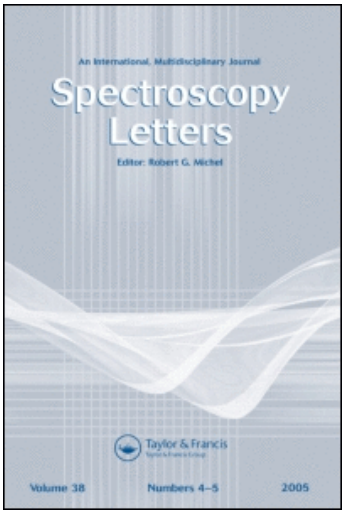

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Far Infrared Spectra of Ammonia-Boron Trifluoride: NH_3BF_3 and ND_3BF_3

A. Anderson[a]; B. A. Bobbie[a]
[a] Department of Physics, University of Waterloo, Waterloo, Ontario, Canada

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FAR INFRARED SPECTRA OF AMMONIA-BORON TRIFLUORIDE: NH_3BF_3 and ND_3BF_3

KEY WORDS: Infrared Absorption; Ammonia-Boron Trifluoride; Lewis Complex; Lattice Vibrations.

A. Anderson and B.A. Bobbie,
Department of Physics, University of Waterloo,
Waterloo, Ontario, N2L 3G1, Canada.

ABSTRACT: Spectra of polycrystalline samples of NH_3BF_3 and ND_3BF_3 at 300 K and 98 K have been recorded in the frequency range 20-400 cm^{-1}. Isotopic frequency ratios are used to interpret the observed features in terms of the known molecular and crystal structures.

INTRODUCTION

Ammonia-boron trifluoride is of considerable interest as a textbook example of a Lewis acid-base complex containing a boron-nitrogen dative bond and has been the subject of many recent spectroscopic and structural investigations. Discrepancies in the data from early experiments were soon found to be caused by water

contamination of the samples, resulting in the presence of impurities such as NH_4BF_4, which is also a white solid, and a consistent picture of the geometry and normal modes of the adduct molecule NH_3BF_3 began to emerge[1,2].

The structure of ammonia-boron trifluoride has been investigated by X-ray diffraction experiments on powder[1] and single crystal samples[3]. The molecule has C_{3v} symmetry with a bond between the boron and nitrogen atoms, with the NH_3 and BF_3 groups in the form of pyramids. A staggered rather than an eclipsed configuration of the fluorine and hydrogen atoms is considered more likely. Although the hydrogen atom positions were not directly determined, they were approximately located by plausible comparisons with related compounds and included in the final refinements[3]. Values of the principal bond lengths and angles are summarized below:

B-N 1.60 Å; B-F 1.38 Å; N-H 1.02 Å.

N-B-F 107°; F-B-F 111°; B-N-H 107°; H-N-H 111°.

The crystallographic unit cell is orthorhombic, space group Pbca (D_{2h}^{15}), and contains 8 molecules on general (C_1) sites. The smallest distances between neighbouring molecules are those between H and F atoms. There are several such contacts which are considerably smaller than the sum of the Van der Waals radii[4], (for example H....F = 2.10 Å, compared to 1.20 + 1.47 = 2.67 Å) and this is evidence for the presence of weak hydrogen bonding in the solid as well as the usual Van der Waals and other electrostatic interactions.

Of the recent spectroscopic investigations of NH_3BF_3,[2,5,6] that by Taylor et al.[2] appears to be the most comprehensive. By using samples enriched with boron -10 and nitrogen -15 isotopes as well as deuterium, these workers were able to observe and identify all vibrational modes except the torsion about the B-N bond, and presented a normal co-ordinate analysis to support their assignments. Our original interest in this compound was to investigate the differences between its vibrational spectrum and those of crystalline NH_3 [7] and BF_3 [8] which have recently been studied in this laboratory, particularly those resulting in the change in geometry in the BF_3 group from planar to pyramidal. When it became clear that our mid-infrared results were identical to those of Taylor et al.[2], the emphasis of our work shifted to the low frequency region, which has received very little attention from previous investigators. Attempts to obtain Raman spectra in the 20-400 cm^{-1} range were unsuccessful, but consistent infrared absorption spectra of NH_3BF_3 and ND_3BF_3 were recorded in this region and are reported in this letter. The results are correlated with the higher frequency data and with the known molecular and crystal structures in an attempt to obtain a more complete understanding of these systems.

EXPERIMENTAL TECHNIQUES

Powder samples of NH_3BF_3 and ND_3BF_3 were prepared by using a modification of the technique of Leane and Richards[9]. Ammonia gas (NH_3, 99.99% pure, from the Matheson Co.; ND_3, 98% isotopically

pure, from Merck, Sharp and Dohme) was slowly bubbled into a mixture of 25 mℓ boron trifluoride-ethyl ether complex (Matheson, Coleman, Bell) and 100 mℓ anhydrous ether (Baker) in a flask flushed by nitrogen gas. The temperature of the mixture was maintained at 15°C by a thermo-electric cooling unit, and the reaction was complete in about 90 minutes. Excess ether was decanted from the flask, and the remaining solid was pumped for 48 hours before being transferred under nitrogen to small vials. Nujol mull samples on polyethylene or sodium chloride substrates were prepared in a nitrogen-purged glove bag. For the far infrared spectra of samples at 98 K, a thin layer of powder was sandwiched between two polyethylene discs, which were then mounted in a conventional glass cryostat, cooled with liquid nitrogen. Temperatures were recorded with a copper-constantan thermocouple, and are estimated to be accurate to ±1 K.

Spectra in the region 300-4000 cm^{-1} were recorded on a Beckman IR 12 filter-grating spectrometer, purged with dry nitrogen gas. Far infrared spectra (20-400 cm^{-1}) were obtained by Fourier transformation of the output of a Michelson interferometer (RIIC-Beckman, FS 620), which was evacuated to minimize water vapour absorption. This instrument used a mercury-in-quartz lamp as source, Mylar film as beam divider, and a germanium bolometer operating at 4.2 K as detector. An on-line mini-computer (Data General, Nova 2) was used to transform the interferograms and to obtain transmission spectra, after ratioing against background intensities. The instrument was calibrated for frequency accuracy

and resolving power by recording the rotational spectrum of water vapour and comparing with standard values [10]. Frequencies of maximum absorption are estimated to be accurate to ±1 cm^{-1}, except for weak broad bands or shoulders (±2 cm^{-1}). A resolving power of 2.5 cm^{-1} (corresponding to a maximum mirror displacement of 2 mm) was used for these spectra.

RESULTS

Spectra recorded in the mid-infrared region are essentially the same as those obtained by Taylor et al.[2], and details will not be repeated here. They serve as a useful check on the purity of the samples. In particular, decomposition of NH_3BF_3 in the presence of moisture can be detected by monitoring the region near 800 cm^{-1}, as shown by Taylor et al.[2]. Commercial samples, used in the early experiments, always showed appreciable contamination, but those prepared and handled as described above appeared to be free of spurious absorptions.

Far infrared spectra of NH_3BF_3 and ND_3BF_3 at 98 K are shown in Fig. 1 and show far more detail than those of samples at room temperature. Frequencies of maximum absorption for samples at 300 K and 98 K are collected in Table 1 and compared with previously measured values where available. Ratios of corresponding frequencies for the two isotopic species are also listed, and assignments of the peaks, to be discussed in the next section, are summarized in the right hand column.

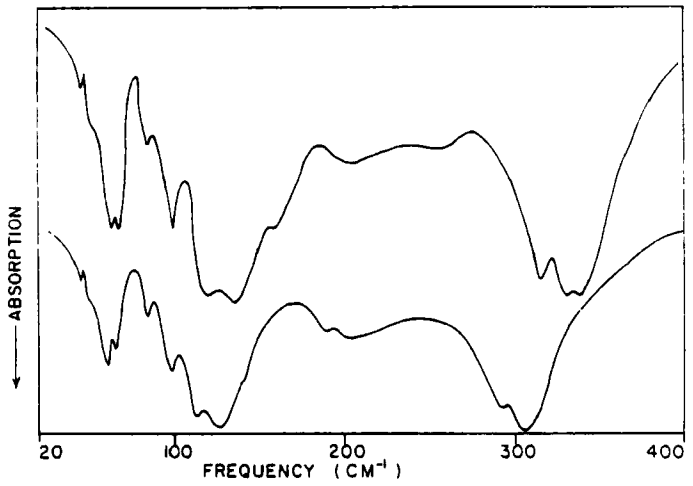

FIG. 1. Far Infrared absorption spectra of NH_3BF_3 (upper curve) and ND_3BF_3 (lower curve). Sample Temperature: 98K Instrumental Resolution: 2.5 cm^{-1}.

DISCUSSION

A comparison of the frequencies in solid NH_3 [7] and BF_3 [8] to those of corresponding modes in NH_3BF_3 [2] reveals some interesting effects. For NH_3, only the symmetric deformation (ν_2, 1058 cm^{-1}) is appreciably shifted in NH_3BF_3 (ν_2, 1438 cm^{-1}). On the other hand, for BF_3 all frequencies are changed, the largest shift being for the anti-symmetric stretch which has a value of ν_3 = 1403 cm^{-1} in BF_3 and becomes ν_9 = 1148 cm^{-1} in NH_3BF_3 or 1090 cm^{-1} in ND_3BF_3. One factor influencing these changes is the coupling between the two parts of the adduct molecule, but this should not be large, since the NH_3 frequencies are considerably higher than the corresponding ones in BF_3. A more

TABLE 1

Far Infrared Spectra of NH_3BF_3 and ND_3BF_3; Frequencies of Maximum Absorption (in cm^{-1})

Present Work				Previous Work		
NH_3BF_3		ND_3BF_3		NH_3BF_3	Isotopic	Assignment
300K	98K	300K	98K	300K	Ratio, 98K	
	45		44		1.02	
	52(sh)		51(sh)		1.02	
62	63	60	61	57[a]	1.03	
	67		65		1.03	ν_T
	85		85		1.00	
	99		98	60-130[a]	1.01	
128	118	118	112		1.05	
	136		127		1.07	ν_L(xy)
	158		140(sh)		1.13	
225	203	193	202[e]		1.00	ν_L(z)
	254		190[e]		1.34	ν_6
	316		293	304[d],308[c]	1.08	
342	331	312		318[b],322[a]		
			306		1.09	ν_{12}
	339			330[d],334[b]		

[a]Ref.6; [b]Ref.2; [c]Ref.2(ND_3BF_3); [d]Ref.5; [e]Note change in ordering, see text; (sh) = shoulder; ν_T = translation; ν_L = libration.

important effect is the change in geometry, particularly for BF_3, which is distorted from its planar configuration: F-B-F, $120^{\circ} \rightarrow 111^{\circ}$; and also undergoes an increase in bond length: B-F, 1.29 Å→1.38 Å [11].

The crystalline environment will also cause changes in the normal mode frequencies, as well as their activities and multiplicities. For the free molecule there are 5 modes of A_1 symmetry and 6 of E symmetry, all of which are infrared and Raman active, and a single A_2 torsional mode, which is optically inactive. As a result of the low site symmetry in the crystal, the E modes lose their degeneracy, and when account is also taken of coupling between molecules in the large unit cell, a group theoretical analysis predicts that all A modes, including the torsion, should show 3 infrared components and all E modes 6 components. In addition, there will be 15 infrared active lattice vibrations, of which 9 are librational and 6 translational in origin.

The lowest frequency feature observed in the comprehensive work of Taylor et al.[2] corresponds to the highest frequency absorption in the present far infrared study, and is assigned to ν_{12}, the asymmetric BF_3 deformation[12]. In the low temperature spectra, there is evidence of crystal field splitting, with 3 components resolved for NH_3BF_3 and 2 for the deuterated sample.

The torsional mode, ν_6, is expected to be only weakly infrared active for the crystal. As shown by Herzberg[13], the isotopic frequency ratio for this mode is given by

$$\nu_6(NH_3BF_3) : \nu_6(ND_3BF_3) = \sqrt{[I(ND_3) \times I(NH_3BF_3) : I(NH_3) \times I(ND_3BF_3)]}$$

where the I's are the moments of inertia about the B-N axis. When the structural data are substituted, a value of 1.39_5 is obtained. For librations about the B-N axis, which differ from the torsion only in that both parts of the molecule rotate in phase instead of anti-phase, and which are also expected to be weakly absorbing, the isotopic freqeuncy ratio is equal to that of the square roots of the total moments of inertia, a value of 1:01. From Fig. 1, it is seen that the spectral region just below the strong ν_{12} absorption is characterized by two weak broad overlapping bands, the more intense of the two being at a lower frequency in NH_3BF_3 and at a higher in ND_3BF_3. The frequency ratio of the weaker bands is about 1.37 and that of the stronger is about unity. These features are therefore tentatively assigned as originating from the torsion, ν_6, and libration, $\nu_L(z)$, respectively.

Librations about axes perpendicular to the B-N bond, $\nu_L(xy)$ are expected to be characterized by the following factors:

(a) Since there is an oscillatory dipole directly associated with this motion, the infrared absorption will be much stronger than for ν_6 and $\nu_L(z)$.

(b) The absorption will be quite broad, since the centre of mass is close to the boron atom and so the H atom amplitudes will be fairly large and hence subject to anharmonic effects.

(c) The isotopic frequency ratio, based on moments of inertia about axes through the centre of mass, is calculated to be 1.12.

These arguments lead to the assignment of the strong absorptions in the 100-160 cm^{-1} region to components of $\nu_L(xy)$.

Translational modes, which involve displacements of the molecular centres of mass relative to each other, usually result in sharper absorptions than librations, and for polar molecules, as for example in the hydrogen halides[14] and hydrogen sulfide[15], also less intense ones. Their frequencies are proportional to the square root of molecular mass, and this leads to an isotopic frequency ratio of 1.02 in this case. In the region below 100 cm^{-1}, all 6 infrared active translations (ν_T) predicted by group theory may be identified in this way.

CONCLUDING REMARKS

All observed features in the far infrared spectra of NH_3BF_3 and ND_3BF_3 have been interpreted in a straightforward manner. However, not all components of the torsional and librational modes have been resolved, and alternative assignments to those suggested here are quite possible. In fact, because of the low symmetry of the crystal and the proximity of many of the peaks, mixing between different modes is quite likely, so that the conventional labels may be inappropriate. Further research, such as neutron diffraction experiments to locate the hydrogen positions more definitely, and Raman studies to observe the other lattice modes, is needed to complete our understanding of these interesting crystals.

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