To calculate the ratio, we have used intensity formulas for Zeeman components in a Russell-Saunders scheme.

We have seen no resonance of the 3250A and 3536A lines of Cd II. Possibly, the polarization of the ${}^2D_{3/2}$ state of Cd II is too low.

With our detection methods we have not been able to observe the 6215A and 7479A lines of Zn II.

We believe that this is the first time that magnetic dipole resonance of free ions has been observed.

The observation of the magnetic resonance of atomic ions might, possibly, be of use for the determination of local magnetic fields in a plasma containing these ions as impurities.

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ANOMALOUS LOSS OF RESOLUTION OF PARAMAGNETIC RESONANCE HYPERFINE STRUCTURE IN LIQUIDS*

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Hausser[1] has recently observed a remarkable temperature dependence in the resolution of hyperfine splittings for paramagnetic molecules in liquid solution. Typically, he finds that increasing temperature from a point of high solvent viscosity ultimately brings out a well-resolved structure which surprisingly blurs and disappears at still higher temperatures. We propose here an explanation for the anomalous loss of structure.

Invoking theories of motional narrowing,[2-4] one can understand the initial appearance of structure as temperature increases by recognizing that the correlation time for molecular re-orientation,

$$\tau_C = 4\pi\mu a^3/(3kT), \qquad (1)$$

decreases until its reciprocal is comparable to the frequency magnitude of anisotropic hyperfine splittings, which are then averaged out by the molecular tumbling.[5] The characteristic isotropic hyperfine pattern then emerges. On this supposition, Eq. (1), together with the solvent viscosity μ appropriate to the lowest temperature at which structure appears and $(2\pi\tau_C)^{-1}$ comparable to the expected anisotropic coupling, yields reasonable values of a, the equivalent Stokes' law spherical radius for the free-radical molecule in solution.

The motional narrowing theory, which predicts for decreasing τ_C a monotonic decrease of each hyperfine component's width (including static and dynamic contributions[4]), cannot explain the loss of hyperfine resolution with further temperature increase. We suggest instead that this phenomenon arises from smearing out of the isotropic hyperfine structure by the exchange interaction, as in the concentration dependence of hyperfine resolution in solutions of diphenyl picryl hydrazyl (DPPH).[6]

We suppose the following model. A paramagnetic solute molecule in moderately low concentration swims through the solvent ultimately into the vicinity of a like solute molecule. If the two approach closely enough for appreciable overlap of their unpaired electron distributions, the exchange interaction $-2J\vec{S}_1\cdot\vec{S}_2-$is "turned on." Assuming that the exchange integral J exceeds the Zeeman interaction $g\beta H_0$ with the external magnetic field, the electron spins will undergo appreciable relative precession about each other, provided they hover long enough in close interaction. The phases of their Larmor precessions about H_0 will have been interrupted, and when the interruption rate is comparable to the width of the hyperfine components, they will be broad-

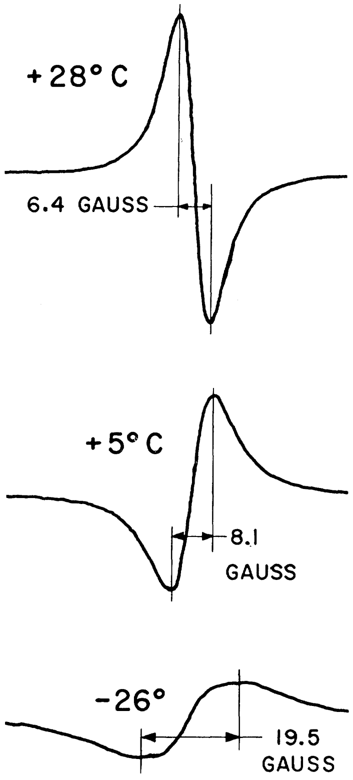

FIG. 1. Temperature dependence of exchange narrowing in 0.14*M* DPPH-toluene solution. The resonance is observed at 9.2 kMc/sec.

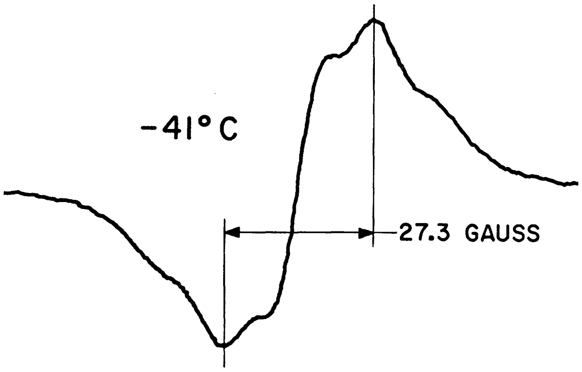

FIG. 2. Emergence of hyperfine structure in the spectrum of a 0.14*M* DPPH-toluene solution at -41°C.

ened and the structure will begin to blur.

Figures 1 and 2 show spectra observed at 9.2 kMc/sec in a 0.14*M* solution of DPPH in toluene. It is clear that further temperature increases above -41°C, where the structure has already begun to smear out, lead to further narrowing even of the single resonance, as observed with exchange narrowing when concentration increases.[6,7]

Our analysis of this model is crude but perhaps instructive. If we suppose the diffusion of the free-radical solute molecule to take place in steps of rms length λ from one molecular environment to another at an average rate of n steps per second, the diffusion constant D is [8]

$$D = n\lambda^2/6. \tag{2}$$

If the average number of new molecular neighbors encountered with each step is z, the number of molecules encountered per unit time is zn. A fraction N_r/N_S of these are other solute molecules, where N_r and N_S are the volume concentrations of free-radical and solvent molecules. Therefore, the rate at which a paramagnetic molecule encounters another one is znN_r/N_S. If p is the probability that appreciable spin precessions about each other occur upon such encounters, the frequency of phase-interrupting collisions is

$$f_e = znN_r p/N_S = 6zN_r Dp/(\lambda^2 N_S). \tag{3}$$

Because N_r will be fairly small, N_S^{-1} may be replaced by the solute molecular volume $(4\pi/3)a_S^3$, a_S being the equivalent spherical radius of a solute molecule. D is related to the viscosity μ through the Stokes-Einstein relation,

$$D = kT/(6\pi a_r \mu). \tag{4}$$

Then,

$$f_e = \frac{N_r kT}{\mu}\left[\frac{4zpa_S^3}{3\lambda^2 a_r}\right]. \tag{5}$$

The dimensionless bracket involves ratios of quantities comparable to molecular radii. The probability p depends upon the time t_i of interaction between paramagnetic molecules, which must be comparable to the period $\hbar/J$ of mutual spin precession about each other if appreciable mutual precession and thus phase interruption of the Larmor precession are to occur. Presumably, $t_i \approx 1/n$. For $\mu = 10^{-2}$ poise, Eqs. (2) and (4) with reasonable values of λ and a_r yield $1/n$ in the range of 10^{-10} to 10^{-11} sec, which is comparable to $\hbar/J$ during the interaction. (J is estimated for close interaction distance from exchange narrowing in crystalline DPPH.) We can only guess that p is not very small and that the bracket in Eq. (5) should be near unity.

For DPPH the splitting to be obscured is about $\Delta\nu = 30$ Mc/sec, and a component width half that, corresponding to $f_e \approx 1.5\times10^7$, would effectively remove structure. From Figs. 1 and 2, this circumstance nearly obtains at -41°C in 0.14*M* solution. Since $\mu = 1.5\times10^{-2}$ poise, the bracket becomes

$$[\ ] = \mu f_e/(N_\gamma kT) \approx 10^{-1}.$$

The same solution's spectrum at +28°C should again yield the bracket. The exchange-narrowing theory[4] relates the observed width $\delta\nu$ of the single narrowed line to the second moment $\langle\Delta\nu^2\rangle$ of the hyperfine pattern and f_e as

$$\delta\nu \approx \langle\Delta\nu^2\rangle/f_e\ . \quad (6)$$

The value of $\delta\nu$ corresponding to 6.4 gauss and $\langle\Delta\nu^2\rangle$ corresponding to the measured[9] 180 gauss^2 thus fix f_e as about 8×10^7 sec^{-1}. The viscosity of toluene at 28°C and Eq. (5) then yield about 10^{-1} again for the bracket.

Hausser's data on $10^{-3}M$ α,γ-bisdiphenylene β-phenyl allyl in ethanol at 0°C give the bracket a value 2 for that system. Considering the crudeness of our model, including its spherical approximation for aromatic molecules, the bracket values lend credence to the suggested mechanism. If less complicated systems can be found with which to test these ideas, they might merit theoretical refinement.

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DISSOCIATION OF H_2^+ IONS BY HYDROGEN

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Interest in the dissociation of H_2^+ ions by hydrogen and other gases has been stimulated recently by the injection problems of thermonuclear devices and accelerators. In particular, the injection current required for a thermonuclear experiment such as OGRA is critically dependent on the cross section for this process, yet there is a discrepancy of a factor 3 between the values obtained by different workers. In some of this work, the importance of the charge exchange cross section and the cross section for double proton production at energies of about 100 kev does not appear to have been realized and none of the techniques so far used has enabled all these processes to be resolved.

In the present work, the cross sections for the four processes contributing significantly to loss of the H_2^+ ions are separately determined. These processes are:

$$H_2^+ \rightarrow H^0 + H^+, \quad (1)$$

$$H_2^+ \rightarrow H^+ + H^+ + e, \quad (2)$$

$$H_2^+ \rightarrow H^0 + H^0 - e, \quad (3)$$

$$H_2^+ \rightarrow H_2{}^0 - e, \quad (4)$$

with cross sections σ_1 to σ_4, respectively.

H_2^+ ions accelerated in a 3-Mv Van de Graaff machine were passed through a differentially pumped gas chamber. The beams of neutral particles, H_2^+ ions, and protons were then separated by a magnetic field and detected by 1-in. CsI crystals mounted on photomultiplier tubes. The entry of two protons simultaneously into the crystal from process (2) was recorded as a pulse of double the height of that from a single proton [process (1)]. Similarly processes (3) and (4) produced pulses in the neutral particle counter of double the height of those due to neutral particles from process (1). By differential discrimination of the output from the crystals it was possible to separate very clearly double from single events and hence the partial cross sections for the processes (1), (2), and (3) + (4).