

EXCHANGE-ORDERING AND OBSERVATION OF FORBIDDEN SPIN RESONANCE TRANSITIONS IN CRYSTALLINE ORGANIC RADICALS*

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In examining the electron spin resonance spectrum of polycrystalline samples of the organic free radicals picryl-*n*-amino carbazyl (PAC),¹ 1-3-bisdiphenylene-2-phenyl allyl (BDPA),² and Wurster's blue perchlorate (WB)¹ at low temperatures and low frequencies, we have observed a resonance at $g=4$. We believe that this line may arise from a "forbidden" transition made possible by the dipolar interaction between spins. In the frequency range from 20 Mc/sec to 200 Mc/sec the g value is four to within 3% independent of temperature. At fixed temperature the ratio of the peak intensity of the $g=4$ resonance absorption to that of the $g=2$ absorption decreases with the increasing frequency. At fixed frequency the intensity ratio decreases with increasing temperature and vanishes above a temperature T^* characteristic of the particular free radical (see Figs. 1 and 2). The intensity ratio decreases with increasing values of the radio-frequency power. The width of the $g=4$ resonance appears to be essentially independent of temperature and is of the same order of magnitude as that of the $g=2$ resonance. In some cases there is evidence for a $g=6$ resonance in the form of a weak bump on the low-field side of the $g=4$ resonance.

Various types of measurement have shown that the electron exchange plays an important role in

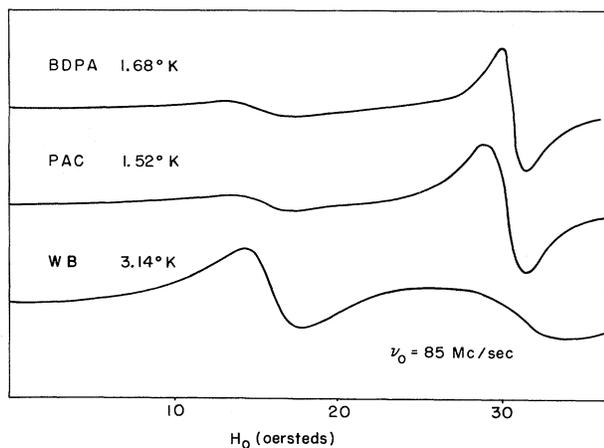


FIG. 1. Absorption spectra of BDPA, PAC, and WB in perpendicular radio-frequency and static magnetic fields. At fixed marginal oscillator frequency of 85 Mc/sec the static field, H_0 , is increased from zero.

these free radicals. Estimates of the dipolar interaction (≈ 100 oersteds) indicate that the Larmor ($g=2$) resonances are strongly exchange-narrowed. Both the resonant and static magnetic susceptibility measurements shown in Fig. 2 give further evidence of exchange and show that the exchange coupling is antiferromagnetic. In each radical the susceptibility goes through a maximum at a temperature presumably indicative of the strength of the exchange coupling. At low temperatures the resonant susceptibilities of PAC and WB again increase with a greatly reduced effective spin density. This behavior may be attributable to magnetic dilution effects.³

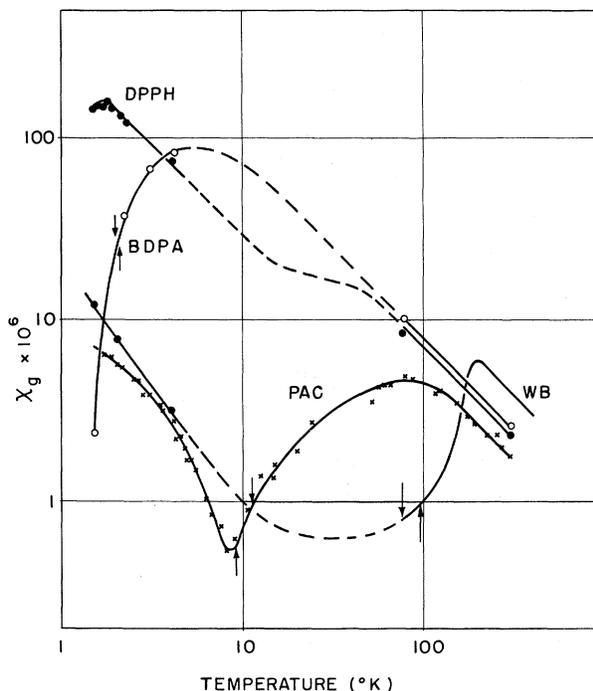


FIG. 2. Mass susceptibilities of free radicals vs temperature. The experimental points represent the intensity of the Larmor resonance at 25 Mc/sec (except WB at 10 kMc/sec). WB is reproduced from static susceptibility measurements by N. Elliott and M. Wolfsberg [Phys. Rev. **91**, 435(A) (1953)]. DPPH is extrapolated in the $4^\circ\text{K} - 77^\circ\text{K}$ region with reference to L. S. Singer and E. G. Spencer [J. Chem. Phys. **21**, 939 (1953)]. Arrows below curves indicate temperatures below which we have observed $g=4$ resonances. Arrows above curves indicate position of $g=2$ linewidth peaks.

Other evidence of exchange is provided by measurements of low-temperature specific heat, electron and proton relaxation times, and Knight shifts.⁴

It is significant that in all three radicals the maximum temperature T^* at which the $g=4$ absorption was observed falls below the peak in the susceptibility. Here the correlation time of the exchange "motion" has been sufficiently lengthened by spin ordering to broaden the Larmor line by a factor of two or more. Moreover, in BDPA at 85 Mc/sec, T^* is very near the temperature at which the width between derivative maxima of the Larmor line shows a sharp peak. Near 1.85°K, ΔH_{pp} reaches a sharp maximum several times the 300°K value, decreases rapidly, and then rises again as the temperature is lowered. The line also deviates from its normal Lorentz form in this region, the tails becoming more prominent.

From similar measurements on other free radicals picryl-*n*-amino carbazyl (PAC), Wurster's blue perchlorate (WB), and 1,1-bisdiphenyl- β -picryl hydrazyl (DPPH), it appears that the susceptibility maximum, Larmor linewidth peak, $g=4$ resonance pattern is common to all these substances. PAC exhibits a Larmor resonance intensity maximum near 70°K, a linewidth maximum near 12°K, and a $g=4$ resonance below 12°K. For WB the static and resonant susceptibility maximum, linewidth peak, and first appearance of $g=4$ resonance occur near 180°K, 80°K, and 100°K, respectively. In DPPH the resonance intensity maximum⁵ occurs near 1.8°K. No linewidth peak or $g=4$ resonance was observed, presumably because the temperature was not low enough.

Resonances at $H_0/2$ have been observed before in copper acetate by Lancaster and Gordy, in cobalt ammonium sulfate by Bleaney and Ingram, and in iron and aluminum alums by Ubbink, Poullis, and Gorter⁶ but no correlation with susceptibility was made. The static susceptibility of copper acetate does decrease rapidly below 300°K. Bleaney and Bowers⁷ attribute these properties to pairs of exchange-coupled spins giving singlet and triplet levels. J is negative so that the singlet is the lower state. The resonance at $H_0/2$ is due to $\Delta M=2$ transitions within the triplet levels made possible by the crystalline electric field interaction. This model predicts a temperature dependence for the $g=4$ resonance intensity which is opposite to that which we observe in the free radicals. Moreover,

the predicted susceptibility peak is not sharp enough to fit the data.

The occurrence of resonances at fields harmonically related to the Larmor resonance field suggest the "forbidden" dipolar transitions discussed by Van Vleck.⁸ However, the electron dipolar interactions in these free radicals is much too large to be regarded as a small perturbation on the Zeeman energy at the frequencies employed. Nevertheless, a perturbation method may be employed under the assumption that electron exchange averages the dipolar coupling, leaving a small secular interaction proportional to the exchange correlation time τ_e . On this model the appearance of the $g=4$ transition is expected only at low temperatures where linewidth and susceptibility data indicate that the exchange correlation time has become long. A proper theoretical treatment following Kubo and Tomita's general theory⁹ is required for a detailed explanation of the effects of exchange in the width, intensity, and saturation properties of the $g=4$ resonance.¹⁰

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⁵C. Jeffries of the University of California has observed a rapid decrease in the X-band absorption intensity of DPPH near 1.1°K (private communication).

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¹⁰A. Wright has indicated that if the external field H_0 is much larger than the dipolar and exchange fields, the effect of exchange is to broaden the $g=4$ resonance [*Phys. Rev.* **76**, 1826 (1949)].