

INTRAMOLECULAR FORCE FIELDS, COMPLIANCE CONSTANTS AND VIBRATIONAL AMPLITUDES OF III-A GROUP TRIHALIDES AND FeCl_3

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(Received May 17, 1979)

Three sets of force constants have been calculated for planar GaCl_3 , $^{115}\text{In}^{35}\text{Cl}_3$, GaBr_3 , GaI_3 employing OVFF, UBFF and GVFF models and two sets of force constants for pyramidal FeCl_3 employing UBFF and GVFF models, using recent vibrational data. Compliance constants have also been calculated. The trend of force constants and relative strength of chemical bonds are discussed. The effect of oxidation state on the stability of chemical bonds in various isoelectronic sequences is also discussed. The mean amplitudes of vibration have also been evaluated at three temperatures 0 K, 298.15 K and 500 K and the results are briefly discussed. The computations have been done with a TDC-316 computer.

1. Introduction

Goel et al. [1] have studied the molecular constants of trichlorides of III-B group elements using the vibrational data of Beattie et al. [2]. But very recently Pong et al. [3] have studied the i.r. spectra of $^{115}\text{In}^{35}\text{Cl}_3$ in solid argon, Drake and Rosenblatt [4] studied the Raman spectra of the vapours over CaCl_3 , GaI_3 at various temperatures and Pong et al. [5] studied the i.r. spectra of gallium trihalides in an argon matrix. They analysed the spectra assuming D_{3h} symmetry for these molecules. In order to extend this study to gallium trihalides these molecules have been considered, in this investigation, using recent Raman data [4] for GaCl_3 , GaI_3 and i.r. data [5] for GaBr_3 (in argon matrix). In order to study the relative stability of chemical bonds of III-A group trichlorides, the recent vibrational data [3] in solid argon for $^{115}\text{In}^{35}\text{Cl}_3$ has also been selected. Similarly, to compare the relative stability of chemical bonds in GaCl_3 , ZnCl_3 [6] and FeCl_3 , the recent vibrational data of FeCl_3 , given by Givan and Lowenschuss [6] (who contradicted its previous planar geometry and have analysed the spectra assuming C_{3v} point group symmetry), has also been considered in the present study. The best results of their computer fit are compared in Table I. The present paper thus includes, (i) the three sets of force constants using the

general valence force field (GVFF), orbital valence force field (OVFF) and the Urey-Bradley force field (UBFF) models, for the molecules belonging to D_{3h} symmetry and two sets using GVFF and UBFF for $FeCl_3$, (ii) compliance constants to have another check, (iii) vibrational amplitudes for bonded and non-bonded atom-pairs at three temperatures (0 K, 298.15 K and 500 K), and (iv) the effect of oxidation state on the chemical bonding in the isoelectronic series. All computations have been carried out on a TDC-316 computer.

2. Method of computation and results

The molecules in the present study belonging to D_{3h} and C_{3v} symmetries give rise to four fundamental frequencies which are distributed in various symmetry species as follows:

$$C_{3v}, \Gamma_{vib} = 2a_1 + 2e,$$

$$D_{3h}, \Gamma_{vib} = a'_1 + a'_2 + 2e'.$$

All the fundamentals belonging to the C_{3v} point group are infrared and Raman active. Under D_{3h} the vibration a'_1 is Raman active and a'_2 is infrared active, while those belonging to the e' species are active in both. Wilson's FG-matrix method [8] has been used to calculate the force constants in GVFF, OVFF and UBFF models. The F and G matrices are taken from the literature [9-11]. The mean amplitudes of vibration have been calculated using Cyvin's secular equation [11] $|\sum G^{-1} - \Delta E| = 0$. Compliance constants have been evaluated using the expressions from literature [11]. Muller's L-matrix approximation [12-14] has been followed to solve the 2×2 determinant occurring in $a_1, e/e'$ species.

TABLE I
GVFF constants (in mdyn/Å) of some III-A group trihalides and $FeCl_3$

Molecules	f_r	f_{rr}	f_a	f_{aa}	f_r/f'_{ra}	$(f_{ra} - f'_{ra})/f_{ra}$
$GaCl_3$	2.690 (2.766) ^a (3.133) ^b	0.171 (0.141) ^a -(0.042) ^b	0.053 (0.053) ^a (0.053) ^b	-0.026 -(0.026) ^a -(0.026) ^b	0.058 (0.052) ^a	-0.068 -(0.057) ^a
$^{115}In^{35}Cl_3$	2.369 (2.424) ^a (2.493) ^b	0.077 (0.119) ^a (0.033) ^b	0.035 (0.050) ^a (0.031) ^b	-(0.018) -(0.025) ^a -(0.016) ^b	0.039 (0.055) ^a	-0.029 -(0.039) ^a
$FeCl_3$	2.409 (2.39) ^c	0.042 (0.077) ^c	0.068 (0.070) ^c	-0.002	0.041	-0.011
$GaBr_3$	2.266 (3.159) ^b	-0.004 -(0.257) ^b	0.050 (0.044) ^b	-0.025 -(0.022) ^b	0.041	-0.083
GaI_3	1.992	0.382	0.034	-0.017	0.015	-0.066

^a From Ref. [1], ^b From Ref. [15], ^c From Ref. [7].

TABLE II

OVFF constants (in mdyn/Å) of some planar III-A group trihalides

Molecules	K_1	A	K'_z	B/R
GaCl ₃	2.410 (2.523) ^a	0.104 (0.087) ^a	0.048 (0.077) ^a	0.016 (0.014) ^a
¹¹⁵ In ³⁵ Cl ₃	2.236 (2.224) ^a	0.048 (0.073) ^a	0.070 (0.090) ^a	0.007 (0.011) ^a
GaBr ₃	2.093	0.027	0.181	0.004
GaI ₃	1.556	0.200	-0.198	0.031

^a From Ref. [1].

TABLE III

UBFF constant (in mdyn/Å) of some III-A group trihalides and FeCl₃

Molecules	K	F	H
GaCl ₃	2.253 (2.391) ^a	0.260 (0.219) ^a	-0.004 (0.008) ^a
¹¹⁵ In ³⁵ Cl ₃	2.159 (2.106) ^a	0.122 (0.185) ^a	0.014 (0.015) ^a
FeCl ₃	2.460	0.046	-0.010
GaBr ₃	2.057	0.067	0.055
GaI ₃	1.284	0.491	-0.099

^a From Ref. [1].

TABLE IV

Compliance constants (in Å/mdyn) of some III-A group trihalides and FeCl₃

Molecules	c_r	c_{rr}	c_α	$c_{\alpha\alpha}$	$c_r/c'_{r\alpha}$	$(c_{r\alpha} - c'_{r\alpha})/c_{r\alpha}$
GaCl ₃	0.379 (0.367) ^a	-0.025 -(0.020) ^a	8.511 (8.506) ^a	-4.256 -(4.253) ^a	17.253	0.290
¹¹⁵ In ³⁵ Cl ₃	0.425 (0.471) ^a	-0.014 -(0.021) ^a	12.705 (8.982) ^a	-6.352 -(4.491) ^a	25.706	0.230
FeCl ₃	0.420	-0.009	14.767	0.273	-0.243	0.062
GaBr ₃	0.453	-0.005	9.167	-4.583	24.704	0.479
GaI ₃	0.558	-0.097	13.509	-6.755	65.315	0.793

^a From Ref. [1].

The potential model includes five (D_{3h}) and six (C_{3v}) force constants, viz. f_r (bond-stretching), f_α (angle-bending), and $f_{\gamma\gamma}$, f_r , $f_{r\alpha}$, $f'_{r\alpha}$, $f_{\alpha\alpha}$ (interaction constants). OVFF and UBFF models include $K_1(K)$ as bond-stretching, $K'_\alpha(H)$ as angle bending, $A(F)$ and B/R as interaction constants. The GVFF constants are presented in Table I while Tables II and

TABLE V
Mean amplitudes of vibration (in Å) of some III-A group trihalides and FeCl₃

Molecules	U_{x-y}			$U_{y\dots y}$		
	0 K	298.15 K	500 K	0 K	298.15 K	500 K
GaCl ₃	0.0405 (0.0401) ^a (0.0388) ^b	0.0458 (0.0453) ^a (0.0431) ^b	0.0543 (0.0536) ^a (0.0506) ^b	0.0648 (0.0681) ^a (0.0646) ^b	0.1048 (0.1047) ^a (0.0646) ^b	0.1328 (0.1326) ^a (0.1323) ^b
¹¹⁵ In ³⁵ Cl ₃	0.0403 (0.0400) ^a (0.0397) ^b	0.0472 (0.0468) ^a (0.0463) ^b	0.0568 (0.0563) ^a (0.0554) ^b	0.0703 (0.0676) ^a (0.0713) ^b	0.1257 (0.1089) ^a (0.1335) ^b	0.1603 (0.1382) ^a (0.1686) ^b
FeCl ₃	0.0423	0.0481	0.0571	0.0743	0.1407	0.1800
GaBr ₃	0.0374 (0.0342) ^b	0.0471 (0.0410) ^b	0.0578 (0.0496) ^b	0.0549 (0.0552) ^b	0.1067 (0.1110) ^b	0.1368 (0.1425) ^a
GaI ₃	0.0378	0.0509	0.0635	0.0517	0.1227	0.1581

^a From Ref. [1]. ^b From Ref. [15].

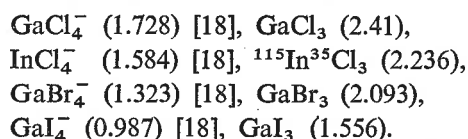
III include the OVFF and UBFF constants respectively. Compliance constants are depicted in Table IV. The vibrational amplitudes for bonded and non-bonded atom-pairs at the three temperatures (0 K, 298.15 K, 500 K) are shown in Table V.

3. Discussion

From Tables I, II, III it is observed that the stretching force constant f_r (K_1 or K) shows a similar trend of variation, i.e., it decreases as the mass of the central atom increases, i.e., the strength of the chemical bond decreases from Ga—Cl to In—Cl. A similar trend has been observed for GaBr₃ (2.09) Table II and InBr₃ (1.78) [16] and for GaI₃ (1.56) Table II and BI₃ (1.74) [17]. It is in agreement with the trend observed by Goel et al. [1] and Sarkar and Singh [15]. Their results are also included in Tables I, II, III. The compliance constants c_r from Table IV are in the ratio $c_r(\text{GaCl}_3) < c_r(^{115}\text{In}^{35}\text{Cl}_3)$ which also support the above trend. It is interesting to note that stretching force constants f_r from Table I for gallium trihalide is in the order $f_r(\text{GaCl}_3) > f_r(\text{GaBr}_3) > f_r(\text{GaI}_3)$, which is in accordance with the electronegativities of the halogen atoms. A similar trend has been observed by Sanyal et al. [6] in the case of the II-B group metal trihalogeno systems.

It is also interesting to study the relative strength of chemical bonds for III-A group halides having the same oxidation state but different coordination number. From the

stretching force constant K_1 (OVFF) these results are summarized as



From this it is concluded that K_1 increases with a decrease in coordination number i.e. the chemical bonds in a trihalogeno species are more stable than in a tetrahalogeno species. A similar trend has been observed in the literature [16].

The stretching force constants f_r from Table I for the isoelectronic series GaCl_3 , ZnCl_3^- and FeCl_3 are III (2.690), II (1.169) [6], III (2.409) respectively. From this it is inferred that a higher oxidation state is more stable than the lower oxidation state. A similar trend has been reflected from the isoelectronic series, (i) ZnCl_3^- II (1.169) [6], GaCl_3 (2.69), (ii) ZnBr_3^- (0.904) [6], GaBr_3 (2.26), and (iii) for K_1 from Table II for CdCl_3 (1.125) [18], $^{115}\text{In}^{35}\text{Cl}_3$ (2.236). The UBFF constants for FeCl_3 are also included in Table III. But in this case the % deviation in observed and calculated frequencies (using this set of force constants) is found to be 2.3% for ν_1, ν_3 and 68% for ν_2, ν_4 . Thus the UBFF set of force constant does not seem reliable in the case of FeCl_3 , however, the stretching force constant K is in good agreement with the corresponding GVFF stretching force constant f_r (Table I).

When the vibrational amplitudes U_{x-y} of GaCl_3 and $^{115}\text{In}^{35}\text{Cl}_3$ are compared at room temperature from Table V, it is found that $U_{x-y}(\text{GaCl}_3) < U_{x-y}(^{115}\text{In}^{35}\text{Cl}_3)$ which is a reverse trend, as was discussed for their stretching force constants. Similarly the trend U_{x-y} for gallium trihalides is in the order $U_{x-y}(\text{GaCl}_3) < U_{x-y}(\text{GaBr}_3) < U_{x-y}(\text{GaI}_3)$, which is also opposite to the trend of their stretching force constant f_r or K . When the trend of the mean amplitude of vibration U_{x-y} at room temperature is studied in various isoelectronic series, (i) ZnCl_3^- (0.063) [6], GaCl_3 (0.045), (ii) ZnBr_3^- (0.066) [6], GaBr_3 (0.047), (iii) ZnI_3^- (0.073) [6], GaI_3 (0.051) and (iv) CdCl_3^- (0.061) [18], $^{115}\text{In}^{35}\text{Cl}_3$ (0.047), it is observed that the mean amplitude decreases with the increase in oxidation number which is also opposite to the trend observed for their stretching force constant. It is also apparent from Table V that mean amplitudes increase with the rise in temperature and the U_{x-y} for the non-bonded distances is greater than that for bonded distances.

One of the authors (R.K.G.) is thankful to U.G.C., New Delhi, India, for financial assistance.

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