

Molecular-dynamics study of phase I of RbCN

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(Received 20 April 1981)

We report molecular-dynamics calculations on the orientationally disordered phase I of RbCN at 138 and 298 K. The results are compared with recent Raman and neutron scattering data.

Partly because the pure single crystals are difficult to prepare,¹ RbCN has received less attention than the cyanides of sodium and potassium. However, dielectric,¹ Raman,^{1,2} Brillouin,³ ultrasonic,⁴ and inelastic neutron scattering⁵ studies have all recently been reported. In the high-temperature phase I, the (CN)⁻ ions undergo rotational diffusion and the structure is the same as that of the sodium and potassium salts, namely *Fm3m*. Under zero pressure at 132 K, there is a first-order transition to phase II, space group *B6*, in which the (CN)⁻ ions are oriented along $\langle 111 \rangle$ directions but have their dipole moments disordered.^{1,3}

On cooling RbCN towards the I→II phase transition, a strong softening of the elastic constant C_{44} is observed with the use of both ultrasonic⁴ and Brillouin techniques.³ This behavior is similar to that found in NaCN and KCN, and is suggestive of a coupling^{6,7} between C_{44} and fluctuations of T_{2g} symmetry in the orientational probability distribution $f(\vec{u})$ (\vec{u} is a unit vector directed along the C—N bond). Additional evidence for the importance of rotation-translation coupling comes from an analysis⁵ of the phonon dispersion curves measured at 300 K.

In an effort to shed further light on the structure and dynamics of phase I of RbCN, we have undertaken a series of molecular-dynamics (MD) calculations. Classical calculations of this type are appropriate here, since even the highest-frequency optic modes will be significantly populated at the temperatures at which phase I exists. The MD calculations were carried out for a system of 64 ions interacting through atom-atom potentials of the form

$$V_{\alpha\beta}(R) = A_{\alpha\beta}\exp(-a_{\alpha\beta}R) - B_{\alpha\beta}/R^6, \quad (1)$$

($\alpha, \beta = \text{C, N, Rb}$) to which a Coulomb term

$q_{\alpha}q_{\beta}/R$ was added ($q_{\text{Rb}} = |e|$). The potential parameters were constructed from literature values,⁸⁻¹⁰ using standard combining rules. As in our earlier work on NaCN,¹⁰ we used a bond length of 1.19 Å for the (CN)⁻ ion and a charge distribution represented by $q_{\text{C}} = -1.28|e|$, $q_{\text{N}} = -1.37|e|$, and $q_{\text{c.m.}} = +1.65|e|$, $q_{\text{c.m.}}$ being placed at the center of mass. This choice of fractional charges yields values of the dipole and quadrupole moments which are in reasonable agreement with *ab initio* self-consistent-field (SCF) results¹¹ for the free ion. Two simulations were carried out, for temperatures of 138 and 298 K.

The orientational distribution of the (CN)⁻ ions, $f(\vec{u})$, may be specified by the coefficients c_i of its expansion¹² in Kubic harmonics K_i , given by

$$f(\vec{u}) = (1/4\pi)(1 + c_4K_4 + c_6K_6 + \dots). \quad (2)$$

The c_i are ensemble averages of the K_i and, therefore, easily calculable from the MD data. Results for c_4 , c_6 , and c_8 are given in Table I, where comparison is made with the experimental neutron scattering results⁵ and with the values which would be obtained if all (CN)⁻ ions were oriented along

TABLE I. Kubic harmonic expansion coefficients for the orientational distribution of (CN)⁻ ions in phase I of RbCN.

	c_4	c_6	c_8
$\langle 111 \rangle$ order	-1.53	2.27	0.88
MD 138 K	-0.85	0.45	0.29
MD 298 K	-0.41	0.05	0.12
EXPT 150 K	-0.15		
EXPT 300 K	-0.35	0.51	

$\langle 111 \rangle$ directions. At room temperature there is satisfactory agreement with experiment. However, as the temperature is reduced, there is a tendency for the model to freeze into $\langle 111 \rangle$ pockets, though even at 138 K the alignment is far from complete. This trend is not apparent in the neutron scattering results.

The calculated mean-square amplitudes $\langle u_{\pm}^2 \rangle \simeq 0.12 \text{ \AA}^2$ were found to be almost independent of temperature, as are the experimental results¹³ for the orientationally disordered phases of NaCN and KCN. The values are smaller than the experimental results ($\langle u_{\pm}^2 \rangle \sim 0.19 \text{ \AA}^2$). Additional calculations on cyanide crystals containing larger numbers of ions indicate that most of this discrepancy is due to our use of a small system. The calculated pressure was large and negative (~ -5 kbar), suggesting that in the model we have used, the hard-core repulsions are too weak.

Polarized Raman scattering experiments¹ may be used to probe the reorientational dynamics of $(\text{CN})^-$ ions in RbCN. The E_g and T_{2g} spectra measure the Fourier transforms of the correlation functions

$$R_{11}(t) = \sum_{i,j} \langle A_1(t) A_1^*(0) \rangle_{ij} (E_g), \quad (3)$$

$$R_{33}(t) = \sum_{i,j} \langle A_3(t) A_3^*(0) \rangle_{ij} (T_{2g}),$$

where the A 's are related^{6,14} to the spherical harmonics Y_2^m . For our classical MD calculations, $A_1 = \frac{1}{2}(3z^2 - 1)$ and $A_3 = \sqrt{3}(xz)$. The summations in (3) extend over all the cyanide ions.

Figure 1 compares the observed¹ and calculated low-temperature E_g and T_{2g} spectra. The difference between the MD peak positions ($\sim 80 \text{ cm}^{-1}$)

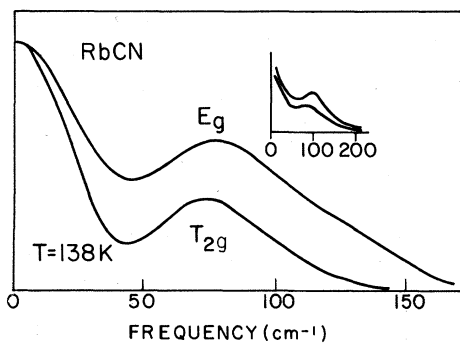


FIG. 1. Power spectra associated with the E_g and T_{2g} reorientational correlation functions (see text). Inset shows the experimental Raman data from Ref. 1.

and experiment ($\sim 100 \text{ cm}^{-1}$) is consistent with the large negative pressure found in the simulation, corresponding to a crystal which is overexpanded. However, so far as the shapes of the spectra are concerned, calculation and experiment are in good agreement. At 300 K, the 100-cm^{-1} peak is poorly resolved in both the experimental and simulated spectra. However, in the simulation the E_g mode displays a stronger peak and the T_{2g} mode a weaker one than is observed.

The coherent inelastic scattering cross section $S(\vec{Q}, \omega)$ and the intermediate scattering function $F(\vec{Q}, t)$ have been calculated for various values of the momentum transfer $\hbar\vec{Q}$, utilizing both the experimental coherent neutron scattering lengths and scattering lengths of $+1$ for the cations and -1 for the anion centers of mass. As would be expected of a rigid-ion model, the calculated longitudinal optic (LO) frequencies are rather high in comparison with the experimental results. However, the acoustic modes agree more closely with experiment (see Fig. 2). The transverse acoustic (TA) phonon at

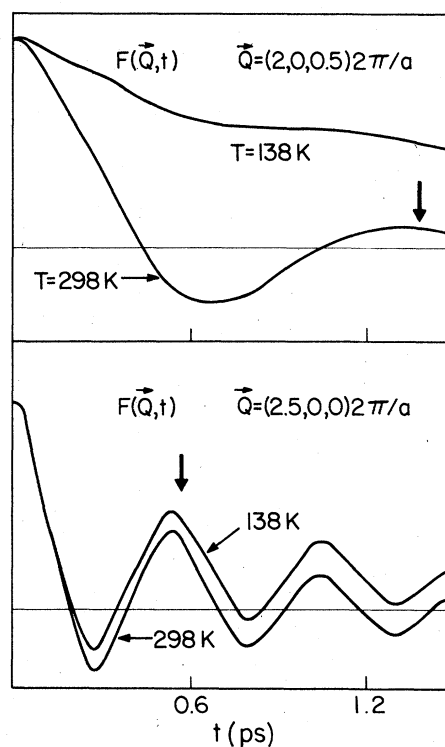


FIG. 2. Temperature dependence of $F(\vec{Q}, t)$ for $\vec{Q} = (2, 0, 0.5) 2 \pi / a$ (LA) and $\vec{Q} = (2.5, 0, 0) 2 \pi / a$ (LA), calculated using the coherent scattering lengths of the nuclei. The arrows indicate the experimental periods of the appropriate TA and LA phonons Ref. 5).

$\vec{Q} = (2,0,0.5)2\pi/a$ develops a central peak as the temperature is lowered, an effect seen also in experiments¹⁵ on KCN. This behavior can be seen in the top part of Fig. 2, where $F(\vec{Q},t)$ is displayed for both high and low temperatures. An interesting observation is the appearance of central peaks in the MD $S(\vec{Q},\omega)$ for longitudinal as well as transverse modes. In both examples shown in Fig. 2 the low temperature $F(\vec{Q},t)$ is not oscillating about zero, but about a weak positive level, even after 2 ps.

In summary, at room temperature the results of the MD simulation are in broad agreement with

those of Raman and neutron experiments. However, at lower temperatures our model shows a greater tendency for the $(\text{CN})^-$ ions to order into $\langle 111 \rangle$ pockets. The simulation predicts the appearance of central peaks in both the longitudinal and transverse neutron scattering response. It will be interesting to see if this prediction is confirmed experimentally.

We thank J. M. Rowe, J. J. Rush, F. Lüty, and A. Anderson for useful discussions. This work was supported in part by the U.S. National Bureau of Standards Reactor Radiation Division.

¹Y. Kondo, D. Schoemaker, and F. Lüty, *Phys. Rev. B* **19**, 4210 (1979).

²E. Rehder and W. Dultz, in *Proceedings of the International Conference on Raman Scattering, Ottawa, 1980*, edited by W. F. Murphy (North-Holland, Amsterdam, 1980), p. 42.

³W. Krasser, B. Janik, K. D. Ehrhardt, and S. Haussühl, *Solid State Commun.* **30**, 33 (1979).

⁴S. Haussühl, *Solid State Commun.* **32**, 181 (1979).

⁵K. D. Ehrhardt, W. Press, J. Lefebvre, and S. Haussühl, *Solid State Commun.* **34**, 591 (1980); K. D. Ehrhardt, thesis, Saarbrücken (1981) (unpublished).

⁶K. H. Michel and J. Naudts, *J. Chem. Phys.* **67**, 547 (1977); **68**, 216 (1978).

⁷M. Boissier, R. Vacher, D. Fontaine, and R. M. Pick, *J. Phys.* **39**, 205 (1978); **41**, 1437 (1980).

⁸F. L. Hirshfeld and K. Mirsky, *Acta Crystallogr. Sect.*

A **35**, 366 (1979).

⁹M. P. Tosi and F. G. Fumi, *J. Phys. Chem. Solids* **25**, 45 (1964).

¹⁰M. L. Klein and I. R. McDonald, *Chem. Phys. Lett.* **78**, 383 (1981).

¹¹J. E. Gready, G. B. Bacskay, and N. S. Hush, *Chem. Phys.* **31**, 467 (1978).

¹²W. R. Fehlner and S. H. Vosko, *Can. J. Phys.* **54**, 2159 (1976); R. S. Seymour and A. W. Pryor, *Acta Crystallogr. Sect. B* **26**, 1487 (1970).

¹³J. M. Rowe, D. G. Hinks, D. L. Price, S. Susman, and J. J. Rush, *J. Chem. Phys.* **58**, 2039 (1973).

¹⁴D. Fontaine and R. M. Pick, *J. Phys. (Paris)* **40**, 1105 (1979).

¹⁵J. M. Rowe, J. J. Rush, N. J. Chesser, K. H. Michel, and J. Naudts, *Phys. Rev. Lett.* **40**, 455 (1978).