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Chimica-Fisica. — *Heisenberg exchange between unlike free radicals.*

Nota di GIORGIO MORO (*), PIER LUIGI NORDIO (*) e ULDERICO SEGRE (*), presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — Il formalismo della matrice densità usato in precedenza per tener conto dell'effetto dello scambio di Heisenberg sullo spettro ESR di soluzioni, è stato esteso al caso di più specie radicaliche tra loro interagenti. Come esempio, vien discusso il caso di una molecola variamente sostituita con specie isotopiche.

I. INTRODUCTION

The Heisenberg exchange interaction constitutes the most important spin relaxation mechanism in relatively concentrated solution of free radicals, by far outdoing the intermolecular magnetic dipole interactions. The effect of the Heisenberg exchange on the ESR spectra in solids has been known for many years, but the first quantitative description of the phenomenon in solution must be ascribed to Ruth Lynden-Bell [1], even if she focused her attention on a somewhat different physical context.

Freed [2] later reformulated the problem, emphasizing the analogies with the theoretical treatments formerly derived to account for the effect of the chemical exchange [3].

The powerful spin relaxing ability of the Heisenberg exchange interaction is often exploited to allow the detection of NMR spectra of paramagnetic system [4]. In such cases, it may happen that a particular spin system is relaxed by means of a different paramagnetic species. This fact motivated our investigation of the effects of the Heisenberg exchange in mixed solutions of free radicals.

II. THEORY

Following the Lynden-Bell treatment, we shall start with the equations of motion of the density matrix for any single radical p ("monomer") and any radical pair pq ("dimer"):

$$i\,\frac{d\rho^p}{dt} = [\mathcal{H}^p, \rho^p] + i\left(\frac{d\rho^p}{dt}\right)_{ex} \tag{1 a}$$

$$i\,\frac{d\sigma^{pq}}{dt} = [\mathcal{H}^{pq}, \sigma^{pq}] + i\left(\frac{d\sigma^{pq}}{dt}\right)_{ex}. \tag{1 b}$$

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In these expressions $\mathscr{H}^p$ is the Hamiltonian for the p-th radical species, which in the frame rotating with angular velocity ω has the form:

$$\mathscr{H}^p = \mathscr{H}^p_0 + \mathscr{H}^p_1 = (\omega^p_0 - \omega)\, S^p_z + \sum_i a^p_i\, I^p_{zi}\, S^p_z + \omega^p_1\, S^p_x \tag{2}$$

$$\omega^p_k = \gamma^p\, B_k \qquad k = 0\,,\, 1$$

whereas $\mathscr{H}^{pq}$ is the total Hamiltonian for the dimer:

$$\mathscr{H}^{pq} = \mathscr{H}^p + \mathscr{H}^q + \mathscr{H}^{pq}_J \quad , \quad \mathscr{H}^{pq}_J = J^{pq}(r)\, \mathbf{S}^p \cdot \mathbf{S}^q . \tag{3}$$

The exchange integral $J^{pq}(r)$ is treated as a function which assumes the value J^{pq} for $r = d^{pq}$ and zero for $r > d^{pq}$, d^{pq} being the distance of closest approach between the radical moieties. Under this assumption, the time dependence of the density matrices is determined by the translational diffusion of the molecules. On the basis of the kinetic equations for bimolecular processes, one can write [1, 5]:

$$\left(\frac{d\rho^p}{dt}\right)_{ex} = \sum_q \frac{1 + \delta_{pq}}{\tau^{pq}_2}\, (\mathrm{Tr}_q\, \sigma^{pq} - \rho^p) \tag{4 a}$$

$$\left(\frac{d\sigma^{pq}}{dt}\right)_{ex} = \frac{1}{\tau^{pq}_1}\, (\rho^p \times \rho^q - \sigma^{pq}) \tag{4 b}$$

where Tr_q stands for the sum over the states of the other component of the dimer, $\rho^p \times \rho^q$ is the tensorial product of the matrices ρ^p and ρ^q, and

$$\tau^{pq}_1 = (1/k^{pq}_1) = \tau^{qp}_1 \tag{5}$$

$$\tau^{pq}_2 = (1/k^{pq}_2\, [Q]) \tag{6}$$

k_1, k_2 being the rate constants for the unimolecular dissociation and bimolecular association processes respectively, and [Q] the concentration of the radical q. Since the concentrations of the dimers are very small under normal experimental conditions ($\tau_1/\tau_2 \ll 1$), [Q] practically corresponds to the stoichiometric concentration of the radical. For this reason, only the monomer species give rise to the spectrum, and therefore the exchange energy terms with the radiofrequency field B_1 can be neglected in the dimer Hamiltonian of eq. (3). For molecules with an approximately spherical shape, the expressions for the rate constants are [5]:

$$k^{pq}_1 = \frac{3\,(D^p + D^q)\, f^{pq}}{(d^{pq})^2}\, \exp\,[U^{pq}\,(d^{pq})/kT] \tag{7}$$

$$k^{pq}_2 = \frac{4\,\pi d^{pq}\,(D^p + D^q)}{(1 + \delta_{pq})\, 1000}\, f^{pq}\, \mathscr{N} \tag{8}$$

where D^p is the diffusion coefficient for the p-radical in the solution, $U^{pq}(r)$ is the interaction potential for a radical pair, $\mathcal{N}$ the Avogadro number and f^{pq} is defined as

$$[f^{(pq)}]^{-1} = d^{pq} \int_{d^{pq}}^{\infty} \exp\,[U^{pq}(r)/kT]\, \frac{dr}{r^2}\,. \tag{9}$$

If degenerate transitions are not present, the monomer density matrix elements can be expressed on the basis of the eigenstates of $\mathcal{H}_0^p$, that shall be denoted by $|m\,,\,M\rangle \equiv |m\rangle\, \Pi_i\, |M_i^p\rangle$. The relevant elements to be calculated are those appearing in the expression for the absorbed power as a function of frequency, which defines the spectral shape:

$$P(\omega) = -\mathcal{N}\hbar\omega \sum_p \omega_1^p\,[P]\, \mathrm{Im} \sum_M \langle \alpha M\,|\,\rho^p\,|\,\beta M\rangle\,. \tag{10}$$

Under stationary conditions and the high temperature approximation, after calculation of the necessary matrix elements of σ^{pq} and their substitution into the equation for ρ^p, one ends up with the following system of linear algebraic equations in the unknowns $\langle \alpha M\,|\,\rho^p\,|\,\beta M\rangle$:

$$\begin{aligned}
(11)\quad & \left\{\sum_q \frac{1+\delta_{pq}}{\tau_2^{pq}} \left[1 - \sum_{M'} F_{pq}(M\,,\,M')\right] + i\left(\omega_0^p - \omega + \sum_i a_i^p\, M_i^p\right)\right\} \times \\
& \times \langle \alpha M\,|\,\rho^p\,|\,\beta M\rangle - i \sum_q \frac{1+\delta_{pq}}{2\,\tau_2^{pq}}\, \tau_1^{pq}\, J^{pq} \sum_{M'} G_{pq}(M\,,\,M')\, \langle \alpha M'\,|\,\rho^q\,|\,\beta M'\rangle = \\
& = -\frac{i\hbar\omega_1^p\,\omega_0^p}{2\,N_p\,kT} \equiv \eta_p/N_p\,.
\end{aligned}$$

$$\begin{aligned}
(12)\quad & F_{pq}(M\,,\,M') = [K_{qp}^{+}(M')/L_{pq}^{+}(M\,,\,M') + K_{qp}^{-}(M')/L_{pq}^{-}(M\,,\,M')]/2\,N_q \\
& G_{pq}(M\,,\,M') = [1/L_{pq}^{+}(M\,,\,M') - 1/L_{pq}^{-}(M\,,\,M')]/2\,N_p \\
& K_{pq}^{\pm}(M) = 1 + i\tau_1^{pq}\left(\omega_0^p - \omega + \sum_i a_i^p\, M_i^p \pm J^{pq}/2\right) \\
& L_{pq}^{\pm}(M\,,\,M') = K_{pq}^{\pm}(M)\, K_{pq}^{\pm}(M') + (\tau_1^{pq}\, J^{pq}/2)^2.
\end{aligned}$$

N_p being the dimension of the nuclear spin space of the p-radical, i.e. $N_p = \Pi_i(2\,I_i^p + 1)$. The system of equations (11) is much simplified under two limiting circumstances which are very likely to be met with in practical cases. After defining the exchange frequency for each component of the pairs as

$$\omega^{pq} = \omega^{0pq}\,[Q] \quad , \quad \omega^{0pq} = k_2^{pq}\, \frac{(\tau_1^{pq}\, J^{pq})^2}{1 + (\tau_1^{pq}\, J^{pq})^2} \tag{13}$$

the two simplifying conditions are the following:

i) $1/\tau_1^{pq} \gg a_i^p , a_i^q$

$\omega^{pq} \ll a_i^p , a_i^q$ (slow exchange)

ii) $1/\tau_1^{pq} \gg a_i^p , a_i^q$

$J^{pq} \gg \mathcal{H}_0^p + \mathcal{H}_0^q .$

Note that the condition on τ_1^{pq} is always verified for relatively small molecules in non-viscous solvents.

One obtains in both cases:

$$\left[\sum_q (1 + \delta_{pq})\, \omega^{pq}/2 + i\left(\omega_0^p - \omega + \sum_i a_i^p \mathrm{M}_i^p\right)\right] (\alpha\mathrm{M} \mid \rho^p \mid \beta\mathrm{M}) - \tag{14}$$

$$- (1/\mathrm{N}_p) \sum_q (1 + \delta_{pq})\, \omega^{pq} \sum_{\mathrm{M}'} (\alpha\mathrm{M}' \mid \rho^q \mid \beta\mathrm{M}') = \eta_p/\mathrm{N}_p .$$

Let us consider $\sqrt{\mathrm{N}_p}\, (\alpha\mathrm{M} \mid \rho^p \mid \beta\mathrm{M})$ as the component X_j of a column vector **X**, in such a way that each value of the index $j \left(= 1 , \cdots \sum_p \mathrm{N}_p\right)$ corresponds to a definite pair (p , M). Then eq. (14) can be rewritten in matrix form [6].

$$[i\,(\omega_0 - \omega)\, \mathbf{I} + \mathbf{U}]\, \mathbf{X} = \mathbf{Y} \tag{15}$$

where **I** is the unity matrix, ω_0 is the average of the ω_0^p, which in general will be not very different, and

$$\mathrm{U}_{jk} = - \frac{\omega^{pq}}{2\sqrt{\mathrm{N}_p \mathrm{N}_q}} + \delta_{pq} \left\{ - \frac{\omega^{pp}}{2\,\mathrm{N}_p} + \right. \tag{16}$$

$$\left. + \delta_{\mathrm{MM}'} \left[\sum_{q'} \frac{1 + \delta_{pq'}}{2}\, \omega^{pq'} + i \left(\omega_0^p - \omega_0 + \sum_i a_i^p \mathrm{M}_i^p \right) \right] \right\}$$

$$\mathrm{Y}_j = \eta_p/\sqrt{\mathrm{N}_p} \qquad (p , \mathrm{M}) \rightarrow j \quad , \quad (q , \mathrm{M}') \rightarrow k .$$

The symmetric matrix **U** can be diagonalized with an orthogonal transformation **T**, and the solution of eq. (15) is given by

$$\mathbf{X}(\omega) = \mathbf{T}\, [\mathbf{\Lambda} + i\,(\omega_0 - \omega)\, \mathbf{I}]^{-1}\, \widetilde{\mathbf{T}}\, \mathbf{Y} \tag{17}$$

with $\mathbf{\Lambda} = \widetilde{\mathbf{T}}\, \mathbf{U}\, \mathbf{T}$. The diagonalization is performed only once, then ω is varied to obtain $\mathrm{X}_j(\omega)$, and the lineshape is calculated through eq. (10). In the case of slow exchange, a first order approximation solution can be obtained by considering only the diagonal terms of the **U** matrix. Accordingly, we put $\mathbf{T} = \mathbf{I}$ in eq. (17), and the expression for the lineshape is:

$$(18) \qquad \mathrm{P}(\omega) = \frac{\mathcal{N}\hbar^2 \omega_1^2 \omega_0 \omega}{2kT} \sum_p \frac{[\mathrm{P}]}{\mathrm{N}_p} \sum_{\mathrm{M}} \frac{\mathrm{T}_{2p}}{1 + \left(\omega_0^p - \omega + \sum_i a_i^p \mathrm{M}_i^p\right)^2 \mathrm{T}_{2p}^2}$$

$$(19) \qquad \mathrm{T}_{2p}^{-1} = \sum_q \frac{1 + \delta_{pq}}{2} \omega^{pq} - \frac{\omega^p}{\mathrm{N}_p} .$$

To conclude this section, it is worth noting that the approximate equation system for the transition density matrix elements given in eq. (14) can be obtained from the following expression for the rate equation of the density matrix, which is the generalization of the case of several different radical species of the equation derived by Freed [2]:

$$(20) \qquad i \frac{d\rho^p}{dt} = [\mathscr{H}^p, \rho^p] + \frac{i}{2} \sum_q (1 + \delta_{pq}) \omega^{pq} [\mathrm{Tr}_q (\hat{\mathrm{P}}\rho^p \times \rho^q \hat{\mathrm{P}} - \rho^p)]$$

where $\hat{\mathrm{P}}$ is the permutation operator [2].

III. DISCUSSION

A particularly simple system to test the validity of the theory is one in which the radical species differ only by isotopic substitution. In such a case the diffusion constants D^p and the exchange integrals J^{pq} are all the same. Let us consider for example the di-*tert*-butyl ketyl radical anion. Because of the very small hyperfine coupling of the butyl protons, this radical shows only one line. However, satellite lines due to ^{13}C in natural abundance in the α or γ position are easily detected [7]. From eq. (19) we obtain the following values for the widths of the lines corresponding to the different species

unsubst. radical $\quad \mathrm{T}_{2u}^{-1} = \delta_0 + 7\,\omega^0 c\mathrm{X}_0/2$

α- or γ-subst. $\quad \mathrm{T}_{2\alpha}^{-1} = \mathrm{T}_{2\gamma}^{-1} = \delta_0 + \omega^0 c\,(1 - 7\,\mathrm{X}_0)/2$

where c is the actual concentration of the radical, X_0 is the natural abundance of ^{13}C, and δ_0 is the residual line width resulting from factors other than the Heisenberg exchange.

It follows that if we plot against increasing concentration of the parent ketyl radical the ratio of the widths $\mathrm{T}_{2u}/\mathrm{T}_{2\alpha}$ or $\mathrm{T}_{2u}/\mathrm{T}_{2\gamma}$ (or conversely, the square roots of the inverse ratios of the corresponding peak heights), we shall obtain straight lines, the slope of which is determined by the exchange frequency ω^0

$$(h_u/h_\alpha)^{1/2} = (6\,h_u/h_\gamma)^{1/2} \simeq \sqrt{2/\mathrm{X}_0}\,[1 + \omega^0 c\,(1 - 14\,\mathrm{X}_0)/2\,\delta_0]$$

neglecting higher order terms in X_0. Experimentally, straight lines are indeed obtained in agreement with the theory, but uncertainties as to the actual radical concentration and the formation of radical aggregates except for the very diluted samples [7] prevent the exact value of ω^0 from being measured. If this were not the case, careful analysis of the line width of unsubstituted radicals, which is predicted to be very little influenced by the exchange process, could provide experimental information on the magnitude of the dipolar relaxation effects.

A few words regarding the exchange integral itself are now in order. Preliminary measurements on the temperature dependence of the line widths show for the di-*tert*-butyl ketyl radical in THF the same behaviour as for the di-*tert*-butyl nitroxide radical [2], indicating that the condition $\tau_1^2 J^2 \gg 1$ holds also in this case. Therefore any information on the magnitude of J is lost, the relaxation effects being governed by the diffusion coefficients, as seen from eqs (8) and (13).

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