Calculations of the Oxygen Isotope Fractionation between Hydration Water of Cations and Free Water

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The oxygen isotope fractionation factors between the hydration complex of the alkali ions in the gas phase and a free water molecule have been computed on the basis of the energy surfaces calculated by Kistenmacher, Popkie and Clementi for a water molecule in the field of an alkali ion. For comparison with recently measured oxygen isotope fractionation factors in aqueous alkali halide solutions, the gas phase values are multiplied with the corresponding separation factors between water vapor and liquid water thus relating the hydration complex in the gas phase with pure water. Qualitative agreement between computed and observed fractionation factors has been found for H_2O and D_2O even neglecting the isotope effect connected with the transfer of the hydration complex from the gas phase to the solution. This transfer effect is estimated for H_2O by a quantitative comparison of computed and observed oxygen isotope fractionation factors.

I. Introduction

In a paper recently published[1] the fractionation of the oxygen isotopes in aqueous electrolyte solutions, studied by the CO_2-equilibration technique, has been reported. The alkali chloride and the potassium halide solutions have been investigated in H_2O and D_2O. The solvent isotope effect found has led to the conclusion that two separation factors are necessary to describe the fractionation of the oxygen isotopes in aqueous solutions, $\alpha_{\mathrm{HW-BW}}$ the separation factor between hydration water of the cations and bulk water, and $\alpha_{\mathrm{BW-PW}}$ a concentration dependent separation factor between bulk water and pure water describing the influence of the anions on the structure of water. ($\alpha_{\mathrm{HW-BW}}$ and $\alpha_{\mathrm{BW-PW}}$ here are identical with $\bar{\alpha}_{\mathrm{HW-FW}}$ and $\alpha_{\mathrm{FW-RW}}$ in the previous paper[1] respectively.) There is no doubt that $\alpha_{\mathrm{HW-BW}}$ is the dominating separation factor.

Clementi, Popkie and Kistenmacher[2–4] have calculated the energy surface of a water molecule in the field of the alkali ions. Their investigations provide the possibility to determine the force constants necessary to calculate the gas phase separation factor for the oxygen isotopes between the hydration complex and a free water molecule. Accepting their calculations, almost all of the arbitrariness in the choice of the force constants disappears and the computed oxygen isotope separation factors should be directly comparable with experimental results.

The gas-phase oxygen isotope fractionation between cationic hydration water and free water has not been measured. In order to relate $\alpha_{\mathrm{HW-BW}}$ in aqueous solution with the corresponding separation factor in the gas phase, information on the transfer of free water to bulk water and of the hydration complex from gas phase to the solution is necessary. The relation between free water and bulk water is directly given by the vapor pressure isotope effect[5]. There exists no similar obvious relationship for the transfer of the hydration complex. It might be expected that by forming the hydrogen bonds between the first and the second hydration sphere in the solution the ion-oxygen bond becomes weaker, while librational and wagging frequencies increase. In respect to the oxygen isotope effect both changes tend to cancel, at least partly. Therefore, it seems to be justified in a first approximation to use the same partition function ratio for the hydration complex in the gas phase as well as in solution. A difference in geometry of the hydrated ion seems to exist between gas phase and solution. Clementi and coworkers have found that the absolute minimum of the potential energy occurs when the dipole moment of the water molecule is directed towards the ion, while x-ray and neutron diffraction studies[6] as well as molecular dynamics calculations[7a] indicate that in the solution a lone pair orbital of the water molecule is directed towards the ion. This difference in geometry can be taken into consideration in the gas phase computations.

In principle, it would be possible to calculate also the influence of the anions on the oxygen isotope fractionation in aqueous solutions, $\alpha_{\mathrm{BW-PW}}$,

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on the basis of the gas phase calculations of Kistenmacher, Popkie and Clementi[8]. But the separation factor α_{BW-PW} is much smaller than α_{HW-BW} and, in addition, the uncertainty in respect to the transfer of the anion hydration complex from the gas phase to the solution is appreciably larger because the oxygen atoms become directly involved in hydrogen bonds in the solution. Any quantitative conclusions drawn from such calculations would be unjustified.

In this paper gas phase calculations on the oxygen isotope fractionation between cationic hydration water and free water are reported on the basis of the work by Clementi and coworkers[2-4]. The comparison of these results with the experimental values for aqueous alkali halide solutions by employing the corresponding vapor pressure isotope effects, are discussed.

II. Details of the Calculations

The calculations were performed using the Wolfsberg and Stern version[9] of the Schachtschneider program to obtain the equilibrium isotope effects from the normal frequencies of vibration on the basis of the Bigeleisen formalism. Thus, the isotope effects are developed within the harmonic approximation in terms of geometries, internal coordinates and corresponding force constants.

The oxygen isotope fractionation was calculated between a free water molecule and the hydration complexes of Li^+, Na^+, K^+ and Cs^+. Experimental[6] and theoretical[7] considerations yield a hydration number of 4 for the Li^+ in aqueous solutions. Therefore, four water molecules are tetrahydrally arranged around the ion with the dipole moment directed towards the ion, in agreement with the configuration found to have the lowest minimum for the ion-water pair potential in the gas phase[2-4] (Figure 1 a). The question if for the larger alkali ions a hydration number of four is reasonable is of no importance here because of the strong decrease of the interaction between the water molecules in the hydration complex with increasing ion size. Test runs have shown that the difference in the computed oxygen isotope fractionation factors between an ion-water pair and a tetrahedral arrangement of four water molecules around an ion is small compared with other uncertainties to be discussed later. Therefore, the tetrahedral arrangement of the water molecules was preserved for all ions. As the x-ray and neutron diffraction studies[6], as well as the molecular dynamics calculations[7a], indicate that in LiCl solutions a lone pair orbital, and not the dipole moment, of the hydration water molecule is directed towards Li^+, additional calculations for Li^+ were performed for this geometry (Figure 1 b). The geometry of the free water molecule was chosen to be the same as that for the water molecule in the hydration complex: O – H distance 0.96 Å, HOH angle 106°. The ion-oxygen equilibrium distances, R_{IO}, were taken from the minima of the potential energy plots[2, 3] and are given in the first column of Table 1.

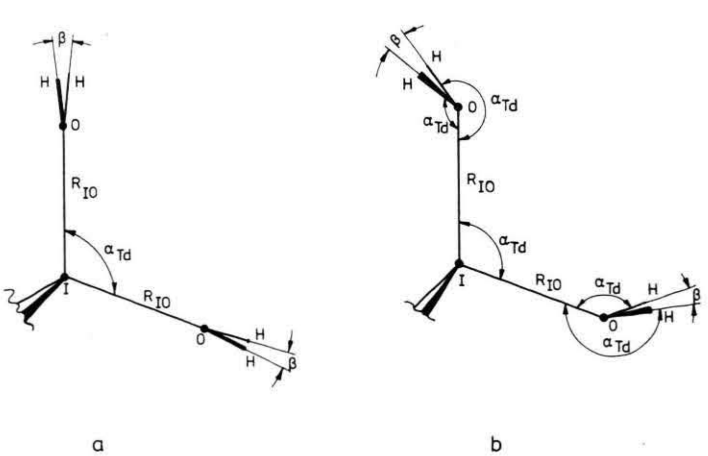

Fig. 1. Geometrical arrangements of the hydration complexes. Dipole moment (a) and lone pair orbital, (b) of the water molecule directed towards the ion. The tetrahedral angle $\alpha_{Td} = 109°47'$ and $\beta = 106°$. The O – H distance is 0.96 Å and R_{IO} distances for the various ions are given in Table 1.

Table 1. The ion-oxygen equilibrium distances and the force constants for the various hydration complexes. R_{IO} is given in Å, f_{OH} and f_{IO} in mdyn/Å and all others in mdyn·Å.

Ion	R_{IO}	f_{OH}	f_{IO}	f_{HOH}	f_{OIO}	f^{ip}_{HOHI}	f^{op}_{HOHI}	f_{HOIO}
Li^+	1.84	9.816	0.6830	0.812	0.068	0.270	0.095	0.008
Na^+	2.22	9.816	0.3542	0.812	0.035	0.211	0.077	0.008
K^+	2.67	9.816	0.2553	0.812	0.026	0.153	0.067	0.008
Cs^+	3.14	9.816	0.1794	0.812	0.018	0.121	0.060	0.008

Force constants were developed for the following set of internal coordinates:

8 stretches	OH
4 stretches	IO
4 bends	HOH
6 bends	OIO
4 in plane wags	HOHI
4 out of plane wags	HOHI
6 torsions	HOIO

The force constants employed for the various ions are given in Table 1.

The values of the force constants for the water molecules were taken from Ermler and Kern [10]. The same values were used for the free water molecule and for the water molecules in the hydration complex. Therefore the computed isotope effect is very insensitive to changes of the force constants. A decrease of 40% leads to a change in the isotope effect of 0.1‰.

The force constants of the ion-oxygen stretches and both kinds of wags were deduced from the calculations of Clementi et al. [2–4] by using a least square routine to fit harmonic potentials to their potential surface. The vibrational frequencies of the hydration complexes calculated on the basis of these force constants agreed with the ones determined by Kistenmacher, Popkie and Clementi [4] in the limits of the computational error. The uncertainty in the stretching and wagging force constants determined in the described way is estimated to be less than 10% which means that the error in the calculated oxygen isotope fractionation factor is less than 1‰ in the case of Li^+, and remarkably less for the heavier ions. As the potential surfaces for a water molecule in the field of an alkali ion are only available for Li^+, Na^+ and K^+, the force constants for the hydration complex around Cs^+ have been determined by an extrapolation procedure based on the size of the alkali ions.

The values of the force constants for the OIO bend and for the torsions have been estimated. The bending force constant has been determined from the fact that for other tetrahedral atomic arrangements the range of the ratio of the stretching to the unweighted bending force constant lies between 10 and 40 [11]. As a test run showed that an increase of the bending force constant by 500% only resulted in a change of the isotope effect of 0.5‰, it can be concluded that the error caused by the uncertainty in the bending force constant is, even for Li^+, less than 0.5‰. The torsion force constants were estimated as being very small, essentially being necessary to satisfy the normal coordinate mathematical conditions [12].

Accepting the potential surfaces given by Kistenmacher, Popkie and Clementi [2–4], the overall accuracy of the calculated oxygen isotope fractionation factors between the hydrated complex and the free water molecule in the gas phase should be better than 1.5‰.

The calculations were performed on the CDC 3300 of the computer centre at the University of Mainz.

III. Results and Discussion

The computed oxygen isotope fractionation factors between hydration water and free water in the gas phase, α_{HW-FW}, are given in the temperature range 0 – 100 °C as a function of $1/T$ for Li^+, Na^+, K^+ and Cs^+ in Figure 2. The computations are based on the force constants as given in Table 1, derived from the energy surfaces calculated by Kistenmacher, Popkie and Clementi [2–4]. For Li^+ two different geometries are employed: (a) the dipole moments and (b) a lone pair orbital of the water molecules are directed towards Li^+ (see Figure 1). The full lines show the results for H_2O and the dashed lines for D_2O. The difference between H_2O and D_2O for Li^+(b), K^+ and Cs^+ is too small to be shown on the graph.

The fractionation factors show the expected decrease with increasing ion size and increasing tem-

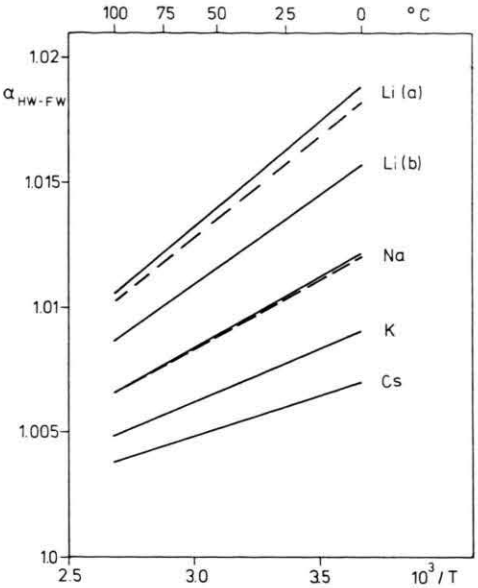

Fig. 2. The computed oxygen isotope fractionation factors between hydration water and free water in the gas phase, α_{HW-FW}, for various alkali ions. Full lines: H_2O, dashed lines: D_2O. The difference between H_2O and D_2O for Li^+(b), K^+ and Cs^+ is too small to be shown on the graph.

perature. The difference between H_2O and D_2O decreases strongly with increasing mass of the central ion. The difference between Li^+(a) and Li^+(b) for H_2O and the result that in the case of Li^+(b) the difference between H_2O and D_2O is very small are a consequence of the different geometries employed because the force constants are kept the same for both cases.

In order to compare the computed oxygen isotope fractionation factors between hydration water and free water in the gas phase with the ones measured in aqueous solutions [1], a fractionation factor α'_{HW-BW} is defined by

$$\alpha'_{HW-BW} = \alpha_{HW-FW} \cdot \alpha_{W(g)-W(l)} \tag{1}$$

where $\alpha_{W(g)-W(l)}$ is the oxygen isotope separation factor between water vapor and liquid water.

All α's in this paper mean:

$$\alpha_{A-B} = (^{18}O/^{16}O)_A/(^{18}O/^{16}O)_B .$$

By Eq. (1) the $^{18}O/^{16}O$ ratio of the hydration complex in the gas phase is related to $^{18}O/^{16}O$ in pure liquid water. In order to complete the transfer from the gas phase to the solution a fractionation factor would be necessary relating the oxygen isotope ratio of the hydration complex in the gas phase with the one in the aqueous solutions. But there is no information available for quantitative statements. Qualitatively it can be expected that the ion-oxygen bond becomes looser while the force constants for the bends, wags and torsions increase by going from the gas phase to the solution. As these changes might at least partly cancel in respect to the oxygen isotope effect, it seems to be justified to compare the α'_{HW-BW} with the measured values in a first approximation. In addition it should be kept in mind that by doing this comparison the influence of the anion on the structure of the bulk water is neglected.

The fractionation factors $\alpha_{W(g)-W(l)}$ for H_2O as well as for D_2O employed here are from Szapiro and Steckel [5]. It should be mentioned that especially for D_2O at temperatures below 30 °C their values are connected with remarkable errors.

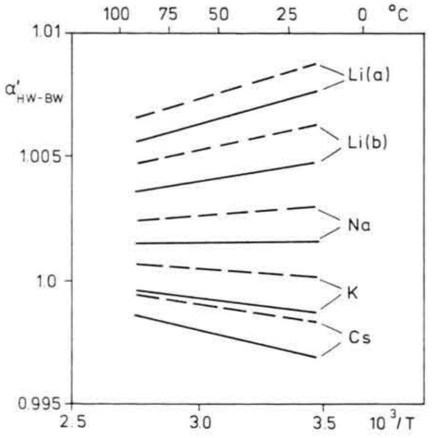

Fig. 3. The oxygen isotope fractionation factors α'_{HW-BW} as defined by Eq. (1) in the temperature range 15—90 °C. Full lines: H_2O, dashed lines: D_2O.

The fractionation factors α'_{HW-BW} are given in Fig. 3 in the temperature range $15-90$ °C, the range for which $\alpha_{W(g)-W(l)}$ values are available. The full lines refer to H_2O and the dashed lines to D_2O. In Table 2 the α'_{HW-BW} values are compared with the measured fractionation factors between hydration water and bulk water in aqueous alkali chloride solutions at 25 °C [1]. As there is good evidence [6, 7a] that in solution a lone pair orbital of the water molecule is directed towards Li^+ only Li^+(b) should be considered for the comparison with the experimental results.

The interesting features of the results can be seen qualitatively in Figure 3. In H_2O for the whole

Table 2. The computed $\alpha'_{\mathrm{HW-BW}}$ and the measured oxygen isotope fractionation factors in aqueous solutions at 25 °C for assumed hydration numbers $n=4$ and $n=6$.

Ion	H_2O			D_2O		
	calc.	obs.		calc.	obs.	
		$n=4$	$n=6$		$n=4$	$n=6$
Li^+ (a)	1.0072	—	—	1.0083	—	—
Li^+ (b)	1.0046	1.0030	(1.0020)	1.0060	1.0092	(1.0061)
Na^+	1.0016	1.0000	1.0000	1.0028	1.0000	1.0000
K^+	0.9989	(0.9981)	0.9987	1.0002	(1.0036)	1.0024
Cs^+	0.9965[b]	(0.9967[a])	0.9978[a]	0.9986	(0.9982)	0.9988

a measured at 4 °C; b determined for 4 °C by extrapolation of the $1/T$ curve in Figure 3.

temperature range $\alpha'_{\mathrm{HW-BW}}>1$ for Li^+ and $\alpha'_{\mathrm{HW-BW}}<1$ for K^+ and Cs^+. This is in agreement with the measured fractionation factors in aqueous solutions at 25 °C (see Table 2) and with other kinds of measurements if positive and negative hydration of ions are defined by the enrichment and depletion of the heavy oxygen isotope in the hydration water relative to bulk water respectively (see e. g. Samoilov[13]). In spite of the approximation in respect to the transfer of the hydration complex from the gas phase to the solution, the absolute values of the isotope effects $|\alpha'_{\mathrm{HW-BW}}-1|$ decrease with increasing temperature as expected for all ions except Na^+ which shows no temperature dependence. As $\alpha'_{\mathrm{HW-BW}}>1$ for Na^+ the temperature independence combined with the fact that in the measurements no isotope effects has been found for a NaCl solution seems to indicate that a systematic deviation exists between computations and measurements. Possible reasons for this systematic deviation are discussed below where the shift is employed for a quantitative discussion of the results.

The general increase of the $\alpha'_{\mathrm{HW-BW}}$ by going from H_2O to D_2O explains qualitatively the results of the measurements in aqueous solutions (see Table 2), except for Na^+ where no isotope fractionation has been found neither in H_2O nor in D_2O. Even the change from negative to positive hydration found for a KCl solution is reproduced. The fact that there is a slight increase of $\alpha'_{\mathrm{HW-BW}}$ for K^+ with increasing temperatures could be a consequence of the relatively large errors in $\alpha_{\mathrm{W(g)-W(l)}}$ for D_2O at temperatures below 30 °C. As the computations are restricted to cation hydration they are not expected to explain the strong anion dependence of the oxygen isotope fractionation measured for KCl, KBr and KJ solutions in D_2O[1].

For a quantitative comparison the computed as well as the measured fractionation factors in aqueous alkali chloride solutions are given in Table 2 for 25 °C, with the exception of Cs^+ where the measurements have been made at 4 °C[14] and $\alpha'_{\mathrm{HW-BW}}$ being determined for the same temperature by linear extrapolation from the $1/T$ dependence in Figure 3. As the observed fractionation factors depend upon the assumed hydration number n, these values are given for $n=4$ and $n=6$. There seems to be no doubt that for Li^+ $n=4$ is correct[6, 7] while for K^+ and Cs^+ $n=6$ might be more appropriate. It should be kept in mind for the following discussion that the error for the observed values is about ± 0.0005.

From the temperature independence of $\alpha'_{\mathrm{HW-BW}}$ for Na^+ in H_2O it might be concluded that a correction of about 1.6‰ should be applied, leading to agreement with the observed value. There are three reasons for a correction: a) the possibility of a wrong choice for the force constants; b) the neglect of the influence of the anions on the structure of bulk water and c) the approximation that the value of the partition function ratio of the hydration complex is the same in the gas phase and in the solution.

Accepting the energy surfaces of Kistenmacher, Popkie and Clementi[2-4] there is no reason for a change of the IO stretching and the wagging force constants. The OIO bending force constants are chosen to have the lowest value in the range given by the relation of Herzberg (see above); an increase would lead to a higher isotope effect for Na^+ and therefore a larger deviation from the measured value. A change of the force constants for the hydration complex in the gas phase in order to achieve agreement seems not to be justified.

The effect of the anions on the structure of bulk water can not explain the difference between computations and measurements because it would result in a structure breaking which means a larger computed isotope effect for the positively hydrated cations and therefore an increased deviation from the observed values.

The transfer of the hydration complex from the gas phase to the liquid results in an additional interaction of the hydration water with the bulk water. This additional interaction is expected to lead to a lowering of the IO stretching force constants and an increase of the force constants for bends, wags and torsions. In other words, the hydration water becomes more bulk water like. Therefore the absolute value of the isotope effect $|\alpha'_{\mathrm{HW-BW}} - 1|$ should become smaller and the amount of the shift should depend upon the size of the isotope effect. Taking the difference between computed and observed values for Na^+ as a measure of the transfer effect, slightly larger shifts are expected for Li^+(b) and Cs^+. In both cases practically quantitative agreement is achieved for both of these ions in the limits of error, if for Li^+ a hydration number of 4 and for Cs^+ $n = 6$ is assumed. In the case of K^+ there is agreement between computed and observed isotope effect without a transfer shift if $n = 6$ is considered as reasonable. The shift is expected to be smaller for K^+ than for Li^+ and Cs^+, but it is hard to guess if agreement is still given in the limits of error. Concluding the discussion of the isotope effects in H_2O it can be stated that the computed isotope effects can explain the experimental results almost quantitatively if the difference for Na^+ is taken as a measure of the effect occurring during the transfer of the hydration complex from the gas phase to the liquid.

In D_2O the discrepancies between computed and observed isotope effects are more complex. There is quantitative agreement in the case of Cs^+ in the limits of error. While for K^+ the change of sign of the isotope effect is reproduced in the computation, the absolute value of it is much smaller compared with the measurements. As in the case of Li^+(b) the value for $n = 4$ has to be used for comparison, again a remarkably larger effect has been measured. In the case of sodium no isotope effect has been measured but a large effect has been computed. It is obvious that in D_2O the transfer of the hydration complex from the gas phase to the liquid alone can not explain the discrepancies as it was possible for H_2O. The strong anion dependence found for KCl, KBr and KJ solutions indicates that in D_2O the influence of the anions on the structure of bulk water is not negligible. As discussed above, this effect would lead to an increase of the isotope effect for positively hydrated ions and could at least partly explain the higher measured values for K^+ and Li^+. For quantitative statements it would be necessary to calculate the isotope fractionation between hydration water of anions and free water. The energy surfaces are available [8] but the problem is that the uncertainty about the isotope effect connected with the transfer of the anion complex from the gas phase to the solution is much bigger than in the case of the cations because the oxygen atoms become directly involved in hydrogen bonds in the liquid. Therefore, computed and measured oxygen isotope fractionation factors can be compared only on a qualitative basis in the case of D_2O.

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