

Force constants, coriolis constants, vibrational amplitudes and shrinkage effects of some linear triatomic systems

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Force constants employing GVFF model have been evaluated for linear thioborine (HBS). The frequencies for the five isotopes have been calculated applying isotopic substitution rule. Coriolis constants ($\Sigma^+X\pi$ type) for six isotopes of thioborine have been calculated. Mean amplitudes of vibration and Bastiansen-Morino shrinkage effects at three temperatures, viz., 0°K, 298·15°K and 500°K, have also been calculated for six isotopes of HBS and linear magnesium dihalides, MgX_2 ($X = F, Cl, Br, I$) and the trends are discussed.

1. INTRODUCTION

The nature of bonding and structure about the unstable species can be beautifully understood by high resolution and matrix isolation techniques. Sams & Maki (1975) on the basis of gas phase-high resolution infrared absorption spectrum of linear thioborine (HBS) determined the unobserved vibrational fundamentals (ν_2 and ν_3) using force constants and observed fundamental ν_1 . The infrared and Raman spectra of matrix isolated magnesium dihalides have been interpreted assuming linear structure by Lesiecki & Nibler (1976). The present paper reports the force constants, Coriolis coupling constants, mean amplitudes of vibration and Bastiansen-Morino shrinkage effects using these complete and accurate fundamental frequencies of HBS and its six isotopes and MgX_2 (X halogens). Wilson's FG matrix method (1955) has been used to calculate the force constants employing GVFF model. The G and F matrices are taken from literature (Cyvin 1968). The mean amplitudes of vibration have been calculated using Cyvin's secular equation (1968) $|\Sigma G^{-1} - \Delta E| = 0$. L-F approximation method (Pandey *et al* 1976) has been followed to solve the 2×2 determinant occurring in Σ^+ species. The expressions for computing Coriolis constants and Bastiansen-Morino shrinkage effects are taken from literature (Cyvin 1968).

Table 1. GVFF constants (in mdyn/Å) of linear thioborine

Molecule	K_{B-H}	K_{B-S}	K_c	K'
H ¹¹ B ³² S	4.2130	7.3367	0.2538	0.5653
	4.08 ± 0.42 ^a	6.95 ± 0.64 ^a	0.253 ± 0.058 ^a	-0.45 ± 0.15 ^a

^a-Values from Sams and Maki (1975).

Table 2. Comparison of observed and calculated frequencies (in cm⁻¹) of linear thioborine.

Molecule		Observed ^a	Calculated
H ¹¹ B ³² S	ν_1	2768.5	2768.5
	ν_2	1194	1194
	ν_3	635	635
H ¹⁰ B ³² S	ν_1	2784.2	2780.5
	ν_2	1234	1232.4
	ν_3	641	641.7
H ¹¹ B ³⁴ S	ν_1	2768.4	2768.5
	ν_2	1185	1184.4
	ν_3	634	634.7
H ¹⁰ B ³⁴ S	ν_1	2784.1	2780.5
	ν_2	1225	1223.1
	ν_3	641	641.4
D ¹¹ B ³² S	ν_1	2080	2054.6
	ν_2	1151	1151.1
	ν_3	497	497.2
D ¹⁰ B ³² S	ν_1	2106	2076.3
	ν_2	1184	1181.1
	ν_3	505	505.7

^a-Frequencies from Sams and Maki (1975).

The computed force constants for HBS are compared with the values reported by Sams & Maki (1975) in Table-1, where K represents stretching, K_c the bending the K' the interaction force constants. The frequencies calculated for other five isotopes, using these constants, are compared with the original frequencies (Sams & Maki 1975) in Table-2 and it is found that the calculated frequencies are well comparable, which proves the reliability of force constants. Table-3 includes the mean amplitudes of vibration, Coriolis constants and shrinkage effects of thioborine and magnesium dihalides at three temperatures viz. 0°K, 298.15°K and 500°K. From Table-3, it is observed that the mean amplitudes for thioborine for bonded atom-pairs B-H and B-S differ considerably.

Table 3. Mean amplitudes of vibration (in Å) Shrinkage effect (in Å) and Coriolis constants ($\Sigma^+X\pi$ type) of linear thioborine and magnesium dihalides.

Molecule	Mean amplitudes of vibration			Shrinkage Effect δ_{H-S} or δ_{X-X}	Coriolis Constant $\zeta(\Sigma^+X\pi$ type)
	σ_{B-H} or σ_{Mg-X}	σ_{H-S} or σ_{X-X}	σ_{B-S}		
H ¹¹ B ³² S	0°K	0.0812	0.0846	0.0408	0.976
	298.15°K	0.0812	0.0846	0.0409	
	500°K	0.0812	0.0852	0.0421	
H ¹⁰ B ³² S	0°K	0.0813	0.0844	0.0415	0.975
	298.15°K	0.0813	0.0844	0.0416	
	500°K	0.0813	0.0850	0.0427	
H ¹¹ B ³⁴ S	0°K	0.0812	0.0844	0.0406	0.976
	298.15°K	0.0812	0.0845	0.0407	
	500°K	0.0812	0.0851	0.0419	
H ¹⁰ B ³⁴ S	0°K	0.0813	0.0843	0.0413	0.975
	298.15°K	0.0813	0.0844	0.0414	
	500°K	0.0813	0.0849	0.0425	
D ¹¹ B ³² S	0°K	0.0690	0.0706	0.0412	0.963
	298.15°K	0.0690	0.0707	0.0413	
	500°K	0.0691	0.0716	0.0426	
D ¹⁰ B ³² S	0°K	0.0690	0.0703	0.0420	0.962
	298.15°K	0.0690	0.0703	0.0421	
	500°K	0.0692	0.0711	0.0433	
MgF ₂	0°K	0.0464	0.0568	0.0052
	298.15°K	0.0482 (3.226) ^a	0.0609	0.0096
	500°K	0.0533	0.0700	0.0150
MgCl ₂	0°K	0.0477	0.0540	0.0092
	298.15°K	0.0533 (2.048) ^a	0.0666	0.0416
	500°K	0.0623	0.0815	0.0691
MgBr ₂	0°K	0.0463	0.0462	0.0084
	298.15°K	0.0559 (1.669) ^a	0.0693	0.0432
	500°K	0.0674	0.0877	0.0718
MgI ₂	0°K	0.0465	0.0424
	298.15°K	0.0590 (1.454) ^a	0.0726
	500°K	0.0719	0.0928

(X = F, Cl, Br, I).

+ Stretching force constants (in mdyne/Å) from Lesiecki and Nibler (1976).

This difference is because of the significant difference in the respective force constants K_{B-H} and K_{B-S} respectively (Table 1). It is also inferred from Table-3

that mean amplitudes for thioborine do not vary with temperature upto 500°K which is due to the strong chemical bondings. The mean amplitudes show variation only when H-atom is replaced by deuterium (D), i.e., the replacement of B or S isotopes, does not affect the mean amplitudes of vibration. The Bastiansen-Morino shrinkage effect shows the usual trend of vibration with temperature. An inspection of the values of mean amplitudes for magnesium dihalides at room temperature ($T = 298.15^\circ\text{K}$) shows that they increase with the mass of halogen atoms, whereas the corresponding stretching force constant (included in Table 3) decreases, which favours this trend. Further, the mean amplitudes for magnesium dihalides (Table 3) show the usual trend of variation with temperature.

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