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LABORATORY DETECTION OF THE C_9H RADICAL

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ABSTRACT

The linear carbon chain radical C_9H in its $^2\Pi_{1/2}$ electronic ground state has been detected in a Fourier transform microwave spectrometer with a supersonic pulsed-jet discharge nozzle. The frequencies of 44 rotational transitions between 5.4 and 16.1 GHz have been measured to a few parts in 10^7, from which precise values for the rotational, centrifugal distortion, lambda doubling, and hyperfine constants have been determined. These allow calculation of the entire radio spectrum of the ground state of C_9H to a fraction of 1 km s^{-1} in equivalent radial velocity.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

On Earth, linear acetylenic carbon chains explosively polymerize, but in space, where chain-chain collisions almost never occur, they are the dominant structural theme. Most of the nearly 90 polyatomic molecules now identified in interstellar clouds or in circumstellar shells are carbon chains, and nearly all of these are unsymmetrical for a reason of little fundamental importance: to provide the permanent electric dipole moment required for radio astronomical detection. Carbon chain radicals with the elemental formula C_nH are highly polar, and all but one with $n < 9$ have now been discovered in at least one astronomical source. Recently, the laboratory spectrum of the missing chain, C_7H (Travers et al. 1996), was detected, and with exact rest frequencies in hand, astronomical detection is probably only a matter of time. Here we report the laboratory detection of the largest member of the series yet: C_9H, shown in Figure 1.

At room temperature, hundreds of rotational transitions are excited in a molecule as large as C_9H, resulting in a weak thicket of radio lines that is extremely difficult to detect. The C_9H radical was detected with a new reactive molecule Fourier transform microwave (FTM) spectrometer in a pulsed supersonic nozzle molecular beam where the rotational temperature is only about 3 K, and as a result, the rotational partition function is 2 orders of magnitude smaller than in a conventional gas discharge cell. The radicals were produced by a low-current 1000 V DC gas discharge synchronized with a gas pulse 280 μs long, the gas sample consisting of 1% diacetylene (HC_4H) in Ar at a backing pressure of approximately 2 atm.

The FTM technique consists of coherently exciting a transition with a short (1 μs) microwave pulse and monitoring the free induction decay (Fig. 2*a*), the Fourier transform of which provides the desired power spectrum (Balle & Flygare 1981). In our spectrometer, the supersonic beam is directed through one of the mirrors parallel to the axis of the Fabry-Perot confocal cavity (70 cm long, 36 cm in diameter), and the line shape as a consequence is double peaked as shown in Figure 2*b*, the separation of the two peaks resulting from the different Doppler shifts of the molecular beam with respect to the two traveling waves composing the confocal Fabry-Perot mode. The line width of the individual peaks, only 7 kHz or 0.2 km s^{-1} in the example shown in Figure 2*b*, is determined mainly by the time of flight of the molecules through the Fabry-Perot cavity. As Figure 2*b* shows, it is this line width, not the separation of the two Doppler peaks, that is the essential limitation in the spectral resolution.

As with C_7H (Travers et al. 1996) and C_8H (McCarthy et al. 1996a), lambda doubling is well resolved in the rotational spectrum, and, owing to the high resolution of the FTM technique, hyperfine structure (hfs) is resolved as well. A typical line is shown in Figure 2*d*. Because of the very low temperature in our beam, only the ground fine-structure ladder $^2\Pi_{1/2}$ has been detected; initial attempts to detect C_9H in our free space gas discharge millimeter-wave spectrometer, where the $^2\Pi_{3/2}$ ladder would be readily excited, have so far been unsuccessful.

The spectroscopic constants were derived by least-squares fitting the standard Hamiltonian for a molecule in a $^2\Pi$ state (Brown et al. 1978; 1979; Amiot, Maillard, & Chauville 1981) to the frequencies in Table 1, on the assumption that the spin-orbit constant A for C_9H is 25 cm^{-1}, i.e., comparable to that of C_7H (Travers et al. 1996). Only six free parameters: the rotational constant B, centrifugal distortion constant D, lambda-doubling constant $p + 2q$, and hyperfine constants a_-, d, and b are required to fit the data to an rms of 1 kHz (Table 2). An almost equally good fit is obtained if the constant b is neglected: the rms of the fit is only 3 kHz, but there are small systematic offsets of 3–5 kHz in the residuals.

The entire radio spectrum of C_9H in the ground $^2\Pi_{1/2}$ ladder can be calculated to the accuracy required for nearly all radio astronomical applications (e.g., to a fraction of a line width in TMC-1 for transitions above 5 GHz) by neglecting the very small coupling between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ ladders:

$$\nu_{J+1\to J} = 2B_{\rm eff}(J+1) - 4D_{\rm eff}(J+1)^3$$
$$\pm \frac{p_{\rm eff}}{2} + \frac{[\pm a_- \pm d/2]}{4(F+1/2)(F+3/2)},$$

where $F = J \pm 1/2$, $B_{\rm eff} = 413.02959$ MHz, $D_{\rm eff} = 1.80 \times 10^{-6}$ MHz, and the values of $p_{\rm eff}$, a_-, and d are as in Table 2. Owing to lambda doubling, each rotational transition is split by $p_{\rm eff}$ (and by the hyperfine-doubling term in d); each lambda component is further split into two hyperfine components of

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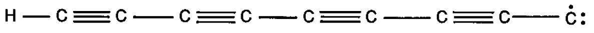

FIG. 1.—Geometry of the C_9H radical. The valence structure shown is approximate; several resonance structures contribute to the $^2\Pi$ electronic ground state, but for simplicity only one is shown.

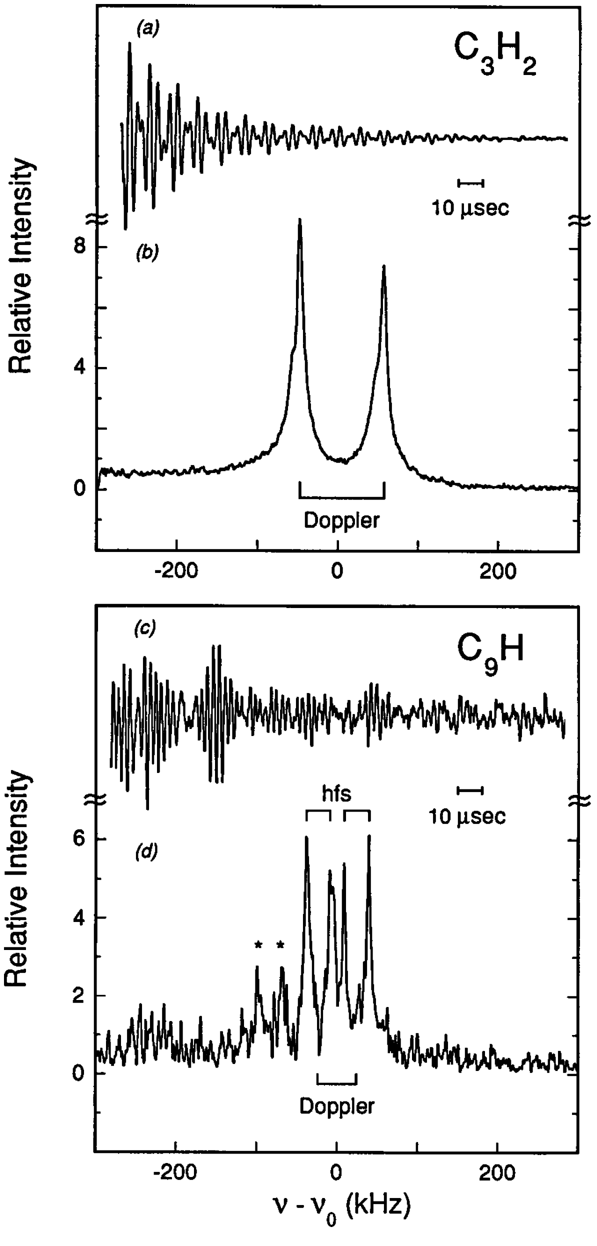

FIG. 2.—Rotational transitions of c-C_3H_2 and C_9H. (a) The free induction decay (FID) of the $1_{1,0}$–$1_{0,1}$ transition of c-C_3H_2 at $\nu_0 = 18{,}343.143$ MHz and (b) its Fourier transform showing the double-peaked line profile resulting from the interaction of the supersonic molecular beam with the two traveling waves of the Fabry-Perot mode. (c) The FID of the $J = 11.5$–10.5, f transition of C_9H at $\nu_0 = 9500.060$ MHz and (d) its Fourier transform. The more complicated spectrum of C_9H, an average of about 2400 gas and microwave pulses at a 2 Hz repetition rate requiring about 20 minutes collection time, is a consequence of the comparable hyperfine and Doppler splitting. The asterisks designate weak ghosts of the lower frequency e component, present because transitions lying both slightly higher and lower in frequency with respect to the pump frequency are observed with the current detection scheme.

TABLE 1

MEASURED ROTATIONAL TRANSITIONS OF C_9H

TRANSITION $J' \leftarrow J$	TRANSITION $F' \leftarrow F$	e/f[a] Λ COMPONENT	FREQUENCY[b] (MHz)	$O-C$ (MHz)
6.5 ← 5.5	7 ← 6	e	5368.954	0.000
	6 ← 5	e	5369.030	−0.001
	7 ← 6	f	5369.743	0.000
	6 ← 5	f	5369.826	0.000
7.5 ← 6.5	8 ← 7	e	6195.019	−0.002
	7 ← 6	e	6195.081	0.000
	8 ← 7	f	6195.808	0.001
	7 ← 6	f	6195.870	0.000
8.5 ← 7.5	9 ← 8	e	7021.085	0.000
	8 ← 7	e	7021.137	0.004
	9 ← 8	f	7021.867	−0.001
	8 ← 7	f	7021.918	−0.001
11.5 ← 10.5	12 ← 11	e	9499.267	0.001
	11 ← 10	e	9499.295	−0.001
	12 ← 11	f	9500.045	0.000
	11 ← 10	f	9500.075	−0.001
13.5 ← 12.5	14 ← 13	e	11151.382	0.001
	13 ← 12	e	11151.406	0.001
	14 ← 13	f	11152.160	0.001
	13 ← 12	f	11152.185	0.002
14.5 ← 13.5	15 ← 14	e	11977.437	0.000
	14 ← 13	e	11977.459	0.000
	15 ← 14	f	11978.214	0.000
	14 ← 13	f	11978.236	0.000
15.5 ← 14.5	16 ← 15	e	12803.492	0.000
	15 ← 14	e	12803.513	0.001
	16 ← 15	f	12804.270	0.001
	15 ← 14	f	12804.288	−0.002
16.5 ← 15.5	17 ← 16	e	13629.546	−0.001
	16 ← 15	e	13629.566	0.001
	17 ← 16	f	13630.322	−0.001
	16 ← 15	f	13630.341	−0.001
17.5 ← 16.5	18 ← 17	e	14455.600	0.000
	17 ← 16	e	14455.617	−0.001
	18 ← 17	f	14456.377	0.000
	17 ← 16	f	14456.394	0.000
18.5 ← 17.5	19 ← 18	e	15281.653	0.000
	18 ← 17	e	15281.668	−0.001
	19 ← 18	f	15282.429	0.000
	18 ← 17	f	15282.447	0.002
19.5 ← 18.5	20 ← 19	e	16107.705	0.000
	19 ← 18	e	16107.720	0.000
	20 ← 19	f	16108.481	0.001
	19 ← 18	f	16108.496	0.000

NOTE.—All transitions are in the ground $^2\Pi_{1/2}$ fine-structure ladder. The parallel $^2\Pi_{3/2}$ ladder, an estimated 35 K higher, remains undetected.

[a] Designation of e and f levels on the assumption that the hyperfine constant d is positive.

[b] Measurement uncertainties are 2 kHz.

nearly equal intensity by the term in a_-. Care is required with respect to the signs: the $p_{\rm eff}$ and d terms are positive for the f lambda components and negative for the e components; the a_- term is negative when $F = J + 1/2$ and positive when $F = J - 1/2$.

Sixth-order centrifugal distortion has been neglected in all the analysis here. It probably amounts to a small fraction of 1 km s^{-1} at most, at the highest frequencies of interest to astronomers.

Is it certain that we are observing C_9H and not some other molecule produced in our discharge, perhaps from an impurity? As Table 2 shows, the spectroscopic constants derived here are so close to those expected for C_9H that the identification is subject to little doubt on spectroscopic grounds alone. Specifically, (i) B is within 0.25% of that calculated ab initio (Pauzat, Ellinger, & McLean 1991); (ii) D is within 17% of

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TABLE 2

SPECTROSCOPIC CONSTANTS OF C_9H (in MHz)

Constant	Measured[a]	Expected
A	750,000[b] (25 cm^{-1})	...
B	413.25759 (3)	412 ± 1[c]
$D \times 10^6$	1.92 (6)	2.39[d]
$p_{eff} = p + 2q$	0.7741 (9)	0.73[e]
$a_- = a - (b + c)/2$..........	5.99 (92)	9[f]
b..............................	−13.7 (16)	−29[f]
d..............................	2.94 (34)[g]	4[f]

[a] The 1 σ uncertainties (in parentheses) are in units of the last significant digit.

[b] Estimated from C_7H (Travers et al. 1996).

[c] Pauzat et al. 1991.

[d] From the L^{-7} dependence of D on chain length L in the C_nH radicals.

[e] Scaled from C_7H (Travers et al. 1996) on the assumption of pure precession.

[f] From C_5H and C_7H (McCarthy et al. 1996b).

[g] Assumed positive.

that calculated from the smaller C_nH radicals, for which D closely follows an L^{-7} dependence on chain length L; and (iii) the remaining terms are in good agreement with those estimated from smaller members of the C_nH series (Gottlieb et al. 1996). In addition, the identification passes several standard tests for a carbon chain radical:

1. Our molecule is almost certainly a hydrocarbon because (*a*) it was detected under similar experimental conditions to those that optimize the lines of C_5H and C_7H; (*b*) it can also be produced in an acetylene discharge, indicating that it does not come from an impurity specific to the diacetylene synthesis; (*c*) it was not observed in a discharge through deuterated acetylene; (*d*) the hfs implies that it contains a hydrogen atom; and (*e*) the absence of quadrupole structure rules out a nitrogen or chlorine containing species.
2. The new molecule is a radical: the lines are harmonically related by half-integer quantum numbers, as predicted; the absence of lines at subharmonic frequencies confirms the rotational assignments.
3. The ground state of the new molecule is $^2\Pi_{1/2}$: lines of C_9H are not modulated by a magnetic field of a few G, confirming that the ground state does not possess a large magnetic moment—as expected for a $^2\Pi_{1/2}$ state near the Hund's coupling case (*a*) limit; the constant splitting in successive rotational transitions is consistent with lambda doubling in the $^2\Pi_{1/2}$ state.

We have found no evidence for C_9H in published astronomical spectral line surveys, including the recent Nobeyama study of the circumstellar envelope of the carbon-rich star IRC +10216 (Kawaguchi et al. 1995). Because Cernicharo & Guélin (1996) were able recently to identify several lines of C_8H in this survey, and long integrations at specific frequencies could probably achieve significantly higher sensitivity, the likelihood of detecting C_9H in at least IRC +10216 would appear to be quite high.

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