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Statistical Method to Describe Molecular Spectra

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The method to reproduce optical spectra by statistical treatment of quantum-mechanical calculations of energy states and photophysical properties in molecular conformers obtained during molecular-dynamical simulation was developed. Polycyclic organic molecules in solvents under thermodynamical conditions were considered. This technique was employed to build the first absorption band of estradiol, benzene, and anthracene. Increasing of the spectral intensity in benzene under temperature growth was demonstrated for the lowest excited state. Anthracene emission spectrum was built as well.

Keywords: photophysical properties, organic compounds, molecular dynamics, semi-empirical Hartree-Fock.

Introduction

Recently the method to reproduce optical absorption spectra by statistical treatment has been presented [1] where quantum-mechanical calculations of excited energy states in molecular conformers obtained during molecular-dynamical (MD) simulation were involved and compared with the various earlier similar methods [2a-d, 3e-g].

The statistical absorption spectra between 240-320 nm of estradiol in ethanol, hexane, or dimethyl sulfoxide (DMSO) solvents were considered. Dependence of the first electronic band in benzene surrounded by cyclohexane molecules on temperature was described. Transition between ground state and the lowest excited energy level is forbidden by symmetry for the equilibrium structure but according to

several experimental data spectral intensity of the corresponding band is observed. Finally, both absorption and emission spectra of anthracene were reconstructed and compared with the reliably confirmed data.

Methodology and computational details

Absorption and emission spectra are formed due to electronic transitions and core vibrations proceeding in molecules. In order to study the spectral-luminescent properties the recently developed theoretical model of statistical electronic spectra was employed [1].

Supplementary agreement to this method concerns fluorescence. The relative radiation intensity can be estimated as a product of probabilities $I_{\Delta\lambda} = p_{\Delta\lambda} \cdot k_r \cdot \gamma_{\Delta\lambda}$ and the fluorescent

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quantum yield $\gamma_{\Delta\lambda}$ also averaged on this spectral interval is the inverse relationship of the radiative rate constant k_r and summarized transition probabilities of all photoprocesses proceeding from same state $\gamma = k_r / (k_r + \sum k_{pf})$ were k_{pf} are the electronic radiationless transition rates. The averaged absorption band $\Delta\lambda$ intensity is defined through the relative absorptivity $\varepsilon_{\Delta\lambda} = p_{\Delta\lambda} f_{\Delta\lambda}$ if $p_{\Delta\lambda} = N_{\Delta\lambda}/N$ is probability (N is a total number of conformers with calculated QC parameters) [1,3] In most cases, such as anthracene, only S_1 has an appreciable fluorescent quantum yield that depends on k_r and the rate of cross-section (singlet-triplet) conversion $\sum k_{1f} \approx k_{ST}$ [4] N conformers of fluorescent spectrum prepared in the same excited state emit photons and relative intensities depend on the constant radiative rates and fluorescent quantum yields.

The following chromophores and surrounding molecules were under consideration: i) the female natural hormone estradiol is a luminescent hormone due to existence of the phenol ring with rich π -system [5]; ii) benzene and anthracene are well tested molecules and basics for many substituted derivatives, which have high absorption possibilities and quantum yields of luminescence in visible and UV spectra [6]; iii) hexane, cyclohexane, ethanol, and DMSO are used as solvents in experimental investigations of spectral-luminescent molecular properties.

A canonical NVT ensemble included one of chosen chromophores solvated among 56 surrounding molecules for MD modeling. Each simulation performed during 0.5 nanosecond with time step 1.0 femtosecond (500000 steps). The chromophores and molecules of solvent were completely flexible according to the force-field potentials. Tinker MD software with the standard MM3 force-field parameterization was applied excepting bond stretching and angle bending parameters on the phenyl cycles. The ideal bond length of carbon hexagonal ring was

taken as 1.40 Å on estradiol and anthracene and 1.38 Å for benzene, ideal angle was 120° to both cases. These parameters were changed a little for fluorescent state.

After single thermo-dynamical run excited states and oscillator strengths of 5000 conformers were calculated by INDO/s and CIS implemented in a trial version of the GAMESS package to construct statistical spectra. Additionally, the rate constants of radiation decays and cross-section conversions were defined for fluorescence. All spectral intensities were normalized to unity except the benzene sample whose maxima of experimental and the most intensive (at 300K) model spectrum were normalized but the rest of spectra were rescaled to this intensity according to the normalization multiplier. Once calculated, charge distribution over atoms (atomic partial charges) for the starting equilibrium structure was invariable during whole MD simulation, consequently, the charge fluctuation was not considered.

Results and discussion

ESTRADIOL. This hormone, having first long-wavelength absorption peak $\lambda = 288.6$ nm, is a typical representative of estrogens. The formation of low-lying energy states of the $\pi\pi$ type is determined by the system of π electrons, whose occurrence is associated with the phenyl cycle [5]. The calculated lowest singlet state of the molecule frozen in equilibrium position coincided pretty well with the empirical maximum (Fig. 1). The estradiol structure was optimized by the ChemOffice soft but benzene ring was taken with all bonds 1.4 Å and angles 120°. The QC calculation of equilibrium structure gave some information about the excited states. Electronic levels define spectral maxima and oscillator strengths estimate intensities as well as the empirical ratio for the molar absorption constant $\varepsilon_{\max} = f \times 4.63 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ [5d].

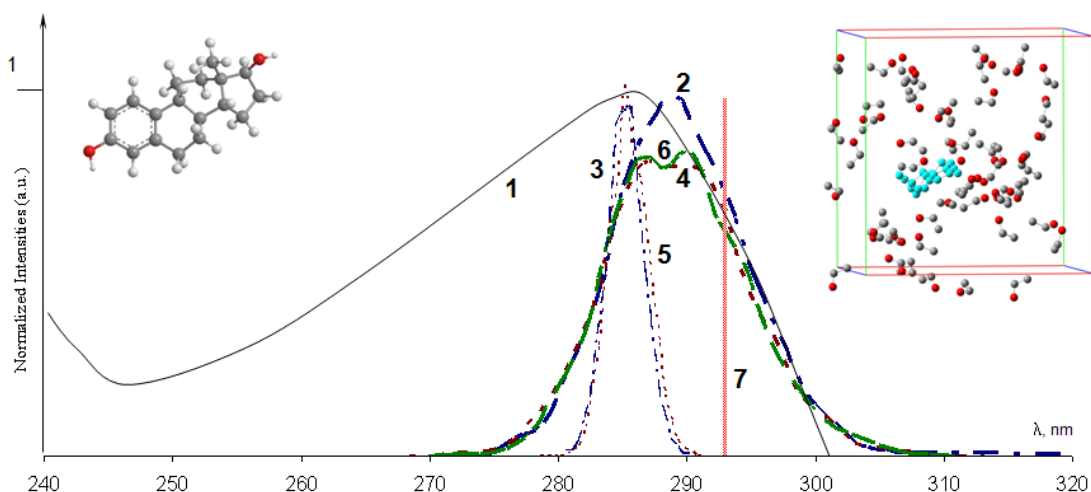


Fig. 1. Estradiol. Empirical absorption spectrum in alcohol at 20°C (solid, 1) [5]. Statistical profiles in ethanol (dot-dashed, 2 at 300°K and narrow 3 at 30°K), in DMSO (dotted, 4 at 300°K and narrow 5 at 30°K), and in hexane (dashed, 6 at 300°K). The lowest electronic state in equilibrium position (straight vertical line, 7). There are stereo-chemical structure on the left side and a snapshot of ethanol solution on the right side

Spectra of estradiol dissolved in ethanol, DMSO, and hexane at 30°K and 300°K (Fig. 1) have almost the same width in different solutions but they are narrower at the lowest temperature. It is obviously that molecular oscillations are weaker in a colder system that defines shorter spectrum. Maxima of bands are shifted into shorter-wavelength UV region relative to the energy of equilibrium molecule and they describe the picks of realistic absorption more precisely. The empirical spectrum in alcohol at 20°C is a smooth curve without a vibration relief. The spectral shapes obtained with frequency resolution 0.5 nm in the cold systems and 2.0 nm under higher temperature are different and depend on the surrounding molecules. It could be noted that the profiles are strong determined by MD force-field parameterization. At least, increasing the ideal bond of benzene ring leads to a displacement into the long-wavelength part of spectrum and, vice versa, decreasing occasions a short-wavelength shift. Parameters for excited molecules and the MD/QC method should be developed in future to build spectra closer to

realistic conditions. Constructed solvents have to affect on spectral profiles and positions much deeper but currently the simplest conditions on interactions were involved during the MD simulation and conformers are taken isolated from the surrounding shells. Nevertheless, the experimental spectrum was reproduced by the statistical curves with very good agreement.

BENZENE. The oscillator strength of the first singlet state in equilibrium positions is negligible that makes absorption $S_0 \rightarrow S_1$ by benzene impossible, however, according to the empirical data there is a weak excitation into the first band. The experimental absorption spectrum in cyclohexane at 23°C (Fig. 2) [7a].

The molar absorption coefficient is $210 \text{ M}^{-1}\text{cm}^{-1}$ in maximum = 255 nm. Transition between these states forbidden by symmetry can be permitted in non-equilibrium structures. Theoretical spectra with nonvanishing intensities are constructed due to the MD statistical technique (Fig. 2). Intensity mounts together with temperature growth. Calculated excitation to state $S_1=250.7 \text{ nm}$ of benzene in

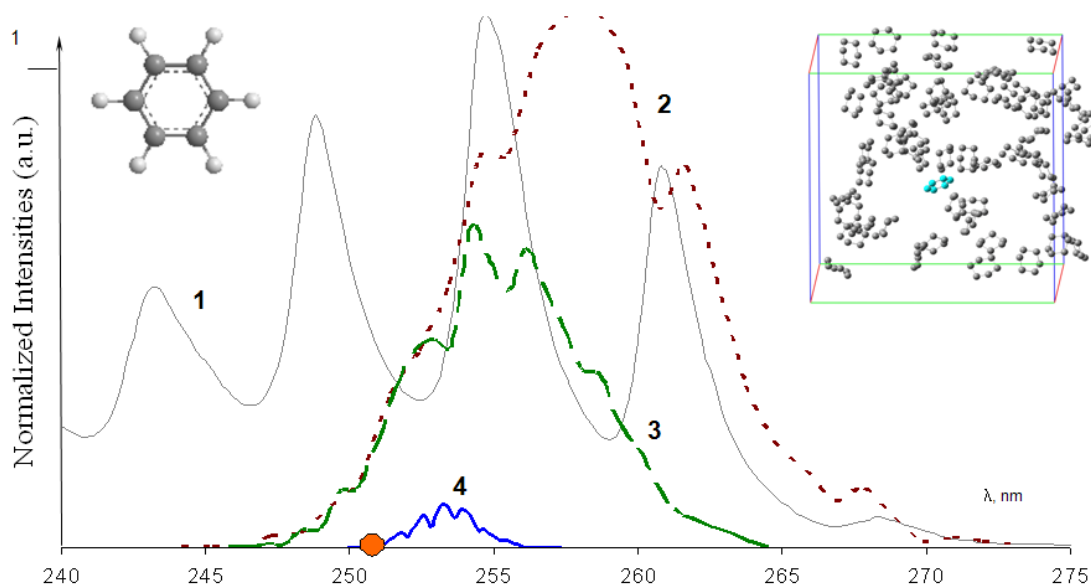


Fig. 2. Benzene absorption spectra. Experimental curve at 23°C in cyclohexane (solid, **1**) [7a]. Statistical graphs at T=300K (dotted, **2**), T=150K (dashed, **3**), and T=30K (solid smallest, **4**). First electronic state in 250.7 (nm) of equilibrium structure with zero oscillator strength (circle)

equilibrium position is not intensive absolutely $f=0.0000$ but conformers in cyclohexane solution under 30°, 150° and 300°K provide oscillator strengths balancing between zero and maximal values 0.0008, 0.0086, 0.0190, respectively to temperatures. These correspondences are reflected by the spectral heights and areas under curves (the total intensities). The respective frequency resolutions of 0.266, 0.643, and 2.129 nm were defined if spectral widths are divided into 29 partitions. This number was chosen to keep frequency resolutions near 2 nm in the system under T=300°K. Spectrum expands into the long-wavelength region starting from zero point. The statistical spectra do not coincide with empirical one very well but the main characteristics on vibration structure are reflected quite precisely. Five maxima can be recognized according to the original curve. Four intensive picks and weak maximum on the end of long-wavelength wing define the spectral profiles. The statistical graphs are narrower and

they do not have sharp reliefs. These variances also concern the mentioned problems of force-field parameters and environment influence.

ANTHRACENE. The Experimental emission and absorption spectra (Fig. 3) are founded from the PhotochemCAD under same conditions [7b] where the molar extinction coefficient is 9,700 M⁻¹cm⁻¹ at 356.25 nm in cyclohexane. Additionally, the narrow absorption curve of anthracene obtained at T = 300K and under atmosphere pressure in a slowly flowing gas mixture is presented as well [7b]. The statistical absorption spectrum in cyclohexane at T=300°K was built in the same manner as the described cases of benzene and estradiol. The maximum is shifted relative to energy of the equilibrium structure and the contour can be recognized as absorption by comparing with experimental one due to 5 vibration picks.

An emission spectrum was constructed if force-field bond stretching, angle bending, and torsion parameters are chosen according to the

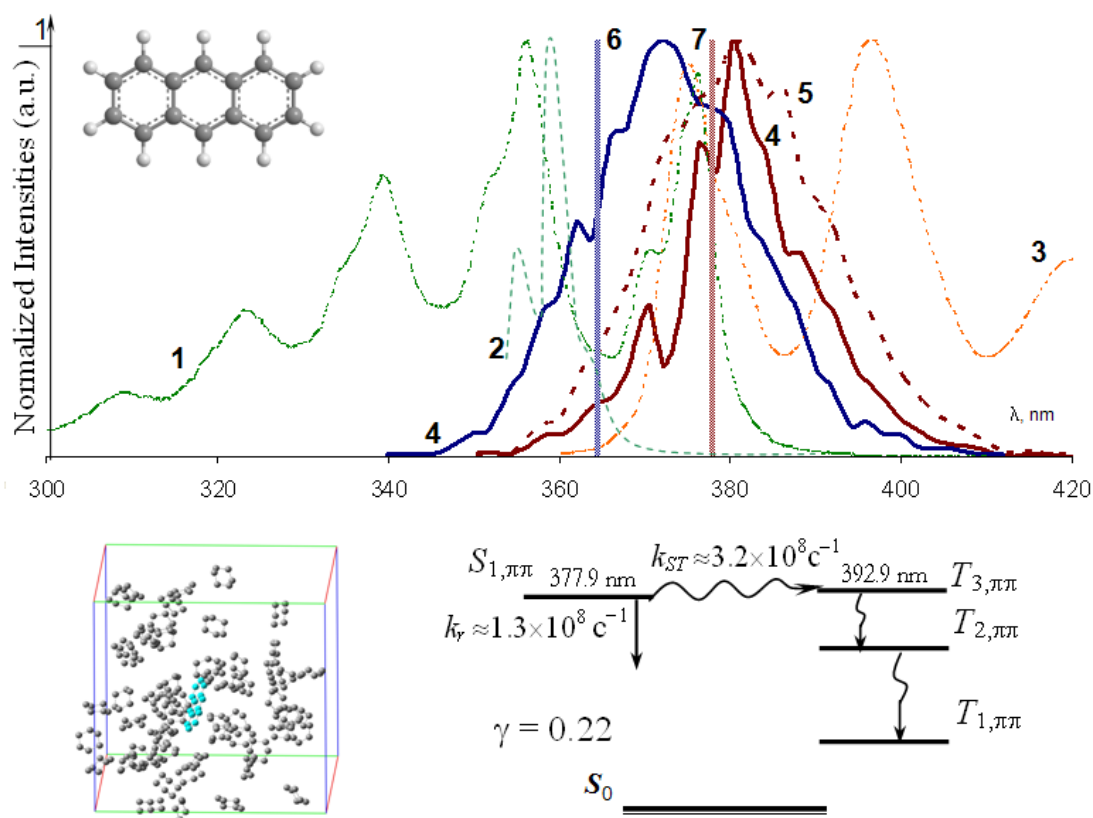


Fig. 3. Anthracene in cyclohexane solvent. Experimental absorption (dashed, 1 and 2) and fluorescent (dashed, 3) spectra [7]. The statistical absorption (solid on short-wavelength wing, 4), fluorescence (solid, 5), and the probability distribution of excited conformers over wavelengths (dotted, 6). Energies of equilibrium structures of ground state (left vertical line, 6) and lowest state (right line, 7). The Jablonski vertical energy diagram with photoprocesses on the right bottom part

spatial structures of molecules in excited state. Every changing in molecular energy leads to a modification in the electronic cloud and then atomic skeleton. One of the simplest way to obtain stereo-chemical structures of excited states, among other, is an evaluative formula to change bond-lengths $\Delta R_{AB} \approx -0.46 \Delta P_{AB}$ where ΔR is the change of the interatomic distance and ΔP is the change of the bond population (order) at the transition from one state to another.

The described idea was applied to construct conjunct phenyl circles in equilibrium position of first excited state. The left vertical line (Fig. 3) represents the emission maximum of this structure. The quantum yield of fluorescence

$\gamma = 0.22$ was estimated due to the vertical Jablonski diagram presented in right bottom part of the Fig. 3, where S and T are singlet and triplets, respectively, marked with numbers and types of transition between molecular orbitals which all are π symmetry. The significant portion of excited energy decays through the cross-section channel since spin-orbital coupling between $S_{1,\pi\pi}$ and $T_{3,\pi\pi}$ is strong that makes the probability of singlet-triplet $k_{ST} \approx 3.2 \times 10^8$ conversion comparable with fluorescence $k_r \approx 1.3 \times 10^8$. Different sources [7a] give the fluorescence yields between 0.27 and 0.36 and maximum about 376 nm. Each local γ was calculated according to the probabilities k_r and k_{ST} of a current molecular snapshot when the

triplet state was chosen as the same to $T_{3,\pi\pi}$ in the equilibrium structure as possible for all obtained conformers. Each magnitude of quantum yield was averaged over the correspondent wavelength interval $\Delta\lambda_k$ and multiplied on $p_{\Delta\lambda}$ and averaged k_r . These obtained relative radiation intensities were integrated to a fluorescent curve. Emissive spectral contour differs from ordinary distribution $p_{\Delta\lambda}$ (dashed red-brown curve over solid one on Fig. 3) because fluorescent quantum yields of different vibronic structures undergo substantial fluctuations between 0.00 and 0.96.

The best absorption and emission contours are narrower and they have smooth reliefs comparing with the experimental curves. These parameters should be modified in such manner that will lead to sharper and broader spectra. Moreover, the applied model was based on adiabatic transition between ground and electronic excited vibration sublevels. A non-adiabatic approach should be employed as well. Another problem remained after all described samples needs to be noted and considered for a further development. Time-resolutions accepted as an interval between two neighboring QC calculations is near 0.1 ps and very short comparing with vibrational relaxation times that can be about and longer than 1 ps. Therefore, some separated calculations on energies seem not to be corresponded to realistic transition between quantum sublevels but possible errors and fluctuations during the quasi-classical QM/MD procedure have to be disappeared after averaging and integrating. In any case, this

might be a reason to exist unexpected distortions in spectral shape that is a subject to study.

Conclusions

There are three main results of this work.

1. Electronic transitions proceeding in conformers obtained after MD simulation can be integrated in such way to outline a curve that is associated with a statistical absorption spectrum.

2. The vibrational structures permit to find non-zero transition probabilities that are forbidden for equilibrium structure. In the case of first long-wavelength band in benzene the bigger distortions are responsible for broader and more intensive absorption spectrum.

3. Emission spectra also can be constructed in the same manner if all photoprocesses comparable with radiative are taken into account as well as MD force-field parameters are modified according to a stereo-chemical structure of excited molecule.

Currently there are several disadvantages since the rude model and approaches are employed that should be improved in future. Force-field bonds stretching, bending and torsion parameters among others should be arranged more precisely for photo-physical purposes involving temperature and pressure dependencies. Solvent influence and solvatochromic shift has to take more part in building spectral curve. Perhaps, the correlation between computed "time-resolution" and vibrational relaxation time should be discussed and defined more accurately. Some non-adiabatic correction should be involved.

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Статистический метод описания молекулярных спектров

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Предложен метод для воспроизведения оптических спектров статистической обработкой квантово-механических расчетов энергетических состояний и фотофизических свойств в молекулярных конформерах, полученных в течение молекулярно-динамической симуляции. Обсуждены некоторые полициклические органические молекулы в растворах при различных термодинамических состояниях. Данный метод был применен для построения первых полос поглощения эстрадиола, бензола и антрацена. Продемонстрировано увеличение спектральной интенсивности бензола с ростом температуры для низшего возбужденного состояния. Также построен спектр излучения антрацена.

Ключевые слова: фотофизические свойства, органические соединения, молекулярная динамика, полуэмпирический Хартри-Фок.
