



Theoretical calculation of the pyrene emission properties in different solvents



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ABSTRACT

Due to its high quantum yield and long fluorescence lifetime, pyrene molecule is a widely used fluorescence probe. From a theoretical–computational viewpoint, the modeling of its emission properties in different environments still represents a challenge, mainly because the coupling with the environment severely affects its emission behavior. We employed our computational–theoretical approach to quantitatively model the pyrene emission, which combines quantum chemical calculations with all-atom molecular dynamics simulations. Our calculated fluorescence properties, well matching the experimental data, highlight that even slight geometrical fluctuations of pyrene at room temperature can provide relevant effects on its radiative lifetime.

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1. Introduction

Pyrene, a polycyclic aromatic hydrocarbon, is an important fluorescent probe because of its high quantum yield, a long fluorescence lifetime and its sensitivity to the environment. Its emission spectrum exhibits five major vibronic bands – associated to different vibronic transitions – and their relative intensities change with the environment.

The pyrene fluorescence spectrum, although well defined, have raised in the past contradictory interpretations. The observed dependence of the relative vibronic peaks intensity present in the pyrene emission spectrum was initially explained as due to the solvent polarity, generating the so-called Py-scale [1]. More recently, such a signal variability was associated to the solute–solvent vibronic coupling [2]. In summary, the essential features of the pyrene emission signal are experimentally well reproducible and defined [3–5,2,1,6,7], but the remarkable variations of the radiative lifetimes in different solvents – spanning between tens and several hundreds of nanoseconds – is not yet fully understood [2]. Therefore, it is not surprising that several theoretical research papers focusing on the pyrene absorption and emission properties have appeared in the past [8–13]. In fact, theoretical–computational approaches can help to understand the pyrene emission

dependence on the environment at an atomistic level of detail and thus, to rationalize experimental data [14–18]. Despite differences in the calculated pyrene emission and absorption maxima in gas-phase conditions, mainly depending on the calculation details, all the theoretical works reasonably reproduce the pyrene emission and absorption essential spectrum features [10]. The effect of the environment was recently addressed by Freidzon et al. [9], showing that the experimental absorption and emission spectra of pyrene in water matrices can be well reproduced when including tens of water molecules in the quantum-mechanical calculations. However, because pyrene and similar molecules are widely used as microenvironment probe in solutions, an accurate modeling of its emission properties, and in particular its radiative lifetime, should include the dynamical coupling with the environment.

In this respect, we have recently shown that our theoretical–computational procedure, based on molecular dynamics (MD) simulations and the perturbed matrix method (PMM) [19–22], is able to reproduce the experimental absorption spectrum of pyrene in water in a quantitative manner [11]. Therefore, we apply such a procedure to the pyrene emission to shed light on its fluorescence properties. In this letter, we compare our theoretical estimates of the pyrene emission properties in gas-phase, acetonitrile, methanol and water with the experimental findings. Our procedure, confirming its ability of modeling the emission spectrum of molecules in solution [23], provides radiative lifetimes in reasonable agreement, within the noise, with the experimental data in gas-phase and in all the solvents considered in this work (i.e. acetonitrile, methanol and water) [4,5,24–29,2,30,3,31],

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pointing out that although the spectrum shape is quite insensitive to the solvent, changing only the relative vibronic peak intensities, the value of the radiative lifetime significantly depends on the pyrene structural fluctuations – affected by the interaction with the solvent – which are associated to relevant changes of its unperturbed electronic properties (the electronic properties of the isolated molecule). Noticeably, our quantum-mechanical calculations based on the density functional theory also confirm that different functionals (BLYP, gradient corrected and B3LYP, hybrid) result in quite different values of the transition dipole moments as reported in literature [10].

2. Methods

Pyrene geometry was optimized by means of Density functional theory calculations on the first excited state, using the B3LYP and BLYP functionals and the 6-31+G* basis set. For determination of the unperturbed electronic properties needed to apply the PMM method [19–22], TD-DFT calculations (with the same functionals and basis set) in the linear and quadratic response approximation were performed using the Dalton program [32]. For pyrene, the atomic charges were estimated using the ESP method of Merz–Kollman, after BLYP/6-31G* geometry optimization, and the ground state parameters available in the GROMOS 53A6 set were used for bonded and non-bonded interactions. The SPC model was used for water [33], whereas the methanol and acetonitrile models were taken from literature [34].

MD simulations, in the NVT ensemble, with fixed bond lengths [35] and a time step of 2 fs for numerical integration were performed with the GROMACS software package [36]. A nonbond pairlist cut-off of 1.1 nm was used, and the pairlist was updated every four time steps. The long-range electrostatic interactions were treated with the particle mesh Ewald method. The isokinetic temperature coupling was used to keep the temperature constant. For the simulation, an initial energy minimization of both solute and solvent has been carried out. Then, the system was gradually heated from 50 K to 300 K using short (200 ps) MD simulations. The trajectory was propagated up to 100 ns in the NVT ensemble at 300 K.

The emission spectra of pyrene in different solvents were calculated following the theoretical–computational procedure described in our recent work, where the pyrene vibronic properties in different solvents have been modeled [11]. Briefly, the unperturbed properties and the molecular dynamics simulations were combined within the PMM framework [19,18,20–22] to obtain the electronic emission spectrum. Note that, due to the high computational efficiency of the PMM procedure, we used all the MD snapshots as provided by the 100 ns long simulations. In this work, due to the relevant variations of the unperturbed electronic properties with the pyrene geometrical fluctuations, the DFT calculations were performed for 8 conformational basins as provided by means of the essential dynamics analysis [37] of the pyrene molecule (for details, see for example our previous work [38]). For each conformational basin, one representative structure was extracted and used for the calculation of the (unperturbed) isolated electronic properties (i.e. dipole moments and excitation energies), which were then used in the PMM framework, to obtain the corresponding perturbed properties. The representative structures and their corresponding isolated (unperturbed) properties are available as Supporting Information. The classical and quantum vibrational effects were estimated – in gas-phase – using a computational efficient procedure relying on the explicit evaluation of the vibrational broadening and on the Frank–Condon principle [23,39]. The default parameters as implemented in G09 were used in the calculation of the vibrational broadening and, thus the electronic dipole moment

is assumed constant during the transition (such an approximation is usually reasonable for fully-allowed transitions). In this work, the vibrational broadening, calculated only for the isolated pyrene in its optimized geometry (which is the representative structure of one of the 8 conformational basins) and added “a-posteriori” to the overall (electronic) spectrum, is considered independent both from the slight pyrene geometrical deviations and from the solvent (i.e. the vibronic contributions are not perturbed by the solvent).

3. Theory

The emission spectra of pyrene in different solvents were calculated following the theoretical–computational procedure described in our recent work, where the pyrene vibronic properties in different solvents have been modeled [11], based on the joint application of PMM and MD simulation, termed as PMM-MD method, whose theoretical basis are reported elsewhere [40,41,22,18,23,42]. PMM-MD, essentially originating from the Perturbation-Theory, similarly to the most popular QM/MM methods [43] is based on the determination of the quantum states of a pre-defined portion of a complex atomic-molecular system, e.g. the solute (hereafter termed as Quantum Centre, QC) interacting with the environment, e.g. the solvent molecules. The main peculiarity of the method is to preserve, as much as possible, both the configurational complexity of the system and a good definition of the quantum observables of the perturbed QC. For this purpose the system, e.g. the solute and the solvent, is first simulated through MD simulation in order to exhaustively explore the related configurational space. Then, after a careful and critical selection of the QC (in general – but not necessarily always – the solute molecule) a set of unperturbed (gas-phase) electronic states Φ_l^0 is evaluated using standard quantum-chemical calculations. In the simplest case the QC is a rigid (i.e. no semi-classical internal coordinates) or semi-rigid (i.e. the semiclassical internal coordinates only provide vibrations around the mean structure) species, hence not involving conformational transitions. In such a condition the unperturbed states are evaluated only at a single semi-classical QC geometry corresponding to the QC mean structure (reference structure) as obtained by the MD simulation, i.e. averaging over the semi-classical vibrations. Note that in the reference structure the quantum vibrational degrees of freedom are always relaxed at their unperturbed minimum energy positions, i.e. for each MD frame the minimum energy positions of the quantum vibrational coordinates as obtained for the unperturbed QC, at the semi-classical reference geometry, in its electronic state best corresponding to the perturbed QC electronic state involved in the MD simulation (for the *i*th perturbed state typically, but not always, the *i*th unperturbed state). Note that: (i) for fluid–liquid state systems at ordinary temperatures the molecular roto-translational coordinates can be considered as semiclassical degrees of freedom; (ii) for all the electronic states of interest we assume the same semi-classical internal coordinates, i.e. for each electronic state the corresponding quantum vibrational modes are defined within the same configurational subspace; (iii) the environment perturbation provides variations of the minimum energy positions which are negligible for electronic state calculations, hence allowing the unperturbed positions; (iv) we always consider the absorption or emission process as starting from the electronic ground or excited state in its vibrational ground state, i.e. with relaxed quantum vibrational modes. When a flexible QC is concerned, a collection of unperturbed electronic states Φ_l^{0-j} is calculated for each QC *j*th sampled conformation at the corresponding reference structure, termed as representative configuration (RC) extracted through a clustering-procedure, with each conformation hence equivalent to a semi-rigid QC. Therefore in the case of flexible QC at each MD step, the root mean square

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