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Elucidating the Magnitude of Internal Reorganization Energy of Molecular Excited States from the Perspective of Transition Density

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ABSTRACT: Quantifying vibronic couplings in molecular excited states is crucial for the elucidation of a broad range of photophysical phenomena. In this study, we compare different theoretical approaches for the calculation of reorganization energy, a measure of vibronic coupling strength, and provide a rigorous derivation to show that molecular transition density characterizing electron—hole excitation could be used to quantify the magnitude of reorganization energy. The theory enables a descriptor based on molecular-orbital coefficients and atomic transition densities to quantify the magnitude of reorganization energies in molecular excited states. Applying the approach to low-lying excited states of polyacenes, we demonstrate that transition density distribution explains the difference in the magnitude of the reorganization energy of different excited states. Furthermore, to clarify the applicability of the transition density descriptor in molecular design for small-reorganization energy molecules, we investigate a broad range of molecular chromophores to show the effectiveness of the proposed



theory. With this perspective on the relationship between reorganization energy and transition density, we successfully provide a quantitative rule to identify π -conjugated systems with small reorganization energy in the excited state, which should be useful for the development of novel optoelectronic materials.

INTRODUCTION

Vibronic coupling, the interaction between an electronic state and molecular vibrations, plays critical roles in a broad range of photophysical phenomena, and therefore its determination is essential for the elucidation of chemical dynamics after photoexcitation.¹⁻³ Experimentally, the vibrational structure observed in the absorption spectrum of a molecular system can be analyzed to estimate the Huang-Rhys factors,^{4,5} which describe the strength of vibronic coupling.⁶ The energy dissipation during the vibrational relaxation process in the molecular excited state, called the internal reorganization energy (λ), can be calculated from the Huang-Rhys factors and used as an indicator of the strength of vibronic coupling. Theoretically, λ can be evaluated readily using quantum chemical calculations, and it has been the focus of numerous theoretical studies.^{8–10} The magnitude of λ affects excited-state properties of molecular systems. For example, in many optoelectronic applications, conventional wisdom suggests that a small λ would suppress radiationless relaxation and enhance the quantum yield of the photoconversion process.^{11–14} Nevertheless, theoretical determination of λ requires geometry optimization or derivative calculations in the excited state and thus is computationally expansive. It is also often challenging to rationalize different magnitudes of λ in excited states with different characteristics. Therefore, to identify novel high-performance organic materials, a molecular design principle able to control the magnitude of λ is highly desirable. It would be even more useful if a quantitative descriptor for

reorganization energy of molecular excited states could be developed, as an easy-to-calculate descriptor would enable new computational approaches for high-throughput screening of low- λ chromophores using available material databases.^{15,16}

In general, enhancement of the molecular rigidity and extension of the π -conjugated system are two widely accepted strategies to reduce λ of molecular excitations.^{17–21} However, these qualitative rules often fail to quantitatively explain the magnitude of the λs . For example, a molecule could have a similar molecular rigidity and extended π -region in different excited states and yet show drastically different couplings to vibrational motions in different electronically excited states. A representative example of drastically different vibronic couplings in different electronic transitions of the same molecule can be found in polycyclic aromatic hydrocarbons (PAHs).²²⁻²⁴ The three lowest excited states of PAHs are the ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states in Platt's notation (Figure 1).^{25,26} In this nomenclature, B and L states refer to the total angular momentum |J| = 1 and |J| = 2x + 1 in the perimeter freeelectron model, where x is the number of condensed rings. B

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Figure 1. (a) Frontier molecular orbitals and (b) major electron configuration of the low-lying electronic transitions of naphthalene, a representative PAH molecule.

and L also correspond to the momentum allowed and forbidden transitions, respectively. The subscripts a and b denote, respectively, whether the nodal planes cut through the bonds or atoms in the transition density. Thus, the ¹L_a state is dominated by HOMO \rightarrow LUMO transition that yields a transverse dipole moment (along the short axis of the molecule). On the other hand, the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states are both contributed by the HOMO \rightarrow LUMO + 1 and HOMO - $1 \rightarrow$ LUMO transitions, where the longitudinal transition dipole momentums of these two configurations are additive in the ¹B_b state and subtractive in the ¹L_b state. The characters of these excited states for PAHs have been thoroughly investigated, and it is well known that these states exhibit quite different vibronic coupling strengths.²⁷⁻²⁹ We believe that the origin of the different vibronic coupling strengths in the ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states of PAHs is an important issue; yet, the challenge to provide a simple explanation of the different vibronic couplings in these excited states remains to be met.^{23,24,30}

In this regard, it is desirable to develop a theory that can be used to quantify the magnitude of the reorganization energy of molecular excited states in terms of molecular-orbital (MO) properties. For electron transfer processes, Chao et al. have illustrated on the basis of a one-orbital approximation that the local nonbonding character in frontier orbitals plays an important role in determining the magnitude of the reorganization energy.^{31,32} Bonding or antibonding character in the lowest unoccupied molecular orbital (LUMO) leads to strong reorganization energy in the electron transfer process because when electron transfer occurs between molecules, the bond length strongly varies at the region where two neighboring atoms exhibit bonding or antibonding character in the LUMO. In contrast, if the LUMO exhibits nonbonding relationships between neighboring atoms, the bond-length changes would be small, leading to small reorganization energy. The same argument also applies to hole transfer in the highest occupied molecular orbital (HOMO). This finding provides a powerful way to understand the relative magnitude of chargecarrier mobilities in different molecular crystals and to design molecules with small reorganization energy in the charged state.³³ Therefore, it would be desirable to formulate a similar structure-function relationship for radiationless transition in molecular excited states. To this end, we apply theoretical density functional theory (DFT) calculations to investigate λ for excited states in a series of representative π -conjugated systems to formulate a general rule for relating λ to MO properties.

In a recent computational study, we observed that the phases in transition density is highly correlated with the magnitude of reorganization energies in many molecular systems.³⁴ In this work, we aim to compare different theoretical approaches for the calculation of λ of organic molecules and to develop a MO theory for the quantification of the reorganization energy of molecular excited states using transition density distributions. We first review ab initio quantum chemistry methods for the estimation of λ of molecular excitations and then provide a simple theory based on an independent-electron approximation and the bond order-bond length relationship to show that molecular transition density characterizing electron-hole excitation could be used to gauge the magnitude of λ , just as coefficients of frontier MOs can be used to estimate reorganization energy in charge-transfer properties. We calculated λ of the three lowest-lying excited states of polyacenes to benchmark the accuracy of different theoretical methods. In addition, we demonstrate that these polyacene excited states exhibit entirely different transition densities, which lead to different magnitudes of reorganization energies. The acquired results enabled us to propose a descriptor based on the transition density distribution to quantify the magnitude of λ in molecular excited states. We also calculate λ and the descriptor for a broad range of molecular dyes to show the effectiveness of the descriptor proposed in this work. Finally, we provide a perspective based on the relationship between reorganization energy and transition density to suggest a general rule for identifying π -conjugated systems with small λ in excitation energy relaxation.

THEORETICAL BACKGROUND

Reorganization Energy. We consider the total Hamiltonian for a molecular system given by

$$\hat{H}_{\text{total}}(r, Q) = \hat{T}_{\text{N}}(Q) + \hat{T}_{\text{e}}(r) + \hat{U}(r, Q)$$
 (1)

where $\hat{T}_{\rm N}(Q)$ is the nuclear kinetic energy operator, $\hat{T}_{\rm e}(r)$ is the electronic kinetic energy operator, $\hat{U}(r, Q)$ is the total potential energy operator, and r and Q denote the electronic and nuclear mass-weighted normal coordinates, respectively. Within the Born–Oppenheimer approximation, the electronic Schrödinger equation includes the terms in the molecular Hamiltonian that depend on the electronic coordinates and can be written as

$$\hat{H}_{e}(r, Q)\psi_{n}(r, Q) = E_{n}(Q)\psi_{n}(r, Q)$$
 (2)

where the electronic Hamiltonian is given by

$$\hat{H}_{e}(r, Q) = \hat{T}_{e}(r) + \hat{U}(r, Q)$$
 (3)

In eq 2, $E_n(Q)$ is the potential energy surface of the *n*th electronic state (the ground (n = 0) and the *n*th excited state). The electronic transition occurs without changes in the molecular geometry according to the Franck–Condon principle. After the vertical excitation, the molecule reorganizes from the equilibrium structure of the ground state to that of the excited state through vibrational relaxation, and the reorganization energy (λ) is the total energy dissipated during this process. In this study, we will introduce how to calculate λ by three computational methods.

Adiabatic Potential Method. For a molecular system, λ of the *n*th excited state can be calculated readily using quantum chemical calculations of the adiabatic potential energy surfaces of the ground and the *n*th excited state, since excited-state energy and geometry optimization calculations are commonly implemented in popular quantum chemistry software packages. If we denote Q_0^{eq} and Q_n^{eq} as the ground state and the *n*th excited-state equilibrium geometries, respectively, λ can be directly obtained from the energy difference of these two geometries in the excited state

$$\lambda_n^{\rm AP} = E_n(Q_0^{\rm eq}) - E_n(Q_n^{\rm eq}) \tag{4}$$

Scheme 1a illustrates the potential energy diagram used in such a calculation. This approach is called the adiabatic potential

Scheme 1. Illustration of λ Calculated by the (a) Adiabatic Potential, (b) Crude Adiabatic, and (c) Linear Orbital Vibronic Coupling Methods



(AP) method.⁷ In the AP method, the equilibrium geometries are obtained by geometry optimization without approximations to the forms of the potential energy surface, so the quality of the values is determined fully by the level of quantum chemistry employed in the calculations, and the λ_n^{AP} calculated in this approach includes full nonlinear vibronic couplings and Duschinsky rotation effects.³⁵ In this work, we use the density functional theory and the time-dependent density functional theory to determine the energies, and the computational details will be given shortly.

Crude Adiabatic Method. The AP method requires a full geometry optimization calculation on the excited-state potential energy surface, which can be avoided when the structural change in the excited state is small. In that case, $E_n(Q)$ can be accurately determined by taking a Taylor expansion around the Franck–Condon point, Q_0^{eq} . As a result, the potential energy surface can be approximated up to the second order in the displacement coordinates as

$$E_n(Q) = E_n(Q_0^{\text{eq}}) + \sum_{\alpha} V_{n,\alpha}q_{\alpha} + \frac{1}{2} \sum_{\alpha,\beta} V_{n,\alpha\beta}q_{\alpha}q_{\beta}$$
(5)

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$$V_{n,\alpha} = \left. \frac{\partial E_n(Q)}{\partial Q_\alpha} \right|_{Q = Q_0^{eq}}$$
(6)

$$V_{n,\alpha\beta} = \frac{\partial^2 E_n(Q)}{\partial Q_\alpha \partial Q_\beta} \bigg|_{Q=Q_0^{eq}}$$
(7)

and $q_{\alpha} = Q_{\alpha} - Q_{0,\alpha}^{eq}$ is the displacement in the α th vibrational mode. In this expression, the electronic energy depends on the properties at a fixed geometry Q_0^{eq} , which is known as the crude adiabatic approximation.³⁶ The evaluation of the derivatives yields $V_{n,\alpha}$ and $V_{n,\alpha\beta}$, which are the linear and quadratic vibronic coupling constants, respectively. Furthermore, we use the harmonic potential $U_{n,\alpha} = (1/2)\omega_{n,\alpha}^2 q_{\alpha}$ where $\omega_{n,\alpha}$ is the vibrational angular frequency of the α th mode in the *n*th electronic state, and assume no Duschinsky effect. Therefore, eq 5 can be rewritten in the normal-mode coordinate of the electronic ground state to reach the following form

$$E_n(Q) = E_n(Q_0^{\text{eq}}) + \sum_{\alpha} \left[\frac{1}{2} \omega_{n,\alpha}^2 \left(q_{\alpha} + \frac{V_{n,\alpha}}{\omega_{n,\alpha}^2} \right)^2 - \frac{V_{n,\alpha}^2}{2\omega_{n,\alpha}^2} \right]$$
(8)

Here, we assume that the molecule is rigid, so the normalmode frequencies of the *n*th excited state are the same as those of the ground state, i.e., $\omega_{n,\alpha} = \omega_{0,\alpha}$. Clearly, this approximation results in a displaced harmonic oscillator model with the excited-state minimum at the α th normal coordinate shifted to $q_{\alpha} = -V_{n,\alpha}/\omega_{n,\alpha}^2$ and λ for the *n*th excited state can be evaluated as

$$\lambda_n = \sum_{\alpha} \lambda_{n,\alpha} = \sum_{\alpha} \frac{V_{n,\alpha}^2}{2\omega_{n,\alpha}^2} = \sum_{\alpha} S_{n,\alpha} \hbar \omega_{n,\alpha}$$
(9)

where we have also defined the Huang–Rhys factor for the α th mode in the *n*th excited state, $S_{n,\alpha} = V_{n,\alpha}^2/2\hbar\omega_{n,\alpha}^3$. The Huang–Rhys factor S_{α} indicates the number of vibrational excitations involved in the α th mode after the Franck–Condon transition and determines the strength of vibronic coupling.⁶ This equation indicates that λ is contributed by the sum of the couplings between the electron and each vibrational normal mode. The method for the calculation of λ is illustrated in Scheme 1b.

The crude adiabatic approximation gives rise to a simple vibronic model, and the relationship between vibronic coupling and λ is clearly defined. The dimensionless linear vibronic coupling constant of the α th mode in the *n*th excited state is defined as

$$g_{n,\alpha} = \frac{1}{\hbar\omega_{0,\alpha}} \frac{\partial E_n(Q)}{\partial \tilde{q}_{\alpha}} \bigg|_{Q = Q_0^{eq}}$$
(10)

where $\tilde{q}_{\alpha} = \sqrt{\omega_{0,\alpha}/\hbar} Q_{\alpha}$ is the dimensionless normal coordinate. As shown in Scheme 1b, for each normal mode, we apply the finite difference method to obtain the $g_{n,\alpha}$ value with a step size of 0.05 in the mass-weighted coordinate. Therefore, λ in the crude adiabatic approximation can be calculated by the expression

$$\lambda_n^{CA} = \sum_{\alpha} \lambda_{n,\alpha}^{CA} = \frac{1}{2} \sum_{\alpha} g_{n,\alpha}^2 \hbar \omega_{0,\alpha}$$
(11)

where

Orbital Vibronic Coupling Method. It is often desirable to express λ in terms of MO properties. In this regard, the linear orbital vibronic coupling (OVC) method developed by Kato et al. provides a quantitative approach for the calculation of λ based on derivatives of MO energies in the crude adiabatic basis.^{37,38} The OVC method focuses on the relationship between the excitation energy of a singly excited configuration and the energy gap between the MOs involved in the transition. Consider the linear vibronic coupling constant of the *i*th MO to the α th normal mode, defined as

$$g_{i,\alpha} = \frac{1}{\hbar\omega_{0,\alpha}} \frac{\partial\varepsilon_i}{\partial\tilde{q}_{\alpha}} \bigg|_{Q=Q_0^{eq}}$$
(12)

where ε_i is the MO energy, and the linear vibronic coupling constant for the electronic transition from the occupied orbital *i* to the virtual orbital *a* can be estimated

$$g_{ia,\alpha} = \frac{1}{\hbar\omega_{0,\alpha}} \left(\frac{\partial(\varepsilon_a - \varepsilon_i)}{\partial \tilde{q}_{\alpha}} \right) |_{Q=Q_0^{\text{eq}}}$$
$$= \begin{cases} |g_{a,\alpha}| - |g_{i,\alpha}|, & \text{for correlated coupling} \\ |g_{a,\alpha}| + |g_{i,\alpha}|, & \text{for anti - correlated coupling} \end{cases}$$
(13)

Here, ε_a and ε_i are the orbital energies obtained from the oneelectron approximation. The orbital energy difference should be calculated from the energy gap coupling constant $g_{ia,a}$ which considers either the correlated coupling or anticorrelated coupling conditions. The correlated coupling case is when both the energies of orbitals *a* and *i* rise or fall simultaneously as the molecule shifts away from the equilibrium structure; in this case, the energy gap is less perturbed than the orbital energy, and the energy gap coupling is the difference between the orbital couplings. Otherwise, it is the anticorrelated coupling case in which the energy gap coupling is the sum of the orbital couplings. The basic picture of the OVC method is illustrated in Scheme 1c.

The OVC method can be generalized to an electronically excited state $|n\rangle$ that involves multiple singly excited configurations

$$|n\rangle = \sum_{ia \in n} c_{n,ia} |i \to a\rangle \tag{14}$$

where c_{ia} is the configuration interaction coefficient of the $i \rightarrow a$ single excitation configuration in the wave function of the *n*th excited state, and the reorganization energy of the state is given by the sum

$$\lambda_n^{\text{OVC}} = \frac{1}{2} \sum_{\alpha} \sum_{ia \in n} c_{n,ia}^2 g_{ia,\alpha}^2 \hbar \omega_{0,\alpha}$$
(15)

The correlated versus anticorrelated relationship in the OVC method deserves further attention. In particular, it is critical that one can distinguish between the two cases in terms of the electron distribution of MOs. For simplicity, we consider the S_1 excited state that is dominated by the HOMO \rightarrow LUMO transition. Under this condition, eq 15 becomes

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$$\begin{aligned} \lambda_{S_{1}}^{OVC} &= \frac{1}{2} \sum_{\alpha} (|g_{H,\alpha}| \pm |g_{L,\alpha}|)^{2} \cdot \hbar \omega_{0,\alpha} \\ &= \lambda_{H} + \lambda_{L} + \sum_{\alpha} \pm |g_{H,\alpha}| |g_{L,\alpha}| \hbar \omega_{0,\alpha} \end{aligned}$$
(16)

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where the linear OVC constants between the α th mode and the HOMO and LUMO are denoted $g_{H,\alpha}$ and $g_{L,\alpha}$, respectively, and the orbital reorganization energies are $\lambda_H = (1/2) \sum_{\alpha} g_{H,\alpha}^2 \hbar \omega_{0,\alpha}$ and $\lambda_L = (1/2) \sum_{\alpha} g_{L,\alpha}^2 \hbar \omega_{0,\alpha}$. In addition to λ_H and λ_L , the magnitude of the $\lambda_{S_1}^{OVC}$ is also determined by a cross-term that describes the dependence in the case of correlated or anticorrelated couplings. As a result, the strength of vibronic coupling between the S₁ state and a normal mode depends on whether the HOMO and LUMO energies vary simultaneously in the same direction or not as the molecular geometry is shifted along the normal mode. Note that the variations of orbital energy depend on the distribution of local antibonding/bonding characters in the molecular orbital along the vibrational displacement. A simple model in Scheme 2

Scheme 2. Illustration of Anticorrelated versus Correlated Coupling between HOMO and LUMO in the OVC Method



demonstrates that when HOMO and LUMO have different phases across a bond, as in Scheme 2a, where the HOMO is bonding and LUMO is antibonding, a shortened bond distance would cause the energy gap between the two MOs to increase, leading to the anticorrelated coupling case. On the other hand, when HOMO and LUMO have the same phases across a bond, the situation is correlated coupling. As the product of HOMO and LUMO orbital coefficients can be described by the transition density of the excitation, it is clear that transition density is an important property function to determine the phase relation between two MOs in the OVC method. As shown in Scheme 2, if the transition density is out-of-phase between the two bonding atoms, the vibronic coupling of this transition configuration to the bond stretching mode must be anticorrelated coupling. On the other hand, the correlated coupling can be identified as the neighboring atoms exhibit an in-phase relationship in the transition density. As a result, the distribution and phase of the transition density for an excitation can be used to gauge the amplitude of its vibronic

couplings. For excitation with strong vibronic couplings, the transition density should exhibit many nodal planes cutting through the bonds, i.e., antibonding relation across bonds.

Bond-Order–Bond-Length Relationship and Reorganization Energy. The orbital vibronic coupling method provides a means to rationalize the magnitude of molecular excited-state reorganization energies in terms of the distribution of the transition density. However, the correlated and anticorrelated molecular-orbital relationships with respect to vibrational motions are often difficult to determine and quantify. It is thus desirable to have a more well-defined molecular property that can better correlate the magnitude of reorganization energy with the MO properties of a molecular excited state. To this end, we propose to use the transition density of a molecular electronic transition as a theoretical tool to elucidate vibronic couplings. Here, we provide a derivation of such connection for π -conjugated excitations based on the bond-order–bond-length (BOBL) relationship.

By inspecting a large data set of bond lengths and quantitatively comparing several different mathematical expressions relating bond orders to bond lengths, Paolini has demonstrated the generality of the BOBL relationship, showing that the shortening of a bond is solely a function of the number of additional electrons in the bond.³⁹ More recent calculations correlating bond lengths with bond orders obtained from ab initio wave functions further validated this great insight, and further extension of the BOBL relationship beyond ground-state geometries was shown to be very successful.40-43 In particular, the BOBL relationship in the scenario of electronic excitation can be interpreted as a function relating the displacement in the structural relaxation (bond shortening or elongation) to the differences in the number of electrons in the bond, which enables calculations of reorganization energies from bond-order changes upon excitation based on the BOBL relationship.⁴⁴ In the following, we demonstrate that this concept can be used to furthermore relate the reorganization energy of an excited state to its transition density.

For simplicity, we consider a π -conjugated system in the Hückel MO model. The π bond order between the μ th and ν th carbon atoms can be calculated by⁴⁴

$$P_{\mu\nu} = \sum_{i=1}^{N} n_i C^i_{\mu} C^i_{\nu}$$
(17)

where n_i is the occupation number for the *i*th Hückel MO and C^i_{μ} and C^i_{ν} are the MO coefficients for *i*th MO on p_z at the μ th and ν th atoms, respectively. According to the BOBL relationship, the bond length can be calculated from the bond order

$$R_{\mu\nu} = -0.2P_{\mu\nu} + 1.534 \tag{18}$$

Equation 18 allows one to calculate the bond-length change upon excitation. For the sake of simplicity, we consider the HOMO \rightarrow LUMO S₁ excited state. The bond-order difference with respect to the ground state S₀ is

$$\delta P_{\mu\nu} = P^{S_1}_{\mu\nu} - P^{S_0}_{\mu\nu} \tag{19}$$

$$=C^{\rm L}_{\mu}C^{\rm L}_{\nu} - C^{\rm H}_{\mu}C^{\rm H}_{\nu} \tag{20}$$

Note that we use H and L to denote HOMO and LUMO, respectively. Combining eqs 18 and 20, we can calculate the change in the bond length using the change in the bond order.

Assuming a harmonic potential, the reorganization energy due to all of the bond-length changes can then be obtained by

$$\lambda_{S_{1}}^{\text{BOBL}} = \frac{1}{2} \sum_{\mu\nu \in \text{bonds}} k_{\mu\nu} \delta R_{\mu\nu}^{2}$$

= 0.02 $\sum_{\mu\nu \in \text{bonds}} k_{\mu\nu} (C_{\mu}^{\text{L}} C_{\nu}^{\text{L}} - C_{\mu}^{\text{H}} C_{\nu}^{\text{H}})^{2}$
= 0.02 $\sum_{\mu\nu \in \text{bonds}} k_{\mu\nu} [(C_{\mu}^{\text{H}} C_{\nu}^{\text{H}})^{2} + (C_{\mu}^{\text{L}} C_{\nu}^{\text{L}})^{2}$
 $- 2 \cdot C_{\mu}^{\text{H}} C_{\nu}^{\text{H}} C_{\nu}^{\text{L}} C_{\nu}^{\text{L}}]$
= $\lambda_{\text{H}}^{\text{BOBL}} + \lambda_{\text{L}}^{\text{BOBL}} - 0.04 \cdot \sum_{\mu\nu \in \text{bonds}} k_{\mu\nu} C_{\mu}^{\text{H}} C_{\nu}^{\text{H}} C_{\nu}^{\text{L}}$
(21)

where $k_{\mu\nu}$ is the force constant of the bond between the μ th and ν th atoms. Equation 21 indicates that the reorganization energy can be partitioned into HOMO ($\lambda_{\rm H}^{\rm BOBL}$), LUMO (λ_L^{BOBL}) , and cross-term contributions. The result corroborates the OVC method (eq 16) and provides a clear mathematical explanation of the correlated and anticorrelated orbital effects. When the HOMO and LUMO coefficients on the two bonding atoms are in phase $(C^{\rm H}_{\mu}C^{\rm H}_{\nu}C^{\rm L}_{\mu}C^{\rm L}_{\nu} > 0)$, the cross-term is negative and thus λ is reduced. It is otherwise when the HOMO and LUMO coefficients on the two bonding atoms are out of phase $(C^{\rm H}_{\mu}C^{\rm L}_{\nu}C^{\rm L}_{\mu}C^{\rm L}_{\nu} < 0)$. To better quantify this relationship, we recognize that the product $C_{\mu}^{\rm H} C_{\mu}^{\rm L}$ corresponds to the Hückel transition density of the HOMO \rightarrow LUMO transition on the μ th atom; hence, the cross-term is actually determined by the products of the atomic transition densities on the two bonding atoms. Therefore, eq 21 clearly shows that the transition density can be adopted as a quantitative proxy for understanding the magnitude of λ for excited states of π -conjugated systems. The excited state tends to have a reduced reorganization energy when the values of its transition density on neighboring atoms are in phase (bonding-like), whereas out-of-phase (antibonding-like) values of transition density on neighboring atoms tend to increase λ .

The result can be generalized to estimate λ of an excited state contributed by one-electron transition configurations in the form of eq 14

$$\lambda_{n}^{\text{BOBL}} = 0.02 \sum_{ia \in n} c_{n,ia}^{2} \sum_{\mu\nu \in \text{bonds}} k_{\mu\nu} [(C_{\mu}^{i}C_{\nu}^{i})^{2} + (C_{\mu}^{a}C_{\nu}^{a})^{2} - 2 \cdot C_{\mu}^{i}C_{\nu}^{i}C_{\mu}^{a}C_{\nu}^{a}]$$
(22)

In the general form, the reorganization energy in the BOBL relationship depends on two parameters, η and ϕ , which are defined as

$$\eta = \sum_{ia \in n} c_{n,ia}^2 \sum_{\mu\nu \in \text{bonds}} \left[(C_{\mu}^i C_{\nu}^i)^2 + (C_{\mu}^a C_{\nu}^a)^2 \right]$$
(23)

$$\phi = -\sum_{ia \in n} c_{n,ia}^2 \sum_{\mu\nu \in \text{bonds}} C^i_{\mu} C^a_{\nu} C^i_{\nu} C^a_{\nu}$$
(24)

Here, $c_{n,ia}$ is the configuration interaction coefficient of the *n*th excited state obtained from the time-dependent DFT (TDDFT) calculations. η corresponds to the coefficients of the occupied orbital *i* and the virtual orbital *a*, which are determined by the electron densities of the corresponding molecular orbital between the bonded atoms. Note that

molecular orbitals with strong local nonbonding characters cause η to approach zero and reduce λ . On the other hand, ϕ is a parameter that quantitatively describes the in-phase and outof-phase characters in the transition density. The positive ϕ value indicates strong out-of-phase character in the transition density, which would increase λ . On the other hand, the transition density with strong in-phase character leads to a negative ϕ value and decreased λ . To focus on the relationship between the densities and λ , we assume that the force constants of the bond stretching mode between the carbon atoms are the same (i.e., $k_{\mu\nu}$ is a constant independent of μ and ν). Then, according to eq 22, λ is proportional to the following BOBL density parameter

$$\kappa = \eta + 2\phi \tag{25}$$

 κ can be used as a descriptor to quantify the magnitude of λ . We will examine this hypothesis in this work.

We further note that although eq 21 is derived based on the overly simplified Hückel model, the general picture should be applicable to excited states of π -conjugated systems calculated using modern first-principle quantum chemical methods. Specifically, η and ϕ can be determined using the MO coefficients obtained from TDDFT calculations. η can be evaluated from the Mulliken atomic densities of MOs and ϕ from Mulliken atomic transition densities. These parameters based on the Mulliken densities not only provide a simple physical picture in describing the transition density but also a direct relationship to λ . It is worth noting that the atomic charge densities could be described by many other models, and the Mulliken density is often not the best choice. Nevertheless, in this initial study, we should focus on using the Mulliken density, and other models for atomic densities shall be explored and benchmarked in a future study. In this work, we intend to investigate the qualitative aspect of the BOBL relationship and the correlation between the BOBL density parameter κ and λ for molecular excited states of PAHs. In this regard, the molecular orbitals and configuration coefficients obtained from a single-point TDDFT calculation at the Franck-Condon geometry will be sufficient for the determination of κ .

Computational Details. In this study, all quantum chemistry calculations were carried out using the program Gaussian 09.45 All geometries of the ground and excited states were optimized by DFT and TDDFT calculations at the CAM-B3LYP/6-31G(d,p) level.⁴⁶ Compared with the conventional B3LYP method, the range-separated CAM-B3LYP functional better describes excitation energies and band shapes, especially for large molecules and excited states with a charge-transfer character.^{47–49} Moreover, the calculated λ is expected to be proportional to the percentage of Hartree-Fock percentage in density functionals.⁵⁰ The BLYP and B3LYP functionals were also examined in this study, and the results showed that the overall trend is consistent with those obtained using the CAM-B3LYP functional. Therefore, all DFT and TDDFT results reported in this work used the CAM-B3LYP/6-31G(d,p) level of theory. To prepare the figures, the molecular orbitals and transition densities were drawn for surface isovalues of 2 \times 10^{-2} and 8 × 10^{-4} au, respectively.

We employed linear response TDDFT to calculate the electronic excitation energy, which can be obtained by solving a non-Hermitian eigenvalue equation in the matrix form 51,52

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$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$
(26)

where the matrix elements of the pure functional are defined as

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ialjb) + (ialf_{xc}|jb)$$
(27)

$$B_{ia,jb} = (ialbj) + (ialf_{xc}|bj)$$
⁽²⁸⁾

The four-index integrals are expressed in the chemists' notation. The first term of the A matrix is the energy difference between the Kohn–Sham occupied orbital *i* and the virtual orbital a. The last two terms of the A matrix are the coupling-matrix terms and can be represented as the Coulomb and exchange-correlation kernel terms, respectively. The B matrix also contains the coupling-matrix terms and corresponds to the de-excitation contributions. The Tamm-Dancoff approximation (TDA), which neglects the coupling B matrix, is a popular approximation used for TDDFT to improve computational efficiency.53 Compared to full TDDFT calculations, TDA has been shown to yield more accurate excitation energies for PAHs but could also underestimate the relative intensities of vibronic peaks.^{54,55} To examine the effect of neglecting the B matrix terms, we also take TDDFT/TDA into consideration to estimate λ .

RESULTS AND DISCUSSION

Reorganization Energies of Naphthalene Excited States. We first consider the λ s of naphthalene excited states calculated by the AP method, as presented in Figure 2. The λ



Figure 2. Theoretical reorganization energies and transition densities for low-lying excited states of naphthalene. (a) λs of the ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states obtained from the AP, CA, and OVC methods. (b) Transition densities of the ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states.

of the ${}^{1}L_{a}$ state exhibits the largest value compared to that of ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states. In addition, although both arise from a combination of the HOMO \rightarrow LUMO + 1 and HOMO - 1 \rightarrow LUMO transitions, the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states have different λ . The general trend is that $\lambda({}^{1}L_{a}) \gg \lambda({}^{1}L_{b}) > \lambda({}^{1}B_{b})$. Therefore, intrinsic electronic properties of the excited states play an important role in determining the magnitude of λ . It is also

worth noting that the BLYP and B3LYP calculations follow the same trend of λ as the CAM-B3LYP calculations (Figure S1).

To clarify the source of different vibronic couplings in different excited states, λ s are decomposed into contributions from different normal modes as shown in Figure 3. Clearly, the



Figure 3. Decomposition of λ into contributions from each normal mode for naphthalene ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states.

magnitudes of λ are dominated by couplings to the C–C stretching modes. In addition, the λ associated with C–C stretching modes in the ${}^{1}L_{a}$ state (323 meV) is significantly higher than that in the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states (100 and 33 meV, respectively). In contrast, the total contributions of ring deformation and ring breathing modes to λ of the ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states are 38, 34, and 44 meV, respectively, which only represent negligible differences between the excited states. Also, the effects of C–H bending and C–H stretching modes on λ are negligible. Therefore, we can confidently state that the difference in the magnitude of λ s among the different low-lying excited states of naphthalene is due to the fact that the C–C stretching modes are strongly coupled to the ${}^{1}L_{a}$ state rather than the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states.

 π -Conjugated systems often accompany strong vibronic coupling to stretching vibrational modes, which have been illustrated by the importance of the bond-length alternation mode in various π -conjugated system problems.^{56–58} The BOBL relationship (eq 21) describes the bond-length changes in the excited state and provides an explanation of the magnitude of λ in terms of the BOBL density parameters (eqs. 23-25). The different couplings to the C–C stretching mode in the excited states of naphthalene should be attributed to the difference in transition density distributions. Figure 2b shows the transition density of the naphthalene excited states and the corresponding η and ϕ values. The transition density of the ¹L_a state, which is dominated by the HOMO \rightarrow LUMO transition, is clearly characterized by the nodal planes passing through the C–C bond. We emphasize that this phenomenon is general for all HOMO \rightarrow LUMO transitions of alternant PAHs. The pairing theorem dictates that the wave-function coefficients of HOMO and LUMO are the same but with changes in the phase at the alternant positions.^{59,60} According to this theorem, the paired molecular-orbital transition in the ¹L_a state always leads to a transition density with a strong out-of-phase character, which will result in the ϕ parameter with a sizable positive value. The positive ϕ value of 0.066 for the ${}^{1}L_{a}$ state represents the strong out-of-phase character in the transition density and the resulting large λ contributed by the C-C stretching modes.

On the other hand, both the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states are originated from the HOMO \rightarrow LUMO + 1 and HOMO - 1 \rightarrow LUMO transitions, which are not transitions from paired molecular orbitals. In contrast to the ${}^{1}L_{a}$ state, the nodes of the transition density are located at the atomic positions for the ¹L_b and ¹B_b states, so the transition density does not exhibit an out-of-phase character. The much smaller ϕ value of 0.001 in the ${}^{1}L_{b}$ state reflects that the reduction of out-of-phase character in the transition density and the small ϕ correspond to a small λ contributed by the C–C stretching modes. More interestingly, the strong in-phase character in the ¹B_b state leads to a negative ϕ value of -0.023, indicative of the lower contribution to λ from the C–C stretching modes. Clearly, the distribution of transition density, which is measured by ϕ , provides a powerful MO picture that elucidates the relative magnitudes of λ in excited states with different electronic transition characters.

Performance of the CA and OVC Methods. Figure 2a also shows reorganization energies of the low-lying excited states of naphthalene calculated using the CA and OVC methods. The results show that the CA method provides excellent quantitative agreement with the AP method, which confirms that the Duschinsky effect and the nonlinear vibronic coupling terms are negligible in the naphthalene system³⁵ because naphthalene is a rigid structure and the potential energy surfaces of the ground and excited states are well described by a harmonic oscillator with constant frequency.

Furthermore, Figure 2a shows that the OVC method systematically overestimates λ for all of the excited states investigated here, especially for the ${}^{1}L_{a}$ and ${}^{1}B_{b}$ states. The discrepancy can be attributed to the fact that the OVC method considers the vibronic coupling of the molecular-orbital energy differences and excludes the effect of electron–electron interactions. Interestingly, the λ of the ${}^{1}L_{b}$ state is not significantly affected by the two-electron terms. This is because the ${}^{1}L_{b}$ state is mainly generated by subtraction of the nearly degenerate configurations (HOMO \rightarrow LUMO + 1 and HOMO $-1 \rightarrow$ LUMO transitions) with paired two-electron terms. As a result, terms in the coupling-matrix elements are largely canceled out in the ${}^{1}L_{b}$ state.

Moreover, TDDFT/TDA calculations using the CA method provides further evidence that the **B** matrix is also less important in the ${}^{1}L_{b}$ state. Figure S2 shows that applying TDA, which ignores the **B** matrix, has negligible effect on the values of λ for the ${}^{1}L_{b}$ state. On the other hand, the λ s of ${}^{1}L_{a}$ and ${}^{1}B_{b}$ states calculated using the TDDFT/TDA approach are significantly smaller than those calculated without TDA, indicating that considering the coupling-matrix terms in the **B** matrix leads to significantly increased λ values. It is interesting to note that λ calculated by the OVC method, which ignores the coupling-matrix terms, could be viewed as an upper bound to the exact value.

It is worth noting that the OVC method also provides a MO rationale for the extralarge λ of the ${}^{1}L_{a}$ state. In the OVC method, the vibronic coupling problem is simplified to how the MO energy gap is modulated by the vibrational mode. For the ${}^{1}L_{a}$ state, the vibronic coupling of the HOMO–LUMO gap is mainly determined by the HOMO and LUMO relative energy shifts. However, as shown in Figure 4a, anticorrelated interactions between the HOMO and LUMO occur in all totally symmetric normal modes because the strong out-of-phase character in the HOMO–LUMO overlap density between any two bonding atoms ensures that the energy of





Figure 4. Decomposition of λ s calculated by the linear OVC method into contribution from each normal mode for naphthalene excited configurations. (a) HOMO \rightarrow LUMO, (b) HOMO \rightarrow LUMO – 1, and (c) HOMO – 1 \rightarrow LUMO. Note that (A) and (C) denote the anticorrelated and correlated couplings, respectively, between the occupied and virtual orbitals. The orbital overlap density for each excited configuration is also depicted.

the paired molecular orbitals changes oppositely in each normal mode. Therefore, these anticorrelated vibronic couplings increase the λ of the ${}^{1}L_{a}$ state.

On the other hand, as shown in Figure 4b,c, the orbital overlap density of these two nearly degenerate configurations generates the transition density of the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states by subtraction and addition, respectively. Because HOMO and LUMO + 1 (HOMO – 1 and LUMO) are unpaired molecular orbitals, the orbital overlap density exhibits less out-of-phase character. The vibronic interactions between the orbitals have a chance to become correlated coupling in some vibrational modes. For example, compared to the HOMO \rightarrow LUMO transition, the vibrational mode at 1672 cm⁻¹ (Figure S4)

shows dramatically reduced λs by a value of nearly 200 meV in the HOMO \rightarrow LUMO + 1 and HOMO - 1 \rightarrow LUMO transitions. This normal mode has significant C-C bond stretching components at the in-phase regions of the transition density, so the vibronic interaction between the HOMO and LUMO + 1 (HOMO - 1 and LUMO) is weakened. Hence, such correlated couplings cause lower λs in the ¹L_b and ¹B_b states. We also note that the λ of ¹L_b and ¹B_b states is similar in the OVC method but is different in the AP and CA methods. This is because, as mentioned above, the coupling-matrix terms weaken the vibronic interaction of the ¹B_b state, resulting in the OVC method incorrectly predicting that $\lambda(^{1}B_{h}) > \lambda(^{1}L_{h})$.

 λ s of the Low-Lying Excited States of Polyacenes. We further carried out a systematic study on the λ s of the low-lying excited states of polyacenes to elucidate the effects of the intrinsic excitation property and the molecular size. The calculation results are summarized in Table 1. λ s calculated by different theoretical methods for different sizes of systems from naphthalene to pentacene consistently show that the AP and CA methods are in quantitative agreement, while the OVC method gives overestimated values. Furthermore, the relative magnitudes of λ are $\lambda({}^{1}L_{a}) \gg \lambda({}^{1}L_{b}) > \lambda({}^{1}B_{b})$ in the AP and CA methods for each polyacene, indicating that the trend is general as predicted by the pairing theorem and analysis of transition density distribution.

The delocalization size of the π -conjugated system has been regarded as a major molecular design factor for small- λ molecules. Indeed, Table 1 shows that this is generally true, as λ decreases with increasing molecular size for a particular excited state in polyacenes. However, the molecular size cannot explain the relative magnitudes of λ s between different excited states. For example, λ of the pentacene ${}^{1}L_{a}$ state is higher than that of the naphthalene ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states. Therefore, molecular delocalization size alone cannot explain the relative magnitude of λ in different excited states, and the analysis of electronic characteristics in different excited states plays a vital role in predicting the magnitude of λ .

To include the characteristics of electronic excitations in the discussion, we examine the η and ϕ parameters for polyacene excited states. Table 1 shows that the ϕ parameters of the polyacene ${}^{1}L_{a}$ states are all positive. This is expected. According to the pairing theorem, the strong out-of-phase character in the transition density of the ${}^{1}L_{a}$ state is general for polyacenes (Figure S3). In addition, both ϕ and η decrease as the molecular size increases, corresponding to smaller λ of bigger systems. Clearly, the molecular size effect is also captured by the η and ϕ parameters.

For the ${}^{1}L_{b}$ states of polyacenes, the ϕ values are small and close to zero because all of the nodal planes in the transition density cut through atom centers. On the other hand, the transition densities with in-phase character in the ${}^{1}B_{h}$ state result in negative ϕ values, reflecting the correlated coupling and hence the smallest λ in the ${}^{1}B_{b}$ state. Overall, for different excited states of a given polyacene molecule, the order of ϕ follows $\phi({}^{1}L_{a}) \gg \tilde{\phi}({}^{1}L_{b}) > \phi({}^{1}B_{b})$. According to eq 21, the relative magnitude of λ in the three lowest excited states estimated by the ϕ value is ${}^{1}L_{a} \gg {}^{1}L_{b} > {}^{1}B_{b}$, which is consistent with the TDDFT calculations. According to eq 23, the η parameter is associated with the electronic transition between the occupied and virtual molecular orbitals. The different electron-hole pairs exhibit similar η values in the same molecule (see Table S1). Therefore, the value of η does not show significant change for different excited states of the

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Table 1	l. 1	'heoretical	Reorg	anization	Energies	and	BOBL	Density	Parameters	of 1	the	Polya	cene	Excited	States
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		$\lambda_n^{ m AP}$	λ_n^{CA}	$\lambda_n^{ m OVC}$	η	ϕ	$\lambda_{ m H1}^{ m OVC}$	$\lambda_{ m H}^{ m OVC}$	$\lambda_{ m L}^{ m OVC}$	$\lambda_{\rm L1}^{ m OVC}$
naphthalene	${}^{1}L_{a}$	348	337	442	0.136	0.066	119	113	156	149
	${}^{1}L_{b}$	140	149	161	0.150	0.001				
	${}^{1}B_{b}$	85	86	163	0.151	-0.023				
anthracene	${}^{1}L_{a}$	289	295	372	0.083	0.041	100	94	126	121
	${}^{1}L_{b}$	115	121	135	0.104	0.001				
	${}^{1}B_{b}$	65	67	141	0.106	-0.015				
tetracene	${}^{1}L_{a}$	245	254	328	0.058	0.029	87	81	107	103
	${}^{1}L_{b}$	101	107	117	0.079	0.001				
	${}^{1}B_{b}$	55	57	124	0.081	-0.011				
pentacene	${}^{1}L_{a}$	216	226	290	0.044	0.022	77	73	94	91
	${}^{1}L_{b}$	89	96	103	0.063	0.001				
	${}^{1}B_{b}$	49	51	111	0.065	-0.008				
^{<i>a</i>} In meV.										

same molecule. Nevertheless, η shows a strong size dependence and can be considered as mainly capturing the delocalization size effect. In other words, the η values in a particular excited state decrease with the molecular size increasing. Overall, the ϕ parameter rationalizes the λ in the different excited states and represents an excellent descriptor.

BOBL Density Parameter. To better examine the effectiveness of using the BOBL relationship in quantifying the magnitude of λ , we calculated the BOBL density parameter κ (eq 25) and correlated κ to λ calculated using the TDDFT method (Figure 5). Note that the BOBL density parameter $\kappa =$



Figure 5. Correlation between the BOBL density parameter and the TDDFT-calculated reorganization energy.

 $\eta + 2\phi$ includes contributions from the electron density of the occupied and virtual orbitals (η) as well as the transition density (ϕ). As shown in Figure 5, the BOBL density parameter provides an excellent linear relationship to λ for polyacene excited states with the same characteristics. The results indicate that κ also quantitatively describes the delocalization effect across polyacenes with different numbers of rings, which is associated with the extension of the π -conjugated system, and is consistent with the inversely proportional relationship between the λ and the number of π -atoms in aromatic molecules.⁶¹ Hence, the BOBL density parameter κ provides an excellent descriptor to compare λ in similar excited-state systems.

A closer inspection of the data presented in Table 1 shows that the key parameter that controls the variation in λ among different excited states is ϕ rather than η . For polyacene excited states, the electron density parameter η and the transition density parameter ϕ are on the same order of magnitudes. For each polyacene, η values of different excited states are not much different; therefore, ϕ , which ranges from positive to negative values, determines the magnitude of λ . In other words, the transition density with strong in-phase character leading to the negative value in ϕ contributes more significantly to lowering the magnitude of λ_i , exemplified by the ¹B_b state of polyacenes. Here, the BOBL density parameters only consider the simplest π -molecular-orbital coefficients but capture the significant features of λ . However, these parameters can be improved by many perspectives to increase the correlation with λ . The different regression lines between different kinds of states are mainly a constant shift in λ , which might be due to σ bonding effects or electron correlations. Note that the BOBL density parameters build upon a simplified model depending only on bond-length changes, and the deviations in the bond force constants are also neglected. Therefore, the results derived from polyacene molecules (Figure 5) require further scrutiny for applications to other systems. A more general scheme that could apply likewise BOBL density parameters to excited states with different characters and systems with heteroatoms is currently under study and will be published in a separate work.

Designing Molecules with Small λ in the S₁ State. The BOBL relationship connects the distribution of transition density to the magnitude of reorganization energy and provides a powerful MO picture to identify molecular excitations with small λ . Here, we present a prescription to construct a molecule with small λ in the S₁ state. The idea is based on applying chemical modifications to a polyacene core to tune the relative energies of the frontier orbitals in a manner that allows the small- λ ¹L_b-like state to become the S₁ state. To this end, anthracene with a small energy gap between the ¹L_a and ${}^{1}L_{b}$ states would be an ideal molecular core to design small- λ S₁ excitation. However, the S_1 state of anthracene is the ${}^{1}L_{a}$ state, which exhibits paired molecular-orbital transition and out-ofphase transition density between bonds and hence a large λ . To reduce λ , we must break the paired molecular orbitals, which can be achieved by oxygen substitution at the center position. Figure 6a shows the MO diagrams for anthracene and the oxygen-substituted xanthene molecule. In the cationic xanthene molecule, the oxygen atom stabilizes the orbital energies and destroys the two nearly degenerate transition configurations, i.e., HOMO \rightarrow LUMO + 1 and HOMO - 1 \rightarrow LUMO transitions, because the strong electronegativity of the oxygen atom at the position where both HOMO and LUMO



Figure 6. Evolution of molecular-orbital properties under perturbation by chemical substitution. (a) Frontier orbitals of anthracene, cationic xanthene, and pyronine. The orbital energies in the unit of electronvolts are labeled beside the energy levels. (b) Transition densities of the excited states of the molecules.

have large wave-function coefficients significantly lowers the energy. Consequently, the HOMO $-1 \rightarrow$ LUMO transition dominates the S₂ state of cationic xanthene and exhibits strong in-phase character in the transition density (Figure 6b).

Furthermore, we can add an electron-donating dimethylamino group to xanthene to raise the HOMO -1 energy so that the S₁ state of the resulting compound originates from the unpaired MO transition. The ideal positions of substituents are at the atoms with large wave-function coefficients in the HOMO -1 of xanthene, leading to the pyronine molecule. Figure 6 also shows the MO diagrams and transition density of the pyronine S_1 state. The transition density of pyronine in the S1 state is mainly contributed by the HOMO to LUMO transition and exhibits a strong in-phase character. Most importantly, the λ of pyronine in the S₁ state is calculated to be 41 meV, which is only about one-seventh of that of the anthracene S1 state. Pyronine is one of the well-known molecules with a small Stokes shift (roughly twice that of λ),⁶² and the MO picture based on transition density distribution and the perturbation MO theory provides a general framework to understand the small- λ property of pyronine in terms of the excited states of PAHs. This molecular design scheme demonstrates that exploring molecules with small λ from the viewpoint of transition density is a powerful method.

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Hetero- π -Conjugated Molecules with Small λ . To confirm our observations on the strong correlation between inphase transition density and small λ in systems beyond polyacenes, we identified six hetero- π -conjugated molecules well known for their small Stokes shift (less than 25 nm) in the S₁ state and calculated their theoretical reorganization energy and BOBL density parameters (Table 2). These molecules

Table 2. Theoretical Reorganization Energies and BOBL
Density Parameters of Selected Hetero- π -Conjugated
Molecules ^a

	$\lambda^{\mathrm{AP}}_{\mathrm{S}_1}$	$\lambda_{S_1}^{CA}$	$\lambda_{S_1}^{OVC}$	η	ϕ	$\lambda_{\rm H}^{\rm OVC}$	$\lambda_{\rm L}^{ m OVC}$
pyronine	41	41	72	0.059	-0.016	55	154
oxazine	48	46	81	0.070	-0.019	58	179
cy5	70	67	153	0.059	-0.016	82	201
DABNA	64	62	86	0.053	-0.016	64	89
BDP	58	57	115	0.051	-0.012	73	113
phthalocyanine	41	42	113	0.047	-0.010	29	142
^{<i>a</i>} In meV.							

include the xanthene dyes (pyronine and oxazine),⁶² the cyanine dye (cy5), DABNA,⁶³ the boron-dipyrromethene derivative (BDP),⁶⁴ and the porphyrinoid (phthalocyanine).⁶⁵ These molecular core structures cover a very broad chemical space of organic functional chromophores used in contemporary optoelectronic applications, as these molecules with small λ are widely used in bioimaging and organic optoelectronics. Interestingly, despite the large variations in the molecular structures, these molecules all exhibit small λ and transition densities with significant in-phase character in the S1 state (Figure 7). Consequently, the calculated transition density parameter ϕ is negative for these molecules, indicating that λ contributed by bond-length changes is significantly reduced in the S₁ state. These results can also be collaborated by the viewpoint of the OVC method. The lowest excited state of these hetero- π -conjugated molecules is mainly contributed by the HOMO to LUMO transition. As listed in Table 2, the sum of $\lambda_{\rm H}^{\rm OVC}$ and $\lambda_{\rm L}^{\rm OVC}$ is larger than $\lambda_{\rm S_1}^{\rm OVC}$. According to eq 16, it indicates that the cross-term lowers the reorganization energy, i.e., the correlated vibronic couplings dominate in the vibrational modes. Therefore, the strong in-phase character in the transition density presents a negative ϕ value and causes the small λ .

It is worth noting that the in-phase character of the transition densities shown in Figure 7 can be interpreted as a separation of the transition density into a positive region and a negative region, which without exception leads to a large transition dipole. Indeed, these small Stokes shift molecules sometimes suffer from the disadvantage of self-absorption, which hinders their applications.^{66–68} Following the analysis performed in this research, we conclude that in general molecular excitations with a small Stokes shift tend to have in-phase transition densities and large transition dipole moments. On the other hand, molecules with an extended out-of-phase region in the transition densities would have a large Stokes shift and a small transition dipole moment. This general guideline could be an important factor to be considered in the strategic design of molecular chromophores.



Figure 7. Selected hetero- π -conjugated molecules and their transition density in the S₁ state. These are representative molecules that have been shown to exhibit small Stokes shifts experimentally.

CONCLUSIONS

In this study, we have proposed a simple theory based on the bond-order-bond-length relationship to connect MO coefficients with the reorganization energy of molecular excited states. We show that the relative phase of transition densities at two bonding atoms is an important factor determining the magnitude of the reorganization energy for bond stretching modes. An out-of-phase character in the transition densities across a bond leads to strong vibronic coupling and hence large reorganization energy, whereas an in-phase character indicates reduced reorganization energy. The theory allows us to reveal a BOBL density parameter that can be used to quantify the magnitude of the reorganization energies. We also applied computational methods to evaluate reorganization energies of the ¹L_a, ¹L_b, and ¹B_b states of polyacenes. TDDFT calculations showed that these excited states exhibit very different reorganization energies, and a general trend of $\lambda(^{1}L_{a}) \gg$ $\lambda({}^{1}L_{b}) > \lambda({}^{1}B_{b})$ for each polyacene is revealed. We then showed that our BOBL analysis based on the transition density distribution provides an illuminating MO picture to explain the different magnitude of state-dependent reorganization energies. The ¹L_a state originates from an electronic transition between paired molecular orbitals, which ensures that the excitation has a strong out-of-phase transition density and a large reorganization energy. In contrast, the electronic transitions involved in the ${}^{1}L_{b}$ and ${}^{1}B_{b}$ states are not limited by the pairing theorem. Instead, the transition densities of ${}^{1}L_{b}$ and ¹B_b show nonbonding and in-phase characters, respectively, which leads to significantly smaller reorganization energies compared to that of the ${}^{1}L_{a}$ state. Besides, we show that the ${}^{1}B_{b}$ state with in-phase character exhibits the lowest reorganization energy because of the contributions from the two-electron integral terms. As a result, for polyacenes, the relative magnitude of reorganization energies in the three lowest-lying excited states can be fully elucidated.

Moreover, we examined the effectiveness of using the BOBL density parameter κ to quantify the magnitude of reorganization energies. A comparison of the TDDFT-calculated reorganization energies to κ shows a strong linear correlation in the same excited state of different polyacenes, confirming that the BOBL MO picture is quantitative and that κ can be used to quantify the magnitude of reorganization energies. We believe that the analysis based on the transition density distribution provides significant physical insights into the MO characteristics that control molecular reorganization energies, and the theory would be extremely useful for the design of small- λ chromophores. To demonstrate this point, we proposed that a molecular-orbital perturbation scheme can be adopted to derive molecules with small- λ S₁ transition from the low-lying excited states of polyacenes. As an example, the S1 excited state of pyronine is shown to be connected to the ¹L_b state of anthracene and exhibits a strong in-phase distribution of the transition density and as a result a small reorganization energy. A small reorganization energy value of 41 meV for the pyronine S_1 state is obtained computationally to confirm the validity of the scheme.

Finally, we examined the transition densities and BOBL density parameter for a representative set of small Stokes shift molecules, which are experimentally well-known molecules that have small reorganization energies. We show that the MO picture and transition density distribution rules for estimating the magnitude of reorganization energies are valid even for these hetero- π -conjugated systems. The results confirm the generality of the theory proposed in this work. Furthermore, our MO picture also suggests a general guideline for chromophores. Small- λ excited states tend to have large transition dipole moments as well, whereas excited states with large λ would also exhibit small transition dipole moments.

In summary, we have revealed a quantitative relationship between the transition density distribution and strength of vibronic couplings in molecular excited states. The relationship provides a MO picture to explain the relative reorganization energies of the low-lying excited states of PAHs and more general hetero- π -conjugated organic molecules, and the new insights allow us to propose a new MO descriptor and strategy to design small- λ organic chromophores. The BOBL density parameter κ can be used as a quantitative descriptor to rationalize the strengths of λ in a broad range of molecular excited states. Note that a rigorous and quantitative expression for the relationship between λ and the transition density obtained from modern many-electron wave functions is a much more difficult task that is out of the scope of this work. Nevertheless, we believe that the molecular design principle based on the transition density distribution would be extremely useful for identifying novel organic optoelectronic materials by more strategically tuning the reorganization energy. We also note that compared to HOMO/LUMO properties, reorganization energy is often overlooked in high-throughput screening of organic optoelectronic materials, $^{69-72}$ likely due to the significantly higher computational cost for determining λ . The BOBL density descriptor provides a much more cost-efficient

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alternative to quantify the magnitude of λ ; hence, we expect it to play a role in future computational studies on screening of small- λ chromophores.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c06482.

 λ s for naphthalene in the ${}^{1}L_{a}$, ${}^{1}L_{b}$, and ${}^{1}B_{b}$ states calculated by the adiabatic potential method in different DFT methods and by different computational methods; transition densities for the three lowest excited states of polyacenes; BOBL density parameters of polyacenes (PDF)

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Notes

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