only in the cold, outer part of the circumstellar shell, unlike CO, C_2H_2, HCN, and CS (*18, 24*), which occur abundantly throughout the stellar envelope. Our discussion in the C_3 paper (*3*) also applies to C_5 and, indeed, it is possible that C_3 and C_5 originate from the same mechanisms.

It is very likely that C_5 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 C_5 could result directly from the photolysis of larger molecules, such as C_5H and C_6H, or of carbonaceous grains. Alternately, C_5 could be produced through ion-molecule chemistry, although no ions have been detected yet in IRC+10216. The necessary parent ions such as $C_2H_2^+$ (*25, 26*) would also be produced by the interstellar ultraviolet flux, supplemented by cosmic ray ionization.

REFERENCES AND NOTES

1. R. F. Curl and R. E. Smalley, *Science* **242**, 1017 (1988).
2. H. Kroto, *ibid.*, p. 1139.
3. K. W. Hinkle, J. J. Keady, P. F. Bernath, *ibid.* **241**, 1319 (1988).
4. K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).
5. D. W. Ewing and G. V. Pfeiffer, *Chem. Phys. Lett.* **134**, 413 (1987).
6. K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
7. G. Pacchioni and J. Koutecky, *ibid.* **88**, 1066 (1988).
8. J. Kurtz and L. Adamowicz, private communication; J. M. L. Martin, J. P. Francois, R. Gijbels, *J. Chem. Phys.* **90**, 3403 (1989).
9. J. Berkowitz and W. A. Chupka, *J. Chem. Phys.* **40**, 2735 (1964).
10. J. Drowart, R. P. Burns, G. DeMaria, M. G. Ingram, *ibid.* **31**, 1131 (1959).
11. K. R. Thompson, R. L. DeKock, W. Weltner, Jr., *J. Am. Chem. Soc.* **93**, 4688 (1971); W. R. M. Graham, K. I. Dismuke, W. Weltner, Jr., *Astrophys. J.* **204**, 301 (1976).
12. M. Vala, T. M. Chandrasekhar, J. Szczepanski, R. Van Zee, W. Weltner, Jr., *J. Chem. Phys.* **90**, 595 (1989).
13. W. Kratschmer, N. Sorg, D. R. Huffman, *Surf. Sci.* **156**, 814 (1985).
14. W. P. Kraemer, P. R. Bunker, M. Yoshimine, *J. Mol. Spectrosc.* **107**, 191 (1984).
15. J. Heath, A. Cooksy, M. Gruebele, C. Schmuttenmaer, R. Saykally, *Science* **244**, 564 (1989).
16. M. Moazzen-Ahmadi, A. R. W. McKellar, T. Amano, private communication.
17. D. N. B. Hall, S. T. Ridgway, E. A. Bell, J. M. Yarborough, *Proc. Soc. Photo-Optical Instrum. Eng.* **172**, 121 (1978).
18. J. J. Keady and K. H. Hinkle, *Astrophys. J.* **331**, 539 (1988).
19. P. G. Wannier *et al.*, *ibid.* **230**, 149 (1979); H. Olofsson, L. E. B. Johansson, Å. Hjalmarson, N.-Q. Rieu, *Astron. Astrophys.* **107**, 128 (1982).
20. C. P. Rinsland, M. A. H. Smith, J. M. Flaud, C. Camy-Peyret, V. Malathi Devi, *J. Mol. Spectrosc.* **130**, 204 (1988).
21. S. Saito, K. Kawaguchi, H. Suzuki, M. Ohishi, N. Kaifu, S. Ishikawa, *Publ. Astron. Soc. Jpn.* **39**, 193 (1987).
22. J. Cernicharo, M. Guélin, K. M. Menten, C. M. Walmsley, *Astron. Astrophys.* **181**, L1 (1987).
23. J. Cernicharo, C. Kahane, J. Gómez-González, M. Guélin, *ibid.* **167**, L5 (1986).
24. J. J. Keady, D. N. B. Hall, S. T. Ridgway, *Astrophys. J.* **326**, 832 (1988).
25. A. E. Glassgold *et al.*, *Astron. Astrophys.* **157**, 35 (1986); A. E. Glassgold, G. A. Mamon, A. Omont, R. Lucas, *ibid.* **180**, 183 (1987).
26. L. A. M. Nejad and T. J. Millar, *ibid.* **183**, 279 (1987).
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Diode-Laser Absorption Spectroscopy of Supersonic Carbon Cluster Beams: The ν_3 Spectrum of C_5

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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 C_5 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 C_5 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 $^1\Sigma$ ground states and the even-numbered clusters were to have $^3\Sigma$ 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, 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 C_3. Spectroscopy of C_3 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 C_3 has been observed in space by Hinkle *et al.* (*16*) and in the laboratory by Matsumura *et al.* (*17*) by diode-laser

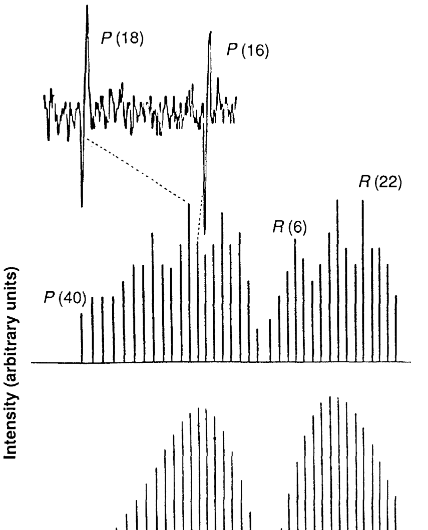

Fig. 1. Stick spectra of calculated (bottom) and observed (middle) rotational lines of the ν_3 (σ_u) band of C_5. The $P(18)$ and $P(16)$ transitions (top) were observed in a 0.4-cm^{-1} scan beginning at 2166.1 cm^{-1} (1000 samples per point and 15 μs (per sample).

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kinetic spectroscopy. High-resolution absorption spectroscopy has not been extended to larger carbon clusters largely because of the lack of suitable cluster sources. In a carbon plasma, the C_4 and C_5 concentration may only be 10^{-3} that of C_3 (*18*). Weltner and co-workers have overcome this problem by building up a carbon cluster population in a rare gas matrix (*19*). Recently these workers used Fourier transform infrared spectroscopy on isotopically substituted carbon clusters trapped in an argon matrix to establish that the ν_3 vibrational band origin of C_5 lies near 2164 cm^{-1} (*20*).

We report the development of a general new technique that allows one to perform high-resolution infrared absorption spectroscopy on relatively large clusters. We have used this technique to record the rovibrational spectrum of the highest frequency $\nu_3(\sigma_u)$ asymmetric stretch of C_5 (the 2164-cm^{-1} band observed by Weltner and coworkers). The C_5 cluster is found to be linear with a center of symmetry and a $^1\Sigma$ ground state. It has an effective ground-state C–C bond length of 1.2833(5) Å, a ground-state rotational constant of 0.085305(31) cm^{-1}, and a band origin of 2169.4404(18) cm^{-1} (numbers in parentheses are the errors expressed as the variation in the last digit or digits).

A brief description of the experiment is as follows (*21*). The clusters are created by 308-nm excimer laser vaporization (the fluence of the focused laser was 1000 mJ/cm^2) of a rotating and translating graphite rod placed in the throat of a supersonic nozzle. The vaporized carbon plasma is entrained in a continuous flow of argon (or neon). The nozzle is specifically designed to decrease the Doppler linewidth and to enhance the cluster concentration within the optical path of a diode-laser beam. The diode laser makes 16 to 20 passes in a White cell that is mounted inside a Roots-blown vacuum chamber. The diode laser is frequency-modulated at 100 kHz, and the absorption signal is processed with a fast, custom-built lock-in amplifier coupled with boxcar detection and background subtraction. The boxcar samples the diode-laser signal during each cluster pulse for 15 μs, and the experiment is recycled at a rate of 200 Hz.

In a typical experiment, the laser was scanned in steps of 25 to 35 MHz, and each step was signal-averaged for 300 to 3000 points. The minimum Doppler-limited linewidths were about 100 MHz, but most of the lines were modulation-broadened to roughly 190 MHz. The rotational temperature of the beam was about 8 K with an argon carrier, although it may be varied somewhat by choice of carrier gas and backing pressure. Absorption frequencies were calibrated with a subsequent scan of N_2O to obtain absolute frequencies. A germanium single-crystal etalon was scanned so as to obtain frequency calibration of the reference lines. This sensitivity of the experiment was initially tested by measuring the $R(2)$ line of the ν_3 band of C_3. On a fast scan (100 points and 15 μs per point), this line was observed with a signal-to-noise ratio of 500. The line intensities for C_5 were, in general, reduced by a factor greater than 100. The experimental frequency precision was dominated by laser drift during the signal scan. For the weakest transitions, the uncertainty arose from low signal-to-noise ratios.

Based on Weltner's reliable matrix value, we searched the region from 2161.5 to 2174.5 cm^{-1} and observed a set of P- and R-branch transitions characteristic of a linear molecule. The observed and calculated spectra are shown in Fig. 1. The rotational temperature of the beam was altered to allow observation of the lowest and highest (up to $J = 40$) J states (where J is the rotational angular momentum quantum number). We identify the carrier of this band as C_5 based on the following considerations: (i) the band origin agrees well with Weltner's value for C_5; (ii) the rotational constant agrees with ab initio predictions of the molecular structure of C_5; (iii) the observed chemistry with respect to the addition of H_2 and O_2 to the buffer gas is consistent with that for a bare carbon cluster (*22*); and (iv) the molecular symmetry of C_5 forbids the existence of states of odd J in the ground vibrational level; consequently, transitions arising from these states are absent in the spectrum. It was sufficient to fit this spectrum with the simplest possible rotational Hamiltonian, $E = BJ(J + 1)$, where E is the energy and B is the rotational constant, since distortion effects may be small for a molecule possessing a moment of inertia as large as that for C_5. Indeed, inclusion of the centrifugal distortion parameters in the Hamiltonian had no effect on the final fit of the spectrum, and the distortion parameters were not determined. The molecular parameters ν_3, B'', and B' were determined by least-squares analysis, and the uncertainties were evaluated from the resulting covariance matrix. The values of the rotational constants are consistent with ab initio predictions of the structure carried out at the Hartree-Fock level (*7, 12*). Raghavachari and Binkley's theoretical value for this vibrational frequency (2344 cm^{-1}) is high by about 7.5%, in accord with their own estimated error. Their calculations indicate that the outer equilibrium C–C bond length is slightly shorter than that of the inner carbon atoms. From our single value for B_0, we extracted an effective bond length of 1.283 Å, assuming all carbon bonds are equal.

In view of the very low bending vibrational frequencies predicted for this molecule (*12*), C_5 may be presumed to be quasilinear with a small barrier to linearity in the bending potential surface. A consequence of quasilinearity in molecules such as C_3 (*16, 17*) and C_3O_2 (*23*) is that the upper-state rotational constant is greater than that in the ground state, which is indicative of an average structure that actually becomes more compact with excitation. The reverse is observed for rigid linear molecules. We do not observe this effect in the ν_3 spectrum of C_5

Table 1. The $\nu_3 = 1 \leftarrow 0$ transitions in C_5 (ν_{obs}) observed in this work. The calculated values (ν_{calc}) are from a fit to a model (Table 2).

J	$P(J)$ (cm^{-1})	$\nu_{obs} - \nu_{calc}$ (10^{-3} cm^{-1})	$R(J)$ (cm^{-1})	$\nu_{obs} - \nu_{calc}$ (10^{-3} cm^{-1})
0			2169.6073	−2.9
2	2169.0984	0.0	2169.9476	0.3
4	2168.7555	2.5	2170.2872	6.2
6	2168.4101	5.8	2170.6046	−6.9
8	2168.0563	4.0	2170.9379	−0.7
10	2167.6955	−1.5	2171.2562	−6.2
12	2167.3376	−0.8	2171.5824	−0.5
14	2166.9691	−7.3	2171.9035	3.5
16	2166.6151	3.9	2172.2085	−5.4
18	2166.2436	1.0	2172.5290	4.6
20	2165.8690	−1.7	2172.8318	0.2
22	2165.4932	−2.2	2173.1381	2.6
24	2165.1180	1.1	2173.4352	−0.9
26	2164.7344	−0.6	2173.7324	−1.0
28	2164.3457	−4.2	2175.0259	−1.4
30	2163.9599	−1.5	2174.3175	−0.5
32	2163.5678	−1.8		
34	2163.1760	1.6		
36	2162.7731	−2.9		
38	2162.3733	−0.9		
40	2161.9768	7.6		

Table 2. Molecular constants (cm^{-1}) and effective bond distances (Å) for C_5. For the first column the uncertainties in the last digit or digits are 2 SD (SD of the fit was 0.0036 cm^{-1}).

Parameter	This work	Ab initio
ν_3	2169.4404 (18)	2344
B''	0.085305 (31)	0.0866
B'	0.084900 (32)	
r_0*	1.2833 (5)	1.271, 1.275† 1.277, 1.280‡

*Ground state–effective C–C bond length, compared with ab initio equilibrium values. †From (*12*). ‡From (7).

and surmise that the average structure does not become dramatically more bent in the $\nu = 1$ upper state.

During the course of this project we learned of the detection of C_5 in the carbon star IRC+10216 by Bernath and co-workers (*24*). This discovery highlights the importance of carbon cluster chemistry in astrophysical contexts. The C_5 molecule is a well-known product of carbon condensation and is even observed in low-pressure benzene-O_2 and C_2H_2-O_2 flames under sooting conditions (*3*). In addition, the well-known interstellar molecules, the polycyanoacetylenes (HC_nN; $n = 3, 5, 7, 9$, and 11), are easily produced in a nitrogen- and hydrogen-rich condensing carbon environment (*2, 22*). It is possible that the bare carbon clusters, as well as the cyanoacetylenes, all originate from a similar chemical environment. A short-term goal of such work is to study other carbon clusters (C_4, C_6, C_7, and so forth) that are likely to exist in space and play an important role in interstellar chemistry. Our experiment is quite general and should certainly be applicable to these other carbon clusters. For both future laboratory and astronomical studies, reliable estimates are needed of the absolute absorption strength for the ν_3 band of C_5 as well as for allowed transitions in other carbon clusters. Such results would allow molecular densities to be extracted from the observations. Such work should also stimulate quantum chemists to begin high-level calculations for the small carbon clusters.

Note added in proof: We have received a preprint by A. R. W. McKellar *et al.* (*25*) reporting the observation of these same spectra in a discharge.

REFERENCES AND NOTES

1. E. A. Rohlfing, D. M. Cox, A. Kaldor, *J. Chem. Phys.* **81**, 3322 (1984).
2. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1984).
3. J. R. Heath, S. C. O'Brien, H. W. Kroto, R. F. Curl, R. E. Smalley, *Astrophys. J.* **314**, 352 (1987).
4. Ph. Gerhardt, S. Loffler, K. H. Homann, *Chem. Phys. Lett.* **137**, 306 (1987).
5. K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).
6. R. Hoffman, *Tetrahedron* **22**, 521 (1966).
7. D. W. Ewing and G. V. Pfeiffer, *Chem. Phys. Lett.* **134**, 413 (1987).
8. R. A. Whiteside *et al.*, *ibid.* **78**, 538 (1981).
9. J. P. Ritchie, H. F. King, W. S. Young, *J. Chem. Phys.* **85**, 5175 (1986).
10. D. H. Magers *et al.*, *ibid.* **84**, 3284 (1986).
11. R. Krishnan *et al.*, *ibid.* **85**, 6623 (1986).
12. K. Raghavachari and J. S. Binkley, *ibid.* **87**, 2191 (1987).
13. W. Huggins, *Proc. R. Soc. London* **33**, 1 (1882).
14. G. Herzberg, *Astrophys. J.* **96**, 314 (1942).
15. A. E. Douglas, *ibid.* **114**, 466 (1951).
16. K. H. Hinkle, J. J. Ready, P. F. Bernath, *Science* **241**, 1319 (1988).
17. K. Matsumura, H. Kanamori K. Kawaguchi, E. Hirota, *J. Chem. Phys.* **89**, 3491 (1988).
18. J. Drowart, R. P. Burns, G. DeMaria, M. G. Inghram, *ibid.* **31**, 1131 (1959).
19. R. J. Van Zee *et al.*, *ibid.* **88**, 3465 (1988).
20. M. Vala *et al.*, *ibid.* **90**, 595 (1989).
21. A more detailed description of the experiments (J. R. Heath *et al.*, unpublished results) will appear elsewhere.
22. J. R. Heath *et al.*, *J. Am. Chem. Soc.* **109**, 359 (1987).
23. L. Fusina and I. M. Mills, *J. Mol. Spectrosc.* **79**, 101 (1980).
24. P. F. Bernath *et al.*, *Science* **244**, 562 (1989).
25. A. R. W. McKellar *et al.*, *Chem. Phys. Lett.*, in press.

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AP1/*jun* Function Is Differentially Induced in Promotion-Sensitive and Resistant JB6 Cells

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Tumor promoters may bring about events that lead to neoplastic transformation by inducing specific promotion-relevant effector genes. Functional activation of the trans-acting transcription factor AP-1 by the phorbol ester 12-O-tetradecanoylphorbol-13-acetate (TPA) may play an essential role in this process. Clonal genetic variants of mouse epidermal JB6 cells that are genetically susceptible (P^+) or resistant (P^-) to promotion of transformation by TPA were transfected with 3XTRE-CAT, a construct that has AP-1 cis-enhancer sequences attached to a reporter gene encoding chloramphenicol acetyltransferase (CAT). Transfected JB6 P^+, but not P^- variants, showed TPA-inducible CAT synthesis. Epidermal growth factor, another transformation promoter in JB6 cells, also caused P^+ specific induction of CAT gene expression. These results demonstrate an association between induced AP-1 function and sensitivity to promotion of neoplastic transformation.

By MEANS OF GENETICALLY BRED carcinogenesis-sensitive or resistant strains of mice, it was demonstrated that susceptibility to promotion of neoplastic transformation in vivo is inheritable and genetically controlled (*1*). Colburn *et al.* subsequently developed the JB6 mouse epidermal cell system of clonal genetic variants of promotion-sensitive (P^+) and promotion-resistant (P^-) cells that permitted the study of genetic susceptibility to transformation promotion at the molecular level (*2*). In P^+ JB6 cells TPA and EGF induce the formation of large, tumorigenic, anchorage-independent colonies in soft agar at a high frequency (10 to 40% of the cell population). In contrast, the P^- cells exhibit a response to the tumor-promoting agents that is 0.1 to 1% that of P^+ cells, and the colonies are much smaller (*3*). From the promotion-sensitive variants, two cloned sequences, designated *pro*-1 and *pro*-2, were isolated, either of which confers promotion-sensitivity when transfected into the P^- cells (*4*).

The expression of genes transcriptionally induced by TPA is among the events thought to be required to implement the process of tumor promotion. The list of such inducible genes has grown to include at least 30 (*5, 6*), among them, proto-oncogenes [such as c-*myc* and c-*fos* (*5*)] and genes encoding proteases, including collagenase and plasminogen activator (*5*). All of these genes are observed at elevated levels of expression in the genesis or maintenance of neoplasia (*6*). The AP-1 protein is a trans-acting transcription factor that controls expression of some of these genes in cells treated with TPA (*7, 8*). The AP-1 transcript is itself induced by TPA (*9*), epidermal growth factor (*10*), and serum (*9, 11*) and is encoded by a recently discovered proto-

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