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# Spectral Faraday rotation in tripyridinium bis[tetrachloroferrate(III)] chloride molecular magnet at room temperature due to electronic transition

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ABSTRACT

The physical mechanism responsible for Faraday rotation (FR) in magnetic molecules under the irradiation of visible light is under intense investigations. In this paper, a quantum mechanical description of the Faraday rotation is provided based on the electronic transitions between the molecular states. The method is applied on bis[tetrachloroferrate(III)]chloride magnetic molecule showing significant FR under irradiation of the visible light ($\lambda = [450, 775]$ nm) at room temperature. Use of dielectric tensor for the molecule in terms of oscillator strengths between HOMOs (highest occupied molecular orbital) and LUMOs (lowest unoccupied molecular orbital) leads to magnetization curve as a function of frequency. The results are obtained in view of quantitative ab initio simulation of electronic structure in the framework of density functional theory (DFT), and the wave functions are calculated making use of Gaussian 03 software within the scheme of B3LYP hybrid functional approximation. The simulation method works for discrete molecules in acetonitrile solvent and considers effect of the solvent as well. The refractive index and the oscillator strengths between molecular states are calculated using the simulated wave functions and the angle of rotation versus wavelength is presented. Comparison of the theoretical results with those of the experiment justifies reasonably the role of electronic transitions between molecular states which have not been emphasized as a mechanism of Faraday rotation in iron-based complexes.

## 1. Introduction

Magneto-optical properties of molecular magnets (MMs), such as Faraday rotation (FR), have been the focus of theoretical and experimental investigations in last few decades [1–3]. Almost all of the applications of these molecules, such as magnetic sensing and memories, qbits *etc*. [4], depend critically upon controlling and tuning the molecule's magnetization with light [1–5]. To understand the physical mechanism of these processes, many theoretical works have been conducted to describe the magnetic behavior of MMs, but most of them refer to classical quantified and phenomenological description of the magneto-optical effects [6,7]. These effects are quantum mechanical in nature and without the quantum physics one can't understand the fascinating magnetization behavior of molecule [8].

Various quantum mechanical studies, empirical or theoretical [9–11], aiming at interpreting of mechanism of photoinduced magnetism (PIM) in MMs, indicate that the light-induced magnetization can be evidenced by several mechanisms due to electronic transitions between the ground state and the excited states of the material [12–15]. Therefore, quantum physics of charge transfer between HOMOs and LUMOs is essential for gaining power of predictive insight into experimental results [16–18]. Among many methods for qualitative and/or quantitative investigation of magneto-optical properties in MMs, density functional theory (DFT) has been employed reliably for modeling and simulating molecule systems, having the main advantage of low computational cost of time of DFT over other various first-principles methods and quantum Monte Carlo (QMC). DFT studies of MMs show good agreement between theoretical and experimental physical parameters of the magnetic molecules [9].

Our incentive to this field of research (PIM) is the recently observed Faraday rotation in bis[tetrachloroferrate(III)] chloride magnetic molecule, a metal complex of empirical formula $[py.\ H]_3[FeCl_4]_2Cl$ in the group of Tetrahaloferrate(III) that belongs to the category of MMs [11]. The solution of this complex in acetonitrile solvent becomes magnetized (non-magnetized) under irradiation of green light with wavelength $\lambda = 532$ nm (red light with $\lambda = 635$ nm) at room temperature. We are trying in this work, to justify theoretically the refractive index and FR in $[py.\ H]_3[FeCl_4]_2Cl$ molecular magnet. The Faraday rotation in the

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molecule under consideration is attributed to electronic transitions between HOMO and LUMO, which is also verified previously [11,10], and is justified here by simulating the experimental curve. This conclusion can't verify the interpretation of the small magnetic interaction in terms of the distortion of the octahedral on formation of the binuclear complex [19,20]. As we demonstrate here, the magnetic exchange coupling is directly related to the special kind of paramagnetic transitions between electronic HOMO and LUMO levels.

The method is fully quantum mechanical and the calculations are performed in the framework of DFT. Use has been made of GAUSSIAN 03 (G03) software [21] and the calculations are performed within the scheme of B3LYP hybrid functional approximation [22–24], taking into account the solvent effect. The hardware used for performing the optimizations and calculations of all energy and frequency is SARMAD cluster of Shahid Beheshti University having 640 cores.

The paper is organized as follows: next section assigns a brief description of the quantum theory of FR (QFR) and introduces required parameters. In Section 3, the molecule and its geometrical structure is introduced; the superexchange coupling constant, found in another previous work, is provided for quantum calculations. The results of our calculations, wave functions, refractive index as a function of frequency and FR curve are presented in Section 4, and the theoretical and experimental results for FR are compared. Section 5 includes a summary of obtained results and we end by summing up the results and concluding the arguments.

## 2. Theoretical background and simulation method

Faraday effect, as the major effect in the field of nonlinear optical spectroscopy, provides us a satisfactory criterion for measuring magnetization of materials. This effect occurs when the energy of light excitation is the same as the energy difference between the ground state molecular orbitals (filled) and excited molecular orbitals (empty) [25,26].

The Faraday rotation, is explained vastly and commonly within the classical mechanics' scheme [27,28]. However, the external magnetic field and the exchange interaction between spins of electrons in the molecule lead to splitting of ground state molecular orbitals (MOs), which should essentially be explained making use of quantum mechanics. By irradiation of magnetic molecule by light, the electrons transfer between HOMOs and LUMOs. The electron transitions has been vastly considered for getting a comprehensive perception of magneto-optical effects in many references [26,29,33,34].

The quantum mechanical description of Faraday effect versus angle of rotation is given by employing transition of electron from energy level $n$ to $l$ as:

$$\theta_{ln} = \frac{L\omega^2\omega_\mathrm{p}^2}{4nc}\sum_{i,j}\frac{\beta_i}{\omega_{ij}}\frac{(f_{ij}^{+}-f_{ij}^{-})(\omega_{ij}^2-\omega^2-\gamma_{ij}^2)}{(\omega_{ij}^2-\omega^2+\gamma_{ij}^2)^2+4\omega^2\gamma_{ij}^2},\qquad \theta=\sum_{n,l}\theta_{ln}, \tag{1}$$

where, these parameters are used: plasma frequency $\omega_\mathrm{p}^2 = N\mathrm{e}^2/m_0\varepsilon_0$, probability $\beta_i$ of electron to be found in the state $i$, line-width $\gamma_{ij}$, optical line path $L$, transition frequency $\omega_{ij}$, electron rest mass $m_0$, oscillator strength for right and left circular polarization $f_{ij}^{\pm}$, $4nc$ including refraction coefficient and the famous velocity of light in the medium [33].

Oscillator strength, $f_{ij}^{\pm}$, are described by the dipole transition matrix element $p_{ij}^{\pm}$,

$$\begin{aligned}&f_{ij}^{\pm} = \tfrac{m_0}{\hbar\mathrm{e}^2}\,|p_{ij}^{\pm}|^2,\\ &p_{ij}^{\pm} \equiv \mathrm{e}\langle i|\ x \pm iy\ |j\rangle = \mathrm{e}\int \psi_i^*(x \pm iy)\psi_j\mathrm{d}r \equiv \mathrm{e}(x_{ij} \pm iy_{ij})\end{aligned} \tag{2}$$

The sign of oscillator strengths depends on two types of electronic transitions, paramagnetic or diamagnetic transition. The paramagnetic transition is shown in Fig. 1 and includes the criteria (Eq. (3))

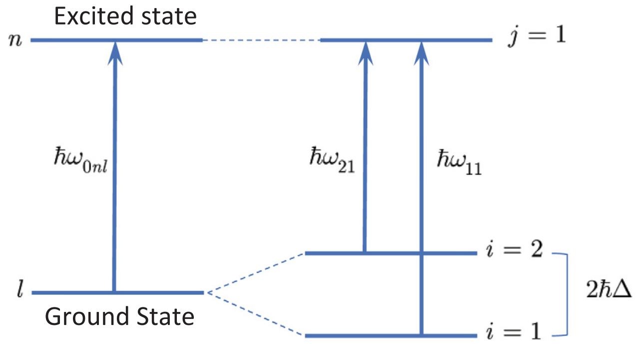

**Fig. 1.** Schematic diagram of paramagnetic transition.

$$\begin{aligned}&f_{11}^{+} = 0, f_{21}^{+} = f^{+}, f_{11}^{-} = f^{-}, f_{21}^{-} = 0,\\ &\gamma_{11} = \gamma_{21} = \gamma,\\ &\omega_{11} = \omega_{0nl} + \Delta = \tfrac{(E_\mathrm{H}-E_\mathrm{L})}{\hbar} + \Delta,\\ &\omega_{21} = \omega_{0nl} - \Delta = \tfrac{(E_\mathrm{H}-E_\mathrm{L})}{\hbar} - \Delta,\end{aligned} \tag{3}$$

Using these abbreviations, Eq. (1) simplifies as

$$\theta(\omega) = \frac{L\omega^2\omega_p^2}{4nc}\sum_{j=1}^{2}\frac{\beta_j}{\omega_{j1}}\frac{f^{\,j}(\omega_{j1}^2-\omega^2-\gamma)}{(\omega_{j1}^2-\omega^2-\gamma)^2+4\omega^2\gamma};\quad f^{1,2} \equiv f^{-,+} \tag{4}$$

The transition energies $\hbar\omega_{0nl}$ are defined as the difference between the energies of HOMO ($E_\mathrm{H}$) and LUMO ($E_\mathrm{L}$) in the absence of the external field ($H_\mathrm{ext}$). Zeeman energy ($\hbar\Delta$), generated by the molecular field ($H_\mathrm{mo}$) and the external field, reads

$$\Delta = \frac{mg\mu_0\mu_B}{2\hbar}(H_\mathrm{ext} + H_\mathrm{mo}),\quad H_\mathrm{mo} = \frac{2J}{3k_BT}S(S+1)H_\mathrm{ext} \tag{5}$$

where, $J$, $\mu_B$, $k_B$, $T$, $S$ are exchange coupling constant, Bohr magneton, Boltzmann constant, temperature, total spin, respectively.

In the case of weak magnetic field and at temperatures above Curie's ($T > T_C$), the thermal energy is larger than Zeeman energy [29]. Under the conditions of having paramagnetic media and weak external field, level occupation probabilities are simplified as:

$$\beta_1 = \mathrm{e}^{-\beta E_1}/\sum_l \mathrm{e}^{-\beta E_l},\qquad \beta_2 = \mathrm{e}^{-\beta E_2}/\sum_l \mathrm{e}^{-\beta E_l} = \beta_1\mathrm{e}^{-2\beta\hbar\Delta} \tag{6}$$

where, $E_1 = E_l - \hbar\Delta = E_\mathrm{H} - \hbar\Delta$ and $E_2 = E_l + \hbar\Delta = E_\mathrm{H} + \hbar\Delta$.

### 2.1. Semi-classical description of real part of the refractive index

The real part of refractive index $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$ as a function of the incident light frequency $\omega$is calculated via [35]

$$n(\omega) = \sqrt{\frac{1}{2}\left(\varepsilon'(\omega) + \sqrt{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}\,\right)} \tag{7}$$

where, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are real and imaginary parts of dielectric function, respectively and $\varepsilon(\omega) = 1 + 4\pi\chi(\omega)$.

Making use of the time dependent perturbation theory and the interaction picture for atoms in classical light field, semi-classical equation for $\chi(\omega)$ is obtained [36],

$$\chi(\omega) = \frac{n_0e^2}{m_0}\sum_{n,l}\frac{f_{ln}}{\omega_{0ln}}\left(\frac{1}{\omega + \omega_{0ln} + i\gamma} - \frac{1}{\omega - \omega_{0ln} + i\gamma}\right) \tag{8}$$

where, $n_0$ is the density of atoms in the system.

### 2.2. Quantum simulation and keywords used

For quantum simulation of the molecule and justifying the electronic transitions between HOMOs and LUMOs, use has been made of B3LYP exchange–correlation potential in combination with the basis set