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On the nature of solvatochromic effect: The riboflavin absorption spectrum as a case study

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ABSTRACT

We present here the calculation of the absorption spectrum of riboflavin in acetonitrile and dimethyl sulfoxide using a hybrid quantum/classical approach, namely the perturbed matrix method, based on quantum mechanical calculations and molecular dynamics simulations. The calculated spectra are compared to the absorption spectrum of riboflavin previously calculated in water and to the experimental spectra obtained in all three solvents. The experimentally observed variations in the absorption spectra upon change of the solvent environment are well reproduced by the calculated spectra. In addition, the nature of the excited states of riboflavin interacting with different solvents is investigated, showing that environment effects determine a recombination of the gas-phase electronic states and that such a recombination is strongly affected by the polarity of the solvent inducing significant changes in the absorption spectra.

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1. Introduction

Flavins are redox-active chromophores that play important roles in a very wide range of biological processes [1]. In addition, there is an increasing interest in their photochemical properties since their discovery as chromophores in blue-light sensing photoreceptors [2]. Therefore, the photophysics and photochemistry of flavin molecules have recently attracted much attention [3–12]. In particular, spectroscopical approaches such as UV/VIS absorption and emission spectroscopy were successfully used to unravel details of the early photophysics and photochemistry in flavins [5,9,11,13].

Riboflavin (RBF, Fig. 1), also known as vitamin B2, is one of the simplest flavins and has been used as model compound among the biologically relevant flavin-based chromophores. RBF absorption and emission spectroscopic characterization has been addressed both experimentally [7,8,11,13,14] and theoretically [15–23]. Despite the computation of the absorption spectrum of RBF and some of its derivatives has been addressed by several groups with accurate quantum chemical calculations at different levels of theory, most of the calculated spectra considerably deviate from the corresponding experimental spectra [15–18,21,23]. The main determinant to such a disagreement has been recognized to be the lack of inclusion of

solvation effects in the computation [24]. The interaction between the chromophore and the environment affects indeed the chromophore electronic degrees of freedom, relevantly modifying the chromophore properties with respect to those calculated in vacuo. In addition, an extensive sampling of the chromophore/environment configurational space is crucial to properly model the interaction between the solute and the solvent. As a matter of fact, the explicit inclusion of solvent effects in the calculation of the absorption spectrum of RBF using only a few structures, obtained from molecular dynamics (MD) simulations [23] led to a high variability of the calculated spectral line shapes often mis-reproducing the experimental relative intensities of the peaks and to an average wavelength of the peaks still in disagreement with the experimental ones.

Very recently, we used an approach based on the joint use of extended MD simulations and a mixed quantum/classical theoretical computational methodology, the Perturbed Matrix Method (PMM) [25,26], to compute the absorption spectra of RBF in water [27] and bound to riboflavin binding protein [28] obtaining results in good agreement with the corresponding experimental results. Along with other approaches that address the inclusion of environmental effects into the calculation of spectral properties in complex systems using hybrid quantum/classical models [29–31], the MD-PMM approach is based on the approximation of dividing the system in a subpart to be treated at the electronic level (the quantum center, QC), while the rest of the system (i.e., the environment) is described at a classical atomic level exerting an electrostatic effect on the QC. In the MD-PMM

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the electronic properties of the QC are at first evaluated in the gas-phase and then, for each configuration generated by a fully classical MD simulation of the whole system (the QC and the environment), the electrostatic effect of the environment on the QC is calculated providing the electronic properties of the QC embedded in the perturbing environment at each MD frame. Being the phase space sampling of the whole system provided by a fully classical MD simulation, the MD-PMM can be applied to a very large set of molecular configurations, hence providing the dynamic coupling of electronic properties with classical degrees of freedom. Differently from other methodologies that use a limited number of snapshots extracted from an MD simulation to perform electronic calculations on a solute embedded in its first solvent hydration shell [30–33], the MD-PMM thus allows, with a relatively low computational cost, both an extensive sampling of the whole system configurations and the inclusion of the effect of the whole environment. The fact that a statistically relevant sampling of the system configurations is achieved, essential for an accurate calculation of the spectra of complex systems, is the main strength of the MD-PMM approach. This methodology has been used successfully to model several relevant experimental observables such as reduction potentials [34,35], charge transfer rates [28,36,37], amide I infrared spectra [38,39] and to compute the absorption spectra of molecules in solution [27,37,40].

Here, we apply the MD-PMM approach to calculate the absorption spectrum of RBF in two organic solvents: acetonitrile (ACN) and dimethyl sulfoxide (DMSO). After validation by comparison with experimental results, the solvent sensitivity of the absorption spectrum of RBF is explained by investigating how the excited electronic states of RBF are affected by the interaction with different solvents. The understanding of solvatochromic effects on RBF spectrum allows a deeper insight into the electronic properties of RBF and thus into its photochemical properties.

2. Theory and Methods

2.1. Perturbed Matrix Method Calculations

The basic features of the application of the MD-PMM approach [25,26] for the calculation of absorption spectra are hereafter briefly described.

As already mentioned, in the MD-PMM the whole atomic-molecular system is divided into a quantum center (QC) (to be treated at the electronic level) where the quantum processes of interest occur, and its environment which is modeled as an atomic-molecular semi-classical subsystem interacting with the QC. In the present case, the QC is lumiflavin (the isoalloxazine moiety saturated with a methyl group) while the ribityl tail and the solvent are included in the perturbing environment (see Fig. 1).

In the MD-PMM the electronic properties of the isolated QC (unperturbed properties) are at first calculated quantum-chemically in vacuum (i.e., in the gas-phase). Then a fully classical molecular dynamics (MD) simulation of the whole system is performed, providing the instantaneous atomistic configurations of both the environment and the QC. Such configurations are used to evaluate the perturbation exerted by the environment on the electronic properties of the QC: for each configuration generated by all-atoms classical MD simulations of the whole system, the electrostatic effect of the instantaneous atomistic configurations of the environment is included as perturbing term to the electronic properties of the isolated QC providing the electronic properties of the QC embedded in the perturbing environment. If the considered QC is rigid (or quasi-rigid), as in the present case, the quantum calculations are performed on a single reference structure (i.e. the ground state geometry optimized in vacuum) and the perturbation effect of the whole simulation environment is included a posteriori by diagonalizing the perturbed Hamiltonian matrix of

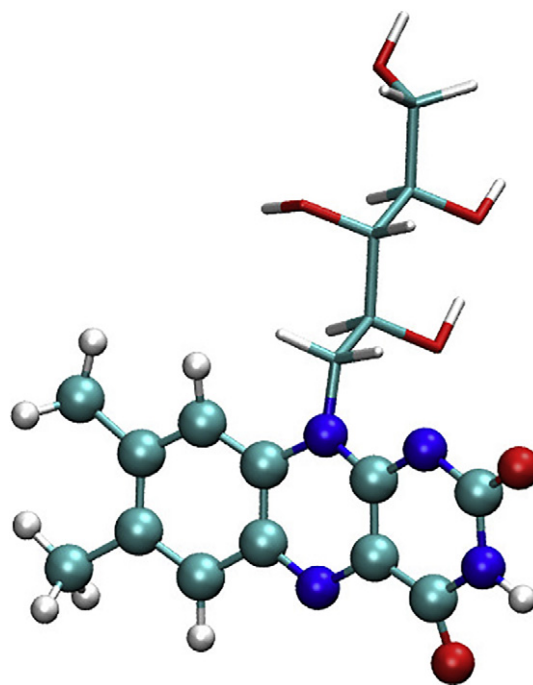


Fig. 1. Representative structure of riboflavin (RBF). The isoalloxazine ring is highlighted in ball and sticks and the ribityl tail is represented in licorice.

the QC at each frame of the MD simulation, i.e. all the configurations/frames of the MD simulation are used (in the present case, the MD simulation is sampled every ps).

A set of unperturbed electronic eigenstates ϕ_j^0 , eigenfunctions of the QC unperturbed (gas-phase) electronic Hamiltonian matrix (\tilde{H}^0), are thus at first evaluated. These eigenstates are used as basis set for constructing the QC perturbed electronic Hamiltonian matrix (\tilde{H}) in which the perturbing effect of the environment is included:

$$\tilde{H} \simeq \tilde{H}^0 + \tilde{I}q_T\nu + \tilde{Z}_1 + \Delta V\tilde{I} \quad (1)$$

$$[\tilde{Z}_1]_{j,j'} = -\mathbf{E} \cdot \langle \phi_j^0 | \hat{\boldsymbol{\mu}} | \phi_{j'}^0 \rangle \quad (2)$$

where q_T and $\hat{\boldsymbol{\mu}}$ are the QC total charge and the dipole operator, ν and \mathbf{E} are the electrostatic potential and field, respectively, exerted by the environment on the QC center of mass at each frame of the simulation. Finally, ΔV includes all the other terms treated as a simple short range potential and \tilde{I} is the identity matrix.

The QC quantum properties in the presence of the perturbing environment (i.e., including the perturbing effect of the electrostatic potential and electric field exerted by each atom of the environment) are then recalculated: at each frame of the simulation the electronic Hamiltonian matrix \tilde{H} is constructed according to the instantaneous values of the perturbing electric field and then diagonalized producing a continuous trajectory of perturbed eigenvalues and eigenvectors to be used for evaluating whatever QC instantaneous perturbed quantum observable.

To calculate the absorption spectrum, once the perturbed frequencies (ν) and transition dipoles ($\boldsymbol{\mu}_{j,i}$) are obtained at each of the N frames of the trajectory, we can evaluate their distribution using an appropriate number of bins in the frequency space. The obtained distributions are then utilized for calculating the molar extinction coefficient $\varepsilon_{0,i}$ for the ground to the i th excited state transition,

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