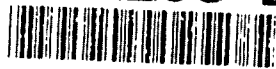




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METHYL TORSIONAL LEVELS OF SOLID ACETONITRILE--  
A NEUTRON SCATTERING STUDY

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## INTRODUCTION

The rotational properties of methyl groups in the solid state have been measured in the past for many different molecular systems of which the methyl group is a part (ref 1). The most interesting properties have been found for those systems in which the hindering potential is small (rotational barrier less than 50 meV) (ref 2). For the most part, these low barriers occur in molecules which have a very small internal barrier due to the arrangement of the other atoms of the molecule with respect to the methyl group resulting in a cancellation of forces. In this case, the intermolecular interactions predominate in determining the potential hindering of the rotation of the methyl group about its three-fold axis. These interactions are due to many neighbors of the methyl hydrogens. When these in turn lead to a small barrier, the detailed shape of the barrier can have substantial structure (consistent with the overall required three-fold symmetry). Perturbations of the crystalline parameters caused by pressure, for example, can produce dramatic effects on the rotational potential. The fact that this potential is a result of the addition of many interactions makes it difficult to predict the result or to foresee when this result has properties which have not been previously found. It seems worthwhile to study those systems for which the possibility of interesting phenomena exists. Detailed spectroscopic information resulting from these studies also make it possible to obtain more reliable information on the intermolecular potentials in the solid.

Acetonitrile ( $\text{CH}_3\text{CN}$ ), because of its rod-like shape, produces no internal barrier to rotation. This is the principle reason for choosing this molecule as a reasonable candidate for further investigation. The crystal structure of the low temperature phase has been previously determined with x-ray and neutron diffraction (ref 3). It reveals one assymmetric unit in the primitive cell. This simplifies the description of the methyl rotations in that there is but one unique methyl group in the crystal. This structural determination did not, however, result in a clear description of the thermal vibrations of the hydrogen atoms. The magnitude of these thermal parameters often can be correlated with the rotational barrier. Accurate neutron diffraction is capable of obtaining this information. For this reason, a neutron powder diffraction measurement on the deuterated molecular at 4 K is reported for the purpose of confirming the details of the previous study and obtaining the thermal parameters of the deuterium atom. A proton magnetic resonance determination of the activation energy for methyl rotations is available (ref 4). The value of the activation energy given by this study is 91 meV. The value of this activation energy is rather large compared to that (9 meV) of the compound, nitromethane (ref 2), whose properties have proved most interesting. This last property was not encouraging in our search for an interesting candidate; however, because it was only obtained for temperatures above 100 K and because inelastic neutron scattering gives more direct information on the nature of the potential, a series of inelastic scattering measurements on both protonated and deuterated isotopic molecules are reported.

## EXPERIMENTAL METHODS

The triple axis neutron spectrometers (BT9 and BT4) in the present inelastic scattering work are located on the neutron beam scattering reactor (NBSR) at the National Institute of Standards and Technology (NIST). Several configurations of the instrument were used corresponding to different regions of energy transfer. For energy transfers below 20 meV, the monochromator and analyzer are PG (002) crystals with an incident energy of 28 meV. Above energies of 20 meV, the analyzer is a cooled Be-PG filter corresponding to a narrow (~1.6 meV) band pass filter centered at 1 meV and a copper (220) monochromator for energy transfers above 40 meV. The spectra obtained in the several energy regions are normalized to each other in those regions for which the energies overlap.

The powder diffractometer (BT1) uses neutrons of wavelength 0.1553 nm. These are obtained from a crystal of copper using the (2,2,0) reflection in transmission geometry. Five detectors measure the neutrons scattered by the sample simultaneously. These detectors are separated by 20 deg from each other with respect to the direction of the beam incident on the sample. Collimations of 10 ft, 20 ft, and 10 ft define the beam direction between the reactor and the monochromator, the monochromator and sample, and the sample and detectors, respectively.

The preparation of a sample for the purpose of a measurement of the diffraction from a powder requires some care. In particular, it is necessary to obtain a good powder by mechanical means in order to ensure that there be no large crystallites which distort the intensities of the diffraction lines due to preferred orientation. This is usually accomplished by grinding or pounding the sample in a mortar and pestle. The melting temperature of acetonitrile is 229 K. The above procedure cannot be accomplished at ambient temperatures. The melting temperature is, however, substantially higher than the sublimation temperature (194 K) of CO<sub>2</sub>. The following procedure has been successfully used in the past for several materials whose melting temperature is between 194 K and ambient. A mortar and pestle, sample container, spatula, and flat plate of some metal (AA1, Fe...) are placed on ground solid CO<sub>2</sub>. The sample is sprayed on the cold metal plate to form a thin film. The film is transferred from the plate to the mortar where it is gently crushed. Care is taken during this operation so that none of the tools become warm enough to melt the sample. The powder is transferred to the sample container until it is full. If a standard cryostat is to be used for the measurements, it is cooled with liquid nitrogen, for example. A closed circuit refrigerator, if used, should also be cooled. The cryostat vacuum is broken with dry nitrogen gas, the vacuum can be removed, and sample attached quickly to the cold block. Radiation shields and vacuum cans are reattached, and the cryostat pumped

out. This last procedure takes about 10 min. There is some water ice formed on the cold surfaces, but not enough to prevent it from being pumped out with a good pumping system. In any case, no ice was detected in the subsequent neutron scattering measurements. The final test of a good powder is the constancy of the intensity of a diffraction peak as the sample is rotated. The above procedure has never failed this test.

Acetonitrile shows a phase transition at 217 K. There exists in the literature a description of a laborious procedure by which the low temperature phase is to be ensured (ref 5). In preparation of the powder sample, we simply formed the sample as described above, cooled to 4.2 K, and performed the diffraction measurement. No evidence of the presence of the high temperature phase was detected in the sample as evidenced by the successful refinement of the structure as described below.

## EXPERIMENTAL RESULTS

### Crystal Structure

The neutron powder diffraction data, at a sample temperature of 4.20 K, were obtained from the high-resolution powder diffractometer at the NIST reactor. The 100 K structure reported by Antson et al. (ref 3) was used for the initial model of the refinement. The refinement with isotropic bulk temperature converged to  $R_{wp} = 12\%$  which suggested that the model structure was correct. A comparison of the observed data to the calculated pattern at the early stage of refinement indicated clearly that the observed powder pattern was contaminated by the diffraction from the Ti sample container. There were a total of 16 Ti peaks within the observed powder pattern of which 8 Ti peaks had significant intensity that was removed from the observed data. The final refinement, with an anisotropic temperature factor to each atom, converged to  $R_B = 2.67$ ,  $R_p = 4.79$ ,  $R_{wp} = 6.63$ , and the expected residual factor  $R_c = 5.32$ . The R values of this study are considerably lower than those of the earlier study (ref 3). The final least-squares parameters are given in table 1.

The crystal symmetry and the constrained  $C_{3v}$  type molecular structure reported by Anston et al. (ref 3) were essentially correct except the precision of the bond parameters. The molecule is positioned on the mirror plane of the  $Cmc2_1$  space group with the three molecular skeleton atoms and one of the methyl hydrogen (D1) on the mirror plane. The molecular axis, C1-C2=N, has a true linear form within the experimental error ( $179.6 \pm 0.5$  deg) and tilted by 48.4 deg from the c-axis. The ORTEP drawing of the molecule is presented in figure 1. The three D atoms of the methyl group are arranged in the normal tetrahedral form with the deviation less than 2 deg in bond angles. The C1-C2 bond was found to be the normal single bond with

the bond length of 1.460(5) Å, unlike the shortened bond length of 1.311(11) Å as reported in reference 3. The bond parameters of this study are given in table 2.

The thermal ellipsoids of the methyl D atoms were about twice as large as those of the C and N atoms, and their orientations were consistent with the molecular libration motion (about the molecular axis). The rigid-body motions (T, L, and S) were obtained from the atomic anisotropic thermal motions by the method of Schomaker and Trueblood. The results are given in table 3. The largest librational motion occurs about the molecular axis with the root mean square amplitude of about 6 deg which is consistent with the rigid-body motion model. It is expected that the thermal motions of the methyl D atoms become much larger at 100 K since the libration motion should increase with the increase of the temperature. Nevertheless, the Debye-Waller factor of the D atoms at 100 K (ref 3) was considerably smaller than those of the skeleton atoms, which is obviously inconsistent with the rigid-body motion model.

### Inelastic Scattering

Spectra were obtained for CH<sub>3</sub>CN at 4 K and 100 K and for CD<sub>3</sub>CN at 4 K (fig. 2). The samples and temperatures for each of the three spectra are indicated in the figure as are the assignments of the peaks. The solid lines in these figures are the result of fits with gaussians whose energy assignments to specific motions are listed in table 4. These assignments are arrived at in the following manner: The two peaks ca 9 and 16 meV are due to intermolecular phonons since they are of the energy expected for these modes and do not shift substantially upon deuteration. The next higher energy peak (also the most intense) in all three spectra is assigned to the rotational (0 - 1) ground state to first excited state transition (here denoted as  $\tau_1$ ). This assignment is strongly supported by the intensity of the peak and the shift upon deuteration. This shift in energy upon deuteration can be obtained from the standard description of the simplest potential hindering a three-fold rotor, namely

$$V(\theta) = V_3/2 (1 - \cos 3\theta)$$

where  $\theta$  is the rotation angle of the methyl group about the three-fold axis, and  $V_3$  is the height of the potential. The solution of the quantum problem for the values of the energy levels as a function of  $V_3$  and moment of inertia of the rotor is well known (ref 6). The results of this calculation for the two isotopic rotors and for a value of  $V_3 = 125$  meV is given in table 5. The agreement with the value of  $\tau_1$  confirms the above assignment. The internal mode  $\nu_8$  (the N-C-C angle bend) of the protonated molecule in the liquid has been identified as occurring at an energy of 47.1 meV (380 cm<sup>-1</sup>) (ref 6). This mode is expected to increase in energy in the solid so that the assignment of the sharp peak at 49.4 meV to this mode is reasonable. This assignment can be strengthened by a normal mode calculation using the potential function of reference 7.

In that work, the N-C-C angle bend force constant is given as  $0.155 \times 10^5$  dynes/cm. Using a value of  $0.171 \times 10^5$  dynes/cm produces a value for  $\nu_8$  of 49.4 meV. This normal mode calculated for the deuterated molecule then shifts to 45.2 meV in the deuterated specimen which is to be compared with the measured value of 45.2 meV. With the above assignments, it was concluded that the  $\tau_2$  mode for the deuterated sample was measured at 36.4 meV and that this mode is accidentally degenerate with the  $\nu_8$  mode in the protonated sample. The spectrum of the protonated molecule at 100 K resolves the question in favor of this assignment. At 100 K, the  $\tau_1$  mode has shifted to 24.9 meV, and a mode at approximately 47 meV is now clearly moved away from the  $\nu_8$  mode which has not changed with temperature. The remaining weak features in the spectra of the protonated molecule are easily assigned as combination bands as indicated in figure 2 and table 5 (where the assignments of all the peaks are given). All the resonances are thus accounted for. This rotational potential produces an activation energy of  $\sim 112$  meV in reasonable agreement with the measured values of 91 meV by proton magnetic resonance. Finally, in the harmonic approximation, a deuterated methyl group in the ground state whose first excited state is 19 meV above the ground state is expected to have a root mean square amplitude of rotational vibration of 7.5 deg. This compares well with the value of 6 deg obtained from the neutron diffraction measurement.

## CONCLUSION

The motivation for this study was the hope of obtaining another low barrier methyl rotor whose properties might prove interesting. Both the neutron diffraction determination of the thermal parameters of the deuterium atom and the neutron spectroscopic determination of the rotational energy levels conform to a substantial potential for the methyl rotation. The measured activation energy obtained from the temperature dependence of  $T_1$  from proton magnetic resonance is consistent with the single particle potential at 4 K. This conforms to this relationship for moderate to high barrier systems. The complete identification of the features in the inelastic neutron spectra and the consistency with the nuclear magnetic resonance measurements is satisfying. Unfortunately, novel phenomena are not forthcoming.

Table 1. Final least-squares parameters of the acetonitrile at 4.2 K

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B11(Å<sup>2</sup>)</u>	<u>B22(Å<sup>2</sup>)</u>	<u>B33(Å<sup>2</sup>)</u>	<u>B23(Å<sup>2</sup>)</u>
C1	0	-0.0695(8)	0	1.1(2)	0.5(2)	1.4(2)	0.1(2)
C2	0	-0.2789(8)	0.1244(7)	1.1(2)	1.1(3)	0.2(2)	-0.1(2)
N	0	-0.4440(5)	0.2240(6)	1.2(2)	0.8(1)	0.4(1)	0.1(1)
D1	0	0.1159(8)	0.0693(7)	2.4(2)	1.0(2)	1.7(2)	0.1(1)
D2	0.1481(4)	-0.0792(7)	-0.0780(6)	1.9(2)	2.4(2)	2.0(2)	0.1(2)

\* B12 = -0.3(2)      B13 = 0.4(1)

NOTE: The elements of the anisotropic temperature factor B12 and B13 are nil for all the atoms in the mirror plane and are not given here. The \* symbol indicates the parameters of the elements B12 and B13 of D2 atoms.

Table 2. Bond lengths and angles of CD<sub>3</sub>CN at 4.2 K

<u>Bonds-lengths (Å)</u>		<u>Bond-angles (°)</u>	
C1-C2	1.460(5)	C1-C2-N	179.7(5)
C2-N	1.159(5)	D1-C1-C2	109.5(4)
C1-D1	1.109(6)	D2-C1-C2	109.6(3)
C1-D2	1.079(3)	D1-C1-D2	108.3(4)
		D2-C1-D2'	111.4(5)

NOTE: The atom symbol D2' indicates the mirror symmetric pair of D2 atom.

Table 3. Tensor elements, T(i,j) and L(i,j), of the rigid-body motions

<u>(i,j)</u>	<u>T(i,j) (Å<sup>2</sup>)</u>	<u>L(i,j) (Å<sup>2</sup>)</u>
11	0.0083(39)	0.0022(21)
22	0.0122(25)	0.0078(52)
33	0.0095(33)	0.0074(61)
23	-0.0031(25)	-0.0024(24)

NOTE: Elements (1,2) and (1,3) are nil because of the mirror symmetry of the site.

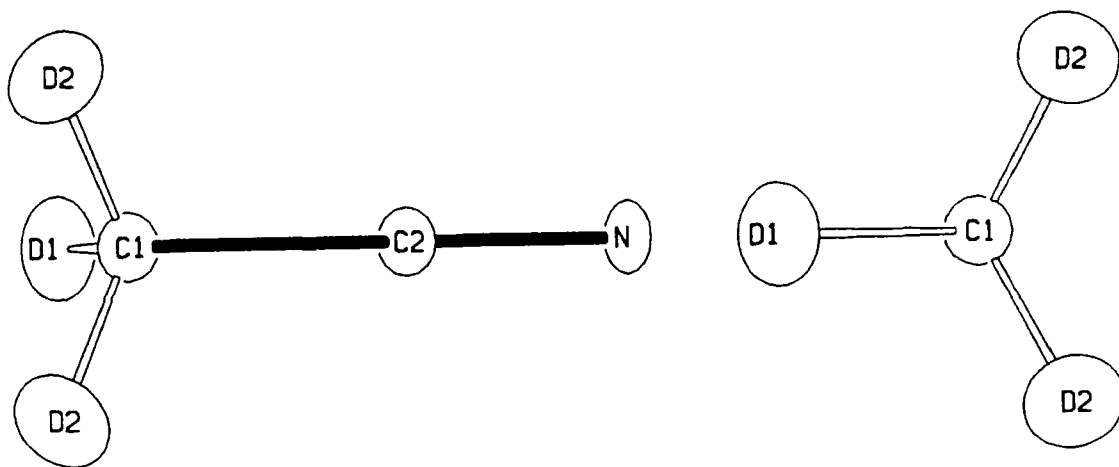
Table 4. Measured and calculated rotational energy levels of acetonitrile

	<u>1st level</u>		<u>2nd level</u>	
	<u>Calculation</u>	<u>Observed</u>	<u>Calculation</u>	<u>Observed</u>
CH <sub>3</sub> CN	25.8	25.9	49.9	49.4
CD <sub>3</sub> CN	18.6	19.0	36.4	37.1

Table 5. Observed neutron inelastic scattering peaks and their assignment for CH<sub>3</sub>CN at 4 and 100 K and for CD<sub>3</sub>CN at 4 K

<u>CH<sub>3</sub>CN</u>		<u>CD<sub>3</sub>CN</u>	<u>Assignment</u>
<u>4 K</u>	<u>100 K</u>	<u>4 K</u>	
9.45	8.9	9.2	Phonon
16.0	15.7	15.6	Phonon
25.9	24.9	19.0	$\tau_1$
34.75	33.8	28.2	Phonon + $\tau_1$
42.0	40.5	34.6	Phonon + $\tau_1$
49.4	46.8	37.1	$\tau_2$
49.4	49.3	45.2	$\nu_8$
58.9			Phonon + ( $\tau_2$ and $\nu_8$ )
66.8			Phonon + ( $\tau_2$ and $\nu_8$ )
74.9			$\tau_1 + \nu_8$

NOTE: Energies are in meV



**Figure 1. Two views of the molecular geometry of CD<sub>3</sub>CN as determined by powder neutron diffraction at 4 K**

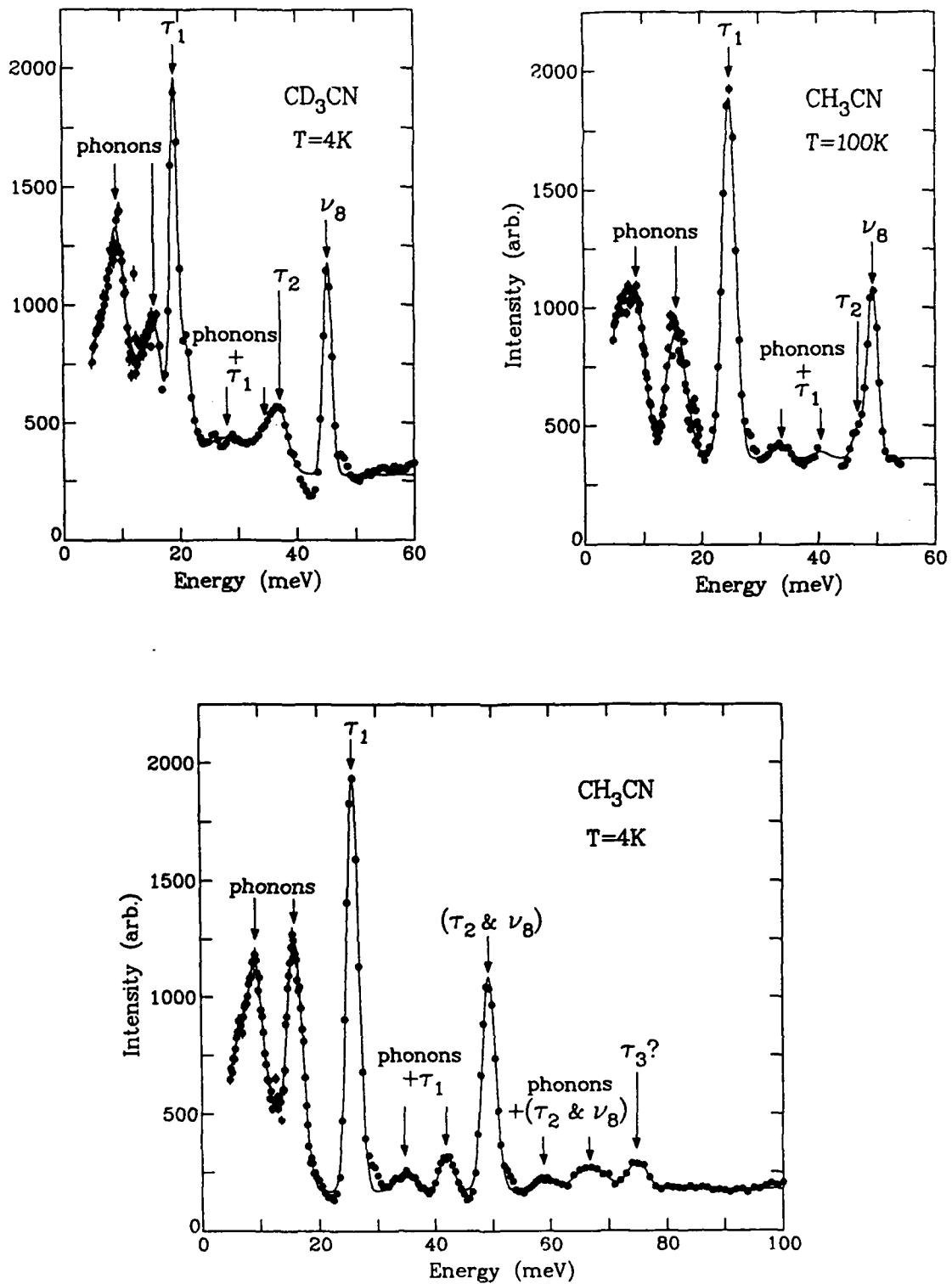


Figure 2. Inelastic neutron spectra for CH<sub>3</sub>CN at 4 K and 100 K and for CD<sub>3</sub>CN at 4 K

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