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Improving the simulation of vibrationally resolved electronic spectra of phenanthrene: A computational Investigation

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ABSTRACT

Based on the density functional theory and its time-dependent extension, the properties of the ground and the first excited states of phenanthrene were calculated. In harmonic and anharmonic approximations, the well-resolved absorption and emission spectra of phenanthrene were simulated using the Franck–Condon approximation combined with the Herzberg–Teller and Duschinsky effects, and the results reproduced the experimental spectra very well. The mirror symmetry breakdown between absorption and emission spectra is induced mainly from the Herzberg–Teller effect and Duschinsky mode mixing. Moreover, most of the vibrational modes were tentatively assigned and compared with the experiment.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the largest class of mutagens and carcinogens as far as we know [1,2]. Phenanthrene, as the prototypical molecule of non-linear PAHs, has been studied extensively [3–19]. Its X-ray structure was reported by Trotter and Mason et al. [3,4] and refined by Kay et al. [5]. The lowest excitation energy was investigated by Otokozawa et al. [6] who concluded that the $S_1 \leftarrow S_0$ (S_0 is ground state and S_1 is first excited state) absorption is weak and should be identified as ^1L_b and similar result could be found in Grimme's work [7]. The Raman [8,9], IR [10], fluorescence and fluorescence excitation [11–14] spectra were also reported. The optical spectra enable us to have a further understanding of the excitation energies and equilibrium geometries. However, drawbacks were that only the main vibrational bands in the experimental spectra were assigned and the tentative assignments in the experimental spectra [12] needed to be confirmed based on the theoretical simulations. The reasons of mirror symmetry breakdown between the excitation and fluorescence spectra also needed to be analyzed in theory. As for quantum mechanical methods, if reliable vibrational structures were obtained, it may provide a direct link between the spectral property and geometrical parameters [15]. Therefore, a number of theoretical studies were performed to explore the properties of phenanthrene [16–19]. Although the equilibrium geometries and vibrational frequencies were reported in many theoretical investigations, little effort was made in the theoretical simulation of the high-resolved absorption and emission spectra together with the intensity, symmetries and frequencies. Therefore, the simulations of well-resolved spectra and the detailed assignments of vibrational modes are helpful to understand the relationship between equilibrium geometries and vibrational structures of phenanthrene.

It is well-known that the transition dipole moments of strong dipole-allowed transitions could be considered independent of the nuclear coordinates (Condon approximation) [20]. This approximation is usually satisfactory for transitions characterized by large oscillator strengths, giving rise to the so-called Franck–Condon (FC) spectrum. However, it is often inadequate for weak and forbidden transitions like the $S_1 \leftrightarrow S_0$ band of phenanthrene [21]. Therefore, it is necessary to consider the Herzberg–Teller effect, causing the phenomenon of intensity borrowing [22]. The Duschinsky mixing of normal coordinates in initial and final states should be included for a proper description of Herzberg–Teller effect [13,23–26]. In addition, although the harmonic approximation could provide a relatively effective general treatment of vibrational structure, the obtained harmonic frequencies usually have some systematic errors as the specific anharmonicity in the fundamental frequencies is ignored. Therefore, the anharmonic effect should also be taken into account for the spectra simulation and the assignments of vibrational modes [27,28].

In this Letter, the properties of the S_0 and S_1 states were obtained using the density functional theory (DFT) and its time-dependent extension (TD-DFT) with different basis sets. The excitation

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energies were used to compare with the experimental values and the S_1 state was identified as ^1L_b. The spectra simulated in harmonic and anharmonic approximation were compared with the experimental findings, and a good agreement between the simulated and experimental spectra could be found. The breakdown of mirror symmetry between the absorption and emission spectra was reproduced very well, and the possible reasons were given. Especially, the main vibrational modes in the absorption and emission spectra were assigned, which is meaningful to understand the photophysical properties of phenanthrene.

2. Computational methods and theoretical details

Geometry optimizations and frequency calculations: The excitation energies, equilibrium geometries and frequencies of vibrational modes in both S_0 and S_1 states were calculated using the density functional theory and its time-dependent extension with different hybrid exchange functionals (B3LYP, PBE0 and BHandHLYP containing 20%, 25%, and 50% of exact HF exchange) with TZVP, QZVP and cc-pVDZ basis sets in this work. As a comparison, the geometrical structure and frequencies of the ground state were also calculated by MP2 and the first excited state was carried out using the meta-GGA (M062X) and long-range corrected (CAM-B3LYP) functionals. The result calculated by B3LYP/cc-pVDZ was adopted to compare with the previous theoretical and experimental data. Other results were provided in the Supplementary material as a reference. All computations above were carried out using the GAUSSIAN09 software package [29].

Simulation of well-resolved spectra: The absorption and emission spectra were simulated using the FCclasses program [30]. The Huang–Rhys factor and the first-order anharmonic corrected spectra were calculated using our own code and the values were given in Table S7 (see Supplementary material). With the harmonic oscillator approximation, the absorption or emission coefficient for the electronic transition $m \rightarrow n$ in Condon approximation can be expressed as [22]

$$a(\omega) = \frac{4\pi^2\omega}{3\hbar c}\left|\vec{\mu}_{nm}\right|^2 \int_{-\infty}^{\infty} dt \exp[it(\omega_{nm} - \omega)] \cdot G(t) \tag{1}$$

where $\hbar$ is Planck's constant, c is the speed of light, $\vec{\mu}_{\mathrm{nm}}$ denotes the electronic transition dipole moment. Using the relation of Slater sum, Eq. (1) can be rewritten as

$$\alpha(\omega) = \frac{2\pi\omega}{3\hbar}\left|\vec{\mu}_{nm}\right|^2 \int_{-\infty}^{\infty} dt e^{it(\omega_{nm} - \omega) - \gamma_{nm}|t|} \times \exp\left[-\sum_j s_j\{2\bar{\nu}_j + 1 - (\bar{\nu}_j + 1)e^{it\omega_j} - \bar{\nu}_j e^{-it\omega_j}\}\right] \tag{2}$$

Considering the general case, a molecular system consists of N_d modes exhibiting the Duschinsky effect and N modes without mode-mixing. In this case, $G(t)$ can be written as

$$G(t) = G_{1,2,\ldots,N_d}(t) \prod_{l}^{l \neq 1,2,\ldots,N_d} G_l(t) \tag{3}$$

$G_{1,2,\ldots,N_d}(t)$ and $G_l(t)$ denote the correlation functions defined by

$$G_l(t) = \sum_{\nu l}\sum_{\nu' l} P_{m\nu_l}\left|\left\langle \chi_{n\nu_l'}(Q_l') \,\middle|\, \chi_{m\nu_l}(Q_l) \right\rangle\right|^2 \exp\left[it\left\{\left(\nu_l' + \frac{1}{2}\right)\omega_l' - \left(\nu_l + \frac{1}{2}\right)\omega_l\right\}\right] \tag{4}$$

and

$$G_{1,2,\ldots,N_d}(t) = \sum_{\nu_1}\cdots\sum_{\nu_{N_d}}\sum_{\nu'_{\alpha 1}}\cdots\sum_{\nu'_{\alpha N_d}} P_{m\nu_1\ldots\nu_{Nd}}\left|\left\langle \chi_{n\nu'_{\alpha 1}}(Q'_{\alpha_1})\ldots\chi_{n\nu'_{\alpha Nd}}(Q'_{\alpha_{Nd}}) \times \,\middle|\, \chi_{m\nu_1}(Q_1)\ldots\chi_{m\nu_{Nd}}(Q_{N_d}) \right\rangle\right|^2 \times \exp\left[it\left\{\sum_{\alpha=\alpha_1}^{\alpha N_d}\left(\nu'_\alpha + \frac{1}{2}\right)\omega'_\alpha - \sum_{j=1}^{N_d}\left(\nu_j + \frac{1}{2}\right)\omega_j\right\}\right] \tag{5}$$

That is, $G_{1,2,\ldots,N_d}(t)$ represents the correlation function of the mixing modes (i.e., the Duschinsky effect).

The electronic transition dipole moment $\vec{\mu}_{nm}$ depends on the nuclear coordinates,

$$\vec{\mu}_{nm} = \vec{\mu}_{nm}(0) + \left(\frac{\partial\vec{\mu}_{nm}}{\partial Q}\right)_0 Q + \cdots \tag{6}$$

The zero-order term of this expansion is generally referred as the Franck–Condon approximation for strongly allowed transitions, while the first-order term is the so-called Herzberg–Teller effect for weakly allowed or forbidden transitions.

The absorption coefficient for the electronic transition $m \rightarrow n$ in the anharmonic correction can be expressed as [27]

$$\alpha(\omega) = \frac{2\pi\omega}{3\hbar}\left|\vec{\mu}_{nm}\right|^2 \int_{-\infty}^{\infty} dt e^{it(\omega_{nm} + \Omega_0 - \omega) - \gamma_{nm}|t|} \times \exp\left[-\sum_j s_j(1 - 3\eta_j)\{2\bar{\nu}_j + 1 - (\bar{\nu}_j + 1)e^{it\omega_j} - \bar{\nu}_j e^{-it\omega_j}\}\right] \tag{7}$$

The quantities Ω_0 and η_j stand for the first-order anharmonic correction given by

$$\Omega_0 = -2\sum_j \eta_j S_j \omega_j \tag{8}$$

and

$$\eta_j = \frac{a_{j3}d_j}{a_{j2}} = \frac{a_{j3}d_j}{0.5\omega_j^2} \tag{9}$$

where ω_j is harmonic vibrational normal-mode frequency, S_j is Huang–Rhys factor, d_j denotes the displacement.

3. Results and discussion

3.1. Excitation energies and equilibrium geometries

Generally for PAHs, the low-energy absorption spectrum is mainly characterized by two low-lying excited states, the so-called ^1L_a and ^1L_b states, with different absorption intensity that will determine the relative position of these two states. The ^1L_a has a strong absorption in ultraviolet region while the ^1L_b has a weak transition [14,31]. For phenanthrene, our calculations display that S_1 state has a very weak absorption with a small oscillator strength (f = 0.0011). This indicates that the characteristic of S_1 could be identified as ^1L_b, which was consistent with the published work from Otokozawa et al. [6]. The calculated vertical excitation energies (ΔE) and oscillator strengths (f) from S_0 to S_1 together with the experimental data [12] were listed in Table S1.