

Raman spectra and calculated vibrational frequencies of size-selected C₁₆, C₁₈, and C₂₀ clusters

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The surface plasmon polariton-enhanced Raman spectra of size-selected C₁₆, C₁₈, and C₂₀ 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 C₂₀ are compared to the experimental frequencies. Systematic shifts in the series of peaks in the 200 cm⁻¹ region for C₁₆, C₁₈, and C₂₀ suggest that the observed isomers have the same geometry, thereby ruling out the bowl and cage isomers for C₂₀. 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 experimental¹⁻¹⁰ and theoretical¹¹⁻¹⁵ work, mainly due to the discovery of the fullerene structure of C₆₀. Of particular interest is the C₂₀ cluster, which is possibly the smallest fullerene,^{16,17} and has been proposed as a precursor to formation of fullerene C₆₀.^{18,19} C₂₀ has several isomers with approximately the same energies,²⁰⁻²⁶ 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^{2,4,27} measurements suggest that the monocyclic ring is the dominant isomer for C₂₀⁺, while the bicyclic ring, monocyclic ring, linear chain, and tadpole (ring and chain)²⁸ isomers have been observed for C₂₀⁻. Electronic absorption spectroscopy^{5,29} of matrix-isolated C_n⁻ anions produce evidence of linear chain structures of C₄⁻-C₂₀⁻ and the start of cyclic structures for C₁₀ and C₁₂ neutral species. Photoelectron spectroscopy^{9,10} measurements are consistent with the monocyclic ring structure for C₁₆⁻, C₁₈⁻, and C₂₀⁻. Infrared vibrational spectroscopy^{3,8,30,31} and surface-enhanced Raman spectroscopy⁶ results are available for neutral clusters, but experiments have not been performed for molecules larger than C₁₃.

In this communication, we present the first vibrational spectra of medium-sized, mass-selected carbon clusters. The surface plasmon polariton (SPP) Raman spectra of C₁₆, C₁₈, and C₂₀ 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.³²⁻³⁴ 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 C₁₆⁺, C₁₈⁺, and C₂₀⁺. Following the deposition of a 50 Å N₂ buffer layer, carbon cluster ions are codeposited with N₂ 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 × 10¹¹ clusters in an 1100 Å thick matrix. After cluster deposition, a 1-2 μm thick capping layer of N₂ 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 100.³⁵⁻³⁸ The 458, 488, and 515 nm lines of an Ar⁺ laser (Spectra-Physics

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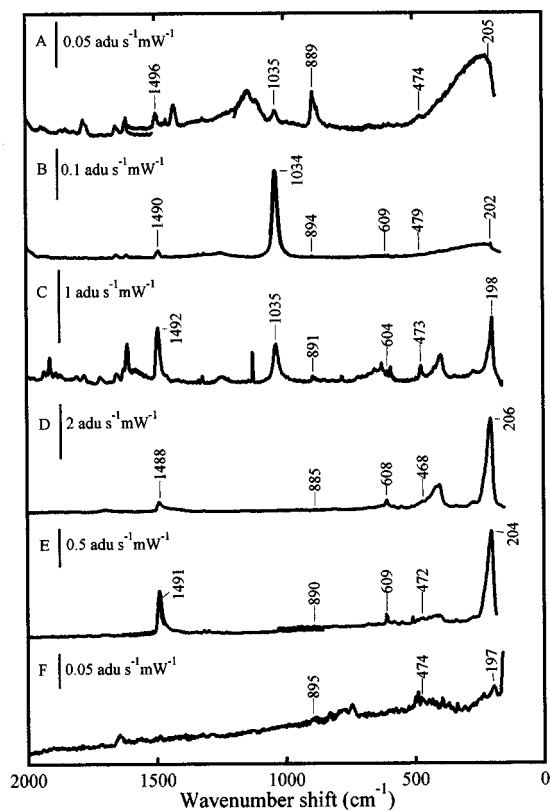


FIG. 1. Raman spectra of matrix-isolated C_{20} clusters over the energy region 100–2000 cm^{-1} for excitation wavelengths of 457.9 (A), 488.0 (B), 514.5 (C), 635 (D), 647 (E), and 670 (F) nm.

model 164) and the 635, 647, and 670 nm lines of an 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 g/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 (cm^{-1}). The spectra show strong resonance enhancement as evidenced by the drastic changes in intensity of the feature at 1035 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 cm^{-1} energy region. Resonance Raman scattering is again indicated by the large peaks present above 2500 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.^{39–42} The lack of features in this region at

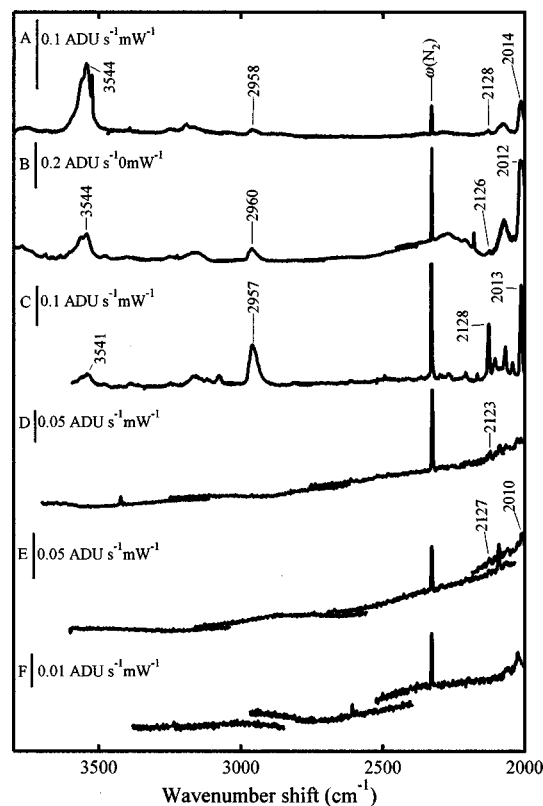


FIG. 2. Raman spectra of matrix-isolated C_{20} clusters over the energy region 2000–4000 cm^{-1} for excitation wavelengths of 457.9 (A), 488.0 (B), 514.5 (C), 635 (D), 647 (E), and 670 (F) nm.

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 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 cm^{-1} and their first overtones at 500, 447, and 397 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),⁴³ using

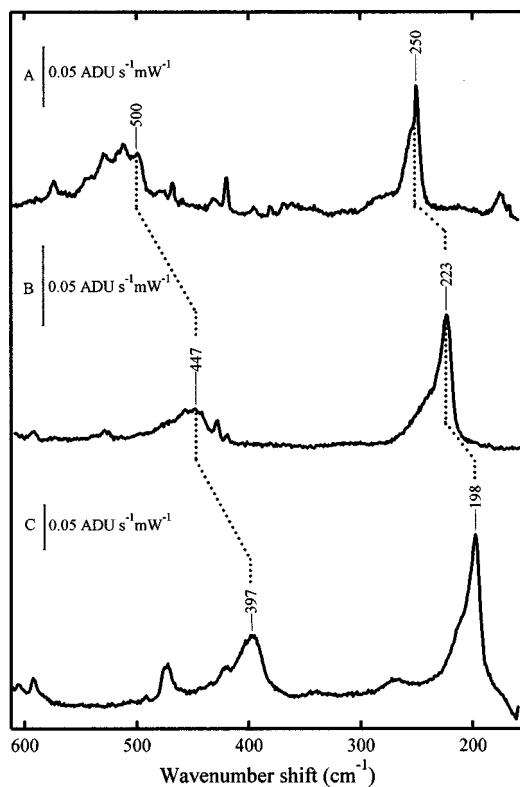


FIG. 3. Raman spectra of matrix-isolated C_{16} (A), C_{18} (B), and C_{20} (C) clusters over the energy region $100\text{--}650\text{ cm}^{-1}$ excited at 514.5 nm .

the B3LYP (Becke three-parameter–Lee–Yang–Parr) functional⁴⁴ and the cc-pVDZ [correlation consistent polarized valence double zeta, a $[3s2p1d]$ contraction of the $(9s4p1d)$ primitive set] basis set.⁴⁵ 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 eV higher in energy. In addition, $D_{\infty h}$ cumulene and polyacetylene chains are found at 2.1 and 4.2 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 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 eV higher in energy. $D_{\infty h}$ cumulene and polyacetylene chains are found at 2.9 and 4.9 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.^{13,14}

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

^aExperimental SPP-enhanced Raman frequencies in cm^{-1} .

^bCalculated Raman-active frequencies in cm^{-1} .

^cCumulene chain isomer.

mers. The chain structures appear to give the closest matches to the experimental frequencies. The measured frequencies at 250, 223, and 198 cm^{-1} and at 735, 650, and 605 cm^{-1} match the first two totally symmetric fundamentals calculated for the chain isomers of C_{16} , C_{18} , and C_{20} , respectively. The calculated lowest frequency A mode of the ring isomers increases along the series C_{16} , C_{18} , and 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 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 (Σ_g) of the linear chain are as much as 10^4 times greater than the asymmetric modes (Π_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 C_{20} .

Although the existence of linear chains is indicated by the data, the ring is the dominant isomer for C_{16}^+ , C_{18}^+ , and C_{20}^+ clusters in the gas phase.^{2,4} The deposited clusters must, therefore, convert from rings to chains upon neutralization. From charge-transfer brocketing experiments, the ionization potentials of C_{16} , C_{18} , and C_{20} are approximately 8 eV,⁴⁶ 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 cm^{-1} for C_{20} and 1373 cm^{-1} for C_{16} are more than 350 cm^{-1} from the nearest frequency predicted for the ring. For the chain the nearest frequency is closer, but still close to 150 cm^{-1} away. This may indicate the presence of another isomer.

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¹W. J. Weltner and R. J. Van Zee, *Chem. Rev.* **89**, 1713 (1989).

²G. von Helden, M.-T. Hsu, N. Gotts, and M. T. Bowers, *J. Phys. Chem.* **97**, 8182 (1993).

³S. L. Wang, C. M. L. Rittby, and W. R. M. Graham, *J. Chem. Phys.* **107**, 7025 (1997).

⁴K. B. Shelimov, J. M. Hunter, and M. F. Jarrold, *Int. J. Mass Spectrom. Ion Processes* **138**, 17 (1994).

⁵P. Freivogel, M. Grutter, D. Forney, and J. P. Maier, *J. Chem. Phys.* **107**, 4468 (1997).

⁶T. L. Haslett, S. Fedrigo, and M. Moskovits, *J. Chem. Phys.* **103**, 7815 (1995).

⁷H. J. Hwang, A. Van Orden, K. Tanaka, E. W. Kuo, J. R. Heath, and R. J. Saykally, *Mol. Phys.* **79**, 769 (1993).

⁸J. Szczepanski, S. Ekern, and M. Vala, *J. Phys. Chem. A* **101**, 1841 (1997).

⁹T. Wakabayashi, M. Kohno, T. Momose, T. Shida, K. Naemura, and Y. Tobe, *J. Chem. Phys.* **107**, 4783 (1997).

¹⁰S. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, *Chem. Phys. Lett.* **144**, 431 (1988).

¹¹J. Hutter, H. P. Lüthi, and F. Diederich, *J. Am. Chem. Soc.* **116**, 750 (1994).

¹²D. A. Plattner and K. N. Houk, *J. Am. Chem. Soc.* **117**, 4405 (1995).

¹³R. O. Jones and G. Seifert, *Phys. Rev. Lett.* **79**, 443 (1997).

¹⁴J. M. L. Martin, J. El-Yazal, and J.-P. Francois, *Chem. Phys. Lett.* **242**, 572 (1995).

¹⁵K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).

¹⁶B. N. Cyvin, E. Brendsdal, J. Brunvoll, and S. J. Cyvin, *J. Mol. Struct.* **352/353**, 481 (1995).

¹⁷V. Parasuk and J. Almlöf, *Chem. Phys. Lett.* **184**, 187 (1991).

¹⁸C. J. Barbec, E. B. Anderson, B. N. Davidson, S. A. Kajihara, Q.-M. Zhang, J. Bernholc, and D. Tomanek, *Phys. Rev. B* **46**, 7326 (1992).

¹⁹H. W. Kroto and K. McKay, *Nature (London)* **331**, 328 (1988).

²⁰P. R. Taylor, E. Bylaska, J. H. Weare, and R. Kawai, *Chem. Phys. Lett.* **235**, 558 (1995).

²¹J. M. L. Martin, J. El-Yazal, and J.-P. Francois, *Chem. Phys. Lett.* **248**, 345 (1996).

²²J. C. Grossman, L. Mitas, and K. Raghavachari, *Phys. Rev. Lett.* **75**, 3870 (1995).

²³Z. Wang, P. Day, and R. Pachter, *Chem. Phys. Lett.* **248**, 121 (1996).

²⁴G. Galli, F. Gygi, and J.-C. Golaz, *Phys. Rev. B* **57**, 1860 (1998).

²⁵K. Raghavachari, D. L. Strout, G. K. Odom, G. E. Scuseria, J. A. Pople, B. G. Johnson, and P. M. W. Gill, *Chem. Phys. Lett.* **214**, 357 (1993).

²⁶C. J. Barbec, E. B. Anderson, B. N. Davidson, S. A. Kajihara, Q.-M. Zhang, J. Bernholc, and D. Tomnek, *Phys. Rev. B* **46**, 7326 (1992).

²⁷N. G. Gotts, G. von Helden, and M. T. Bowers, *Int. J. Mass Spectrom. Ion Processes* **149/150**, 217 (1995).

²⁸P. Dugourd, R. R. Hudgins, J. M. Tenenbaum, and M. F. Jarrold, *Phys. Rev. Lett.* **80**, 4197 (1998).

²⁹D. Forney, P. Freivogel, M. Grutter, and J. P. Maier, *J. Chem. Phys.* **104**, 4954 (1996).

³⁰S. L. Wang, C. M. L. Rittby, and W. R. M. Graham, *J. Chem. Phys.* **107**, 6032 (1997).

³¹T. F. Giesen, A. V. Orden, H. J. Hwang, R. S. Fellers, R. A. Provençal, and R. J. Saykally, *Science* **265**, 756 (1994).

³²E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, *Nature (London)* **366**, 42 (1993).

³³E. C. Honea, J. S. Kraus, J. E. Bower, and M. F. Jarrold, *Z. Phys. D* **26**, 141 (1993).

³⁴J. E. Bower and M. F. Jarrold, *J. Chem. Phys.* **97**, 8312 (1992).

³⁵Y. J. Chen, W. P. Chen, and E. Burstein, *Phys. Rev. Lett.* **36**, 1207 (1976).

³⁶K. Sakoda, K. Ohtaka, and E. Hanamura, *Solid State Commun.* **41**, 393 (1982).

³⁷K. Kurosawa, R. M. Pierce, S. Ushioda, and J. C. Hemminger, *Phys. Rev. B* **33**, 789 (1986).

³⁸H. Knobloch, H. Brunner, A. Leitner, F. Aussenegg, and W. Knoll, *J. Chem. Phys.* **98**, 10093 (1993).

³⁹D. L. Rousseau, J. M. Friedman, and P. F. Williams, *Topics in Current Physics* (Springer, New York, 1979).

⁴⁰K.-S. K. Shin and J. I. Zink, *Inorg. Chem.* **28**, 4358 (1989).

⁴¹R. J. H. Clark and T. J. Dines, *Angew. Chem. Int. Ed. Engl.* **25**, 131 (1986).

⁴²A. B. Myers, *Laser Techniques in Chemistry* (Wiley, New York, 1995).

⁴³M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

⁴⁴A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

⁴⁵T. H. J. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).

⁴⁶S. B. H. Bach and J. R. Eyler, *J. Chem. Phys.* **92**, 358 (1990).