Vibrational Properties of Bismutine, BiH_3

Enrique J. Baran

Centro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina

Reprint requests to Prof. Dr. E. J. B.; Fax: (54) 0221 4259485; E-mail: baran@quimica.unlp.edu.ar

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Structural and vibrational-spectroscopic data of BiH_3 have recently been reported for the first time. On the basis of these data the force constants, mean amplitudes of vibration and thermodynamic functions have been calculated. Some comparisons with the structurally related SbH_3 molecule are made.

Key words: BiH_3; SbH_3; Force Constants; Mean Amplitudes of Vibration; Bond Properties; Thermodynamic Functions.

Bismutine, BiH_3, is the least stable of the group-15 trihydrides. F. Paneth first detected it in minute traces in 1918 using a radiochemical technique involving $^{212}Bi_2Mg_3$ [1]. The best preparation method seems to be the one proposed by Amberger in 1961, based on the disproportionation of CH_3BiH_2 at -45 °C [2]. This relatively complex synthesis has recently been successfully reproduced and allowed to obtain the vibrational and rotational spectra of BiH_3 [3]. Using the spectroscopic and structural data reported in this study, we have now performed the calculation of the most important vibrational properties and thermodynamic functions of this molecule. For comparative purposes, similar calculations have also been made for SbH_3, the immediately adjacent lower-mass trihydride in group-15 of the Periodic System.

It is expected that on going from NH_3 to BiH_3 an increase of the p-orbital character in the three bonding orbitals occurs, generating a stepwise diminution of the respective bond angle [4]. This expectation is clearly fulfilled, as BiH_3 presents the lowest bond angle (90.48°) [3], even lower as that of SbH_3 (91.55°) [5]. This means that in the vibrational ground state BiH_3 is an oblate symmetric top molecule ($I_a = I_b < I_c$) close to a spherical top ($I_a = I_b = I_c$), even more than SbH_3.

A parameter that can be used to quantify the spherical character of an oblate top molecule is the relation between the rotational constants C and B, i.e., $\gamma = (C_c - B_c)/1/2(C_c + B_c)$ [5]. Bismutine with $\gamma = -0.015$ represents the most quasi-spherical oblate top so far investigated, whereas for stibine $\gamma = -0.052$.

Table 1. Force constants (mdyn/Å) of BiH_3 and SbH_3.

	f_r	f_{rr}	f_α	$f_{\alpha\alpha}$
BiH_3	1.79	0.01	0.16	−0.003
SbH_3	2.11	−0.002	0.19	−0.005

For the calculation of force constants the geometrical and vibrational data reported by Jerzembeck et al. [3] were used. **G**- and **F**-matrixes were constructed as detailed in [6] and a modified valence force field (MVFF) ($F_{12} = F_{34} = 0$) was employed. Results of this calculation are shown in Table 1, in which f_r refers to the Bi-H bonds and f_α to the H-Bi-H angle, whereas f_{rr} and $f_{\alpha\alpha}$ refer to the bond/bond and angle/angle interactions, respectively.

A similar calculation was performed for SbH_3. In this case the structural parameters and vibrational frequencies were taken from the paper of Fusina et al. [5] (cf. also [7]). The results are included in Table 1.

As can be seen, Sb-H bonds are somewhat stronger than Bi-H bonds, whereas the deformational constants are comparable. In both cases interaction constants are negligible. The potential energy distribution of both molecules showed that all the vibrations are highly characteristic, as expected for species with heavy central atoms.

With the now obtained results it is interesting to compare the bond characteristics of the full series of the trihydrides of group-15 elements. A plot of the force constants of the X-H bonds as a function of the atomic number is presented in Fig. 1 (the force constants of the three lighter trihydrides were taken from the book of Siebert [8]). From this figure it becomes

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Table 2. Mean vibration amplitudes (in Å) of BiH_3 and SbH_3.

Tempera-ture (K)	BiH_3		SbH_3	
	u_{Bi-H}	$u_{H...H}$	u_{Sb-H}	$u_{H...H}$
0	0.0984	0.179	0.0944	0.171
100	0.0984	0.179	0.0944	0.171
200	0.0984	0.180	0.0944	0.171
298.16	0.0985	0.183	0.0944	0.173
300	0.0985	0.183	0.0944	0.173
400	0.0986	0.188	0.0945	0.177
500	0.0991	0.195	0.0948	0.183
600	0.1000	0.204	0.0954	0.190
700	0.1013	0.212	0.0963	0.197
800	0.1030	0.221	0.0976	0.204
900	0.1048	0.230	0.0991	0.212
1000	0.1069	0.239	0.1008	0.220

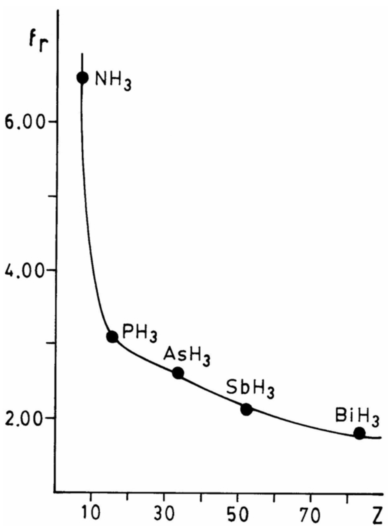

Fig. 1. X-H force constant f_r (in mdyn/Å) of the X-H bond as function of the atomic number (Z) of the group-15 trihydrides.

evident that with increasing p-orbital character of the bonds, which occurs with increasing Z-values, a continuous diminution of the X-H bond strength takes place. The comparatively high value of ammonia is clearly supported by the involvement of the sp^3 hybrid orbital from the N-atom in bonding, and this is the only trihydride of this group in which this hybrid orbital is used (NH_3 bond angle = 107° [4, 9]). Already in the next compound of the series, PH_3, the s-contribution can be considered as practically negligible (PH_3 bond angle = 94° [4, 9]). In going from the second row elements to higher rows, the bonding overlap is mainly concentrated on the p orbitals, were the s electron density is concentrated into the lone pair regions [9].

Table 3. Statistical thermodynamic functions of BiH_3 and SbH_3 (values in cal/deg.mole).

T(K)	C_p	$(H^0-H_0^0)/T$	$-(G^0-H_0^0)/T$	S^{00}
BiH_3:				
100	7.96	7.95	40.22	48.17
200	8.77	8.10	45.76	53.86
298.16	10.30	8.57	49.08	57.65
300	10.32	8.58	49.13	57.71
400	11.80	9.21	51.68	60.89
500	13.11	9.86	53.80	63.66
600	14.22	10.49	55.66	66.15
700	15.15	11.10	57.32	68.42
800	15.91	11.65	58.84	70.49
900	16.62	12.16	60.24	72.40
1000	17.02	12.62	61.55	74.17
1100	17.42	13.04	62.77	75.81
1200	17.74	13.42	63.92	77.34
SbH_3:				
100	7.96	7.95	38.38	46.33
200	8.54	8.05	43.91	51.96
298.16	9.89	8.43	47.19	55.61
300	9.91	8.43	47.24	55.67
400	11.30	8.98	49.74	58.72
500	12.56	9.57	51.81	61.38
600	13.67	10.17	53.60	63.77
700	14.61	10.74	55.21	65.95
800	15.41	11.27	56.68	67.96
900	16.06	11.77	58.04	69.81
1000	16.60	12.23	59.30	71.53
1100	17.04	12.64	60.49	73.13
1200	17.41	13.03	61.61	74.63

For a wider characterization of the metal-hydrogen bonds the mean amplitudes of vibration of BiH_3 and SbH_3 were also calculated. These calculations were performed with the method of characteristic vibrations of Müller et al. [10] (cf. also [11, 12]). The obtained results, in the temperature range between 0 and 1000 K, are shown in Table 2.

The mean amplitudes for the metal-hydrogen bonds show the expected trend; i.e., they are lower in the case of SbH_3, as this molecule presents the higher bond force constant. Interestingly, both hydrides present relatively low temperature dependencies, and this dependency is also lower in the case of stibine. On the other hand, and as expected, the calculated mean amplitudes are somewhat higher than those of AsH_3 [11], PH_3 [11] and NH_3 [13], which present stronger bond force constants (cf. Fig. 1). Regarding the amplitudes for the non bonded H···H pairs, they lie also slightly higher in bismutine.

Finally, we have calculated the thermodynamic functions, in a wide temperature range, for the ideal gaseous state (unit fugacity) using the rigid rotator, harmonic oscillator approximation [14, 15]. The moments of inertia were calculated with the MOLDRAW program [16]. The symmetry number is 3.

The results, specific heat (C_p), reduced enthalpy $[(H^0 - H_0^0)/T]$, reduced free enthalpy $[(G^0 - H_0^0)/T]$ and entropy (S^0), in the temperature range between 100 and 1200 K, are presented in Table 3. A comparison of the tabulated data shows comparable values for the thermodynamic functions of both species which are, as expected, slightly higher in the case of BiH_3 in the whole temperature range.

To conclude, these calculations provide a first insight into the most important vibrational properties of BiH_3, the heaviest group-15 trihydride, and show that this molecule follows very well the expected general trends, when compared with its lighter congeners [9].

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