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Theoretical DFT study of phosphorescence from porphyrins

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Abstract

Geometrical structure of free-base porphin (H_2P) and Mg- and Zn-porphyrins together with their vibrational frequencies and vibronic intensities in phosphorescence are investigated by density functions theory (DFT) with the standard B3LYP functional. These molecules have a closed-shell singlet ground state (S_0) and low-lying triplet (T_1) excited states of $\pi\pi^*$ type. The S_0–T_1 transition probability and radiative lifetime of phosphorescence (τ_p) of these molecules are calculated by time-dependent DFT utilizing quadratic response functions for account of spin–orbit coupling (SOC) and electric-dipole transition moments including displacements along active vibrational modes. The infrared and Raman spectra in the ground singlet and first excited triplet states are also studied for proper assignment of vibronic patterns. The long radiative lifetime of free-base porphin phosphorescence ($\tau_p \sim 360$ s at low temperature limit, 4.2 K) gets considerably shorter for the metalloporphyrins. An order of magnitude reduction of τ_p is predicted for Mg-porphyrin but no change of phosphorescence polarization is found. A forty times enhancement of the radiative phosphorescence rate constant is obtained for Zn-porphyrin in comparison with the H_2P molecule which is accompanied by a strong change of polarization and spin-sublevel radiative activity. A strong vibronic activity of free-base porphin phosphorescence is found for the b_{2g} mode at 430 cm^{-1}, while the 679 and 715 cm^{-1} vibronic bands of b_{3g} symmetry are less active. These and other out-of-plane vibrations produce considerable changes in the radiative constants of different spin sublevels of the triplet state; they also promote the $S_1 \rightarrow T_1$ intersystem crossing. Among the in-plane vibrations the a_g mode at 1614 cm^{-1} is found very active; it produces a long progression in the phosphorescence spectrum. The time-dependent DFT calculations explain the effects of the transition metal atom on phosphorescence of porphyrins and reproduce differences in their phosphorescence and EPR spectra.

Keywords: Free-base porphin; Mg-porphyrin; Zn-porphyrin; Phosphorescence; Radiative lifetime; Vibronic bands

1. Introduction

Porphyrins constitute an important class of π-conjugated organic chromophores, which can be doped by metal ions. These derivatives are involved in a number of biological processes (photosynthesis, dioxygen transport and activation) which are of crucial importance for the Earth biosphere [1–3]. In recent time the porphyrins have been employed for applications in dye industry, solar energy conversion, artificial photosynthesis, photodynamic therapy, electrooptics and nonlinear optics [4–6], to mention a few out of many examples. To elucidate the mechanisms of this biophotonics and biomachinery, the electronic structure and spectra of porphyrins have been widely investigated [2–20].

Studies of triplet state spectroscopy present most interesting aspects of porphyrins [4,8–14]. The intense triplet–triplet (T–T) absorption in the visible region is now utilized in nonlinear optical devices and optical storage applications [4,8,9]. Lifetimes of triplet-excited porphyrins and triplet quantum yields are important quantities also in photobiology since they determine the singlet oxygen $O_2(^1\Delta_g)$ generation [1,6,21] under

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irradiation of tissues with visible light. High concentration of porphyrin pigments in the skin and in the blood can cause damage by the $O_2(^1\Delta_g)$ generation upon light, since the singlet oxygen is a hazardous molecule that oxidizes biopolymers [1,6]. In cancer treatment with photodynamic therapy the $O_2(^1\Delta_g)$ generation by porphyrins is used in a controlled manner to oxidize a tumor [1,22].

Porphyrin derivatives which contain zinc, palladium and platinum ions are known to exhibit phosphorescence even at room temperature (zinc - to a less extent) [2,4,11–14]. The phosphorescence (radiative transition from the first excited triplet state, T_1, to the ground singlet state, S_0), depends on spin–orbit coupling (SOC), which increases with atomic number. This notion explains the so-called heavy atom effect [23], which is observed also in phosphorescence of porphyrins [2,12,24]. At the same time the closed shell porphyrins without heavy atoms provide some exception from common rules of luminescence of organic π-conjugated compounds [10,12,13]. Such porphyrins have extremely weak phosphorescence though they have a very efficient nonradiative $S_1 \rightsquigarrow T_1$ intersystem crossing [12,25]. For example, free-base porphin (H_2P), which is the basic building block and the electronic "heart" of porphyrins, has a quantum yield of the intersystem crossing equal to 0.9 [25], which is typical for many other tetrapyrrole compounds [10,14]. The weak phosphorescence means that sufficient triplet state population can be created by high-intensity laser sources [4,8] and intense T–T absorption can make the transparent porphyrins become opaque in some part of the visible spectrum. Thus, the efficient intersystem crossing of porphyrins, which maintains a high concentration of triplet-excited molecules, is used in a wide variety of applications from photodynamic therapy to nonlinear optics and optical limiting devices [8].

The photophysical properties of porphyrins are not completely understood in spite of their fundamental significance for numerous applications [10,12,26,27]. The main puzzle of the luminescence of porphyrin free-bases and their complexes with light metals (Mg, Al) is connected with the question why their $T_1 \to S_0$ decay is almost completely dark in solid organic solvents [13], though these molecules have nitrogen atoms with lone pairs of electrons. Usually such molecules with *n*-electrons exhibit strong phosphorescence with a relatively short lifetime because of the effective SOC-induced mixing between $^1n\pi^*$ and $^3\pi\pi^*$ states [23].

The study of luminescence of porphyrins and their relative fluorescence and phosphorescence intensities was pioneered by Becker et al. [28–31]. They established that only porphyrins with heavy metal ions exhibit appreciable phosphorescence. In porphyrins with a diamagnetic ground state, the phosphorescence grows with the weight of the ion. van der Waals et al. [13,32] studied the fine structure and kinetics of populating and depopulating of the lowest triplet state of free-base porphin from a pulsed microwave technique. They analyzed transient changes in the fluorescence intensity induced by microwaves, which depend on the S_1–T_1 coupling, but did not detect phosphorescence itself in *n*-octane at 1.3 K [13]. Tsvirko et al. [12,25] detected phosphorescence of many porphyrin free bases in EPA and other organic solids. They found the phosphorescence quantum yield to be equal to about $\phi_p \sim 10^{-4}$. Since the measured phosphorescence lifetime (τ) is of the order 0.1 s this leads to a very small radiative rate constant of phosphorescence $k_p = \phi_p/\tau \sim 0.001\ s^{-1}$. Even pure hydrocarbons (benzene, naphthalene) have higher k_p values (0.1–0.01 s^{-1}) [23,33].

The time-dependent DFT calculations with quadratic response functions [33–37] can be useful in solving this puzzle in order to understand the very weak phosphorescence of free-base porphin and its strong sensitivity to the external heavy atom effect. For more systematic studies of the photophysics of porphyrins one needs to consider the vibrational movements and their interaction with electrons and spins.

Infrared (IR) and Raman spectra of porphyrins are now well documented and analyzed [20,24,38–41,43–45]. The knowledge of the force field, vibrational frequencies and their intensities are important for correlating IR and Raman spectroscopy measurements with structural information and with luminescence vibronic activity. It is difficult to obtain the empirical force field for such large molecules like porphyrins, making quantum chemical calculations of the force constants the only effective way to solve the problem [20]. Pulay et al. [20,44,45] calculated the force field of free-base porphin (H_2P) and metalloporphyrins by the DFT B3LYP method [46,47] with the 6-31G* basis set [48]. For the Zn ion [20] they used the TZV basis set of Ahlrichs group [49]. Using scaling factors optimized on the H_2P isotopomers Pulay et al. [44,45] interpreted the IR active fundamental frequencies (a_{2u},e_u) and Raman spectra (a_{1g},b_{1g},b_{2g},e_g) in agreement with empirical force fields [40,43]. Time-resolved resonance Raman spectra recently applied to excited states of porphyrins [50–52] provide very important information about changes of vibrational modes on excitation to the triplet state. The simplest molecule studied so far is free-base octaethylporphyrin [50]. Though the time-resolved resonance Raman spectra are not available for the molecules studied in the present work, we will make a qualitative comparison of our triplet state data with those known for more complicated derivatives [50–52].

In this paper, we are going to address the issue of triplet state radiative properties and calculate the $T_1 \to S_0$ transition dipole moments of a number of porphyrins in the framework of time-dependent DFT using quadratic response (QR) functions. This method has