

Excitonic Splittings in Jet-Cooled Molecular Dimers

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Abstract: In more than 60 years of research on molecular excitons, there has been extensive theoretical work but few experimental investigations have rigorously tested the predictions of exciton coupling theories. In centrosymmetric doubly H-bonded molecular dimers with identical chromophores, the $S_0 \rightarrow S_1$ electronic transition dipole moments of the monomers combine in a parallel and antiparallel fashion, giving the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the dimer. One of these is strictly symmetry-forbidden and the other fully allowed. Minimal perturbations such as $^{12}\text{C}/^{13}\text{C}$ or H/D isotopic substitution lift the symmetry restrictions sufficiently to render both transitions allowed. The excitonic (Davydov) splitting can then be measured as the energy difference between the respective vibrationless 0_0^0 bands. We have measured the mass-specific vibronic spectra of the centrosymmetric H-bonded dimers (2-pyridone)₂ and (2-aminopyridine)₂ that are supersonically cooled to a few K and isolated in molecular beams, using two-color resonant two-photon ionization spectroscopy. Comparison of the *all-¹²C*- and ¹³C- isotopomer spectra yield excitonic splittings of $\Delta_{\text{exp}} = 43.5$ and 10.5 cm^{-1} , respectively. The corresponding splittings calculated by high-level *ab initio* methods (RI-CC2/aug-cc-pVTZ) are 20 to 50 times larger. These purely electronic *ab initio* exciton splittings need to be reduced ('quenched') by vibronic coupling to the optically active vibrational modes. Only after quenching are the experimentally observed exciton splittings correctly reproduced.

Keywords: Energy transfer · Exciton splitting · Hydrogen-bonding · Molecular dimers · Molecular exciton

1. Introduction

Molecular excitons are collective excited states that are important in a wide range of biological and chemical systems including photosynthetic light-harvesting antenna systems, conjugated polymers, molecular crystals and nucleic acids.^[1] The excitonic interactions have a significant impact on their electronic structure and functions. Below, we discuss the vibronically resolved ultraviolet spectra of centrosymmetric molecular homo-dimers that are formed, cooled and isolated in supersonic jets. The spectra of these simple and paradigmatic systems provide strict benchmarks for testing the predictions of exciton coupling theories. Current improvements of these theories give new insights and provide a solid basis for the bottom-up understanding of excitonic interactions in multichromophoric systems.

2-Pyridone (2PY) and 2-aminopyridine (2AP) are structural mimics of the Watson-Crick hydrogen binding sites of uracil and adenine, respectively, and have been em-

ployed to model doubly hydrogen-bonded DNA base pairs in the gas phase.^[2–6] In the corresponding self-dimers (2PY)₂ and (2AP)₂, two antiparallel H-bonds hold the chromophores at well-defined intermolecular distances and angles. Using (2PY)₂ and (2AP)₂ as model dimers, we focus on the excitonic splitting between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ vibrationless transitions (0_0^0 bands or electronic origins). The observed exciton splittings are 20–50 times smaller than those obtained from *ab initio* calculated $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitation energies. This large disagreement can only be resolved by considering the reduction ('quenching') of the excitonic splitting by the molecular and intermolecular vibrations of the dimer.

2. Electronic Treatment of Excitonic Interactions: The Frenkel-Davydov Model

Excitonic couplings in molecular dimers are small (typically 1–5 kJ/mol) and are usually treated by weak-coupling (Frenkel-Davydov) exciton theory.^[7,8] For centrosymmetric homo-dimers consisting of two identical monomers labeled *A* and *B*, the monomer electronic S_0 wave functions are denoted $|A\rangle$ and $|B\rangle$ and the dimer S_0 wave function is approximated as $|\Psi_0\rangle = |A\rangle|B\rangle$. The monomer $S_0 \rightarrow S_1$ excited state wave functions $|A^*\rangle$ and $|B^*\rangle$ combine to

give the delocalized dimer excited state wavefunctions

$$\begin{aligned} |\Psi^+\rangle &= (|A^*\rangle|B\rangle + |A\rangle|B^*\rangle)/2 \\ |\Psi^-\rangle &= (|A^*\rangle|B\rangle - |A\rangle|B^*\rangle)/2 \end{aligned}$$

The corresponding excited-state energies are obtained from 1st-order perturbation theory:^[7,8]

$$E^{+/-} = \left\{ V_{AA} + V_{BB} \pm \sqrt{(V_{AA} - V_{BB})^2 + 4V_{AB}^2} \right\} / 2 \quad (1)$$

where V_{AA} and V_{BB} are the monomer excitation energies of *A* and *B* and V_{AB} is the excitonic coupling matrix element. The excitonic splitting (Davydov splitting) between E^+ and E^- is

$$\Delta E = \sqrt{(V_{AA} - V_{BB})^2 + 4V_{AB}^2} \quad (2)$$

For symmetric dimers, $V_{AA} = V_{BB}$, and the excitonic splitting becomes $\Delta E = 2V_{AB}$, see Fig. 1.

In the Frenkel model, *A* and *B* are rigid (clamped-nuclei approximation) and the coupling to the molecular vibrations is neglected in the ground and excited states. Therefore, the $S_0 \rightarrow S_1$ electronic transitions for separated *A* and *B* are line-like, similar to atomic absorption lines as shown schematically in Fig. 2a,b. The electronic respective monomer oscillator strengths $f_e(A)$ and $f_e(B)$ are concentrated in the 0_0^0 bands.

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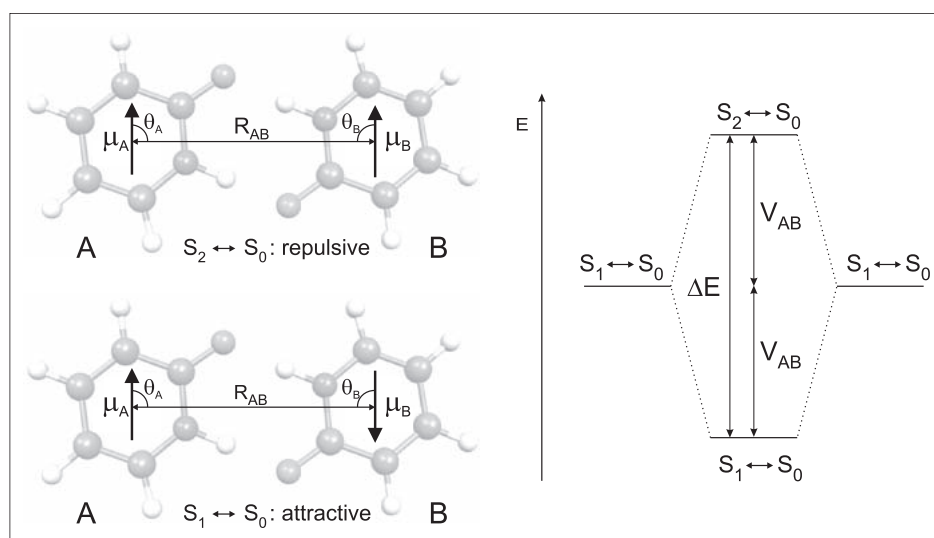


Fig. 1. Dipole-dipole interaction and energy level diagram in the Frenkel-Davydov exciton model for a symmetric molecular homodimer A-B.

Upon dimer formation, the coupling between the monomer $S_0 \rightarrow S_1$ transitions leads to dimer S_1 and S_2 states that are energetically separated by $\Delta E = 2V_{AB}$ as shown in Fig. 2c. At typical intermolecular distances, V_{AB} can be approximated by the dipole-dipole interaction of the local electric transition dipole moments of A and B, which results in $V_{AB} \sim |\vec{\mu}_{el}(A) \cdot \vec{\mu}_{el}(B)|^2 \sim f_{el}$, i.e. V_{AB} is proportional to the monomer $S_0 \rightarrow S_1$ oscillator strength. For centrosymmetric molecular dimers, such as $(2AP)_2$, one of the transitions becomes electric-dipole forbidden and the other fully allowed, as indicated in Fig. 2c.

3. Effect of Vibronic Coupling on the Excitonic Splitting

The interaction of the electronic excitations with the molecular vibrations changes the excitonic coupling between A and B: So-called *vibronic coupling models* for molecular homodimers have been developed from the late 1950s onwards.^[9–11] For the weak-coupling case and linear vibronic coupling, Förster has shown that in absorption from the $v'' = 0$ ground state, the excitonic splitting between a given pair of *vibronic* bands is $\Delta E_{vibronic} = 2V_{AB} \cdot |\langle \phi_{v'} | \phi_0 \rangle|^2$, where v' is the excited-state quantum number of a given vibrational mode and $|\langle \phi_{v'} | \phi_0 \rangle|^2$ is the Franck-Condon factor (FCF).^[11] Since FCFs are always < 1 and often $\ll 1$, this implies that the *electronic* Davydov splitting $2V_{AB}$ is reduced ('quenched') by the FCF. The FCF of the electronic origin is $|\langle \phi_0 | \phi_0 \rangle|^2 = \exp(-\sum_i S_i) = \Gamma$, where S_i is the Huang-Rhys factor of the i -th vibrational mode, the sum extends over all excited-state totally-symmetric vibrations, and Γ is the *quenching factor* which reduces the electronic splitting ΔE_{el} . For harmonic vibrations and similar S_0 and S_1 frequencies, $S_i = FCF(i_0)/FCF(0_0) \geq 0$. Aromatic chromophores typi-

cally have 5–10 totally symmetric vibrations with S_i in the range 0.1–1. Consequently, the quenching factor can become very small $\Gamma = \exp(-\sum_i S_i) = 0.001$ –0.1.

Fig. 3a,b illustrates this with schematic vibronic spectra of A and B, where only two intramolecular vibrations are included for clarity. In contrast to Fig. 2a,b the oscillator strength f_{el} is now fragmented over many vibronic transitions spanning a range of several 1000 cm^{-1} . Fig. 3 assumes the quenching factor Γ to be $\Gamma = 0.05$, that is $f_{(0-0)} = 0.05 f_{el}$ (compare the vertical axes in Figs 2 and 3).

Hence the splitting between the S_2 and S_1 origin (Fig. 3c) is strongly reduced relative to Fig. 2c. The excitonic coupling of A and B now occurs between *individual pairs* of vibronic transitions; the latter are typically spaced apart much farther than the individual excitonic splittings. Vibronic coupling occurs for both intra- and intermolecular vibrations, see ref. [12] for details. The intermolecular couplings are neglected in Figs 2 and 3.

4. Spectroscopic Determination of Excitonic Splittings: (2-Pyridone)₂ and (2-Aminopyridine)₂

The $(2PY)_2$ and $(2AP)_2$ dimers were produced and cooled in pulsed neon supersonic jet expansions. The pulsed nozzle containing the 2PY or 2AP sample was heated to 50–60 °C. Two-color resonant two-photon ionization (2C-R2PI) spectra were recorded by overlapping the excitation and ionization lasers in the source of a time-of-flight mass spectrometer.^[12,13]

The mass selective 2C-R2PI spectra of $(2PY)_2$ and $(2AP)_2$ around their respective electronic origins are shown in Fig. 4a,b.

The $(2PY)_2$ dimer is C_{2h} symmetric in both electronic states, and only the $S_0 \rightarrow S_2$

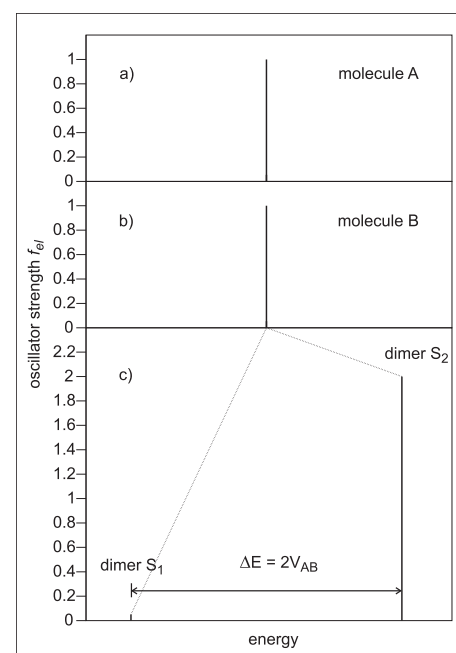


Fig. 2. Schematic representation of the purely electronic excitonic interaction of two molecular electronic transitions in the clamped-nuclei approximation (neglecting all effects of molecular vibrations).

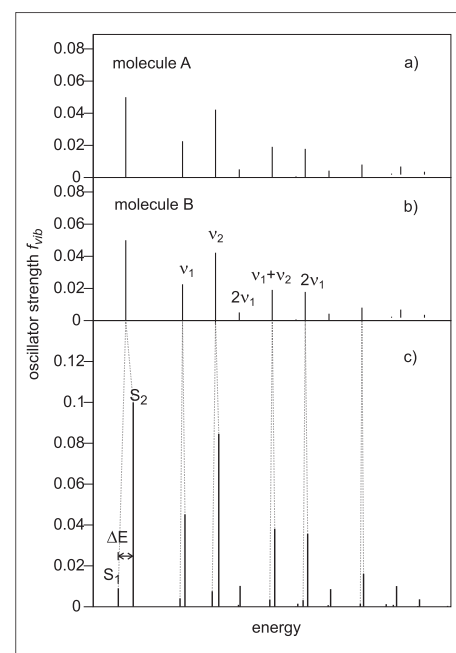


Fig. 3. Excitonic interaction of molecular chromophores A and B including excited-state vibrations. The oscillator strength of each monomer is distributed over many vibrational levels resulting in a significant reduction of the excitonic splitting between the electronic origins. The S_1 and S_2 state dimer spectra are indicated below.

transition is observed at 30778 cm^{-1} , see also ref. [5]. $(2AP)_2$ is C_{2h} symmetric in its excited states but in the S_0 state it is C_2 symmetric, which renders the $S_0 \rightarrow S_1$ transition also weakly allowed.^[14] We assign the intense band at 31808 cm^{-1}

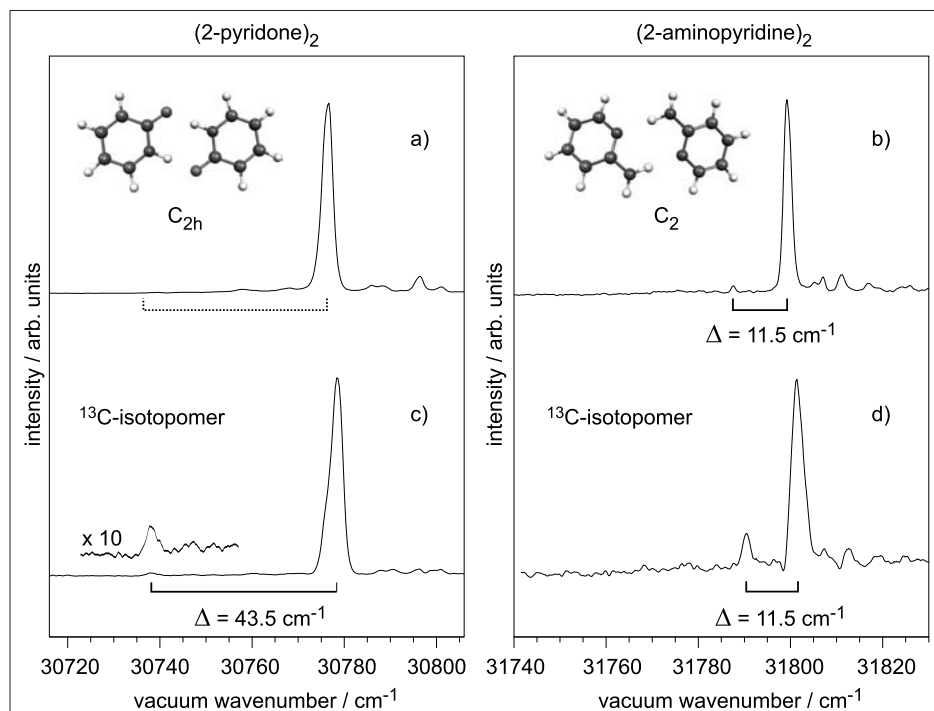


Fig. 4. Experimental two-color resonant two-photon ionization spectra of (2-pyridone)₂ and (2-aminopyridine)₂ in the ¹²C- and ¹³C isotopomer mass channels and near the electronic origin or 0₀⁰ bands.

in Fig. 4b to the $S_0 \rightarrow S_2$ 0₀⁰ band and the weak band at 31797 cm⁻¹ to the $S_0 \rightarrow S_1$ origin. For (2AP)₂, the excitonic splitting between the 0₀⁰ bands is directly measurable and amounts to $\Delta_{\text{exp}} = 11.5$ cm⁻¹. Both assignments were verified by measuring the 2C-R2PI spectra of the corresponding ¹³C-isotopomers, shown in Fig. 4c,d: The natural ¹³C/¹²C ratio results in a ¹³C-isotopomer signal of ~11%. Since the ¹³C atom can substitute at any ¹²C-position within the dimer, the spectra in Fig. 4c,d arise from the overlapping absorption spectra of five slightly inequivalent ¹³C-isotopomers. ¹³C-substitution lowers the dimer symmetry from C_{2h} to C_s for (2PY)₂ and from C₂ to C₁ for (2AP)₂. The symmetry-

breaking allows the $S_0 \rightarrow S_1$ transitions to appear weakly in Fig. 4c,d.

5. Calculations of the Electronic and Vibronic Excitonic Splitting

We optimized the (2PY)₂ and (2AP)₂ ground state structures using the approximate coupled cluster RI-CC2 method with the aug-cc-pVTZ basis set, and calculated the vertical S₁ and S₂ excitation energies at the same level. The results are summarized in Table 1. Note that the *ab initio* calculations employ clamped nuclei, hence the *ab initio* splitting ΔE_{calc} corresponds to the atom-like case, as in Fig. 2.

Table 1. Calculated vertical RI-CC2/aug-cc-pVTZ excitation energies (cm⁻¹), oscillator strengths $f_{\text{el,calc}}$ and electronic S₁/S₂ splittings Δ_{calc} , for (2AP)₂ and (2PY)₂ (at RI-CC2/aug-cc-pVTZ optimized geometries). The quenching factors Γ are determined from experiment,^[13,14] and vibronic splitting energies $\Delta_{\text{quenched}} = \Delta E_{\text{calc}} \cdot \Gamma$ are compared to the observed splittings Δ_{exp} .

(2-aminopyridine) ₂			(2-pyridone) ₂			
	Irrep	Energy	$f_{\text{el,calc}}$	Irrep	Energy	$f_{\text{el,calc}}$
$S_0 \rightarrow S_1$	a	35326 cm ⁻¹	0.003	a _g	34137 cm ⁻¹	0.000
$S_0 \rightarrow S_2$	b	35742 cm ⁻¹	0.109	b _u	35262 cm ⁻¹	0.173
ΔE_{calc}		416 cm ⁻¹			1125 cm ⁻¹	
Γ_{exp}		0.025			0.035	
Δ_{quenched}		10 cm ⁻¹			44 cm ⁻¹	
Δ_{exp}		11.5 cm ⁻¹			43.5 cm ⁻¹	

To calculate the quenching factor $\Gamma = \exp(-\sum S_i)$, we employed the Huang-Rhys factors S_i from experimental fluorescence spectra of the 2PY and 2AP monomers,^[13,15] which gave $\Gamma = 0.025$ for (2AP)₂ and 0.035 for (2PY)₂. The vibronic coupling to intramolecular vibrational modes is seen to quench the Davydov splittings by factors of 40 and 30, respectively! As Table 1 shows, the predicted quenched excitonic splittings of 10 and 44 cm⁻¹ are in excellent agreement with the experimental splittings of 11.5 and 43.5 cm⁻¹.

We also calculated purely theoretical quenching factors: For this, the S₁ state potentials of the 2PY and 2AP monomers were computed at the RI-CC2 level along the totally-symmetric ground state normal vibrations. The ground state geometries were distorted by $\pm 1Q_i$ and $\pm 2Q_i$ along each normal mode and the Huang-Rhys factors determined as $k_i^2 / (2\omega_i^2)$, where k_i is the first derivative of the S₁ potential along the *i*-th mode at $Q_i = 0$ and ω_i is the vibrational frequency. The quenching factors so obtained are $\Gamma_{\text{calc}} = 0.019$ and 0.102, resulting in estimated excitonic splittings of $\Delta_{\text{calc}} = 21.4$ cm⁻¹ for (2AP)₂ and $\Delta_{\text{calc}} = 42.4$ cm⁻¹ for (2PY)₂. Compared to the splittings obtained *via* the experimental quenching factors Γ_{exp} , these values are in slightly less good agreement. Nevertheless, the consistency and level of agreement of both approaches clearly demonstrates that the quenching of the excitonic splitting is large. There are many repercussions for the fields of natural light-harvesting and energy transfer as well as in nanoscale and device-oriented systems.^[1]

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