Ab initio study of optical properties of rhodamine 6G molecular dimers

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Equilibrium atomic geometries of rhodamine 6G (R6G) dye molecule dimers are studied using density-functional theory. Electron-energy structure and optical properties of R6G H and J dimers are calculated using the generalized gradient approximation method with \textit{ab initio} pseudopotentials. Our theory predicts substantial redshifts or blueshifts of the optical absorption spectra of R6G dye molecules after aggregation in \textit{J} or \textit{H} dimers, respectively. Predicted optical properties of R6G dimers are interpreted in terms of interatomic and intermolecular interactions. Results of the calculations are discussed in comparison with experimental data. © 2006 American Institute of Physics. [DOI: 10.1063/1.2158987]

I. INTRODUCTION

The use of dyes in dye lasers and various photoinduced reactions caused extensive studies of their electronic and optical properties. More recently, dyes have become the subject of renewal interest, which has been focused on the phenomenon of molecular aggregation. Rhodamine 6G (R6G) dye is one of the most efficient laser dyes characterized by a high-efficiency luminescence band around 560 nm (see, e.g., Ref. 6 and references therein). However, optical properties of high-concentrated R6G dyes differ from those of isolated dye molecules. The R6G dye has a high tendency to form \textit{H}-type nonluminescent dimer sandwichlike aggregates with parallel-aligned molecular axes. Another configuration of R6G molecules with head-to-tail aligned dipole moments (\textit{J}-type dimers) was normally observed in the presence of an additional external potential (by intercalation, on solid surfaces, etc.). \textit{H}-type R6G dimers are associated with a remarkable blueshift in the optical absorption band with respect to R6G monomers. On the other hand, \textit{J}-type R6G dimers are characterized by a redshifted luminescence band.

It has been demonstrated for decades that Kohn-Sham density-functional theory (DFT) realistically predicts the electronic structure of different systems, such as atoms, molecules, and solids. Various generalized gradient approximation (GGA) methods describing exchange and correlation (XC) interaction have been shown to systematically improve the local density approximation (LDA) predictions of equilibrium atomic geometries. In atomic systems (such as large single molecules, inorganic solids, etc.) the geometry optimization study primarily requires accurate prediction of the short-range interatomic interaction which is well reproduced within a standard DFT approach (see, e.g., Refs. 10 and 11). However, in addition to the short-range interaction, a geometry optimization study in the molecular system requires also realistic predictions of the long-range (electrostatic) interaction which is not straightforward within a DFT. In order to be able to realistically calculate the dipole (van der Waals) term of the interaction energy one needs to reliably predict a charge distribution in the system. This is a many-body effect which requires realistic modeling of the XC interaction, and it is more challenging for the DFT-GGA. The Perdew-Wang (PW) model for XC has been used in Ref. 14 to study simple organic molecular dimers. The Perdew-Burke-Ernzerhof (PBE) functional accounting for XC interaction leads to further improvements against PW in predictions of equilibrium geometry and electronic properties of molecular systems. The PBE model of XC interaction was modified in Ref. 16 by introduction of several new formal parameters into the original PBE-XC functional, the extended PBE (xPBE) method, which shows some improvement for simple molecular systems. The last method, however, is less transparent for understanding the physics of the interaction because of the new parameters which could not be easily interpreted. Comparative study of predicted equilibrium distances and bonding energies clearly indicated that the PBE (and xPBE) methods predict these parameters with better than 10% accuracy for a number of simple molecular dimers. However, for more complex molecular systems these methods could result in bigger deviations, consequently the predicted values should be taken cautiously. This point is addressed below in this work by discussing equilibrium geometries of R6G dimers predicted in this work.

Electronic excitations are key points of most of the commonly measured optical spectra. The first-principle studies of excited states, however, require much larger effort than computations of the ground state. Theoretical approaches for computation optics could be roughly separated into two large groups. In first group methods the system of independent particles excited by an external light field is considered within perturbation theory [the random phase approximation (RPA)]. The DFT is used as a zero-order solution and other corrections to the electron self-energies (such as many-body, local-field effects, quasi particle (QP) shifts) are applied. Optical response functions are calculated by solving a set of Green’s function equations. An alternative approach to predict electronic excitation energies is the time-dependent den-
sity functional theory (TDDFT). For many systems the last approach offers practical advantages (e.g., excitonic effects in both organic and inorganic materials). Comparative analysis of both approaches is given in a recent review. For predictions of linear and nonlinear optical responses both approaches are equivalent as demonstrated in Ref. 19.

Nonradiative and luminescent characters of $H$ and $J$ dimers, respectively, have been semiqualitatively interpreted in the literature using excitonic theory. It has been argued that observed blueshifts of eigenvalues is achieved with $E_{\text{R6G single molecule}}$. An accuracy of better than 10\% for the R6G single molecule. An accuracy of better than 10\% for the approach offers practical advantages. A comparative analysis of both approaches is given in a recent review. For predictions of linear and nonlinear optical responses both approaches are equivalent as demonstrated in Ref. 19.

In this study, we present the results of the numerical analysis of electron-energy structure and optical properties associated with molecular R6G dimers based on the state-of-the-art first-principle methods in computational physics and chemistry.

II. METHOD

We have used both commercial and research computational packages based on $ab\ initial$ pseudopotentials (PP). The electron-energy structure and eigenfunctions of R6G single molecules and molecular dimers were calculated within DFT-GGA using fully separable $ab\ initial$ PP generated according to the Troullier-Martins scheme. An energy cutoff up to 60 Ry is taken for a generated fully separable PP. Convergence of the ground state has been proved by test calculations with an energy cutoff ($E_{\text{cut}}$) up to 100 Ry for the R6G single molecule. An accuracy of better than 10\% for eigenvalues is achieved with $E_{\text{cut}}=45$ Ry. The QP corrections are calculated as in Ref. 18 only for the monomer. For the atomic relaxation of single-molecule and molecular dimers the supercell method is used. The GGA-PBE functional was used to model XC interaction. Dimensions of the supercell are determined from the following consideration. The main purpose to introduce the supercell is to simulate a virtual crystal in order to define periodical pseudopotentials. On the other hand, it should be large enough to avoid additional intermolecular interactions between molecules from the neighboring cells. However, increase of the supercell dimensions immediately results in a dramatic increase of the plane wave numbers in the evaluation of the PPs. No effect on the results has been found for the systems studied if the volume of the supercell exceeds $20 \times 15 \times 15$ Å$^3$.

The optimized geometries of the dimers were obtained in a few steps. First, the equilibrium atomic geometry of the single molecule was determined. Then every single molecule was kept frozen in order to get the molecular dimer configuration. After that boundary atoms were allowed to relax. The last steps were repeated until the full convergence of the geometry of dimers.

Optical absorption spectra were calculated within RPA approach according to

$$\alpha(\omega) = 2\omega k(\omega),$$

The extinction coefficient $k$ was determined through real and imaginary parts of the dielectric permittivity function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$ according to the formula

$$k(\omega) = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1},$$

The isotropic dielectric susceptibility function $\varepsilon(\omega)$ is given through the components of the second-rank dielectric tensor $e_{\alpha\beta}(\omega)(\alpha, \beta = x, y, z)$,

$$\varepsilon = \frac{1}{2}(e_{xx} + e_{yy} + e_{zz}).$$

The evaluation of $e_{\alpha\beta}(\omega)$ in this work is based on the independent particle approximation. The time-dependent linear optical susceptibility function follows from the equation of motion for the density matrix (the RPA picture). The function of $e_{\alpha\beta}(\omega)$ is given by

$$e_{\alpha\beta}(\omega) = 1.0 + 8\pi \sum_{n,m} \frac{f_{nm}(n|\nu_\alpha|m)(m|\nu_\beta|n)}{\omega_{nm} - \omega - i\Gamma},$$

where $\nu_\alpha$ and $\nu_\beta$ are Cartesian components $(\alpha, \beta = x, y, z)$ of the velocity operator, $\omega_{nm}=E_n-E_m$, $f_{nm}$ is electron occupation function (taken here at zero temperature), and indices $n$ and $m$ denote empty and filled electronic states. The intraband electron transitions are excluded in this study because of the negligible contributions. Note, that we use atomic system units: $m_0=h=e=c=1$. We also neglected the optical momentum nonlocality effects and replaced velocity operator $\vec{\nu}$ for momentum operator $(\vec{p}=\vec{\mu}=-\vec{e})$. In this case Eq. (4) agrees with that given in Ref. 19 for linear optical response. Neglect of the effects of nonlocality may cause errors in the predictions of the shape of optical spectra, which could be not small in molecular systems. However, this point is beyond the scope of the present study and will be addressed explicitly elsewhere.

III. RESULTS AND DISCUSSION

Equilibrium atomic configuration of the single R6G molecule was determined by geometry optimization as described above. Comparison with the results provided by other commercial packages [GAUSSIAN-03 and JAGUAR 4.2 (Refs. 30 and 31)] indicate that the latter packages, based on quantum chemistry methods, are faster for this system than the PP method in producing equilibrium geometries of the single molecule. The $ab\ initial$ PP theory is more often used for crystals. For molecular systems, it is applied in a supercell version, which requires more extensive computational work. However, agreement of the results predicted by PP theory...
with experimental optical data is better, as it has been proven in this work.

We found that the H-type configuration is energetically favorable against the J type,

\[ \Delta E_{\text{tot}} = E_{\text{tot}}^H - E_{\text{tot}}^J = -0.064 \text{ eV}. \]  

The relatively small energy difference (\( \Delta E_{\text{tot}} \approx 3kT \)) indicates that both configurations of free standing R6G dimers could coexist at room temperature with a concentration ratio of H- to J-type dimers of at least one order of magnitude. In Figs. 1 and 2, fully relaxed atomic configurations of H- and J-type R6G molecular dimers are shown. The molecular axes in H type are antiparallel with a twisted angle \( \theta_J = 28^\circ \). The predicted angular value perfectly matches the experimental one (\( \theta_J^{\text{exp}} = 29^\circ \)) recently reported in Ref. 5 for R6G molecules intercalated in fluor-taeniolite (TN) film. For J-type dimers, our analysis predicts only one equilibrium configuration with the angle between molecular axes \( \theta_J = 93^\circ \) (T-shape configuration shown in Fig. 2). This value is in reasonable agreement with reported torsion angle values of 105° and 109° obtained in Ref. 7 using excitonic theory\(^{20}\) from optical absorption spectra of R6G dimers intercalated in Laponite Clay. The predicted distance between geometrical centers of the molecules in J dimer, 0.803 nm, is lower than the value of 0.95 nm obtained from the optical absorption in Ref. 7. However, the predicted intermolecular distance of the free standing H-type dimer, \( \Delta R = 0.24 \) nm, is much smaller than the reported experimental value of 0.71 nm of intercalated dimers.\(^5\) These discrepancies require some comments. On one hand experimental data in Refs. 5 and 7 were obtained from optical absorption using semiquantitative analysis based on the excitonic theory.\(^{20}\) Within this model intermolecular interaction is assumed of pure van de Waals type, and neglect of the short-range interaction may cause errors. The intermolecular distance may also increase by intercalation in the TN system\(^5\) or in Laponite Clay.\(^7\) On the other hand, the predicted value of intermolecular distances should also be taken cautionary. Our model incorporates both short- and long-range (dipole-dipole) interactions. The short-range interaction is determined straightforward from DFT-GGA electronic structure through the calculations of corresponding overlap integrals. However, dipole-dipole interaction is incorporated through self-consistent calculations of the charge distribution over molecules in dimers. This essentially many-body part requires a realistic description of XC interaction, and it is still challenging for the DFT-GGA approach. Several models for XC were proposed within the last decades. In this work we used the PBE (Ref. 15) approach for XC interaction which was proved in Ref. 16 by a geometry optimization study of the dimers formed from relative small molecules. The limitations of this approach may result in discrepancies observed. One can expect that further development of the XC model will result in better agreement between predictions and experiment.

For a better understanding of the numerical results, it is instructive to refer to the electrostatic theory. The calculated static dipole moment (\( \mu \)) is found to be parallel to the molecular axis oriented along benzene rings of the R6G molecule. Assuming all molecules have been identical, the attractive potential energy describing dipole-dipole interaction is given by\(^{29}\)
nant peak located at 483 nm also another small peak located at 526 nm.

\[ \text{Absorption (cm}^{-1}\text{)} \]

\[ \text{Wavelength (nm)} \]

FIG. 3. Predicted optical absorption spectrum of the single R6G molecule (solid line) in comparison with experimental data (dots) (Ref. 31).

\\[ V(r) = \frac{|\mu|^2}{|r|^6} f(\theta), \quad \text{with } f(\theta) = (1 - 3 \cos^3 \theta), \quad (6) \]

where \( \theta \) is an angle between \( r \) (location in direct space) and \( \mu \). The energy of the dipole-dipole interaction is determined through a calculation of overlap integrals with the potential (6) after integration over entire space. It is proportional to \( |r|^{-6} \), which represents the van der Waals type of interaction. Equation (6) demonstrates that a strong attractive (negative) value is expected for dipoles aligned antiparallel if aggregated in \( H \)-type dimers which should be the most energetically favorable configuration resulting in quenching the radiation. This is in agreement with direct computations of this work: total energy of the \( H \) dimer is lower than that of the \( J \) dimer [see Eq. (5)], and the predicted value of \( \mu \) for the \( H \)-type dimer is 34 times smaller than that of the \( J \) dimer.

Optical absorption spectra of the R6G single molecule as well as those of molecular dimers are calculated from Eqs. (1)–(4). The self-consistently calculated eigenfunctions and eigenenergies of dimers include QP shift of monomer. Calculated optical absorption spectrum for the isolated R6G molecule is shown in Fig. 3 in comparison with the experimental data.32 Absolute values of the absorption coefficient are normalized according to the molecular concentration followed from the dimension of the supercell.28 Electronic eigenvalues related to singlet-type electronic states are represented with better than 10% accuracy. The theoretically calculated absorption spectrum shown in Fig. 3 reproduces most of characteristic features measured experimentally. Thus, the dominant calculated absorption peak is located at 511 nm, while the same peak is seen in the experimental absorption spectrum at about 528 nm.5,30,33

The predicted optical absorption spectrum corresponding to the singlet transitions of \( H \)-type dimers shows the dominant peak located at 483 nm (2.567 eV); see Fig. 4. There is also another small peak located at 526 nm (2.357 eV). The splitting (\( \Delta E_{H} = 0.210 \text{ eV} \)) is caused by the strong intermolecular interaction between \( \pi \)-type electrons of the neighboring molecules in \( H \) dimer. In terms of excitonic theory20 these peaks correspond to antibonding (dipole-allowed) and bonding (dipole-forbidden) electronic states, respectively. Due to the twisting of the molecular axes (see Fig. 1), optical transitions to a dipole-forbidden unoccupied electronic state in \( H \)-type dimers are weakly allowed (see also Refs. 3 and 6). The predicted absorption maximum of R6G monomers (Fig. 3) is located at 511 nm. Therefore, our theory predicts a strong blueshift (\( \Delta \lambda = 28 \text{ nm} \)) in optical absorption of R6G due to the creation of \( H \)-type dimers. Very close to this value are reported experimental data of absorption maxima at 501 nm (Ref. 5) and 500 nm (Ref. 7) [as compared to a 528 nm maximum in initial spectrum (Refs. 5 and 7)] of R6G molecules intercalated in a fluor-taeniolite film5 or in a Laponite Clay,7 which were interpreted as an indication of \( H \)-type dimers. On the other hand, our recent study33 does not reveal any remarkable changes in optical absorption with increase of the concentration of R6G molecules in methanol solution from 0.1 to 3.8 g/l. One can speculate that intercalation substantially increases the probability of aggregation of R6G molecules.

For \( T \)-shaped \( J \)-type R6G dimers, our theory predicts splitting of the main absorption peak into two maxima located at 527 nm (2.353 eV) and at 506 nm (2.451 eV); see Fig. 5. The splitting (\( \Delta E_{J} = 0.098 \text{ eV} \)) is caused by the hydrogen-bonding interaction of boundary atoms from one molecule with delocalized \( \pi \) electrons from the other molecule in the \( J \) dimer. In terms of the excitonic theory,20 this situation corresponds to the oblique mutual orientation of molecular dipoles when electronic transitions to both electronic unoccupied levels are allowed (see discussion in Refs. 3, 6, and 7), in agreement with our results. Obtained values of the total energy minima as well as values of \( \Delta E_{H} \) and \( \Delta E_{J} \) clearly indicate that intermolecular interaction in \( H \) type is substantially stronger then that in \( J \)-type R6G dimers.

Theoretical results above are consistent with the experimental data presented in our recent publication.33 In Ref. 33, optical absorption, emission, and excitation spectra of a pure solution of R6G in methanol at a concentration of the mixture in the range from 0.1 to 16.7 g/l have been measured.
Based on the emission and absorption spectra of R6G dye in 0.1 g/l methanol solution (recorded using straightforward procedures described in Ref. 33) and the luminescence decay time of a low-concentrated R6G, $\tau_{em}=5 \times 10^{-9}$ s, we observed the appearance of the second emission band at 600 nm. The quantum yield of luminescence of the donor, $\eta_0$, was redshifted with respect to the single R6G molecule, which was redshifted with respect to the absorption spectrum. A theoretical prediction of a strong blueshift in optical absorption spectra due to H dimers (see Fig. 4) agrees with experiment of intercalated R6G. On the other hand in Ref. 33 we have not observed any new blueshifted peaks in the optical absorption of free-standing R6G aggregates even at a very high concentration of R6G where well-pronounced splitting in luminescence has been measured (at 16.7 g/l; see also Fig. 6). One can speculate that the stability of free-standing dimers at room temperature is very low, but it could be enhanced through surface adsorption and/or intercalation.

In order to answer the second half of the question above, why in this case there is a relatively strong second band (the $J$ band because $H$ dimers are nonradiative, as discussed above) in the emission, we use assumption 2: there is an efficient energy transfer from monomers to dimers. In support of this assumption, we estimated the energy transfer in R6G aggregates. Our approach exploits the readily achievable coupling via incoherent long-range dipolar interaction, which allows intermolecular communication via Förster energy transfer (see, e.g., Ref. 34 and references therein). The intermolecular distance $R_0$ at which the efficiency of the energy transfer is equal to 50% (Förster radius) is given by

$$R_0^2 = \frac{3}{2(2\pi)^2} \eta_0 \int F(\bar{\nu}) \sigma_{abs}(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4}.$$  

(7)

where $\bar{\nu}=\omega/2\pi c$ is the wave number (cm$^{-1}$), $\sigma_{abs}(\bar{\nu})$ is the effective cross section of acceptor absorption, $n$ is the refractive index [dispersion of $n$ is neglected in Eq. (7)], $\eta_0$ is the quantum yield of luminescence of the donor, and $F(\bar{\nu})$ is the normalized radiation spectrum expressed as the number of quanta per unit frequency range,

$$\int F(\bar{\nu}) d\bar{\nu} = \int F(\lambda)\lambda d\lambda = 1.$$  

(8)

In expressions (7) and (8), we used a conventional relationship of argument scale conversion for radiation spectrum (see, e.g., Ref. 35). Following Ref. 36, the effective emission cross section $\sigma_{em}(\lambda)$ can be calculated as

$$\sigma_{em}(\lambda) = \frac{1}{8\pi n^2 c \tau_{em}} \eta_0 \lambda^5 F(\lambda),$$  

(9)

where $\tau_{em}$ is the emission lifetime, and $c$ is the light speed. Combining Eqs. (7) and (8), we obtain a convenient formula for calculating the Förster radius,

$$R_0^2 = \frac{3}{8\pi^4} \frac{c \tau_{em}}{n^2} \int \sigma_{em}(\lambda)\sigma_{abs}(\lambda) d\lambda.$$  

(10)

did we not see the presence of dimers in absorption while we observed $J$ dimers in emission? To answer the first half of this question, we use assumption 1: the concentration of dimers was low. Our prediction of a strong blueshift in optical absorption spectra due to $H$ dimers (see Fig. 4) agrees with experiment of intercalated R6G. On the other hand in Ref. 33 we have not observed any new blueshifted peaks in the optical absorption of free-standing R6G aggregates even at a very high concentration of R6G where well-pronounced splitting in luminescence has been measured (at 16.7 g/l; see also Fig. 6). One can speculate that the stability of free-standing dimers at room temperature is very low, but it could be enhanced through surface adsorption and/or intercalation.
which results in a bigger value of the Förster radius $R_F$.

$R_F$ is characterized by a strong interaction of the electronic cross sections of R6G monomers, and the luminescence of the R6G dye is determined through optical absorption spectra. The results of this work are discussed in comparison with available experimental data.

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