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Reply to the 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 recent article[1] on the water-exchange mechanism of the $[UO_2(OH_2)_5]^{2+}$ ion, I objected that in two previous studies[2,3] inadequate quantum chemical methods have been used: i) static (non-dynamical) electron correlation has been neglected in the geometry optimizations of the uranyl(VI) complexes, and ii) static electron correlation has not been taken into account for the energy computations. The adequacy of these approximations has not been assessed in these two studies.[2,3]

In the preceding Comment,[4] Vallet, Wahlgren, and Grenthe (VWG) present MP2, MP3, and MP4 energies based on my[1] CAS-SCF(12/11)-PCM geometries (Table 1 of reference [4]). Compared with Hartree–Fock (HF), CAS-SCF(12/11) improves the too short axial U=O bond lengths by 0.056 Å (Table 4 of reference [4]), whereas the equatorial U−O bonds get slightly worse (elongation by 0.014 Å). It should be noted that in most, if not all metal aqua ions, the computed metal–water bond lengths are too long due to the approximations in the solvation models and in the treatment of electron correlation. For the A mechanism, which operates for the water-exchange reaction of $[UO_2(OH_2)_5]^{2+}$, VWG’s MP2 (and also MP3 and MP4) data based on my geometries are much closer to the experimental value than the MP2 energy based on their[3] HF-CPCM geometries. These entries prove the higher accuracy of the CAS-SCF(12/11)-PCM geometries over VWG’s HF-CPCM geometries (the two solvation models, PCM and CPCM, produce virtually equal geometries and energies). Therefore, VWG demonstrate that reaction and activation energies are susceptible to the U=O bond lengths, which are computed more accurately with CAS-SCF(12/11)-PCM than with HF-CPCM.

In the following, I shall present a detailed analysis of electron correlation in $[UO_2(OH_2)_5]^{2+}$ (CAS-SCF(12/11)-SCRF geometry[1]) and corroborate the importance of static electron correlation in uranyl(VI) complexes.

The key issue in this controversy is, whether the MP2 technique, for whose application two conditions must be fulfilled, can be applied for uranyl(VI) complexes. All of the methods for the treatment of electron correlation with ab initio methods are based on simplifications of the computationally very demanding and in most cases prohibitive exact solution, the full configuration interaction (CI) method. The MP2 method involves excited configurations that are generated via the displacement of one and two electrons; higher excitations are not included. Furthermore, MP2 is based on second-order perturbation theory (PT2), requiring that the perturbation is small.

As a tool for the assessment of the applicability of methods for the treatment of electron correlation, its nature is often referred to as “static” or “dynamic”. I shall use these terms in the sense of Tew et al.,[5] who stated that “.. static and dynamical correlation are not physically different, both arising from Coulomb interactions. Rather, their distinction is an operational one, connected to the machinery we employ to treat them.”

One extreme situation, with static electron correlation of the near-degeneracy type, is frequently seen in excited states. The other extreme is the complete absence of any static electron correlation. In the latter situation, excitations of more than two electrons do not contribute to the correlation energy, the natural orbital (NO) occupations diminish smoothly and are always close to integral numbers. In the $[Ca(OH_2)_7]^{2+}$ ion, exhibiting the same charge and a similar size as $[UO_2(OH_2)_5]^{2+}$, static electron correlation is absent or nearly so. As it will be shown below, static electron correlation in $[UO_2(OH_2)_5]^{2+}$ arises from excitations exceeding 2, and from a large number of determinants involving molecular orbitals (MOs) of the (12/11) active space,[1] viz. the σ(U=O), π(U=O), σ*(U=O), and π*(U=O) MOs. These determinants exhibit higher CI coefficients than those observed

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in systems with only dynamical electron correlation and, more noticeably, their NO occupations deviate from 2 and 0 in a pronounced manner.

The NO occupations arising from CI singles-doubles (CISD) calculations (the 1s MOs of oxygen were treated as frozen cores) on $[Ca(OH_2)_7]^{2+}$ and $[UO_2(OH_2)_5]^{2+}$ are shown in Figure 1 and Figure 2. The computations were performed with GAMESS,[6,7] using the same basis sets as in the previous study,[1] whereby for Ca, the basis set of Wadt and Hay[8] was taken (which was supplemented with a d polarization function of 0.20). For $[Ca(OH_2)_7]^{2+}$, the NO occupations of the oxygen 2s MOs are around 1.992, and the other NO occupations are somewhat lower and diminish continuously to ~1.985 (Figure 1). For $[UO_2(OH_2)_5]^{2+}$, the occupations of the oxygen 2s, mixed with uranium 6s/6p orbitals, as well as those of the H_2O ligands are as in $[Ca(OH_2)_7]^{2+}$. There are, however, 6 NOs with significantly lower occupations (NOs 34–39) being the two σ(U=O), and the 4 π(U=O) NOs shown in Figure 1a and 1b of reference [1]. A similar phenomenon is observed for the formally empty NOs (Figure 2): for $[UO_2(OH_2)_5]^{2+}$, 5 NOs exhibit considerably higher occupations than the others and those of $[Ca(OH_2)_7]^{2+}$. These five NOs are the four π^*(U=O) and the σ^*(U=O) with a higher occupation (Figure 1c and Figure 1d of reference [1]). These 11 NOs are involved in static electron correlation and constitute the (12/11) active space. All of the CI coefficients for $[Ca(OH_2)_7]^{2+}$ are smaller than 0.01, whereas for $[UO_2(OH_2)_5]^{2+}$, more than 100 of them are ≥ 0.01, and virtually all of these determinants involve MOs of the (12/11) active space. Static electron correlation (as manifested by the NO occupations) in $[UO_2(OH_2)_5]^{2+}$ is due to *a large number of determinants of the (12/11) active space* (exhibiting CI coefficients that are higher than in systems with only dynamical electron correlation). In other words: in the case of $[UO_2(OH_2)_5]^{2+}$, static electron correlation does not arise from a few determinants with relatively large coefficients ("near-degeneracy" type static correlation), but it is due to a large number of determinants exhibiting coefficients higher than those seen in dynamical electron correlation and furthermore, these determinants involve a small set of MOs. Precisely these MOs constitute the active space, within which static electron correlation has to be treated. This is the application of the operational criterion for the construction of the MCQDPT2(12/11) wavefunction in the sense of Tew et al.[5] The NO occupations (Figure 1 and Figure 2) indicate, that the MP2 technique cannot be applied to uranyl(VI) complexes without reservations. The other condition for the application of MP2, namely that configurations arising from the excitation of more than two electrons are negligible, is less straightforward to assess.

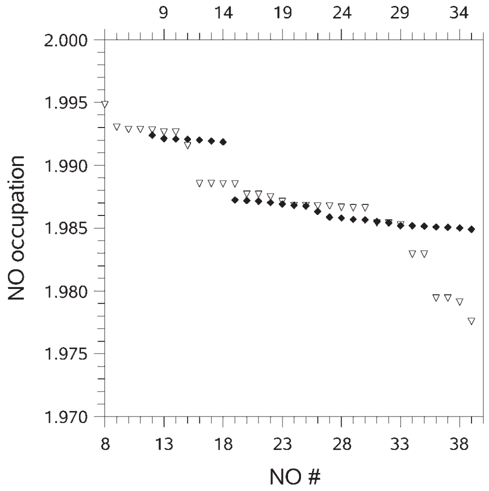

Figure 1. Natural orbital (NO) occupations of the formally doubly occupied orbitals of $[Ca(OH_2)_7]^{2+}$ (◆, upper scale) and $[UO_2(OH_2)_5]^{2+}$ (▽, lower scale).

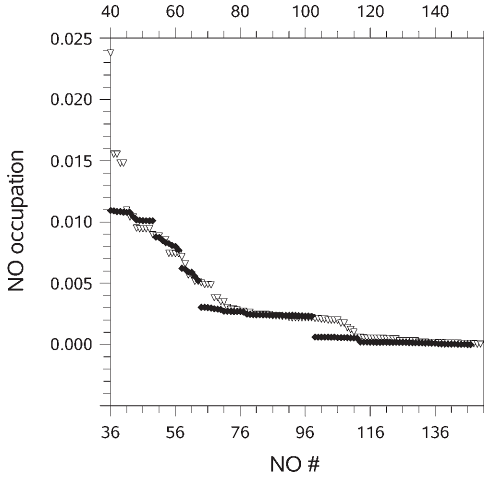

Figure 2. Natural orbital (NO) occupations of the formally empty orbitals of $[Ca(OH_2)_7]^{2+}$ (◆, lower scale) and $[UO_2(OH_2)_5]^{2+}$ (▽, upper scale).

Some further explanations concerning the data in Table 3 of reference [1] are appropriate. It is true that *within the (12/11) active space* singles-doubles excitations make the largest energetic contribution, but triple and quadruple excitations contribute to the non-negligible energy of 4.8 kJ mol^{-1}. With an excitation level of 6 (within the (12/11) active space), CAS-SCF(12/11) accuracy is reached. It is important to note that singles-doubles excitations *within the small (12/11) active space* give rise to the appreciable correlation energy of 68.3 kJ mol^{-1}. The dynamic correlation arising from each of these configurations (generated via the excitation of one and two electrons) is unknown and cannot be computed today (this is only possible for the HF and the CAS-SCF wavefunctions). *If singles-doubles excitations within the (12/11) active space are sufficient, a total excitation level of 4 would be required* for the description of the *entire* correlation energy. To be within 4.8 or 0.1 kJ mol^{-1} with respect to MCQDPT2(12/11), a total excitation level of 6 or 8 would be required. Whether perturbation theory is adequate for the excited configurations within the (12/11) active space remains an open question. Based on these considerations, it cannot be expected that the MP2 energies agree with MCQDPT(12/11). Even MP4 is not entirely converged as the excitation level is concerned. The condition, that excited configurations involving the displacement of more than two electrons are negligible, is not established.

The energy for the water addition reaction (1)

$$UO_3 + H_2O \rightarrow UO_2(OH)_2 \qquad (1)$$

was studied by Vallet et al.[9] at the MP2 and CCSD(T) level (based on B3LYP gas phase geometries) using various basis sets. For equal basis sets, the MP2 and CCSD(T) reaction energies differ by 33 and 32 $kJ\,mol^{-1}$ (Table 6 of reference [9]). These large MP2-CCSD(T) differences are accurate because they were determined for equal geometries and basis sets. They are a clear indication for the inadequacy of MP2. Doubtless, CCSD(T) is superior, since it takes into account excitations of more than two electrons, and since it is not based on PT2 (which requires the perturbation to be small). For the other reactions reported in Table 6 in reference [9] the MP2-CCSD(T) differences are similar or larger except in one case. At variance with the assertation by Vallet et al.,[9] this data proves that the absence of near-degeneracy type electron correlation is not a sufficient condition for the applicability of (single-reference) MP2. (For UO_3 and $UO_2(OH)_2$, I verified with CISD calculations that static correlation of the near-degeneracy type is absent.[10]) The statement[9] that ".. methods such as MP2 are in general applicable to uranyl(VI) complexes, .." is not correct either because, as shown, MP2 is not applicable *in general* to uranyl(VI) complexes, but only in certain cases, in which error cancellation takes place. Furthermore, their statement[9] ".. the agreement between CCSD(T) and MP2 is within 50 $kJ\,mol^{-1}$, which is satisfactory .." is unacceptable and at variance with the error limit of 10 $kJ\,mol^{-1}$ considered as "satisfactory" in VWG's Comment.[4] It should be noted that, in contrast to the water-exchange reactions, those in Table 6 in reference [9] involve variations of the U=O bonds (as verified for reaction 1[10]). The reaction with a MP2-CCSD(T) difference of ~10 $kJ\,mol^{-1}$ is likely to exhibit small structural changes in the UO_2^{2+} fragments. This data[9] shows unequivocally a failure of MP2, and suggests that, because of a cancellation of errors, MP2 is only applicable in cases, in which the geometry of the UO_2^{2+} fragments does not alter significantly in the course of the reaction.

Based on the above-discussed considerations, the MP2 technique cannot be applied without reservations to uranyl(VI) complexes. This might have been the reason why in a recent study, Hagberg et al.[11] applied the CASPT2 method in their $[UO_2(OH_2)_5]^{2+}$ study. They investigated its water-exchange reaction on the basis of classical molecular dynamics (MD) simulations. They constructed the potential using the CASPT2(12/12) technique, whereby they could have saved a considerable amount of CPU time by using MP2. They reported[11] that in previous studies,[12–15] they found "that it was important to include in the active space the oxygen 2p orbitals and the corresponding UO antibonding orbitals of σ- and π-type." These are precisely the MOs (Figure 1 of reference[1]) involved in static electron correlation (whereby they included the second σ^* orbital with a much lower NO occupation[1] into the active space). Doubtless, they intended to avoid errors arising from a possible inappropriate application of MP2.

The CISD calculations on $[UO_2(OH_2)_5]^{2+}$ (Figure 1 and Figure 2) suggest a (12/11) active space. Preferably, active spaces are chosen to be composed of the corresponding bonding and antibonding pairs of MOs, which gives rise to the same number of electrons and orbitals for closed shell systems. This principle has been applied in the cited[11–15] CASPT2(12/12) studies. There is no loss of accuracy, when the σ^*(U=O) MO with a much lower occupation than the other antibonding MOs is excluded from the active space.[10] With limited computational resources, the ~3 times faster MCQDPT2(12/11) calculations might be a remaining option.

In their Comment, VWG present further unsubstantiated or incorrect statements:

1) VWG's contention that electron correlation in $[VO(OH_2)_5]^{2+}$ is not relevant for the situation in uranyl(VI) complexes, and that it is entirely proper to use the MP2 method in computational studies of these complexes, is not correct. The unpaired 3d electron in $[VO(OH_2)_5]^{2+}$ is located in the lowest d_π (t_{2g} type) MO and does not give rise to any near-degeneracy effects. In both systems the MOs, which are strongly correlated, are of the same type: σ(M=O), π(M=O), σ^*(M=O), and π^*(M=O). In a study on the permanganate oxidation of alkenes,[17] Wiberg et al. observed a complete failure of MPx ($x=2$, 3, 4) methods in the computation of the FeO_4, $[MnO_4]^-$, and $[CrO_4]^{2-}$ geometries. I wish to emphasize that, although the MPx methods failed in all of these systems, *near-degeneracy effects are absent* as verified by CISD calculations on $[MnO_4]^-$.[10] Furthermore, the NO occupations are only marginally different from those in $[UO_2(OH_2)_5]^{2+}$. *Thus, the absence of near-degeneracy effects is not a sufficient condition for the applicability of MP2.* Since in uranyl(VI) complexes, the nature of electron correlation is similar to that in the vanadyl(IV) and the tetra-oxo transition metal complexes, VWG's statement ".. demonstrate very clearly that it is entirely proper to use the MP2 method in computational studies of the uranyl(VI) ion." is definitely wrong. Rather, as shown above, the applicability of MP2 for the water-exhange reactions on $[UO_2(OH_2)_5]^{2+}$ is likely to be due a cancellation of errors, which might arise from the inertness of the O=U=O fragment (the U=O bond lengths alter by ≤ 0.004 Å) in these reactions.[1] The above-discussed examples show that MP2 is not applicable to systems, in which sizable variations of U=O bonds take place.
2) VWG's claim that in the comparison of activation energies for different mechanisms, for example A and D, a model with the same number of H_2Os should be used, lacks any basis. VWG's criticism, that I used "a poor structure model!", by using one fewer H_2O for the D mechanism, is untenable. The model representing the

metal complex together with the entering ligand is rather simple. Whether, instead of the entire second coordination sphere, one or two H_2Os are located in the second sphere (of the intermediate for the D mechanism, for example) is irrelevant as shown 10 years ago for the water-exchange reaction on $[Ni(OH_2)_6]^{2+}$, $[Mn(OH_2)_6]^{2+}$, and $[Cu(OH_2)_6]^{2+}$.[18,19] Rather, with two H_2Os in the second sphere, many isomers exist, but there are no criteria for the elucidation of the "right" isomer. Thus, VWG should have studied all of these isomers instead of only one.

3) VWG criticize that I made ".. an extensive discussion .." on ".. lifetime of intermediates, conformation of water ligands, ..", which ".. will therefore remain speculations." In the section on lifetimes of intermediates,[1] I presented physical criteria for the distinction of the step-wise from the concerted mechanism. This is novel and an important issue, since on the basis of experimental data, typically activation volumes, this distinction is only possible in rare cases.[20] The approximations and limitations are presented in detail and, furthermore, I wrote[1] "This is an example showing that small deviations, lying well within the error of the calculations, can have a determining influence on the conclusions." VWG's criticism is absolutely unnecessary. Furthermore, my study on the water-exchange mechanism of $[UO_2(OH_2)_5]^{2+}$ does not just ".. support the conclusion that the water-exchange in the uranyl aqua ion follows an associative pathway as noted previously." but, for the first time, the thermodynamic activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$, which agree with experiment, have been computed. Since it could not be expected a priori that these parameters, determined on the basis of the rather simple cluster model, agree with experiment, I described limitations and artifacts of the model in detail. As the conformations of the H_2O ligands are concerned, I pointed out that the entropy might depend critically on such factors. It is important to inform the reader about such limitations or artifacts. Also this criticism is undue. I made all of these statements with the due care.
4) VWG disagree with my criticism on their incorrect attribution of the water-exchange mechanism on $[UO_2(C_2O_4)_2OH_2]^{2-}$. Also in this matter, their arguments are not correct. The mechanism for the oxalato complex was compared with that for the aqua ion[3] and found to be associative as that for the aqua ion. These two ions are quite different because of their opposite charges and, furthermore, the oxalato complex exhibits a permanent dipole moment. On the other hand, VWG reported[21] a dissociative mechanism for $[UO_2F_4OH_2]^{2-}$. It is certainly appropriate to say that the two anionic complexes are similar, especially in comparison with the positively charged aqua complex. The $U-O_{oxalate}$ and U–F average bonds are not the only relevant parameters. More important are the $U-O_{aqua}$ bond lengths in the fluoro and oxalato complexes, whereby this bond is longest in the oxalato complex (with the reservation that the geometry might be inaccurate due to the neglect of hydration and static correlation in the geometry optimizations). This longer bond is expected to give rise to an even higher preference for the D mechanism than in the fluoro complex.
5) In the Conclusion, VWG state "The discussion above based on Rotzinger's own reaction energy calculations, shows that his conclusions on the MP2 method are wrong." This assertion is certainly not correct: I have shown that MP2 should not be applied to uranyl(VI) complexes without assessment of its validity. In the case of the present water-exchange reaction, MP2 is applicable because of a cancellation of errors, which arises from the small geometrical variations in the U=O bond lengths. However, MP2 is not applicable to reactions involving sizable changes in the U=O bond lengths.
6) Finally, VWG object that I did not cite work, which was published after the submission of my article. In general, at that stage, I add only references suggested by the reviewers or references of high relevance. I did not include reference [9] because, as discussed above, several statements and conclusions are incorrect; I did not want to lengthen my article with additional discussions and criticism.

To conclude, single-reference MP2 can be applied without reservations, if two conditions are met: i) the perturbation must be small, and ii) excitations of more than two electrons must be negligible. In uranyl(VI) complexes, both conditions are not fulfilled as shown by the NO occupations of the present CISD calculations (Figure 1 and Figure 2) and the data in Table 3 of reference [1]. It should be noted that the absence of static correlation of the near-degeneracy type is not a sufficient condition for the applicability of MP2 (the pertinent statements in reference [9] and in VWG's synopsis are wrong). The neglect of electron correlation in the geometry optimizations of uranyl(VI) aqua ions gives rise to a sizable error in the U=O bond lengths and total energies (Table 4 of reference [1]). Simplifications, for example the neglect of electron correlation in geometry optimizations, or the computation of energies with MP2 when static electron correlation is present, are acceptable, *provided that their validity has been established*. Precisely this has not been done in the two criticized $[UO_2(OH_2)_5]^{2+}$ studies.[2,3] In their Comment,[4] VWG present an a posteriori validation of the MP2 method for water-exchange reactions on uranyl(VI) complexes, whereby this approximation is not valid for reactions, which involve variations of the O=U=O geometry.

Finally, I would like to give a recommendation for the elucidation of the adequate method for the treatment of electron correlation: after having obtained the Hartree–Fock orbitals, a CISD calculation should be performed; for large systems, the iterative natural orbital method[22] can be used. The NO occupations provide information on the nature of the correlation, static and dynamic or only dynamic, and for the former case, they supply a clue, which MOs should be included into the CAS-SCF active space. In doubtful cases, the applicability of MP2 has to be validated via the comparison with higher-level ab initio methods (for example CCSD(T), MCQDPT2, CASPT2).

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