

Mean Amplitudes of Vibration for Tetrahedral Molecules and Ions

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Mean amplitudes of vibration for 38 tetrahalides and 15 tetraoxides have been computed at temperatures $T=0^\circ\text{K}$, $T=298.15^\circ\text{K}$ and $T=500^\circ\text{K}$ employing most recent vibrational data. Müller's method has been followed in solving the two dimensional Cyvin's secular determinant. The results have been briefly discussed.

Introduction

Recent advancement in the analysis of electron diffraction results demands a deeper understanding of the mean amplitudes of vibration for bonded and non-bonded interatomic distances computed from spectroscopic data. The knowledge of mean amplitudes throws light on the non-rigid molecular model. Such studies for tetrahedral molecules and ions exist in literature and have been reviewed by Cyvin^{1,2}. Most of the results quoted in literature employ the vibrational data prior to 1970. Since then laser technique has played an important role in the analysis of vibrational spectral studies and therefore, more and more tetrahedral molecules and ions have been studied by this method. Certainly, the frequency assignments can now be considered to be more reliable than previous results. Thus, it was thought worthwhile to examine the mean amplitude of vibration from more reliable vibrational data. Recently Basile et al.³ have studied the force fields for 146 tetrahedral systems and compiled the I.R. and Raman spectral data. In the present study the same vibrational frequencies have been employed for 38 tetrahalides and 15 tetraoxides to compute mean amplitudes of vibration for bonded as well as for non-bonded interatomic distances at temperatures $T=0^\circ\text{K}$; $T=298.15^\circ\text{K}$ and $T=500^\circ\text{K}$. The

results have been used to discuss the trend of variation in mean amplitudes.

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 $a_1 + e + 2f_2$. The mean amplitudes of vibration have been computed by Cyvin's secular equation¹ $|\Sigma G^{-1} - \Delta E| = 0$ where the symbols have their usual meaning¹. The analytical expressions for the mean amplitudes of vibration and kinetic energy matrices are taken from Cyvin's book. Müller's method⁴⁻⁶ has been followed for the solution of 2×2 secular determinants in f_2 species. The vibrational frequencies employed in this computation are taken from Basile et al. paper³.

Results and Discussion

The computed values of mean amplitudes of vibration for bonded and non-bonded distances at temperatures $T=0^\circ\text{K}$; $T=298.15^\circ\text{K}$ and $T=500^\circ\text{K}$ are collected in Table 1 and 2 for tetrahalides and tetraoxides respectively.

From the observation of the Table 1 for tetrahalides it is apparent that at room temperature the mean amplitudes are nearly the same in the gas, liquid and solid phases. In contrast to this stretching force constants³ in different phases show marked variations. Thus it is concluded that the effect of change in phase is more pronounced in the stretching force constants than the corresponding mean amplitudes. Comparing the mean amplitudes for IVB and IVA group tetrahalides, it is found that the values show a slightly decreasing tendency with the increase of mass of the central atom. This variation is more pronounced in IVA group tetrahalides than IVB group. The values are almost the same for Ti and Zr tetrahalides. The trend of variation is changed for Sn and Pb tetrahalides. This may be due to change in the non metallic to metallic character. Comparing the mean amplitude values in XY_4 type tetrahalides having the same central atom it is found that the values increase with the increase in the mass of the peripheral atom while the force constants^{3,7} show an opposite trend. This is consistent with the electronegativity difference. On examining the mean amplitudes for bonded distances at room temperature for tetrahalides from Table 2 for the oxyanions of the same group, it is found that the values decrease with the increase of the mass of the central atom whereas corresponding stretching force constants³ show the opposite trend. It is interesting to study the trend of variation in the oxoanions of the same group. From Table 2 it is

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Table 1. Mean amplitudes of vibration of tetrahalides.

Molecule or Ion	Mean Amplitude of Vibration (in Å)					
	$T=0\text{ }^{\circ}\text{K}$	X-Y $T=298.15\text{ }^{\circ}\text{K}$	$T=500\text{ }^{\circ}\text{K}$	$T=0\text{ }^{\circ}\text{K}$	Y...Y $T=298.15\text{ }^{\circ}\text{K}$	$T=500\text{ }^{\circ}\text{K}$
TiF ₄ (gas)	0.0399	0.0409	0.0445	0.0729	0.1018	0.1266
TiCl ₄ (gas)	0.0416	0.0461	0.0540	0.0696	0.1183	0.1507
TiCl ₄ (sol.)	0.0416	0.0461	0.0450	0.0691	0.1163	0.1479
TiCl ₄ (solid)	0.0417	0.0463	0.0543	0.0690	0.1154	0.1468
ZrCl ₄ (gas)	0.0401	0.0461	0.0552	0.0729	0.1329	0.1697
HfCl ₄ (gas)	0.0383	0.0447	0.0538	0.0710	0.1270	0.1621
VCl ₄ (liq.)	0.0416	0.0464	0.0546	0.0709	0.1229	0.1567
MnCl ₄ ²⁻	0.0529	0.0691	0.0858	0.0805	0.1539	0.1972
FeCl ₄ ⁻	0.0458	0.0544	0.0658	0.0710	0.1196	0.1523
CuCl ₄ ²⁻	0.0535	0.0721	0.0900	0.0741	0.1272	0.1622
CdCl ₄ ²⁻ (solid)	0.0497	0.0675	0.0843	0.0777	0.1409	0.1802
CCl ₄ (liq.)	0.0503	0.0520	0.0571	0.0530	0.0671	0.0824
CCl ₄ (solid)	0.0498	0.0515	0.0564	0.0530	0.0671	0.0824
SiCl ₄ (liq.)	0.0427	0.0454	0.0517	0.0601	0.0868	0.1089
SiCl ₄ (solid)	0.0430	0.0459	0.0523	0.0601	0.0865	0.1085
GeCl ₄ (liq.)	0.0400	0.0451	0.0534	0.0637	0.0979	0.1237
GeCl ₄ (solid)	0.0399	0.0449	0.0532	0.0638	0.0982	0.1241
SnCl ₄ (liq.)	0.0395	0.0459	0.0551	0.0693	0.1188	0.1513
SnCl ₄ (solid)	0.0395	0.0458	0.0550	0.0694	0.1185	0.1508
PbCl ₄ (solid)	0.0404	0.0492	0.0600	0.0732	0.1330	0.1699
TiBr ₄ (gas)	0.0391	0.0470	0.0569	0.0604	0.1292	0.1663
TiBr ₄ (sol.)	0.0392	0.0473	0.0574	0.0594	0.1242	0.1597
ZrBr ₄ (gas)	0.0364	0.0466	0.0575	0.0635	0.1467	0.1890
HfBr ₄ (gas)	0.0339	0.0451	0.0562	0.0614	0.1390	0.1790
AlBr ₄ ⁻	0.0467	0.0556	0.0672	0.0566	0.1103	0.1415
CBr ₄	0.0502	0.0535	0.0604	0.0468	0.0743	0.0944
SiBr ₄ (liq.)	0.0421	0.0777	0.0565	0.0523	0.0945	0.1209
GeBr ₄ (liq.)	0.0377	0.0474	0.0584	0.0551	0.1066	0.1368
SnBr ₄ (liq.)	0.0363	0.0482	0.0600	0.0596	0.1279	0.1646
MnBr ₄ ²⁻	0.0482	0.0690	0.0868	0.0635	0.1395	0.1796
TiI ₄ (gas)	0.0400	0.0519	0.0642	0.0563	0.1386	0.1788
ZrI ₄ (gas)	0.0365	0.0513	0.0643	0.0597	0.1605	0.2073
HfI ₄ (gas)	0.0328	0.0483	0.0610	0.0544	0.1313	0.1698
SiI ₄ (solid)	0.0439	0.0530	0.0642	0.0504	0.1086	0.1399
GeI ₄ (sol.)	0.0383	0.0529	0.0663	0.0520	0.1167	0.1504
SnI ₄ (sol.)	0.0362	0.0536	0.0677	0.0575	0.1487	0.1920
MnI ₄ ²⁻	0.0492	0.0777	0.0987	0.0622	0.1654	0.2136
ZnI ₄ ²⁻	0.0490	0.0808	0.1031	0.0607	0.1561	0.2027

Table 2. Mean amplitudes of vibration of tetraoxides.

Molecule or Ion	Mean Amplitude of Vibration (in Å)					
	$T=0\text{ }^{\circ}\text{K}$	X-Y $T=298.15\text{ }^{\circ}\text{K}$	$T=500\text{ }^{\circ}\text{K}$	$T=0\text{ }^{\circ}\text{K}$	Y...Y $T=298.15\text{ }^{\circ}\text{K}$	$T=500\text{ }^{\circ}\text{K}$
CrO ₄ ²⁻	0.0397	0.0403	0.0431	0.0623	0.0704	0.0825
MoO ₄ ²⁻	0.0379	0.0386	0.0414	0.0638	0.0745	0.0885
WO ₄ ²⁻	0.0366	0.0372	0.0399	0.0625	0.0722	0.0853
ReO ₄ (solid)	0.0350	0.0354	0.0375	0.0600	0.0678	0.0792
FeO ₄ ²⁻	0.0413	0.0422	0.0457	0.0659	0.0770	0.0916
FeO ₄ ³⁻	0.0412	0.0420	0.0455	0.0670	0.0799	0.0957
RuO ₄ (solid)	0.0366	0.0370	0.0393	0.0627	0.0724	0.0856
RuO ₄ ²⁻ (Ba-salt)	0.0383	0.0389	0.0419	0.0636	0.0732	0.0864
RuO ₄ ²⁻ (K-salt)	0.0392	0.0401	0.0434	0.0645	0.0747	0.0886
RuO ₄ ²⁻ (Aq. sol.)	0.0383	0.0390	0.0420	0.0637	0.0735	0.0868
OsO ₄ (liq.)	0.0345	0.0349	0.0368	0.0607	0.0696	0.0818
OsO ₄ (solid)	0.0346	0.0349	0.0369	0.0610	0.0701	0.0825
ClO ₄ ⁻	0.0375	0.0377	0.0392	0.0534	0.0562	0.0626
BrO ₄ ⁻	0.0383	0.0388	0.0416	0.0615	0.0691	0.0806
IO ₄ ⁻	0.0376	0.0383	0.0412	0.0662	0.0794	0.0952

apparent that for bonded and non-bonded distances, at room temperature, the values in general show a decreasing tendency with the increase of the mass of the central atom in case of transition metal anions while for oxoanions of VII A group elements the opposite trend is noted.

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