rate. Some investigators have reported that this phenomenon arises simply from an inhibitory action of norepinephrine or dopamine on the cell, which depresses background firing rate more than it depresses stimulus elicited responses [for example, (5); E. T. Rolls, S. J. Thorpe, M. Boytim, I. Szabo, D. I. Perret, *Neuroscience* **12**, 1201 (1984)]. In this report, we focus on a set of observations that suggests a different mechanism: a potentiation of responses to both excitatory and inhibitory inputs with minimal or no influence on background firing rate [for example, (6, 7)]. Furthermore, in considering these changes in cellular response, we are not attempting to address the underlying biochemical mechanisms. Our focus, and our results, concern the informational and behavioral consequences of neuromodulation, at the cellular level and above.

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$$u_0(x) = \begin{cases} 0 \text{ for } x \leq 0 \\ 1 \text{ for } x > 0 \end{cases}$$

A sequence of functions $\{g_n\}$ converges almost everywhere to the function g if the set of points where it diverges, or converges to the wrong value, is of measure zero. For a rigorous discussion of convergence almost everywhere, consult A. J. Weir, *Lebesgue Integration and Measure* (Cambridge Univ. Press, Cambridge, 1973).
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The C_7 Cluster: Structure and Infrared Frequencies

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Observation and characterization of the C_7 cluster are reported. Carbon clusters are produced by laser vaporization of a graphite target followed by supersonic expansion of the vaporized material within a gas dynamically focused argon jet. Thirty-six sequential rovibrational lines of the ν_4 antisymmetric stretch fundamental of C_7 are probed by gated detection of diode laser absorption. The observed spectrum is characteristic of a symmetrical linear molecule. Analysis of the spectrum indicates an effective average bond length of 1.2736(4) angstroms and a vibrational frequency of 2138.1951(10) reciprocal centimeters, in excellent agreement with ab initio calculations. This work will facilitate the astrophysical detection of this cluster.

SMALL CARBON CLUSTERS (LESS THAN 12 atoms) have recently attracted the attention of numerous investigators from a wide variety of disciplines. This is largely due to the ubiquitous nature of these species; they have been observed in astrophysical sources (*1*), in sooting flames (*2*), in acetylene photolysis (*3, 4*), and in plasmas produced by laser vaporization of graphite (*5–7*). This suggests that unsaturated carbon clusters play a critical, if not central, role in the high-temperature chemistry of carbon-rich environments.

Ab initio and semiempirical theory of small carbon clusters has been under constant development for several decades (*8, 9*). Much of this work has recently been reviewed by Weltner and Van Zee (*10*). Odd-numbered clusters of up to 11 atoms are expected to have linear $^1\Sigma$ ground states, with the lowest triplet states existing at much higher energy. Even-numbered clusters of up to 10 atoms are predicted to have two low-energy configurations: an open shell linear $^3\Sigma$ state and a monocyclic singlet state. There is much debate regarding the detailed properties of these even clusters (*10*). Odd-numbered clusters up to C_7 are predicted to be more stable than the adjacent even clusters (*9*).

Despite this high level of theoretical activity, experimental results have been sparse. The development of tandem mass spectrometric technologies has enabled researchers to study carbon cluster cation photofragmentation (*6*) and anion photoelectron spectroscopy (*7*). Results from these experiments have been consistent with theory. Only recently, however, have definitive experiments capable of testing detailed theoretical predictions been possible. Over the past 2 years a number of research groups have characterized the C_3 cluster with high-precision laser techniques and have obtained sufficient information for the construction of an accurate molecular potential surface (*3, 12–14*). Last year we accomplished a detailed laboratory characterization of the C_5 cluster (*5*) using infrared laser spectroscopy. That experiment was reported simultaneously with the detection of C_5 in the carbon star IRC+10216 by Bernath, Hinkle, and Keady (*1*). Additional bands of C_5 have been detected and analyzed by Moazzen-Ahmadi, McKellar, and Amano (*4, 15*). Ab initio calculations are in close agreement with those experimental results.

In this paper we describe direct observation and characterization of the C_7 cluster, carried out with an infrared laser spectroscopy technique similar to that used in our study of C_5. Thirty-six sequential rovibrational lines have been measured and assigned to the ν_4 antisymmetric stretch vibrational transition of C_7. The observed spectrum is characteristic of a symmetrical linear molecule with a closed electronic shell. Analysis of the spectrum indicates a ground state rotational constant of 0.030929(21) cm^{-1},

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and an effective average carbon-carbon bond length of 1.2736(4) Å. This supports the theoretical prediction of cumulene-like bonding in this system, although the inner, middle, and outer carbon-carbon bond lengths are not expected to be identical (*9*).

In a previous report, we discussed a technique for studying the infrared spectra of supersonically cooled carbon clusters at high resolution (*5*). Both the experimental detection system and the cluster source have been substantially improved, and a description of these modifications is provided here. The carbon cluster beam is generated by focusing a KrF excimer laser (248 nm) onto a graphite target placed in the throat of a pulsed planar nozzle (2 mm by 10 mm). The nozzle (20-atm Ar backing pressure) is fired such that maximum carrier gas density passes over the target coincident with laser ablation. The carrier gas entrains and cools the carbon clusters, and the cluster-gas mixture expands into a vacuum chamber pumped by a 2800 cfm Roots pump, where it intersects an infrared diode laser beam. A multipass optical cell (*16*) is used to align 10 to 12 passes of the diode laser through the supersonic expansion. Absorption resonances are detected by monitoring the diode laser power with an InSb detector. The diode laser frequency is typically incremented 20 MHz after signal averaging for 30 excimer shots. Frequency calibrations are performed as previously described (*5*).

Two fundamental experimental difficulties have been addressed with the current generation of this apparatus. The first involves the time profile of the absorption signal. This signal lasts only about 15 μs, which, when coupled with a repetition rate of 100 Hz, produces an experimental duty cycle of 0.15%. The transient nature of the signal implies a corresponding broad frequency spectrum, and it is difficult to filter diode laser and detector noise without significantly altering the time profile and amplitude of an absorption signal. This problem has been addressed by careful selection of high- and low-pass signal filters, which reduce laser and detector noise by approximately a factor of 100. Such filtering modifies the absorption signal because of ac coupling, giving it both positive and negative voltage components, and causes a 70% amplitude reduction. Two boxcar signal averagers are triggered 12 μs apart, and each samples the filtered detector output for 3 μs. When the laser is on resonance the boxcars sum negative and positive signal components, and when the laser is off resonance the boxcars subtract background fluctuations.

A second experimental problem emanates from the nature of a supersonic expansion through a circular orifice. Such an expansion, when interrogated at right angles by a high-resolution laser operating near 2100 cm^{-1}, will exhibit Doppler-broadened absorption linewidths of 200 to 300 MHz. The diode laser, however, has a frequency bandwidth of only 30 to 40 MHz. Thus, at an absorption maximum, the laser may only probe 10% of the clusters. This difficulty has been addressed by gas-dynamic focusing of the molecular beam through a slit. Clusters are generated at the center of the slit where the expanding gas has a compressed Doppler width along the diode laser axis (*17*). Single pass measurements of C_3 and C_5 absorption resonances indicated a reduced Doppler width of 45 MHz. The use of a multipass cell increases that width to about 60 MHz. The slit orifice also allows for 200 to 300 mJ of the vaporizing laser to be focused to a line on the target, thereby increasing the effective path length of the clusters in the infrared laser beam. These source and detection system improvements have increased the experimental sensitivity by a factor of 10, and the spectral resolution by a factor of 3.

Table 1. The $\nu_4 = 1 \leftarrow 0$ transitions in C_7 (ν_{obs}) measured 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			(2138.2567)	—
2	2138.0713	0.1	2138.3854	6.1
4	2137.9445	−1.8	2138.5055	4.7
6	2137.8155	−4.9	2138.6173	−4.2
8	2137.6937	0.0	2138.7383	−2.8
10	2137.5668	0.9	2138.8642	4.3
12	2137.4309	−6.3	2138.9800	2.3
14	2137.3008	−6.8	2139.0885	−6.0
16	2137.1762	0.8	2139.2059	−4.5
18	2137.0485	3.0	2139.3306	5.2
20	2136.9130	0.0	2139.4384	−0.9
22	2136.7787	−0.8	2139.5554	3.0
24	2136.6479	2.7	2139.6719	7.4
26	2136.5182	8.3	2139.7713	−4.4
28	2136.3698	−3.8	2139.8920	6.1
30			2139.9944	−0.7
32			2140.0989	−4.5
34			2140.2110	0.2
36			2140.3137	−3.5
38			2140.4216	−1.1
40			2140.5278	0.6
42			2140.6313	0.5

Table 2. Molecular constants and effective bond distance for C_7. The effective bond distance is calculated assuming all bond lengths are equal. For the first column the uncertainties in the last digits are 2 SD (SD of the fit was 0.0041 cm^{-1}). All ab initio values taken from (*9*).

Parameter	This work	Ab initio
ν_4 (cm^{-1})	2138.1951(10)	2281
B'' (cm^{-1})	0.030928(21)	0.03099
B' (cm^{-1})	0.030809(20)	
r_o* (Å)	1.2736(4)	1.270, 1.280, 1.264

*Ground state effective C-C bond length, compared with ab initio equilibrium values. Ab initio values correspond to the outer, central, and inner C-C bond distances, respectively.

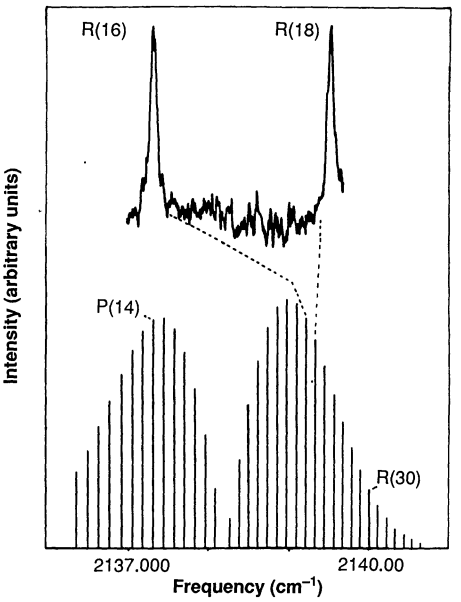

Fig. 1. Calculated rovibrational spectra for the ν_4 (σ_u) fundamental C_7. The R(16) and R(18) transitions (top) were observed in a 0.2 cm^{-1} scan beginning at 2139.2 cm^{-1} (30 samples per point and 6 μs per sample).

A set of P- and R-branch transitions characteristic of a linear closed electronic shell carbon cluster was observed near the end of an exhaustive search over the region 2020 to 2142 cm^{-1}. The measured transitions and their spectral assignments are presented in Table 1. Typical data and the calculated spectrum are shown in Fig. 1. The spectrum is assigned to the C_7 cluster based on the following observations: (i) the behavior of this absorber with respect to experimental conditions is similar to that of C_5 and C_3; (ii) the rotational constant is in excellent agreement with ab initio predictions (*9*); and (iii) the vibrational band origin is in good agreement (6% lower) with theoretical predictions (*9*), roughly the same error as analogous predictions for the C_5 and C_3 clusters. The rotational temperature of the C_7 cluster in the beam is estimated to be about 15 K.

The observed spectrum was fit with the

standard formula for rovibrational levels of a linear molecule (*18*). Three molecular parameters, the vibrational band origin (ν_4) and the lower and upper state rotational constants (B″ and B′), were determined by least-squares analysis, and the uncertainties were evaluated from the resulting covariance matrix. Statistical analysis indicated that the two rotational constants are highly correlated (0.99).

C_3 is thought to be slightly quasi-linear (*13, 14*). Quasi-linearity is a result of a small barrier to linearity in the molecular bending potential (*11*). Molecules exhibiting this phenomenon are characterized by highly anharmonic low-frequency bending vibrations and strong stretch-bend interactions. Quasi-linearity manifests itself in the antisymmetric mode of the C_3 cluster in the average molecular structure becoming more compact (the rotational constant increases by 1.2%) upon excitation of the antisymmetric stretch vibration. The rotational constant of a normal linear molecule would be expected to decrease upon similar vibrational excitation. C_5 and C_7 have low-energy bending vibrations and are also potentially quasilinear. Recent spectroscopic measurements on C_5 indicate that its bending vibrations are reasonably harmonic, and no evidence for quasi-linearity is observed (*15*). The results presented here similarly do not evidence quasi-linearity in the case of C_7. Upon excitation of the ν_4 vibration the rotational constant is found to decrease by about 0.35%, and thus the average length of the molecule increases. While this is not suggestive of quasi-linearity in C_7, it does not rule it out either.

The detection of the C_5 and C_3 clusters in the carbon star IRC+10216 by Bernath and co-workers (*1, 19*) with infrared astronomy highlights the importance of carbon clusters in astrophysical processes. The following ion-molecule reaction scheme has been proposed by Suzuki (*20*) for astrophysical production of carbon chains:

$$\begin{aligned} C^+ + C_n &\rightarrow C_{n+1}^+ + h\nu \\ C_{n+1}^+ + H_2 &\rightarrow C_{n+1}H^+ + H \\ C_{n+1}H^+ + e &\rightarrow C_{n+1} + H \end{aligned} \quad (1)$$

Calculations done by Freed, Oka, and Suzuki (*21*) compared unimolecular dissociation rates versus rates for infrared emission. Cluster growth was shown to proceed at the Langevin rate for $n \geq 4$. This may explain the high C_5 abundance observed in IRC+10216 (*1*). It follows from the model that C_7 should also be abundant. The C_7 absorption spectrum reported here was a factor of 3 to 5 less intense than the ν_3 spectrum observed for C_5. This is expected if the oscillator strength of the ν_4 transition of C_7 is similar to that of the ν_3 transition of C_5. The observed decrease of absorption intensity comes from an increased ground-state partition function for the larger C_7 cluster and an expected slight decrease in the relative density of C_7 in the molecular beam (*6, 22*). If the interstellar C_7/C_5 abundance ratio is not too small, then the frequencies reported here will make astronomical observation of this molecule possible. This, in turn, will constitute an important step in understanding the nature and distribution of carbon in the interstellar medium.

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Tunable Far-IR Laser Spectroscopy of Jet-Cooled Carbon Clusters: The ν_2 Bending Vibration of C_3

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Seven rovibrational transitions of the $(01^10) \leftarrow (00^00)$ fundamental bending band of C_3 have been measured with high precision with the use of a tunable far-infrared laser spectrometer. The C_3 molecules were produced by laser vaporization of a graphite rod and cooled in a supersonic expansion. The astrophysically important ν_2 fundamental frequency is determined to be 63.416529(40) cm^{-1}. These measurements provide the basis for studies of C_3 in the interstellar medium with far-infrared astronomy.

THE STUDY OF CARBON CLUSTERS BY both theory and experiment has received a great deal of recent attention (*1–3*). These species have proven to be remarkably ubiquitous. They are observed, for example, in flames and electrical discharges, in carbon stars, and in laser-produced plasmas of various polymers. They are implicated in the process of soot formation and in the aggregation of interstellar dust grains. Many investigations have evidenced new closed structures of carbon composed of five and six membered rings.

The elucidation of the roles of carbon clusters in these various contexts has been seriously impeded by the absence of spectral and structural data for them. In fact, detailed laboratory spectra have been measured only for C_2, C_2^-, C_2^+, C_3, and C_5, although both infrared and electron spin resonance data have been obtained for several other species from studies in cryogenic matrices (*4*). We are attempting to improve this situation. In a previous report (*5*) we described a general new technique for measuring carbon clusters with mid-infrared laser absorption spectroscopy, and infrared (IR) spectra of the C_5 cluster were presented as an initial demonstration of the method. The detection of C_5 in the carbon star IRC+10216 by infrared astronomy was presented at the same time by Bernath *et al.* (*6*). In this report, we describe a new experiment for measuring far-infrared (FIR) (10 to 350 cm^{-1}) spectra of carbon clusters with high precision (1×10^{-6}) and high sensitivity, and present the first direct measurement of the astrophysically important 63 cm^{-1} bending mode of

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