Vibrational spectra of tungsten oxytetrachloride

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Abstract. Raman spectroscopy has been applied to study the vibrational modes of WOCl$_4$. The symmetry of the vibrations is reported. Ab initio calculations are employed to determine the equilibrium lattice parameters and to calculate phonon frequencies in several Brillouin zone points.

1. Introduction
The tungsten-oxygen compounds have crystal lattices with different topologies. The WOCl$_4$, WO$_2$Cl$_2$ and WO$_3$ form crystal lattices with one-, two- and three-dimensional networks of W-O bonds respectively. It determines vibrational behaviour of the crystal lattice.

WOCl$_4$ crystallizes in a tetragonal body centered structure with space group of C$_4$ (Fig.1) [1]. The crystal lattice is made by WO$_2$Cl$_4$ octahedra. Two oxygen atoms in the octahedra are in a trans-position with each other. W - O bonds are asymmetric. The chlorine atoms are in the plain perpendicular with the W – O bond. Octahedra are linked together by corners, where an oxygen atom is shared by two neighboring octahedra. The crystal structure consists of linear chains. These chains are parallel in the crystal lattice. In the chain the long bonds interchange with the short ones. Van der Waals forces attract chains together. The vibrational properties of WOCl$_4$ have not been widely studied. The Raman spectra were reported earlier in [2,3].

WOCl$_4$ is model crystal for materials with more complicated structure. Tl$_6$[WOCl$_4$]$_2$ [4], Tl[NbOCl$_4$] and Tl[NbOBr$_4$] [5] have linear metal-oxygen chains.

This work presents experimental and theoretical investigations of vibrational properties of WOCl$_4$.

![Figure 1. Crystal structure of WOCl$_4$. a) chain parallel to c-axe; b) projection on the plain (001); c) first Brillouin zone.](image)

2. Experimental and computational details
Good optical quality WOCl$_4$ single crystals were grown by the reaction of WO$_3$ and SOCl$_2$ at 200°C in closed ampule. The dimensions of the crystals are nearly 0.5x0.5x10 mm$^3$. Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd
The Raman spectra were measured with 1 cm$^{-1}$ resolution using a 1403 double grating Spex Ramalog spectrophotometer with a conventional photon counting system. The spectra were excited with the 633 nm line of a He-Ne ion laser. The power of the excitation was 10 mW.

Calculations were performed by using hybrid exchange density functional theory to determine equilibrium geometries and phonon frequencies. The Grimme dispersion correction for energy and gradient was used in combination with the B3LYP functional. The CRYSTAL09 computer code was used [6].

The group theoretical analysis have been applied to determine symmetries of vibrational modes.

3. Results and analysis

Relationship between symmetry of vibrations of different WOCl$_4$ lattices are given in table 1. The highest possible hypothetical symmetry of WOCl$_4$ chain is D$_{4h}$, as W − O bond lengths are equal. Actually existing WOCl$_4$ structure has asymmetric bonds, this leads to lowering of symmetry to C$_{4v}$. Symmetry lowers to C$_4$, if chains join in a crystal lattice.

The chain with symmetrical W − O bonds in WO$_2$Cl$_4$ octahedra has four Raman active optical vibrations A$_{1g}$+B$_{1g}$+B$_{2g}$+E$_g$. To the chain with asymmetrical W − O bonds the number of Raman active vibrations rise to 10: 3A$_1$+2B$_1$+B$_2$+4E. Only one symmetry A$_2$ vibration stays inactive in the Raman scattering. Finally, if the chains joining in crystal lattice and having symmetry C$_4$ all optical vibrations 4A+3B+4E are Raman active. If the hypothetical WOCl$_4$ crystal is made by symmetrical W − O bonds, five optical vibrations 2A$_g$+2B$_g$+E$_g$ are Raman active.

| Crystal with symmetric chains | Symmetric chain | Asymmetric chain | Crystal with asymmetric chains |
|-----------------------------|-----------------|-----------------|-------------------------------|
| C$_{4h}$                    | D$_{4h}$        | C$_{4v}$        | C$_4$                         |
| 2A$_g$ (R)                  | A$_{1g}$ (R)    | 4A$_1$ (R,IR)   | 5A (R,IR)                     |
| 2B$_g$ (R)                  | A$_{2g}$        | A$_2$           | 3B (R,IR)                     |
| E$_g$ (R)                   | B$_{1g}$ (R)    | 2B$_1$ (R)      | B$_2$ (R)                     |
| 3A$_u$ (IR)                 | B$_{2g}$ (R)    | 5E (R,IR)       | 5E (R,IR)                     |
| B$_u$                       | 3A$_{2u}$ (IR)  |                 |                               |
| 4E$_u$ (IR)                 | B$_{2u}$        |                 |                               |
|                             | 4E$_u$ (IR)     |                 |                               |

Raman spectrum of WOCl$_4$ crystal is shown in Fig.2. Thirteen bands are well observed in the Raman spectrum (Fig.2). Symmetry calculations of lattice vibrations provide for 11 Raman active vibrations (Tab.2).
Figure 2. Raman spectrum of WOCl$_4$ at room temperature.

For further Raman spectra interpretation ab initio calculations of lattice vibrations have been performed. These calculations were performed for optimized crystal lattice. Optimized lattice parameters are shown in Table 3, where they are compared to the experimental parameters [1] of crystal lattice. The obtained sizes of a lattice cell do not differ from the experimental data of more than 1%.

Table 2. Experimental and calculated phonon frequencies of WOCl$_4$. Calculations were performed in the Brillouin zone points $\Gamma$, X and Z.

|        | $\Gamma$ |          | $X$ |          | $Z$ |          |
|--------|----------|----------|-----|----------|-----|----------|
|        | Calculation | Experiment | Calculation | Calculation |
|        | Frequency, cm$^{-1}$ | Symmetry | Frequency, cm$^{-1}$ | Symmetry | Frequency, cm$^{-1}$ | Frequency, cm$^{-1}$ |
| 85     | A        | 70       | A   | 69       | 45; 56 |
| 119    | B        | 109      | B   | 109      | 63; 77 |
| 136    | E        | 122      | E   | 135      | 114   |
|        |          | 136      | A   |          | 133   |
| 153    | E        | 147      | E   | 162      | 169   |
| 175    | A        | 173      | A   | 180      | 205   |
| 231    | B        | 218      | B   | 220      | 227   |
| 329    | B        | 322      | B   | 348      | 330   |
| 350    | E        | 330      | E   | 367      | 358   |
| 378    | E        | 390      | E   | 390      | 361   |
| 409    | A        | 400      | A   | 406      | 403   |
| 845    | A        | 877      | A   | 845      | 1013  |
|        |          | 889      | A   |          |       |

Table 3. Ab initio optimized and experimental [1] lattice parameters of WOCl$_4$.

|        | Calculation | Experiment [1] |
|--------|-------------|----------------|
| a, Å   | 8.53        | 8.48           |
| c, Å   | 3.95        | 3.99           |
| R$_{W\cdot O}$, Å | 2.21      | 2.18           |
| R$_{W\cdot O}$, Å | 1.74      | 1.81           |
| R$_{W\cdot Cl}$, Å | 2.30      | 2.28           |
The frequencies of lattice vibrations were calculated in Brillouin zone center $\Gamma$ and in two points $X$ and $Z$ on the Brillouin zone boundary. The calculations provide for one Raman active W-O stretching high frequency vibration in the Brillouin zone center $\Gamma$. Experimental Raman spectrum show doublet at 877-889 cm$^{-1}$. In [2] it was suggested that this is due to a multiphonon process in resonance with the fundamental W-O stretching vibration. This does not compare with computed and experimental vibrational frequencies. The highest possible two phonon frequency is equal to 800-820 cm$^{-1}$. It is too low for the experimentally observed 889 cm$^{-1}$.

If the sequence of experimentally obtained and theoretically calculated vibrational symmetry is compared, according to theoretical calculations 136 cm$^{-1}$ Raman band should not be in Raman spectrum.

4. Conclusions
Theoretical calculations describe lattice parameters and Raman spectra of WOCl$_4$, It is possible by using the Grimme dispersion correction for energy and gradient in computations. However, calculations do not explain existence of Raman bands 136 and 889 cm$^{-1}$. The issues of further investigations is to clarify the nature of additional Raman bands.

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