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# LABORATORY DETECTION OF THE $C_3H$ RADICAL

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## ABSTRACT

Following the astronomical identification of the $C_3H$ radical reported in an accompanying *Letter*, 34 millimeter-wave lines of this linear carbon chain, including six of the lines observed in space, were detected in a laboratory glow discharge through a flowing mixture of $C_2H_2$, He, and CO. Each of the 10 rotational transitions measured, five between 98 and 185 GHz in the $^2\Pi_{1/2}$ ladder and five between 80 and 194 GHz in the $^2\Pi_{3/2}$ ladder, is split by lambda-type doubling, and all but three possess resolved hyperfine structure. The excellent agreement between the fine-structure, rotation, lambda-doubling, and hyperfine constants derived from the laboratory data and from the astronomical observations conclusively confirms the identifications in IRC +10216 and TMC-1 by Thaddeus and colleagues. An accurate set of spectroscopic constants, which allow calculation of the entire radio spectrum of $C_3H$ to a radial velocity of 0.1 km $s^{-1}$, was derived from a simultaneous fit to the laboratory frequencies and to the well-resolved hfs observed in the narrow-line astronomical source TMC-1.

*Subject headings:* laboratory spectra — molecular processes

Detection of the carbon chain molecules CCH and $C_4H$ in a discharge through helium and acetylene (Gottlieb, Gottlieb, and Thaddeus 1983; Gottlieb *et al.* 1983) prompted us to search in the laboratory for $C_3H$, the simplest odd carbon chain radical. At first we were unsuccessful, owing to uncertainties about the frequencies and the proper discharge conditions. Subsequently, as shown in the preceding *Letter*, Thaddeus *et al.* (1985) identified $C_3H$ in the molecular envelope of IRC +10216, enabling us to determine the principal fine-structure, rotation, and lambda-doubling constants ($A$, $B$, $D$, $p$, and $q$) and to predict, to an accuracy of 10 MHz, the $C_3H$ spectrum in the region 150–200 GHz where our spectrometer is most sensitive. The laboratory lines were then detected at 185 GHz under discharge conditions that yield peak $C_4H$.

In all, 10 rotational transitions were measured—five in the $^2\Pi_{1/2}$ ladder and five in the $^2\Pi_{3/2}$ ladder. The laboratory profiles in the $^2\Pi_{1/2}$ ladder were characterized by nearly resolved hyperfine structure, as shown in Figure 1; hyperfine splittings in the $^2\Pi_{3/2}$ ladder are several times smaller and were observed only in transitions arising from lower rotational levels. A complete analysis of the $C_3H$ laboratory spectrum was performed. The four $\Delta F = 1$ hyperfine components in the lowest rotational transition ($^2\Pi_{1/2} J = 3/2 \rightarrow 1/2$) were afterward detected in TMC-1 with the Onsala 20 m telescope (see the preceding *Letter*) at the predicted frequencies, culminating in a highly accurate determination of the hyperfine constants and providing a good example of a profitable interplay between laboratory spectroscopy and astronomical observations.

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The spectrometer used to detect $C_3H$ was previously used to detect $C_3N$ and $C_4H$ (Gottlieb *et al.* 1983). As before, klystron modulation and second harmonic detection were used to suppress noise; magnetic modulation, applied on alternate klystron sweeps for the $^2\Pi_{3/2}$ transitions, was, owing to the small $g$ factor, ineffective for the $^2\Pi_{1/2}$ transitions. The strongest $C_3H$ signals were observed in a liquid nitrogen–cooled DC discharge (0.4 A) through $C_2H_2$ (with a flow rate of 0.2 $cm^3$ $s^{-1}$), He (0.01 $cm^3$ $s^{-1}$), and CO (0.04 $cm^3$ $s^{-1}$), at a total pressure of 25 millitorr. The yield of $C_3H$ was estimated by comparing the strength of the $C_3H$ signal at 171.958 GHz with $^{18}OC^{34}S$ at 166.784 GHz; assuming the kinetic temperature is 100 K and the $C_3H$ dipole moment is 3.1 $D$ (Green 1980), the $C_3H$ concentration is $1.2 \times 10^{10}$ $cm^{-3}$ and the mole fraction is $3 \times 10^{-6}$.

A mass spectrometric study by Vasile and Smolinsky (1977) shows that $C_3H_x^+$ ions are produced in a $C_2H_2$ discharge at concentrations of a few percent relative to $C_4H_y^+$ ions. The reaction (Schiff and Bohme 1979) expected is:

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

but electron-ion recombination of $C_3H_2^+$ or $C_3H_3^+$, not $C_3H^+$, is conjectured to produce $C_3H$ (Herbst, Adams, and Smith 1984). Why the $C_3H$ signals increased in strength by a factor of 10 when CO was added to the He and $C_2H_2$ discharge is puzzling.

The rest frequencies (Table 1), measured as before (Gottlieb *et al.* 1983), are generally the mean of four scans; the total integration time of a scan varied between 20 minutes for the



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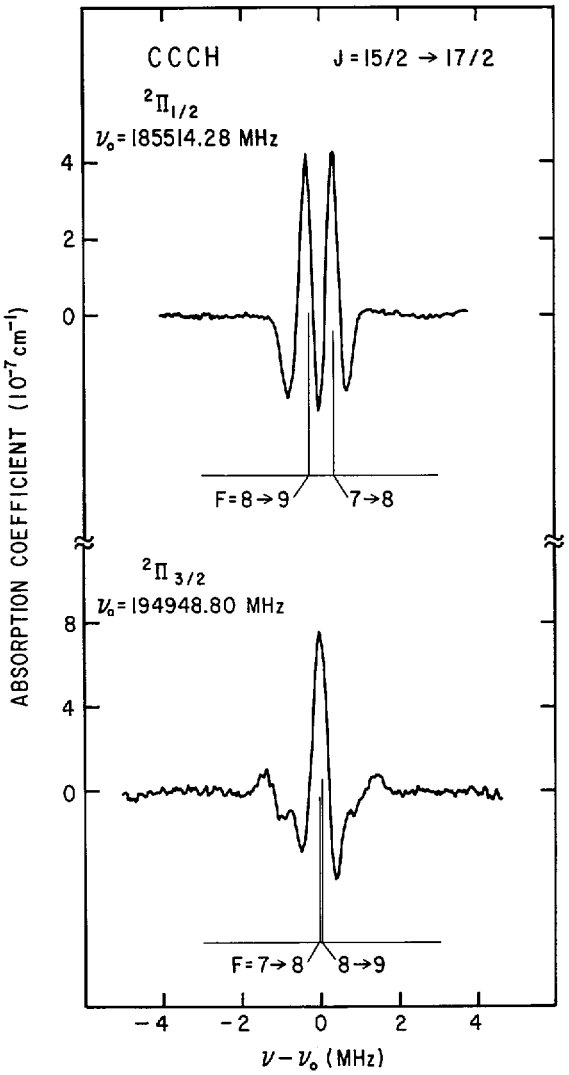


FIG. 1.—Sample laboratory spectra: the upper lambda component of the $J = 15/2 \rightarrow 17/2$ rotational transition in both fine-structure ladders. Frequency modulation was used to suppress noise, and in the $^2\Pi_{3/2}$ spectrum Zeeman modulation was used as well to suppress baseline distortion from standing waves. In the $^2\Pi_{3/2}$ ladder (*bottom spectrum*), hyperfine structure is unresolved, and the line shape is essentially the second derivative instrumental profile (with some slight distortion on the wings owing to Zeeman components). For each spectrum the total integration time was approximately 60 minutes.

$15/2 \rightarrow 17/2$ transitions to 60 minutes for the $^2\Pi_{3/2} 5/2 \rightarrow 7/2$ transition. Line widths (HWHM) varied between 400 and 600 kHz, narrowing with a reduction of pressure (to 15 millitorr) that resulted in a loss of 2 in signal strength. Transitions above 119 GHz were observed with the smallest possible line width in order to resolve the hyperfine structure, which collapses with increasing $J$. The uncertainties in the frequencies are estimated to be 50 kHz.

For the analysis, we used the Hamiltonian of Brown *et al.* (1978, 1979) in the $N^2$ representation with the hyperfine terms diagonal in $J$ and the fourth-order lambda-doubling terms added empirically (Meerts 1977). The energy of a particular $|\pm; J, \Omega, F\rangle$ level was obtained by numerically diagonalizing a $2 \times 2$ matrix; then the parameters were least-squares fitted, using explicit expressions for the derivatives.

The first step in the analysis was to determine the minimum number of parameters needed to describe the $C_3H$ millimeter-wave spectrum. When $A$, $B$, and $D$ were fitted to the frequencies in the absence of hyperfine structure and lambda-doubling, it became clear that the spin-rotation term was needed. Since the spin-rotation interaction is indistinguishable from the centrifugal correction to the spin-orbit interaction in a $^2\Pi$ molecule (Brown and Watson 1977), $A_D$ was constrained to zero. Analysis of the lambda-doubling revealed that the higher order terms $p_D$, $q_D$, $p_H$, and $q_H$ were needed.

Assignments of hyperfine components from intensities proved impossible, because in the high rotational transitions (i.e., above 150 GHz) relative intensities of the two $F \rightarrow F + 1$ hyperfine components are the same to 6%. Instead, the hyperfine constants were least-squares fitted to the $^2\Pi_{1/2} 7/2 \rightarrow 9/2$ and $9/2 \rightarrow 11/2$ transitions, while the fine-structure constants were constrained to the values determined in a fit to the $C_3H$ frequencies without hyperfine structure. The remaining transitions were assigned by comparison with the calculated frequencies.

Having determined the number of parameters and the assignments of the transitions, we were now able simultaneously to least-squares fit 14 spectroscopic constants to the 34 laboratory frequencies shown in Table 1. Until still higher frequency transitions are measured, inclusion of higher order fine- or hyperfine-structure terms in the Hamiltonian appears unjustified (some of the parameters, especially $A$ and $\gamma$, may be refined by spectroscopic investigations in the infrared).

It is impossible to determine the signs of the lambda-doubling parameters ($p$, $q$, $p_D$, $q_D$, $p_H$, $q_H$, and $d$) from our transitions. Since the molecular orbital containing the unpaired electron is a linear combination of $C$ $2p$ orbitals, we assumed $d$ is positive, implying that $p$ and $q$ are negative. In the isoelectronic $X^2\Pi$ CCN radical $p$ and $q$, as expected, are positive (Kakimoto and Kasuya 1982), since the lowest $\Sigma$ state is $A^2\Sigma^-$ (Merer and Travis 1965).

A set of recommended constants (Table 2) was derived from a simultaneous analysis of the laboratory frequencies and the four highly resolved $J = 3/2 \rightarrow 1/2$ $\Delta F = 1$ hyperfine components observed in TMC-1 (see the preceding *Letter*). The accuracy of the hyperfine parameters improved dramatically when astronomical data were included, owing to the large splittings in the $J = 3/2 \rightarrow 1/2$ transition and the 40 times smaller widths of the TMC-1 lines. The frequencies calculated with the recommended constants are in excellent agreement with the laboratory data. In the fit to the combined data we treated the radial velocity in TMC-1 as a free parameter and obtained a value of $V_{\rm LSR} = 5.4 \pm 0.3$ km s$^{-1}$, in fairly good agreement with that of other molecules in this source.

The value calculated for the spin-orbit constant of 29.8 cm$^{-1}$ (Cooper 1983) is 2 times larger than the measured value; however, owing to the Renner-Teller effect, the measured value is likely to be smaller than the calculated value. The rotational constant calculated by Green (1980) agrees with the measured value to within his estimated uncertainty of

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TABLE 1

LABORATORY CCCH FREQUENCIES

| J → J' | Ω | Λ Component[a] | F → F' | Measured Frequencies[b] (MHz) | Measured–Calculated[c] (MHz) |
|---|---|---|---|---|---|
| 5/2 → 7/2 | 3/2 | a | 3 → 4 | 80,388.107 | -0.006 |
| | | | 2 → 3 | 80,389.442 | 0.016 |
| | | b | 3 → 4 | 80,420.646 | -0.056 |
| | | | 2 → 3 | 80,422.052 | -0.038 |
| 7/2 → 9/2 | 1/2 | b | 4 → 5 | 97,995.166 | -0.008 |
| | | | 3 → 4 | 97,995.913 | -0.016 |
| | | a | 4 → 5 | 98,011.611 | 0.015 |
| | | | 3 → 4 | 98,012.524 | -0.014 |
| 7/2 → 9/2 | 3/2 | a | 4 → 5 | 103,319.276 | -0.033 |
| | | | 3 → 4 | 103,319.786 | -0.040 |
| | | b | 4 → 5 | 103,372.483 | -0.016 |
| | | | 3 → 4 | 103,373.094 | -0.015 |
| 9/2 → 11/2 | 1/2 | b | 5 → 6 | 119,804.682 | 0.014 |
| | | | 4 → 5 | 119,805.322 | 0.004 |
| | | a | 5 → 6 | 119,847.476 | 0.034 |
| | | | 4 → 5 | 119,858.259 | 0.007 |
| 11/2 → 13/2 | 1/2 | * | 6 → 7 | 141,635.793 | -0.033 |
| | | | 5 → 6 | 141,636.431 | 0.031 |
| | | * | 6 → 7 | 141,708.728 | -0.023 |
| | | | 5 → 6 | 141,709.494 | 0.016 |
| 11/2 → 13/2 | 3/2 | a | 5 → 6, 6 → 7 | 149,106.972 | 0.069 |
| | | b | 5 → 6, 6 → 7 | 149,212.667 | 0.090 |
| 13/2 → 15/2 | 1/2 | a | 7 → 8 | 163,491.035 | -0.012 |
| | | | 6 → 7 | 163,491.557 | -0.002 |
| | | b | 7 → 8 | 163,597.232 | -0.033 |
| | | | 6 → 7 | 163,597.900 | -0.033 |
| 13/2 → 15/2 | 3/2 | a | 6 → 7, 7 → 8 | 171,958.650 | 0.055 |
| | | b | 7 → 8, 6 → 7 | 172,094.778 | 0.059 |
| 15/2 → 17/2 | 1/2 | a | 8 → 9 | 185,371.952 | 0.004 |
| | | | 7 → 8 | 185.372.417 | 0.009 |
| | | b | 8 → 9 | 185,513.968 | 0.019 |
| | | | 7 → 8 | 185,514.589 | 0.021 |
| 15/2 → 17/2 | 3/2 | a | 7 → 8, 8 → 9 | 194,780.373 | -0.062 |
| | | b | 7 → 8, 8 → 9 | 194,948.795 | -0.071 |

[a] Following the convention of Brown *et al.* 1975, a transition between Λ doublets of lower energy is designated as an *a* component and the upper as a *b* component. The * denotes that the order reverses in the $^2\Pi_{1/2}$ ladder between $J = 11/2$ and 13/2.

[b] Estimated 1 σ uncertainties: ±50 kHz.

[c] Calculated with the recommended constants in Table 2.

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TABLE 2

SPECTROSCOPIC CONSTANTS OF CCCH IN THE $X^2\Pi$ STATE

| Molecular Constant | Laboratory (this work) | Laboratory Plus Astronomical (recommended constants) |
|---|---|---|
| $A_{\rm eff}$ ..... | 430830 ± 44 | 430828 ± 41 |
| $B$ ..... | 11186.335 ± 0.002 | 11186.335 ± 0.002 |
| $D \times 10^3$ ..... | 5.55 ± 0.02 | 5.55 ± 0.02 |
| $\gamma_{\rm eff}$ ..... | 36.8 ± 1.1 | 36.9 ± 1.1 |
| $p$ ..... | −7.1 ± 0.2 | −7.20 ± 0.07 |
| $q$ ..... | −16.60 ± 0.04 | −16.62 ± 0.03 |
| $p_D \times 10^3$ .... | 46 ± 3 | 47.4 ± 2.4 |
| $q_D \times 10^3$ .... | 1.3 ± 0.7 | 1.6 ± 0.6 |
| $p_H \times 10^6$ .... | 53 ± 12 | 45 ± 6 |
| $q_H \times 10^6$ .... | 4.2 ± 2.7 | 3.1 ± 2.1 |
| $a$ ..... | 12 ± 2 | 12.3 ± 0.2 |
| $b + \frac{c}{3}$ ..... | −13.8 ± 0.6 | −13.8 ± 0.6 |
| $c$ ..... | 29 ± 6 | 28.3 ± 1.4 |
| $d$ ..... | 15 ± 4 | 16.2 ± 0.1 |

NOTE.—Units: MHz. Uncertainties are 1 $\sigma$ derived from a least-squares fit.

4%; Green calculated the hyperfine parameters $a$, $c$, and $d$, and, while his calculated and our measured values of $a$ agree very well, his $c$ and $d$ are too small by a factor of 2.

Under the most favorable laboratory discharge conditions, we detected little decline with size in the mole fraction of the three carbon chain radicals; even longer ones, which should be detectable with slightly improved instrumental sensitivity, are therefore probably present. A complete list of the calculated frequencies of the lines in the millimeter-wave spectrum of $C_3H$ and a fuller account of the present analysis are deferred to another paper.

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REFERENCES

Brown, J. M., *et al.* 1975, *J. Molec. Spectrosc.*, **55**, 500.
Brown, J. M., Colbourn, E. A., Watson, J. K. G., and Wayne, F. D. 1979, *J. Molec. Spectrosc.*, **74**, 294.
Brown, J. M., Kaise, M., Kerr, C. M. L., and Milton, D. J. 1978, *Molec. Phys.*, **36**, 553.
Brown, J. M., and Watson, J. K. G. 1977, *J. Molec. Spectrosc.*, **65**, 65.
Cooper, D. L. 1983, *Ap. J.*, **265**, 808.
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.
Green, S. 1980, *Ap. J.*, **240**, 962.
Herbst, E., Adams, N. G., and Smith, D. 1984, *Ap. J.*, **285**, 618.
Kakimoto, M., and Kasuya, T. 1982, *J. Molec. Spectrosc.*, **94**, 380.
Meerts, W. L. 1977, *Chem. Phys. Letters*, **46**, 24.
Merer, A. J., and Travis, D. N. 1965, *Canadian J. Phys.*, **43**, 1795.
Schiff, H. I., and Bohme, D. K. 1979, *Ap. J.*, **232**, 740.
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.
Vasile, M. J., and Smolinsky, G. 1977, *Int. J. Mass Spectr. Ion Phys.*, **24**, 11.

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