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Comment on “The Water-Exchange Mechanism of the $[UO_2(OH_2)_5]^{2+}$ Ion Revisited: The Importance of a Proper Treatment of Electron Correlation” [F. P. Rotzinger *Chem. Eur. J.*, 2007, *13*, 800]

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In a previous paper (page 2019 of reference [1]), Rotzinger has discussed what he refers to as static and dynamic correlation and states “In $UO_2(OH_2)_5^{2+}$, there is static electron correlation, arising from the population of σ*(M=O) and π*(M=O)s by σ(M=O) and π(M=O) electrons as in $VO(OH_2)_5^{2+}$”. In that paper, Rotzinger did not study the uranyl(VI) aqua ion and his statements in reference [1] are therefore not supported by any computations. His claim that quantum-chemical calculations describing the structure of uranyl complexes and their dynamics using wave function based methods at the MP2 levels are flawed due to neglect of static correlation[1] is erroneous as we have pointed out in a previous publication.[2] In a recent paper[3] Rotzinger has found it expedient to base his previous claim on computational evidence and we applaud this. Despite considerable computational efforts his conclusions are still flawed; his own calculations (and some additional ones made by us) demonstrate very clearly that it is entirely proper to use the MP2 method in computational studies of the uranyl(VI) ion.

There is no strict division between static and dynamic correlation. An operational definition which is often used is that dynamic correlation is what remains after a MC-SCF calculation, normally in a Complete Active Space (CAS) framework. A “full” CAS comprises Configuration State Functions resulting from distributing the valence electrons in all the bonding and antibonding orbitals in the system. Static correlation is also used to describe a situation with one or a few configurations in the reference space, which interacts strongly with the leading configuration due to the presence of nearly degenerate orbitals in the valence space. This situation can conveniently be referred to as static correlation of the near degeneracy type. Strong atomic coupling, which is not quenched by the ligands, can also give rise to several dominating configurations in the wave function, and this can also be regarded as static correlation. If neither of this occurs, there will normally be only one dominant configuration in the wave function. It is therefore reasonable to make a distinction between valence correlation, when the CAS wave function only has one dominant configuration, and static correlation, where the wave function must be described by several configurations with comparable weight. Another possible way of underlining this distinction is to use two concepts for static correlation namely static correlation of the near-degeneracy type and static correlation of the valence correlation type, but this is in our opinion cumbersome.

Second-order Møller–Plesset perturbation theory (MP2) may not be applicable if the reference wave function has more than one dominant configuration. This can occur in systems with nearly degenerate orbitals in the valence space or for open shell systems where strong atomic coupling is important. The possible failure of MP2 in the first case is evident since the difference between orbital energies (or diagonal Fock matrix elements) appears in the denominators in the perturbation expansion. If atomic coupling effects remain important in open-shell systems, as for example in plutonyl(VI), no single reference method is applicable. However, if the valence space does not contain nearly degenerate orbitals, and if there are no appreciable atomic coupling effects, which is the case for example for closed shell systems and systems with only one open shell, there is

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It presents the computational details of the calculation of the binding energy of one water molecule to a uranyl(VI) ion.

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no a priori reason why MP2 should fail. Technically, valence correlation is of the same type as dynamic correlation from the point of view of MP2 if no static correlation of the near degeneracy type is present. It should be pointed out that near degeneracies may appear in a system if the valence orbitals used in the calculation are inappropriate, but this will manifest itself in the calculations (small reference weight in the MP2). A full CAS calculation must lengthen the bonds, since the CI space is dominated by antibonding configurations. In the case of the uranyl ion, which has a closed-shell ground state, a full CAS comprises 12 electrons in twelve orbitals (the bonding and antibonding U−O σ- and π-orbitals). The importance of valence correlation in the bare uranyl(VI) ion, UO_2^{2+}, is shown by the lengthening of the U−O bond from 1.64 to 1.68 Å, and a weight on the leading configuration of 87 % (coefficient 0.93). The natural orbital occupation in the bonding orbitals is between 1.945 and 1.959, and the antibonding between 0.020 and 0.062. No configuration has a weight larger than 0.006 in the CASSCF wave function and there is no indication of small denominators in the MP2 calculation. Valence correlation is thus important, but there is no indication of strong static correlation of the near degeneracy type. There is thus no reason why MP2 should fail for uranyl(VI) complexes. However, in order to ascertain this we have calculated the binding energy of one water molecule to a uranyl(VI) ion with MP2 and with a CASPT2 based on a (12/12) CASSCF reference space. The geometry was optimized by using B3LYP, a method that generally gives good geometries for actinide complexes. The binding energies obtained with MP2 and the large CASPT2 are 285.4 and 287.6 $kJ\,mol^{-1}$, a result, which shows that at least for this property MP2 is accurate. The BSSE is also similar between MP2 and CASPT2, 4.92 versus 4.86 $kJ\,mol^{-1}$. Rotzinger's claim that MP2 is not applicable to uranyl(VI) complexes is thus incorrect.

Rotzinger has also calculated multi-configuration self-consistent field energies in his Table 3 of reference [3] for uranyl(VI) with an increasing number of excitations from the bonding and to the antibonding valence orbitals. The energy drops by 68.3 $kJ\,mol^{-1}$ when the number of excitations increases from zero to two, but remains essentially constant when the excitation level is further increased. This demonstrates the importance of valence correlation (doubly excited configurations). In the MCSCF calculation, the CI expansion is very short, only 1261 determinants for excitation level 2, and includes only excitations within valence orbitals, while excitations from both the valence and the outer core into all virtual orbitals are included in the MP2 calculation. In fact, the calculation of the binding energy of one water molecule to a uranyl(VI) ion mentioned in the previous paragraph shows that the difference between the SCF and CASSCF results is corrected at the MP2 level. Rotzinger finds a weight of 87.6 % of the HF electron configuration in the CAS(12/11) wave-function; this is very close to the value reported above and also to that reported in our review article (see ref. [2], p. 156). Valence correlation is certainly important in uranyl(VI), accounting for about 12 % of the total weight in the CASSCF wave function. However, we do not agree with Rotzinger that 87.6 % weight on the HF reference rules out the use of MP2, when there are no apparent near degeneracy effects. On the contrary, both our results presented here and in reference [2] (p. 156), and the results presented in Table 1 in the article by Rotzinger, clearly show that MP2 can be used on uranyl(VI) complexes. The ground state of metal ions with open d-shells can in principle be described by one determinant, but for this to be true, in particular in strong ligand fields, the electron configuration must be chosen with care. Systems with more than one open f-shell must in the majority of cases be described by a multi-reference wave function.

Rotzinger has calculated the reaction energy for the gas-phase reaction $[UO_2(OH_2)_5^{2+}] \rightarrow [UO_2(OH_2)_4^{2+}],(H_2O)$. The difference between the reaction energy calculated using the HF, MP2, CCSD(T) and MCQDPT2 approximations at constant geometry of reactant and product and reported in Table 1 of reference [3] is only 0.1 $kJ\,mol^{-1}$, between MCQDPT2 and MP2. Rotzinger states "··· that the HF data are, fortuitously, quite close to MCQDPT2. Due to the presence of static electron correlation it is uncertain whether (single reference) MP2 is adequate". As shown in the previous section there is no evidence of static correlation of the near degeneracy type in the uranyl ion and a more reasonable conclusion is that the comparison in Table 1 of reference [3] demonstrates that the use of the MP2 method in uranyl(VI) systems is justified. The difference between the MP2 and CCSD(T) reaction energies for the associative and dissociative exchange mechanisms is below 3 $kJ\,mol^{-1}$.[3] This has been further verified in a more general study using geometries optimized at the B3LYP rather than the SCF level.[4] We furthermore tested the convergence behavior of the Møller–Plesset perturbation series up to fourth-order. The reaction energies reported in Table 1 vary by at most 3 $kJ\,mol^{-1}$ along the MP(n) series, indicating that the convergence of the MP(n) series is fast and the MP2 numbers are reliable.

The reaction energies for dissociative and associative water exchange reactions are reported in Table 6 of reference [3]. The observed difference between Rotzinger's data using CAS-SCF(12/11) geometries and MCQDPT2(12/11) energies and our data obtained with SCF geometries and the energy calculated by using MP2,[5] are then used to support the claim that the MP2 method is unreliable. To begin with his own calculations reported in Table 1 of reference [3] using CASSCF(12/11)-PCM geometries, show that there is *no* significant energy difference between the different methods used to calculate the reaction energy, hence a more likely reason for the discrepancies found is that they are due to the difference in geometry between Rotzinger's calculations and ours. In this context it is worth noticing that the HF bond lengths in the equatorial plane are in better agreement with experimental observations than the CAS-SCF (12/11) geometry. Especially, the hydrogen bond lengths in the CAS-SCF(12/11) geometry are much longer than those obtained at other levels of calculations.[2,5] The reaction energy varies with the geometry and with the basis set; in a previous study[2] we have compared the reaction energy obtained at the MP2-CPCM level for the dissociative reaction path, using HF and MP2 geometries in the gas phase. We find that the former gives a higher energy of reaction by 13 kJ mol^{-1} (65.8 kJ mol^{-1} vs. 52.9 kJ mol^{-1}). This difference is small though not negligible.

In Table 1 we compare our results from reference [5] with those of Rotzinger. To compare the reaction energy (for simplicity only the electronic energy, ΔE using the CPCM/PCM models) for different mechanisms one should of course use chemical models with the same number of water molecules, not one with five and the other with six as used by Rotzinger.

Table 1. Reaction energies in the solvent (the PCM model[6–9] was used in refence [3] and CPCM model[6–9,10] in reference [5] and in this study) for the dissociative (D) and associative (A) water exchange mechanisms in the uranyl(VI) ion. The first value is the activation energy and the one within parenthesis refers to the corresponding intermediate. The basis sets used for the MP(n)-CPCM calculations are detailed in Supporting Information.

Reaction	CAS-SCF(12/11)-PCM geometry[3]				HF-CPCM geometry[5]
	MCQDPT2 (12/11) [3]	MP2	MP3 [this study]	MP4	MP2 [5]
D-reaction					
$[UO_2(OH_2)_5]^{2+} \rightarrow [UO_2(OH_2)_4]^{2+},(H_2O)$	52.6	50.7	54.2	51.1	59.2
	(47.9)	(45.3)	(49.5)	(46.5)	(54.5)
D-reaction					
$[UO_2(OH_2)_5]^{2+},(H_2O) \rightarrow [UO_2(OH_2)_4]^{2+},(H_2O)_2$	–	–			74.0
					(61.8)
A-reaction					
$[UO_2(OH_2)_5]^{2+},(H_2O) \rightarrow [UO_2(OH_2)_6{}^{2+}]$	31.0	29.6	28.9	26.3	18.7
	(26.0)	(24.3)	(23.9)	(20.3)	(15.8)

The data in columns 2 and 3 in Table 1, calculated with the CAS-SCF(12/11)-PCM geometry, show that the energy difference between the MCQDPT2(12/11)-PCM and MP2-CPCM calculations is within 2 kJ mol^{-1}, in agreement with the findings of Rotzinger in reference [3] (p. 802). The energy difference between the *D* and *A* values in Rotzinger's MCQDPT2(12/11)-PCM calculation[3] using CAS-SCF-(12/11)-PCM geometry, 21.9 kJ mol^{-1}, is much smaller than the MP2-CPCM energies in Vallet et al.[5] using HF geometry (Table 1, columns 2 and 5), 39.7 kJ mol^{-1}. Thus the difference that Rotzinger ascribes to an improper treatment of electron correlation is in fact due to the different geometries. This confirms our previous findings that differences in the geometry model used can easily result in differences in reaction energies up to about 10 kJ mol^{-1}. In view of this it is surprising that Rotzinger has used a poor structure model!

The results in Table 1 indicate that the method used for geometry optimization that in general results in small differences, say 0.05 Å, results in an uncertainty in the calculated reaction energy that can amount to about 10 kJ mol^{-1} and has opposite signs for the D and A reaction. There are also, as demonstrated by Rotzinger in Table 6 of reference [3], small (a few kJ mol^{-1}) differences in reaction energy depending on the solvent model (SCRF or PCM) used. When comparing experimental and calculated quantities it is necessary to consider the uncertainties related to different model assumptions. This is particularly important when comparing experimental and calculated reaction energies because of the much stronger model dependence of the latter; this is why one always should use the structure model that is in best agreement with the experimental data. In previous publications[2,11,12] we have suggested that an agreement between experimental and calculated activation energies within 10 kJ mol^{-1} must be considered satisfactory; we consider it doubtful to select reaction mechanisms based on a smaller difference in activation energy between different mechanisms. Rotzinger has studied a model world and made an extensive discussion on details of the reaction mechanism but only the activation energy can be compared with experimental data, quantitative conclusions from other calculated quantities such as the life-time of intermediates, conformation of the water ligands, hydrogen bonds etc., will therefore remain speculations.

Rotzinger (see ref. [3], p. 2) comments on the mechanism for water exchange in $[UO_2(oxalate)_2(OH_2)]^{2-}$ and $[UO_2F_4(OH_2)]^{2-}$ and finds it "incomprehensible that the rather similar oxalate and fluoro complexes should undergo the water-exchange process with opposite mechanisms". Most chemists would not consider these two complexes as "rather similar", for example there is a very significant difference in the experimental $U{-}O_{oxalate}$[13] and the $U{-}F$ average distances,[14] 2.38 Å and 2.26 Å, respectively that might facilitate a dissociative mechanism in the fluoride complex.

Conclusion

To summarize: Rotzinger concludes:

- that it is not appropriate to use the MP2 method in quantum chemical calculations on uranyl(VI) systems because this method does not take electron correlation into account in a proper way, resulting in erroneous values of the calculated reaction energy.
- that the water exchange in $UO_2(OH_2)_5{}^{2+}$ follows an associative mechanism.

The discussion above based on Rotzinger's own reaction energy calculations, shows that his conclusions on the MP2 method are wrong. His statement that the conclusions of Vallet et al. "that these water exchange reactions proceeds

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by means of the A mechanism is based on inappropriate computational techniques" for reactions involving the uranyl(VI) ion is not supported by any computational evidence. Our calculations demonstrate that the observed difference in reaction energy depends on geometry differences, but that this does not affect the chemical conclusions, the difference in activation energy between the two pathways is 65.3 kJ mol^{-1}. We agree with Rotzinger that when one has accurate methods for geometry calculations, they should be used; these were not available in the studies discussed in reference [3], but have been used in later studies with a comparison of methods given in reference [2]. We can also note that even the HF geometry gives satisfactory values for the reaction energy in the uranyl aquo ion (in this case within 10 kJ mol^{-1} of the CCSD(T) value). Rotzinger's calculations support the conclusion that the water exchange in the uranyl aquo ion follows an associative pathway as noted previously.[5,15–17] Finally, we and other quantum chemists have of course always been aware of the fact that the geometry differences result in changes in reaction energies. As more accurate methods for geometry optimization became computationally affordable, we have used them and also compared their different performance. We were therefore both surprised and disturbed by the fact that Rotzinger has not made a reference to the more recent methodological discussions[2,18] related to this study that were published before this paper was presented in its final form.

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