QUANTUM CHEMICAL STUDY OF THERMODYNAMICAL FRACTIONATION OF STABLE ISOTOPES IN THE PROCESS OF CRYSTAL GROWTH FROM SOLUTION.

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In [1, 2] it has been shown that the quantum chemistry methods can be used successfully in calculating of isotope reduced partition function ratio $(s/s')f$ ("β-factors") of molecules and ions for which information about vibrational frequencies is inaccessible, in particular, for complexes in water solutions.

The special interest causes a question on value of $(s/s')f$ for hydrated cations of calcium and magnesium, as calcium and magnesium minerals, on the one hand, are widely distributed in nature and have practical importance, and, on the other hand, isotope fractionation of magnesium and calcium at the sedimentation of their salts (in the laboratory and in nature) has not been studied. The calculation of $(s/s')f$ of aqua complexes of cations of these metals could help to clear up a nature of isotope fractionation of calcium and magnesium and to find out an opportunity to use the data on isotope structure of the natural minerals as instrument of research, first of all in isotope geochemistry.

Hydration of cations.

Hydration of cations Mg^{2+} and Ca^{2+} in water solutions has been studied both experimentally and theoretically (see review [3] and references given there). Mg^{2+} cation is strongly hydrated, and its coordination number is always equal to 6, the coordination is close to octahedral.

On the contrary, the calcium cation is weakly hydrated. The coordination number of an ion Ca^{2+} is usually (according the data of X-ray researches) is accepted equal 6. However, modeling by methods of molecular dynamics gives greater values of coordination number (up to 9.6). It is necessary to note that the researches by diffraction methods give rather unsharp maxims. This may be due to asymmetry of the first coordination sphere. The *ab initio* calculations of geometry and vibrational frequencies of ion $Ca(H_2O)_n^{2+}$ in the literature are absent, that has forced us to carry them out.

Calculation of vibration frequencies and $(s/s')f$ values of hydrated cations Mg^{2+} and Ca^{2+}.

The most detailed review on the spectral data on frequencies of vibrations of magnesium aqua complex is given in work [4]. In this work *ab initio* calculation of vibrational frequencies of hexaaquacomplex $Mg(H_2O)_6^{2+}$ (symmetry T_h) has been carried out (basis RHF MP2/6-31++G*). The experimental and calculated frequencies of $Mg(H_2O)_6^{2+}$ are given in the Tab. 1 (in this table only those frequencies are given which contribution to value of $\ln(s/s')f$ exceeds 1%).

It should be noted the discrepancy between our assignment and those given in [4]. In the mentioned work the frequency 421.8 cm^{-1} (MP2/6-31+G*) is assigned to valent asymmetrical vibration ν(Mg–O). However, it is obvious from the contributions of various frequencies to the value of $\ln(s/s')f$ presented in Tab. 1 that to the ν(Mg–O) vibration it is necessary to assign frequency 371.9 cm^{-1}, which the authors [4] have assigned to ω − HOH (in basis MP2/6-31+G* this frequency is equal to 390.4 cm^{-1}). Really, the rule that valent vibrations including the isotopically substituted atom bring main (usually more than 50%) contribution to the value of $\ln(s/s')f$, has no exceptions.

Table 1: Experimental and calculated frequencies (cm^{-1}) of ion $Mg^{2+} - (H_2O)_6$. Only frequencies for light isotopic form (^{24}Mg) are given.

Experiment	MP2/6-31+G* [4]	MP2/6-311++G**			Symmetry	Assignment
		^{24}Mg	^{26}Mg	Contribution to $\ln(s/s') f$ in %		
	151.5	162.1	160.6	$1.8 \times 3 = 5.4$	F_u	$\delta - OMgO$
370	390.4	380.7	374.8	$16.5 \times 3 = 49.5$	F_u	$\nu - MgO$
420	421.8	418.2	417.6	$2.0 \times 3 = 6.0$	F_u	$\omega - HOH$?
	582.5	560.4	557.1	$12.9 \times 3 = 38.7$	F_u	$\rho - HOH$

The calculations of $\ln(s/s') f$ of hydrated cations Ca^{2+} and Mg^{2+} have not been carried out earlier. The experimental data on vibrational frequencies for calcium aqua complex necessary for such calculations are absent in the literature. For magnesium aqua complex only few frequencies are determined and there are no data on frequencies of the isotopic forms.

The calculation of $\ln(s/s') f$ for aqua complexes has been carried out by us on the basis of the frequencies of the isotopic forms calculated by *ab initio* methods as in detail described by us in [2]. In all calculations of geometry, vibrational frequencies and $\ln(s/s') f$ of hydrated cations the program PC GAMESS [5, 6] has been used. We have used RHF method and bases built-in in PC GAMESS. In all calculations the effective core potentials (ECP) such as SBK [7] and HW [8] were used, as the preliminary computations have shown that use of these potentials practically does not influence resulting value of $\ln(s/s') f$. In case of magnesium aqua complex the bases RHF/6-311++G**(3df,3p) and MP2/6-311++G**(3df, 3p) were used. Calcium aqua complexes were calculated in bases RHF/DZV (Ca(14s,9p,3d)/[5s,3p,1d], O(10s,5p)/[3s,2p], H(5s,3p)/[3s,3p], effective core potential HW) and RHF/TZV (Ca (14s,9p,3d)/[8s,4p,3d], O (11s,6p,3d,1f)/[5s,3p,3d,1f], H (6s,3p)/[4s,3p], effective core potential HW). Before calculation of vibrational frequencies the optimization of geometry of complexes in the same bases has been carried out. The results of calculations are given in the tables 2 and 3.

Table 2: $\ln(s/s') f$ values for aqua complexes of Mg^{2+} cation (T=300K).

Complex	Basis	
	RHF/6-311++G**(3df,3p)	MP2/6-311++G**(3df,3p)
$Mg(H_2O)^{2+}$	0.0101^s, 0.0104^h	0.0092^s, 0.0095^h
$Mg(H_2O)_2^{2+}$	0.0186^s, 0.0191^h	0.0170^s, 0.0174^h
$Mg(H_2O)_3^{2+}$	0.0252^h	0.0235^h
$Mg(H_2O)_4^{2+}$	0.0285^h	—
$Mg(H_2O)_5^{2+}$	0.0261^h	0.0258^h
$Mg(H_2O)_6^{2+}$ (symmetry T_h)	0.0239^h	0.0247^h
$Mg(H_2O)_{10}^{2+}$ (symmetry C_1)	0.0249^h	—

^{h} HW ECP has been used
^{s} SBK ECP has been used

Experimental data on fractionation of isotopes of calcium and magnesium. Comparison of the calculated data with experiment.

Unlike isotopes of carbon and oxygen, fractionation of which at sedimentation of carbonate minerals is well studied, fractionation of isotopes of calcium and magnesium in natural systems and in experiment was studied only in few works. In [9, 10, 11] the separation

of calcium isotopes between a $Ca(HCO_3)_2$ solution and $CaCO_3$ sediment formed at slow evaporation of a solution was studied. In these works it was not revealed fractionation of calcium isotopes between a solution and sediment, isotope separation factor ($^{44}Ca/^{40}Ca$) was found to be 1.000 ± 0.002.

Table 3: $\ln(s/s')f$ values for solid calcite and aqua complexes of Ca^{2+} cation (T=300K)

Complex	Basis		
	RHF/DZV	RHF/TZV	MP2/TZV
$Ca(H_2O)^{2+}$	0.0031	0.0036	0.0033
$Ca(H_2O)_2^{2+}$	0.0054	0.0067	0.0061
$Ca(H_2O)_3^{2+}$	0.0086	0.0099	0.0091
$Ca(H_2O)_4^{2+}$	0.0111	0.0123	0.0115
$Ca(H_2O)_5^{2+}$	0.0113	0.0123	0.0121
$Ca(H_2O)_6^{2+}$ (T_h)	—*	0.0118	0.0114
$CaCO_3$ (calcite)	—*	—	—

*according to [12], for $Ca(H_2O)_6^{2+}$ (T_h) $\ln(s/s')f$=0.01365, for $CaCO_3$ (calcite) $\ln(s/s')f$=0.00628.

At the theoretical description of process of isotope fractionation of Ca^{2+} and Mg^{2+} it is necessary to take into account that (i) the isotope exchange at every moment occurs not between solution and internal space of a crystal, but between solution and crystal surface, and $\ln(s/s')f$ of superficial ions differs from $\ln(s/s')f$ of a crystal; (ii) the system has complex chemical composition, in particular include not only aqua complexes, but also sulfate complexes $MgSO_4$ and $CaSO_4$.

Influence of an exchange with a surface

For a theoretical estimation of separation factor in system $^{40}CaCO_3$(solid) $+ ^{44}Ca^{2+}$(aq) $\rightleftharpoons$ $^{44}CaCO_3$(solid)$+^{40}Ca^{2+}$(aq) it is necessary to have the data about $(s/s')f$ for aqua complexes of calcium and for solid calcite. The results of calculation of $\ln(s/s')f$ of complexes and $CaCO_3$ crystal are given in Tab. 3. The value of $\ln(s/s')f$ given in the table for calcite has been calculated in [12] on the basis of isotope frequencies of calcite vibrations. As one can see from Tab. 3, the logarithm of isotope separation factor of calcium $\ln\alpha_{^{40}Ca/^{44}Ca}$ for an exchange between a water solution of calcium salt and calcite, calculated on the basis of $\ln(s/s')f$ of a calcite and hydrated calcium ion in assumption that the isotope equilibrium between internal space of a crystal and solution is established, is equal to 0.004. Such value of separation factor, if it were really realized, would be easy found out experimentally. However in view of stated in [13] (exchange between *surface* of a crystal and solution, and $\ln(s/s')f$ of superficial and internal ions differ) it is necessary to reduce this factor approximately twice, which gives value 0.002, agreed with above mentioned experimental data.

Influence of complex formation in system

While considering a question about separation of isotopes of calcium and magnesium in the process of sedimentation of calcium and magnesium salts from solutions in nature it is necessary to mean that calcium and magnesium present in water phase not only as aqua complexes, but also (provided the corresponding anion presents) as enough strong sulfate complexes [14]. The constant of instability of a complex $CaSO_4$ at 298K is $4.9 \cdot 10^{-3}$, of complex $MgSO_4$ — $4.4 \cdot 10^{-3}$.

Separation factor of isotopes at presence of several reactions of exchange with various substances can not be calculated any more as the simple relation of $(s/s')f$ for two substances

(this question has been considered, for example, in [15]). If in one phase of the system there are the thermodynamic equilibrium between two substances AX and BX exchanging an isotope X with one substance in other phase CX

$$AX^* + CX \rightleftarrows AX + CX^*$$

$$BX^* + CX \rightleftarrows BX + CX^*$$

$$A \rightleftarrows B,$$
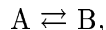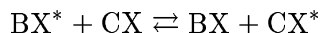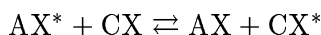
and equilibrium constants of these reactions are

$$K_A = \frac{\beta_C}{\beta_A} = \frac{[AX]\,[CX^*]}{[AX^*]\,[CX]}; \quad K_B = \frac{\beta_C}{\beta_B} = \frac{[BX]\,[CX^*]}{[BX^*]\,[CX]}; \quad K_{AB} = \frac{[B]}{[A]} = \frac{[BX]+[BX^*]}{[AX]+[AX^*]}. \quad (1)$$

Then the expression for separation factor is

$$\begin{aligned} \alpha = \frac{\beta_C}{2\beta_A\beta_B r\,(1+K_{AB})} \Big[&-\beta_A - K_{AB}\beta_B + \beta_B r + K_{AB}\beta_A r \\ &+ \big(2K_{AB}\beta_A\beta_B + 2\beta_A\beta_B r + 8K_{AB}\beta_A\beta_B r + \beta_A^2 \\ &-2K_{AB}\beta_A^2 r - 2K_{AB}\beta_B^2 r + 2K_{AB}\beta_A\beta_B r^2 + 2K_{AB}^2\beta_A\beta_B r+ \\ &K_{AB}^2\beta_B^2 + \beta_B^2 r^2 + K_{AB}^2\beta_A^2 r^2\big)^{1/2}\,\Big], \end{aligned} \qquad (2)$$

where

$$r = \frac{[X^*]}{[X]} = \frac{[AX^*]+[BX^*]}{[AX]+[BX]}. \qquad (3)$$

As one can see, one of features shown in case of presence of concurrent reactions of isotope exchange with different equilibrium constants, is the dependence of isotope separation factor upon the relation of concentration of isotopes in system. It is necessary, however, to note that $(s/s')\,f$ of a substance is defined first of all by number and type of bonds formed by isotopically substituted atom, and in aqua complexes and sulfate complexes of calcium and magnesium (having a structure $Me(H_2O)_5(SO_4)$) these types and numbers do not differ. Therefore the $(s/s')\,f$ values for them should be close, and complex formation with a sulfate ion should not influence separation factor of isotopes of calcium and magnesium.

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