Vigasina M.F., Orlov R.Yu. Possibilities of application of the quantum-mechanical calculations for the interpretation of the oscillation spectra, estimations of Δ_rG in aqueous solution and thermodynamic parameters of species

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Application of the quantum mechanics for the description of the properties of aqueous species and conditions of geochemical reactions is interesting, since, firstly, most of geochemical processes proceeds in the aqueous media and, secondly, the amounts of the additional data used for such calculations are insignificant. Therefore, the quantum-mechanical calculations are independent and informative. The last factor is the most valuable, since desired natural parameters can not be reproduced in some cases.

Some possibilities of the quantum-mechanical calculations were demonstrated by the study of protonation reaction of molibdate-ion in water:

$MoO_4^{2-} + H^+ = HMoO_4^-$

Free Gibbs energy of the reaction $\Delta_rG^0_{298}$ and free Gibbs energy of the formation of the $HMoO_4^-$ complex $\Delta_fG^0_{298}$ were calculated.

All calculations were performed in the approximation of a restricted Hurtry-Fock's method with the use of quantum-chemical programs PC GAMESS. The description of molybdenum atom was carried out with the use of effective potential SBK [3], for atoms of oxygen and hydrogen the basis DH [4] was used with the addition of the polarized p-orbital of oxygen.

In order to calculate energetic characteristics of reactions and the $HMoO_4^-$ complex, equations of the energetic balance at standard conditions were deduced:

$$\mathbf{E^G[MoO_4^{2-}{}_{aq}] + E^G[H^+_{aq}] + \Delta_rG^o_{298} = E^G[HMoO_4^-{}_{aq}]} \quad (1)$$

$$\mathbf{\Delta_fG^o_{298}[MoO_4^{2-}{}_{aq}] + \Delta_fG^o_{298}[H^+_{aq}] + \Delta_rG^o_{298} = \Delta_fG^o_{298}[HMoO_4^-{}_{aq}]}\ , \quad (2)$$

where $E^G = E_{form.} + G^0_{298}$ is a total energy of the complex (for $HMoO_4^-$ and MoO_4^{2-}complexes, the total energy was obtained from the quantum-mechanical calculations, for H^+_{aq} the total energy was calculated from the published data).

On the first stage of calculation, an equilibrium geometry and frequencies of normal oscillations of $HMoO_4^-$ and MoO_4^{2-} ions in the aqueous media were deduced. Two models of the dissolving media were applied: the model of the self-consistent reaction field [5] (SCRF) and the model of effective fragment potentials [6]. Within the model of effective fragment potentials, a deduction of the equilibrium geometry of the molybdenum ions was performed in surrounding of four, twelve, and twenty water molecules. The most adequate geometry of the solvated molybdenum ions was chosen on the basis of the maximal consistency of the calculated frequency of hole-symmetrical stretching vibration of the $HMoO_4^-$ and MoO_4^{2-}complexes with the experimentally derived frequencies (the experiment by authors) and published data (Table 1).

Table 1. Frequency of the valent symmetric oscillation of molibdate-ions, ν (cm^{-1})

	SCRF	EFP (+4 H_2O)	EFP (+12 H_2O)	EFP (+20 H_2O)	Experiment	Nakamoto, 1991
MoO_4^{2-}	866	877	898	903	895	897
$HMoO_4^-$	946	946	944	944	941	-

Table 2. The calculated energy of formation $E_{form.}$ and the Gibbs free energy G^0_{298} of solvated molybdate-ions, (kcal/mol).

	$E_{form.}$	$G^0_{298} \equiv G^o_o - G^0_{298}$
MoO_4^{2-}	-230367.585	-9.142
$HMoO_4^-$	-230667.786	-4.904

Analysis of the calculated frequencies showed that the best consistency of theoretical and experimental frequencies of the solvated $HMoO_4^-$ and MoO_4^{2-}ions was achieved in the EFP model with the surrounding of 12 water molecules. The obtained result allowed unambiguous identification of the experimental ionic forms and application of the calculated equilibrium geometries of the molybdenum complexes and the aqueous surrounding in further calculations.

In order to estimate $\Delta_rG^0_{298}$ by the equation (1), we calculated the complete energy of the formation $E_{form.}$ and the Gibbs free energy G^0_{298} of molybdate-ions in the SCRF model (Table 2). Radiuses of the cavities accommodated by molybdate-ions was taken to be equal of the radiuses of the first coordination sphere, estimated from the calculation of the equilibrium geometry of the solvated molybdate-ions in the EFP model: R_0 = 3.14 E for $HMoO_4^-$ and R_0 = 3.07 E for MoO_4^{2-}.

The value of the complete energy of the solvated proton $E^G[H^+_{aq}]$ was calculated from the published data by the following scheme:

$$\mathbf{E^G[H^+_{aq}] = E^G[H^+_{gas}] + \Delta_{sol}G^o_{298}\ [H^+]}, \quad (3)$$

where $\Delta_{sol}G^0_{298}(H^+)$ is the Gibbs free energy of the proton solvation, $E^G[H^+_{gas}]$ is the complete energy of proton in gas. In turn, this value was found from the equation

$$\mathbf{E^G[H^+_{gas}] = E_{form}\cdot[H^+_{gas}] + G^o_{298}\ (H^+_{gas}) = G^o_{298}\ [H^+_{gas}]}\ , \quad (4)$$

since the energy of the proton formation in gas $E_{form.}[H^+_{gas}]$ is taken to be zero and serves as a zero point of entry in the quantum chemistry. The Gibbs free energy of proton in gas $G^0_{298}[H^+_{gas}]$ was calculated from the well-known relation:

$$\mathbf{G^o_{298}\ [H^+_{gas}] = H^o_{298}\ [H^+_{gas}] - T \cdot S^o_{298}\ [H^+_{gas}]\ .} \qquad (5)$$

Enthalpy and entropy of proton in gas are taken from [8]: $H^0_{298}[H^+_{gas}]$ = 6.2 kJ/mol, $S^0_{298}[H^+_{gas}]$ = 108.8 J/(mol K). Thus, the complete energy of proton is

$$\mathbf{E^G[H^+_{gas}] = 6.2 - 108.8 \cdot 298.15 = -26.24 (кJ/mol) = -6.28 (kcal/mol).}$$

A value of the Gibbs free energy of solvated proton in (3) was calculated from the equation similar to (5), related to the thermodynamic values of the solvation process. An enthalpy of solvation $\Delta_{sol}H^0_{298}[H^+]$ = -1153 kJ/mol is calculated in [9], whereas the entropy change during solvation is calculated in accordance with [10]:

$$\mathbf{\Delta_{sol}S^o_{298}[H^+] = S^o_{298}[H^+_{aq}] - S^o_{298}[H^+_{gas}] + 26.57\ J/(mol \bullet K)}$$

where a correction 26.57 J/(mol•K) is added to account for the difference in standard states of an ion in gas and in solution, while $S^0_{298}[H^+_{aq}]$ = -20.9 J/(mol K) [10]. Thus, the entropy of the proton solvation is $\Delta_{sol}S^0_{298}[H^+]$ =-20.9-108.8+26.57 = -103.13 J/(mol K) = -24.67 (cal/mol), whereas the Gibbs free energy of the proton solvation is -$\Delta_{sol}G^0_{298}[H^+]$ = -1153 – 298.15*(-103.13)= -1122.25 (kJ/mol) = -268.48 (kcal/mol). Substituting into (3) of the complete energy of proton in gas and the Gibbs free energy of the proton solvation, we calculated a value of the complete energy of proton in the aqueous phase:

$$\mathbf{E^G[H^+_{aq}] = -26.24 – 1122.25 = -1148.5\ (kJ/mol) = -274.8\ (kcal/mol).}$$

Equation (1) allowed determination of the Gibbs free energy of the reaction of protonation of the molybdate-ion in the aqueous media:

$$\mathbf{\Delta_rG^o_{298} = E^G[HMoO_4{}^-_{aq}] - E^G[MoO_4{}^{2-}_{aq}] - E^G[H^+_{aq}] = (E_{обр} + G^o_{298})[HMoO_4{}^-_{aq}] - (E_{обр} + G^o_{298})[MoO_4{}^-_{aq}] - E^G[H^+_{aq}] = (-230667.8-4.9) - (-230367.6-9.1) - (-274.8) = -21.2 (kcal/mol).}$$

Thus, the value of the Gibbs free energy of the reaction regarding the errors (which does not exceeds 15 kcal/mol [11]) is $\Delta_rG^0_{298}$ = -21±15 kcal/mol. This result is in accordance with the value of the Gibbs free energy of the above reaction, estimated from our experiment on combination light dissipation, i.e. $\Delta^{exp}{}_rG^0_{298}$ = -8.6 kcal/mol.

The calculated value of the Gibbs free energy of the reaction of protonation of molybdate-ion allowed estimation of the Gibbs free energy of the formation of the aqueous complex $HMoO_4{}^-_{aq}$ from the equation (2). Since the value $\Delta_fG^0_{298}[H^+]$ is taken to be equal to zero, whereas the Gibbs free energy of the $MoO_4{}^{2-}$ complex is known, $\Delta_fG^0_{298}[MoO_4{}^{2-}]$ = - 200.4 kcal/mol [12], the value

$$\mathbf{\Delta_fG^0_{298}[HMoO_4{}^-] = \Delta_fG^0_{298}[MoO_4{}^{2-}] + \Delta_rG^0_{298} = -200-21 = -221\ kcal/mol\ (\pm 15\ kcal/mol).}$$

The calculated entropy of the $HMoO_4{}^-$ aqueous complex is $S^0_{298}[HMoO_4{}^-]$ = 79.98 cal/mol K and of the $MoO_4{}^{2-}$ aqueous complex is $S^0_{298}[MoO_4{}^{2-}]$ = 68.8 cal/mol K

Conclusion. The above results of calculation of thermodynamic parameters for the aqueous reation of protonation of the $HMoO_4{}^-$ aqueous complex demonstrate possibilities of application of the quantum-mechanical calculations in the study of aqueous geochemical reactions. Taking to account a constant improvement of the models for description of solvent, such calculations are shown to be very perspective.

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