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Detection of C₅ in the Circumstellar Shell of IRC+10216

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The C₅ molecule has been identified in the infrared spectrum of the prototypical obscured carbon star, IRC+10216. In addition to their astrophysical importance, pure carbon chain molecules such as C₅ are of interest in the chemistry of flames and propellants.

PURE CARBON MOLECULES ARE CURRENTLY under intense experimental and theoretical scrutiny. A large number of geometrical structures are possible for C_n molecules, including chains, rings, and sheets, as well as spheroidal fullerenes (1, 2) such as C₆₀. These molecules are believed to play an important role in the formation of soot in flames (1, 2). In astrophysics, they may be both the building blocks and photo-fragments of carbonaceous materials.

Recently we detected the C₃ molecule in the high-resolution circumstellar absorption spectrum of a carbon star, IRC+10216 (3). The C₃ absorption features were very sharp (<0.014 cm⁻¹ wide, full width at half-maximum) and remarkably strong (almost 50% absorbing). Inspired by these results, we searched for the "next" member of the carbon chain series, C₅.

We skipped searching for C₄ in favor of C₅ for a variety of reasons: (i) C₅ is predicted to be linear and symmetric with a closed-shell $\tilde{X}^1\Sigma_g^+$ electronic ground state similar to

the C₃ molecule (4–8); (ii) the C₄ molecule is known to be less abundant than C₅ (9, 10) in high-temperature carbon vapors (although this is not necessarily the case in a circumstellar shell); and (iii) the previous infrared spectrum of C₄ (11) recorded near 2164 cm⁻¹ in inert gas matrices was recently reassigned to C₅ (12).

The C₅ molecule has no dipole moment and thus cannot be monitored by pure rotational microwave spectroscopy. The optical spectrum of C₅ is not known with any degree of confidence, although some published experimental (13) and theoretical (7) suggestions are available.

The infrared vibration-rotation transitions are ideal for the detection of C₅. Of the seven vibrational modes of C₅, ν_3 (σ_u^+ symmetry) near 2164 cm⁻¹ (12) is predicted to have the largest transition dipole moment (0.48 D) (8). The ν_3 mode of C₅ is an "antisymmetric stretching mode" similar to ν_3 (σ_u^+) of C₃ near 2040 cm⁻¹ (3). The ν_3 mode of C₃ is also predicted to have a remarkably strong transition dipole moment of 0.44 D (14).

Our search for the high-resolution vibration-rotation spectrum of C₅ was successful. Guided by our preliminary results, C₅ has been detected in the laboratory by two research groups. Our astronomical measure-

ments are in excellent agreement (15, 16) with the subsequent laboratory measurements.

On 17 January 1989, spectra of the prototypical obscured carbon star IRC+10216 and the moon were observed with an unpolarized resolution of 0.010 cm⁻¹ (1.4 km s⁻¹, full width at half-maximum) by means of the Kitt Peak National Observatory 4-meter telescope and the Fourier transform spectrometer located at the coudé focus (17). The 218-min integration on IRC+10216 resulted in a peak signal-to-noise (1 SD) ratio of 360. The spectrum was limited to 2115 to 2195 cm⁻¹ by a cold blocking filter. The moon, which is an intrinsically featureless source in the 2100 to 2200 cm⁻¹ region, was observed at the same air mass as IRC+10216. We used the ratio of the lunar spectrum, which had a peak signal-to-noise ratio of 460, to the IRC+10216 spectrum to remove the telluric spectrum.

The observed 2170-cm⁻¹ line positions of C₅ needed to be corrected for the Doppler shift caused by the motion of the circumstellar shell relative to the Fourier transform spectrometer. To do this we assumed, in analogy to other molecules observed in the infrared with similar line shape and excitation temperature (see below), that the lines exist in the circumstellar shell at the terminal expansion velocity, -14 km s⁻¹, relative to the center of mass (18). We used this velocity and corrected for a local standard-of-rest velocity of -26 km s⁻¹ for IRC+10216 (19) and for the earth's velocity at the time of observation to measure the frequencies. Telluric ozone lines (20) were used to obtain the frequency zero point.

In the spectrum (Fig. 1), a series of six

Table 1. Line positions of C₅ observed in the 4.6- μ m spectrum of IRC+10216.

Line	Frequency (cm ⁻¹)	Central depth* (%)
P(28) [†]	2164.347	1.9
P(26)	2164.733	2.1
P(20)	2165.870	2.3
P(18)	2166.241	2.3
P(16)	2166.612	2.4
P(14)	2166.977	2.9
P(12)	2167.339	3.9
P(10)	2167.699	2.4
P(8)	2168.052	3.1
R(6)	2170.613	2.8
R(14)	2171.901	3.5
R(16)	2172.214	3.6
R(18) [†]	2172.525	3.6
R(22) [†]	2173.135	3.7
R(24)	2173.433	3.2
R(26)	2173.731	2.8

*The C₅ lines are underresolved, so the linewidths (full width at half-maximum) of 0.010 cm⁻¹ are determined by the instrumental resolution. [†]Slightly blended lines with higher uncertainties.

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Table 2. Spectroscopic constants for the ν_3 mode of C_5 . The uncertainty in the last two digits (1 SD) is given in parentheses. These errors are determined from the least-squares fit of the 16 line positions of Table 1.

Constant	Value (cm^{-1})
ν_3	2169.44205 (40)*
B'' (ground state)	0.0853085 (62)
B' (excited state)	0.0848879 (60)

equally spaced, weak lines (2 to 4% deep) were identified first. The observed line spacing of $0.35 cm^{-1}$ is consistent with the ab initio predictions of the molecular structure of C_5 (4-8). This series of lines turned out to be a P branch ($\Delta J = -1$, J the rotational angular momentum quantum number). The R branch lines ($\Delta J = +1$) were then assigned by prediction from the P branch with the use of the usual rotational energy level expression

$$F(J) = B J(J + 1) \quad (1)$$

where B is the rotational constant.

At this point in our analysis, the attribution of the spectrum to C_5 was secure, as was the relative rotational numbering between the P and R branch lines. However, the absolute rotational assignment and the location of the band origin was not certain. Fortunately, by this time Heath *et al.* (15) had detected the first lines, $R(0)$ and $P(2)$, in their cold laboratory spectrum of C_5 . This work provided us with the correct absolute rotational quantum number assignments for our lines. The low J lines near the origin in our spectrum are very weak and, in the case of $R(0)$ and $P(2)$, are obscured by atmospheric absorption.

The 16 observed line positions of C_5 (Table 1) were reduced to three molecular constants (Table 2) with Eq. 1. The observed band origin of $2169.442 cm^{-1}$ agrees with the argon matrix value of $2164 cm^{-1}$ (11, 12) and the neon matrix value of $2167 cm^{-1}$ (11).

The rotational constants of Table 2 agree well with the ab initio predictions, for example $B_e = 0.0866 cm^{-1}$ (6), although we measure vibrationally averaged constants, whereas the quantum chemical calculations usually provide equilibrium B_e values. These calculations (4-8) also predict that C_5 has a cumulene type of structure with all of the C-C bonds almost identical in length. If the bonds are identical in length, then from our ground-state rotational constant (Table 2) we predict an r_0 value for the bond lengths of 1.283 \AA . The corresponding r_0 for C_3 is 1.277 \AA (3).

We assumed an infrared transition dipole moment for C_5 of $0.48 D$ (8) and used an

observer's frame radiation transport code (18) to synthesize the C_5 lines. The spectrum synthesis indicates that the observed rotational strength distribution is consistent with a rotational temperature of approximately 40 K. There is no a priori reason to expect a Boltzmann population distribution, and a range of temperatures, 20 to 70 K, was required for C_3 (3). However, the C_5 data are not of sufficiently high signal-to-noise ratio to determine if a range of temperatures is also required for C_5 .

The derived column density of C_5 is $n(C_5) = 0.9 \pm 0.25 \times 10^{14} cm^{-2}$, implying a fractional abundance relative to molecular

H_2 , $x(C_5) = n(C_5)/n(H_2) = 1.0 \times 10^{-7}$. Thus C_5 is a factor of 11 less abundant than C_3 . The C_5 temperature (40 K) and abundance are similar to those of the C_6H [$n = 3 \times 10^{14} cm^{-2}$ and $T = 30 K$, (21, 22)] and C_5H [$n = 1.5 \times 10^{14} cm^{-2}$ and $T = 20 K$ (22, 23)]. The detection limits now available in infrared astronomy compare favorably with those achieved in radio astronomy.

The production mechanisms for C_5 in IRC+10216 are unclear. Like C_3 , the rotational lines of C_5 are very sharp ($<0.010 cm^{-1}$, full width at half-maximum) and cold (40 K). This result implies that C_5 occurs

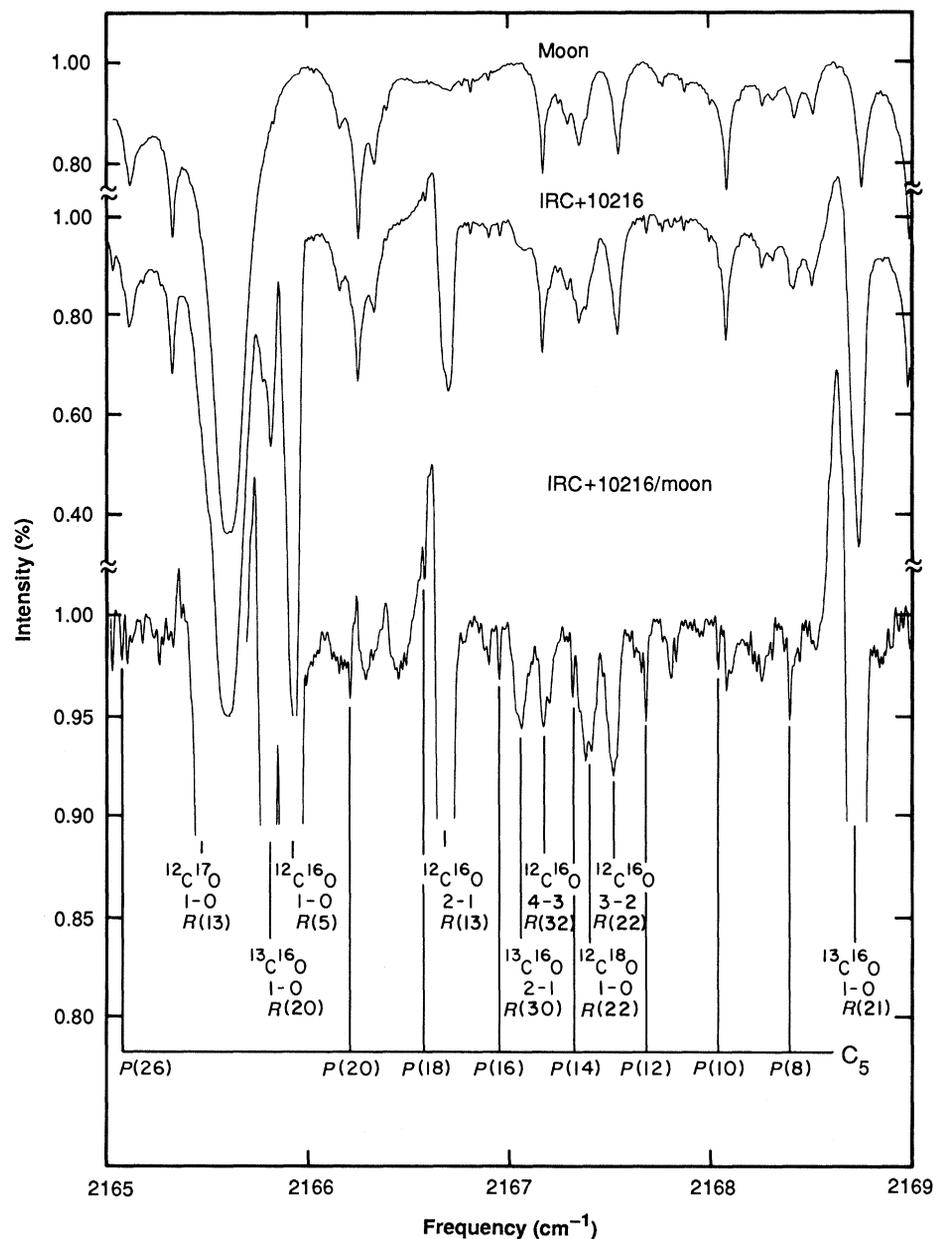


Fig. 1. A short section of the spectrum of the moon, IRC+10216, and the ratio IRC+10216/moon showing most of the observed C_5 P branch. Also identified are CO lines of various isotopic species. The CO lines are formed throughout the circumstellar shell and have a different line shape and excitation temperature from the C_5 . The frequency scale has not been corrected for the earth's velocity. See text to convert the C_5 frequencies to laboratory values. Note that the intensity scale for the ratioed spectrum has been expanded by a factor of 4.

only in the cold, outer part of the circumstellar shell, unlike CO, C₂H₂, HCN, and CS (18, 24), which occur abundantly throughout the stellar envelope. Our discussion in the C₃ paper (3) also applies to C₅ and, indeed, it is possible that C₃ and C₅ originate from the same mechanisms.

It is very likely that C₅ is a direct or indirect result of photochemistry in the outer part of the envelope. The ultraviolet flux present in the interstellar medium can only penetrate into the outer portions of the dusty shell of IRC+10216. The C₅ could result directly from the photolysis of larger molecules, such as C₅H and C₆H, or of carbonaceous grains. Alternately, C₅ could be produced through ion-molecule chemistry, although no ions have been detected yet in IRC+10216. The necessary parent ions such as C₂H₂⁺ (25, 26) would also be produced by the interstellar ultraviolet flux, supplemented by cosmic ray ionization.

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Diode-Laser Absorption Spectroscopy of Supersonic Carbon Cluster Beams: The ν_3 Spectrum of C₅

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A new spectroscopic experiment has been developed in which rovibrational transitions of supersonically cooled carbon clusters, which were produced by laser vaporization of graphite, have been measured by direct-absorption diode-laser spectroscopy. Thirty-six sequential rovibrational lines of the ν_3 band of the C₅ carbon cluster have been measured with Doppler-limited resolution. The absorption spectrum is characteristic of a linear molecule with a center of symmetry. Least-squares analysis of the spectrum indicates an effective carbon-carbon bond length of 1.283 angstroms, in good agreement with ab initio quantum chemical calculations. This work confirms the detection of C₅ in IRC+10216 reported in the accompanying paper.

THE INVESTIGATION OF CLUSTERS OF refractory elements has been one of the fastest growing fields in chemistry and physics during the past 6 to 7 years. Carbon clusters in particular have received much attention because of their relevance to interstellar chemistry and combustion chemistry (1-4). The first theoretical calculations on carbon clusters date to the pioneering work of Pitzer and Clementi (5) and Hoffman (6). Those calculations postulated that carbon clusters of n atoms were either linear (for $n \leq 10$) or formed monocyclic rings (for $n > 10$). Odd-numbered linear clusters were predicted to have ¹Σ ground states and the even-numbered clusters were to have ³Σ ground states. Several recent theoretical papers have not qualitatively changed these results, but instead have given more detailed structural and spectroscopic predictions (7-9). One major new result from high-level quantum chemistry is the calculated existence of low-lying cyclic isomers of small even-numbered clusters ($n = 4, 6, \text{ or } 8$) (10-12).

Complementary high-resolution spectroscopy experiments that can rigorously test these theories have not been possible. Prior to this work, the largest carbon cluster to be studied by high-resolution spectroscopy is the relatively stable cluster C₃. Spectroscopy of C₃ dates to cometary detection in 1881

(13), laboratory detection by Herzberg in 1942 (14), and the spectral assignment by Douglas in 1951 (15). Recently, the 2040-cm⁻¹ ν_3 band of C₃ has been observed in space by Hinkle *et al.* (16) and in the laboratory by Matsumura *et al.* (17) by diode-laser

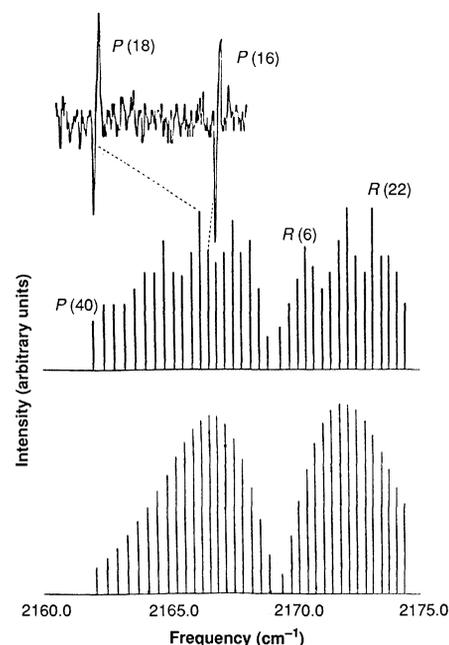


Fig. 1. Stick spectra of calculated (bottom) and observed (middle) rotational lines of the ν_3 (σ_u) band of C₅. The P(18) and P(16) transitions (top) were observed in a 0.4-cm⁻¹ scan beginning at 2166.1 cm⁻¹ (1000 samples per point and 15 μ s (per sample)).

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