

# Raman spectra and calculated vibrational frequencies of size-selected C<sub>16</sub>, C<sub>18</sub>, and C<sub>20</sub> clusters

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(Received 31 August 1998; accepted 1 October 1998)

The surface plasmon polariton-enhanced Raman spectra of size-selected C<sub>16</sub>, C<sub>18</sub>, and C<sub>20</sub> clusters isolated in nitrogen matrices are presented along with the calculated vibrational frequencies for the ring and linear chain isomers. The Raman spectra, recorded at a range of excitation wavelengths from 457.9 to 670 nm, show strong resonance enhancement for the three clusters. The calculated vibrational frequencies for ring and linear chain isomers and the cage and bowl structures for C<sub>20</sub> are compared to the experimental frequencies. Systematic shifts in the series of peaks in the 200 cm<sup>-1</sup> region for C<sub>16</sub>, C<sub>18</sub>, and C<sub>20</sub> suggest that the observed isomers have the same geometry, thereby ruling out the bowl and cage isomers for C<sub>20</sub>. The measured spectra appear to be most consistent with the linear chain isomer. This high-energy isomer may be produced during neutralization of the deposited cluster ions. © 1998 American Institute of Physics. [S0021-9606(98)02346-0]

## I. INTRODUCTION

Determining the structures of carbon clusters has recently been the subject of much experimental<sup>1-10</sup> and theoretical<sup>11-15</sup> work, mainly due to the discovery of the fullerene structure of C<sub>60</sub>. Of particular interest is the C<sub>20</sub> cluster, which is possibly the smallest fullerene,<sup>16,17</sup> and has been proposed as a precursor to formation of fullerene C<sub>60</sub>.<sup>18,19</sup> C<sub>20</sub> has several isomers with approximately the same energies,<sup>20-26</sup> including the monocyclic ring, the corannulene-like bowl, and the fullerene cage.

Experimental measurements on neutral carbon clusters are scarce, but much information is available for cluster ions. Ion mobility<sup>2,4,27</sup> measurements suggest that the monocyclic ring is the dominant isomer for C<sub>20</sub><sup>+</sup>, while the bicyclic ring, monocyclic ring, linear chain, and tadpole (ring and chain)<sup>28</sup> isomers have been observed for C<sub>20</sub><sup>-</sup>. Electronic absorption spectroscopy<sup>5,29</sup> of matrix-isolated C<sub>n</sub><sup>-</sup> anions produce evidence of linear chain structures of C<sub>4</sub><sup>-</sup>-C<sub>20</sub><sup>-</sup> and the start of cyclic structures for C<sub>10</sub> and C<sub>12</sub> neutral species. Photoelectron spectroscopy<sup>9,10</sup> measurements are consistent with the monocyclic ring structure for C<sub>16</sub><sup>-</sup>, C<sub>18</sub><sup>-</sup>, and C<sub>20</sub><sup>-</sup>. Infrared vibrational spectroscopy<sup>3,8,30,31</sup> and surface-enhanced Raman spectroscopy<sup>6</sup> results are available for neutral clusters, but experiments have not been performed for molecules larger than C<sub>13</sub>.

In this communication, we present the first vibrational spectra of medium-sized, mass-selected carbon clusters. The surface plasmon polariton (SPP) Raman spectra of C<sub>16</sub>, C<sub>18</sub>, and C<sub>20</sub> neutral atomic clusters isolated in nitrogen matrices are presented as well as the calculated vibrational frequen-

cies for their isomers. The observed spectra appear to be most consistent with a linear chain structure. The linear chains are likely formed upon neutralization of the deposited cluster ions to form neutral clusters.

## II. EXPERIMENT

The experimental apparatus has been described previously.<sup>32-34</sup> Carbon cluster cations are created via laser ablation (308 nm, 100 Hz) of a graphite rod in a continuous flow of He buffer gas (99.9999%) at 11-15 Torr. A 1 kV electron beam is injected into the buffer gas flow to enhance the production of cations. The cluster ions are focused into a low-energy beam, injected into a quadrupole mass spectrometer for size selection, and passed through a double-bend quadrupole deflector into the ultrahigh vacuum (UHV) chamber. The cluster source typically produces an ion-beam current of 25 pA for C<sub>16</sub><sup>+</sup>, C<sub>18</sub><sup>+</sup>, and C<sub>20</sub><sup>+</sup>. Following the deposition of a 50 Å N<sub>2</sub> buffer layer, carbon cluster ions are codeposited with N<sub>2</sub> onto a silver-coated (550 Å thickness) hemicylindrical sapphire prism cooled to 10 K. The cluster ions were deposited at 5-25 eV. The measured spectra were independent of the deposition energy, indicating that fragmentation did not occur during deposition. The ions in the matrix are neutralized by low-energy electrons from a hot filament during deposition. The sample contains approximately 5 × 10<sup>11</sup> clusters in an 1100 Å thick matrix. After cluster deposition, a 1-2 μm thick capping layer of N<sub>2</sub> is added to provide the correct conditions for the surface plasmon enhancement and to protect the cluster sample from contamination.

The surface plasmon polariton-enhanced Raman spectroscopy configuration allows for an enhancement of the Raman signal by approximately a factor of 100.<sup>35-38</sup> The 458, 488, and 515 nm lines of an Ar<sup>+</sup> laser (Spectra-Physics

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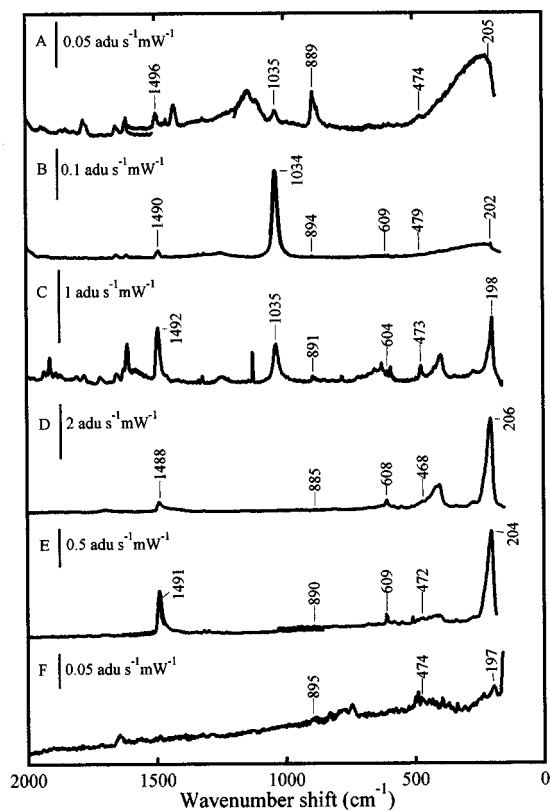


FIG. 1. Raman spectra of matrix-isolated  $C_{20}$  clusters over the energy region 100–2000  $\text{cm}^{-1}$  for excitation wavelengths of 457.9 (A), 488.0 (B), 514.5 (C), 635 (D), 647 (E), and 670 (F) nm.

model 164) and the 635, 647, and 670 nm lines of an  $\text{Ar}^+$  laser (Spectra-Physics model 2060) pumped dye laser (Coherent model 590) using DCM are used for excitation. Raman scattered light is focused into a triple grating spectrometer (SPEX Triplemate) with either 600 or 1800  $\text{g}/\text{mm}$  gratings and is imaged onto a charge-coupled device (CCD) detector (Princeton Instruments model LN/ccd-512). Data acquisition times range from 60 to 300 s at laser powers between 10 and 200 mW.

### III. RESULTS

#### A. Experiment

Figure 1 shows the Raman signal for  $C_{20}$  in analog-to-digital converter units ( $\text{ADU s}^{-1} \text{mW}^{-1}$ ) at excitation wavelengths 457.9 (A), 488.0 (B), 514.5 (C), 635 (D), 647 (E), and 670 nm (F) as a function of energy shift ( $\text{cm}^{-1}$ ). The spectra show strong resonance enhancement as evidenced by the drastic changes in intensity of the feature at 1035  $\text{cm}^{-1}$  as the incident wavelength changes.

Figure 2 shows the Raman spectra for  $C_{20}$  at excitation wavelengths 457.9 (A), 488.0 (B), 514.5 (C), 635 (D), 647 (E), and 670 nm (F) in the 2000–4000  $\text{cm}^{-1}$  energy region. Resonance Raman scattering is again indicated by the large peaks present above 2500  $\text{cm}^{-1}$ , where fundamental frequencies are not predicted. The conditions for resonance Raman spectroscopy (RRS) produce large signal enhancements for overtones and combination bands depending on the excitation frequency.<sup>39–42</sup> The lack of features in this region at

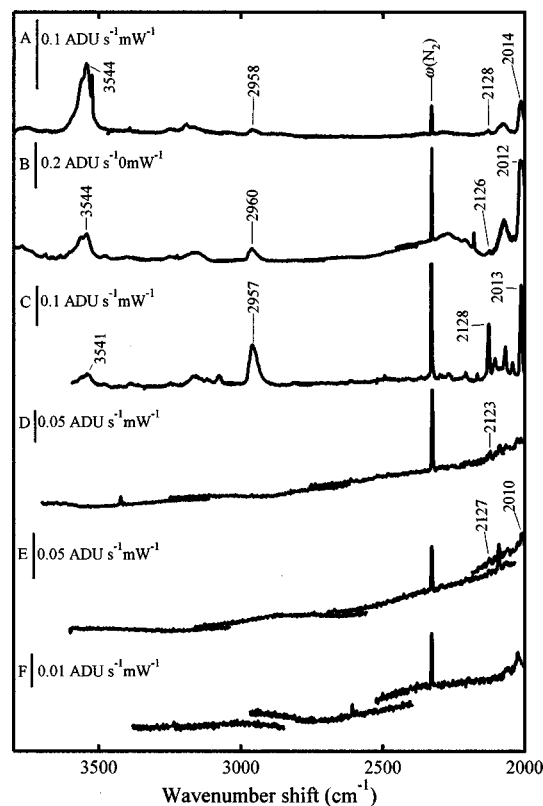


FIG. 2. Raman spectra of matrix-isolated  $C_{20}$  clusters over the energy region 2000–4000  $\text{cm}^{-1}$  for excitation wavelengths of 457.9 (A), 488.0 (B), 514.5 (C), 635 (D), 647 (E), and 670 (F) nm.

excitation wavelengths of 635, 647, and 670 nm indicates that the resonance enhancement is less strong for these longer wavelengths.

The Raman spectra (not shown here) for  $C_{18}$  excited at 457.9, 488.0, 514.5, 635, and 647 nm also showed resonance enhancement. Further, strong fluorescence from  $C_{18}$  was observed between 620 and 860 nm at excitation wavelengths of 457.9, 488.0, and 514.5 nm. Resonance Raman spectra were also observed for  $C_{16}$  clusters excited at 457.9, 488.0, 514.5, and 635 nm, though fluorescence was not detected for  $C_{16}$  or  $C_{20}$ .

Figure 3 shows the Raman spectra at an excitation wavelength of 514.5 nm in the 200–600  $\text{cm}^{-1}$  region for  $C_{16}$  (A),  $C_{18}$  (B), and  $C_{20}$  (C). The systematic shifts in frequencies for the series of peaks at 250, 223, and 198  $\text{cm}^{-1}$  and their first overtones at 500, 447, and 397  $\text{cm}^{-1}$  for  $C_{16}$ ,  $C_{18}$ , and  $C_{20}$ , respectively, indicate that the three clusters share similar structures. This progression suggests that the spectra do not result from a bowl or a cage isomer since analogous isomers are not structurally feasible for  $C_{16}$  and  $C_{18}$ . Instead, the spectra are probably due to ring or chain isomers.

#### B. Theory

Table I presents the experimental vibrational frequencies and the predicted Raman-active vibrational frequencies for the ring and linear chain isomers of  $C_{16}$ ,  $C_{18}$ , and  $C_{20}$  from *ab initio* calculations. The vibrational properties were calculated using density functional theory (DFT). All calculations were performed using GAUSSIAN 94W (Revision E.1),<sup>43</sup> using

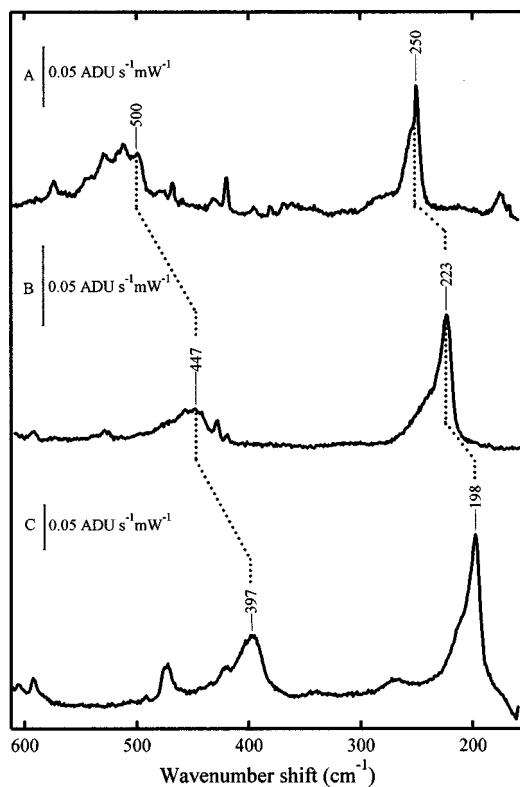


FIG. 3. Raman spectra of matrix-isolated  $C_{16}$  (A),  $C_{18}$  (B), and  $C_{20}$  (C) clusters over the energy region  $100\text{--}650\text{ cm}^{-1}$  excited at  $514.5\text{ nm}$ .

the B3LYP (Becke three-parameter–Lee–Yang–Parr) functional<sup>44</sup> and the cc-pVDZ [correlation consistent polarized valence double zeta, a  $[3s2p1d]$  contraction of the  $(9s4p1d)$  primitive set] basis set.<sup>45</sup> The B3LYP/cc-pVDZ

harmonic frequencies were uniformly scaled down by 2% to account for the systematic overestimation that results from the neglect of anharmonic effects.

Of the ring and chain structures considered, the lowest-energy isomer of  $C_{16}$  is a  $C_{8h}$  polyacetylene ring, with a  $D_{8h}$  cumulene ring lying  $1.0\text{ eV}$  higher in energy. In addition,  $D_{\infty h}$  cumulene and polyacetylene chains are found at  $2.1$  and  $4.2\text{ eV}$  above the  $C_{8h}$  ring structure, respectively. The lowest-energy ring or chain  $C_{18}$  cluster is a  $D_{9h}$  cumulene ring, with a  $D_{\infty h}$  cumulene chain lying  $3.5\text{ eV}$  higher in energy. The lowest-energy ring or chain isomer of  $C_{20}$  is a  $C_{10h}$  polyacetylene ring, with a  $D_{10h}$  cumulene ring lying  $1.2\text{ eV}$  higher in energy.  $D_{\infty h}$  cumulene and polyacetylene chains are found at  $2.9$  and  $4.9\text{ eV}$  above the  $C_{10h}$  structure, respectively. The alternating energies of the cumulene and polyacetylene ring geometries with cluster size are consistent with trends calculated in the literature.<sup>13,14</sup>

#### IV. DISCUSSION

The experimental frequencies presented in Table I were determined by matching spectral peaks present at nearly all of the excitation laser wavelengths. Definitive determination of the fundamental frequencies for  $C_{20}$  from the spectra is complicated by the strong resonance enhancement that can produce peaks for overtones and combination bands which are more intense than some fundamentals. While excitation with higher input laser wavelength can clarify these ambiguities by reducing the resonance contribution, a corresponding decrease in signal-to-noise ratio is unavoidable.

The experimental frequencies are compared in Table I to the calculated frequencies for the ring and linear chain iso-

TABLE I. Vibrational parameters for  $C_{16}$ ,  $C_{18}$ , and  $C_{20}$ .

$C_{16}^a$	$C_{16}(C_{8h})^b$		$C_{16}(D_{\infty h})^{b,c}$		$C_{18}^a$	$C_{18}(D_{9h})^b$		$C_{18}(D_{\infty h})^{b,c}$		$C_{20}^a$	$C_{20}(C_{10h})^b$		$C_{20}(D_{\infty h})^{b,c}$	
	70	$E_2$	45	$\Pi_g$		60	$E_2$	36	$\Pi_g$		48	$E_{2g}$	29	$\Pi_g$
			137	$\Pi_g$				111	$\Pi_g$				91	$\Pi_g$
			252	$\Pi_g$				211	$\Pi_g$				178	$\Pi_g$
249	260	A	258	$\Sigma_g$	223			230	$\Sigma_g$	200			207	$\Sigma_g$
			380	$\Pi_g$	430	320	$A_1$	311	$\Pi_g$				273	$\Pi_g$
468											363	$A_g$	377	$\Pi_g$
	488	$E_2$			457	465	$A_1$	452	$\Pi_g$		426	$A_g$		
	532	A	524	$\Pi_g$	478	480	$E_2$	465	$\Pi_g$	473	483	$E_{2g}$		
	538	$E_1$			650	653	$E_1$	674	$\Sigma_g$				493	$\Pi_g$
646								710	$\Pi_g$	605			603	$\Pi_g$
			674	$\Pi_g$				895	$\Pi_g$				609	$\Sigma_g$
			752	$\Sigma_g$		976	$E_2$				716	$E_{1g}$	744	$\Pi_g$
735			855	$\Pi_g$				1087	$\Sigma_g$	889		843	$E_{2g}$	
					1215								935	$\Pi_g$
	1012	$E_2$			1380					1035			988	$\Sigma_g$
			1205	$\Sigma_g$				1465	$\Sigma_g$				1340	$\Sigma_g$
1372								1747	$\Sigma_g$	1489				
			1616	$\Sigma_g$				1807	$\Sigma_g$				1661	$\Sigma_g$
			1814	$\Sigma_g$	1905								1682	$\Sigma_g$
1920			1929	$\Sigma_g$				2022	$\Sigma_g$				1912	$\Sigma_g$
	1986	A			2088					2014				
2096			2128	$\Sigma_g$		2158	$E_2$	2149	$\Sigma_g$		2076	$A_g$	2086	$\Sigma_g$
	2160	$E_2$	2175	$\Sigma_g$				2172	$\Sigma_g$	2128			2132	$\Sigma_g$
2200					2212						2195	$E_{2g}$	2185	$\Sigma_g$

<sup>a</sup>Experimental SPP-enhanced Raman frequencies in  $\text{cm}^{-1}$ .

<sup>b</sup>Calculated Raman-active frequencies in  $\text{cm}^{-1}$ .

<sup>c</sup>Cumulene chain isomer.

mers. The chain structures appear to give the closest matches to the experimental frequencies. The measured frequencies at 250, 223, and 198  $\text{cm}^{-1}$  and at 735, 650, and 605  $\text{cm}^{-1}$  match the first two totally symmetric fundamentals calculated for the chain isomers of  $\text{C}_{16}$ ,  $\text{C}_{18}$ , and  $\text{C}_{20}$ , respectively. The calculated lowest frequency  $A$  mode of the ring isomers increases along the series  $\text{C}_{16}$ ,  $\text{C}_{18}$ , and  $\text{C}_{20}$  in contrast to the experimental data, where a systematic decrease occurs (see Fig. 3).

One key to matching experiment and theory is the number of Raman-active fundamental vibrations. There are eight Raman-active fundamentals for the  $\text{C}_{20}$  cluster determined from the experiment and calculated for the polyacetylene ring isomer. Although the chain structure has 19 Raman-active fundamentals, the calculated intensities of the ten totally symmetric modes ( $\Sigma_g$ ) of the linear chain are as much as  $10^4$  times greater than the asymmetric modes ( $\Pi_g$ ), and the experiment may only detect the totally symmetric modes. The cage and bowl structures have 54 and 28 Raman-active vibrations, respectively, providing further evidence to rule out these structures as the carrier of the spectrum for  $\text{C}_{20}$ .

Although the existence of linear chains is indicated by the data, the ring is the dominant isomer for  $\text{C}_{16}^+$ ,  $\text{C}_{18}^+$ , and  $\text{C}_{20}^+$  clusters in the gas phase.<sup>2,4</sup> The deposited clusters must, therefore, convert from rings to chains upon neutralization. From charge-transfer brocketing experiments, the ionization potentials of  $\text{C}_{16}$ ,  $\text{C}_{18}$ , and  $\text{C}_{20}$  are approximately 8 eV,<sup>46</sup> and neutralization of the clusters could provide enough energy to break apart the rings to form chains. A further possibility is that both rings and chains exist in the sample, but that the resonance Raman effect is much stronger for the chain structures, thereby making the chain fundamentals the dominant features of the spectra. Note that the chain and ring isomers do not seem to account for all of the observed features. For example, the intense features at 1489  $\text{cm}^{-1}$  for  $\text{C}_{20}$  and 1373  $\text{cm}^{-1}$  for  $\text{C}_{16}$  are more than 350  $\text{cm}^{-1}$  from the nearest frequency predicted for the ring. For the chain the nearest frequency is closer, but still close to 150  $\text{cm}^{-1}$  away. This may indicate the presence of another isomer.

## ACKNOWLEDGMENT

This work was supported by a multidisciplinary university research initiative (MURI) grant (DAAG-55-97-0133) from the Army Research Office.

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