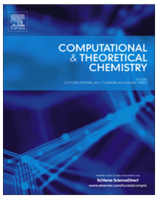
Computational and Theoretical Chemistry 1115 (2017) 197–207

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Time-evolution study of photoinduced charge-transfer in tertiary amine-fluorophore systems

Demeter Tzeli *, Theodoros Mercouris, Giannoula Theodorakopoulos, Ioannis D. Petsalakis *

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., Athens 116 35, Greece

ARTICLE INFO

Article history:
Received 9 June 2017
Received in revised form 22 June 2017
Accepted 22 June 2017
Available online 27 June 2017

Keywords:
Photoinduced charge transfer
Sensors
Tertiary amine-pyrene molecules
Fluorophores
DFT
Calculations

ABSTRACT

Photoinduced charge transfer in a fluorescent sensor of organophosphorus nerve agents is examined by solution of the time dependent Schrödinger equation, under the influence of an external electromagnetic field and employing potential energy curves obtained by density functional theory (DFT) and time dependent DFT (TDDFT) calculations for the ground and the excited states, respectively. The systems of interest here consist of a tertiary amine-pyrene molecule, with different numbers of CH_2 spacer units between the t-amine and the pyrene. Quenching of pyrene emission has been observed in these systems, to different extent depending on the number of spacer units, which is due to photoinduced electron transfer from the t-amine to pyrene. Here, we present a new approach based on time-evolution for the explanation of the experimental observation of the quenching of pyrene emission. In this work the inversion coordinate at nitrogen is considered as a generalized coordinate for the charge-transfer process. Vibrational levels, dipole moments and dipole transition moments of the ground, excited, and charge transfer electronic states along the inversion coordinate are computed by DFT and TDDFT calculations. The time evolution of the excitation probability between the vibrational levels of the ground state and the first excited state and the charge transfer state has been calculated for different excitation frequencies. The results are in agreement with experimental observations regarding the photoinduced electron transfer and decreasing probability for charge transfer with increasing number of CH_2 spacer units between the t-amine and the pyrene.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Intramolecular or intermolecular electron or charge transfer reactions are very important in biological processes, [1] in material science, [2] in the fabrication of optoelectronic devices, [3] in energy convention, [4,5] in chemical sensors and fluorescent probes [5–8]. In the last decades a lot of research has been conducted on the study of intramolecular electron or charge transfer between a group that acts as an electron donor and a group that acts as an electron acceptor connected by a spacer, i.e., molecular bridge [7–14].

Photoinduced electron transfer, [15–22] or PET, may be described as follows: there is a system consisting of an electron donor (D) part and an electron acceptor (A). The whole system is in the ground state. In some cases, e.g. the case of *photovoltaics*, the first step is absorption of radiation to yield an excited state corresponding to excitation of the donor part ($D \rightarrow D^*$). Then the system is converted fully or partially to a CT state where an electron or a part of electron charge is transferred from D^* to A ($D^* \rightarrow D^+\text{-}A^-$). In the case of *fluorescent sensors*, which are the systems of interest of the present work, the acceptor moiety absorbs light and emission by $A*$ is *suppressed* by PET from D to A, see Scheme 1. Sensing involves a chemical reaction that prevents the PET process and hence enhances emission.

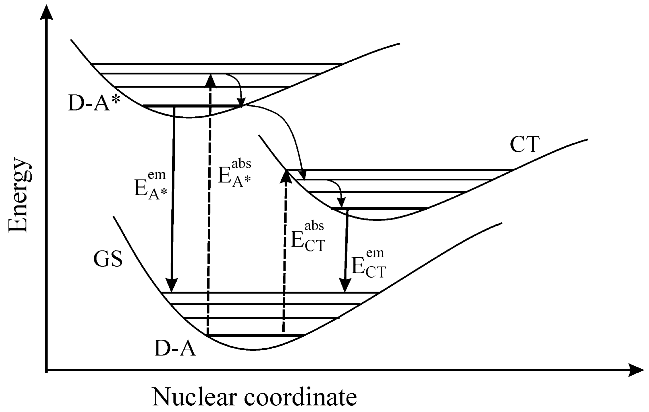
There are different theories aiming the treatment of and understanding of charge transfer (CT) phenomena, for a review see Ref. [15] and reference therein. Most commonly the theory of R. A. Marcus [23] for the calculation of the rates of charge transfer has been evoked over the past 50 years. This theory is based on a model of coupling between the electronic potential energy surfaces of donor and acceptor states, and application of this model would require detailed knowledge of the potential energy surfaces of the electronic states of the donor and acceptor systems, something, however, which is practically impossible to achieve for polyatomic systems, with the existing theoretical methods. The normal practice is to draw simplified schematic diagrams of the variation of energy along a one-dimensional "reaction coordinate" or a generalized coordinate, corresponding to the most critical nuclear motion accompanying the electron transfer process and proceed

---

* Corresponding authors.

E-mail addresses: dtzeli@eie.gr (D. Tzeli), idpet@eie.gr (I.D. Petsalakis).

http://dx.doi.org/10.1016/j.comptc.2017.06.019
2210-271X/© 2017 Elsevier B.V. All rights reserved.

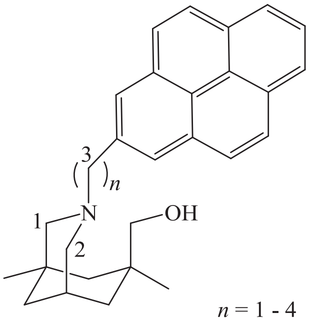


Scheme 1. Photoinduced electron transfer for fluorescent sensors.

in this manner. In the present work we will follow this approach, namely by employing a one-dimensional reaction coordinate for the study of PET in a fluorescent sensor.

In our previous study, [8] we have studied via DFT and TDDFT calculations a series of tertiary amine-fluorophore systems that exhibit suppression of emission due to a photoinduced electron transfer (PET) process from amine to the fluorophore. In the case of pyrene as the fluorophore, cf. Scheme 1 below, it was shown that the PET process, indicated by a change in the character of the excited state, accompanies its geometry optimization. In agreement with the experimental observations the suppression of emission diminishes with the number of the aliphatic spacers between the amine and pyrene [7]. In Ref. [8] the geometries of the minimum structures of the ground state and of the charge transfer (CT) state were computed. Additionally, the absorption transitions from the ground to low-lying excited electronic states at the geometry of the minimum structures of the ground state and the emission transition at the minimum of the CT state were calculated at the B3LYP/def2-SVP level of theory.

Here, we present a new approach for the explanation of the suppression of emission based on time-evolution. We examine the photoinduced charge transfer in the system of interest, (Scheme 2), by solution of the time-dependent Schrödinger equation including an external electromagnetic field to simulate the absorption of light, in order to determine the evolution of the population of the charge transfer state for different exciting frequencies and for different spacer units between the t-amine and pyrene. The variation of energy along a "reaction coordinate" or a generalized coordinate, corresponding to the most critical nuclear motion for the electron transfer process will be calculated with the excitation probability of the charge transfer state obtained by time evolution calculations, described below. Here we focus on the calculation of the optimized path from the 1st excited state, corresponding to absorption by pyrene, to the CT state. In our previous study [8] only the minimum energy structure of the CT state was calculated. Here we focus also on the calculation of the vibrational levels of the calculated curves and on the change of the absorption and emission spectra as well as the variation of the dipole moments along the path. The approximate model considered here is relevant to the actual process since it has been found that the important geometric feature accompanying the electron transfer is planarity at N [8].



Scheme 2. Calculated structures of the **1C**-**4C** molecules.

2. Computational details

The tertiary amine alcohols of pyrene (cf. Scheme 2) having one to four CH_2 units as spacers have been computed via DFT and TDDFT calculations using the B3LYP, [24] CAM-B3LYP, [25] PBE0, [26] and M06-2X [27] functionals in conjunction with the 6-31G(d,p) basis set [28]. The four systems were fully optimized in the ground, the first excited and the CT states. It was demonstrated previously that the critical geometry variation accompanying the potential energy surface (PES) in these systems is the pyramidalization at the nitrogen atom, where a nearly planar conformation at N corresponds to the geometry of the CT state. Therefore a generalized reaction coordinate, cf. Marcus's theory for charge transfer processes, [23] is defined by the pyramidalization motion at the N atom, and more specifically the generalized coordinate here is given by the dihedral angle around the N atom which is the dihedral angle between the C_1NC_3 and C_2NC_3 planes. The potential energy curves along the generalized coordinate have been determined for the ground, the first excited and the charge transfer (CT) states, and will be discussed below. For these curves, full geometry optimization (except for the $C_1NC_3C_2$ dihedral angle) was carried out at each point.

The applicability of the B3LYP functional was tested in our previous study [8] by comparison of the theoretical results with experimental quantities, [7] also see below, and it was found to be sufficient for the calculation of the minimum energy structures in the ground and the CT state of the present system. It is well established [25] that use of the B3LYP functional yields good excitation energies except for the charge-transfer states where it leads to underestimation of the excitation energy. On the other hand, functionals more appropriate for the charge-transfer states, e.g. CAM-B3LYP, can lead to an overestimation of the excitation energies [29,30]. The applicability of B3LYP, CAM-B3LYP, PBE0 and M06-2X functionals were tested here for the pyrene molecule, see Table 1S and Fig. 1S of the Electronic Supplementary Material (ESM). The absorption spectrum of pyrene using the B3LYP functional has been calculated before [31]. A detailed study of the absorption and emission spectra of pyrene using a variety of TDDFT functionals and ab initio methodologies such as coupled cluster, multi-reference configuration interaction methodologies have been published by our group [32]. Experimentally [33] has been found that the absorption spectra of pyrene present two close lying bands, a weak first absorption band and an intense second absorption band. Both B3LYP and PBE0 predict absorption maxima in good agreement with the experiment, [33] while M06-2X and CAM-B3LYP overestimate the excitation energy values, see Table 1S of the ESM. However, B3LYP and PBE0 interchange the order of the two bands while M06-2X and CAM-B3LYP predict the correct order of the bands, but the excitation energies are overestimated. A comprehensive comparison of different theoretical approaches employed on the calculation of the lowest two electronic states of pyrene has been presented previously [32]. It is well known that there are factors that cause a certain degree of allowance or forbiddenness to absorption and emission [34]. If the planarity of the pyrene group changes slightly, the oscillator strengths and the order of the bands can change, too [34,35]. In

Download English Version:

https://daneshyari.com/en/article/5392330

Download Persian Version:

https://daneshyari.com/article/5392330

Daneshyari.com