Nonadiabatic coupling in UO_{2+x}

Ge Yao[1], Dmitri S. Kilin[2], Jianwei Wang[1]*

1. Department of Geology and Geophysics, State University of Louisiana, Baton Rouge, LA

2. Department of Chemistry, the University of South Dakota, Vermillion, South Dakota

As both nuclear fuel in reactor and used fuel, UO_2 is one of the most thoroughly studied materials. In stoichiometric uranium dioxide, uranium ions have a valence of 4+. However, uranium dioxide can be easily deviated from its stoichiometry, leading to mixed valences of uranium ions, which are represented as UO_{2+x} in different condensed oxide or oxyhydroxide phases. The Born–Oppenheimer approximation for such system may not be appropriate due to the heavy mass weight of the uranium. The nonadiabatic coupling, the interaction between electrons and nucleus vibrational motion, needs to be considered for the properties of the material at finite temperature. Base on previous studies of the UO_2 system, [1,2,3] a nonadiabatic coupling was simulated by combining time-dependent density matrix methodology, *ab initio* molecular dynamics, and on-the-fly nonadiabatic couplings for nonradiative transitions between electronic states at interested temperatures.[4] The fluctuation of orbital energies in molecular dynamics, the probability of electronic excitation, and the nonradiative decay rates in electronic dissipation processes were computed and compared to the adiabatic manner. The significance of nonadiabatic effect were evaluated, which would benefit for better understanding of the properties of UO_{2+x} systems.

1. Wang, J.; Ewing, R. C.; Becker, U., Average structure and local configuration of excess oxygen in UO2+x. *Sci. Rep.* **2014,** *4*.
2. Wang, J.; Ewing, R.; Becker, U., Electronic structure and stability of hyperstoichiometric UO2+x under pressure. *Physical Review B* **2013,** *88* (2), 024109.
3. Wang, J.; Becker, U., Activation energetics of actinide diffusion in UO2 from first-principles calculations. *Journal of Nuclear Materials* **2013,** *433* (1–3), 424-430.
4. Yao, G.; Meng, Q.; Berry, M. T.; May, P. S.; S. Kilin, D., Molecular dynamics in finding nonadiabatic coupling for β-NaYF4: Ce3+ nanocrystals. *Molecular Physics* **2014,** (DOI 10.1080/00268976.2014.972475).