

The dynamics of tetrahedral XY_4 molecules

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Abstract. A physical understanding of the nature of the force constants and kinetic constants in molecules leads to a stringent application of the provisions of the group theoretical techniques introduced by Wilson in the study of molecular vibrations. This procedure is applied here to the evaluation of force constants and the mean amplitudes of eighteen tetrahedral XY_4 molecules with highly satisfactory results.

Keywords. Molecular dynamics; molecular constants.

1. Introduction

The general quadratic valence force field, abbreviated as GQVFF, has been one of the widely adopted force fields in the study of molecular constants. A physical understanding of the problem has shown that there are at least two classes of force constants, *viz.*, independent force constants and non-independent force constants in molecules. The non-independent force constants may be eliminated from consideration and our attention may be confined to the independent force constants only, for evaluation from spectroscopic data. Secondly, the kinetic constants of molecules are found to be effective participants in molecular dynamics. These kinetic constants have their own intrinsic characteristics and, in addition, they have interesting applications in the study of molecular constants as amply demonstrated in studies relating to XY_3 (D_{3h}), XY_3 (C_{3v}), XY_4 (D_{4h}), XY_6 (O_h), XYZ_2 (C_{2v}) and XYZ_3 (C_{3v}) molecules (Thirugnanasambandam and Srinivasan 1969; Thirugnanasambandam and Mohan 1974 *a,b*; 1975 *a,b,c*; Thirugnanasambandam and Karunanidhi 1975, 1976). Thus a new procedure, based on independent force constants as well as kinetic constants, seems to be now available in a stringent, and at the same time, straightforward application of Wilson's F - G matrix method (Wilson 1939, 1941) to the study of molecular constants.

2. Theoretical considerations

2.1. Internal coordinates

A look at the general tetrahedral XY_4 molecule reveals that there are four bonds and six planes in the molecule (figure 1). There are two angles in each of the planes and therefore the number of angles to be taken into account becomes twelve instead of the usual six interbond angles. Thus the number of internal coordinates

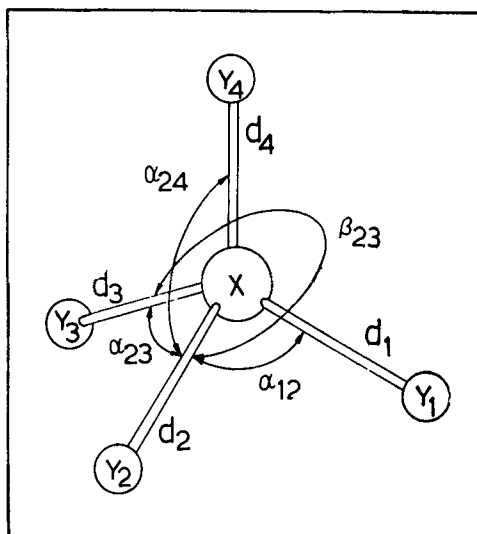


Figure 1. Geometry, bond distances and interbond angles of the tetrahedral XY_4 type of molecules.

in this molecule is found to be sixteen, four contributed by the four bond distances, six contributed by the usual six interbond angles and six more contributed by the reflex angles in the planes concerned.

2.2. Symmetry coordinates*

On the basis of the sixteen internal coordinates viz., $\Delta d_1, \Delta d_2, \Delta d_3, \Delta d_4, \Delta \alpha_{12}, \Delta \alpha_{23}, \Delta \alpha_{31}, \Delta \alpha_{41}, \Delta \alpha_{42}, \Delta \alpha_{43}, \Delta \beta_{12}, \Delta \beta_{23}, \Delta \beta_{31}, \Delta \beta_{41}, \Delta \beta_{42}, \Delta \beta_{43}$, sixteen symmetry coordinates are formed subject to the well-known group theoretical considerations.

2.3. Redundancy constraints*

Following Ford and Orville Thomas (1967), the seven redundant symmetry coordinates are found to lead to ten redundancy constraints. The redundancy constraints show that ten of the force constants are non-independent force constants so that the number of independent force constants involved in the tetrahedral XY_4 molecule turns out to be only five in number viz., f_a the stretching force constant, f_{aa} the bond-bond interaction force constant, f_α the bending force constant, $f'_{\alpha\alpha}$ the force constant relating to the interaction between two interior distant angles and $f'_{a\alpha}$ the interaction force constant between a bond and the corresponding distant interior angle.

2.4. F matrix

By incorporating the redundancy constraints in the general F matrix, the condensed F matrix elements are obtained and they are given below:

A_1 Type :

$$F_{11} = f_a + 3f_{aa}$$

* Symmetry coordinates, redundancy constraints and G matrix elements are available from the authors on request.

E Type:

$$F_{22} = 3d^2 (f_a + f'_{a\alpha})$$

F₂ Type:

$$F_{33} = f_u - f_{aa}$$

$$F_{44} = 2d^2 (f_a - f'_{a\alpha})$$

$$F_{34} = -4df'_{u\alpha}$$

2.5. Kinetic constants

The *G* matrix elements are obtained as usual by Wilson's method. The kinetic constants arise out of the expression

$$2T = S G^{-1} S$$

and are given below:

$$k_{\ddot{u}} = (\mu_y + 3\mu_x)/4\mu_y$$

$$k_{\ddot{a}\ddot{a}} = \mu_x/3A\mu_y$$

$$k_{\alpha\alpha} = (1/144 \mu_y) (B/A)$$

$$k'_{\alpha\alpha} = - (1/144 \mu_y) (C/A)$$

$$k'_{\ddot{a}\alpha} = - \mu_x/3\sqrt{2} A \mu_y$$

where

$$A = \mu_y + 4\mu_x$$

$$B = 13\mu_y + 28\mu_x$$

$$C = 5\mu_y - 4\mu_x$$

2.6. Reduction of equations

The kinetic constants are utilised to eliminate the off-diagonal elements in the *F* matrix, through the equation

$$F_{34}/F_{44} = K_{34}/K_{44}$$

Thus F_{34} is eliminated and the equations relating to F_{11} , F_{22} as well as the equations involving F_{33} and F_{44} are available in a straightforward solution of the problem. (Thirugnanasambandam *et al.* 1969 1974 *a,b*, 1975 *a,b,c*, 1976).

2.7. Mean amplitudes

Making use of the force constants obtained from the sequential steps mentioned above, the mean amplitudes of vibration are calculated by adopting Cyvin's procedure (Cyvin 1968).

3. Results and Discussion

Results relating to eighteen tetrahedral XY_4 molecules are discussed here. Table 1 gives the structural parameters and vibrational frequencies of the molecules studied in the present investigation. Table 2 deals with the kinetic constants of these molecules. The evaluated individual force constants of these molecules are presented here in table 3. The mean square amplitudes and the mean amplitudes are given in tables 4 and 5 respectively.

Table 1. Structural parameters and the vibrational frequencies

Sl. No.	Molecule	Bond distance d in A	$\nu_1 (A_1)$	$\nu_2 (E)$ (Wave numbers cm^{-1})	$\nu_3 (F_2)$	$\nu_4 (F_2)$	Refererce
1.	CH ₄	1.091	3143	1573	3145	1357	a, b
2.	CD ₄	..	2224	1113	2333	1027	a, b
3.	CT ₄	..	1817	910	1990	880	a, b
4.	NH ₄	1.016	3040	1680	3145	1400	b, c
5.	ND ₄	..	2214	1215	2346	1065	b, c
6.	SiH ₄	1.48	2187	974.6	2190.6	914.2	d
7.	SiD ₄	..	1545	689	1597	681	e, f
8.	GeH ₄	1.527	1990	833	2110	933	g, h, i
19.	GeD ₄	..	1504	665	1522	596	b, j
10.	SiO ₄	1.61	800	500	1050	625	b, g
11.	PO ₄	1.61	970	358	1080	500	b, e
2.	ClO ₄	1.49	932	460	1110	626	b, h
13.	MoO ₄	1.75	936	220	895	365	b, h
14.	RuO ₄	1.74	880	293	913	330	a, b
15.	IO ₄	1.81	795	280	840	340	b, g
16.	XeO ₄	1.736	767.1	277	867	303	k, l
17.	ReO ₄	1.761	965	332	916	332	b, m
18.	OsO ₄	1.66	965	335	954	335	b, g, m

- (a) Nagarajan (1962) (h) Venkateswarlu and Sundaram (1955)
 (b) Sutton (1958) (i) Pistorius (1957)
 (c) Radhakrishnan (1964) (j) Lindeman and Wilson (1956)
 (d) Radhakrishnan (1962) (k) Huston and Claassan (1970)
 (e) Meal and Wilson (1956) (l) Gunderson and Hedberg
 (f) Kovalev (1957) (m) Venkateswarlu and Sundaram (1955)
 (g) Venkateswarlu and Thanalakshmi (1962)

Table 2. Kinetic constants (10^{-23} g)

Sl. No.	Molecule	k_a	k_{aa}	k_α	$k'_{\alpha a}$	$k'_{\alpha a}$
1.	CH ₄	0.1568	0.0035	0.0134	-0.0041	-0.0025
2.	CD ₄	0.3011	0.0112	0.0246	-0.0060	-0.0079
3.	CT ₄	0.4391	0.0210	0.0348	-0.0069	-0.0149
4.	NH ₄	0.1581	0.0032	0.0136	-0.0043	-0.0022
5.	ND ₄	0.3041	0.0102	0.0251	-0.0065	-0.0072
6.	SiH ₄	0.1622	0.0018	0.0142	-0.0049	-0.0012
7.	SiD ₄	0.3161	0.0062	0.0271	-0.0085	-0.0044
8.	GeH ₄	0.1652	0.0008	0.0147	-0.0054	-0.0005
9.	GeD ₄	0.3274	0.0024	0.0288	-0.0102	-0.0020
10.	SiO ₄	2.1949	0.1539	0.1629	-0.0153	-0.1088
11.	PO ₄	2.2090	0.1492	0.1652	-0.0177	-0.1055
12.	ClO ₄	2.2291	0.1425	0.1686	-0.0210	-0.1007
13.	MoO ₄	2.3908	0.0886	0.1955	-0.0480	-0.0626
14.	RuO ₄	2.3991	0.0858	0.1969	-0.0439	-0.0607
15.	IO ₄	2.4338	0.0742	0.2027	-0.0551	-0.0525
16.	XeO ₄	2.4387	0.0725	0.2034	-0.0560	-0.0513
17.	ReO ₄	2.4866	0.0566	0.2115	-0.0639	-0.0400
18.	OsO ₄	2.4893	0.0557	0.2120	-0.0644	-0.0394

Table 3. Force constants (10^8 dynes cm^{-1})

Sl. No.	Molecule	f_d	f_{dd}	f_a	f'_{aa}	f'_{da}
1.	CH ₄	5.4183	0.1506	0.0980	-0.0163	-0.0016
2.	CD ₄	5.4798	0.1328	0.0983	-0.0165	-0.0297
3.	CT ₄	5.5225	0.1210	0.0984	-0.0164	-0.0408
4.	NH ₄	5.4065	0.0284	0.1085	-0.0154	-0.0153
5.	ND ₄	5.6118	0.0712	0.1125	-0.0150	-0.0290
6.	SiH ₄	2.7529	0.0297	0.0441	-0.0128	-0.0037
7.	SiD ₄	2.7894	0.0158	0.0450	-0.0137	-0.0072
8.	GeH ₄	2.5367	-0.0612	0.0427	-0.0197	-0.0016
9.	GeD ₄	2.6724	0.0053	0.0392	-0.0100	-0.0024
10.	SiO ₄	6.4945	-0.1527	0.1891	-0.0581	-0.1509
11.	PO ₄	7.4288	0.4820	0.1147	-0.0476	-0.0936
12.	ClO ₄	7.9368	0.0854	0.1873	-0.0765	-0.1402
13.	MoO ₄	6.7474	0.5053	0.0703	-0.0449	-0.0296
14.	RuO ₄	6.7300	0.1914	0.0823	-0.0129	-0.0235
15.	IO ₄	5.7898	0.0572	0.0735	-0.0324	-0.0215
16.	XeO ₄	5.9817	-0.1438	0.0624	-0.0222	-0.0167
17.	ReO ₄	7.5351	0.4161	0.0974	-0.0104	-0.0157
18.	OsO ₄	7.9982	0.2617	0.0991	-0.0110	-0.0157

Table 4. Mean square amplitudes (10^{-3} A²) at 298.16 K

Sl. No.	Molecule	σ_d σ_{dd}	σ_a σ'_{aa} σ_{da}	σ_q σ'_{qq} σ_{dq}	σ_{dq} σ'_{dq}
1.	CH ₄	5.765 -0.148	25.610 -4.325 0.421	15.232 1.774 -1.043	4.343 0.001
2.	CD ₄	4.230 -0.157	19.155 -3.988 0.567	10.746 1.243 -0.678	2.999 0.072
3.	CT ₄	3.574 -0.168	16.548 -3.989 0.665	8.803 1.000 -0.524	2.397 0.109
4.	NH ₄	5.747 -0.082	24.121 -4.199 0.361	14.913 2.008 -0.937	4.417 0.075
5.	ND ₄	4.131 -0.118	17.645 -3.801 0.484	10.320 1.365 -0.669	2.997 0.087
6.	SiH ₄	7.911 -0.088	37.959 -3.028 0.258	22.597 2.188 -0.757	6.239 0.006
7.	SiD ₄	5.662 -0.081	28.668 -2.586 0.355	16.321 1.440 -0.416	4.352 0.073
8.	GeH ₄	8.157 0.083	39.808 1.812 0.104	24.059 2.136 1.021	6.668 0.195
9.	GeD ₄	5.652 -0.028	30.461 -3.197 0.144	17.381 1.440 -0.869	4.509 0.037
10.	SiO ₄	1.684 -0.104	6.652 -1.609 0.546	3.296 0.496 0.216	0.976 0.146
11.	PO ₄	1.526 -0.140	9.346 -0.918 0.480	4.337 0.036 0.506	0.854 0.049
12.	ClO ₄	1.440 -0.095	6.531 -0.835 0.408	3.202 0.296 0.238	0.863 0.081

Table 4 (Contd.)

Sl. No.	Molecule	σ_d	σ_a	σ_q	σ_{dq}
		σ_{dd}	σ'_{aa} σ'_{da}	σ'_{qq} σ'_{dq}	σ'_{dq}
13.	MoO ₄	1.396 -0.182	15.516 4.184 0.190	6.566 -0.874 1.535	0.963 -0.024
14.	RuO ₄	1.382 -0.050	12.494 -0.685 0.176	5.608 -0.163 -0.029	0.986 0.020
15.	IO ₄	1.484 -0.033	12.361 0.419 0.154	5.763 -0.143 0.342	1.095 0.035
16.	XeO ₄	1.453 -0.003	13.700 -0.676 0.144	6.228 -0.123 0.037	1.101 0.078
17.	ReO ₄	1.263 -0.050	10.556 -1.009 0.095	4.956 -0.053 -0.290	0.935 -0.027
18.	OsO ₄	1.218 -0.035	10.378 0.974 0.089	4.868 -0.042 -0.250	0.914 -0.006

Table 5. Mean amplitudes (A) at 298.16 K

Sl. No.	Molecule	$(\sigma_d)^{1/2}$	$(\sigma_q)^{1/2}$
1.	CH ₄	0.07593	0.12342
2.	CD ₄	0.06504	0.10366
3.	CT ₄	0.05978	0.09382
4.	NH ₄	0.07581	0.12212
5.	ND ₄	0.06427	0.10159
6.	SiH ₄	0.08895	0.15032
7.	SiD ₄	0.07524	0.12775
8.	GeH ₄	0.09032	0.15511
9.	GeD ₄	0.07518	0.13184
10.	SiO ₄	0.04104	0.05741
11.	PO ₄	0.03906	0.06586
12.	ClO ₄	0.03795	0.05659
13.	MoO ₄	0.03736	0.08103
14.	RuO ₄	0.03718	0.07489
15.	IO ₄	0.03852	0.07591
16.	XeO ₄	0.03812	0.07892
17.	ReO ₄	0.03554	0.07040
18.	OsO ₄	0.03490	0.06977

The kinetic constants given in table 2 may be grouped under three heads :

1. those belonging to the bond-angle interactions ; 2. those belonging to the bending and angle-angle interactions ; 3. those belonging to the stretching and bond-bond interactions.

The bond-angle interaction kinetic constants may be seen to possess mutually complementary roles such that their algebraic sum vanishes in every case.

Thus

$$\sum k'_{aa} + \sum k''_{aa} + \sum k'_{a\beta} + \sum k''_{a\beta} = 0$$

i.e.,

$$12(2k'_{aa}) + 12(2k''_{aa}) + 12(2k'_{a\beta}) + 12(2k''_{a\beta}) = 0$$

i.e.,

$$24k'_{aa} + 24k''_{aa} + 24k'_{a\beta} + 24k''_{a\beta} = 0.$$

i.e.,

$$k'_{aa} + k''_{aa} + k'_{a\beta} + k''_{a\beta} = 0.$$

In addition to this, the bond-angle interaction kinetic constants satisfy the following relation also,

$$(k'_{aa} - k''_{aa}) + (k'_{a\beta} - k''_{a\beta}) = 0.$$

The second group of complementary kinetic constants relating to bending kinetic constants and angle-angle interaction kinetic constants behave such that their algebraic sum also vanishes on summation.

$$\begin{aligned} \sum k_{\alpha} + \sum k'_{\alpha\alpha} + \sum k''_{\alpha\alpha} + \sum k_{\beta} + \sum k'_{\beta\beta} + \sum k''_{\beta\beta} + \sum k_{\alpha\beta} \\ + \sum k'_{\alpha\beta} + \sum k''_{\alpha\beta} = 0 \end{aligned}$$

i.e.,

$$\begin{aligned} 6(k_{\alpha}) + 3(2k'_{\alpha\alpha}) + 12(2k''_{\alpha\alpha}) + 6(k_{\beta}) + 3(2k'_{\beta\beta}) + 12(2k''_{\beta\beta}) \\ + 6(2k_{\alpha\beta}) + 6(2k'_{\alpha\beta}) + 24(2k''_{\alpha\beta}) = 0 \end{aligned}$$

i.e.,

$$\begin{aligned} 6k_{\alpha} + 6k'_{\alpha\alpha} + 24k''_{\alpha\alpha} + 6k_{\beta} + 6k'_{\beta\beta} + 24k''_{\beta\beta} + 12k_{\alpha\beta} \\ + 12k'_{\alpha\beta} + 48k''_{\alpha\beta} = 0 \end{aligned}$$

i.e.,

$$\begin{aligned} k_{\alpha} + k'_{\alpha\alpha} + 4k''_{\alpha\alpha} + k_{\beta} + k'_{\beta\beta} + 4k''_{\beta\beta} + 2k_{\alpha\beta} \\ + 2k'_{\alpha\beta} + 8k''_{\alpha\beta} = 0. \end{aligned}$$

Here again, there are few additional relationships between bending kinetic constants and angle-angle interaction kinetic constants. They are,

$$k_a + k'_{aa} + 4k''_{aa} = 0$$

$$k_\beta + k'_{\beta\beta} + 4k''_{\beta\beta} = 0$$

$$(k_a + k'_{aa} - 2k''_{aa}) - (k_\beta + k'_{\beta\beta} - 2k''_{\beta\beta}) = 0$$

$$(k_a + k_{aa} - 2k''_{aa}) + (k_\beta + k_{\beta\beta} - 2k''_{\beta\beta}) + 2(k_{a\beta} + k'_{a\beta} - 2k''_{a\beta}) = 0$$

$$(k_a - k'_{aa}) - (k_\beta - k'_{\beta\beta}) = 0$$

$$(k_a - k'_{aa}) + (k_\beta - k'_{\beta\beta}) + 2(k_{a\beta} - k'_{a\beta}) = 0.$$

The third group of kinetic constants involving stretching and bond-bond interaction constants, on summation, leads to

$$\begin{aligned} \Sigma k_{ij} + \Sigma k'_{ij} &= 4k_a + 6(2k_{aa}) \\ &= 4k_a + 12k_{aa} \\ &= 4m_y. \end{aligned}$$

Further, when the mass of the X atom increases, the kinetic constants k_a , k_α and k'_{aa} exhibit increasing trends while the other kinetic constants k_{aa} , and k'_{aa} exhibit decreasing trends in all the cases studied here. The kinetic constants k'_{aa} and k'_{aa} assume negative signs in all the cases.

Applying the method developed in the earlier papers (Thirugnanasambandam and Srinivasan 1969; Thirugnanasambandam and Mohan 1974 *a,b*; 1975 *a,b,c*; Thirugnanasambandam and Karunanidhi 1976) the symmetry force constants of these molecules are evaluated. The individual force constants deduced from the symmetry force constants are listed in table 3. The following observations relating to the force constants may be made from a study of this table.

- (1) The stretching and the bending force constants are sensibly the same in sets of isotopically substituted molecules.
- (2) The bond-bond interaction force constant f'_{aa} appears to be determined by the atoms constituting the molecule.
- (3) The interaction force constants f'_{aa} and f'_{aa} are negative in all the molecules studied here while their magnitudes appear to be characteristic of the molecule concerned.
- (4) The extraordinary regularities in the unique sets of force constants obtained in relation to the four sets of isotopically substituted molecules studied here confirm similar results relating to the bent symmetrical XY_2 and the pyramidal XY_3 molecules (Thirugnanasambandam and Mohan 1974 *a*, 1975*b*). Indeed, these results do bring out the validity of the significant statement made by Herzberg (1956) in relation to the invariance of the potential functions relating to isotopic molecules.

- (5) It is interesting to note that the stretching force constants in the oxygenated molecules hover around 7×10^5 dynes cm^{-1} whereas the bending force constants in these cases appear to have values of about 0.1×10^5 dynes cm^{-1} .

Comparing the present results with the results of earlier investigators relating to these molecules, it may be mentioned that systematic sets of force constants appear to be available for the first time in this type of molecules. As usual, f_d seems to be in good comparison with the values of the earlier authors. The bond-bond interaction force constant f_{dd} values agree favourably with some of the authors in some of the cases. The bending force constants and the interaction force constants are found to be considerably reduced as a result of the recognition of the reflex angles.

Using the symmetry force constants in the Cyvin's secular equation, the symmetrized mean square amplitudes have been obtained at the temperature 298.16 K. The valence mean square amplitudes of vibration for all the molecules have been computed from the symmetrized mean square amplitude values. The values of the mean amplitude appear to be reasonable in all these cases. Further, these values agree favourably with those obtained from the electron diffraction data wherever such results are available (Cyvin 1968). The mean amplitude $\sigma_d^{1/2}$ and $\sigma_q^{1/2}$ corresponding to the bonded and the non-bonded distances respectively are found to decrease in the isotopically substituted cases. The present values will be useful in the interpretation of electron diffraction data relating to these molecules.

4. Conclusion

The GQVFF force constants of eighteen molecules of the tetrahedral XY_4 structure are evaluated on the basis of a new set of symmetry coordinates. The kinetic constants and certain simplifying considerations are used in evaluating the force constants by Wilson's F - G matrix method. It may be seen that highly systematic and reasonable sets of independent force constants relating to these molecules have been obtained here for the first time. The interaction force constants appear to assume in magnitude as well as in sign, significant values characteristic of the molecules and the molecular type. Further, the mean amplitudes evaluated in the present study, using the force constants, are in the expected range. The force constants and the mean amplitudes of the molecules studied here are found to be very interesting from the point of view of molecular dynamics.

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