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REGULAR ARTICLE

Interaction of uranyl ion with few molecules of water: thought (computational) scenarios with hydrogen bonding motif

One short Festschrift story

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Abstract The interaction of the uranyl ion UO_2^{2+} with one, two and three molecules of water is computationally modeled. It is demonstrated that the dihydration potential energy surface of UO_2^{2+} is partitioned into two bonding regions which correspondingly determine the weak and strong regime of solvation: if the former describes the traditional filling of the first solvation shell, the latter develops, via the hydrogen bonding interaction, to the metastable complex $[UO_2(OH)]^+ - H_3O^+$ with a rather short lifetime. An addition of water molecule from infinity to its H_3O^+ side results in the formation of the Zundel cation and spontaneous dissociation into the latter and $[UO_2(OH)]^+$.

Keywords Uranyl ion · Water · Hydrogen bonding · Hydration · Hydrolysis · H_3O^+ · Zundel ion $H_5O_2^+$

Dedicated to Nino Russo on the occasion of his 60th birthday.

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> "… we are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation."
>
> Joseph Louis Gay-Lussac
> Memoires de la Sociétè d'Arcueil 2, 207 (1808)[1]

0 Exordium: Festschrift thoughts

It is pretty obvious that writing on the special occasion is a fair work allowing to explore rather curious, even bizarre ideas, thoughts, including the 'Gedanken' quantum chemical computational experiments, and concepts which partly endow some paradigm shifts and which might not be so fully appropriate for the standard mode of a scientific paper, though perfectly suitable for the Festschrift one.

Aiming to write this particular story, we have not only intended to take full advantage of the aforementioned authors' freedom that any Festschrift certainly offers, rather to address the topic that we have been thinking for the last 2–3 years to some degree or other, though, looking deeper, in retrospective, even associatively, these thoughts are likely rooted to the Chernobyl disaster, and that, quite surprisingly to us, has become one of the hot topics of Nino Russo's current activity [1,2]. Since the protagonist of our story is the uranyl U(VI) ion, UO_2^{2+}, or the uranium dioxo cation, we do believe that Nino Russo, whose 60th birthday this Festschrift is honorably dedicated to, will not be so displeased with our contribution. Having this apology, we embark on exposing our thoughts about the extremely simple and quite mysterious interaction between molecules of water and UO_2^{2+} that

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[1] From Boorse HA, Motz L (eds) (1966) The world of the atom, vol 1. Basic Books, New York (translation: Alembic Club Reprint No. 4).

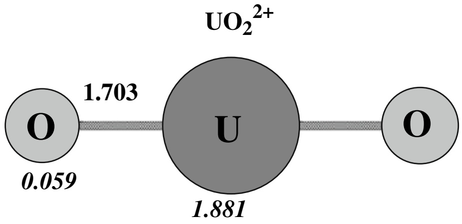

Fig. 1 The uranium ion UO_2^{2+}. The U–O bond is given in Å. The early computational data: R(U–O) = 1.701 – 1.703 Å [16] and 1.688 Å [17]. Mulliken charges are indicated in *italic*

paradoxically continues, since the 1840s' studies of its optical properties [3,4], to unveil novel, rather perplexed features of its ubiquitous nature and reactivity which still wonder the scientists [5–9] and that is of primary importance and of sustained interest for the development of novel waste reprocessing technologies and speciation of radioactive metals in the environment [10–15].

1 Uranyl ion and its hydration

Our focus is precisely on the subtle features of the potential energy surface (PES) of the multiple-stage hydration of UO_2^{2+} which, on the one hand, are straightforwardly related to its intrinsic tendency to accept neutral ligands such as H_2O in the gas phase and which, on the other, underlie two different patterns of hydration (or, speaking generally, solvation), either the direct hydration or the hydrolysis, and govern the dynamics of hydrated water molecules. First, however, what is the uranyl ion?

1.1 Uranyl ion

The uranyl ion, UO_2^{2+}, is a linear triatomic molecule which in its closed-shell ground state $^1\Sigma_g^+$ structurally coordinates, according to Fig. 1, the oxygen ligands to the U atom in the equatorial plane. Its U–O equatorial bond of 1.703 Å long is rather strong (see e.g. the recent works [16,17] and references therein). The symmetric and asymmetric U–O stretches, ν_{sym} (U–O) and ν_{asym} (U–O), of the UO_2^{2+} moiety in aqueous solution are observed at 870 and 962 cm^{-1}, respectively [18]. Note also that the computational level which is invoked in the present work and outlined in Appendix predicts correspondingly 994 and 1,090 cm^{-1} for the harmonic modes ν_{sym} (U–O) and ν_{asym} (U–O) of the isolated uranyl ion in the gas phase[2]. The positive charge is largely localized on U, as indicated by its Mulliken charge q_M (U) equal to 1.88 |e|.

According to its molecular orbital bonding picture [19–21], the ground-state UO_2^{2+} accommodates 12 valence electrons and, generally speaking, behaves as a strong Lewis acid, thus accepting lone-pair electrons from ligands. This particularly determines the bonding patterns of UO_2^{2+} with water molecules that results in that, as well known, the uranyl ion features a high solubility in water and a strong tendency to hydrolyze in aqueous solution, yielding protons and forming uranyl hydroxides [6]. To proceed with performing the 'Gedanken' quantum chemical computational experiments on the interaction of UO_2^{2+} with few water molecules, let us first briefly outline the working concept of solvation.

1.2 Working concept of solvation: general remarks

Since Mendeleyev's work [22,23] on solutions as balanced chemical systems composed of solvent, solute, and the products of their total solvent–solute interaction or solvation that instantly takes place when a solute molecule is immersed into a solvent, the concept of solvation has been gradually changed and currently admits a variety of possible interpretations [24–29]. On the one side, the solvation usually refers to the class of the solvent–solute interactions that are not strong enough (a so-called 'weak regime') and hold the solute largely intact, as though partly and separately reorganized to minimize these interactions. Within this regime, the solute establishes contacts with a surrounding solvent through one or more solvent molecules which form a first solvation (coordination) shell via van der Waals, hydrogen bonding, or covalent bonding interactions, or via charge transfer. The weak-regime solvation patterns are developed via the 'external' scenarios [30,31] that usually cast in neutral solutions.

On the other side, the solvation is viewed as involving the chemical reactions of dynamical solvent–solute clustering (a so-called 'strong regime') that may occur on the PES of the solvent–solute interactions and may cause a solute–solute, solute–solvent and solvent–solvent re-bonding and re-structuring. The corresponding solvation patterns are mostly developed via the 'internal' scenarios. A strong solvation regime may eventually lead to the product clusters which no longer hold the identity of solute ('solvolysis'). This regime of solvation particularly appears with such solutes that are sufficiently strong to enhance the structure of solvent ('bond or structure maker', or 'kosmotrope') or, on the contrary, to weaken it ('bond or structure breaker', or 'chaotrope') [24–29,32–36].

In a broad meaning, the general picture of solvation is based on a variety of the reaction scenarios emerging from the entire PES of the solvent–solute interactions and varying between the aforementioned two extreme regimes of weak and strong interactions: either yielding a well-defined 'external' solvation patterns or developing via a 'restructive–destructive' scenarios partly including the 'internal' ones.

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[2] The comparison of the experimental and computational ν_{sym} (U–O) and ν_{asym} (U–O) of the UO_2^{2+} are thoroughly discussed by Gutowski and Dixon (p. 8844 of [16]).

The 'restructive-destructive' scenarios make illusive a partition of the total solution system into solvent and solute, that is, in the other words, the total system behaves as a whole entity—this is a so-called solvent–solute entanglement.

How to quantify the solvation phenomenon in micro-dimensions? It seems that a natural way is to choose some physically measurable quantities, related in particular to the structural, energetic, and spectroscopic properties of the solvent–solute system, and to quantify the solvation in terms of the complete list of changes in these quantities that occur under their composition with respect those measured on infinitely separated solvent and solute. These are precisely the changes that are caused by the solvent–solute intermolecular interactions. Quite often, this list of changes is interpreted as the definition of the solvation [28]. It is intuitively clear that such definition does not entirely reflect the many-body interaction and multi-product nature of the solvation phenomenon, particularly those its subtle features as the reaction routes whose appearances strongly depend on the external conditions and the energetic landscape of the saddle structures. If there are few reaction scenarios developed on the PES of the solvent–solute interactions that lead to different products, the solute–solvent system is definitely the ensemble of products, and therefore, any measurement on this ensemble hides the changes in solvent and solute along any reaction route. True, this definition is rather based on the list of the observable differences between the reactants (solvent and solute) and a single product.

1.3 Hydration of uranyl ion: experimental and computational facts

The following scenarios underlie the general picture [6,9,37–41] of the solvent–solute interaction of UO_2^{2+} with molecules of water that result, depending on the pH, in ligands of either water or hydroxide on the solvation or hydration PES:

$$\begin{array}{l} UO_2^{2+}+H_2O \equiv \\ UO_2^{2+}+H_2O \equiv \end{array}\left\{\begin{array}{ll}[UO_2(H_2O)]^{2+} & (1a)\\ {[UO_2(OH)]^{+}+H^{+}} & (1b)\end{array}\right.$$

$$\begin{array}{l} [UO_2(H_2O)]^{2+}+H_2O \equiv \\ {[UO_2(H_2O)]^{2+}+H_2O \equiv} \end{array}\left\{\begin{array}{ll}[UO_2(H_2O)_2]^{2+} & (2a)\\ {[UO_2(OH)(H_2O)]^{+}+H^{+}} & (2b)\end{array}\right.$$

$$[UO_2(OH)]^{+}+H_2O \equiv UO_2(OH)_2+H^{+} \tag{3}$$

and so on. The question that is really puzzling is not about how these PESs bestow two absolutely different scenarios, rather how and under which conditions, one of them is selected and operates, and the other is substantially undermined?

Reactions 1a and 2a simply represent the reactions of the mono- and dihydration of UO_2^{2+} which are correspondingly displayed in Figs. 2 and 3. In general, such reaction scenarios describe a weak solvation regime and lead to that water molecules coordinate to UO_2^{2+} to form the first, second, and higher coordination or hydration shells. What is now widely understood and accepted is that the first coordination shell is represented by the fivefold uranyl $[UO_2(H_2O)_5]^{2+}$ where the uranyl ion is preferentially surrounded by five water molecules which are arranged in a pentagonal geometry within the plane which is perpendicular to UO_2^{2+} [7,16,41–54].

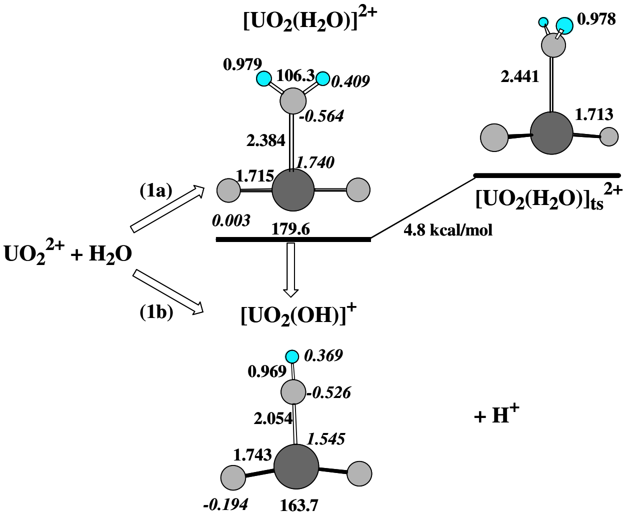


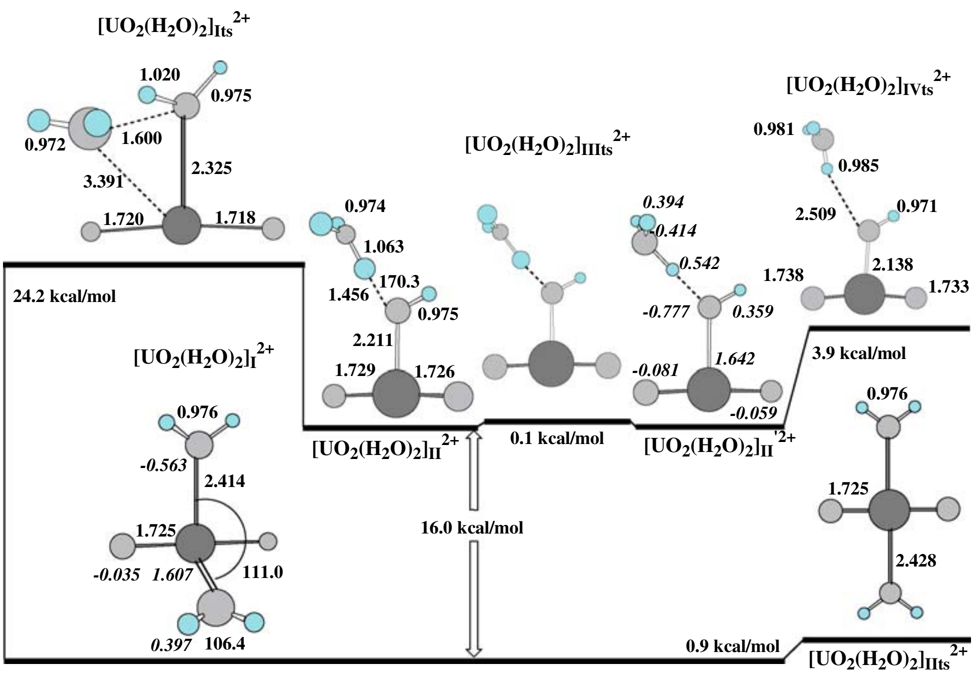
Fig. 2 The monohydration PES of UO_2^{2+}. Selected bond lengths are given in Å and bond angles in degrees. The early computational data: R(U–O) = 1.708 Å and $R(\mathrm{U{-}O_w})$ = 2.351 Å [17]. Mulliken charges are indicated in *italic*

Reactions 1b and 3 are the reactions of the hydrolysis which, respectively, take place on the same PESs as the reactions 1a and 2a (see Figs. 2 and 3) and which correspond to the strong solvation regime. Generally speaking, the hydrolysis of the uranyl ion is represented as [6,9]:

$$mUO_2^{2+}+nH_2O \equiv [(UO_2)_m(OH)_n]^{(2m-n)+}+nH^{+} \tag{4}$$

where m and n are the relative ratios (stoichiometric coefficients) of uranyl and water molecules involved in reaction 4. The limiting complex for the hydrolysis scenarios is $[UO_2(OH)_5]^{3-}$. The reactions of type 2b are mixtures of the reactions of hydration and hydrolysis. As an example, the reaction path 2b yields the formation of the monohydrate $[UO_2(OH)(H_2O)]^{+}$ that occurs in terms of the donation of electron density by the strongly basic OH^- to the uranyl metal and the reduction of Lewis acidity of U [48,55]. Reacting with water, this monohydrate forms dihydrate and trihydrate. The rates for formation of the dihydrate $[UO_2(OH)(H_2O)_2]^{+}$ is nearly three times faster than the formation of the monohydrate [48]. Since, as believed, the hydroxide complexes are in general formed by dissociation of a proton from coordinated water [41], the precursor of $[UO_2(OH)_5]^{3-}$ must be $[UO_2(OH)_4(H_2O)]^{2-}$. A mixture of water and hydroxide

Fig. 3 The dihydration PES of UO_2^{2+}. Selected bond lengths are given in Å and bond angles in degrees. ν_{sym} (U–O) and ν_{asym} (U–O) of $[UO_2(H_2O)_2]_I^{2+}$ are equal to 954 and 1,045 cm^{-1}. Mulliken charges are indicated in *italic*



ligands are coordinated to UO_2^{2+} in neutral solution [56], and four or five hydroxide ligands in highly alkaline solutions [57,58].

Summarizing, we conclude that absolutely different scenarios, either describing the weak or strong regimes, may occur on the solvation PES of the solvent–solute interaction of UO_2^{2+} with molecules of water. This looks quite disappointed since it is not quite clear which one(s) would be preferential, even in the gas phase, and whether it would be possible to classify them. This viewpoint was not previously fully addressed, though it was considered as a quite substantial problem. We partly address it in the present work that actually aims to pursue a thorough study of the microsolvation PESs of $[UO_2(H_2O)_{1\leq n\leq 3}]^{2+}$ and to unveil those their features which are related, on the one hand, to the reaction scenarios with a hydrogen bonding motif and, on the other, which are directly linked to the dynamical aspects of the first-shell solvation and inter-shell water exchange.

2 Hydrogen bonding reaction scenarios on PESs of $[UO_2(H_2O)_{1\leq n\leq 3}]^{2+}$

According to the reaction scenarios (1a) and (1b), the simplest uranyl–water interaction results either in the formation of the monohydrate $[UO_2(H_2O)]^{2+}$, characterized by the energy and enthalpy of formation $\Delta E_f\{[UO_2(H_2O)]^{2+}\} = -64.3(-61.9)$ kcal mol^{-1} and $\Delta H_f\{[UO_2(H_2O)]^{2+}\} = -62.9$ kcal mol^{-1} with respect to (wrt) the asymptote $UO_2^{2+} + H_2O$, or in the formation of the complex $[UO_2(OH)]^{+}$, which is characterized by $\Delta E_f = -378.2(-375.8)$ kcal mol^{-1} and $\Delta H_f = -376.8$ kcal mol^{-1} wrt the asymptote $UO_2^{2+} + OH^-$. Notice that the difference in energy between the asymptotes $UO_2^{2+} + H_2O$ and $UO_2^{2+} + OH^- + H^+$ (that is actually between H_2O and $OH^- + H^+$) amounts to circa 396.0 (388.1) kcal mol^{-1}. Both reaction scenarios (1a) and (1b) evidently involve the complex $[UO_2(H_2O)]^{2+}$ shown in Fig. 2: if for the former, it is the final product of reaction, for the latter it is the intermediate.

$[UO_2(H_2O)]^{2+}$ is originated from a new U–O$_w$ bond that arises between the uranyl ion and water molecule. Its formation, first, slightly lengthens the U–O bonds of the former molecule by ∼0.01 Å and correspondingly red-shifts its symmetric and asymmetric U–O stretches by 21 and 24 cm^{-1} and, second, induces a redistribution of the electronic charge therein so that the positive charge initially localized on U is partly transferred to the hydrogen atoms of water molecule. Also, there takes place a weakening of the O$_w$–H bonds of water and this is particularly manifested by their elongation by ∼0.02 Å and shift of their O–H stretches by 198 and 243 cm^{-1} to lower wavenumbers.

The reaction manifold of the weak-regime scenario (1a) also includes the transition state $[UO_2(H_2O)]_{ts}^{2+}$ placed only 4.8 kcalmol^{-1} above $[UO_2(H_2O)]^{2+}$. This transition state governs the rotation of water molecule perpendicular to the $[UO_2(H_2O)]^{2+}$ plane characterized by the transition-state frequency $\nu_{TS} = 300i$ cm^{-1}. The strong-regime reaction scenario (1b) proceeds further via deprotonation of the intermediate complex $[UO_2(H_2O)]^{2+}$ (see Fig. 2) that is considerably facilitated by a weaker O$_w$–H bonding compared to that in water molecule since the deprotonation energy DPE

$\{[\mathrm{UO_2(H_2O)}]^{2+}\} = 82.1(72.9)\ \mathrm{kcal\,mol^{-1}} \ll \mathrm{DPE}\{\mathrm{H_2O}\} = 378.2(375.8)\ \mathrm{kcal\,mol^{-1}}$.

Adding another molecule of water to the reaction manifold (1a) yields the reaction pathway (2). Instead of its rather simplistic representation given by the above equation, it actually splits into two sub-pathways, both shown in Fig. 3 and separated from each other by the transition-state linker $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{Its}}$ with $\nu_{\mathrm{TS}} = 122i\ \mathrm{cm^{-1}}$. The latter in fact defines the verge that partitions the whole three-dimensional space into three bonding attractors. One of these attractors, a so-called the coordination one, is associated with a direct coordination of $\mathrm{H_2O}$ to U of $[\mathrm{UO_2(H_2O)}]^{2+}$ and a subsequent formation of the ground-state dihydrated complex $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{I}}$, that is accompanied by the energy release $\Delta E_{\mathrm{f}}\{[\mathrm{UO_2(H_2O)_2}]^{2+}_{I}\} = -56.0(-58.5)\ \mathrm{kcal\,mol^{-1}}$ and characterized by the enthalpy of formation $\Delta H_{\mathrm{f}}\{[\mathrm{UO_2(H_2O)_2}]^{2+}_{I}\} = -54.2\,\mathrm{kcal\,mol^{-1}}$. A relative smallness, by the absolute value, of $|\Delta E_{\mathrm{f}}\{[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{I}}\}|$, compared to $|\Delta E_{\mathrm{f}}\{[\mathrm{UO_2(H_2O)}]^{2+}\}|$, indicates a weaker character of the second $\mathrm{U{-}O_{w'}}$ bonding that relocates a partial positive charge to the hydrogens. Geometrically, the second water ligand w′ coordinates to U via the bonding angle $\angle \mathrm{O_wUO_{w'}} = 111.0°$. The negligible barrier of $0.9\,\mathrm{kcal\,mol^{-1}}$, formed by the planar transition state $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{IIts}}$ and characterized by $\nu_{\mathrm{TS}} = 19i\ \mathrm{cm^{-1}}$, is thus easy to access at moderate temperatures, and that is why it more likely smears out this coordination bonding angle.

The existence of the novel transition state $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{Its}}$ as placed $24.2\,\mathrm{kcal\,mol^{-1}}$ (without ZPVE) above $[\mathrm{UO_2(H_2O)_2}]^{2+}_{I}$ significantly modifies the present picture of the solvation patterns of the uranyl ion and its dynamics, and originates the two equivalent hydrogen bonding attractors, contiguous to the coordination one. Building a solution by adding a solvent molecule at a time [59], the latter can approach $[\mathrm{UO_2(H_2O)}]^{2+}$ from infinity by means of two different routes: either via a direct coordination route to the uranyl moiety which passes through the coordination attractor or via a direct hydrogen bonding route to the water moiety which passes through one of two hydrogen bonding attractors. Relative to the asymptote $[\mathrm{UO_2(H_2O)}]^{2+} + \mathrm{H_2O}$, the barrier of $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{Its}}$ is seen as $31.8\,\mathrm{kcal\,mol^{-1}}$ (without ZPVE and $34.8\,\mathrm{kcal\,mol^{-1}}$ with ZPVE) high above it, meaning that two regions are sufficiently well separated and more likely are hardly penetrable into each other. This implies that there actually exist two scenarios: the one that occurs on the coordination attractor and leads to the formation of $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{I}}$ and the other that takes place on one of two hydrogen bonding attractors. These scenarios are both equivalent in a sense that there is no preference in approaching of a second molecule of water to $[\mathrm{UO_2(H_2O)}]^{2+}$ from infinity.

The second scenario develops in a quite unexpected manner. While the second water molecule $\mathrm{H_2O_{w'}}$ approaches one of the water hydrogens of $[\mathrm{UO_2(H_2O_w)}]^{2+}$ (see Fig. 3) which, as being participated in the formation of the water–water $\mathrm{O_w - H \cdots O_{w'}}$ hydrogen bonding, transfers barrierlessly, yielding the complex $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$. The latter represents itself the uranyl ion bonded to the ionic pair $\mathrm{OH^- \cdots H_3O^+}$. The difference in energy between this ionic-pair complex and $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{I}}$ amounts to $\Delta \mathrm{E_{I-II}} = 17.3(16.0)\ \mathrm{kcal\,mol^{-1}}$.

Actually, there are two nearly iso-energetic conformers of $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$, characterized either by a downward or upward bending of the $\mathrm{H_3O^+_{w'}}$ wrt the $\mathrm{UO_2^{2+}}$ moiety (see Fig. 3), which are linked to each other via the transition state $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{IIIts}}$ with the transition frequency $\nu_{\mathrm{TS}} = 295i\ \mathrm{cm^{-1}}$, that gives rise to tiny ($\sim 0.1\,\mathrm{kcal\,mol^{-1}}$; without ZPVE) and hence absolutely transparent barrier. A remarkable feature of $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$ is that its oxygen atom $\mathrm{O_{w'}}$ is distanced from $\mathrm{O_w}$ by 4.484 Å, that approximately corresponds to the position of the second coordination shell of the uranyl ion (see e.g. [16,50] and references therein). This particularly implies that the transition state $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{Its}}$, which is identified in the present work for the first time, can be interpreted as governing the exchange of water molecule(s) between the first and second solvation shells.

It is, however, not a last surprise at all that brings us the ionic-pair conformer $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$ which, first, partly resembles the strong-regime hydrolysis scenario (1b) and operates, within the present picture, with the hydroxonium ion $\mathrm{H_3O^+}$ rather than with a simple 'naked' proton $\mathrm{H^+}$. Actually, lying below the asymptote $[\mathrm{UO_2(OH)}]^{+} + \mathrm{H_3O^+}$ by 50.3 (51.4) $\mathrm{kcal\,mol^{-1}}$, $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$ gains its relative stability due to the existence of a rather facile transition state $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{IVts}}$ with the barrier height of $3.9\,\mathrm{kcal\,mol^{-1}}$ (without ZPVE and $4.0\,\mathrm{kcal\,mol^{-1}}$ with) and with $\nu_{\mathrm{TS}} = 100i\ \mathrm{cm^{-1}}$ which, however, does not confer $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$ a substantial lifetime. For this reason, the latter finally dissociates due to the Coulomb explosion. Second, the formation of the hydroxide complex $[\mathrm{UO_2(OH)}]^{+}$ occurs due to the dissociation of the first-shell coordinated water to particularly this proton and its simultaneous transfer to the second-shell one (see also [41] and references therein). This charge transfer invokes the formation of the above transition-state linker $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{IVts}}$. Notice that a similar mechanism of the Coulomb explosion of some doubly hydrated metal dications has recently been discussed in the work [60].

Let us, however, suggest that the barrier generated by $[\mathrm{UO_2(H_2O)_2}]^{2+}_{\mathrm{IVts}}$ is sufficiently high to prevent $[\mathrm{UO_2(OH)^-(H_3O)^+}]^{2+}_{\mathrm{II}}$ from exploding Coulombically. Hence, the latter does exist as a metastable species. Let us further suggest that it interacts with another water molecule that approaches its hydronium from an infinity. The scenario of such thought

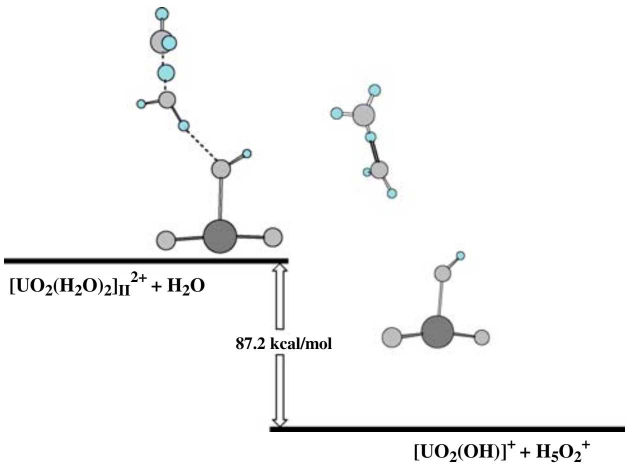


Fig. 4 The spontaneous dissociation of $[UO_2(H_2O)_2]_{II}^{2+}$ after interacting with water molecule via hydrogen bonding and forming the Zundel ion $H_5O_2^+$

(computational) experiment is portrayed in Fig. 4. According to this scenario, the interaction of the hydronium ion and water molecule leads to the formation of the ion $H_5O_2^+$, the well-known Zundel ion [61–63]. The resultant complex $[UO_2(OH)^-(H_5O_2)^+]^{2+}$ spontaneously decays due to the Coulomb explosion. Assume that the difference between the complexes $[UO_2(OH)^-(H_3O)^+]_{II}^{2+}$ and $[UO_2(OH)^-(H_5O_2)^+]^{2+}$ consists in that the Zundel ion carries a larger positive charge than H_3O^+—say +1|e| vs. +0.916|e|, in accordance to their calculated Mulliken charges,[3] since the proton affinity of water dimer exceeds that of water monomer. We therefore may speculate that the Coulomb repulsion energies of both systems are correspondingly equal to $1/R$ and $0.99/R$: a slightly smaller Coulomb repulsion energy of the complex with the Zundel ion compared to that with H_3O^+ predetermines instability of the former and its spontaneous dissociation, whereas the latter features a small barrier which partially, on small time scales, prevents it from a similar Coulomb explosion.

3 Summary

What we have shown in the present work is that the PES of solvation of the monohydrated uranyl ion, $[UO_2(H_2O)]^{2+}$, is quite rich, mostly due to the existence of the subtle hydrogen bonding attractors which encumber the traditional scenario of solvation to occur. Paraphrasing a Feynman quote, we may conclude: "Like it or not, that's the way the world is." These attractors predetermine two solvation scenarios. On the one hand, it is the strong-regime scenario that leads to the realistic hydrolysis processes ending either with the metastable ion pair $[UO_2(OH^-)]^{2+} - H_3O^+$ or with the Coulombically dissociated pair $[UO_2(OH)]^+$ and $H_5O_2^+$. It might be worth to draw some parallel with the above ion pairs and the solvent-separated ion pairs which appear under solvation of some molecules, such as HCl, HBr, etc., in small water clusters (see [64,65] and references therein). On the other, they are more likely to govern the water-exchange mechanism that takes places between the first and second solvation shells.

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Appendix: computational modus operandi

All calculations of the studied complexes reported in the present work were performed with the hybrid exchange-correlation density functional B3LYP within the Kohn–Sham density functional self-consistent field theory, using the *GAUSSIAN 03* suite of programs [66]. The basis set composed of the energy-consistent relativistic effective core potential (RECP) on U developed by Hay [67] and standard Pople basis set 6-311++G(d, p) on H and O [68] was invoked. All geometrical optimizations were carried out with the options "Tight" and "Int=UltraFine". The harmonic vibrational frequencies were also calculated in order to adequately characterize stationary points and to evaluate the unscaled zero-point vibrational energies (ZPVE) and thermodynamic quantities, such as enthalpy and entropy. The latter are estimated from the partition functions calculated at room temperature (298.15 K) under a pressure of 1 atm, using Boltzmann thermostatistics and the rigid-rotor-harmonic-oscillator approximation. The energy $\Delta E_f\{AB\}$ of formation of the complex $A \cup B$ is defined in a standard way as the energy difference $E[A \cup B] - (E[A] + E[B])$ and its ZPVE-corrected value is also reported throughout this work for the stable complexes (in parentheses).

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[3] Since the total charge of the complexes $[UO_2(OH)^-(H_3O)^+]_{II}^{2+}$ and $[UO_2(OH)^-(H_5O_2)^+]^{2+}$ is equal to +2 |e|. Assuming that the charge of the Zundel ion is +1 |e| and H_3O^+ 0.916 |e|, the charges of the remaining parts of the above complexes, $[UO_2(OH)^-(H_5O_2)^+]^{2+}$ and $[UO_2(OH)^-(H_3O)^+]_{II}^{2+}$ are +1 |e| and +1.084 |e|. Therefore, to a zeroth order, the Coulomb repulsion energies of $[UO_2(OH)^-(H_5O_2)^+]^{2+}$ and $[UO_2(OH)^-(H_3O)^+]_{II}^{2+}$ are, respectively, $1 \times 1/R$ and $0.99/R$ (= $0.916 \times 1.084/R$).

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