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Exchange Effects in Alkali Ozonates*

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Resonance absorption has been observed in polycrystalline samples of potassium and cesium ozonate. The absorptions are characterized by nearly free electron spin g values with line widths ranging from 26 to 49 oersteds. Analysis of line shapes based on the Anderson-Weiss model for exchange interaction between equivalent magnetic ions and calculations of line shape moment ratios based on the Van Vleck theory, strongly suggest exchange interaction narrowing. Values of exchange frequencies for potassium and cesium ozonate are estimated to be 6×10^{11} rad sec^{-1} and 3×10^{11} rad sec^{-1}, respectively.

IN the absence of exchange interactions, which is the case for dilute paramagnetic salts and nuclear paramagnetism, the Gaussian function becomes a fair approximation to magnetic resonance absorption line shapes whose broadening is due principally to dipole-dipole interactions.[1,2] For such interactions, the mean square width of resonance absorption lines is given by[2]

$$\langle\Delta H\rangle^2=\tfrac{3}{4}S(S+1)g^2\beta^2\sum_k\left[\frac{1-3\cos^2\theta}{r^3}\right]_{jk}^2, \qquad (1)$$

where the transitions are between magnetic levels having spin quantum number S, spectroscopic splitting factor g, and interionic distance $r_{j,k}$. For the case of undiluted paramagnetic salts, an exchange potential of the form $\sum_k J\mathbf{S}_j\cdot\mathbf{S}_k$ must be added to the interaction Hamiltonian to account for the shapes and widths of resonance absorption lines. The role of this potential, as pointed out by Gorter and Van Vleck,[3] is much the same as that of thermal motion and molecular collisions in that the rapid exchange of spins tend to diminish the coherence of dipole-dipole interactions. A consequence of this loss of coherence is the enhancement of peak absorption intensity of resonance absorption lines with an accompanying narrowing of the shape factor. A classic example of such narrowing is the resonance absorption of 1, 1-diphenyl-2-picryl hydrazl (dpph).

Another example of exchange narrowing of resonance absorptions lines has been observed in potassium ozonate and cesium ozonate which are formed by the action of ozone with the corresponding water free alkali hydroxide.[4,5] The resonance absorptions of these two compounds are characterized by g values of 2.008 and 2.006 and line widths of 26 and 49 oersteds for KO_3 and CsO_3, respectively. Figure 1 is a reproduction of the absorption signal derivative *versus* magnetic field for KO_3 taken at 78°K.

From x-ray powder diffraction data,[6] the mean distance $r_{j,k}$ between neighboring O_3^- ions in KO_3 is determined to be 4.8×10^{-8} cm. Substituting this value into Eq. (1) and averaging the factor $(1-3\cos^2\theta)^2$ over all orientations to account for the polycrystalline sample, a line width of 380 oersteds is obtained which is an order of magnitude greater than the observed width. This lack of agreement between the observed and calculated absorption line widths is interpreted to be the result of exchange interaction.

Further indication of exchange narrowing in resonance absorption lines is provided by line shape analysis. In the analysis due to Van Vleck,[1] the ratio of root mean fourth moment to root mean square moment is calculated for absorption lines broadened by dipole-dipole interactions. This ratio is found to lie between 1.16 for a box-like shape and 1.32 for the Gaussian shape. When the potential $\sum_k J\mathbf{S}_j\cdot\mathbf{S}_k$ due to exchange is added to the interaction Hamiltonian, the mean fourth moment of the absorption is found to increase while the mean second moment remains unchanged so that the ratio of moments experiences a net increase over the ratio 1.32 corresponding to dipole-dipole interaction broadening. In the two ozonate compounds, the ratio of moments have been determined to be 1.38 and 1.35 for KO_3 and CsO_3. These ratios are to be compared with the ratio 1.37 for undiluted dpph which is strongly narrowed by exchange interaction.

In the Anderson-Weiss treatment of exchange narrowing,[7] the physical picture underlying the diminution of magnetic dipole effects is given in sufficient detail to predict absorption shape factors. The shape factor for an exchange narrowed absorption line given by this treatment is that of the Lorentz damped oscillator

$$S(w,w_0)=\frac{w_{pp}^2/w_{\text{ex}}}{(w-w_0)^2+(w_{pp}^2/w_{\text{ex}})^2}, \qquad (2)$$

where w_0 is the frequency at peak absorption, w_{pp} is

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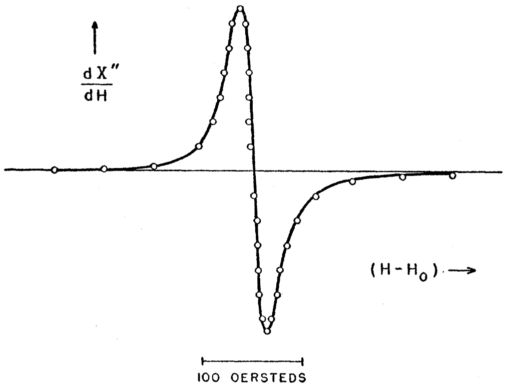

FIG. 1. Absorption signal derivative *vs* magnetic field for potassium ozonate.

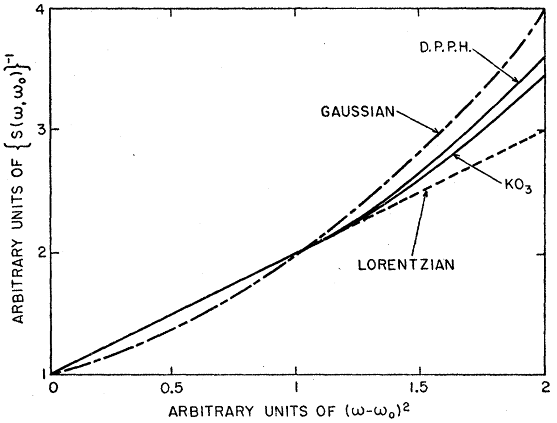

FIG. 2. Plot of reciprocal shape factor $S^{-1}(w,w_0)$ *vs* $(w-w_0)^2$ for the Gaussian shape, Lorentzian shape, dpph, and potassium ozonate.

the line width frequency due to dipole-dipole interaction, and w_{ex} is the exchange frequency which is proportional to the exchange integral J. Between points of half absorption intensity, this shape factor is predicted to accurately describe the exchange narrowed resonance absorption line. Beyond these points, however, the theory predicts the exchange narrowed line must drop off more rapidly than the Lorentz shape so as to ensure the convergence of the mean second moment which is unaffected by the exchange potential.

By inverting Eq. (2), a linear relation is established between the reciprocal of the shape factor and the square of the frequency deviation from maximum absorption. Plotting $S^{-1}(w,w_0)$ *versus* $(w-w_0)^2$ for an absorption line, a direct comparison can be made with the Lorentz damped oscillator shape function to see if the line in question is exchange narrowed. Such a plot is shown in Fig. 2 for polycrystalline KO_3 and for dpph as a comparison. A plot for CsO_3 is not given since its behavior is almost identical to that of KO_3. It will be noted that between maximum intensity and half intensity both the KO_3 and dpph absorptions follow the Lorentz damped oscillator absorption. Beyond the point of half intensity the absorptions drop off more rapidly than the Lorentz damped oscillator absorption but not as rapidly as the Gaussian function. This is in complete agreement with the behavior predicted by the Anderson-Weiss treatment.

Assuming exchange interactions to be operative in these two ozonate compounds, the values of w_{ex}/w_{pp}^2 are determined to be 2.2×10^{-9} sec^{-1} and 1.2×10^{-9} sec^{-1} for KO_3 and CsO_3, respectively. Using these values of w_{ex}/w_{pp}^2, the exchange frequencies for KO_3 and CsO_3 are determined to be 6×10^{11} rad sec^{-1} and 3×10^{11} rad sec^{-1}, respectively, by making use of the relation

$$w_{pp}^2=5\cdot1[g^2\beta^2/\hbar]^2N^2S(S+1), \qquad (3)$$

where N is the number of ozonate ions per cubic centimeter. Applying the same procedure, the exchange frequency for dpph is estimated to be 5.6×10^{11} rad sec^{-1} which is in fair agreement with 6.4×10^{11} rad sec^{-1} obtained by Bruin and Bruin.[8]

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