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Modeling processes of non-radiative relaxation of electronically excited states of fluorescent probe 4-dimethylaminochalcone and its complexes with water using non-adiabatic molecular dynamics

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ABSTRACT

One of the most important parameters registered in fluorescent probes method is fluorescence quantum yield. For fluorescent probe DMAC (4-dimethylaminochalcone) it could vary by thousand times depending on its environment.

Fluorescence quantum yield value is defined by rates of non-radiative processes – internal conversion and intersystem crossing. Those rates could be determined using non-adiabatic molecular dynamics.

In the present work the rates of non-radiative decay from lowest excited singlet level to ground state were determined for DMAC molecule, and its complexes with one and two water molecules. Molecular dynamics modeling was performed in Newton-X package with addition of Turbomole, using TDDFT. Probability of non-adiabatic transition was obtained using Tully's fewest switches algorithm.

Various factors that can influence the rates of non-adiabatic decay were evaluated, such as energy gap between the levels, values of coupling vectors. It was shown that the probability of non-radiative transition is mostly influenced by vibrational mobility of polyene chain in the middle of the molecule. That hypothesis agrees well with experimental data.

1. Introduction

Fluorescent probes are frequently used as indicators of research object structure. Fluorescence parameters, such as its spectrum shape and quantum yield, react to changes in the probe's microenvironment. But determining the reason behind such sensitivity is often a complicated task. One approach to solving this task is computer simulation using quantum chemistry methods. That way it is possible, for example, to investigate non-radiative relaxation of lowest excited singlets through non-adiabatic transition to a ground state. This process is with the fluorescence, so the rate of non-radiative relaxation can influence the fluorescence quantum yield.

The most consistent way of modeling this relaxation is to perform molecular dynamics calculations that include the non-adiabatic events—that is, hops between adiabatic potential energy surfaces (APES) representing different electronic states. Those methods are based on an approximation, in which movement-associated vibrational degrees of freedom are modeled using Newtonian dynamics. This means, that the simulation of a vibrational wave packet is replaced with modeling of an ensemble of classical trajectories of movements along APES, which could be obtained using molecular dynamics.

For the simulation of non-adiabatic events, Tully's surface hopping algorithm of fewest switches is widely used [1]. For an acceptable approximation of a non-adiabatic process in a molecular system one has to gather an ensemble of trajectories to obtain the required statistics on probabilities of transitions between APESes.

Energy and energy gradient values, needed for such calculation, can be obtained directly during the motion along the trajectory (through "on-the-fly" gradient calculation). This method does not have any restrictions related to the size of a molecule, and can be therefore more useful for simulations of electronic excited state relaxation in an organic fluorophore.

For example, the processes of photoisomerization of azobenzene [2,3] and photochemical synthesis of vitamin D [4] were investigated this way. The Tully's surface hopping algorithm, combined with semi-empirical quantum-chemical calculations,

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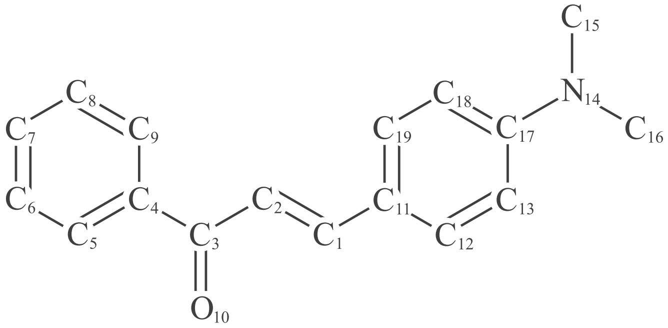

Fig. 1. Atomic numeration of a DMAC molecule.

was also used to study the non-adiabatic transitions that lead to photodegradation of adenine [5], and processes of energy redistribution in a phenylene–ethynylene dendrimer [6]. Non-adiabatic processes in condensed media (transitions in organic semiconductors) were modeled in [7].

In present study the relaxation cascade processes in photoexcited DMAC molecule were investigated for the first time by the means of nonadiabatic molecular dynamics. The probability of non-adiabatic transition from excited electronic to ground state was evaluated, i.e. the rate of non-radiative relaxation was established. To understand how the surrounding media can influence the relaxation process, we performed the molecular dynamics calculations for a single DMAC molecule, and also for its complexes with one and two water molecules. It is known that DMAC fluorescence quantum yield changes significantly upon hydrogen bond formation between the probe's carbonyl group and a water molecule. In non-polar solvents the interaction between DMAC and hydroxyl-bearing additives increases the DMAC fluorescence intensity. At the same time, in polar solvents, such as dimethylformamide or acetone, the formation of hydrogen-bonded DMAC complexes with alcohols or water decreases its quantum yield.

The factors responsible for quantum yield increase, i.e. lowering of fluorescent π–π^* state energy, were studied earlier [8]. The processes that lead to the decrease in the quantum yield are discussed in this study. DMAC structure and its atomic numeration are depicted in Fig. 1.

2. Materials and methods

Solvents used in the work were obtained from Acros Organics (>98.7% purity grade). The polarity of solvents and its mixtures had been estimated using the function of orientation polarizability [9]:

$$f(\varepsilon, n) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \left(\frac{n^2 - 1}{2n^2 + 1}\right).$$

The absorption spectra were obtained using a Beckman DU-7 spectrophotometer. The corrected steady-state fluorescence spectra were produced with a Hitachi MPF-4000 spectrofluorometer, at 20 °C and 420 nm excitation wavelength. The concentration of DMAC in all experiments was 3.5 μM.

DMAC fluorescence quantum yield in solvents was calculated from steady state fluorescent data by comparison with a standard known quantum yield [9]. The quantum yield of DMAC luminescence in acetone was used as the standard [10].

Molecular dynamics calculations and accessing of nonadiabatic transition probabilities by Tully's method were performed using Newton-X software package [11]. Calculations were performed using Lomonosov's MSU supercomputer center resources [12]. Wave function and energy gradients on every step of the molecular dynamics were calculated using TDDFT method with BHLYP functional in def2-SVP basis using Turbomole [13]. Andersen thermostat [14] was employed throughout the calculation with time constant 5 fs and temperature of 300 K.

In previous works, analysis of electronic orbitals' shape and properties was performed for a single DMAC molecule [15] and its complexes with water [8]. The analysis determined that the lowest singlet $^1(\pi\pi^*)$ state of DMAC is dominated by intramolecular charge transfer (ICT). It is known that the precision of TDDFT method used in the present work is sometimes unsatisfactory for excited states dominated by ICT [16]. To determine whether TDDFT results could be considered valid, a comparison of excitation energy for DMAC lowest singlet state, calculated by TDDFT and more rigorous ab-initio calculation method RICC2 (coupled clusters method CC2 with resolution of identity, RI [17]), was performed, and did not reveal any significant difference. The comparison itself is contained below in the results section. The corresponding comparative RICC2 calculations were performed using Turbomole in the same basis (def2-SVP) as TDDFT for 100 equidistant points on a single randomly chosen trajectory, sampled every 5 fs.

Three sets of 100 molecular dynamics trajectories were obtained—one for a single DMAC molecule, one for DMAC complex with single water molecule and one for DMAC complex with two water molecules. Each trajectory was 500 fs long, with a 0.5 fs step. Initial conditions were set differently for each trajectory. To obtain the initial conditions, first, a minimum was located on the ground state APES, and normal vibrational modes were calculated in that point. Then, the initial deviations and velocities were determined using Monte-Carlo procedure from Wigner distribution for a multi-dimensional harmonic oscillator with zero vibrational quantum numbers [18]. Such choice of initial conditions means that in accordance with Franck–Condon principle the photo excitation of the molecule causes an instantaneous transition from one APES to another with conservation of atom's instantaneous velocities and coordinates at the moment of transition. Visualization of molecular dynamics was performed using VMD [19].

To evaluate a kinetic parameter of molecular system transition from lowest excited to ground state, the simple exponential decay kinetic model $P = \exp(-t/\tau_0)$ was assumed. At each step of a trajectory the probability of the nonadiabatic transition from first excited to the ground state was evaluated. Since the probabilities turned out to be rather small, it was not expected that Tully's fewest switches algorithm would perform a switch to the ground state during a simulation of an acceptable duration. That implies a situation in which the trajectory length is sufficiently smaller than the expected lifetime of excited state. In such case one could obtain the initial portion of the excited state decay curve by plotting the time dependency of probability P_Π for the system to remain on the excited state APES after N steps, where

$$P_{\prod} = \prod_{i=1}^{N} (1 - p_i).$$

here p_i is the probability of non-adiabatic transition to the ground state at each step of molecular dynamics trajectory. Probability for an ensemble of trajectories was determined by averaging over all trajectories. This value can also be interpreted as the size of the excited state population. Since trajectory length is significantly shorter than the characteristic decay time of the excited state τ_0, the obtained plot of probability P_Π vs. simulation time is close to the straight line, which is tangential to the decay exponent at $t = 0$. The characteristic decay time for the excited state population (by nonadiabatic relaxation into the ground state) can be determined from the slope ratio of this line: $t_g(\varphi) = 1/\tau_0$.

The non-adiabatic coupling vectors (ground state with first excited singlet) were calculated in the framework of TDDFT