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Applications of Magnetic Circular Dichroism for Studies of Organic Molecules

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Abstract. Magnetic circular dichroism (MCD) spectroscopy provides extended information about molecular electronic structure and transitions. Because the chirality is induced by static magnetic field it can also be used for non-chiral compounds. However, interpretation of the spectra is difficult, and precise computations using quantum mechanical approaches were implemented in publicly available software packages only recently. We present introduction to the theory of MCD, explaining physical origins of the phenomenon. The ADF and Dalton software packages available for first principle calculations of MCD are compared. A short overview of the instrumentation is given. Finally we give an example of our ongoing study on 5,10,15,20-tetraphenyl-21H,23H-porphyrintetrasulfonic acid (TPPS) and its protonated, where the MCD spectra were interpreted by TDDFT (time dependent density functional theory).

Introduction

Magnetic circular dichroism (MCD) spectroscopy is a method which uses circularly polarized light to study transitions between molecular states. In contrast to other chiroptical spectroscopies like ECD (Electronic Circular Dichroism), VCD (Vibrational Circular Dichroism) or ROA (Raman Optical Activity) it can study nonchiral molecules. The effect of MCD can be observed as different absorption of right- and left- circularly polarized light by the system in a static magnetic field oriented along the direction of propagation of the measuring light beam. MCD can be observed for number of molecular transitions, and in a wide spectral range. X-ray MCD is used in studies of solid state materials where it can probe the magnetic properties of the matter [*Funk, 2005*]. UV-vis and near IR region is characteristic for valence shell electronic transitions. MCD in this spectral range is usually used in studies of molecules in diluted solutions, much like absorption or ECD measurements. Finally, one can measure MCD even in mid IR region, and observe the effect of magnetic field on the vibrational transitions [*Bour, 1996*]. In our laboratory we are focusing on the most usual UV-vis MCD measurements.

History of MCD is dated back to the times of Michael Faraday when he in 1845 observed that linearly polarized light was rotated by application of a longitudinal magnetic field. This effect, referred to as the magneto-optical rotation (MOR), was the first experimental evidence of a relation between electromagnetism and light. Dependence of MOR on the wavelength—so called MORD (Magnetic Optical Rotatory Dispersion)—is related to the MCD spectrum by Kramers-Kronig relations, similarly as the natural circular dichroism is related to the optical rotatory dispersion [*Buckingham, 1966*].

First theoretical explanations of MCD were attempted in 1930s [*Serber, 1932*]. Before the quantum mechanics fully developed to be able to describe molecules exactly, semiempirical approaches to interpretation of MCD were proposed [*Michl, 1978a; Michl, 1978b*]. In spite of the complicated MCD expressions, the complete theory was recently implemented in common quantum chemical software [*Dalton; ADF*; *Seth, 2008*a–*c*].

In recent years a lot of work has been done on calculating of MCD of metaloporphyrins [*Solheim, 2008*], [*Peralta, 2007*], but much less on free base species. In our laboratory, we are currently studying effects of protonation of free-base 5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine-*p*,*p'*,*p''*,*p'''*-tetrasulfonic acid (TPPS) (Fig. 1). Because the phenyl-sulfogroups are relatively strongly acidic, they are not protonated until very low pH. The protonation occurs on the nitrogen atoms of the central ring [*Farjtabar, 2010*]. While there have been some studies of protonation of 5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine (TPP) [*Mack, 2005*] to the best of our knowledge there are no MCD studies with TPPS.

Theory

The theory of MCD is complicated by many terms that have to be included, and for detailed derivation we refer the reader to ref. [*Stephens, 1970*]. MCD is usually described by three parameters, denoted by $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$. Each of these parameters is obtained by differentiation of the transition probability (Fermi golden rule). For the light, we have to use the time dependent perturbation theory. There is also present a second perturbation in the form of the static magnetic field. Total Hamiltonian of the system can then written as sum of the time dependent and time independent parts,

$$\hat{H}(t) = \hat{H}_1 + \hat{H}_2(t)\,. \tag{1}$$

$\hat{H}_1$ contains all terms independent of the light field, including possible spin effects. We will neglect these relativistic effects, which are in detail analyzed elsewhere [*Seth, 2008C*]. We assume that we know the eigenfunctions of $\hat{H}_1$. Using these states we can apply the time dependent perturbation theory and obtain the transition rate from ground state to the continuum of states, proportional to the molar absorption coefficient ε.

$$\varepsilon_{\pm} = \eta \frac{N_a - N_j}{N}\left(\left|\left\langle a \mid \hat{\mu}_x \pm i\hat{\mu}_y \mid j\right\rangle\right|^2\right)\rho(E) \tag{2}$$

N_a and N_j are number of molecules in ground state $\left|a\right\rangle$ and excites state $\left|j\right\rangle$ respectively. Total number of molecules is N. $\hat{\mu}_x, \hat{\mu}_y$ are electronic transition dipole moment operators in x and y direction respectively, $\rho(E)$ is function describing the shape of the absorption band associated with the transition, *E* is energy, η is a factor containing fundamental physical constants.

Magnetic field affects the states of the molecule, their populations and band shape function. We will now look how these quantities are changed when molecule is put into nonzero magnetic field and how we can relate these changes to the field free quantities.

First, we consider the effect of magnetic field on the populations of molecules in states $\left|a\right\rangle$ and $\left|j\right\rangle$. If the electronic levels are well separated, i.e. non-degenerate, there is usually no effect on the populations, because the electronic energies are much larger than the magnetic perturbation and Boltzmann *kT* factor. However, if the states are degenerate, application of the magnetic field will result in breaking of the degeneracy, i.e. splitting of the electronic levels. For usual fields B the splitting will be small, and the resulting levels will be thermally accessible at the room temperature. We express these energy shifts using standard time independent perturbation theory. We introduce subscript λ to distinguish degenerate levels of the state $\left|a\right\rangle$ and superscript ^{0} for field-free quantities. For field-free λ—fold degenerate ground state $\left|a_\lambda^0\right\rangle$ with field-free energy E_a^0 the partition function in the presence of magnetic field B in the direction of *z*-axis is

$$Q = \sum_{\lambda} \exp(-E_a^0/kT + \left\langle a_\lambda^0 \mid \hat{m}_z \mid a_\lambda^0\right\rangle B/kT)\,, \tag{3}$$

where k is the Boltzmann constant, T is temperature and $\hat{m}_z$ is the *z*-component of the magnetic dipole moment operator. Assuming that there are no electronically excited molecules, we can write

$$\frac{N_{a\lambda} - N_j}{\sum_{\lambda} N_{a\lambda}} \approx \frac{N_{a\lambda}}{\sum_{\lambda} N_{a\lambda}} = e^{-E_a^0/kT + \left\langle a_\lambda^0|\hat{m}_z|a_\lambda^0\right\rangle B/kT} / Q \tag{4}$$

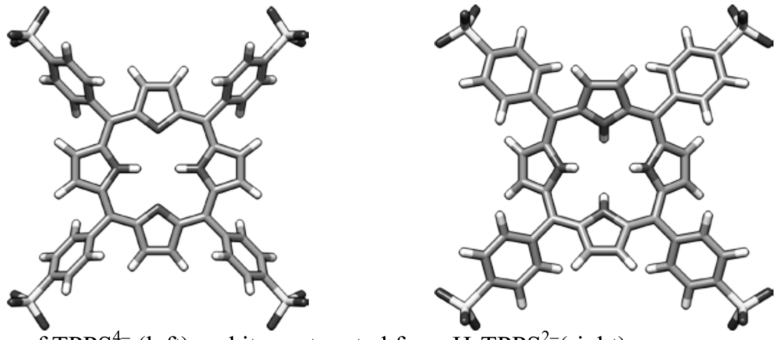

Figure 1. The structure of TPPS^{4-} (left) and its protonated form H$_2$TPPS^{2-}(right).

For small fields we can expand exponential function using Taylor expansion and to the first order in B we obtain

$$\frac{N_{a\lambda}-N_j}{N}\sim\frac{1}{|n_{a\lambda}|}\left(1+\left\langle a_\lambda^0\,|\,\hat{m}_z\,|\,a_\lambda^0\right\rangle B/kT\right),\tag{5}$$

where $n_{a\lambda}$ is number of degenerate sublevels of $\left|a\right\rangle$. Now, we will look at how the eigenfunctions of $\hat{H}_0$ relate to the unperturbed functions of field free Hamiltonian. We assume that the magnetic field is weak in comparison to internal molecular fields, and again use time independent perturbation theory. By introducing ν as a label for degenerate sublevels of excited states $\left|j_\nu^0\right\rangle$, we get expression for field dependent wavefunctions in the basis of field independent wavefunctions $\left|a_\lambda^0\right\rangle$, $\left|j_\nu^0\right\rangle$ and $\left|k^0\right\rangle$.

$$\left|a_\lambda\right\rangle=\left|a_\lambda^0\right\rangle-\sum_{k^0,k^0\neq a_\lambda^0}\frac{\left\langle k^0\middle|\hat{m}_z\middle|a_\lambda^0\right\rangle}{E_a^0-E_k^0}\left|k^0\right\rangle B\tag{6}$$

$$\left|j_\nu\right\rangle=\left|j_\nu^0\right\rangle-\sum_{k^0,k^0\neq j_\nu^0}\frac{\left\langle k^0\middle|\hat{m}_z\middle|j_\nu^0\right\rangle}{E_j^0-E_k^0}\left|k^0\right\rangle B,$$

where $\left|k^0\right\rangle$ are electronically excited states and E_a^0, E_j^0, E_k^0 are corresponding energies. Finally, we investigate how the band shape changes under influence of magnetic field. This can be in principle very difficult to calculate rigorously because the band shape is influenced by vibronic motions and collisions. Fortunately, in most cases we can impose so called rigid shift approximation, assuming that the magnetic field just shifts the bands in energy, and that it does not change their shape. We express this as

$$\rho\left(E_{aj}\right)=\rho\left(E_{aj}^0-\left(\left\langle j_\nu^0\,|\,\hat{m}_z\,|\,j_\nu^0\right\rangle-\left\langle a_\lambda^0\,|\,\hat{m}_z\,|\,a_\lambda^0\right\rangle\right)B\right).\tag{7}$$

Using the first two terms of the Taylor expansion we obtain dependence on the field,

$$\rho\left(E_{aj}\right)=\rho\left(E_{aj}^0\right)-\frac{\partial\rho}{\partial E}\left(\left\langle j_\nu^0\,|\,\hat{m}_z\,|\,j_\nu^0\right\rangle-\left\langle a_\lambda^0\,|\,\hat{m}_z\,|\,a_\lambda^0\right\rangle\right)B.\tag{8}$$

Inserting expression 5, 6 and 8 into 2, retaining only terms linear in B, and performing averaging over molecular orientations for isotropic sample we get the terms $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$

$$\mathcal{A}=\frac{\varepsilon_{\alpha\beta\gamma}}{2n_{a\lambda}}\sum_{\lambda,\nu}\left(\left\langle j_\nu^0\middle|\hat{m}_\alpha\middle|j_\nu^0\right\rangle-\left\langle a_\lambda^0\middle|\hat{m}_\alpha\middle|a_\lambda^0\right\rangle\right)\mathrm{Im}\left\langle a_\lambda^0\middle|\hat{\mu}_\beta\middle|j_\nu^0\right\rangle\left\langle j_\nu^0\middle|\hat{\mu}_\gamma\middle|a_\lambda^0\right\rangle\tag{9}$$

$$\mathcal{B}=\frac{\varepsilon_{\alpha\beta\gamma}}{n_{a\lambda}}\sum_{\lambda,\nu}\mathrm{Im}\left[\sum_{k\neq a}\frac{\left\langle k^0\middle|\hat{m}_\alpha\middle|a_\lambda^0\right\rangle}{E_k-E_a}\left\langle a_\lambda^0\middle|\hat{\mu}_\beta\middle|j_\nu^0\right\rangle\left\langle j_\nu^0\middle|\hat{\mu}_\gamma\middle|k^0\right\rangle\right.$$
$$\left.+\sum_{k\neq j}\frac{\left\langle j_\nu^0\,|\,\hat{m}_\alpha\,|\,k^0\right\rangle}{E_k-E_j}\left\langle a_\lambda^0\middle|\hat{\mu}_\beta\middle|j_\nu^0\right\rangle\left\langle k^0\middle|\hat{\mu}_\gamma\middle|a_\lambda^0\right\rangle\right]$$

$$\mathcal{C}=\frac{\varepsilon_{\alpha\beta\gamma}}{2n_{a\lambda}}\sum_{\lambda,\nu}\left\langle a_\lambda^0\middle|\hat{m}_\alpha\middle|a_\lambda^0\right\rangle\mathrm{Im}\left\langle a_\lambda^0\middle|\hat{\mu}_\beta\middle|j_\nu^0\right\rangle\left\langle j_\nu^0\middle|\hat{\mu}_\gamma\middle|a_\lambda^0\right\rangle.$$

The Einstein summation convention is invoked for the Cartesian indices α, β and γ, $\varepsilon_{\alpha\beta\gamma}$ is Levi–Civita symbol. In summary, the total MCD intensity can then be expressed using these three contributions according to

$$\Delta\varepsilon\sim\mathcal{A}\left(-\frac{\partial\rho}{\partial E}\right)+\left(\mathcal{B}+\mathcal{C}\frac{1}{kT}\right)\rho.\tag{10}$$

The derivative-like $\mathcal{A}$ term is describing the breaking of degeneracies of the ground and excited states of the molecule. The $\mathcal{B}$ term describes the field induced "mixing" of electronic states. The temperature dependent $\mathcal{C}$ term describes population differences in the ground state given by breaking of the degeneracy. When ground state is non-degenerate, the $\mathcal{C}$ term is not present. When neither ground nor excited states are degenerate neither the $\mathcal{A}$ term is present. The $\mathcal{B}$ term is always present, for any molecule. Therefore while natural CD is a property of only limited set of molecules, MCD is observed for all matter.

Methods

Computational details

The geometry was obtained by optimization using the BP86 functional and def-TZVPP basis set with Turbomole 6.0 [*Turbomole*]. The resolution of identity was used. Rotating of dihedral angles of phenyl groups with respect to the porphine core can generate five stable conformers. We used the lowest energy conformer to calculate all MCD spectra.

MCD spectra were calculated by TDDFT method using the ADF 2010 software package and a development version of Dalton. For calculation in ADF 2010 we used the SAOP functional with TZP basis set and the COSMO model for solvent. The calculated line spectrum was convoluted with Lorentzian bands with full-width at half-height of 0.2 eV. In Dalton, we used the B3LYP functional and the 6-31G basis set and IEF-PCM model. Spectra generated in Dalton are obtained as a set of MCD intensities at discrete frequencies, i.e. the broadening is explicitly set in calculation. We used the same value of 0.2 eV as above.

For all MCD calculations we used simplified molecule based on $TPPS^{4-}$ and H_2TPPS^{2-} geometries where we have replaced the sulfogroups with hydrogen atom. This could be done because the central conjugated system is relatively isolated from the sulfogroups and the simplification allowed us to speed up the calculations without degrading too much the results.

Experiment

The MCD experiment for measurement in UV-VIS region can be set up very easily using commercially available ECD (Electronic Circular Dichroism) spectrometers. The only difference in instrumentation is that the sample compartment must be equipped with suitable magnet. These magnets are either permanent, with field of up to 1.5 T, or electromagnets with strengths up to 8 T. They are generally commercially available from instrument suppliers. A useful extension for more sophisticated measurements is an inclusion of cryostat allowing for low temperature measurements. In our laboratory, we use Jasco J-815 spectrometer equipped with a permanent magnet, with a field of 1.5 T. Our experimental set up does not allow temperature dependent measurements.

The spectra shown in Fig. 2 were recorded in 1 cm quartz cell using wavelengths from 300 nm to 800 nm, with a resolution of 0.5 nm, time constant 1s, and scanning speed 50 nm/min. Spectra from 300 to 500 nm were recorded with 2 accumulations. The region from 500 to 800 nm was recorded with 3 accumulations due to smaller signal to noise ratio. The spectra were recorded in water in concentration 4 μmol/l. Stock solution of concentration 10 μmol/l was prepared by dissolving tetrasodium salt of TPPS in water. Non-protonated TPPS was obtained by diluting in pure water, the protonated species by a drop wise addition of 0.1 mol/l HCl before diluting to desired concentration. pH of prepared samples was 6 and 2 for non-protonated and protonated form, respectively. Because the pK_a constant of the protonation is 4.8 [*Farjtabar2010*] we can assume that the species were prepared predominantly in the indicated forms as $TPPS^{4-}$ and H_2TPPS^{2-}.

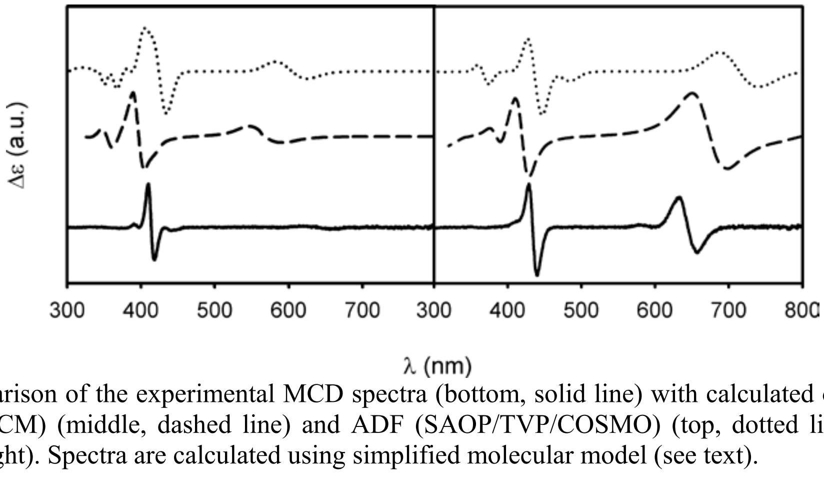

Figure 2. Comparison of the experimental MCD spectra (bottom, solid line) with calculated ones using Dalton (B3LYP/6-31G/PCM) (middle, dashed line) and ADF (SAOP/TVP/COSMO) (top, dotted line). $TPPS^{4-}$ (left) and H_2TPPS^{2-} (right). Spectra are calculated using simplified molecular model (see text).

Results and discussion

The measured spectra of the free and protonated TPPS are shown in Fig. 2, together with the calculated ones. For the calculations, both the Dalton and ADF software packages were used. We can clearly see that upon protonation the Soret band shifts to lower energy. This shift is well reproduced in the calculated spectra. The Q-band MCD, which is very small in non-protonated form, gains large intensity upon protonation. Both calculations well reproduce this change, although it is worth noting that the predicted intensity of this band relative to the Soret band is higher than in experiment. It is also worth noting that the SAOP functional provided more transitions in the same energy region than B3LYP, while still maintaining similar shape of the spectrum. This is a common feature often observed in the TDDFT theory, although not yet completely understood. A more detailed analysis of the spectrum is beyond the scope of this overview, and will be performed in a separate study.

Conclusion

The MCD technique can be applied for a broad range of molecules, and the experiments become increasingly useful as they can be interpreted accurately using the first principles calculations. We have shown that the effect in MCD spectra induced by the protonation of the nitrogen atoms can be successfully reproduced both in the observed frequency shift and change of intensity. This further broadens the applicability of MCD for studies of free-base porphyrins. So far MCD studies focused mainly on metaloporphyrins. The detailed nature of the experimental and calculated MCD spectra of the model system, and of the differences observed for the two computational approaches will be analyzed in the future.

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