

Spectroscopic Study of a Representative Polar Cap of Buckminsterfullerene: Cyclopentacorannulene

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The spectroscopic properties of corannulene and cyclopentacorannulene are examined by use of absorption and steady-state fluorescence measurements. A red shift in the emission maxima of cyclopentacorannulene is noted with respect to the emission maxima in the corannulene spectrum. Similar differences in the absorption spectra of both molecules are also observed. Reasons for the dissimilarities in the absorption and emission spectra of these molecules are discussed. The fluorescence quantum yields and lifetimes of the molecules measured in organic solvents are reported. The fluorescence quantum yield and lifetime of cyclopentacorannulene are lower than those of corannulene. This difference is attributed to the highly strained and nonplanar structure of cyclopentacorannulene. The effectiveness of nitromethane as a quencher of corannulene and cyclopentacorannulene fluorescence is examined. In contrast to previously reported results, the fluorescence of these molecules is quenched by nitromethane. Fluorescence quenching of the molecules has been attributed to complex formation in the ground state, i.e., static quenching.

KEY WORDS: Fluorescence; cyclopentacorannulene; corannulene; spectroscopic properties.

INTRODUCTION

In spite of numerous reports on the spectroscopic characterization of large polycyclic aromatic hydrocarbons (PAHs),⁽¹⁻¹⁴⁾ only a few studies report on the photophysical properties of curved, nonpolar PAHs such as the corannulenes (COR).⁽¹⁵⁾ The inspiration for investigating the COR in the present work arose from this lack of data as well as increased interests in fullerenes. Fullerenes or buckyballs, are composed of as many as 60 to 70 carbon atoms and have intrigued scientists, largely because of their novel cage geometry, high stability, and

interesting reactivities.⁽¹⁶⁻¹⁹⁾ Therefore, the fluorescence and phosphorescence spectra and excited state properties of fullerenes have been studied extensively.⁽²⁰⁾

Corannulene (COR) and cyclopentacorannulene (CCOR) can be classified as curved, nonalternant bowl-shaped PAHs that are structurally represented on the surface of one side of buckminsterfullerene. The shaded area in the buckminsterfullerene structure (Fig. 1) depicts the corannulenes examined in this paper. The curvature of these molecules is the result of molecular distortion or strain due mainly to the presence of a central five-membered ring surrounded by five fused six-membered rings. The parent compound COR (1) was first synthesized in the mid 1960s⁽²¹⁾ and is a prime example of a nonplanar molecule possessing considerable aromatic character.⁽²²⁾ Despite their significant curvature, however, COR undergoes rapid bowl-to-bowl inversion in solution, during which the molecule passes through

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an "intermediate" planar, conformation.^(23,24) In fact, some researchers suggest that COR can invert as many as 200,000 times per s at room temperature.⁽²⁵⁾ The inversion process can be inhibited on the NMR time scale by incorporation of another fused five-membered ring to form CCOR (2).

Cyclopentacorannulene is a derivative of corannulene that was first synthesized within the last few years and is composed of two additional carbon atoms to form a cyclopentene ring fused to two of the outer six-membered rings.⁽²⁶⁾ These additional carbons effectively extend the depth and rigidity of the bowl and reduce its ability to invert in solution. The additional carbons also extend molecular conjugation, introduce asymmetry, and add geometrical tension to the corannulene framework. The incorporation of an ethylene bridge into PAH structures can also change relative energies of the electronic excited states. For example, the energy gap between the S_1 and the S_2 states increases from 1400 cm^{-1} for pyrene to 7000 cm^{-1} for cyclopenta[*cd*]pyrene.⁽²⁷⁾ This large energy gap has been reported to influence the photophysical processes of these molecules. These include unusual phenomena such as dual fluorescence and intersystem crossing from the upper excited states.⁽²⁷⁻²⁹⁾ Hence, fluorescence measurements may prove to be useful as a comparison tool for examining the spectroscopic behavior of COR and CCOR.

In this work, the absorption and fluorescence properties of corannulene and cyclopentacorannulene in organic solvents are characterized and compared. The influence of the fluorescence quencher, nitromethane, on the fluorescence intensity of the corannulenes is also examined.

EXPERIMENTAL

Materials

All solvents were HPLC, AR, or spectroquality grade and were purchased from either Mallinckrodt or EM Science. Nitromethane (97%) and 9,10-diphenylanthracene (98%) were purchased from Aldrich Chemicals (Milwaukee, WI). Corannulene and cyclopentacorannulene were synthesized in the laboratory of one of us (PWR) and were recrystallized once from ethanol. The synthetic procedures for the corannulenes are reported elsewhere.⁽²⁶⁾

The purity of COR and CCOR was analyzed by use of GC/MS. It was found that corannulene was >99% pure. However, trace amounts of COR (5-10%) were found to be present in CCOR sample as an impurity.

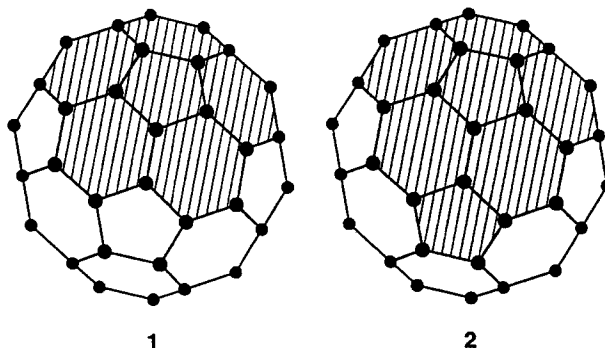


Fig. 1. Structures (shaded area) of corannulene (1) and cyclopentacorannulene (2).

Therefore, the CCOR was purified by use of reversed-phase HPLC. The liquid chromatographic system consisted of a Bio-Rad Model 2700 solvent delivery system equipped with an automatic sampling system (20-ml sample loop) and a Bio-Rad Bio-Dimension UV/Vis monitor set at 254 nm. A Zorbax C8 column (4.6 mm \times 15 cm, Dupont Chromatography) and an 80% acetonitrile/water mobile phase at a flow rate of 1.0 ml/min were used. The chromatogram of CCOR consisted of a large peak with a retention time of 6 min and a smaller peak at 5 min. These peaks were assigned to CCOR and COR, respectively. The COR peak was identified by running a pure COR sample. Other small impurity peaks appeared in the chromatogram but were well separated from the major peak. Fractions (0.5 ml) were collected by use of a Bio-Rad fraction collector. The solvent was then evaporated to obtain a solid sample.

Method

Solution Preparation A $5.0 \times 10^{-4}\text{ M}$ stock solution of COR in cyclohexane was prepared. A small aliquot of the stock solution was pipetted in 10-ml vials, and the cyclohexane was evaporated to dryness by use of extradry nitrogen. The contents of the vial were then diluted with appropriate volume of solvent to obtain a $1.0 \times 10^{-6}\text{ M}$ solution of the corannulene. The absorption and fluorescence spectra of CCOR were measured by using the dilute solution obtained directly from the HPLC column. The solvent was evaporated and redissolved in appropriate solvent. The solutions containing quencher were prepared using purified samples of COR and CCOR. For quenching studies of CCOR, the effluent collected from the column was used as a stock solution. The concentration range of quencher was 0.0 to 0.2 M.

Measurement of Fluorescence Quantum Yield and Lifetime. Fluorescence quantum yields were measured

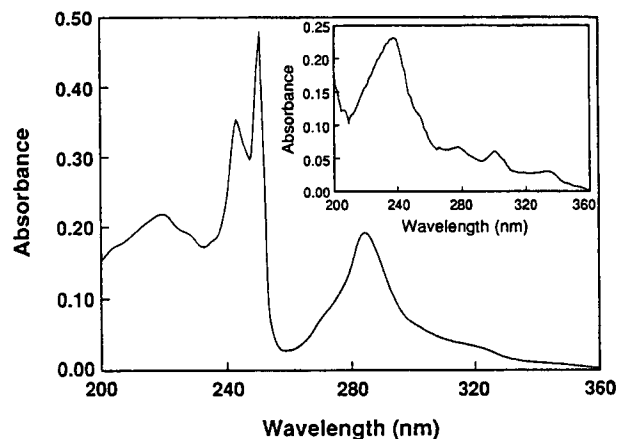


Fig. 2. Absorption spectrum of cyclopentacorannulene in cyclohexane. (Inset) Absorption spectrum of corannulene in cyclohexane; [corannulene] = 1.0×10^{-6} M.

using 9,10-diphenylanthracene in ethanol as a fluorescence standard ($\Phi = 1.0$).⁽¹⁾ The absorbance of the sample solution at the excitation wavelength was maintained at <0.05 . Fluorescence lifetimes were measured by using a PTI Inc LS-100 luminescence spectrometer. A flash lamp using a N_2 and He gas mixture was used as an excitation source. A dilute solution of colloidal starch was used as a scatterer to estimate the lamp profile. The 316-nm emission of N_2 was used for excitation. The decay curves were obtained by the use of the time correlated single-photon counting (TC-SPC) method. To obtain decay curves, 2×10^4 counts were collected at the peak channel. Each data set was collected in 512 channels. The data were analyzed using a multiexponential decay analysis program. The goodness of fit between experimental and computed decay curves was evaluated by use of the reduced χ^2 value (0.9–1.2) and by the randomness of the weighted residuals and the autocorrelation function. The measurements were repeated, if necessary, to obtain a good data set.

Apparatus

Absorption measurements were performed on a double-beam Shimadzu UV-3101PC UV-vis-NIR scanning spectrophotometer. All absorption scans were blank subtracted by use of the solvent. Steady-state fluorescence spectra were obtained on a Perkin Elmer Model LS-50 spectrofluorometer at room temperature. Samples were measured in a 1-cm^2 quartz cell by use of excitation and emission slit widths of 8.6 and 1.7 nm, respectively, unless otherwise noted.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of COR and CCOR, as measured in cyclohexane solvent, are shown in Fig. 2. The absorption spectrum of corannulene is characterized by a weak band at 285 nm and an intense band system at 250 nm. The essential separation between the intense peak at 250 nm and the band at 285 nm suggests that the electronic transitions involved are associated with two independent energy levels. The molar absorptivities were determined from a calibration plot of absorbance versus corannulene concentration. Values of 33,000 and 80,000 $\text{cm}^{-1} M^{-1}$ for the peaks at 285 and 250 nm, respectively, were obtained and are consistent with values reported in the literature.⁽²¹⁾

The absorption spectra of CCOR (Fig. 2, inset) extends over a broader wavelength region and is characterized by an intense band at 235 nm, two smaller peaks at 285 and 300 nm, and a shoulder at 330 nm. The molar absorptivities of CCOR could not be measured because the exact concentration of the solution was unknown. It is interesting to note that the longer wavelength region appears to be more vibronically structured than the band at shorter wavelength. Absorption at the longer wavelengths can be attributed to the additional π -electrons incorporated into the fused cyclopentene ring. A similar phenomenon has been observed for a comparison between the spectra of naphthalene⁽¹⁾ and acenaphthalene.^(28,29) A blue shift in the highest-absorptivity band relative to the highest band for the corannulene absorption is also noted. This band appears at 235 nm for CCOR and at 250 nm for COR, suggesting that a larger energy difference occurs between the corresponding energy levels for CCOR compared to COR. Similar effects were observed when an ethylene bridge was incorporated into the naphthalene^(28,29) or pyrene⁽²⁷⁾ molecule.

Steady-State Fluorescence Spectra

The fluorescence spectrum for COR (Fig. 3) consists of an unresolved doublet at 417 and 432 nm and two shoulder bands at 395 and 460 nm. The spectrum is very similar to the spectra in n-hexadecane, butylacetate, dichloromethane, and dimethylsulfoxide reported by Tucker *et al.*⁽¹⁵⁾ The bowl-to-bowl inversion of corannulene at room temperature has been reported to be approximately on the submicrosecond time scale.^(23,24) Since the fluorescence lifetime of aromatic molecules is normally on the nanosecond time scale, COR is not expected to undergo a full inversion during the emission

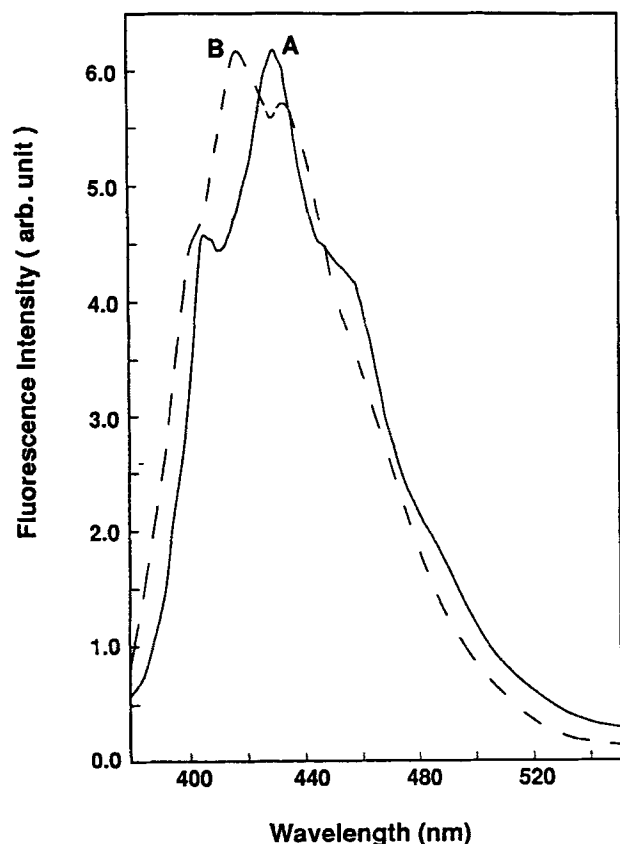


Fig. 3. Fluorescence spectra of purified samples of (A) cyclopentacorannulene and (B) corannulene. Excitation wavelength = 285 nm.

process. Hence, the fluorescence spectrum of COR in Fig. 3 represents an average of the rapidly inverting PAH.

Figure 3 also depicts the fluorescence spectrum of a sample of CCOR that was purified by the use of HPLC. The CCOR spectrum appears in the same wavelength region as the corannulene spectrum. However, the emission maxima of CCOR appear at 410, 429, and 455 nm (shoulder) and are red-shifted with respect to the emission maxima in COR. This phenomenon reflects the extended molecular conjugation in the CCOR molecule resulting from the additional fused cyclopentene ring. The structured fluorescence spectrum suggests that the geometry of the molecule does not change upon electronic excitation. Thus, the molecule is more rigid as compared to corannulene in both the S_0 and the S_1 states.

The photophysical data for the corannulenes, including radiative and nonradiative rate constants, are listed in Table I. The k_r and k_{nr} values were obtained, respectively, from the equations $k_r = \Phi_f/\tau_f$ and $k_{nr} (1 - \Phi_f)/\tau_f$. The fluorescence quantum yield of cyclopenta-

corannulene was measured in ethanol and a value of 0.01 was estimated. This value is relatively low compared to that of corannulene (0.07) in the same solvent. The k_{nr} values of the compounds, within the limit of experimental error, are essentially identical. However, the radiative rate constant of CCOR is lower than that of COR. Thus, the low fluorescence quantum yield value of the former compound is due to the lower radiative rate constant relative to that of the latter. As stated earlier, the low Φ_f value of cyclopentacorannulene is consistent with a decrease in fluorescence quantum yields for some parent PAHs after incorporation of the cyclopentene ring.⁽²⁷⁻²⁹⁾ These results may seem unlikely considering the inherent increase in molecular rigidity of acenaphthalene derivatives compared to the respective parent compounds. However, molecular rigidity is apparently counterbalanced by the distortion or strain further induced in these molecules by the additional cyclopentene ring, which may give rise to the lower quantum yield for CCOR. The very high strain in CCOR structure is further manifested in its low k_r value. The nonplanar strained ring structure of the molecule may cause a reduction of oscillator strength (f) and hence the radiative rate constant, k_r . The estimates of the photophysical properties clearly explain the higher bowl depth of CCOR (1.05 Å) in comparison to that of COR (0.89 Å).⁽³⁰⁾

Fluorescence Quenching

Fluorescence signals of many PAHs can be eliminated or suppressed in the presence of fluorescence quenching agents. For this reason, fluorescence quenching has been proposed to be a useful tool in the separation of structurally similar PAHs by HPLC.⁽³¹⁾ Nitromethane, for example, is a documented quencher of many select alternant PAHs.⁽³¹⁾ Other studies report that nitromethane quenches the fluorescence of fewer nonalternant acenaphthalene derivatives.⁽¹⁵⁾ Quenching studies using nitromethane have been performed in polar solvents, including acetonitrile and aqueous-acetonitrile solvent mixtures. It has been reported that the fluorescence intensity of COR in neat acetonitrile is not quenched by nitromethane. In the present work, we found that nitromethane significantly decreases the fluorescence intensity of CCOR in an 80% acetonitrile/water solutions. Figure 4 shows the Stern-Volmer plots for COR as well as CCOR. At low quencher concentrations (0.0–0.1 M), the fluorescence quenching of both fluorophores can be described by a simple Stern-Volmer relationship:⁽³²⁾

$$F_0/F = 1 + K_{sv}[Q] \quad (1)$$

Table I. Photophysical Properties of Corannulene and Cyclopentacorannulene in Ethanol

Property	Corannulene (COR)	Cyclopentacorannulene (CCOR)
Fluorescence maxima, λ_{\max} (nm)	423 <u>417^a</u> 395 (s)	455 (s) <u>429^a</u> 410
Fluorescence quantum yield (Φ_f)	0.070 (± 0.001) ^b	0.010 (± 0.001) ^b
Fluorescence lifetime, τ_f (ns)	10.3	9.60
Radiative rate constant, k_r (s ⁻¹)	6.80×10^6	1.04×10^6
Nonradiative rate constant, k_{nr} (s ⁻¹)	9.03×10^7	10.3×10^7

^a The underlined wavelengths represent emission maxima; (s) shoulder,

^b The uncertainties listed represent the average deviation.

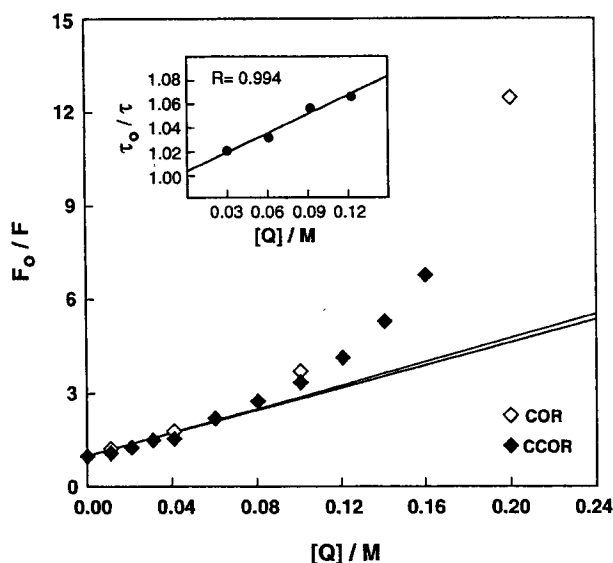


Fig. 4. Stern–Volmer plots for the fluorescence quenching of corannulene and cyclopentacorannulene by nitromethane in 80% acetonitrile/water solutions. (Inset) Stern–Volmer plot showing the change in the fluorescence lifetime of corannulene as a function of the concentration of nitromethane in acetonitrile.

where F_0 and F are the fluorescence intensities in the presence and absence of quencher, Q , respectively, and K_{SV} is the Stern–Volmer constant. The K_{SV} values obtained from the slope of the plots, within the limit of experimental error, are identical (18.4 and $18.0 M^{-1}$, respectively, for corannulene and cyclopentacorannulene). Thus, both fluorophores are equally quenched by nitromethane. However, at higher concentrations, the plots curve upward. Normally, this would suggest the existence of both static and dynamic quenching processes. To examine further the nature of the quenching mechanism, we have measured the fluorescence lifetime of corannulene in acetonitrile–water (80:20) mixed solvent

containing various concentrations of nitromethane. The lifetime decreased from 9.6 ns in pure solvent to 9.0 ns in the presence of 120 mM nitromethane. Such a small decrease in lifetime even at a relatively high concentration of nitromethane suggests that the contribution of the dynamic quenching mechanism is negligible as compared to static quenching. The Stern–Volmer plot obtained by use of these lifetime data is shown in Fig. 4 (inset). The dynamic quenching constant, K_D , is given by the slope and is estimated to be $0.55 M^{-1}$. The quenching constant, k_q , calculated from the equation $K_D = k_q \tau_0$ (where τ_0 is the fluorescence lifetime in the absence of quencher) is equal to $5.7 \times 10^7 M^{-1} s^{-1}$, which is much lower than the diffusion-controlled rate constant ($k_d \sim 10^{10}$). Thus, the fluorescence of both molecules is quenched mainly by a static mechanism. This is consistent with the reported results that corannulene forms a light-colored charge–transfer complex with picric acid and trinitrobenzene in the S_0 state.⁽³³⁾ The upward curvature of the Stern–Volmer plots may be due to a second type of static quenching, which probably occurs as a result of close contact between the quencher and the fluorophore at high concentrations.

CONCLUSIONS

An examination of the absorption and fluorescence spectra of corannulenes has indicated that incorporation of the ethylene bridge to form cyclopentacorannulene alters the photophysical properties of the parent compound, corannulene. We have observed a lower fluorescence quantum yield and a red shift in the emission spectra for cyclopentacorannulene. In addition, we have also noted a more vibronically structured emission spectrum of the latter molecule. The radiative rate constant of cyclopentacorannulene is much lower than that of cor-

annulene. Although the molecules examined in this study are classified as nonalternant PAHs, the fluorescence of both molecules is equally quenched by nitromethane and the quenching is essentially static, which likely involves the formation of a charge-transfer-type complex with a nitromethane molecule(s) in the S_0 state.

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REFERENCES

- I. B. Berlman (1971) *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York.
- R. Waris, M. A. Rembert, D. M. Sellers, W. E. Acree Jr., K. W. Street Jr., C. F. Poole, P. H. Shetty, and J. C. Fetzer (1988) *Appl. Spectrosc.* **42**, 1525.
- S. A. Tucker, W. E. Acree Jr., K. W. Street Jr., and Fetzer J. C. Fetzer (1989) *Appl. Spectrosc.* **43**, 162.
- R. Waris, M. A. Rembert, D. M. Sellers, W. E. Acree Jr., K. W. Street Jr., and J. C. Fetzer (1989) *Analyst* **114**, 195.
- R. Waris, K. W. Street Jr., W. E. Acree Jr., and J. C. Fetzer (1989) *Appl. Spectrosc.* **43**, 845.
- K. W. Street Jr., W. E. Acree Jr., J. C. Fetzer, P. H. Shetty, and C. F. Poole (1989) *Appl. Spectrosc.* **43**, 1149.
- S. A. Tucker, S. E. Cretella, R. Waris, K. W. Street Jr., W. E. Acree Jr., and J. C. Fetzer (1990) *Appl. Spectrosc.* **44**, 269.
- W. E. Acree Jr., S. A. Tucker, A. I. Zviagnze, K. W. Street Jr., J. C. Fetzer, and H.-F. Grutzmacher (1990) *Appl. Spectrosc.* **44**, 477.
- W. E. Acree Jr., A. I. Zviagnze, and J. C. Fetzer (1990) *Appl. Spectrosc.* **44**, 1193.
- S. A. Tucker, W. E. Acree Jr., and M. J. Tanga (1991) *Appl. Spectrosc.* **45**, 911.
- S. A. Tucker, W. E. Acree Jr., M. Zander, P. Demerseman, and J.-P. Buisson (1993) *Appl. Spectrosc.* **47**, 317.
- A. Munoz de Pena, T. T. Ndou, J. B. Zung, and I. M. Warner (1991) *J. Phys. Chem.* **95**, 3330.
- G. Patony and I. M. Warner (1991) *J. Inclusion Phenom. Mol. Rec. Chem.* **11**, 313.
- J. M. Schutte and I. M. Warner (1994) *Talanta* **41**, 647.
- S. A. Tucker, W. E. Acree Jr., J. C. Fetzer, R. G. Harvey, M. J. Tanga, P.-C. Cheng, and L. T. Scott (1993) *Appl. Spectrosc.* **47**, 715.
- H. F. Kroto, R. E. Smalley, R. F. Curl, J. R. Heath, and O'Brien (1985) *Nature* **318**, 168.
- W. Kratschmer and D. R. Huffman (1990) *Chem. Phys. Lett.* **170**, 167.
- R. F. Curl, H. F. Kroto, and R. E. Smalley (1985) *J. Am. Chem. Soc.* **107**, 7779.
- D. R. Huffman, L. D. Lamb, W. Kratschmer, and K. Fostiropoulos (1990) *Nature* **347**, 354.
- W. C. Hung, C.-D. Ho, C. P. Liu, and Y.-P. Lee (1996) *J. Phys. Chem.* **100**, 3927, S. H. Gallagher, R. S. Armstrong, P. A. Lay, and C. A. Reed (1995) *J. Phys. Chem.* **99**, 5817, I. Renge (1995) *J. Phys. Chem.* **99**, 15955, D. J. van den Heuvel, G. J. B. van den Berg, E. J. J. Groenen, J. Schmidt, I. Holleman, and G. Meijer (1995) *J. Phys. Chem.* **99**, 11644; D. J. van den Heuvel, I. Y. Chan, E. J. J. Groenen, J. Schmidt, and G. Meijer (1994) *Chem. Phys. Lett.* **231**, 111, J. Catalan (1994) *Chem. Phys. Lett.* **223**, 159; R. V. Bensasson, E. Bienvenue, M. Dellinger, S. Leach, and P. Seta (1994) *J. Phys. Chem.* **98**, 3492.
- W. E. Barth and R. G. Lawton (1966) *J. Am. Chem. Soc.* **88**, 380.
- J. C. Hanson and C. E. Nordman (1976) *Acta. Cryst.* **B32**, 1147.
- L. T. Scott, M. M. Hashemi, and M. S. Bratcher (1991) *J. Am. Chem. Soc.* **113**, 7082.
- L. T. Scott, M. M. Hashemi, and M. S. Bratcher (1992) *J. Am. Chem. Soc.* **114**, 1920.
- A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldrige, and J. S. Siegel (1992) *J. Am. Chem. Soc.* **114**, 1921.
- A. H. Abdourazak, A. Sygula, and P. W. Rabideu (1993) *J. Am. Chem. Soc.* **115**, 3010; A. H. Abdourazak and P. W. Rabideu (1996) *J. Am. Chem. Soc.* **118**, 339.
- B. F. Plummer and Z. Y. Al-Saigh (1983) *J. Phys. Chem.* **87**, 1579.
- A. Samanta, C. Devadoss, and R. W. Fessenden (1990) *J. Phys. Chem.* **94**, 7106.
- A. Samanta (1991) *J. Am. Chem. Soc.* **113**, 7427.
- P. W. Rabideau and A. Sygula (1995) in R. P. Thummel (Ed.), *Advances in Theoretically Interesting Molecules*, Vol. 3, JAI Press, London, p. 1, P. W. Rabideau and A. Sygula (1996) *Acc. Chem. Res.* **29**, 235.
- G.-P. Blumer, M. Zander, and Z. Fresenius (1979) *Anal. Chem.* **296**, 409.
- J. R. Lakowicz (1983) *Principles of Fluorescence Spectroscopy*, Plenum Press, New York.
- W. E. Barth and R. G. Lawton (1971) *J. Am. Chem. Soc.* **93**, 1730.