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Quasielastic neutron scattering of $-NH_3$ and $-BH_3$ rotational dynamics in orthorhombic ammonia borane

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ABSTRACT

Energy barriers for rotation of $-NH_3$ and $-BH_3$ in the orthorhombic phase of ammonia borane, NH_3BH_3, were determined using quasielastic neutron scattering (QENS). QENS confirms the 3-site jump model of rotational diffusion and yields barrier heights of 23.6 ± 1.0 kJ/mol and 14.8 ± 0.4 kJ/mol for the borane and amine groups, respectively, which are comparable to barrier heights determined by recent ^2H and ^{15}N NMR studies suggesting no significant isotope effect on rotational motion in the orthorhombic phase of ammonia borane.

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1. Introduction

The donor–acceptor complex of ammonia with borane $H_3N \rightarrow BH_3$ is a molecular crystal at ambient temperature and pressure due to the polarized nature of the hydrogen bond in the molecular crystal shown in Fig. 1 [1,2]. The H attached to the more electronegative N is positively charged and the H attached to the more electropositive boron is negatively charged, leading to an extended network of NH···HB *dihydrogen bonding* interactions. The local fluctuations and large amplitude motions in ammonia borane (AB) that are affected by dihydrogen bonding have been studied by computational and experimental approaches. Calculations predict a cohesive energy of 76–96 kJ/mol or ca. 13–16 kJ/dihydrogen bond in AB [3,4]. The large cohesive energy is consistent with the negligible vapor pressure of AB at room temperature [5]. Dillen and Verhoeven [2], using *ab initio* SCF (MP2) methods, predicted that the torsional frequency in solid AB consists of two moieties, a lower energy 188 cm^{-1} frequency for NH_3 and a higher energy 328 cm^{-1} frequency for BH_3. The predicted split in the frequency for NH_3–BH_3 torsion is consistent with the observed rotational energy barriers in the low temperature orthorhombic phase of AB determined by ^2H and ^{15}N NMR T_1 relaxation methods, 9–14 kJ/mol for the amine end of the molecule and 24 kJ/mol for the borane end of the molecule [6–8]. Neutron scattering techniques are ideally suited to directly probe H in materials due to the large incoherent scattering cross-section of hydrogen and have been invaluable in providing direct insight into the local fluctuations and large amplitude motions in AB. Neutron diffraction was used to determine the average structure of AB at 200 K and confirmed the close proximity of the NH···HB hydrogen in neighboring molecules at 2.02 Å [1]. Local fluctuations or vibrational modes inactive in both IR and Raman spectra, i.e., a torsional mode at 334 cm^{-1} were observed using inelastic neutron scattering [9]. Quasielastic neutron scattering (QENS) [10] was used to confirm the 3-site jump model for amine and borane rotation in the orthorhombic phase of AB that could only be assumed in the NMR experiments. The sum of these spectroscopic and computational studies suggests that dihydrogen bonding plays a significant role in determining both the structure and the dynamics of AB. In more general terms, dihydrogen bonding may have a significant affect on materials to be used to store hydrogen for fuel-cell powered applications. We have noticed a trend of low temperature release of H_2 in materials composed of hydridic and protonic hydrogen [11–13]. This phenomenon has caught our attention and motivated our interest to gain more insight into how dihydrogen bonding interactions affect the structure and dynamics of AB [14–17]. This fundamental insight will also provide greater understanding of the critical pathways leading to the low temperature release of hydrogen release from AB in the solid state [18,14], ionic liquids [19], organic [20] or aqueous solutions [21,22].

Here we present results from a thorough QENS investigation of diffusive hydrogen motion in $NH_3{}^{11}BH_3$ and $ND_3{}^{11}BH_3$ to obtain (1) a direct measure of the rotational energy barriers of the protonated species and (2) a confirmation of the 3-site jump model for rotational motion. The amplitude of the energy barrier of rotation of

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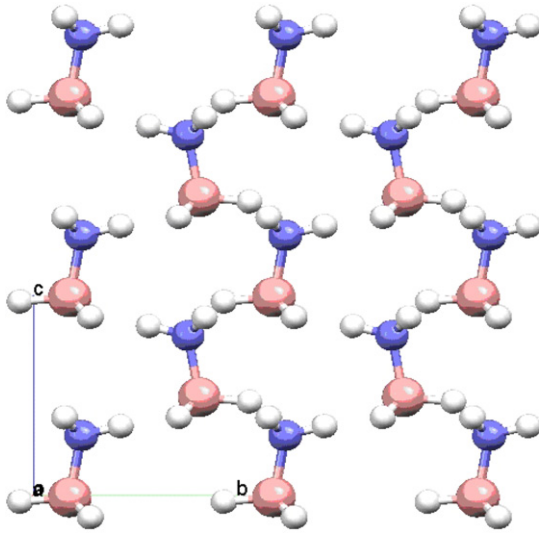

Fig. 1. Orthorombic structure of $^{11}BD_3ND_3$ from NPD. N atoms in blue, B atoms in red (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

BH_3 (23.6 ± 1.0 kJ/mol) and NH_3 (14.8 ± 0.4 kJ/mol) determined by QENS are compared to those determined for BD_3 and ND_3 determined by ^2H NMR studies.

2. Materials and methods

Synthesis of $NH_3{}^{11}BH_3$ followed the procedure of Schlesinger et al. [23]. ^{11}B enriched boric acid, purchased from Eagle Pricher, was refluxed in excess MeOH to yield trimethylborate [$B(OMe)_3$] and distilled from the reaction mixture. The [$B(OMe)_3$] was added to a stirred paste consisting of an excess NaH heated to 200 °C. Sodium borohydride ($Na^{11}BH_4$) was extracted from the resulting mixture with propyl amine. Any impurities were removed by dissolving $Na^{11}BH_4$ in diglyme. Pure $Na^{11}BH_4$ was retrieved by filteration *in vacuo*. Finally, equal molar ratios of $Na^{11}BH_4$ and NH_4-formate were dissolved in tetrahydrofurane (THF) and sonicated for 1 h. The reaction mixture was filtered and THF solvent was removed to yield $NH_3{}^{11}BH_3$. Exchange of deuterium for hydrogen on the amine end of ammonia borane was accomplished by repeatedly dissolving $NH_3{}^{11}BH_3$ in an excess of D_2O.

The high flux backscattering spectrometer [24] (HFBS) at the NIST Center for Neutron Research (NCNR) was used to study $ND_3{}^{11}BH_3$. The sample was loaded into annular aluminum cells in a He atmosphere and cooled in a closed cycle refrigerator. The reorientational diffusive motions of the borane end of the molecule were measured using a $ND_3{}^{11}BH_3$ sample at 5, 140, 160, 170, 180, and 200 K with a dynamic energy range of ±17 μeV about the elastic line. The total reorientational diffusive motions of the $NH_3{}^{11}BH_3$ sample were measured at 140, 160, 180, 200, and 220 K with a dynamic energy range of ±35 μeV about the elastic line. Dynamic data at momentum transfer values, or Q values, ranging from 0.25 to 1.75 $Å^{-1}$. The amine contribution was then isolated and analyzed by accounting for the borane contribution from the data analysis of the $ND_3{}^{11}BH_3$ sample. Data were reduced and fitted using DAVE software available at the NCNR [25].

2.1. Preliminary QENS analysis

The reorientational diffusive motions of the borane end of the molecule were analyzed first by investigating $ND_3{}^{11}BH_3$. At 5 K, there were no diffusive motions present on the time-scale of the HFBS instrument, and these data were used to define the instrument resolution function. The data at the other temperatures were analyzed as follows. First the data for all 16 detectors were analyzed using a model consisting of a delta function and a single Lorentzian. This simple model is sufficient to determine whether or not diffusive motions on the time-scale of the instrument are present, and in the case of two or threefold reorientations, the model is capable of exactly modeling the motion. Next, using the results of the simple model fit above, a FWHM for the Lorentzian for all detectors was determined by using a least-squares technique to fit a constant value to the results of the model fits for all detectors used within the analysis. Lastly, using the constant FWHM determined above, a threefold jump rotation model was fit to the data using H–H jump distances determined from neutron powder diffraction data [26].

3. Results and discussion

The reorientational diffusive motions of the hydrogen associated with the BH_3 in AB were measured on a $ND_3{}^{11}BH_3$ sample, which effectively masks the contribution due to the reorientational diffusive motions of the NH_3 end of the molecule. Analysis of the QENS data using a delta function and single Lorentzian confirmed the appropriateness of a threefold jump rotation model [23]. The incoherent dynamical scattering function, $S(Q,\omega)$ corresponding to a threefold jump reorientation is represented as

$$S_i(Q,\omega) = \frac{1}{3}\left[1 + 2j_0(Qr\sqrt{3})\right]\delta(\hbar\omega) + \frac{2}{3}\left[1 - j_0(Qr\sqrt{3})\right]\frac{1}{\pi} \times \frac{(3\hbar/2\tau)}{(3\hbar/2\tau)^2 + (\hbar\omega)^2}$$

where Q is the magnitude of the momentum transfer for the scattering interaction, $\sqrt{3}\,r$ is the H–H jump distance determined from neutron powder diffraction data [26], τ is the residence time between jumps, and j_0 is the zeroth order spherical Bessel function [27]. This equation was used to determine the residence time at each temperature. The residence times were then fit to an Arrhenius function of the form, $\tau = \tau_\infty \exp(E_a/kT)$ where E_a is the activation energy for the diffusive process, k is Boltzmann's constant, and T is temperature in Kelvin. The activation energy and τ_∞ determined from the fit were 23.6 ± 1.0 kJ/mol and 8.4×10^{-5} ps, respectively. The fit of the threefold jump model at 190 K is shown in Fig. 2. The agreement with the experimental data as a function of Q is excellent, illustrating that the reorientational diffusive motion of

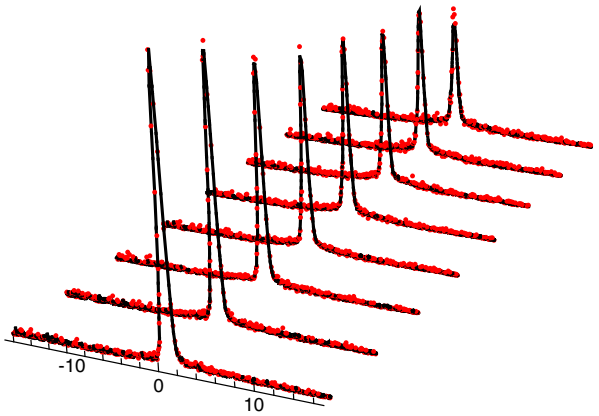

Fig. 2. Fit of the threefold jump rotation model to the $ND_3{}^{11}BH_3$ QENS data at 190 K for HFBS detectors ranging from $Q = 0.8707$ $Å^{-1}$ to $Q = 1.5980$ $Å^{-1}$ (plots are layered from low to high Q). The data have been renormalized such that the area under each curve is 1.0, and the energy transfer axis is in units of μeV.

the borane end of the molecule is accurately represented by the threefold jump rotation model. Following a similar procedure, the QENS data for $NH_3{}^{11}BH_3$ were analyzed. The contribution from the BH_3 end of the molecule was calculated using the results of the $ND_3{}^{11}BH_3$ QENS analysis. Fitting a threefold jump rotation model to the NH_3 data, resulted in an activation energy of 14.8 ± 0.4 kJ/mol and a τ_∞ of 5.2×10^{-3} ps.

Our earlier analysis of the $NH_3{}^{11}BH_3$ data resulted in lower energy barrier for NH_3 rotations, namely 7.98 kJ/mol. The amine dynamics measured on the $NH_3{}^{11}BH_3$ sample above 170 K included contributions from the borane group that were not expected to contribute to quasielastic scattering based on the available NMR data at the time [7]. However, the measurements reported here with $ND_3{}^{11}BH_3$ sample has allowed the borane dynamics to be isolated and its contribution subsequently removed from the total dynamics measured on the $NH_3{}^{11}BH_3$ sample. The corrected energy barriers for the NH_3 and independently determined barriers for BH_3 rotations are compared to determinations by ^{1}H, ^{2}H, and ^{15}N NMR methods in Table 1.

An energy barrier of 23.6 kJ/mol measured for borane rotation in $ND_3{}^{11}BH_3$ as determined by QENS measurement is in excellent agreement with the values determined by ^{1}H NMR T_1 analysis on NH_3BH_3 [7] as well as the ^{2}H NMR T_1 and lineshape analysis on NH_3BD_3.[6] Similarly, the energy barrier of 14.8 kJ/mol value for amine rotation in $NH_3{}^{11}BH_3$ determined by QENS agrees well with values determined on BH_3ND_3 using ^{2}H NMR T_1 [4] and ^{15}N NMR T_1 analysis [8]. However, it is in poorer agreement with the value of 9.6 kJ/mol measured by Reynhardt and Hoon whose low value may result from either difficulty in spectrally isolating the amine and borane hydrogen dynamics without the benefit of deuteration or approaching the amine quantum tunneling regime [7].

An Arrhenius plot, shown in Fig. 3, comparing the calculated experimental energy barrier determinations with the stated errors in E_a reveals that if spectral isolation is used, the experimental determinations are equivalent within experimental error regardless of whether QENS or NMR is used to measure the dynamics.

Table 1
Comparison of rotational energy barriers and τ_∞ determined by QENS and NMR

	E_a (kJ/mol)	τ_∞ (s)	Sample/Ref.
Borane			
QENS	23.6 ± 1.0	8.4×10^{-17}	ND_3BH_3/TW
^{1}H NMR T_1	25.0 ± 0.4	6.7×10^{-18}	NH_3BH_3/[7]
^{2}H NMR T_1	26.4 ± 1.4	1.2×10^{-17}	NH_3BD_3/[6]
^{2}H NMR LS	24.3 ± 1.9	4.3×10^{-17}	NH_3BD_3/[6]
Amine			
QENS	14.8 ± 0.4	5.2×10^{-15}	NH_3BH_3/TW
^{15}N NMR T_1	14.5 ± 0.4	4.8×10^{-15}	$^{15}NH_3BH_3$/[8]
^{1}H NMR T_1	9.6 ± 0.4	9.5×10^{-14}	NH_3BH_3/[7]
^{2}H NMR T_1	13.7 ± 0.9	5.7×10^{-15}	ND_3BH_3/[6]

TW = this work and LS = lineshape.

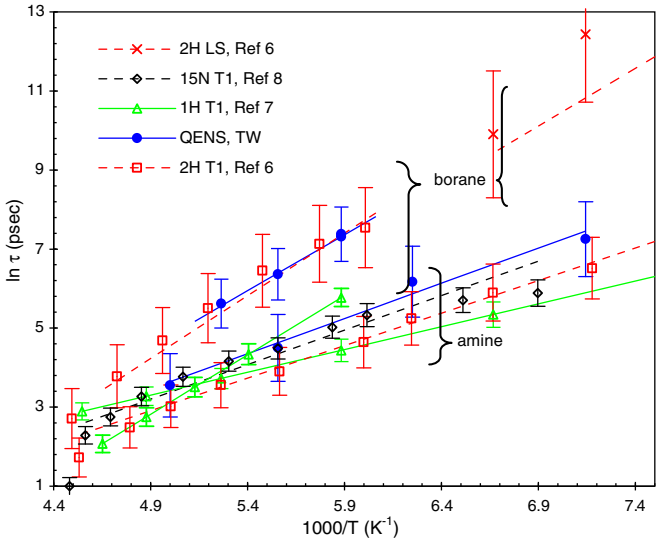

Fig. 3. Arrhenius plot of the calculated rotational energy barriers and experimental errors determined by different techniques for the borane and amine groups. TW = this work, LS = lineshape.

4. Conclusion

The results reported here conclusively demonstrate that the threefold jump model accurately represents the diffusive motion of the amine and borane groups and that spectral isolation of the amine and borane groups is necessary for the correct determination of their rotational energy barriers. Future work is planned to determine the dynamics of motion of hydrogen in the tetragonal phase of AB as well as the dynamics of AB in mesoporous scaffolds [28].

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References

[1] T. Klooster, T.F. Koetzle, Per E.M. Siegbahn, T.B. Richardson, R.H. Crabtree, J. Am. Chem. Soc. 121 (1999) 6337.
[2] J. Dillen, P. Verhoeven, J. Phys. Chem. 107 (2003) 2570.
[3] C.A. Morrison, M.M. Siddick, Angew. Chem. Int. Ed. 43 (2004) 4780.
[4] M.H. Matus, K. Anderson, D.M. Camaioni, S.T. Autrey, D.A. Dixon, J. Phys. Chem. A 111 (2007) 4411.
[5] E.R. Alton, R.D. Brown, J.C. Carter, R.C. Taylor, J. Am. Chem. Soc. 81 (1959) 3550.
[6] G.H. Penner, Y.C. Phillis Chang, J. Hutzal, Inorg. Chem. 38 (1999) 2868.
[7] E.C. Reynhardt, C.F. Hoon, J. Phys. C: Solid State Phys. 16 (1983) 6137.
[8] O. Gunaydin-Sen, R. Achey, N.S. Dalal, A. Stowe, T. Autrey, J. Phys. Chem. B 111 (2007) 677.
[9] D.G. Allis, M.E. Kosmowski, B.S. Hudson, J Am. Chem. Soc. 126 (2004) 7756.
[10] C.M. Brown et al., Physica B 385 (2006) 266.
[11] P. Chen, Z. XiongXiong, G. Wu, Y. Liu, J. Hu, W. Luo, Scripta Mater. 56 (2007) 817.
[12] F.E. Pinkerton, G.P. Meisner, M.S. Meyer, M.P. Balogh, M.D. Kundrat, J. Phys. Chem. B. 109 (2005) 6.
[13] Z. Xiong, et al., Nat. Mater. (2008), doi:10.1038/nmat2081.
[14] A.C. Stowe, W.J. Shaw, J.C. Linehan, B. Schmid, T. Autrey, Phys. Chem. Chem. Phys. 9 (2007) 1831.
[15] N.J. Hess, V.M. Parvanov, M.E. Bowden, C. Mundy, S. Kathmann, G. Schenter, T. Autrey. J. Chem. Phys. 128 (2008) 034508.
[16] H. Cho et al., J. Phys. Chem. 112 (2008) 4277.
[17] V. Parvanov et al., J. Chem Soc., Dalton Trans., in press.
[18] G. Wolf, J. Baumann, F. Baitalow, F.P. Hoffmann, Thermochim. Acta 343 (2000) 19.
[19] M.E. Bluhm, M.G. Bradley, R. Butterick III, U. Kusari, L.G. Sneddon, J. Am. Chem. Soc. 128 (2006) 7748.
[20] J.S. Wang, R.A. Geanangel, Inorg. Chim. Acta 148 (1988) 185.
[21] J-M.J.-M. Yan, X-B.X.-B. Zhang, S. Han, H. Shioyama, Q. Xu, J. Power Sources 156 (2006) 190.
[22] M. Chandra, Q. Xu, Angew. Chem. Int. Ed. 120 (2008) 2319.

[23] H.I. Schlesinger, H.C. Brown, J.R. Gilbreath, J.J. Katz, J. Am. Chem. Soc. 75 (1953) 195.
[24] A. Meyer, R.M. Dimeo, P.M. Gehring, D.A. Neumann, Rev. Sci. Instrum. 74 (2003) 2759.
[25] The DAVE software package was used for elements of the data reduction and analysis. See <http://www.ncnr.nist.gov/dave>.
[26] N.J. Hess, G.K. Schenter, A. Stowe, L.L. Daemen, T. Proffen, T. Autrey, in preparation.
[27] M. Beé, Quasielastic Neutron Scatter – Principles and Applications in Solid State Chemistry, Biology, and Materials Science, Adam Hilger, Bristol, 1988.
[28] A. Gutowska, et al., Angew. Chem. Int. Ed. 44 (2005) 3578.