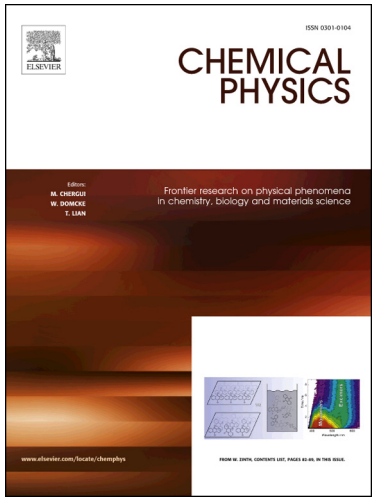

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Theoretical Study on Electronic Excitation Spectra: A Matrix Form of Numerical Algorithm for Spectral Shift

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ABSTRACT: In this work, a matrix form of numerical algorithm for spectral shift is presented based on the novel nonequilibrium solvation model that is established by introducing the constrained equilibrium manipulation. This form is convenient for the development of codes for numerical solution. By means of the integral equation formulation polarizable continuum model (IEF-PCM), a subroutine has been implemented to compute spectral shift numerically. Here, the spectral shifts of absorption spectra for several popular chromophores, *N,N*-diethyl-*p*-nitroaniline (DEPNA), methylenecyclopropene (MCP), acrolein (ACL) and *p*-nitroaniline (PNA) were investigated in different solvents with various polarities. The computed spectral shifts can explain the available experimental findings reasonably. Discussions have been made on the contributions of solute geometry distortion, electrostatic polarization and other non-electrostatic interactions to spectral shift.

Highlights

► A novel expression of nonequilibrium solvation energy is presented by introducing the constrained equilibrium approach, which is different from the traditional ones. ► A matrix form of numerical formula for spectral shift is presented and the computational codes have been implemented by combining with PCM. ► Solvent effects on electronic excitation spectra of several chromophores were investigated and discussed.

Keywords: Nonequilibrium solvation, Spectral shift, Constrained equilibrium, Vertical excitation energy, Numerical algorithm

1. Introduction