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## Nearly free quantum rotations of ammonia groups in Ni–Ni–Bz(d<sub>6</sub>) Hofmann clathrate

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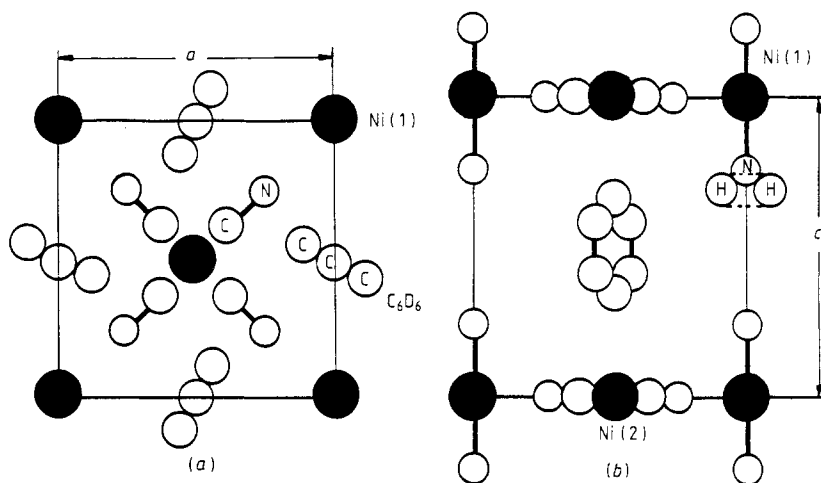
**Abstract.** In the inelastic neutron scattering spectra of Ni–Ni–Bz(d<sub>6</sub>) obtained at 1.8 K we observed transitions differing only slightly, but systematically, from those between uniaxial free rotator levels of ammonia groups. We interpreted the deviations as the influence of a weak hindering potential. A twelve-fold cosine potential with a barrier height  $V_{12}$  of  $16 \pm 3$  meV together with a rotational constant of  $0.71 \pm 0.02$  meV for NH<sub>3</sub> gave a satisfactory description of the experimental results. Spectra obtained at higher temperatures (up to 51 K) showed qualitatively the transition from quantum to classical behaviour.

### 1. Introduction

Hofmann-type clathrates are compounds with the general formula  $M(\text{NH}_3)_2M'(\text{CN})_4 \cdot 2G$ , usually abbreviated as  $M-M'-G$ . Here  $M$  is a six-coordinated and  $M'$  a four-coordinated divalent metal ion. Examples of  $M$  and  $M'$  respectively are Ni, Fe, Co, Cd and Ni, Pt, Pd. The guest molecule  $G$  is mostly an aromatic compound (e.g. benzene, aniline or pyrrole) [1]. New classes of analogous compounds are described in [2]. They are generated by substituting for example ethylenediamine for NH<sub>3</sub> ligand pairs and/or replacing the  $M'(\text{CN})_4$  complex by a tetrahedral Cd(CN)<sub>4</sub> or Hg(CN)<sub>4</sub> complex.

The crystal structure of the  $M-M'-G$ -type compounds is built up of stacked sheets containing  $M$ ,  $M'$  and the cyanide groups [3]. From the  $M$  ions, NH<sub>3</sub> groups are protruding at both sides of these planes in a *trans* configuration. It is between these ammonia groups and the adjacent layers where the guest molecules are caged. This arrangement gives Hofmann-type clathrates partially the character of intercalation compounds.

The first example prepared of this type is the 'Hofmann compound' Ni–Ni–Bz containing benzene guest molecules [4]. It has a tetragonal crystal lattice with the space group  $P4/m$  and one formula in the unit cell [3]. The benzene rings are oriented vertically to the metal ion layers (figure 1). The motions of host lattices and guest molecules have been studied with Raman [5], IR [1, 6] and NMR [7, 8] spectroscopy for  $M-M'-Bz$  and other Hofmann-type clathrates. The magnetic moment per Ni ion has been determined



**Figure 1.** Projections of the Hofmann clathrate unit cell. Only one of the ammonia groups and one of the benzene guest molecules are shown in (b).

in [9], and antiferromagnetic ordering of the  $M'$  ions has been found in measurements of susceptibility and specific heat (Néel temperature, 2.39 K; Weiss temperature,  $-2.7$  K) [10, 11]. DSC measurements [12] showed that in Ni–Ni–Bz, at about 370 K, liberation of benzene and, at about 470 K, liberation of ammonia from the residual host lattice takes place. More references can be found in [2] and in [13], where also some technical applications of benzene enclathration are mentioned.

In [14] a constant proton resonance line width has been found for Cd–Ni–Bz at temperatures between 80 and 420 K; therefore rotational tunnelling motion of  $\text{NH}_3$  groups about their threefold axis (aligned with the  $c$  axis of the lattice) was assumed in [14]. The authors suggest that corresponding results for Ni–Ni–Bz( $d_6$ ) reported in [8] have to be interpreted in the same way. Notable changes in the IR [1] and Raman [5] spectra have been observed in the ammonia bands during gradual removal of guest molecules. From the differences in the behaviour of particular  $\text{NH}_3$  modes it is concluded that the interaction between the ammonia groups of adjacent layers can be neglected and that only weak interactions exist with the remaining lattice. Furthermore large IR linewidths for antisymmetric vibrations compared with those of symmetric vibrations are explained by almost free internal rotations of the  $\text{NH}_3$  groups.

In this paper a neutron scattering study is presented of the ammonia motions in the host lattice of Ni–Ni–Bz. This technique has been used for many systems to investigate rotational tunnelling of molecular groups (see, e.g., [15]). We have searched for inelastic lines in the incoherent neutron energy loss spectra at low temperatures. This provides a more direct way to identify the nature of the ammonia rotations in Ni–Ni–Bz and allows us to gain additional information about the hindering potential.

## 2. Experiments and results

Powder samples were prepared according to [4]; to avoid loss of  $\text{C}_6\text{D}_6$ , they were not dried, kept under vacuum or ground [1]. Samples containing different ammonia species

(NH<sub>3</sub>, NDH<sub>2</sub>, ND<sub>2</sub>H and ND<sub>3</sub>) were obtained using for the reaction about three quarters NH<sub>3</sub> and one quarter ND<sub>3</sub>. X-ray diffraction and IR spectra served as a check for the specimens. Additional IR lines found for the deuterated samples could be assigned using the results published in [1, 6, 16], confirming the presence of the different ammonia species. A precise determination of the fractions for the different degrees of deuteration (e.g. using NMR) has not been carried out. For the neutron measurements the samples were sealed under a He atmosphere into flat aluminium containers of 0.8 mm thickness. Their transmission for neutrons of wavelength 5 Å was about 91%.

A first series of exploratory measurements were carried out on the TOF spectrometer at the BR2 reactor in Mol, with an energy resolution of 0.25 meV for the incoming wavelength of 4.16 Å. The spectra obtained at different temperatures (4.4, 21, 31 and 52 K) for a non-deuterated specimen are shown in figure 2. At 4.4 K, several clearly separated inelastic lines at about ±0.7, 1.4 and 2.1 meV are visible. With increasing temperature they become broader and not well resolved. Going from 4.4 to 22 K, one can find a small broadening and a shift to smaller energy transfers in the positions of the first peaks, but for the highest *T*-values this trend cannot be verified using these data, nor can the existence of a quasi-elastic broadening of the elastic peak be checked. For the deuterated specimen, two additional peaks appeared at energy transfers lower than 0.7 meV but are not well resolved.

A second set of experiments was carried out on the TOF spectrometer MIBEMOL at the Orphée reactor in Saclay with incoming neutron wavelengths between 2.3 and 7.0 Å and a sample temperature of 1.8 ± 0.1 K for all runs. The spectra, corresponding to scattering angles ranging from 86° to 141°, were summed. For the non-deuterated specimen in the energy loss parts of the spectra in total 13 inelastic lines could be found corresponding to energy transfers ranging from 0.7 to 6.5 meV.

Figure 3 shows examples of peaks; additional data are given in table 1 (most transitions appeared in more than one spectrum).

For the deuterated sample the spectrum obtained with an incoming wavelength of 7 Å contains three well defined peaks at 0.44, 0.54 and 0.72 meV (figure 4). For 5 Å, three additional peaks corresponding to transitions up to 2.2 meV appear.

The third column of table 1 gives an overview over the inelastic lines used in the analysis. The peak positions have been determined by least-squares fits with a Gaussian and a linear background for each peak individually.

### 3. Discussion

#### 3.1. Non-deuterated species

In NMR, IR and Raman studies [1, 11, 14] it has been suggested that the ammonia groups (being all equivalent) can be regarded as weakly hindered uniaxial quantum rotators. The corresponding energy level scheme can be calculated easily (see, for instance, [17, 18]), if the dependence of the hindering potential  $V(\theta)$  from the orientation  $\theta$  is approximated by

$$V(\theta) = \frac{1}{2} \sum_n V_n \cos[n(\theta + \theta_{n0})] \quad n = 1, 2, 3 \dots \quad (1)$$

with  $V_n$  and  $\theta_{n0}$  being the height and the phase shift of the  $n$ -fold symmetric contribution to the barrier. This approach assumes that no coupling exists of the internal rotation

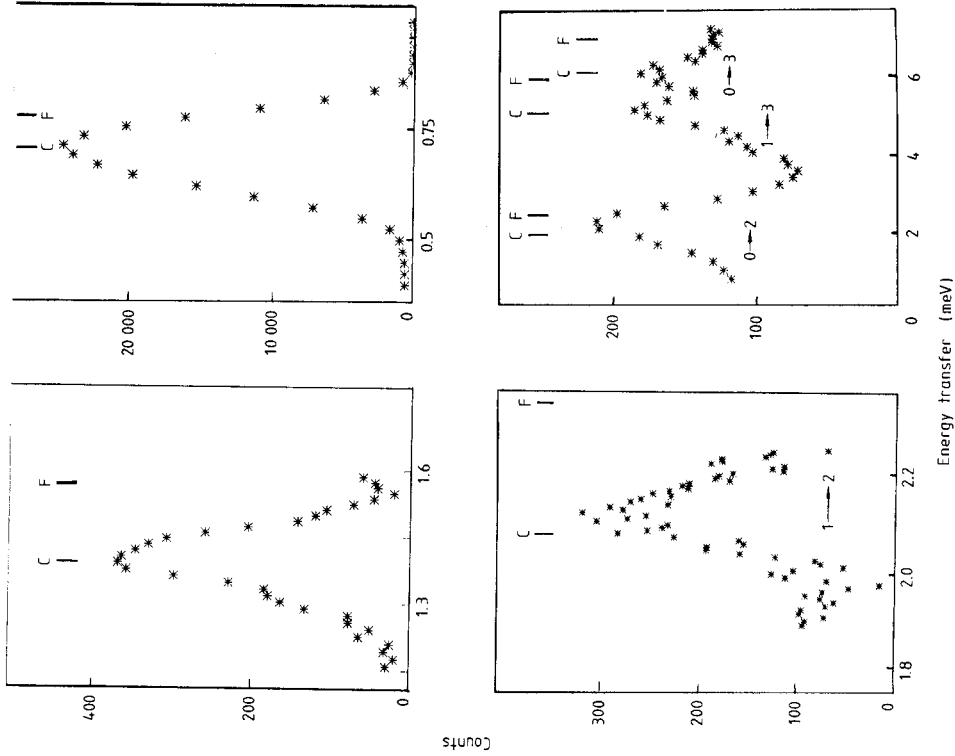


Figure 3. Examples of peaks in inelastic neutron scattering spectra of Ni-Ni-Bz(d<sub>6</sub>) at 1.8 K, containing NH<sub>3</sub> only; C, position calculated with the model potential; F, position corresponding to freely rotating NH<sub>3</sub> groups.

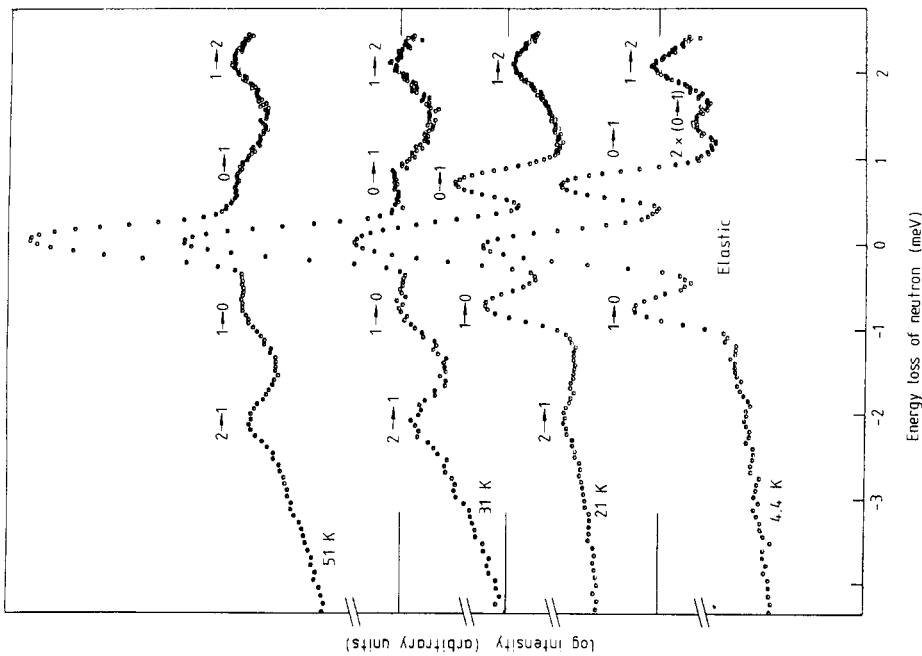


Figure 2. Semilogarithmic plot of neutron spectra obtained with Ni-Ni-Bz(d<sub>6</sub>) at different temperatures. The highest peaks correspond to elastic scattering; for the inelastic lines the corresponding transitions of NH<sub>3</sub> rotators are indicated.

**Table 1.** Transitions identified in the neutron spectra: *i*, initial level; *f*, final level; *E*(calc), level distance calculated with *V*<sub>12</sub> and *B* fitted to all levels; *E*(exp), peak position; *E*(free) – *E*(exp), deviation from free rotator level; HWHM, half-width at half-maximum.

<i>i</i> → <i>f</i>	<i>E</i> (calc) (meV)	<i>E</i> (exp) (meV)	<i>E</i> (free) – <i>E</i> (exp) (meV)	HWHM (meV)
NH <sub>3</sub>				
0 → 1	0.70	0.68	0.10	0.07
0 → 1	0.70	0.72	0.06	0.12
0 → 1	0.70	0.72	0.06	0.02
0 → 1	0.70	0.68	0.10	0.12
2 × (0 → 1)	1.40	1.36	0.20	0.06
2 × (0 → 1)	1.40	1.43	0.13	0.10
2 × (0 → 1)	1.40	1.39	0.17	0.10
2 × (0 → 1)	1.40	1.45	0.11	0.06
1 → 2	2.09	2.02	0.32	0.05
1 → 2	2.09	2.12	0.22	0.08
0 → 2	2.79	2.84	0.28	0.18
0 → 2	2.79	2.75	0.37	0.25
0 → 2	2.79	3.25	–0.13	0.62
0 → 2	2.79	2.64	0.58	0.86
1 → 3	5.57	5.50	0.74	0.50
0 → 3	6.29	6.50	0.52	0.47
0 → 3	6.29	6.33	0.69	0.67
NDH <sub>2</sub>				
0 → 1	0.53	0.54	0.05	0.02
0 → 1	0.53	0.60	–0.01	0.08
ND <sub>2</sub> H				
0 → 1	0.42	0.44	0.03	0.02
0 → 1	0.42	0.44	0.03	0.08
0 → 1	0.42	0.46	0.01	0.13

with other modes of the lattice or the rotator itself. In the case of Ni–Ni–Bz restrictions imposed by molecular and site symmetry (threefold and fourfold respectively) lead to

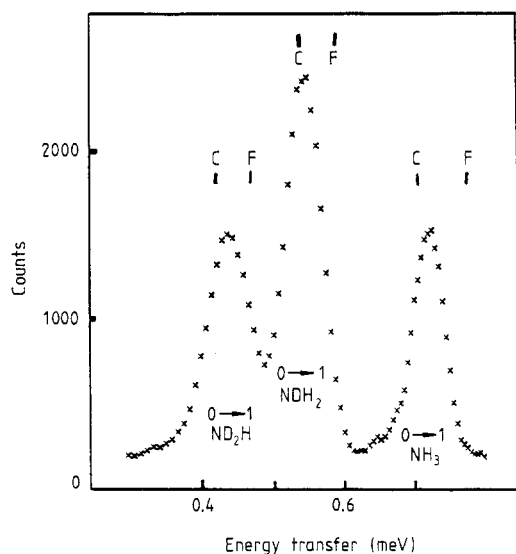
$$V(\theta) = \frac{1}{2} \sum_n V_n \cos[n(\theta + \theta_{n0})] \quad n = 12, 24, 36 \dots \quad (2)$$

This is valid for the non-deuterated and the fully deuterated ammonia groups having three-fold symmetry; for the partially deuterated groups the situation is more complicated (see section 3.2). From the Schrödinger equation

$$[-B d^2/d\theta^2 + V(\theta)]\Psi = E\Psi \quad (3)$$

(with  $B = \hbar^2/2I$ , where *I* is the moment of inertia of ammonia with the C<sub>3v</sub> rotation axis) the energy levels are then obtained as a function of *V<sub>n</sub>*. In this study, only the first term in the expansion equation (2) was used.

Scanning the *V*<sub>12</sub>-parameter in the range  $0 < V_{12} < 300$  meV with the *B*-value for a free ammonia molecule [19], only one single region could be found where the calculated level distances nearly coincided with peak positions found in the neutron spectra. This



**Figure 4.** Examples of peaks in inelastic neutron scattering spectra of Ni-Ni-Bz(d<sub>6</sub>) at 1.8 K, containing differently deuterated ammonia species: C, position calculated with the model potential; F, approximate position corresponding to freely rotating ammonia groups.

led to a unique assignment, which was used for a fit to determine the best values of  $V_{12}$  and  $B$  as

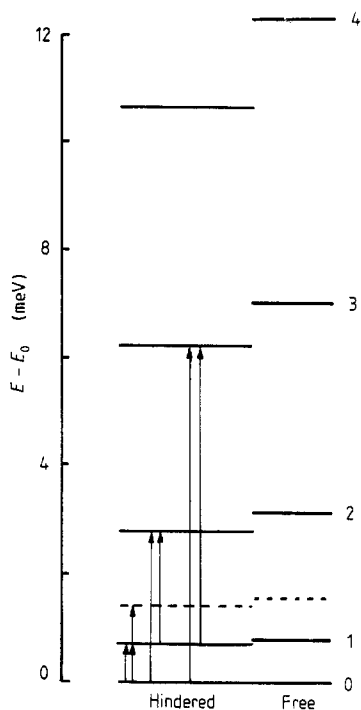
$$V_{12} = 16 \pm 3 \text{ meV} \quad B = 0.71 \pm 0.02 \text{ meV}.$$

In this fit, 22 peak positions were used (including data obtained with pure NH<sub>3</sub> and with partially deuterated samples).

One small peak (at 1.4 meV) was assigned to neutrons having caused twice a  $0 \rightarrow 1$  transition. This seems reasonable, since this peak is much less intense than that of the  $0 \rightarrow 1$  transition and since it vanishes rapidly with increasing temperature (see figure 2). The  $0 \rightarrow 3$  level distance was the highest included in the analysis. Indications of intensity at energy transfers higher than 6.5 meV were visible in some spectra, but no attempt was made to analyse them, since in these regions the TOF method causes the signal-to-noise ratio to deteriorate. All remaining peaks could be assigned, and all transitions up to  $0 \rightarrow 3$  could be found in the spectra. The agreement between calculated transition energies and peak positions is satisfying: the deviations are, with one exception, less than the HWHM of the instrumental resolution, in most cases even less than  $\frac{1}{4}$  (see figures 3 and 4). This gives a clear confirmation of the twelve-fold single-particle potential model for the non-deuterated species. Admixture of lower symmetry terms ( $V_3$ ,  $V_6$ ,  $V_9$  and combinations) produced fits of lesser quality (the physical reason for such terms could be a coupling to vibrational modes of the crystal lattice [20]). The calculated level schemes for free groups and for hindered NH<sub>3</sub> groups are shown in figure 5, together with the six distinct transitions identified in the neutron spectra. Transitions  $i \rightarrow f$  with  $i > 1$  could not be observed since at  $T = 1.8$  K the occupation is too low for the initial levels.

From the IR results derived in [1] an upper limit of about 52 meV for the rotational barrier height and of about 4 meV for the first rotational level; this is consistent with our data derived from neutron results.

The value of 16 meV for the hindering potential suggests that van der Waals interactions should be assumed between hydrogen atoms of NH<sub>3</sub> and of benzene guest



**Figure 5.** Calculated rotational levels of NH<sub>3</sub> groups in a twelve-fold cosine potential ( $V_{12} = 16$  meV) with  $B = 0.71$  meV. The arrows indicate transitions found in the inelastic neutron spectra. For comparison the levels of the corresponding free rotator are indicated also.

molecules but, considering the distances (greater than  $2.8 \text{ \AA}$ ) and the van der Waals radius of H ( $1.2 \text{ \AA}$ ), this seems less plausible than the conclusion that a 'weak' H bond exists between the ammonia and the  $\pi$  electrons of the benzene molecules [1].

Figure 2, showing results of preliminary measurements, gives a qualitative picture of the temperature dependence of the inelastic lines. Their increasing widths reflect the transition from the quantum mechanical regime to the classical regime, with increasing statistical fluctuations of the hindering potential due to lattice vibrations. No clear trend in the peak positions could be found.

### 3.2. Partially deuterated species (NDH<sub>2</sub> and ND<sub>2</sub>H)

The deuterated specimen contained different species of partially deuterated ammonia groups, enabling simultaneous measurements of the corresponding transitions. Equations (2) and (3) are, however, not adequate for the 'mixed' cases NDH<sub>2</sub> and ND<sub>2</sub>H, since the  $C_{3v}$  symmetry is lost. In [21] such a case has been treated using an effective hindering potential containing, in addition to the purely rotational part ( $V_3$  and  $V_6$ ), terms which approximate the coupling between rotation and vibrational stretching modes of the rotating groups. Some simplifying assumptions reduced the number of additional parameters to four. Combining optical, calorimetric and neutron data, in [21] a consistent set of these parameters could be derived giving a detailed description of the rotational barrier.

This approach was not possible in the case of Hofmann clathrates, since on the one hand the number of parameters would have been too large (up to  $V_{12}$  instead of  $V_6$ ), and on the other hand less experimental information was available (no specific heat, no



Raman data and no first torsional frequency). Instead an estimation of the first excited levels was used for the fit, just taking into account the changed moment of inertia for the partially deuterated groups. Even for this rough approximation the agreement is relatively good. Peaks observed at 0.72 and 1.39 meV correspond to  $0 \rightarrow 1$  and  $2 \times (0 \rightarrow 1)$  transitions for  $\text{NH}_3$ , and those at 0.44 and 0.54 meV to  $0 \rightarrow 1$  for  $\text{ND}_2\text{H}$  and  $\text{NDH}_2$ . The first  $\text{ND}_3$  peak would be at 0.27 meV, but it is invisible because of the small incoherent scattering cross section of D and because of the small number of  $\text{ND}_3$  groups present. Some peaks between 1.0 and 1.5 meV belong very probably to  $2 \times (0 \rightarrow 1)$  transitions, combining different species. Their assignment is uncertain, and they were not used in the analysis. Higher transitions were not calculated, since the uncertainty would be too high. In table 1, only peaks are included which have been used for the fit.

### 3.3. Significance of deviations from free rotator levels

The fourth column in table 1 compares the transition energies derived from neutron data with those calculated for freely rotating undistorted ammonia groups (for deuterated species approximately). With two exceptions the free-rotator values are systematically the higher ones. The relative deviations are about 10%; they are significant, as can be seen from the resolution values given in the fifth column, and from the positions F included in figures 3 and 4. These deviations are ascribed partially to the influence of the hindering and partially to a flattening of the ammonia groups (a fit of  $V_{12}$  alone resulted in  $V_{12} = 50$  meV). The situation is comparable with that of Cd-Ni-Bz, where also a rotational tunnelling of distorted  $\text{NH}_3$  was found [14].

## 4. Conclusions

From the analysis of the inelastic neutron scattering spectra we draw the following conclusions.

(i) The model of the ammonia groups as uniaxial quantum rotators, as suggested by IR studies, is confirmed.

(ii) The observed transitions for  $\text{NH}_3$ ,  $\text{NDH}_2$  and  $\text{ND}_2\text{H}$  are located systematically about 10% lower than those for the corresponding free rotators. This indicates the presence of a weak hindering and/or distortion.

(iii) Assuming a cosine potential of twelvefold symmetry ( $V_{12} = 16 \pm 3$  meV) and  $B = 0.71 \pm 0.02$  meV one can obtain a good description of the observed neutron scattering data. The  $V_{12}$ -value and the energy of the first excited states are consistent with limits derived from IR results. Lower-symmetry admixtures could not improve the model; this indicates that coupling with vibrational modes is not important.

(iv) Above about 21 K a transition from the quantum mechanical to the classical regime is observed.

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