

A DFT study on the vibrational spectroscopy of protoporphyrin IX

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Abstract

Infrared and Raman spectra of protoporphyrin IX were recorded. DFT quantum chemical calculations were performed. Optimised molecular geometry, electric charge distribution, vibrational force constants were computed. The normal coordinate analysis and the scaling of the force constants yielded all the necessary data for the simulation of the infrared and Raman spectra and the potential energy distribution calculations. The result was the interpretation of all vibrational modes of the molecule. Conclusions were drawn from the difficulties arisen during the assignment of the vibrational spectra of such large molecules.

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1. Introduction

Protoporphyrin IX (PPP) is an important component of hemoglobin. Hemoglobin is an iron contained oxygen-transport metalloprotein in the red blood cells. The iron-PPP (heme, more precisely heme B) is the prosthetic group of this metalloprotein.

The articles dealing with porphyrin and PPP pay more attention on the metal complexes of PPP and on porphyrins and less on PPP itself. Only few articles were published about the vibrational spectroscopy and the quantum chemistry of the free porphyrin base and non-metal complexes of PPP.

We found only one article dealing with the experimental molecular geometry of the non-complexed PPP. Caughey and Ibers [1] measured the crystal and molecular structure of the dimethyl ester of PPP (DME-PPP) together with that of the porphyrin base with X-ray diffraction. According to their results, the unit cell contains two DME-PPP molecules. It crystallizes in the triclinic space group $C_1^1 = P\bar{1}$. The authors established that, the vinyl groups in DME-PPP are not coplanar with the porphyrin core.

Some articles dealt with the calculation of the structure of PPP metal complexes. Olkhova et al. [2] carried out molecular dynamic calculations and for one input data set of this calcula-

tions they computed the optimised structure of heme (Fe-PPP) using 3-21G basis set. They did not present these results. Jensen and Ryde [3] applied DFT calculations for the comparison of the properties of the three tetrapyrroles, most important in biology: iron porphyrin, cobalt corrin and nickel hydrocorphine. Their geometric, electronic and functional properties were computed. The results revealed that the porphyrin ring shows the lowest flexibility of them.

Several authors recorded spectra of PPP metal complexes. Bizzarri and Cannistraro [4] studied the surface enhanced resonance Raman spectra (SERRS) of iron-PPP. They found that the spectra exhibit drastic temporal fluctuations. They revealed the fluctuations arose from the colloid continuum. Larsen et al. [5] used optical absorption and UV-resonance Raman spectroscopies (UV-RRS) for the study of the steady state optical absorption and transition vibrational states of CO-Fe-PPP. Their results refer to the formation of a five coordinate and high-spin transient species. de Vito et al. [6] examined the peripheral vinyl stretch frequencies of PPP on the bis(cyanide) complexes of iron-PPP and 2-methyl-2-devinyl iron-PP. They applied similarly UV (220 nm) excited resonance Raman spectroscopy. Their results suggested that the two vinyl groups of PPP are vibrationally decoupled. Li and Imae [7] investigated zinc-PPP in air/water interface and in LB films. Long alkyl chain surfactants were used to Langmuir monolayer and LB film behaviours. The FT-IR spectra of the LB monolayers suggested the transformation of the PPP carboxylic acids groups into carboxylates.

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Radziszewski et al. [8] measured the polarized infrared spectra of the free-base porphyrin and some of its hydrogen and nitrogen substituted isotopomers in xenon matrix. They calculated the vibrational frequencies of the molecule using ab initio HF/3-21G* method and basis set. The force constants were scaled and the recalculation of the isotopomer frequencies proved the applicability of the force field.

Li et al. [9] elaborated a consistent porphyrin vibrational force field. The calculation of the force field was based on XRD geometric parameters and resonance Raman spectroscopic data. Spectra of Ni-porphyrin and tetraphenyl Ni-porphyrin and some of their isotopomers were measured. It was concluded that the phenyl groups have little influence on the porphyrin skeletal mode frequencies. In their next article [10] they applied the force field to the octaethyl derivative of Ni-porphyrin and some of its isotopomers. They concluded that the ethyl group has a marked influence on the low-frequency region of the vibrational spectra.

The same working group published [11] the in-plane normal modes of porphyrin base applying XRD measured geometric parameters and the vibronic and infrared spectra of several deuterated derivatives. They concluded that there are three types of metal sensitive frequencies of the porphyrin base: sensitive to the metal size, to the metal-ring d-r⁺ backbonding, and to the strength of the metal–nitrogen bond.

There exist calculations also on more complicated PPP derivatives. Harris et al. [12] calculated the optimised geometry of a PPP derivative, the oxyferryl methylmercaptide PPP in $S=1/2$ and $S=3/2$ electronic states using the DFT method with BPW91 functional. They simulated also the electronic spectrum of the compound. Pudzianowski [13] calculated PPP-based models for cytochrom P-450 iron-binding inhibitors. The iron(III) PPP low-spin doublet state with constant ethyl sulfide ligand was completed with second ligands, e.g. imidazoles and pyridines. The structures of the complexes were computed with the SAM1 semiempirical method. These ligands replace the water molecule since they bonds to the iron are stronger. Therefore they block the P-450 enzyme catalyzed cycle.

To our best knowledge up to now article was not published that dealt with the quantum chemically supported assignment of the vibrational spectra of PPP.

2. Experimental

The applied protoporphyrin IX was the product of Aldrich Chemical Company and was applied without any further purification.

Infrared spectra of the compound were recorded in the medium IR region on a Nicolet Magna 750-FT-IR spectrometer in the 4000–400 cm⁻¹ region with 4 cm⁻¹ resolution in KBr pellet. Far infrared spectra were measured on a Bio-Rad Digilab FTS 40 spectrometer in the 500–100 cm⁻¹ region with 2 cm⁻¹ resolution in “Nujol” suspension.

Raman spectra were recorded using a Labram type Raman microscope of Jobin–Yvon. The spectra were measured with the fIXD310 microscope objective in the 4000–150 cm⁻¹ region and excited with the 1064 nm line of the Nd:YAG laser.

3. Calculations

For the quantum chemical calculations the Gaussian program package [14] was applied, with the DFT Becke3LYP functional and the 3-21G* standard basis set.

During the first step of the calculations the molecular geometry was optimised and the charge distribution was calculated using both Mulliken's approach [15] and the natural bond orbital (NBO) model [16] and the molecular energy. The most important results of the second step were the (unscaled) vibrational frequencies, the vibrational force constants and the thermodynamic functions of the molecule.

The yielded quantum chemical results needed further elaboration. Internal coordinates were defined for the molecule. The force constants were transformed into this coordinate system. The inverse kinetic energy matrix (G matrix) was calculated, based on the optimised molecular geometry, similarly in this system. The force constants (F matrix) were scaled to the experimental vibrational frequencies. For the characterization of the vibrational modes the potential energy distributions (PED matrix) were also calculated. Simulated infrared and Raman spectra were performed for the visualization of the results and comparison with the experimental ones. These calculations were carried out with home made computer programs.

The complicate experimental spectral bands were resolved.

4. Results and discussion

4.1. Molecular structure

Protoporphyrin IX is a relatively large molecule. It contains 76 atoms. Their numbering is presented in Fig. 1, the shape of the optimised B3LYP/3-21G* structure is shown in Fig. 2.

The optimised molecular parameters are listed in Table S1. This table includes also the X-ray data of the PPP dimethyl ester [1] and the results of our B3LYP/3-21G* calculations. The very large table is deposited. The skeleton of the molecule (atoms numbered from 1 to 24) is planar. One of the carboxylic groups (atoms numbered from 49 to 52) is coplanar with the skeleton, while the other one (atoms numbered from 59 to 62) is perpendicular to it. A hydrogen bond exists between the two carboxylic groups. The distance between the two head atoms H₆₂ and O₅₁ was found 1.724 Å (see Fig. 1). Comparing the calculated and the measured results, the deviations between the corresponding bond lengths and valence angles are in the magnitude of hundred of angstroms or some degrees, respectively. These distances reflect the difference in the state of the molecule and the quantum chemical approximation. Only one exclusion exists, the carbon–carbon distances of the vinyl groups. The measured C₃₄–C₃₆ distance is 1.225 Å, while the calculated is 1.340 Å. The corresponding values are for the C₅₉–C₆₁ bond length 1.290 and 1.339 Å, respectively. The measured bond lengths are in the magnitude of a C–C triple bond length and are between the length of a triple and a double C–C bond, respectively. Therefore our calculated bond lengths seem more realistic than the measured ones.

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