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Spectroscopic Studies of Lewis Acid–Base Complexes. II. Isotopic Frequencies and Force Constant Calculations for Ammonia–Boron Trifluoride

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The vibrational spectrum of the Lewis complex NH_3BF_3 has been investigated and data for five isotopic species preserving C_{3v} symmetry are presented. The isotopic substitutions involve deuterium, ^{10}B, and ^{15}N. All results are for the solid state. Some errors and inconsistencies in previous work have been cleared up and the new and extended data provide the basis for a new frequency assignment. Normal-coordinate calculations have been carried out to support the proposed assignment and provide information on force constants and the nature of the vibrational modes.

Introduction

Ammonia–boron trifluoride is one of the simpler and more stable Lewis complexes and often is cited as a textbook example of this particular class of compounds. X-Ray diffraction results[1] have confirmed that a bond exists between the boron and nitrogen atoms and that the molecule has C_{3v} symmetry. Despite the frequency with which this compound is mentioned in textbooks, it has not received a great deal of spectroscopic attention. In 1958 Goubeau and Mitschelen[2] reported the infrared and Raman spectra of solid NH_3BF_3 and the Raman spectrum of an aqueous solution. In the same year, Babuskin, Kovalev, and Emil'yanova[3] also reported the infrared spectrum of the solid and the Raman spectrum of the aqueous solution. The latter authors included the deuterated compound in their experimental work and carried out a normal-coordinate analysis. Preliminary results from the present investigation have appeared,[4] and in 1965 Sawodny and Goubeau, in a paper on $X_3Z \cdot NR_3$ compounds,[5] presented some new data plus the results of force constant calculations.

Comparison of the experimental results from the two 1958 papers shows a number of striking differences not explained in later papers. For example, frequencies assigned as fundamentals by one group were not reported by the other while differences in frequency larger than the normal limits of experimental uncertainty were present for other bands. All investigations heretofore have relied on natural boron and the infrared spectrum only of the deuterium compound has been examined. In the present study, Raman and infrared spectra have been obtained of five isotopic species in the solid state including species enriched in boron-10 and nitrogen-15 which have not been studied before. It is believed that the source of the discrepancy between the two 1958 investigations has been identified. Assignments are made which differ from previous proposals[5] and a normal-coordinate analysis has been carried out to support the assignment.

Experimental Section

Preparation and Purification of Compounds.—Although boron trifluoride–ammonia is regarded as a fairly stable compound, it may undergo slow decomposition with time, particularly when exposed to moisture. The principal decomposition reaction with water leads to the formation, probably by successive stages, of various hydroxyfluoroborates, the ultimate product being a boric acid. Inasmuch as the hydroxyl group is isoelectronic with fluorine and has nearly the same mass, the spectra of many of these decomposition products undoubtedly resemble the spectrum of the parent compound.

In the present study, the complex was prepared by allowing the purified acid and base to react in excess diethyl ether under anhydrous conditions. Cooling with ice or Dry Ice was necessary to reduce the possibility of decomposition due to localized heating during the reaction. A slight excess of ammonia was retained at the conclusion of the reaction to prevent the possibility of contamination at later stages by the hydrolysis of residual traces of boron trifluoride etherate. Direct combination of undiluted gaseous reactants did not seem to yield as pure a product as the solution method.

After the reaction, excess ether and ammonia were removed from the precipitated solid by pumping or by evaporation in a stream of dry nitrogen. Traces of impurities causing fluorescence in the Raman spectra were largely eliminated by dissolving the compound in cold water or cold, dry acetone, treating with Norit, partially removing the solvent by pumping, and collecting and drying the crystallized product. No alteration of the infrared spectrum was noted as a result of this treatment providing the solutions were kept cold and the procedure was carried out fairly rapidly.

Further identification of the compound was made by means of its X-ray powder diagram. The original X-ray powder data reported by Laubengayer and Condike[6] do not agree with the data later reported by Keenan and McDowell.[7] Since this disagreement has been a source of confusion in the literature, theoretical powder pattern lines were calculated from the cell dimensions and crystal symmetry found in the single-crystal work[1] and were found to agree with the pattern observed for the product prepared in the present study as well as with the data of Keenan and McDowell. No extraneous lines were observed in the experimental patterns which could not be indexed.

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(1) J. L. Hoard, S. Geller, and W. M. Cashin, *Acta Cryst.*, **4**, 396 (1951).

(2) J. Goubeau and J. Mitschelen, *Z. Physik. Chem.*, **14**, 61 (1958).

(3) A. A. Babuskin, J. F. Kovalev, and V. M. Emil'yanova, *Opt. i Spektroskopiya*, **4**, 486 (1958).

(4) R. C. Taylor, "Proceedings of the Duke Symposium on Boron–Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 59.

(5) W. Sawodny and J. Goubeau, *Z. Physik. Chem.* (Frankfurt), **44**, 227 (1965).

(6) A. W. Laubengayer and G. F. Condike, *J. Am. Chem. Soc.*, **70**, 2274 (1948).

(7) C. W. Keenan and W. M. McDowell, *ibid.*, **75**, 6348 (1953).

During one of the recrystallizations from acetone, the solution inadvertently was allowed to stand exposed to the atmosphere for a period of time during which it picked up water and warmed to room temperature. The infrared spectrum of the product obtained was significantly altered from that of the starting material indicating appreciable decomposition had occurred. Comparison of the infrared spectrum of this decomposed product with the spectrum published by Babuskin[3] for NH_3BF_3 showed that the two were remarkably similar. In particular, the spectrum of the decomposed product showed a broad band centered at about 800 cm^{-1} and a weaker but sharper band at about 1260 cm^{-1}, both of which appeared to be characteristic of the decomposed material and were not present in the spectrum of the pure compound. Conversely, the characteristic strong band near 990 cm^{-1} in the spectrum of pure NH_3BF_3 was very weak in the spectrum of the decomposed product. Other less striking differences were also present. The infrared spectrum of the decomposition product recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer is shown in Figure 1.

Isotopic Materials.—Deuterioammonia was prepared from the reaction of freshly prepared magnesium nitride with D_2O (99.8%) in a steel tank. Spectra of ND_3BF_3 prepared from this material showed no hydrogen bands. Isotopically enriched boron was obtained in the form of KBF_4 from the Oak Ridge National Laboratory; the boron-10 material was enriched to 92 atom % and the boron-11 to 99.4 atom %. Most of the boron-11 data were obtained from compounds containing the normal boron isotopic ratio, approximately 80 atom % boron-11. A small amount of NH_3BF_3 containing nitrogen-15 in 98.5% enrichment was prepared from boron-11-enriched BF_3. The nitrogen-15 was obtained in the form of ammonium sulfate through the courtesy of Dr. C. W. Heitsch.

Spectroscopic Equipment and Procedures.—The infrared equipment used initially in this investigation[4] comprised two Perkin-Elmer Model 21 spectrophotometers equipped with CaF_2, NaCl, and KBr prisms. The infrared data listed in the present paper were obtained with a Beckman IR-12 spectrophotometer which extended the frequency range to 200 cm^{-1} as well as checked the accuracy of the earlier measurements. General agreement well within the experimental uncertainty of the earlier measurements was noted.

The Raman equipment and procedures have been described previously.[8] Spectra were obtained only of polycrystalline solids, usually in the form of small pressed disks. Wavelength measurements were made directly on the plates with a comparator and also on microphotometer tracings. Owing to halation from the exciting line, frequencies below about 400 cm^{-1} were not observable. The scattering power of NH_3BF_3 is not very great and exposure times up to 48 hr were sometimes used without obtaining a very intense spectrum.

For infrared examination, the samples were dispersed in KBr pellets using standard procedures except for precautions to minimize water pickup. Various concentrations were employed to delineate the various bands as clearly as possible. The few spectra of mulls obtained showed insignificant differences from the KBr pellet spectra. Mulls between polyethylene plates were used to survey the region between 200 and 300 cm^{-1} but no additional features were observed.

Despite efforts at reproducibility and precision in frequency measurement, the uncertainties in most of the bands remained of the order of 1–5 cm^{-1} (see tables). Although satisfactory for many purposes, these uncertainties were too high to allow most of the small heavy isotope shifts to be determined with a high degree of accuracy. The principal factor contributing to the uncertainties appeared to be the strong intermolecular forces in the crystal which, under the conditions of the experiments, broadened bands, caused the apparent maxima of infrared and Raman frequencies to differ, and caused some sensitivity of the band maxima to temperature and the degree of dispersion. Overlapping of bands in certain regions of the spectrum also contributed.

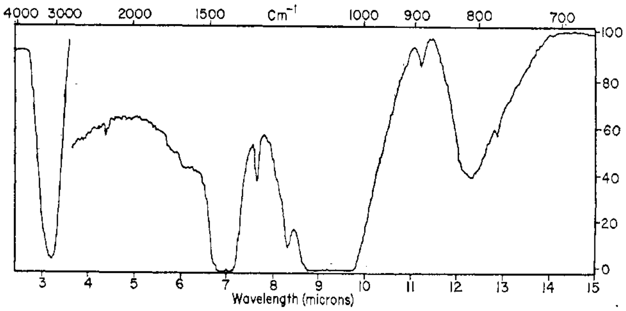

Figure 1.—Infrared spectrum of decomposed NH_3BF_3 (KBr pellet).

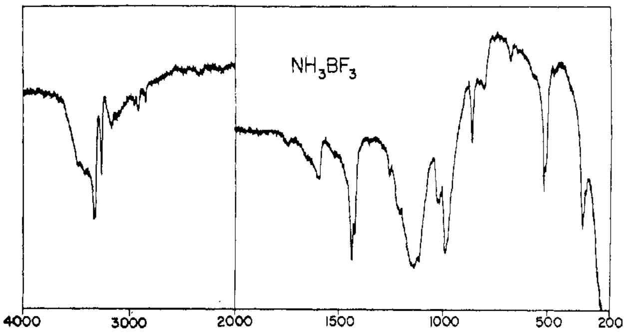

Figure 2.—Infrared spectrum of NH_3BF_3 prepared from normal isotopic boron (KBr pellet) (cm^{-1}).

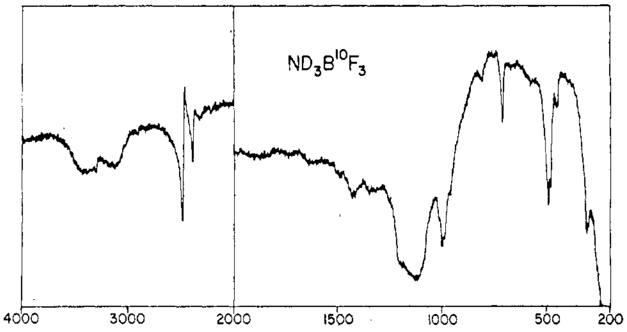

Figure 3.—Infrared spectrum of ND_3BF_3 prepared from boron enriched in ^{10}B (KBr pellet) (cm^{-1}).

Results and Assignments

The observed infrared and Raman frequencies for the three hydrogen-containing isotopic species are listed in Table I. Similar data for the two deuterium species are presented in Table II. The values presented represent averaged results from several spectra on more than one sample. A representative tracing of the infrared spectrum of the normal hydrogen compound as well as one for a deuterated variety are presented in Figures 2 and 3. The frequencies reported for the normal hydrogen compound agree well with those of Goubeau[2,5] but, for reasons cited previously, are at variance with those of the Russian workers.

In their discussion of the X-ray diffraction results for the single crystal, Hoard and Geller[1] remarked on the strong nonspecific electrostatic interactions involving

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[8] R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964).

TABLE I[a]

OBSERVED INFRARED AND RAMAN FREQUENCIES FOR SOME ISOTOPIC VARIETIES OF SOLID NH_3BF_3 (CM^{-1})

$H_3{}^{14}NBF_3$[b]				$H_3{}^{14}N^{10}BF_3$				$H_3{}^{15}N^{11}BF_3$		
Ir	δ	Raman	δ	Ir	δ	Raman	δ	Ir	δ	Assignment
318 vvw	1			317 vvw	1			314 vvw	1	
334 m	1			333 m	1			329 m	1	ν_5
468 vvw	2	461 vvw	5	467 vvw	2	461 vvw	5	457 vvw	1	
476 vvw	2			476 vvw	2			476 vvw	1	ν_{12}
509 w	1	505 vw	5	509 w	1	501 vw	3	501 w	1	
518 m	1			518 m	1			510 m	1	ν_{11}
568?		578 vvw	8	570?		587 vvw	8	570?		
680 vw, br	6							677 vvw	3	$2\nu_5$
		741 s	1			741 s	1			ν_4
807 vw	3			810 vw	3					
830 vvw	3									
863 m	2	871 w	2	865 m	1	874 w	2	858 m	1	ν_{10}
		963 vvw	6							
988 s, br	3	995 w	4	985 vw	3	991 w	4	990 s	3	ν_3 $\{^{11}B\}$
								999 s	2	
				1016 s	2					
1027 m, br	3	1027 vvw	6	1031 s	2	1036 w	2			ν_3 $\{^{10}B\}$
1112 w, br	2			1124 w, br	8			1110 sh	8	
								1134 s	2	
1148 s, br	2			1170 s, br	3			1146 s	2	ν_9
1180 sh	10			1186 s, br	3			1177 w	2	$\nu_5 + \nu_{10}$
1212 w, br	3			1221 w, br	4			1206 w, br	3	$\nu_4 + \nu_{12}$
1426 w	1			1426 w	1			1418 w	1	
1438 m	1	1450 vvw	8	1438 m	1	1455 vvw	10	1431 m	1	ν_2
1599 w	2	1601 m	2	1596 w	2	1601 m	2	1595 w	3	ν_8
								1608 w		$\nu_9 + \nu_{12}$
1746 vw, br	4	1765 vvw	8	1747 vw, br	4	1758 vvw	8			$\nu_3 + \nu_4$?
2856 vw	3			2852 vw	3					$2\nu_2$
2927 vw	3			2912 vw	3			2935 w, br	4	
2960 vvw	4			2960 vvw	4					
3116 vvw, br	5	3124 w	2	3120 vw, br	5	3122 w	2			
3185 vw, br	4			3195 vw, br	4					$2\nu_8$
3279 m	2	3273 s	2	3278 m	3	3275 s	2	3277 m	2	ν_1
3343 m	2	3335 m	2	3341 m	3	3336 m	3	3337 m	2	ν_7

[a] Abbreviations: br, broad; sh, shoulder; s, strong; m, medium; w, weak; v, very; δ, estimated experimental uncertainty. [b] Compound prepared from natural boron.

the fluorine atoms which must exist in the solid. This conclusion is borne out by the present investigations as evidenced by the breadth of the bands associated with the fluorine stretching frequencies and the fact that other bands were found to be split into two or more components.

In the absence of information provided by polarization results and band contours, assignments had to be made largely by analogy with related molecules plus the results of the normal-coordinate calculations. Vibrational frequencies and assignments for both BF_4^- and the isoelectronic CH_3CF_3, including those for the deuterated species of the latter, are available.[9,10] In addition, data and assignments for $(CH_3)_3NBF_3$,[8] $(CH_3)_2OBF_3$,[11] and the coordinated ammonia molecule[12–14] have been published.

Although the hydrogen atoms were not located in the X-ray study of NH_3BF_3, a staggered configuration for the molecule seems most probable. The vibrational structure and symmetry (C_{3v}) of the molecule, however, do not depend on this assumption. The numbering scheme, symmetry, and approximate description of the 12 vibrational fundamentals are listed in Table III.

The N–H stretching frequencies agreed closely with those found for many transition metal ammine perchlorates[12] but were significantly sharper and higher in frequency than the N–H stretching frequencies in halogen-containing metal ammine complexes where hydrogen bonding appears to exist.[14] The results thus support the conclusions from the X-ray study which found no evidence for specific hydrogen bonds between nitrogen and fluorine. The band at 1430 cm^{-1} assigned to the symmetric NH_3 deformation is appreciably higher in frequency than the symmetric deformation in metal ammine complexes where it usually is identified in the range between 1100 and 1350 cm^{-1}. In all three hydrogen compounds, this band appeared as a doublet in the infrared spectrum with a 12-cm^{-1} separation between components. The ND_3 deformation bands unfortunately fell in the congested 1000–12000-cm^{-1} re-

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(9) J. Goubeau and W. Bues, *Z. Anorg. Allgem. Chem.*, **268**, 221 (1952).

(10) (a) T. R. Stengle, Dissertation, The University of Michigan, 1961; (b) B. Lafon and J. R. Nielsen, *J. Mol. Spectry.*, **21**, 175 (1966).

(11) G. M. Begun, W. H. Fletcher, and A. A. Palko, *Spectrochim. Acta*, **18**, 655 (1962); see also J. R. Moyer, Dissertation, The University of Michigan, 1958; J. LeCalve, Thesis, The University of Bordeaux, 1966.

(12) J. M. Terasse, H. Poulet, and J. P. Mathieu, *Spectrochim. Acta*, **20**, 305 (1964).

(13) T. Shimanouchi and I. Nakagawa, *Inorg. Chem.*, **3**, 1805 (1964).

(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y., 1963, pp 143–150.

TABLE II[a]

OBSERVED INFRARED AND RAMAN FREQUENCIES FOR TWO ISOTOPIC VARIETIES OF SOLID ND_3BF_3 (CM^{-1})

$D_3{}^{14}NBF_3$[b]				$D_3{}^{14}N^{10}BF_3$				
Ir	δ	Raman	δ	Ir	δ	Raman	δ	Assignment
308 m	1			307 m	1			ν_5
329 sh				310?				ν_5 (H)
449 vvw	2			449 vvw	2			
455 vvw	2			455 vvw	2			ν_{12}
483 w	1			484 w	1			
493 m	1	488 vw	5	492 m	1			ν_{11}
		574 vvw	6	567 vvw	4	569 vvw	5	
714 m	2			714 m	2			ν_{10}
		720 m	2			718 m	2	ν_4
805 vw	3			805 vw	3			$\nu_5 + \nu_{11}$
964 vw	3			960 vw, sh	8			
977 m	2	975 w	4					ν_3 (^{11}B)
				988 m	2			$2\nu_{11}$
1002 w	5			999 m	2	1004 w	4	ν_3 (^{10}B)
				1010 vw, sh	5			$\nu_3 + \nu_{10}$
1060 vw, sh	10			1080 vw, sh	10			
1090 s, br	4							ν_9 (^{11}B)
1110 w, br	8			1117 s, br	4	1113 w	3	ν_9 (^{10}B)
1130 s, br	5			1135 s, br	5			ν_2
1161 m, br	4			1165 m, br	3	1176 vw	6	ν_8
				1202 w, br	5			$\nu_{10} + \nu_{11}$
1335 vw, br	5			1353 vvw, br	5			$3\nu_{12}$?
				1423 w, br	5			$\nu_5 + \nu_9$, $2\nu_{10}$
2357 vw	5			2353 vw	5			$2\nu_8$?
2402 w	2	2394 m	4	2400 w	2			ν_1
2494 m	2	2493 w	6	2496 m	2	2495 w	6	ν_7
2926 vvw	5			2920 vvw				$\nu_7 + \nu_{12}$
2962 vvw	3							$\nu_7 + \nu_{11}$

[a] Abbreviations: br, broad; sh, shoulder; s, strong; m, medium; w, weak; v, very; δ, estimated experimental uncertainty. [b] Natural isotopic boron.

TABLE III

DESCRIPTION AND NUMBERING OF THE FUNDAMENTAL VIBRATIONS OF NH_3BF_3

A_1 class		E class	
ν_1	Sym N–H str	ν_7	Asym N–H str
ν_2	Sym NH_3 def	ν_8	Asym NH_3 def
ν_3	Out-of-phase NBF_3 str	ν_9	Asym BF_3 str
ν_4	In-phase (breathing) NBF_3 str	ν_{10}	NH_3 rock
ν_5	Sym BF_3 def	ν_{11}	BF_3 rock
		ν_{12}	Asym BF_3 def

A_2 class	
ν_6	Torsion

gion and not only was it impossible to determine whether the same splitting existed here but even the identification of the bands was difficult. The 1130-cm^{-1} band was finally selected as the symmetric ND_3 deformation. Goubeau[5] assigned this mode to the strong band at 1090 cm^{-1} and the 1130-cm^{-1} band to the asymmetric BF_3 stretch. However, the large boron-10 isotope shift in the 1090-cm^{-1} band, as well as its high intensity, favors the reverse assignment proposed here and the normal-coordinate calculations support this reversal.

Another disagreement with Goubeau's assignments involving the NH_3 half of the molecule occurs in the case of the asymmetric ND_3 deformation mode which was assigned[5] to a weak infrared band at 1349 cm^{-1}. However, this band, although observed in the present work, seems abnormally weak compared to this mode in other molecules and the shift in frequency from the hydrogen band at 1599 cm^{-1} likewise seems too small. A frequency ratio of about 1.35, which is usual for this type of vibration, would predict a position around 1180 cm^{-1}. The spectrum between 1000 and 1200 cm^{-1} is confused because of the presence of other fundamentals but a band at 1161 cm^{-1} appears to be a suitable choice for ν_8 and is consistent with the product rule ratios.

In the hydrogen species, the complexity of the 1000–1200-cm^{-1} region appears due partly to the breadth of the B–F frequencies but also to the fact that several overtones and combinations fall in this region. The strongest absorption with maximum at about 1150 cm^{-1} is attributed principally to ν_9, the asymmetric B–F mode. The second principal maximum at 988 cm^{-1} is sharper and less complex than the first and is a logical candidate for the BF_3 symmetric mode. Since the NH_3 group is similar in mass to a fluorine atom, the normal-coordinate calculations show that the 988- and 741-cm^{-1} frequencies actually are mixed modes involving both the B–N and B–F bonds. In the higher frequency band, the boron atom moves in a direction opposite to the motion of the nitrogen and three fluorines causing the B–N bond to lengthen as the B–F bonds contract. The high infrared intensity and appreciable boron isotope shift are consistent with this description. The band at 741 cm^{-1} is the breathing motion in which all B–F and B–N bonds stretch simultaneously; it has a low infrared intensity, high Raman intensity, and low sensitivity to the mass of the boron atom.

The NH_3 rocking motion, ν_{10}, is assigned to the band at 863 cm^{-1} in agreement with Goubeau[5] but his assignment of the corresponding deuterated frequency to a band at 524 cm^{-1} does not seem correct since the limiting 1.41 ratio is greatly exceeded. The assignment of the deuterated mode to the 714-cm^{-1} band is consistent with other work and is confirmed by the calculations.

The most difficult aspect of the assignments was to decide how to distribute the three low-frequency modes involving the BF_3 group. The spectra of related molecules predict that all three should occur below about 600 cm^{-1} and, since fluorine atom motions are involved in each, that all might be expected to have appreciable infrared intensity. Three bands indeed were observed in this region but their assignment was complicated by the fact that the two highest bands were both doublets having about a 10-cm^{-1} separation and by the fact that the intensity of one band was quite low. The absence of data on infrared band shapes or Raman depolarization ratios unfortunately prevents any clear decision. However, after lengthy consideration of the small amount of evidence available, the a_1 mode has been assigned to the 518-cm^{-1} band and the two e modes to the bands at 476 and 334 cm^{-1}. This assignment parallels the assignment in the isoelectronic CH_3CF_3 molecule which also, on quite convincing evidence, places the a_1 mode highest and is consistent with results from most other molecules containing the BF_3 group. Goubeau[5] has proposed that the weak band at 476 cm^{-1} is the a_1 mode and that the e modes occur at 518 and 334 cm^{-1}. However, the product rule ratios (Table IV), particularly the $^{14}N/^{15}N$ ratios, do not agree as well for his assignment as for the one proposed here. The normal-coordinate calculations did not prove of any decisive value since either assignment could be fitted about equally well and there seemed to be no physical basis for preferring the results of one set of calculations over the other.

TABLE IV

PRODUCT RULE RATIOS FOR H_3NBF_3

Isotope pair	Isotopic species	Theoret	This work	Goubeau (ref 5)	Goubeau (revised)[a]
			A_1 Class		
H/D	^{11}B	1.964	1.900	1.986	1.891
H/D	^{10}B	1.964	1.912	. . .	1.900
$^{10}B/^{11}B$	H	1.042	1.028	. . .	1.028
$^{10}B/^{11}B$	D	1.043	1.021	. . .	1.023
$^{14}N/^{15}N$	H	1.029	(1.030)[b]	. . .	(1.014)[b]
			E Class		
H/D	^{11}B	2.633	2.666	2.897	2.678
H/D	^{10}B	2.633	2.641	. . .	2.657
$^{10}B/^{11}B$	H	1.042	1.016	. . .	1.016
$^{10}B/^{11}B$	D	1.043	1.026	. . .	1.024
$^{14}N/^{15}N$	H	1.018	1.027	. . .	1.043

[a] Assignments for ν_5, ν_{11}, and ν_{12} as proposed by Goubeau;[5] other assignments from this work; all frequency values from this work. [b] Computed using the value from normal-coordinate results for ν_4 of the $^{15}NH_3BF_3$ species.

Two other possible assignments for these BF_3 modes were considered. One assigns the a_1 fundamental to the lowest band at 334 cm^{-1} and the e fundamentals to the two higher frequencies. This distribution could be fitted satisfactorily in the normal-coordinate calculations and also gave fairly good agreement with the product rule ratios. However, it was felt that the value of 334 cm^{-1} was too much at variance with assignments in related molecules to be very likely. In addition, the potential energy distribution derived from the normal coordinates seemed less satisfactory from a physical point of view than when the a_1 fundamental was assigned to the 518-cm^{-1} band. However, this assignment, like that of Goubeau, cannot be ruled out on the basis of the present evidence.

The other assignment regards the 518-cm^{-1} band as an accidentally degenerate pair of fundamentals (it is actually a doublet) containing the a_1 and an e mode. The 476-cm^{-1} band is attributed to a combination involving the torsional mode and the 334-cm^{-1} band is the remaining e fundamental. This assignment was discarded on the basis that the splitting of the 518- and 476-cm^{-1} bands was independent of isotopic substitution whereas the calculations showed that this should not be the case if two fundamentals were involved. It seems likely that the splitting is due to crystal effects.

Normal-Coordinate Calculations

Iterative least-squares procedures for the calculation of molecular force constants using computer techniques have been described by a number of authors[15–17] and by now are fairly standard. Almost all current calculations, including those described here, are cast in the familiar *GF* framework of Wilson. In the usual procedure, elements of the inverse kinetic energy matrix (G) calculated from their definition or from the expressions of Decius[18] are used in conjunction with a trial force constant matrix, F°, to compute a secular equation, $GF^\circ - \lambda I = 0$, which is solved in the form $(G \cdot F^\circ)L = L \cdot \Lambda$. Here, L is the amplitude or eigenvector matrix and Λ is a vector of the roots of the secular equation. After normalizing the eigenvector matrix by the condition $L \cdot L' = G$, its elements may be used to compute the elements of the Jacobian matrix $J_{ij}^k = (\partial\lambda_k/\partial F_{ij})$.[15] The Jacobian matrix in turn is used in the least-squares formulation

$$J' \cdot W \cdot J \cdot \delta F = J' \cdot W \cdot \delta\Lambda \qquad (1)$$

to calculate a vector of corrections, δF, to the trial force constants. W is a diagonal weight matrix and $\delta\Lambda$ is a vector of differences between calculated and experimental frequency values. After adding the corrections to the original trial constants, the process is repeated and iterated until no further improvement in the calculated frequency values results.

In the present calculations, the problem was formu-

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(15) J. Overend and J. R. Scherer, *J. Chem. Phys.*, **32**, 1289 (1960).
(16) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).
(17) J. Aldous and I. M. Mills, *ibid.*, **18**, 1073 (1962).
(18) J. C. Decius, *J. Chem. Phys.*, **16**, 1025 (1948).

lated in terms of valence symmetry coordinates and symmetry force constants since these represent a general approach. The constants of more specialized force fields such as valence or Urey–Bradley can be obtained from symmetry force constants with a knowledge of the defining equations. The program used was written in MAD for an IBM 7090 computer with 32,000 words of storage. In each cycle, the secular equation for each isotopic species was symmetrized by the method described by Mills[17] and solved by the Jacobi method. The resulting eigenvector matrices were then used to construct a composite Jacobian matrix of dimensions $(n \times n_i) \times n_f$ relating all isotopic frequencies of the symmetry class being treated. Here, n is the dimension of the symmetry class, n_i the number of isotopic species (five in this case), and n_f the number of symmetry force constants.

In any force constant analysis, it is generally true that certain force constants prove rather insensitive to the frequencies despite the fact that the problem formally may be overdetermined, as it was here. Since such constants contribute little to the fitting process, they usually are constrained during the calculations. In the present work, these insensitive constants were identified by trial and error methods, by inspection of the Jacobian matrix, or by numerical methods.[19] They were relatively few in number (four in the A_1 class and seven in the E) and in general involved coordinates between which, on physical grounds, one would not expect much interaction. In the calculations, they were constrained to zero and an initial frequency fit was obtained for the remaining (sensitive) constants. At this point, the sensitive constants were constrained to the values they had assumed, the insensitive constants were relaxed, and the calculations were continued. Under these conditions, the insensitive constants proved well behaved and converged to values most of which were quite small. Since some improvement in the frequency fit was found, in the final step the insensitive constants were reconstrained to their new nonzero values and the sensitive constants were refitted. The changes which occurred in this last step were slight indicating that the effect of the constraints was quite small. It was felt that this procedure was preferable to the use of other more highly constrained potential functions such as the Urey–Bradley force field.

Oscillations in the calculations were effectively damped using the method described by Pliva.[20] Although the problem was sufficiently overdetermined (after constraining) that no particular difficulties were encountered in the solution of eq 1 in the present work, double precision could be employed if problems of ill conditioning arose.

Molecular parameters used in the calculations were based on the X-ray data[1] and are tabulated in Table V. The symmetry-coordinate expressions based on nontetrahedral angles are given in the same table. The numbering scheme is the same as that given by Clark and Weber[21] for H_3CGeD_3 and gives a correct set of coordinates transforming properly under the C_{3v} operations. Two redundant coordinates orthogonal, respectively, to S_2 and S_5 have been omitted.

TABLE V

MOLECULAR PARAMETERS AND COORDINATES FOR NH_3BF_3[a]

Bond lengths, Å	Bond angles, deg
r = N–H = 1.020	α = HNH = 108.00
R = B–N = 1.600	β = HNB = 110.91
d = B–F = 1.380	γ = FBF = 111.00
	δ = NBF = 107.90

Symmetry Coordinates[b]

A_1 class

$$S_1 = 1/\sqrt{3}[\Delta r_1 + \Delta r_2 + \Delta r_3]$$
$$S_2 = 1/\sqrt{c_1}[b_1(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$$
$$S_3 = 1/\sqrt{3}(\Delta d_1 + \Delta d_2 + \Delta d_3)$$
$$S_4 = \Delta R$$
$$S_5 = 1/\sqrt{c_3}[b_3(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3) - (\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)]$$

E class

$$S_7 = 1/\sqrt{2}[\Delta r_2 - \Delta r_3]$$
$$S_8 = 1/\sqrt{2}[\Delta\alpha_2 - \Delta\alpha_3]$$
$$S_9 = 1/\sqrt{2}[\Delta d_2 - \Delta d_3]$$
$$S_{10} = 1/\sqrt{2}[\Delta\beta_2 - \Delta\beta_3]$$
$$S_{11} = 1/\sqrt{2}[\Delta\delta_2 - \Delta\delta_3]$$
$$S_{12} = 1/\sqrt{2}[\Delta\gamma_2 - \Delta\gamma_3]$$

[a] Atom masses from "American Institute of Physics Handbook," McGraw-Hill Book Co., New York, N. Y., 1957. [b] $b_1 = -\sqrt{3}\cos\beta/[(\cos\alpha)/2]$, $c_1 = 3(b_1^2 + 1)$, $b_3 = -\sqrt{3}\cos\delta/[(\cos\gamma)/2]$, and $c_3 = 3(b_3^2 + 1)$.

The calculated values for the frequencies of all species are tabulated in Table VI together with the deviations from the observed values. The over-all average deviations of 0.33 and 0.22% for the A_1 and E classes are quite satisfactory. Symmetry force constants are given in Table VII together with their dispersions, the constrained constants being underlined. Unless values are assumed for the symmetry force constants associated with the redundant coordinates, it is not possible to solve for all valence force constants from the symmetry constants. Valence stretching force constants, however, can be obtained and their values are also tabulated in Table VII.

The potential energy distribution in symmetry-coordinate space for the normal molecule is tabulated in Table VIII. That for the deuterated species is similar. It will be noted that most of the frequencies are fairly well described by the corresponding symmetry coordinate. The principal exceptions are the 988- and 741-cm^{-1} frequencies in the A_1 class and the 1148-, 863-, and 476-cm^{-1} frequencies in the E class which show significant mixing of coordinates. Inspection of the eigenvector matrices (not given) shows that the phases of S_3 and S_4 are opposite in the 988-cm^{-1} frequency and alike in the 741-cm^{-1} frequency giving rise to the descriptions of ν_3 and ν_4 in Table III.

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(19) L. Nemes, *Spectrochim. Acta*, **24A**, 300 (1968).

(20) D. Papousek, S. Toman, and J. Pliva, *J. Mol. Spectry.*, **15**, 502 (1965).

(21) E. A. Clark and A. Weber, *J. Chem. Phys.*, **45**, 1759 (1966).

TABLE VI[a]

CALCULATED FUNDAMENTAL FREQUENCIES AND DIFFERENCES FROM OBSERVED VALUES FOR FIVE ISOTOPIC VARIETIES OF NH_3BF_3 (CM^{-1})

		$H_3{}^{14}N{}^{11}BF_3$		$H_3{}^{14}N{}^{10}BF_3$		$H_3{}^{15}N{}^{11}BF_3$		$D_3{}^{14}N{}^{11}BF_3$		$D_3{}^{14}N{}^{10}BF_3$	
		Calcd	Δ	Calcd	Δ	Calcd	Δ	Calcd	Δ	Calcd	Δ
						A_1 Class					
ν_1	(ν_{N-H})	3281	−2	3281	−3	3274	3	2399	3	2399	1
ν_2	(δ_{NH_3})	1440	−2	1440	−2	1432	−1	1128	2	1131	4
ν_3	(ν_{-NBF_3})	991	−3	1022	−6	989	1	971	6	998	1
ν_4	(ν_{+NBF_3})	742	−1	744	−3	733	...	714	6	719	−1
ν_5	(δ_{BF_3})	518	0	521	−3	514	−4	488	5	490	2
						E Class					
ν_7	(ν_{N-H})	3344	−1	3344	−3	3332	5	2495	−1	2495	1
ν_8	(δ_{NH_3})	1597	2	1598	−2	1594	1	1162	−1	1165	0
ν_9	(ν_{B-F})	1146	2	1174	−4	1145	1	1088	2	1118	−1
ν_{10}	(ρ_{NH_3})	860	3	866	−1	860	−2	713	1	713	1
ν_{11}	(ρ_{BF_3})	476	0	477	−1	476	0	454	1	455	0
ν_{12}	(δ_{BF_3})	334	3	334	−1	327	2	309	−1	311	−4

[a] A_1 class: average deviation = 3.5 cm^{-1} (0.33%); E class: average deviation = 2.1 cm^{-1} (0.22%); $\Delta = \nu(\text{exptl}) - \nu(\text{calcd})$.

TABLE VII

SYMMETRY AND VALENCE FORCE CONSTANTS FOR NH_3BF_3[c]

				A_1 Class				
F_{11}	5.847	0.047[a]	F_{12}	−0.626	0.044[a]	F_{24}	0.008	0.013[a]
F_{22}	0.587	0.015	F_{13}	0.000	0.573	F_{25}	−0.167	0.073
F_{33}	6.870	0.595	F_{14}	0.000	0.044	F_{34}	0.546	0.376
F_{44}	3.969	0.420	F_{15}	0.008	0.061	F_{35}	0.430	0.318
F_{55}	1.331	0.050	F_{23}	−0.247	0.069	F_{45}	−1.086	0.231
				E Class				
F_{77}	5.850	0.036	F_{78}	0.388	0.048	F_{811}	0.001	0.04
F_{88}	0.674	0.012	F_{79}	−0.024	0.35	F_{812}	−0.002	0.02
F_{99}	4.467	0.675	F_{710}	−0.008	0.05	F_{910}	0.523	0.249
F_{1010}	0.538	0.017	F_{711}	0.032	0.41	F_{911}	−0.163	0.269
F_{1111}	1.898	0.471	F_{712}	0.040	0.06	F_{912}	0.898	0.537
F_{1212}	2.122	0.794	F_{89}	−0.018	0.050	F_{1011}	−0.252	
			F_{810}	−0.160	0.046	F_{1012}	−0.631	0.374
						F_{1112}	0.943	0.386

Valence Force Constants[b]

	mdyn/Å		mdyn/Å		mdyn/Å
f_R	3.969	f_{rr}	−0.001	f_{dR}	0.315
f_r	5.849	f_{dd}	0.801	f_{rd}	0.031
f_d	5.268	f_{rR}	0.000	f_{rd}'	−0.016

[a] Force constant dispersions: $\sigma^2\{F_i\} = (J'WJ)_{ii}{}^{-1}\sigma^2$. [b] R = B–N, d = B–F, r = N–H. [c] Units of symmetry force constants: mdyn/Å, mdyn/radian, or mdyn-Å/radian^2.

Discussion

The additional isotopic data provided in the present work have made it possible to clear up a number of questions and errors in the literature and have provided a satisfactory and consistent set of assignments for this important example of a Lewis complex. A parameter of continuing interest in these compounds is the force constant associated with the dative bond. The B–N bond in the present molecule was found to have a constant of 3.97 mdyn/Å which is significantly larger than the value of 3.11 mdyn/Å given by Sawodny and Goubeau.[5] A number of factors undoubtedly contribute to the difference including small differences in most of the experimental frequency values used, the fact that they assumed tetrahedral angles, and the more limited set of experimental data available to them. They gave no information on their "goodness of fit" also. Interestingly enough, the effect of the different assignment of ν_5 on the B–N constant appeared very small. Calculations carried out using the Goubeau assignment for ν_5 changed the value of the B–N constant by less than 1%.

It is of interest to compare the value of the B–N constant with that found for the trimethylamine–boron trifluoride complex. Goubeau[5] reported 3.36 mdyn/Å for the latter compound but recent calculations in this laboratory[22] based on data from five isotopic species

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(22) P. H. Clippard, Dissertation, The University of Michigan, 1969.

TABLE VIII

DISTRIBUTION OF POTENTIAL ENERGY OF NORMAL MODES OF $^{14}NH_3{}^{11}BF_3$ AMONG SYMMETRY COORDINATES

A_1 Class

	cm^{-1}				
	3279	1438	988	741	518
S_1 (ν_{N-H})	0.94	0.06	0.00	0.00	0.00
S_2 (δ_{NH_3})	0.06	0.88	0.02	0.00	0.04
S_3 (ν_{B-F})	0.00	0.01	0.60	0.35	0.04
S_4 (ν_{B-N})	0.00	0.05	0.29	0.66	0.00
S_5 (δ_{BF_3})	0.00	0.00	0.09	−0.01	0.92

E Class

	cm^{-1}					
	3343	1599	1148	863	476	334
S_7 (ν_{N-H})	0.96	0.00	0.00	0.00	0.00	0.00
S_8 (δ_{NH_3})	0.04	0.96	0.00	−0.01	0.00	0.02
S_9 (ν_{B-F})	0.00	0.00	0.70	0.11	0.27	−0.08
S_{10} (ρ_{NH_3})	0.00	−0.01	0.22	0.58	0.07	0.13
S_{11} (ρ_{BF_3})	0.00	0.00	0.07	0.39	0.60	−0.06
S_{12} (δ_{BF_3})	0.00	0.01	0.01	−0.07	0.06	0.99

without assuming point mass methyl groups have given the value of 3.54 mdyn/Å. In either case, the present calculations place the B–N constant for the ammonia complex higher than that for the amine, a reversal of the order found by Goubeau but in agreement with data published for the BH_3 complexes. The value of 3.97 mdyn/Å for the B–N constant in NH_3BF_3 is comparable to, though somewhat less than, the values found in the literature for the force constants of isoelectronic carbon–carbon single bonds. In general, values for the latter fall somewhere around 4.5 mdyn/Å. The only force constant analysis for the analogous CH_3CF_3 molecule so far available[10b] is based on a Urey–Bradley force field and the value reported for the C–C constant, 3.7 mdyn/Å, consequently is not strictly comparable with that from the present analysis. The B–N bond in NH_3BF_3 appears to be a reasonably strong bond in agreement with the general chemical behavior and thermal stability of the compound.

A word might be said at this point regarding the reliability of the potential function obtained. It has been pointed out already that several constants were constrained in the fitting process and the function consequently is not completely general. However, there is some basis on physical grounds to believe that these constrained constants probably are small and likely are not significant. A more worrisome concern is the fact that Mills and others have pointed out quite graphically in the case of small molecules that isotopic frequency data alone generally are insufficient to determine a complete force field with a high degree of precision and that supplementary data such as the Coriolis interaction constants are desirable, if not essential, for satisfactory results. Although published work has dealt with molecules the size of chloroform or smaller, little hope has been given that the situation will be any better with larger molecules. On the other hand, practically all of such studies have dealt with the substitution of only one isotope, deuterium for hydrogen, and very limited evidence is available for molecules where extensive isotope substitution of both light and heavy atoms has been made. In view of the fact that atoms belonging to different equivalent sets contribute in different ways to the various normal coordinates, there is some reason to believe that extensive isotope substitution of several atom species may be more effective in the determination of potential functions than has been the case when deuterium substitution alone has been used. In any case, for substances which cannot be studied in the gas phase, as in the present instance, extensive isotopic data are about the only recourse since other types of data cannot be obtained.

One unsatisfactory feature of the present work is the residual uncertainty regarding the assignment of the lowest a_1 fundamental. Although the value of the B–N constant probably will not be much affected should later data provide evidence for an assignment different than that proposed here, it would be desirable to have an unequivocal answer. In view of the physical properties of the compound, this probably will have to come from single-crystal work.

Finally, it should be noted that observed frequencies have been fitted instead of the true harmonic frequencies. Incorporation of anharmonicity corrections undoubtedly would alter the values of the force constants to some extent although the effect on the potential energy distributions probably would be minimal. The force constant dispersions in Table VII, of course, do not reflect this uncertainty.

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