

Mean Amplitudes of Vibration of the Halogen Molecules

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Dedicated to Prof. Achim Müller on the occasion of his 65th birthday

Mean amplitudes of vibration of the halogen molecules F_2 , Cl_2 , Br_2 , and I_2 have been calculated from known spectroscopic data in the temperature range between 0 and 1000 K. The results are briefly discussed, and some comparisons with the results of the related diatomic interhalogen molecules, as well as with experimental values obtained by electron diffraction experiments, are made.

Key words: F_2 , Cl_2 , Br_2 , I_2 ; Mean Amplitudes of Vibration; Bond Properties.

During the last years, we have performed systematic calculations on the vibrational properties of simple molecules and ions containing interhalogen bonds. Surprisingly, during our literature searches we found that detailed information on the mean amplitudes of vibration of the halogen molecules themselves are not available. In the classic work of Cyvin [1] only a brief mention of these values for Cl_2 , I_2 , and $^{79}Br^{81}Br$, at two selected temperatures, are given. There is no information about F_2 [1, 2].

In order to fill this gap and to complement and extend our studies, we have now performed a calculation of the mean amplitudes of vibration of the four halogen molecules.

The calculations are relatively simple due to the fact that diatomic species present only one vibrational degree of freedom. The vibrational frequencies were taken from the book of Siebert [3]. They correspond to the gaseous F_2 , Cl_2 , and Br_2 molecules and to a chloroformic solution of I_2 . These data, together with the corresponding force constants, calculated using the “two-masses model” [4], are presented in Table 1.

According to Kimura and Kimura [5]; mean-square amplitudes of vibration for a normal coordinate with

Table 1. Vibrational frequencies (in cm^{-1}) and force constants (in $mdyn/\text{Å}$) for the halogen molecules.

Molecule(X_2)	$\nu(X-X)$	Force constant (f_{X-X})
F_2	892	4.46
Cl_2	558	3.25
Br_2	317	2.36
I_2	207	1.60

one characteristic vibrational frequency can be calculated with the expression

$$u_{XY}^2 = G_{XY} \cdot \bar{V}_1 \quad (1)$$

where

$$G_{XY} = \mu_X + \mu_Y \quad (1a)$$

$$\bar{V}_1 = [h/8\pi^2\nu_1] \coth(h\nu_1/2kT) \quad (1b)$$

(μ_X and μ_Y are the reduced masses of the atoms X and Y, in the present case being $Y = X$, and ν_1 is the characteristic vibrational frequency of the X–X bond, in cm^{-1}).

Using these relations we have calculated the mean amplitudes of vibration for the four halogen molecules between 0 and 1000 K. The obtained results are presented in Table 2, and the respective temperature dependencies are depicted in Figure 1.

The analysis of these results shows an unexpected behaviour at the lowest temperatures, as the molecules with the lowest vibrational frequencies and force constants show the lowest amplitude values. Only with increasing temperature the values show the expected trends, i.e. molecules with higher force constants and therefore stronger X–X bonds present lower mean amplitudes of vibration. Such anomalies, usually denominated “low temperature anomalies”, become always evident when the vibrations are dominated by mass effects rather than by the force constant effects (cf. for example [6, 7]). A similar

Table 2. Calculated mean amplitudes of vibration (in Å) of the four halogen molecules between 0 and 1000 K.

T (K)	F_2	Cl_2	Br_2	I_2
0	0.0446	0.0413	0.0365	0.0358
100	0.0446	0.0413	0.0369	0.0377
200	0.0446	0.0420	0.0404	0.0451
298.16	0.0452	0.0442	0.0455	0.0527
300	0.0452	0.0442	0.0455	0.0529
400	0.0464	0.0472	0.0508	0.0601
500	0.0482	0.0506	0.0558	0.0666
600	0.0502	0.0540	0.0606	0.0727
700	0.0524	0.0574	0.0650	0.0782
800	0.0547	0.0606	0.0692	0.0835
900	0.0570	0.0638	0.0733	0.0886
1000	0.0593	0.0669	0.0771	0.0931

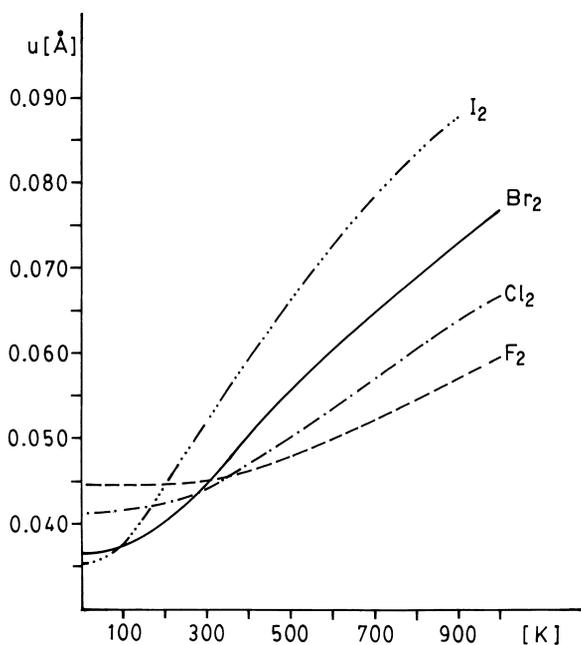


Fig. 1. Temperature dependence of the mean amplitudes of vibration of the four halogen molecules.

behaviour has been observed in the case of the related diatomic XY interhalogen molecules [8].

In such cases, and at low temperatures, the higher masses of the vibrating units generate smaller vibrational amplitudes, solely as a consequence of a weight effect. Only at higher temperatures, the mean amplitudes of vibration become dominated mainly by the strength of the interatomic bonds, diminishing or canceling the mass effect. This fact is also clearly defined in the Theory of Molecular Vibrations, through the so-called “classical mean amplitudes of

vibration”, which only depend on the corresponding force constant [1, 6].

There exists another simple expression between the mean amplitudes of vibration and the force constants, which allows a wider insight into this peculiar problem [9, 10]:

$$u_{xx}^2 = kTf_{xx}^{-1} + [h/64\pi^2kT](\mu_x + \mu_x). \quad (2)$$

This expression clearly shows that at low temperatures the second term can dominate the u -values, whereas with rising temperatures the first term acquires increasing impact, finally constituting the determinant factor.

A further comparison of the present results with those previously obtained for simple diatomic interhalogen molecules, using the same methodology of calculation [8], seems interesting. To support these comparisons, we present in Table 3 some relevant data for these molecules (force constants were taken from this work and from [8], whereas the other data are from [11]).

As can be seen from this table, with only one exception (the pair ICl/Br₂, for which the force constants are practically identical) the bond lengths increase stepwise, with diminution of the respective force constants. Regarding the bond energies, the particularly low value of F_2 is well known and is discussed in all standard Inorganic Chemistry textbooks [12–14]. For all the other species, although the variations are not totally regular, a general trend becomes also evident, as the bond energies decrease in the same direction as the corresponding force constants.

Table 3. Force constants (mdyn/Å), bond energies (kcal/mol) and bond lengths (Å) for the halogen and diatomic interhalogen molecules.

Molecule	Force constant	Bond energy	Bond length
F_2	4.46	37.0	1.418
ClF	4.36	59.5	1.628
BrF	4.07	59.6	1.756
IF	3.62	66.4	1.91
Cl_2	3.25	57.3	1.988
BrCl	2.80	51.6	2.138
ICl	2.38	49.7	2.321
Br_2	2.36	45.45	2.284
IBr	2.06	41.9	(2.45) ^{a)}
I_2	1.60	35.60	2.666

^{a)} Estimated with the Schomaker-Stevenson relation [11].

On the basis of the above trends it is possible to make also some comparisons between the mean amplitudes of vibration. Although the force constant of F_2 is by about 2% higher than that of ClF, its bonding energy is appreciably lower. Consequently the mean amplitudes of vibration of F_2 are slightly higher in the full temperature range. Only above 600 K the values for both molecules become comparable. In agreement with their similar bonding energy, BrF and ClF present similar amplitudes, and those of BrF become again comparable with those of F_2 at temperatures above 600 K.

The mean amplitudes of vibration of IF are markedly lower than those of Cl_2 in the whole temperature range, in good agreement with its higher force constant and bonding energy. On the other hand, since Br_2 and ICl present very similar bond properties one may expect similar mean amplitudes of vibration for both species, a fact that is better fulfilled at the highest temperatures, and the values between 800 and 1000 K are identical. At temperatures above 300 K, the values of Br_2 are always slightly higher than those of BrCl, also in agreement with the somewhat stronger bond of the latter molecule.

Also the IBr/ I_2 pair fulfills the expectations derived from its bonding characteristics: the mean amplitudes of vibration of the halogen molecule are always higher than those of the diatomic interhalogen compound.

Finally, it was also interesting to compare the now calculated values with those obtained from electron diffraction data, if available. For Cl_2 the experimental values of 0.0446 Å [15] and 0.044 Å [16] obtained at 300 K, are in excellent agreement with that calculated in the present work at the same temperature (0.0442 Å). For Br_2 a value of 0.045 Å was found experimentally, also at 300 K [17], again in good agreement with that calculated here (0.0455 Å). In the case of I_2 different values, obtained under different experimental conditions, were reported at 360 K, ranging between 0.055 and 0.063 Å [17]. We have also calculated the mean amplitude of vibration at the mentioned temperature, obtaining 0.0572 Å, in relatively good agreement with the electron diffraction data.

For F_2 only the internuclear distance has been determined by means of electron diffraction experiments, without mentioning the value of the mean amplitude of vibration [18, 19].

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