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On the structure and relative stability of uranyl(VI) sulfate complexes in solution

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Abstract

The mode of coordination, mono-, bidentate, sulfate in $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$, and the relative energy of the various isomers have been studied at the DFT and MP2 levels using DFT-optimized geometry in a CPCM solvent model. The U–S distances in the mono- and bidentate coordination, 3.63 and 3.08 Å, respectively, agree very well with experimental observations from solutions. The U–O_{sulfate} distance is significantly different in complexes with mono- and bidentate coordination, 2.23, vs. 2.37 Å, an observation difficult to deduce from the experimental studies. The experimental distance between uranium and the equatorial oxygen atoms, U–O_{eq}, is very close to the calculated average distance in a five-coordination model, but significantly longer in a six-coordination model, indicating a preference for the former; this finding is supported by energy calculations, where the five-coordinated isomers for the $\text{UO}_2(\text{SO}_4)$ have the lowest Gibbs energy. For $\text{UO}_2(\text{SO}_4)_2^{2-}$, the calculated Gibbs energy of reaction indicates that the six-coordinated isomer is slightly more stable than the five-coordinated one; however, the difference is small and less than the expected uncertainty in calculations of this type. Bidentate coordination of the sulfate group is always preferred over monodentate coordination. However, all differences in Gibbs energy between the different isomers is small, indicating that the mode of coordination may change with the composition of test solutions used, as observed experimentally. The U–O–S_{mono} angle is close to 143° in complexes with a monodentate sulfate group; this is traced to steric effects, which overcome the electronic preference for a linear U–O–S bond. This study demonstrates the significant increase in chemical information that may be obtained by combining experimental data on structures and thermodynamics with quantum chemical methods. **To cite this article:** V. Vallet, I. Grenthe, *C. R. Chimie* 10 (2007).

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Résumé

Le mode de coordination, monodentate ou bidentate, de l'ion sulfate dans $\text{UO}_2(\text{SO}_4)$ et $\text{UO}_2(\text{SO}_4)_2^{2-}$ et la stabilité relative des différents isomères conformationnels en phase aqueuse ont été étudiés par des calculs de chimie quantique au niveau DFT et MP2, utilisant des géométries optimisées au niveau DFT avec le modèle de solvant CPCM. Les distances U–S sont de 3,63 Å et 3,08 Å pour une coordination monodentate et bidentate, respectivement, et sont en très bon accord avec les mesures expérimentales en solution. La distance U–O_{sulfate} est sensiblement plus courte dans les complexes monodentés, 2,22 Å, que dans les complexes bidentés, 2,37 Å, une disparité qu'il est difficile de déduire des données expérimentales. La distance expérimentale entre l'uranium et

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les oxygènes coordonnés dans le plan équatorial, $U-O_{\text{eq}}$, est très proche de la valeur calculée dans les isomères pentacoordinés, alors que cette distance est plus longue dans les modèles hexacoordinés, indiquant une préférence pour une coordination 5. Cette observation est corroborée par les valeurs calculées des énergies libre relatives, qui indiquent que les isomères pentacoordinés ont l'énergie libre la plus basse pour le complexe $UO_2(SO_4)$. Pour $UO_2(SO_4)_2^{2-}$, l'énergie libre de réaction indique que l'isomère hexacoordiné est légèrement plus stable que celui pentacoordiné; cependant, la différence est, très faible et plus petite que l'incertitude des calculs de ce type. Nous observons aussi une préférence pour la coordination bidentate des ions sulfate dans les deux composés mono- et bisulfate. Or, l'énergie libre de réaction entre les différents isomères structuraux est faible, indiquant que le mode de coordination de l'ion sulfate peut changer avec la composition chimique de la solution ionique utilisée. Dans les complexes monodentés, l'angle $U-O-S_{\text{mono}}$ est proche de 143° ; ceci est attribué aux effets stériques qui dominent les effets d'interaction électronique tendant à rendre la liaison linéaire. Cette étude illustre comment l'analyse des données expérimentales concernant les structures et la thermodynamique, couplée aux calculs de chimie quantique, permet d'accroître la compréhension de la chimie des actinides en solution. **Pour citer cet article** : V. Vallet, I. Grenthe, C. R. Chimie 10 (2007).

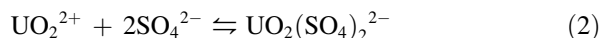
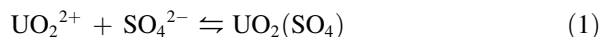
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Keywords: Structure; Bonding; Equilibria; Uranyl; Sulfate; Complexes; Quantum chemistry

Mots-clés : Structure ; Liaison ; Équilibres chimiques ; Uranyl ; Sulfate ; Complexes ; Chimie quantique

1. Introduction

Quantitative information on chemical equilibria and the thermodynamics of actinide complex formation in aqueous solution is, in addition to its pure scientific interest, also important in many applications, such as separation technology and speciation in ground and surface water systems. Solution thermodynamic data provide information on the stoichiometry of the complexes formed, but little or no information on the structure of the first coordination sphere, i.e. the mode of coordination of ligands and the possible formation of isomers of various types. There is extensive information [1] on the chemical thermodynamics of actinide complex formation reactions, including the following uranyl(VI) sulfate reactions that will be discussed in this communication:



We will use experimental and quantum chemical data to provide information on the mode of coordination of the sulfate ion and the number of coordinated water molecules in the uranyl(VI) sulfate complexes formed in reactions (1) and (2).

Single-crystal X-ray structures of a number of uranyl(VI) sulfate compounds reveal that the sulfate ion can be coordinated both in bidentate [2] and monodentate [3] fashion, but with predominance of the latter type. A characteristic feature of the bond distances in solid compounds that contain both mono- and bidentate

sulfate coordination is that the $U-O_{\text{sulfate}}$ bond distance is about 0.15 \AA shorter in the former than in the latter. Structure studies of uranyl(VI) sulfate complexes in solution have been made by Moll et al. using EXAFS [4] and by Neufeind et al. using large-angle X-ray diffraction (LAXS) [5]. Both methods provide accurate information on bond distances, but much less precise information on coordination numbers. These two studies demonstrate that the sulfate ion also in solution can be coordinated both in a monodentate [5] and bidentate fashion [4]. The solution structure determinations are complicated by the fact that the test solutions may contain a mixture of different uranyl species, as will be discussed in the following.

The equilibrium constants for the formation of uranyl(VI) sulfate complexes are moderately large at zero ionic strength, $\log \beta_1^0 = 3.15$ and $\log \beta_2^0 = 4.14$, respectively [1] for the reactions (1) and (2). These equilibrium constants decrease substantially with increasing ionic strength [1], cf. Appendix, and from their magnitude it is not possible to make a reliable prediction of the mode of coordination of sulfate and the number of donor atoms in the equatorial plane of the UO_2^{2+} ion. We have therefore used quantum chemical methods to determine the structure and bond distances in various isomers of $UO_2(SO_4)$ and $UO_2(SO_4)_2^{2-}$ and their relative electronic and Gibbs energies of formation. The bond distances can be directly compared with experimental data, while the relative energies are used to corroborate the conclusions drawn from the bond distances.

The quantum chemical calculations refer to a model where the complexes are dissolved in a model solvent

where the water is described by a conductor-like polarizable continuum model (CPCM) with the macroscopic dielectric constant of water [6]. This differs in two ways from the experimental situation: hydrogen bonding is treated in a simple way and interactions between the dissolved complexes and the counter ions, Na^+ in most experimental test solutions, are not taken into account, i.e. the calculation refers to a medium with zero ionic strength. For this reason we have tested how sensitive the geometry and the relative energy of the complexes are for different model assumptions.

The M–O–S bond angle in most solid-state structures of metal sulfates differs significantly from 180° , the configuration that is expected to minimize electrostatic repulsion. To rationalize this observation, we have probed the interaction between the uranyl unit and a unidentate sulfate group through the energy decomposition scheme [7] in ADF [8,9] (see Section 2.1) to determine whether the angular preference is driven by electronic or steric effects.

2. Quantum chemical calculations and results

2.1. Computational details

The small-core relativistic effective core potential of the Stuttgart–Bonn group was employed for uranium [10], along with the segmented (14s13p10d8f6g)/[10s9p5d4f3g] basis set [11]. The valence triple- ζ plus polarization basis sets were used for sulfur [12a], oxygen [12b], and hydrogen [12b] atoms. The correlation-consistent double- ζ plus polarization basis set (cc-pVDZ) from Woon et al. [13] was used for the sodium counterion. The structures of the various isomers of $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ species were optimized with the gradient-corrected hybrid functional B3PW91 [14], as this is known to result in geometries that are close to the experimental values. Single-point MP2 calculations were also performed at the DFT-optimized geometries, with the 1s core orbitals of oxygen, the 1s, 2s, and 2p orbitals of sulfur and 5s, 5p, 5d orbitals of uranium frozen. Thermochemical corrections to the electronic energies to obtain free energies were computed using the geometries and vibrational partition functions computed at the DFT level for a temperature of 25°C and a pressure of 1 atm. Solvent effects on geometries, partition functions and energies were accounted for through the use of the conductor-like polarizable continuum model (CPCM) [6], with the United Atom Kohn Sham (UAKS) formula for the atomic radii [15]. All calculations were performed with the Gaussian 03 package [16].

2.2. Comment on the energy calculations

There is no significant difference in electronic energy of reaction calculated at the DFT and MP2 levels (Table 2) for reactions that do not involve a change in coordination number. This is not the case for reactions where the coordination number changes from 5 to 6, in which the DFT values are 10–20 kJ/mol higher than the MP2 values. The reason for this is known and related to the known tendency of current exchange correlation functions to underestimate the stability of high coordination numbers. These errors may compensate when comparing two isomers that differ by the number of bound water molecules and the mode of coordination of the sulfate group. Further details have been discussed by Rotzinger [17] for transition metals and by Wählin et al. [18] in the context of the uranyl aqua ion. It is thus important to compare DFT-based numbers for energetics to those obtained with wave-function-based correlated methods, such as MP2. The difference between the electronic and Gibbs energy of reaction is strongly dependent on the contribution of low-frequency vibration modes originating from shallow potential wells. In some cases it was not possible to obtain structures with only real frequencies; in other cases, such as $[\text{UO}_2(\text{SO}_{4\text{-chelate}})_2(\text{OH}_2)_2] \cdot (\text{H}_2\text{O})$, the difference between the electronic and Gibbs energy of reaction was fairly large, around 10 kJ/mol. We conclude that the calculated free energy of reaction may have an uncertainty of about the same magnitude.

2.3. Details of the energy decomposition calculations

To analyze the interaction between uranyl and monodentate sulfate groups, we have computed the total interaction energy between the uranyl fragment and one monodentate sulfate group, using the energy decomposition scheme [7] implemented in the Amsterdam density functional (ADF) package [8,9]. For these calculations, we considered a simplified molecular system involving the uranyl unit and one monodentate sulfate group, without additional water molecules in the first coordination sphere. All-electron calculations were performed using the scalar relativistic zero-order regular approximation (ZORA) – DFT method [19] with the hybrid B3LYP functional [20]. All atoms were described with the uncontracted triplet- ζ Slater-type orbital (STO) augmented by two polarization functions (TZ2P) [21]. The various contributions to the total interaction energy are given in Table S3. The geometry was optimized at the B3LYP level without symmetry constraints. We then explored the evolution of the total

bonding energy between the uranyl and the monosulfate groups for various U–O–S bending angles ranging from 120° to 180°, with steps of 10°.

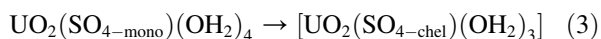
2.4. Quantum chemical results

The bond distances for the various isomers of the uranyl monosulfate and uranyl bis-sulfate complexes calculated at the DFT-B3PW91 level in the CPCM solvent are given in Table 1. The total energy and coordinates of the different complexes are given as supporting data, Tables S1 and S2. The only other theoretical data available is that of Craw et al. [22]. They optimized the structure of uranyl monosulfate at the Hartree–Fock level, assuming a bidentate coordination and imposing C_{2v} symmetry on the structure. They did not consider the lower-symmetry monodentate isomer, certainly because of lack of computational capacity at that time. Our calculated equatorial distances are generally shorter, by 0.20 Å, than those obtained by Craw et al. This is a result of relaxing the symmetry constraints and of the effect of electron correlation and solvent effects, as discussed for other uranyl structures by Wahlgren et al. and Vallet et al. [23]. In the experimental test solutions, there are counterions present (Na^+ or H^+), and we therefore explored if the Na^+ counterions present in the test solutions might influence the quantum mechanical (QM) bond distances in the mono- and bidentate isomers; we found no significant changes. It is noteworthy that it was not possible to optimize the

structure of the monodentate isomer in gas phase because of proton abstraction of one non-coordinated oxygen atom in the sulfate from a neighboring coordinated water molecule.

2.4.1. Five-coordinated $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$

Two different isomers, $[\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{OH}_2)_4]$ and $[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_3]$ (cf. Fig. 1) were identified for $\text{UO}_2(\text{SO}_4)$. The U–S distances are 3.61 and 3.08 Å, respectively, the corresponding U–O_{sulfate} distances 2.22 and 2.37(2) Å are also significantly different. The average U–OH₂ distances in the two isomers are 2.48(3) and 2.46(3) Å, slightly longer than the experimental EXAFS distance, 2.43(1) Å in $\text{UO}_2(\text{OH}_2)_5^{2+}$ [23a]. The negative Gibbs energy of reaction, $\Delta G^0 = -17.0$ kJ/mol (cf. Table 2) for:



indicates that the complex with chelate bonded sulfate is the most stable isomer.

There are three five-coordinated isomers of $\text{UO}_2(\text{SO}_4)_2^{2-}$, $[\text{UO}_2(\text{SO}_{4\text{-mono}})_2(\text{OH}_2)_3]^{2-}$, $[\text{UO}_2(\text{SO}_{4\text{-chel}})_2(\text{OH}_2)]^{2-} \cdot (\text{H}_2\text{O})_2$ and $[\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{SO}_{4\text{-chel}})(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$, cf. Fig. 2. The U–S distances in the mono- and bidentate sulfate groups are close to those in the $\text{UO}_2(\text{SO}_4)$ isomers and the same is true for the U–O distances. The quantum chemical bond distances for the isomer $[\text{UO}_2(\text{SO}_{4\text{-chel}})_2(\text{OH}_2)]^{2-} \cdot (\text{H}_2\text{O})_2$ are in good agreement with the experimental EXAFS data

Table 1

Geometries of the monodentate (mono) and bidentate (chelate) $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ complexes optimized in the solvent using the B3PW91 functional

Chemical model	N^a	U–O _{yl}	U–O _{wat}	U–O _{chel}	U–O _{mono}	U–O _{aver}	U–S _{chel}	U–S _{mono}
$[\text{UO}_2(\text{OH}_2)_5]^{2+} \cdot (\text{H}_2\text{O})$	5	1.746	2.43(1)	–	–	2.43(1)	–	–
EXAFS Ref. [23]	5	1.77	2.41	–	–	–	–	–
$\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{OH}_2)_4$	5	1.759	2.48(3)	–	2.22	2.43(8)	–	3.61
$[\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{OH}_2)_4] \cdot \text{Na}^+$	5	1.758	2.46(1)	–	2.25	2.42(7)	–	3.64
$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_3] \cdot (\text{H}_2\text{O})$	5	1.765	2.46(3)	2.37(2)	–	2.42(4)	3.08	–
$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_3] \cdot (\text{H}_2\text{O}), \text{Na}^+$	5	1.760	2.43(2)	2.39	–	2.42(3)	3.07	–
$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_4]$	6	1.760	2.52(3)	2.41	–	2.51(6)	3.13	–
$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_3]^b$	5	1.74	2.64	2.562	–	–	3.08	–
EXAFS Ref. [4]	5	1.78	–	–	–	2.42	3.12	–
$[\text{UO}_2(\text{SO}_{4\text{-mono}})_2(\text{OH}_2)_3]^{2-}$	5	1.769	2.49(3)	–	2.29	2.4(1)	–	3.67
$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{SO}_{4\text{-mono}})(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$	5	1.769	2.46(1)	2.42(1)	2.27	2.41(6)	3.11	3.67
$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{SO}_{4\text{-mono}})(\text{OH}_2)_3]^{2-}$	6	1.765	2.58(9)	2.47(1)	2.38	2.49(7)	3.17	3.74
$[\text{UO}_2(\text{SO}_{4\text{-chel}})_2(\text{H}_2\text{O})]^{2-} \cdot (\text{OH}_2)_2$	5	1.768	2.43	2.40(1)	–	2.41(1)	3.09	–
$[\text{UO}_2(\text{SO}_{4\text{-chel}})_2(\text{H}_2\text{O})_2]^{2-} \cdot (\text{OH}_2)$	6	1.769	2.54	2.46(1)	–	2.49(3)	3.16(1)	–

For comparison we have also reported the bond distances in $[\text{UO}_2(\text{OH}_2)_5]^{2+} \cdot (\text{H}_2\text{O})$, calculated with the same functional.

^a N is the coordination number of uranyl(VI).

^b From Ref. [22]: structure optimized at the Hartree–Fock level in gas phase.

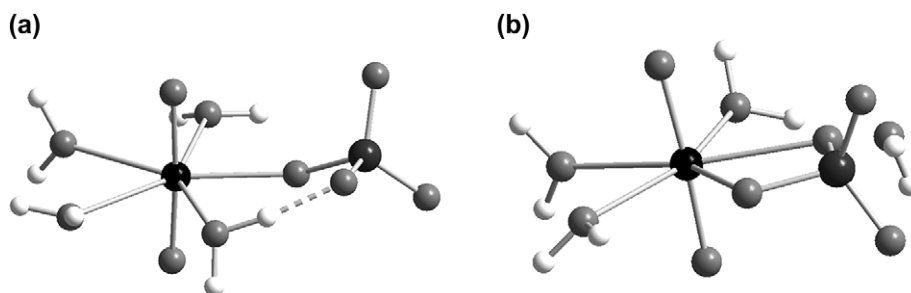
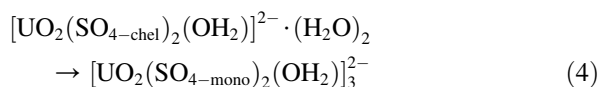
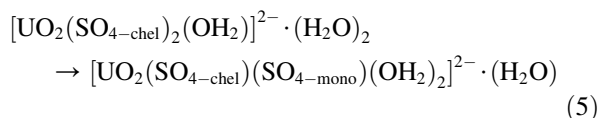


Fig. 1. The structure of the two five-coordinated isomers of $\text{UO}_2(\text{SO}_4)$: (a) $[\text{UO}_2(\text{SO}_4\text{-mono})(\text{OH}_2)_4]$ and (b) $[\text{UO}_2(\text{SO}_4\text{-chelate})(\text{OH}_2)_3] \cdot (\text{H}_2\text{O})$ based on DFT geometry optimizations in the CPCM solvent. The dashed line indicates a hydrogen bond where the distance $\text{H}_{\text{water}}\text{-O}_{\text{sulfate}}$ is about 1.60 Å and the angle $\text{O}_{\text{water}}\text{-H-O}_{\text{sulfate}}$ is 168°; the water outside the first coordination sphere in $\text{UO}_2(\text{SO}_4\text{-chelate})$ forms only very weak hydrogen bonds.

[4], indicating that this is the stable isomer. The calculated Gibbs energy of reaction for reaction (4):



is 13 kJ/mol, indicating that the chelate bonded isomer is the most stable one. However, the electronic energy of reaction indicates the reverse as ΔE (MP2) is -8.6 kJ/mol; caution is therefore necessary when using the electronic energy to estimate the relative stability of isomers.



It was not possible to calculate the Gibbs energy of reaction for reaction (5) because of the appearance of imaginary frequencies, but as this complex contains two

different U–S distances that are not evident in the experimental EXAFS data, we conclude that also this isomer is less stable than $[\text{UO}_2(\text{SO}_4\text{-mono})(\text{SO}_4\text{-chel})(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$.

2.4.2. Six-coordinated $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$

There is only one stable six-coordinated isomer of $\text{UO}_2(\text{SO}_4)$, $[\text{UO}_2(\text{SO}_4\text{-chel})(\text{OH}_2)_4]$, cf. Fig. S1a; all bond distances are longer than in the corresponding five-coordinated isomer, the U–S distance is 3.13 Å, the U– O_{chel} , 2.41 Å and the U– OH_2 2.52(3) Å. The average U–O distance in the first coordination sphere is 2.51(6) Å, larger than the value for the five-coordinated isomer, 2.42 Å, which is in good agreement with the experimental EXAFS distance, 2.40–2.44 Å [4].

There are two stable six-coordinated isomers of $\text{UO}_2(\text{SO}_4)_2^{2-}$, $[\text{UO}_2(\text{SO}_4\text{-chel})_2(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$ and $[\text{UO}_2(\text{SO}_4\text{-chel})(\text{SO}_4\text{-mono})(\text{OH}_2)_3]^{2-}$, cf. Fig. S1b,c. All bond distances in these isomers are significantly longer than in the corresponding five-coordinated

Table 2

Relative electronic and Gibbs free energies in kJ/mol between the different isomers of $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ computed in the CPCM solvent using both the DFT-B3PW91 and the MP2 method, in both cases using the DFT geometry with B3PW91 functional

Chemical model	N^a	DFT-B3PW91		MP2	
		ΔE	ΔG^0	ΔE	ΔG^0
$[\text{UO}_2(\text{SO}_4\text{-chelate})(\text{OH}_2)_3] \cdot (\text{H}_2\text{O})$	5	0.0	0.0	0.0	0.0
$\text{UO}_2(\text{SO}_4\text{-mono})(\text{OH}_2)_4$	5	12.3	13.0	16.3	17.0
$[\text{UO}_2(\text{SO}_4\text{-chelate})(\text{OH}_2)_4]$	6	22.2	32.4	12.0	22.2
$[\text{UO}_2(\text{SO}_4\text{-chelate})(\text{OH}_2)_3] \cdot (\text{H}_2\text{O}), \text{Na}^+$	5	0.0	– ^b	0.0	– ^b
$[\text{UO}_2(\text{SO}_4\text{-mono})(\text{OH}_2)_4], \text{Na}^+$	5	12.5	– ^b	10.3	– ^b
$[\text{UO}_2(\text{SO}_4\text{-chelate})_2(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$	6	0.0	0.0	0.0	0.0
$[\text{UO}_2(\text{SO}_4\text{-chelate})_2(\text{OH}_2)]^{2-} \cdot (\text{H}_2\text{O})_2$	5	12.7	–9.0	26.4	4.7
$[\text{UO}_2(\text{SO}_4\text{-mono})_2(\text{OH}_2)_3]^{2-}$	5	–3.0	–3.1	17.8	17.7
$[\text{UO}_2(\text{SO}_4\text{-chelate})(\text{SO}_4\text{-mono})(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$	5	–0.3	– ^b	18.7	– ^b
$[\text{UO}_2(\text{SO}_4\text{-chelate})(\text{SO}_4\text{-mono})(\text{OH}_2)_3]^{2-}$	6	21.5	26.5	28.9	33.9

^a N is the coordination number of uranyl(VI).

^b The computation of the thermal contributions was not possible because of spurious imaginary frequencies obtained with the CPCM solvent model.

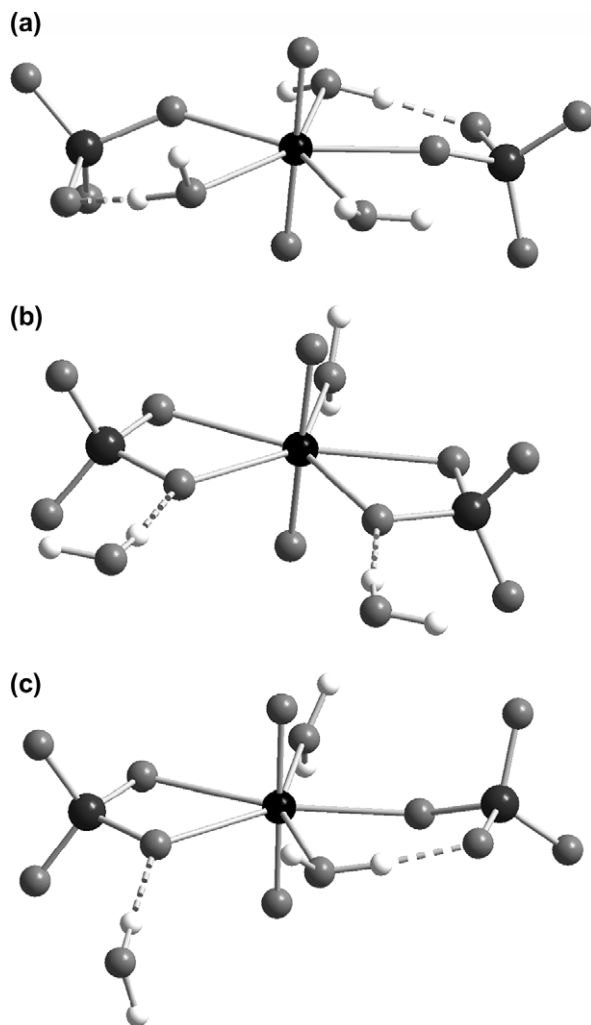
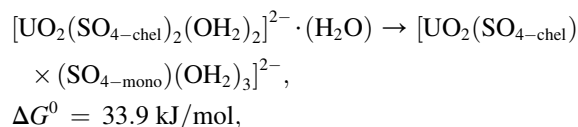


Fig. 2. The structures of the three different five-coordinated isomers of $\text{UO}_2(\text{SO}_4)_2^{2-}$: (a) $[\text{UO}_2(\text{SO}_{4\text{-mono}})_2(\text{OH}_2)_3]^{2-}$, (b) $[\text{UO}_2(\text{SO}_{4\text{-chelate}})_2(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})_2$ and (c) $[\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{SO}_{4\text{-chelate}})(\text{OH}_2)_2(\text{H}_2\text{O})_2]^{2-} \cdot (\text{H}_2\text{O})$, based on DFT geometry optimizations in the CPCM solvent. The dashed line indicates a hydrogen bond where the distances $\text{H}_{\text{water}}\text{-O}_{\text{monosulfate}}$ and $\text{H}_{\text{water}}\text{-O}_{\text{chel-sulfate}}$ are about 1.60, 1.94 Å in structures (a), (b) and (c), respectively. The angles $\text{O}_{\text{water}}\text{-H-O}_{\text{monosulfate}}$ and $\text{O}_{\text{water}}\text{-H-O}_{\text{chel-sulfate}}$ are 168° and 177° , respectively.

isomers and neither of these structures is consistent with the experimental EXAFS data. The positive Gibbs energy for reaction:

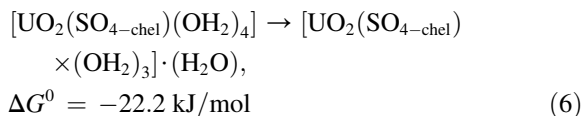


at the MP2 level, indicates that the isomer $[\text{UO}_2(\text{SO}_{4\text{-chel}})_2(\text{OH}_2)_2]^{2-} \cdot (\text{H}_2\text{O})$ is the most stable

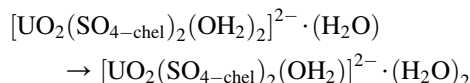
one and confirms that bidentate sulfate coordination is preferred in six-coordinated isomers.

2.4.3. The relative stability of five- and six-coordinated isomers

Five-coordination is preferred for the UO_2SO_4 isomer as indicated by the negative Gibbs energy of reaction for:



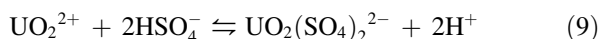
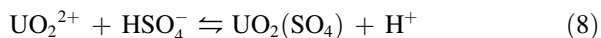
For $\text{UO}_2(\text{SO}_4)_2^{2-}$, the Gibbs energy of reaction for reaction (7), $\Delta G^0(\text{MP2}) = 4.7 \text{ kJ/mol}$, indicates that the six-coordinated isomer is more stable. However, the free-energy change is small and we can see no chemical reason why six-coordination should be preferred in $\text{UO}_2(\text{SO}_4)_2^{2-}$ when this is not the case in $\text{UO}_2(\text{SO}_4)$. In addition the EXAFS data are in better agreement with the five-coordinated model.



We have made several test of models where additional water molecules have been added to the second coordination sphere, but all of them indicate a small preference for six-coordination.

3. Discussion

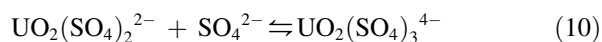
The interpretation of experimental EXAFS and LAXS data rests both on assumptions of the chemical composition of the tests solutions and on the physical models used. The chemical composition of the test solutions, that is the stoichiometric concentrations of the various species present, can be estimated from published equilibrium constants. There is extensive information in the literature on the equilibrium constants formed in the uranyl(VI) sulfate system [1] and the species $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ are well established. The formation of $\text{UO}_2(\text{SO}_4)_3^{4-}$ has been suggested by Ahrlund [24], but this proposal has not been accepted in the reviews [1a,1b]. The equilibrium constants for the complex formation reactions depend on the ionic strength and the ionic medium composition, as described in the reviews by Grenthe et al. [1a,25] and Guillaumont et al. [1b]. For the reactions:



in sulfuric acid solutions, the ionic strength/ionic medium variation of the equilibrium constant can be

described using the specific ion interaction theory (SIT) as described in the Appendix and Ref. [25]. The relationship between $\log K^0$ and the $\log K^I$, the equilibrium constants at ionic strengths zero and I , is particularly simple in test solutions where sulfuric acid is the predominant component because here $m_{\text{H}^+} \approx m_{\text{HSO}_4}$, resulting in the cancellation of interaction terms, cf. Appendix. We have used this method to re-evaluate the speciation in the EXAFS test solutions used by Moll et al. [4] and find, in agreement with them, that only a minor amount of $\text{UO}_2^{2+}(\text{aq})$ is present in their test solution A (1.00 M H_2SO_4). However, they have underestimated the amount of $\text{UO}_2(\text{SO}_4)_2^{2-}$, cf. Appendix. The sulfate concentration in test solutions B (10.0 M H_2SO_4) and C (2.00 M NaClO_4 , 0.50 M Na_2SO_4 , pH 2.00) is higher than in test solution A and accordingly the relative amount of $\text{UO}_2(\text{SO}_4)_2^{2-}$ is higher, as suggested by Moll et al. The SIT expression is not accurate in test solutions with ionic strengths larger than 3–4*m*. It is also difficult to use in uranyl sulfate test solutions that contain other ionic species in high concentrations because of the many ionic interactions that have to be taken into account. The total concentration of uranium in the test solutions used by Neufeind et al. [5] is so high that the SIT method is inaccurate. However, from the total concentrations of uranium and sulfate in their test solutions, it seems quite clear that the predominant complex is $\text{UO}_2(\text{SO}_4)(\text{aq})$.

The most straightforward experimental method to determine if sulfate is coordinated through one or two oxygen donors is to determine the U–S distance and this method has been used both by Moll et al. [4] and Neufeind et al. [5]. Moll et al. find a U–S distance of 3.12 Å in test solutions A, B, and C, indicating that the sulfate is bidentate coordinated in all sulfate complexes present. The number of U–S distances in test solution C is close to 2, confirming the predominance of $\text{UO}_2(\text{SO}_4)_2^{2-}$. Ahrland [24] has suggested that the complex $\text{UO}_2(\text{SO}_4)_3^{4-}$ is formed at high sulfate concentrations:



As the stepwise equilibrium constant for the reaction (9) is small, $K(9) \approx 6 \text{ M}^{-1}$, it seems unlikely that a third sulfate ligand forms a chelate; if this complex is formed one would expect to see a second U–S distance for monodentate coordination at about 3.7 Å. There is no such evidence and we conclude that complexes with a maximum of two chelating sulfate groups are formed in the test solutions in accordance with the evaluation made by Grenthe et al. [1a].

Neufeind et al. [5] used LAXS data from two test solutions containing the same concentration of uranyl(VI), the first without and the second with sulfate present. In this way they could to a large extent eliminate the contributions of the solvent in the difference radial distribution functions, allowing a clear identification of the U–S distance and the difference in the average U–O distances in the two complexes. They find a U–S distance of 3.67 Å, in excellent agreement with the QM value, 3.64 Å, for a complex with monodentate sulfate coordination. In both studies [4,5] there is no evidence of a mixture of mono- and bidentate coordination; however, the experimental method is not sensitive enough to detect small amounts of the two isomers.

In the EXAFS study of Moll et al. [4], only one U–O_{eq} distance, 2.42 (2) Å, was found for test solutions A, B and C; O_{eq} denotes the oxygen atoms in the equatorial plane of the uranyl sulfate complex(es). This distance is equal to the average U–O_{eq} distance, 2.42 Å in the five-coordinated complexes obtained using QM, but significantly shorter than the corresponding average distance, 2.51 Å, computed for the six-coordinated complexes. The average U–OH₂ distance in the five-coordinated complexes, 2.46 Å, is somewhat longer than in aqua ion $\text{UO}_2(\text{OH}_2)_5^{2+}$, 2.43 Å, obtained in this study using the B3PW91 functional and 2.41 Å, obtained from the experimental EXAFS data [23].

The average difference between the U–O distances in the equatorial plane of $\text{UO}_2^{2+}(\text{aq}) \equiv \text{UO}_2(\text{OH}_2)_5^{2+}$ and in the sulfate test solutions used by Neufeind et al. [5] is 0.017 Å. This value is very close to the difference between the average U–O distances in $[\text{UO}_2(\text{OH}_2)_5]^{2+} \cdot (\text{H}_2\text{O})$ and $[\text{UO}_2(\text{SO}_4)(\text{H}_2\text{O})_4] \cdot (\text{H}_2\text{O})$, 0.008 Å, obtained using the QM optimized structures in the PCM solvent (see Table 1) where systematic errors in the distances will cancel to a large extent. It is not clear to us if the difference method used by Neufeind et al. is precise enough to identify individual variations in the bond distances, in particular the appearance of one shorter U–O distance in the presence of four longer ones in the uranyl(VI) sulfate solution. The quantum chemical results show a significantly shorter U–O distance, 2.22 Å, in the monodentate sulfate isomer than in the chelate, 2.37 Å, for $\text{UO}_2(\text{SO}_4)$. The trend is the same in the various isomers of $\text{UO}_2(\text{SO}_4)_2^{2-}$ and we find it unlikely that this difference is a computational artifact. In this context it is worth noticing that the U–O_{mono} distance is significantly shorter, about 0.15 Å, than the U–O_{chel} distance in $\text{KNa}_5(\text{UO}_2)(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ [3a] and in $\text{K}_4(\text{UO}_2)(\text{SO}_4)_3$ [3b], which contain both mono- and bidentate coordination.

Both the average $U-O_{eq}$ distances and the Gibbs energy of reaction suggest that the uranyl(VI) moiety has five donor atoms in the equatorial plane; this is consistent with the fact that there are no known crystal structures in the uranyl(VI) sulfate system with six-coordination [26].

The $U-O_{sulfate}-S$ angle is 141.5° and 143° in $[UO_2(SO_4\text{-mono})(OH_2)_4]$ and $[UO_2(SO_4\text{-mono})_2(OH_2)_3]$, respectively. These values agree with that obtained by Neufeind et al. [5], and is in the range of the values, 139° to 146° , with a grand average of 143° , found in crystal structures. Neufeind et al. [5] suggested that the bent angle might be either an intrinsic property of uranyl–sulfate bonding, or due to hydrogen bond interactions. A screening of structure of crystals with unidentate sulfate and transition metal ions or alkali ions indicate that the $M-O-S$ angle is always bent, around 130° or slightly larger; this property does not seem to be specific for the bonding to uranium. To rationalize this observation, we have probed the interaction between the uranyl unit and a unidentate sulfate group through the energy decomposition scheme [7] in ADF [8,9] (see Section 2.1) to determine whether the angular preference is driven by electronic or steric effects. The total bonding energy (E_B) between the two fragments (the uranyl moiety and the sulfate group) was calculated for various bending angles ranging from 120° to 180° with steps of 10° . It is decomposed into a steric component (sum of the electrostatic and Pauli terms) and an electronic component (so-called orbital interaction). Fig. 3 shows the variation of the various contributions with the $U-O-S$ angle. To facilitate the

comparison, we have assigned the binding energy 0 kJ/mol at 180° to each of the contributions and calculated the energy at other angles relative to that reference. From the shape of the curve of the orbital interaction (electronic) component, it is clear that there is an electronic preference for linearity. However, steric interactions favor the bent structure, because the classical electrostatic interaction offsets the unfavorable Pauli repulsion upon bending. A plot of the total interaction energy indicates that there is an energy minimum around 125° and that the energy gain upon bending is about 16 kJ/mol. The bond angle is smaller than observed experimentally, but this might very well be due to the fact that the calculations were made using a model without water in the first coordination sphere. The key point is that the “driving force” for a bent $U-O-S$ angle is the steric interaction energy, which overcomes the electronic preference for a linear $U-O-S$ angle. Such steric interactions are most likely also important for the coordination of monodentate sulfate in other metal complexes and thus provide a rationalization for the general observation of bent $M-O-S$ bonds.

It is very clear from the experimental observations that the composition of the test solutions, (total concentration of uranium, ionic strength, and ionic medium) results in different modes of coordination of sulfate. This indicates that the difference in Gibbs energy between the two isomers is small, as also found in the quantum chemical calculation (Table 2) that refers to reactions (4)–(6). These reactions involve a transfer of water from the first to the second

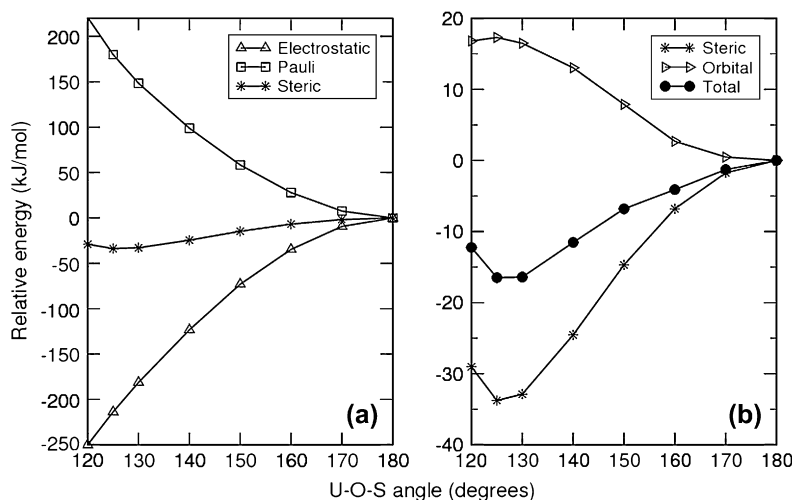


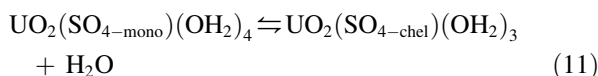
Fig. 3. Contributions to the total bonding energy of $UO_2(SO_4\text{-mono})$ for different $U-O-S$ angles: (a) the steric contribution is the sum of the electrostatic interaction and Pauli repulsion; (b) the total bonding energy is the sum of the steric contributions and orbital interaction and has a minimum around 125° .

Table 3

Ratio between the concentrations $[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_3]/[\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{OH}_2)_4]$ at different values of the Gibbs energy of reaction

ΔG^0 (kJ/mol)	$[\text{UO}_2(\text{SO}_{4\text{-chel}})(\text{OH}_2)_3]/[\text{UO}_2(\text{SO}_{4\text{-mono}})(\text{OH}_2)_4]$
-5.0	7.5
0	1.00
+5.0	0.133

coordination sphere of U(VI), while in the test solutions the reactions describe the transfer of water from the first coordination sphere to the bulk solvent, as exemplified by:



Reaction (11) shows that the relative stability of the mono- and bidentate isomers depends on the water activity, where a low water activity will favor the chelate. As the water activity decreases with increasing ionic strength and temperature, it seems possible to test this by performing LAXS and EXAFS studies at higher temperatures. A very small change in Gibbs energy of reaction for reaction (11) will result in a substantial change in the relative amounts of the two isomers, as shown in Table 3. With the approximations used in the chemical and quantum chemical models, it seems difficult to claim a higher accuracy than 10 kJ/mol in the Gibbs energy and this uncertainty range spans the range of ΔG^0 values in Table 3, for which there is a substantial change in the relative amounts of the isomers.

4. Conclusions

Standard solution chemical methods give information on the stoichiometry of the complexes with respect to the reactants, in this case UO_2^{2+} and SO_4^{2-} , but not on the mode of coordination of the ligand and the number of coordinated water ligands. Structure chemical methods such as EXAFS provide this information, but the structure models are not always unique. In addition, EXAFS methods require information on the speciation, i.e. the concentration of the different species in the test solutions used. In systems where several different complexes occur in comparable concentrations, it is very difficult to deduce structure information. Quantum chemistry provides tools to obtain both the geometry and relative energy of different complexes and this information, combined with experimental solution chemical and EXAFS data, makes it possible to obtain

a better understanding of the chemistry of aqueous complex formation than using the experimental or theoretical methods alone. In the present system we conclude that there are several possible isomers of the complexes $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ that have very near the same energy. These isomers consist both of species where the sulfate ligand is coordinated in bi- and monodentate fashion. However, the number of donor atoms in the equatorial plane of the UO_2 moiety is five in all isomers, as supported both by experimental and calculated average bond distances and the relative energy of isomers with the same mode of coordination of sulfate, but a different number of coordinated water ligands. The relative stability of the different isomers is small and the mode of coordination of the sulfate ligand seems therefore to be dependent on the water activity, as also noted experimentally.

Acknowledgments

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Appendix

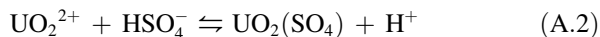
The experimental EXAFS and LAXS investigations have been made in test solutions that contain $\text{UO}_2^{2+}(\text{aq})$, $\text{UO}_2(\text{SO}_4)(\text{aq})$ and $\text{UO}_2(\text{SO}_4)_2^{2-}(\text{aq})$, and it is important to know these concentrations for the analysis of the experimental data. Such calculations are based on the known total concentrations of the components and known equilibrium constants for the formation of the two sulfate complexes. The latter are tabulated in data bases [1] and usually refer to standard state conditions; they have therefore to be recalculated to the actual ionic medium of the test solutions. We have reanalyzed the composition of the test solutions described by Moll et al. [4] using the specific ion interaction theory (SIT), as described in the example given below. The theoretical basis for the SIT is described in Refs. [1,25].

The activity coefficient of an ion, i , is described by Eq. (A.1):

$$\log \gamma_i = -\frac{AZ_i^2 I^{1/2}}{1 + 1.5 I^{1/2}} + \sum_j \varepsilon_\gamma(i, j) m_j \quad (\text{A.1})$$

where Z_i is the charge of ion, I the ionic strength and A the Debye–Hückel parameter ($A = 0.5100 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ at 25 °C). $\varepsilon(i, j)$ is the specific ion interaction parameter between the ions i and j and m_j the molality of the ion j . If i is a cation, the summation involves all anions, j , present in solution, and the reverse if i is an anion. Note that the summation includes all pair ion interactions. The SIT model ignores both binary interactions between species of the same charge, and the contribution of ternary interactions to the activity coefficients.

The activity correction is particularly simple in sulfuric acid solutions, as shown by the following example for the reactions:



$$\log \gamma(\text{UO}_2^{2+}) = -4D + \varepsilon(\text{UO}_2^{2+}, \text{HSO}_4^-) m_{\text{HSO}_4} \quad (\text{A.3})$$

$$\log \gamma(\text{HSO}_4^-) = -D + \varepsilon(\text{HSO}_4^-, \text{UO}_2^{2+}) m_{\text{UO}_2^{2+}} + \varepsilon(\text{HSO}_4^-, \text{H}^+) m_{\text{H}^+} \quad (\text{A.4})$$

$$\log \gamma(\text{H}^+) = -D + \varepsilon(\text{H}^+, \text{HSO}_4^-) m_{\text{HSO}_4} \quad (\text{A.5})$$

The relationship between the standard state equilibrium constant at zero ionic strength, K^0 , and in m molal H_2SO_4 , $K^{(m)}$ is then:

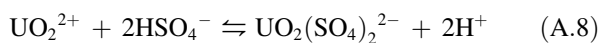
$$\begin{aligned} \log K^0(\text{A.2}) = \log K^{(m)} + 4D + \varepsilon(\text{H}^+, \text{HSO}_4^-) m_{\text{HSO}_4} \\ - \varepsilon(\text{HSO}_4^-, \text{UO}_2^{2+}) m_{\text{UO}_2^{2+}} \\ - \varepsilon(\text{HSO}_4^-, \text{H}^+) m_{\text{H}^+} \\ - \varepsilon(\text{UO}_2^{2+}, \text{HSO}_4^-) m_{\text{HSO}_4} \end{aligned} \quad (\text{A.6})$$

D is the Debye–Hückel term $A\sqrt{I}/(1 + 1.5\sqrt{I})$; in pure sulfuric acid $m_{\text{H}^+} = m_{\text{HSO}_4^-}$. As the concentration $[\text{UO}_2^{2+}]$ is often much smaller than $[\text{HSO}_4^-]$, the term $\varepsilon(\text{HSO}_4^-, \text{UO}_2^{2+}) m_{\text{UO}_2^{2+}}$ can be neglected and Eq. (A.6) is then:

$$\log K^0(\text{A.2}) = \log K^{(m)} + 4D - \varepsilon(\text{UO}_2^{2+}, \text{HSO}_4^-) m_{\text{HSO}_4} \quad (\text{A.7})$$

The interaction coefficient $\varepsilon(\text{HSO}_4^-, \text{UO}_2^{2+})$ has been estimated to be 0.35 ± 0.11 based on the experimental interaction coefficients $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$ and $\varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-)$.

The equilibrium constant for the reaction:



is obtained in the same way:

$$\begin{aligned} \log K^0(\text{A.8}) = \log K^{(m)} + \varepsilon(\text{UO}_2^{2+}(\text{SO}_4)_2^{2-}, \text{H}^+) m_{\text{H}^+} \\ + 2\varepsilon(\text{H}^+, \text{HSO}_4^-) m_{\text{HSO}_4} \\ - 2\varepsilon(\text{HSO}_4^-, \text{H}^+) m_{\text{H}^+} \\ - \varepsilon(\text{UO}_2^{2+}, \text{HSO}_4^-) m_{\text{HSO}_4^-} \end{aligned}$$

The specific ion interaction parameters used are taken from Ref. [1b] and are listed in Table A.1.

Using the equilibrium constants at zero ionic strength from Ref. [1] ($\log K^0(\text{A.2}) = 1.17$ and $\log K^0(\text{A.8}) = 0.18$) and the interaction coefficients from Table A.1, we obtain the following equilibrium constants valid in 1.0 M H_2SO_4 : $\log K(\text{A.2}) = 0.71$ and $\log K(\text{A.8}) = 0.56$; the uncertainty in these quantities is at least 0.10 log units. The composition of test solution A in the paper by Moll et al. [4] is then $[\text{UO}_2^{2+}(\text{aq})] = 5.6 \pm 1.4 \text{ mM}$, $[\text{UO}_2(\text{SO}_4)(\text{aq})] = 26.5 \pm 0.2 \text{ mM}$ and $[\text{UO}_2(\text{SO}_4)_2^{2-}] = 17.8 \pm 1.7 \text{ mM}$; the uncertainty ranges have been estimated using the uncertainty in the equilibrium constants. In their calculation of the composition of test solution A, Moll et al. do not seem to have taken the formation of

Table A.1
Specific ion interaction coefficients [1b] for the estimate of activity coefficients in the uranyl(VI)– H^+ – SO_4^{2-} system

Ion interaction coefficient	$E(i, j)$ (kg mol ⁻¹)	Comments
$\varepsilon(\text{UO}_2^{2+}, \text{HSO}_4^-)$	0.35 ± 0.11	The interaction coefficient is estimated from the known values $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46$ and $\varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = 0.24$.
$\varepsilon(\text{HSO}_4^-, \text{H}^+)$	0.15	The interaction coefficient is estimated from the known value $\varepsilon(\text{HSO}_4^-, \text{Li}^+) = 0.15$.
$\varepsilon(\text{H}^+, \text{HSO}_4^-)$	0.15	$\varepsilon(\text{HSO}_4^-, \text{H}^+) \equiv \varepsilon(\text{H}^+, \text{HSO}_4^-)$
$\varepsilon(\text{UO}_2(\text{SO}_4)_2^{2-}, \text{H}^+) \approx \varepsilon(\text{UO}_2(\text{SO}_4)_2^{2-}, \text{Li}^+)$	-0.02 ± 0.06	The interaction coefficient is estimated by increasing the known value $\varepsilon(\text{UO}_2(\text{SO}_4)_2^{2-}, \text{Na}^+) = -0.12 \pm 0.06$ by 0.10, the difference found between Li^+ and Na^+ .

For details about the comments, see Ref. [1b], Table B-5, pp. 731–733.

$\text{UO}_2(\text{SO}_4)_2^{2-}$ into account. It seems clear that the predominant complex in the test solution is $\text{UO}_2(\text{SO}_4)(\text{aq})$, but with a significant amount of $\text{UO}_2(\text{SO}_4)_2^{2-}$. It is not possible to make an accurate estimate of the speciation in test solution B because of the high ionic strength in 10 M H_2SO_4 ; however, as a result of the higher total concentration of HSO_4^- , it seems clear that the predominant complex is $\text{UO}_2(\text{SO}_4)_2^{2-}$. It is not possible to make an accurate analysis of the speciation in test solution C using the SIT, as the test solution contains large amounts of both ClO_4^- and HSO_4^- and has a high ionic strength. To conclude: the reanalysis of the test solutions used in the EXAFS measurements of Moll et al.[4] are only to a minor degree affected by the presence of $\text{UO}_2^{2+}(\text{aq})$, and the predominant complexes are $\text{UO}_2(\text{SO}_4)(\text{aq})$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.crci.2007.03.004](https://doi.org/10.1016/j.crci.2007.03.004).

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