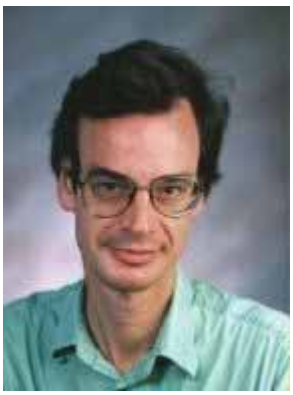
第206回触媒化学研究センター談話会
第15回創成科学セミナー

Non-equilibrium solvation in density functional theory based molecular dynamics simulation



Professor Michiel SPRIK
Department of Chemistry, University of Cambridge, United Kingdom

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北海道大学創成科学研究棟5階大会議室

Solvent effects are particularly strong when the reacting solutes are charged and the reaction takes place in a polar solvent (foremost water). Solvation affects the reaction free energy change as well as the free energy barriers. The effect on the equilibrium constant is due to stabilization of charged species and is studied with the solvent orientation (polarization) fully equilibrated to the charge distribution of the solute. However, the same approach is not always appropriate for understanding the solvent effect on the free energy of a transition state. Non-equilibrium solvation becomes important when the motion of the solvent is slow in comparison to the time scale of the rearrangement of the solute charge densities. In that case the solvent must move first and its configuration must be treated as an explicit reaction coordinate. Electron and proton transfer in water are familiar examples where these conditions are realized. This type of non-equilibrium solvation has been extensively studied using a continuum representation of the solvent and simulated numerically using valence bond models. Both approaches go back to the Marcus theory of electron transfer. After a short introduction about non-equilibrium solvation, we will highlight in this talk some of the issues encountered when a similar approach is extended to density functional theory based *ab initio* molecular dynamics ("Car-Parrinello") simulation which treats solute and solvent at the same level of electronic structure calculation and statistical mechanical theory. As illustration we will use some of the results of recent work on the Car-Parrinello simulation of redox reactions in solution. In the same context we will comment on the simulation of proton transfer by Car-Parrinello methods.

連絡先:　触媒化学研究センター・界面分子化学分野・大澤雅俊 (011-706-9123・osawam@cat.hokudai.ac.jp)
創成科学共同研究機構・特定研究部門・寺倉清之 (011-706-9217・terakura@cris.hokudai.ac.jp)

主　催:　触媒化学研究センター・創成科学共同研究機構