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High-Pressure Raman Spectroscopic Study of the Ammonia–Borane Complex. Evidence for the Dihydrogen Bond

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The Raman spectra of the ammonia–borane complex, NH_3BH_3, have been investigated as a function of pressure up to 40 kbar. Vibrational modes involving the NH_3 group show negative pressure dependences, supporting the existence of the dihydrogen bond, but the vibrations of the BH_3 group have a positive dependence. Two transitions were observed in the solid phase under pressure, in contrast to the temperature behavior, where a single transition occurs. Factor group splitting occurs for the degenerate vibrations, and this allows the correct assignment of the observed vibrations.

Introduction

There has been considerable interest in recent years in the concept of the “dihydrogen bond”, an analogue of the conventional hydrogen bond but one which involves the interaction between a positively charged (protonic) hydrogen and a hydrogen bonded to a less electronegative atom, a hydridic proton.[1,2] The major evidence for the dihydrogen bond is based on structural information and characterized by short distances between the two hydrogen atoms. For example, the structure of the low-temperature phase of the ammonia–borane complex, NH_3BH_3, has been re-examined by neutron diffraction[3] and the H···H distance of 2.02 Å is less than the sum of the van der Waals radii, 2.4 Å. This complex, as a well-known example of a dative bond, has been widely studied by a variety of experimental methods. The crystal structure[4] at room temperature is tetragonal, and a transition to an orthorhombic form occurs at 225 K. The molecular motions that occur in the solid phases have been investigated by NMR methods.[5,6] The vibrational spectra of NH_3BH_3 have been reported both for solution (in liquid ammonia) and as the isolated species in an argon matrix.[7,8]

It is well-known that the hydrogen stretching frequencies, X–H (X = O, N), show large shifts to lower wavenumbers upon the formation of a hydrogen bond,[9] and, by analogy with the normal hydrogen bond, it would be expected that a similar effect might occur upon formation of the dihydrogen bond. For example,[10] the vibrational frequency of the N–H stretch in the complex between 2-pyridone (as the proton donor) and trimethylamine–borane has been reported to shift by 155 cm^{-1}. Calculations of the vibrational frequencies for complexes where C–H acts as a proton donor and Li–H as the acceptor have been reported,[11] and the frequencies are to lower and higher energy, respectively.

The vibrational frequencies in a hydrogen-bonded system, X–H···Y, are strongly dependent on the X···Y distance,[9] and it is possible to reduce this distance by the application of high external pressures. Normally, vibrational frequencies increase with increasing pressure, but, in the case of a hydrogen bond, the frequency decreases until the hydrogen bond is symmetrical and then increases.[12,13] A comparison of the vibrational frequencies in the solid state with those of

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(1) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348.
(2) Custalcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963.
(3) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.
(4) Hoon, C. F.; Reynhardt, E. C. *J. Phys. C, Solid State Phys.* **1983**, *16*, 6129.
(5) Hoon, C. F.; Reynhardt, E. C. *J. Phys. C, Solid State Phys.* **1983**, *16*, 6137.
(6) Penner, G. H.; Chang, Y. C. P.; Hutzal, J. *Inorg. Chem.* **1999**, *38*, 2868.
(7) Taylor, R. C. *Adv. Chem. Ser.* **1964**, *42*, 59.
(8) Smith, J.; Seshadri, K. S.; White, D. *J. Mol. Spectrosc.* **1973**, *45*, 327.
(9) Pimentel, G. C.; McLellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960.
(10) Naresh Patwari, G.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2001**, *105*, 8642.
(11) Alkorta, I.; Elguero, J.; Mó, O.; Yáñez, M.; Del Bene, J. E. *J. Phys. Chem.* **2002**, *106*, 9325.
(12) Moon, S. H.; Drickhamer, H. G. *J. Chem. Phys.* **1974**, *61*, 48.
(13) Hamann, S. D.; Linton, M. *Austr. J. Chem.* **1975**, *28*, 2567.
(14) Markwell, R. D.; Butler, I. S. *Can. J. Chem.* **1995**, *73*, 1019.

10.1021/ic026275s CCC: $25.00

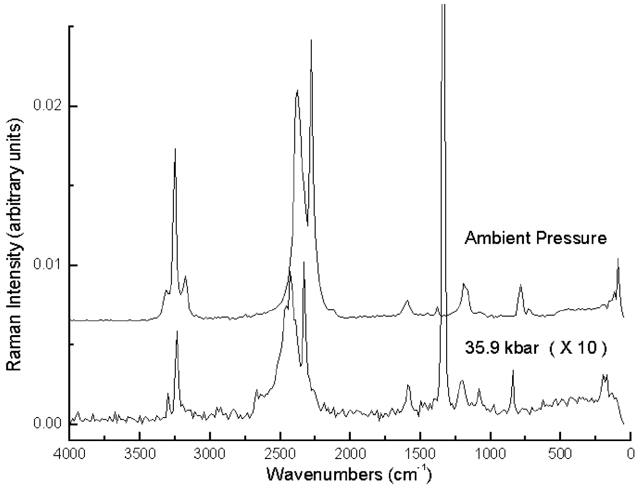

Figure 1. Raman spectra of the ammonia−borane complex at ambient pressure and at 35.9 kbar. The intense peak at 1300 cm^{-1} is due to the diamond.

Table 1. Vibrational Frequencies (cm^{-1}) and Their Pressure Dependences (cm^{-1} kbar^{-1})

frequency			pressure dependence		
matrix[a]	solid	assignment	0−4 kbar	4−13 kbar	14−40 kbar
3386	3315	ν_7	−3.45	−0.03	−0.44
3337	3251	ν_1	−1.58	−0.09	−0.4/−0.13[b]
2415	2374	ν_8	8.41	0.45	1.56/0.60[b]
2340	2332	ν_3	3.08	0.38	0.91
	2280		8.64	0.28	0.77
1186	1175	ν_{11}	2.01	0.21/0.15	0.62/0.01
1052	1026	ν_4	5.4	−0.09	0.30

[a] Reference 12. [b] Factor group splitting.

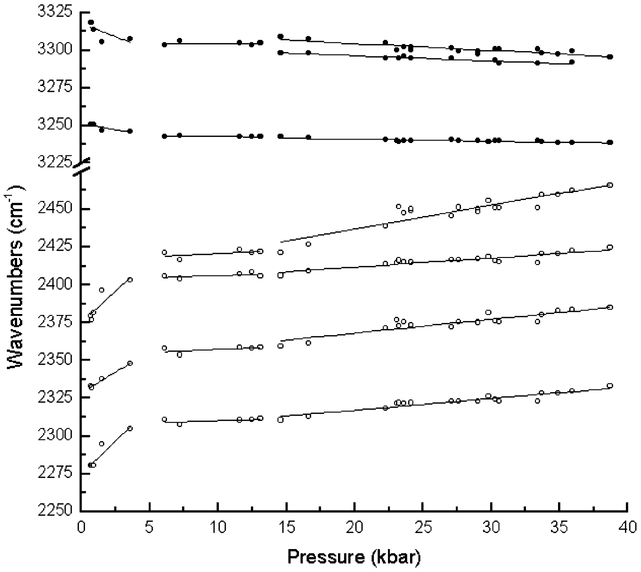

Figure 2. Pressure dependence of the N−H and B−H stretching frequencies in NH_3BH_3.

the matrix-isolated molecule, which would not be involved in a dihydrogen bond, would be useful. In this study, we report on the effect of pressure on the Raman spectra of the NH_3BH_3 complex as a method of confirming the existence of a dihydrogen bond.

Experimental Section

The ammonia−borane complex was purchased from Aldrich Chemicals and recrystallized from cold anhydrous diethyl ether. FT-Raman spectra were measured, using a Bruker IFS88 spectrometer with a Nd^{3+}:YAG laser (1064.1 nm) equipped with liquid nitrogen cooled detector, with a resolution of 2.6 cm^{-1}. The diamond anvil cell (High-Pressure Diamond Optics, Tucson, AZ) was mounted on the translation stage of a microscope attached to the spectrometer. The pressure was measured using the 1332.5 cm^{-1} vibration of the diamond itself.[14]

Results and Discussion

The Raman spectra at atmospheric pressure and at 35.9 kbar are shown in Figure 1. The dν/dP values of selected vibrations are given in Table 1.

The differences between the vibrational frequencies of the solid NH_3BH_3 (Raman) and those of the matrix-isolated compound (infrared)[8] show reductions in frequency of 74 and 92 cm^{-1} for ν_1 and ν_7 (the symmetric and antisymmetric N−H stretching modes, respectively) and of 38 and 8 cm^{-1} for ν_2 and ν_8, the corresponding vibrations of the BH_3 group. In the case of the ammonia−boron trifluoride complex, NH_3-BF_3, where a dihydrogen bond cannot occur, the vibrational spectra of the crystalline material and the matrix-isolated material (in nitrogen) have been reported.[15,16] The frequency of the symmetric N−H stretch decreases from 3309 to 3279 cm^{-1} and the antisymmetric N−H stretching frequency decreases from 3432 to 3343 cm^{-1} on going from the matrix to the crystalline environment. Thus there are significant differences in vibrational frequency in both the borane and boron trifluoride cases, and a shift in frequency to lower wavenumbers is not a sufficient indicator of the presence of the dihydrogen bond in NH_3BH_3.

The pressure dependences of the peaks arising from the N−H and B−H stretching modes are shown in Figure 2. The slopes of the N−H antisymmetric and symmetric stretching mode frequencies are negative, but they are positive for the corresponding B−H stretches.

A survey of structures exhibiting intermolecular dihydrogen bonds[3] showed that the N−H···H angles are more linear, in the range 150−170°, and the B−H···H angles more acute, between 95° and 115°. In the ammonia−borane complex, these angles are 106° and 156°, respectively. The extension of the N−H direction is directed, not at the (B)−H atom, but at the electron dense region of the B−H σ-bond,[17] and the pressure-induced decrease in distance increases the strength of the dihydrogen bond at the expense of the N−H bond. The (B)−H atom is not directly involved in the interaction, and so positive dν/dP values are observed for the B−H stretching frequencies. An alternative explanation of this negative pressure dependence follows from the proposal of Li and co-workers[18] that the dihydrogen bond involves donation of charge from the B−H σ-bond to the

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(15) Taylor, R. C.; Gabelnick, H. S.; Aida, K.; Amster, R. L. *Inorg. Chem.* **1969**, *8*, 605.

(16) Nxumalo, L. M.; Andrzejak, M.; Ford, T. A. *Vibr. Spectrosc.* **1996**, *12*, 221.

(17) Richardson, T. B.; de Gala, S.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875.

(18) Li, J.; Zhao, F.; Jing, F. *J. Chem. Phys.* **2002**, *116*, 25.

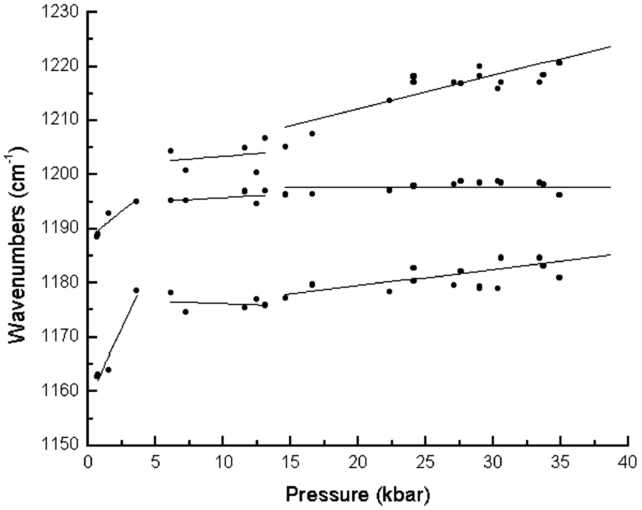

Figure 3. Pressure dependence of the frequencies in the BH_3 bending mode region.

N−H σ^* orbital. An increase in antibonding character would lower the bond strength and, therefore, the force constant of the stretching vibration. However, the loss of charge from the bonding orbital should also weaken the B−H bond, but the B−H stretching vibration increases with increasing pressure.

There are changes in the slopes, $d\nu/dP$, at 5 and 14 kbar indicating two solid−solid phase transitions, and factor group splitting occurs as all e modes split into two peaks. The assignment of the symmetric and antisymmetric bending modes of the BH_3 group has been the subject of disagreement. The original assignment by Taylor[7] placed the symmetric mode at higher frequency (1175 cm^{-1}) than the antisymmetric (1026 cm^{-1}), but this was reversed by Smith and co-workers[8] on the grounds that antisymmetric modes should be at higher frequency. Several theoretical studies[19−21] have not resolved the problem.

Figure 3 shows the BH_3 bending mode region, and the splitting of the peak at 1188 cm^{-1} in the highest pressure phase shows that this must be the e mode.

There was no evidence, up to the 40 kbar pressure reached in this study, of the decomposition of ammonia−borane and the formation of molecular hydrogen.

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(19) Brint, P.; Sangchakr, B.; Fowler, P. W. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 29.
(20) Vijay, A.; Sathayanarayana, D. N. *Chem. Phys.* **1995**, *198*, 345.
(21) Leboeuf, M.; Russo, N.; Salahub, D. R.; Toscano, M. *J. Chem. Phys.* **1995**, *103*, 7408.