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The Influence of Thermodynamical Conditions on the Photophysical Properties of Cyanoanthracene

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Semi-empirical Quantum-Chemical calculations of the photophysical molecular properties of cyanoanthracene and surrounding argon cell under different thermodynamical conditions were performed using the MD DL_POLY code. Photophysical scheme of the lowest energy levels and transition probabilities was plotted for the individual molecule. Vibrational profiles of the long-wave absorption electronic band and the first excited Frank-Condon singlet state with fluorescent live-times of the oscillating molecule were obtained. Based on the theoretical results, experimental spectroscopic data have been interpreted.

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

Introduction

One of the most important directions in chemical photophysics or photonics is the investigation of the interdependency between polyatomic molecular structures and spectral-luminescent properties such as electronic state energies, rates of decay transitions etc. A theoretical analysis of these properties is required for a better understanding of the processes involved, in particular for organic compounds. Obtaining of the experimental spectral-luminescent parameters supported by theoretical calculations can be discussed more precisely, so this allow us to determine correct electron states and to estimate the probabilities of photophysical processes between them. The quantum-chemical (QC) approach is an effective tool to study the

photophysical and photochemical properties of various compounds [1,2]. A calculation of electronic energy levels using QC approach gives energy lines corresponding to narrow spectral peaks. Molecular-Dynamics (MD) simulation could provide a capability for studying photophysical properties of organic compounds under thermodynamical influence to obtain spectral profiles [3].

QC calculations often meets serious troubles to give clear pictures of photo-physical processes within and between complex systems, such as: the transfer or exchange energy of unbound compounds (anthracene-naphthalene complex) [4,5]; the spectral-luminescent properties of molecules strongly dependent on environment behavior (tryptophan in different solvents)

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[6,7]; or the same qualities under different thermodynamical conditions (cyanoanthracene under high pressure) [8]. In some cases one can guess about structure of several separate snapshots but a lot of points are needed to describe realistic photo-processes. Instead of contrived structure modifications there is a more direct, simple and clear way to use QC and MD codes [9]. MD simulations could give an opportunity to consider interactions of a chosen molecule with external forces and solution while spectral properties of the flexible structure are calculated by QC. Hybrid MD simulation and a series of QC calculations along this process provide photophysical parameters of all possible conformers and probability to meet them for building a statistical molecular spectrum.

One of the simplest examples is cyanoanthracene under high pressure. This well-studied cyclic organic molecule has substantial experimental photophysical data. The idea to use cyanoanthracene came from the experimental research devoting to influence of different pressures on lifetime of fluorescence state of both 4-(10-cyano-9-anthracenylmethyl)-N,N-dimethylaniline (CADMA) or more simple structure 9-cyanoanthracene (9CNA or CADM, Fig. 1) and their solvent with Polymethylmethacrylate (PMMA) into chloroform [8]. These molecular fluorescent spectra are very similar and photophysical CADM properties in general define CADMA characteristics.

Method of calculation

Quantum-Chemical methods determine electronic spectra and probabilities of transitions for an isolated molecule into vacuum under low temperature. There are several ways to solve the Hartree-Fock equation using both *ab initio* and semi-empirical techniques. Semi-empirical approaches reduce the number of Matrix Element

(ME) calculations and exceed DFT in economy for many cases [10,11,12]. Photophysical processes in polyatomic systems are described by probabilities and quantum yield. The photophysical scheme of energy decay depends on transition probabilities or, in other words, rate constants of an electronic transition (k_{if}) [4,13,14].

One of the simplest way to obtain stereochemical structures of excited states, among other, is an evaluative formula to change bond-lengths $\Delta R_{AB} \approx -0.46 \Delta P_{AB}$ [6], 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. This method was applied to obtain the first excited structure of CADM whose luminescent core is flat such as the anthracene molecule (AN).

Coupling between particles was simulated by the MD DL_POLY package [15]. Noose-Hover canonical (conserved pressure and temperature NPT) for high pressure and microcanonical (conserved volume and energy NVE) for dilute gas ensembles with periodical cubic boundary conditions, were used. The Van der Waals non-bonded, bond-length, bending (valent) and torsion (dihedral) parameters were taken from or calculated according to the AMBER force field [16,17]. The molecule remained geometry as close as possible to be flat. Columbic interaction was calculated but changing of charge distribution on CADMA during the MD simulation was not considered. About 1000 particles were involved in MD run with a time-step of 0.015 ps and total time interval of 15 to 250 ps. The frequency resolution was accepted as 4.365 nm except in the 30K case where it was 1.200 nm.

The MD simulations of intermolecular interactions were used to facilitate calculation of the vibrational profiles of absorption and fluorescence spectra. The method in details has been described earlier [9] but it is needed to

mention several important points to calculate statistical spectra. The averaged absorption band $\Delta\lambda$ intensity is defined through the relative absorptivity $\varepsilon_{\Delta\lambda} = p_{\Delta\lambda} f_{\Delta\lambda}$ when $p_{\Delta\lambda} = N_{\Delta\lambda}/N$ is probability (N is a total number of conformers with calculated QC parameters). The oscillator strength $f_{\Delta\lambda}$ is accepted to be an average over wavelength interval $\Delta\lambda$. The relative radiation intensity can be estimated as a product of probabilities $I_{\Delta\lambda} = p_{\Delta\lambda} k_r \gamma_{\Delta\lambda}$ and the fluorescent 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.

Results and Discussion

Single point quantum-chemical calculation

Before discussion of the oscillating molecule under thermo-dynamical conditions the structure and properties of the isolated rigid cyanoanthracene should be studied. This molecule belongs to the anthracene class (Figs. 1a, 2a) with well-known spectral-luminescence properties and can be discussed as a cyano-substituted anthracene [7,18-20] Its photophysical processes and energy scheme have to be close to AN while the cyano-group $C\equiv N$ can make a perturbation in the system.

The absorption structure corresponded to the usual conception of aromatic carbon cyclic compounds: all bonds in the rings had lengths of 1.4 Å and valent angles of 120°. Single non-ring carbon-carbon (C–C) and carbon-nitrogen (C≡N) bonds were chosen as 1.42 and 1.16 Å, respectively. Calculated energy or frequency absorption to the first band maximum respectively to the red spectral region was $\nu(S_{0,0} \rightarrow S_{1,n}) = 27432 \text{ cm}^{-1}$ for AN and $= 26392 \text{ cm}^{-1}$ for CADM ν . A long-wave shift appeared due to the influence of the nitrogen AOs participating in electron transition from

HOMO to LUMO; this mathematically means that there is significant coefficient MO expansion over the AOs (Figs. 1a, 2a). These MOs are linear combinations of atomic orbitals (MO LCAO)

$$i = \sum_{\mu} C_{i\mu} \chi_{\mu} = \sum_A \sum_{\mu} C_{i\mu}^A \chi_{\mu}^A, \text{ where } i \text{ and } k \text{ are the}$$

occupied and unoccupied MOs, respectively, and χ_{μ} are the AOs of s - or p -type ($\chi_{\mu}, \mu = ns, np_x, np_y, np_z$). The square coefficients of expansion $|C_{i\mu}|^2$ determine the contribution of each AO χ_{μ} to the MO $|i\rangle$. The wave function of the excited state

$$\Phi = \sum_{ik} A_{ik} |i \rightarrow k\rangle, \text{ the configuration interaction}$$

(CI), is the linear combinations of single excited configurations $|i \rightarrow k\rangle$ formed by electron transitions from occupied to unoccupied MOs [1,2].

The energies were calculated using 17 occupied MOs and 15 vacant MOs. Such CI matrix included all important $\pi\pi$ MOs, giving an exact photophysical picture, but could overestimate energy levels by more than 1500 cm^{-1} for complete CI = 33×30 , not breaking the molecular luminescent properties, but significantly reducing the calculation time.

Different experimental data give maxima of the first absorption band of AN as 27700 cm^{-1} and CADM as 26170 cm^{-1} [17]. High oscillator strengths of AN and CADM $f_x = 0.27$ and $f_x = 0.34$ provide the molar absorption coefficients as $\varepsilon_{\max} \approx 1.25 \times 10^4$ and $\varepsilon_{\max} \approx 1.57 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$. It can be seen that the CADM absorption possibility is a little better than AN. The next effective absorption maximum is $\nu = 41092 \text{ cm}^{-1}$ with $f_y = 2.47$ for AN and for CADM $\nu = 40720 \text{ cm}^{-1}$ with $f_y = 2.29$. Again, the CADM maximum is shifted to the long side but has a lower $\varepsilon_{\max} \approx 10.60 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ than for AN with $\varepsilon_{\max} \approx 11.44 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$. It is possible to conclude that the presence of the cyano-group, perhaps due to lone electron pair

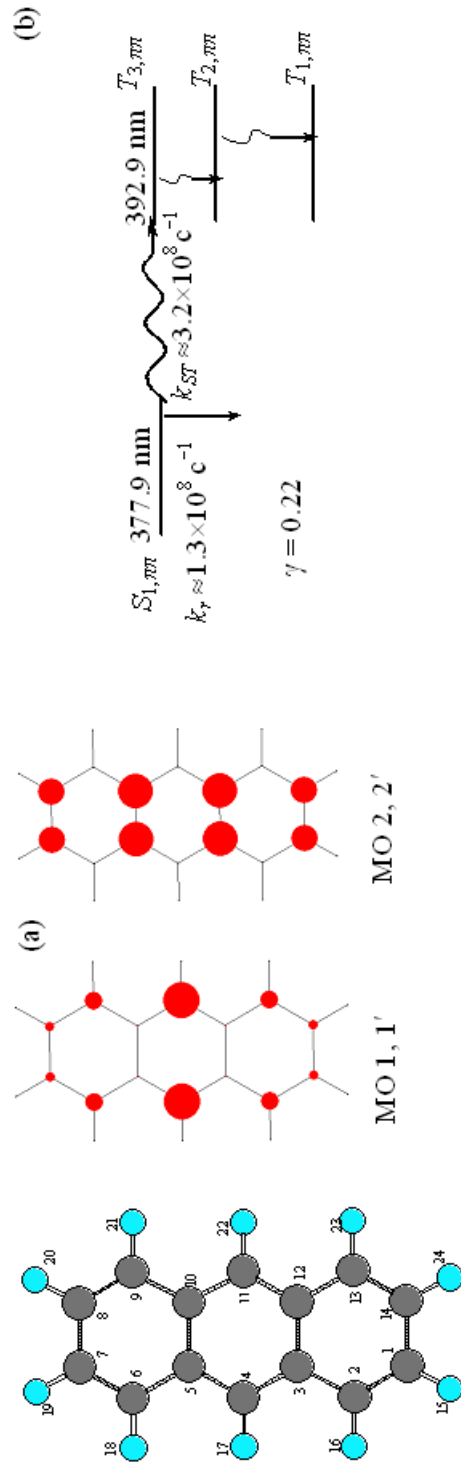


Fig. 1. Distribution MO over AO (a) and the photophysical scheme of AN (b)

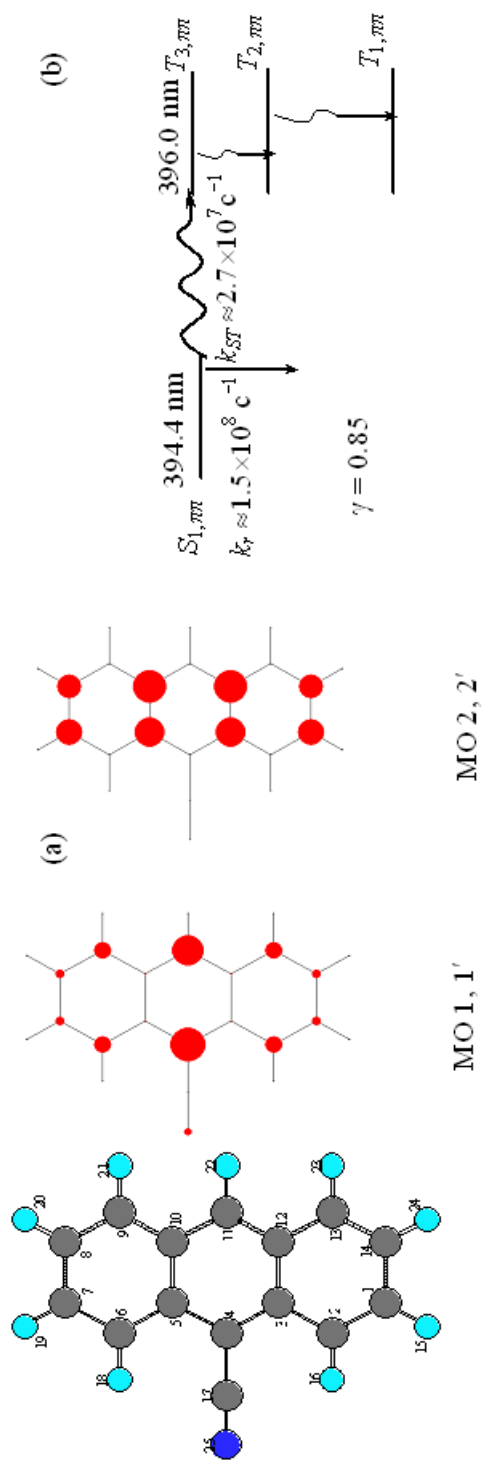


Fig. 2. Localization of MO (a) and the photophysical scheme of CADM (b)

of nitrogen, lowers the energies of all visible and violet spectra.

In order to calculate the fluorescent maximum the molecular geometries were changed to an excited structure. The excited state decays according to the probabilities of photophysical processes proceeding in the molecule that can be detected and confirmed by an experimental quantum yield of fluorescence. An analysis on the computed electronic states and rate constants of the internal, spin-orbital and radiation processes provided the schemes of the lowest energy levels and their degradation (Figs. 1b, 2b). Predominant processes were fluorescence and spin-orbital transitions. The internal conversion was very small and hence neglected. Both molecules had almost equal probabilities of radiation, due to the very developed π -systems but very different quantum yields due to less effective the spin-orbital interaction of CADM. The fluorescence of AN had efficiency about 20% and close to 90% for CADMA [19,20] The CADM fluorescent lifetime τ_f in the gas phase was shot $\tau_f \approx 3$ ns compared with that in solution $\tau_f \approx 14-15$ ns and the normal mode (0-0) of the observed vibrational bands was 382.1 nm (26173 cm^{-1}). Spin-orbital interaction between S_1 and closest Triplet is stronger in An (ME is $\langle S_1 | H_{SO} | T_3 \rangle = 0.32 \text{ cm}^{-1}$) than in CADM ($\langle S_1 | H_{SO} | T_3 \rangle = 0.07 \text{ cm}^{-1}$) that, perhaps, determined by lone electron pairs (n -type AOs) localized on N atoms. Both molecules were calculated in equilibrium flat position "in-plane" when there is no mixing of π - and σ -orbitals.

If molecules are flexible then their high symmetry can be broken under external impacts and in the "out-of-plane" case the distortion in the molecular plane structure leads to mixing of the π - and σ -orbitals, to increasing spin-orbital interaction and to quenching the fluorescence. This effect, among others, could be studied

involving MD simulation of thermo-dynamical influence.

MD and QC simulation of the oscillating molecules.

There are no experimental absorption spectra dependent upon the high pressure and the present research on this process was more predictive than comparative case except for under weak conditions. Initially, The MD system was prepared with low temperature = 30 K and pressure ≈ 0.4 bar.

The absorbent systems under temperature 300 K with two significantly different pressures of almost normal 4 Bar and very high 20 kBar were studied as well (Fig. 3a). According to QC theory the absorption goes to the band maximum. The straight dotted line marks the absorption electronic state of the flat rigid molecule. Spectral peaks of the molecule in dilute gas under low temperature can be seen to be pretty close to its wavelength. The main reason for the visible shift in absorption maxima is temperature growth. This shift is substantial for 30 and 300 K but for rest of curves the outlines almost coincide. CADM under various pressures has spectra with similar molar coefficients and different shapes while temperature defines spectral widths. The system under 20 kBar has a liquid or is close to a solid condition and perhaps due to this has a more relief profile than the smooth curve which is under 4 bar in the gas phase.

There are two lowest plots (Figs. 3b and 3c) to show a relationship between the fluorescent intensity of the vibrating molecule and its quantum yield. In the given model, taking into account the weakly changing radiation constant, the intensity depends only on the spin-orbital interaction. This can be expressed experimentally through the fluorescent quantum yield. The average quantum yield was calculated for every chosen wavelength interval (Fig. 3c). The divergence from the initial

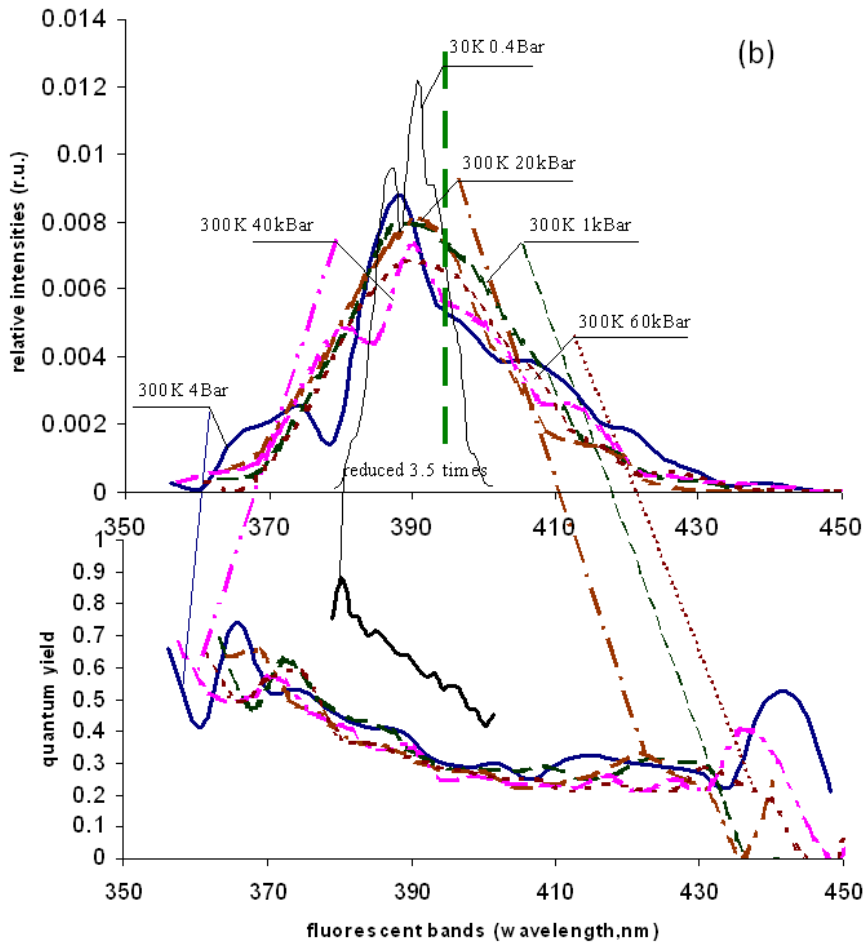
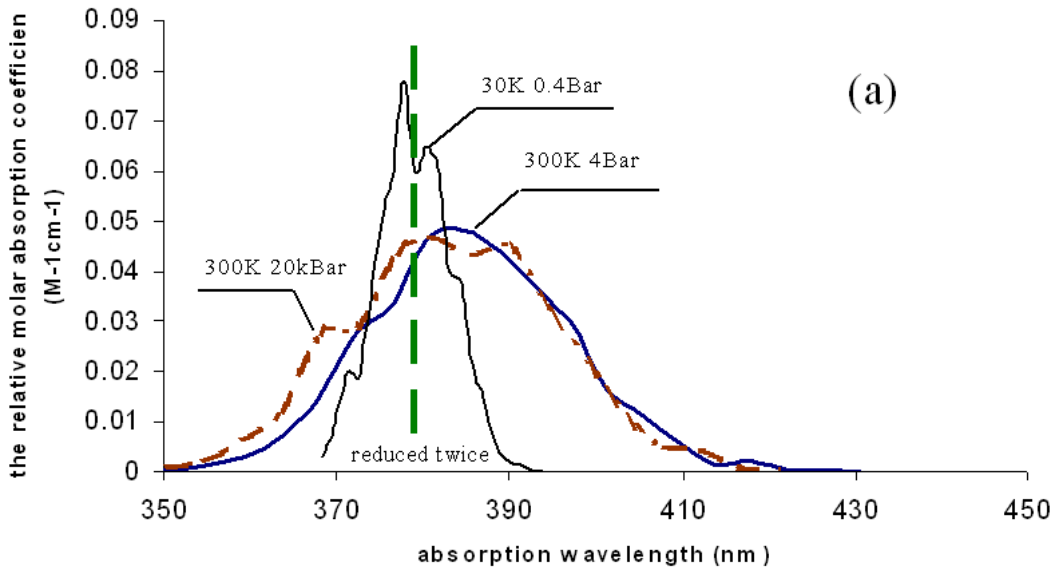


Fig. 3. Spectral bands of CyanoAnthracene

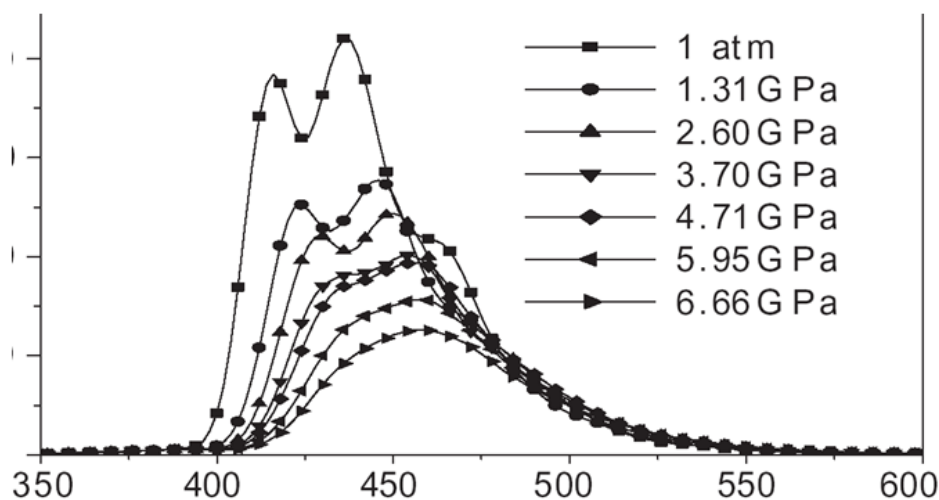


Fig. 4. Experimental spectra under pressure

Table 1: Final vibrational energy averages and (r.m.s. fluctuation) of one CADM in the argon cell [kcal/mol]

ENERGY	chemical bond	angle bending	dihedral torsion
T=33.9±0.9 K P=0.35±0.15 Bar	1.04±0.24	1.16±0.29	0.85±0.20
T = 300 K P = 4.3±0.5 Bar	10.03±2.55	8.68±2.38	8.03±2.18
T = 300 K P = 1 kBar	10.08±2.37	8.21±2.21	7.17±1.99
T = 300 K P = 20 kBar	9.16±2.27	7.16±2.14	6.74±1.87
T = 300 K P = 40 kBar	10.94±2.57	8.65±2.39	8.25±2.41
T = 300 K P= 60 kBar	9.79±2.38	7.73±2.23	8.24±2.44

structure leads to an increase of the quantum yield but there is a tendency for it to decrease on the long-wave side. Only the middle part under these curves are of interest because their quantum yields, at the end of the spectral wings, are averaged over only a few sets of the values and do not give the real picture. Moreover, the intensities of these parts are low.

Comparing with the absorption plot (Fig 3a) it can be noted that the peaks are shifted to the long-wave side due to an initial energy split between the first electronic singlet levels of the flat frozen absorption and fluorescent molecular structures. Profiles of absorption and fluorescent spectra under T=30K have mirror symmetrical

relief profiles. Two evident vibrational maxima of anthracene and the ordinary Stokes shift are observed.

Temperature increases make the spectra wider and practically in one wavelength interval for all pressure cases. But under different pressures the profiles vary. At room temperature the spectral shape becomes less sharp and washes out with applied pressures of 1 to 20 kBar. Below 40 kBar a distinct structure comes back and again is lost below 60 kBar. This phenomenon can be explained as an attempt to join the phase condition of solvent and spectral properties. The solvent remains liquid at 20 kBar and become solid above this.

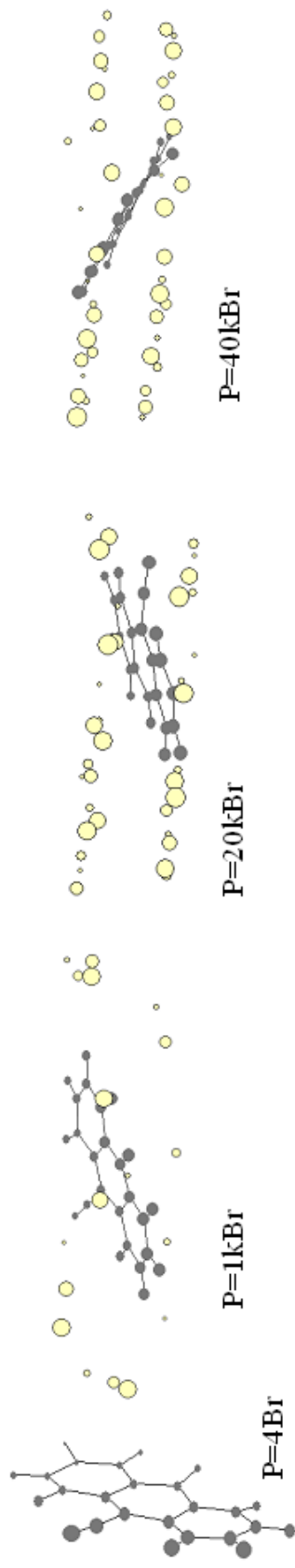


Fig. 5. Final XZ-plane snapshots of MD system under different pressure and temperature = 300°

The molecule is more flexible in fluid and has more degrees of freedom than in solid. A pressure of 40 kBar can be in the transitional phase and have mixed properties but at 60 kBar becomes completely solid and quenches oscillations. This is only a supposition and not an assertion. It seems to be possible to support this idea by the following comparative and calculated data.

In order to connect with experimental and theoretical data it can be noted that both calculated (under 40 kBar, Fig. 3) and experimental (under 2.60 GPa = 26 kBar, Fig. 4) look very similar. The total vibrational energies of bond-lengths, valent and dihedral angles (Table 1) give a sense that the oscillation activity falls along the pressure mounting under constant temperature, but in the 40 kBar region the total energy leaps and then decreases. This is consistent with the snapshots having sides of approximately 30 Å from the MD region (Fig. 5). Concentration and argon atom positions reflect thermodynamical conditions. The solvent rearranges to the crystal state. Argon and atoms of the molecule are captured near some positions and oscillate over the fixed sites. A pressure of 40 kBar is critical for the argon solvent whereas for PMMA films a pressure of 26 kBar is critical. The radiation probability is maintained between 10^7 and $1.5 \times 10^8 \text{ sec}^{-1}$ through the entire MD run. Neither valent angles nor dihedrals reach critical magnitudes. There is no significant change in these angles, probably because the molecule undergoes a uniform impact from argon solvent under different thermodynamical condition and therefore there is not big wavelength shift. Probably if

the solvent is not neutral like argon and impact is not homogeneous it is possible to obtain a stronger dependence of CCN angle on the thermodynamical condition.

The simplified model has the following evident restrictions. The scheme of interactions is incomplete. The argon solvent was applied instead of PMMA. Using only one molecule excludes intermolecular interaction and at the same time "concentration quench" of fluorescent intensity. A more complete model in future must involve an intricate medium in which organic molecules really dissolved, several molecules of the studying type, and a longer time for the MD run, comparable with the lifetime of the fluorescent state, as well as, taking into account Coulombic coupling.

Conclusions

The photophysical schemes of the lowest anthracene and cyanoanthracene electron energy levels and transitions between them look very similar but the presence of the CN bond changes the ratio between probabilities of the radiation and cross-section transitions apparently through contribution of AOs of this bond to MOs of the interacting states.

The vibrational width depends on temperature but together with pressure they define spectral outline and structure, and the spectral shape is strongly connected to the thermodynamical phase of the condition.

CADM embedded to argon solvent deals with homogeneous thermo-dynamical impact and there is no reason to expect radical structure changing. The spectral shifts can be obtained for more realistic compounds and solvents (complex CADM-PMMA) in future works.

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Влияние термодинамического состояния на фотофизические свойства цианоантрацена

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Проведены полуэмпирические квантово-химические расчеты фотофизических свойств цианоантрацена в ячейки с аргоновым растворителем при различных термодинамических условиях. Использован MD DL_POLY пакет. Построена фотофизическая схема низших уровней с вероятностями переходов для изолированной молекулы. Получены колебательные профили длинноволновой электронной полосы поглощения и первого возбужденного Франк-Кондоновского синглетного состояния с учетом флуоресцентного времени жизни для осциллирующей молекулы. Дана интерпретация экспериментальных спектроскопических данных.

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