

## Orientational Freezing in KCN-KBr Studied by Magnetic Resonance

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The NMR line shape and spin-echo behavior of  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR in powder samples of  $\text{K}(\text{CN})_{0.5}\text{Br}_{0.5}$  are reported. The line shape and spin-echo data are best explained by the molecules' developing increasingly preferred orientations as the temperature is decreased. Models in which the molecular reorientations simply slow down with decreasing temperature do not fit our data. The quadrupolar freezing is nearly complete at temperatures well above the dielectric freezing temperature. The NMR results from KCN-KBr are compared to results from the orientational glasses  $o\text{-H}_2\text{-}p\text{-H}_2$  and  $\text{N}_2\text{-Ar}$ .

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$\text{K}(\text{CN})_x\text{Br}_{1-x}$  is a site-disordered solid solution, a random substitution of  $\text{Br}^-$  for  $\text{CN}^-$  on the anionic sublattice. Pure KCN ( $x=1$ ) occurs in three phases differing in their extents of orientational disorder.<sup>1,2</sup> At high temperature the  $\text{CN}^-$  molecules are orientationally disordered; below a first-order transition at 168 K the  $\text{CN}^-$  exhibit quadrupolar order (molecular "alignment"), but with head-tail (electrical) disorder. Finally, head-tail order is established at a higher-order transition at 83 K. With sufficient dilution ( $x \leq 0.6$ ) these sharp transitions disappear.<sup>3,4</sup> Much of the current interest in KCN-KBr concerns the nature of the continuous freezing in the diluted solutions that replaces the sharp phase transitions in pure KCN. Further, the KCN-KBr system is similar to the randomly diluted orientational-glass-forming systems of  $\text{N}_2\text{-Ar}$ <sup>5-7</sup> and  $o\text{-H}_2\text{-}p\text{-H}_2$ .<sup>8,9</sup> As such, the orientational freezing of KCN-KBr is pertinent to an entire class of disordered materials.

The electric dipole moment of  $\text{CN}^-$  is small,  $\text{CN}^-$  being a nearly symmetric molecule. As a consequence, quadrupolar orientational order develops in pure KCN at a temperature well above the electrical ordering temperature. In the diluted material, the weakness of the  $\text{CN}^-$  asymmetry may cause the quadrupolar components of orientation to freeze at a higher temperature than the dipolar components (i.e., head-tail coordinates). That is, previous dielectric studies<sup>10-12</sup> that observed a slowing of molecular reorientations may have been following  $180^\circ$  flips,<sup>13-15</sup> reorientations which do not modulate the stronger interactions of quadrupolar symmetry. On the other hand, the ratio of the quadrupolar and dipolar ordering temperatures in KCN is only about 2; this argues that there may be just one combined freezing in KCN-KBr. Thus, the first question to be addressed by this work is, "Are the quadrupolar and dipolar freezing temperatures different?"

The orientational freezing of KCN-KBr has been observed with several techniques including neutron scattering,<sup>10,16-19</sup> softening of the shear stiffness  $C_{44}$ ,<sup>10,20,21</sup> and dielectric spectroscopy.<sup>10-12,22</sup> Each technique has its own time scale and each is sensitive

to a particular function of molecular orientation. For example, dielectric spectroscopy is an  $l=1$  (in the sense of spherical harmonics) technique and is sensitive to head-tail flips as well as smaller reorientations. The principal strain-coupled interactions<sup>3</sup> are of quadrupolar symmetry because of the nearly symmetric molecules. Hence, elastic-stiffness measurements primarily probe functions of even  $l$  and are insensitive to the head-tail states of the molecules. The nuclear-magnetic-resonance (NMR) line-shape studies reported here are sensitive directly to an  $l=2$  function of molecular orientation.<sup>23</sup>

Because the various techniques monitor different functions of molecular orientation with different time scales, different physical pictures of the freezing have evolved. Thus, this work addresses the questions, "Does the orientational freezing occur gradually or with some singularity?" "Does the freezing occur kinetically (i.e., a simple slowing down, as in window glass) or in some other way?"

Finally, because much of the work on other orientational glasses involved NMR, the NMR study of KCN-KBr should allow an answer to the last question: "In what ways is the orientational freezing of KCN-KBr related to those of  $\text{N}_2\text{-Ar}$  and  $o\text{-H}_2\text{-}p\text{-H}_2$ ?"

All of the samples studied were polycrystalline. As a result, we are unable to identify the orientation of the frozen rotators with respect to crystal axes. All spectra are Fourier transforms of free-induction decays and echoes.

In the  $^{15}\text{N}$  NMR, chemical-shift anisotropy is the dominant source of line broadening. The extent to which the electrons of a  $\text{CN}^-$  shield or enhance the external magnetic field from the  $^{15}\text{N}$  nucleus depends on the angle  $\theta$  between the  $\text{CN}^-$  long axis and the magnetic field. Thus, the resonance frequency  $\omega$  of a nucleus becomes<sup>23</sup>

$$\omega = \omega_0 \left( 1 - \Delta\sigma \langle \cos^2\theta - \frac{1}{3} \rangle \right), \quad (1)$$

where  $\omega_0$  is the resonance frequency for a randomly tumbling molecule as in a liquid,  $\Delta\sigma$  is the anisotropic shift, and the brackets represent time averaging over any fast motions. Thus NMR monitors an  $l=2$  func-

tion of single-molecule orientations. The intermolecular dipolar interactions are all small by virtue of their  $r^{-3}$  dependence and only slightly broaden the features of the spectra. The  $^{15}\text{N}$  spectrum calculated for randomly oriented nonrotating  $\text{CN}^-$  molecules may be calculated and is shown as the dashed curve in Fig. 1 for  $\Delta\sigma = 520$  ppm.

In the  $^{13}\text{C}$  spectra the intramolecular dipolar coupling to the  $^{14}\text{N}$  and anisotropic shift are both important; fortunately, the angular dependences are the same. Thus, the resonance frequency of a  $^{13}\text{C}$  is<sup>23</sup>

$$\omega = \omega_0 \left( 1 - [\Delta\sigma - m_s 3\gamma_I \gamma_S \hbar / \omega_0 r^3] (\cos^2\theta - \frac{1}{3}) \right), \quad (2)$$

where  $m$  specifies the  $^{14}\text{N}$  spin state and  $r$  is the  $^{13}\text{C}$ - $^{14}\text{N}$  distance. In effect, the three available  $^{14}\text{N}$  spin states (1,0,-1) can either decrease, not affect, or increase the effective anisotropy. The  $^{13}\text{C}$  spectrum calculated for randomly oriented nonrotating  $\text{CN}^-$  molecules (with  $^{14}\text{N}$  spins uniformly distributed among the three  $m$  states) is shown in Fig. 2; the value of  $\Delta\sigma$  was taken as 360 ppm. The value of  $3\gamma_I \gamma_S \hbar / \omega_0 r^3$  is 172 ppm for  $r = 1.21$  Å. Thus the anisotropic shift and intramolecular dipole interactions are of comparable magnitudes. In Eq. (2) above we have neglected  $^{14}\text{N}$  quadrupole effects and have assumed the  $^{14}\text{N}$  quantization axis to be along the external field, a fair approximation in our 2-T field (the  $^{14}\text{N}$  Zeeman frequency is 6 MHz, while the pure quadrupole frequency in  $\text{CN}^-$  is only 3 MHz<sup>24</sup>).

We remark that the time averaging in Eqs. (1) and (2) is over time scales of order  $T_{2\text{RL}}^* \equiv \Delta\omega_{\text{RL}}^{-1}$  ( $\Delta\omega_{\text{RL}}$  is the rigid-lattice linewidth, where  $\Delta\omega_{\text{RL}} \approx \omega_0 \Delta\sigma$ ).<sup>23</sup> Thus the relevant time scale is  $\sim 10^{-4}$  s, much longer

than the reciprocal of the resonance frequency.

The spectra from the 90%  $^{13}\text{C}$ -enriched sample were taken at 21.38 MHz and are displayed in Fig. 2. The 20%  $^{13}\text{C}$  data are similar, but with lower signal-to-noise ratio. The  $^{15}\text{N}$  line shapes were obtained at 8.62 MHz with a 99%  $^{15}\text{N}$ -enriched sample and are presented in Fig. 1. For both nuclei the line shapes evolve continuously from narrow lines at high temperatures ( $\sim 160$  K) to fully broadened patterns (see theoretical curves) by 20 K. Because NMR is sensitive only to the  $l=2$  part of orientations, we can conclude that the quadrupolar freezing in KCN-KBr is a *continuous* process at  $x = 0.50$ . This agrees with previous findings in KCN-KBr and appears to be the case in *o*-H<sub>2</sub>-*p*-H<sub>2</sub> as well.<sup>25</sup>

The spectra obtained below 40 K show little motional narrowing, having the same approximate widths as the calculated rigid powder patterns. This is at first surprising, since the dielectric constants at 2.5 kHz<sup>11</sup> and at 10 kHz<sup>12</sup> are still nearly Curie at 40 K (these frequencies were chosen because they are nearly equal to the relevant NMR frequency,  $\Delta\omega_{\text{RL}}/2\pi$ ). That is, the dielectric loss peaks occur at a lower temperature (27 K<sup>10</sup>, 30 K<sup>11</sup>). In fact, to narrow the NMR lines in Figs. 1 and 2 by a factor of 2, temperatures of 60–80 K (double the dielectric freezing temperature) are required. Clearly, the dielectric measurements are seeing a motion to which NMR is insensitive: 180°  $\text{CN}^-$  flips [see Eqs. (1) and (2); changing  $\theta$  to  $180-\theta$  does not change  $\omega$ ]. The quadrupolar degrees of orientational freedom ( $l=2$ ) are frozen at temperatures well above the dipolar ( $l=1$ ) freezing temperature. Thus, the quadrupolar and dipolar freezings are separate.

The motional narrowing present at high tempera-

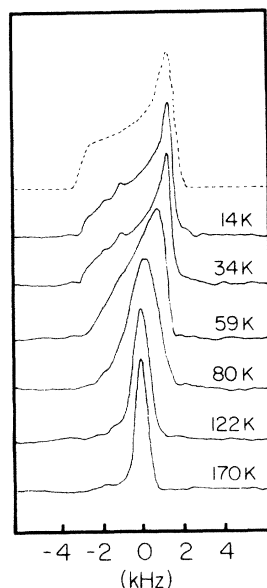


FIG. 1.  $^{15}\text{N}$  magnetic resonance line shapes from KCN-KBr at several temperatures. The dashed curve is a calculated rigid powder pattern.

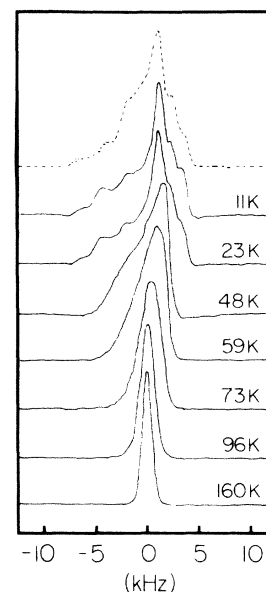


FIG. 2.  $^{13}\text{C}$  spectra from KCN-KBr at several temperatures. The dashed curve is a calculated rigid powder pattern.

tures disappears as the temperature is decreased. One way that this can occur is for the  $\text{CN}^-$  reorientation time  $t_c$  simply to increase with decreasing temperature. This "kinetic" model was treated in the classic NMR paper of Bloembergen, Purcell, and Pound.<sup>26</sup> Another way to defeat motional narrowing is the model of "favored orientations." In this case, as temperature is decreased the magnitude of  $\langle \cos^2\theta - \frac{1}{3} \rangle$  in Eqs. (1) and (2) increases because the molecules no longer spend equal times at all orientations.<sup>18</sup> At very high temperatures the orientation probability function is expected to be spherical, yielding  $\langle \cos^2\theta - \frac{1}{3} \rangle = 0$  and narrow lines (like the kinetic model). At low temperatures, one expects a strongly peaked orientation probability function, yielding a powder pattern (because the peak will occur in an arbitrary direction; also, our samples are polycrystalline). This, too, is like the prediction of the kinetic model. Hence, it is only at intermediate temperatures that the two models lead to different predictions. This has been discussed in connection with the  $\text{H}_2$  system along with a detailed comparison of the two models.<sup>27</sup>

We measured the decay-time constant  $T_2$  of spin echoes using a  $90_x - \tau - 180_y$  pulse sequence. The  $180^\circ$  pulse reverses dephasing due to anisotropic chemical shift and unlike-spin dipolar interactions. However, as with any spin echo, only dephasing from *static* interactions can be refocused.<sup>23</sup> The  $T_2$  results from the 20%  $^{13}\text{C}$  and 99%  $^{15}\text{N}$  samples are shown in Fig. 3 along with  $T_2^*$  data.  $T_2^*$  is the time for the free-induction decay to decrease to  $1/e$  of its initial value;  $T_2^*$  is essentially the reciprocal of the linewidth.  $T_2$  was deter-

mined by fitting the echo envelope with  $e^{-2\tau/T_2}$ .

Clearly, the data in Fig. 3 show that  $T_2 \gg T_2^*$ , typically by a factor of 10. Thus the principal line-broadening (dephasing) interactions are *static* (at least on a  $T_2$  time scale), even at temperatures such that narrowing occurs. It is a well known property of the kinetic model<sup>23</sup> that  $T_2 = T_2^*$  in the region of motional narrowing: For narrowing to occur,  $\tau_c$  must be less than  $T_2^*$ ; given that  $T_2^*$  cannot be longer than  $T_2$ , it must be true that  $\tau_c < T_2$ . Thus, the molecular orientations are not static on the  $T_2$  time scale, and thus echoes cannot be refocused. The kinetic model is ruled out by the spin-echo  $T_2$  data.

On the other hand, the favored-orientation model can readily explain the  $T_2$  data. If each molecule rapidly samples all orientations (though not with equal time weighting), the anisotropic shift will contain an unimportant rapidly fluctuating part and a nonzero dc (average) part.<sup>27</sup> The dephasing from the static (dc) part of the shift is readily refocused. Interestingly, the spin-echo behavior of *o*- $\text{H}_2$ -*p*- $\text{H}_2$  is similar to that reported here.<sup>28,29</sup>

The line shapes at intermediate temperatures also indicate that the kinetic model is not appropriate for KCN-KBr. Note in Fig. 2 that the  $^{13}\text{C}$  spectrum at 59 K has roughly one-half of its low-temperature width. Nevertheless, a pronounced asymmetry is present and there are no long, Lorentzian tails on the spectrum. By comparison, the kinetic model predicts<sup>26</sup> Lorentzian line shapes in the region of narrowing. At higher temperatures such line-shape analysis is unreliable, since the narrow linewidths will be determined by other interactions (intermolecular dipole).

Dipolar reorientation in KCN-KBr is characterized by a distribution of correlation times as much as ten decades wide.<sup>12</sup> Consider the NMR spectrum that would result from the kinetic model if each molecule had its own  $\tau_c$  value with a wide distribution of  $\tau_c$  values over the molecules. Those molecules with  $\tau_c \ll T_{2RL}^*$  would produce very narrow lines while those molecules with  $\tau_c \gg T_{2RL}^*$  would produce rigid powder patterns. For a wide enough distribution of  $\tau_c$  values, there would be comparatively few molecules with  $\tau_c \approx T_{2RL}^*$ ; thus the spectrum would consist primarily of a sharp line on top of a powder pattern; only the relative intensities of the two parts would change with temperature. Clearly the observed spectra do not fit a kinetic model with a wide distribution of  $\tau_c$  values.

In the favored orientation model, any single molecule's orientation probability function  $P(\Omega)$  evolves from nearly spherical at high temperatures to strongly peaked at low temperatures. Sullivan *et al.*<sup>9</sup> and Meyer *et al.*<sup>8,30</sup> have used this model to explain successfully the NMR spectra of *o*- $\text{H}_2$ -*p*- $\text{H}_2$  and of  $\text{N}_2$ -Ar.<sup>5</sup> These workers assume that  $P(\Omega)$  is uniaxi-

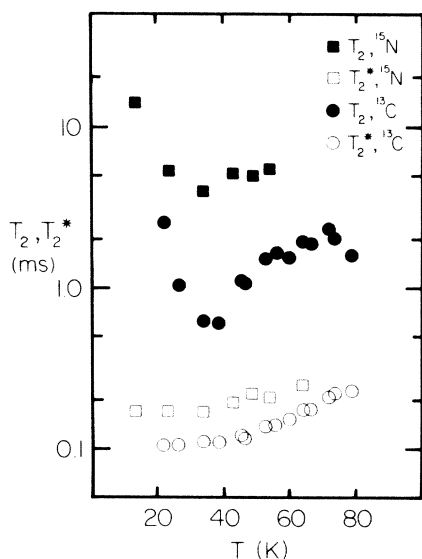


FIG. 3. Relaxation time  $T_2$  (solid symbols), the decay-time constant of the spin-echo envelope. The  $e^{-1}$  decay time of the free-induction decay,  $T_2^*$ , is indicated by open symbols. The principal source of line broadening is *static*, as indicated by  $T_2 \gg T_2^*$ .

ally symmetric (to simplify the problem) with randomly directed local symmetry axis. Although there is some influence on the local symmetry axis exerted by the crystal axes,<sup>30</sup> this has been generally regarded as small. The local order parameter  $\sigma$  for a given molecule is

$$\sigma = \langle \cos^2\psi - \frac{1}{3} \rangle^{\frac{3}{2}}, \quad (3)$$

where the brackets denote time averaging the  $\psi$  is the instantaneous angle between the local symmetry axis and the molecular axis. Thus  $\sigma$  is a measure of the  $l=2$  deviation from sphericity of  $P(\Omega)$ :  $\sigma=0$  for a sphere and  $\sigma=1$  for a strongly peaked function.

All molecules with a given  $\sigma$  produce an NMR powder pattern, but scaled in width by  $\sigma$ . The distributions of order parameter values  $\sigma$  required to reproduce the  $H_2$  and  $N_2$ -Ar line shapes were computed.<sup>5,8,9,30</sup> At this point, in KCN-KBr we believe that the actual distribution of  $\sigma$  values is of less significance than the fact that the spectra *can* be fitted with the favored-orientation model. For example, the distribution of  $\sigma$  values one obtains is directly dependent upon the assumption of a uniaxially symmetric probability function. Our  $KC^{15}N$ -KBr spectra, when symmetrized by reflection through the center, strikingly resemble the  $H_2$  spectra<sup>8,9,30</sup> (symmetric because of the  $m_l = -1 \rightarrow 0$  and  $0 \rightarrow 1$  doublet); the same distributions of  $\sigma$  values present in  $H_2$  evidently fit the KCN-KBr data. The similarities in the NMR spectra suggest that the underlying physics in  $H_2$  and in KCN-KBr is the same, even though the anisotropic molecular interactions are very different in the two cases.

Recent  $^{23}Na$  NMR experiments on NaCN-NaCl indicate that the quadrupolar orientational freezing in this material also occurs by development of favored orientations.<sup>31</sup> Volkmann *et al.*<sup>32</sup> have extended measurements of shear softening in KCN-KBr to the kilohertz range using a torsional pendulum. They find that the quadrupolar and dipolar freezings are separate at frequencies below  $10^8$  Hz, in agreement with our NMR results. However, they also find a weak frequency dependence of the quadrupolar freezing temperature for  $x=0.5$  (30% variation from  $10^2$  to  $10^{12}$  Hz) and a stronger dependence for  $x=0.2$ . This is *not* predicted by the model of favored orientations and indicates that dynamic (rate) effects may also be present.

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