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Electron impact excitation of the merocyanine molecule in the gas phase

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ABSTRACT

Electronic transitions in a merocyanine dye were studied in the gas phase using electron energy loss spectroscopy and compared with the optical absorption spectra. It was found that the most intense band of the $S_1 \leftarrow S_0$ polymethine transition lies at 2.8 eV in vapor and 2.4 eV in *n*-hexane. Higher electronic transitions in the range of 3.7–7 eV were also analyzed. Besides, the singlet-triplet transition was revealed near 1.8 eV. TDDFT simulation of singlet-singlet transitions in the studied molecule was performed using B97D3, B3LYP, B3PW91 and wB97xD functionals. The calculated energy of the long-wavelength transition is closest to the experimental value with the latter. Other functionals result in the energy 0.2–0.4 eV exceeding experimental. The interpretation of higher transitions/bands is complicated due to their superposition and difference between experimental and calculated data. The excitation anisotropy spectra were measured in glycerol for more reliable determination of higher transitions and comparison with the TDDFT/PCM simulation.

1. Introduction

Merocyanines are conjugated donor-acceptor systems with the essential redistribution of electron density from the donor to acceptor group and strong charge alternation along the polymethine chain [1,2]. Such a structure results in a high polarizability of their molecules, which is manifested in the essential solvatochromism. It means that merocyanine electronic structure is determined not only by the donor-acceptor properties of the terminal groups and polymethine chain length but also by environment polarity.

The tunable electronic structure enables the extensive applications of merocyanines as functional dyes for nonlinear optics [3], photorefractive materials [4], dye-sensitized and bulk heterojunction solar cells [5–7], as well as polarity probes for physical-chemical and biomedical studies [2,8]. However, the available data about the positions of long-wavelength absorption and fluorescence bands are insufficient for targeted search of dyes with required properties for a number of modern applications. For example, the HOMO and LUMO energies are crucial for solar cells, higher electronic transitions $S_n \leftarrow S_0$ are of current interest for nonlinear optics, and triplet level positions are important for dye-sensitized photo-semiconducting and electroluminescent materials [9,10]. The $S_n \leftarrow S_0$ positions can be found using excitation anisotropy spectra [11], however, these studies can be impeded by the presence of closely located transitions $S_n \leftarrow S_0$, as well as by low fluorescence quantum yields. Besides, the measurements of fluorescence excitation spectra are limited by solvents UV-cutoffs – it is possible to study transitions in the range of ≥200 nm, typically of ≥280 nm. The probability of intersystem crossing in merocyanines is very low due to a much quicker competing excited state decay channel – photoisomerisation [12,13]. Triplet absorption and emission (phosphorescence) in merocyanines can be observed in solid matrixes, e.g. in frozen solutions, in which case one should take into account both their solvatochromism and thermochromism [14,15].

Quantum chemistry is an important tool for studying the electronic structure and properties of functional molecules. Quantum chemistry calculation of merocyanines is complicated owing to both high polarizability of the donor-acceptor conjugated π-system and essential redistribution of electron density between neighbor (odd and even) chromophore positions, the so-called charge resonance, at the long-wavelength transition in polymethine dyes [1]. With the latter, the problem of accuracy of TDDFT

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calculation of electronic transitions in these molecules is usually associated [16–18]. Also, it is not clear, when comparing experimental and calculated data, whether the observed discrepancies are related to the inaccuracy of the calculation method itself or to the incorrect consideration of solvation. The existing SCRF models are incomplete because they do not take into account the specific non-covalent solute-solvent interactions, e.g. the formation of hydrogen bonds [19,20]. Thus, it is interesting to study an isolated molecule for both calibration of quantum chemical tools and evaluation of solvation effect on the solute electronic structure and properties. This task is not trivial, since functional dyes are seldom volatile and thermally stable enough for their effective evaporation. Fortunately, low-molecular weight merocyanines can be evaporated without decomposition.

The study of the electronic structure in a wide energy range in the gas phase is achieved with electron energy loss spectroscopy (EELS). Passing through a material, some of the electrons of an electron beam will lose energy and change their trajectories randomly because of inelastic scattering on electrons of the substance. If the electron energy is nearly monokinetic, the energy loss can be measured with an electron spectrometer and used for analysis of the ongoing processes [21,22]. In valence/molecular EELS, electron beams with the energy from 1 eV to tens eV and higher are used. These electrons interact with a thin-film [23] or gas-phase [24] substance and cause electron transitions between molecular orbitals. Similar to the optical spectroscopy, interaction of electrons with the substance has an electromagnetic nature, and valence EELS is an analog of optical absorption spectroscopy because the same electronic transitions are registered. However, they have several important differences. First, EELS spectra can contain symmetry or dipole forbidden transitions caused by polarization of molecular electron shell through interaction with the incident electrons. Second, the possible electron exchange between scattered and molecular electrons removes spin restriction on singlet-triplet transitions. This phenomenon gives the possibility to study the position of triplet states. Third, interaction of electrons with the substance (including electron exchange) occurs at relatively long distances, resulting in big cross sections. As a result, the sensitivity threshold of vapor density is only 10^{-4}–10^{-3} Torr that facilitates investigation of weakly evaporating substances. Fourth, EELS allows to study high-energy transitions in the vacuum UV region (up to ~12 eV), thus providing the full diagram of energy levels in a molecule.

Interest to EELS of organic molecules in the gas phase is growing from the end of 1980s, after improvement of the corresponding devices. Except inorganic gases, the main objects were simple and easy evaporating substances such as halogens, alcohols, carbonyl and aromatic compounds [25,26]. Functional molecules for optoelectronics were studied seldom [24,27,28].

The aim of this work was to study the electronic structure of a merocyanine molecule in the gas phase by means of EELS and to juxtapose the data obtained with the UV/Vis spectra in solutions and TDDFT simulation. To the best of our knowledge, such studies have not been conducted for merocyanines hitherto. The molecule was chosen by the criteria of low molecular weight and relative simplicity of the structure (i.e. the absence of labile functional groups), providing its stability and volatility. The latter parameters depend on the electronic structure as well – less polar positively solvatochromic merocyanines have to be more volatile owing to weaker dipole-dipole interactions between molecules. The polymethine chain length is another crucial factor – the thermal stability is known to decrease strongly even in going from tetra- to hexamethinemerocyanines [29]. From these considerations, as an object of study we chose positively solvatochromic tetramethinemerocyanine **1** (Fig. 1) derivative of benzothiazole and malononitrile [30].

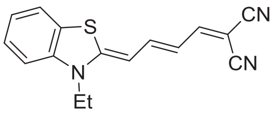

Fig. 1. Representation of merocyanine **1**.

2. Experimental

Dye **1** was synthesized and purified according to Ref. [30].

A special electron spectrometer was used for the EEL spectra measurements [24]. A monoenergetic electron beam with a diameter of 1.5 mm was formed by an electron gun consisting of a heated oxide cathode and an electron-optical system. The electron beam current did not exceed 10 μA. The spectrometer operated in a continuous mode. The organic vapor density in the collision chamber was less than 10^{-3} Torr to prevent multiple collisions and secondary processes. The necessary vapor pressure was obtained by heating the chamber and the container in which the organic powder sample was placed with special molybdenum heaters. To avoid vapor condensation, the chamber temperature was ca. 30 °C higher than in the container. Electrons scattered at an angle of 90° relative to the direction of the electron beam were detected by a 127° electrostatic analyzer and a channel electron multiplier detector. Scattering at an angle of 90° facilitates detection of spin forbidden singlet-triplet exchange transitions, because the probability of these transitions depends weakly on angle, while the probability of singlet-singlet direct transitions decreases with scattering angle. The analyzer energy resolution was 0.05 eV. The full-energy resolution of the spectrometer found using the elastic scattering peak was 0.6 eV. The incident electron beam current was measured with a 35 mm Faraday cup. The length of the collision range inside the chamber was 5 mm.

Optical absorption spectra were recorded using a spectrophotometer Shimadzu UV-3100 in 1-cm cuvettes. Fluorescence spectra were registered on a spectrofluorometer Solar CM2203 (Belarus). To minimize the inner filter effects, the optical densities in the dye's absorption maximum did not exceed 0.1 in fluorescence measurements. The fluorescence quantum yields (φ_f) of dye **1** were calculated in relation to Rhodamine 6G in ethanol (φ_f = 95% [31]). The excitation polarization spectra of merocyanine **1** were recorded in glycerol. All solution spectra were measured at 293 K.

DFT/TDDFT calculations were performed on a Gaussian-09 program suite [32] using B3LYP, B3PW91, wB97XD, and B97D3 hybrid functionals. In all cases the ground state structural optimization had been preliminary carried out with the split-valence 6–31G(d, p) basis set; the calculation of force constants and vibrational frequencies was performed to verify that the geometry located was a minimum. The convolution of the obtained TDDFT spectra was carried out using the gauss broadening with the FWHM (full width at half maximum) parameter of 0.5 eV, which is comparable with FWHMs of long-wavelength spectral bands of typical polymethine dyes.

3. Results and discussion

3.1. UV/Vis absorption spectra

The solvent polarity growth in going from *n*-hexane to toluene and further to dichloromethane and DMF results in a batochromic shift, intensity increase and narrowing of the long-wavelength absorption band of dye **1** (Fig. 2), i.e. this merocyanine possesses positive solvatochromism. This means that its electronic structure varies within the range of structures from the nonpolar polyene to the ideal polymethine [1,2]. A significant contribution of the nonpolar polyene structure in low-polarity *n*-hexane is confirmed by