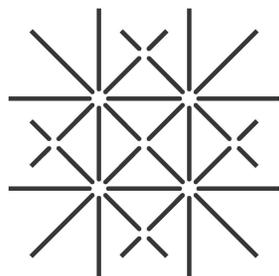


Energetics and Solvation Dynamics of the excited $\text{Ru}(\text{bpy})_3$ complex in water

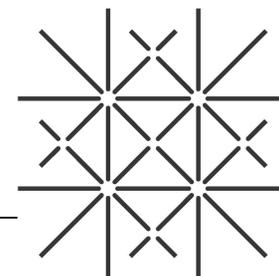
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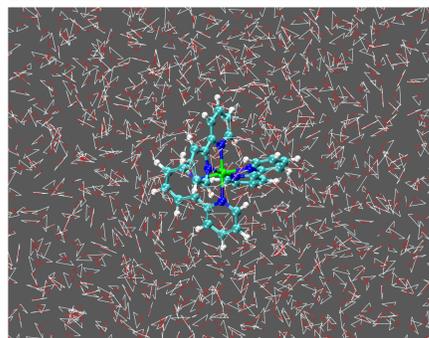
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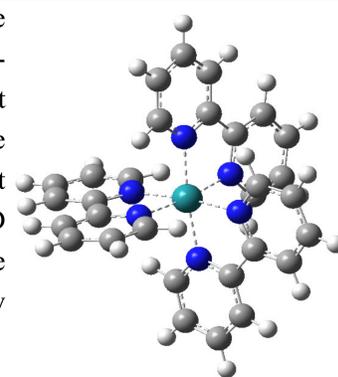
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Efficient MD simulations of inorganic chromophores such as pyridinated ruthenium complexes were carried out to study the behavior of water solvation shells. After electronic excitation of a pseudo-octahedral ruthenium complex in explicit solvent, a reorganization process of the corresponding solvent can be obtained, which is mainly related to the solvent electronic interactions.^[1] The geometry of the complex is flexible during the MD process in order to study the internal motions in the time-dependent solvation process. The structure of the solvation shell and the reorganization time can be obtained by MD simulations and TD-IR spectroscopy derived from correlation function of the dipole moments.^[2] Using the VALBOND TRANS^[3] force field with different water models it was verified experimental data gained by spectroscopy with modern laser techniques.^[4]



Motivation

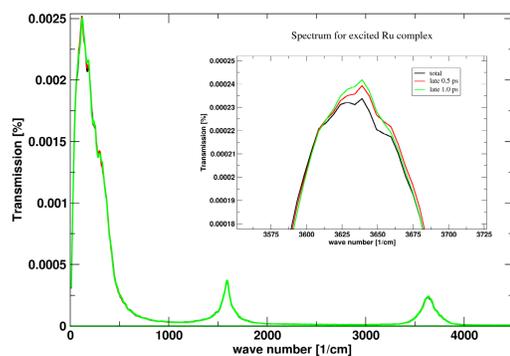
The progress in ultrafast spectroscopic techniques brought new insights about structural changes on the sub-picosecond scale. Experimental findings alone, however, are not able to explain the complex and heterogeneous dynamics.^[3] Therefore MD simulations are the method of choice helping better understanding of related processes. Ruthenium(II)-tris-(2,2'-bipyridine) is known to be photostable, also in its excited state,^[5] therefore $\text{Ru}(\text{bpy})_3$ plays an important role in solar-energy research.^[6] These features of $\text{Ru}(\text{bpy})_3$ made it the complex of our choice.

Theoretical setup

VALBOND TRANS (VBT) force field was used for MD simulations with TIP3P^[7] and flexible KKY^[8] water models. For TIP3P setup a 1 fs time step was used and SHAKE for constraining the hydrogen atoms, whereby for the KKY flexible water model a timestep of 0.2 fs was used. Verlet dynamics (NVE) were carried out at 300K in explicit water (1694 water molecules). The excitation has been modeled by instantaneous change of force field parameters for the ruthenium complex from Ru(II) to Ru(III). Both force fields were first reparameterized to the data obtained from *ab initio* calculations, with TRANS parameters adjusted according to the previous work in our group.^[3]

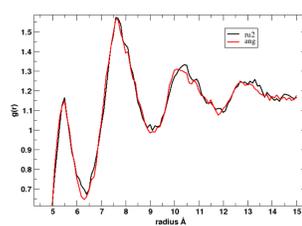
Results

Spectrum for excited Ru complex



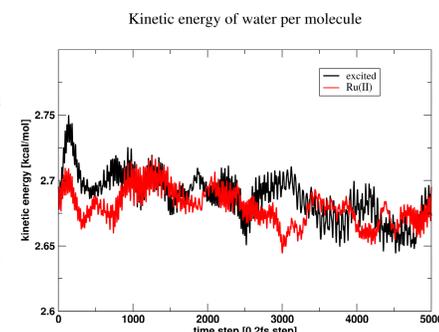
Classical IR spectra of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ averaged over 100 trajectories evaluated at different time after excitation. Spectrum is obtained from the Fourier transform of the dipole-dipole correlation function. Black: total spectra after excitation, red: spectrum after 0.5 ps and green: spectrum after 1.0 ps. The inset is a amplification of the peak at $\sim 3600 \text{ cm}^{-1}$.

VALBOND TRANS (VBT) force field is used the first time for applications in spectroscopy, where an instantaneous excitation of ruthenium was investigated and the magnitude of energy transfer which occurs to the surrounding water shells. Since changes in the signal recorded for all the water is weak we concentrated on the water closest to Ru complex that would stay within the shell of 11Å from the centre of the complex. Considering the RDF, usage of an 11 Å radius was reasonable to make sure that the first three water-shells around the transition metal were taken into account. After excitation, an increase in kinetic energy of 0.04 kcal/mol per water molecule is determined, having approximately 120 water molecules within this radius makes an overall energy increase of almost 5 kcal/mol. This intermolecular charge transfer occurs in 40-50 fs, followed by a decay of this signal within 400 fs.

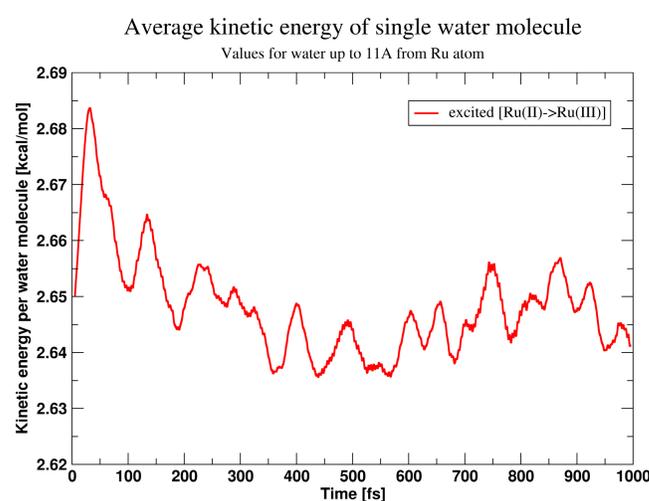


Radial distribution function of solute-solvent distances recorded for before and after excitation.

Energy transfer and RDF were also determined for the rigid TIP3P water model, but to generate an IR spectra, it was necessary to use flexible water model. The classical IR spectra is calculated from the time-dependence of the dipole moment function. According to experimental data the O-H symmetrical and asymmetrical stretches lay around 3600 cm^{-1} and the bending mode around 1600 cm^{-1} and the out of plane asymmetrical stretch below 700 cm^{-1} . By comparing the full spectra and “late spectra” (determined 0.5, 1.0, 1.5 ps) one observes no shifts in positions of the peak, but there is a visible change in amplitudes of the peaks. To verify our findings we performed simulations with artificially large charge changes, to show the same effect, but more intensive. The most pronounced change in quantities, that we can directly obtain from MD simulation, is the energy transfer to the solvent manifesting in raise of kinetic energy of water. At the current state it is an open question how this change would be seen by the experiment.



Kinetic energy of a single water after excitation and in the equilibrated state, values averaged over 100 trajectories.



Energy transfer to the solvent expressed in terms of kinetic energy of a single water molecule

Goal

The reorganization process of solvent (water) after excitation is studied to capture the time-dependent solute-solvent interaction and the solvent response which includes the energy transfer from the metal complex to surrounding solvent. The time scales of the energy transfer process as well as signal decay time are estimated from non-equilibrium MD simulations. The measured quantities involve radial distribution function, kinetic energy of water and changes in the theoretically obtained IR spectrum recorded during the relaxation of the photo-excited complex. The obtained information is expected to be helpful in answering the question if there is an energy transfer to the surrounding solvent or if energy is rather redistributed to the low frequency modes as suggested by Chergui and co-workers^[9]

Conclusion

ValBond Trans force field has been proven to perform well giving qualitatively good decay signal times comparable with predicted decay values available from QM/MM calculations (300ps).^[1] On the contrary to suggestion in previous work^[9], we observed a significant energy transfer from the excited transition metal complex to the surrounding water within 40-50 fs, decaying within 400 fs. The IR spectra of the full trajectory compared to the “late spectra” registered within 0.5 ps delay periods after excitation, shows differences in magnitude of the intensities of the peak; however, no shift in frequencies has been observed.

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