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where

$$K_m = \bar{v}_{1s}^{\infty}/(RT) - \beta_{mT} \quad (4)$$

$$K_s = [1/(1 - x_{3s}) - (\partial \ln \varphi_{1s}^{\infty}/\partial x_{3s})](\partial x_{3s}/\partial P)_T - \bar{v}_{1s}^{\infty}/(RT) - (V_s/V_m)\beta_{sT} \quad (5)$$

In eqs 3-5, P is the pressure, x_{3s} is the equilibrium mole fraction of the mobile-phase fluid in the stationary phase, φ_{1s}^{∞} is the infinite-dilution fugacity coefficient of the solute in the stationary phase, \bar{v}_{1s}^{∞} is the infinite-dilution partial molar volume of the solute in the stationary phase, β_{sT} is the isothermal compressibility of the stationary phase, and V_s and V_m are the volumes of the stationary and the mobile phases in the column, respectively. The derivation and discussion of eqs 3-5 may be found elsewhere.^{25,26} It should only be emphasized here that k_1 in eq 3 is a *local* value at some particular position within the column rather than the experimentally observed, average value over the pressure drop across the column.

In a similar way, the derivative with respect to the molar density of the mobile phase may be written as

$$(\partial \ln k_1/\partial \rho_m)_T = Q_m + Q_s = K_m/(\rho_m \beta_{mT}) + K_s/(\rho_m \beta_{mT}) \quad (6)$$

The quantities \bar{v}_{1s}^{∞} and β_{mT} in eq 4 combine in such a way that straightforward relationships result between K_m (or Q_m) and the molecular quantities of eqs 1 and 2. After simple rearrangements, one obtains

$$\int c_{31}^{\infty}(\mathbf{r}) \, d\mathbf{r} = -K_m/(N_A \rho_m \beta_{mT}) = -Q_m/N_A \quad (7)$$

$$\zeta = -RT \rho_m K_m = -RT \rho_m^2 \beta_{mT} Q_m \quad (8)$$

(25) Roth, M. *J. Phys. Chem.* **1990**, *94*, 4309.

(26) Roth, M. *J. Supercrit. Fluids*, in press.

In principle, therefore, eqs 3-8 provide a way to estimate the molecular characteristics of the dilute mixture of the solute 1 with the mobile-phase fluid 3 from the pressure (or density) course of the solute retention in SFC. The respective procedure may be broken down to three basic steps, namely (a) calculation of $(\partial \ln k_1/\partial P)_T$ or $(\partial \ln k_1/\partial \rho_m)_T$ from experimental retention data, (b) application of appropriate expressions for K_s or Q_s to obtain K_m or Q_m , respectively, and (c) use of eqs 7 or 8 to calculate the direct correlation function integral or mean cluster size, respectively. As the column pressure drop has to be minimized in order to obtain meaningful values of $(\partial \ln k_1/\partial P)_T$ from the experimental retention data, an open tubular capillary column is to be preferred to a packed column. A major problem in applying the above procedure lies in the term $(\partial \ln \varphi_{1s}^{\infty}/\partial x_{3s})$ in eq 5. This term is not accessible experimentally so that a molecular or an equation-of-state model is required for a theoretical evaluation.

Conclusion

Relationships have been shown between the correlation and fluctuation integrals in dilute, binary, supercritical mixtures and the solute retention in SFC. Ensuing from these relationships is a possibility of using SFC as a potential technique to determine the correlation and fluctuation integrals. However, the interesting information hidden in the pressure (or density) course of solute retention cannot be exploited until significant progress is made in the understanding of the effect on solute retention of the absorption of the mobile-phase fluid into the stationary phase. To this end, more experimental data on equilibrium absorption of supercritical fluids by chromatographic stationary phases are needed, and improved models for the effect of composition on the solute fugacity coefficient in the stationary phase will have to be developed.

¹³C NMR Study of the C60 Cluster in the Solid State: Molecular Motion and Carbon Chemical Shift Anisotropy

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¹³C NMR spectra of solid buckminsterfullerene, the soccerball-like cluster of 60 carbon atoms, have been obtained at temperatures down to 77 K. The ambient spectrum shows rapid isotropic rotational motion. The motion is sufficiently slow at 77 K that a measurement of the chemical shift tensor of the carbon nucleus can be made. The tensor components (220, 186, 40 ppm) have values that are typical for an aromatic carbon. Spectra at intermediate temperatures suggest the possibility of either growth of a low-temperature phase in which C60 rotation is inhibited or a distribution of rotational correlation times.

The recent success in generating macroscopic quantities of the C60 cluster¹⁻³ has stimulated intense interest and activity.⁴ A variety of spectroscopic studies have been made to explore the properties of the C60 moiety.^{1,2,4-7} Infrared^{1,2} and vibrational

Raman spectra⁵ of C60 strongly support the soccerball geometry for this molecule, and solution NMR spectra⁶ have shown that the molecule has icosahedral point group symmetry. The pseudospherical symmetry of this molecule suggests potential for facile isotropic motion in the solid state,⁵ and solid-state NMR spectroscopy is uniquely suited as a probe of this kind of molecular dynamics.

The sample was prepared by toluene extraction of soot produced by arc heating graphite in 100 Torr of He.⁸ The dried powder consists mainly of C60 and C70 in a ratio of ~10:1 and also shows a strong, sharp (1.5-G width) EPR signal at $g \sim 2$.

¹³C spectra of approximately 1 g of sample have been obtained at 1.4 T (15 MHz). Figure 1 shows spectra at several temper-

(1) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167-170.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354-358.

(3) Meijer, G.; Bethune, D. S. *J. Chem. Phys.* **1990**, *93*, 7800-7802.

(4) For an overview of some of the current work, see: Baum, R. M. *Chem. Eng. News* **1990**, Oct 29, 22-25.

(5) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.* **1990**, *174*, 219-222.

(6) (a) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983-8984. (b) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *Chem. Commun.* **1990**, *20*, 1423-1425.

(7) Ajje, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630-8633.

(8) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634-8636.

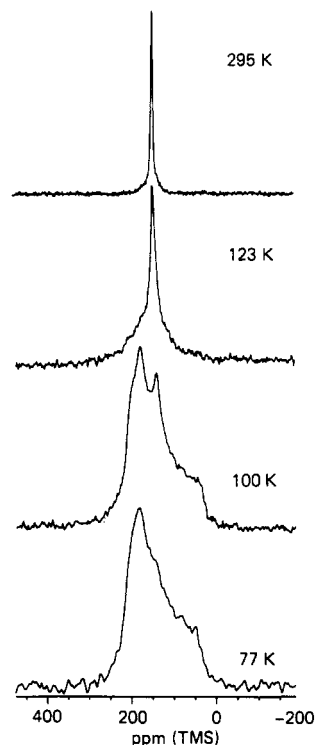


Figure 1. ^{13}C NMR spectra of solid C60 obtained at ambient and 123, 100, and 77 K. Recycle times (seconds/number of scans at each temperature) are as follows: ambient, 8/3108; 123 K, 1/1520; 100 K, 8/14400; 77 K, 8/7342.

atures. The spectrum at ambient consists of a narrow (70-Hz fwhm) single peak with a chemical shift (143 ppm) close to that found in the solution NMR spectrum.⁶ In the absence of molecular motion, the ^{13}C NMR spectrum of solid C60 is expected to be a broad resonance, the features of which are defined by the chemical shift anisotropy of the ^{13}C nucleus.⁹ The narrow width thus proves that the molecule is rotating isotropically and rapidly relative to the NMR time scale defined by the inverse of the spectral spread due to the chemical shift anisotropy. Since the

chemical shift anisotropy is expected to extend over ~ 200 ppm⁹ (3 kHz at 1.4 T), the relevant time scale is $\sim 10^{-4}$ s. Measurements of the ^{13}C spin-lattice relaxation time at 7.04 T show a T_1 minimum at 233 K, indicating that the correlation time for molecular motion at this temperature is $\sim 10^{-9}$ s. Thus, C60 molecules must be rotating at rates $>10^9$ s⁻¹ at ambient temperatures. The spectrum at 123 K shows that a broad skirt has developed at the base of the main resonance at 143 ppm. At 100 K, the spectrum is predominantly a powder pattern characteristic of a chemical shift anisotropy⁹ with minor intensity in the narrow peak at 143 ppm. At 77 K the same powder pattern is observed with little evidence of the narrow line at 143 ppm. A fit of the powder pattern yields an asymmetric chemical shift tensor⁹ as expected for a carbon in the C60 cluster. The components of the tensor, 220, 186, and 40 ppm, confirm the aromatic character of the carbons in C60.^{8,9}

As shown in Figure 1, as the temperature is lowered, the intensity of the narrow peak due to rapidly rotating C60 decreases while a spectrum reflecting static molecules builds up. This evolution may be explained either by growth, as the temperature is lowered, of a phase in which cluster rotation is inhibited¹⁰ or by a distribution of rotational correlation times and a concomitant distribution of motional barriers.¹¹

In conclusion, we report results that show that the C60 cluster rotates rapidly and isotropically in the solid state at ambient temperatures and that by lowering the temperature this motion can be slowed to the extent that the carbon chemical shift anisotropy can be measured. The resulting chemical shift tensor confirms the aromatic nature of the carbons in C60. The ^{13}C spectra also suggest either growth of a new phase as the temperature is lowered or a distribution of motional dynamics, possibly due to sample heterogeneity. Experiments that may permit us to distinguish between these two possibilities are in progress. A careful study of the temperature dependence of the ^{13}C NMR line shape to probe the details of the motional dynamics is also planned. A further implication of these results is that it may be necessary to cool C60 to low temperatures to explore its structure by diffraction methods or to image individual atoms by using STM.

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(9) (a) Veeman, W. S. *Progress in Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1984; Vol. 16, pp 193-237. (b) Mehring, M. *High Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: Berlin, 1983; Chapter 7.

(10) Shiao, W.-I.; Duesler, E. N.; Paul, I. C.; Curtin, D. Y.; Blann, W. G.; Fyfe, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 4546-4548.

(11) Garroway, A. N.; Ritchey, W. M.; Moniz, W. B. *Macromolecules* **1982**, *15*, 1051-1063.