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## COMMUNICATIONS

## The C<sub>9</sub> cluster: Structure and infrared frequencies

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Small carbon clusters (< 15 atoms) have been the focus of considerable theoretical study over the past 25 years.<sup>1-7</sup> Most of this effort has centered on structural calculations, which indicate that these clusters are dominated by two morphologies: monocyclic rings are favored for even C<sub>n</sub> (n > 4), while small odd clusters (n = 3, 5, 7, 9) are predicted to have linear <sup>1</sup>Σ<sub>g</sub><sup>+</sup> cumulenic ground states. For the smallest clusters, the odd-numbered cumulenes are predicted to be relatively more stable than the adjacent even-numbered rings. However, this trend gradually weakens with increasing cluster size, and at n = 9, it actually reverses. C<sub>10</sub> is more stable than C<sub>9</sub> and for larger clusters, ring structures are the predicted ground states for odd as well as even clusters.

Negative ion photoelectron spectroscopy indicates that a structural transition probably does occur at C<sub>11</sub>.<sup>8</sup> Although carbon clusters containing up to 7 atoms have been observed in recent spectroscopy experiments,<sup>9-17</sup> direct experimental structural determinations of clusters in the "transition" size regime (n = 9-12) have been nonexistent. In this Letter we announce the first structural characterization of C<sub>9</sub>, the largest cluster predicted to have a linear ground state. We have used infrared diode laser absorption spectroscopy of a supersonic carbon cluster jet to measure 51 lines of the ν<sub>6</sub> (σ<sub>u</sub>) antisymmetric stretch fundamental transition within the linear <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground electronic state of C<sub>9</sub>. The measured ground state rotational constant [429.30(50) MHz] indicates an effective C-C bond length of 1.278 68(75) Å, in good agreement with *ab initio* theory and consistent with cumulenic bonding in this cluster. In addition, the molecule is found to have unusually large ground-state and upper-state distortion constants, and several discrete perturbations are observed in the upper state.

The diode laser spectrometer used in these experiments was identical to that described previously.<sup>16,17</sup> Absolute frequency calibrations were performed by simultaneously recording a reference gas (OCS) spectrum while the carbon cluster absorption spectrum was monitored. Relative frequency calibrations were made by recording the fringe spectrum of an temperature-stabilized air-spaced germanium etalon immediately following the completion of each 0.4 cm<sup>-1</sup> scan.

The difficulties involved with scanning diode lasers over large frequency ranges are well established. Our spectral search was largely guided by the calculations of Martin, Francois, and Gijbels,<sup>18</sup> who pointed out that a matrix absorption observed by Thompson and co-workers<sup>19</sup> at 1997 cm<sup>-1</sup> was very likely due to the ν<sub>6</sub> fundamental (second highest frequency antisymmetric stretch) of C<sub>9</sub>. Based on these results, the region from 1995-2023 cm<sup>-1</sup> was searched. Fifty-one rotational lines attributable to a single vibrational transition of a linear molecule having a center of symmetry and a <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground electronic state were recorded in the wavelength region 2013.0-2017.0 cm<sup>-1</sup>. A typical scan is presented in Fig. 1, and the observed absorption frequencies are presented in Table I. This band was assigned to C<sub>9</sub> based on the following criteria: (1) the chemistry of this absorber with respect to added impurities (H<sub>2</sub>, O<sub>2</sub>) in the argon carrier gas is similar to that observed previously for C<sub>3</sub>, C<sub>5</sub>, and C<sub>7</sub>; (2) the measured rotational constant is with-

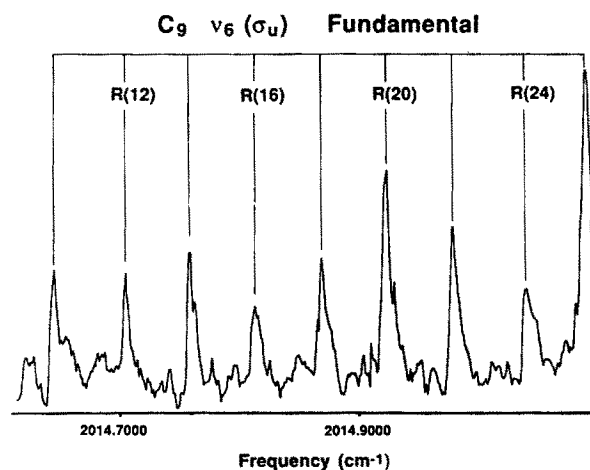


FIG 1. Experimental data showing nine rovibrational transitions assigned to the ν<sub>6</sub> antisymmetric stretch fundamental of C<sub>9</sub>. C<sub>9</sub> is generated by 248 nm laser ablation of a graphite target in the throat of a gas-dynamically focused pulsed planar argon jet. This 0.4 cm<sup>-1</sup> region was scanned in steps of approximately 20 MHz. At each step the experiment was cycled for 60 shots. The data were averaged with a 300 shot time constant, which improves the signal-to-noise ratio but distorts and broadens the line-shapes. The frequency scale is not exactly linear.

TABLE I. Measured frequencies assigned to the  $\nu_6$  ( $\sigma_u$ ) antisymmetric stretch fundamental of  $C_9$ . The standard deviation of the fit was  $0.0035 \text{ cm}^{-1}$ .

$J$	$R(J)$	obs-calc ( $\times 10^{-3}$ )	$P(J)$	obs-calc ( $\times 10^{-3}$ )
2	2014.4271	3.3		
4	2014.4838	3.3		
6	2014.5376	0.7	2014.1687	3.2
8	2014.5872	-5.9	2014.1077	0.3
10	2014.6445	-4.5	2014.0418	-7.3
12	2014.7063	1.6	2013.9845	-6.0
14	2014.7600	-0.1	2013.9322	0.5
16	2014.8157	0.4	2013.8703	-2.4
18	2014.8720	1.8	2013.8160	2.4
20	2014.9273	-2.4	2013.7569	2.2
22	2014.9790	-0.4	2013.6979	3.3
24	2015.0314	-2.3	2013.6353	0.4
26	2015.0825	-5.2	2013.5728	-2.2
28	2015.1379	-3.7	2013.5123	-2.7
30			2013.4497	-5.1
32	2015.2484	-0.4	2013.3974	2.8
34	2015.3013	-0.9		
36			2013.2710	-2.8
38	2015.4121	3.9	2013.2188	5.5
40	2015.4649	3.9	2013.1553	2.5
42	2015.5128	-0.8	2013.0976	5.5
44	2015.5618	-4.2		
46	2015.6176	-0.7		
48	2015.6710	0.6		
50	2015.7166	-5.6		
52	2015.7676	-6.3		
54	2015.8220	-3.3		
56	2015.8779	1.4		
58	2015.9248	-2.5		
60	2015.9790	1.1		
68	2015.1796	4.0		
70	2016.2235	-0.1		
74	2016.3159	-1.6		
76	2016.3695	3.8		
80	2016.4540	-1.3		

in 1.4% of the *ab initio* prediction; and (3) the measured band origin is in good agreement with the *ab initio* band origin prediction.

The measured band exhibits at least three discrete perturbations to the upper state. The number of unperturbed lines was insufficient for obtaining reliable upper-state constants from  $R(J)$ - $P(J)$  combination differences. Thus, the perturbations themselves could not be reliably analyzed. Ground state constants were extracted from a fit to the combination differences  $R(J)$ - $P(J+2)$ . This fit had a standard deviation of  $0.0014 \text{ cm}^{-1}$ , more representative of the characteristics of our apparatus than the fit presented in Table I. In the latter case the ground-state parameters were held fixed while the  $\nu_6$  band origin and upper-state parameters were determined. The resulting molecular parameters are presented in Table II.

The three observed perturbations come from dark state crossings of the upper state near  $J' = 7, 23$ , and 45. The first perturbing state splits the transitions from  $J'' = 2-10$  into doublets. Since the perturbation is localized to the upper state,  $R$ -branch and  $P$ -branch lines with the same upper-state rotational quantum number are split identically. These splittings were critical for making absolute  $J$  assignments

TABLE II.  $C_9$  molecular parameters derived from least squares analysis of the  $\nu_6$  ( $\sigma_u$ ) stretching fundamental frequencies. Quoted uncertainties are  $1\sigma$ .

Quantity	Value	<i>Ab initio</i> theory
$\nu_6$ ( $\text{cm}^{-1}$ )	2014.3383(10)	2084 (Ref. 6) 2042 (Ref. 18) 1817 (Ref. 20) <sup>a</sup> 435 (Ref. 6)
$B''$ (MHz)	429.30(48)	
$D''$ (kHz)	0.42(20)	
$r_{\text{eff}}^b$	1.27868(75) Å	1.269, 1.261 1.283, 1.269 Å <sup>c</sup>
$B'$ (MHz)	428.31 (45)	
$D'$ (kHz)	0.33(15)	
$H'$ (Hz)	-1.11(29)	

<sup>a</sup> Value scaled by 0.9.

<sup>b</sup> Assumes all C-C bonds are of identical length.

<sup>c</sup> Calculated values of C-C bond distances from innermost (left) to outermost. From Ref. 6.

since  $R(0)$  and  $P(2)$  were not observed. The other two crossings manifest themselves as perturbations to the absorption line strengths, and as systematic deviations of the observed line positions from calculated values. The high degree of perturbation in the vibrational spectrum of  $C_9$  is not really surprising, even at excitation energies as low as  $2000 \text{ cm}^{-1}$ .  $C_9$  is predicted to have four degenerate bends at or below  $250 \text{ cm}^{-1}$ , and 16 of its 22 normal modes lie below  $1000 \text{ cm}^{-1}$ .<sup>6,18,20</sup> A simple, semiclassical approximation to the density of vibrational states<sup>21</sup> indicates that, at  $2000 \text{ cm}^{-1}$  the vibrational state density in  $C_9$  is already  $10^8/\text{cm}^{-1}$ !

The upper-state quartic and sextic centrifugal distortion constants are quite large, but due to the perturbed nature of the upper state, it is difficult to draw many conclusions based on these parameters. The ground state quartic distortion constant is also quite large, however. The normalized constant ( $D''/B''$ ) is 15 times that of  $C_5$  and only 3 times smaller than that of  $C_3$ . The available evidence indicates that  $C_5$  is a rigid cluster with harmonic bending potentials.<sup>15</sup>  $C_3$ , on the other hand, is quite nonrigid and its vibrational manifold is characterized by strong stretch-bend and Coriolis interactions.<sup>9-12</sup> The  $C_9$  cluster has been calculated to have low-lying  $\pi_g$  bending vibrations at 114, 252, and  $658 \text{ cm}^{-1}$ .<sup>6</sup> The large ground-state distortion constant observed for  $C_9$  may indicate strong  $\Sigma$ - $\Pi$  Coriolis interactions between the  $^1\Sigma_g^+$  ground state and one or more of these bends. Similar evidence of such perturbations has recently been obtained for the  $C_7$  cluster,<sup>16,17</sup> which also has several predicted low-frequency bending vibrations.<sup>6</sup>

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- <sup>1</sup>W. Weltner, Jr., and R. J. Van Zee, *Chem. Rev.* **89**, 1713 (1989).  
<sup>2</sup>K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).  
<sup>3</sup>R. Hoffman, *Tetrahedron* **22**, 521 (1966).  
<sup>4</sup>R. A. Whiteside, K. Raghavachari, D. J. Defrees, J. A. Pople, and P. v. R. Schleyer, *Chem. Phys. Lett.* **78**, 538 (1981).  
<sup>5</sup>K. Raghavachari, R. A. Whiteside, and J. A. Pople, *J. Chem. Phys.* **89**, 6623 (1986).  
<sup>6</sup>K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).  
<sup>7</sup>D. E. Bernholdt, D. H. Magers, and R. J. Bartlett, *J. Chem. Phys.* **89**, 3612 (1988).  
<sup>8</sup>S. H. Yang, C. L. Pettiette, J. Conceicao, O. Chesnovsky, and R. E. Smalley, *Chem. Phys. Lett.* **139**, 233 (1987).  
<sup>9</sup>K. Kawaguchi, K. Matsumura, H. Kanamori, and E. Hirota, *J. Chem. Phys.* **91**, 1953 (1989).  
<sup>10</sup>(a) R. S. Smith, M. Anselment, L. F. DiMauro, J. M. Frye, and T. J. Sears, *J. Chem. Phys.* **89**, 2591 (1988); (b) F. J. Northrup and T. J. Sears, *Chem. Phys. Lett.* **159**, 421 (1989); (c) F. J. Northrup and T. J. Sears, *J. Opt. Soc. Am.* **B7**, 1924 (1990).  
<sup>11</sup>(a) E. A. Rohlfing, *J. Chem. Phys.* **89**, 6103 (1988); (b) E. A. Rohlfing and J. E. Goldsmith, *ibid.* **90**, 6804 (1989); (c) E. A. Rohlfing and J. E. Goldsmith, *J. Opt. Soc. Am.* **B7**, 1915 (1990).  
<sup>12</sup>C. A. Schmuttenmaer *et al.*, *Science* **249**, 897 (1990).  
<sup>13</sup>J. R. Heath, A. L. Cooksy, M. H. W. Gruebele, C. A. Schmuttenmaer, and R. J. Saykally, *Science* **244**, 565 (1989).  
<sup>14</sup>P. F. Bernath, K. H. Hinkle, and J. J. Keady, *Science* **244**, 562 (1989).  
<sup>15</sup>N. Moazzen-Ahmadi, A. R. W. McKellar, and T. Amano, *J. Chem. Phys.* **91**, 2140 (1989).  
<sup>16</sup>J. R. Heath, R. A. Sheeks, A. L. Cooksy, and R. J. Saykally, *Science* **249**, 895 (1990).  
<sup>17</sup>J. R. Heath and R. J. Saykally, *J. Chem. Phys.* (in press).  
<sup>18</sup>J. M. L. Martin, J. P. Francois, and R. Gijbels, *J. Chem. Phys.* (in press).  
<sup>19</sup>K. R. Thompson, R. L. DeKock, and W. Weltner, Jr., *J. Am. Chem. Soc.* **93**, 4688 (1971).  
<sup>20</sup>D. W. Ewing (private communication).  
<sup>21</sup>R. A. Marcus and O. K. Rice, *J. Phys. and Colloid Chem.* **55**, 894 (1951).