

MEAN AMPLITUDES OF VIBRATION AND CORIOLIS COUPLING CONSTANTS FOR THE AMMONIA-BORON TRIFLUORIDE COMPLEX

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Recently vibrational spectroscopic studies of inorganic complexes have attracted some interest. Some good vibrational assignments have also been made for complexes like ammonia-boron trifluoride,¹ trimethylamine-boron trifluoride,² acetonitrile-boron trifluoride,³ etc. In some cases these assignments were followed up by normal coordinate analysis.⁴ As it was felt that the theoretical determination of other molecular constants like mean amplitude of vibration, Coriolis coupling constants, etc. for these complexes, would be of great use in future experimental studies, the present investigations were taken up. The first theoretical studies were made on the complex acetonitrile-boron trifluoride.⁵ In the present work the molecular constants for the complex ammonia-boron trifluoride with all its isotopic modifications have been determined.

The complex $\text{H}_3\text{N}\cdot\text{BF}_3$ has a C_{3v} symmetry with the vibrational modes distributed as $5A_1 + A_2 + 6E$. The A_2 mode which represents the torsional motion is inactive both in Raman and infrared spectra. For the present calculations the vibrational assignment, internal and symmetry coordinates, and the molecular parameters were taken from Taylor *et al.*¹ The initial set of symmetry force constant (F) values were also taken from Taylor *et al.* However, when the eigenvalues of the $\mathbf{GF}$ product matrix were evaluated for $\text{H}_3^{14}\text{N}\cdot^{11}\text{BF}_3$, whereas the agreement with the observed frequency values was good for A_1 species, the frequency reproduction for E species was poor. This may be due to the fact that the dispersion values even for the diagonal F matrix elements in the E species are large in the procedure of Taylor *et al.* Hence the E species force constants were improved iteratively till the experimentally observed frequencies were exactly reproduced for $\text{H}_3^{14}\text{N}\cdot^{11}\text{BF}_3$. When these symmetry force constants were used to calculate the vibrational frequencies of the isotopic series $\text{H}_3^{14}\text{N}\cdot^{10}\text{BF}_3$, $\text{H}_3^{15}\text{N}\cdot^{11}\text{BF}_3$, $\text{D}_3^{14}\text{N}\cdot^{11}\text{BF}_3$, and $\text{D}_3^{14}\text{N}\cdot^{10}\text{BF}_3$ the agreement with the observed frequency values was fairly good. The symmetry F matrix elements are given in Table 1. The calculated and observed vibrational frequencies are given in Table 2.

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¹ Taylor, R. C., Gabelnick, H. S., Aida, K., and Amster, R. L., *Inorg. Chem.*, 1969, **8**, 605.

² Clippard, P. D. H., Ph.D. Thesis, University of Michigan, 1969.

³ Swanson, B., and Shriver, D. F., *Inorg. Chem.*, 1970, **9**, 1406.

⁴ Sawodny, W., and Goubeau, J., *Z. phys. Chem., Frankf. Ausg.*, 1965, **44**, 227.

⁵ Devarajan, V., and Cyvin, S. J., *Z. Naturf. (A)*, in press.

The mean amplitudes of vibration for all the isotopic species were calculated using Cyvin's procedure⁶ and these values are given in Table 3. To check the dependence of non-bonded mean amplitudes on torsional vibrations, a torsional symmetry

TABLE 1
SYMMETRY F MATRIX ELEMENTS FOR NH_3BF_3
Symmetry force constants in mdyne $\text{\AA}^{-1}$, mdyne rad^{-1} , mdyne $\text{\AA} \text{rad}^{-2}$

A ₁ class	F_{11}	5.854	F_{12}	-0.626	F_{14}	0.008
	F_{22}	0.588	F_{13}	0	F_{25}	-0.167
	F_{33}	6.904	F_{14}	0	F_{34}	0.542
	F_{44}	3.984	F_{15}	0	F_{35}	0.430
	F_{55}	1.334	F_{23}	-0.247	F_{45}	-1.088
E class	F_{66}	5.846	F_{68}	-0.004	F_{711}	0.008
	F_{77}	0.667	F_{69}	-0.019	F_{89}	0.305
	F_{88}	3.223	F_{610}	0.018	F_{810}	0.129
	F_{99}	0.417	F_{611}	0.032	F_{811}	0.114
	F_{1010}	1.616	F_{78}	0.105	F_{910}	-0.219
	F_{1111}	1.669	F_{79}	-0.150	F_{911}	-0.407
	F_{67}	0.391	F_{710}	-0.023	F_{1011}	0.616

TABLE 2
CALCULATED AND OBSERVED VIBRATIONAL FREQUENCIES (cm^{-1}) FOR FIVE ISOTOPIC VARIETIES OF NH_3BF_3

Species	ν	$\text{H}_3^{14}\text{N},^{11}\text{BF}_3$		$\text{H}_3^{14}\text{N},^{10}\text{BF}_3$		$\text{H}_3^{15}\text{N},^{11}\text{BF}_3$		$\text{D}_3^{14}\text{N},^{11}\text{BF}_3$		$\text{D}_3^{14}\text{N},^{10}\text{BF}_3$	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
A ₁	ν_1	3283	3283	3282	3284	3275	3271	2400	2396	2400	2398
	ν_2	1442	1442	1441	1442	1432	1433	1129	1126	1132	1127
	ν_3	994	994	1025	1028	992	988	973	965	1000	997
	ν_4	743	743	746	747	734	733	715	708	720	720
	ν_5	518	518	521	524	514	518	487	483	490	488
E	ν_6	3345	3345	3343	3347	3331	3327	2496	2496	2496	2494
	ν_7	1595	1595	1583	1600	1577	1593	1207	1163	1236	1165
	ν_8	1144	1144	1173	1178	1130	1144	1071	1086	1088	1119
	ν_9	857	857	877	867	876	862	694	712	694	712
	ν_{10}	476	476	476	478	471	476	459	453	459	455
	ν_{11}	331	331	335	335	334	325	308	310	308	315

coordinate was introduced and the mean amplitudes were determined for two different torsional frequencies, viz. 25 and 150 cm^{-1} in the case of $\text{H}_3^{14}\text{N},^{11}\text{BF}_3$ only. It was found that *gauche* $\text{H} \cdots \text{F}$ mean amplitude alone was dependent on torsional vibrations.

The Coriolis coupling constants were evaluated using the procedure of Meal and Polo.⁷ The most important amongst them, i.e. the diagonal elements of

⁶ Cyvin, S. J., "Molecular Vibrations and Mean Square Amplitudes." (Universitetsforlaget: Oslo 1968.)

⁷ Meal, J. H., and Polo, S. R., *J. chem. Phys.*, 1956, **24**, 1119, 1126.

$\zeta^z(E_a \times E_b)$, are given in Table 4 for all the isotopic species. All the abovementioned calculations were carried out on a UNIVAC 1108 computer at the computer centre in Norges Tekniske Høgskole, Trondheim.

TABLE 3
MEAN AMPLITUDES ($\text{\AA}$) OF VIBRATION OF THE ISOTOPIC SPECIES

Vibration	$\text{H}_3^{14}\text{N}, ^{11}\text{BF}_3$		$\text{H}_3^{14}\text{N}, ^{10}\text{BF}_3$		$\text{D}_3^{14}\text{N}, ^{11}\text{BF}_3$		$\text{H}_3^{15}\text{N}, ^{11}\text{BF}_3$		$\text{D}_3^{14}\text{N}, ^{10}\text{BF}_3$	
	0°K	298°K	0°K	298°K	0°K	298°K	0°K	298°K	0°K	298°K
N-H	0.0748	0.0748	0.0748	0.0748	0.0639	0.0639	0.0748	0.0748	0.0639	0.0639
N-B	0.0544	0.0553	0.0550	0.0559	0.0544	0.0554	0.0541	0.0550	0.0550	0.0559
B-F	0.0494	0.0513	0.0502	0.0519	0.0496	0.0515	0.0495	0.0515	0.0506	0.0523
H...H	0.1293	0.1297	0.1293	0.1297	0.1096	0.1106	0.1293	0.1297	0.1093	0.1103
F...F	0.0597	0.0686	0.0595	0.0682	0.0590	0.0679	0.0599	0.0692	0.0587	0.0673
H...B	0.1186	0.1241	0.1186	0.1239	0.1029	0.1110	0.1185	0.1241	0.1081	0.1110
F...N	0.0593	0.0654	0.0592	0.0651	0.0589	0.0653	0.0588	0.0651	0.0587	0.0650
(D)H...F (<i>trans</i>)	0.1012	0.1043	0.1010	0.1041	0.0889	0.0934	0.1008	0.1040	0.0888	0.0933
(D)H...F (<i>gauche</i>) ^a	0.2465	0.8469								
(D)H...F (<i>gauche</i>) ^b	0.1608	0.2064	0.1603	0.2058	0.1335	0.1701	0.1608	0.2068	0.1331	0.1692

^a At torsional frequency 25 cm^{-1} .

^b At torsional frequency 150 cm^{-1} .

TABLE 4
THE IMPORTANT FIRST-ORDER CORIOLIS COUPLING COEFFICIENTS $\zeta^z(E_a \times E_b)$ FOR THE ISOTOPIC SPECIES

$\zeta^z(E_a \times E_b)$	$\text{H}_3^{14}\text{N}, ^{11}\text{BF}_3$	$\text{H}_3^{14}\text{N}, ^{10}\text{BF}_3$	$\text{H}_3^{15}\text{N}, ^{11}\text{BF}_3$	$\text{D}_3^{14}\text{N}, ^{11}\text{BF}_3$	$\text{D}_3^{14}\text{N}, ^{10}\text{BF}_3$
ζ_{66}	0.3574	0.3575	0.3500	0.4574	0.4576
ζ_{77}	-0.4496	-0.4367	-0.4451	0.2029	0.4388
ζ_{88}	0.8990	0.8921	0.8993	0.1936	-0.0289
ζ_{99}	-0.0418	-0.0438	-0.0414	-0.2695	-0.2695
ζ_{1010}	0.3374	0.3397	0.3267	0.3344	0.3357
ζ_{1111}	-0.6350	-0.6414	-0.6321	-0.4868	-0.4917

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