Tetrahedral XY_4 Molecules: Application of the Keating Bendings to the Degenerate Vibrations

S. J. Cyvin [a], B. N. Cyvin [a], M.-A. Einarsrud [b], J. Brunvoll [a], and G. Díaz Fleming [c]

Z. Naturforsch. **41 a**, 615–618 (1986); received January 29, 1986

The Keating force field of tetrahedral XY_4 molecules is defined in analogy with valence and central force fields. The applicability of the Keating coordinates versus valence and central coordinates is tested by different approaches. The general conclusion goes in favour of the Keating coordinates.

Introduction

The theory of Keating bendings [1, 2] was formulated in the conventional terms of molecular vibration studies by Cyvin [3]. This new internal coordinate has been successfully applied to the E′ species of the molecular vibration of planar symmetrical XY_3 molecules [4–8]. In all these works the Keating force field (for a definition, see below) proved to the better than the valence and central force fields. Furthermore, force fields based on the Keating bendings appeared to be better than those with Decius' bendings [9] to reproduce the experimental frequencies of naphthalene, benzene, other condensed aromatics, and the dodecaborane ion [10–12]. The applicability of Keating bendings was also tested in bent symmetrical XY_2 molecules [13]. In this case no general conclusion could be drawn with regard to the superiority of the different coordinate types.

The purpose of the present work is to test the applicability of Keating coordinates to the T_2 species of the molecular vibrations of tetrahedral XY_4 type molecules, in comparison with valence and central coordinates.

[a] Division of Physical Chemistry, The University of Trondheim, Norway.
[b] Laboratory of Inorganic Chemistry, The University of Trondheim, Norway.
[c] Academia Superior de Ciencias Pedagogicas, Valparaiso, Chile.

Reprint requests to Prof. Dr. S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway.

Theory

Valence Coordinates

The symmetrical XY_4 (T_d) molecular model is treated on pp. 121–124 of Cyvin's book [14] in terms of the stretchings, r_i, and scaled bendings, $R\alpha_{ij}$. One degenerate pair of symmetry coordinates of the species T_2 is

$$S_{1a}(T_2) = \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4),$$

$$S_{2a}(T_2) = 2^{-\frac{1}{2}} R(\alpha_{24} - \alpha_{13}).$$

The corresponding **G** matrix block is

$$\mathbf{G}(T_2) = \begin{bmatrix} \frac{4}{3}\mu_X + \mu_Y & \frac{8}{3}\mu_X \\ & 2(\frac{8}{3}\mu_X + \mu_Y) \end{bmatrix}.$$

Central Coordinates

The central coordinates are obtained from the valence coordinates on replacing Decius' bendings ($R\alpha_{ij}$) by nonbond stretchings, d_{ij}, as shown on pp. 143–146 of the cited book [14]. Accordingly one obtains the central symmetry coordinates, $S^c(T_2)$ as

$$S_1^c = S_1, \quad S_2^c = -\tfrac{2}{3} 3^{\frac{1}{2}} S_1 + 3^{-\frac{1}{2}} S_2.$$

These expressions are applicable to all degenerate pairs (a, b, c). In consequence, the **G** matrix block of species T_2 in terms of the central symmetry coordinates becomes

$$\mathbf{G}^c(T_2) = \begin{bmatrix} \frac{4}{3}\mu_X + \mu_Y & -\frac{2}{3} 3^{\frac{1}{2}} \mu_Y \\ & 2\mu_Y \end{bmatrix}.$$

0340-4811 / 86 / 0400-0615 $ 01.30/0. – Please order a reprint rather than making your own copy.

The connection between the symmetry valence force constants (F_{ij}) and the symmetry central force constants (F^c_{ij}) is

$$F^c_{11} = F_{11} + 4F_{12} + 4F_{22},$$

$$F^c_{12} = 3^{\frac{1}{2}} F_{12} + 12^{\frac{1}{2}} F_{22},$$

$$F^c_{22} = 3F_{22}.$$

Keating Coordinates

In Keating coordinates, the Decius bendings are replaced by Keating bendings, $\varkappa_{ij}$, given by

$$\varkappa_{ij} = \alpha_{ij} \sin 2A - (r_i + r_j) \cos 2A.$$

Here A is the half of the YXY angle, which here is tetrahedral. The symmetry coordinates follow:

$$S^k_1 = S_1, \quad S^k_2 = -\tfrac{1}{3} 2^{\frac{1}{2}} S_1 + \tfrac{2}{3} 2^{\frac{1}{2}} S_2.$$

The $\mathbf{G}^k(T_2)$ and $\mathbf{F}^k(T_2)$ matrices obtained through this transformation are given by

$$\mathbf{G}^k(T_2) = \begin{bmatrix} \frac{4}{3}\mu_X + \mu_Y & \frac{1}{3} 2^{\frac{1}{2}}(4\mu_X - \mu_Y) \\ & 2(\frac{4}{3}\mu_X + \mu_Y) \end{bmatrix},$$

$$F^k_{11} = F_{11} + F_{12} + \tfrac{1}{4} F_{22},$$

$$F^k_{12} = \tfrac{3}{2} 2^{-\frac{1}{2}} F_{12} + \tfrac{3}{4} 2^{-\frac{1}{2}} F_{22},$$

$$F^k_{22} = \tfrac{9}{8} F_{22}.$$

Principles of Analysis

The validity of the Valence Force Field (VFF), Central Force Field (CFF) and Keating Force Field (KFF) can be judged by assuming $F_{12} = 0$ (VFF), $F^c_{12} = 0$ (CFF) and $F^k_{12} = 0$ (KFF). In this approach F_{11} and F_{22} are determined in each case so that they reproduce exactly the observed frequencies of one isotopic molecule. The calculated frequencies of the other isotopic species of the molecule give a measure of the superiority of the different approximations.

Another approach to this problem is possible when a reliable force field is available, as based on accurate experimental data as isotopic shifts, Coriolis coupling constants, mean amplitudes of vibration, etc., in addition to the vibrational frequencies of the main isotopic species. Such a force field has been referred to as "exact". It may be expressed by symmetry **F** matrices in terms of valence (VAL), central (CEN) and Keating (KEA) coordinates. The lowest magnitude of the interaction constant (i.e. F_{12}, F^c_{12} or F^k_{12}) is considered as an indication of the coordinate system which is best suited as a basis for approximations.

Numerical Computations

In the first approach (i.e. $F_{12} = 0$, $F^c_{12} = 0$ and $F^k_{12} = 0$) we have considered the most recent vibrational data of some tetrahedral XY_4 molecules. They include accurate frequencies of different isotopically substituted species [15–17]. The two nonvanishing force constants of the T_2 species were adjusted to fit exactly the experimental frequencies of one isotopic species; they are collected in Table 1. The observed and calculated frequencies of the different isotopic species are shown in Table 2.

In the second approach we have collected "exact" force fields from the literature [15–17]; they have been obtained from Coriolis coupling constants and isotopic shifts of vibrational frequencies as additional data. In Table 3 we present these force fields in terms of the three coordinate sets of the present study (i.e. VAL, CEN and KEA).

Conclusion

From the results in Table 2 we can infer that the Keating force field (KFF) is definitely the best of

Table 1. Valence (VFF), central (CFF) and Keating (KFF) force field approximations; force constants in mdyne/Å.

Isotopic species	Ref.	(*ij*)	VFF	CFF	KFF
$^{12}CH_4$	[15]	(11)	5.2600	[a]	5.2310
		(22)	0.4610		0.5213
$^{12}CF_4$	[16]	(11)	[a]	5.3200	4.6300
		(22)		3.1550	1.3600
$^{28}Si^{19}F_4$	[17]	(11)	5.7380	5.6100	6.1390
		(22)	0.4731	1.4525	0.4977
$^{74}Ge^{19}F_4$	[17]	(11)	5.2490	4.4850	5.3200
		(22)	0.2731	0.9840	0.3105
$^{28}Si^{35}Cl_4$	[17]	(11)	2.4820	2.8290	2.8290
		(22)	0.2721	0.7165	0.2687
$^{74}Ge^{35}Cl_4$	[17]	(11)	2.5650	2.3400	2.6750
		(22)	0.1788	0.5880	0.1930
$^{116}Sn^{35}Cl_4$	[17]	(11)	2.4470	2.2140	2.4860
		(22)	0.1082	0.3588	0.1198
$^{28}Si^{79}Br_4$	[17]	(11)	1.8360	2.4040	2.2070
		(22)	0.2170	0.4970	0.2031
$^{74}Ge^{79}Br_4$	[17]	(11)	1.9195	2.0426	2.0790
		(22)	0.1488	0.4185	0.1541
$^{116}Sn^{81}Br_4$	[17]	(11)	1.9180	1.9035	1.9940
		(22)	0.0940	0.2837	0.1017

[a] Outside the range of real force constants.

Table 2. Calculated and experimental T_2 frequencies (cm^{-1}); calculations from the VFF, CFF, and KFF approximations.

Isotopic species	$\nu(T_2)$	Calculated frequencies			Exp.	Ref.
		VFF	CFF	KFF		
$^{12}CH_4$	3	3156.8	–	3156.8	3156.8	[15]
	4	1367.4	–	1367.4	1367.4	
$^{12}CD_4$	3	2352.8	–	2332.1	2336.2	[15]
	4	1025.7	–	1034.7	1034.1	
$^{13}CH_4$	3	3143.8	–	3146.0	3145.6	[15]
	4	1360.0	–	1358.8	1358.9	
$^{12}CF_4$	3	–	1283.2	1283.2	1283.2	[16]
	4	–	631.2	631.2	631.2	
$^{13}CF_4$	3	–	1256.2	1240.6	1241.7	[16]
	4	–	622.6	630.6	629.3	
$^{14}CF_4$	3	–	1233.8	1203.6	1208.7	[16]
	4	–	614.3	629.8	627.3	
$^{28}Si^{19}F_4$	3	1030.9	1030.9	1030.9	1030.9	[17]
	4	389.3	389.3	389.3	389.3	
$^{29}Si^{19}F_4$	3	1020.9	1024.3	1021.8	1022.1	[17]
	4	388.1	386.9	387.6	387.7	
$^{30}Si^{19}F_4$	3	1011.6	1021.7	1013.2	1013.7	[17]
	4	386.9	386.0	386.4	386.2	
$^{74}Ge^{19}F_4$	3	799.6	799.6	799.6	799.6	[17]
	4	272.9	272.9	272.9	272.9	
$^{70}Ge^{19}F_4$	3	806.3	803.6	805.4	805.3	[17]
	4	271.2	275.5	274.8	274.9	
$^{76}Ge^{19}F_4$	3	796.6	797.7	796.0	797.0	[17]
	4	268.6	271.7	272.0	272.0	
$^{28}Si^{35}Cl_4$	3	621.3	621.3	621.3	621.3	[17]
	4	222.3	222.3	222.3	222.3	
$^{28}Si^{37}Cl_4$	3	616.9	613.9	616.0	615.7	[17]
	4	216.7	217.9	217.1	217.2	
$^{29}Si^{35}Cl_4$	3	613.4	615.3	613.9	614.5	[17]
	4	221.9	221.2	221.7	221.5	
$^{29}Si^{37}Cl_4$	3	608.9	607.8	608.6	609.0	[17]
	4	216.4	216.8	216.5	216.4	
$^{30}Si^{35}Cl_4$	3	605.9	609.7	607.0	608.1	[17]
	4	221.5	220.2	221.2	220.7	
$^{30}Si^{37}Cl_4$	3	601.3	602.0	601.5	602.3	[17]
	4	216.0	215.8	216.0	215.7	
$^{74}Ge^{35}Cl_4$	3	461.3	461.3	461.3	461.3	[17]
	4	171.3	171.3	171.3	171.3	
$^{70}Ge^{35}Cl_4$	3	467.1	465.1	466.2	466.3	[17]
	4	172.3	173.0	172.5	172.6	
$^{74}Ge^{37}Cl_4$	3	454.3	452.3	453.8	453.7	[17]
	4	167.6	168.3	167.8	167.8	
$^{76}Ge^{35}Cl_4$	3	458.6	459.6	458.8	459.1	[17]
	4	170.8	170.4	170.7	170.6	
$^{116}Sn^{35}Cl_4$	3	411.3	411.3	411.3	411.3	[17]
	4	127.5	127.5	127.5	127.5	
$^{116}Sn^{37}Cl_4$	3	403.5	402.6	402.3	403.3	[17]
	4	124.8	125.1	124.9	125.1	
$^{124}Sn^{35}Cl_4$	3	407.1	408.3	407.4	407.7	[17]
	4	126.5	126.2	126.4	126.3	
$^{124}Sn^{37}Cl_4$	3	399.3	399.5	399.4	399.6	[17]
	4	123.8	123.8	123.8	123.8	
$^{28}Si^{79}Br_4$	3	499.3	499.3	499.3	499.3	[17]
	4	134.7	134.7	134.7	134.7	
$^{28}Si^{81}Br_4$	3	498.5	497.8	498.3	498.6	[17]
	4	133.1	133.2	133.1	133.0	
$^{29}Si^{79}Br_4$	3	491.6	492.5	492.0	492.4	[17]
	4	134.6	134.3	134.5	134.4	
$^{29}Si^{81}Br_4$	3	490.9	491.1	491.0	491.5	[17]
	4	133.0	132.9	132.9	132.8	
$^{30}Si^{79}Br_4$	3	484.5	486.3	485.1	485.7	[17]
	4	134.5	133.9	134.3	134.1	
$^{30}Si^{81}Br_4$	3	483.7	484.8	484.1	484.8	[17]
	4	132.9	132.5	132.7	132.6	
$^{74}Ge^{79}Br_4$	3	334.6	334.6	334.6	334.6	[17]
	4	111.3	111.3	111.3	111.3	
$^{70}Ge^{79}Br_4$	3	341.0	339.6	340.6	340.1	[17]
	4	111.7	112.2	111.8	112.0	
$^{70}Ge^{81}Br_4$	3	339.7	337.7	339.1	339.0	[17]
	4	110.5	111.2	110.7	110.7	
$^{74}Ge^{81}Br_4$	3	333.3	332.7	333.1	333.4	[17]
	4	110.1	110.3	110.1	110.0	
$^{76}Ge^{79}Br_4$	3	331.7	332.3	331.8	331.9	[17]
	4	111.1	110.9	111.0	111.0	
$^{76}Ge^{81}Br_4$	3	330.3	330.4	330.3	330.8	[17]
	4	109.9	109.9	109.9	109.7	
$^{116}Sn^{81}Br_4$	3	285.6	285.6	285.6	285.6	[17]
	4	85.8	85.8	85.8	85.8	
$^{116}Sn^{79}Br_4$	3	287.2	287.7	287.4	287.0	[17]
	4	86.7	86.5	86.6	86.7	
$^{124}Sn^{79}Br_4$	3	282.4	283.8	282.8	282.6	[17]
	4	86.1	85.6	85.9	85.9	
$^{124}Sn^{81}Br_4$	3	280.6	281.7	280.9	280.9	[17]
	4	85.3	84.8	85.1	85.1	

the three approximations for CH_4, CF_4, SiF_4 and GeF_4. Also in the majority of the other cases KFF appears to be best, but the conclusion is not so clear all the time. Many of the shifts are relatively small, and the test can hardly be considered as significant within the experimental limits of error.

The results from the second approach are reflected in Table 3. The conclusions from this test are more significant than those from Table 2 since also the Coriolis constants have been invoked. These quantities are known to be sensitive for relatively small changes in force constants. In all cases it is found that

$$|F_{12}^{k}| < |F_{12}| < |F_{12}^{c}|.$$

Hence it is concluded unequivocally that the Keating coordinates are superior to either valence or central coordinates as a basis of force field approximations for the investigated XY_4 molecules.

Table 3. Previous ("exact") T_2 force fields in terms of valence (VAL), central (CEN) and Keating (KEA) coordinates; mdyne/Å.

Molecule	Coordinates	(11)	(12)	(22)	Ref.
CH_4 [a]	VAL	5.3780	−0.2036	0.4655	[15]
	CEN	6.4256	1.2599	1.3965	
	KEA	5.2900	0.0309	0.5235	
CF_4 [b]	VAL	6.1200	−0.7750	1.0560	[16]
	CEN	7.2440	2.3157	3.1680	
	KEA	5.6090	−0.2620	1.1180	
SiF_4	VAL	6.3700	−0.2800	0.4380	[17]
	CEN	7.0020	1.0323	1.3140	
	KEA	6.1995	−0.0647	0.4928	
GeF_4	VAL	5.4100	−0.1500	0.2760	[17]
	CEN	5.9140	0.6963	0.8280	
	KEA	5.3290	−0.0127	0.3105	
$SiCl_4$	VAL	3.2500	−0.2500	0.2260	[17]
	CEN	3.1540	0.3499	0.6780	
	KEA	3.0565	−0.1453	0.2543	
$GeCl_4$	VAL	2.8000	−0.1400	0.1710	[17]
	CEN	2.9240	0.3499	0.5130	
	KEA	2.7028	−0.0578	0.1924	
$SnCl_4$	VAL	2.5500	−0.0800	0.1070	[17]
	CEN	2.6580	0.2321	0.3210	
	KEA	2.4968	−0.0281	0.1204	
$SiBr_4$	VAL	2.6100	−0.1800	0.1660	[17]
	CEN	2.5540	0.2633	0.4980	
	KEA	2.4715	−0.1029	0.1868	
$GeBr_4$	VAL	2.3400	−0.1600	0.1320	[17]
	CEN	2.2280	0.1801	0.3960	
	KEA	2.2130	−0.0997	0.1485	
$SnBr_4$	VAL	2.0500	−0.0600	0.0900	[17]
	CEN	2.1700	0.2078	0.2700	
	KEA	2.0125	−0.0159	0.1013	

[a] Converted into mdyne/Å by means of $R = 1.085$ Å.
[b] Converted into mdyne/Å by means of $R = 1.320$ Å.

Acknowledgement

Financial support to BNC from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

[1] P. N. Keating, Phys. Rev. **145,** 637 (1966)
[2] W. Weber and M. F. Thorpe, J. Phys. Chem. Solids **36,** 967 (1975).
[3] S. J. Cyvin, Spectroscopy Letters **17,** 489 (1984).
[4] S. J. Cyvin, Spectroscopy Letters **17,** 493 (1984).
[5] S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, Spectroscopy Letters **17,** 511 (1984).
[6] S. J. Cyvin and B.N. Cyvin, Spectroscopy Letters **17,** 525 (1984).
[7] S. J. Cyvin, B. N. Cyvin, T. Mogstad, J. Brunvoll, and G. Díaz Fleming, Spectroscopy Letters **17,** 537 (1984).
[8] S. J. Cyvin, B. N. Cyvin, and G. Díaz Fleming, Spectrochim. Acta **41 A,** 351 (1985).
[9] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.
[10] J. Brunvoll, B. N. Cyvin, and S. J. Cyvin, Spectroscopy Letters **17,** 551 (1984).
[11] B. N. Cyvin, J. Brunvoll, S. J. Cyvin, and P. Klaeboe, Spectroscopy Letters **17,** 559 (1984).
[12] B. N. Cyvin, J. Brunvoll, and S. J. Cyvin, Spectroscopy Letters **17,** 569 (1984).
[13] S. J. Cyvin and B. N. Cyvin, Spectroscopy Letters **17,** 541 (1984).
[14] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo and Elsevier, Amsterdam 1968.
[15] D. L. Gray and A. G. Robiette, Mol. Phys. **37,** 1901 (1979).
[16] L. H. Jones, C. Kennedy, and S. Ekberg, J. Chem. Phys. **69,** 833 (1978).
[17] F. Königer, A. Müller, and W. J. Orville-Thomas, J. Mol. Struct. **37,** 199 (1977).