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### **Abstract**

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Keywords: NMR, NMR spectroscopy, HR-NMR, Linewidth, Relaxation, Molecular reorientation

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# Linewidths in High-Resolution NMR Spectra of Coupled Nuclear Systems. Broadening Mechanisms Induced by Molecular Reorientation

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The perturbation theory of energy-level widths in coupled nuclear systems is applied to the relaxation processes activated by molecular reorientation, i.e., to the dipolar relaxation, the quadrupolar relaxation, the relaxation due to the chemical shift anisotropy, the intermolecular relaxation, and the relaxation due to the spin-rotation interaction. The relaxation processes are divided into two groups with respect to their behavior under rotations of molecular coordinates; the first three are of tensor character while the last two are of vector character. For each of the two groups a theory is developed based on the properties of normed spherical operators. This sheds some new light on the two previously studied cases, i.e., the dipolar relaxation and the intermolecular relaxation, and leads to the solutions of the other cases. The theory of the quadrupolar relaxation is documented by two simple examples. It turns out that in the case of molecules containing quadrupolar nuclei useful information about the molecular structure can be obtained from the linewidth patterns. The same also holds, of course, for the other relaxation processes provided they lead to experimentally accessible effects. Explicit formulas are given for the cross-term contributions due to simultaneous action of two different relaxation mechanisms.

In the preceding two papers<sup>1,2</sup> (henceforth referred to as I and II, respectively), the theory of homogeneous broadening in coupled nuclear systems was developed and applied to the intramolecular dipolar broadening (I) and to the broadening due to intermolecular effects (II). In the present paper two general types ( $\Pi$  and  $\Delta$ ) of random processes are distinguished on the basis of their behavior under rotations of coordinates. To each of these classes the general theory of homogeneous broadening is applied. The resulting formulae enable one to treat very easily any individual random process. The relaxation mechanisms discussed in detail in this paper are all characterized by their dependence on molecular reorientation. Apart from dipolar relaxation these are: quadrupolar relaxation, relaxation due to spin-rotation interaction, and relaxation due to the chemical shift anisotropy. The existence of cross-term contributions has been mentioned in I; in the present paper the cross terms are studied in a more detailed manner.

## I. THE THEORY OF $\Delta$ -TYPE PROCESSES

First, the following operators are defined:

$$\begin{aligned} \mathbf{F}_{ij} &= (1/2)(\mathbf{K}_i\mathbf{K}_j - \mathbf{I}_i^+\mathbf{I}_j^- - \mathbf{I}_i^-\mathbf{I}_j^+), \\ \mathbf{T}_{ij}^{\pm} &= (6^{1/2}/4)(\mathbf{K}_i\mathbf{I}_j^{\pm} + \mathbf{I}_i^{\pm}\mathbf{K}_j), \\ \mathbf{D}_{ij}^{\pm} &= (6^{1/2}/2)\mathbf{I}_i^{\pm}\mathbf{I}_j^{\pm}, \end{aligned} \quad (1)$$

with  $\mathbf{I}_i^+$ ,  $\mathbf{I}_i^-$ , and  $\mathbf{K}_i = 2\mathbf{I}_i^z$  being the usual spin operators for the nucleus  $i$ . The operators (1) behave under rotations of laboratory coordinates like the second-order spherical harmonics<sup>3</sup>  $Y_{2,\mu}$ , where  $\mu=0$  for the flip-flop operators  $\mathbf{F}$ ,  $\mu=\pm 1$  for the transition operators  $\mathbf{T}$ , and  $\mu=\pm 2$  for the double-transition operators  $\mathbf{D}$ . From these transformation properties the "spectroscopic" designation of the individual types of processes is also derived.

Any random interaction with zero average value which is of second order in the spin coordinates can be written in the form

$$\begin{aligned} \mathbf{H}^V &= \sum_{ij} \mathbf{H}_{ij}^V, \\ \mathbf{H}_{ij}^V &= F_{ij}^{V,0}\mathbf{F}_{ij} + F_{ij}^{V,1}\mathbf{T}_{ij}^- + F_{ij}^{V,-1}\mathbf{T}_{ij}^+ \\ &\quad + F_{ij}^{V,2}\mathbf{D}_{ij}^- + F_{ij}^{V,-2}\mathbf{D}_{ij}^+, \end{aligned} \quad (2)$$

where  $V$  specifies the interaction and  $F_{ij}^{V,\mu}$  are pseudo-scalar functions behaving under molecular rotations like spherical harmonics  $Y_{2,\mu}$ . Because of this property, the  $F_{ij}^{V,\mu}$  can always be expressed by means of the components of a traceless second-order tensor  $\tilde{F}_{ij}^V$ :

$$\begin{aligned} F_{ij}^{V,0} &= (1/2)(\tilde{F}_{ij}^V)_{ZZ}, \\ F_{ij}^{V,\pm 1} &= (1/6^{1/2})[(\tilde{F}_{ij}^V)_{ZX} \pm i(\tilde{F}_{ij}^V)_{ZY}], \\ F_{ij}^{V,\pm 2} &= [1/2(6)^{1/2}][(\tilde{F}_{ij}^V)_{XX} - (\tilde{F}_{ij}^V)_{YY} \pm 2i(\tilde{F}_{ij}^V)_{XY}], \end{aligned} \quad (3)$$

where  $X$ ,  $Y$ , and  $Z$  denote the laboratory axes of coordinates. The tensor  $\tilde{F}_{ij}^V$  is fixed with respect to the molecule; if the molecule reorients, its components become random functions of time. In such a case, the correlation functions  $G_{ij,kl}^{V,\mu}(\tau)$  are introduced by the relations

$$G_{ij,kl}^{V,\mu}(\tau) = \mathbf{A}_\sigma [F_{ij}^{V,-\mu}(t)F_{kl}^{V,+\mu}(t+\tau)], \quad (4)$$

where  $\mathbf{A}_\sigma$  is the statistical-averaging operator. The corresponding spectral densities  $J_{ij}^{V,\mu}(\omega)$  are then defined as

$$J_{ij,kl}^{V,\mu}(\omega) = \int_{-\infty}^{+\infty} \exp(-i\omega\tau) G_{ij,kl}^{V,\mu}(\tau) d\tau. \quad (5)$$

If  $\mathbf{Y}_{k,\mu}$ ,  $\mathbf{Y}_{k,\nu}$  are any two spherical tensor operators<sup>3</sup> transforming like  $Y_{k,\mu}$  and  $Y_{k,\nu}$ , respectively, and if  $r$

and  $s$  denote any two eigenstates of the system, then

$$\langle \mathbf{Y}_{k,\mu} \rangle_{rs} \langle \mathbf{Y}_{k,\nu'} \rangle_{sr} \neq 0 \text{ only if } \mu + \nu = 0. \quad (6)$$

(Throughout this paper,  $\langle \mathbf{W} \rangle_{rs} = \langle s | \mathbf{W} | r \rangle$  for any operator  $\mathbf{W}$ .) This rule (6) is a generalization of the rules (I, Eq. 11); it leads to a substantial simplification of the expressions for the transition probabilities

$$\begin{aligned} \mathfrak{W}^V(r \rightarrow s) &= \int_{-\infty}^{+\infty} \exp(-i\omega_{rs}\tau) \\ &\times \mathbf{A}_\sigma \langle s | \mathbf{H}^V(t) | r \rangle \langle r | \mathbf{H}^V(t+\tau) | s \rangle. \end{aligned} \quad (7)$$

In the case of a molecule in an isotropic medium, similar simplification could be obtained also on the basis of the properties of the correlation functions. The rules (6) are, of course, much more general as they do not require the isotropy of the surrounding medium.

The contribution of the random interaction  $V$  to the  $r$ th energy-level width is

$$\Gamma^V(r) = \sum_s^{\neq r} \mathfrak{W}^V(r \rightarrow s). \quad (8)$$

Following the general principles explained in I, this reduces to

$$\begin{aligned} \Gamma^V(r) &= \sum_{ij} \sum_{kl} \Gamma_{ij,kl}^V(r), \\ \Gamma_{ij,kl}^V(r) &= J_{ij,kl}^{V,0}(0) \mathbf{G}_{ij,kl}^{V,0}(r) + J_{ij,kl}^{V,0}(\Phi_i - \Phi_j) \\ &\times \tilde{\mathbf{G}}_{ij,kl}^{V,0}(r) + 2 \operatorname{Re} J_{ij,kl}^{V,1}(\Phi_j) \mathbf{G}_{ij,kl}^{V,1}(r) \\ &+ J_{ij,kl}^{V,1}(\Phi_i) \tilde{\mathbf{G}}_{ij,kl}^{V,1}(r) \\ &+ J_{ij,kl}^{V,2}(\Phi_i + \Phi_j) \mathbf{G}_{ij,kl}^{V,2}(r), \end{aligned} \quad (9)$$

where the  $\mathbf{G}$  functionals have the form<sup>4</sup>

$$\begin{aligned} \mathbf{G}_{ij,kl}^{V,0}(r) &= (1/4) [e_{kl} \langle \mathbf{K}_i \mathbf{K}_j \rangle_{rr} \langle \mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_k^- \mathbf{I}_l^+ \rangle_{rr} \\ &+ e_{ij} \langle \mathbf{I}_i^+ \mathbf{I}_j^- + \mathbf{I}_i^- \mathbf{I}_j^+ \rangle_{rr} \langle \mathbf{K}_k \mathbf{K}_l \rangle_{rr} \\ &- \langle e_{kl} \mathbf{K}_i \mathbf{K}_j (\mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_k^- \mathbf{I}_l^+) - e_{ij} (\mathbf{I}_i^+ \mathbf{I}_j^- + \mathbf{I}_i^- \mathbf{I}_j^+) \mathbf{K}_k \mathbf{K}_l \rangle_{rr}, \\ &+ \langle \mathbf{K}_i \mathbf{K}_j \mathbf{K}_k \mathbf{K}_l \rangle_{rr} - \langle \mathbf{K}_i \mathbf{K}_j \rangle_{rr} \langle \mathbf{K}_k \mathbf{K}_l \rangle_{rr}], \\ \tilde{\mathbf{G}}_{ij,kl}^{V,0}(r) &= (1/4) \{ e_{ij} e_{jk} [ \langle \mathbf{I}_i^+ \mathbf{I}_j^- \mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_i^- \mathbf{I}_j^+ \mathbf{I}_k^- \mathbf{I}_l^+ \rangle_{rr} \\ &- \langle \mathbf{I}_i^+ \mathbf{I}_j^- \rangle_{rr} \langle \mathbf{I}_k^+ \mathbf{I}_l^- \rangle_{rr} - \langle \mathbf{I}_i^- \mathbf{I}_j^+ \rangle_{rr} \langle \mathbf{I}_k^- \mathbf{I}_l^+ \rangle_{rr} ] \\ &+ e_{ik} e_{jl} [ \langle \mathbf{I}_i^+ \mathbf{I}_j^- \mathbf{I}_k^- \mathbf{I}_l^+ + \mathbf{I}_i^- \mathbf{I}_j^+ \mathbf{I}_k^+ \mathbf{I}_l^- \rangle_{rr} \\ &- \langle \mathbf{I}_i^+ \mathbf{I}_j^- \rangle_{rr} \langle \mathbf{I}_k^- \mathbf{I}_l^+ \rangle_{rr} - \langle \mathbf{I}_i^- \mathbf{I}_j^+ \rangle_{rr} \langle \mathbf{I}_k^+ \mathbf{I}_l^- \rangle_{rr} ] \}, \\ \mathbf{G}_{ij,kl}^{V,1}(r) &= (3/8) [ e_{jk} \langle \mathbf{K}_i \mathbf{I}_j^+ \mathbf{K}_k \mathbf{I}_l^- \rangle_{rr} \\ &+ e_{jk} \langle \mathbf{K}_i \mathbf{I}_j^+ \mathbf{I}_k^- \mathbf{K}_l \rangle_{rr} ], \\ \tilde{\mathbf{G}}_{ij,kl}^{V,1}(r) &= (3/8) [ e_{ij} \langle \mathbf{I}_i^+ \mathbf{K}_j \mathbf{K}_k \mathbf{I}_l^- \rangle_{rr} \\ &+ e_{ik} \langle \mathbf{I}_i^+ \mathbf{K}_j \mathbf{I}_k^- \mathbf{K}_l \rangle_{rr} ], \\ \mathbf{G}_{ij,kl}^{V,2}(r) &= (3/2) (e_{ik} e_{jl} + e_{il} e_{jk} - e_{ik} e_{il}) \langle \mathbf{I}_i^+ \mathbf{I}_j^+ \mathbf{I}_k^- \mathbf{I}_l^- \rangle_{rr}. \end{aligned} \quad (10)$$

The indicator  $e_{ij}$  in these equations is equal to 1 if the nuclei  $i$  and  $j$  are of the same kind and is zero otherwise.

Let us return now to the correlation functions (4). In connection with them, two mutually independent approximations are widely used<sup>5</sup>:

(i) The reduced correlation functions are assumed to be identical (the IRCOF approximation), i.e.,

$$G_{ij,kl}^{V,\mu}(\tau) / G_{ij,kl}^{V,\mu}(0) = \chi_2(\tau), \quad (11)$$

where the function  $\chi_2(\tau)$  is the same for all  $\Delta$  processes activated by the same random phenomenon. It is easy to show that in an isotropic medium

$$\begin{aligned} G_{ij,kl}^{V,\mu}(0) &= \mathfrak{G}_{ij,kl}^V \\ &= (1/30) \sum_{\alpha=1}^3 \sum_{\beta=1}^3 (\tilde{F}_{ij}^{V,\alpha})^\alpha (\tilde{F}_{kl}^{V,\beta})^\beta \cos^2(\alpha_{ij} \wedge \beta_{kl}), \end{aligned} \quad (12)$$

where  $(\tilde{F}_{ij}^{V,\alpha})^\alpha$  is the  $\alpha$ th main axis of the tensor  $\tilde{F}_{ij}^{V,\alpha}$  and  $(\alpha_{ij} \wedge \beta_{kl})$  denotes the angle between the  $\alpha$ th axis of  $\tilde{F}_{ij}^{V,\alpha}$  and the  $\beta$ th axis of  $\tilde{F}_{kl}^{V,\beta}$ . Note that the quantities  $G_{ij,kl}^{V,\mu}$  do not depend on  $\mu$ .

The spectral density functions (5) are now

$$J_{ij,kl}^{V,\mu}(\omega) = \mathfrak{G}_{ij,kl}^V \zeta_2(\omega), \quad (13)$$

where  $\zeta_2(\omega)$  is the Fourier transform of  $\chi_2(\tau)$ .

(ii) The exponential-decay approximation (EDA) by which

$$\chi_2(\tau) = \exp(-|\tau|/\tau_2). \quad (14)$$

The function  $\zeta_2(\omega)$  then becomes

$$\zeta_2(\omega) = 2\tau_2 / (1 + \omega^2\tau_2^2). \quad (15)$$

This equation can often be further simplified as either  $\omega\tau_2 \ll 1$  (fast reorientation limit) or  $\omega\tau_2 \gg 1$  (slow reorientation limit).

### A. Broadening Due to Dipolar Interactions ( $D$ )

In the case of dipolar interactions, the tensor  $\tilde{F}_{ij}^{D}$  has the form

$$\begin{aligned} (\tilde{F}_{ij}^{D})_{\alpha\beta} &= (\gamma_i \gamma_j / R_{ij}^3) [\delta_{\alpha\beta} - 3(\bar{p}_{ij})_\alpha (\bar{p}_{ij})_\beta], \\ \alpha, \beta &= X, Y, Z, \end{aligned} \quad (16)$$

where  $\gamma_i$  is the gyromagnetic ratio for the nucleus  $i$ ,  $R_{ij}$  is the distance between the nuclei  $i$  and  $j$ , and  $\bar{p}_{ij}$  is the unit vector along the line connecting these two nuclei. The summation (2) runs over all pairs of nuclei which implies  $i < j$ .

As the dipolar broadening has been discussed in detail in I, no further discussion is given here.

### B. Broadening Due to Quadrupolar Interactions ( $Q$ )

The quadrupolar interaction tensor  $\tilde{F}_{ij}^{Q}$  is<sup>6</sup>

$$\tilde{F}_{ij}^{Q} = [e^2 Q_i / 2S_i (2S_i - 1)] \tilde{Q}^i \delta_{ij}, \quad (17)$$

where  $Q_i$  and  $S_i$  are the quadrupole moment and the total spin of the  $i$ th nucleus, respectively. The symmetric, traceless tensor  $e\tilde{Q}^i$  denotes the anisotropy of

the gradient of the electric field  $\mathcal{E}^i$  at the nucleus  $i$ :

$$e\tilde{Q}^i \equiv e(\tilde{Q}^i)_{\alpha\beta} = -(\mathcal{E}^i)_{\alpha/\beta} + (1/3)\delta_{\alpha\beta} \sum_{\mu} (\mathcal{E}^i)_{\mu/\mu}, \quad (18)$$

where  $\alpha, \beta, \mu = X, Y, Z$ .

Because of the  $\delta_{ij}$  factor in (18), the summation (2) now runs over the nuclei. Substituting the two identical indices by a unique one, the general formulas (1)–(13) can be substantially simplified. The contribution to the  $r$ th energy-level width then becomes

$$\Gamma^Q(r) = \sum_i \sum_k \Gamma_{ik}^Q(r), \quad (19)$$

$$\Gamma_{ik}^Q(r) = J_{ik}^{Q,0}(0) \mathbf{G}_{ik}^{Q,0}(r) + 2 \operatorname{Re}[J_{ik}^{Q,1}(\Phi_i) \mathbf{G}_{ik}^{Q,1}(r) + J_{ik}^{Q,2}(2\Phi_i) \mathbf{G}_{ik}^{Q,2}(r)],$$

where

$$\begin{aligned} \mathbf{G}_{ik}^{Q,0}(r) &= (3/4)^2 [\langle \mathbf{K}_i^2 \mathbf{K}_k^2 \rangle_{rr} - \langle \mathbf{K}_i^2 \rangle_{rr} \langle \mathbf{K}_k^2 \rangle_{rr}], \\ \mathbf{G}_{ik}^{Q,1}(r) &= (3/8) e_{ik} \langle (\mathbf{K}_i \mathbf{I}_i^+ + \mathbf{I}_i^+ \mathbf{K}_i) (\mathbf{K}_k \mathbf{I}_k^- + \mathbf{I}_k^- \mathbf{K}_k) \rangle_{rr}, \\ \mathbf{G}_{ik}^{Q,2}(r) &= (3/2) e_{ik} \langle \mathbf{I}_i^+ \mathbf{I}_i^+ \mathbf{I}_k^- \mathbf{I}_k^- \rangle_{rr}. \end{aligned} \quad (20)$$

In the IRCOF approximation, and assuming that the spectral density functions are real, Eq. (19) can be written as

$$\Gamma_{ik}^Q(r) = \mathcal{G}_{ik}^Q \sum_{\mu=0}^2 \zeta_2(\mu\Phi_i) \mathbf{Q}_{ik}^{\mu}(r), \quad (21)$$

where

$$\begin{aligned} \mathbf{Q}_{ik}^0(r) &= \mathbf{G}_{ik}^{Q,0}(r), \\ \mathbf{Q}_{ik}^1(r) &= (3/8) e_{ik} \langle (\mathbf{K}_i \mathbf{I}_i^+ + \mathbf{I}_i^+ \mathbf{K}_i) (\mathbf{K}_k \mathbf{I}_k^- + \mathbf{I}_k^- \mathbf{K}_k) \\ &\quad + (\mathbf{K}_i \mathbf{I}_i^- + \mathbf{I}_i^- \mathbf{K}_i) (\mathbf{K}_k \mathbf{I}_k^+ + \mathbf{I}_k^+ \mathbf{K}_k) \rangle_{rr}, \\ \mathbf{Q}_{ik}^2(r) &= (3/2) e_{ik} \langle \mathbf{I}_i^+ \mathbf{I}_i^+ \mathbf{I}_k^- \mathbf{I}_k^- + \mathbf{I}_i^- \mathbf{I}_i^- \mathbf{I}_k^+ \mathbf{I}_k^+ \rangle_{rr}. \end{aligned} \quad (22)$$

One-particle ( $i=k$ ) and two-particle ( $i \neq k$ ) terms can be distinguished. In the one-particle case the spectral density functions are necessarily real so that Eq. (21) is valid.

The quantities  $\mathcal{G}_{ik}^Q$  are now

$$\begin{aligned} \mathcal{G}_{ik}^Q &= e^4 Q_i Q_k C_{ik} / 120 S_i S_k (2S_i - 1) (2S_k - 1), \\ C_{ik} &= \sum_{\alpha=1}^3 \sum_{\beta=1}^3 Q_{\alpha}^i Q_{\beta}^k \cos^2(\alpha_i \wedge \beta_k), \end{aligned} \quad (23)$$

where  $Q_{\alpha}^i$  denotes the length of the  $\alpha$ th main axis of the tensor  $\tilde{Q}^i$  and  $(\alpha_i \wedge \beta_k)$  is the angle between the  $\alpha$ th axis of  $\tilde{Q}^i$  and the  $\beta$ th axis of  $\tilde{Q}^k$ . If both  $\tilde{Q}^i$  and  $\tilde{Q}^k$  are axially symmetric then

$$C_{ik} = (3/4) \epsilon_i \epsilon_k (3 \cos^2 \theta_{ik} - 1), \quad (24)$$

where  $\epsilon_i$  is the length of the symmetry axis of  $\tilde{Q}^i$  and  $\theta_{ik}$  is the angle between the symmetry axes of  $\tilde{Q}^i$  and  $\tilde{Q}^k$ .

Another special case concerns the one-particle quantities  $C_{ii}$ . Let  $\epsilon_i = Q_1^i$  be the length of the dominant axis of  $\tilde{Q}^i$  and define the parameter<sup>5</sup>  $\eta_i$  as

$$\eta_i = (Q_2^i - Q_3^i) / Q_1^i. \quad (25)$$

Then

$$C_{ii} = (3/2) \epsilon_i^2 [1 + (1/3) \eta_i^2] \quad (26)$$

In the fast reorientation limit and assuming the validity of the approximations IRCOF and EDA, Eq. (21) becomes

$$\Gamma_{ik}^Q(r) = \frac{e^4 Q_i Q_k \tau_2}{60 S_i S_k (2S_i - 1) (2S_k - 1)} C_{ik} \sum_{\mu=0}^2 \mathbf{Q}_{ik}^{\mu}(r). \quad (27)$$

### 1. Application to an SX System

The aim of this paper is not to give a detailed discussion of relaxation in various systems but rather to give a general feeling of what kind of effects can be expected. For this purpose, only very simple applications based on Eq. (27) will be considered.

Let  $\mathcal{S}$  be a system composed exclusively of spin- $\frac{1}{2}$  nuclei and let  $X$  be a nucleus with spin  $S \geq 1$ . In this case, the quadrupolar broadening is reduced to the one-particle contribution arising from  $X$ .

Because of the  $\mathcal{S}$ - $X$  interaction, each transition in  $\mathcal{S}$  splits into a multiplet of  $(2S+1)$  lines. The present theory may only be applied to the case where the considered multiplet is well resolved (see I, Sec. III; a more detailed discussion of this problem is being prepared). Let us denote the eigenvectors of the composite system by  $|S\rangle |m\rangle$ ,  $m$  being the  $I^z$  value of the nucleus  $X$ . In this case  $\mathbf{Q}^0(r) = 0$  for any eigenstate and the values of  $\mathbf{Q}^1(r)$  and  $\mathbf{Q}^2(r)$  depend on  $m$  but do not depend on the state of the subsystem  $\mathcal{S}$ . Consequently, the  $X$  multiplets arising from the  $\mathcal{S}$ - $X$  interaction are composed of lines of which the widths are identical. The values of  $\mathbf{Q}^1(m)$  and  $\mathbf{Q}^2(m)$  resulting from (22) are

$$\begin{aligned} \mathbf{Q}^1(m) &= 3\{ (4m^2+1)[S(S+1) - m^2] - 4m^2\}, \\ \mathbf{Q}^2(m) &= 3\{ [S(S+1) - m^2][S(S+1) - m^2 - 2] + 3m^2\}. \end{aligned} \quad (28)$$

In the simplest case of  $S=1$  one obtains

$$\begin{aligned} \mathbf{Q}^1(-1) = \mathbf{Q}^1(1) &= 3, & \mathbf{Q}^1(0) &= 6, \\ \mathbf{Q}^2(-1) = \mathbf{Q}^2(1) &= 6, & \mathbf{Q}^2(0) &= 0. \end{aligned}$$

The levels with  $m = \pm 1$  are thus always broader than the levels with  $m = 0$ . In consequence, the sideband components of each of the  $S$ -transition triplets are broader than the central peak. If the quadrupolar broadening is dominant, and assuming that all the above approximations are valid, the ratio of the linewidths in each triplet should be 3:2:3. This is in agreement both with experiment<sup>6</sup> (2.95:2:2.95) and with the previous calculations for this simple case.<sup>5</sup>

Analogous results for  $X$  nuclei with higher spin values are easily obtained from (28). Note that for  $S \geq 2$  each of the lines of the  $X$  multiplet is composed of several components with different linewidths.

The  $SX$  system is, of course, a rather trivial example which can be treated in other ways<sup>7,8</sup> as well. The equa-

TABLE I. The eigenvectors and the values of Q functionals for an AB system composed of spin-1 nuclei.<sup>a</sup>

| $I_z$ | State       | Energy                      | Eigenvector                                      | $Q_{AA}^0$  | $Q_{AA}^1$  | $Q_{AA}^2$                | $Q_{AB}^0$  | $Q_{AB}^1$                     | $Q_{AB}^2$                     |
|-------|-------------|-----------------------------|--|-------------|-------------|---------------------------|-------------|--------------------------------|--------------------------------|
| 2     | 1           | $2\Phi + \delta x$          | $ ++\rangle$                                     | 0           | (3/4)       | 6                         | 0           | 0                              | 0                              |
| 1     | 2           | $\Phi + \delta\epsilon(x)$  | $\cos\varphi +0\rangle + \sin\varphi 0+\rangle$  | $p^2$       | (3/4)(1+r)  | 6s                        | 0           | 2p                             | 0                              |
| 1     | 3           | $\Phi - \delta\epsilon(x)$  | $-\sin\varphi +0\rangle + \cos\varphi 0+\rangle$ | $p^2$       | (3/4)(1+s)  | 6r                        | 0           | -2p                            | 0                              |
| 0     | $i=4, 5, 6$ | $\delta\epsilon_i(x)$       | $A_i +-\rangle + B_i 00\rangle + C_i -+\rangle$  | $v_i^2 u_i$ | (3/4) $U_i$ | 6 <u><math>u_i</math></u> | $v_i^2 u_i$ | -2 <u><math>v_i Z_i</math></u> | 12 <u><math>A_i C_i</math></u> |
| -1    | 7           | $-\Phi + \delta\epsilon(x)$ | $\cos\varphi 0-\rangle + \sin\varphi -0\rangle$  | $p^2$       | (3/4)(1+s)  | 6r                        | 0           | 2p                             | 0                              |
| 1     | 8           | $-\Phi - \delta\epsilon(x)$ | $-\sin\varphi 0-\rangle + \cos\varphi -0\rangle$ | $p^2$       | (3/4)(1+r)  | 6s                        | 0           | -2p                            | 0                              |
| -2    | 9           | $-2\Phi + \delta x$         | $ --\rangle$                                     | 0           | (3/4)       | 6                         | 0           | 0                              | 0                              |

<sup>a</sup>  $\Phi = (\nu_A + \nu_B)/2$ ;  $\delta = \nu_A - \nu_B$ ;  $x = 2\mathcal{J}/\delta = \tan 2\varphi$ ;  $\epsilon(x) = (1+x^2)^{1/2}$ ;  $p = (3/8)\sin 2\varphi$ ;  $r = \sin^2\varphi$ ;  $s = \cos^2\varphi$ ;  $u_i = 1 - B_i^2$ ;  $U_i = 1 + B_i^2$ ;  $v_i = 3B_i/4$ ;  $Z_i = A_i + C_i$ ;  $\epsilon_i(x)$  denote the eigenvalues of the matrix  $M(x)$  defined in text

and ( $A_i, B_i, C_i$ ) are the corresponding eigenvectors of this matrix. The equality  $Q_{BA}^\mu = Q_{AB}^\mu$  holds for all  $\mu$ . If  $r$  and  $s$  are interchanged,  $Q_{BB}^\mu$  values result on the place of  $Q_{AA}^\mu$ .

tion (21) assumes its real importance only in the case of several mutually coupled quadrupolar nuclei.

2. AB System Composed of Spin-1 Nuclei

The AB system is described by the chemical shift  $\delta = \nu_A - \nu_B$  and by the coupling constant  $\mathcal{J}$ . Let us introduce the interaction parameter

$$x = 2\mathcal{J}/\delta = \tan 2\varphi \tag{29}$$

and the matrix

$$M(x) = \begin{bmatrix} 2-x & x & 0 \\ x & 0 & x \\ 0 & x & -2-x \end{bmatrix}. \tag{30}$$

Then the energies, eigenvectors, and the values of the Q functionals can be expressed by means of  $x$  and  $M(x)$  as shown in Table I. Equation (27) now gives

$$\Gamma^Q(r) = (e^4 Q^2 / 60) \tau_2 [C_{AA} \gamma_{AA}(r) + C_{BB} \gamma_{BB}(r) + 2C_{AB} \gamma_{AB}(r)], \tag{31}$$

where  $\gamma_{AA}(r) = Q_{AA}^0(r) + Q_{AA}^1(r) + Q_{AA}^2(r)$ , analogous equations being valid for  $\gamma_{BB}$  and  $\gamma_{AB}$ .

TABLE II. Energy-level widths in a typical AB system composed of spin-1 nuclei.<sup>a</sup>

| Eigenstate |      | $\Gamma(r)/\lambda C_{AA}^b$ |      |      |      |
|------------|------|------------------------------|------|------|------|
| $r$        | Type | i                            | ii   | iii  | iv   |
| 1          | ++   | 6.8                          | 13.5 | 13.5 | 13.5 |
| 2          | +0   | 6.6                          | 8.3  | 8.8  | 7.8  |
| 3          | 0+   | 1.7                          | 8.3  | 7.8  | 8.8  |
| 4          | +-   | 6.5                          | 13.0 | 14.8 | 11.3 |
| 5          | 00   | 1.9                          | 3.8  | 3.6  | 4.0  |
| 6          | -+   | 6.7                          | 13.0 | 11.9 | 14.7 |
| 7          | 0-   | 1.7                          | 8.3  | 8.8  | 7.8  |
| 8          | -0   | 6.6                          | 8.3  | 7.8  | 8.8  |
| 9          | --   | 6.8                          | 13.5 | 13.5 | 13.5 |

<sup>a</sup>  $\delta = 10$ ,  $\mathcal{J} = 1.82$  ( $\varphi = 10^\circ$ );  $\lambda = e^4 Q^2 \tau_2 / 60$ .  
<sup>b</sup> (i)  $C_{BB} = C_{AB} = 0$ ; (ii)  $C_{BB} = C_{AA}$ ,  $C_{AB} = 0$ ; (iii)  $C_{BB} = C_{AB} = C_{AA}$ ; (iv)  $C_{BB} = -C_{AB} = C_{AA}$ .

Instead of a general discussion, let us see the results for some typical cases assuming that (31) is valid. As this discussion is particularly interesting in connection with deuterated compounds, the values  $\delta = 10$  and  $\mathcal{J} = 1.82$  ( $\varphi = 10^\circ$ ) have been chosen which are considered sufficiently characteristic for this type of problem.

The energy-level parameters and the transition parameters are summed in Tables II and III, respectively. As far as the transition frequencies are concerned, the multiplet is always symmetrical with six intense transitions in each half. The transitions are grouped in doublets which may be unresolved. All the characteristics of both components of each doublet are very similar. The following conclusions can be drawn from the data given in Table III:

(i)  $C_{BB} \ll C_{AA}$

The linewidths do not respect the symmetry of the multiplet. If  $C_{BB} = 0$ , the A part of the multiplet is very

TABLE III. Transition parameters for the AB system specified in Table II.

| Transition | Frequency | Intensity | Linewidth $\Delta_{1/2}/\lambda C_{AA}^a$ |      |      |      |
|------------|-----------|-----------|---|------|------|------|
|            |           |           | i   | ii   | iii  | iv   |
| 1          | -17.55    | (0.00)    | 6.9                                       | 15.7 | 14.8 | 16.7 |
| 2          | -14.10    | (0.01)    | 6.7                                       | 15.4 | 16.7 | 14.3 |
| 3          | -7.15     | 0.66      | 9.5                                       | 15.8 | 15.6 | 16.1 |
| 4          | -6.90     | 0.78      | 9.4                                       | 15.7 | 14.2 | 17.2 |
| 5          | -5.55     | 0.82      | 2.5                                       | 9.1  | 9.5  | 8.7  |
| 6          | -5.10     | 0.88      | 2.5                                       | 9.1  | 8.5  | 9.7  |
| 7          | -3.50     | 1.34      | 9.5                                       | 15.8 | 16.1 | 15.6 |
| 8          | -3.45     | 1.51      | 9.3                                       | 15.4 | 17.2 | 13.7 |
| 9          | 3.45      | 1.51      | 6.7                                       | 15.4 | 17.2 | 13.7 |
| 10         | 3.50      | 1.34      | 7.0                                       | 15.8 | 16.1 | 15.6 |
| 11         | 5.10      | 0.88      | 6.9                                       | 9.1  | 8.5  | 9.7  |
| 12         | 5.55      | 0.82      | 6.9                                       | 9.1  | 9.5  | 8.7  |
| 13         | 6.90      | 0.77      | 6.9                                       | 15.7 | 14.2 | 17.2 |
| 14         | 7.15      | 0.66      | 7.0                                       | 15.8 | 15.6 | 16.1 |
| 15         | 14.10     | (0.01)    | 9.3                                       | 15.4 | 16.7 | 14.3 |
| 16         | 17.55     | (0.00)    | 9.4                                       | 15.7 | 14.8 | 16.7 |

<sup>a</sup> See Table II for the description of the individual cases.

regular with no marked differences in linewidths. On the other hand, the lines of the central doublet in the  $B$  part are surprisingly narrower and the other  $B$  transitions somewhat broader than the  $A$ -part transitions. The linewidths ratio between the broad and the narrow components of the  $B$ -part multiplet is almost 4!

(ii)  $C_{AA}=C_{BB}=C$  but  $C_{AB}\ll C$  (i.e.,  $\theta_{AB}\sim 54^\circ$ )

In this case, the linewidth pattern is symmetrical. The central doublets in each half of the multiplet are narrower than the other lines; the linewidth ratio is now about 5:3.

(iii)  $C_{AA}=C_{BB}=\pm C_{AB}$

In the previous two cases the two components of each doublet had roughly the same linewidth but in this case they differ. From the difference one could obtain, at least in principle, both the absolute value and the sign of  $C_{AB}$ . If the coupling is weak the effect does not seem sufficiently pronounced but it increases rapidly with increasing value of  $x$ .

Let us see now the energy-level widths (Table II). It has been noticed in I that the energy-level widths can be "tested" directly through the  $X$ -transition linewidths if another nucleus  $X$  is weakly coupled to the system which determines the relaxation. In the present case it means that in an  $ABX$  system with  $X$  being a spin- $\frac{1}{2}$  nucleus (proton), the  $X$ -part transitions reflect directly the energy-level widths of the  $AB$  subsystem. The  $X$  multiplet is composed of nine transitions with equal integral intensities. The linewidths follow directly from Table II and do not need, I think, any comment.

### C. Broadening Due to the Chemical Shift Anisotropy (S)

Let  $\tilde{\sigma}^k$  be the shielding tensor of the  $k$ th nucleus and  $\tilde{H}_0=H_0\tilde{h}_0$  the intensity of the magnetic field. Then the asymmetric part of the shielding leads to the perturbation

$$\mathbf{H}^S=H_0\sum_k\mathbf{H}_k^S,$$

$$\mathbf{H}_k^S=\tilde{h}_0\cdot\tilde{S}^k\cdot\tilde{\mathbf{I}}_k, \quad (32)$$

where

$$\tilde{S}^k=\tilde{\sigma}^k-(1/3)\text{Tr}\tilde{\sigma}^k. \quad (33)$$

Despite being of first order with respect to the spin operators, the relaxation through (32) is still governed by rotations of a tensor quantity and, hence, belongs to the type  $\Delta$ .

By means of the spherical tensor quantities we have

$$\mathbf{f}_k=h_0^2\mathbf{K}_k-(1/2)(h_0^+\mathbf{I}_k^-+h_0^-\mathbf{I}_k^+)=\mathbf{K}_k,$$

$$\mathbf{t}_k^\pm=(6^{1/2}/2)(h_0^+\mathbf{I}_k^\pm+h_0^-\mathbf{I}_k^\pm)=(6^{1/2}/2)\mathbf{I}_k^\pm,$$

$$\mathbf{d}_k^\pm=(6^{1/2}/2)h_0^\pm\mathbf{I}_k^\pm=0. \quad (34)$$

Equation (32) can be rewritten as

$$\mathbf{H}_k^S=F_k^S\mathbf{f}_k+F_k^S\mathbf{t}_k^-+F_k^S\mathbf{t}_k^+, \quad (35)$$

where

$$F_k^{S,0}=(1/2)\tilde{S}_{ZZ}^k \quad \text{and} \quad F_k^{S,\pm 1}=(1/6^{1/2})(\tilde{S}_{ZX}^k\pm i\tilde{S}_{ZY}^k). \quad (36)$$

For the energy-level widths one obtains

$$\Gamma^S(\mathbf{r})=\sum_i\sum_k\Gamma_{ik}^S(\mathbf{r}),$$

$$\Gamma_{ik}^S(\mathbf{r})=H_0^2\{J_{ik}^{S,0}(0)\mathbf{S}_{ik}^0(\mathbf{r})+2\text{Re}[J_{ik}^{S,1}(\Phi_i)\mathbf{S}_{ik}^1(\mathbf{r})]\}, \quad (37)$$

where

$$\mathbf{S}_{ik}^0(\mathbf{r})=(\mathbf{K}_i\mathbf{K}_k)_{rr}-\langle\mathbf{K}_i\rangle_{rr}\langle\mathbf{K}_k\rangle_{rr},$$

$$\mathbf{S}_{ik}^1(\mathbf{r})=(3/2)e_{ik}\langle\mathbf{I}_i^+\mathbf{I}_k^-\rangle_{rr}. \quad (38)$$

The spectral density functions  $J_{ik}^{S,\mu}(\omega)$  and their properties follow immediately from Eqs. (4), (5), and (11)–(15); it is only necessary to put  $(ij)\equiv i$  and  $(kl)\equiv k$ .

In the fast reorientation limit, and assuming the validity of the approximations IRCOF and EDA, (37) reduces to

$$\Gamma_{ik}^S(\mathbf{r})=2H_0^2\tau_2\mathcal{G}_{ik}^S$$

$$\times[\mathbf{S}_{ik}^0(\mathbf{r})+(3/2)e_{ik}\langle\mathbf{I}_i^+\mathbf{I}_k^-+\mathbf{I}_i^-\mathbf{I}_k^+\rangle_{rr}] \quad (39)$$

with  $\mathcal{G}_{ik}^S$  defined by (12).

In *proton* resonance the perturbations due to the chemical shift anisotropy start, in general, with smaller absolute amplitudes than those due to dipolar interactions.<sup>9</sup> Moreover, the double transition terms do not appear in (37). In the case of dipolar relaxation the  $D$ -transition terms are dominant (I). Consequently, the contributions of the chemical shift anisotropies are expected to be rather small. Because of their dependence on  $H_0^2$ , they could become important in connection with the high-field spectrometers with superconducting magnets which are being developed.

## II. THE THEORY OF $\Pi$ -TYPE PROCESSES

The spherical spin operators of first order are  $\mathbf{K}$  and  $\sqrt{2}\mathbf{I}^\pm$ . Consequently, the random interactions of first order can always be written as

$$\mathbf{H}^V=\sum_k\mathbf{H}_k^V,$$

$$\mathbf{H}_k^V=f_k^{V,0}\mathbf{K}_k+\sqrt{2}(f_k^{V,1}\mathbf{I}_k^-+f_k^{V,-1}\mathbf{I}_k^+), \quad (40)$$

where the pseudoscalar functions  $f_k^{V,\mu}$  ( $\mu=-1, 0, 1$ ) behave under molecular rotations like spherical harmonics  $Y_{k,\mu}$ . A vector  $\tilde{f}_k^V$  exists such that

$$f_k^{V,0}=(1/2)(\tilde{f}_k^V)_Z,$$

$$f_k^{V,\pm 1}=(\sqrt{2}/4)[(\tilde{f}_k^V)_X\pm i(\tilde{f}_k^V)_Y]. \quad (41)$$

As the vector  $\tilde{f}_k^V$  reorientates randomly, the functions  $f_k^{V,\mu}$  are random functions of time. The correlation functions  $g_{ik}^{V,\mu}(\tau)$  are then defined

$$g_{ik}^{V,\mu}(\tau)=\mathbf{A}_\sigma[f_i^{V,-\mu}(t)f_k^{V,\mu}(t+\tau)], \quad (42)$$

which generate the corresponding spectral density

TABLE IV. Values of the  $\mathbf{R}$  functionals for an  $AB$  system composed of spin- $\frac{1}{2}$  nuclei.<sup>a</sup>

| $r$ | Eigenvector   | $\mathbf{R}_{AA}^0$ | $\mathbf{R}_{AA}^1$ | $\mathbf{R}_{AB}^0$ | $\mathbf{R}_{AB}^1$ |
|-----|---|---------------------|---------------------|---------------------|---------------------|
| 1   | $ \alpha\alpha\rangle$  | 0                   | 2                   | 0                   | 0                   |
| 2   | $\cos\varphi \alpha\beta\rangle + \sin\varphi \beta\alpha\rangle$ | $p^2$               | 2                   | $-p^2$              | $2p$                |
| 3   | $\cos\varphi \beta\alpha\rangle - \sin\varphi \alpha\beta\rangle$ | $p^2$               | 2                   | $-p^2$              | $-2p$               |
| 4   | $ \beta\beta\rangle$  | 0                   | 2                   | 0                   | 0                   |

<sup>a</sup>  $p = \sin 2\varphi$ ,  $\tan 2\varphi = \mathcal{J}/\delta$ ;  $\mathcal{J}$  and  $\delta$  are the coupling constant and the chemical shift, respectively. The values of the  $\mathbf{R}$  functionals do not change if  $A$  and  $B$  are permuted.

functions

$$j_{ik}^{V,\mu}(\omega) = \int_{-\infty}^{+\infty} g_{ik}^{V,\mu}(\tau) \exp(-i\omega\tau) d\tau. \quad (43)$$

Following the usual lines, the contribution of the interaction  $V$  to the  $r$ th energy-level width becomes

$$\Gamma^V(r) = \sum_i \sum_k \Gamma_{ik}^V(r),$$

$$\Gamma_{ik}^V(r) = j_{ik}^{V,0}(0) \mathbf{P}_{ik}^0(r) + 2 \operatorname{Re} [j_{ik}^{V,1}(\Phi_i) \mathbf{P}_{ik}^1(r)], \quad (44)$$

where the  $\mathbf{P}$  functionals are given as

$$\begin{aligned} \mathbf{P}_{ik}^0(r) &= \langle \mathbf{K}_i \mathbf{K}_k \rangle_{rr} - \langle \mathbf{K}_i \rangle_{rr} \langle \mathbf{K}_k \rangle_{rr}, \\ \mathbf{P}_{ik}^1(r) &= 2e_{ik} \langle \mathbf{I}_i^+ \mathbf{I}_k^- \rangle_{rr}. \end{aligned} \quad (45)$$

In the approximation IRCOF, the correlation functions are assumed to be

$$g_{ik}^{V,\mu}(\tau) = g_{ik}^{V,\mu}(0) \chi_1(\tau), \quad (46)$$

where  $\chi_1(\tau)$  is a function common to all processes of the  $\Pi$  type activated by the same random phenomenon. In an isotropic case

$$g_{ik}^{V,\mu}(0) = \mathcal{G}_{ik}^V = (1/12) \mathbf{A}_\sigma(\tilde{f}_i^V \cdot \tilde{f}_k^V). \quad (47)$$

The spectral density functions are then independent of  $\mu$ :

$$j_{ik}^{V,\mu}(\omega) = \mathcal{G}_{ik}^V \zeta_1(\omega), \quad (48)$$

$\zeta_1(\omega)$  being the Fourier transform of  $\chi_1(\tau)$ . If, moreover, the approximation EDA is valid then

$$\chi_1(\tau) = \exp(-|\tau|/\tau_1) \rightarrow \zeta_1(\omega) = 2\tau_1/(1+\omega^2\tau_1^2). \quad (49)$$

Once again the fast reorientation limit and the slow reorientation limit can be distinguished.

With (49), the spectral density functions are real; consequently

$$\Gamma_{ik}^V(r) = j_{ik}^{V,0}(0) \mathbf{R}_{ik}^0(r) + j_{ik}^{V,1}(\Phi_i) \mathbf{R}_{ik}^1(r), \quad (50)$$

where

$$\mathbf{R}_{ik}^0(r) \equiv \mathbf{P}_{ik}^0(r), \quad \mathbf{R}_{ik}^1(r) = 2e_{ik} \langle \mathbf{I}_i^+ \mathbf{I}_k^- + \mathbf{I}_i^- \mathbf{I}_k^+ \rangle_{rr}. \quad (51)$$

These functionals are the same for all  $\Pi$  processes. Their values for a simple  $AB$  system composed of spin- $\frac{1}{2}$

nuclei are given in Table IV. If the coupling is not too strong, the main contribution to the linewidths comes from the one-particle terms connected with  $\mathbf{R}_{kk}^1(r)$ . In spin- $\frac{1}{2}$  systems  $\mathbf{R}_{kk}^1(r)$  is equal to 2 for all eigenstates. In the special case of intermolecular relaxation, this uniformity has been already noticed in II.

### A. Intermolecular Relaxation ( $\mathbf{R}$ )

Although intermolecular relaxation is not a typical  $\Pi$  process, it obeys the same equations (40)–(51). The vector  $\tilde{f}_k^R$  is equal to  $\gamma_k \tilde{h}_k$ ,  $\tilde{h}_k$  being the fluctuating magnetic field due to intermolecular interactions. This case has been discussed in detail in II; here it is mentioned only for completeness.

### B. Broadening Due to Spin-Rotation Interaction ( $\mathbf{J}$ )

The general importance of this type of relaxation was demonstrated by Gutowsky *et al.*<sup>10</sup> and, for uncoupled systems, discussed by Hubbard.<sup>11</sup> It seems<sup>10</sup> that for small molecules the spin-rotation relaxation can even be more important than the dipolar one. Let us notice here that the same should hold also for small fragments like methyl groups provided they undergo free rotation.

In a polyatomic molecule, the coupling of the nuclear spins  $\tilde{\mathbf{I}}_k$  with the angular momentum  $\tilde{\mathbf{J}}$  can be approximated by its leading term

$$\mathbf{H}^J = \sum_k \tilde{\mathbf{J}} \cdot \tilde{\mathbf{C}}_k \cdot \tilde{\mathbf{I}}_k, \quad (52)$$

where  $\tilde{\mathbf{C}}_k$  is the coupling tensor for the  $k$ th nucleus. As both  $\tilde{\mathbf{J}}$  and  $\tilde{\mathbf{C}}_k$  follow the molecular rotations, the quantity  $\tilde{\mathbf{J}} \cdot \tilde{\mathbf{C}}_k$  really behaves like a vector under them and can thus be identified with the vector  $\tilde{f}_k^J$ .

In the approximation IRCOF the only parameters to be specified are the  $\mathcal{G}_{ik}^J$ . From (47) one obtains

$$\mathcal{G}_{ik}^J = (1/12) \mathbf{A}_\sigma(\tilde{\mathbf{J}} \cdot \tilde{\mathbf{D}}_{ik} \cdot \tilde{\mathbf{J}}), \quad (53)$$

where  $\tilde{\mathbf{D}}_{ik} = \tilde{\mathbf{C}}_i \tilde{\mathbf{C}}_k^+$ , the cross denoting the transposed tensor.

Note that, because of the ensemble averaging in (47), the  $\Pi$  processes depend on the temperature not only through the correlation times but also through the temperature dependence of the ensemble averages (see Ref. 10 for a very clear demonstration of this effect).

Another important feature of the spin-rotation interaction is that it is governed by the correlation time  $\tau_1$  which is different both from  $\tau_2$  characterizing  $\Delta$  processes and from  $\tau_c'$  characterizing the intermolecular relaxation. Furthermore,  $\tau_1$  is characteristic for the molecular reorientation only if  $\tilde{f}_k^V$  preserves its absolute value; this evidently does not hold for  $\tilde{f}_k^J$ . Gordon<sup>12</sup> has shown, of course, that in many cases the infrared band shapes are consistent with the assumption that the redistribution of the absolute value of  $\tilde{\mathbf{J}}$  is much slower than the redistribution of its direction. If this is true then the random jumps between states with different  $\mathbf{J}$  values have little influence on  $\tau_1$ .

### III. CROSS TERMS BETWEEN VARIOUS TYPES OF INTERACTIONS

The existence of the cross-term contributions to the energy-level widths was mentioned in I but no particular case has so far been treated. They arise from the contributions to the transition probabilities of the type

$$\mathfrak{W}^{UV}(r \rightarrow s) = \int_{-\infty}^{+\infty} \exp(-i\omega_{rs}\tau) \times \mathbf{A}_\sigma[s | \mathbf{H}^U(t) | r \rangle \langle r | \mathbf{H}^V(t+\tau) | s \rangle] d\tau. \quad (54)$$

Many of the cross terms can be immediately excluded. If the time dependence of the two interactions  $U$  and  $V$  is due to two different, uncorrelated random processes then  $\mathfrak{W}^{UV} = 0$  for all transitions. Even if both  $U$  and  $V$  are activated by the same random process, the cross terms between them disappear as long as they are of different symmetry types (provided the medium is isotropic). Consequently, the only nonzero cross terms connected with the above cited interactions are those between the three  $\Delta$ -type mechanisms.

Consider now two different, but correlated, relaxation mechanisms  $U$  and  $V$  and let the orders of magnitude of the linewidth contributions connected with them be in a ratio  $u/v > 1$ . The cross terms are then expected to be of the order of  $(uv)^{1/2}$  and, moreover, they can be both positive and negative. The cross-term contributions thus change the linewidths by a value which is of the order of  $200(u/v)^{1/2}\%$ . For  $u/v \simeq 10^2$  this gives about 20%; it means that the cross terms can be significant even if the direct influence of one of the mechanisms is negligible.

The derivation of the expressions for the cross terms is quite straightforward but the resulting formulas are a little cumbersome. Only the final formulas are given here which result in the fast reorientation limit if the approximations IRCOF and EDA are valid.

#### A. Cross Terms Between the Dipolar Interaction and the Quadrupolar Interaction

The contribution to the energy-level width due to D-Q cross terms is

$$\Gamma^{DQ}(r) = -\frac{3e^2}{80} \tau_2 \sum_i \sum_{k < l} \left[ \frac{Q_i}{S_i(2S_i-1)} \frac{\gamma_k \gamma_l}{R_{kl}^3} \times \sum_\beta Q_\beta^i \cos^2 \gamma_{kl}^\beta \right] \mathbf{C}_{i,kl}(r), \quad (55)$$

where  $\gamma_{kl}^\beta$  is the angle between the vector  $\bar{p}_{kl}$  and the  $\beta$ th main axis of  $\tilde{Q}^i$ . The functional  $\mathbf{C}_{i,kl}(r)$  has the form

$$\begin{aligned} \mathbf{C}_{i,kl}(r) = & 2e_{kl} \langle \mathbf{K}_i^2 \rangle_{rr} \langle \mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_k^- \mathbf{I}_l^+ \rangle_{rr} - 2 \langle \mathbf{K}_i^2 \rangle_{rr} \langle \mathbf{K}_k \mathbf{K}_l \rangle_{rr} \\ & + \langle 2\mathbf{K}_i^2 \mathbf{K}_k \mathbf{K}_l - e_{kl} [\mathbf{K}_i^2, \mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_k^- \mathbf{I}_l^+] \\ & + [\mathbf{K}_i \mathbf{I}_i^- + \mathbf{I}_i^- \mathbf{K}_i, e_{il} \mathbf{K}_k \mathbf{I}_l^+ + e_{ik} \mathbf{I}_k^+ \mathbf{K}_l] \\ & + [\mathbf{K}_i \mathbf{I}_i^+ + \mathbf{I}_i^+ \mathbf{K}_i, e_{il} \mathbf{K}_k \mathbf{I}_l^- + e_{ik} \mathbf{I}_k^- \mathbf{K}_l] \\ & + 4e_{ik} e_{il} \{ [\mathbf{I}_i^+ \mathbf{I}_i^+, \mathbf{I}_k^- \mathbf{I}_k^-] + [\mathbf{I}_i^- \mathbf{I}_i^-, \mathbf{I}_k^+ \mathbf{I}_k^+] \} \}_{rr}, \quad (56) \end{aligned}$$

the bold face brackets denoting anticommutators.

#### B. Cross Terms Between the Dipolar Interaction and the Chemical Shift Anisotropy

The contribution to the energy-level width is

$$\Gamma^{DS}(r) = -(\tau_2/20) \sum_i \sum_{k < l} (\gamma_k \gamma_l / R_{kl}^3) \times (\sum_\beta S_\beta^i \cos^2 \gamma_{kl}^\beta) \mathbf{D}_{i,kl}(r), \quad (57)$$

where  $S_\beta^i$  is the length of the  $\beta$ th main axis of  $\tilde{S}^i$ ,  $\gamma_{kl}^\beta$  is the angle between  $\bar{p}_{kl}$  and the  $\beta$ th main axis of  $\tilde{S}^i$ , and

$$\begin{aligned} \mathbf{D}_{i,kl}(r) = & e_{kl} \langle \mathbf{K}_i \rangle_{rr} \langle \mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_k^- \mathbf{I}_l^+ \rangle_{rr} - \langle \mathbf{K}_i \rangle_{rr} \langle \mathbf{K}_k \mathbf{K}_l \rangle_{rr} \\ & + \langle \mathbf{K}_i \mathbf{K}_k \mathbf{K}_l - (1/2) e_{kl} [\mathbf{K}_i, \mathbf{I}_k^+ \mathbf{I}_l^- + \mathbf{I}_k^- \mathbf{I}_l^+] \\ & + (3/4) [\mathbf{I}_i^+, e_{il} \mathbf{K}_k \mathbf{I}_l^- + e_{ik} \mathbf{I}_k^- \mathbf{K}_l] \\ & + (3/4) [\mathbf{I}_i^-, e_{il} \mathbf{K}_k \mathbf{I}_l^+ + e_{ik} \mathbf{I}_k^+ \mathbf{K}_l] \}_{rr}. \quad (58) \end{aligned}$$

#### C. Cross Terms Between the Quadrupolar Interaction and the Chemical Shift Anisotropy

The contribution to the energy-level width is

$$\Gamma^{QS}(r) = (e^2 \tau_2 / 80) \sum_i \sum_k \{ [Q_i / S_i (2S_i - 1)] \times \sum_\alpha \sum_\beta Q_\alpha^i S_\beta^k \cos^2(\alpha_i \wedge \beta_k) \} \mathbf{E}_{ik}(r), \quad (59)$$

where  $(\alpha_i \wedge \beta_k)$  is the angle between the  $\alpha$ th main axis of  $\tilde{Q}^i$  and the  $\beta$ th main axis of  $\tilde{S}^k$ , and

$$\begin{aligned} \mathbf{E}_{ik}(r) = & 2 \langle \mathbf{K}_i^2 \mathbf{K}_k \rangle_{rr} - 2 \langle \mathbf{K}_i^2 \rangle_{rr} \langle \mathbf{K}_k \rangle_{rr} \\ & + e_{ik} \langle [\mathbf{I}_k^+, \mathbf{K}_i \mathbf{I}_i^- + \mathbf{I}_i^- \mathbf{K}_i] + [\mathbf{I}_k^-, \mathbf{K}_i \mathbf{I}_i^+ + \mathbf{I}_i^+ \mathbf{K}_i] \rangle_{rr}. \quad (60) \end{aligned}$$

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### APPENDIX

#### A. Transition Probabilities

The transition probabilities  $\mathfrak{W}^{UV}(r \rightarrow s)$  due to various random interactions have not been needed in an explicit form in this series of papers. They are, of course, important basic quantities for the study of such problems like saturation and dynamical behavior (spin-echo, saturation recovery) or for problems connected with random perturbations which are too strong to be treated by perturbation methods.<sup>5</sup>

Starting from the corresponding perturbation Hamiltonians and using Eq. (54), the expressions for the transition probabilities can be easily obtained. Their further simplification is possible using the same principles as in the case of linewidths; Eq. (6) is particularly important in this step.



### B. Units

In I it was stated that there is a relation between the mean lifetime  $\Gamma(\tau)$  of an eigenstate and its energy-level width  $\delta_\tau$  of the type  $\delta_\tau = g\Gamma(\tau)$ , where  $g \simeq 1$  depends on the shape of the density profile of the energy level. It can be shown on a quite general basis<sup>13</sup> that, for the Lorentz-shape lines,  $g = 1$ . The resulting energy-level widths are then given in Hz; otherwise the convention  $\hbar = 1$  implies that the energy and frequency units must be  $\text{rad sec}^{-1}$  for all the input parameters.

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<sup>1</sup> S. Sýkora, J. Chem. Phys. **52**, 4818 (1970).

<sup>2</sup> S. Sýkora, J. Chem. Phys. **52**, 5949 (1970). Two numerical errors appeared in I and II. The coefficient  $18/45\pi$  in I, Eq. (28) should be  $4/45$ . In II, a factor of 2 is missing in the second terms of Eqs. (8). In consequence, the values of the  $R_{ij}$  functionals

in II must be multiplied by 2. None of the conclusions in the two papers is influenced by these changes.

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## High-Temperature Heat Contents and Related Thermodynamic Functions of Seven Trifluorides of the Rare Earths: Y, La, Pr, Nd, Gd, Ho, and Lu\*

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The high-temperature heat contents of high-purity YF<sub>3</sub>, LaF<sub>3</sub>, PrF<sub>3</sub>, NdF<sub>3</sub>, GdF<sub>3</sub>, HoF<sub>3</sub>, and LuF<sub>3</sub> were measured from 100–1600°C. The heat capacity, heats of transition, heats of fusion, and related thermodynamic functions were calculated. The smoothed values of  $H^\circ_T - H^\circ_{298}$ ,  $C_p$ ,  $S^\circ_T - S^\circ_{298}$ , and  $-(F^\circ_T - H^\circ_{298})/T$  are tabulated at 100° intervals. A comparison of the values for the transition temperature, melting points, and lattice parameters of the higher-purity fluorides of this work with those of less pure fluorides indicated that a reduction in oxygen content does not affect these properties.

### INTRODUCTION

The rare-earth trifluorides have been of particular interest in the preparation of the rare-earth metals for many years. As part of an effort to improve the purity of the rare-earth metals, a program to prepare and characterize very high-purity rare-earth fluorides was undertaken. A significant part of this program was concerned with the measurement of the high-temperature thermodynamic properties of the trifluorides, including the latent heats of transition and of fusion. This paper is the first of a series from this Laboratory reporting the properties of the fluorides. In this segment of the investigation we have measured the high-temperature heat contents of seven rare-earth trifluorides, specifically, YF<sub>3</sub>, LaF<sub>3</sub>, PrF<sub>3</sub>, NdF<sub>3</sub>, GdF<sub>3</sub>, HoF<sub>3</sub>, and LuF<sub>3</sub>.

The light rare-earth fluorides, LaF<sub>3</sub>, PrF<sub>3</sub>, and NdF<sub>3</sub>, were originally thought to have a hexagonal structure.<sup>1–3</sup> Recent single-crystal data<sup>4–6</sup> show LaF<sub>3</sub> has a trigonal structure rather than the hexagonal structure. No crystalline transformation was reported for the light

fluorides. The heavy rare-earth fluorides, GdF<sub>3</sub>, HoF<sub>3</sub>, LuF<sub>3</sub>, and YF<sub>3</sub> have an orthorhombic structure at room temperature.<sup>2,7</sup> However, the heavy fluorides have been reported to transform to a high-temperature hexagonal structure.<sup>2,8</sup> The high-temperature transitions for GdF<sub>3</sub>, LuF<sub>3</sub>, and YF<sub>3</sub> have been observed by Dennison using differential thermal analysis,<sup>9</sup> but the transition for HoF<sub>3</sub> has been detected only by high-temperature x-ray diffraction.<sup>8</sup>

Very little thermodynamic data are available for the rare-earth fluorides. As far as we know, the only previous experimental data on the high-temperature heat contents or heat capacities of the rare-earth fluorides are the measurements on PrF<sub>3</sub>, NdF<sub>3</sub>, GdF<sub>3</sub>, and YbF<sub>3</sub> over the temperature range of 500–1400°K,<sup>10</sup> and both the low- and high-temperature data for CeF<sub>3</sub>.<sup>11,12</sup>

### MATERIALS AND EQUIPMENT

The rare-earth fluorides were prepared by a two-step process.<sup>13</sup> In the first step, high-purity rare-earth oxide