UDC 577.322

QUANTUM-CHEMICAL CALCULATIONS OF THE STRUCTURE AND ELECTRON TRANSITIONS OF MULTIMOLECULAR FILMS

Kopbalina K.B.[1], Mazhenov N.A.[1], Bimbetova G.M.[2]

[1]Karaganda State Technical University, Karaganda, Kazakhstan, kopbalina82@mail.ru

[2]L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

Dynamic and static quenching of fluorescence occurs upon contact interaction of oxygen molecules. Of the simplest models of the complex of oxygen and anthracene, a complex consisting of one molecule of oxygen and anthracene molecule is proposed. Quantum-chemical calculations were performed by using the Gaussian 98 software package. Equilibrium geometry of the ground electron state was obtained for a complex of oxygen and anthracene molecules. The electron absorption spectrum is calculated for this complex. It is established that this complex of oxygen and anthracene is not photo-stable.

Keywords: molecular oxygen, anthracene molecule, computer modeling, molecular orbitals, wave function.

Introduction

Molecular oxygen plays an important role in many natural oxidative reactions and technological processes. The establishment of the mechanism of photosensitized oxidative processes involving molecular oxygen is of fundamental interest for photochemistry and photobiology. Collision of the oxygen molecule with the luminophore in the excited state leads to non-radiative energy transfer. The degree of quenching depends on the frequency of collisions, consequently, on the concentration and temperature of the oxygen-containing medium, therefore an oxygen molecule generates a number of interesting photophysical phenomena, the mechanisms of which are not completely clear. In this regard, the study of photoprocesses involving molecular oxygen retains its relevance.

Computer modeling is one of the effective methods for studying complex systems. In recent decades, it is one of the components of almost any research in physics and chemistry. There are many methods of such modeling, oriented on solution various problems and differing both in a strategic approach and in software implementation. Computer modeling is to conduct a series of computational experiments on a computer, the purpose of which is to analyze, interpret and compare the modeling results with the real behavior of the study object and, if necessary, refine the model.

Molecular modeling begins with the formation of a computer model of an object by specifying spatial coordinates. Information on the initial geometry can be obtained by different ways: X-ray structural data bases, search of standard geometries in libraries, construction of structural models by using various software. The next stage of computer modeling of the molecule is the optimization of the geometric structure. Optimization is the search for a structure with minimal energy. There are computational methods for optimizing geometry. Method of molecular mechanics is separately distinguished. In this method atoms in a molecule composition are considered as set material points, which interacting with each other as in the harmonic oscillator model. The other methods (algorithms) of minimization can be divided into two classes: methods based on gradient techniques (method of steepest descent, conjugate gradient method) and methods using the second derivative (Newton-Raphson method and related methods).

1. Quantum-chemical calculations

The calculations were carried out by using the density functional method and the Gaussian 98 software package [1]. Geometry optimization was performed by using the Beke three-parametric hybrid method with gradient-correction correlation of the Lee, Yang and Para functional (B3LYp) and the standard basis set 6-31G (d). The theoretical UV and visible spectra were obtained with considering the time dependence of the density functional method [1–13], where the discrete excitation spectra and the corresponding oscillator strengths were estimated from several dozens of low-energy singlet transitions. The optimized geometries of anthracene and oxygen molecules were calculated. The sequence of energy levels of molecular orbitals (MO) of oxygen is presented in table 1.

Table 1. The sequence of MO energy levels of oxygen.

MO	**Energy**	**MO**	**Energy**
SGG	-1.82017	SGG	-1.69635
SGU	-1.04054	SGU	-0.91208
SGG	-0.78167	SGG	-0.73081
PIU	-0.70022	PIU	-0.54924
PIU	-0.70022	PIU	-0.54924
PIG	-0.49006		
PIG	-0.49006		

Electron spectra for the optimized geometry of anthracene molecules were obtained by using the Gaussian program. The distribution of effective charges on the atoms of the anthracene molecule is obtained. Electron configurations for the S_0 state are constructed based on the molecular orbitals of the anthracene molecule (φ_n-n-number of MO in the ground singlet state) (Table 2). Wave functions of the excited states Φ_i are constructed from these configurations.

Table 2. Energies and wavelengths of electron transitions for S_0 state of the anthracene molecule

Nature of transition	Transition energy, eV	Wave function	Wavelength, nm	Oscillator strength
$S_1\left({}^1\pi \to \pi^*\right)$	3.33	${}^1\Phi_1 = -0.16(\varphi_{32} \to \varphi_{35}) + 0.67(\varphi_{33} \to \varphi_{34})$	371	0.2224
$T_1\left({}^3\pi \to \pi^*\right)$	1.86	${}^3\Phi_1 = 0.24(\varphi_{32A} \to \varphi_{37A}) + 0.73(\varphi_{34A} \to \varphi_{35A}) + 0.18(\varphi_{30B} \to \varphi_{35B}) - 0.57(\varphi_{32B} \to \varphi_{33B})$	665	0.0047

An analysis of the wave function ${}^1\Phi_1 = -0.16(\varphi_{32} \to \varphi_{35}) + 0.67(\varphi_{33} \to \varphi_{34})$ of the excited $S_1\left({}^1\pi \to \pi^*\right)$ state shows that absorption at 371 nm with an oscillator strength of 0.2224 occurs when the transition of π-electrons of conjugated bonds to the π^* vacant molecular orbital of the anthracene molecule (Table 2, MO $\varphi_{32} \to \varphi_{35}, \varphi_{33} \to \varphi_{34}$), which corresponds to the experimentally observed absorption value of 370 nm. Thus, the calculated electron transition at 371 nm occurs from the S_0 state of the anthracene molecule, which is in the global minimum to the S_1 excited state [9–11]. Molecular orbitals for the S_0 structure of the anthracene molecule are given in Table 3.

Table 3. Molecular orbitals for the S_0 structure of the anthracene molecule

Energy of MO, eV	MO(φ) and contributions AO (χ)
-0,31150	$\varphi_{32} = -0{,}31\chi_Z^4 - 0{,}39\chi_Z^{12} - 0{,}39\chi_Z^{16} - 0{,}31\chi_Z^{24} - 0{,}39_Z^{36} - 0{,}39\chi_Z^{40} + 0{,}31_Z^{49} + 0{,}31\chi_Z^{53}$
0,01054	$\varphi_{35} = -0{,}30\chi_Z^4 + 0{,}39\chi_Z^{12} - 0{,}39\chi_Z^{16} + 0{,}30\chi_Z^{24} + 0{,}39_Z^{36} - 0{,}39\chi_Z^{40} + 0{,}30_Z^{49} - 0{,}30\chi_Z^{53}$
-0,26840	$\varphi_{33} = -0{,}23\chi_Z^4 - 0{,}30\chi_Z^8 + 0{,}10\chi_Z^{12} - 0{,}10\chi_Z^{16} + 0{,}30_Z^{20} + 0{,}23\chi_Z^{24} + 0{,}40_Z^{28} - 0{,}43\chi_Z^{32}$ $- 0{,}10\chi_Z^{36} + 0{,}10\chi_Z^{40} + 0{,}30\chi_Z^{44} - 0{,}23\chi_Z^{49} + 0{,}23\chi_Z^{53} + 0{,}30\chi_Z^{57}$
-0,02679	$\varphi_{34} = 0{,}23\chi_Z^4 - 0{,}30\chi_Z^8 + 0{,}11\chi_Z^{12} - 0{,}11\chi_Z^{16} - 0{,}30_Z^{20} + 0{,}23\chi_Z^{24} + 0{,}42_Z^{28} + 0{,}42\chi_Z^{32}$ $- 0{,}11\chi_Z^{36} - 0{,}11\chi_Z^{40} - 0{,}30\chi_Z^{44} + 0{,}23\chi_Z^{49} + 0{,}23\chi_Z^{53} - 0{,}30\chi_Z^{57}$
-0,32152	$\varphi_{32A} = -0{,}34\chi_Z^4 + 0{,}34\chi_Z^{12} + 0{,}34\chi_Z^{16} - 0{,}34\chi_Z^{24} - 0{,}34\chi_Z^{36} - 0{,}34\chi_Z^{40} + 0{,}34\chi_Z^{49} + 0{,}34\chi$
0,02758	$\varphi_{37A} = -0{,}13\chi_Z^4 + 0{,}32\chi_Z^8 + 0{,}30\chi_Z^{12} - 0{,}30\chi_Z^{16} + 0{,}32\chi_Z^{20} - 0{,}13\chi_Z^{24} + 0{,}24\chi_Z^{28} + 0{,}24\chi_Z^{32}$ $0{,}30\chi_Z^{36} - 0{,}30\chi_Z^{40} + 0{,}32\chi_Z^{44} - 0.13\chi_Z^{49} - 0{,}13\chi_Z^{53} + 0{,}32\chi_Z^{57}$
-0,35524	$\varphi_{30B} = 0{,}13\chi_Z^4 + 0{,}31\chi_Z^8 + 0{,}30\chi_Z^{12} - 0{,}30\chi_Z^{16} * -0{,}31\chi_Z^{20} - 0{,}13\chi_Z^{24} + 0{,}26\chi_Z^{28} - 0{,}26\chi_Z^{32}$ $0{,}30\chi_Z^{36} + 0{,}30\chi_Z^{40} + 0{,}31\chi_Z^{44} + 0{,}13\chi_Z^{49} - 0{,}13\chi_Z^{53} - 0{,}32\chi_Z^{57}$
-0,06187	$\varphi_{33B} = -0{,}26\chi_Z^4 - 0{,}24\chi_Z^8 + 0{,}20\chi_Z^{12} - 0{,}20\chi_Z^{16} + 0{,}24\chi_Z^{20} + 0{,}26\chi_Z^{24} + 0{,}39\chi_Z^{28} - 0{,}39\chi$ $0{,}20\chi_Z^{36} + 0{,}20\chi_Z^{40} - 0{,}24\chi_Z^{44} - 0{,}26\chi_Z^{49} + 0{,}26\chi_Z^{53} + 0{,}24\chi_Z^{57}$

According to the definition of academician A.N. Terenin, the photonics of molecules is a combination of photophysical and photochemical processes occurring in them after absorption of a quantum of light [9]. In optically excited electron states, chemical or structural changes can occur. Such processes are called photochemical, in contrast to processes that do not lead to such changes and are called photophysical. After the absorption of a quantum of light in a molecule, several photophysical processes of conversion of the excitation energy can occur [14].

The processes leading to a decrease in the energy of electron excitation, i.e. energy deactivation processes, by their nature, can be radiative (radiation, optical) and non-radiative. A characteristic feature of radiation transitions is the absorption or emission of a quantum of light (photon) by a molecule. The study of the photonics of molecules requires knowledge not only of the energies and wave functions of various electron states, but also of the probabilities of transitions of a molecule from one state to another. The absorption spectrum registered in the experiment most often consists of several bands. The absorption band is characterized by the shape, intensity and position of the absorption maximum, measured in wavelengths or energy units.

When interpreting the absorption spectra, the Frank-Condon principle must be taken into account. It consists in the statement that during the electron transition the electron state of the molecule changes so rapidly that the atomic nuclei do not have time to shift from their equilibrium positions. Since calculations of the excited states are carried out on the basis of the geometry of the ground state of the molecules, according to the Frank – Condon principle, calculated energies of the excited states E_i should be compared with the maximum of the band in the electron absorption spectrum $S_0 \rightarrow S_i$ [11].

Fig.1 presents the electron spectrum $S_0 \rightarrow S_1$ of the anthracene molecule, obtained from the calculation by means of the program "Gaussian-09". As can be seen, from the fig.1, the maximum of the spectrum is the λ = 371.96 nm wavelength and corresponds to the transition from the ground state to the first excited singlet state. The oscillator strength is 0.2224. Fig. 2 shows the calculated electron spectrum of the anthracene molecule for the $S_0 \rightarrow T_1$ transition. The maximum of the spectrum is the λ = 665.64 nm wavelength. The oscillator strength is 0.0047. The obtained data are in agreement with the experimental one [12].

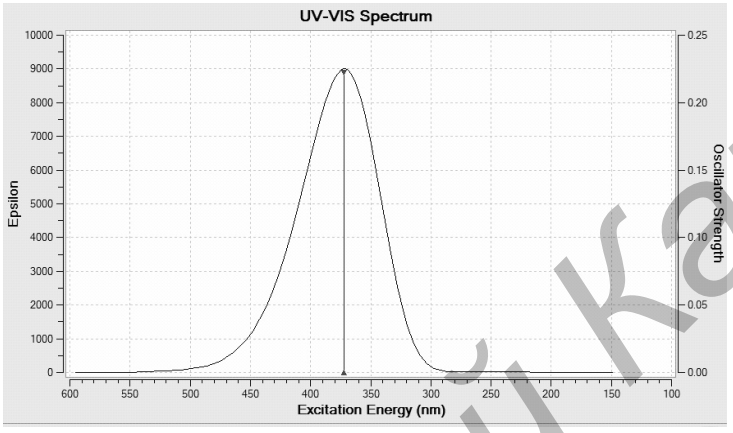

Fig.1. Electron spectrum of anthracene molecule ($S_0 \rightarrow S_1$)

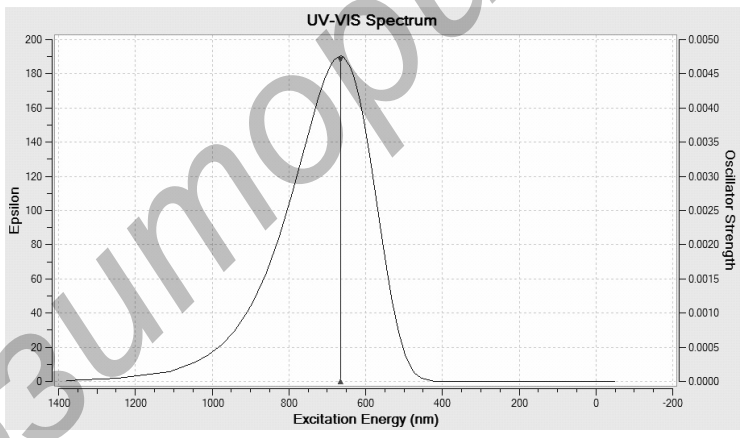

Fig.2. Electron spectrum of anthracene molecule ($S_0 \rightarrow T_1$ **)**

The calculated energies of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ singlet-singlet transitions, as well as their oscillator strengths (f) of the anthracene molecule are shown in Table 4. Quantum-chemical calculations performed by the ZINDO method for this luminophore give quite good agreement of the spectral characteristics obtained from calculations and experiment. As can be seen from Table 4, the wavelength value (λ=665.64 nm) of the $S_0 \rightarrow T_1$ transition is close to the experimental one (λ=650 nm).

If the environment in the film form has a slight effect, then the equilibrium geometry of the ground and the excited electron states can be calculated [13].

Monomer and dimer of anthracene can absorb and fluoresce in the experiment. Therefore, it is necessary to study the spectra of both monomers and dimers of anthracene. At the first stage, it is necessary to determine the geometries of the ground and first excited electron states. Note that in the experiment, an electron vibrational absorption spectrum is observed (0→0, 0→1, 0→2,…).

Monomer and dimer of anthracene can absorb and fluoresce in the experiment. 0→0 is pure electron transition, 0→1, 0→2 is electron oscillatory transition.

2. Results and discussion

We can calculate only pure electron transition. Therefore, it is necessary to first determine the geometry of the ground electron state. The spin of anthracene in the ground state is zero.

Currently, the density functional theory (DFT) method is used to optimize the geometry of large molecules (larger than naphthalene). The most popular is the exchange-correlation functional B3LYP (hybrid functional). Therefore, to solve this problem, the DFT / B3LYP method was chosen. In this case, three exhibitors TZVP were selected. The optimization of the geometry of the ground and excited electron states was carried out in the Gaussian-09 program on the SKIF CYBERIA supercomputer. The equilibrium geometries of the ground and first excited electron states of the anthracene molecule were determined by the DFT / B3LYP / TZVP method.

The truth of the found geometry is confirmed by calculating the oscillation frequencies by the harmonic approximation, all frequencies not imaginary. The geometries of the ground and first excited electron states are significantly different. Therefore, the Stokes shift for the absorption and the fluorescence spectra of anthracene should not be small [14].

To characterize the anthracene electron absorption spectrum, the energy of the first electron transition $S_0 \rightarrow S_1$ and the oscillator strength were calculated by using the temporal dependent density functional theory TDDFT and B3LYP/ TZVP method. In addition, to characterize the fluorescence spectrum, the $S_1 \rightarrow S_0$ transition and the oscillator strength of its were calculated. Calculation results are shown in table 4.

Table 4. Spectra of absorption and fluorescence of anthracene monomers

Absorption Spectrum		
Wavelength, nm		Oscillator strength
$S_0 \rightarrow S_1$	381.84	0.0584
$S_0 \rightarrow S_2$	319.66	0.0002
Fluorescence spectrum		
Wavelength, nm		Oscillator strength
$S_1 \rightarrow S_0$	441.03	0.0607

As shown, modern calculations and experiments, there are 4 types of anthracene. Equilibrium geometries of the ground electron states of anthracene dimers are calculated: slipped-parallel, symmetry C2h, graphite type, symmetry Ci, T-shape, symmetry C2v, Crossed, symmetry D2d. By using the B97D functional the equilibrium geometries of the ground state of 4 anthracene dimers were obtained, the truth of which was confirmed by calculating the frequent oscillations of harmonic approximations (all frequencies not imaginary).

Dynamic and static quenching of fluorescence occurs upon contact interaction of oxygen molecules. Therefore, at the first stage of the study, it is necessary to obtain equilibrium geometry of the complex of oxygen and anthracene. Of the simplest models of the complex of oxygen and anthracene, a complex consisting of one molecule of oxygen and anthracene is proposed. Results of calculations of the electrostatic potential for anthracene molecules show that the surrounding molecules can interact mainly with the central ring. Therefore, it is fair to place the oxygen molecule on the central ring of anthracene (Fig.1).

For such a complex, it is necessary to determine the equilibrium geometry of the ground and first excited electron states. To solve this problem, the B3LYP / TZVP hybrid functional was also

chosen. The interaction with oxygen distorts the geometry of anthracene molecule. The validity of the geometry is confirmed by calculating the oscillation frequencies by the harmonic approximation. Also, the electron absorption spectrum of this complex was calculated, results of which are given in Table 5.

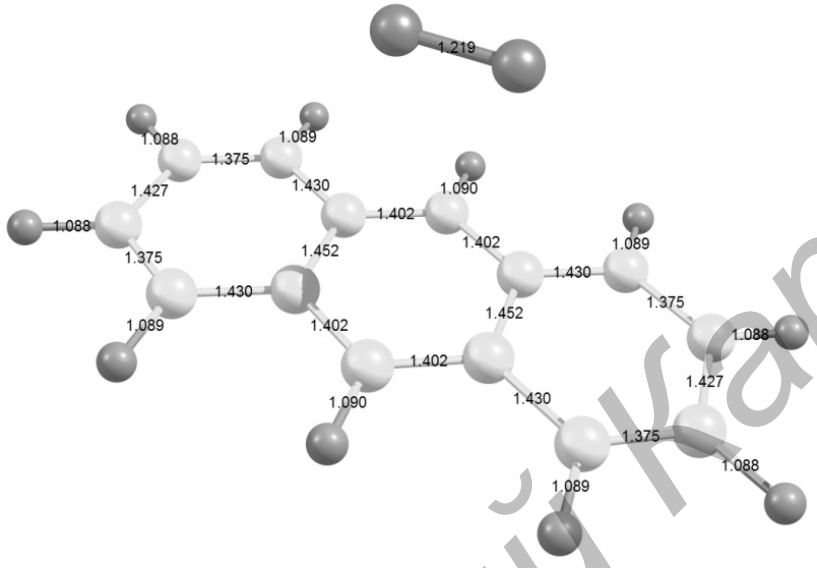

Fig.1. Equilibrium geometry of the ground electron state of the complex of the oxygen and the anthracene molecules

Table 5. The energy of the vertical electron transition for the complex of anthracene and oxygen molecules

Electron Absorption Spectrum	
Wavelength, nm	Oscillator strength
388.53	0.0568

Conclusion

For the same complex, an attempt was made to calculate the equilibrium geometry of the first excited state to characterize fluorescence quenching. It was then planned to calculate the fluorescence spectrum of this complex, which would allow determining how much the intensity of this spectrum changes in the presence of an oxygen molecule, and the band that is rejected by the transition from the first excited state to the ground state is shifted. However, results of preliminary calculations showed that the anthracene-oxygen complex is not photo-stable. Therefore, it is necessary either to use *ab initio* (more precisely) methods or to consider anthracene complexes that already contain two oxygen molecules.

REFERENCES

1 Tang B. Zh., Zhan X.W., Yu G. Efficient blue emission from siloles. *J. Mater. Chem*. 2001, Vol. 11, pp. 2974 – 2978.

2 Casida M.E. *Resent advances in density functional methods.* Part I. Vol. l. Singapore: World scientific, 1995, 428 p.

3 Vosko S.H., Wilk L., Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can.J.A. Phys.*, 1980, Vol. 58, pp. 1200 – 1211.

4 Gurinovich G.P. Kislorod, yego lyuminestsentsiya i vliyaniye na lyuminestsentsiyu organicheskikh molekul [Oxygen, its luminescence, and the effect on luminescence of organic molecules]. *Izvestiya Akademii Nauk SSSR, Ser.fiz*. Bulletin of Academy of Sciences of the USSR. Physics series. 1982, Vol. 46, No. 2, pp. 362 – 366. [in Russian]

5 Aymukhanov A.K., Ibrayev N.Kh., Smagulov Zh.K. Polucheniye i spektral'no-kineticheskiye svoystva nanogibridnykh plenok geptadetsilovogo efira bengal'skoy rozy i poliamfolitnogo polimera. [Production and spectral-kinetic properties of nanohybrid films of Bengal rose heptadecyl ether and polyampholytic polymer]. *Bulletin of the Karaganda University. Chemistry series*. 2010, No. 2(58), pp. 112 – 117. [in Russian]

6 Aymukhanov A.K., Ibraev N.Kh., Kucherenko M.G., Chmereva T.M. Kinetika fotoreaktsiy s uchastiyem molekulyarnogo kisloroda v plenkakh lengmyura-blodzhett. [Kinetics of photoreactions involving molecular oxygen in films of Langmuir-Blodgett]. *Optika i spektroskopiya - Optics and Spectroscopy*. 2013, Vol. 114, No. 4, pp. 120 – 126. [in Russian]

7 Aymukhanov A.K., Ibraev N.Kh., Seliverstova E.V. Mezhsloynyy perenos tripletnoy energii v plenkakh Lengmyura-Blodzhett [Interlayer transfer of triplet energy in Langmuir-Blodgett films]. *Bulletin of the Karaganda University. Physics series*. 2008, No. (51), pp. 20 – 24. [in Russian]

8 Kucherenko M.G. Kinetika staticheskogo nelineynogo samotusheniya lyuminestsentsii v kolloidnykh sistemakh [Kinetics of static nonlinear self-quenching of luminescence in colloidal systems] // - *Kolloid. Zhurnal - Colloid Journal*. - 1998. - Vol.60. No. 3. - pp. 380-388. [in Russian]

9 Rullens F., Divillers M., Laschevsky A. New Regular, Amphiphilic Poly(ampholyte)s: Synthesis and Characterization. *Macromolecular Chemistry and Physics*. 2004, Vol. 205, pp. 1155 – 1166.

10 Terenin A.N. *Fotonika molekul krasiteley - Photonics of dye molecules*. Leningrad: Science, 1967, 616 p. [in Russian]

11 Nurmukhametov R.N. *Pogloshcheniye i lyuminestsentsiya aromaticheskikh soyedineniy. - Absorption and luminescence of aromatic compounds*. M.: Chemistry, 1971. - 216 p. [in Russian]

12 Nurmukhametov R.N., Plotnikov V.G., Shigorin D.N. Priroda vozbuzhdennykh elektronnykh sostoyaniy i lyuminestsentsiya molekul [The nature of the excited electron states and the luminescence of molecules]. *Zhurnal fizicheskoy khimii*. 1966, Vol. 40, No. 5, pp. 1154 – 1157.

13 Birks T.B. *Photophysics of aromatic molecules*. Sidney-London, 1970, 645 p.

14 Mazhenov N.A., Kopbalina K.B., Effect of oxygen on the excited state of complex organic molecules. *Eurasian Physical Technical Journal*. 2012, Vol. 9, No. 2(18), 57 – 60.

Article accepted for publication 05.06.2019