On the Calculation of the Force Constants for Halides AX_4^n (Td) Using an Empirical Constraint $F_{33}(F_2)/F_{11}(A_1) = $ Constant for Similar Molecules and Ions

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An empirical constraint for the determination of the force constants of a General Valence Force Field for the tetrahedral halides with the general formula AX_4^n (where A = an element of the groupe II, III, IV, V and VI; X = F, Cl, Br and I and $n = +1, 0, -1$ and -2) is presented. The model is defined by a constant value of the parameter $p = (f_t - f_{tt})/(f_t + 3 f_{tt})$. The optimum value, $p = 0.73$, obtained for the mixed halides of chlorobromomethane is compared with those calculated from other force fields commonly used.

I. Introduction

1. Definition of the parameter p

An original method [1] of calculating the vibrational frequencies of mixed halides from the frequencies of the simple halides in the series SiX_4, GeX_4, SnX_4 and BX_4 has been successfully applied to fifty tetrahedral halides of the general formula AX_4^n where A = elements of the group II, III, IV, V and VI; X = F, Cl, Br and I and $n = +1, 0., -1$ and -2. This method is based on the knowledge of an unique parameter p with an optimal value of $p = 0.73$ [1–4].

The parameter p is expressed either as a function of the internal force constants f_t and f_{tt} or as a function of the symmetric force constants F_{11} (A_1) and F_{33} (F_2), viz.,

$$p = \frac{f_t - f_{tt}}{f_t + 3 f_{tt}} = \frac{F_{33}(F_2)}{F_{11}(A_1)} . \tag{1}$$

The knowledge of the effective value of p is then sufficient to permit us to determine all the force constants by use of Equation (1). (For expressions of $\mathbf{F}$ and $\mathbf{G}$ see Ref. [5–8].)

2. Mathematical expression for p

It is possible to give an expression for p when one uses the general bi-parametric form of the force constants [9–11]. For example, the elements of the $\mathbf{F}(F_2)$ matrix are given by

$$\begin{aligned} F_{33} &= (\mathbf{G}^{-1})_{33} \left[(\lambda_3 + \lambda_4)/2 + (\lambda_3 - \lambda_4)/2 \cos 2(2\psi_{34} - \alpha_{34}) \right] , \\ F_{34} &= (\mathbf{G}^{-1})_{34} \left[(\lambda_3 + \lambda_4)/2 + \frac{(\lambda_3 - \lambda_4) \sin 2(\alpha_{34} - \psi_{34})}{2 \sin 2\psi_{34}} \right] , \\ \text{and} \quad F_{44} &= (\mathbf{G}^{-1})_{44} \left[(\lambda_3 + \lambda_4)/2 - (\lambda_3 - \lambda_4)/2 \cos 2\alpha_{34} \right] \end{aligned} \tag{2}$$

where

(i) ψ_{34} is the molecular kinematic coupling coefficient [9] between the two symmetry coordinates $\mathbf{S}_3$ and $\mathbf{S}_4$ defined by

$$\sin 2\psi_{34} = -G_{34}/(G_{33} \cdot G_{44})^{1/2} \tag{3}$$

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(ii) α_{34} is the free parameter [9–13] which permits one to generate all of the $\boldsymbol{F}(F_2)$ matrices in such a way that the frequency parameters λ_3 and λ_4 are the eigenvalues of $[\mathbf{G}(F_2) \cdot \boldsymbol{F}(F_2)]$. However, the range of variation of α_{34} is limited by the application of the energy criterion [9–11, 13] and the values of the energy distributions of the vibrations [11–14].

Thus by using the expression of $F_{11}(A_1)$, one obtains

$$p(\alpha, \psi, s) = (\lambda_3 - \lambda_4)/2\,\lambda_1\,[s_{34} + \cos 2\,(2\,\psi_{34} - - \alpha_{34})]\,(G_{11}\,G_{44})/\mathbf{G} \tag{4}$$

where

$$\mathbf{G} = G_{33}\,G_{44} - G_{34}{}^2 \quad \text{and} \quad s_{34} = (\lambda_3 + \lambda_4)/\lambda_3 - \lambda_4)\,.$$

The range of variation of $p(\alpha)$ is then limited by

$$p_{\max} = p(0) = (\lambda_3 + \lambda_4)/2\,\lambda_1\,[\,(s_{34} + \cos 4\,\psi_{34})\,]\,(G_{11}\,G_{44})/\mathbf{G} \tag{5}$$

and

$$p_{\min} = p(\psi - \pi/4) = (\lambda_3 - \lambda_4)/2\,\lambda_1\,[\,(s_{34} + \sin 2\,\psi_{34})\,]\,(G_{11}\,G_{44})\,\mathbf{G}\,. \tag{6}$$

The parameter p is a function of

(i) ψ_{34} which defines the kinematic coupling of the molecule related to the matrix $\mathbf{G}(F_2)$,

(ii) s_{34} which defines the coupling between the frequency parameters λ_3 and λ_4, and

(iii) α_{34} which defines the different $\boldsymbol{F}(F_2)$ matrices which are in agreement with the inverse vibrational problem. However, *one and only one* value of α_{34} corresponds to the physically acceptable solution [11].

The *fixing of a value of* p corresponds to a new model for force field [1]. The optimum value of this parameter, $p = 0.73$, has been determined by Cerf in previous papers [1–4] in such a way as to obtain the best agreement between the calculated and the observed vibrational frequencies of the spectra of the mixed halides [1] (precision 2% for $p = 0.73 \pm 0.1$).

In a similar way as for p, it would be also possible to define as parameter [1–4] $K = F_{44}(F_2)/F_{22}(E)$. However, the actual determination of the numerical value of K is more difficult in this case due to the fact that a greater error is involved in the measurement of the vibrational frequencies ν_2 and ν_4.

II. Comparison of Some Force Fields with the Present Model

With the mathematical properties of p given, it is now possible to determine the effective values obtained by the application of various model force fields to simple halides of the type $AX_4{}^n$ whose vibrational spectra have been recorded.

Numerous works have been published on the determination of the force constants of molecules of the type XY_4 using different force field. (See for example Ref. [15–17].) We will consider here the following force fields:

1. The General Valence Force Fields (Approximations)

The solution of the inverse problem of the eigenvalues of the secular equations is performed by several authors using different additional conditions which depend only on the characteristics of the considered molecules and more particularly on the form of the **G**-matrix. One may distinguish two types of such methods namely the iterative and the non-iterative ones.

(a) The iterative methods

(i) The method of the "nearest solution" of Fadini [18–20]

Fadini uses the following minimisation condition:

$$R_{\min} = \sum_i \sum_{j>i} (F_{ij} - F_{ij}{}^{(0)})^2{}_{\min}\,, \quad \text{where} \quad F_{ii}{}^{(0)} = \lambda_i/G_{ii}\,. \tag{7}$$

This condition can be written in a more general sense as $R_{\min} = \| \boldsymbol{f} - \boldsymbol{f}^{(0)} \|^2{}_{\min}$, where $\boldsymbol{f}$ is a column vector determined from the upper triangular part of the matrix $\boldsymbol{F}$. The symbol $\| \; \|$ represents the Euclidian norm. It has been pointed out that this method is not invariant under scaling [21, 22]. In the second order cases, the results obtained are very close to those obtained by the application of the Eigenvector

Method[18, 24] and of the Matrix Polynomial Expansion Method[22].

(ii) The stepwise coupling methods[15–17, 21, 22, 25]

These methods are based on the general principle of stepwise introduction of the kinematic coupling[25] but use different mathematical procedures. Alix[22] has demonstrated that under some conditions the Logarithmic Steps Method[15–17] (L. S. M.) is a particular case of the Matrix Polynomial Expansion Method[22] which is formally equivalent to the Eigen Vector Method[22–24] (E. V. M.). In this paper we shall use the results of the L. S. M.[15–17].

(b) The non-iterative methods

(i) The model $L^{(0)}$ of Alix[11–13, 32]

This model has been studied in different equivalent forms by a number of workers[26–32] and is a good approximation to the actual physical solution in the case of weak kinematic coupling[10–14] (i. e., $|\sin 2\psi| \ll 1$). Different forms of the model are summarized below:

$(\boldsymbol{G}\,\boldsymbol{F})_{ij}=0,\ \lambda_i>\lambda_j$ for $i<j \Leftrightarrow L_{ij}=0,\ i<j$ (Torkington[26]),

$L_{ij}=0,\ \lambda_i>\lambda_j,\ i<j$; "progressive rigidity method" (Larnaudie[27]),

$L_{34}=0$, approximation method of Müller[28] in the second order case[25–27],

$F_{44}=\min$ (Strey[29, 30], Müller[28]),

and

$L_{ij}^{(0)}=0$, with $\lambda_i>\lambda_j,\ i<j,\ L_{ii}>0 \Rightarrow M_i^{(k)}=\delta_{ik}$ (Alix[12–14]),

i. e., the symmetry coordinates $\boldsymbol{S}_i$ contributes only to the normal coordinates $\boldsymbol{Q}_i$ from the energy point of view. This model corresponds to $\alpha=0$ and gives the maximal value of p compatible with the energy criterion[9, 11–13] [see Equation (5)].

(ii) Solution of Becher and Ballein[33] (P. E. D. Method)

This solution is only defined in the particular cases of second order with a stretching and a bending frequency. In this case the solution imposes that the energetic contribution of the bending force constant is compensated by the interactions (stretching-bending). Thus, $\boldsymbol{V}_{33}^{(3)}=1$, $\boldsymbol{V}_{44}^{(3)}=-(\boldsymbol{V}_{34}^{(3)}+\boldsymbol{V}_{43}^{(3)}) \neq 0$. Recently, Höffler[34] has applied this solution to some halides AX_4 for the determination of their force constants and for the calculation of the frequencies of the mixed halides.

(iii) The force field for the molecules with strongly coupled vibration[32, 35] (S. C. M. F. F.)

This new empirical model, recently proposed by Alix[1, 21, 35], is very convenient for the molecules which are characterized by strong kinematic coupling (with $0.35<|\sin 2\psi|<0.95$). This is the case for almost all the molecules studied in the present paper (see Tables).

This model is defined either by the general expression

$$F_{34}(\alpha_{34}^*) = [(F_{34})_{\min} + F_{34}(F_{44})_{\min}]/2 \qquad (8)$$

from which one deduces

$$p^* = \frac{p_{\min}+p_{\max}}{2} - \frac{G_{11}}{G_{33}} \cdot \frac{\lambda_3-\lambda_4}{4\,\lambda_1} \cdot \left[1-\frac{3+\sin 2\psi_{34}}{1+\sin 2\psi_{34}}\right]^{1/2} \qquad (9)$$

or by the parametric expression derived from Eq. (2) which leads to

$$\sin 2(\alpha_{34}^* - \psi_{34}) = -\tfrac{1}{2}(1+\sin 2\psi_{34}),\ \alpha_{34}^*<0\,. \qquad (10)$$

2. *Modified Valence Force Fields (MVFF)*

(a) MVFF of Uhlig[36]

Uhlig uses the constraint $F_{34}=0$, which defines a Simplified Force Field in the symmetry coordinates. However, this condition is not always compatible with the inverse vibrational problem[9–14, 32]. If one applies this condition one obtains

$$\sin 2(\alpha_{34}-\psi_{34}) = -s_{34}\sin 2\psi_{34}\,. \qquad (11)$$

In the case of the tetrahedral tetrahalomethanes the Eq. (11) is not fulfilled.

(b) MVFF of Meister and Cleveland[6]

It is defined by the constraint $f_{tt}=0$ which corresponds to $p=1$ as in the case of the Simple Valence Force Field. This value is a disagreement with all of the results obtained for the fifty halides studied and for which $p_{\max}<1$.

(c) MVFF of Pistorius[37]

The value of the interaction constant f_{tt} is obtained by equating the elements F_{11} from the matrices corresponding to the Simple Urey Bradley Force Field and the General Valence Force Field. Thus, $f_t=K$, $f_{tt}=(4/3)F$. This condition cannot be applied to the tetrahalomethanes because the value of p obtained does not lie in the range of the permitted values *.

3. *Model Force Fields*

(a) Urey-Bradley Force Field[38] (U.B.F.F.)

In this case

$$p = \frac{K + (4/3)\,F + (4/3)\,F'}{K + 4\,F}\,. \qquad (12)$$

(b) Orbital Valence Force Field[23] (O.V.F.F.)

This is very similar to the U.B.F.F. but with different notation. Its application leads to the relation

$$p = \frac{k_1 + (8/3)\,A - (4/3)\,B/R_e}{k_1 + 8\,A}\,. \qquad (13)$$

III. Results

1. *Tables 1 – 7:* Comparison of the different force fields is given in Tables 1 to 7 for the fifty halides AX_4 (the structure has been assumed to be tetrahedral). The compounds are classified according to the group of the central atom in the periodic table.

The values of p are obtained from data on frequencies and or force constants given in Ref.[17, 19–20, 34]. In each case we give,

Column 1: the ratio ϱ of the masses of the central atom A to the mass of halogen X.

Column 2: the molecular coupling coefficient, $a = \sin 2\,\psi_{34}$ which is related to ϱ by the expression

$$a = \sin 2\,\psi_{34} = \left(1 + \tfrac{9}{8}\,\varrho + \tfrac{9}{32}\,\varrho^2\right)^{-1/2}. \qquad (14)$$

Column 3: $p_{\min}$ = value of the parameter corresponding to the force field defined by $F_{34} = (F_{34})_{\min}$ and given by Equation (6).

Column 4 to 8: The value of p obtained from the calculated force constants in the cases of the U.B.F.F.[38], O.V.F.F.[23], Fadini's method[18–20], Logarithmic steps method[17, 21] and the model $L^{(0)}$[9–14] that gives in particular $p_{\max}$ [see Equation (5)]. The ? indicates that the sign of the calculated force constant is in contradiction to that expected from the application of the force field used[15–17].

Column 9 to 12: the results of the application of the empirical force field for strongly coupled molecules (S.C.M.F.F.)[32, 35] have been summarized in these columns as follows: 9: p^* is the value obtained from the general relation (9). 10: $|\alpha_{34}^*|$ is the absolute value of the angle deduced from the parametric relation (10). The sign of α_{34}^* is negative for all the molecules studied in this work. 11: $M_i^{*(j)}\%$: is the value of the energy coupling, i.e., the contribution $M_3^{(4)}$ of $\mathbf{S}_3$ to $\mathbf{Q}_4$ (or $M_4^{(3)}$, contribution of $\mathbf{S}_4$ to $\mathbf{Q}_3$) (see Refs.[9–14, 32]). 12: $(p^*/p_{\max}) = F_{33}(\alpha_{34}^*)/F_{33}(0)$. This relation for the above constraint, $f_t = K$, is often very bad. This confirms the conclusions given in this paper.

Table 1. Simple metal halides of group II.

Compound	ϱ [a]	a [b]	$p_{\min}$ [c]	U.B.F.F. [d]	O.V.F.F. [d]	Fadini's solution [d]	Log. Steps Method [d]	$p_{\max}$ [c]	p^* [e]	$\|\alpha_{34}^*\|$ [f]	$M_i^*(j)$ % [g]	$p^*/p_{\max}$
BeF_4^{2-}	0.45	0.791	0.45	—	—	—	0.60	0.75	0.65	5°30′	13.2	0.87
$ZnCl_4^{2-}$	1.84	0.498	0.32	0.77 ?	0.77 ?	0.61	0.70	0.75	0.62	9°15′	11.7	0.82
$ZnBr_4^{2-}$	0.82	0.689	0.31	0.67	0.67 ?	0.55	0.56	0.64	0.53	7°10′	13.4	0.82
ZnI_4^{2-}	0.51	0.778	0.31	0.66 ?	0.66 ?	0.52	0.55	0.65	0.54	6°	13.8	0.83
$CdBr_4^{2-}$	1.40	0.564	0.28	0.72 ?	0.72 ?	0.62	0.61	0.66	0.54	8°30′	11.8	0.81
CdI_4^{2-}	0.89	0.672	0.28	0.73 ?	0.73 ?	0.62	0.61	0.67	0.54	7°	12.4	0.80
$HgCl_4^{2-}$	5.65	0.247	0.62	0.82	0.88 ?	0.85	0.83	(0.89) [h]	(0.83) [h]	12°30′	10.1	(0.93) [h]
HgI_4^{2-}	1.58	0.536	0.22	0.60	0.59 ?	—	0.46	0.50	0.41	8′45′	11.7	0.82

[a] Defined by $\varrho = m_A/m_X$ (see text).

[b] Molecular kinematic coupling coefficient given by Eq. (14) [see also Equation (3)].

[c] Given by Eqs. (5) or (6).

[d] Values of p calculated using the indicated force field (see text). For datas see Ref.[17, 19, 20].

[e] Calculated from Equation (9).

[f] Calculated from Equation (10).

[g] Potential or kinetic energy coupling (see Refs.[9–14]).

[h] Unreasonable values are given in parenthesis.

[i] The ? indicates a sign contradiction (see text).

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* During the preparation of this manuscript, a paper by N. Mohan, K. H. Schmidt, and A. Müller appeared (J. Mol. Structure **13**, 155 [1972]) which shows that the above constraint, $f_t = K$, is often very bad. This confirms the conclusions given in this paper.

Table 2. Simple metal halides of group III [a].

Compound	ϱ	a	$p_{\min}$	U.B.F.F.	O.V.F.F.	Fadini's solution	Log. Steps Method	$p_{\max}$	p^*	$\lvert\alpha_{34}^*\rvert$	$M_i^*(j)$ %	$p^*/p_{\max}$
BF_4^-	0.57	0.760	0.46	0.57	0.59	0.59	0.62	0.77	0.67	6°15′	14.4	0.87
BCl_4^-	0.30	0.855	0.44	0.57	—	0.57	—	0.77	0.65	4°30′	13.4	0.84
BBr_4^-	0.14	0.930	0.45	0.58	—	0.55	—	0.84	0.71	3°15′	14.8	0.84
$AlCl_4^-$	0.76	0.704	0.36	0.77?	0.79?	0.70	0.69	0.79	0.65	7°	13.5	0.82
$GaCl_4^-$	1.96	0.482	0.36	0.78	0.78	0.73	0.72	0.78	0.64	9°30′	11.4	0.82
$GaBr_4^-$	0.87	0.675	0.35	0.74	0.74	0.68	0.68	0.77	0.63	7°15′	13.0	0.81
GaI_4^-	0.55	0.766	0.35	0.75	0.75	—	0.63	0.79	0.64	6°	13.5	0.81
$InCl_4^-$	3.23	0.363	0.35	0.81	0.81	0.78	0.77	0.79	0.67	9°	8.5	0.85
$InBr_4^-$	1.44	0.559	0.34	0.80?	0.80?	0.75	0.74	0.80	0.66	8°30′	11.7	0.82
InI_4^-	0.90	0.667	0.32	0.84	0.85	0.71	0.70	0.77	0.62	7°30′	13.3	0.80
$TlCl_4^-$	5.75	0.244	0.33	0.76?	0.76?	—	0.73	0.73	0.64	12°	9.5	0.87
$TlBr_4^-$	2.55	0.418	0.34	0.83	0.83	0.79	0.78	0.81	0.68	10°	10.9	0.83
TlI_4^-	1.61	0.531	0.34	0.77?	0.77?	—	0.71	0.77	0.64	9°	12.1	0.83

[a] See footnotes in Table 1.

Table 3. Simple metal halides of group IV [a].

Compound	ϱ	a	$p_{\min}$	U.B.F.F.	O.V.F.F.	Fadini's solution	Log. Steps Method	$p_{\max}$	p^*	$\lvert\alpha_{34}^*\rvert$	$M_i^*(j)$ %	$p^*/p_{\max}$
CF_4	0.63	0.741	0.48	0.58	0.61	0.63	0.66	0.83	0.71	6°20′	13.3	0.86
CCl_4	0.34	0.841	0.46	0.58	0.60	0.58	0.68	0.81	0.69	5°	14.3	0.85
CBr_4	0.15	0.922	0.47	0.61	0.65	0.63	0.79	0.91	0.75	3°20′	14.2	0.82
CI_4	0.09	0.950	0.48	0.61	0.66?	0.63	0.84	0.93	0.77	2°40′	14.5	0.83
SiF_4	1.48	0.552	0.42	0.85	0.86	0.87	0.85	0.93	0.77	8°45′	12.4	0.83
$SiCl_4$	0.79	0.695	0.39	0.77	0.78	0.76	0.75	0.86	0.71	7°	13.2	0.82
$SiBr_4$	0.35	0.836	0.41	0.77	0.78	0.79	0.83	0.94	0.76	5°	14.0	0.81
SiI_4	0.22	0.890	0.42	0.78	0.80	0.83	0.90	0.99	0.79	4°	14.1	0.80
GeF_4	3.82	0.326	0.40	0.88	0.88	0.87	0.86	0.88	0.75	11°15′	10.1	0.85
$GeCl_4$	2.04	0.472	0.38	0.82	0.82	0.78	0.77	0.83	0.69	9°40′	11.7	0.83
$GeBr_4$	0.91	0.666	0.37	0.80	0.81	0.78	0.77	0.86	0.70	7°20′	13.0	0.81
GeI_4	0.57	0.759	0.39	0.83	0.84	0.82	0.83	0.93	0.75	6°	13.3	0.80
$SnCl_4$	3.35	0.355	0.39	0.87	0.88	0.86	0.86	0.88	0.75	11°	10.8	0.85
$SnBr_4$	1.48	0.551	0.37	0.87	0.87	0.84	0.83	0.88	0.72	4°45′	6.2	0.81
SnI_4	0.93	0.660	0.37	0.87	0.88?	0.86	0.85	0.92	0.74	7°20′	12.8	0.80
$PbCl_4$	5.84	0.241	0.41	0.93	0.94?	0.90	0.92	0.93	0.80	7°15′	4.7	0.86
$PbBr_4$	2.59	0.415	0.36	0.84	0.84	—	0.81	0.84	0.70	10°15′	11.1	0.83
PbI_4	1.63	0.528	0.34	0.85	0.85	—	0.81	0.85	0.70	9°	12.1	0.82
$TiCl_4$	5.75	0.574	0.33	0.84	—	0.79	—	0.83	0.67	8°30′	12.3	0.80
$TiBr_4$	2.55	0.750	0.35	0.90	—	0.89	—	0.96	0.75	6°10′	13.2	0.78
TiI_4	1.61	0.826	0.34	—	—	—	—	0.94	0.73	5°	13.5	0.78
$ZrCl_4$	2.57	0.417	0.34	0.84	—	0.79	—	0.81	0.67	10°	10.9	0.83

[a] See footnotes in Table 1.

ratio ($p^*/p_{\max}$) gives the particular value of the ratio of the force constants F_{33} given by the S.C.M.F.F. to the force constant corresponding to the solution $L^{(0)}$ of non-energetic coupling (i.e., $M_{i \neq j}^{(j)} = 0$; $i, j = 3, 4$).

2. *Table 5* gives the comparison between the special solution of Becher and Ballein [33] and the other related methods.

3. *Table 6* gives the mean values of the results for the different groups to which the central atom A belongs.

IV. Discussions

(i) We should like first to point out that the U.B.F.F. and the O.V.F.F. do not seem to be very

Table 4. Simple metal halides of groups V and VIII [a].

Compound	ϱ	a	$p_{\min}$	U.B.F.F.	O.V.F.F.	Fadini's solution	Log. Steps Method	$p_{\max}$	p^*	$\lvert a_{34}^* \rvert$	$M_i^*(j)$ %	$p^*/p_{\max}$
NF_4^+	0.74	0.710	0.51	—	—	0.70	—	0.86	0.74	7°	13.8	0.86
PCl_4^+	0.87	0.675	0.42	0.78	0.79	0.80	0.79	0.90	0.75	7°15′	13.0	0.83
PBr_4^+ (I)	0.38	0.822	0.43	—	—	—	—	0.97	0.78	5°20′	14.1	0.80
PBr_4 (II)	0.38	0.822	0.51	0.77	0.76?	0.97	—	(1.16)	(0.94)	5°20′	14.1	0.81
$AsCl_4^+$	2.11	0.465	0.41	0.87	0.88?	0.85	0.84	0.89	0.75	9°40′	11.5	0.84
$SbCl_4^+$	3.43	0.350	0.44	0.92	0.94?	0.92	0.90	0.94	0.80	11°	10.6	0.85
VCL_4	1.44	0.559	0.35	0.84	—	0.79	—	0.83	0.68	8°30′	12.0	0.82
$FeCl_4^+$	1.57	0.537	0.33	0.79	—	0.73	—	0.77	0.64	8°45′	11.8	0.83

(I) PBr_4^+ in $P_2Br_4F_6$ (tetrahedral[1]). (II) PBr_4^+ in PBr_5 (not tetrahedral[1]). [a] See footnotes in Table 1.

Table 5. Comparison of the values of p obtained from the solution of Becher-Ballein (B.B.) and the others methods [a].

Compounds	U.B.F.F.	O.V.F.F.	Fadini's solution	Log. Steps Method	p^*	B. B. solution	$p_{\max}$
SiF_4	0.85	0.86	0.87	0.85	0.77	0.82	0.93
$SiCl_4$	0.77	0.78	0.76	0.75	0.71	0.77	0.86
$SiBr_4$	0.77	0.78	0.79	0.83	0.76	0.80	0.94
SiI_4	0.78	0.80	0.83	0.90	0.79	0.81	0.99
$TiCl_4$	0.84	—	0.79	—	0.67	0.83	0.83
$TiBr_4$	0.90	—	0.89	—	0.75	0.84	0.96

[a] See footnotes in Table 1. [b] Datas for B.B.-solution are given in Ref. [34].

Table 6. Mean values of p for the different groups.

Group number	II 8	III 13	IV 22	V 6	VIII 1	50
$p_{\min}$	0.35 ± 0.09	0.37 ± 0.04	0.39 ± 0.04	0.43 ± 0.04		0.38 ± 0.05
U.B.F.F.	0.71 ± 0.06	0.74 ± 0.07	0.80 ± 0.08	0.84 ± 0.05	0.79	0.77 ± 0.07
O.V.F.F.	0.71 ± 0.08	0.77 ± 0.04	0.80 ± 0.07	0.84 ± 0.07	—	0.78 ± 0.07
Fadini's solution	0.63 ± 0.07	0.69 ± 0.07	0.78 ± 0.07	0.84 ± 0.07	0.73	$0.74_5 \pm 0.10$
Log. Step Method	0.62 ± 0.07	0.71 ± 0.03	0.81 ± 0.05	0.84 ± 0.07	—	0.75 ± 0.08
S.C.M.F.F.						
p^*	0.58 ± 0.09	0.65 ± 0.02	0.73 ± 0.02	0.75 ± 0.05	0.64	0.69 ± 0.06
$M_i^*(j)$ %	$12.3\% \pm 1$	$12.3\% \pm 3$	$12.1\% \pm 3$	$12.5\% \pm 2$	11.8%	$12.2_5\% \pm 2$
$p^*/p_{\max}$	$0.82_4 \pm 0.02$	$0.83_2 \pm 0.03$	$0.81_8 \pm 0.04$	$0.83_0 \pm 0.03$	0.83	$0.82_8 \pm 0.03$
$p_{\max}$	0.69 ± 0.08	0.78 ± 0.02	0.89 ± 0.05	0.90 ± 0.04	0.77	$0.83_3 \pm 0.07$

reliable for the ions, in particular to those of group II for which the energy criterion is not fulfilled. It may be expected however that the values of several frequencies are found to be unrealistic for the mixed halides as there are difficulties in obtaining the vibrational spectra of the ions owing to (a) broad bands in the solution and (b) use of different solvents in order to get the complete spectrum. Therefore it is not surprising to find frequently in the literature different spectra for the same simple or mixed halides by different authors. In this case the value of the parameter of Cerf [1], $p = 0.73$ which defines a new model is convenient for the calculation of the frequencies and also it provides a criterion between different solutions [1]. For instance we have given in Table 4 the results for PBr_4^+ either in $P_2Br_4F_6$ or in PBr_5. Only in the first case is the structure effectively tetrahedral and the calculations are in agreement with this symmetry. We see that in the second case, the values obtained for p are not realistic.

(ii) The iterative methods of Fadini [18–20] and Wendling and Mahmoudi [15–17] lead to a number of values of p, very close together and also slightly

Table 7. Comparison of the models: $p =$ constant and the S.C.M.F.F.

			Groups			
	II	III	IV	V	mean value	Remarks
New G.V.F.F. model based on $p = 0.73$ (Cerf[1])						
p			0.73		0.73	constant by definition
f_t/f_{tt}			11.80		11.80	constant
$F_{33}/F_{33}(0)$	1.160	0.933	0.824	0.787	0.895	the value of p is not compatible for the group II
Strongly Coupled Molecule Force Field (Alix[35])						
p^*	0.58	0.65	0.73	0.75	0.69	increasing with the sequence of the group
f_t/f_{tt}	6.5	8.4	11.8	15.1	10.2	increasing with the sequence of the group
$F_{33}^*/F_{33}(0)$	0.824	0.832	0.818	0.830	0.828	constant
$M_i^*(j)$ %	12.3	12.3	12.1	12.5	12.25	constant

below the $p_{\max}$ value. This comes from the fact that the solutions obtained are very close to the model $(L^{(0)})$ of Alix[21, 22].

(iii) The empirical S.C.M.F.F.[1, 35] leads to a mean value of p^* remarkably constant for a given group. In the case of the group IV we have found again the value $p_{\text{mean value}} = 0.73$ proposed in the G.V.F.F. model of Cerf[1] based on the constraint $p =$ constant. This optimal value of p was also numerically determined[1–4] in the study of the halides where A belongs to the group IV.

We notice that in the S.C.M.F.F., the mean values of the ratio $[(p^*/p_{\max})_{\text{mean value}}]$ as well as the energy coupling $[(M_i^{*(j)})\%_{\text{mean value}}]$ are constants with respect to the group. Moreover, the value of $(p^*/p_{\max})$ itself is nearly constant for all the fifty halides studied, i. e., the ratio of $F_{33}^*/F_{33}(0)$ is a constant for the series of the simple halides studied in this work. This result is different from that obtained with the constraint $p = 0.73$. Table 7 gives the comparison between these two models.

(iv) The model of the G.V.F.F. defined by $p =$ constant[1] can be developed in a similar way[1] for other molecules belonging to different symmetry groups. In particular, for the boron-halides BX_3 (D_{3h}) the study of the frequency calculated for their mixed halides for different values of p, leads to an optimal value of $p = 0.70$, which is nearly equal to the mean value between $p = 0.73$ and $p^* = 0.66$ (value obtained for the series BX_3). The calculation based on the force constants of Shimanouchi et al.[39], in the case of the U.B.F.F., gives for the particular value of the parameter p: BF_3 (0.74), BCl_3 (0.68), BBr_3 (0.68) and BI_3 (0.68); values in very good agreement with the above values.

V. Conclusions

The constant value $p = 0.73$ of the parameter of Cerf[1] $p = F_{33}(F_2)/F_{11}(A_1)$ for a series of simple halides AX_4^n with different molecular coefficients of coupling (ψ) or different spectral coefficient of coupling (s), defines a model of G.V.F.F., which gives excellent results in the problem of the calculation of the frequencies of the corresponding mixed halides (see Refs.[1–4]). The above study of the different values of p obtained from the commonly used force fields has permitted us to:

(i) classify the force fields compatible with the solution of the inverse vibrational problem,

(ii) analyse and criticize these force fields to reveal the inadequate methods, and

(iii) compare the values obtained for p with the optimum value of $p = 0.73$.

At this stage, it is also important to note the limitations of the model based on the constraint $p =$ constant ($p = 0.73$). In Table 8 we have given the values of p determined from the exact force field data for some AX_4 (Td) type molecules. It can be immediately noted that the value of p is a constant only for molecules with the same type of chemical bonding. In other words the value of p $[p = (f_t - f_{tt})/(f_t + 3f_{tt})]$ depends on the nature of bonding. The value of p is nearly a constant for chlorides, bro-

Table 8. Exact force constants and values of p for some AX_4 (Td) type molecules.

	$F_{11}(A_1)$[a]	$F_{33}(F_2)$	exact p
CF_4	9.25	6.22 ± 0.25 [b]	0.672 ± 0.027
		6.485 ± 0.07 [c]	0.701 ± 0.007
		6.909 ± 0.459 [d]	0.746 ± 0.049
CCl_4	4.40	2.26 [e]	0.513
		3.35 ± 0.75 [d]	0.761 ± 0.17
SiF_4	7.16	6.201 [f]	0.866
		6.406 ± 0.371 [d]	0.894 ± 0.051
$SiCl_4$	3.75	3.02 [e]	0.805
	3.773 ± 0.018 [d]	2.96 ± 0.09 [d]	0.784 ± 0.003
$SiBr_4$	2.92	2.88 [e]	0.986
GeF_4	6.09	5.807 ± 0.237 [d]	0.953 ± 0.038
$GeCl_4$	3.27	2.76 [e]	0.844
	3.29 ± 0.02 [g]	2.83 ± 0.04 [g]	0.860 ± 0.012
		2.73 ± 0.13 [d]	0.829 ± 0.04
$GeBr_4$	2.60	2.25 [e]	0.865
GeI_4	1.89	1.73 [e]	0.915
$SnCl_4$	2.80	2.67 [e]	0.953
	2.84 [h]	2.55 ± 0.03 [h]	0.897 ± 0.01
$SnBr_4$	2.30	2.35 [e]	1.021
SnI_4	1.66	1.59 [e]	0.957
$TiCl_4$	3.16	3.13 [e]	0.990
	3.16 ± 0.02 [g]	2.64 ± 0.05 [g]	0.835 ± 0.015
		2.56 ± 0.47 [d]	0.810 ± 0.148
BF_4^-	6.62	4.68 [d]	0.706
VCl_4	3.06	2.09 ± 0.16 [d]	0.683 ± 0.05

[a] Calculated according to the frequencies given in H. Siebert, Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie, Springer-Verlag, Berlin 1966.

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mides, iodides whereas it is very different for fluorides. This might be expected on the basis of the values of electronegativity. Moreover for different groups (where the central atom A belongs in the periodic table), one must have different values of p, since the ratio (f_t/f_{tt}) is different for different groups (negative values of f_t/f_{tt} are also possible).

The precision of the frequencies calculated for the mixed halides from only the knowledge of the frequencies of the simple halides is 2% for $p = 0.73 \pm 0.1$. We recall that this "optimal" value of p is based only on a least-squares analysis of the frequency data and not on a least-squares analysis of force constant data. The U.B.F.F., the O.V.F.F., Fadini's solution and the Logarithmic steps method, though not perfect methods for the calculation of the force constants, are however, suitable for the determination of the vibrational frequencies.

The application of S.C.M.F.F. of Alix [35] defined here by p^* is in good agreement with the model of Cerf [1–4]. In particular, the mean value of p^* obtained for the halides AX_4 in which the central atom belongs to the group IV, coincides exactly with the optimum value of p (i. e., $p = 0.73$). The S.C.M.F.F. gives different values of p^* for each group. So the S.C.M.F.F. being nearly equivalent to $p = \text{constant}$ for the calculation of vibrational frequencies seems to be better for the calculation of the force constants.

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