Millimeter-wave spectrum of vibrationally excited cyclopropenylidene, c-C_3H_2

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The millimeter-wave rotational spectrum of c-C_3H_2 in four vibrationally excited states was measured and the rotational and quartic centrifugal distortion constants determined. Of the vibrational states observed here, only ν_3 has been previously detected in the infrared. Assignment of the three new states to ν_6, ν_5, and ν_2 was based on relative intensities, comparison of calculated and measured inertial defects, and symmetry considerations. The spectroscopic constants determined will guide future infrared investigation of c-C_3H_2, needed for a complete elucidation of the vibrational structure of this molecule. The experimental values of the vibration-rotation coupling constants will allow comparison with theoretical calculations that have recently become feasible for molecules of similar size as c-C_3H_2. Detection in space of rotational lines from the lowest vibrationally excited states may be possible.

I. INTRODUCTION

Cyclopropenylidene, c-C_3H_2, the three-membered carbene ring with C_{2v} symmetry, is the most stable molecule with three carbon and two hydrogens atoms.[1] Its gas-phase pure rotational spectrum in the ground vibrational state was detected and assigned in 1985 in the laboratory following radio astronomical observation of lines from a then-unknown carrier.[2] C_3H_2 is widely distributed in space, including molecular clouds, circumstellar shells, and at least one external galaxy.[3–5] The original production of the molecule in the laboratory was in an acetylene-helium dc discharge;[2] subsequently, Bogey *et al.*[6] found a more efficient method of producing C_3H_2 in an rf discharge in allene and studied the deuterium and ^{13}C isotopic species to determine its molecular structure.

The first laboratory detection of cyclopropenylidene is that of Reisenauer *et al.*[7] who reported infrared bands at 1279, 1063, 888, and 789 cm^{-1} attributed to C_3H_2 trapped in a matrix of solid argon. Huang and Graham[8] subsequently studied the infrared spectrum of C_3H_2 as part of a systematic investigation of tricarbon hydride radicals in a low temperature Ar matrix. Although they confirmed the assignment of Reisenauer *et al.* of the band at 1279 cm^{-1} to ν_3, their deuterium isotopic studies did not appear to confirm the assignment of the other bands to cyclopropenylidene.

The only gas-phase high-resolution study of the vibration-rotation transitions of C_3H_2 has been performed by Hirahara *et al.*[9] by high-resolution Fourier transform spectroscopy. They obtained the rotational and centrifugal distortion constants of ν_3, the symmetric C–C stretch coupled with an in-plane symmetric CH bend, which is the vibrational state with the largest predicted infrared absorption coefficient from the ground state.[10] Their constants allowed us to make accurate predictions for the pure rotational transitions of the ν_3 state and to observe them. The strength of the rotational lines of the ν_3 state indicated the feasibility of detecting other vibrationally excited states of the C_3H_2 molecule in our discharge.

II. DESCRIPTION OF EXPERIMENT

The millimeter-wave rotational spectra presented here were obtained with the reactive molecule spectrometer described in detail by Mollaaghababa *et al.*[11] Cyclopropenylidene and its vibrational satellites were produced in a 0.35 A discharge through a 5:1 mixture of allene and helium at a pressure of 30 mTorr with the walls of the discharge cell cooled to 120 K. Lines from the excited vibrational states were found to generally increase in intensity with increasing current, but a systematic study of the dependence of excited state populations on current has not been attempted. The linewidths of the rotational lines varied from ~1 MHz at lower frequencies—largely pressure broadened—to ~2 MHz in the vicinity of 400 GHz—where Doppler broadening is ~1 MHz. In the excited vibrational states, the signal-to-noise ratio of the rotational transitions was typically greater than 15, allowing line frequencies to be measured to 50 kHz or better, i.e., one part in 10^7.

III. OBSERVED SPECTRUM

Cyclopropenylidene is an oblate asymmetric top ($\kappa = +0.69$) with b-type transitions and a permanent electric

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TABLE I. Rotational transitions of vibrationally excited C_3H_2.

						Frequency (MHz)[a]											
J'	K_a'	K_c'	J''	K_a''	K_c''	ν_6		O–C	ν_5		O–C	ν_3		O–C	ν_2		O–C
2	1	2	1	0	1	84 491.357	(0.010)	−0.002	85 293.282	(0.029)	−0.051	85 269.797	(0.029)	−0.030	85 094.247	(0.016)	−0.009
3	0	3	2	1	2	116 791.782	(0.100)	0.379	117 282.486	(0.012)	−0.038						
6	2	4	6	1	5	145 767.572	(0.027)	−0.038				150 597.623	(0.013)	0.004	149 810.664	(0.049)	0.012
6	3	4	6	2	5							150 671.447	(0.010)	−0.003	149 906.375	(0.011)	−0.002
4	0	4	3	1	3							150 841.525	(0.034)	0.033			
4	1	4	3	0	3							150 869.622	(0.024)	0.045	150 404.201	(0.025)	0.141
4	1	3	3	2	2	182 391.982	(0.022)	−0.037				183 618.056	(0.036)	0.006	182 867.192	(0.035)	−0.005
8	3	5	8	2	6				183 601.810	(0.010)	0.010						
8	4	5	8	3	6				183 623.633	(0.010)	−0.011						
5	0	5	4	1	4	184 009.283	(0.041)	0.031	184 556.042	(0.021)	0.055	184 363.409	(0.030)	0.044	183 796.955	(0.027)	0.035
5	1	5	4	0	4	184 010.229	(0.016)	0.215	184 557.669	(0.065)	0.172	184 365.192	(0.091)	0.037	183 799.271	(0.074)	0.022
4	2	3	3	1	2							185 472.101	(0.027)	0.011	184 989.032	(0.036)	0.039
6	0	6	5	1	5	217 560.029	(0.019)	0.038	218 109.762	(0.020)	0.115	217 873.176	(0.020)	0.130	217 209.774	(0.032)	0.137
6	1	6	5	0	5	217 560.029	(0.019)	0.003	218 109.762	(0.020)	0.036	217 873.176	(0.020)	0.027	217 209.774	(0.032)	−0.005
5	1	4	4	2	3							217 894.288	(0.015)	−0.006	217 153.380	(0.033)	0.006
5	2	4	4	1	3							218 092.608	(0.023)	0.059	217 395.789	(0.045)	0.026
7	1	6	7	0	7							218 165.939	(0.029)	−0.021			
6	1	5	5	2	4	250 033.194	(0.015)	0.061									
5	3	3	4	2	2	251 033.194	(0.020)	−0.011									
7	0	7	6	1	6	251 108.912	(0.013)	−0.090	251 661.765	(0.022)	−0.028	251 380.782	(0.010)	−0.033	250 620.413	(0.184)	−0.032
7	1	7	6	0	6	251 108.912	(0.013)	−0.091	251 661.765	(0.022)	−0.032	251 380.782	(0.010)	−0.039	250 620.413	(0.184)	−0.040
6	2	5	5	1	4				251 661.765	(0.022)	0.010	251 486.793	(0.015)	0.020	250 669.785	(0.033)	−0.025
6	2	4	5	3	3							284 817.468	(0.039)	0.020	283 777.906	(0.100)	−0.210
8	0	8	7	1	7	284 656.236	(0.025)	0.016	285 212.585	(0.027)	−0.071	284 886.883	(0.015)	−0.013	284 029.646	(0.029)	−0.134
8	1	8	7	0	7	284 656.236	(0.025)	0.016	285 212.585	(0.027)	−0.071	284 886.883	(0.015)	−0.013	284 029.646	(0.029)	−0.135
7	1	6	6	2	5				285 192.690	(0.031)	−0.081	284 975.039	(0.029)	−0.003	284 056.649	(0.036)	−0.058
7	2	6	6	1	5				285 193.900	(0.100)	0.246	284 976.280	(0.099)	0.097	284 058.229	(0.090)	−0.057
6	3	4	5	2	3							285 612.023	(0.031)	−0.019	284 749.440	(0.039)	−0.050
8	1	7	7	2	6	317 115.455	(0.023)	−0.013	318 733.541	(0.036)	0.158	318 474.948	(0.010)	0.036	317 458.778	(0.034)	0.114
8	2	7	7	1	6	317 115.455	(0.023)	−0.033	318 733.541	(0.036)	0.109	318 474.948	(0.010)	−0.037	317 458.778	(0.034)	0.007
9	0	9	8	1	8	318 201.315	(0.043)	−0.059	318 761.970	(0.043)	−0.052	318 390.987	(0.010)	0.007	317 437.340	(0.030)	−0.033
9	1	9	8	0	8	318 201.315	(0.043)	−0.059	318 761.970	(0.043)	−0.052	318 390.987	(0.010)	0.007	317 437.340	(0.030)	−0.032
7	2	5	6	3	4							318 585.940	(0.042)	−0.014			
7	3	5	6	2	4				318 820.571	(0.021)	−0.001	318 667.220	(0.046)	−0.022	317 618.961	(0.022)	−0.024
8	2	6	7	3	5	349 608.498	(0.019)	−0.025							350 923.357	(0.103)	0.101
8	3	6	7	2	5	349 611.562	(0.061)	0.578				352 094.371	(0.044)	0.053	350 932.847	(0.029)	0.076
9	1	8	8	2	7	350 652.972	(0.036)	−0.071	352 272.881	(0.033)	0.015	351 973.888	(0.010)	0.001	350 859.759	(0.034)	−0.024
9	2	8	8	1	7	350 652.972	(0.036)	−0.072	352 272.881	(0.033)	0.012	351 973.888	(0.010)	−0.003	350 859.759	(0.034)	−0.031
10	0	10	9	1	9	351 744.215	(0.023)	0.003	352 309.608	(0.026)	−0.085	351 892.831	(0.034)	0.053	350 842.945	(0.033)	−0.010
10	1	10	9	0	9	351 744.215	(0.023)	0.003	352 309.608	(0.026)	−0.085	351 892.831	(0.034)	0.053	350 842.945	(0.033)	−0.010
10	1	9	9	2	8	384 187.925	(0.037)	0.016	385 810.485	(0.032)	−0.060				384 259.389	(0.045)	−0.027
10	2	9	9	1	8	384 187.925	(0.037)	0.016	385 810.485	(0.032)	−0.060				384 259.389	(0.045)	−0.028
11	0	11	10	1	10	385 284.523	(0.019)	0.034	385 855.612	(0.031)	0.126				384 246.309	(0.021)	0.032
11	1	11	10	0	10	385 284.523	(0.019)	0.034	385 855.612	(0.031)	0.126				384 246.309	(0.021)	0.032

[a] Uncertainties are an estimated 1σ. The O–C values are obtained from comparison of measured frequencies and those predicted from molecular constants in Table II.

dipole moment of about 3.4 D in the ground vibrational state.[12] Unlike linear and near-prolate asymmetric top molecules, where the frequencies of rotational transitions are related by harmonic ratios, the rotational transitions of oblate asymmetric tops such as C_3H_2 are generally not harmonically related. Owing to this lack of symmetry and the high density of unidentified lines in an allene discharge, we based our strategy for locating lines of new vibrational states on a search for a line pattern with a distinctive signature: a particular *ortho-para* doublet with a characteristic 3:1 intensity ratio which in one of the $J=4\rightarrow5$ transitions ($4_{14}\rightarrow5_{05}$ and $4_{04}\rightarrow5_{15}$) has a splitting of a few MHz. For brevity, we refer to this K-type doublet which has been crucial for identification of the ground and vibrationally excited states as the $4\rightarrow5$ doublet. Specifically, we searched a region of more than 2 GHz above and 3 GHz below the $4\rightarrow5$ doublet of the vibrational ground state at 184 GHz (i.e., more than 1% of the ground state rotational frequency on each side). Some vibrational satellites may lie outside this range due to Coriolis interactions. The doublet of the known ν_3 state was initially identified within 300 kHz of the values predicted from the constants of Hirahara *et al.*[9] Three other *ortho-para* doublets in previously unidentified vibrational states were then observed, two with A and one with B type symmetry (Fig. 1). By a method similar to that used for assignment for the ground state, rotational lines with the same value of K_a but successively higher J were identified in vibrationally excited

TABLE II. Molecular constants of cyclopropenylidene in the ground and four vibrationally excited states.

Constant[a]	Ground[b]	ν_6	ν_5	ν_3	ν_2[c] (?)
A	35 092.5083±0.032	34 157.232±0.061	34 957.495±0.097	34 999.126 ±0.051	34 969.591±0.041
B	32 212.9468±0.032	31 944.546±0.075	32 251.56 ±0.10	32 224.563 ±0.045	32 012.523±0.048
C	16 749.0286±0.032	16 777.999±0.01	16 778.889±0.008	16 757.130 ±0.003	16 708.446±0.007
$\Delta_J \times 10^3$	41.689 ±0.065	210.388±0.003	132.250±0.003	47.015 ±0.002	41.011±0.002
$\Delta_{JK} \times 10^3$	44.017 ±0.055	−412.809±0.005	80.419±0.007	9.882 ±0.004	39.564±0.005
$\Delta_K \times 10^3$	61.871 ±0.038	−499.149±0.014	−603.96 ±0.01	76.130 ±0.005	−90.717±0.008
$\delta_J \times 10^3$	16.4338±0.0086	101.037±0.001	63.328±0.001	18.2591±0.0008	16.387±0.001
$\delta_K \times 10^3$	58.610 ±0.020	41.313±0.004	166.864±0.003	48.682 ±0.001	32.628±0.002
$H_J \times 10^6$	0.00	0.00	0.00	0.00	0.00
$H_{JK} \times 10^6$	6.37 ±0.84	6.37[d]	6.37[d]	12.3[e]	6.37[d]
$H_{KJ} \times 10^6$	−14.7 ±0.12	−14.7[d]	−14.7[d]	−39[e]	−14.7[d]
$H_K \times 10^6$	10.08 ±0.56	10.08[d]	10.08[d]	−30[e]	10.08[d]
$h_1 \times 10^6$	0.477 ±0.075	0.477[d]	0.477[d]	0.00[e]	0.477[d]
$h_2 \times 10^6$	−0.88 ±0.37	−0.88[d]	−0.88[d]	0.00[e]	−0.88[d]
$h_3 \times 10^6$	1.22 ±0.31	1.22[d]	1.22[d]	0.00[e]	1.22[d]
Δ (uÅ^2)	0.083 126 ± 0.000 009	−0.494 643 ± 0.000 046	−0.00693 ± 0.00007	0.036 245 ± 0.000 037	0.008 05 ± 0.000 03

[a] Units are in MHz.

[b] Constants from Ref. 6.

[c] The question mark after ν_2 indicates that the assignment of this mode is tentative.

[d] Fixed at ground state values.

[e] From Ref. 9.

states. After transitions as high as $10_{1,10} \rightarrow 11_{0,11}$ and $10_{0,10} \rightarrow 11_{1,11}$ were assigned, A, B, C, and Δ_J could be well determined, allowing us to identify rotational transitions with higher values of K_a ($K_a = 1,2,3$) with *ortho-para* splittings of 2–6 MHz. In all, approximately 30 rotational transitions between 84 and 386 GHz were measured for each vibrational state (Table I).

The rotational and centrifugal distortion constants obtained by fitting the data in Table I to Watson's A-reduced Hamiltonian[13] are shown in Table II. To ensure correct assignments in the presence of a thicket of unidentified lines, we eliminated rotational lines individually from the data set and recomputed the constants, finding only very small shifts—generally less than one standard deviation. There is no evidence therefore that the fits are biased by the inclusion of single misidentifications. As further evidence that the molecular constants are correct, blind predictions for the frequencies of several rotational transitions in each vibrational state were verified, generally to within a small fraction of a linewidth. The correlation coefficients among the constants are lower than 0.97, with the exception of Δ_J and δ_J that show a correlation coefficient of essentially unity.

IV. ASSIGNMENT OF VIBRATIONAL STATES

The rotational transitions of the C_3H_2 molecule are segregated into *ortho* and *para* lines with 3:1 intensity ratios owing to the two equivalent off-axis hydrogen atoms. Because the vibrational wave functions are either symmetric (A-type symmetry) or antisymmetric (B-type symmetry) with respect to a rotation about the b-axis of the molecule that interchanges the hydrogens, the ordering in frequency of *ortho* and *para* components of K-type doublets is reversed between modes of A and B symmetries. As shown in Fig. 1, by employing this *ortho-para* reversal, the observed vibrational states were separated into two groups,

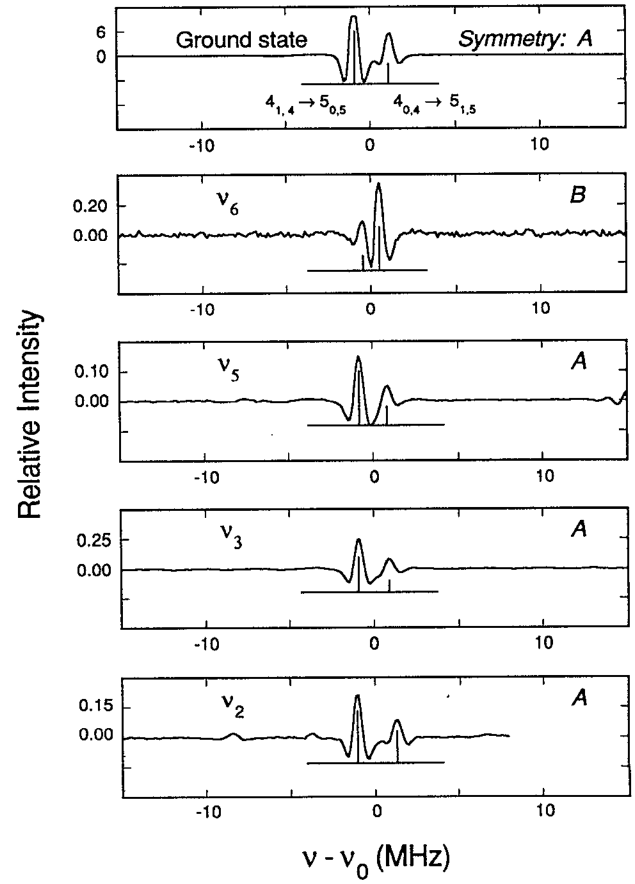

FIG. 1. The K doublets showing characteristic 3:1 intensity ratios of the 4→5 doublet of the ground and four vibrationally excited states of c-C_3H_2. Line shapes are second derivative of a Lorentzian, owing to the modulation scheme.

TABLE III. Comparison of theoretical and experimental inertial defects.

Vibrational mode[a]	Approximate description[b]	Symmetry	Frequency[c] (cm^{-1})	Inertial defect $\Delta(u\text{Å}^2)$ Observed	Inertial defect $\Delta(u\text{Å}^2)$ Calculated
ν_1	Sym. CH str.	A_1	3104		0.09
ν_7	Asym. CH str.	B_2	3070		0.089
ν_2	C=C str.	A_1	1583	0.008 05(3)	0.081
ν_3	Sym. C–C str.+in-plane sym. CH bend	A_1	1277.3711[d]	0.036 25(4)	0.049
ν_8	In-plane asym. CH bend+asym. C–C str.	B_2	1064		0.609
ν_5	Out-of-plane, out-of-phase CH bend	A_2	975	−0.006 93(8)	−0.012
ν_9	Asym. C–C str.+in-plane asym. CH bend	B_2	895		−0.873
ν_4	In-plane sym. CH bend+sym. C–C str.	A_1	890		1.376
ν_6	Out-of-plane, in-phase CH bend	B_1	774	−0.494 63(3)	−0.411
	Ground state	A_1	0	0.083 126[e]	0.091

[a] Designation of the modes is based on the convention in Ref. 37.
[b] From Ref. 10.
[c] From Ref. 1 (calculated).
[d] From Ref. 9 (measured).
[e] From Ref. 6.

three with A and one with B type symmetry. This classification, however, does not uniquely identify the vibrational states. If the vibration-rotation coupling constants were known, a unique assignment might be made, but, in order to obtain accurate values for these constants, the anharmonic part of the potential is needed. Recently, the vibration-rotation coupling constants of H_2CCC, the linear isomer of cyclopropenylidene, have been calculated,[14] but to our knowledge such calculations have not been done for cyclopropenylidene itself.

In planar molecules such as C_3H_2, Oka and Morino[15] showed that to first order the inertial defect, unlike the vibration-rotation coupling constants, does not depend on the anharmonic part of the potential and can be calculated from a normal mode analysis. Comparison of the inertial defect obtained from high-resolution spectroscopy and the calculated values therefore provides a way to assign vibrational states. Recently, Jagod and Oka[16] obtained excellent agreement between the observed and calculated values of the inertial defect for modes of several polyatomic molecules such as benzene, which encouraged us to adopt the same approach for cyclopropenylidene.

Calculation of the vibrational contribution to the inertial defect, Δ_{vib}, requires the normal mode vibrational frequencies and Coriolis couplings. The dependence of of Δ_{vib} on these parameters is given by[17,18]

$$\Delta_{\text{vib}}=\sum_s \Delta_s(v_s+\tfrac{1}{2}), \tag{1}$$

where

$$\Delta_s=\frac{2K}{\omega_s}\sum_{s'}\frac{[(\zeta^c_{ss'})^2-(\zeta^a_{ss'})^2-(\zeta^b_{ss'})^2]}{(\omega^2_{s'}-\omega^2_s)} \times(4\omega^2_{s'}\delta_{si}+(\omega^2_{s'}+3\omega^2_s)\delta_{so}), \tag{2}$$

i refers to in-plane and o to out-of-plane modes, and $K=h/8\pi^2c$. The Coriolis coupling constants, $\zeta_{ss'}$, are between modes s and s', and ω_s is the vibrational frequency of mode s. The ζ matrices are derived from the l matrix which relates the normal coordinates to the mass-weighted Cartesian coordinates (Ref. 15):

$$\zeta^a_{ss'}=\sum_i (l^b_{is}l^c_{is'}-l^b_{is'}l^c_{is}). \tag{3}$$

The frequencies of the normal mode vibrations of C_3H_2 were calculated *ab initio* by DeFrees and McLean.[1] Their harmonic force field[19] in conjunction with the GAUSSIAN 90 and UMAT vibrational packages[20] were used[21] to calculate the l matrix. Both the ground state and ν_3 can be accurately assigned based on comparison of the calculated and observed inertial defects, thus providing a check on the reliability of the calculations (Table III). As in the case of benzene,[16] the agreement for the ground state is better than that for the excited vibrational states.

The state with B symmetry has a large negative inertial defect (Table III). We have assigned it to the lowest vibrational state ν_6, the out-of-plane, in-phase CH bend, by comparison of the observed inertial defect with that calculated. Two states with A type symmetry remain to be assigned. One has a small positive inertial defect, and the other a small negative one. The latter state was tentatively assigned to ν_5, involving the out-of-plane, out-of-phase CH bend, because the agreement with the calculated value for ν_5 was the closest.

The vibrational temperature diagram shown in Fig. 2, which is based on intensities of four rotational transitions in the vibrationally excited states observed relative to ground, can be used as a guide for the assignment of the remaining A symmetry state. The assignment of this state with small positive inertial defect is somewhat uncertain because none of the calculated defects is in good agreement with that observed. We have tentatively assigned it to the C=C stretch (ν_2) based on the following evidence: except for ν_2, there are only two other states with A type symmetry, ν_1 and ν_4. The ν_1 state (symmetric CH stretch) lies approximately 3000 cm^{-1} above ground and is predicted to be too weak to be observed, if the vibrational tempera-

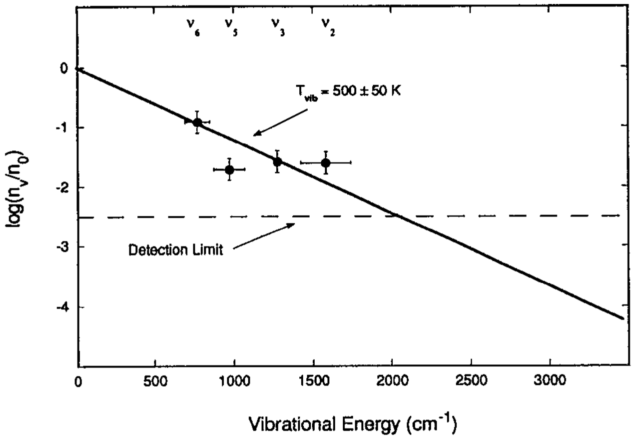

FIG. 2. Vibrational temperature diagram. Points indicate intensities of four sets of rotational transitions ($9_{1,9} \rightarrow 10_{0,10}$, $8_{1,8} \rightarrow 9_{0,9}$, $8_{2,7} \rightarrow 9_{1,8}$, and $7_{2,6} \rightarrow 8_{1,7}$) of ν_2, ν_3, ν_5, and ν_6 relative to the ground state. Uncertainties are estimated by repeated intensity measurements. The line, a least-squares fit, is constrained to pass through the origin; its slope corresponds to a vibrational temperature of 500±50 K. The horizontal error bars were estimated by comparison of the theoretical values from Refs. 1 and 10. The dashed line indicates approximately the sensitivity of our searches reported here.

ture in our discharge is 500±50 K as suggested by Fig. 2. The ν_4 state, on the other hand, has a large Coriolis interaction with ν_9 which probably shifts the readily recognized $4 \rightarrow 5$ doublet in ν_9 out of our search range.

It is unlikely that the state we have assigned to ν_2 is an overtone or a combination state. The overtone state $2\nu_6$ is the closest in energy to ν_2; the inertial defect for this state, however, is large and negative, in disagreement with the observed value for ν_2.

The large discrepancy between the experimental and calculated inertial defects for the ν_2 state could be the result of interaction with the state with two quanta in ν_6. A Fermi interaction between $2\nu_6$ and ν_2 is allowed because both states have the same symmetry. The close proximity of the predicted energies of $2\nu_6$ and ν_2 (~ 35 cm^{-1}), and the fact that admixture of an out-of-plane state (ν_6) will, in general, lower the inertial defect of an in-plane state (ν_2) make such interaction plausible. Such effects on the inertial defect have been observed in other systems. Jagod and Oka,[16] for example, attributed the discrepancy between the measured and calculated inertial defects for ν_{20} of benzene to the interaction with overtone states.

V. DISCUSSION

Aside from the two CH stretches, approximately 3000 cm^{-1} above ground and therefore probably too weak for us to observe, there are three low-lying states that have not been identified (Table III). The calculated Coriolis matrices show that there is a c-type Coriolis interaction between ν_4 and ν_9 that results in anomalous values of the C rotational constant for the two states because of their close proximity to each other (~ 5 cm^{-1}). On the assumption that the major contribution to the vibration-rotation coupling constants is from Coriolis interaction, the $4 \rightarrow 5$ doublet of the ν_4 state is estimated to lie below our search range with a collapsed K-type splitting. The same doublet in ν_9 lies above our search range with a predicted K-type splitting of ~ 180 MHz. As discussed later, our data suggests that the energy difference between the ν_4 and ν_9 states may be ~ 40 cm^{-1}. If we use this splitting instead of the theoretically estimated value (~ 5 cm^{-1}) and assume as before that the dominant contributions to the vibration-rotation coupling constants are from the Coriolis interactions, we estimate that the $4 \rightarrow 5$ doublets of the ν_4 and ν_9 states lie within the range of our survey but with collapsed K-type splittings. The assignment of such isolated lines is a difficult task. Using the Coriolis contributions to the vibration-rotation coupling constants, we estimate that the same $4 \rightarrow 5$ doublet of the ν_8 state probably lies within the range of our survey, and the K-type splitting is ~ 6 MHz compared with ~ 2 MHz for the states that we have identified. An apparent *ortho-para* doublet with a splitting of approximately 6 MHz was tenatively assigned to the $4 \rightarrow 5$ doublet of this state, however, we were unable to assign other rotational transitions possibly owing to large Coriolis interactions.

TABLE IV. Quartic distortion constants in ν_6 and ground vibrational states (units are in MHz).

	Ground state	ν_6
τ_{aaaa}	-0.590	2.806
τ_{bbbb}	-0.298	-1.649
τ_{cccc}	-0.035	-0.033

As for the rotational constants, there are also substantial shifts in the values of the centrifugal distortion constants between the ground and vibrationally excited states. It is worth asking if it might be possible to use these distortion constants as an additional signature for the assignment of the vibrational states.

The difference in the quartic centrifugal distortion constants between the ground and the vibrationally excited states is most pronounced for ν_6, with both Δ_K and Δ_{JK} changing in sign and magnitude. Table IV shows the values of τ_{aaaa}, τ_{bbbb}, and τ_{cccc} for the ground state and ν_6. Although τ_{cccc} is little changed, both τ_{aaaa} and τ_{bbbb} differ significantly between ν_6 and the ground state, with τ_{aaaa} showing the largest shift. The centrifugal distortion constant, τ_{aaaa}, may be expressed as[22]

$$\tau_{aaaa} = 4 \sum_{v' \neq v} \frac{\langle \mu_{aa} \rangle^2_{v,v'}}{E_v - E'_v} + \tau^{Cor}_{aaaa}, \tag{4}$$

where μ is the inverse inertial tensor expressed as a Taylor series in the vibrational coordinates and τ^{Cor}_{aaaa} indicates the Coriolis contribution to τ_{aaaa}. From symmetry considerations, it is readily shown that the interaction of the ground state and ν_6 does not contribute to the sum; contributions of states higher in energy than ν_6 to the sum are negative (i.e., opposite to the observed shift), implying that Coriolis interactions are responsible for the shifts in the distortion constants. The a-type Coriolis interaction between ν_6 and ν_4 causes a change in τ_{aaaa} estimated as[23]

$$\Delta\tau_{aaaa}=\frac{64A^4(\zeta^a_{4,6})^4}{(E_4-E_6)^3}, \tag{5}$$

where $\Delta\tau_{aaaa}$ is the difference in τ_{aaaa} between ν_6 and ground, ζ the Coriolis coupling coefficient, and E_4-E_6 is the separation between the ν_6 and ν_4 states. The energy separation can be estimated from the change of the A rotational constant, ΔA, between the ν_6 and ground state as[23]

$$E_4-E_6=\frac{-4(\zeta^a_{4,6})^2A^2}{\Delta A}. \tag{6}$$

From the observed value of ΔA and the *ab initio* value of $\zeta^a_{4,6}$, a separation between ν_6 and ν_4 of 76 cm^{-1} compared with the *ab initio* value of 112 cm^{-1} was estimated. Using the value of 76 cm^{-1} in Eq. (5), yields $\Delta\tau_{aaaa}=1.53$ MHz, 1.9 MHz lower than the experimental value.

An energy separation of 118 cm^{-1} between ν_6 and ν_9 was estimated on the assumption that the change in the rotational constant B in ν_6 is due to a b-type Coriolis interaction between ν_6 and ν_9. This allowed us to estimate the separation between ν_4 and ν_9 of 42 cm^{-1}, compared with the *ab initio* value of 5 cm^{-1}. The b-type Coriolis interaction between ν_6 and ν_9 should cause an increase of τ_{bbbb} in ν_6 with respect to the ground state, yet, the experimental value is smaller—possibly owing to high correlation between δ_J and the sextic distortion constants.

We therefore conclude that the main cause of large changes in the centrifugal distortion constants are near-resonance interactions, and in the absence of precise information about the vibrational structure and the potential function of the molecule, it is probably not practical to use the centrifugal distortion constants as a basis for the assignment of the states.

A better determination of the vibrational structure of cyclopropenylidene is now largely dependent on infrared studies. All modes other than ν_5 are infrared active, although the small predicted infrared absorption coefficients of several may make detection difficult. The rich vibrational structure can also be a source of confusion in the infrared (Fig. 3). The molecular constants that we have determined for the excited vibrational states should aid detection of the infrared active modes. Perhaps the best candidate for IR detection is ν_6 whose predicted infrared absorption coefficient is only a factor of two less than that of ν_3.[10]

Although it may now be possible to obtain *ab initio* values of the vibration-rotation coupling constants for molecules as large as C_3H_2, there is a paucity of high-resolution spectroscopic data for the vibrationally excited states of polyatomic molecules. Our experimental values of the vibration-rotation coupling constants can be used to test theoretical methods when such calculations are attempted in the future for C_3H_2.

We have considered the possibility of detecting vibrationally excited C_3H_2 in space, particularly in the lowest bending state, ν_6, which is ~1000 K above ground. In various astronomical sources, vibrationally excited states of several diatomic molecules (SiO, CS, SiS) have been observed,[24,25] and excited bending states of C_4H, HCN, and HC_3N have also been observed.[25–27] The ν_2 excited bending state of HCN at ~1025 cm^{-1} was detected, for example, in the hot molecular core of the Orion nebula.[26] The HCN column density in the ground state in the hot core[26] is 2.3×10^{18} cm^{-2}, while the column density in the extended source[28] is 10^{14} cm^{-2}. Blake *et al.* obtained a column density of 2.6×10^{13} cm^{-2} for C_3H_2 in the ground state in Orion,[29] while Vrtilek *et al.*[3] obtained a slightly lower value of 6×10^{12} cm^{-2} averaged over a somewhat larger telescope beamwidth. To our knowledge, there is no evidence for C_3H_2 in the hot core; however, if we assume that column densities toward the extended source and hot core scale the same way as those of HCN, the estimated antenna temperature for the ν_6 state of vibrationally excited C_3H_2 is approximately 5 mK. Although there is no evidence for rotational lines of vibrationally excited C_3H_2 in the published millimeter-wave surveys of Sgr B2 and Orion,[30–36] Sgr B2, where the $\nu_7=1$ bending state of HC_3N at 320 K above ground is among the vibrationally excited species detected,[27] is a plausible source for detection of vibrationally excited C_3H_2. There, we estimate an antenna temperature of a few mK for the ν_6 mode of C_3H_2 based on a column density of 5×10^{14} cm^{-2} in the ground state,[3,4] a possibly detectable value.

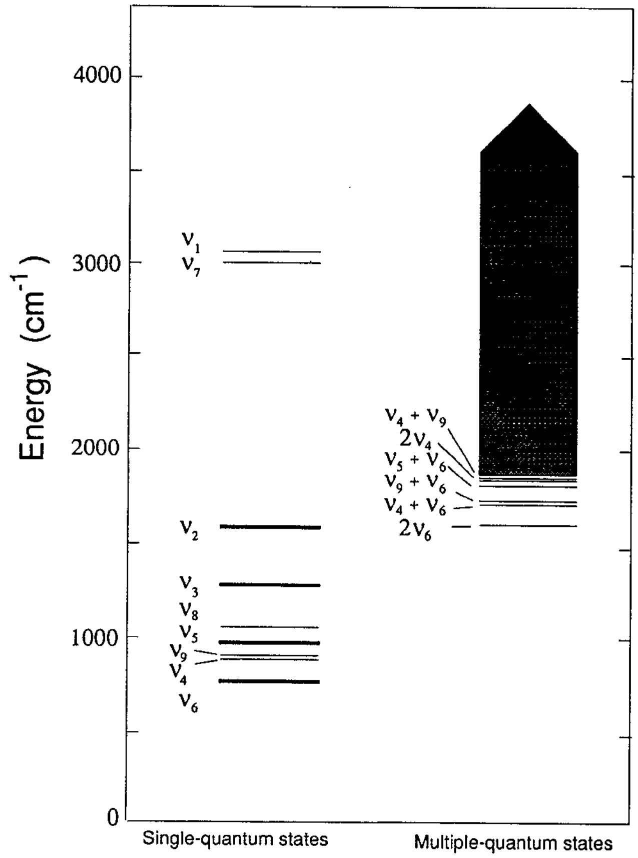

FIG. 3. Energy levels referenced to the ground vibrational state of the nine normal modes. The separation between ν_4 and ν_9 has been exaggerated. Three of the overtone and combination bands are shown. The shaded area indicates a high density of overtone and combination bands.

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