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Molecular reorientation in liquids: a compromise between the strong collision and the rotational diffusion model.

MOLECULAR REORIENTATION IN LIQUIDS: A COMPROMISE BETWEEN THE STRONG COLLISION AND THE ROTATIONAL DIFFUSION MODEL

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SUMMARY - The limits of the Debye model of rotational Brownian motion and of the rotational random jump model when applied to the calculations of the electron resonance line shape for slowly tumbling paramagnetic molecules, are discussed. A more general model, which for molecules having very large or very small mean radii, reduces to the previous ones, is proposed.

RIASSUNTO - Vengono discussi i limiti del modello di Debye per il moto Browniano rotazionale e del modello dei salti casuali rotazionali nei riguardi della loro applicazione al calcolo della forma di riga degli spettri di risonanza elettronica per molecole paramagnetiche in riorientazione lenta. Viene inoltre proposto un modello più generale che, per molecole aventi raggi medi molto piccoli o molto grandi, si riduce ai due precedenti.

The study of the line shape in an electron resonance experiment, may give useful information on the molecular reorientation in viscous solvents. A paramagnetic molecule reorienting in solution may be considered as a spin system interacting with a bath. In the case of

viscous liquids this interaction is strong enough to make necessary to consider in detail the dynamic of the reorientation process [1-4] . If we assume, for the sake of simplicity, to deal with a molecule having cylindrical symmetry and tumbling in an isotropic medium, its orientation is completely specified by the angle ϑ between the molecular axis and the direction of the magnetic field. By dividing the total range of orientations into N sectors identified by the angle ϑ_i bisecting the ith sector, the number of molecules in each site will be, assuming an isotropic distribution of population, $W_i = \sin \vartheta_i$ [5]. The reorientation process induces transitions from one site to the other, perturbing the equilibrium distribution which is restored only after a certain time.

When trying to calculate the esr spectrum of the paramagnetic solute we face with two problems: the evaluation of the possible frequencies from the spin Hamiltonian and the determination of the line shape from a stochastic reorientation model. The line shape function in a frequency sweep experiment may be written, according to the stochastic theory [6-8] , as:

$$I(\omega) \propto \mathrm{Re} \overline{\langle S_x | [i(\omega \underline{1} - \underline{\underline{\mathcal{L}}}) - \underline{\Gamma}]^{-1} | S_x \rangle}$$

where the bar denotes the average over all orientations, $\underline{\underline{\mathcal{L}}}$ is the Liouville superoperator and S_x and $\underline{\Gamma}$ are the transition and evolution operators respectively. When the spin Hamiltonian contains pseudosecular and nonsecular terms, the Liouville operator is non--diagonal so that the stochastic and spin aspects of the problem

can not be separated [1,8].

Since we are interested in the dynamic of the molecular reorientation and then in the stochastic part of the problem, it is useful to separate the two aspects by using the adiabatic approximation which seems to be appropriate when dealing with very viscous solvents [9]. The line shape function for each transition then becomes [10]

$$I(\omega) \propto Re \langle W | \left[i(\omega \underset{\sim}{1} - \underset{\sim}{\Omega}) - \underset{\sim}{\Pi} \right]^{-1} | 1 \rangle$$

where $\langle W |$ is a row vector containing the occupation probabilities of the sites in equilibrium, $|1\rangle$ is a unit vector and $\underset{\sim}{\Omega}$ is a diagonal matrix containing the frequencies ω_i for each site.

The elements of $\underset{\sim}{\Pi}$ are

$$\Pi_{ij} = P_{ij} \qquad\qquad \Pi_{ii} = -\sum_{i \neq j} P_{ij}$$

being P_{ij} the transition probability per unit time from the ith to the jth site.

The transition probabilities depend on the models assumed for the molecular reorientation; those which have received more attention are essentially the Debye rotational diffusion and the strong collision model which, however, are appropriate for very different physical situations. The rotational diffusion model corresponds to the simplest case of random walk, where transitions may occur only between adjacent sites with reflecting barrier at ϑ equal zero and $\pi/2$ [11]. In this case, for sufficiently long times holds the dif-

fusion equation

$$\frac{\partial P(\vartheta_0|\vartheta, t)}{\partial t} = D\nabla_\vartheta^2 P(\vartheta_0|\vartheta, t)$$

for the time evolution of the conditional-probability $P(\vartheta_0 / \vartheta,$ subject to the initial condition

$$P(\vartheta_0|\vartheta, t) = \delta(\vartheta - \vartheta_0)$$

being

$$\nabla_\vartheta^2 \doteq (\sin\vartheta)^{-1}\frac{d}{d\vartheta}\left[\sin\vartheta\left(\frac{d}{d\vartheta}\right)\right]$$

and D the rotational diffusion constant.

The finite difference approximation to the diffusion term [12] gives the elements of the transition matrix as

$$\Pi_{1,1+1} = \frac{D}{\Delta^2}\ \frac{\sin(\vartheta_1 \pm \Delta/2)}{\sin\vartheta_1} \qquad \begin{cases} + : & 1 \leqslant 1 < \\ - : & 1 < 1 \leqslant \end{cases}$$

$$\Pi_{1,1} = -\frac{D}{\Delta^2}\left[\Pi_{1,1+1} + \Pi_{1,1-1}\right]$$

where $\Delta = \vartheta_{1+1} - \vartheta_1 = \pi/2N$

Since the tridiagonal matrix is not symmetric, is more convenient to use the independent variable $x = \cos\vartheta$ instead of ϑ ;

the new $\underset{\sim}{\Pi}$ matrix is now symmetric with elements [1]

$$\Pi_{1,1+1} = -\frac{D}{\Delta^2}(1 - x_1^2 - x_1\Delta) = \Pi_{1+1,1}$$

$$\Pi_{1,1} = \frac{2D}{\Delta^2}(1 - x_1^2) \qquad 1 = 2,3, \ldots, N-1$$

$$\Pi_{1,1} = \frac{D}{\Delta^2}(1 - x_1^2 - x_1\Delta)$$

$$\Pi_{N,N} = \frac{D}{\Delta^2}(1 - x_N^2 + x_N\Delta)$$

The strong collision model assumes that, as a result of a colli-
sion, the molecule jumps to a new orientation which is completely
independent on the previous one.

One should point out that, while in the diffusion model only in-
finitesimal changes of direction are allowed, here the orientation
may change relevantly in a single step. In this case the elements
of the transition matrix are

$$\Pi_{mn} = k\left[W_n - \delta_{mn}\right]$$

where

$$W_n = \sin\vartheta_n / \sum_{i=1}^{N} \sin\vartheta_i$$

and k is a first order rate constant. The asymmetric $\underset{\sim}{\Pi}$ matrix can
be easily symmetrized replacing ϑ_n with the independent variable

$x_n = \sqrt{\sin \vartheta_n} \cdot \vartheta_n$. This is equivalent to perform the similarity transformation

$$\underset{\sim}{\Pi}' = \underset{\sim}{P}^{1/2} \cdot \underset{\sim}{\Pi} \cdot \underset{\sim}{P}^{-1/2}$$

by the diagonal matrix $\underset{\sim}{P}^{1/2}$.

Even if the rotational diffusion and strong collision models have been largely employed in a number of investigations on dielectric and spin relaxation, there are no "a priori" reasons for preferring these models to others. Also the choice between these two models in specific cases is not obvious and is usually justified on the basis of the agreement with the experiment. However, we can expect that the diffusion model is mainly valid for molecules large enough in respect to the dimensions of the surrounding solvent molecules, so that they can be treated as Brownian particles immersed in an homogeneous continuous medium [13]. This seems to be confirmed by the good agreement with the experimental results obtained by McConnell and coworkers [14] when using this model to interpret esr spectra of paramagnetic macromolecules.

For small molecules for which the Brownian motion consist of a number of jumps by finite distances, the strong collision model seems more appropriate. Unfortunately in this model no parameters depending on the molecular dimensions are considered, and also in the diffusional rotation model, althougth the hydrodynamic radius of the molecule appears in the diffusional constant D, the increase of D when reducing the radius implies only a fastening of the motion

while the elementary step remains infinitesimal.

It seems then convenient to develop a more general model containing explicity the molecular dimensions which will determine the average elementary step. A good model should give the strong collision and the rotational diffusion models as limiting cases when dealing with very small or very large molecules. A rotational jump model with the transition probabilities modulated by a step distribution function will satisfy these requirements to a reasonable extent. The elements of the transition probability can be written as

$$\Pi_{mn} = k \left\{ W_n \cdot \exp\left[-(\vartheta_n - \vartheta_m)^2 / a \right] - \delta_{mn} \cdot \xi_m \right\}$$

where

$$\xi_m = \sum_n W_n \exp\left[-(\vartheta_n - \vartheta_m)^2 / a \right],$$

$$a = c/r^3$$

being $\underline{r}$ the hydrodynamic radius.

It can be noticed that by expanding the exponential

$$\exp(-\Delta\vartheta^2/a) = \sum_0^\infty (-\Delta\vartheta^2/a)^n/n! = 1 - \Delta\vartheta^2/a + \Delta\vartheta^4/2a^2 - \ldots.$$

and taking only the first term of the expansion, which can be done for large values of $\underline{a}$, i.e., for very small molecules, the Π matrix become identical to that of the strong collision model. For very large $\underline{r}$, W_n is modulated by a sharp gaussian and only tran-

sitions between neighbouring sites are possible, thus describing a situation very similar to that encountered in the rotational diffusion model.

Further work in in progress to apply the present theory to specific cases; the sensitivity of the esr spectra to the model assumed for reorientation is presently being checked for triplet and quartet states.

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