Vibrational Properties of Hydrogen Astatide, HAt

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A number of theoretical studies on the bond characteristics of HAt, the heaviest hydrogen halide, have recently been reported. On the basis of these data the force constant, mean amplitudes of vibration and thermodynamic functions of this molecule have been calculated. Some comparisons with the related lighter hydracids are made.

Key words: HAt; Force Constant; Mean Amplitudes of Vibration; Thermodynamic Functions.

Astatine ($Z = 85$) is the heaviest member of the elements of group 17 of the Periodic System (halogens). About 20 isotopes are known, and some of them have been identified as short-lived products in the natural radioactive series. The longest-lived isotope is ^{210}At with a half-life of only 8.3 hours. Consequently, macroscopic quantities of this element cannot be accumulated. Our knowledge on its chemistry is mainly based on tracer studies, which show that it behaves in the manner one would expect, by extrapolation from the other halogens [1, 2].

Hydrogen astatide, HAt, is therefore the heaviest hydrogen halide. Although its formation has been detected mass spectroscopically [1], no other experimental studies on its physical and chemical behavior could be undertaken. Notwithstanding, in recent years a number of theoretical studies, has been performed on this molecule [3 – 5]. Therefore, it seems interesting to explore with more detail its vibrational properties and to establish correlations with the other hydrogen halides.

The bond distance, dissociation energy and harmonic frequency for HAt have been calculated on the basis of different theoretical frameworks and at different degrees of sophistication, using relativistic and non-relativistic approaches [3 – 5]. For most of our purposes the knowledge of the harmonic frequency is of central importance. A thorough analysis of the available data shows that the most reasonable values lie between 2155 and 2185 cm^{-1} [3 – 5]. Force constants calculated with these two extreme figures only differ by about 3%. Thus, in all the calculations we have used
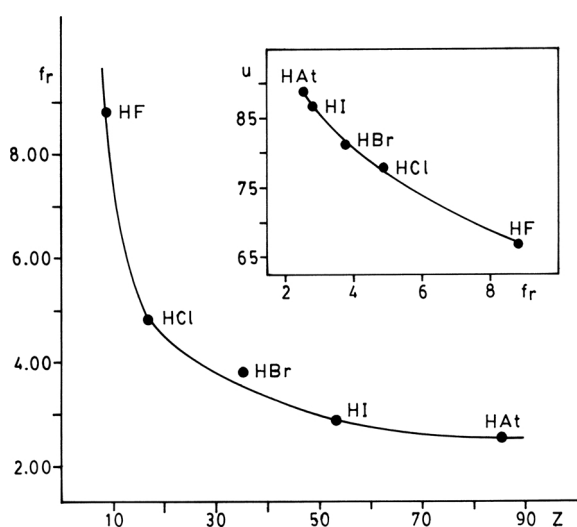

Fig. 1. H-X force constant f_r (in mdyn/Å) for the hydrogen halides as a function of the atomic number (Z) of the halogen atom. **Inset:** Mean amplitudes of vibration (u) $\times 10^3$ (in Å, at 298.16 K) as a function of the force constants f_r (in mdyn/Å) of the hydrogen halides.

the value of 2155 cm^{-1} for the stretching frequency of the H-At bond. The corresponding bond length can be estimated to lie at about 1.70 Å. For the atomic mass of At, a value of 209.9871 [5] has been used in all the performed calculations.

Using the mentioned harmonic frequency and the well-known "two-masses model" [6] a value of 2.74 mdyn/Å can be calculated for the force constant of the H-At bond. As can be seen from Fig. 1 this value correlates very well with those corresponding to the

Table 1. Mean amplitudes of vibration (in Å) for the hydrogen halides in the temperature range between 0 and 1000 K.

T (K)	HF	HCl	HBr	HI	HAt
0	0.0668	0.0772	0.0813	0.0870	0.0883
100	0.0668	0.0772	0.0813	0.0870	0.0883
200	0.0668	0.0772	0.0813	0.0870	0.0883
298.16	0.0668	0.0772	0.0813	0.0870	0.0883
300	0.0668	0.0772	0.0813	0.0870	0.0883
400	0.0668	0.0772	0.0813	0.0870	0.0883
500	0.0668	0.0772	0.0814	0.0871	0.0885
600	0.0668	0.0773	0.0815	0.0874	0.0888
700	0.0668	0.0774	0.0818	0.0879	0.0894
800	0.0668	0.0776	0.0822	0.0886	0.0901
900	0.0669	0.0780	0.0827	0.0895	0.0912
1000	0.0670	0.0784	0.0834	0.0906	0.0924

Table 2. ν(H-X) stretching frequencies (cm^{-1}), force constants (mdyn/Å) and mean amplitudes of vibration (Å) at 298.16 K for the hydrogen halides.

	HF	HCl	HBr	HI	HAt
ν(H-X)*	3961	2886	2559	2227	2155
f(H-X)*	8.87	4.81	3.84	2.92	2.74
u(H-X)	0.0668	0.0772	0.0813	0.0870	0.0883

* all values, except those for HAt, from [7].

other four hydrogen halides (HF = 8.87; HCl = 4.81; HBr = 3.84; HI = 2.92 mdyn/Å [7]).

The mean amplitudes of vibration at different temperatures have been calculated using the relations of Kimura and Kimura [8] (cf. also [9, 10]). Using this same methodology, and in order to allow a wider insight into the vibrational characteristics of this type of compounds, we have extended these calculations to the full series of hydrogen halides. The necessary vibrational frequencies were obtained from the book of Siebert [7]. The obtained results, in the temperature range between 0 and 1000 K, are presented in Table 1.

As can be seen, these values show only a slight temperature dependence, as expected for bonds with $\omega > 2000$ cm^{-1} [11]. This dependence increases from HF to HAt, although even in this last case the increment is only 4.6% from absolute zero to 1000 K.

In Table 2 we compare the X-H stretching frequencies, mean amplitudes of vibration and force constants for the complete series of hydrogen halides. This comparison shows the expected trend, i.e., mean amplitudes of vibration become higher when force constants becomes lower [11, 12]. The inset of Fig. 1 presents the correlation between both values, which confirms

Table 3. Statistical thermodynamic functions of HAt, compared with that of HI (values in cal/deg.mole).

T(K)	C_{p}	$(H^{\mathrm{o}} - H_{\mathrm{o}}^{\mathrm{o}})/T$	$-(G^{\mathrm{o}} - G_{\mathrm{o}}^{\mathrm{o}})/T$	S^{o}
100	7.95	7.95	40.08	48.03
200	7.95	7.95	45.59	53.54
298.16	7.96	7.95	48.76	56.71
300	7.96	7.95	48.81	56.76
400	8.00	7.96	51.10	59.06
500	8.10	7.97	52.88	60.85
600	8.25	8.01	54.33	62.34
700	8.43	8.06	55.57	63.63
800	8.59	8.11	56.65	64.76
900	8.75	8.17	57.61	65.79
1000	8.89	8.24	58.48	66.72
1100	9.01	8.30	59.26	67.57
1200	9.12	8.37	59.99	68.36
1300	9.21	8.43	60.66	69.09
1400	9.29	8.49	61.29	69.78
1500	9.36	8.54	61.88	70.42
Comparison with HI values, at some selected temperatures:				
100	7.95	7.95	38.24	46.19
298.16	7.95	7.95	46.93	54.88
500	7.97	7.97	51.04	59.01
700	8.39	8.04	53.73	61.77
1000	8.85	8.22	56.63	64.85
1200	9.08	8.34	58.14	66.48
1500	9.33	8.52	60.02	68.54

the excellent correlation of all of them and additionally confirms that HAt behaves in the expected manner.

Finally, we have also calculated the thermodynamic functions for HAt, in a wide temperature range, for the ideal gaseous state (unit fugacity) using the rigid rotator, harmonic oscillator approximation [13, 14]. The symmetry number is 1. 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 1500 K, are presented in Table 3.

For comparative purposes similar calculations were performed for the closely related hydrogen iodide molecule. Values obtained at some selected temperatures are also shown in Table 3. As it can be seen, these values are comparable, and only slightly lower, than those obtained for HAt.

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