The Determination of Singlet-Triplet Separation from the Anomalous Hyperfine Structure Observed with a Radical Pair

By Hisaharu HAYASHI, Koichi ITOH and Saburo NAGAKURA
The Institute for Solid State Physics, The University of Tokyo, Azabu, Tokyo

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It has recently been found by ESR studies that radical pairs are stably trapped in the single crystals of several oximes X-irradiated at 77°K.[1-3] In particular, the radical pair, "K", of dimethylglyoxime shows an anomalous hyperfine structure; i. e., the observed central three lines among the nine hyperfine lines corresponding to the $\Delta m=\pm 1$ transitions of the radical pair are not equally spaced.[1] This can not be explained by a first-order treatment which considers only the nonequivalence of the hyperfine tensors of two interacting radicals.[1] We have attempted to interpret the anomaly by considering the mixing between the singlet and triplet states through the hyperfine interaction and the electronic Zeeman term.

The Hamiltonian for the system under consideration consists of the electronic Coulomb, electronic Zeeman, electron spin-spin interaction, hyperfine interaction and nuclear Zeeman terms. The effective energy difference due to the first term between the singlet and triplet states is expressed by the exchange term, $-2\,J\mathbf{s}_1\mathbf{s}_2$, where J is the exchange integral. On the assumptions that the second term is much larger than the third and fourth terms, and that the fourth term is much larger than the fifth term, the energy level, $E(m, M^a, M^b)$, of the triplet state can easily be evaluated by the aid of the second-order perturbation. In this case, the interacting nucleus is only one nitrogen ($I=1$) for each radical.[1,4] The two radical sites are designated as a and b, and m and M^p are the z-components of the electron spin of the triplet state and of the nitrogen nuclear spin on the p site respectively. Only the allowed transitions of $\Delta m=\pm 1$ and $\Delta M^a=\Delta M^b=0$ are considered.

Since the anomaly is noticeable for the hyperfine lines due to $M^a+M^b=0$, the deviation, $\delta_\pm$, defined below should be considered,

$$\delta_\pm=\{\Delta E_\pm(1,\ -1)-\Delta E_\pm(-1,1)\}/2-\Delta E_\pm(0,0) \tag{1}$$

where the transition energies, $\Delta E_+(M^a, M^b)$ and $\Delta E_-(M^a,M^b)$, are represented by $E(1, M^a, M^b)-E(0, M^a, M^b)$ and $E(0, M^a, M^b)-E(-1, M^a, M^b)$ respectively. When the perturbation is applied to the second order, $\delta\pm$ is given as follows:

$$\delta_\pm=\pm A/(2J\mp g\beta H-d/6)\pm B/(2J+d/3)-C_\pm \tag{2}$$

where:

$$A=\{A^a{}_{xx}{}^2+2A^a{}_{xy}{}^2+A^a{}_{yy}{}^2+A^b{}_{xx}{}^2+2A^b{}_{xy}{}^2+A^b{}_{yy}{}^2-2(A^a{}_{xz}+A^b{}_{xz})^2-2(A^a{}_{yz}+A^b{}_{yz})^2\}/16 \tag{3}$$

$$B=\{2(A^a{}_{zz}+A^b{}_{zz})^2-A^a{}_{zx}{}^2-A^a{}_{zy}{}^2-A^b{}_{zx}{}^2-A^b{}_{zy}{}^2\}/8 \tag{4}$$

$$C_\pm=(A+A^a{}_{xz}A^b{}_{zx}/2+A^a{}_{yz}A^b{}_{yz}/2)\times\{2/(g\beta H\pm d/2)-1/(g\beta H\mp d/2)\} \tag{5}$$

The laboratory coordinates are taken as x, y and z, and the external magnetic field is parallel to the z-axis. $A^p{}_{ij}$ is the ij-element of the hyperfine tensor for the p site, g is equal to $(g^a{}_{zz}+g^b{}_{zz})/2$, and d is represented by $D(3\cos^2\Theta-1)/3$, where Θ is the angle between the axis of symmetry and the external magnetic field. D may be of the negative sign, since the odd electron is localized on the =N–O· group of the oxime[1,4] and the distance between the groups of the interactng radicals is very large (5.6 Å).[1] E is negligibly small in this case[1]. The first and second terms of Eq. 2 arise from the mixing of the singlet state with the $m=\pm 1$ and $m=0$ states of the triplet state respectively. On the other hand, the third term is brought about by the mixing within the triplet state.

From the $\delta_\pm$ values measured with four crystal orientations at the X-band, J was evaluated as $-(1.24\pm 0.12)\times 10^{-5}$ eV. In this case the second term of Eq. 2 was found to be predominant. Thus, the system is proved to be a ground-state singlet.

It may be emphasized that magnitudes and signs of J as small as 10^{-5} eV. can be determined by the present method. Details will be published elsewhere.

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1) Y. Kurita, *J. Chem. Phys.*, **42**, 3926 (1964); *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **85**, 833 (1964). $D_\parallel$ and $D_\perp$ in these papers are to be negative and positive, respectively.
2) H. Hayashi, K. Itoh and S. Nagakura, to be published.
3) Y. Kurita, private communication.
4) I. Miyagawa and W. Gordy, *J. Chem. Phys.* **30**, 1590).