Spectroscopic Studies of Molecular Constants in some Polyatomic Molecules

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Force constants have been evaluated by the WILSON group theoretical method for various ij_3 molecules possessing a planar trigonal symmetry. Mean-square amplitude quantities and mean amplitudes of vibration for the bonded as well as nonbonded atom pairs have been computed at the temperatures $T=0$ and $T=298$ °K for C_3, Si_3, and XeF_2 by the CYVIN method. The molar thermodynamic functions from spectroscopic data have been calculated for Si_3 and XeF_2 on the basis of a rigid rotator, harmonic oscillator model. BASTIANSEN–MORINO shrinkage effects have been calculated for various linear asymmetrical ijk, linear symmetrical ij_2 and tetrahedral ij_4 molecules at the temperatures $T=0$ and $T=298$ °K.

Since the molecular structural studies with high degree of accuracy from electron diffraction studies have, nowadays, been well advanced, the spectroscopic studies of mean amplitudes of vibration, shrinkages of chemical bonds, force constants and thermodynamic functions would be very useful for the i) interpretation of the results of electron diffraction studies, ii) study of the nature of chemical bonds, iii) determination of normal frequencies in other related systems having similar chemical bonds with nearly identical internuclear distances and iv) interpretation of the experimental heat capacities and entropies. In undertaking such investigations for various molecular systems, the WILSON group theoretical method [1] for the calculation of force constants, the CYVIN method [2] for the computation of mean amplitudes of vibration and shrinkage effects and statistical-mechanical treatment for the calculations of thermodynamic functions have been adopted here.

Force Constants of some Planar ij_3 Molecules

The molecules such as WO_3, MoO_3, UO_3, BH_3, CH_3, CF_3, AlF_3, and $AlCl_3$ possessing a planar trigonal symmetry have been considered here for the the calculation of force constants by the WILSON group theoretical method [1] and their fundamental frequencies in cm^{-1} are given in Table 1. A schematic representation of normal modes of oscillation for a molecule of the present study has already been given elsewhere [3, 4]; the symmetry coordinates and kinetic energy matrices have been given by CYVIN [5]. The most general quadratic potential energy function used for the present study is given as follows:

$$\begin{aligned} 2V = &\Sigma f_d(\Delta d_i)^2 + 2\Sigma f_{dd}(\Delta d_i \Delta d_j) + \Sigma f_\Theta (d\Delta\Theta_{ij})^2 \\ &+ 2\Sigma f_{\Theta\Theta}(d\Delta\Theta_{ij})(d\Delta\Theta_{jk}) \\ &+ 2\Sigma f_{d\Theta}(\Delta d_i)(d\Delta\Theta_{ij}) \\ &+ 2\Sigma f_{d\Theta}'(\Delta d_i)(d\Delta\Theta_{jk}) + f_\alpha (d\Delta\alpha)^2, \end{aligned}$$

where Δd_i is the change in the length of the ith bond, $\Delta\Theta_{ij}$ the change of the angle between the ith and jth bonds and $\Delta\alpha$ the change in angle due to the out-of-plane vibration. The secular equations giving the

Molecule	$\nu_1(A_1')$	$\nu_2(A_2'')$	$\nu_3(E')$	$\nu_4(E')$	Reference
WO_3	780	298	791	314	a, b
MoO_3	800	390	830	340	a
UO_3	750	320	780	280	a
BH_3	2384	802	2976	1764	b
CH_3	2600	840	2760	1370	b, c
CF_3	890	667	1400	480	d
AlF_3	700	400	900	300	b
$AlCl_3$	345	230	610	135	b

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Table 1. Fundamental frequencies in cm^{-1} in some planar ij_3 molecules.

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Molecule	f_d	f_{dd}	f_Θ	$f_{\Theta\Theta}$	$f_{d\Theta}$	$f'_{d\Theta}$	f_α
WO_3	4.394	0.671	0.430	− 0.215	0.603	− 0.301	0.664
MoO_3	−4.219	0.910	0.477	− 0.239	0.596	− 0.298	0.957
UO_3	3.411	0.949	0.682	− 0.341	0.764	− 0.382	0.804
BH_3	4.033	− 0.329	0.395	− 0.198	0.153	− 0.077	0.299
CH_3	3.999	0.008	0.228	− 0.113	0.015	− 0.008	0.335
CF_3	6.287	1.290	0.440	− 0.220	0.081	− 0.041	0.867
AlF_3	4.264	0.611	0.189	− 0.097	0.151	− 0.075	0.576
$AlCl_3$	2.111	0.187	0.122	− 0.061	0.084	− 0.042	0.224

Table 2. Valence force constants in millidynes/Å in some planar ij_3 molecules.

normal frequencies in terms of the valence force constants were constructed by the WILSON method [1] and solved. Since the equations under the species E' resulted to imaginary values for the diagonal elements, the off-diagonal element was taken into consideration and both the diagonal and off-diagonal elements were evaluated in the manner described by TORKINGTON [6]. The values of valence force constants in millidynes/Å obtained by the method of GOLD, DOWLING and MEISTER [7] are given in Table 2 where f_d is the force constant corresponding to the stretching of the bond $i-j$, f_θ the constant due to the bending $j-i-j$, f_α the constant due to the out-of-plane vibration and the others are the respective interaction constants. The value of the force constant due to the out-of-plane vibration is greater than that due to the $j-i-j$ bending. The values of all the constants in molybdenum trioxide and tungsten trioxide are more or less similar. The values in general are in the decreasing order from aluminium trifluoride to aluminium trichloride. Most of the interaction constants are not much significant in methyl group and boron trihydride. The stretching-bending interaction constant is not a considerable one in all but the trioxides of molybdenum, tungsten and uranium.

Mean Amplitudes of Vibration in C_3, Si_3 and XeF_2

The triatomic carbon molecule C_3 was first identified by HERZBERG [8], its spectrum was observed by SWINGS [9] and its (linear) structure was confirmed by CLUSIUS and DOUGLAS [10]. The positions of the discrete bands were determined by HERZBERG [11] and by ROSEN and SWINGS [12]. The emission spectrum of C_3 was first observed by GARTON [13]. Many investigations [14–20] were undertaken on the so-called continuum of this molecule; the following fundamental frequencies $\nu_1(\Sigma_g^+) = 1300\ \mathrm{cm}^{-1}$, $\nu_2(\Pi_u) = 550\ \mathrm{cm}^{-1}$, and $\nu_3(\Sigma_u^+) = 2200\ \mathrm{cm}^{-1}$ were given by PITZER and CLEMENTI [21]; and the enthalpies were determined by BREWER and ENGELKE [22]. The fundamental frequencies $\nu_1(\Sigma_g^+) = 358\ \mathrm{cm}^{-1}$, $\nu_2(\Pi_u) = 281\ \mathrm{cm}^{-1}$, and $\nu_3(\Sigma_u^+) = 620\ \mathrm{cm}^{-1}$, were reported for Si_3 molecule by DROWART, DE MARIA, and INGHRAM [23]. The molecular configuration, bond distance and force constants for XeF_2 were determined from X-ray diffraction studies by SIEGEL and GEBERT [24] and neutron diffraction studies by LEVY and AGRON [25]. AGRON and his associates [26] proposed three possible structures for XeF_2, confirmed a $D_{\infty h}$ symmetry with

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following assignment of fundamentals $\nu_1(\Sigma_g^+) = 515$ cm^{-1}, $\nu_2(\Pi_u) = 213$ cm^{-1}, and $\nu_3(\Sigma_u^+) = 555$ cm^{-1} and calculated force constants.

The secular equations giving the normal frequencies in terms of the mean-square amplitude quantities were constructed by the CYVIN method [27] at the temperatures $T = 0$ and $T = 298$ °K with help of the above fundamentals and then solved. On account of the greater symmetry of the molecular system, the three fundamental frequencies are well sufficient in evaluating the three vibrational constants. The calculated values of the mean-square amplitude quantities in Å² are given in Table 3 for all these three

Molecule	Symbol	$T = 0$	$T = 298$ °K
C_3	σ_r	0.0014973	0.0014973
	σ_{rr}	− 0.0004173	− 0.0004173
	$\sigma\Theta$	0.0153168	0.0180341
Si_3	σ_r	0.0022933	0.0028944
	σ_{rr}	− 0.0006146	− 0.0003188
	$\sigma\Theta$	0.0128317	0.0238362
XeF_2	σ_r	0.0018927	0.0022453
	σ_{rr}	− 0.0001693	− 0.0001618
	$\sigma\Theta$	0.0107354	0.0232313

Table 3. Mean-square amplitude quantities in Å² in C_3, Si_3, and XeF_2 molecules.

molecules where σ_r is the mean-square amplitude quantity due to the bonded atom pair $i-j$, σ_{rr} the quantity due to the interaction of the bonded atom pairs and σ_Θ the quantity due to the bending of the molecule. The corresponding calculated values of mean amplitudes of vibration for both bonded and nonbonded atom pairs are given in Å in Table 4.

Molecule	Distance	$T = 0$	$T = 298$ °K
C_3	C=C	0.0387	0.0387
	C−C	0.0465	0.0465
Si_3	Si=Si	0.0480	0.0538
	Si−Si	0.0579	0.0717
XeF_2	Xe−F	0.0435	0.0474
	F−F	0.0587	0.0646

Table 4. Mean amplitude of vibration in Å in C_3, Si_3, and XeF_2 molecules.

The quantity due to bending is very much greater than that due to the bonded atom pair in contrast to the corresponding force constant values. The mean-square amplitude quantity due to the interaction of the bonded atom pairs is very small. The mean amplitude of vibration for the nonbonded distance is very higher than that of the bonded atom pair. There are no experimental values from electron diffraction studies available to make a comparison with results of the present study.

Thermodynamic Functions of Si_3 and XeF_2

The molar thermodynamic functions such as heat content, free energy, entropy and heat capacity of Si_3 and XeF_2 were calculated using the vibrational data given above for the temperature range 200 to 2000 °K. A rigid rotator, harmonic oscillator model was assumed and all the quantities were calculated for a gas in the thermodynamic standard gaseous state of unit fugacity (one atmosphere). The standard formulae and tables of functions for the harmonic oscillator contributions given by PITZER [28] were used. Using a value 2.25 Å for the Si = Si bond and a value 2.00 Å for the Xe-F bond [23, 24, 26], the calculated

T(°K)	$(H_0 - E_0^0)/T$	$-(F_0 - E_0^0)/T$	S^0	C_p^0
200	8.708	47.016	55.724	11.459
273.16	9.614	49.867	59.481	12.638
298.16	9.877	50.696	60.573	12.918
300	9.897	50.779	60.676	12.939
400	10.763	53.755	64.518	13.675
500	11.389	56.224	67.613	14.076
600	11.861	58.359	70.220	14.310
700	12.209	60.178	72.387	14.455
800	12.505	61.838	74.343	14.561
900	12.740	63.341	76.081	14.630
1000	12.935	64.714	77.649	14.681
1100	13.146	65.905	79.051	14.718
1200	13.260	67.252	80.512	14.752
1300	13.342	68.127	81.469	14.769
1400	13.442	69.002	82.444	14.787
1500	13.544	70.084	83.628	14.804
1600	13.622	70.979	84.601	14.815
1700	13.683	71.735	85.418	14.824
1800	13.735	72.587	86.340	14.833
1900	13.815	73.347	87.162	14.841
2000	13.859	74.012	87.871	14.847

Table 5. Heat content, free energy, entropy, and heat capacity of Si_3 molecule for the ideal gaseous state at one atmospheric pressure. T is the temperature in degrees Kelvin; the other quantities are in cal. deg^{-1}. $mole^{-1}$ and E_0^0 is the energy of one mole of perfect gas at absolute zero temperature.

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principal moments of inertia are as follows:

$I_{xx} = I_{yy} = 284.1075$ AMU Å^2
(471.9395×10^{-40} g cm^2) for the Si_3 molecule,

$I_{xx} = I_{yy} = 152.0000$ AMU Å^2
(252.4918×10^{-40} g cm^2) for the XeF_2 molecule.

Assumed in the calculations were a symmetry number of 2, singlet ground electronic state and chemical atomic weights. Neglected in the calculations were the contributions due to centrifugal distortion, isotopic mixing and nuclear spins. The calculated values of the thermodynamic quantities in cal. deg.$^{-1}$·mole^{-1} are given in Tables 5 and 6, respectively for the two molecules. The results of the present study would be helpful for the interpretation of calorimetric data. Such calculations were already performed for C_3 molecule by PITZER and CLEMENTI [21].

T(°K)	$(H_0 - E_0^0)/T$	$-(F_0 - E_0^0)/T$	S^0	C_p
200	8.960	48.155	57.115	11.541
273.16	9.625	51.005	60.630	12.260
298.16	10.068	51.954	62.022	12.939
300	10.093	52.026	62.119	12.965
400	10.902	55.029	65.931	13.684
500	11.511	57.556	69.067	14.082
600	11.956	59.683	71.639	14.314
700	12.301	61.535	73.836	14.462
800	12.583	63.233	75.816	14.561
900	12.807	64.715	77.522	14.632
1000	12.984	66.028	79.012	14.681
1100	13.144	67.295	80.439	14.720
1200	13.265	68.384	81.649	14.747
1300	13.388	69.476	82.864	14.772
1400	13.490	70.506	83.996	14.789
1500	13.592	71.554	85.146	14.806
1600	13.661	72.374	86.035	14.817
1700	13.712	73.156	86.877	14.825
1800	13.791	73.978	87.769	14.835
1900	13.488	74.731	88.219	14.486
2000	13.898	75.489	89.387	14.848

Table 6. Heat content, free energy, entropy, and heat capacity of XeF_2 molecule for the ideal gaseous state at one atmospheric pressure. T is the temperature in degrees Kelvin; the other quantities are in cal. deg^{-1}. mole^{-1} and E_0^0 is the energy of one mole of perfect gas at absolute zero temperature.

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Bastiansen–Morino Shrinkage Effect in some Linear *ijk* Molecules

The apparent shortening or shrinkage of the long distances in linear chains observed by BASTIANSEN and his associates [29–32] from electron diffraction studies was theoretically established by MORINO [33] on the basis of the intramolecular motion. This shrinkage which has been attributed to the out-of-linearity vibrations increases with increasing bonds in long chain molecules. MORINO and his coworkers [34] performed their spectroscopic studies and their results are in good agreement with experimental ones. Later, several investigations appeared with the name, "BASTIANSEN–MORINO Shrinkage Effect" and one may refer to CYVIN [35] for a detailed account on this aspect. The analytical expression of BASTIANSEN–MORINO shrinkage effect for a linear asymmetrical $i\,j\,k$ molecule is given by:

$$-\delta = (\langle \Delta x_{ik}^2 \rangle)/r_{ik}^e - (\langle \Delta x_{ij}^2 \rangle)/r_{ij}^e - (\langle \Delta x_{jk}^2 \rangle)/r_{jk}^e$$

where $\langle \Delta x_{ik}^2 \rangle$, $\langle \Delta x_{ij}^2 \rangle$, and $\langle \Delta x_{jk}^2 \rangle$ stand for the mean-square perpendicular amplitudes of vibration corresponding to the $i-k$, $i-j$, and $j-k$ distances and similarly r_{ik}^e, r_{ij}^e, and r_{jk}^e stand for the internuclear distances $i-k$, $i-j$, and $j-k$ at the equilibrium position. The mean-square perpendicular amplitudes of vibration $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are identical for the bonded atom pair. The mean-square parallel or perpendicular amplitudes of vibration can be calculated in the manner described by MORINO and HIROTA [36] for any molecular system.

The molecules such as FCN, ClCN, BrCN, ICN, N_2O, HgClBr, LaC_2, BeC_2, SiC_2, and Si_2C have been considered here for the calculation of shrinkage effect and their fundamental frequencies in cm^{-1} and internuclear distances in Å are given in Table 7. Since the experimental values of internuclear distances for some of the molecules of the present study are not available, they are taken from the related molecules having similar chemical bonds. The calculations were further simplified by the fundamental frequencies of isotopic species for nitrous oxide. The computed values of the mean-square per-

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Molecule	$\nu_1(\Sigma^+)$	$\nu_2(\pi)$	$\nu_3(\Sigma^-)$	$i-j$	$j-k$	Reference
FCN	1077	449	2290	1.165	1.26	a, b
ICCN	714	380	2219	1.163	1.629	c, d
BrCN	575	342.5	2200	1.158	1.79	c, d
ICN	470	321	2178	1.158	1.995	d, e
$N^{14}N^{14}O$	1300.3	596.5	2276.9	1.1297	1.1846	f, g
$N^{14}N^{15}O$	1295.6	582.8	2228.6	1.1289	1.1872	f, g
$N^{15}N^{14}O$	1285.1	593.2	2254.5	1.1289	1.1872	f, g
$N^{15}N^{15}O$	1280.3	578.9	2206.3	1.1296	1.1848	f, g
HgClBr	232	139	347	2.44	2.27	h, i
LaC_2	630	400	1772	1.94	1.395	i, j
BeC_2	1580	423	1947	1.331	1.395	i, j
SiC_2	591	465	1742	1.865	1.395	j, k, l
Si_2C	799	265	446	1.865	2.252	j, k, l

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Table 7. Fundamental frequencies in cm^{-1} and internuclear distances in Å in some linear *ijk* molecules.

pendicular amplitudes of vibration in $Å^2$ for the bonded and nonbonded atom pairs are given in Table 8 at the temperatures $T=0$ and $T=298$ °K and similarly the calculated values of Bastiansen–Morino shrinkage effect in Å are given in Table 9 for all these molecules. Since the experimental values of shrinkages for these molecules are not available, no comparison could be made here.

Molecule	$T=0$	$T=298$ °K
FCN	0.00712	0.0047
ClCN	0.00735	0.01120
BrCN	0.00705	0.01161
ICN	0.00691	0.01215
N_2O		0.00580
HgClBr	0.00595	0.03044
LaC_2	0.00586	0.00819
BeC_2	0.00774	0.01016
SiC_2	0.00532	0.00676
Si_2C	0.00384	0.00733

Table 9. Bastiansen–Morino shrinkage effects in Å in some linear *ijk* molecules.

Bastiansen–Morino Shrinkage Effect in some Linear ij_2 Molecules

The analytical expression of Bastiansen–Morino shrinkage effect for a linear symmetrical ij_2 molecule is given by:

$$\delta = 2(\langle \Delta x_{ij}^2 \rangle)/r_{ij}^2$$

where the symbols have the usual meaning. In this case, the mean-square perpendicular amplitudes of vibration $\langle \Delta x_{jj}^2 \rangle$ and $\langle \Delta y_{jj}^2 \rangle$ for the nonbonded atom pair become vanished by symmetry of the

Molecule	$i-j$		$j-k$		$i-k$	
	$T=0$	$T=298$ °K	$T=0$	$T=298$ °K	$T=0$	$T=298$ °K
FCN	0.0038578	0.0051363	0.0047446	0.0063170	0.0000466	0.0000620
ClCN	0.0035609	0.0054266	0.0061581	0.0093800	0.0003532	0.0005380
BrCN	0.0034321	0.0058291	0.0061927	0.0101100	0.0006514	0.0011025
ICN	0.0034228	0.0061044	0.0062073	0.0110707	0.0008321	0.0014840
N_2O		0.0035140		0.0031956		0.7000076
HgClBr	0.0035525	0.0181710	0.0112411	0.0574986	0.0021545	0.0110202
LaC_2	0.0027843	0.0038927	0.0064883	0.0090712	0.0007713	0.0010783
BeC_2	0.0059147	0.0077660	0.0046306	0.0060799	0.0000780	0.0001024
SiC_2	0.0030063	0.0038222	0.0053087	0.0067494	0.0003259	0.0004144
Si_2C	0.0024095	0.0045991	0.0061781	0.0117920	0.0008084	0.0015430

Table 8. Mean-square perpendicular amplitudes of vibration in $Å^2$ in some linear *ijk* molecules.

molecular system. The mean-square perpendicular amplitudes of vibration $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are identical for the bonded atom pair. The molecules such as ZrO_2, TiO_2, SiO_2, BO_2, CrO_2, mercury dihalides, beryllium dihalides, magnesium fluoride, magnesium chloride, XeF_2, C_3, and Si_3 have been considered here for the calculation of shrinkages and their fundamental frequencies in cm^{-1} and internuclear distances in Å are given in Table 10. The calculated values of the mean-square perpendicular amplitudes of vibration in $Å^2$ for the bonded atom pair and BASTIANSEN–MORINO shrinkage effect in Å are given in Table 11 at the temperature $T = 0$ and $T = 298$ °K. The values of the shrinkages are very significant in some of the metal dihalides at the room temperature. The values are in the increasing order from lower to higher members of the halogen series. This shows that the replacement of end atoms with atoms of higher atomic weight causes lower fundamental frequencies and higher shrinkage effect.

Molecule	$\nu_1(\Sigma_g^+)$	$\nu_2(\pi_u)$	$\nu_3(\Sigma_u^+)$	$i-j$	Reference
ZrO_2	865	271	1003	1.728	a, b, c
TiO_2	874	305	1129	1.94	d, e
SiO_2	885	378	1295	1.61	d, f
BO_2	1070	464	1322	1.2049	g, h
CrO_2	785	259	996	1.627	i, j
HgF_2	593	120	600	1.96	k
$HgCl_2$	360	70	413	2.27	l, m
$HgBr_2$	225	41	293	2.44	l, n
HgI_2	156	33	233	2.61	k, l, n
BeF_2	700	825	1520	1.40	k, o, p
$BeCl_2$	375	482	1113	1.77	k, p, q
$BeBr_2$	230	270	930	1.90	k, q
BeI_2	140	160	820	2.12	k, q
MgF_2	500	400	800	2.07	k, r
$MgCl_2$	300	295	597	2.18	k, o, p
XeF_2	515	213.2	555	2.00	s, t
C_3	1300	550	2200	1.281	u
Si_3	358	281	620	2.25	v

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Table 10. Fundamental frequencies in cm^{-1} and internuclear distances in Å in some linear ij_2 molecules.

Molecule	$i-j$		δ	
	$T=0$	$T=298$ °K	$T=0$	$T=298$ °K
ZrO_2	0.0026267	0.0050136	0.00304	0.00580
TiO_2	0.0028820	0.0050104	0.00297	0.00517
SiO_2	0.0029839	0.0044258	0.00371	0.00550
BO_2	0.0044944	0.0057142	0.00746	0.00949
CrO_2	0.0032865	0.0064129	0.00404	0.00788
HgF_2	0.0043937	0.0267954	0.00448	0.02734
$HgCl_2$	0.0045978	0.0397995	0.00405	0.03507
$HgBr_2$	0.0046213	0.0453651	0.00379	0.03719
HgI_2	0.0045601	0.0485453	0.00349	0.03721
BeF_2	0.0028035	0.0029072	0.00401	0.00415
$BeCl_2$	0.0043719	0.0054675	0.00494	0.00618
$BeBr_2$	0.0073144	0.0139611	0.00770	0.01470
BeI_2	0.0120994	0.0499861	0.01991	0.04716
MgF_2	0.0022735	0.0027960	0.00220	0.00270
$MgCl_2$	0.0031565	0.0057026	0.00290	0.00523
XeF_2	0.0026839	0.0058078	0.00268	0.00581
C_3	0.0038292	0.0045085	0.00598	0.00704
Si_3	0.0032079	0.0059591	0.00285	0.00530

Table 11. Mean-square perpendicular amplitudes of vibration in $Å^2$ and BASTIANSEN–MORINO shrinkage effects in Å in some linear ij_2 molecules.

Bastiansen–Morino Shrinkage Effect in some Tetrahedral ij_4 Molecules

MORINO and his associates [37] derived an analytical expression for the shrinkage effect of non-linear conformation, defined the terms "natural" shrinkage and "practical" shrinkage and proved that both are identical to the first order approximation. Considering non-linear shrinkage effect, the anharmonic term, as in the case of a linear molecule, may not be cancelled out and may be obtained as a linear combination of symmetry coordinates of the totally symmetrical vibrational modes (stretching and angle deformation modes). The contributions from the symmetry coordinates of the stretching modes to the anharmonic terms of the practical shrinkage effect always become vanished while those from the symmetry coordinates of the angle deformation modes do exist. In highly symmetrical molecules having no totally symmetrical deformation modes, anharmonic terms cancel out in the computation of shrinkage

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effect. The analytical expression of BASTIANSEN–MORINO shrinkage effect for a tetrahedral ij_4 molecule is, according th MEISINGSETH and CYVIN [38], given by:

$$\delta = \sqrt{6}[1/(12\, r_{ij}^{e})]\{(1/6)\Sigma_{22} - \Sigma_{33} + (7/6)\Sigma_{44} - \Sigma_{34}\}$$

where the symbols have the usual meaning.

The molecules such as VCl_4, OsO_4, RuO_4, GeF_4, $GeBr_4$, SiF_4, $SiCl_4$, $SiBr_4$, PbF_4, $PbCl_4$, PbI_4, $HfBr_4$, HfI_4, ZrF_4, $ZrCl_4$, $ZrBr_4$, TiF_4, $TiCl_4$, TiI_4, SnH_4, CH_4, CD_4, CT_4, GeH_4, GeD_4, SiH_4, and SiD_4 have been considered here for the calculation of shrinkage effect and their fundamental frequencies in cm^{-1} and internuclear distances in Å are given in Table 12. The value 1.098 Å for the C-T bond in CT_4 has been obtained by extrapolation from the experimental values of CH_4 and CD_4 as given by BARTELL, KUCHITSU, and DE NEUI [39]. In the cases of

Molecule	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	$i-j$	Reference
VCl_4	383	128	475	128	2.03	a, b
OsO_4	971	328	959.7	328	1.66	c, d, e, f
RuO_4	880	293	913	330	1.66	g, h
GeF_4	740	200	800	260	1.67	i, j
$GeBr_4$	235	80	327	112	2.29	k, l
SiF_4	800	268	1031	391	1.55	m, n
$SiCl_4$	424	150	610	221	2.01	k, o
$SiBr_4$	249	90	487	137	2.15	k, p, q
PbF_4	564	158	570	180	2.08	r
$PbCl_4$	326	83	314	99	2.43	r
PbI_4	137	37	168	48	2.77	r
$HfBr_4$	205	54	240	60	2.56	s
HfI_4	142	39	185	46	2.75	s
ZrF_4	630	160	668	190	2.10	t, u, v, w
$ZrCl_4$	382	108	423	114	2.33	x
$ZrBr_4$	224	65	309	78	2.47	x
TiF_4	704	192	804	232	1.73	v, y
$TiCl_4$	385	120	496	144	2.18	l, z
TiI_4	155	57	225	100	2.57	v
SnH_4	1910	829	1860	703	1.76	aa
CH_4	3143	1573	3154	1357	1.106	bb, cc, dd
CD_4	2224	1113	2333	1027	1.102	bb, cc, dd
CT_4	1817	910	1990	880	1.098	bb, cc
GeH_4	1990	833	2110	933	1.527	z, ee
GeD_4	1504	665	1522	596	1.527	ee, ff
SiH_4	2187	978	2182	910	1.477	gg, hh
SiD_4	1547	689	1597	681	1.477	hh, ii, jj

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Table 12. Fundamental frequencies in cm^{-1} and internuclear distances in Å in some tetrahedral ij_4 molecules.

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Molecule	$T = 0$	$T = 298\,°K$
VCl_4	0.00076	0.00117
OsO_4	0.00030	0.00035
RuO_4	0.00041	0.00049
GeF_4	0.00065	0.00103
$GeBr_4$	0.00103	0.00097
SiF_4	0.00076	0.00064
$SiCl_4$	0.00106	0.00139
SiB_4	0.00101	0.00176
PbF_4	0.00052	0.00110
$PbCl_4$	0.00048	0.00109
PbI_4	0.00042	0.00106
$HfBr_4$	0.00031	0.00035
HfI_4	0.00042	0.00018
ZrF_4	0.00089	0.00151
$ZrCl_4$	0.00065	0.00093
$ZrBr_4$	0.00059	0.00070
TiF_4	0.00096	0.00015
$TiCl_4$	0.00071	0.00153
TiI_4	0.00112	0.00157
SnH_4	0.00420	0.00414
CH_4	0.00284	0.00284
CD_4	0.00210	0.00211
CT_4	0.00202	0.00204
GeH_4	0.00312	0.00319
GeD_4	0.00190	0.00187
SiH_4	0.00229	0.00234
SiD_4	0.00202	0.00212

Table 13. Bastiansen–Morino shrinkage effects in Å in some tetrahedral ij_4 molecules.

GeD_4 and SiD_4, experimental values of the internuclear distances are not available and hence the same distances of GeH_4 and SiH_4 have been assumed here. The symmetrized mean-square amplitude matrices (Σ) were obtained by the Cyvin method [40] and used to obtain the values of shrinkage effect. The calculated values of shrinkage effect in Å are given in Table 13 at the temperatures $T = 0$ and $T = 298\,°K$. As obtained in other types of molecules earlier, the values are in the increasing order from lower to higher members of the halogen series at room temperature. Though the values appear small, they are real and they are to be added at the appropriate temperatures to the observed internuclear distances from electron diffraction studies in order to obtaine the actual internuclear distances.

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