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References

[1] R. Steinhaus and E. Gumlich, Verh. dtsch. Phys. Ges. *17*, 369 (1915).
[2] E. Dussler, Z. Phys. *44*, 286 (1927).
[3] S. Shtrikman and D. Treves, J. appl. Phys. *31*, 58 S (1959).
[4] E. P. Wohlfarth, in: *Magnetism*, G. T. Rado and H. Suhl, Eds. (Academic Press, New York 1963), Vol. III, Chap. 7, p. 351–393.
[5] E. Kneller, J. appl. Phys. *39*, 945 (1968).
[6] E. Kneller and E. P. Wohlfarth, J. appl. Phys. *37*, 4816 (1966).
[7] L. Neel, R. Forrer, N. Janet and R. Baffie, Cahiers Phys. *17*, 51 (1943).
[8] L. Neel, Cahiers Phys. *17*, 47 (1943).
[9] S. Middelhoek, IBM Jl. Res. Dev. *6*, 394 (1962).
[10] E. C. Stoner and E. P. Wohlfarth, Phil. Trans. Roy. Soc. (London) *A 240*, 599 (1948).
[11] S. Shtrikman and D. Treves, J. Phys. Radium *20*, 286 (1959).

Group Theory of Angular Correlations Related to Diatomic Rotators in Liquids and Solids

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(3. V. 68)

Abstract. Angular correlations of diatomic rotators (OH^-, OD^-) in crystals (KCl) have recently been measured with the aid of vibration-rotation spectra. Here we examine by group theory the relations between the different angular correlation functions of diatomic rotators in liquids and solids as determined by electric dipole transitions and magnetic resonances.

Résumé. Nous avons récemment mesuré les corrélations angulaires de rotateurs diatomiques (OH^-, OD^-) dans les cristaux (KCl) en observant les spectres de vibration-rotation. C'est pourquoi nous étudions maintenant à l'aide de la théorie des groupes les fonctions de corrélation de ces rotateurs dans les liquides et les solides. Les résultats sont appliqués aux transitions dipolaires et aux résonances magnétiques.

Zusammenfassung. Kürzlich haben wir Winkelkorrelationen von zweiatomigen Rotatoren (OH^-, OD^-) in Kristallen (KCl) mit Hilfe von Rotations-Vibrationsspektren studiert. Zum besseren Verständnis der experimentellen Resultate untersuchen wir in der vorliegenden Arbeit die Winkelkorrelationsfunktionen solcher Rotatoren mit gruppentheoretischen Methoden. Dabei werden besonders jene Korrelationsfunktionen berücksichtigt, welche bei elektrischen Dipolübergängen und magnetischen Resonanzen auftreten.

Introduction

Random rotation of molecules in liquids strongly influences the line shapes observed in nmr, esr, vibrational and even Raman spectra. Considerable effort has

therefore been focussed on the experimental and theoretical study of this statistical phenomenon [1–4]. Since the gamut of rotational relaxation times reaches down to 10^{-13} sec for simple molecules at room temperature, a successful experimental investigation must be based on a probe with much shorter response time. Short-time rotational-relaxation processes cannot be observed by the relatively slow nmr and esr with response times larger than 10^{-7} sec and 10^{-10} sec respectively. Explanations of nmr and esr line shapes [4, 5] are therefore content with an exponential decay of correlation, which has to be considered as the long-time approximation. On the contrary, the vibration-rotation spectra of diatomic linear and symmetric-top molecules with response times of the order 10^{-14} sec provide an almost ideal tool for the study of rapid rotational motion. Experiments [6, 7] and theories [8–10] performed during the last few years are very promising.

Recently the colour center community has been fascinated by the theoretical aspects and the technical possibilities of diatomic rotators as OH^-, OD^- and O_2^- in alkali halides [1, 12, 13]. As a consequence detailed esr [21], uv, ir [12] and dielectric [11] measurements have been started in order to determine the electronic structure of the molecules and their interaction with the host crystal. Recently, KELLER and the author attempted to contribute some additional information on this problem by precise measurement of the vibration-rotation spectra of OH^- and OD^- and subsequent evaluation with the theory of rotational correlations in liquids [14]. But we were not too sure about the relations between the correlations in liquids and those in solids.

The determination of angular correlations by observation of electric dipole transitions such as dielectric relaxation, rotational spectra and vibration-rotation spectra is based on the rotation of the permanent or oscillatory electric dipole $\boldsymbol{p}(t) = p(t)\,\boldsymbol{u}(t)$, where $\boldsymbol{u}(t) = (\sin\vartheta(t)\cos\varphi(t),\ \sin\vartheta(t)\sin\varphi(t),\ \cos\vartheta(t))$ is the randomly rotating unit vector. The quantity measured is essentially the correlation function

$$\langle \boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\rangle = 3\,\langle\cos\vartheta(0)\cdot\cos\vartheta(t)\rangle\,. \tag{1}$$

Relaxation effects in nmr and esr depend on entirely different correlation functions. As an example we consider a paramagnetic diatomic rotator (O_2^- ?) with an axial g-tensor. According to PAKE [5] the spin Hamiltonian as function of the orientation $\Omega = (\vartheta, \varphi)$ can be written as

$$\begin{aligned}\mathcal{H} &= \beta H_0 g S_z + \frac{1}{9}\beta H_0 \Delta g \left(\cos^2\vartheta - \frac{1}{3}\right) S_z \\ &\quad + \frac{1}{2}\beta H_0 \Delta g \cos\vartheta \sin\vartheta\,(e^{+i\varphi} S_- + e^{-i\varphi} S_+);\\ 3g &= g_\parallel + 2g_\perp;\quad \Delta g = g_\parallel - g_\perp\end{aligned}$$

neglecting crystal field terms and hyperfine interactions. Therefore, the contribution of the random rotation to the spin-lattice relaxation is given by the expression

$$\begin{aligned}\left(\frac{1}{2T_1}\right)_{mm'} &= \left(\frac{\beta H_0 \Delta g}{2\hbar}\right)^2 |(m\,|\,S_-\,|\,m')|^2 \\ &\quad\times \int dt\, e^{-i\omega_{mm'}t}\,\langle(\cos\vartheta_0 \sin\vartheta_0\, e^{i\varphi_0})\,(\cos\vartheta_t \sin\vartheta_t\, e^{-i\varphi_t})\rangle\end{aligned}$$

with

$$\langle(\cos\vartheta_0 \sin\vartheta_0 \, e^{i\varphi_0}) \, (\cos\vartheta_t \sin\vartheta_t \, e^{-i\varphi_t})\rangle \tag{2}$$

as the basic correlation function. From Equation (2) it can be easily derived that the contribution to the spin-spin relaxation must be connected to still another correlation function:

$$\left\langle\left(\cos^2\vartheta_0 - \frac{1}{3}\right)\left(\cos^2\vartheta_t - \frac{1}{3}\right)\right\rangle. \tag{3}$$

This demonstrates that different experimental methods for studying angular correlation of diatomic rotators provide us with at least three correlation functions (1), (2) and (3). We are going to show that the relations among these functions differ for rotators in liquids and rotators in solids.

Orientational Probability and Correlation Functions

Before introducing any group theoretical concepts we describe the general properties of orientational probabilities and correlations in analogy to the considerations of WANG and UHLENBECK [15]. We concentrate mainly on the representation of the probability density, the joint probability density and the correlation matrix, which can be determined partially by the experimental methods mentioned above.

The orientation Ω of a diatomic rotator is determined by the polar angles ϑ and φ. Consequently any function f of the orientation Ω can be expressed by linear combination of normalized spherical harmonics $Y_{nm}(\vartheta, \varphi) = Y_{nm}(\Omega)$:

$$f(\Omega) = a^*_{nm} \, Y_{nm}(\Omega) \, . \tag{4}$$

For $Y_{nm}(\Omega)$ and related functions we use the definitions of EDMONDS [20]. Summation is performed over identical indices. A *random rotation* is characterized by an orientation Ω which does not depend in a completely definite way on the time t. Only certain probability distributions are directly observable. If the random rotation is a *Markoff process*, the motion is completely described by the *probability density* $w(\Omega_T)$ and the *joint probability density* $W(\Omega_T/\Omega_{T+t})$. Random rotational motion is not necessarily restricted to Markhoff processes, but for experimental purposes we may confine our theory to $w(\Omega_T)$ and $W(\Omega_T/\Omega_{T+t})$. $w(\Omega_T)\, d\Omega_T$ is defined as the probability of finding the rotator with the orientation in the range $(\Omega_T, \Omega_T + d\Omega_T)$ at the time T. $W(\Omega_T/\Omega_{T+t})\, d\Omega_T \, d\Omega_{T+t}$ represents the probability of finding the rotator with the orientation in the range $(\Omega_T, \Omega_T + d\Omega_T)$ at the time T and with the orientation in the range $(\Omega_{T+t}, \Omega_{T+t} + d\Omega_{T+t})$ at the time $(T + t)$. The two probability densities are functions of the orientations Ω_T and Ω_{T+t} which implies

$$w(\Omega_T) = w^*_{nm}(T) \, Y_{nm}(\Omega_T) \quad \text{and}$$
$$W(\Omega_T/\Omega_{T+t}) = Y^*_{nm}(\Omega_T) \, W_{nm/n'm'}(T, T+t) \, Y_{n'm}(\Omega_{T+t}) \, . \tag{5}$$

In general $w(\Omega_T)$ has to be real and normalized over the unit sphere, whereas $W(\Omega_T/\Omega_{T+t})$ must be a symmetric function in Ω_T and Ω_{T+t}:

$$W(\Omega_{T+t}/\Omega_T) = W^*(\Omega_T/\Omega_{T+t}) \, .$$

This requires

$$w_{00}(T) = w_{00} = (4\pi)^{-1/2} \text{ and } w^*_{nm}(T) = (-1)^m w_{n,-m}(T);$$
$$\text{and } W_{nm/n'm'}(T, T+t) = W^*_{n'm'/nm}(T+t, T). \tag{6}$$

In addition, $w(\Omega_T)$ and $W(\Omega_T/\Omega_{T+t})$ are related by

$$\int W(\Omega_T/\Omega_{T+t})\, d\Omega_{T+t} = w(\Omega_T) \text{ or } W_{nm/00}(T, T+t) = w_{nm}(T)\,(4\pi)^{-1/2}.$$

Because we are dealing with *stationary random rotations* the origin of the time is arbitrary and $w(\Omega_T)$ and $W(\Omega_T/\Omega_{T+t})$ do not depend on T. Some calculations based on this fact and relations (3) show that

$$w_{nm}(T) = w_{nm}; \quad W_{nm/n'm'}(T, T+t) = W_{nm/n'm'}(0, t) = W_{nm/n'm'}(t)$$
$$\text{and} \quad W_{nm/n'm'}(t) = W^*_{n'm'/nm}(-t). \tag{7}$$

Boundary values for $W_{nm/n'm'}(t)$ at the correlation times $t = 0$ and $t = \infty$ are derived from the fact that

$$W(\Omega_0, \Omega_{t=0}) = w(\Omega_0)\,\delta(\Omega_0 - \Omega_{t=0})$$

and the assumption that the correlations are lost after a sufficiently long time:

$$W(\Omega_0, \Omega_{t=\infty}) = w(\Omega_0)\cdot w(\Omega_{t=\infty}).$$

We obtain

$$\begin{aligned} W_{nm/n'm'}(0) &= (4\pi)^{-1}\,\delta_{nm/n'm'} + \text{higher order terms} \\ &= (4\pi)^{-1}(-1)^{m'}\,[(2n+1)(2n'+1)(2n''+1)]^{1/2}\, w^*_{n''m''} \\ &\times \begin{pmatrix} n & n' & n'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n & n' & n'' \\ m & -m' & m'' \end{pmatrix} \text{ and } W_{nm/n'm'}(\infty) = w_{nm}\, w^*_{n'm'}. \end{aligned} \tag{8}$$

Information on $w(\Omega)$ and $W(\Omega_0/\Omega_t)$ can be collected only by experimental determination of averages and correlations. The *average* of a function $f(\Omega)$ is defined as

$$\langle f(\Omega)\rangle = \int f(\Omega)\, w^*(\Omega)\, d\Omega = a^*_{nm}\, w_{nm} \tag{9a}$$

and the *correlation function* of $f_1(\Omega_0)$ and $f_2^*(\Omega_t)$ as

$$\begin{aligned} \langle f_1(\Omega_0)\, f_2^*(\Omega_t)\rangle &= \iint f_1(\Omega_0)\, W(\Omega_0/\Omega_t)\, f_2^*(\Omega_t)\, d\Omega_0\, d\Omega_t \\ &= a^*_{1,nm}\, W_{nm/n'm'}(t)\, a_{2,n'm'}. \end{aligned} \tag{9b}$$

The matrix elements w_{nm} and $W_{nm/n'm'}(t)$ are therefore uniquely determined by the set

$$\langle Y_{nm}(\Omega)\rangle = w_{nm} \quad \text{and} \quad \langle Y_{nm}(\Omega_0)\, Y^*_{n'm'}(\Omega_t)\rangle = W_{nm/n'm'}(t). \tag{10}$$

For this reason $W_{nm/n'm'}$ is called the *correlation matrix*.

The time reversal of the auto-correlation functions is governed by the last equation of (7):

$$\langle f(\Omega_0)\, f^*(\Omega_t)\rangle = a^*_{nm}\, W_{nm/n'm'}(t)\, a_{n'm'}$$
$$= \langle f(\Omega_0)\, f^*(\Omega_{-t})\rangle^* = G(t) + i\, U(t)$$

where $G(t) = G(-t)$ and $U(t) = -U(-t)$ are real functions. Thus $W_{nm/n'm'}(t)$ can be split according to

$$W_{nm/n'm'}(t) = G_{nm/n'm'}(t) + i\, U_{nm/n'm'}(t)\,,$$
$$G_{nm/n'm'}(t) = G^*_{n'm'/nm}(t) = G_{nm/n'm'}(-t)\,,$$
$$U_{nm/n'm'}(t) = U^*_{n'm'/nm}(t) = -\, U_{nm/n'm'}(-t)\,.$$

The relations above are valid for a rotator in a neighbourhood of arbitrary symmetry. If this symmetry is known, a simplification of w_{nm} and $W_{nm/n'm'}(t)$ by group theoretical procedures is possible. We shall illustrate this for rotators in a liquid or a gas corresponding to a vicinity of full rotation symmetry R^3 and in a crystal with cages of symmetry O_h. The latter represents a simple model of OH^- in KCl.

Angular Correlations in Liquids and Gases

In liquids and gases the probability densities $w(\Omega)$ and $W(\Omega_0/\Omega_t)$ remain invariant under all coordinate transformations of the *full rotation group* R^3. The basis of the irreducible representation $D_n^{\pm}$ of R^3 is $Y_{nm}(\Omega)$. No transformation of w_{nm} and $W_{nm/n'm'}(t)$ has to be made. Schur's lemma can immediately be applied.

$$w(\Omega) = w(\Omega, D_0^+) = (4\pi)^{-1}, \quad W_{nm/n'm'}(t) = (4\pi)^{-1}\, k_n(D_n^{\pm}, t)\, \delta_{nn'}\, \delta_{mm}$$

or

$$W(\Omega_0/\Omega_t) = (4\pi)^{-1}\, k_n(D_n^{\pm}, t)\, Y^*_{nm}(\Omega_0)\, Y_{nm}(\Omega_t)$$
$$= (4\pi)^{-2}\,(2n+1)\, k_n(D_n^{\pm}, t)\, P_n(\cos\Delta\Omega) \tag{11}$$

where $\Delta\Omega$ is the angle between the orientations Ω_0 and Ω_t. $D_n^{\pm}$ indicates the $2n+1$-dimensional representation of the full rotation group and $k_n(D_n^{\pm}, t)$ the *normalized correlation function* of the irreducible representation $D_n^{\pm}$. Conditions (8) are fulfilled if

$$k_0(D_0^+, t) = 1,\; k_{n>0}(D_n^{\pm}, 0) = 1,\; k_{n>0}(D_n^{\pm}, \infty) = 0\,. \tag{12}$$

The *correlation functions of special experimental interest* are determined by $k_1(D_1^+, t)$ and $k_2(D_2^+, t)$:

$$\langle\cos\vartheta_0 \cos\vartheta_t\rangle = \frac{1}{3}\, k_1(D_1^-, t)\,, \tag{1a}$$

$$\left\langle\left(\cos^2\vartheta_0 - \frac{1}{3}\right)\left(\cos^2\vartheta_t - \frac{1}{3}\right)\right\rangle = \frac{4}{45}\, k_2(D_2^+, t)\,, \tag{2a}$$

$$\left\langle\langle(\cos\vartheta_0 \sin\vartheta_0\, e^{i\varphi_0})\,(\cos\vartheta_t \sin\vartheta_t\, e^{-i\varphi_t})\right\rangle = \frac{2}{15}\, k_2\,(D_2^+, t)\,. \tag{3a}$$

Specific theories of angular correlations of rotators in liquids and gases should provide us with information on all the different k_n.

This can be illustrated by the most simple theory, called the *Debye limit* of random rotation. Here we assume that the rotator in the liquid acts as a rotating sphere in a liquid of effective viscosity η. The random rotation of this sphere is determined by the equation of diffusion

$$\frac{[\vartheta\, w^{-1}(\Omega_0)\, W(\Omega_0/\Omega_t)]}{\vartheta\, t} = \frac{1}{6\,\tau_2}\, \Delta(\Omega_t)\, [w^{-1}(\Omega_0) W(\Omega_0/\Omega_t)] \tag{13}$$

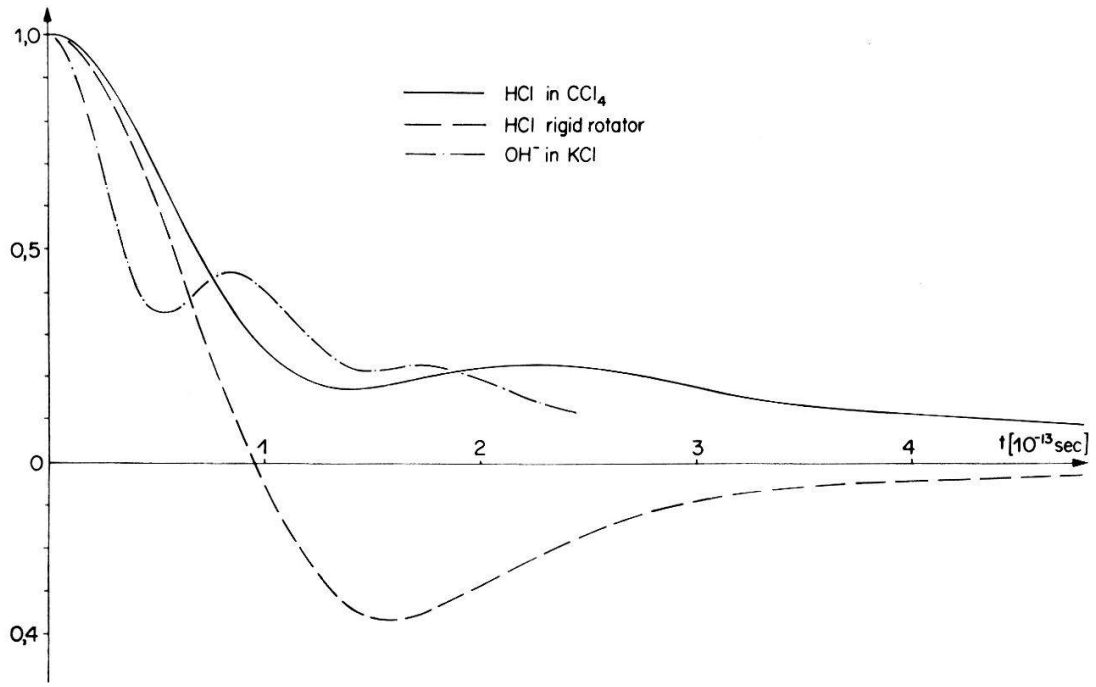
with the Debye relaxation time $\tau_2 = \eta\, V/(k\, T)$.

V is the volume of the sphere, T the absolute temperature. The solution leads to exponential normalized correlation functions (e.g. [4, 16])

$$k_n(D_n^+, t) = \exp\left(-\frac{n\,(n+1)}{6\,\tau_2}\,|t|\right)$$

The exponential decay classifies the Debye limit as a MARKOFF *process* [15].

The Figure shows examples of $k_1(D_1^-, t)$ determined from vibration-rotation spectra. It clearly demonstrates the non-validity of the Debye limit for short correlation times. For long correlation times this limit approaches reality and can therefore be used for the explanation of esr and nmr line shapes. For extremely short times the random rotation may be described by the *inertial limit* [9], in between both limits fail.



Auto-correlation functions of diatomic rotators.
$k_1(D_1^-, t)$ of HCl in an ideal gas (calculated) and in CCl_4 (measured by B. KELLER) at room temperature. $k_{11}(\Gamma_1^-, t)$ of OH^- in KCl (measured by B. KELLER) at room temperature.

Angular Correlations of a Diatomic Rotator in a Vicinity of Symmetry O_h

If the vicinity possesses the symmetry O_h the probability densities remain invariant under the transformations of O_h. Linear combinations $\gamma_v^w(\Gamma_u^\pm, \Omega)$ of the spherical harmonics $Y_{nm}(\Omega)$ form the basis of the five irreducible representations $\Gamma_u^\pm$.

Further information may be obtained from the Tables of TRAMMEL [17] and ALTMANN et al. [18]. Because $w(\Omega)$ is a representation of Γ_n^+ it corresponds to the series

$$\begin{aligned} w(\Omega) &= w_v^*(\Gamma_1^+)\,\gamma_v(\Gamma_1^+, \Omega) \\ &= (4\pi)^{-1} + w_2\left[\frac{7}{\sqrt{84}}\,Y_{40} + \frac{1}{2}\sqrt{\frac{70}{84}}\,(Y_{44} + Y_{4,-4})\right] + + \end{aligned} \tag{15}$$

If an effective cubic field acts on the rotator [13], w_v can be calculated with Boltzmann's law. Taking a sixfold coordination [19, page 13] we obtain for $w_2 = -\sqrt{21}\,D_4/4\pi k T$. $W_{nm/n'm'}(t)$ again is determined by Schur's lemma:

$$\begin{aligned} 4\pi\,W_{00/1m'}(t) &= 4\pi\,W_{00/2m'}(t) = 0\,, \\ 4\pi\,W_{00/00}(t) &= k_{11}(\Gamma_1^+, t) = 1\,, \\ 4\pi\,W_{1m/1m'}(t) &= \delta_{mm'}\cdot k_{11}(\Gamma_4^+, t)\,, \\ 4\pi\,W_{20/20}(t) &= \left[1 + 6\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_5^+, t)\,, \\ 4\pi\,W_{2,\pm1/2,\pm1}(t) &= \left[1 - 4\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_5^+, t)\,, \\ 4\pi\,W_{2,\pm2/2,\pm2}(t) &= +\frac{1}{2}\left[1 + 6\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_3^+, t) + \\ &\quad + \frac{1}{2}\left[1 - 4\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_5^+, t)\,, \\ 4\pi\,W_{2,\pm2/2,\mp2}(t) &= +\frac{1}{2}\left[1 + 6\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_3^+, t)\,, \\ &\quad - \frac{1}{2}\left[1 - 4\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_5^+, t)\,, \\ 4\pi\,W_{2,m/2,m'}(t) &= 0 \quad \text{otherwise.} \end{aligned} \tag{16}$$

$k_{vv'}(\Gamma_u^+, t)$ are the *normalized correlation functions* with the value 1 for the time $t = 0$ and vanishing for t approaching infinity. The Figure shows as an example $k_{11}(\Gamma_4^-, t)$ of OH^- in KCl evaluated from the vibration-rotation spectrum. The correlation functions already mentioned in the introduction and in the section on rotators in liquids depend on three normalized correlation functions:

$$\langle \cos\vartheta_0 \cdot \cos\vartheta_t \rangle = \frac{1}{3}\,k_{11}(\Gamma_4^-, t)\,, \tag{1b}$$

$$\left\langle \left(\cos\vartheta_0 - \frac{1}{3}\right)\left(\cos^2\vartheta_t - \frac{1}{3}\right)\right\rangle = \frac{4}{45}\left[1 + 6\sqrt{\frac{\pi}{21}}\,w_1(\Gamma_1^+)\right] k_{11}(\Gamma_3^+, t)\,, \tag{2b}$$

$$\begin{aligned} &\langle (\cos\vartheta_0 \sin\vartheta_0\, e^{i\varphi_0})\,(\cos\vartheta_t \sin\vartheta_t\, e^{-i\varphi_t}) \rangle \\ &\qquad = \frac{2}{15}\left[1 - 4\sqrt{\frac{\pi}{21}}\,w_2(\Gamma_1^+)\right] k_{11}(\Gamma_5^+, t)\,. \end{aligned} \tag{3b}$$

The remarkable feature of these correlations is that for the rotator in a cubic neighbourhood $k_2(D_2^+, t)$ is split into the group-theoretically independent $k_{11}(\Gamma_3^+, t)$ and $k_{11}(\Gamma_5^+, t)$.

Conclusions

$W_{1m/1m}(t)$, $k_1(D_1^-, t)$ and $k_{11}(\Gamma_4^-, t)$ can be determined by the observation of *electric dipole transitions* such as dielectric relaxation, rotational spectra and vibration-rotation spectra

$$\langle \boldsymbol{u}(0)\ \boldsymbol{u}(t)\rangle = k_1(D_1^-, t) = k_{11}(\Gamma_4^-, t)\,. \tag{1c}$$

No problem arises from this equation if the rotator is brought from a liquid or a gas into a solid with cages of symmetry O_h. Orthorhombic or lower symmetries only split the function $k_1(D_1^-, t)$ into two or three group-theoretically independent components.

Relaxation effects of nmr and esr give information on $W_{2m/2m'}(t)$. Cubic symmetry already separates the correlation functions (2) and (3) related to the spin-lattice relaxation and the spin-spin relaxation into two group-theoretically independent functions. Therefore care has to be taken in determining angular correlations of diatomic rotators in solids using esr or nmr.

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References

[1] P. Debye, *Polar Molecules* (The Chemical Catalog Comp., N.Y. 1929).
[2] F. Perrin, J. Phys. Rad. *5*, 497 (1934).
[3] L. Fabri, Phys. Rev. *119*, 53 (1960).
[4] A. Abragam, *Nuclear Magnetism* (Clarendon Press, 1961).
[5] G. E. Pake, *Paramagnetic Resonance* (Benjamin Inc., N.Y. 1962).
[6] J. Lascombe, P. V. Huong, M. L. Josien, Bull. Soc. Chim. France (1959), 1175.
[7] M. O. Bulanin, N. D. Orlova, Optics and Spectroscopy *15*, 112 (1963).
[8] F. C. Gordon, J. Chem. Phys. *39*, 2788 (1963); *40*, 1973 (1964); *41*, 1819 (1964); *43*, 1307 (1965); *44*, 1830 (1966).
[9] H. Shimizu, J. Chem. Phys. *43*, 2453 (1965); Bull. Chem. Soc. Japan *39*, 2325 (1966).
[10] C. Brot, J. Phys. *28*, 789 (1967); C. Brot, B. Lassier, Chem. Phys. Lett. *1*, 581 (1968).
[11] W. Känzig, H. R. Hart, S. Roberts, Phys. Rev. Lett. *13*, 543 (1964); K. Knop, G. Pfister, W. Känzig, Phys. kondens. Mat. *7*, 107 (1968).
[12] U. Kuhn, F. Lüty, Solid St. Comm. *2*, 281 (1964); H. Paus, F. Lüty, Phys. stat. solidi. *12*, 341 (1965); M. V. Klein et al., Phys. Rev. Lett. *17*, 521 (1966); Bull. Am. Phys. Soc. *11*, 228 (1966); *12*, 78 (1967).
[13] A. S. Devonshire, Proc. Roy. Soc. [A] *153*, 601 (1936); P. Sauer, Z. Phys. *194*, 360 (1966); M. E. Baur, W. R. Salzmann, Phys. Rev. Lett. *18*, 590 (1967).
[14] B. Keller, F. K. Kneubühl, Phvs. Rev. Lett. *21*, 88 (1968).
[15] M. C. Wang, G. E. Uhlenbeck, Rev. mod. Phys. *17*, 323 (1945).
[16] F. K. Kneubühl, J. Chem. Phys. *33*, 1074 (1960).
[17] G. T. Trammel, J. math. Phys. *4*, 431 (1963).
[18] S. L. Altmann, A. P. Cracknell, Rev. mod. Phys. *37*, 19 (1965).
[19] W. Low, *Paramagnetic Resonance in Solids*, Solid St. Phys., Suppl. 2 (Academic Press, 1960).
[20] A. R. Edmonds, *Drehimpulse der Quantenmechanik* (Hochschultaschenbücher Verlag Mannheim 1964) or: *Angular Momentum in QM* (Princeton University Press).
[21] H. R. Zeller, W. Känzig, Helv. phys. Acta *40*, 845 (1967); R. T. Shuey, H. R. Zeller, Helv. phys. Acta *40*, 873 (1967); R. H. Silsbee, J. Phys. Chem. Solids *28*, 2525 (1967).