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The Structural Influence of Ca^{2+} Counter-Ions on Uranyl(VI) Tricarbonate in Aqueous Solution

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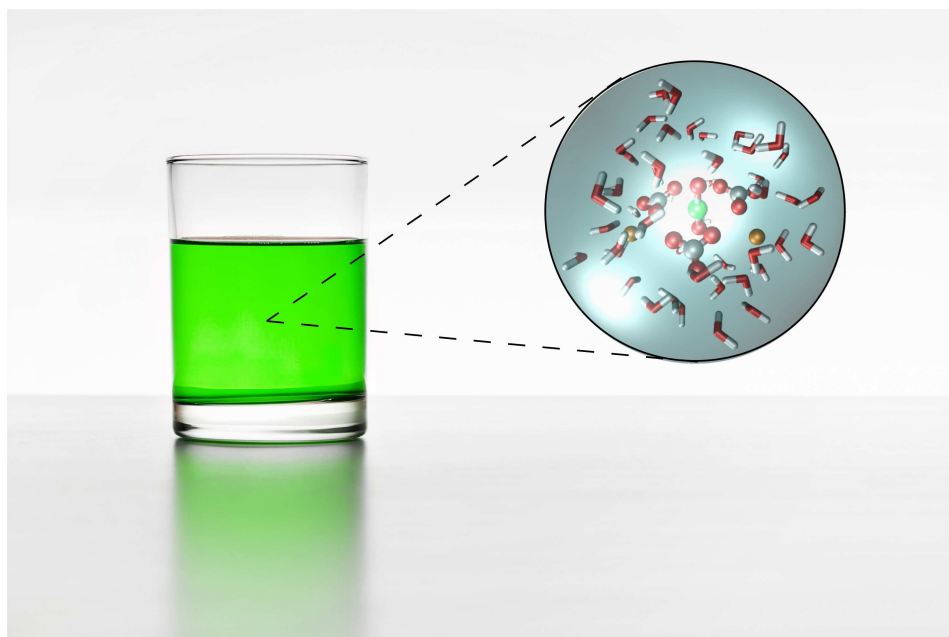
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Abstract

The presented study elucidates the influence of calcium(II) counter-ions on the structure of the environmentally relevant uranyl tricarbonates using hybrid quantum mechanical/molecular mechanical (QM/MM) MD simulations. Since experimental investigations may be subject to limitations in detecting the presence of counter-ions in solution, this investigation is of special importance to gain a profound understanding the effect of counter-ions may have on coordination complexes. It can be concluded from the obtained simulation data that two calcium(II) ions are essential for stabilizing the experimentally observed uranyl tricarbonate complex in aqueous solution. Including only one calcium(II) ion in the coordination sphere was found to be insufficient for obtaining the six-fold equatorial coordination of carbonates, but a five-fold coordination is adopted similar to the counter-ion free case in aqueous solution reported in a previous study.

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The intensive mining of uranium in combination with weathering processes has lead to the mobilization of radionuclides and the associated contamination of water bodies. Among the various radionuclides detected in contaminated soil waters, uranium has the highest concentration[1] and consequently efficient removal strategies are of critical interest. The most abundant species of uranium is the hexavalent oxocation UO_2^{2+}, also referred to as uranyl(VI) ion and is known to form a variety of stable complexes with inorganic ligands present in aqueous solution.[2] Among those the uranyl carbonates are most abundant and, therefore, studied most frequently.[1–16] Several different uranyl carbonates have been reported in the literature so far, with the tricarbonate being the most important one under environmental conditions.[3] Detailed understanding of structure and dynamics of uranyl tricarbonates is essential for its efficient removal from contaminated water bodies and a number of investigations have been conducted in this regard.[1,3,11,16–20] It is found that in the crystal, the uranyl ion is coordinated by three carbonates in a bidentate way corresponding to a six-fold equatorial coordination.[7–9,11,12] However, recently it has been shown that in an aqueous environment and without any stabilizing effect of counter-ions, a five-fold coordination is adopted, with two carbonates coordinating bidentately and one carbonate only coordinating with one oxygen towards uranium.[4] This is due to the formation of a bicarbonate via protonation of a carbonate, thereby lowering the high negative charge of four leading to the stable species $[UO_2(CO_3)_2(HCO_3)]^{3-}$. Since previous studies report solution structures similar as in the crystal, it appeared of interest to investigate the influence of counter-ions on the structure of uranyl tricarbonates in aqueous solution. A recent investigation of the similarly four-times negatively charged hexacyanoferrate(II) complex $[Fe(CN)_6]^{4-}$ revealed that only in the presence of K^+ counterions the complex is stable in an aqueous environment.[21] On the other hand in the absence of counter-ions the negatively charged cyano ligands repel, resulting in the dissociation of two cyanide ions.[21]

Indeed several studies of calcium(II) stabilized uranyl carbonates are reported in the literature.[7–11,13–16] Most of these works are based on simple optimized cluster calculations without or insufficient inclusion of explicit solvent[13,14] or are molecular dynamics (MD) simulations on a classical level of theory.[15,16] Recently, a Car–Parrinello molecular dynamics simulations on generalized-gradient approximation (GGA) level density functional theory (DFT) level of the dicalcium uranyl tricarbontate complex has been reported.[22] Therefore, he present study reports the first MD simulations investigating the structural properties of two relevant calcium(II) coordinated uranyl tricarbonates $Ca[UO_2(CO_3)_3]^{2-}$

and $Ca_2[UO_2(CO_3)_3]$ in aqueous solution on a hybrid quantum mechanical/molecular mechanical (QM/MM) level of theory.

The key question of the present work was to evaluate whether calcium(II) ions are capable to stabilize the six-fold equatorial coordination of the three carbonates reported for the crystal thereby preventing protonation of the carbonate ions as reported in a previous study.[4] In this line, it is of interest to investigate whether only a single counter-ion is sufficient to stabilize a six-fold coordination. The respective computational setup for the MD simulations was identical to previous successful QM/MM studies of uranyl carbonates.[4,5] The starting configuration for the uranyl carbonate with one and two calcium(II) counter-ions was the six-fold bidentate coordination of all three carbonates as observed in the experimentally derived crystal structure. Both systems have been extensively equilibrated for 750000 MD steps (150 ps) on a classical level of theory to properly relax and equilibrate all degrees of freedom. Afterwards the QM/MM treatment was invoked and a trajectory of 30 ps was collected discarding the first 4 ps as re-equilibration of the systems at the QM/MM level. Fig. 1a shows a two-dimensional cross root mean square deviation (rmsd) plot for $Ca[UO_2(CO_3)_3]^{2-}$ (x-axis) and $Ca_2[UO_2(CO_3)_3]$ (y-axis). It is seen that within the first ten picoseconds of simulation hardly any configurational changes occur for $Ca[UO_2(CO_3)_3]^{2-}$. However, after ten picoseconds a sudden configurational change occurs, which corresponds to the switching of one carbonate into a monodentate coordination towards the uranium atom. This configuration is maintained throughout the remainder of the simulation of approx. 16 ps giving no indication of a reversal of the structural rearrangement. In fact a five-fold coordination is adopted which is the stable configuration according to the QMCF-MD simulation. Thus, a similar configuration as the counter-ion free aqueous uranyl tricarbonate $[UO_2(CO_3)_2(HCO_3)]^{3-}$ is adopted.[4] In order to prove this statement a two-dimensional cross rmsd plot of the calcium(II) uranyl tricarbonate (x-axis) and ion-free tricarbonate (y-axis) was created, which is seen in fig. 1b. It should be noted that only the last approx. 16 ps of the trajectory of $Ca[UO_2(CO_3)_3]^{2-}$ showing five-fold coordination have been considered for generating the respective plot. It can be seen that all occurring configurations, adopted by the systems are closely related confirming the structural similarity of these complexes in aqueous solution. The $Ca_2[UO_2(CO_3)_3]$ on the other hand remains in six-fold coordination throughout the entire simulation. The simulation data clearly demonstrates that two calcium(II) ions are necessary to stabilize such a coordination sphere. A schematic illustration of the different complexes is seen in

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fig. 1c. Furthermore, it can be assumed that experimentally derived data measure the calcium(II) stabilized species, although some authors insist that counter-ions are absent in their experimental setup,[10] while another study reports an improvement of the EXAFS fit upon inclusion of the U-Ca shell into the respective structural fitting model.[1]
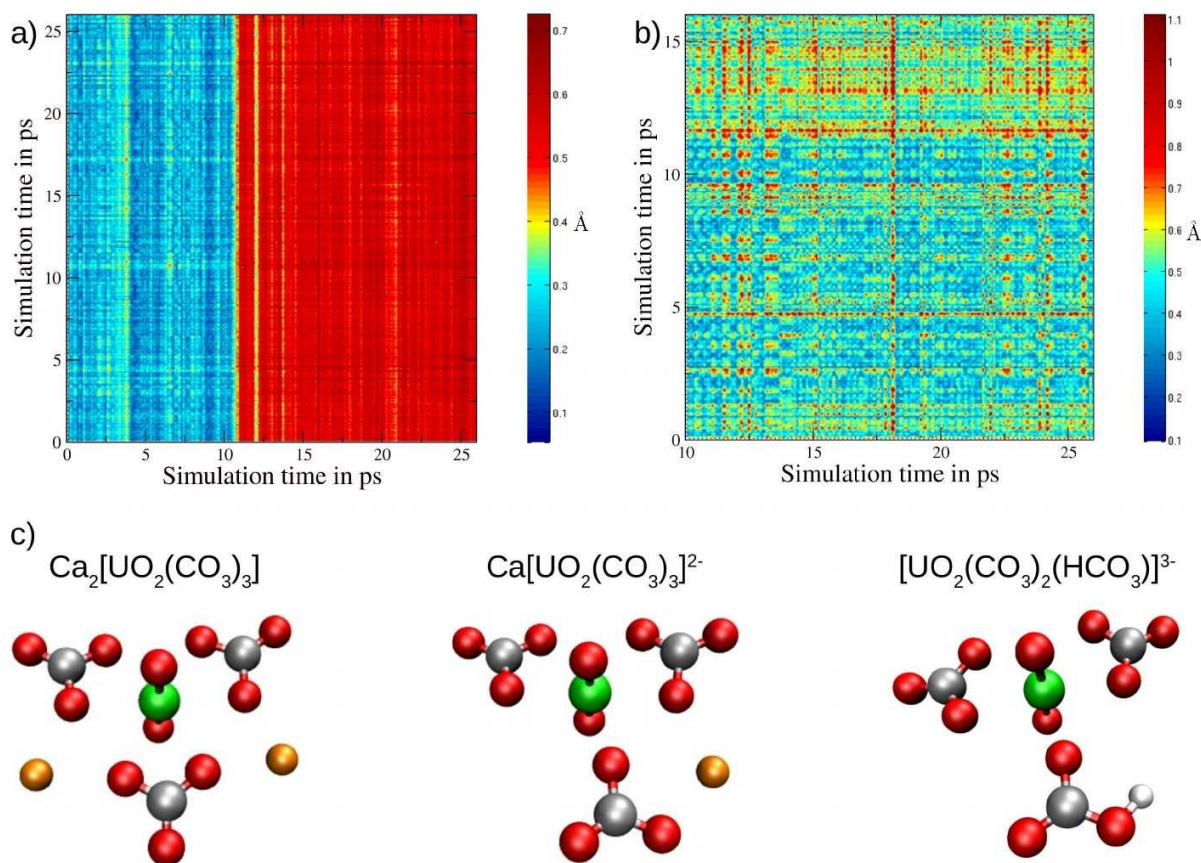

Figure 1: a) 2d-cross rmsd of calcium(II) (x-axis) and dicalcium(II) uranyl tricarbonate (y-axis). b) 2d-cross rmsd of calcium(II) uranyl tricarbonate (x-axis) and the isolated uranyl dicarbonate bicarbonate anion (y-axis). c) Schematic depiction of the three configurations taken into account for the cross rmsds in a) and b).

Fig. 2 depicts the volume slice projections (a and b) and radial distribution functions (RDFs) (c-g) for calcium uranyl tricarbonate and dicalcium uranyl tricarbonate. The principal idea of a volume slice projection is the intersection of a three-dimensional particle density by a number of planes parallel to a preset reference plane. The reference plane was defined via a three-dimensional orthogonal least square fit to the uranium atom and the

coordinating carbonate oxygen atoms. A more detailed information on volume slice projections is provided by Weiss et al.[23] Fig. 2a and b show the volume slice projection of the water oxygen density for calcium uranyl tricarbonate and dicalcium uranyl tricarbonate, respectively. The numbers (± 1, ± 2, ± 3, ± 4) to the left denote the position of the various planes relative to the reference plane (0). The spacing between the individual layers was chosen as 1.6 Å, obtaining 9 slices covering a region of ± 6.4 Å. To facilitate the interpretation a schematic illustration of the considered volume is shown in the left part of fig. 2. The density resulting from the uranyl carbonate and of calcium(II) is shown in a greyish color, whereas water oxygen density is color-coded according to the color bar with reddish regions denoting high oxygen density and blueish regions respective low oxygen density. It can be seen that a high oxygen density can be found in proximity to the calcium(II) ions, while solvent molecules at the carbonate and uranyl oxygens cannot be located at certain positions for a sufficient long time due to the intermolecular flexibility of the ligands.

Fig. 2c shows the U-O_u RDF for both systems. An average uranyl bond distance of 1.74 Å
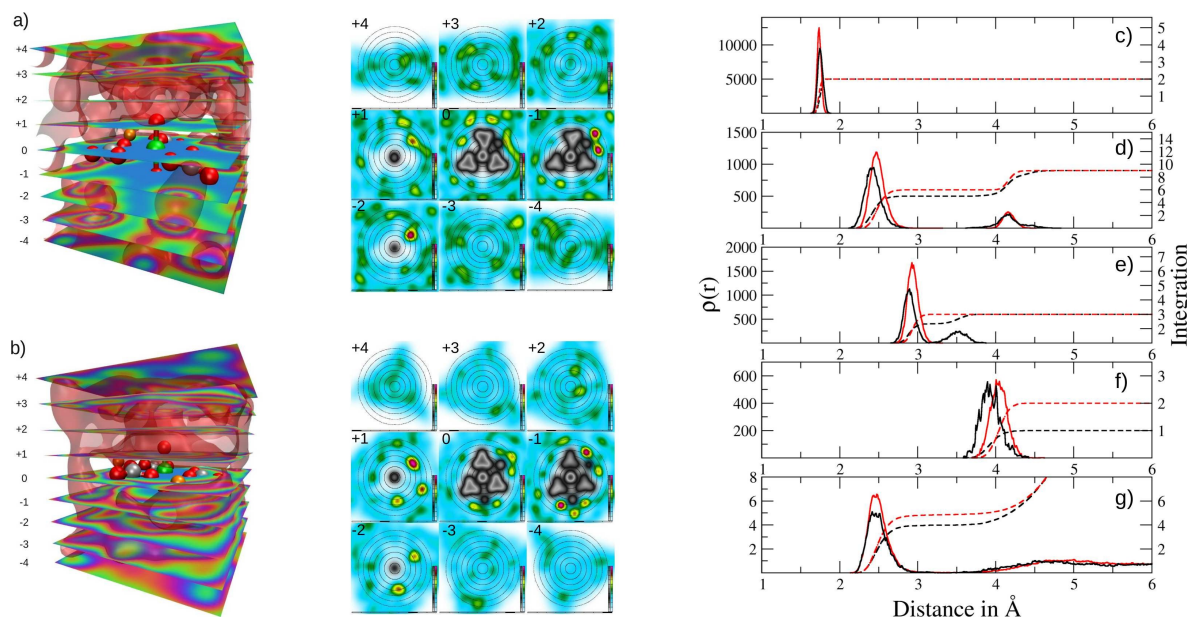

Figure 2: a) Volume slice projection for the calcium(II) uranyl tricarbonate. b) Volume slice projection for the dicalcium(II) uranyl tricarbonate. c) U-Ou RDF d) U-O_c RDF e) U-C RDF f) U-Ca RDF g) Ca-O_w RDF.

for calcium uranyl tricarbonate and 1.73 Å for dicalcium uranyl tricarbonate is obtained. These values compare well to the respective distances in the solid and in liquid samples reported in the literature, which is summarized in Table 1.

Fig. 2d depicts U-O_c RDFs of the coordinatively bound carbonate oxygens and those pointing into the bulk. An average distance of 2.41 Å and 2.47 Å is obtained in case of one and two calcium(II) counter ions, respectively, which is also in accordance with the literature (Table 1). The first peak of the RDF in case of one calcium is less intense. This is due to the fact that one of the three carbonates only coordinates with one oxygen towards uranium and the respective integration yields five. It is seen that upon coordination of a second calcium(II) leads to a bond elongation of 0.06 Å. This is direct result of the change of coordination number from five to six, leading to bond competition of among the ligands, resulting in the observed elongation of the U-O bonds in the equatorial plane. A similar conclusion has been obtained in a study of uranyl monocarboxylates reported by Rösch *et al.*[24] Monitoring the average Mulliken partial charge of the uranium atom changing from +2.62 to +2.71 and +2.77 upon addition of one and two calcium(II) ions, respectively. It is interesting to note that the second peak in Fig. 2c, corresponding to the non-coordinating carbonate oxygens, is only slightly different for the two systems indicating that the calcium(II) ion constrains the configuration of the monodentately coordinating carbonate. It has been shown in a previous study that in absence of the calcium(II) counter ions, the non-coordinating oxygens of the monodentately coordinating carbonate may freely rotate about the associated U-O_c axis adopting several different configurations.[4] The respective average distance of 4.15 Å is obtained in excellent agreement with reported data shown in Table 1. Fig. 2e shows U-C RDFs for both systems. An average U-C distance of 2.88 Å and 2.93 Å is obtained for the bidentately coordinating carbonates of calcium(II) and dicalcium(II) uranyl tricarbonate, whereas an average bond distance of 3.50 Å is seen in case of the monodentately coordinating carbonate. Fig. 2f depicts U-Ca RDFs for both systems and an average distance of 3.92 Å and 4.04 Å is observed uranyl tricarbonate with one and two calcium(II) counter-ions, respectively, also being in excellent agreement with experimental data (*cf.* Table 1). The shorter bond distance in case of calcium(II) uranyl tricarbonate is attributed to the monodentate binding of one carbonate towards uranium enabling the counter-ion to be closer to the uranyl ion. Fig. 2g shows Ca-O_w RDFs for the treated systems. It is seen that in case of calcium(II) uranyl tricarbonate, besides three carbonate oxygens, additional four water molecules form the first coordination sphere of the counter-ion leading to a coordination number of seven for calcium(II). In case of dicalcium(II) uranyl tricarbonate only two carbonate oxygens coordinate towards calcium(II), but additional five water molecules complete the first coordination sphere and coordination number seven is also obtained in this case. The water molecules coordinating

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to calcium(II) can also be seen in fig. 2a and b. A coordination number of seven for aqueous calcium(II) has been previously reported,[15,25,26] but Schwenk et al. and Naor et al. also observed an equilibrium between seven- and eight-fold coordination. However, in presence of negatively charged carbonate ions, a coordination number of eight for the calcium(II) counter-ion can be excluded due to the considerable charge transfer from the carbonate anion to the calcium(II) cation. The average Ca-Ow is 2.46 Å for both systems, which also agrees well with the literature.[9,15,25,26]

In conclusion, we have employed hybrid QM/MM MD simulations to investigate the struc-

system	method	U=O	U-Oc	U-C	U-Ca	Reference
Ca[UO$_2$CO$_3$]$^{2-}$	QMCF-MD	1.74	2.41/4.15	2.88	3.92	this work
	MM-MD	–	2.40/–	–	4.05	Kerisit et al.[15]
	EXAFS ^{a}	1.78	2.45/4.11	2.89	4.02	Kelly et al.[10]
	EXAFS ^{b}	1.79	2.43/4.15	2.88	3.97	Amayri et al.[7]
	EXAFS ^{b}	1.79	2.43/4.15	2.88	–	Amayri et al.[8]
	XRD ^{b}	1.78	2.44/4.12	2.88	3.96	Mereiter et al.[12]
	XRD ^{b}	1.78	2.44/4.11	–	–	Coda et al.[9]
Ca$_2$[UO$_2$CO$_3$]	QMCF-MD	1.73	2.47/4.15	2.93	4.04	this work
	MM-MD ^{a}	–	2.40/–	–	3.99	Kerisit et al.[15]
	MM-MD $^{a,ads.}$	1.83	2.39/3.97	2.79	4.00	Kerisit et al.[16]
	CP-MD ^{a}	1.85	2.45/4.15	2.85	4.07	Priest et al.[22]
	EXAFS ^{a}	1.79	2.45/4.13	2.89	4.04	Kelly et al.[10]
	EXAFS ^{a}	1.80	2.44/4.20	2.89	3.94	Bernhard et al.[6]
	B3LYP ^{a}	1.81	–	2.95	4.05	Kubicki et al.[14]
	B3LYP ^{a}	1.80	2.40/4.13	2.96	3.99	Tsushima et al.[13]
	B3LYP ^{c}	1.79	2.36/4.19	2.97	3.83	Tsushima et al.[13]
	EXAFS ^{b}	1.80	2.43/4.15	2.88	4.05	Amayri et al.[7]
	EXAFS ^{b}	1.80	2.42/4.10	2.89	–	Reeder et al.[11]
	EXAFS ^{b}	1.80	2.43/4.15	2.88	–	Amayri et al.[8]
	XRD ^{b}	1.78	2.43/4.11	2.86	4.07	Coda et al.[9]

Table 1: Average bond distances for selected species in calcium(II) and dicalcium(II) uranyl tricarbonate: Uranium-Uranyl oxygen (U=O), Uranium-Carbonate oxygen (U-Oc), Uranium-Carbon (U-C) and Uranium-Calcium (U-Ca).
$^a)$ Liquid phase $^b)$ Solid state $^c)$ Gas phase calculation $^{ads.)}$ adsorbed

tural influence of calcium(II) counter-ions on the coordination of carbonates towards the uranyl ion. It was found that one single calcium(II) ion is not sufficient to stabilize the experimentally observed uranyl tricarbonate complex. In this case a five-fold coordination with very similar structural behavior as observed in the counter-ion free species is

obtained. If, however, two calcium(II) ions are coordinating to the uranyl tricarbonate complex, the six-fold equatorial coordination is maintained and the experimental findings are reproduced. This situation is similar to the counter-ion effect reported previously in case of $[Fe(CN)_6]^{4-}$. By explicitly including potassium(I) ions in the vicinity of the cyano ligands a stable complex in agreement with experimental data was obtained,[21] while in the absence of counter-ions cyano ligands dissociated from the complex.

Therefore, it is concluded that counter-ions are essential to compensate the highly negative excess charges introduced by the coordinating ligands, leading in both cases to a six-fold coordination. It can be concluded that both experimental hexacyanoferrate(II) as well as carbonate solutions contain counter-ion stabilized complexes upon dissolution of the respective salts.

Nevertheless, it would be very interesting to compare our computational results to experimentally derived data of very dilute $Ca_2[UO_2(CO_3)_3]$ solutions to probe whether the five-fold coordination is observed in absence of counter-ions or whether the calcium(II) ions remain associated to the complex.

Computational Methods

The MD simulations were performed at a hybrid quantum mechanical/molecular mechanical (QM/MM) level of theory using the software package QMCF.[27–29] The cubic simulation box contained the solute and 1000 explicitly treated water molecules. The entire QM region measured a diameter of 14 Å thus including the solute and an average of over 30 quantum mechanically treated solvent molecules. Energies and forces of the QM region were evaluated using the QM software package TURBOMOLE 6.5.[30] Since previous studies gave excellent results and for reasonable comparability the chosen level of theory was Hartree-Fock (HF). As in previous studies on uranyl carbonates, the same basis sets have been used.[4,5] For calcium the respective Stuttgart RSC (Relativistic Small Core) ECP basis set[31] was used. The MM region containing only solvent molecules was treated via the flexible water model SPC-mTR.[32]

Rmsd-values between to configurations generated by chosing the uranium atom plus the atoms of all carbonate ligands (not considering the hydrogen atom in case of ion-free $[UO_2(CO_3)_2(HCO_3)]^{3-}$). After alignment of the respective centres of mass, the systems are rotated until the best alignment is achieved[33] indicated by the smallest possible value for the rmsd being defined as

$$rmsd = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(r_i^a - r_i^b \right)^2} \tag{1}$$

with r_i^a and r_i^b being the coordinates of atom i in configurations a and b, respectively. N corresponds to the number of atoms considered in the analysis. This prodcedure has been repeated for each pair of configurationss in the respective trajectories to obtain the cross-rmsd plots shown in figure 1.

Acknowledgments

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