

## Quantum Dynamics Simulation of Doublet Excitation and Magnetic Field Effect in Neutral Radical Materials

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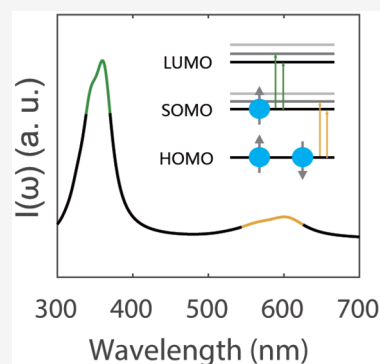


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Supporting Information

**ABSTRACT:** The photon absorption and the relevant magnetic field effect of a doublet in neutral radical materials are investigated by combining the density functional theory and the variational quantum dynamics with Davydov ansatz. The doublet is a perfect model system to study the full-quantum dynamics of a two-level system coupling to a realistic molecular vibrational environment. In this work, we simulate the optical absorption spectroscopy of the neutral radical material, (4-*N*-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)-methyl, and find a good agreement with experiments for both highest occupied molecular orbital–singly occupied molecular orbital (SOMO) and SOMO–lowest unoccupied molecular orbital transitions. The nontrivial role of the intramolecular vibronic couplings is comprehensively discussed with separate spectroscopy and population dynamics, suggesting different contributions and the long time scale effect stemming from the vibrations, according to different symmetries. On the basis of the model, an applied magnetic field is taken into account to qualitatively investigate its magnetic properties in a dynamics manner, leading to a result which can be described by a sum of Lorentzian functions.



Open-shell neutral radical materials have been attracting great attention in multiple different areas of chemistry and physics. In organic luminescence, recent experiments have revealed that the quantum efficiency of these materials can be extremely high. Ai et al.<sup>1</sup> showed that external quantum efficiency up to 27% can be realized with the radical-based organic light-emitting diodes (OLEDs) of TTM-3NCz, and afterward Guo et al.<sup>2</sup> successfully designed non-Aufbau-radical emitters which are able to improve the stability and reach the highest efficiencies for deep-red/NIR OLEDs based on purely organic emitters. Moreover, as the radical materials possess attractive features of quantum coherence and fidelity, they have significant potential in quantum computing and have been used to build covalent donor–acceptor–radical systems for quantum teleportation.<sup>3–5</sup> The advantages of these materials can be attributed to their doublet, which can bypass the spin selection rule in the process of photoelectric conversion.<sup>6</sup>

Radical materials are generally considered to be highly unstable.<sup>7</sup> To lower the reactivity of radicals, one can either kinetically block the active reaction sites with bulky groups or make the radical delocalize on the molecular skeleton, especially in polycyclic hydrocarbons.<sup>8</sup> It is rational to classify radicals into three categories: monoradicals, biradicals (two radicals with couplings), and diradicals (two radicals without couplings).<sup>9</sup> The first provides a singly occupied molecular orbital (SOMO) participating in the photoelectric processes. The SOMO manifests significantly different photophysical features from that of the highest (doubly) occupied molecular orbital (HOMO).<sup>6</sup> When the unpaired electron initially residing on SOMO is excited to the lowest-unoccupied

molecular orbital (LUMO) or the doubly occupied electron on HOMO is excited to SOMO, a hole that no longer has a half-spin is generated. In this situation, the electron with any spin state is allowed to recombine with the hole; that is, the limitation of spin selection rule is circumvented in the monoradical materials.

The doublet needs comprehensive theoretical investigations. Recently, He et al.<sup>10</sup> studied the doublet mechanism by means of the time-dependent density functional theory (TDDFT) and related the photon absorption to HOMO–SOMO transition. In this context, it is meaningful to further study the excitation dynamics, taking the vibronic couplings into account, because the organic materials involve fairly strong phonon vibration. Moreover, it can build up a bridge to understand the coherence, which is demanding in quantum computing. Due to the polaron effect, the electrons in the normal closed-shell molecules are relatively localized such that they usually couple to a small amount of nuclei.<sup>11</sup> On the other hand, however, the radicals are of relatively high activity, so the electrons of radicals are much easier to delocalize on the molecular skeleton. It suggests that the electrons in open-shell molecules couple to much more nuclei than those in closed-shell molecules. This may poorly impact the simulation results because the nonradiative emission might play a considerable

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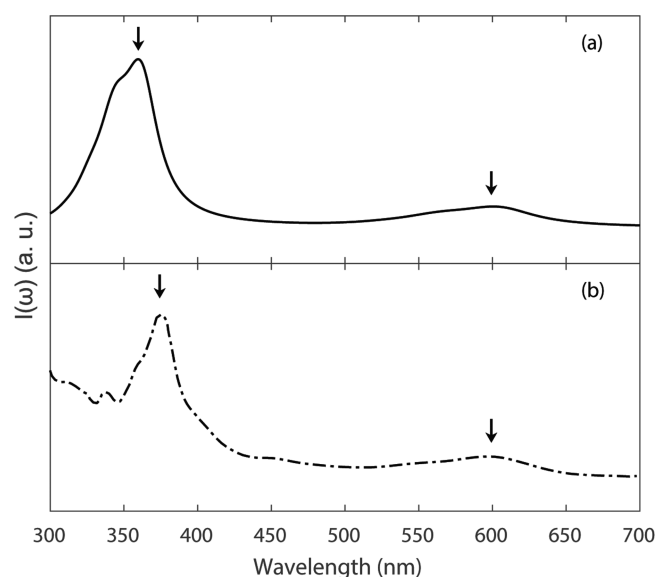
role. Therefore, a quantum dynamics approach is necessary to handle the problem. Such a method should go beyond the Born–Oppenheimer approximation and be capable to provide precise numerical simulations such as the multiconfiguration time-dependent Hartree (MCTDH) method,<sup>12,13</sup> hierarchical equations of motion (HEOM),<sup>14</sup> time-dependent density matrix renormalization group (t-DMRG),<sup>15–17</sup> etc. In this context, we adopt the variational Davydov ansatz to investigate the excitation dynamics and the ultrafast absorption spectroscopy of monoradicals. With each vibrational mode mimicked by multiple coherent states, the variants of this method can provide efficient simulations in both diagonal and off-diagonal coupling cases.<sup>18,19</sup> To get the parameters for the model, the density functional theory (DFT) is performed. Our results will show that photoelectric properties of the doublet can be rebuilt well, consistent with the experiment.

In this work, we take an organic open-shell molecule, (4-N-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)-methyl (TTM-1Cz), as an example to investigate the optical and magnetic properties of neutral radical materials. The doublet can be modeled well as a two-level system coupling to the molecular vibrational modes. The Hamiltonian can be written as ( $\hbar = 1$ )

$$\hat{H} = \begin{pmatrix} \varepsilon^{(1)} & \mu \\ \mu & \varepsilon^{(2)} \end{pmatrix} + \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q + \sum_q \begin{pmatrix} \kappa_q^{(1)} & 0 \\ 0 & \kappa_q^{(2)} \end{pmatrix} (\hat{b}_q^\dagger + \hat{b}_q) \quad (1)$$

Herein, the first term represents the Hamiltonian of electrons, in which  $\varepsilon^{(1)}$  and  $\varepsilon^{(2)}$  are diabatic energies of HOMO and SOMO, respectively. The second term is for the harmonic vibrational modes on two electronic states, where  $\hat{b}_q$  ( $\hat{b}_q^\dagger$ ) is the annihilation (creation) operator of different vibrational modes with characteristic frequency  $\omega_q$ . The last term denotes the linear diagonal coupling between electronic states and vibrations. All the parameters above are obtained with Vienna Ab initio Simulation Package (VASP)<sup>20–23</sup> to perform the dynamics simulations (see Section 1 in the [Supporting Information](#)). The effective off-diagonal coupling  $\mu$  for the charge transfer from HOMO to SOMO determines the intensity strength of photoabsorption, which will be chosen from 0.1 to 0.5 eV. To investigate the system dynamics and the absorption spectroscopy, the approach of variational Davydov ansatz<sup>18,24,25</sup> is utilized to perform our calculations (see Section 2 in the [Supporting Information](#)).

Figure 1a shows our simulation result for the absorption spectrum of the transition from HOMO to SOMO ( $\mu = 0.3$  eV). For a comparison with the relevant experimental measurements, the detected spectrum is extracted from ref 6 (Figure 1b). A main peak located at about 600 nm is visibly observed in both theory and experiment, referring to the transition between adiabatic electron states (the 0–0 transition). A side peak with a distance of about 45 nm (for experiment 50 nm) to the main peak is weak but spotted, which represents the relevant vibrational state, namely the 0–1 transition. The good agreement between theory and experiment demonstrates that our calculations have successfully rebuilt the optical features of doublet in neutral radical materials. In addition, we also simulate the SOMO–LUMO transition ( $\mu = 0.1$  eV) and find a relation to the peak at 375 nm. While it is known that for higher excited state energies there may be deviation in the DFT calculation, vibrational

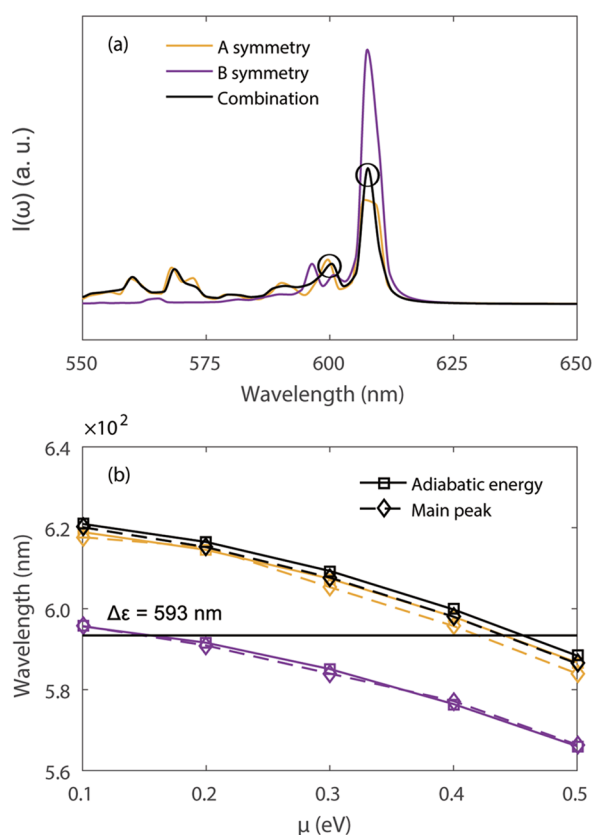


**Figure 1.** (a) Absorption spectrum simulating the HOMO–SOMO ( $\tau = 7$  fs) and SOMO–LUMO ( $\tau = 5.5$  fs) transition and (b) the experimentally detected spectrum reprinted (adapted or reprinted in part) with permission from ref 6. Copyright 2015, John Wiley and Sons.

states are in accordance with the detected spectrum. Absorption in other wavelength regions referring to higher-lying manifolds of electrons is not considered, which will be the scope of our future works.

As the vibrational modes play an essential role in determining the absorption spectra, we discuss more details of the vibrations. Because TTM-1Cz has a  $C_2$  point group, vibrational modes can be classified into A and B symmetries. We can thus perform separate calculations to reveal how the symmetries of vibrational modes impact the spectroscopy (Figure 2a). Because the vibronic spectra are different for the three cases, there are different lineshifts due to the different zero-point vibrations. For clearer comparison, the main peaks are thus shifted to the same point. It can be seen that the fine structure of the combined spectrum is more similar to that of A symmetry rather than B symmetry. Because vibrational modes of B symmetry hardly change the geometry of TTM-1Cz, vibronic transition of 0–0 becomes more pronounced than that of the other two spectra. This is in accordance with the fact that the A symmetry influences the molecular energy in a greater manner (Table S2). It implies that those molecular structures with few excitations of A symmetry vibrations may result in the enhancement of luminescence.

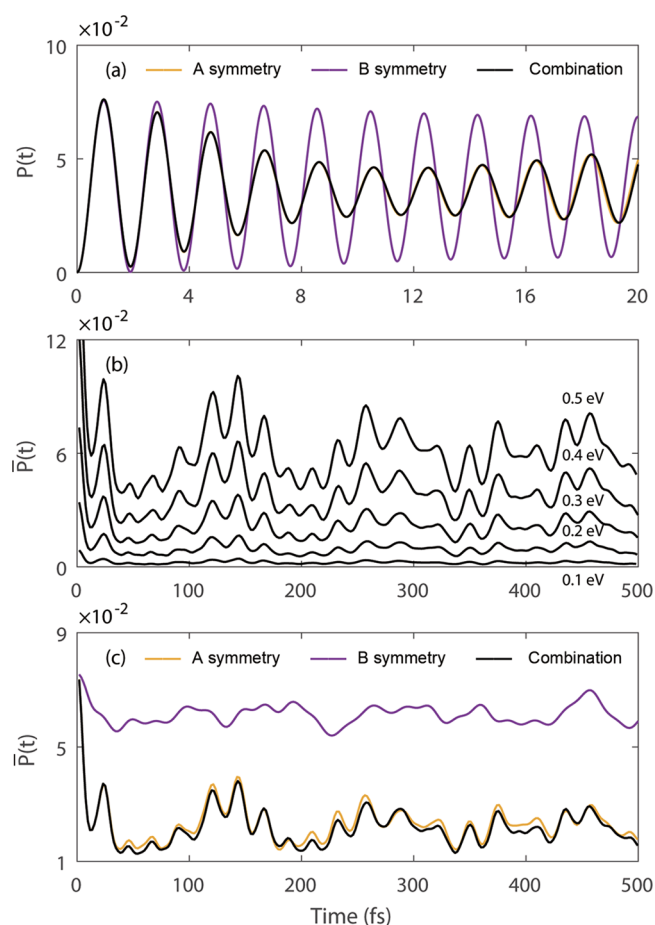
It is worth noting that due to the dissipation of the environment, the detected main peak in Figure 1a is actually the mixture of a main peak, referring to the electronic transition, and a neighboring side peak, referring to the high-frequency vibronic transition, which are marked with circles in Figure 2a. We compare the main peak to the adiabatic energy  $\varepsilon_a^{(2)}$  (Figure 2b). For  $\mu = 0.3$  eV, the location of the marked main peak is almost identical to that of the adiabatic energy. We also change  $\mu$  from 0.1 to 0.5 eV to study the influence of the off-diagonal coupling  $\mu$ . Because structures of absorption spectra are similar among different  $\mu$ , here we merely show the location of the main peak. The redshift effect stemming from the vibrations may be weakened by the changing off-diagonal



**Figure 2.** (a) Absorption spectrum referring to A symmetry (yellow line), B symmetry (purple line), and a combination (black line), calculated with different broadening ( $\tau = 80$  fs). Peaks marked with circles combine into the detected peak. (b) Location of the main peak referring to A symmetry (yellow line), B symmetry (purple line), and a combination (black line).  $\Delta\epsilon$  is the energy gap between the HOMO and SOMO.

coupling, as the average displacement of the phonons decreases.

We then studied the diabatic state population of SOMO during the time evolution with the initial state being HOMO (Figure 3), which describes how the electrons initially populating on the HOMO are transited onto the SOMO. It is found that the evolution of the population involves two components, i.e., a quick oscillation with high frequency ( $\sim 0.5$  fs $^{-1}$ ) and an envelope with low oscillation frequency ( $\sim 0.045$  fs $^{-1}$ ). Figure 3a shows the quick component which originates from the Rabi oscillation between the two levels that are HOMO and SOMO. In the early stage, the dynamics is not influenced by the vibronic couplings, and with time evolving, the oscillation frequency and amplitude are changed to be different for A and B symmetry cases. More interesting is the slow component of the oscillation as it refers to the vibronic coherence in the system (Figures 3b and c). The differential envelope  $\bar{P}(t)$  is defined as the difference of the neighboring local maximum and minimum of the population, through which the features of envelopes can be revealed. For the early 20 fs, it can be clearly viewed that the system experiences a quick dissipation. We find that differential envelopes also manifest an oscillatory trend. This case arises due to the vibronic coupling but not the off-diagonal coupling  $\mu$ , as the changing  $\mu$  hardly impacts the oscillatory behavior (Figure 3b). Furthermore, the system dynamics is dependent on the A symmetry, as the frequency and amplitude of the black line

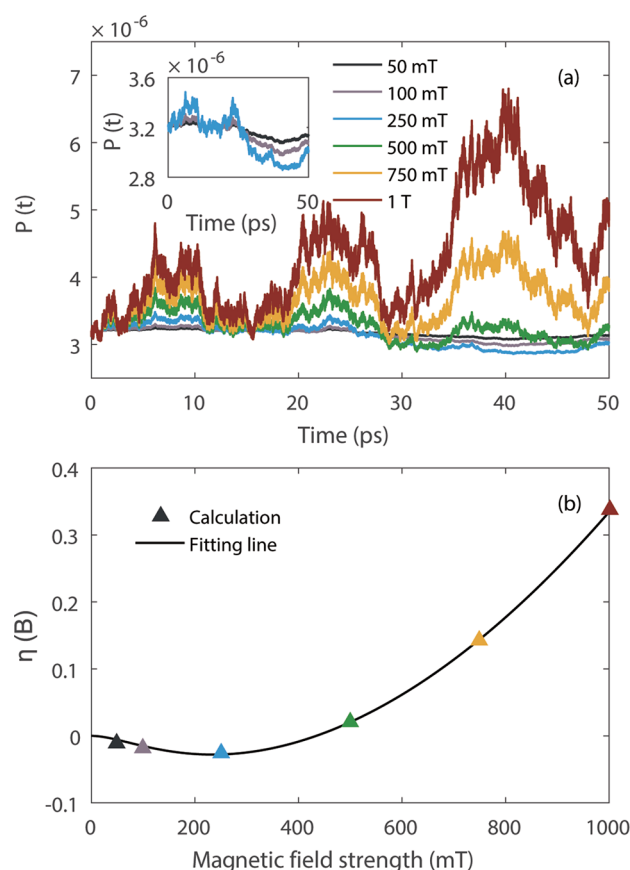


**Figure 3.** (a) Population of SOMO in the early time and differential envelope with respect to (b) off-diagonal coupling  $\mu$  and (c) different symmetries. For (a) and (c), results are calculated with  $\mu = 0.3$  eV, referring to A symmetry (yellow line), B symmetry (purple line), and a combination (black line).

resembles the yellow line (Figure 3c). This agrees with our discussion of the absorption spectrum.

It suggests that radical molecules have a prospective application in not only the optical but also magnetic area<sup>26</sup> due to its unpaired electron and the feature of coherence (Figure S3). Herein, we propose a model Hamiltonian applicable for the doublet in the presence of an external static magnetic field (see Section 4 in Supporting Information) and use it to investigate the spin dynamics. Figure 4a shows the spin-positive population evolution with the magnetic field strength ranging from 50 mT to 1 T. Because of the weak dipole moment, the absolute intensity of the transition is seen to be of a small order of magnitude. We find a critical magnetic field with  $B \sim 250$  mT. Under the weak magnetic field, it is obvious that the population is more suppressed and difficult to flip as the magnetic field increases. Exceeding the critical point, an upsurge as the transition efficiency increases by half every 250 mT can be recognized. It suggests that the spin dynamics is dependent on a couple of competitive mechanisms. To better view this property, we plotted the time-average enhancement with the time windows of the evolutionary duration from 0 to 50 ps and a mixed-Lorentzian function as<sup>27</sup>





**Figure 4.** (a) Population of the spin-positive state as the three with the weakest magnetic field are plotted in the inset and (b) the time-average enhancement with respect to magnetic field strength.

$$\eta(B) = \frac{\bar{P}(B) - \bar{P}(B=0)}{\bar{P}(B=0)} = c_1 \frac{B^2}{B^2 + B_1^2} + c_2 \frac{B^2}{B^2 + B_2^2} \quad (2)$$

is employed to fit the discrete data (Figure 4b). Herein, parameters are optimized to be  $c_1 = 2000$ ,  $c_2 = -0.1101$ ,  $B_1 = 67.76$  mT, and  $B_2 = 0.2468$  mT, respectively. The fitting function reveals that the spin flip involves two components, the positive strong magnetic-field effect and the negative weak magnetic-field effect. The latter, correlating with the occupied-spin promotion, earlier approaches its half-maximum so that the spin flip manifests a negative enhancement when the magnetic field is weak. This property will be canceled as the strong magnetic-field effect begins to work, which flips the spin and makes the system disordered. For extremely large magnetic field strength, the fitting function is incorrect, which may involve a stronger magnetic-field effect. With respect to the quantum control of radical spin, our calculation results may be applicable to the electron paramagnetic resonance experiments.

In conclusion, we investigated the photoelectric and magnetic properties of a radical-based material, TTM-1Cz, by means of the combination of the density functional theory and the quantum dynamics method. It is found that the doublet can be well-described using a vibronic coupling model, and both electronic transition and relevant vibrational state signals are reproduced consistent with earlier experiments. Having probed the effectiveness, calculations of separate spectra were performed and suggest an important role of

vibrational modes especially for the A symmetry ones, which are observed to be more dominant in the system dynamics. Except for the dissipation properties, modes referring to the A symmetry vibrations determine both the high-frequency population and the low-frequency differential envelope. In addition, we propose a spin-interaction Hamiltonian to describe the doublet under an external magnetic field and find the significant spin flip will occur exceeding a critical point. As a full-quantum dynamics method, the advantage of the variational Davydov ansatz is the availability in relatively long time duration, making it a useful approach for the exploration of magnetic field effect in excitation dynamics.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.9b03635>.

Computational details and results, including (1) orbital energy, charge distribution, effective mass and vibronic spectrum calculated by DFT; (2) the expressions for the variational Davydov ansatz and observable quantities; (3) discussion of the autocorrelation function calculated by the Davydov ansatz; and (4) details to calculate the spin dynamics (PDF)

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### Notes

The authors declare no competing financial interest.

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