The Urey-Bradley Force Constants of Boron Halides and their Transferability

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The infrared and Raman spectra of several boron trihalides have been recorded[1-9] and their Urey-Bradley force constants[10], except for those of boron triiodide, have already been calculated.

We have now recalculated the force constants of the boron trihalides BX_3 (X: F, Cl, Br and I) by using the most probable observed values of the fundamental frequencies of ^{10}B and ^{11}B compounds as a means of studying the transferability of force constants from boron trihalides to boron mixed halides.

The force constants for boron mixed halides were estimated by applying the usual additive property[11] to the recalculated values for boron trihalides.

The calculated values of the normal vibrational frequencies of boron mixed halides were obtained by using these constants and were compared with the observed values[7].

Calculations

The boron trihalides have a planar configuration and belong to the point group D_{3h}[12]. These tetraatomic molecules have six normal modes of vibration, of which two are degenerate; $\nu_1(A_1')$, $\nu_2(A_2'')$, $\nu_3(E')$ and $\nu_4(E')$. The A_1' mode is active only in the Raman and the A_2'' only in infrared spectra, while the doubly degenerate E' vibrations are both infrared and Raman active.

Unfortunately we have no configuration data for boron mixed halides. If the boron mixed halides of the BX_2Y type are assumed to have a planar configuration, they belong to the point group C_{2v}. All six normal modes, thus, are nondegenerate; $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(A_1)$, $\nu_4(B_2)$, $\nu_5(B_1)$ and $\nu_6(B_1)$. All the vibrations are both infrared and Raman active.

In this paper, only the in-plane vibrations (BX_3; A_1' and E', BX_2Y; A_1 and B_1) are described.

The following symmetry coordinates are used for the transformation into the factored ***F*** and ***G*** matrices defined by Wilson[13]:

For BX_3 molecules;

$$A_1'; \quad S_1=(\Delta r_1+\Delta r_2+\Delta r_3)/\sqrt{3}$$

$$E'; \quad S_3=(2\Delta r_1-\Delta r_2-\Delta r_3)/\sqrt{6}$$

$$S_4=(2\Delta\alpha_{23}-\Delta\alpha_{12}-\Delta\alpha_{13})/\sqrt{6}$$

For BX_2Y molecules;

$$A_1; \quad S_1=(\Delta R_1+\Delta r_2+\Delta r_3)/\sqrt{3}$$

$$S_2=(2\Delta R_1-\Delta r_2-\Delta r_3)/\sqrt{6}$$

$$S_3=(2\Delta\beta_{23}-\Delta\alpha_{12}-\Delta\alpha_{13})/\sqrt{6}$$

$$B_1; \quad S_5=(\Delta r_2-\Delta r_3)/\sqrt{2}$$

$$S_6=(\Delta\alpha_{12}-\Delta\alpha_{13})/\sqrt{2}$$

The internal coordinates used in boron trihalides and boron mixed halides are shown in Fig. 1.

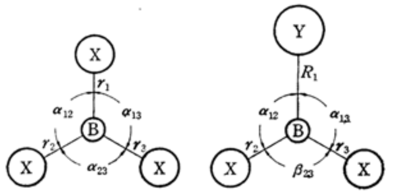

Fig. 1. Definition of internal coordinates for BX_3 and BX_2Y molecules.

The Urey-Bradley force constants of boron trihalides can be calculated uniquely by using the three observed values of fundamental frequencies (ν_1, ν_3 and ν_4) which are listed in Table I.

In the calculation, the force constant F' is

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10) T. Shimanouchi, Private communication, "Force constants of small molecules", (1962), p. 10. (Department of Chemistry, Faculty of Science, The Universtiy of Tokyo, Tokyo, Japan)

11) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

12) J. H. M. Bowen, "Tables of Interatomic Distances and Configuration in Moleculer and Ions", M 17, The Chemical Society, Burlington House, W. 1, London (1958).

13) E. B. Wilson, *J. Chem. Phys.*, **9**, 76 (1941).

TABLE I. TRIHALIDE FREQUENCIES USED TO CALCULATE FORCE CONSTANTS (cm^{-1})

	ν_1	ν_3	ν_4
$^{10}BF_3$[a]	888	1505	482
$^{11}BF_3$[a]	888	1454	480
$^{10}BCl_3$[a]	471	994	—
$^{11}BCl_3$[a]	471	954	243
$^{10}BBr_3$[b]	278	856	150
$^{11}BBr_3$[b]	278	820	150
$^{10}BI_3$[b]	190	737	100
$^{11}BI_3$[b]	190	704	100

a) From Ref. 7
b) From Ref. 9

assumed to be equal to $-0.1\,F$, as usual[11], and the following molecular constants which have been previously reported are used; $r(B\text{–}F)=1.295\,\text{Å}$[14], $r(B\text{–}Cl)=1.73\,\text{Å}$[12], $r(B\text{–}Br)=1.87\,\text{Å}$[15] and $r(B\text{–}I)=2.10\,\text{Å}$[9], while all bond angles$=120°$[12,14,15].

For boron triiodide, the tentative values which had been proposed by Wentink and Tiensuu[9] were used because there are no experimental values.

The force constants calculated for each boron trihalide to fit the most probable fundamental frequencies are shown in Table II.

In Table II, the force constants for the ^{10}B compound of boron trichloride are not given because the frequency ν_4 for this molecule has not been observed, as is shown in Table I.

TABLE II. FORCE CONSTANTS OF BORON TRIHALIDES (10^5 dyn./cm.)

	K	H	F
$^{10}BF_3$	6.032	0.210	0.932
$^{11}BF_3$	6.051	0.212	0.925
$^{10}BCl_3$	—	—	—
$^{11}BCl_3$	3.022	0.055	0.537
$^{10}BBr_3$	2.401	0.058	0.412
$^{11}BBr_3$	2.406	0.059	0.411
$^{10}BI_3$	1.838	0.042	0.287
$^{11}BI_3$	1.838	0.041	0.287

TABLE III. ESTIMATED FORCE CONSTANTS FOR BORON MIXED HALIDES (10^5 dyn./cm.)

K(B–F)	6.051	H(F–B–F)	0.212	F(F⋯F)	0.925
K(B–Cl)	3.022	H(F–B–Cl)	0.134	F(F⋯Cl)	0.731
K(B–Br)	2.406	H(F–B–Br)	0.136	F(F⋯Br)	0.668
K(B–I)	1.838	H(F–B–I)	0.127	F(F⋯I)	0.606
		H(Cl–B–Cl)	0.055	F(Cl⋯Cl)	0.537
		H(Cl–B–Br)	0.057	F(Cl⋯Br)	0.474
		H(Cl–B–I)	0.048	F(Cl⋯I)	0.412
		H(Br–B–Br)	0.059	F(Br⋯Br)	0.411
		H(Br–B–I)	0.050	F(Br⋯I)	0.349
		H(I–B–I)	0.041	F(I⋯I)	0.287

It may be seen in Table II that the values for ^{10}B and ^{11}B compounds are approximately equal, as was expected. The force constants of boron mixed halides are estimated by applying

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES OF BORON MIXED HALIDES (cm^{-1})

		ν_1	ν_2	ν_3	ν_5	ν_6
$^{10}BF_2Cl$	Obs.	1286	701	—	1470	366
	Calcd.	1265	708	428	1485	367
$^{11}BF_2Cl$	Obs.	1242	696	427	1421	366
	Calcd.	1223	703	428	1428	365
$^{10}BF_2Br$	Obs.	1247	637	—	1468	—
	Calcd.	1228	646	363	1483	339
$^{11}BF_2Br$	Obs.	1208	632	—	1417	—
	Calcd.	1188	639	363	1431	337
$^{10}BF_2I$	Obs.	—	—	—	—	—
	Calcd.	1197	615	326	1480	322
$^{11}BF_2I$	Obs.	—	—	—	—	—
	Calcd.	1161	608	325	1428	320
$^{10}BCl_2F$	Obs.	1355	—	—	1031	—
	Calcd.	1360	575	268	1035	376
$^{11}BCl_2F$	Obs.	1312	—	—	993	—
	Calcd.	1315	571	267	993	375
$^{10}BCl_2Br$	Obs.	916	—	—	991	—
	Calcd.	915	409	214	991	208
$^{11}BCl_2Br$	Obs.	878	405	218	951	—
	Calcd.	878	409	213	952	207
$^{10}BCl_2I$	Obs.	—	—	—	—	—
	Calcd.	854	378	196	985	185
$^{11}BCl_2I$	Obs.	—	—	—	—	—
	Calcd.	820	377	196	946	185
$^{10}BBr_2F$	Obs.	1344	—	—	901	—
	Calcd.	1342	442	178	915	324
$^{11}BBr_2F$	Obs.	1302	—	—	862	—
	Calcd.	1298	439	178	876	324
$^{10}BBr_2Cl$	Obs.	954	—	—	864	—
	Calcd.	952	346	166	860	192
$^{11}BBr_2Cl$	Obs.	918	—	—	827	195
	Calcd.	913	346	166	824	192
$^{10}BBr_2I$	Obs.	—	—	—	—	—
	Calcd.	834	230	141	850	128
$^{11}BBr_2I$	Obs.	—	—	—	—	—
	Calcd.	798	230	141	813	128
$^{10}BI_2F$	Obs.	—	—	—	—	—
	Calcd.	1319	378	123	818	302
$^{11}BI_2F$	Obs.	—	—	—	—	—
	Calcd.	1277	374	123	782	302
$^{10}BI_2Cl$	Obs.	—	—	—	—	—
	Calcd.	916	287	118	750	170
$^{11}BI_2Cl$	Obs.	—	—	—	—	—
	Calcd.	880	286	118	717	170
$^{10}BI_2Br$	Obs.	—	—	—	—	—
	Calcd.	812	220	108	746	124
$^{11}BI_2Br$	Obs.	—	—	—	—	—
	Calcd.	777	220	108	713	124

The observed values are cited from the Ref. 7.

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14) A. H. Nielsen, ibid., **22**, 659 (1954).
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the usual additive property to the constants for ^{11}B compounds of boron trihalides.

The bending force constant, H, and the repulsive force constant, F, are evaluated from the following equation;

$$H(\mathrm{X{-}B{-}Y}) = [H(\mathrm{X{-}B{-}X}) + H(\mathrm{Y{-}B{-}Y})]/2$$

$$F(\mathrm{X}\cdots\mathrm{Y}) = [F(\mathrm{X}\cdots\mathrm{X}) + F(\mathrm{Y}\cdots\mathrm{Y})]/2$$

The stretching force constant, K, is assumed to be equal to one in boron trihalides.

The values estimated for boron mixed halides are shown in Table III.

The normal vibrational frequencies of boron mixed halides are calculated by using these constants.

The molecular constants for these compounds have not been given. Since it may be assumed that the nature of bonds of these molecules does not differ greatly from that of boron trihalides, their values are taken from those of the boron trihalides.

Results

It has been described how Urey-Bradley potential function is quite suitable for calculating the normal vibrational frequencies of saturated hydrocarbons and their halogen compounds[11].

Making use of this function with reference to boron halides, we have obtained a good agreement between the observed and the calculated values of vibrational frequencies for boron mixed halides, as Table IV shows.

The frequencies for ν_4 corresponding to the out-of-plane bending vibration are omitted in Table IV.

The greatest difference between the observed and the calculated values was about ±2%, while the average deviation was about ±1%.

It has thus been found that the transferability of Urey-Bradley force constants from boron trihalides to boron mixed halides was reasonable and that the error due to the assumed planar configuration and molecular constants of boron mixed halides had no great effect to the transferability of the force constants.

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