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Molecular reorientations in the ordered phases of KCN and NaCN studied by NMR

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We have measured ^{13}C and ^{23}Na NMR spin-lattice relaxation times as a function of temperature in KCN and NaCN in order to study the head-to-tail reorientations of the CN^- molecules in the two low-temperature ordered phases. We have combined our data with those of dielectric-response and ionic-thermal-conductivity measurements and have determined the correlation time τ_c of the reorientations over more than five decades. We found τ_c to be continuous through the electric-ordering phase transition with the same activation energy in both phases. In the elastically ordered phase of KCN, we detected small-angle CN^- reorientations about directions nearly parallel to the orthorhombic b axis, leading to a small disorder in the CN^- orientation along that axis. We found the rms average of the angle between the C—N and b axes to be 3.9°. Our experiments resulted in the first direct observations of NMR relaxation arising from chemical-shift anisotropy in a solid.

I. INTRODUCTION

Potassium cyanide (KCN) and sodium cyanide (NaCN) both exhibit an elastically ordered phase (below 168 K in KCN and 288 K in NaCN) in which the CN^- molecules are aligned parallel to the b axis in an orthorhombic crystal structure[1,2] (Fig. 1). In this phase, the CN^- molecules are disordered with respect to head-and-tail alignment and undergo random head-to-tail reorientations.[3] At a lower temperature, both KCN and NaCN undergo a second-order phase transition (at 83 K in KCN and 172 K in NaCN) in which the CN^- molecules are *ordered* with respect to head and tail in an antiparallel fashion.[3–5] This is an *electrically* ordered phase.

The structure and dynamics of these two phases have been of considerable interest in recent years. The reorientational motions of the CN^- molecules have been studied by dielectric response,[6,7] ionic thermal conductivity[8,7] (ITC), EPR,[9] and NMR.[10] We[11,12] have studied these motions by NMR of ^{13}C in KCN and NaCN and by NMR of ^{23}Na in NaCN. Combining our results with dielectric-response[6,7] and ITC measurements,[8,7] the correlation time of the reorientations has been obtained over a wide range of temperature, extending into both phases. We find that the correlation time is continuous through the electric-ordering phase transition and follows an Arrhenius relationship with the same activation energy on *both* sides of the phase transition.

Furthermore, we have also detected a small-angle reorientational motion of CN^- molecules in the elastically ordered phase of KCN. We propose that this motion arises from interactions *between* the CN^- molecules, so that a given CN^- not only reorients head-to-tail itself, but also reacts to the head-to-tail reorientations of its CN^- neighbors by changing its own orientation by some small angle. This model leads us to conclude that in the elastically ordered phase, the CN^- molecules are slightly disordered with respect to alignment along the b axis.

II. THEORY

Nuclear spins, when placed in an external dc magnetic field $\vec{H}_0$, develop a macroscopic magnetization along $\vec{H}_0$. The time evolution of this nuclear magnetization towards its thermal-equilibrium value is often exponential with a time constant T_1, the spin-lattice relaxation time. Here, we develop some expressions for T_1 due to mechanisms present in KCN and NaCN. Reorientational motions of the CN^- molecules cause fluctuations in various nuclear-spin interactions. These fluctuations in turn cause spin-lattice relaxation. The interactions considered here are (1) the nuclear spin-spin dipolar interaction, (2) the chemical shift, and (3) the nuclear-quadrupolar interaction. In the cases discussed here, we consider only polycrystalline samples, thus allowing us to simplify our expressions for T_1 by averaging over Ω, the direction of $\vec{H}_0$ with respect to the crystalline axes.

A. Dipolar interaction

Molecular reorientations cause the nuclear spin-spin dipolar interaction to fluctuate, thus giving rise to spin-lattice relaxation. For interactions between unlike spins (I and S spins), we obtain the dipolar contribution $1/T_{1,\mathrm{dip}}$ to the I spin-lattice relaxation rate[13] of the I spins,

$$1/T_{1,\mathrm{dip}} = 2\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left[\tfrac{1}{12}J^{(0)}(\omega_I-\omega_S)+\tfrac{3}{2}J^{(1)}(\omega_I)+\tfrac{3}{4}J^{(2)}(\omega_I+\omega_S)\right], \quad (1)$$

where ω_I and ω_S are the NMR frequencies, $\gamma_I H_0$ and $\gamma_S H_0$, of the I and S spins, respectively, and $J^{(p)}(\omega)$ are spectral density functions of the motion. In a powder sample, we have[14]

$$J^{(0)}(\omega):J^{(1)}(\omega):J^{(2)}(\omega)=6:1:4\ , \tag{2}$$

and, accordingly,

$$1/T_{1,\mathrm{dip}}=\tfrac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)[\tfrac{1}{2}J^{(0)}(\omega_I-\omega_S)+\tfrac{3}{2}J^{(0)}(\omega_I)+3J^{(0)}(\omega_I+\omega_S)]\ . \tag{3}$$

The spectral density function is given by

$$J^{(0)}(\omega)=\int_0^\infty d\tau\cos(\omega\tau)\sum_k G_{jk}^{(0)}(\tau)\ , \tag{4}$$

where $G_{jk}^{(0)}(\tau)$ is a correlation function,

$$G_{jk}^{(0)}(\tau)=\langle \delta F_{jk}^{(0)}(t)\delta F_{jk}^{(0)}(t+\tau)\rangle_{t,\Omega}\ . \tag{5}$$

The symbol $\langle\ \rangle_{t,\Omega}$ denotes an average over time t and solid angle Ω. The summation in Eq. (4) is over all S spins (labeled k) which interact with some given I spin (labeled j). The term $\delta F_{jk}^{(0)}$ is the fluctuating part of the dipolar coupling function,

$$F_{jk}^{(0)}=-2r_{jk}^{-3}P_2(\cos\theta_{jk})\ , \tag{6}$$

where $\vec{r}_{jk}$ is the vector from the I spin to the S spin, θ_{jk} is the angle between $\vec{r}_{jk}$ and $\vec{H}_0$, and P_2 is the Legendre polynomial $P_2(x)=\frac{1}{2}(3x^2-1)$.

By fluctuating part of $F_{jk}^{(0)}$, we mean

$$\delta F_{jk}^{(0)}(t)\equiv F_{jk}^{(0)}(t)-\langle F_{jk}^{(0)}(t)\rangle_t\ . \tag{7}$$

Consequently, we have

$$\langle \delta F_{jk}^{(0)}(t)\rangle_t=0\ , \tag{8}$$

and, if the motion is uncorrelated for large τ,

$$\lim_{\tau\to\infty} G(\tau)=0\ . \tag{9}$$

Thus, we write the correlation function as

$$G_{jk}^{(0)}(\tau)=\langle F_{jk}^{(0)}(t)F_{jk}^{(0)}(t+\tau)\rangle_{t,\Omega}-\langle[\langle F_{jk}^{(0)}(t)\rangle_t]^2\rangle_\Omega\ . \tag{10}$$

If the correlation function is assumed to be exponential, i.e.,

$$G_{jk}^{(0)}(\tau)=G_{jk}^{(0)}(0)\exp(-\tau/\tau_c)\ , \tag{11}$$

where τ_c is the correlation time of the motion, we then obtain from Eqs. (3) and (4),

$$1/T_{1,\mathrm{dip}}=\tfrac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left[\sum_k G_{jk}^{(0)}(0)\right]\left[\frac{1}{2}\frac{\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2}+\frac{3}{2}\frac{\tau_c}{1+\omega_I^2\tau_c^2}+3\frac{\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\right]\ , \tag{12}$$

where

$$G_{jk}^{(0)}(0)=\langle[F_{jk}^{(0)}(t)]^2\rangle_{t,\Omega}-\langle[\langle F_{jk}^{(0)}(t)\rangle_t]^2\rangle_\Omega\ . \tag{13}$$

1. C-Na dipolar interaction

The major source of fluctuations in the ^{13}C-^{23}Na dipolar interaction is the head-to-tail reorientations of the CN^- molecules. Each ^{13}C nucleus can occupy one of two positions, and the time averages in Eq. (13) can be calculated using statistical averages over these two positions.

Assuming the occupation of each position to be equally probable, we obtain

$$\langle[F_{jk}^{(0)}(t)]^2\rangle_{t,\Omega}=\tfrac{2}{5}(r_{1,jk}^{-6}+r_{2,jk}^{-6}) \tag{14}$$

and

$$\langle[\langle F_{jk}^{(0)}(t)\rangle_t]^2\rangle_\Omega=\tfrac{1}{5}[r_{1,jk}^{-6}+r_{2,jk}^{-6}+2r_{1,jk}^{-3}r_{2,jk}^{-3}P_2(\hat{r}_{1,jk}\cdot\hat{r}_{2,jk})]\ , \tag{15}$$

where $\vec{r}_{1,jk}$ and $\vec{r}_{2,jk}$ are the vectors from the ^{13}C nucleus to the ^{23}Na nucleus for the two positions of the ^{13}C nucleus, respectively. Setting these expressions into Eq. (13), we obtain

$$G_{jk}^{(0)}(0)=\tfrac{1}{5}[r_{1,jk}^{-6}+r_{2,jk}^{-6}-2r_{1,jk}^{-3}r_{2,jk}^{-3}P_2(\hat{r}_{1,jk}\cdot\hat{r}_{2,jk})]\ . \tag{16}$$

Usually, expressions for $T_{1,\mathrm{dip}}$ are written in terms of ΔM_2, the motionally "averaged out" part of the dipolar second moment. We can write $\Delta M_{2,\mathrm{C-Na}}$ in terms of $G_{jk}^{(0)}(0)$:

$$\Delta M_{2,\mathrm{C-Na}}=\tfrac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\sum_k G_{jk}^{(0)}(0)\ . \tag{17}$$

Combining this with Eq. (12), we obtain the expression of Albert and Ripmeester,[15]

$$1/T_{1,\mathrm{C-Na}}=\Delta M_{2,\mathrm{C-Na}}\left[\frac{1}{2}\frac{\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2}+\frac{3}{2}\frac{\tau_c}{1+\omega_I^2\tau_c^2}+3\frac{\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\right]\ . \tag{18}$$

2. C-N dipolar interaction

In the case of ^{13}C-^{14}N interactions, we can greatly simplify Eq. (10) since only the interaction with the ^{14}N nucleus in the same CN^- molecule as the ^{13}C nucleus needs to be considered. The dipolar interaction between ^{13}C and ^{14}N of different CN^- molecules is negligible in comparison because of the much greater separation in distance.

Let $\hat{r}_1$ and $\hat{r}_2$ be the directions of $\vec{r}_{jk}$ for two different orientations of the molecule. Using Eq. (6), we obtain

$$\langle F_{jk}^{(0)}(\hat{r}_1)F_{jk}^{(0)}(\hat{r}_2)\rangle_\Omega=\tfrac{2}{5}r_0^{-6}[3(\hat{r}_1\cdot\hat{r}_2)^2-1] , \tag{19}$$

where $r_0=r_{jk}$, the C—N distance, which we assume to be constant under reorientation. From Eqs. (9) and (10), we see that

$$\langle[\langle F_{jk}^{(0)}(t)\rangle_t]^2\rangle_\Omega=\lim_{\tau\to\infty}\langle F_{jk}^{(0)}(t)F_{jk}^{(0)}(t+\tau)\rangle_{t,\Omega} . \tag{20}$$

Combining Eqs. (10), (19), and (20), we finally obtain

$$\begin{aligned} G_{jk}^{(0)}(\tau)&=\tfrac{6}{5}r_0^{-6}\{\langle[\hat{r}(t)\cdot\hat{r}(t+\tau)]^2\rangle_t\\ &\quad-\lim_{\tau'\to\infty}\langle[\hat{r}(t)\cdot\hat{r}(t+\tau')]^2\rangle_t\}\\ &=\tfrac{6}{5}r_0^{-6}G_R(\tau) , \end{aligned} \tag{21}$$

where we have introduced here a "rotational" correlation function $G_R(\tau)$, given by

$$G_R(\tau)=\langle[\hat{r}(t)\cdot\hat{r}(t+\tau)]^2\rangle_t-\lim_{\tau'\to\infty}\langle[\hat{r}(t)\cdot\hat{r}(t+\tau')]^2\rangle_t . \tag{22}$$

Using an exponential correlation function as in Eq. (11), we obtain from Eq. (12),

$$\begin{aligned} 1/T_{1,\mathrm{C-N}}&=\tfrac{2}{5}\gamma_I^2\gamma_S^2\hbar^2S(S+1)r_0^{-6}G_R(0)\\ &\quad\times\left[\frac{1}{2}\frac{\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2}+\frac{3}{2}\frac{\tau_c}{1+\omega_I^2\tau_c^2}\right.\\ &\quad\left.+3\frac{\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\right] , \end{aligned} \tag{23}$$

where

$$G_R(0)=1-\lim_{\tau\to\infty}\langle[\hat{r}(t)\cdot\hat{r}(t+\tau)]^2\rangle_t . \tag{24}$$

The information about the type of reorientations taking place is contained in $G_R(0)$, as we will demonstrate below.

a. Head-to-tail reorientations. First, let us evaluate $G_R(0)$ for simple head-to-tail reorientations of the CN^- molecules. Since $[\hat{r}(t)\cdot\hat{r}(t+\tau)]^2=1$ for all values of t and τ in this case, we see from Eq. (24) that $G_R(0)$ is zero. Simple head-to-tail reorientations cannot cause relaxation in this case. This is due to the fact that the intramolecular dipolar energy is invariant under 180° rotations. As a result, $T_{1,\mathrm{C-N}}$ is very sensitive to other types of reorientations which might otherwise be masked by the large head-to-tail reorientations.

b. Intermediate orientations. von der Weid *et al.*[9] suggested that CN^- molecules in KCN reorient head-to-tail via intermediate orientations along the orthorhombic $\langle 111\rangle$ directions. This model would give ten possible directions for the CN^- molecule: the orthorhombic [010] and $[0\bar{1}0]$ directions (the b axis) and the eight intermediate $\langle 111\rangle$ directions. The time average in Eq. (24) can be expressed as a statistical average using occupation probabilities Q_i (direction $\vec{r}_i$ is occupied with probability Q_i):

$$G_R(0)=1-\sum_{i=1}^{10}\sum_{k=1}^{10}(\hat{r}_i\cdot\hat{r}_k)^2Q_iQ_k . \tag{25}$$

The occupation probability Q_i of the $\langle 111\rangle$ directions is less than that of the [010] and $[0\bar{1}0]$ directions by the Boltzmann factor $\epsilon=\exp(-\Delta/kT)$, where Δ is the difference in energy for the two types of orientations. Imposing the normalization requirement

$$\sum_{i=1}^{10}Q_i=1 , \tag{26}$$

we easily obtain $Q_i=(2+8\epsilon)^{-1}$ for the [010] and $[0\bar{1}0]$ directions, and $Q_i=\epsilon(2+8\epsilon)^{-1}$ for the $\langle 111\rangle$ directions. Setting this into Eq. (25), we obtain

$$G_R(0)=1-(1+4\epsilon)^{-2}\left[1+4\epsilon^2+\frac{8\epsilon b^2}{a^2+b^2+c^2}+4\epsilon^2\frac{(-a^2+b^2+c^2)^2+(a^2-b^2+c^2)^2+(a^2+b^2-c^2)^2}{(a^2+b^2+c^2)^2}\right] , \tag{27}$$

where a,b,c are the orthorhombic lattice constants (Fig. 1).

c. Small-angle orientations. For reasons to be discussed in a later section, we also want to consider the possibility of small-angle reorientations about the b axis. For this case, we consider a continuum of possible CN^- directions $\hat{r}$ with an associated probability density function $Q(\hat{r})$ such that the probability of finding a CN^- molecule oriented in a direction within the solid angle $d\hat{r}$ is given by $Q(\hat{r})d\hat{r}$. Similar to Eq. (25), we write

$$G_R(0)=1-\int d\hat{r}\int d\hat{r}'(\hat{r}\cdot\hat{r}')^2Q(\hat{r})Q(\hat{r}') . \tag{28}$$

To evaluate this expression, let us choose the x,y,z axes to be along the orthorhombic c,a,b axes, respectively. Also, let us use polar coordinates, r,θ,ϕ with their usual meaning. In terms of ϕ and θ, we have

$$\begin{aligned} \hat{r}\cdot\hat{r}'&=\cos\phi\,\sin\theta\,\cos\phi'\,\sin\theta'\\ &\quad+\sin\phi\,\sin\theta\,\sin\phi'\,\sin\theta'+\cos\theta\,\cos\theta' \end{aligned} \tag{29}$$

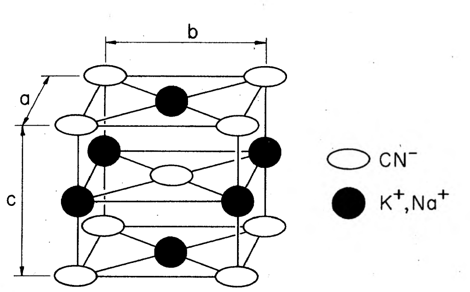

FIG. 1. Orthorhombic crystal structure of KCN and NaCN.

and

$$d\hat{r}=\sin\theta\, d\theta\, d\phi\ . \tag{30}$$

By symmetry, we have

$$Q(-\theta,\phi)=Q(\theta,\phi)\ ,$$
$$Q(\theta,-\phi)=Q(\theta,\phi)\ ,$$

and

$$Q(\pi-\theta,\phi)=Q(\theta,\phi)\ . \tag{31}$$

Using these relations, we obtain from Eq. (28),

$$\begin{aligned} G_R(0)=1&-4\left[\int_0^{\pi/2}d\theta\sin\theta\int_0^{2\pi}d\phi\, Q(\theta,\phi)\cos^2\phi\sin^2\theta\right]^2\\ &-4\left[\int_0^{\pi/2}d\phi\sin\int_0^{2\pi}d\phi\, Q(\theta,\phi)\sin^2\phi\sin^2\theta\right]^2\\ &-4\left[\int_0^{\pi/2}d\theta\sin\theta\int_0^{2\pi}d\phi\, Q(\theta,\phi)\cos^2\theta\right]^2 . \end{aligned} \tag{32}$$

Now, for small-angle reorientations about the b axis (z axis), $Q(\theta,\phi)$ is nonzero only near $\theta=0$ and π. Since the integrals in Eq. (32) include only values of $Q(\theta,\phi)$ between $\theta=0$ and $\pi/2$, we can expand the expression about $\theta=0$. Keeping only the lowest-order term in θ, we have

$$\begin{aligned} G_R(0)&=4\int_0^{\pi/2}d\theta\sin\theta\int_0^{2\pi}d\phi\, Q(\theta,\phi)\theta^2\\ &=2\langle\theta^2\rangle\ . \end{aligned} \tag{33}$$

If we replace θ by α which is also defined to be the angle between the C—N axis and the macroscopic b axis, then

$$G_R(0)=2\alpha_{\mathrm{rms}}^2\ , \tag{34}$$

where α_{rms} is the root-mean-square average of α over all the CN^- molecules in the crystal.

B. Chemical shift

Molecular reorientations cause nuclei with an anisotropic chemical shift (CS) to experience a fluctuating magnetic field. This in turn causes spin-lattice relaxation.[16] From Soda and Chihara,[14] we obtain

$$\begin{aligned} 1/T_{1,\mathrm{CS}}=2\omega_I^2\int_0^\infty d\tau\cos(\omega_I\tau)&\\ \times\langle\delta\sigma_{xz}(t)\delta\sigma_{xz}(t+\tau)\rangle_{t,\Omega}&\ , \end{aligned} \tag{35}$$

where $\delta\sigma_{xz}(t)$ is the fluctuating part of any off-diagonal element of the chemical shift tensor σ. The choice of off-diagonal element is arbitrary in this case since we average over all orientations Ω of σ.

Consider a chemical shift with axial symmetry. Let $\hat{r}_1$ and $\hat{r}_2$ be the axes of symmetry for two different orientations of the tensor σ. We show in the Appendix that

$$\langle\sigma_{xz}(\hat{r}_1)\sigma_{xz}(\hat{r}_2)\rangle_\Omega=\tfrac{1}{30}(\Delta\sigma)^2[3(\hat{r}_1\cdot\hat{r}_2)^2-1]\ , \tag{36}$$

where $\Delta\sigma$ is the anisotropy of σ. Noticing the similarity between this expression and Eq. (19), we can immediately obtain

$$1/T_{1,\mathrm{CS}}=\tfrac{1}{5}\omega_I^2(\Delta\sigma)^2G_R(0)\frac{\tau_c}{1+\omega_I^2\tau_c^2}\ , \tag{37}$$

where $G_R(\tau)$ here is the same correlation function as that given in Eq. (22), assuming that the axis of symmetry for σ lies along the C—N axis.[17]

If we use the approximation $\omega_S\ll\omega_I$ in Eq. (23), we obtain

$$1/T_{1,\mathrm{C-N}}\cong2\gamma_I^2\gamma_S^2\hbar^2S(S+1)r_0^{-6}G_R(0)\frac{\tau_c}{1+\omega_I^2\tau_c^2}\ . \tag{38}$$

Note that $\omega_S\cong0.35\omega_I$, so this approximation is very rough. Combining Eq. (38) with Eq. (37), we obtain a very useful relation between $T_{1,\mathrm{CS}}$ and $T_{1,\mathrm{C-N}}$:

$$\frac{T_{1,\mathrm{C-N}}}{T_{1,\mathrm{CS}}}\cong\frac{\omega_I^2(\Delta\sigma)^2r_0^6}{10\gamma_I^2\gamma_S^2\hbar^2S(S+1)}\ . \tag{39}$$

Note that this ratio does not depend on $G_R(\tau)$, i.e., it does not depend on the nature of the reorientations.

C. Quadrupolar interaction

Nuclei with spin $I>\frac{1}{2}$ possess electric quadrupole moments and thus interact with electric field gradients. Motions of electric charges (such as CN^- reorientations) cause fluctuating electric field gradients and thus spin-lattice relaxation. From O'Reilly,[18] we obtain for the case $I=\frac{3}{2}$ (as in ^{23}Na),

$$1/T_{1,Q}=\tfrac{1}{16}e^2Q^2\hbar^2\left[\langle|\delta V_{xz}(t)+i\delta V_{yz}(t)|^2\rangle_{t,\Omega}\frac{\tau_c}{1+\omega_I^2\tau_c^2}+\langle|\delta V_{xx}(t)-\delta V_{yy}(t)+2i\delta V_{xy}(t)|^2\rangle_{t,\Omega}\frac{\tau_c}{1+4\omega_I^2\tau_c^2}\right]\ , \tag{40}$$

where e is the electronic charge, Q is the nuclear quadrupole moment, and $\delta V_{xz}(t)$, $\delta V_{yz}(t)$, etc. are the fluctuating parts of $V_{xz}\equiv\partial^2V/\partial x\partial z$, $V_{yz}\equiv\partial^2V/\partial y\partial z$, etc., respectively, and V is the electric potential at the I spin. Here, correlation functions are again assumed to be exponential.

III. SAMPLES

The ^{13}C NMR measurements were made on isotopically enriched (90 at. % ^{13}C) samples of KCN and NaCN (obtained from Prochem (Summit, NJ). The ^{23}Na NMR measurements were made on a sample of NaCN (nonenriched) obtained from the University of Utah Crystal Growth Laboratory (Salt Lake City, Utah) as well as the enriched sample of NaCN mentioned above.

IV. EXPERIMENTAL RESULTS

A. KCN

We measured the T_1 of ^{13}C in KCN as a function of temperature at three different fields (Fig. 2). At each field

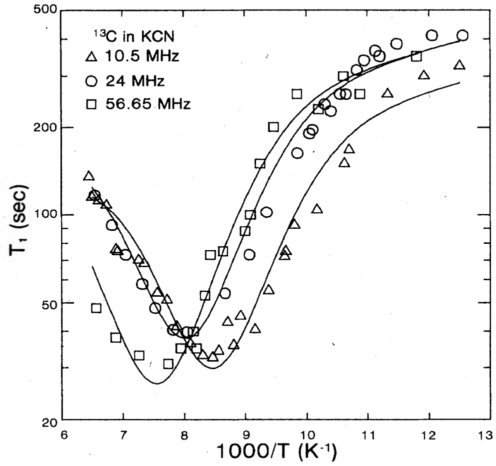

FIG. 2. Spin-lattice relaxation time T_1 of ^{13}C in KCN.

a minimum in T_1 is observed. The field dependence of T_1 exhibited here is very unusual. On the cold side of the minima ($1000/T > 9$ K^{-1}), T_1 decreases with decreasing field, whereas on the hot side ($1000/T < 7$ K^{-1}), T_1 *increases* with decreasing field, in contrast to the expected behavior for dipolar relaxation. Furthermore, the T_1 minima at 10.5 and 56.65 MHz are *both* deeper than the minimum at 24 MHz.

This field dependence can be explained by considering T_1 to be due to a *combination* of two different interactions, dipolar and chemical shift. The T_1 due to the dipolar interactions usually decreases with decreasing field on the cold side of its minimum and is field independent on the hot side. On the other hand, the T_1 due to chemical shift anisotropy usually *increases* with decreasing field on the hot side of its minimum and is field independent on the cold side. If *both* interactions are present in comparable strength, we might expect to see a field dependence like that exhibited by our data.

In KCN both such interactions are present: the ^{14}N-^{13}C dipolar interaction and the ^{13}C chemical shift. Spin-lattice relaxation, of course, is caused by *fluctuations* in these interactions. We propose that the mechanism in KCN which produces such fluctuations is molecular reorientations of the CN^- ion. The observed T_1, then, is given by

$$1/T_1 = 1/T_{1,\text{C-N}} + 1/T_{1,\text{CS}} \quad (41)$$

where $T_{1,\text{C-N}}$ and $T_{1,\text{CS}}$ are given by Eqs. (23) and (37), respectively.

To test Eq. (41), we examine the ratio $T_{1,\text{C-N}}/T_{1,\text{CS}}$ given by Eq. (39). This ratio is independent of the nature of the reorientations, as long as the fluctuations in the dipolar and chemical-shift interactions are caused by the *same* reorientations, which, of course, they must be.

It is easy to show from Eqs. (41), (37), and (38) that T_1 should have its most shallow minimum when $T_{1,\text{C-N}} \cong T_{1,\text{CS}}$. If we set $T_{1,\text{C-N}} = T_{1,\text{CS}}$ in Eq. (39) and use values of $\Delta\sigma$ and r_0 published in the literature ($\Delta\sigma = 290$ ppm in Ref. 17 and $r_0 = 1.13$ Å in Ref. 19), we predict that the most shallow minimum should occur when $\omega_I/2\pi = 23$ MHz. [Note that this result is only approximately correct since it is based on Eq. (38) which is an approximation to Eq. (23).] At this frequency, the T_1 minimum should have a value larger than the T_1 minimum at frequencies above or below. This predicted result is in agreement with our 24-MHz data which is intermediate between the two extremes where either $T_{1,\text{C-N}}$ or $T_{1,\text{CS}}$ dominates T_1.

The above agreement strongly confirms our hypothesis that the observed relaxation is due to CN^- reorientations which cause fluctuations in the ^{13}C chemical shift and the ^{14}N-^{13}C dipolar interactions. We emphasize that this conclusion does not depend on the type of reorientations, since $T_{1,\text{CS}}$ and $T_{1,\text{C-N}}$ *both* depend in the same way on the correlation function $G_R(\tau)$ which is the only parameter dependent upon the details of the motion.

Now, in order to determine the nature of the reorientations present, we must investigate $G_R(\tau)$. From Eq. (37), we find the value of $T_{1,\text{CS}}$ at its minimum,

$$1/T_{1,\text{CS,min}} = \tfrac{1}{10}\omega_I(\Delta\sigma)^2 G_R(0) \ . \quad (42)$$

At $\omega_I/2\pi = 24$ MHz, we have already shown that $T_{1,\text{CS}} \cong T_{1,\text{C-N}}$. From Fig. 2 we find that $T_{1,\text{min}} \cong 40$ s at 24 MHz, and thus, using Eq. (41), we obtain $T_{1,\text{CS,min}} \cong 80$ s. Solving Eq. (42) for $G_R(0)$, we finally calculate $G_R(0) \cong 0.01$. We determine $G_R(0)$ more accurately at the end of this section.

We can conclude that simple head-to-tail reorientations cannot cause our observed relaxation since such motions correspond to $G_R(0) = 0$, as shown in Sec. II. Thus the relaxation exhibited by our data must be due to departures from this simple head-to-tail reorientation.

From the very small value of $G_R(0)$, we know that these departures must be small, i.e., the CN^- molecules spend most of their time oriented in directions near or along the orthorhombic b axis. The fact that $G_R(0)$ is *nonzero*, though, indicates that the CN^- molecules must spend at least part of the time oriented in directions *not* parallel to the b axis. This can be accomplished in two different ways: (1) The CN^{-1} molecules spend a very small fraction of their time oriented at large angles with the b axis, or (2) the CN^- molecules spend *most* of their time oriented at *small* angles with the b axis. The first possibility is the case of intermediate orientations, and the second is the case of small-angle reorientations. In Sec. II we calculated $G_R(0)$ for both of these cases. We now try to fit these calculations to the data for each case.

First, let us consider the case of intermediate orientations. von der Weid *et al.*[9] made EPR measurements on HCN^- defects in KCN and found some of them in the orthorhombic $\langle 111 \rangle$ orientations as well as the [010] and [0$\bar{1}$0] directions, suggesting that a head-to-tail reorientation might proceed, for example, from [010] to [111] to [1$\bar{1}$1] and finally to [0$\bar{1}$0]. From the fractional occupation of these $\langle 111 \rangle$ orientations detected by EPR, they determined that the minima of the $\langle 111 \rangle$ potential wells were only 0.0074 eV greater than that of the [010] and [0$\bar{1}$0] potential wells. The similarity between HCN^- and CN^- molecules led them to suggest that the information obtained about the HCN^- reorientations from EPR might also be true for the CN^- reorientations.

We can rule out the model of von der Weid *et al.*[9] for the CN^- reorientations in KCN. Using $\Delta=0.0074$ eV from Ref. 9 and $a=4.22$ Å, $b=5.07$ Å, and $c=6.13$ Å from Ref. 1, we evaluate our expression for $G_R(0)$, Eq. (27), at the temperature ($T=125$ K) of our T_1 minimum for 24 MHz and obtain $G_R(0)\cong 0.6$, which is about 60 times larger than our experimental value. The model of von der Weid *et al.* would cause T_1 to be less than 1 s at the minimum instead of the 40 s which we observed (Fig. 2).

In order for this model of intermediate orientations to fit our value of $G_R(0)$, a much larger value of Δ is required. For large Δ, we have $\epsilon \ll 1$, and Eq. (27) may then be written to first order in ϵ as

$$G_R(0)=8\epsilon\frac{a^2+c^2}{a^2+b^2+c^2} . \tag{43}$$

In this case, the relaxation rate is decreased by a factor $\epsilon=\exp(-\Delta/kT)$, a feature which is typical of reorientational motion between unequal potential wells.[20] Using $G_R(0)=0.01$, we find from Eq. (43) that $\Delta=0.07$ eV.

One striking consequence of such a large Δ is an asymmetry of the slope of T_1 on the two sides of the minimum.[20] On a plot of $\ln T_1$ versus $1/T$, the slope of the line on the cold side of the minimum would be $E_A+\Delta$ and on the hot side $-(E_A-\Delta)$. The difference in the absolute values of these slopes would be equal to $2\Delta\cong 0.14$ eV. Such a great difference is clearly in disagreement with our data.

Thus although the value $\Delta=0.07$ eV may give the correct value for T_1 at the minimum, it would produce too great an asymmetry in the slopes of T_1. We therefore conclude that our T_1 data in KCN does *not* arise from reorientations between $\langle 111\rangle$ directions and [010] or [0$\bar{1}$0] directions. If there are any intermediate orientations in $\langle 111\rangle$ directions, the resulting relaxation must be so weak so that it is masked by the relaxation which we do observe. We can thus place a lower limit on Δ in KCN. This limit is more than ten times the value measured by von der Weid *et al.* for HCN^- reorientation. Even though the CN^- and HCN^- are very similar, their reorientational motions here are strikingly different. Apparently, von der Weid *et al.* were not justified in suggesting that CN^- reorients similar to HCN^- in KCN.

Reorientations between other possible intermediate orientations which are at large angle with the b axis would give similar results: large Δ and asymmetric slopes in T_1, which disagrees with our data. We can simply rule out this type of mechanism as being responsible for the observed relaxation.

This leaves us with the other possibility: small-angle reorientations. In Sec. II we calculated $G_R(0)$ for this model. Using $G_R(0)\cong 0.01$ in Eq. (34), we obtain $\alpha_{\rm rms}\cong 4°$. Later in this section we obtain more accurate values for $G_R(0)$ and $\alpha_{\rm rms}$. We discuss the possible origin of these small-angle reorientations in a following section.

The correlation time τ_c for the reorientations can be obtained from the positions of the T_1 minima. We see from Eqs. (37) and (38) that the T_1 minima occur when $\omega_I\tau_c\cong 1$, which allows us to determine the values of τ_c at the temperatures of the three T_1 minima shown in Fig. 2. We plot the resulting values of τ_c in Fig. 3.

Values of the correlations times τ_c obtained at lower temperatures from dielectric response[6,7] and ITC measurements[8,7] are also plotted in Fig. 3. As can be seen, a single straight line can be drawn through *all* the data. Thus we conclude that the correlation times obtained from dielectric response and ITC data describe the same motion as the correlation times obtained from our NMR data. Using the Arrhenius relation,

$$\tau_c=\tau_0\exp(E_A/kT) , \tag{44}$$

we obtain $E_A=0.154$ eV and $\tau_0=3.8\times 10^{-15}$ s from a least-squares fit to the data. (These values are more accurate than our previously reported values[12] due to improved dielectric response data.[7]) The activation energy $E_A=0.154$ eV which we obtain from data in Fig. 3 is consistent with the slopes of the T_1 data in Fig. 2 if the background relaxation rate is first subtracted off. We note that τ_c is continuous through the electric-ordering phase transition and that the activation energy E_A appears to have the same value on both sides of the phase transition. Thus, the phase transition does not appear to have a measurable effect on the CN^- reorientational motion.

With an expression for τ_c we can now fit our data with

$$1/T_1=1/T_{1,\text{C-N}}+1/T_{1,\text{CS}}+1/T_{1,\text{other}} , \tag{45}$$

where $T_{1,\text{C-N}}$ and $T_{1,\text{CS}}$ are given by Eqs. (23) and (37), respectively. [Here we used Eq. (23) instead of the approximate expression, Eq. (38).] The last term, $1/T_{1,\text{other}}$, is the relaxation rate from other sources (such as paramagnetic impurities) which determine T_1 at low temperatures. The form we choose for $T_{1,\text{other}}$ is rather arbitrary and does not affect the results of the fit significantly. We use

$$1/T_{1,\text{other}}=A\exp(T_0/T) , \tag{46}$$

which is a straight line on a graph such as Fig. 2. We allow the coefficient A to take on different values for the three frequencies ω_I.

In the expressions for $T_{1,\text{C-N}}$ and $T_{1,\text{CS}}$ we allow only two adjustable parameters: $G_R(0)$ and $\Delta\sigma$. The resulting

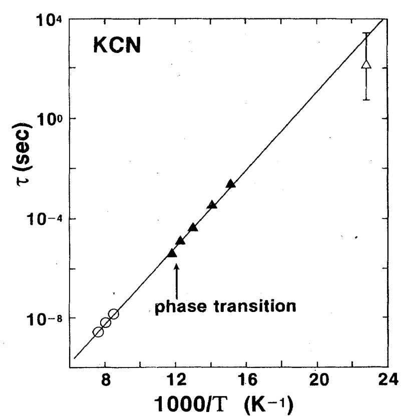

FIG. 3. Correlation time τ_c of CN^- reorientations in KCN. Our NMR data (○). Dielectric response data (▲) and ITC data (△) from Ref. 7.

best fit is shown by the solid lines in Fig. 2 and yields $G_R(0)=0.0093$ and $\Delta\sigma=300$ ppm. The value of $\Delta\sigma$ has not been directly measured in KCN, but in other compounds containing CN groups, similar values for $\Delta\sigma$ have been obtained: 280 ppm in HCN (Ref. 21) and 290 ppm in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (Ref. 17). From the best fit value of $G_R(0)$, we obtain $\alpha_{rms}=3.9°$. (We reported earlier[12] that $\alpha_{rms}=2.6°$ and subsequently found a numerical error in that calculation.)

In our analysis of the ^{13}C relaxation in KCN, we have neglected the ^{13}C-^{13}C dipolar interaction. To demonstrate the validity of this approximation, we measured T_1 in a sample containing only 10 at. % ^{13}C and found no significant difference in T_1 from the data in Fig. 2. Since ^{13}C—^{13}C distances are very different in the two samples, our data shows that the ^{13}C-^{13}C dipolar interaction does not make any significant contribution to our relaxation data.

B. NaCN

We measured T_1 for ^{13}C in NaCN as a function of temperature at two different fields (Fig. 4). The relaxation here is dominated by ^{13}C-^{23}Na dipolar interactions and is described by Eq. (18). Since the NMR frequencies of ^{13}C and ^{23}Na are very close to each other (about 1.2 MHz when $\omega_I/2\pi=24$ MHz, for example), the first term in Eq. (18) should have a much larger value at its minimum than the other two terms. Thus T_1 should have a rather prominent minimum when $|\omega_I-\omega_S|\tau_c=1$, which allows us to determine the values of τ_c at the two T_1 minima shown in Fig. 4.

We plot in Fig. 5 these values of τ_c along with values obtained from dielectric response[6,7] and ITC measurements.[8,7] We see again that τ_c obeys the Arrhenius relation of Eq. (44) with $E_A=0.284$ eV and $\tau_0=9.4\times10^{-16}$ s. As in KCN, τ_c is continuous through the electric ordering phase transition, and E_A has the same value in both phases.

Using these values, we can now fit the data to

$$1/T_1=1/T_{1,\mathrm{C-Na}}+1/T_{1,\mathrm{C-N}}+1/T_{1,\mathrm{CS}}+1/T_{1,\mathrm{other}}\ . \tag{47}$$

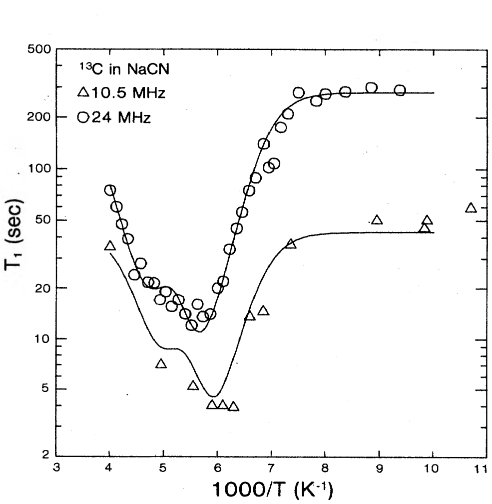

FIG. 4. Spin-lattice relaxation time T_1 of ^{13}C in NaCN.

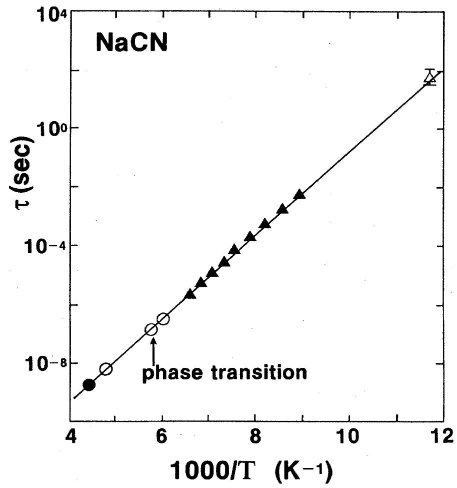

FIG. 5. Correlation time τ_c of CN^- reorientations in NaCN. Our NMR data (○). NMR data (●) from Ref. 10. Dielectric response data (▲) and ITC data (△) from Ref. 7.

Expressions for these terms are given by Eqs. (18), (23), (37), and (46), respectively. Equation (47) for T_1 in NaCN is identical in form to Eq. (45) for T_1 in KCN except for the addition of the C—Na relaxation term. The ^{13}C-^{39}K dipolar interaction is very weak and can be neglected for ^{13}C relaxation in KCN. In contrast, the ^{13}C-^{23}Na dipolar interaction is very strong and in fact dominates ^{13}C relaxation in NaCN. Using the value of $\Delta\sigma$ determined for KCN, we allow only two adjustable parameters [$\Delta M_{2,\mathrm{C-Na}}$ and $G_R(0)$] in our expressions for $T_{1,\mathrm{C-Na}}$, $T_{1,\mathrm{C-N}}$, and $T_{1,\mathrm{CS}}$.

The resulting best fit is shown by the solid lines in Fig. 4 and yields $\Delta M_{2,\mathrm{C-Na}}=2.5\times10^6\ \mathrm{s}^{-2}$ and $G_R(0)=0.006$. There is a much larger uncertainty in $G_R(0)$ here than for KCN since the effect of small-angle reorientations are now largely masked by the $1/T_{1,\mathrm{C-Na}}$ term. However, we do obtain a value which is approximately the same as in KCN, showing that the same small-angle reorientations which we observed in KCN are probably also present in NaCN with about the same amplitude.

We can calculate $\Delta M_{2,\mathrm{C-Na}}$ from Eq. (17) assuming simple head-to-tail reorientations of the CN^- molecules along the b axis. We neglect the small-angle reorientations which make a relatively minor contribution to $\Delta M_{2,\mathrm{C-Na}}$. Using this model, we obtain $\Delta M_{2,\mathrm{C-Na}}=5.0\times10^6\ \mathrm{s}^{-2}$ which is twice as large as the value obtained from the data. This disagreement suggests either that this simple model used in calculating $\Delta M_{2,\mathrm{C-Na}}$ from Eq. (17) does not completely describe our data or that we have made a computational error. At present, we cannot account for this disagreement.

We also measured the T_1 of ^{23}Na in NaCN as a function of temperature (Fig. 6). The relaxation here is due to the quadrupolar interaction of ^{23}Na with fluctuating electric field gradients arising from CN^- reorientations. The strong nature of this interaction gives rise to a rather short T_1 at the minimum. We see from Eq. (40) that the T_1 minimum should be at $\omega_I\tau_c\cong1$. Using this relation, we obtain $\tau_c\cong7\times10^{-9}$ s at the minimum, and we plot

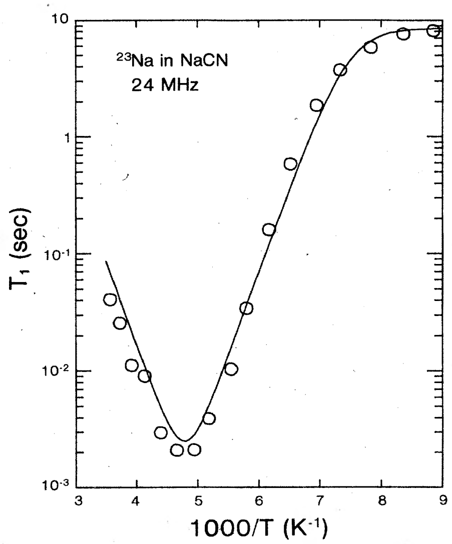

FIG. 6. Spin-lattice relaxation time T_1 of ^{23}Na in NaCN.

this point in Fig. 5.

We fit the data to

$$1/T_1 = 1/T_{1,Q} + 1/T_{1,\mathrm{other}} \,, \tag{48}$$

where we use, as an approximation for Eq. (40),

$$1/T_{1,Q} \cong \frac{A_Q \tau_c}{1+\omega_I^2 \tau_c^2} \,, \tag{49}$$

and treat $T_{1,\mathrm{other}}$ as a constant. In the expression for $T_{1,Q}$, we have only one adjustable parameter, A_Q. The resulting best fit is drawn as a solid line in Fig. 6. We do not attempt to calculate A_Q here.

Buchheit *et al.*[10] also measured T_1 of ^{23}Na in NaCN and found the minimum to be at $1000/T = 4.4$ K^{-1} for $\omega_I/2\pi = 79.38$ MHz. Using $\omega_I \tau_c = 1$ at their minimum, we obtain $\tau_c = 2.0\times10^{-9}$ s. This point is also plotted in Fig. 5. They also measured $T_{1\rho}$, the spin-lattice relaxation time in the rotating reference frame, and found a very shallow minimum at $1000/T = 7.5$ K^{-1}, using an rf field $H_1 = 2$ G. From the approximate relation $\gamma_I H_1 \tau_c \cong 1$ at the minimum, we obtain $\tau_c \cong 7.1\times10^{-5}$ s, in rough agreement with the data shown in Fig. 5. (Actually, this determination of τ_c is not rigorously correct in weak rf fields at a $T_{1\rho}$ minimum.[22] The effect of the local field should be included, in which case a smaller value of τ_c would be obtained, in better agreement with our data.)

V. DISCUSSION

We have shown from our data in KCN that the CN^- molecules reorient among directions which are very nearly parallel to the orthorhombic *b* axis. However, we can see from Fig. 3 that the observed reorientations cannot be simple librations of the CN^- molecules since the measured correlation times are much too long. The correlation times observed for these small reorientations are comparable in magnitude to those expected for the head-to-tail reorientations. Certainly, head-to-tail reorientations are also taking place here although they do not affect the relaxation directly.

The observed values of τ_c lead us to propose the following model. These small-angle reorientations of any given CN^- molecule are caused by the head-to-tail reorientations of *nearby* CN^- molecules. In the elastically ordered phase, the CN^- molecules are disordered with respect to head-and-tail alignment. Since the CN^- molecule is slightly different with respect to head and tail, this disorder breaks the orthorhombic symmetry of the lattice on a microscopic scale and distorts the lattice randomly throughout the crystal. This distortion causes each CN^- molecule to be misoriented slightly from its otherwise equilibrium orientation along the *b* axis. This misorientation varies randomly from molecule to molecule such that, over *macroscopic* distances, the misorientation averages to zero and the lattice has overall orthorhombic symmetry as detected by x-ray and neutron diffraction.

Each time a CN^- molecule reorients head-to-tail, the local distortion of the lattice changes, thereby causing the CN^- molecules in the vicinity to change their orientations slightly so that they are now all misoriented in *new* directions. Thus, a given CN^- molecule reorients both in small-angle steps (due to head-to-tail reorientations of neighbors) as well as large-angle steps (180°, due to its own head-to-tail reorientations). The small-angle steps provide the mechanism for relaxation of ^{13}C in KCN. In contrast, the large-angle steps are not *directly* observable in the ^{13}C relaxation even though they are responsible for the small-angle steps of nearby CN^- molecules.

From this model, we see that the small-angle reorientations observed in our data are indirectly caused by *head-to-tail* reorientations. The frequency of the small-angle reorientations is much greater than that of the head-to-tail reorientations since a given CN^- undergoes a small-angle reorientation whenever any one of the neighboring CN^-'s reorients head-to-tail. Nevertheless, the correlation time of the small-angle reorientations is *not* equal to the mean time between such reorientations since each reorientation is very small and arises from the head-to-tail reorientations of any one of a number of neighboring CN^-'s. In fact, since the head-to-tail reorientations *drive* the small-angle reorientations, their correlation times must be equal. Thus the values of τ_c which we obtained from our data are identical to those for head-to-tail reorientations.

If these small-angle reorientations and resulting disorder are present in KCN, we would expect them to be present in NaCN as well. However, these effects are masked in NaCN largely by the strong ^{13}C-^{23}Na dipolar interactions which produce ^{13}C relaxation via head-to-tail CN^- reorientations *directly* and which are rather insensitive to the small-angle reorientations, if present. However, our ^{13}C relaxation data in NaCN does allow these small-angle reorientations to be present. In fact, we get a slightly better fit of our calculated relaxation to the data if we assume the presence in NaCN of small-angle reorientations of the same amplitude as in KCN.

ACKNOWLEDGMENTS

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APPENDIX: CALCULATION OF $\langle \sigma_{xz}(\hat{r}_1)\sigma_{xz}(\hat{r}_2)\rangle_\Omega$

Consider a chemical-shift tensor σ with axial symmetry. Let $\hat{r}_1$ and $\hat{r}_2$ be the axes of symmetry for two different orientations of σ. Calculation of the powder average of $\sigma_{xz}(\hat{r}_1)\sigma_{xz}(\hat{r}_2)$ is accomplished by averaging over all possible orientations of the coordinate axes x,y,z. To do this, we use the transformation matrix $\underline{A}(\theta,\phi,\psi)$ which reorients the coordinate axes through Eulerian angles θ,ϕ,ψ. We have from Goldstein[23]

$$\begin{aligned}
A_{xx} &= \cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi\ ,\\
A_{xy} &= \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi\ ,\\
A_{xz} &= \sin\psi\sin\theta\ ,\\
A_{yx} &= -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi\ ,\\
A_{yy} &= -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi\ ,\\
A_{yz} &= \cos\psi\sin\theta\ ,\\
A_{zx} &= \sin\theta\sin\phi\ ,\\
A_{zy} &= -\sin\theta\cos\phi\ ,\\
A_{zz} &= \cos\theta\ .
\end{aligned} \tag{A1}$$

Under a reorientation θ,ϕ,ψ of the coordinate axes, the components of σ become

$$\sigma_{ik} \to \sum_{m,n} A_{im}(\theta,\phi,\psi)\sigma_{mn}[\underline{A}^{-1}(\theta,\phi,\psi)]_{nk}\ . \tag{A2}$$

Thus, we write

$$\langle \sigma_{xz}(\hat{r}_1)\sigma_{xz}(\hat{r}_2)\rangle_\Omega = \frac{1}{8\pi^2}\int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \sum_{i,k} A_{xi}(\theta,\phi,\psi)\sigma_{ik}(\hat{r}_1)[\underline{A}^{-1}(\theta,\phi,\psi)]_{kz} \times \sum_{m,n} A_{xm}(\theta,\phi,\psi)\sigma_{mn}(\hat{r}_2)[\underline{A}^{-1}(\theta,\phi,\psi)]_{nz}\ . \tag{A3}$$

Now, since we are averaging over all possible orientations of the coordinate axes, we are free to choose the original axes which define the components $\sigma_{ik}(\hat{r}_1)$ and $\sigma_{ik}(\hat{r}_2)$. Therefore, let us choose the z axis along $\hat{r}_1$ and the x and y axes such that $\hat{r}_2$ lies in the y-z plane. Then we have

$$\underline{\sigma}(\hat{r}_1) = \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix}, \tag{A4}$$

and

$$\sigma_{ik}(\hat{r}_2) = \sum_{m,n} A_{im}(\gamma,0,0)\sigma_{mn}(\hat{r}_1)[\underline{A}^{-1}(\gamma,0,0)]_{nk}\ , \tag{A5}$$

where γ is the angle between $\hat{r}_1$ and $\hat{r}_2$. In Eq. (A4), $\sigma_{xx} = \sigma_{yy}$ because of axial symmetry. Now, using $(\underline{A}^{-1})_{ik} = A_{ki}$ and Eqs. (A4) and (A5), we finally obtain

$$\langle \sigma_{xz}(\hat{r}_1)\sigma_{xz}(\hat{r}_2)\rangle_\Omega = \sum_{i,k,m,n} A_{mk}(\gamma,0,0)A_{nk}(\gamma,0,0)\sigma_{ii}(\hat{r}_1)\sigma_{kk}(\hat{r}_1) \times \frac{1}{8\pi^2}\int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta A_{xi}(\theta,\phi,\psi)A_{zi}(\theta,\phi,\psi)A_{xm}(\theta,\phi,\psi)A_{zn}(\theta,\phi,\psi)\ . \tag{A6}$$

The evaluation of this expression is straightforward, though tedious, and we obtain

$$\langle \sigma_{xz}(\hat{r}_1)\sigma_{xz}(\hat{r}_2)\rangle_\Omega = \tfrac{1}{30}(\Delta\sigma)^2(3\cos^2\gamma - 1)\ , \tag{A7}$$

where $\Delta\sigma = \sigma_{zz} - \sigma_{xx}$, the anisotropy of σ.

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