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LABORATORY AND ASTRONOMICAL SPECTROSCOPY OF C_3H_2, THE FIRST INTERSTELLAR ORGANIC RING

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ABSTRACT

The first laboratory and astronomical observations of the carbene ring molecule C_3H_2 briefly reported in a recent *Letter* are described in detail. In the laboratory, 22 millimeter-wave lines have been measured in a He and C_2H_2 discharge. From these the three rotational constants and the five fourth-order centrifugal distortion constants of C_3H_2 have been determined to high precision, allowing, in turn, calculation to 0.1 km s^{-1} of the most important lines in the radio and far-IR spectrum; 123 lines in the rotational spectrum with $E/k < 100$ K are tabulated. Eleven astronomical transitions have been identified, and in Sgr B2 and Orion KL, rotational temperatures and column densities were derived and compared with those of other hydrocarbons with a similar number of C atoms. Owing to the ubiquity in space of its strongest low-lying transitions, C_3H_2 promises to be a generally useful molecular probe; further, it may be the first of a new class of ring molecules in space. Detection of a carbene ring in an He and C_2H_2 discharge suggests searches for other hydrocarbon rings and cyclopropenylidene derivatives.

Subject headings: interstellar: molecules — laboratory spectra — line identifications

I. INTRODUCTION

Cyclopropenylidene, C_3H_2, the compact ring shown in Figure 1, is one of the most unusual and interesting interstellar molecules, the first organic ring observed in an astronomical source (Thaddeus, Vrtilek, and Gottlieb 1985, hereafter TVG) and—with a highly reactive bivalent carbon atom—the first carbene. Long postulated by theoretical chemists as the most stable compound with three carbon and two hydrogen atoms (Hehre *et al.* 1976), C_3H_2 is conspicuous in many Galactic sources and widely distributed in the interstellar gas, with at least nine velocity components in absorption at 18 GHz against the distant H II region W49 (Matthews and Irvine 1985); the same line, the lowest lying transition of the ortho symmetry species, has recently been detected in absorption against the nucleus of the radio galaxy Centaurus A (Seaquist and Bell 1986).

The first evidence for C_3H_2 was astronomical, and identification afterward occurred in the laboratory. A decade ago the strong astronomical line at 85338 MHz was observed toward several sources as part of a fortuitous triplet of "nonterrestrial" lines, two members of which were soon identified (Thaddeus, Guélin, and Linke 1981). Searches for harmonically related lines had been unsuccessful, no additional astronomical lines could be assigned conclusively, and attempts to detect the carrier in the laboratory failed. The crucial step leading to identification occurred in 1984 August, when, motiviated by recent success in producing the carbon-chain radicals C_2H, C_3H, and C_4H in an acetylene discharge, we searched for and detected a laboratory line in the same discharge at the precise astronomical frequency. Our purpose here is to amplify TVG, where we described the discovery of C_3H_2, presenting our laboratory data in greater detail than was possible there and discussing more fully the astronomical lines we attribute to C_3H_2.

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II. EVIDENCE FOR CYCLOPROPENYLIDENE

The carrier of U85338 was produced in a DC discharge (0.3 A) through C_2H_2 and He in the absorption cell of our millimeter-wave spectrometer,[2] a large glass tube cooled by liquid nitrogen flowing through a surrounding copper coil. Impurities (mainly acetone), which contribute a thicket of unrelated lines, were removed by bubbling the acetylene through concentrated sulfuric acid and next passing it through a soda-lime column to absorb sulfur contaminants. The total pressure in the cell was typically 20–30 milli torr; flow rates, measured at atmospheric pressure and 20° C, were about 0.4 cm^3 s^{-1} for C_2H_2 and 0.01 cm^3 s^{-1} for He. The line widths (FWHM) were typically 700–1200 kHz.

When an adequate signal-to-noise ratio of at least 5 was achieved in a few minutes' integration by optimizing flow rates and discharge conditions (see Fig. 3 of TVG), assays were performed to identify the elemental constituents of the carrier and to determine whether it is a radical or a molecular ion. On adding small amounts of N_2 or O_2 to the discharge, no change in the intensity of the 85338 MHz line was observed, indicating that contaminants from the air were not the source of the carrier, which therefore had to be either a hydrocarbon or a pure carbon molecule. With the same sample of 99% deuterium-enriched acetylene previously used in our CCD measurements (Vrtilek *et al.* 1985) substituted for normal acetylene, the line vanished, indicating that the carrier contains H as well as C. Next, since no line was detected with 1 Hz Zeeman modulation in a magnetic field of 12 G, the carrier is

[2] The spectrometer used to detect C_3H_2 has been gradually modified from that described by Gottlieb, Gottlieb, and Thaddeus (1983). The klystron phase-lock loop is similar to that described by Henry (1976). The 800 MHz phase-lock-loop reference is derived by doubling the output of a frequency synthesizer (HP 5105A) which is swept under computer control and is now phase-modulated at 100 kHz. The modulation system has been eliminated by using a lock-in-amplifier that measures signals near 200 kHz. A preamplifier (Perry 604-40) better matched to the InSb bolometer is now used. The flow rates are measured at the gas inlet port with Matheson model 610 flow meters.

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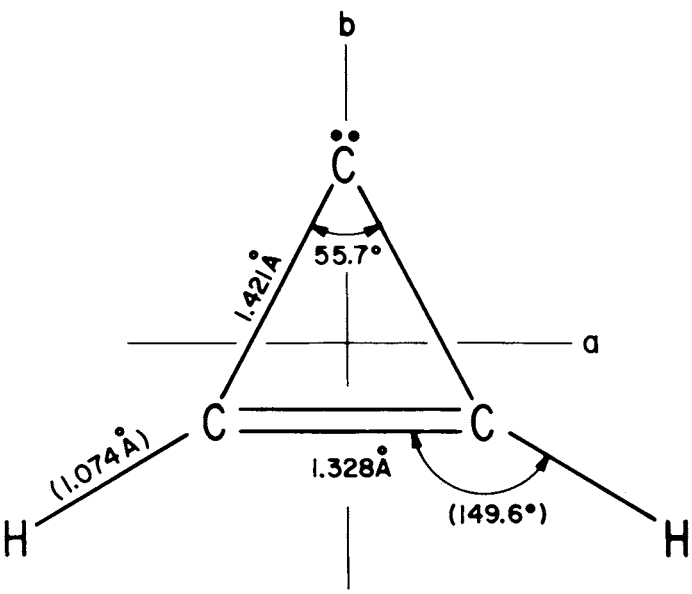

FIG. 1.—Molecular geometry of C_3H_2. The C–C and C=C distances were derived from the measured rotational constants (Table 3) for the C–H distance and the H–C=C angle (in parentheses) from the ab initio calculation of Lee, Bunge, and Schaefer (1985; double zeta plus polarization two-configuration self-consistent field I calculation).

not a radical and, further, the number of H atoms is even, since a hydrocarbon with an odd number would possess a net magnetic moment. Application of an even stronger static 50 G field, which, by comparison, enhanced the production of HCO^+ by a factor of 9, did not affect the line intensity, indicating that the carrier is probably not a molecular ion (DeLucia *et al.* 1983). We therefore concluded that we were observing a neutral hydrocarbon with an even number of H atoms.

When all hydrocarbons with three or fewer C atoms were considered, and after eliminating those without a permanent electric dipole moment, only CH_2, C_3H_4, and C_3H_8 (molecules with known spectra) and C_3H_2 remained. Complex hydrocarbons with more than three C atoms were vulnerable to the general objection that they should produce many more unidentified astronomical lines comparable in strength to U85,338 than were observed in the Sagittarius B2 survey of Cummins, Linke, and Thaddeus (1986). No molecule with the formula C_3H_2 had been observed in its free state prior to our work, although tentative evidence at IR wavelengths for C_3H_2 trapped in an argon matrix had recently been reported (Reisenauer *et al.* 1984). Many theoretical studies of the structure of C_3H_2 (e.g., Hehre *et al.* 1976; Lee, Bunge, and Schaefer 1985) indicate that cyclopropenylidene, a singlet carbene ring with C_{2v} symmetry, is the most stable isomer. Owing to the two unpaired electrons on the bivalent carbon atom, C_3H_2 is predicted to be exceptionally polar for a hydrocarbon, with a dipole moment calculated to be 3.3 debyes.

III. SPECTROSCOPY OF CYCLOPROPENYLIDENE

Finding and assigning related lines to prove that U85338 is produced by C_3H_2 was the most difficult and time-consuming part of the investigation, requiring much trial and error. The uncertainties of the ab initio structure calculation, $\sim 1\%$, imply uncertainties of one or more GHz in the predicted frequencies of the rotational spectrum, posing a severe problem in the search for weak lines with a spectrometer that covers at most 40 MHz at one setting.

The spectrum of cyclopropenylidene is that of an oblate asymmetric top ($\kappa = +0.69$) with *b*-type transitions and ortho-para symmetry species with relative statistical weights of 3:1. If C_3H_2 were strictly planar and rigid, two parameters would suffice to determine the entire spectrum: three moments of inertia constrained by the Pythagorean theorem; but to describe the actual deformable molecule to satisfactory accuracy requires three rotational and five centrifugal distortion constants. To determine these, at least eight lines of C_3H_2 must be identified and correctly assigned.

The strategy adopted to find other lines of C_3H_2 was to search for a series of strong, *R*-branch ortho and para doublets from levels along the backbone (i.e., the lower right edge) of the energy level diagram (Fig. 2) predicted to occur near 85, 117, 151, 184, and 217 GHz. The splittings of these doublets decrease rapidly with increasing J from ~ 3000 MHz, for the $J = 1 \rightarrow 2$ doublet at 82 and 85 GHz, to 0.1 MHz, for the $J = 5 \rightarrow 6$ doublet at 217 GHz. We began by searching in the laboratory for the 151 GHz $J = 3 \rightarrow 4$ doublet, because the ortho-para splitting was predicted to be small (~ 20 MHz), yielding a distinct signature; at this frequency our spectrometer was particularly sensitive.

In 1985 February, a doublet with the expected 3:1 intensity ratio was detected at 150820 and 150851 MHz. We immediately extended the search to the next higher lying line pair, and soon a similar, more closely spaced doublet with exactly the predicted splitting of 2 MHz was detected near 184330 MHz in a striking confirmation that we were observing a new molecule with the spectrum of an asymmetric top and the ortho-para alternation expected of C_3H_2. At nearly the same time, E. Sutton communicated to us the frequency of an unidentified line detected in Orion in the recent Caltech survey (Sutton *et al.* 1985), which we realized was the unresolved $J = 6 \rightarrow 5$ doublet.

We also attempted, in retrospect mistakenly, to assign the strong, unidentified line at 45379 MHz (Suzuki *et al.* 1984), with astronomical properties similar to those of U85,338, to the $3_{2,1} \rightarrow 3_{1,2}$ transition, predicted ab initio to lie only 32 MHz away. However, when a Hamiltonian for an asymmetric rotor with centrifugal distortion was fitted to the 45, 85, 151, 184, and 217 GHz lines, unreasonably large values of the fourth-order centrifugal distortion parameters and of the inertial defect were derived. The omission of one transition at a time from the fit confirmed that U45379 does not originate from the same carrier as the others; its carrier is still unknown.

Removing this misassigned line dramatically improved the fit, and hence our ability to predict the frequencies of new lines, and quickly enabled us to locate in the laboratory the $J = 2 \rightarrow 3$ ortho-para doublet at 117 GHz and higher J transitions arising from levels on the left side of the energy level diagram. The assignment of several previously unidentified astronomical lines soon followed, including four from the Sgr B2 survey of Cummins, Linke, and Thaddeus (1986), among them the weak para counterpart at 82 GHz of the 85338 MHz line and the 151 GHz ortho-para doublet observed by Hollis *et al.* (1983). It had been clear to us for some time that astronomical detection of the lowest lying ortho transition of C_3H_2 near 18 GHz, too weak to be observed in the laboratory and below the range of our spectrometer, was a crucial test of our assignment. Before we could undertake a search ourselves, we learned from H. Matthews and W. Irvine that they had

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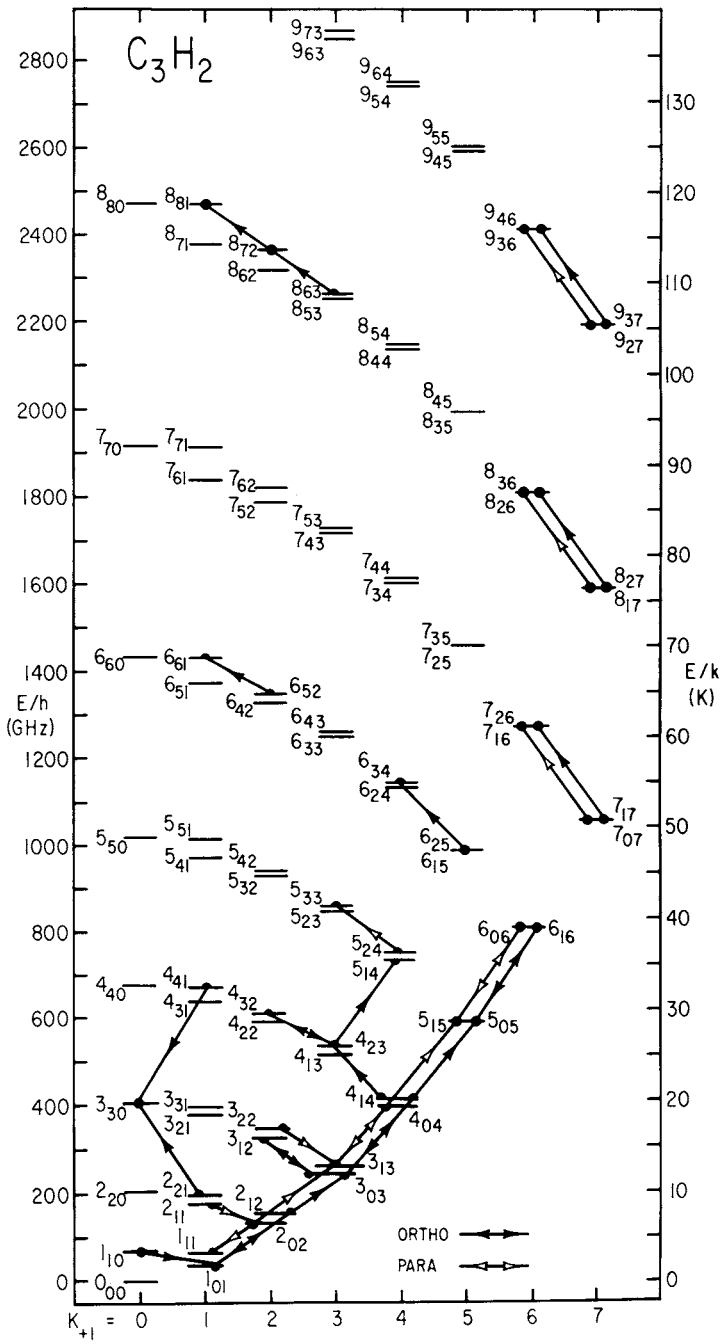

FIG. 2.—Rotational levels of C_3H_2. Downward arrows indicate astronomical transitions, mainly in emission; upward ones indicate laboratory transitions, all in absorption.

detected a ubiquitous interstellar line at 18343 MHz with just the required properties. This is the $1_{1,0} \rightarrow 1_{0,1}$ transition. Our current prediction of the frequency of this transition from laboratory data agrees with that derived from astronomical data to 0.1 parts per million.

In all, 22 laboratory lines have now been very accurately measured (Table 1). Several of these, in particular the important pairs at 117 and 184 GHz, are inaccessible to astronomical observation from the ground because of atmospheric O_2 and H_2O. Measurements of the peak intensities of transitions close in frequency allowed determination of ortho-para ratios (see sample spectra in Fig. 3). The measured ratios (Table 2) are in good agreement with the theoretical ratio, providing additional support for the identification of cyclopropenylidene.

The 19 unblended laboratory transitions were very accurately fitted with an asymmetric rotor Hamiltonian with five determinable fourth-order centrifugal distortion parameters (Kirchhoff 1972). Specifically, the reduced χ^2 was near unity (0.67 for 11 degrees of freedom), the molecular constants (Table 3) were well determined, and in only two cases were the off-diagnonal elements of the correlation coefficient matrix (Table 4) greater than 0.9. There is no evidence for either missing

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TABLE 1

LABORATORY C_3H_2 FREQUENCIES

Transition (lower → upper)	Measured Frequency[a] (MHz)	Measured Minus Calculated (MHz)	S[c]	E/k[d] (K)
$6_{5,2} \rightarrow 6_{6,1}$	82583.434 ± 0.011	−0.001	2.21	62.4
$3_{0,3} \rightarrow 3_{1,2}$	82966.200 ± 0.013	−0.013	0.98	9.7
$1_{0,1} \rightarrow 2_{1,2}$	85338.893 ± 0.014	−0.012	1.50	0.0
$4_{2,3} \rightarrow 4_{3,2}$	85656.431 ± 0.017	+0.011	1.75	22.6
$8_{6,3} \rightarrow 8_{7,2}$	100400.778 ± 0.006	0.000	4.02	106.3
$8_{7,2} \rightarrow 8_{8,1}$	104904.155 ± 0.009	0.000	2.40	111.1
$2_{1,2} \rightarrow 3_{0,3}$	117151.191 ± 0.009	0.000	2.44	4.1
$2_{0,2} \rightarrow 3_{1,3}$	117546.214 ± 0.026	−0.023	2.45	6.4
$5_{2,4} \rightarrow 5_{3,3}$	117550.392 ± 0.020	+0.004	1.85	35.4
$4_{1,4} \rightarrow 4_{2,3}$	117731.821 ± 0.009	+0.003	0.99	17.0
$3_{1,3} \rightarrow 4_{0,4}$	150820.665 ± 0.018	−0.004	3.45	12.1
$3_{0,3} \rightarrow 4_{1,4}$	150851.908 ± 0.007	+0.007	3.45	9.7
$6_{2,5} \rightarrow 6_{3,4}$	151039.173 ± 0.014	+0.002	1.89	45.1
$4_{1,4} \rightarrow 5_{0,5}$	184327.966 ± 0.005	−0.001	4.45	17.0
$4_{0,4} \rightarrow 5_{1,5}$	184330.026 ± 0.016	+0.003	4.45	19.3
$2_{2,1} \rightarrow 3_{3,0}$	216278.756 ± 0.021	−0.004	1.42	6.7
$5_{1,5} \rightarrow 6_{0,6}$	217822.148 ± 0.004	+0.112	5.45	28.1
$5_{0,5} \rightarrow 6_{1,6}$		−0.010	5.45	25.8
$4_{2,3} \rightarrow 5_{1,4}$	217940.046 ± 0.007	−0.001	3.43	22.6
$9_{2,7} \rightarrow 9_{3,6}$	218054.783 ± 0.014	+0.007	2.82	103.1
$9_{3,7} \rightarrow 9_{4,6}$	218057.545 ± 0.041	−0.071	2.82	105.3
$8_{1,7} \rightarrow 8_{2,6}$	218449.439 ± 0.023	+0.579	1.96	76.4
$8_{2,7} \rightarrow 8_{3,6}$		+0.002	1.96	74.1
$7_{0,7} \rightarrow 7_{1,6}$	218732.732 ± 0.018	+0.016	1.03	48.3
$7_{1,7} \rightarrow 7_{2,6}$		−0.068	1.03	50.7

[a] Each frequency is the mean of four measurements, two made with frequency swept upward and two downward. The uncertainties were estimated as the quadrature sum of two terms: (1) the 1 σ statistical uncertainty obtained from the least-squares fit of a theoretical (second derivative Lorentzian) profile superposed on a polynomial baseline, and (2) the standard deviation of the four frequencies from the separate means of the upward and downward scans.

[b] Calculated frequencies from constants in Table 3.

[c] Asymmetric rotor line strength.

[d] E is the energy of the lower level of the transition above the para ground state $0_{0,0}$ or the ortho ground state $1_{0,1}$, 2.3 K higher; k is Boltzmann's constant.

terms in the Hamiltonian or systematic errors in the measurements; when new transitions are measured, the molecular constants should not change by more than the standard deviations. This Hamiltonian yielded in addition very accurate blind predictions: the most recently detected lines, for example, were found within a fraction of a line width of the predicted

TABLE 2

MEASURED ORTHO-PARA DOUBLETS

Transition (lower → upper)	Calculated Frequency (MHz)	Symmetry	ortho/para Ratio
$2_{1,2} \rightarrow 3_{0,3}$	117151.191	ortho	3.7 ± 0.8
$2_{0,2} \rightarrow 3_{1,3}$	117546.237	para	
$3_{1,3} \rightarrow 4_{0,4}$	150820.669	para	3.1 ± 1.2
$3_{0,3} \rightarrow 4_{1,4}$	150851.901	ortho	
$4_{1,4} \rightarrow 5_{0,5}$	184327.967	ortho	3.4 ± 0.4
$4_{0,4} \rightarrow 5_{1,5}$	184330.023	para	
$9_{2,7} \rightarrow 9_{3,6}$	218054.776	ortho	2.9 ± 0.3
$9_{3,7} \rightarrow 9_{4,6}$	218057.616	para	

NOTE.—Uncertainties are an estimated 1 σ. The lower two ratios, each measured on single scans, are somewhat more accurate than the upper two, each measured on separate scans. Ortho-para ratios are expected to equal the ratio of statistical weights, 3, at high temperature, but are 1%–2% higher at 100 K owing to the slight difference between the ortho and para ground states.

TABLE 3

MOLECULAR CONSTANTS OF C_3H_2

Parameter	Measured[a] (this work)	Expected[b]
Rotational and centrifugal distortion constants (MHz):[c]		
A''	35092.5963 ± 0.0018	35094
B''	32212.9314 ± 0.0018	32789
C''	16749.3147 ± 0.0013	16951
τ_1	−0.6765 ± 0.0004	−0.4866
τ_2	−0.1628 ± 0.0002	−0.1220
τ_3[d]	+15.3792 ± 0.0035	+4.1633
τ_{aaaa}	−0.5901 ± 0.0001	−0.2072
τ_{bbbb}	−0.2982 ± 0.0002	−0.1548
τ_{cccc}	−0.0361 ± 0.0001	−0.0267
Inertial defect (amu Å^2):		
Δ	0.083115 ± 0.000002	...
Bond lengths (Å) and angle:		
r(C=C)	1.328[e]	1.314
r(C–C)	1.421[e]	1.418
r(C–H)	...	1.074
<(HC=C)	...	149°6

[a] Uncertainties: 1 σ in least-squares fit to 19 unblended laboratory lines.

[b] Rotation constants from the ab initio structure of Lee *et al.* 1985 (double zeta plus polarization two-configuration self-consistent field I calculation). Centrifugal distortion constants from the stable, three-membered ring cyclopropene (Vrtilek *et al.* 1986).

[c] Watson's (1967) determinable parameters.

[d] Not fitted; calculated from the other τ's on the assumption of planarity (Kirchhoff 1972).

[e] Calculated from A and B, adopting for the C–H bond and angle the theoretical values (last column).

frequency. The laboratory data are so accurate that including the astronomical data in the fit offers little improvement of the spectroscopic constants while leaving the rms essentially unchanged. Uncertainties in the molecular constants calculated from the fit (Kirchhoff 1972) agree well with those derived by fitting the constants to fictitious data sets, i.e., obtained by adding to the measured line frequencies Gaussian random deviates with standard deviations equal to the quoted uncertainties.

The general pattern of the millimeter-wave spectrum and the derived spectroscopic constants both provide exceptionally strong evidence to support the identification. The laboratory spectrum was analyzed with a standard Hamiltonian for a semirigid asymmetric top with b-type transitions and no fine or hyperfine structure, appropriate to a molecule with the structure shown in Figure 1: the ortho-para doublets were in the correct theoretical 3:1 ratio, and the splittings decreased with increasing J, supporting the assignment. Five transitions have been observed in space, including the fundamental ortho transition, at the exact frequencies predicted from the laboratory measurements. The measured rotational constants agree (to within 1.8%) with those calculated by Lee, Bunge, and Schaefer (1985); the inertial defect ($\Delta = 0.0831$, where $\Delta = I_C - I_A - I_B$) is comparable to that of the planar molecules H_2CO (0.056), H_2CS (0.061), and HCOOH (0.076); and the fourth-order distortion constants are nearly the same as those for cyclopropene (Vrtilek *et al.* 1986), the three-membered hydrocarbon ring with two hydrogens attached to the bivalent carbon in C_3H_2.

Table 5 lists the calculated frequencies, based entirely on laboratory data, for the strongest lines of C_3H_2 below 400 GHz whose upper levels are within 100 K of ground. The frequencies predicted are accurate to 0.1 km s^{-1} or better,

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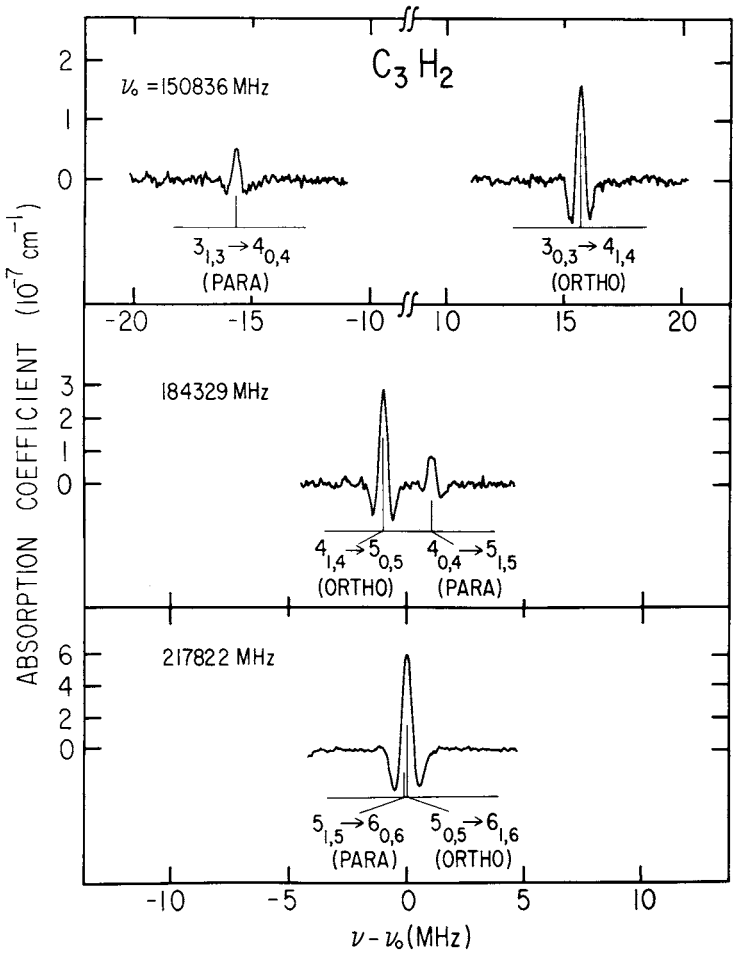

FIG. 3.—Sample laboratory spectra of three successive ortho and para *R*-branch transitions at 151, 184, and 217 GHz, illustrating the 3:1 intensity ratios and splittings that decrease with increasing *J*. The total integration time for spectra at 151 and 184 GHz was 60 minutes and for the spectrum at 217 GHz 20 minutes; the spectra shown were smoothed to an effective resolution of 180 kHz.

even in the far-infrared. Using these predictions, we identified a total of 11 lines of C_3H_2 in space (six of them also measured in the laboratory), and it should now be possible to find many more. For a rather light molecule, C_3H_2 is unusual in having many strong transitions at low frequencies (see Table 5) which should be observable with existing centimeter-wave telescopes.

Detection of partially deuterated cyclopropenylidene, C_3HD, which should now be straightforward in the laboratory, will provide additional information on the molecular structure. To judge from $CH_2(CH)_2$ (cyclopropene) and CH_2CHCD, the important transitions of C_3HD below 110 GHz can be predicted to within 50 MHz: the counterparts of the 18343 and 85338 MHz transitions lie at 19560 and 79330 MHz.

IV. ASTRONOMICAL IDENTIFICATION

Although cyclopropenylidene has been detected toward many directions in the Galaxy (Matthews and Irvine 1985;

TABLE 4

CORRELATION COEFFICIENT MATRIX

	A	B	C	τ_1	τ_2	τ_3	τ_{aaaa}	τ_{bbbb}	τ_{cccc}
A	+1.0000	+0.3882	+0.6351	−0.5712	−0.5248	+0.7457	−0.9399	−0.4099	−0.5135
B		+1.0000	+0.5964	−0.7541	−0.7313	+0.7910	−0.4029	−0.5766	−0.3154
C			+1.0000	−0.6157	−0.5729	+0.7974	−0.7545	−0.6922	−0.8647
τ_1				+1.0000	+0.9966	−0.8215	+0.5804	+0.2232	+0.2192
τ_2					+1.0000	−0.7722	+0.5255	+0.1569	+0.1580
τ_3						+1.0000	−0.8210	−0.6678	−0.6089
τ_{aaaa}							+1.0000	+0.5927	+0.6880
τ_{bbbb}								+1.0000	+0.8229
τ_{cccc}									+1.0000

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TABLE 5

CALCULATED RADIO TRANSITIONS OF C_3H_2

Frequency (MHz)	Transition Upper	Lower	Sym	S	E/k (K)
18343.143 ± 0.005	$1_{1,0}$	$1_{0,1}$	O	1.50	0.9
21587.395 ± 0.006	$2_{2,0}$	$2_{1,1}$	P	2.28	9.7
27084.336 ± 0.009	$3_{3,0}$	$3_{2,1}$	O	2.76	17.1
35360.902 ± 0.013	$4_{4,0}$	$4_{3,1}$	P	2.91	32.5
42139.184 ± 0.006	$5_{4,1}$	$5_{3,2}$	O	4.37	44.4
42231.256 ± 0.007	$4_{3,1}$	$4_{2,2}$	P	3.25	30.9
44104.788 ± 0.007	$3_{2,1}$	$3_{1,2}$	O	2.09	15.8
44624.874 ± 0.007	$6_{5,1}$	$6_{4,2}$	P	5.24	65.9
46645.012 ± 0.018	$5_{5,0}$	$5_{4,1}$	O	2.84	46.6
46755.621 ± 0.006	$2_{1,1}$	$2_{0,2}$	P	1.05	8.7
50262.658 ± 0.017	$7_{6,1}$	$7_{5,2}$	O	5.71	86.0
51841.416 ± 0.006	$1_{1,1}$	$0_{0,0}$	P	1.00	2.5
55027.767 ± 0.006	$2_{2,1}$	$2_{1,2}$	O	0.83	6.7
59557.893 ± 0.008	$3_{3,1}$	$3_{2,2}$	P	1.37	19.0
60613.857 ± 0.022	$6_{6,0}$	$6_{5,1}$	P	2.69	68.8
65674.683 ± 0.009	$4_{4,1}$	$4_{3,2}$	O	1.76	29.9
67932.543 ± 0.027	$7_{5,2}$	$7_{4,3}$	O	4.91	83.6
72515.739 ± 0.023	$6_{4,2}$	$6_{3,3}$	P	3.71	63.7
73373.207 ± 0.010	$5_{5,1}$	$5_{4,2}$	P	2.03	48.8
76449.826 ± 0.025	$7_{7,0}$	$7_{6,1}$	O	2.58	89.6
77100.066 ± 0.016	$5_{3,2}$	$5_{2,3}$	O	2.70	42.4
80723.203 ± 0.010	$4_{2,2}$	$4_{1,3}$	P	1.82	28.8
82093.559 ± 0.006	$2_{0,2}$	$1_{1,1}$	P	1.37	6.4
82583.435 ± 0.010	$6_{6,1}$	$6_{5,2}$	O	2.21	66.3
82966.213 ± 0.007	$3_{1,2}$	$3_{0,3}$	O	0.98	13.7
84727.696 ± 0.006	$3_{2,2}$	$3_{1,3}$	P	0.96	16.1
85338.905 ± 0.006	$2_{1,2}$	$1_{0,1}$	O	1.50	4.1
85656.420 ± 0.006	$4_{3,2}$	$4_{2,3}$	O	1.75	26.7
87435.316 ± 0.008	$5_{4,2}$	$5_{3,3}$	P	2.45	45.3
90344.073 ± 0.008	$6_{5,2}$	$6_{4,3}$	O	3.06	62.4
93162.007 ± 0.009	$7_{7,1}$	$7_{6,2}$	P	2.33	91.9
94613.974 ± 0.008	$7_{6,2}$	$7_{5,3}$	P	3.59	87.5
112490.804 ± 0.030	$7_{4,3}$	$7_{3,4}$	O	3.47	80.3
115231.921 ± 0.017	$6_{3,3}$	$6_{2,4}$	P	2.66	60.3
116770.809 ± 0.009	$5_{2,3}$	$5_{1,4}$	O	1.85	38.7
117151.191 ± 0.007	$3_{0,3}$	$2_{1,2}$	O	2.44	9.7
117457.183 ± 0.011	$6_{4,3}$	$6_{3,4}$	O	2.64	58.0
117530.689 ± 0.007	$4_{1,3}$	$4_{0,4}$	P	0.99	24.9
117546.237 ± 0.007	$3_{1,3}$	$2_{0,2}$	P	2.45	12.1
117550.388 ± 0.008	$5_{3,3}$	$5_{2,4}$	P	1.85	41.1
117647.100 ± 0.017	$7_{5,3}$	$7_{4,4}$	P	3.39	82.9
117731.818 ± 0.007	$4_{2,3}$	$4_{1,4}$	O	0.99	22.6
122023.529 ± 0.007	$2_{2,1}$	$1_{1,0}$	O	1.50	6.7
145089.636 ± 0.009	$3_{1,2}$	$2_{2,1}$	O	1.25	13.7
150283.509 ± 0.015	$7_{3,4}$	$7_{2,5}$	O	2.72	74.9
150436.575 ± 0.008	$2_{2,0}$	$1_{1,1}$	P	0.63	9.7
150584.631 ± 0.014	$7_{4,4}$	$7_{3,5}$	P	2.72	77.3
150820.669 ± 0.006	$4_{0,4}$	$3_{1,3}$	P	3.45	19.3
150851.901 ± 0.006	$4_{1,4}$	$3_{0,3}$	O	3.45	17.0
150954.715 ± 0.007	$6_{2,4}$	$6_{1,5}$	P	1.89	54.7
151039.171 ± 0.007	$6_{3,4}$	$6_{2,5}$	O	1.89	52.4
151343.898 ± 0.011	$5_{1,4}$	$5_{0,5}$	O	1.01	33.1
151361.125 ± 0.011	$5_{2,4}$	$5_{1,5}$	P	1.01	35.4
155518.311 ± 0.008	$3_{2,2}$	$2_{1,1}$	P	1.67	16.1
183623.662 ± 0.006	$4_{1,3}$	$3_{2,2}$	P	2.42	24.9
184276.307 ± 0.013	$8_{3,5}$	$8_{2,6}$	P	2.78	95.8
184307.976 ± 0.012	$8_{4,5}$	$8_{3,6}$	O	2.78	93.4
184327.967 ± 0.006	$5_{0,5}$	$4_{1,4}$	O	4.45	25.8
184330.023 ± 0.006	$5_{1,5}$	$4_{0,4}$	P	4.45	28.2
184738.148 ± 0.009	$7_{2,5}$	$7_{1,6}$	O	1.93	67.7
184745.602 ± 0.009	$7_{3,5}$	$7_{2,6}$	P	1.93	70.0
185047.787 ± 0.021	$6_{1,5}$	$6_{0,6}$	P	1.02	47.5
185049.048 ± 0.021	$6_{2,5}$	$6_{1,6}$	O	1.02	45.1
185617.507 ± 0.007	$4_{2,3}$	$3_{1,2}$	O	2.46	22.6
193488.810 ± 0.009	$3_{3,1}$	$2_{2,0}$	P	2.08	19.0
204788.971 ± 0.012	$4_{2,2}$	$3_{3,1}$	P	1.04	28.8
216278.760 ± 0.009	$3_{3,0}$	$2_{2,1}$	O	1.42	17.1
217822.036 ± 0.012	$6_{0,6}$	$5_{1,5}$	P	5.45	38.6
217822.158 ± 0.012	$6_{1,6}$	$5_{0,5}$	O	5.45	36.3
217940.047 ± 0.007	$5_{1,4}$	$4_{2,3}$	O	3.43	33.1
218160.459 ± 0.008	$5_{2,4}$	$4_{1,3}$	P	3.44	35.4
218448.860 ± 0.021	$8_{2,6}$	$8_{1,7}$	P	1.96	86.9
218449.437 ± 0.021	$8_{3,6}$	$8_{2,7}$	O	1.96	84.6
218732.716 ± 0.037	$7_{1,6}$	$7_{0,7}$	O	1.03	58.8
218732.800 ± 0.037	$7_{2,6}$	$7_{1,7}$	P	1.03	61.2
227169.139 ± 0.009	$4_{3,2}$	$3_{2,1}$	O	1.92	26.7
244222.191 ± 0.011	$3_{2,1}$	$2_{1,2}$	O	0.23	15.8
249054.437 ± 0.007	$5_{2,3}$	$4_{3,2}$	O	2.38	38.7
251314.316 ± 0.024	$7_{0,7}$	$6_{1,6}$	O	6.45	48.3
251314.323 ± 0.024	$7_{1,7}$	$6_{0,6}$	P	6.45	50.7
251508.698 ± 0.012	$6_{1,5}$	$5_{2,4}$	P	4.43	47.5
251527.308 ± 0.012	$6_{2,5}$	$5_{1,4}$	O	4.43	45.1
252409.867 ± 0.061	$8_{1,7}$	$8_{0,8}$	P	1.04	76.5
252409.872 ± 0.061	$8_{2,7}$	$8_{1,8}$	O	1.04	74.1
254987.644 ± 0.010	$5_{3,3}$	$4_{2,2}$	P	2.51	41.1
260479.820 ± 0.021	$5_{3,2}$	$4_{4,1}$	O	0.80	42.4
265759.485 ± 0.009	$4_{4,1}$	$3_{3,0}$	O	2.80	29.9
282381.130 ± 0.009	$4_{4,0}$	$3_{3,1}$	P	2.37	32.5
284805.147 ± 0.041	$8_{0,8}$	$7_{1,7}$	P	7.45	64.3
284805.148 ± 0.041	$8_{1,8}$	$7_{0,7}$	O	7.45	62.0
284913.025 ± 0.014	$6_{2,4}$	$5_{3,3}$	P	3.44	54.7
284997.985 ± 0.022	$7_{1,6}$	$6_{2,5}$	O	5.42	58.8
284999.336 ± 0.022	$7_{2,6}$	$6_{1,5}$	P	5.42	61.2
285795.669 ± 0.015	$6_{3,4}$	$5_{2,3}$	O	3.45	52.4
286081.453 ± 0.094	$9_{1,8}$	$9_{0,9}$	O	1.04	91.0
286081.454 ± 0.094	$9_{2,8}$	$9_{1,9}$	P	1.04	93.3
300191.704 ± 0.012	$5_{4,2}$	$4_{3,1}$	P	2.26	45.3
312709.631 ± 0.013	$6_{3,3}$	$5_{4,2}$	P	2.25	60.3
318294.253 ± 0.065	$9_{0,9}$	$8_{1,8}$	O	8.45	77.3
318294.253 ± 0.065	$9_{1,9}$	$8_{0,8}$	P	8.45	79.6
318482.214 ± 0.036	$8_{1,7}$	$7_{2,6}$	P	6.42	76.5
318482.303 ± 0.036	$8_{2,7}$	$7_{1,6}$	O	6.42	74.1
318696.962 ± 0.025	$7_{2,5}$	$6_{3,4}$	O	4.44	67.7
318790.223 ± 0.025	$7_{3,5}$	$6_{2,4}$	P	4.44	70.0
326152.785 ± 0.019	$6_{4,3}$	$5_{3,2}$	O	2.58	58.0
336948.610 ± 0.013	$4_{4,1}$	$3_{1,2}$	O	0.22	29.9
338204.008 ± 0.009	$5_{5,1}$	$4_{4,0}$	P	3.65	48.8
349264.017 ± 0.009	$5_{5,0}$	$4_{4,1}$	O	3.41	46.6
351523.288 ± 0.024	$7_{3,4}$	$6_{4,3}$	O	3.43	74.9
351781.372 ± 0.095	$10_{0,10}$	$9_{1,9}$	P	9.45	96.5
351781.372 ± 0.095	$10_{1,10}$	$9_{0,9}$	O	9.45	94.1
351965.835 ± 0.057	$9_{1,8}$	$8_{2,7}$	O	7.41	91.0
351965.840 ± 0.057	$9_{2,8}$	$8_{1,7}$	P	7.41	93.3
352185.472 ± 0.041	$8_{2,6}$	$7_{3,5}$	P	5.42	86.9
352193.593 ± 0.041	$8_{3,6}$	$7_{2,5}$	O	5.42	84.6
354142.933 ± 0.027	$7_{4,4}$	$6_{3,3}$	P	3.47	77.3
359019.127 ± 0.051	$7_{5,2}$	$6_{6,1}$	O	0.42	83.6
368293.687 ± 0.019	$5_{4,1}$	$4_{3,2}$	O	1.06	44.4
373670.019 ± 0.028	$7_{4,3}$	$6_{5,2}$	O	2.02	80.3
374357.674 ± 0.019	$6_{5,2}$	$5_{4,1}$	O	2.71	62.4
385877.148 ± 0.042	$8_{3,5}$	$7_{4,4}$	P	4.45	95.8
386218.060 ± 0.043	$8_{4,5}$	$7_{3,4}$	O	4.45	93.4
399274.294 ± 0.033	$7_{5,3}$	$6_{4,2}$	P	2.71	82.9

NOTE. —Frequencies calculated from the constants in Table 3. Errors are 1 σ from the least-squares fit and contain an estimated systematic error of 5 kHz added in quadrature. Sym: symmetry species, ortho (O) or para (P); S: asymmetric rotor line strength; and E: energy of the upper level of the transition above the para ground state $0_{0,0}$ or the ortho ground state $1_{0,1}$, 2.3 K above. Only O transitions with $S > 0.2$ and P transitions with $S > 0.6$ are listed, for $E/k < 100$ K in either case.

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TABLE 6

ASTRONOMICAL LINES OF C_3H_2

Transition (upper → lower)	Rest Frequency[a] (MHz)	Source[b]	Telescope[c]	$\Delta\theta$	v_{LSR} (km s^{-1})	T_R (K)	Δv[d] (km s^{-1})	W (K km s^{-1})	References
$1_{1,0} \rightarrow 1_{0,1}$	18343.143	Orion KL	GB	1'.65	7.8	0.17 ± 0.03[e]	5.0	0.85 ± 0.15	1
		TMC-1	GB	1.65	5.7	3.6 ± 0.7[e]	0.59	2.1 ± 0.4	1
$2_{1,1} \rightarrow 2_{0,2}$	46755.621	TMC-1	N	0.6	5.9	1.54 ± 0.30	0.46	0.71 ± 0.14	2
$2_{0,2} \rightarrow 1_{1,1}$	82093.559	Sgr B2	BTL	2.6	62 ± 8	0.13 ± 0.04(?)	(13 ± 7)	3.1 ± 1.0[f]	3
$3_{1,2} \rightarrow 3_{0,3}$	82966.213	Orion KL	BTL	2.6	9 ± 4	0.058	5 ± 1	0.29	3
		Sgr B2	BTL	2.6	58 ± 2	0.17 ± 0.02	24 ± 3	4.0 ± 0.7	4
$3_{2,2} \rightarrow 3_{1,3}$	84727.696	Sgr B2	BTL	2.5	60 ± 6	0.04 ± 0.01	(29 ± 17)	1.0 ± 0.3	4
$2_{1,2} \rightarrow 1_{0,1}$	85338.905	IRC +10216	BTL	2.5	−26 ± 4	0.036 ± 0.01	30 ± 4	1.1 ± 0.3	3
		Orion KL	BTL	2.5	9 ± 4	0.26 ± 0.03	5 ± 1	1.3 ± 0.3	3
		Sgr B2	BTL	2.5	~62 (blend)	0.42 ± 0.03	(<50)	10.1 ± 1.5	4
		TMC-1	NRAO	1.4	5.8 ± 0.1	3.1	0.53	1.6	5
$4_{3,2} \rightarrow 4_{2,3}$	85656.420	Orion KL	BTL	2.5	...	<0.06	5	<0.3	3
		Sgr B2	BTL	2.5	62 ± 8	0.05 ± 0.02(?)	24	1.2 ± 0.5(?)	4
$4_{0,4} \rightarrow 3_{1,3}$	150820.669	Sgr B2	NRAO	1.1	60 ± 2	0.30 ± 0.04	13.9 ± 2.0	4.2 ± 0.8	6
$4_{1,4} \rightarrow 3_{0,3}$	150851.901	Sgr B2	NRAO	1.1	64 ± 2	0.30 ± 0.04	17.9 ± 2.0	5.4 ± 0.9	6
$6_{0,6} \rightarrow 5_{1,5}$	217822.036	Orion KL	OVRO	0.5	9 ± 1	0.7	7.0	4.9	7
$6_{1,6} \rightarrow 5_{0,5}$	217822.158								
$4_{4,1} \rightarrow 3_{3,0}$	265759.485	Orion KL	MMWO	1.2	10.5 ± 1.5	0.25	7.5	1.85	8

[a] From Table 5.

[b] To within a few arseconds, source coordinates (α, δ [1950]) are: Orion KL ($5^h32^m47^s$, $-5°24'21''$); Sgr B2 ($17^h44^m11^s$, $-28°22'30''$); and TMC-1 ($4^h38^m38^s$, $+25°35'45''$).

[c] GB, NRAO 43 m telescope at Green Bank; N, 45 m Nobeyama telescope; BTL, Bell 7 m telescope; NRAO, NRAO 11 m telescope at Kitt Peak; OVRO, Owens Valley Radio Observatory 10 m telescope; MMWO, 5 m telescope of the Millimeter Wave Observatory at Fort Davis.

[d] Parentheses indicate line widths estimated from the data but not used to compute the integrated line intensity W. For Sgr B2, the best measurement with the Bell 7 m telescope, 24 ± 3 km s^{-1} from the $3_{1,2} \rightarrow 3_{0,3}$ transition, was used to obtain W for all lines from 82 to 86 GHz.

[e] Estimated beam efficiency of the 43 m telescope at 18 GHz: 0.5 ± 0.1.

[f] Unpublished data obtained with the NRAO 11 m telescope, not analyzed here because of uncertain calibration, confirm the detection of this line in Sgr B2.

REFERENCES.—(1) Matthews and Irvine 1985. (2) Suzuki *et al.* 1986. (3) Thaddeus 1986. (4) Cummins *et al.* 1986. (5) Thaddeus *et al* 1981. (6) Hollis *et al.* 1983. (7) Sutton *et al.* 1985. (8) Loren 1984.

Thaddeus, Guélin, and Linke 1981), the sources most extensively studied so far are Sgr B2, Orion Kleinmann-Low, and TMC-1 (Table 6). Our aim here is to show that in these sources the line frequencies and intensities are consistent with the identifications, and that in two of these three it is possible to derive rough estimates of the rotational temperature and column density of C_3H_2. Source radial velocities, derived using the rest frequencies in Table 5, are consistent with those of other molecules.

Eight lines of C_3H_2, the most yet observed in a single source, have been detected toward Sgr B2, all seen in emission except the $1_{1,0} \rightarrow 1_{0,1}$ transition at 18 GHz, which shows a complex absorption profile (Matthews and Irvine 1985). A rotational temperature of 11 ± 2 K, at the low end of the 10–30 K range found from other molecules (Cummins, Linke, and Thaddeus 1986), and a column density of $(6 \pm 1) \times 10^{13}$ cm^{-2}, are implied by the five emission lines between 82 and 86 GHz observed with the Bell Telephone Laboratories 7 m antenna. The ortho-para doublet at 151 GHz, observed by Hollis *et al.* (1983) with a much smaller beam, lies fairly close to the best-fit line to the 80 GHz data (Fig. 4), an agreement that may indicate that C_3H_2 is not strongly peaked within several arcminutes of Sgr B2; the observed intensity ratios of this doublet are closer to unity than the expected 3:1, with noise, interfering lines, or uncertainties in the baseline possibly accounting for the discrepancy.

Five C_3H_2 lines, all in emission, have been detected toward Orion KL; from those observed with the same telescope and nearly the same beamwidth, $3_{1,2} \rightarrow 3_{0,3}$ at 83 GHz and $2_{1,2} \rightarrow 1_{0,1}$ at 85 GHz, we obtained, with uncertainties of order 50%, $T_{rot} = 9$ K, an unusually low value compared with 20–90 K for most molecules in the extended ridge (Johansson *et al.* 1984), and $N = 6 \times 10^{12}$ cm^{-2}. The other three transitions fall above the line defined by those two on the rotational temperature diagram (Fig. 5); normalized to a uniform 2'.5 beamwidth, these three transitions move, although probably only coincidentally, very near the line. A small, hot source may contribute to the observed emission in the higher lying lines, even though the velocity and line widths are characteristic of molecules observed in the extended, low-density ridge in Orion A.

A reliable rotational temperature diagram could not be constructed in TMC-1, because only three C_3H_2 lines were observed, with radiation temperatures comparable to the kinetic temperature, thus with optical depths of order unity. Detection of C_3HD, which should be feasible in TMC-1 following completion of laboratory spectroscopy, will provide a better understanding of deuterium enhancement and optical depth effects.

V. DISCUSSION

Both in the laboratory and in space, cyclopropenylidene can be formed by electronic recombination with the cyclopropenyl cation $C_3H_3^+$, the simplest aromatic molecule and the product of many bimolecular ion-molecule reactions. In space, $C_3H_3^+$ may be produced by the fast bimolecular reaction (Bohme, Raksit, and Schiff 1982)

$$C_2H_2 + C^+ \rightarrow C_3H^+ + H ,$$

followed by radiative association of C_3H^+ with H_2 (Herbst, Adams, and Smith 1984),

$$C_3H^+ + H_2 \rightarrow C_3H_3^+ .$$

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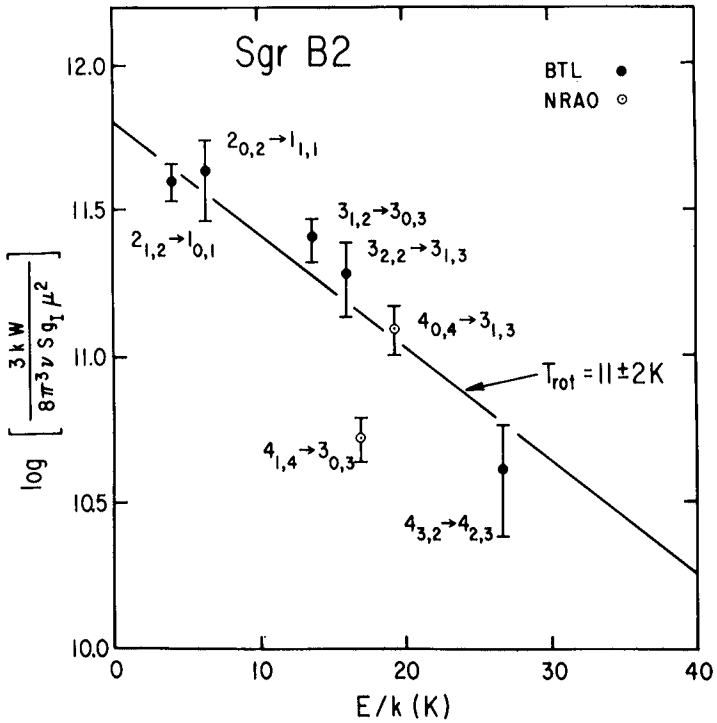

FIG. 4

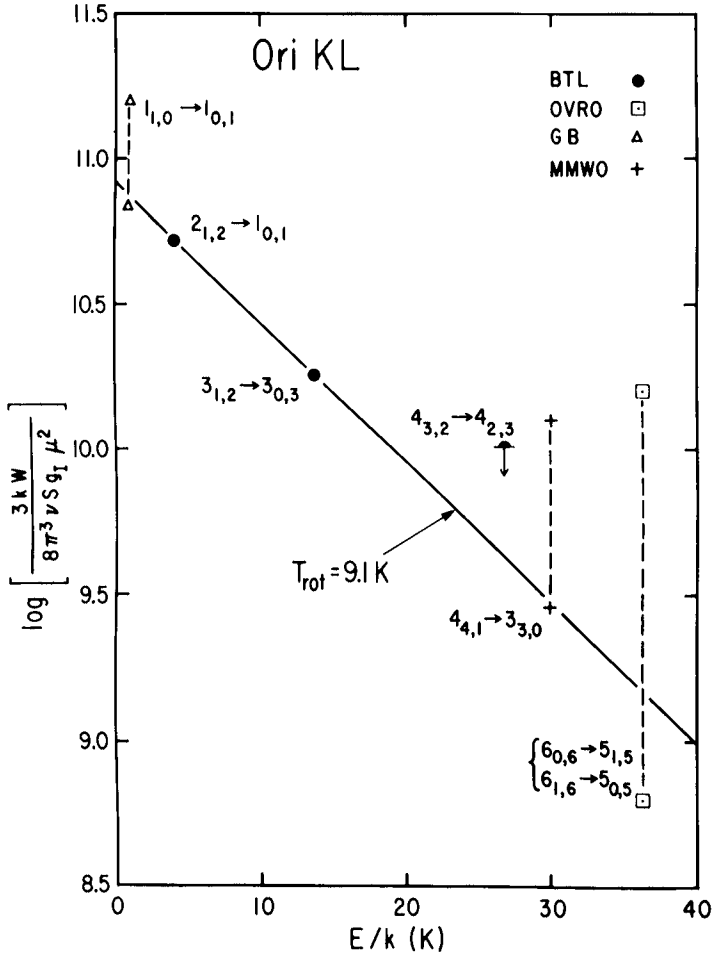

FIG. 5

FIG. 4.—Rotational temperature diagram of C_3H_2 in Sgr B2. The line is from a fit to the five transitions measured between 82 and 86 GHz with the Bell 7 m telescope (BTL); the remaining two transitions were observed with the 11 m telescope at Kitt Peak (NRAO) with a smaller beam.

FIG. 5.—Rotational temperature diagram of C_3H_2 in Orion KL. The line is drawn through two transitions measured with the same telescope and beamwidth: $2_{2,1} \rightarrow 1_{0,1}$ at 83338 MHz and $3_{1,2} \rightarrow 3_{0,3}$ at 82966 MHz. Other measurements shown in their upper positions were observed with different beamwidths and in their lower positions were normalized to a 2'.5 beam on the assumption that the source is small.

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Mass spectrometric evidence indicates that in an acetylene discharge $C_3H_3^+$ is produced at a concentration ~ 10 times less than that of the more abundant ions $C_2H_2^+$, $C_2H_3^+$, $C_4H_2^+$, and $C_4H_3^+$ (Vasile and Smolinsky 1977). Indirect evidence suggests that the reaction paths by which $C_3H_3^+$ forms in the discharge differ from those by which it forms in interstellar clouds. In the laboratory the reaction of C^+ with C_2H_2 is apparently not important to the production of $C_3H_3^+$, since the concentration of C_3H_2, unlike that of C_3H (Gottlieb *et al.* 1985), does not increase when CO is added to the He and C_2H_2 discharge. The reaction expected (Huntress 1977) is

$$He^+ + CO \rightarrow He + C^+ + O ,$$

followed by the reaction of C^+ with C_2H_2. The chemistry of the discharge may be more complicated, as illustrated by the observation of gaseous CCH in a discharge through pure Ar over a cell previously coated with polymeric material produced in an Ar and C_2H_2 discharge (Carrick, Merer, and Curl 1983). However, we do not believe that the heavy polymeric deposits produced in the C_2H_2 and He discharge and present on the walls of our cell directly affected the production of C_3H_2, because in a C_2D_2 and He discharge C_3H_2 was not observed.

A comparison of the abundance of C_3H_2 in Galactic sources and the abundances of C_3H and CH_3CCH (methyl acetylene), both hydrocarbons with three C atoms, is informative, since larger, stable rings, e.g., pyrrole (Myers, Thaddeus, and Linke 1980), are apparently less abundant in space than molecules of comparable size with a linear heavy atom backbone. In TMC-1, surprisingly, the column density of C_3H_2 estimated by Matthews and Irvine (1985) is 10 times greater than that of C_3H (Thaddeus *et al.* 1985) and is comparable to that of CH_3CCH (Askne *et al.* 1984). The column density of C_3H_2, unlike that of most other molecules, is nearly the same in Sgr B2 and TMC-1, owing perhaps to the much higher predicted CI abundance in the earlier stages of cloud evolution (Leung, Herbst, and Huebner 1984); in methyl acetylene the same trend is predicted but not observed. In contrast to SiCC, the first ring detected by astronomers and primarily observed in the molecular envelope of the carbon star IRC+10216 (Thaddeus, Cummins, and Linke 1984), C_3H_2 is most readily observed in cold molecular clouds. The column density of C_3H_2 is nearly 20 times less than that of CH_3CCH in Sgr B2 (Churchwell and Hollis 1983) and 200 less in Orion KL (Sutton *et al.* 1985).

It is possible that the carriers of some of the remaining U lines are also reactive rings. Our demonstration of the formation of ring molecules in a C_2H_2 discharge suggests further searches in the same discharge at the U-line frequencies. Detection of one carbene ring in an acetylene discharge implies others, e.g., the known five-membered carbene ring cyclopentadienylidene (C_5H_4).

Douglas (1977) hypothesized that the carriers of the diffuse interstellar optical bands are carbon chains with an odd number of carbon atoms. The molecules shown in Figure 6 can be considered carbon chains (HC_nH) with an odd number of carbon atoms that have undergone intramolecular cyclization. They can also be regarded as derivatives of cyclopropenylidene, with either C_2H or C_4H chains substituted for the hydrogens. All have large dipole moments, and the uppermost molecule in Figure 6 (C_5H_2), for example, has the readily identifiable radio spectrum of a nearly symmetric top with harmonically related transitions every 7 GHz. In the C_2H_2 and He discharge, the abundances of C_3H_2 and of the carbon chains CCH (Gottlieb, Gottlieb, and Thaddeus 1983) and C_4H (Gottlieb *et al.* 1983) are comparable. If these ring-chain molles are stable isomers, they may be present in our C_2H_2 and He discharge.

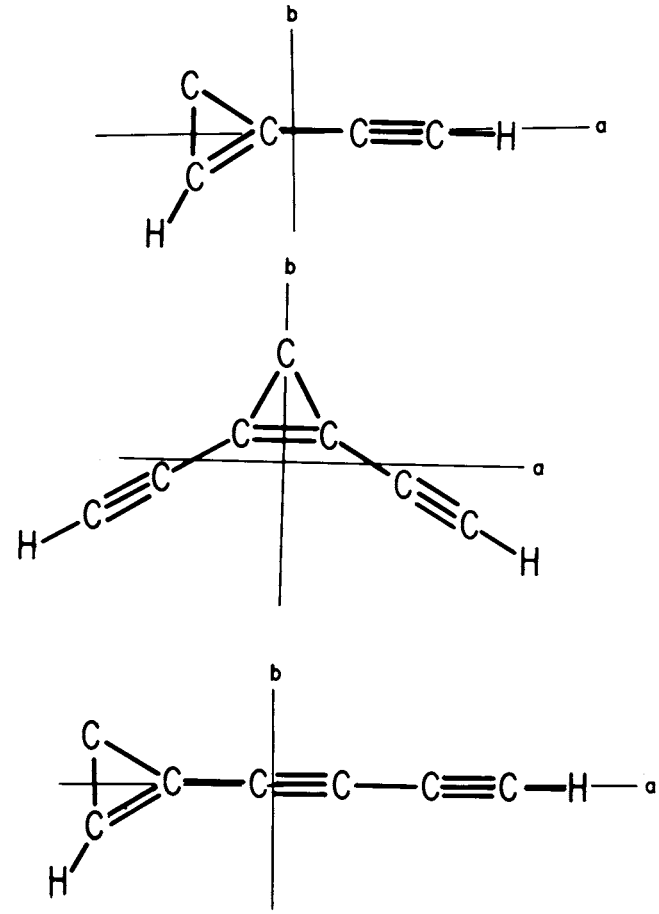

FIG. 6.—Hypothetical ring-chain hybrids formed by substitution of C_2H or C_4H groups for the H atoms in cyclopropenylidene.

VI. SUMMARY

The existence of a new molecule was established from the pattern of the millimeter-wave spectrum observed in the laboratory and the derived spectroscopic constants. This new molecule is identified as cyclopropenylidene, the singlet three-membered carbene ring with C_{2v} symmetry and the most stable molecule with the elemental formula C_3H_2. The rotational constants derived from 19 laboratory measured transitions are in excellent agreement (to within 1.8%) with those derived ab initio; the inertial defect is small (0.08), as expected for a planar molecule; the intensities of ortho and para transitions are observed in the required 3:1 ratio; and laboratory assays demonstrated that the carrier contains C and H but not N or O and that it is not a radical and probably not a molecular ion.

Additional support for the identification comes from the assignment of 11 transitions in space, including the ground-state ortho transition at 18343 MHz and four others not observed in the laboratory, at the exact frequencies predicted

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from the laboratory data. The intensities of the astronomical lines in Sgr B2 and Orion KL are consistent with the identification. The column density of C_3H_2 in TMC-1 is similar to that of methyl acetylene and 10 times greater than that of C_3H but is much less than methyl acetylene in Sgr B2 and Orion KL. The relatively large column density in TMC-1, the low rotational temperatures in Sgr B2 and Orion KL, and the detection of many absorption components of the 18343 MHz line toward distant continuum sources suggest that C_3H_2 is an important molecule in cold molecular clouds, for which it may be a good tracer.

Detection of a reactive carbene ring in a laboratory discharge through acetylene and helium implies other carbenes and rings, some of them possibly the carriers of known U lines.

After this paper was submitted, we received copies of recent work by Bogey, Demuynck, and Destombes (1986), in which a detailed centrifugal distortion analysis of C_3H_2 is presented, and by Bogey and Destombes (1986), in which the laboratory detection of ^{13}C-substituted cyclopropenylidene is reported. Where direct comparison is possible, their work and ours are in excellent agreement.

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REFERENCES

Askne, J., Höglund, B., Hjalmarson, Å., and Irvine, W. M. 1984, *Astr. Ap.*, **130**, 311.
Bogey, M., Demuynck, C., and Destombes, J. L. 1986, *Chem. Phys. Letters.*, **125**, 383.
Bogey, M., and Destombes, J. L. 1986, *Astr. Ap.*, **159**, L8.
Bohme, D. K., Raksit, A. B., and Schiff, H. I. 1982, *Chem. Phys. Letters*, **93**, 592.
Carrick, P. G., Merer, A. J., and Curl, R. F. 1983, *J. Chem. Phys.*, **78**, 3652.
Churchwell, E., and Hollis, J. M. 1983, *Ap. J.*, **272**, 591.
Cummins, S. E., Linke, R. A., and Thaddeus, P. 1986, *Ap. J. Suppl.*, **60**, 819.
DeLucia, F. C., Herbst, E., Plummer, G. M., and Blake, G. A. 1983, *J. Chem. Phys.*, **78**, 2312.
Douglas, A. E. 1977, *Nature*, **269**, 130.
Gottlieb, C. A., Gottlieb, E. W., and Thaddeus, P. 1983, *Ap. J.*, **264**, 740.
Gottlieb, C. A., Gottlieb, E. W., Thaddeus, P., and Kawamura, H. 1983, *Ap. J.*, **275**, 916.
Gottlieb, C. A., Vrtilek, J. M., Gottlieb, E. W., Thaddeus, P., and Hjalmarson, Å. 1985, *Ap. J.*, (*Letters*), **294**, L55.
Hehre, W. J., Pople, J. A., Lathan, W. A., Radom, L., Wasserman, E., and Wasserman, Z. R. 1976, *J. Am. Chem. Soc.*, **98**, 4378.
Henry, P. S. 1976, *Rev. Sci. Instr.*, **47**, 1020.
Herbst, E., Adams, N. G., and Smith, D. 1984, *Ap. J.*, **285**, 618.
Hollis, J. M., Suenram, R. D., Lovas, F. J., and Snyder, L. E. 1983, *Astr. Ap.*, **126**, 393.
Huntress, W. T. 1977, *Ap. J. Suppl.*, **33**, 495.
Johansson, L. E. B., *et al.* 1984, *Astr. Ap.*, **130**, 227.
Kirchhoff, W. H. 1972, *J. Molec. Spectrosc.*, **41**, 333.
Lee, T. J., Bunge, A., and Schaefer, H. F. 1985, *J. Am. Chem. Soc.*, **107**, 137.
Leung, C. M., Herbst, E., and Huebner, W. F. 1984, *Ap. J. Suppl.*, **56**, 231.
Loren, R. B. 1984, Tech. Rept. University of Texas Elec. Eng. Res. Lab.
Matthews, H. E., and Irvine, W. M. 1985, *Ap. J.* (*Letters*), **298**, L61.
Myers, P. C., Thaddeus, P., and Linke, R. A. 1980, *Ap. J.*, **241**, 155.
Reisenauer, H. P., Maier, G., Riemann, A., and Hoffmann, R. W. 1984, *Angew. Chem., Internat. Ed. English*, **23**, 641.
Seaquist, E. R., and Bell, M. B. 1986, *Ap. J.* (*Letters*), **303**, L67.
Sutton, E. C., Blake, G. A., Masson, C. R., and Phillips, T. G. 1985, *Ap. J. Suppl.*, **58**, 341.
Suzuki, H., Kaifu, N., Miyaji, T., Morimoto, M., Ohishi, M., and Saito, S. 1984, *Ap. J.*, **282**, 197.
Suzuki, H., Kaifu, N., Ohishi, M., Morimoto, M., and Miyaji, T. 1986, in preparation.
Thaddeus, P. 1986, unpublished.
Thaddeus, P., Cummins, S. E., and Linke R. A. 1984, *Ap. J.* (*Letters*), **283**, L45.
Thaddeus, P., Gottlieb, C. A., Hjalmarson, Å., Johansson, L. E. B., Irvine, W. M., Friberg, P., and Linke, R. A. 1985, *Ap. J.* (*Letters*), **294**, L49.
Thaddeus, P., Guélin, M., and Linke, R. A. 1981, *Ap. J.* (*Letters*), **246**, L41.
Thaddeus, P., Vrtilek, J. M., and Gottlieb, C. A. 1985, *Ap. J.* (*Letters*), **299**, L63 (TVG).
Vasile, M. J., and Smolinsky, G. 1977, *Internat. J. Mass Spectrom. Ion Phys.*, **24**, 11.
Vrtilek, J. M., Gottlieb, C. A., Langer, W. D., Thaddeus, P., and Wilson, R. W. 1985, *Ap. J.* (*Letters*), **296**, L35.
Vrtilek, J. M., Gottlieb, C. A., LePage, T. J., and Thaddeus, P. 1986, *Ap. J.*, in press.
Watson, J. K. G. 1967, *J. Chem. Phys.*, **46**, 1935.

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