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# Spin-Resonance Transitions of Free Radicals in the Zeeman Region

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**BD2. Nuclear-Magnetic-Resonance Measurements of Self-Diffusion in Noninfinite Media.*** R. C. WAYNE† AND R. M. COTTS, *Cornell University.*—An extension of the Hahn spin–echo method for measuring self-diffusion is made to the case of noninfinite sample size. A sample is noninfinite from the point of view of NMR if $T_2 \gg t_x$, where $t_x$ is the average time for a molecule to diffuse once across the sample width **a**. From the spin–echo experiment, an effective self-diffusion coefficient $D'$ is defined[1] where $D' = \{-3\ln(M(2\tau)/M_0)/2\gamma^2G^2\tau^3\}$. $G$ is a linear magnetic-field gradient parallel to $\mathbf{H}_0$. From test measurements made on infinite samples, $D' = D$. However, when $t_x \ll T_2$, $D'/D < 1$ and $D'$ depends on $\tau$. The measurement of $D'$ is made by holding the time of an echo $2\tau$ constant and by varying $G$. Experimental data are presented for $D'(2\tau)$ vs $2\tau$ for four values of the sample size **a**. These data are compared with a theoretical calculation of $D'(2\tau)$, using Torrey's modification of the Bloch equations and requiring that boundary conditions be satisfied. A "universal" curve of $D'/D$ vs $2\tau/t_x$ is plotted illustrating that $D'$ is independent of $G$. It is further shown that $M(2\tau) \propto \exp(-K_1\tau^3)$ for $\tau \ll t_x$ and that $M(2\tau) \propto \exp(-K_2\mathbf{a}^4\tau)$ for $\tau > t_x$.

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[1] D. E. Woessner, J. Phys. Chem. **67**, 1365 (1963).

**BD3. Temperature Dependence of $F^{19}$ NMR in $CeF_3$.** K. LEE, *Varian Associates.*—The temperature dependence of the $F^{19}$ nuclear magnetic resonance in a single crystal of pure $CeF_3$ has been studied from 88° to 530°K. As in $LaF_3$ (Ref. 1), which has the same tysonite crystal structure, motional narrowing of the linewidth, due to the presence of Schottky defects, is observed near room temperature. At 16.022 MHz and with the magnetic field along the $c$ axis, four Gaussian-shaped lines with the intensities in a ratio of 3:3:2:1 are observed at 88°K. This is in agreement with the proposed[2] crystal structure ($P6_3cm$–$C_{6v}^3$), which includes four different $F^{19}$ sites. Between 245° and 500°K, the two types of $F^{19}$ in $c$ sites are in rapid motion and the $F^{19}$ in $a$ and $b$ sites are in relatively slow motion. The activation energy measured in this region is 0.13 eV. Above 500°K, the $F^{19}$ in the $a$ and $b$ sites also begin to move rapidly. This is compatible with the model for motion of $F^{19}$ in $LaF_3$.[3]

[1] K. Lee and A. Sher, Phys. Rev. Letters **14**, 1027 (1965); A. Sher, R. Solomon, K. Lee, and M. W. Muller, Phys. Rev. **144**, 593 (1966).
[2] L. O. Andersson and W. G. Proctor (to be published).
[3] M. Goldman and L. Shen, Phys. Rev. **144**, 321 (1966).

**BD4. Temperature Variation of $La^{139}$ Nuclear Quadrupole Resonance in $LaF_3$.** A. SHER, K. LEE, L. O. ANDERSSON, AND W. G. PROCTOR, *Varian Associates.*—The temperature dependence of the pure quadrupole transitions of $La^{139}$ in $LaF_3$ has been studied from 88° to 447°K. $La^{139}$ has a nuclear spin of $\frac{7}{2}$, so three $|\Delta m| = 1$ transitions were observed. A spectrometer of crossed-coil geometry was used. The Bayer torsional motion mechanism and an Einstein phonon spectrum are used to interpret the measurements. The characteristic (or Einstein) temperatures are 465° and 641°K. Values for the quadrupole coupling constant, asymmetry parameter, and electric-field-gradient components at the La sites are tabulated. The observed temperature variation is approximately 2 orders of magnitude larger than predicted by the simple theory employed. Mechanisms are discussed to account for this discrepancy.

**BD5. Hyperfine Structure in the Arc Spectrum of Argon 39.*** MERTON M. ROBERTSON, *Sandia Corporation*, W. TRAUB, F. L. ROESLER, *University of Wisconsin*, AND V. W. COHEN, *Brookhaven National Laboratory.*—The nuclear spin and magnetic moment of argon 39 have been determined by high-resolution optical-spectroscopic methods, using a pressure-swept Fabry–Perot interferometer and photoelectric detection. The argon 39 was produced through the $K^{39}(n,p)Ar^{39}$ reaction by pile-neutron irradiation of KF and then processing the KF to obtain the $Ar^{39}$. The arc spectrum of $Ar^{39}$ was excited in a liquid-nitrogen-cooled miniature hollow cathode, utilizing helium as a carrier gas. By application of the intensity rules, the nuclear spin was determined to be $\frac{7}{2}$, in agreement with the shell model. Apparent deviations from a spin of $\frac{7}{2}$ was noted in some levels but can be explained by self-absorption from excited states. The nuclear magnetic moment has been determined to be $-1.3\pm0.3$ nm from the $A$ value of $-23.7\pm0.2$ mK measured for the $1s_2$ level, which is involved in the 7503-Å transition, and using a previous result for $Ar^{37}$ (Ref. 1.). The measured $B$ value for the $1s_2$ level is $B = 3.2\pm0.5$ mK. The structure of other levels is reported.

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[1] M. M. Robertson, J. E. Mack, and V. W. Cohen, Phys. Rev. **B140**, 820 (1965).

**BD6. Dynamic Polarization of Protons in Frozen Toluene.*** R. J. WAGNER AND R. P. HADDOCK, *University of California, Los Angeles.*—We have conducted a series of experiments in which sizable polarization of protons has been obtained in frozen toluene, $C_6H_5(CH_3)$. Concentrations of diphenyl picrylhydrazyl (DPPH) ranging from 0.1% to 3% have been dissolved in toluene and the protons are polarized by the "solid-state effect."[1] This work has been done in a magnetic field of 20 400 Oe, using a microwave frequency of 57 GHz in a temperature range from 1° to 4.2°K. Polarizations of 30% have been obtained in 200 mg, 2% samples near 1°K. The chief limitation to higher polarizations in this material is the relatively short proton $T_{1n}$. Measurements have also been made of the electron relaxation rates at 9400 MHz, and the behaviors of $T_{1n}$ and $T_{1e}$ as functions of temperature and DPPH concentration are discussed.

* Work supported in part by the U. S. Atomic Energy Commission.
[1] C. D. Jeffries, Phys. Rev. **106**, 164 (1957).

**BD7. Spin-Resonance Transitions of Free Radicals in the Zeeman Region.** J. V. ACRIVOS, *San Jose State College.*—The transitions $\Delta F = 0, \pm1$, $\Delta F_z = \pm1$ of the spin system of an unpaired electron, 4 equivalent protons and 2 sodium nuclei, have been studied for $p$-benzosemiquinone and its ion cluster $(Na^+)_2\cdot(C_6H_4O_2^-)$ in solution. The nuclear-spin eigenfunctions decompose within the operations of the $D_{2h}$ symmetry group into the presentation:

$$\Gamma = \Gamma(4-{}^1\mathrm{H}) \times \Gamma(2-{}^{23}\mathrm{Na})$$
$$= ({}^5A_g + {}^2{}^1A_g + {}^3B_{1g} + {}^3B_{2u} + {}^3B_{3u}) \times ({}^7A_g + {}^5B_{2u} + {}^3A_g + {}^1B_{2u}).$$

The $^{23}Na$ hyperfine structure was resolved not at room temperature but at $t = -50$°C. Owing to their finite widths of 0.29 Mc/sec, proton hyperfine resonance absorptions were detected about zero field for $\nu = 16.217$ and 9.916 Mc/sec, where $h\nu = 2.5|A|$ and $1.5|A|$, $|A| = 6.631\pm0.003$ Mc/sec. Also, since anisotropic proton hyperfine interactions appear to be the main source for spin relaxation in the Paschen–Back field region,[1] the proton spin states $^1Ag$ were investigated for saturation effects. At room temperature, they were found to saturate 15%–25% more readily than the nonzero proton-spin states. A study of the relaxation mechanism for these $F = \frac{1}{2}$ states led to the discovery of the 3-ion cluster, where the sodium hyperfine coupling constant is $0.4\pm0.1$ Mc/sec at $t = -50$°C.

[1] G. K. Fraenkel *et al.*, J. Chem. Phys. **39**, 326 (1963); **42**, 4275 (1965).

**BD8. Phenomenological Theory of Optical Pumping.*** ROBERT E. SLOCUM, *The University of Texas.*—The phenomenological theory of optical pumping previously used to describe magnetic-resonance absorption in optically oriented free-spin