# 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 °K, $T$ = 298.15 °K and $T$ = 500 °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 than 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 °K; $T$ = 298.15 °K and $T$ = 500 °K. The results have been used to discuss the trend of variation in mean amplitudes.

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## *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 equation [1] $|\Sigma G^{-1} - \Delta E| = 0$ where the symbols have their usual meaning [1]. The analytical expressions for the mean amplitudes of vibration and kinetic energy matrices are taken from Cyvin's book. Müller's method [4–6] has been followed for the solution of $2 \times 2$ secular determinants in $f_2$ species. The vibrational frequencies employed in this computation are taken from Basile et al. paper [3].

## *Results and Discussion*

The computed values of mean amplitudes of vibration for bonded and non-bonded distances at temperatures $T$ = 0 °K; $T$ = 298.15 °K and $T$ = 500 °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 constants [3] 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 IV B and IV A 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 IV A group tetrahalides than IV B 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 constants [3] 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

Table 1. Mean amplitudes of vibration of tetrahalides.

| Molecule or Ion | Mean Amplitude of Vibration (in Å) X−Y $T=0$ °K | $T=298.15$ °K | $T=500$ °K | Y...Y $T=0$ °K | $T=298.15$ °K | $T=500$ °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) X−Y $T=0$ °K | $T=298.15$ °K | $T=500$ °K | Y...Y $T=0$ °K | $T=298.15$ °K | $T=500$ °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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[1] S. J. Cyvin, Molecular Vibration and Mean Square Amplitudes, Elsevier publishing Co. Ltd., Amsterdam 1968.
[2] S. J. Cyvin, Molecular Structures and Vibrations, Elsevier publishing Co. Lt., Amsterdam 1972.
[3] L. J. Basile, J. R. Ferraro, P. LaBonville, and M. C. Wall, Coordination Chemistry Reviews **11**, 21 [1973].
[4] A. Müller and C. J. Peacock, Mol. Phys. **14**, 393 [1968].
[5] A. Müller, Z. Phys. Chem. **238**, 116 [1968].
[6] C. J. Peacock and A. Müller, J. Mol. Spectroscopy **26**, 454 [1968].
[7] A. N. Pandey, D. K. Sharma, and H. P. Mital, Z. Naturforsch. **27 a**, 1211 [1972].