 \quad \Delta J = +1 \end{aligned} \quad (3.28)$$

The electric dipole moment is independent of nuclear spin when relativistic interactions are ignored:

$$\Delta I = 0 \quad (3.29)$$

The nuclear spin selection rule (3.29) combined with the nuclear spin statistics leads to a new selection rule:

$$\Delta g = 3n \quad (3.30)$$

3.7. Simulated Spectrum

The intensity of a transition is given by:

$$I \propto N'' |\langle \psi' | \boldsymbol{\mu} | \psi'' \rangle|^2 = \frac{g_{I,J} e^{-E''/k_B T} |\langle \psi' | \boldsymbol{\mu} | \psi'' \rangle|^2}{Q} \quad (3.31)$$

Where Q is the partition function and $g_{I,J}$ is the degeneracy of the rotational level:

$$g_{I,J} = (2I + 1)(2J + 1) \quad (3.32)$$

For an allowed transition $|\langle \psi' | \boldsymbol{\mu} | \psi'' \rangle|^2$ is proportional to the Hönl-London factor $A(J, K)^{30}$. In the rigid rotor-harmonic oscillator approximation, the partition function is:

$$Q = \sum_{I,J} g_{I,J} e^{-E_{rot}(J,K)/k_B T_{rot}} \prod_{\nu} (1 - e^{-h\nu/k_B T_{vib}}) \quad (3.33)$$

Using (3.22), (3.23), and (3.31), Rade has prepared a simulated spectrum of the ν_4 vibrational band at 800 K³¹ (Figure 2). Rade used the rotational constants of Lee, *et al.*²⁴, the vibrational band center of Craig *et al.*^{19,20}, and the Coriolis coupling constant of the degenerate CH stretching band of CH₃⁺¹⁰:

$$B = 1.0254 \text{ cm}^{-1} \quad C = 0.5127 \text{ cm}^{-1} \quad \nu_4 = 3137 \text{ cm}^{-1} \quad \zeta = 0.1141 \quad (3.34)$$

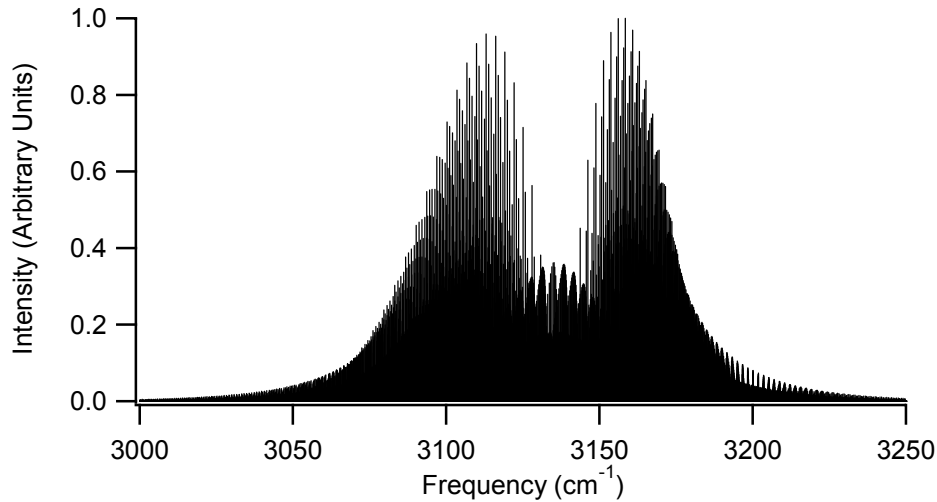


Figure 2. Simulated ν_4 fundamental band of $c\text{-C}_3\text{H}_3^+$ at 800 K

4. Production of Cyclopropenyl Cation

The most critical aspect of obtaining the high-resolution gas-phase rovibrational spectrum of $c\text{-C}_3\text{H}_3^+$ is the production of enough $c\text{-C}_3\text{H}_3^+$ such that spectroscopy is possible. In this section, three methods for producing the $c\text{-C}_3\text{H}_3^+$ cation are proposed.

4.1. Positive Column Discharge

The positive column discharge is the standard source of molecular plasmas studied by the Oka group. In addition to producing an abundance of positive molecular ions, the positive column discharge allows the use of velocity modulation. Velocity modulation is a technique first developed by Saykally and Gudeman³². A large AC potential, typically several kV, drives the discharges. Because of the AC potential, the velocity distribution of ions in the discharge is time-dependent, at the frequency of the discharge. Thus, the effective frequency of an absorption line is time-dependent, due to the Doppler effect. The spectrum of ions in the plasma are therefore said to be velocity modulated at the frequency of the discharge.

The velocity-modulated signal can be demodulated using a phase sensitive detector; the resulting signal is the Fourier component of the modulated signal at the frequency and specific phase shift of the AC discharge. Because only ions are velocity modulated, neutrals do not show up in the demodulated signal. This ion-neutral selectivity is crucial for the identification of ion absorptions, which are typically 3 – 6 orders of magnitude less intense than neutral absorptions. Further sensitivity improvements are possible by using multipass and noise subtraction techniques.

Rade proposed searching for $c\text{-C}_3\text{H}_3^+$ in plasma conditions suitable for the production of $c\text{-C}_3\text{H}_2$ ³¹. Thaddeus, *et al.* obtained the first laboratory spectrum of $c\text{-C}_3\text{H}_2$ using a mixture of acetylene, helium, and hydrogen¹⁵. Bogey, *et al.* obtained a higher concentration using allene and helium³³. Because the proton affinity of $c\text{-C}_3\text{H}_2$ is extremely high—9.86 eV^{34,35}—it is reasonable to expect a detectable amount of $c\text{-C}_3\text{H}_3^+$ in plasma conditions that produce $c\text{-C}_3\text{H}_2$. We therefore plan to search for $c\text{-C}_3\text{H}_3^+$ in discharges including allene or acetylene.

Rade estimated the intensity of the ν_4 band of $c\text{-C}_3\text{H}_3^+$ relative to the degenerate CH-stretching ν_3 band of CH_3^+ . CH_3^+ is efficiently made in a discharge of methane, helium, and hydrogen. The ν_3 band of CH_3^+ was recorded with a signal-to-noise ratio of 500:1 by Crofton, *et al.* using a difference frequency system¹⁰. The transition dipole moment of the ν_3 band of CH_3^+ is comparable to that of the ν_4 band of $c\text{-C}_3\text{H}_3^+$. Hence, the ratio of the intensities of these two bands should approximately be given by the ratio of their partition functions.

Based on (3.31), it is clear that the partition function should be as small as possible for maximum sensitivity. The partition function is lowered by cooling the plasma. We typically cool the positive column discharge using liquid N₂, water, or air. The plasma used to study CH₃⁺ was liquid N₂ cooled. Unfortunately, allene and acetylene both freeze at the temperature of liquid N₂; therefore, discharges of allene or acetylene must be water cooled or perhaps cooled by an acetone/dry ice bath. Thus, the rotational temperature of *c*-C₃H₃⁺ is expected to be a factor of two larger than for CH₃⁺. The rotational constants of *c*-C₃H₃⁺ are about an order of magnitude smaller than the rotational constants of CH₃⁺. Thus, Rade concluded that the overall spectrum should be about 50 times weaker than CH₃⁺, corresponding to a signal-to-noise ratio of 10:1. However, the color center laser system is more powerful than the difference frequency system used by Crofton, *et al*, so some improvement in sensitivity is expected.

Rade's estimate is optimistic for a number of reasons. First of all, it assumes that *c*-C₃H₃⁺ can be made in concentrations equivalent to CH₃⁺, which is probably not realistic. Additionally, a more detailed estimate of the rotational partition function of *c*-C₃H₃⁺ places it about 50 to 100 times larger than CH₃⁺. Furthermore, because *c*-C₃H₃⁺ has six more vibrational modes than CH₃⁺, the vibrational partition function of *c*-C₃H₃⁺ is necessarily larger than the vibrational partition function of CH₃⁺, possibly by more than an order of magnitude. For these reasons, the estimated signal-to-noise ratio for *c*-C₃H₃⁺ is likely to lie between 1:2 and 10:1, before considering the gains due to a more powerful laser source. Thus, it is prudent to consider other methods for producing *c*-C₃H₃⁺. It is impossible to know *a priori* the concentration of *c*-C₃H₃⁺ that may be formed in the discharge, so it is still quite possible that *c*-C₃H₃⁺ can be studied in the positive column. Therefore, the initial attempt at recording the high-resolution spectrum will involve the positive column.

4.2. Supersonic Slit-Jet Discharge

Lindsay has recently built a slit-jet discharge²¹. The slit jet provides rotational and translational cooling. Thus, sensitivity is improved in the slit jet by a lowering of the rotational partition function, and a narrowing of the Doppler profile. Lindsay's supersonic slit-jet design is different from other such apparatuses in that it uses a pump large enough to allow continuous flow of gas through the slit. Traditionally, spectroscopists have opted for smaller pumps, requiring the flow of gas through the slit to be pulsed. The duty cycle increase afforded by a continuous flow of gas leads to a substantial gain in sensitivity.

The mass spectrum of the cyclopropenyl cation has clearly been observed in a supersonic slit-jet discharge by Dopfer. Dopfer has recorded the IR photodissociation spectra of both *c*-C₃H₃⁺ and linear C₃H₃⁺ ions complexed with N₂ ligands with resolution of K structure³⁶. Dopfer's experimental apparatus differs from Lindsay's apparatus³⁷⁻³⁹ in several ways: his vacuum source is pulsed and his ion source is

slightly different than ours. In addition, Dopfer's source of IR-radiation is a Nd:YAG pumped 0.02 cm^{-1} resolution pulsed OPO system. None of these differences should prevent using his experimental conditions to produce the $c\text{-C}_3\text{H}_3^+$ radical in adequate concentration for studying the high-resolution spectrum.

4.3. Supersonic Jet Flash Pyrolysis

Deyerl, *et al.* have reported the photoelectron spectrum of the propargyl radical, linear $\text{C}_3\text{H}_3^{40,41}$. They were able to create a molecular beam of internally cold propargyl radicals by supersonic jet flash pyrolysis⁴² of propargyl bromide, which is commercially available. 3-Halocyclopropenes are not commercially available, as these molecules deteriorate after a few days even when stored at low temperature. The synthesis 3-chlorocyclopropene⁴³ is the initial step in the synthesis of cyclopropenyl salts. The preparation of 3-fluorocyclopropene⁴⁴ by fluorination of 3-chlorocyclopropene is also known. Thus, supersonic jet flash pyrolysis of 3-halocyclopropenes followed by ionization may be a viable method for the production of $c\text{-C}_3\text{H}_3^+$ in the gas phase. If this method works, there should be no problem in recording the high-resolution infrared spectrum. However, because of the difficulty of working with 3-halocyclopropenes, this method is not preferred.

5. Conclusion

A rotationally-resolved spectrum of the cyclopropenyl cation has not been recorded to date because of the difficulty in producing this cation in the gas phase. Three methods of producing $c\text{-C}_3\text{H}_3^+$ in concentrations suitable for recording this spectrum have been proposed. The analysis of this spectrum is of great use to theoretical chemists, because $c\text{-C}_3\text{H}_3^+$ is the simplest aromatic hydrocarbon. In addition, the analysis of the high-resolution spectrum may lead to the astronomical detection of $c\text{-C}_3\text{H}_3^+$. Finally, once the spectrum of $c\text{-C}_3\text{H}_3^+$ is recorded, recording the spectra of deuterated isotopomers should be straightforward, allowing the high deuterium fractionation of $c\text{-C}_3\text{H}_2^+$ to be explored.

6. References

- 1 S. V. Krivun, O. F. Alferova, and S. V. Sayapina, *Usp. Khim.* **43**, 1739-70 (1974).
- 2 T. McAllister and A. J. C. Nicholson, *J. Chem. Soc., Faraday Trans. 1* **77**, 821-5 (1981).
- 3 K. C. Smyth, S. G. Lias, and P. Ausloos, *Chem. Phys. Processes Combust.*, 187-90 (1981).
- 4 K. C. Smyth, S. G. Lias, and P. Ausloos, *Combust. Sci. Technol.* **28**, 147-54 (1982).
- 5 J. Eyler, M. Zerner, and F. Wiseman,, (Univ. Florida, Gainesville, FL, USA., 1988), pp. 188 pp.
- 6 E. Herbst and W. Klemperer, *Astrophys. J.* **185**, 505-533 (1973).
- 7 T.-K. Ha, F. Graf, and H. H. Guenthard, *J. Mol. Struct.* **15**, 335-50 (1973).
- 8 Y. G. Byun, S. Saebo, and C. U. Pittman, Jr., *J. Am. Chem. Soc.* **113**, 3689-96 (1991).
- 9 T. Oka, *Phys. Rev. Lett.* **45**, 531-4 (1980).
- 10 M. W. Crofton, M. F. Jagod, B. D. Rehfuss, W. A. Kreiner, and T. Oka, *J. Chem. Phys.* **88**, 666-78 (1988).
- 11 T. Oka, *Philos. Trans. R. Soc. London, A* **324**, 81-95 (1988).
- 12 M. W. Crofton, M. F. Jagod, B. D. Rehfuss, and T. Oka, *J. Chem. Phys.* **91**, 5139-53 (1989).
- 13 R. Breslow and J. T. Groves, *J. Amer. Chem. Soc.* **92**, 984-7 (1970).
- 14 R. Hückel, *Z. Phys.* **70**, 204 (1931).
- 15 P. Thaddeus, J. M. Vrtilik, and C. A. Gottlieb, *Astrophys. J.* **299**, L63-L66 (1985).
- 16 M. B. Bell, L. W. Avery, H. E. Matthews, P. A. Feldman, J. K. G. Watson, S. C. Madden, and W. M. Irvine, *Astrophys. J.* **326**, 924-30 (1988).
- 17 M. B. Bell, P. A. Feldman, H. E. Matthews, and L. W. Avery, *Astrophys. J.* **311**, L89-L92 (1986).
- 18 D. Talbi and F. Pauzat, *Chem. Phys. Lett.* **244**, 269-74 (1995).
- 19 N. C. Craig, J. Pranata, S. J. Reinganum, J. R. Sprague, and P. S. Stevens, *J. Am. Chem. Soc.* **108**, 4378-86 (1986).
- 20 N. C. Craig, J. Pranata, J. R. Sprague, and P. S. Stevens, *J. Am. Chem. Soc.* **106**, 7637-8 (1984).
- 21 C. M. Lindsay, Research Prospectus, University of Chicago, 1997.
- 22 M. Born and J. R. Oppenheimer, *Ann. d. Phys.* **84**, 457 (1927).
- 23 C. Eckart, *Phys. Rev.* **47**, 552 (1935).
- 24 T. J. Lee, A. Willetts, J. F. Gaw, and N. C. Handy, *J. Chem. Phys.* **90**, 4330-40 (1989).
- 25 J. Wilson, E. B. and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).
- 26 J. Wilson, E. B., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955).
- 27 J. K. G. Watson, *Mol. Phys.* **15**, 479 (1968).
- 28 T. Oka and Y. Morino, *J. Mol. Spectrosc.* **6**, 472-482 (1961).
- 29 B. J. McCall and T. Oka, *J. Chem. Phys.* **113**, 3104-3110 (2000).
- 30 H. Hönl and F. London, *Z. Phys.* **33**, 803 (1925).
- 31 R. M. Rade Jr., Research Prospectus, University of Chicago, 2000.
- 32 C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **50**, 727-31 (1983).
- 33 M. Bogey, C. Demuynck, and J. L. Destombes, *Chem. Phys. Lett.* **125**, 383-8 (1986).
- 34 L. J. Chyall and R. R. Squires, *Int. J. Mass Spectrom. Ion Processes* **149**, 257-66 (1995).
- 35 R. G. A. R. Maclagan, *Theochem* **90**, 175-8 (1992).
- 36 O. Dopfer, Personal Communication, September 20, 2000
- 37 R. V. Olkhov, S. A. nizkorodov, and O. Dopfer, *J. Chem. Phys.* **108**, 10046-60 (1998).
- 38 E. J. Bieske, S. A. Nizkorodov, F. R. Bennett, and J. P. Maier, *J. Chem Phys.* **102**, 5152-5164 (1995).
- 39 E. J. Bieske, A. M. Soliva, and J. P. Maier, *J. chem. Phys.* **94**, 4749-4755 (1991).
- 40 H.-J. Deyerl, I. Fischer, and P. Chen, *J. Chem. Phys.* **111**, 3441-3448 (1999).
- 41 T. Gilbert, R. Pfab, I. Fischer, and P. Chen, *J. Chem. Phys.* **112**, 2575-2578 (2000).
- 42 D. W. Kohn, Clauberg, H., Chen, P., *Rev. Sci. Instrum.* **63**, 4003 (1992).
- 43 R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.* **92**, 988-93 (1970).
- 44 N. C. Craig, K. L. Sloan, J. R. Sprague, and P. S. Stevens, *J. Org. Chem.* **49**, 3847-8 (1984).