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The Mechanism of ESR Relaxation in Peroxylamine Disulfonate Ion $\cdot ON(SO_3)_2^{2-}$

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The mechanism of ESR relaxation in $\cdot ON(SO_3)_2^{2-}$ is discussed. As the line width in an aqueous solution is plotted against the concentration, it is almost concentration independent in the range lower than 7×10^{-3} mol/*l*, but the dependence increases in the higher range. Powles and Moseley showed that the anisotropy of the *g*-value contributes to the line width in the lower concentration range, but the line width in the higher-concentration range, which is investigated in the present investigation, can not be accounted for by the *g*-tensor anisotropy. Hence, it is supposed that electron spin exchange or nuclear quadrupole interaction contributes in the higher-concentration range. The latter can, however, be eliminated by the line width measurement in a deuterium measurement in a deuterium oxide solution, and so it may be concluded that electron spin exchange is the main contribution to the line width in the higher-concentration range. This is in accordance with the proposal of Jones. Furthermore, we could show that, by calculation of the line shape for Bloch's equation, including exchange interactions, the exchange frequency of 5.4×10^7 sec^{-1} can give a line fitting the observed line shape for the 7.8×10^{-2} mol/*l* solution. This result can be taken as another evidence showing that the electron spin exchange is the main source of the line width in the higher-concentration range.

The widths of ESR hyperfine lines, ΔH, have attracted the interest of many investigators. For example, a very careful examination of ΔH in organic radicals has proven useful for the elucidation of molecular motion of free radicals.¹⁾ Rogers and Pake²⁾ observed the dependence of ΔH on the nuclear quantum number, m_I; McConell interpreted this phenomena in terms of a model where the electron spin which carries anisotropy relaxes with the hyperfine field.³⁾ This model worked nicely and excited more detailed investigations.⁴⁾ For example, Powles and Moseley,^4a)^ working on the peroxylamine disulfonate ion ($\cdot ON(SO_3)_2^{2-}$) in mixed solvents of glycerine and water, noted viscosity dependence of the each hyperfine line width. Although this study presented several interesting features, they are not suitable for the general discussion of relaxation mechanisms, for the chemical surroundings of the paramagnetic ion change with the change in the concentration of glycerine. Kivelson classified the mechanisms of the spin relaxation in detail, and one of the present authors applied his results to the case of an aqueous solution of cupric ions. In the latter investigation, the relaxation of cupric ions in a dilute aqueous solution was found to be determined mainly by the perturbation of the spin-orbit interaction of isotropically-hydrated $[Cu(H_2O)_6]^{2+}$ ions and, in higher-concentration regions, by anisotropies of the *g*-values and by electron spin exchange.⁵⁾ A similar conclusion has also been obtained experimentally with respect to the Ti(III) ion.⁶⁾ Jones has studied an aqueous solution of $\cdot ON(SO_3)_2^{2-}$ and analyzed the line width, assuming that electron spin exchange is the main effect of the relaxation.⁷⁾

Besides the electron spin exchange and the spin-orbit interaction, the nuclear quadrupole effect is a possible source of relaxation. Kubo presented a theoretical treatment of the contribution of the quadrupole effect to the nuclear spin relaxation, and much experimental evidence has been put forward with regard to this mechanism.⁸,⁹⁾ As this evidence

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is related to NMR, we have become interested in investigating to what extent, if any, this effect is related to the relaxation of the electron system which couples with a nucleus carrying quadrupole moment. We chose peroxylamine disulfonate ion $\cdot ON(SO_3)_2^{2-}$ as the sample, because it reveals a well-resolved hyperfine interaction with nitrogen,[10] and we can find pertinent results on such related compounds as di-tertiary butyl nitroxide (DTBN).[11] This paper will show that the contribution of the quadrupole interaction is small and that the line width is, as has been noted by Jones, dominated by the electron spin exchange.

Experimental

Spectra were measured on a Japan Electron Optics X-band ESR spectrometer, Model JES-3BS-X, with 100 kHz/sec field modulation. The modulation amplitude is 30 mgauss, and the microwave power is kept low so as not to saturate the signal. All measurements were carried out at room temperature (20°C).

Solutions of the peroxylamine disulfonate ion $\cdot ON(SO_3)_2^{2-}$ were made by dissolving Fremy's salt in a 0.1 N aqueous solution of sodium carbonate. The concentration of the sample was determined by optical method, taking the molar extinction coefficient of this compound as $\varepsilon=20.8$ (at 545 mμ).[12] Water and deuterium oxide were used as solvents. The ESR intensities of the sample solutions were found constant over several hours, hence, we assume that they are stable over the period of measurement. The concentration of the sample solutions varied from 5×10^{-4} to 8×10^{-2} mol/*l*. No degassing procedure was carried out.

For the calculation of the line shapes, the RA-5 electronic digital computer made by Japan Electron Optics Company was used.

Results and Discussion

The width was measured as the separation of the maximum slope points of the derivatives of the absorption spectrum, which can be shown as a function of the concentration shown in Fig. 1. The results in Fig. 1 suggest that, the lower concentration range, the width is almost independent of the concentration, having a value of 0.24 gauss. It is also found that the width is the same in both H_2O and D_2O, which have different viscosities 1.0 and 1.2 cps respectively. These findings eliminate the spin-spin dipole interaction, the quadrupole interaction, and the anisotrpy due to the nuclear quantum number as the dominant sources of the electron spin relaxation, because if the spin-spin interaction is working as the dominant factor, the line width should be concentration dependent, while if the quadrupolar interaction or the anisotropy due to the nuclear quantum number works, then the width should be viscosity dependent. Using the B. P. P.[13] model, the dipolar line width is evaluated as 0.18 gauss for the solution of 0.01 mol/*l*. This is about two-thirds of the observed line width of 0.3 gauss. Hence, we assume that complexity exists in the system; *i. e.*, the spin-orbit interaction or the electron spin exchange interaction contributes to the relaxation as well as the dipolar interactions, and also that the apparent features of the concentration dependence can not be simply interpreted. This can be presented in a different way by manipulating the line shape. We construct an absorption line of three hyperfine components, each of a Lorentzian shape and of a definite width, the hyperfine components being separated from each other by 13 gauss. The calculated line is as shown in Fig. 2, where the line width of the hyperfine component is given two values, 2.9 gauss and 4 gauss. It may be seen in the figure that the outer peak is higher than the central peak; moreover, the line width is broader than the latter, contrary to the experimental observations. In the latter, the

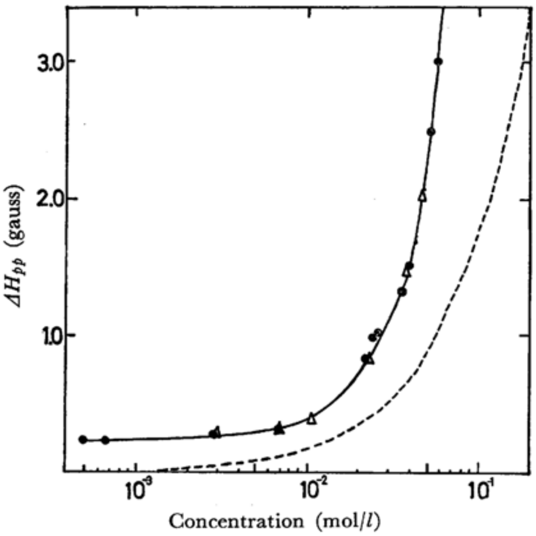

Fig. 1. Concentration dependence of line width in water (•) and in deuterium oxide (△). Dotted line is line width calculated on the bases of intermolcular dipole interaction.

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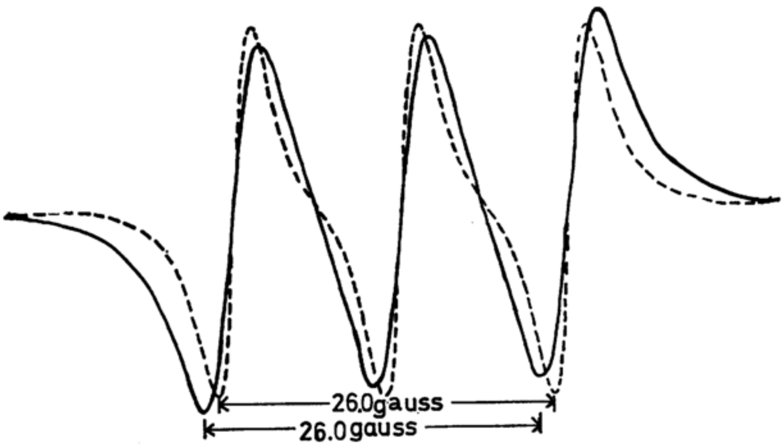

Fig. 2. Calculated line shape with the assumption of equal line width of each hyperfine component separated by 13 gauss from each other. Dotted curve refers to the line of 2.9 gauss of ΔH_{pp}, the peak to peak line width of the hyperfine component, and the full line to that of 4.0 gauss of ΔH_{pp}.

central line width is slightly narrower in the range of about 6×10^{-2} mol/*l*, and then it becomes broader in the higher concentration range ($\sim 1\times 10^{-1}$ mol/*l*). This suggests that the line shape could not be analyzed simply by the overlap of Lorentzian hyperfine lines of the same line width. This investigation supports that of Kivelson.11) As to the nonequivalence of the hyperfine component, the line width in this system can be produced by the spin exchange mechanism. We manipulate the line shape on the basis of a modification of Bloch's equation which carries an exchange interaction term by which we can evaluate the magnitude of this interaction roughly. We write first modifications of the Bloch equation for three sites,14) assuming that the fraction of each spin state is equal and that the spin state are mixed through electron exchange. The imaginary part, v, of the total magnetization, M, is given below;

$$v=\frac{M(PZ+RM)}{P^2+R^2}$$

where;

$$P=3(\Delta\nu+4\tau\Delta\nu/T_2+3\tau^2\Delta\nu/T_2{}^2-\tau^2\Delta\nu^3+\Delta\nu\tau^2\delta\nu^2)$$

$$R=3/T_2+6\tau/T_2{}^2-6\Delta\nu^2\tau+2\tau\delta\nu^2+3\tau^2/T_2{}^3$$
$$-9\Delta\nu^2\tau^2/T_2+3\tau^2\delta\nu^2/T_2$$

$$W=3+6\tau/T_2+3\tau^2/T_2{}^2-3\Delta\nu^2\tau^2+\delta\nu^2\tau^2$$

$$Z=6(\tau\Delta\nu+\Delta\nu\tau^2/T_2)$$

where T_2 refers to the spin-spin relaxation time in the absence of electron spin exchange, and where $1/\tau$ is the exchange frequency, $\delta\nu$, the coupling constant, and $\Delta\nu$, the frequency from the center.

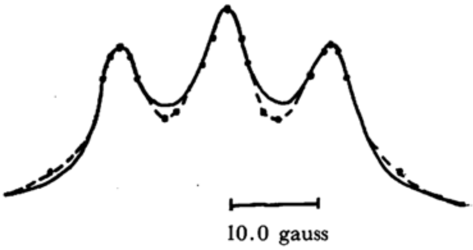

Fig. 3. —— The integrated line shape for a solution of 7.8×10^{-2} mol/*l* of $\cdot\mathrm{ON(SO_3)_2}^{2-}$.
-●- The calculated line shape for the modified Bloch's equation.

As the exchange frequency is taken as 5.4×10^7 sec^{-1}, $1/T_2$, as 0.36×10^7 sec^{-1}, and $\delta\nu$, as 3.6×10^7 sec^{-1}, the line shape is calculated to be as shown by the dotted curve in Fig. 3. It agrees fairly well with the curve observed with the solution of 7.8×10^{-2} mol/*l*, which is shown in Fig. 3 by the straight curve. Jones investigated the electron spin exchange in his study of the line width. However, the present analysis of the total line shape should be more efficient.

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