Theoretical investigation of electron and nuclear dynamics in the $Au_{25}(SH)_{18}^{-1}$ thiolate-protected gold nanocluster

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The electron nuclear correlations in photoexcited systems should be treated with nonadiabatic dynamics as they cannot be treated by Born-Oppenheimer molecular dynamics. In the present study, the electronic and nuclear dynamics of the nonplasmonic nanocluster $Au_{25}(SH)_{18}^{-1}$ are studied to understand the electronic excited states and decay to lower energy states using molecular dynamics with nonadiabatic couplings. A combination of time-dependent Kohn-Sham (TDKS)[1, 2] and linear response time-dependent density functional theory (LR-TDDFT) is used to examine the thiolate-protected nanoparticle using the fewest switches surface hopping (FSSH) scheme [3] to examine the nonadiabatic effects.

Several important electronic excited states that contribute to the two main peaks in the optical absorption spectrum of $Au_{25}(SH)_{18}^{-1}$ in the energy range of 0.0 - 2.2 eV were studied in order to calculate the decay times of the excited states. The decay times were calculated including decoherence both 'with' and 'without' an energy correction to the calculated excited states. The energy correction is used to compensate for underestimation in the calculated density functional theory (DFT) band gaps compared to the experimental gaps.

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[2] Akimov, V.A., Prezhdo, O. V, *J. Chem. Theor. Comput.* **9**, 4959 (2013).
[3] Tully, J. C, *Faraday Discuss*. **110**, 407 (1998).