Pseudo-exact Force Constants for Tetramethyls of Group IVA Metals and Molecular Force Fields for Some Tetrahedral Molecules or Ions

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Recently reported Coriolis constants of tetrahedral tetramethyls of group IVA metals from the vapour phase IR spectra have been used to determine the pseudo-exact force constants with the aid of the point mass model. The symmetrized force constants for tetramethyls of group IVA and some tetrahedral molecules and ions have also been computed following thhe L-F approximation method. The results are compared with exact or pseudo-exact force constants and with those force constants obtained from different approximation methods. The validity of the method has been tested.

Introduction

Recently Bosworth et al.[1] have reported Coriolis constants of tetramethyls of group IVA metals from the vapour phase IR spectra. In the present communication it is aimed (i) to fix the molecular force fields for the tetramethyls of group IVA metals using the point mass model (P.M.M.) in conjunction with Coriolis coupling constants as additional data, and (ii) to evaluate the symmetrized force constants for tetramethyls of group IVA metals and ten other tetrahedral molecules and ions viz: BeF_4^{2-}, MgX_4^{2-} (X = Cl, Br or I), AlX_3^- (X = Cl, Br or I), TiI_4, $Os^{16}O_4$ and $Os^{18}O_4$, following the methods of Müller [2–4], Pandey et al.[5] and Thakur and Rai [6]. A comparison of the various results, is also made.

Method of Computation

Molecules and ions of the type XY_4 belong to the point group T_d, and the fundamental vibrations are distributed as $\Gamma = 1\,A_1 + 1\,E + 2\,F_2$.

In order to make use of experimentally known Coriolis coupling data for determining the three symmetrized force constants appearing in two dimentional secular equation of species F_2, the following equations [7] have been used:

$$G_{ii} F_{ii} + 2\, G_{ij} F_{ij} + G_{jj} F_{jj} = \lambda_i + \lambda_j \,, \tag{1}$$

$$(G_{ii} G_{jj} - G_{ij}^2)\ (F_{ii} F_{jj} - F_{ij}^2) = \lambda_i \lambda_j \,, \tag{2}$$

and

$$F_{ii}(G_{ii} - C_{ii}) + 2\, F_{ij}(G_{ij} - C_{ij}) + F_{jj}(G_{jj} - C_{jj}) = \lambda_i(1 - \zeta_i) + \lambda_j(1 - \zeta_j) \,. \tag{3}$$

In the above equations $\lambda_i = 4\,\pi^2 c^2 \nu_i^2$, and G_{ij} and C_{ij} elements depend only on the reciprocal of the masses of the constituent atoms and the equilibrium parameter of the molecules. Two sets of force constants are obtained with the help of Eqs. (1) – (3), one of which is rejected on physical grounds. The second one is the unique set of force constants which is considered here.

Since we are reporting a unique set of pseudo-exact force constants for the first time, it will be interesting to examine the validity of a few approximation methods. The L-F approximation, Müller's L-matrix approximation and the method of Thakur and Rai have been selected for this purpose.

Results and Discussion

The pseudo-exact force constants and the force constants for F_2 species obtained by different approximation methods for tetramethyls of group IVA metals are collected in Table 1. It is apparent from Table 1 that the symmetrized force constants for tetramethyls of germanium, tin and lead determined by the methods of L-F approximation and L-matrix approximation, are in excellent agreement with the pseudo-exact force constants, but this is not true for tetramethyls of carbon and silicon. This is on account of strong mixing between the skeletal

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Table 1. Comparison of symmetrized force constants of F_2 species for tetrahedral tetramethyls of group IV A metals obtained from different approximation methods.

Molecule	Wave number (in cm^{-1})	Force constants (in mdyn/Å)			Method
		F_{11}	F_{12}	F_{22}	
$C(CH_3)_4$	$\nu_1(F_2)=1257$	4.83	0.14	0.31	PE−PMM
	$\nu_2(F_2)=414.8$	5.31	0.30	0.30	L−F approx.
		5.38	0.36	0.30	$L_{12}=0$
		5.29	0.24	0.35	$^*F_{12}=F_{12}^c$
		5.99	0.64	0.32	PE−PMM **
$Si(CH_3)_4$	$\nu_1(F_2)=694.5$	2.57	0.25	0.13	PE−PMM
	$\nu_2(F_2)=239.0$	2.34	0.09	0.12	$L-F$ approx.
		2.36	0.09	0.12	$L_{12}=0$
		2.48	0.05	0.14	$^*F_{12}=F_{12}^c$
$Ge(CH_3)_4$	$\nu_1(F_2)=599.2$	2.25	0.06	0.10	PE−PMM
	$\nu_2(F_2)=188.5$	2.24	0.04	0.10	L−F approx.
		2.24	0.04	0.10	$L_{12}=0$
		2.48	0.01	0.11	$^*F_{12}=F_{12}^c$
$Sn(CH_3)_4$	$\nu_1(F_2)=527.0$	1.84	−0.02	0.07	PE−PMM
	$\nu_2(F_2)=148.0$	1.86	0.02	0.07	L−F approx.
		1.86	0.02	0.07	$L_{12}=0$
		2.10	0.00_4	0.07	$^*F_{12}=F_{12}^c$
$Pb(CH_3)_4$	$\nu_1(F_2)=476.1$	1.60	0.005	0.05	PE−PMM
	$\nu_2(F_2)=120$	1.60	0.007	0.05	L−F approx.
		1.60	0.007	0.05	$L_{12}=0$
		1.60	0.001	0.05	$^*F_{12}=F_{12}^c$

* Thakur and Rai method (Reference[6]).

** Pseudo-exact force constants using ζ constants from Raman band contour analysis.

PE-PMM: Pseudo exact point mass model.

and methyl group fundamentals for $C(CH_3)_4$ and $Si(CH_3)_4$ as pointed by Bosworth et al.[1], and therefore, the approximation of treating methyl groups as a point mass is unjustified in case of $C(CH_3)_4$ and $Si(CH_3)_4$ while for the remaining tetramethyls of group IVA metals it is justified. In order to further test the validity of the point mass model and L-F approximation and L-matrix approximation for $M(CH_3)_4$ (M = Ge, Sn, Pb) we have computed the Coriolis coupling constants by making use of the computed force constants, tabulated in Table 1 and an empirical relation[8]. The results are presented in Table 2 together with the experimental data. A comparison of these values from Table 2 shows that the calculated values are more near to the experimental values in case of the tetramethyls of Ge, Sn and Pb as compared to C and Si which justify our assumption.

Table 2. Coriolis constants for tetrahedral tetramethyls of group IV A metals.

Molecule	Coriolis constants $\zeta_3(F_2 \times F_2)$		
	Calculated *	L-F approx. method	Exptl. **
$C(CH_3)_4$	0.59	0.60	0.68
			0.48 †
$Si(CH_3)_4$	0.38	0.38	0.22
$Ga(CH_3)_4$	0.19	0.19	0.17
$Sn(CH_3)_4$	0.12	0.13	0.17
$Pb(CH_3)_4$	0.08	0.08	0.08

* Mass influence on coriolis constant relation[8]. Using relation $\zeta_3(F_2 \times F_2) = 1 - [1/\{(4/3) m_y/m_x\} + 1]$.

** Reference 1.

† From Raman band contour analysis.

The symmetrized force constants for ten tetrahetral molecules of the type XY_4, where in most cases $m_x < m_y$, are tabulated in Table 3. It is interesting to note that symmetrized force constants for $Os^{16}O_4$, evaluated by L-matrix approximation method and L-F approximation method are in excellent agreement with the exact force field[9]. It is noted from Table 3, that the force constants, evaluated by the method of Thakur and Rai[6] are generally in agreement with OVFF constants as reported in our earlier work[10, 11] for the tetrahedral molecules and ions under present study. It is interesting to note that the force constants evaluated by $L_{12} = 0$ and L-F approximation method are in better agreement with each other than OVFF constants. The value of interaction term F_{34} in L-F approximation method is smaller as compared to that obtained by L-matrix approximation method. It is essential to quote that generally, the L-matrix approximation method tends to over estimate the interaction term[12] for molecules of the type XY_n where $M_x < M_y$.

Table 3. Comparison of symmetrized force constants of F_2 species for some tetrahedral XY_4 type molecules or ions obtained from approximation methods.

Molecule/ Ion	Wave number (in cm^{-1})	Force constants (in mdyn/Å)			Method	Ref.
		F_{11}	F_{12}	F_{22}		
BeF_4^{2-}	$\nu_1(F_2) = 800$	2.61	0.49	0.33	$L_{12} = 0$	PW
	$\nu_2(F_2) = 385$	2.37	0.42	0.34	L−F approx	PW
		1.87	0.30	0.39	$*F_{12} = F_{12}^{c}$	PW
		1.72	0.29	0.41	OVFF	11
MgC_4^{2-}	$\nu_1(F_2) = 330$	0.93	0.12	0.09	$L_{12} = 0$	PW
	$\nu_2(F_2) = 142$	0.89	0.10	0.09	L−F approx	PW
		0.78	0.07	0.10	$*F_{12} = F_{12}^{c}$	PW
		0.81	0.10	0.09	OVFF	11
$MgBr_4^{2-}$	$\nu_1(F_2) = 290$	0.93	0.12	0.07	$L_{12} = 0$	PW
	$\nu_2(F_2) = 90$	0.88	0.10	0.07	L−F approx	PW
		0.78	0.08	0.08	$*F_{12} = F_{12}^{c}$	PW
		0.75	0.07	0.08	OVFF	11
MgI_4^{2-}	$\nu_1(F_2) = 259$	0.78	0.09	0.05	$L_{12} = 0$	PW
	$\nu_2(F_2) = 60$	0.75	0.08	0.05	L−F approx	PW
		0.67	0.06	0.05	$*F_{12} = F_{12}^{c}$	PW
		0.65	0.05	0.05	OVFF	11
$AlCl_4^-$	$\nu_1(F_2) = 496$	2.12	0.20	0.16	$L_{12} = 0$	PW
	$\nu_2(F_2) = 186$	2.07	0.18	0.16	L−F approx	PW
		1.84	0.12	0.16	$*F_{12} = F_{12}^{c}$	PW
		1.88	0.13	0.16	OVFF	10
$AlBr_4^-$	$\nu_1(F_2) = 409$	1.89	0.19	0.12	$L_{12} = 0$	PW
	$\nu_2(F_2) = 114$	1.83	0.17	0.12	L−F approx	PW
		1.66	0.12	0.12	$*F_{12} = F_{12}^{c}$	PW
		1.59	0.10	0.12	OVFF	10
AlI_4^-	$\nu_1(F_2) = 336$	1.43	0.16	0.09	$L_{12} = 0$	PW
	$\nu_2(F_2) = 82$	1.38	0.14	0.09	L−F approx	PW
		1.24	0.11	0.09	$*F_{12} = F_{12}^{c}$	PW
		1.16	0.09	0.10	OVFF	10
TiI_4	$\nu_1(F_2) = 324$	1.89	0.10	0.06	$L_{12} = 0$	PW
	$\nu_2(F_2) = 67$	1.87	0.10	0.06	L−F approx	PW
		1.77	0.06	0.06	$*F_{12} = F_{12}^{c}$	PW
		1.77	0.06	0.07	OVFF	10
$Os^{16}O_4$	$\nu_1(F_2) = 976.9$	8.11	0.10	0.47	Exact	12
		±0.08	±0.10	±0.01		
	$\nu_2(F_2) = 345$	8.10	0.09	0.47	$L_{12} = 0$	PW
		8.10	0.09	0.47	L−F approx	PW
		8.07	0.01_3	0.47	$*F_{12} = F_{12}^{c}$	PW
$Os^{18}O_4$	$\nu_1(F_2) = 926.6$	7.78	0.10	0.45	$L_{12} = 0$	PW
	$\nu_2(F_2) = 328.3$	7.78	0.09	0.45	L−F approx	PW
		8.16	0.23	0.47	OVFF	10

PW: Present work. * Thakur and Rai method (Reference [6]).

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