

first triplet state. The best hypothesis appears to be that, at 2537 Å., 1,3-butadiene is excited to the upper singlet state. It follows that the 0-0 level must lie at even longer wave lengths. The simplest conjugated diene from which fluorescence has been observed is ergosterol.¹⁰ In this case, the fluorescent spectrum exactly reproduces the absorption spectrum but is shifted by nearly 1000 Å. to the red. A similar situation obtains in lumisterol, another cyclic 1,3-diene.¹⁰ In both molecules, there is no detectable absorption which corresponds to the 0-0 band from the ground singlet to the upper singlet. It seems possible that in 1,3-butadiene the 0-0 band may lie at a wave length as low in energy as 90 kcal./mole (~ 3200 Å.). Since the lowest triplet lies at 60 kcal./mole,⁹ the gap that separates these two levels is in no sense "large." [The upper singlet-lowest triplet separation in benzene is 25.5 kcal./mole.¹¹]

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On the Equations Used to Analyze Isotropic Nuclear Magnetic Resonance Shift Data for Systems Involving a Rapid Equilibrium

Sir:

The equation

$$\frac{\Delta H_i}{H} = \frac{\Delta f_i}{f} = -\frac{A_i \gamma_e g \beta S(S+1)}{2S \gamma_H kT} [3 + \exp(\Delta G/RT)]^{-1} \quad (1)$$

has been used many times¹⁻¹¹ to analyze the results of isotropic n.m.r. shifts of nickel chelates in solution where there is a square-planar (singlet) \rightleftharpoons tetrahedral (triplet) equilibrium in solution. In this equation ΔH_i and Δf_i are the isotropic shifts from the diamagnetic position of the resonance magnetic field and frequency, respectively, of a given nucleus. A_i is the isotropic hyperfine coupling constant for the i th proton, γ_e and γ_H are the magnetogyric ratios of the electron and proton, respectively, g is the spectroscopic splitting factor for the paramagnetic species, and ΔG is the free energy change for the above-mentioned equilibrium. The other symbols have their usual significance.

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As noted in footnote 31a of ref. 8, the $2S$ in the denominator of eq. 1 is involved with the relationship between the unpaired electron spin density and the A_i values. This point will not concern us further here. Equation 1 reduces (when $\Delta G \rightarrow -\infty$) correctly to eq. 2¹² which is applicable to fully paramagnetic systems in which the isotropic shifts obey the Curie law

$$\frac{\Delta H_i}{H} = -\frac{A_i \gamma_e g \beta S(S+1)}{2S \gamma_H 3kT} \quad (2)$$

The observed isotropic shifts for a system in rapid equilibrium will be the isotropic shifts for the diamagnetic species (zero by definition) and paramagnetic species, weighted by their mole fractions in solution. If we call the mole fraction of triplet molecules N_T , then the isotropic shifts are given by

$$\frac{\Delta H_i}{H} = -\frac{A_i \gamma_e g \beta S(S+1)}{2S \gamma_H 3kT} N_T \quad (3)$$

It is easily shown that the equilibrium constant K for the singlet-triplet equilibrium is $K = [(1/N_T) - 1]^{-1}$, and also since $\Delta G = -RT \ln K$ we have: $\Delta G = RT \ln [(1/N_T) - 1]$.¹³ We get immediately that $N_T = [\exp(\Delta G/RT) + 1]^{-1}$, so that the correct equation for isotropic shifts, when an equilibrium is involved, is

$$\frac{\Delta H_i}{H} = -\frac{A_i \gamma_e g \beta S(S+1)}{2S \gamma_H 3kT} [\exp(\Delta G/RT) + 1]^{-1} \quad (4)$$

Furthermore, the equation given^{6,8} for the molar magnetic susceptibility of these systems

$$\chi_M = \frac{2g^2 N \beta^2}{3kT} [1 + 1/3 \exp(\Delta G/RT)]^{-1} \quad (5)$$

and the corollary equation^{6,8,10,11} for the free energy change in terms of the measured effective magnetic moment values, μ_{eff}

$$\Delta G = RT \ln 3 \left[\frac{\mu_{\infty}^2}{\mu_{\text{eff}}^2} - 1 \right] \quad (6)$$

are incorrect and should in fact be, respectively

$$\chi_M = \frac{2g^2 N \beta^2}{3kT} [\exp(\Delta G/RT) + 1]^{-1} \quad (7)$$

and

$$\Delta G = RT \ln \left[\frac{\mu_{\infty}^2}{\mu_{\text{eff}}^2} - 1 \right] \quad (8)$$

The error no doubt arose from a misapplication of the formula¹⁴ for the magnetic susceptibility of a substance which has a singlet ground state and a thermally accessible triplet state separated from the ground state by an energy J . The molar susceptibility of such a system is correctly given by

$$\chi_M = \frac{2g^2 N \beta^2}{3kT} [1 + 1/3 \exp(J/kT)]^{-1} \quad (9)$$

However, it is not permissible to replace the energy quantity J by a free energy ΔG , while retaining the degeneracy factor $1/3$. The degeneracy factor is embodied

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(13) The analogous eq. 5 of ref. 6 is in error.

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