δ 5.7; the ultraviolet spectrum has λ_{max} 240 mμ (ε 12,400). Attempts to dehydrogenate VII to octalene itself, either with N-bromosuccinimide and base or with dichlorodicyanoquinone, have so far led only to nonvolatile tarry materials, suggesting that octalene does not have striking stability.

Perhaps the most relevant evidence concerns cyclo-octatetraenocycloheptatriene (IX), produced in 15% yield by reaction of III with VIII. After vpc purification, IX shows m/e 168 and a large fragment at m/e 167; hydrogenation in benzene over Pd–C gives material with m/e at 180 and 178. The nmr spectrum of IX is as expected, with the CH_2 at δ 2.27 and a complex ten-proton vinyl pattern. With trityl fluoroborate, IX is converted to the tropylium salt X, mp 99–100° (*Anal.* Found: C, 61.17; H, 4.69; nmr: five protons at δ 9.10, four protons at δ 6.16, two protons at δ 4.77). Since the anion XI derived from IX has a total of 14 π electrons, aromaticity of XI should be reflected in an increased kinetic acidity of IX compared with cyclo-heptatriene. However, with potassium *t*-butoxide in deuterated DMSO-*t*-butyl alcohol[8] IX exchanges 20–30-fold more slowly than does cycloheptatriene. Apparently fusion of tropylium anion to cycloocta-tetraene does not appreciably stabilize it. We conclude that if there is any aromaticity associated with such fused ring systems it is not sufficient to induce planarity in our compounds, and it thus remains undetected.[9]

(8) This is the inverse of the system used by W. von E. Doering and P. P. Gaspar, *J. Am. Chem. Soc.*, **85**, 3043 (1963), to exchange protons into deuteriocycloheptatriene.

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Paramagnetic Relaxation of Trapped Electrons in Irradiated Alkaline Ices

Sir:

Electrons produced by γ radiation are trapped in alkaline ices at 77°K.[1,2] At hydroxide concentrations greater than 0.5 M the trapped electron is characterized by an epr singlet at $g = 2.001$[2,3] and a blue absorption band[1] with a maximum at 5850 A. Proof that the epr signal and the absorption band are associated with a trapped electron is demonstrated by experiments with electron scavengers.[3,4] Scavenging experiments show that a mobile electron, e_m^-, is formed in irradiated ice; the electron moves through the lattice until it finds a suitable site at which to be trapped or a species with which to react.[4] The nature of the trapping site has been discussed in terms of an F-center model in which the electron is trapped in a hydroxide anion vacancy.[4–6] We report here paramagnetic relaxation experiments which support this model. The anion vacancy should

(1) D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, **17a**, 445 (1962); **18a**, 199 (1963).

(2) B. G. Ershov, A. K. Pikaev, P. Ya. Glazunov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **149**, 363 (1963).

(3) P. N. Moorthy and J. J. Weiss, *Phil. Mag.*, **10**, 659 (1964).

(4) L. Kevan, *Progr. Solid-State Chem.*, **2**, 304 (1965).

(5) L. Kevan, *J. Am. Chem. Soc.*, **87**, 1481 (1965).

(6) M. J. Blandamer, L. Shields, and M. C. R. Symons, *Nature*, **199**, 902 (1963).

be formed in a radiation produced "spur"; the present results do indicate that the trapping site is located in a "spur." In addition, it is found that the trapped electron relaxes *via* cross relaxation with O^- which is also formed in irradiated alkaline ices.

Frozen solutions of 10.0 M NaOH and 7.3 M NaOD were irradiated at 77°K with cobalt-60. Slow passage progressive power saturation measurements at a modulation frequency of 40 cps were made over a 40-db power range on a Varian-4500 epr spectrometer. Measurements were made at 77°K unless otherwise noted. The electron line shape is nearly Gaussian and the saturation curves were interpreted as due to inhomogeneous broadening. The curves do not fit the ideal inhomogeneous case discussed by Portis,[7] but can be accounted for by the intermediate case discussed by Castner.[8] The inhomogeneous line is the envelope of individual spin packets where each spin packet is composed of those spins which "see" the same local magnetic field.[7,8] $(T_1T_2)^{1/2}$ was determined from the saturation curves; T_1 denotes the spin–lattice relaxation time and T_2 denotes the spin–spin relaxation time.

$(T_1T_2)^{1/2}$ was found to be about 2×10^{-5} sec. The most important results are: (a) $(T_1T_2)^{1/2}$ is independent of radiation dose from 0.3 to at least 2 Mrads (megarads) in both H_2O and D_2O matrices, (b) $(T_1T_2)^{1/2}$ is independent of temperature from 77 to 150°K, and (c) $(T_1T_2)^{1/2}$ is about 50% larger in D_2O as compared to H_2O matrices; this is on the borderline of being equal within our experimental error.

Observation a indicates no spin–spin interaction between trapped electrons at doses up to 2 Mrads. Thus the spin-packet width is due to spin–spin interactions within a radiation produced "spur" or it is limited by spin–lattice interactions. The lack of a temperature dependence eliminates the latter alternative. At higher doses at which the electron radiation yield has reached saturation (10^{19} electrons/g for both H_2O and D_2O), $(T_1T_2)^{1/2}$ does decrease as expected owing to *inter* "spur" interactions. We conclude that the electron trap is located within a "spur." This is to be expected if the trap is a hydroxide anion vacancy produced by the radiation.

Observations b and c yield information about the spin–lattice relaxation mechanism of the trapped electron. At temperatures of the order of and above the Debye temperature ($\theta_D = 192$°K for H_2O),[9] a two-phonon (Raman) spin–lattice relaxation mechanism is expected to dominate.[10] Since the trapped electron resonance line is broadened by hyperfine interaction with surrounding nuclear spins,[5] the logical candidate for the dominant spin–lattice relaxation mechanism is modulation of the hyperfine interaction by the lattice vibrations.[11] This and all other two-phonon processes in H_2O or D_2O matrices above 100°K predict $(T_1T_2)^{-1/2} \propto T^2$ where T is in °K. Instead a T^0 dependence is observed. Furthermore, hyperfine modulation by the phonons would require $(T_1T_2)^{1/2}$ to be several times

(7) A. M. Portis, *Phys. Rev.*, **91**, 1071 (1953).

(8) T. C. Castner, *ibid.*, **115**, 1506 (1959); a detailed analysis of the saturation curve shape will be published shortly.

(9) W. F. Giauque and J. W. Stout, *J. Am. Chem. Soc.*, **58**, 1144 (1936).

(10) G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 121–133; eq 6–51 should have $1/T_1 \propto T^2$ instead of T^0.

(11) This mechanism is observed for F centers in KCl; see D. W. Feldman, R. W. Warren, and J. G. Castle, *Phys. Rev.*, **135**, A470 (1964).

greater in D_2O than in H_2O. This is also not observed. The only reasonable mechanism compatible with these experimental results appears to be a cross-relaxation process which occurs *via* spin–spin interaction with another paramagnetic species. The only other known paramagnetic species in 10 M hydroxide ices is O^-. We tentatively conclude that O^- is involved in a cross-relaxation process with the trapped electron.

Further paramagnetic relaxation studies are under way. It appears that such studies can yield quite useful insights into the nature of the trapping sites of ions and radicals in solids.

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Kerr-Constant Dispersion for an Electronic Absorption

Sir:

The Kerr constant of a material can be used in the estimation of the anisotropy of the polarizability when measurements are carried out in a region of little or no absorption.[1] If the Kerr constant is measured as a function of frequency in a region of absorption (*i.e.*, the dispersion is determined), then it is possible to assign the polarization of the transition as well as to estimate the properties of the excited state.[2] Kerr-constant dispersion was used in a recent communication[3] to infer the direction of a dipole moment from determinations made at two or three widely scattered frequencies.

We are now reporting the measurement of the dispersion of the Kerr constant throughout an entire absorptive region. The system chosen is the acridine orange–polyglutamic acid complex which has previously been examined by the techniques of optical rotatory dispersion[4] (ORD) and circular dichroism[5] (CD).

The Kerr effect (linear electric birefringence) arises from anisotropies in the electrostatic and electrooptic polarizabilities; the effect is quadratic in the applied field. For the case of a dipolar molecule with the dipole moment lying along one of the principal axes of the molecule (the z axis), the Kerr constant (B) can be expressed as

$$B = \frac{\pi N}{27n\lambda}(n^2 + 2)^2(\epsilon + 2)^2\frac{\mu_z^2}{45k^2T^2}(2\alpha_z - \alpha_x - \alpha_y) \quad (1)$$

where N is the number of molecules/unit volume, n and ϵ are the index of refraction and dielectric constant of the

(1) C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem.*, **5**, 261 (1955), and succeeding papers.
(2) A. D. Buckingham, *Proc. Roy. Soc.* (London), **267**, 271 (1962).
(3) W. H. Orttung, *J. Am. Chem. Soc.*, **87**, 924 (1965).
(4) L. Stryer and E. R. Blout, *ibid.*, **83**, 1411 (1961).
(5) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Biopolymers*, **4**, 97 (1966).
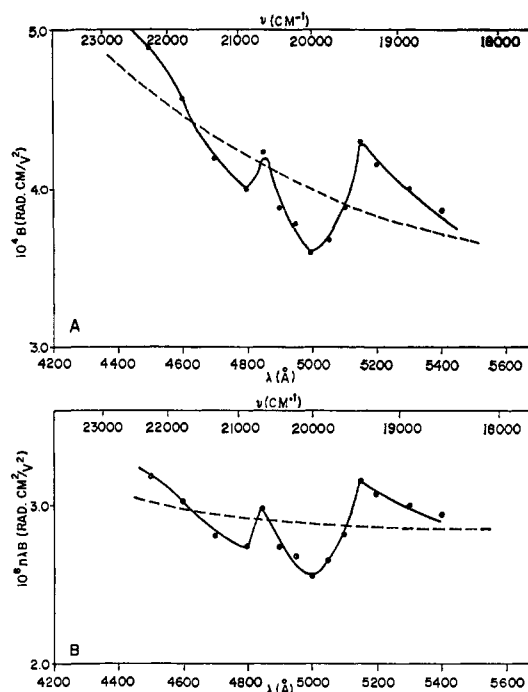

Figure 1. (A) Dispersion of the Kerr constant (B) for the AO–PGA complex (solid line) and PGA (dotted line). (B) Dispersion of $n\lambda B$ for the AO–PGA complex (solid line) and PGA (dotted line).

medium, λ is the wavelength of the light, and μ_i and α_i are the components of the dipole moment and electro-optic polarizability along the principal axes. From the definition of the polarizability,[6] it can be seen that in the vicinity of an absorption of frequency ν_i, the Kerr constant will vary as $1/(\nu_i - \nu)$. If $2\alpha_z > (\alpha_x + \alpha_y)$, the dispersion is positive and the transition is parallel; a negative dispersion arises from a perpendicular transition. Buckingham and Pople[7] have considered deviations from a linear polarization law (hyperpolarizability); in the vicinity of an absorption, this gives rise to a dispersion that varies as $1/(\nu_i - \nu)^3$ for the axially symmetric case. The width of the absorption will cause a broadening of the dispersion curve with maxima and minima occurring at the half-width frequencies.[2] The polarization of a transition is easily determined by the initial rise or fall of B as ν approaches ν_i.

The acridine orange (AO)–polyglutamic acid (PGA) complex was formed by mixing the appropriate stock solutions. The dye was zinc free. The solvent used was DMF because of its relatively low conductivity. In this solvent, the polymer is in the helical conformation. The spectrum of the complex in DMF closely resembles that obtained in water; a maximum is found at 4950 A with a shoulder appearing around 4650–4700 A. These absorptions can be assigned to the free protonated dye and aggregated dye, respectively.[8] The Kerr constants were measured by a conventional photoelectric method. The light source was a 1000-w Osram lamp, the appropriate wavelengths being selected by a Bausch and Lomb monochromator; the width of the output beam was about 10 A. Full details of these experiments will be published elsewhere.

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(7) A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 905 (1958).
(8) V. Zanker, *Z. Physik. Chem.*, **199**, 225 (1952).