RAMAN-SPECTROSCOPY AND AB-INITIO CALCULATIONS OF THE OXYCOMPLEXES OF TUNGSTEN FROM NA_2WO_4-HCL-H_2O SYSTEM

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The vibrational spectrometric methods are of great importance at the hydrothermal investigations. The existence and the concentrations of some tungsten complexes in the water solution of $Na_2WO_4 \cdot H_2O$ was obtained by the Raman spectrometric study at room temperature. The known frequencies of the aquacomplex WO_4^{-2} (931cm^{-1} [1]) and data of our quantum-chemical calculations were used for their identification.

The Raman lines at the frequencies 931, 960 and 980 cm^{-1} were observed during the lowering pH of the solution from 9 to 4. The line 960 cm^{-1} was assigned to the HWO_4^- complex owing to the experiment in which the solutions at pH=7.4 and three initial concentrations of the salt equal to 0.1, 0.05 and 0.025 mol/l were studied. It was observed that the relatition of intensity of the line at 960cm^{-1} to the intensity of the line at 931cm^{-1} remaind constant. So, the conclusion was done that the both lines belong to the tungsten monomeres.

The equilibrium $WO_4^{-2} + H^+ = HWO_4^-$ (1) was studied also at different value of pH. In the range pH=7.95-7.05 the linear dependence $\lg(I_{960}/I_{931}) = -pH + Const$ with the angle of incidence nearly 45^o was observed. It confirms the assignment of the line at 980cm^{-1} to the HWO_4^--complex.

The equality of the concentrations of WO_4^{-2} and HWO_4^- species was obtained at pH=7.3±0.1, hence logarithm of the equilibrium quotient is $\lg K_1$ *= 7.3±0.2 At the same manner the line 980cm^{-1} was attributed to H_2WO_4 species and $\lg K_2$ *= 4.6±0.2 was obtained for the equilibrium $HWO_4^- + H^- = H_2WO_4$(2).

The activity coefficients of the tunsten complexes in the second approximation of the Debye-Hückel theory are: $\lg\gamma(WO_4^{-2}) = -0.53$, $\lg\gamma(HWO_4^-) = -0.13$. Hence the equilibrium constants are: $\lg K_1 = 7.7 \pm 0.2$ è $\lg K_2 = 4.7 \pm 0.2$. Applying the known value of the Gibbs free energy of formation of the species WO_4^{-2} in water solution $\Delta G_f^{\circ}{}_{298.15} = -916$ kJ/mol [2], and our values of $\lg K_1$ and $\lg K_2$ we obtained the Gibbs free energy of formation for the studied aquacomplexes:

$$\Delta G_f^{\circ}{}_{298.15}(HWO_4^-) = \Delta G_f^{\circ}{}_{298.15}(WO_4^{-2}) - R \cdot T \cdot \ln K_1 = -(916+44) \text{ kJ/mol} = -960 \text{ kJ/mol}$$

$$\Delta G_f^{\circ}{}_{298.15}(H_2WO_4) = \Delta G_f^{\circ}{}_{298.15}(HWO_4^-) - R \cdot T \cdot \ln K_2 = -(958+27) \text{kJ/mol} = -987 \text{ kJ/mol}.$$

The calculations of the equilibrium geometries, vibrational frequencies and thermodynamic properties of free complexes WO_4^{-2}, HWO_4^- and H_2WO_4 were carried out for the interpretation of the experimental results. Our calculations were made at the restricted Hartree-Fock level. For tungsten we used SBK effective core potential. The atoms of oxygen, chlorine and hydrogen were calculated with the triple zeta valence basis sets with adjusted the polarization orbitals d-type at oxygen and chlorine and p-type at hydrogen. Theoretical equilibrium structures and vibrational frequencies for this complexes were also obtained using second order of Möller-Plesset pertubation theory.

Vibrational frequencies (×0.89) of WO_4 -frame accumulated in the table (*-experiment):

WO_4^{-2}	HWO_4^-	H_2WO_4
883 / 931*	958 / 960*	1026 / 980*
763(3)	869 866 573	962 695 690
301(3)	315 303 271	350 264 241
296(2)	235	231
	224	193

The assignment of the lines at 960cm^{-1} and 980cm^{-1} to the protonated species is confirmed by our calculations which show that the highest vibrational frequency of the W-O bond increases with the increasing the number of the protons as 1:1.07:1.16.

The equilibrium structure of WO_4^{-2} related to the T_d -symmetry point group with the bond lengths r(W-O)=1.77Å.

The structure of $WO_2(OH)_2$ may be with equal correctness related to point groupes C_s and C_2 due to existence of the two isomeres. In both case two hydrogen atoms are attached to different oxygen atoms O_1 and O_2. Bond lengths and angles of this isomeres are: $r(H_1\text{-}O_1)$=0.94Å, $r(W\text{-}O_1)$=1.86Å, $r(W\text{-}O_3)$=1.68Å, $\angle O_1\text{-}W\text{-}O_2 \cong 110^o$, $\angle O_3\text{-}W\text{-}O_4 \cong 108^o$, $\angle O_1\text{-}W\text{-}O_3 \cong 110^o$, $\angle O_1\text{-}W\text{-}O_4 \cong 110^o$, $\angle W\text{-}O_1\text{-}H_1 \cong 137^o$.

The equilibrium structure of HWO_4^- related to C_s point group and may be described as deformed tetrahedron with bond lengths r(W-OH)=1.94Å, r(W-O)= =1.72Å and $r(H\text{-}O^1)$=0.94Å. The hydrogen atom is placed at cis-form with respect to the one of three non-bonded oxygen (O^1) with the bond angle equal to ∠

O^1-W-OH=≅107°, the other bond angles are ∠W-O-H≅122°, ∠O-W-O≅111° and two angles equal to ∠HO-W-O≅109°.

The absolute entropy $S^o_{298.15}$ calculated for free complex HWO_4^- is equal to 355 kJ/mol·K. The tabulated values for entropies of related substances [3] were used for the entropy of formation of HWO_4^- calculation according to reaction $1/2 \cdot H_2 + 2O_2 + W_{crys} = HWO_4^-$: $\Delta S_f^o{}_{298.15}$ (HWO_4^-)= -156 J/mol·K. Then, using the experimental enthalpy of formation [4], we calculated the free Gibbs energy of formation for the free complex: $\Delta G_f^o{}_{298.15}(HWO_4^-)$= -1093 kJ/mol.

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