Anomalous Pressure Dependence of the Torsional Levels in Solid Nitromethane

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Inelastic neutron-scattering measurements of the torsional levels of CH_3NO_2 and CD_3NO_2 are presented as functions of pressure and temperature. In contrast to all previously observed pressure dependence of hindered rotors, the ground-state tunnel splitting increases and the energies of the bound torsional levels decrease with pressure. A potential which reproduces these anomalous effects is found and the source of the anomaly explained.

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Nitromethane (CH_3NO_2) in the solid state has proven to be a prototypical system for the study of the properties of the potential governing the rotational motion of a molecular group (in this case CH_3) subjected to weak intermolecular forces.[1] Interest in the study of rotational motions in molecular crystals is longstanding[2] and has intensified in recent times because of the availability of high-resolution neutron spectrometers capable of probing the microscopic details of the rotational motions.[3] Many of the systems studied are complicated by the existence of phase transitions, multiple rotational axes, different environments surrounding the various molecules, or uncertainties concerning the crystal structure; any or all of these make the interpretation of the measurements difficult. In the case of nitromethane, these complications do not exist. The molecular group (CH_3) is constrained to rotate about a single axis, the C-N bond; the crystal structure is well established[4] and is the same for both protonated and deuterated species from the melt to 4.2 K; and all the molecules are related by symmetry leading to a single potential describing the rotational motion. In addition, the intramolecular rotational potential is very small[5] so that the contribution due to intermolecular interactions in the solid is dominant.

We have reported in the past the measurement of several dynamical properties of the rotational motion of both isotopic species, but, with the interpretation given in Ref. 1, we have been unable to discover a potential which correctly describes all the measured quantities. In this Letter we present new inelastic neutron-scattering measurements of the level scheme, including tunneling levels and first and second torsional levels, of both isotopic species and their temperature and pressure dependence (in which quite unexpected behavior was found). Also presented is a potential which reasonably reproduces the measured levels and is qualitatively consistent with one derived from intermolecular interactions. This study represents a thorough characterization of a low-barrier rotational potential in the solid state.

In a previous study,[1] a feature centered at ~7-meV energy transfer in an inelastic neutron spectrum of CH_3NO_2 was interpreted as resulting from two broad levels corresponding to the tunnel-split first-excited torsional level. The source of the width was attributed to interactions with virtual phonons since the torsional level was thought to exist near the top of the potential well. In order to test this assignment we have measured the torsional level as a function of pressure; we expected that the levels would move deeper into the potential well, and thus increase their lifetime (narrowing the energy width). The result of this measurement at two pressures[6] (1 bar and 4.8 kbar) is presented in Fig. 1. The measurements were performed on the triple-axis spectrometer at BT4 of the National Bureau of Standards research reactor with an energy resolution of 1 meV. The broad feature centered at 7 meV at 1 bar splits into two well resolved peaks, one of which moves to 5.8 meV and the other remains at 7.8 meV. Because the lower-energy peak is more intense and because it is more pressure sensitive, it must be assigned to the torsional level. The higher-energy peak should be assigned to a phonon density of states. We therefore revise the interpretation of the broad peaks observed at 1 bar as consisting of one torsional peak and a phonon density of states rather than the

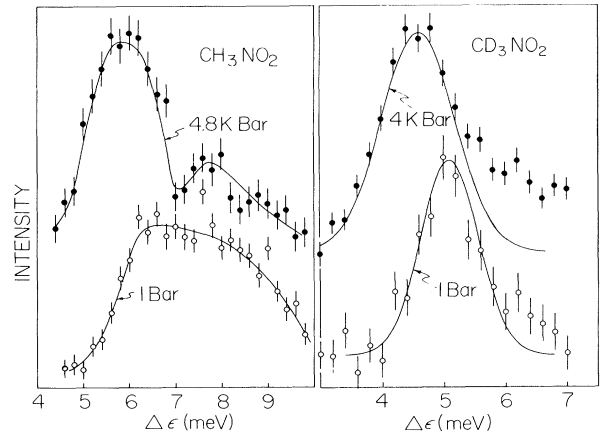

FIG. 1. Inelastic neutron-scattering spectrum of CH_3NO_2 and CD_3NO_2 at two pressures and 4.2 K. For CH_3NO_2 $Q = 1.9$ Å^{-1} and for CD_3NO_2 $Q = 1.3$ Å^{-1}. This is a measurement of the pressure dependence of the first excited torsional level of both isotopic species. Solid lines are fits with resolution-broadened Gaussians. The intrinsic width of the torsional peak in CH_3NO_2 is about 1 meV, whereas that for CD_3NO_2 is resolution limited.

two levels resulting from tunnel splitting of the first excited torsional state. This assignment is supported by a recent Raman spectroscopic[7] study in which the temperature dependence of the torsional peak was studied (see also Fig. 4). The pressure dependence of the torsional level in the deuterated species is also presented in Fig. 1 and also shows its energy decreasing with increasing pressure.

The changes in the potential with pressure resulting in this unexpected downshift can be further investigated by measuring the pressure dependence of the ground-state tunnel splitting of both isotopic species. These measurements were performed with the high-resolution backscattering instruments IN13 with a resolution of 7 μeV full width at half maximum for CH_3NO_2 and IN10 with a resolution of 0.4 μeV full width at half maximum for CD_3NO_2, both instruments located at the Institut Laue-Langevin.[8] The results of the measurement at two pressures are presented in Fig. 2. In contrast to all previously investigated systems of hindered rotors in the solid,[9] here the tunnel splitting of the ground state increases with increasing pressure. From data at several pressures, not presented here, the increase is found to be linear with pressure in the case of CH_3NO_2 and almost exponential for CD_3NO_2.

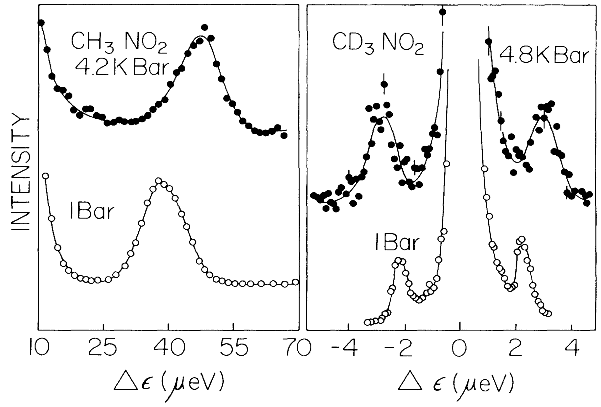

FIG. 2. The pressure dependence of the ground-state splitting of CH_3NO_2 and CD_3NO_2 at 4.2 K. The data at 1 bar are taken from Ref. 1.

Several conclusions concerning the potential can be inferred from these measurements. The first excited state of CH_3NO_2 is deeper in the potential well than previously thought, since its tunnel splitting is substantially less than the ~1 meV of the original assignment,[1] and the changes caused by pressure affect the bottom of the well as reflected by the larger relative change of the deuterated-species ground-state tunnel splitting compared to the protonated species, the former ground state being nearer the bottom. A potential of the form

$$V(\theta) = V_3(1-\cos 3\theta) + V_6[1-\cos(6\theta+\delta)]$$

can be made to produce such effects. Values of the

TABLE I. Measured and calculated levels of the two isotopic species of nitromethane at two pressures and 5 K. The values of the potential parameters at the two pressures are, for 1 bar, $V_3 = 25.5$ meV, $V_6 = -15.5$ meV, $\delta = 30°$; for 4.8 kbar, $V_3 = 22.5$ meV, $V_6 = -17.2$ meV, $\delta = 25°$.

	Ground-state splitting (μeV)		First-excited state (meV)		Second-excited state (meV)		
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Pressure
CH_3NO_2	35	34	6.7	6.9	17.5	16.7	1 bar
CD_3NO_2	1.7	1.3	5.3	5.2	10.6	11.4	
CH_3NO_2	54	54	5.6	5.6	· · ·	15.8	4.8 kbar
CD_3NO_2	2.8	2.5	4.4	4.1	· · ·	10.7	

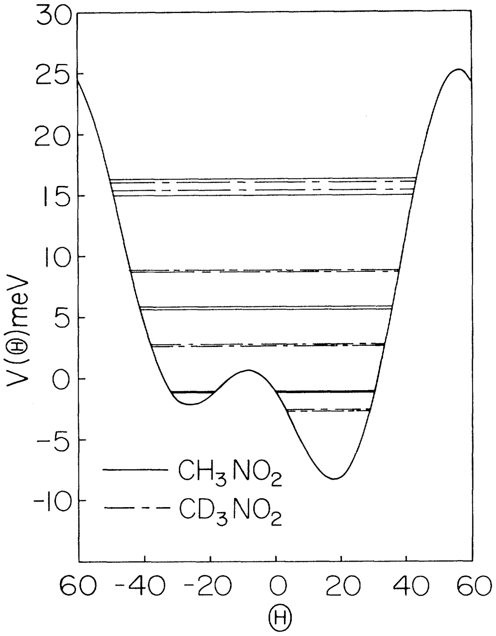

FIG. 3. The rotational potential as a function of methyl rotation with parameters corresponding to 1 bar (see text and Table I). Also presented are the calculated levels for CH_3NO_2 (solid lines) and CD_3NO_2 (dashed lines). The level splittings are only schematic for the lower levels; they are drawn to scale only for the highest level.

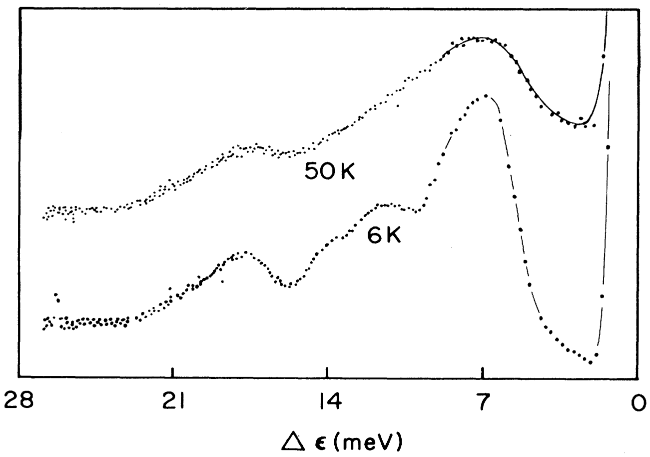

FIG. 4. An inelastic neutron-scattering spectrum from CH_3NO_2 at two temperatures. The first (7 meV) and second (17.5 meV) excited torsional levels are evident.

parameters V_3, V_6, and δ which reproduce the measured properties of the torsional levels are given in Table I for both pressures. Figure 3 displays the potential resulting from the parameters appropriate to the 1-bar measurements along with the levels for both isotopic species. The agreement between the calculated and observed quantities is very satisfactory. Note that this potential predicts several bound torsional levels for both species. Inspection of the spectrum previously obtained for CD_3NO_2 reveals a peak centered at 10.6 meV, which we now assign to the second torsional level in agreement with the results of the calculation. As further confirmation of the predictions of the potential, an inelastic neutron-scattering spectrum, extending to 26 meV, from CH_3NO_2 was obtained at two temperatures, 4 and 50 K, with the time-of-flight spectrometer (IN4) at Institut Laue-Langevin and is presented in Fig. 4. In addition to the 7-meV peak which contains the first torsional level, there is a peak at 17.5 meV which is in reasonable agreement with the calculated value of 16.7 meV. The temperature dependence, viz., a dramatic broadening at 50 K, further supports this assignment.

In an attempt to investigate the source of the various terms in the above potential, we have used a simple Lennard-Jones pairwise potential $V(r)=E[(r_1/r)^{12}-(r_2/r)^6]$ to describe the interaction between the methyl hydrogens and their neighboring oxygen atoms. The rotational potential is obtained by calculation of the total interaction potential as a function of methyl-group orientation within the approximation that the neighboring oxygen atoms are rigid as a function of methyl orientation. Values of $E=283$ meV, $r_1=2.19$ Å, and $r_2=2.17$ Å produce a potential which is in qualitative agreement with that presented in Fig. 3. These calculations reveal that the source of the V_6 term is the repulsive part of the pair potential (if r_0 is adjusted so that no repulsive interaction contributes, there is no V_6 feature present), and that the phase angle δ is due to the nonsymmetric distribution of oxygen atoms *vis-à-vis* the equilibrium orientation of the methyl groups. Scaling the lattice constants to simulate pressure[10] produces an increase of V_6 with respect to V_3 in agreement with the pressure dependence of the hindering potential deduced from our experimental results.

The work described here provides a thoroughly characterized low-barrier rotational potential for a molecule in the solid state, as well as an understanding of the reason for the anomalous behavior of this potential with pressure.

We make a final comment concerning the activation energy observed for thermally activated hopping in CH_3NO_2 as measured by quasielastic neutron scattering.[1] The value of the activation energy, ~10 meV, is substantially smaller than the observed bound state at 17.5 meV. It is possible that one must invoke one or more mechanisms such as enhanced hopping due to interactions with phonons, band tunneling through thermally broadened excited states, or substantial change of the barrier with temperature. In any case, for systems with very low barriers, the simple relation between activation energy and single-particle potential derived from 4.2-K data seems not to be straightforward.[11]

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