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Infrared Spectra of Difluoroborane and Difluoroborane-*d*

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Gaseous H–BF$_2$ and D–BF$_2$ were obtained by a new method of preparation. Analysis of high-resolution ir spectra gave approximate values for the B–F distance (1.30±0.15 Å) and the F–B–F angle (120°±5°). Five of the six fundamentals were observed and assigned unambiguously: $\nu_2=2620$ and 1962 cm^{-1}, B–H and B–D stretches; $\nu_1=1166$ and 1128 cm^{-1}, ^{11}B–F symmetric stretches in H–BF$_2$ and D–BF$_2$; $\nu_3=545$ and 540 cm^{-1}, F–^{11}B–F bending in H–BF$_2$ and D–BF$_2$; and $\nu_4=1402$, 1392, 1419 cm^{-1}, ^{11}B–F asymmetric stretches in H–BF$_2$ and D–^{11}BF$_2$ and ^{10}B–F stretch in D–^{10}BF$_2$, respectively; $\nu_6=944$, 924, 810, 790 cm^{-1}, out-of-plane deformation in H–^{10}BF$_2$, H–^{11}BF$_2$, D–^{10}BF$_2$, and D–^{11}BF$_2$, respectively. The H–B–F bending appears to have a frequency $\nu_5=1200$ cm^{-1} for H–^{11}BF$_2$ and is estimated at 887 cm^{-1} for D–^{11}BF$_2$. A force-constant calculation was made, obtaining the following values (in millidynes per angstrom): $f_D=3.66$, $f_d=6.625$, $f_d'=0.725$, $f_{Dd}=0.37$, $f_\tau=0.772$.

THE complete assignment of the ir spectra of HBX$_2$ (X=F, Cl, Br) would allow the calculation of the force constants of these compounds, and a comparison of these with the corresponding ones of the boron trihalides might yield interesting results on the nature of the B–X bonds. Bass *et al.*[1] have obtained the ir spectra of mixtures of HBCl$_2$–BCl$_3$ and HBCl$_2$–DBCl$_2$–BCl$_3$ in the gas phase and made a complete assignment utilizing Green's function. A quite different assignment was made by Mandirola and Westerkamp,[2] who calculated vibrational frequencies using reasonable force constants. A straightforward assignment is difficult, owing to the unavoidable presence of BCl$_3$ with strong bands in regions where there are bands of HBCl$_2$ and of DBCl$_2$. Even in matrix isolation spectra,[3] there is still some superposition of bands.

The ir spectrum of HBBr$_2$ is shown in a paper by Rietti and Lombardo,[4] and the complete assignment has been made by Mandirola and Westerkamp.[5]

The ir spectrum of gaseous HBF$_2$ has been reported recently by Coyle *et al.*[6] By a different method of preparation we have obtained the mixtures HBF$_2$–BF$_3$–H$_2$ and DBF$_2$–BF$_3$–D$_2$. Practically all the bands of H–BF$_2$ and D–BF$_2$ are well separated from those of BF$_3$ and show a well-resolved and intense rotational structure. The quality of the spectra enabled us to obtain approximate values of molecular parameters, make a complete and unambiguous assignment of the observed bands, and calculate force constants by Wilson's method.

EXPERIMENTAL

The mixtures were obtained by irradiation with a high-frequency discharge (in the megacycles-per-second range) on a 1:7 mixture of B$_2$F$_4$, prepared by the method of Finch and Schlesinger,[7] with H$_2$ or D$_2$. We irradiated for about 5 min in the gas cell; after this time the B$_2$F$_4$ had reacted completely. Longer irradiation times produced B$_2$H$_6$ or B$_2$D$_6$, which are also obtained after a period of weeks by decomposition of H–BF$_2$ and D–BF$_2$. The total pressure of the mixtures was of ≈40 mm: ($p_{\text{HBF}_2(\text{DBF}_2)}\approx3$ mm; $p_{\text{BF}_3}\approx3$mm). The spectra were obtained with a Beckman IR-9 spectrometer, over the range 400–4000 cm^{-1}, using 10-cm-path-length gas cells with NaCl, KBr, and CsI windows. We also ran a spectrum in the 400–200-cm^{-1} region, but observed no bands. The resolution of the spectra scanned over the whole range was of 1.5 cm^{-1}, the absorption peaks of H–BF$_2$ and D–BF$_2$ were also obtained with 0.5-cm^{-1} resolution, in order to analize the rotational structure. The calibration was done using the rotational structure of H$_2$O. All spectra of the HBF$_2$ mixture were taken with an empty cell, a cell with BF$_3$, and a cell containing B$_2$H$_6$ in the reference beam. Those of DBF$_2$ were taken with an empty cell and with BF$_3$ in the reference beam.

SPECTRA

The gas-phase spectra of H–BF$_2$ and D–BF$_2$ are shown in Fig. 1. We include the well-known spectra of pure B$_2$H$_6$ and of pure BF$_3$ in order to show clearly the peaks corresponding to the compounds under study.

The spectra of the H–BF$_2$ mixture show well-defined bands not attributable to either BF$_3$ or B$_2$H$_6$; the positions and prominent features of those bands are the following: a medium-intensity doublet with peaks at ≈2630 and ≈2602 cm^{-1} showing resolvable fine

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[1] C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames, J. Chem. Phys. **40**, 3611 (1964).

[2] O. Brieux de Mandirola and J. F. Westerkamp, Spectrochim. Acta **20**, 1633 (1964).

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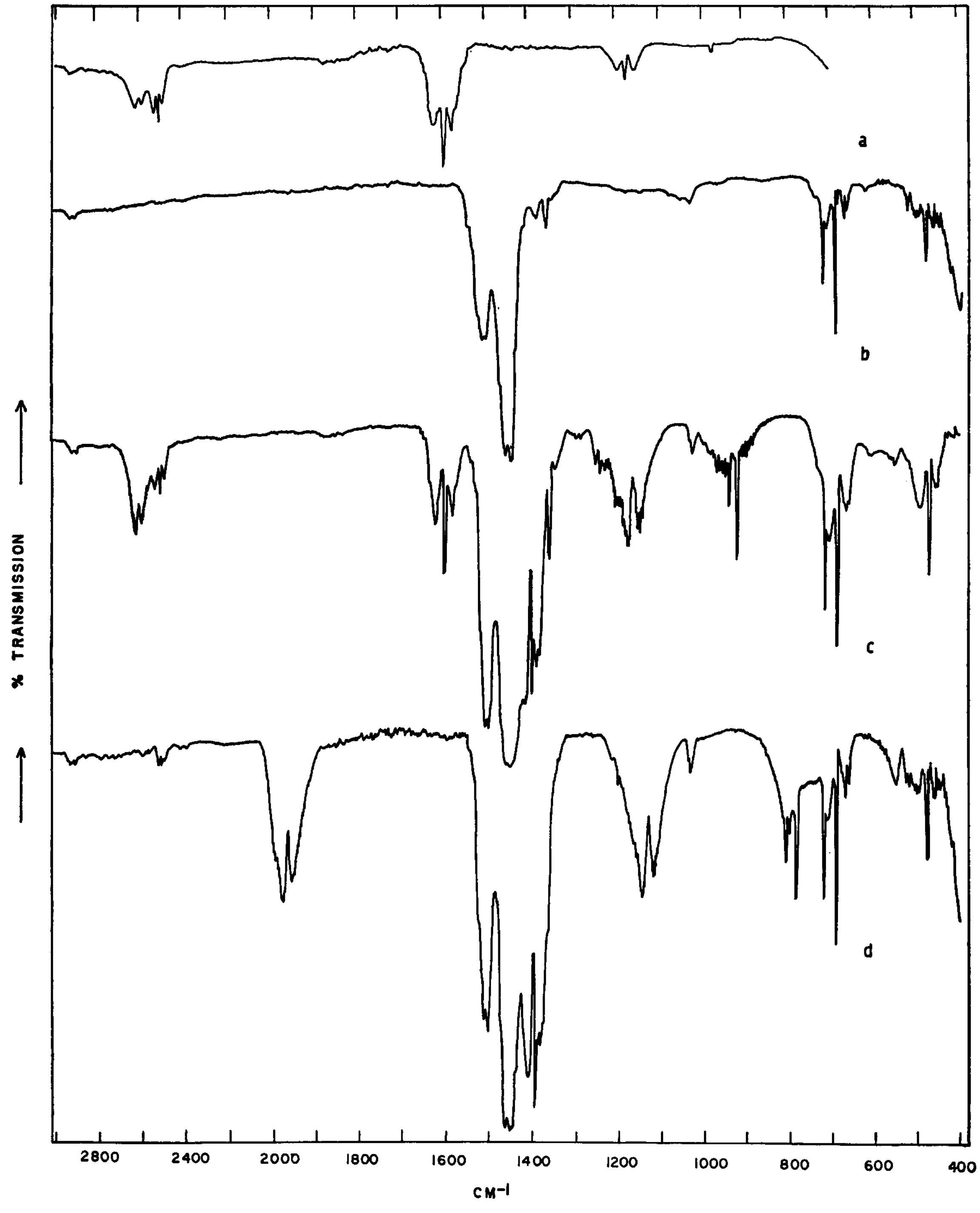

FIG. 1. Infrared spectra at 1.5-cm^{-1} resolution. (a) B_2H_6, $p \approx 4$ mm, taken with NaCl windows; (b) BF_3, $p \approx 2$ mm, with KBr windows; (c) $HBF_2 + BF_3 + H_2 + B_2H_6$, 1:1:10:1.3, $p_T \approx 40$ mm, with CsI windows; (d) $DBF_2 + BF_3 + D_2$, 1:1.2:11, $p_T \approx 40$ mm, with KBr windows. The peak at 1030 cm^{-1} is due to SiF_4.

structure; a very intense triplet with peaks at 1417, 1402, and 1391 cm^{-1}; a medium-intensity doublet with resolvable fine structure and maxima at $\approx$1177 and 1150 cm^{-1} and a shoulder at $\approx$1200 cm^{-1}; two sharp peaks at 924 and 944 cm^{-1} superimposed on a fine-structure background; and a weak broad maximum with fine structure at $\approx$560 cm^{-1}. Coyle *et al.*[6] reported bands at: 2645 sh, 2631, 2607 m; 1462, 1455, 1449 sh, s; 1417, 1405, 1392 sh, vs; 1200 sh, 1176, 1145 s; 944 m, 924 s; 555, 530 w[8]; their spectrum coincides with

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[8] sh, shoulder; m, medium; s, strong; v, very; w, weak.

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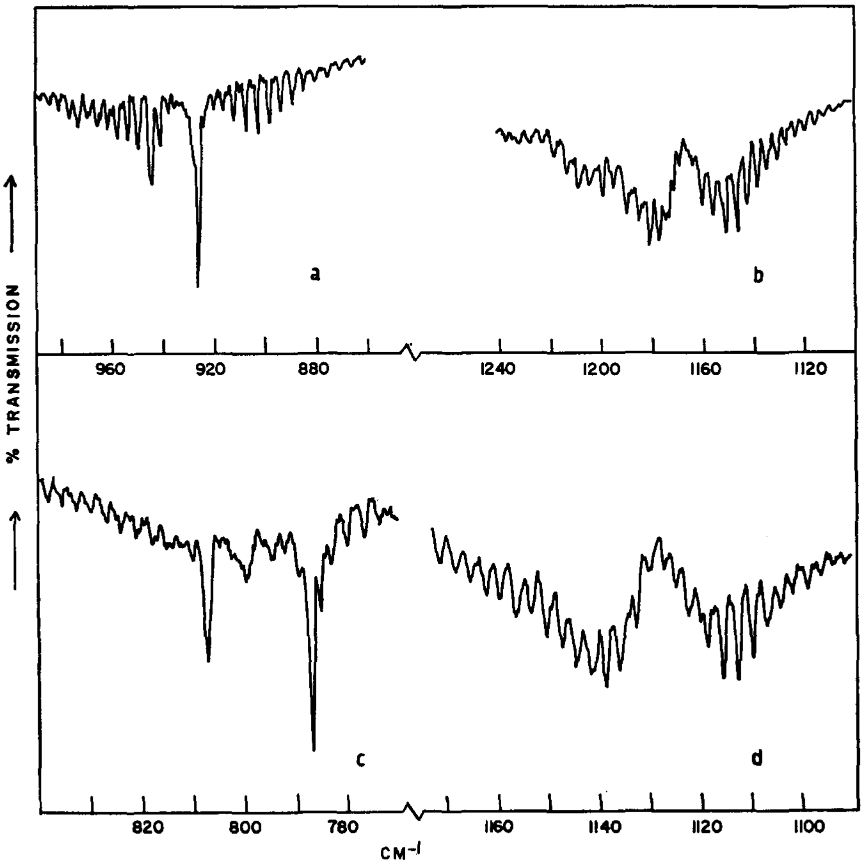

FIG. 2. Infrared spectra at 0.5-cm^{-1} resolution. (a) HBF_2 compensated with B_2H_6, NaCl windows; (b) HBF_2 compensated with B_2H_6, NaCl windows; (c) DBF_2, KBr windows; (d) DBF_2, KBr windows.

ours except for the bands at 1462, 1455, 1449 cm^{-1}, which we cannot observe due to the presence of a very strong BF_3 band, and the band at 530 cm^{-1}, also obscured in our spectra by a BF_3 band.

The deuterated compound has a spectrum with bands at the following frequencies: a medium intensity doublet having resolvable fine structure with maxima at $\approx$1956 and $\approx$1970 cm^{-1}; strong peaks at 1419, 1410, 1392, and 1380 cm^{-1}; a doublet with fine structure and maxima at $\approx$1145 and $\approx$1118 cm^{-1}; two sharp peaks superimposed on a background with fine structure at 810 and 790 cm^{-1}; and, finally, a broad peak with structure at $\approx$552 cm^{-1}.

The high-resolution spectra of these bands are shown in Figs. 2 and 3; the lowest frequency bands of H- and D-BF_2 gave a poor spectra and are not included in the figures.

MOLECULAR PARAMETERS

The bands with center at 2620 and at 1166 cm^{-1} in the spectra of HBF_2 and those with center at 1962 and at 1128 cm^{-1} of DBF_2 show a regular and intense rotational structure. Since the appearance of these bands is similar to that due to the H-B stretching mode of $HBCl_2$,[9] we tried to interpret the fine structure assuming that H-BF_2 and D-BF_2 are also accidental symmetric tops. Although our data do not fit as well as those of $HBCl_2$ in the expression for the energy levels of a symmetric rotor, the separation of neighboring peaks was sufficiently constant to allow an estimate of the moments of inertia.

In these perpendicular-type bands, assuming that the rotational constants are the same for the excited and the fundamental vibrational levels, the energy difference between succesive ^{R}Q and ^{P}Q branches is

$$2(A-\bar{B})=2[A-\tfrac{1}{2}(B+C)],$$

where A is the rotational constant corresponding to the unique axis, parallel to the F-F line.

The measurements made on the high-resolution spectra gave the following values:

for HBF_2, $4.1<2(A-\bar{B})<4.7$ cm^{-1};

for DBF_2, $2.8<2(A-\bar{B})<3.2$ cm^{-1}.

Since the assignment of the bands is consistent with a symmetry C_{2v}, there are three molecular parameters to determine. In order to obtain values for two of them we fixed the H-B distance (the moment of inertia is less sensitive to its variation) and calculated the values of $(A-\bar{B})$, varying the B-F distance between 1.10-1.50 Å in steps of 0.05 Å, and the F-B-F angle between 90°-130° in steps of 2.5°.

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[9] L. Lynds and C. D. Bass, J. Chem. Phys. **40**, 1590 (1964).

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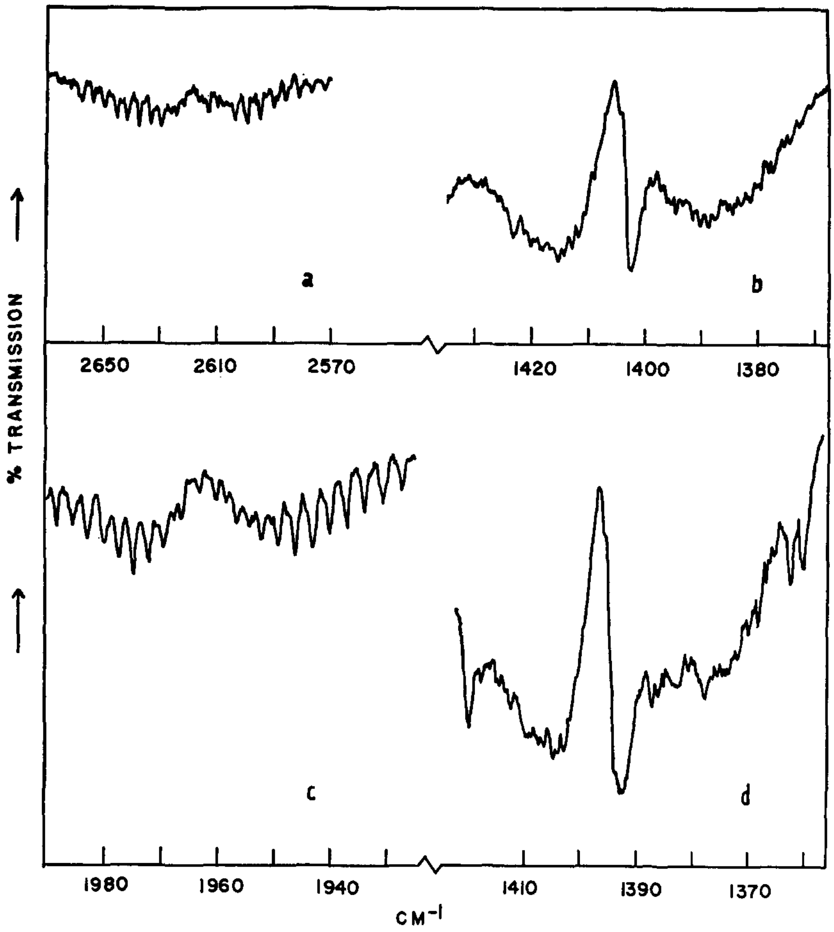

FIG. 3. Infrared spectra at 0.5-cm^{-1} resolution. (a) HBF_2 compensated with B_2H_6, NaCl windows; (b) HBF_2, NaCl windows; (c) DBF_2, KBr windows; (d) DBF_2, KBr windows.

The values of the molecular constants agreeing best with the mean measured value of $(A-\tilde{B})$, and their range of variation compatible with the experimental results, are given in Table I.

These parameters have too much error to draw any conclusion about bond distances but indicate that there is little distortion with respect to BF_3 ($r_{FB}=1.295$ Å)[10] and to CH_3BF_2 ($r_{FB}=1.30$ Å).[11]

ASSIGNMENT

In Table II we give the symmetry, description, rotational type, and expected isotope shift for the six modes of H– and D–BF_2 molecules of symmetry C_{2v}. These features, together with the frequencies of related modes in similar molecules allowed us to make an unambiguous assignment of the observed modes, as shown in Table III.

A_1 Modes

These modes should have bands with no central peak and resolvable fine structure (the separation of the Q branches is ≈ 4.4 cm^{-1} in HBF_2 and ≈ 3.0 cm^{-1} in DBF_2). The frequency of the B–H stretching mode (D) of HBF_2 is expected to be similar to that of $HBCl_2$ (2617 cm^{-1}); the frequency of the B–F symmetric stretching mode (d_s) should be in the neighborhood of

TABLE I. Molecular parameters.

	I_A (amu×Å^2)	I_B (amu×Å^2)	I_C (amu×Å^2)	$\rho=I_A/I_B$	$(A-\tilde{B})$ (cm^{-1})	<FBF	r_{BF}	r_{BH}
HBF_2	6.55	47.18	53.73	0.140	2.23	120±5°	1.30±0.15 Å	1.15 Å (assigned)[a]
DBF_2	9.18	47.18	56.36	0.195	1.50			

[a] See Ref. 9.

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[10] A. H. Nielsen, J. Chem. Phys. **22**, 659 (1954).

[11] S. H. Bauer and J. M. Hastings, J. Am. Chem. Soc. **64**, 2686 (1942).

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TABLE II. Description of vibrational modes.

No.	Mode	Band type	Description	Expected isotope shift (ν_H/ν_D)
1	A_1	B (⊥)	d_s; B–F symmetric stretch	1
2	A_1	B (⊥)	D; B–H stretch	1.40
3	A_1	B (⊥)	A; F–B–F bending	1
4	B_1	A (||)	d_a; B–F asymmetric stretch	1
5	B_1	A (||)	a; H–B–F bending	1.35
6	B_2	C (⊥)	τ; out-of-plane deformation	1.18

1200 cm^{-1}, by comparison with CH_3BF_2[12] (1250 cm^{-1}); and the F–B–F bending mode (A) is responsible for a band at ≈500 cm^{-1}, where it appears in CH_3BF_2 (479 cm^{-1}). Deuteration of H–BF_2 will shift the D mode by a factor of ≈0.7 but will not much alter the frequencies of the other modes. We can thus assign with certainty the doublet with band center at 2620 cm^{-1} in the spectra of HBF_2 (1962 cm^{-1} in DBF_2) to the D mode, the doublet with center at 1166 cm^{-1} (1128 cm^{-1}) to the d_s mode, and the band with maxima at 560 cm^{-1} (552 cm^{-1}) to the ^PQ branches of the A mode. The ^RQ branches of this band are obscured by the spectrum of BF_3, but the valley, corresponding to the band center, can be clearly distinguished at 545 cm^{-1} (540 cm^{-1}). All these bands correspond to the molecules with ^{11}B, the bands of the ^{10}B isotope could not be distinguished in these A-type modes. We checked the Teller–Redlich product rule, which gave us a 1.0% agreement.

B_2 Modes

The appearance of a C-type band can be imagined as a composition of two extreme forms, namely a perpendicular and a parallel band, depending on the value of ρ. If ρ is not too small, there will be a central peak in addition to the peaks of the ^RQ and ^PQ branches. Since there are molecules with ^{10}B and with ^{11}B, two sharp peaks of different intensity are expected (the smaller peak at higher frequency). The product rule predicts a ratio of 1.18 between the frequency of this mode in HBF_2 with respect to DBF_2. Hence we assigned the bands at 944 cm^{-1} (810 cm^{-1}) and 924 cm^{-1} (790 cm^{-1}) to the out-of-plane (τ) mode of $H^{10}BF_2$ ($D^{10}BF_2$) and of $H^{11}BF_2$ ($D^{11}BF_2$).

B_1 Modes

The B_1 modes will have bands without resolvable fine structure and will show the envelopes of the P, Q, and R branches. The frequency of the B–F asymmetric stretching mode (d_a) is expected to be near to that of the corresponding mode in CH_3BF_2 (1363 cm^{-1}). In the spectra of H–BF_2, we can thus assign the triplet with a central peak at 1402 cm^{-1} to the d_a mode of the molecule with ^{11}B (the triplet with central peak at 1455 cm^{-1} observed by Coyle *et al.*[6] can be assigned to the d_a mode of the ^{10}B isotope). The spectrum of

TABLE III. Calculated and observed spectra and assignments.[a]

	Coyle *et al.*[b]		This work[c]			
	$H^{11}BF_2$	$H^{10}BF_2$	$H^{11}BF_2$	$H^{10}BF_2$	$D^{11}BF_2$	$D^{10}BF_2$
1	1176, 1145	···	Obs 1166	···	1128	···
			Calc 1168	···	1126	··
2	2631, 2607	2645[d]	Obs 2620	···	1962	···
			Calc 2618	···	1961	···
3	555, 530	···	Obs 545	···	540	···
			Calc 544	···	538	···
4	1417, 1405, 1392	1462, 1455, 1449	Obs 1402	···	1392	1419
			Calc 1408	1455	1375	1426
5	1200[d]	···	Obs 1200[d]	···	887[e]	···
			Calc 1186	1190	887	887
6	924	944	Obs 924	944	790	810
			Calc 925	944	789	810

[a] All frequencies are given in cm^{-1}.
[b] Peak positions reported in Ref. 6.
[c] Band centers are given.
[d] Doubtful assignments.
[e] Deduced by applying the product rule.

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[12] H. J. Becher, Z. Anorg. Allgem. Chem. **291**, 151 (1957).

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TABLE IV. Jacobian matrices.[a]

	$H^{11}BF_2$			$D^{11}BF_2$		
j	$i=2$	$i=1$	$i=3$	$i=2$	$i=1$	$i=3$
11	97	50	2	52	62	1
12	316	−56	−7	206	−38	−6
13	73	−186	50	95	−184	40
22	258	15	7	205	6	8
23	119	103	−100	189	56	−106
33	14	172	346	43	137	347

	$H^{11}BF_2$		$D^{11}BF_2$		$H^{10}BF_2$		$D^{10}BF_2$	
j	$i=4$	$i=5$	$i=4$	$i=5$	$i=4$	$i=5$	$i=4$	$i=5$
44	91	28	114	4	100	23	118	4
45	−561	321	−385	135	−560	306	−401	136
55	869	926	325	1031	788	1019	341	1029

[a] The elements are defined by $J_{ij}=\partial\nu_i/\partial F_j$.

D–BF_2 shows this band shifted to 1392 cm^{-1} and also a peak at 1419 cm^{-1} assigned to the Q branch of the d_a mode of the ^{10}B isotope.

It is not obvious where we should expect the band of the H–B–F bending mode (a), since there are no ir studies of other molecules with modes involving a H–B–F bending. As a first try, we can deduce a likely frequency for this mode, applying the product rule between the equivalent B_1 modes of CH_3BF_2 and HBF_2. This gave us a value of $\approx$1100 cm^{-1} for the a mode in H–B–F, and led us to assign the shoulder at $\approx$1200 cm^{-1} in the spectra of HBF_2 to this mode. This band should shift by a factor of $\approx$0.7 when deuterating the molecule. Unfortunately, we could not see this band in the spectra of DBF_2, which makes this the only uncertain feature of our assignment.

FORCE CONSTANTS

We made a force-constant calculation using Lindeman and Wilson's[13] general force field and their symmetry coordinates, modifying the angular coordinates by multiplication by $(d_0D_0)^{\frac{1}{2}}$ and changing the signs of F_{45} and G_{45}.[14] We used frequencies uncorrected for anharmonicity, since we observed only fundamentals.

The out-of-plane mode gave us directly four values of f_τ, the mean of which is given in Table V. They agree very well, considering the uncertainty in the molecular parameters and anharmonicity. The mean value of f_τ, 0.772 mdyn/Å, is smaller than for BF_3, 0.866 mdyn/Å, as can be expected from the likely reduction of conjugated π bonding in going from BF_3 to HBF_2.

For the other species, we started with the set of force constants deduced for CH_3BF_2. We found a suitable set of elements of the F matrix after calculating the Jacobian matrix J ($J_{ij}=\partial\nu_i/\partial F_j$) and adjusting the F's by inspection of the system of linear equations

$$J\Delta F=\Delta\nu.$$

We felt that there was no justification for a least-squares refinement since: (a) the number of assigned frequncies (11) is nearly equal to the number of independent F's (9); (b) the data are not corrected for anharmonicity; (c) the frequency of the H–B–F mode is critical in determining the elements of the F elements

TABLE V. Force constants (millidynes per angstrom).

	f_d:	f_d'	f_τ	f_D	f_{Dd}			
HBF_2	6.625	0.725	0.772	3.66	0.37			
BF_3[a]	7.221	0.802	0.866					
	F_{11}	F_{12}	F_{13}	F_{22}	F_{23}	F_{33}	F_{44}	F_{45}	F_{55}
HBF_2	6.60	−1.56	0.12	4.40	0.10	0.64	5.90	0.27	0.37

[a] See Ref. 13.

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[13] L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).

[14] We had to recalculate the elements of F and G due to the typographical errors in Lindeman and Wilson's paper.

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of symmetry B_1; and (d) inspection of J shows that isotopic data alone are not sufficient to fix the force constants of the A_1 and B_1 species uniquely, as is also the case for a number of other molecules.[15] It is necessary to use centrifugal stretching constants and/or Coriolis interaction constants to fix the general force field constants uniquely.

We also tried a Urey–Bradley potential with two of its eight constants fixed by the relation

$$-0.25 < F'/F < 0,$$

but we could not reach a good enough agreement between ν_{obs} and ν_{calc}.

The calculated frequencies are given in Table III, the elements of the Jacobian are given in Table IV, and the F matrix and force constants that are determined univocally from the F matrix are given in Table V. We could not compare our results with those of $(CH_3)BF_2$ because Becher[12] used a restricted potential to calculate the force constants. The force constants estimated for $HBCl_2$[2] are too uncertain to use them to compare the pair $HBCl_2$–BCl_3 and the pair HBF_2–BF_3. The comparison with BF_3 (Table V) shows clearly that the stretching force constants for B–F is smaller in HBF_2, indicating weaker bonding.

ACKNOWLEDGMENTS

Part of the equipment used in this work was obtained with a Ford Foundation Grant. The Argentine Atomic Energy Commission provided us with D_2. We are indebted to Ing. E. Silbermann for helpful discussion and assistance in the use of the spectrometer. Dr. G. Videla, Dr. S. B. de Rietti, and J. Lombardo have had a great part in enabling us to obtain the compounds.

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[15] J. L. Duncan and I. M. Mills, Spectrochim. Acta **20**, 523 (1964).

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Infrared Absorption by Symmetrical NO_3 Free Radical in the Gas Phase*

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(Received 8 April 1965)

A new infrared absorption band between 1325 and 1375 cm^{-1} has been observed in the N_2O_5–O_3 system at low pressure in an 80-m path-length cell. In such systems the presence of the symmetrical NO_3 free radical is well known in terms of its visible absorption spectrum, which varies in the unusual way of $K_{ss}[N_2O_5]^{\frac{1}{3}}[O_3]^{\frac{1}{3}}$. The new infrared band lies at a frequency just below that for the antisymmetric stretch of the symmetrical planar nitrate ion; the absorption optical density varies as $[N_2O_5]^{\frac{1}{3}}[O_3]^{\frac{1}{3}}$; and the new absorption has been assigned to the symmetrical NO_3 free radical.

INTRODUCTION

The kinetics of the N_2O_5-catalyzed decomposition of O_3 is well understood.[1,2] Dinitrogen pentoxide catalyzes the decomposition of ozone according to the rate equation

$$-d[O_3]/dt = k[N_2O_5]^{\frac{2}{3}}[O_3]^{\frac{2}{3}}, \tag{1}$$

which is quantitatively explained by the mechanism[1a]

$$N_2O_5 \underset{B(M)}{\overset{A(M)}{\rightleftarrows}} NO_2+NO_3,$$

$$NO_2+O_3 \xrightarrow{h} NO_3+O_2,$$

$$2NO_3 \xrightarrow{g} 2NO_2+O_2. \tag{2}$$

Both nitrogen dioxide and the symmetrical NO_3 free radical are low-concentration intermediates in this system. These intermediates are related to the catalyst N_2O_5 by the equilibrium constant

$$K = A(M)/B(M) = [NO_2][NO_3]/[N_2O_5]. \tag{3}$$

In the N_2O_5–O_3 system the steady-state concentration

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