I. INTRODUCTION

The 2-pyridone dimer (2PY)₂ consists of two equivalent pyridine-based chromophores which are connected by two antiparallel N–H···O=C hydrogen bonds, see Fig. 1. It may be viewed as a model for hydrogen-bonded nucleotide base pairs, e.g., the noncanonical uracil dimer. The electronic coupling and excitation transfer in dimers which can model hydrogen-bonded DNA and RNA base pairs are of great interest: In nucleic acids, exciton optical effects are complicated, since there are numerous different nearest-neighbor interactions between bases, both on the same and on opposite strands of a double helix. Also, exciton splittings or shifts are not visible in the relatively broad near-UV absorption bands of DNA. Here, we investigate by laser gas-phase spectroscopy a base pair analogue which exhibits only the coupling between two transition dipoles across the hydrogen bonds linking the two strands, without further stacking-type interactions with other bases.

Due to this pair of strong hydrogen bonds (2PY)₂ is planar and C₂ᵥ symmetric both in its ground (S₀) and lowest optically allowed excited state (S₂), see Fig. 1. The rotational constants and hydrogen-bonded distance of (2PY)₂ have been precisely measured in both electronic states. The S₀ and S₁ states both transform as Aₐ and the S₂ state as Bₐ, hence the electronic S₂→S₀ transition is one-photon electric-dipole allowed in C₂ᵥ, while the S₁→S₀ transition is strictly forbidden. These selection rules can be understood in terms of an in-phase excitation of the two 2PY units for the S₂→S₀ (Bₐ→Aₐ) transition, see Fig. 1(a), and an out-of-phase excitation for the forbidden S₁→S₀ (Aₐ→Aₐ) transition, Fig. 1(b). High-resolution spectroscopic investigations of the 2PY monomer by Pratt et al. showed that its S₁→S₀ transition moment is oriented by −51° relative to the inertial a axis. The inversion symmetry of the dimer requires the two monomer transition moments to be exactly parallel or antiparallel, see Fig. 1. Measurement of a ≃ 95% polarization of the (2PY)₂ S₂→S₀ transition along the dimer inertial b axis showed that the two monomer transition moments must be in-plane and nearly perpendicular to the line connecting the two centers of mass. (2PY)₂ is thus a very well characterized dimer which can be used to model and investigate exciton coupling effects of biological relevance.

The electronic coupling and excitation transfer in dimers has traditionally been treated by Frenkel exciton theory. The local ground state wave functions of the two chromophores are usually denoted |A⟩ and |B⟩ and the corresponding excited state wave functions as |A⟩* and |B⟩*. The totally symmetric electronic ground state S₀ is written as |Ψ₀⟩=|A⟩·|B⟩. For the excited states, the coupling of the two local excitations results in the excited dimer wave functions

\[ S₂: \quad |\Psi^{+}\rangle=\left(|A^{*}\rangle \cdot |B\rangle + |A\rangle \cdot |B^{*}\rangle\right)/\sqrt{2}, \]

\[ S₁: \quad |\Psi^{-}\rangle=\left(|A^{*}\rangle \cdot |B\rangle - |A\rangle \cdot |B^{*}\rangle\right)/\sqrt{2}. \]

The Davydov splitting between these two excitonic states can be treated by first order perturbation theory with Vₐₐ and V₀₀ being the Coulomb integrals of the individual chromophores, S is the overlap integral of the two localized wave functions, and V₁₁ is the coupling matrix element of the exciton interaction, often denoted β. The overlap integral S is neglected for intermonomer distances larger than 5 Å. Solving the secular equation yields the interaction energy

\[ E^{\pm}=E_{₀}^{\pm} \pm \sqrt{\left(E_{0}^{\pm}-V_{BB}\right)^{2}+4V_{AB}^{2}}/2. \]

The exciton splitting is

\[ \Delta E=|E^{+}-E^{-}|=\sqrt{(V_{AA}-V_{BB})^{2}+4V_{AB}^{2}}. \]
Equation (4) shows that the in-phase \( S_2 \rightarrow S_0 \) transition occurs at higher energy compared with the out-of-phase \( S_1 \rightarrow S_0 \) transition, as discussed by Held and Pratt.\(^5\) A schematic diagram showing the energy levels and exciton splitting is given in Fig. 2. The matrix element \( V_{AB} \) consists of a part describing the electrostatic interaction and another part for the exchange interaction; the latter can usually be omitted for a sufficiently large distance between the two chromophores.\(^6\)–\(^13\) The electrostatic interaction is then modeled by the point dipole interaction between the two transition dipole moments, denoted \( V_{dd} \), and given by\(^14\)

\[
V_{dd} = - \frac{\mu_1 \cdot \mu_2}{4 \pi \varepsilon_0 R_{AB}^3} \left[ 2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos \varphi \right]
\]

where \( R_{AB} \) is the distance between the centers of the two chromophores, \( \theta_A \) and \( \theta_B \) are the angles of the transition dipole moment with the line joining the two centers according to Fig. 1, and \( \varphi \) is the dihedral angle between the two transition dipoles. More accurate calculations take into account the Coulomb interaction between the actual charge distributions.

The Frenkel exciton model has been extended to incorporate vibronic coupling.\(^5\)–\(^8\),\(^12\),\(^15\),\(^16\) These models usually consider one allowed electronic excited state and one intramolecular vibrational coordinate per monomer. Typically, the vibrational mode is assumed to have the same frequency \( h\nu \) in the ground and excited state, but the excited state equilibrium position along the single vibrational coordinate is shifted by an amount \( \lambda \), the electronic–vibronic coupling or Huang–Rhys factor.\(^8\),\(^15\),\(^16\) Numerical treatments of the weak, intermediate, and strong coupling cases of the dimer spectra that arise from the relative sizes of \( V_{AB} \), \( \lambda \), and \( h\nu \) have been given.\(^8\),\(^15\),\(^16\)

Considerable effort has been devoted to the spectroscopic study of dimers of the simplest aromatic molecules such as benzene\(^11\),\(^17\)–\(^20\) and naphthalene,\(^21\)–\(^23\) for which supersonic-beam techniques have made it possible to obtain detailed information about the geometries, intermolecular interactions and vibrations. Following the pioneering studies of the benzene dimer by Smalley et al.\(^17\)–\(^19\) and Levy et al.,\(^17\)–\(^19\) Schlag et al. measured and analyzed the exciton splitting energies in different isotopomers of benzene dimers by R2PI spectroscopy. They observed a small splitting of \( \Delta E = 1.7 \) cm\(^{-1}\) for \( C_6H_{62} \) and of \( \Delta E = 2.3 \) cm\(^{-1}\) for \( C_6D_{62} \). These were analyzed in terms of an exciton coupling matrix element of \( V_{AB} = 0.8 \) cm\(^{-1}\) together with further effects from isotopic shifts and the excitation of localized chromophores.\(^11\) Later measurements of the benzene trimer and tetramer yielded exciton coupling matrix element of very similar sizes.\(^20\) For the naphthalene dimer broad bands were observed even in the supersonic jet spectra, precluding an analysis of the exciton splitting. For the naphthalene trimer and tetramer, band splittings were observed which were interpreted in terms of coupling elements \( V_{AB} = 10\)–15 cm\(^{-1}\).\(^21\)

In contrast to the benzene dimer, no direct observation of the electronic \( S_1 \rightarrow S_0 \) transition nor of the \( S_1/S_2 \) exciton splitting has so far been reported for the 2-pyridone dimer, due to its higher symmetry. From the analysis of H/D isotopic shifts of the origins, Held and Pratt postulated an upper limit of 20 cm\(^{-1}\) to the exciton splitting.\(^2\) Here we report the breakdown of the \( C_{2v} \) symmetry selection rules in \( (2PY)_2 \) by single asymmetric isotope substitutions; H/D exchange at either the N–H group or a single \(^12\)C/\(^13\)C isotopic exchange within either ring (due to the natural \( 1.1% \) abundance of \(^13\)C) lowers the symmetry of the dimer from \( C_{2v} \) to \( C_\gamma \). This leads to a slight change in the vibrationally averaged structure, a change of vibrational zero point energy, and a slight realignment of the transition dipole in the particular mono-
mer subunit, which renders the $S_{1} \leftrightarrow S_{0}$ transition weakly allowed. Double H/D exchange at both N–H groups in $(2\text{PY})_{2} \rightarrow d_{2}$ restores the $C_{2h}$ symmetry of the dimer and re-introduces the strict $g \leftrightarrow u$ selection rule.

Section II presents *ab initio* ground and excited state calculations on 2PY and all four $(2\text{PY})_{2}$ isotopomers including normal mode analyses, as well as transition dipole moment calculations for 2PY, giving theoretical exciton splittings. In Sec. III we present the experimental spectra and vibrational analyses for the $S_{0}$, $S_{1}$, and $S_{2}$ states, which partially builds on our earlier analysis of $(2\text{PY})_{2} \rightarrow h_{2}$. In Sec. IV we discuss the observed exciton splittings in terms of the Frenkel exciton model and examine possible modifications.

II. THEORETICAL METHODS AND RESULTS

A. Computational procedure

Minimum-energy structures and harmonic wave numbers of the 2-pyridone dimer were calculated as reported earlier. Normal coordinate analyses were performed for the singly and doubly N–D deuterated $(2\text{PY})_{2}$ dimer, both at the SCF/6-31G($d,p$) and at the B3LYP/6-311+ + G(2d,2p) levels. For the 2PY monomer, configuration interaction singles (CIS) calculations with the 6-31G($d,p$) basis set were also performed, to obtain an estimate for the size and direction of the $S_{1} \leftrightarrow S_{0}$ transition dipole moment. CIS structure optimizations for excited state $(2\text{PY})_{2}$ were also attempted; these failed due to convergence problems associated with the close-lying $S_{1}$ and $S_{2}$ excited states. All calculations were performed using the GAUSSIAN 98 program.

B. Calculated vibrational wave numbers

The wave numbers of the six intermolecular modes and of the lowest intramolecular vibrations of the four studied isotopomers of $(2\text{PY})_{2}$ are compiled in Table I. Comparison of the intermolecular vibrations $v'_{i}$ to $v''_{i}$ of the nondeuterated with the doubly deuterated species reveals that all wave numbers are reduced by approximately 0.7 cm$^{-1}$ at the SCF level. The $v'_{9}$ slanting mode shows the largest shift of 1.0 cm$^{-1}$. The deuteration shifts of the intermolecular wave numbers at the B3LYP/6-311+ + G(2d,2p) level are significantly larger than at the SCF level: $v'_{9}$ is reduced by 4.4 cm$^{-1}$ while $v''_{9}$ increases by 0.9 cm$^{-1}$. The $v'_{6}$ and $v''_{6}$ wave numbers are reduced by 1.4 and 1.5 cm$^{-1}$. The $v''_{9}$ "opening" vibration wave number is reduced by 2.4 cm$^{-1}$ and the $v''_{6}$ stretch by 3.1 cm$^{-1}$.

The low wave number intramolecular modes also exhibit deuteration shifts of several cm$^{-1}$, as can be seen in Table I. As expected, much larger shifts are calculated for the N–H bending and stretching modes. The out-of-plane bending modes show wave number decreases of 218.7 and 287.5 cm$^{-1}$, the in-plane bends decreases of 563.8 and 560.1 cm$^{-1}$, and the largest shifts of 874.7 and 887.0 cm$^{-1}$ are calculated for the two N–H stretching modes (see Table II).

C. Calculated transition dipole moments and exciton splitting energies

Full geometry optimizations of $S_{1}$ state 2-pyridone was performed with the CIS/6-31G($d,p$) method. The optimized $S_{1}$ structure is nonplanar with the N atom displaced out of the ring plane by 23$^\circ$ and the N–H bond oriented pseudoequatorially. Such a structure was proposed by Held et al., based on the $S_{1}$ state rotational constants. The alternative pseudoaxial N–H bond conformation, also suggested by Held et al., was not found to be a stable minimum with the CIS/6-31G($d,p$) method.

The $S_{1} \leftrightarrow S_{0}$ transition dipole moment calculated with the nonplanar $S_{1}$ state optimized structure is $|\mu| = 1.17 \times 10^{-29}$ Cm. The calculated angle between this $\mu$ and the $a$...
TABLE II. SCF/6-31G(d,p) and B3LYP/6-311++G(2d,2p) calculated intramolecular wave numbers for the N–H stretching and bending modes of (2PY)₂–h₂ and (2PY)₂–d₂ which undergo the largest wave number shifts.

<table>
<thead>
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<th>Mode</th>
<th>Description</th>
<th>Irrep.</th>
<th>SCF</th>
<th>B3LYP</th>
<th>SCF</th>
<th>B3LYP</th>
<th>Shift/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₂₇</td>
<td>N–H oop. bend</td>
<td>b₉</td>
<td>896.9</td>
<td>945.9</td>
<td>678.2</td>
<td>709.5</td>
<td>−218.7 −236.4</td>
</tr>
<tr>
<td>ν₂₈</td>
<td>N–H oop. bend</td>
<td>a₉</td>
<td>942.5</td>
<td>950.1</td>
<td>655.0</td>
<td>716.8</td>
<td>−287.5 −233.3</td>
</tr>
<tr>
<td>ν₄₉</td>
<td>N–H ip. bend</td>
<td>b₉</td>
<td>1531.8</td>
<td>1513.3</td>
<td>968.0</td>
<td>1056.6</td>
<td>−563.8 −456.7</td>
</tr>
<tr>
<td>ν₅₀</td>
<td>N–H ip. bend</td>
<td>a₉</td>
<td>1538.7</td>
<td>1521.8</td>
<td>978.6</td>
<td>1060.2</td>
<td>−560.1 −461.6</td>
</tr>
<tr>
<td>ν₅₇</td>
<td>N–H stretch</td>
<td>a₅</td>
<td>3329.2</td>
<td>3027.1</td>
<td>2454.5</td>
<td>2246.9</td>
<td>−874.7 −780.2</td>
</tr>
<tr>
<td>ν₅₈</td>
<td>N–H stretch</td>
<td>b₅</td>
<td>3360.4</td>
<td>3095.8</td>
<td>2473.4</td>
<td>2286.6</td>
<td>−887.0 −809.2</td>
</tr>
</tbody>
</table>

principal axis is 56°, in good agreement with the measured value of 51°.²⁴ Using Eq. (5), with an interdipole separation taken to be R = 5.36 Å, the separation of the monomer centers of mass in the SCF/6-31G(d,p) optimized structure, and angles θ₄ = θ₅ = 94.7° (see Fig. 1), we obtain the dipole–dipole interaction energy V₆ = ±0.485 cm⁻¹, corresponding to an exciton splitting energy of ΔE = 817.0 cm⁻¹. Analogous CIS calculations with the 2PY monomer fixed in the planar ground-state SCF/6-31G(d,p) geometry as calculated for the (2PY)₂ dimer yielded a very similar transition dipole moment |µ| = 1.11×10⁻²⁹ Cm, and angles θ₄ = θ₅ = 86.9°, giving an interaction energy of V₆ = ±363.2 cm⁻¹ or ΔE = 726.3 cm⁻¹. The calculated angle between the a principal axis and the calculated transition dipole is also 56°. This means that a moderate degree of nonplanarity has only a relatively minor effect on the size and direction of the S₁ ← S₀ transition dipole moment.

III. EXPERIMENTAL RESULTS

A. Experiment

(2PY)₂ dimers were synthesized and cooled in a 20 Hz pulsed supersonic expansion, using Ne carrier gas at 1.4 bar backing pressure. 2-Hydroxypyridine Aldrich, 97% purity) was placed in a home made pulsed nozzle with a thin-walled 0.4 mm diameter orifice at a temperature of 67°C. For deuteration experiments, the carrier gas was flowed through a reservoir containing D₂O at room temperature for a few hours giving ~50% degree of deuteration. During the measurements, the D₂O reservoir was removed and the carrier gas was led directly into the nozzle, to minimize the formation of 2PY- (D₂O)ₙ clusters.

Two-color resonant two-photon ionization (2C–R2PI) spectra were measured by crossing the skinned beam with overlapping excitation and ionization laser beams inside the source of a linear time-of-flight mass spectrometer. Excitation was performed with the frequency-doubled UV output of a pulsed DCM dye laser with ~0.5 cm⁻¹ resolution, pumped by the 532 nm output of a Nd:YAG laser. The excitation intensity was kept very low, <10 kW/cm² (<50 µJ/pulse), to avoid optical saturation effects. For the ionization step, the 10 times more intense (500 µJ/pulse) 266 nm output of the same Nd:YAG laser was employed, which was spatially and temporally fully overlapped with the excitation pulse.

Dispersed fluorescence spectra were recorded at an excitation energy of 200 µJ/pulse. The UV laser beam crossed the jet 20 mm downstream from the nozzle. The emitted fluorescence was dispersed with a SOPRA F1500 UHRS 1.5 m monochromator used with a 2160 groove/mm grating in first order at a spectral bandpass of 5 cm⁻¹. The dispersed fluorescence was detected by a LN2 cooled UV-enhanced CCD array with 15×15 µm pixels (Princeton Instruments).

FIG. 3. 2C–R2PI spectra of four (2PY)₂ isotopomers: (a) (2PY)₂–h₂, (b) (2PY)₂–H⁺, (c) (2PY)₂–d₁, (d) (2PY)₂–d₂. Band wave numbers are relative to the S₁ origin, except for band wave numbers followed by (Sₙ), which are relative to the S₁ origin. For (2PY)₂–h₂ and (2PY)₂–d₂ the origins are not observed, but are inferred from the modeling, see text. Bands marked with × are due to the dissociation of the corresponding Ne complex upon ionization, those marked with ○ are due to the 2PY–2–HP isomer and its isotopomers (Ref. 26).
Spectra were accumulated for 20 minutes to 1 hour. Other experimental details were given previously.

### B. Resonant two-photon ionization spectra, exciton splitting

2C–R2PI spectra of (2PY)$_2$, (2PY)$_2$–$^{13}$C, (2PY)$_2$–$d_1$, and (2PY)$_2$–$d_2$ were measured over the 30 000–31 600 cm$^{-1}$ range. The low wave number part of the $S_1\leftarrow S_0$ and $S_2\leftarrow S_0$ transitions of the four isotopomers is shown in Fig. 3. The band maxima of the $S_2\leftarrow S_0$ electronic origins lie at 30 776.3 cm$^{-1}$ for (2PY)$_2$–$h_2$, at 30 778.2 cm$^{-1}$ for the arbitrarily substituted $^{13}$C isotopomer, at 30 785.8 cm$^{-1}$ for the singly deuterated (2PY)$_2$–$d_1$ and at 30 781.1 cm$^{-1}$ for the doubly deuterated (2PY)$_2$–$d_2$. The single asymmetric substitution of the hydrogen bonded H by D causes a spectral shift of +9.5 cm$^{-1}$ to higher wave number, while the symmetry-conserving substitution of both H bonded hydrogens leads to a slightly smaller blueshift of +8.8 cm$^{-1}$. In fluorescence excitation, this leads to the overlapping of the electronic origins of (2PY)$_2$–$d_1$ and (2PY)$_2$–$d_2$.

The blue shift induced by a single $^{13}$C substitution is +1.9 cm$^{-1}$, smaller than both the deuteration shifts but clearly resolvable from the (2PY)$_2$–$h_2$ origin. However, the spectra of the asymmetrically $^{13}$C and D isotope-substituted dimers shown in Figs. 3(b) and 3(c) both reveal a second, weaker origin to lower wave number. These appear due to the lowering of the nuclear framework symmetry from $C_{2h}$ to $C_s$, which removes the $g\leftrightarrow u$ restriction from the optical selection rules; now the $S_1\leftarrow S_0$ transitions, which are $A'\leftrightarrow A'$ in $C_s$, can also be observed. The origins are at 30 734.6 cm$^{-1}$ for (2PY)$_2$–$^{13}$C and at 30 733.4 cm$^{-1}$ for (2PY)$_2$–$d_1$, with intensities of 10% and 22% relative to the corresponding $S_2\leftarrow S_0$ origins, respectively. From the wave number difference of the corresponding electronic origins, the $S_1/S_2$ state exciton splitting energies are obtained as 43.6 cm$^{-1}$ for the $^{13}$C-substituted (2PY)$_2$ and as 52.4 cm$^{-1}$ for (2PY)$_2$–$d_1$.

### C. $S_2$ and $S_1$ excited state vibrations

The intermolecular vibrational structure of the $S_2\leftarrow S_0$ transition of (2PY)$_2$–$h_2$ was measured and first analyzed in Ref. 3. There, the in-plane intermolecular $v_4'$ shear and $v_0'$ stretching mode excitations were identified at 91.5 and 153.1 cm$^{-1}$, respectively. The 2C–R2PI spectra of the other three isotopomers shown in Figs. 3(b)–3(d) exhibit analogous $A_0'$ and $A_1'$ bands at about 91 and 151 cm$^{-1}$. The vibrational wave numbers of the (2PY)$_2$–$^{13}$C isotopomer agree with those of (2PY)$_2$–$h_2$ to within $\pm 0.5$ cm$^{-1}$, whereas mono- and di-deuteration shift the $v_4$ and $v_6$ fundamentals slightly to lower wave numbers. Generally, the shifts increase in the order $^{13}$C<$d_2$<$d_1$. Table III lists these excitation frequencies together with their respective combination and overtone bands.

The (2PY)$_2$–$h_2$ band at 190.2 cm$^{-1}$ exhibits relatively large deuteration shifts, increasing by 1.4 cm$^{-1}$ to 191.6 cm$^{-1}$ for (2PY)$_2$–$d_1$ and decreasing by 5.9 cm$^{-1}$ to 184.3 cm$^{-1}$ for (2PY)$_2$–$d_2$ (see Table III). For (2PY)$_2$–$h_2$, the band at 190.2 cm$^{-1}$ was tentatively assigned as the 2$v_6'$ overtone. This must now clearly be revised, since for both (2PY)$_2$–$d_1$ and (2PY)$_2$–$^{13}$C the $S_1$ state $v_5'$ wave number of 107 and 110 cm$^{-1}$ would lead us to expect an overtone at $\approx 215$–220 cm$^{-1}$. A possible assignment would be as the 2$v_4'$ overtone of the “slanting” mode, which is at 90.5 cm$^{-1}$ in the ground state.

In Ref. 3 we proposed that the excitations of (2PY)$_2$–$h_2$ at 62 and 68 cm$^{-1}$, denoted X and Y, are $b_u$ intermolecular vibrations of the $S_1(A_g)$ electronic state which appear through vibronic coupling to the close lying $S_2(B_u)$ electronic state. For (2PY)$_2$–$^{13}$C and (2PY)$_2$–$d_2$, the X and Y excitations show very small isotopic shifts. However, as seen in Fig. 3(c), the corresponding X and Y bands of (2PY)$_2$–$d_1$ are about 12 cm$^{-1}$ lower than for the other three isotopomers. Comparing the R2PI spectra of the (2PY)$_2$–$^{13}$C and (2PY)$_2$–$d_1$ isotopomers, one notices that the spacing between the $S_1$ origins and the X and Y bands remains approximately constant, being 105 and 110 cm$^{-1}$ for (2PY)$_2$–$^{13}$C.
and 103 and 107 cm\(^{-1}\) for \((2PY)_2-d_1\). This near constancy with respect to the \(S_1\) origins supports the previous proposal as \(b_u\) intermolecular levels of the \(S_1\) state. The more intense \(Y\) bands at 110 cm\(^{-1}\) \([(2PY)_2-^{13}C]\) and 107 cm\(^{-1}\) \([(2PY)_2-d_1]\) are assigned as the \(v_4\) “opening” or “cog-wheel” fundamental, based on the B3LYP calculated \(v_5^\#\) wave number of 107.7 cm\(^{-1}\). The less intense \(X\) excitations at 105 and 103 cm\(^{-1}\) are tentatively assigned to the \(v_1^0 + v_2^0, v_6^\#\) combination. A third intermolecular vibrational \(b_u\) state, \(v_2^0 + v_3^0 + v_6^\#\), is tentatively assigned to a band 170 cm\(^{-1}\) above the \(S_1\) origin. These three excitations are the only low-lying \(b_u\) states.

In the \(S_1\) state of \((2PY)_2-d_1\), the two other \(a^g\) intermolecular vibrational fundamentals \(v_4^0\) and \(v_6^\#\) are observed at 90.8 cm\(^{-1}\) and 155.9 cm\(^{-1}\), as well as the 2\(v_3^0\) overtone at 189.3 cm\(^{-1}\), see Table IV. In the spectrum of \((2PY)_2-^{13}C\), these fundamentals are too weak to be identified.

### D. Dispersed fluorescence

Figure 4 compares the \(S_2\) fluorescence spectra of the \((2PY)_2-d_2\) and \((2PY)_2-h_2\) isotopomers when exciting at their electronic origins. We note that the 0\(_0\) band maxima of \((2PY)_2-d_1\) and \((2PY)_2-d_2\) are separated by only 0.7 cm\(^{-1}\), less than the 1.5 cm\(^{-1}\) half-width of the rotational band contours.\(^2\) We carefully optimized the excitation wavelength to the red side of the \(S_2\) band maxima, and analysis of the fluorescence bands did not reveal any significant signals due to \((2PY)_2-d_1\). The fluorescence bands of \((2PY)_2-d_2\) at 97.6 cm\(^{-1}\) and at 162.4 cm\(^{-1}\) are assigned to the \(a_g\) in-plane \(v_4^\#\) shearing and \(v_6^\#\) stretching fundamentals. The \(v_4^0 + v_6^\#\) combination is observed at 258.3 cm\(^{-1}\) and the 2\(v_3^0\) overtone at 321.4 cm\(^{-1}\). The main intramolecular vibrational fundamentals observed are \(v_1, v_5^0\) and \(v_8^\#\) at 545.7 cm\(^{-1}\) and 611.5 cm\(^{-1}\). Between 600 and 900 cm\(^{-1}\) a number of combination bands of \(v_5^\#\) with the intermolecular fundamentals, overtones and combinations are observed. The band assignments agree very well with those of \((2PY)_2-h_2\), see also Table V, and the overall appearance of the two spectra is similar. Some weak features in the emission spectrum, e.g., at 296.7, 400.1, 419.2, and 503.9 cm\(^{-1}\) are narrower than the 5 cm\(^{-1}\) bandpass of the monochromator, and are due to cosmic ray background on the CCD.

Excitation of the \((2PY)_2-d_2\) band at 91.0 cm\(^{-1}\), which was assigned above as the \(S_2\) state \(v_4^0\) level, yields the fluorescence spectrum shown in Fig. 5(a). The strongest band at 97.5 cm\(^{-1}\) is assigned as the \(v_4^\#\) shearing fundamental, with 3\(v_3^0\) and 3\(v_4^\#\) overtones at 193.9 cm\(^{-1}\) and 289.6 cm\(^{-1}\), respectively. The \(v_6^\#\) \(H\) bond stretching fundamental is ob-

![FIG. 4.](image)

**FIG. 4.** (a) Dispersed fluorescence spectra of \((2PY)_2-d_2\) and (b) \((2PY)_2-h_2\), excited at the \(S_2\) electronic origins at 30 785.8 cm\(^{-1}\) and 30 776.3 cm\(^{-1}\). The wave number scale is relative to the excitation. For band assignments, see Table V.

### Table IV. Experimental intermolecular \(S_1\) state vibrational wave numbers of \((2-pyridone)_2-h_2, -^{13}C, -d_1,\)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>((2PY)_2-h_2)</th>
<th>((2PY)_2-^{13}C)</th>
<th>((2PY)_2-d_1)</th>
<th>((2PY)_2-d_2)</th>
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<tr>
<td>(v_4^0)</td>
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<td>90.8</td>
<td>106</td>
<td>260</td>
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<tr>
<td>(v_4^0 + v_3^0)</td>
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<td>103.2</td>
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<td>106</td>
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<tr>
<td>(v_5^#)</td>
<td>109.9</td>
<td>107.4</td>
<td>111</td>
<td>260</td>
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<tr>
<td>(v_4^0 + v_4^#)</td>
<td>155.5</td>
<td>151.3</td>
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<td>107</td>
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<tr>
<td>(v_4^0 + v_3^0 + v_4^#)</td>
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<td>163.6</td>
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<td>219</td>
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<td>(v_4^0 + v_3^0 + v_4^#)</td>
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<td>128</td>
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<td>(2v_4^0)</td>
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<td>215.2</td>
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<td>219</td>
</tr>
<tr>
<td>(v_4^0 + v_3^0 + v_4^#)</td>
<td>239</td>
<td>260</td>
<td>260</td>
<td>1.4</td>
</tr>
<tr>
<td>(v_4^0 + v_3^0 + v_4^#)</td>
<td>262</td>
<td>264</td>
<td>264</td>
<td>2.6</td>
</tr>
</tbody>
</table>

\(^{a}\)Intensity of respective \(S_2\) origin band = 100.
TABLE V. Experimental $S_0$ state vibrational wave numbers of (2-pyridone)$_2$--$h_2$, --$d_1$, and --$d_2$ (in cm$^{-1}$) from dispersed fluorescence spectra. Accuracy ± 1 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Excitation at assignment</th>
<th>(2PY)$_2$--$h_2$</th>
<th>(2PY)$_2$--$d_1$</th>
<th>(2PY)$_2$--$d_2$,--$d_1$</th>
<th>(2PY)$_2$--$d_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freq.$^b$</td>
<td>Int.$^c$</td>
<td>Freq.$^b$</td>
<td>Int.$^c$</td>
</tr>
<tr>
<td>$\nu_4^d + \nu_4^d$</td>
<td>98.0</td>
<td>22.4</td>
<td>98.2</td>
<td>16.0</td>
</tr>
<tr>
<td>$\nu_4^d$</td>
<td>107.9</td>
<td>26.1</td>
<td>115.0</td>
<td>7.1</td>
</tr>
<tr>
<td>$\nu_5^d$</td>
<td>162.6</td>
<td>42.6</td>
<td>162.7</td>
<td>24.5</td>
</tr>
<tr>
<td>$\nu_6^d$</td>
<td>179.6</td>
<td>2.0</td>
<td>193.9</td>
<td>216.5</td>
</tr>
<tr>
<td>$\nu_7^d + \nu_7^d$</td>
<td>259.2</td>
<td>7.8</td>
<td>257.6</td>
<td>8.5</td>
</tr>
<tr>
<td>$\nu_8^d + \nu_8^d$</td>
<td>266.6</td>
<td>7.1</td>
<td>266.3</td>
<td>4.4</td>
</tr>
<tr>
<td>$\nu_9^d + \nu_9^d$</td>
<td>322.0</td>
<td>7.0</td>
<td>322.0</td>
<td>7.0</td>
</tr>
<tr>
<td>$\nu_{10}^d + \nu_{10}^d$</td>
<td>350.7</td>
<td>3.2</td>
<td>351.4</td>
<td>6.6</td>
</tr>
<tr>
<td>$\nu_{11}^d + \nu_{11}^d + \nu_4^d$</td>
<td>416.2</td>
<td>22.0</td>
<td>423.3</td>
<td>14.5</td>
</tr>
<tr>
<td>$\nu_{12}^d + \nu_{12}^d + \nu_{13}^d + \nu_4^d$</td>
<td>541.5</td>
<td>57.7</td>
<td>607.2</td>
<td>5.7</td>
</tr>
<tr>
<td>$\nu_{13}^d + \nu_{13}^d + \nu_4^d + 2 \nu_4^d$</td>
<td>613.8</td>
<td>5.2</td>
<td>611.5</td>
<td>6.4</td>
</tr>
<tr>
<td>$\nu_{14}^d + \nu_{14}^d + \nu_4^d + \nu_4^d$</td>
<td>647.5</td>
<td>5.8</td>
<td>642.3</td>
<td>6.6</td>
</tr>
<tr>
<td>$\nu_{15}^d + \nu_{15}^d + \nu_2^d$</td>
<td>669.3</td>
<td>5.3</td>
<td>663.3</td>
<td>6.1</td>
</tr>
<tr>
<td>$\nu_{16}^d + \nu_4^d$</td>
<td>712</td>
<td>11.3</td>
<td>706.4</td>
<td>11.3</td>
</tr>
<tr>
<td>$\nu_{17}^d + \nu_4^d$</td>
<td>712</td>
<td>11.3</td>
<td>706.4</td>
<td>11.3</td>
</tr>
<tr>
<td>$\nu_{18}^d + \nu_4^d$</td>
<td>712</td>
<td>11.3</td>
<td>706.4</td>
<td>11.3</td>
</tr>
<tr>
<td>$\nu_{19}^d + \nu_4^d$</td>
<td>775</td>
<td>6.9</td>
<td>765.4</td>
<td>47.5</td>
</tr>
<tr>
<td>$\nu_{20}^d + \nu_4^d$</td>
<td>844</td>
<td>14.0</td>
<td>868.6</td>
<td>862.5</td>
</tr>
</tbody>
</table>

$^a$Excitation mainly at (2PY)$_2$--$d_2$ origin, see text.

$^b$Relative to the wave number of the excitation band.

$^c$Intensity of origin = 100.

served at 162.5 cm$^{-1}$. A $\nu_4^d$ progression appears in combination with $\nu_6^d$, i.e., $\nu_4^d + \nu_6^d$ at 257.8 cm$^{-1}$ and $2 \nu_4^d + \nu_6^d$ at 353.6 cm$^{-1}$. The strong enhancement of $\nu_4^d$ and its overtone and combination bands in this emission spectrum as compared to the spectrum shown in Fig. 4(a) confirm the assignment of the 91.0 cm$^{-1}$ excitation as $\nu_4^d$. The band at 107.5 cm$^{-1}$ can only be assigned to the $\nu_5^d$ “opening” vibration of the asymmetric (2PY)$_2$--$d_1$, for which this in-plane vibration is totally symmetric ($a'$. Due to the near-perfect overlap of the 14$_0^0$ bands of (2PY)$_2$--$d_2$ and (2PY)$_2$--$d_1$, $\nu_5^d$ and the 2 $\nu_5^d$ overtone of the latter also appear in the fluorescence spectrum. The band at 118.4 cm$^{-1}$ is assigned to the overtone of the “propeller twist” vibration 2 $\nu_2^d$ of (2PY)$_2$--$d_2$. The analogous emission band was previously observed for (2PY)$_2$--$h_2$ at 119.7 cm$^{-1}$ when exciting the 14$_0^1$ transition.$^5$ At higher wave numbers, the intramolecular in-plane ring deformation $\nu_{15}^d$ at 546.7 cm$^{-1}$ is comparatively weak.

A very interesting fluorescence spectrum is observed following excitation of the (2PY)$_2$--$d_2$ band at 111 cm$^{-1}$, which we assigned above as 5$_1^1$. We recall that the $\nu_4^d$ excited state is vibrationally $b_u$ and vibrationally $B_u$, gaining intensity through vibronic interaction with the $S_2(B_u)$ electronic state. The fluorescence spectrum shown in Fig. 5(b) exhibits an intense progression with a spacing of $\approx 82$ cm$^{-1}$. The first member of this progression cannot be assigned to any of
the $a_g$ fundamentals; the only vibrational state with the required $a_g$ vibrational symmetry in this region is $\nu_1^0 + \nu_5^0$. The formation of a progression by such a combination level is quite unusual. It may be enhanced by the excited state Fermi resonance of $\nu_5'$ with the close-lying $\nu_1' + \nu_5'$ state. As would be expected, the allowed $2\nu_5^{\text{ov}}$ overtone, observed at 212 cm$^{-1}$, is rather intense in this emission spectrum.

The $S_1\rightarrow S_0$ fluorescence spectrum of (2PY)$_2$–$d_1$ excited at the electronic origin is shown in Fig. 6. Similar to the $S_1\rightarrow S_0$ 2C–R2PI spectrum, the fluorescence spectrum exhibits all three totally symmetric ($a'$) intermolecular vibrational fundamentals $\nu_4''$, $\nu_5''$ and $\nu_6''$ at 98.2 cm$^{-1}$, 107.9 cm$^{-1}$, and 162.7 cm$^{-1}$, see Table V. The intramolecular vibrational fundamentals $\nu_{15}'$, $\nu_{16}'$, and $\nu_{17}'$ are observed at 546.6 cm$^{-1}$, 559.6 cm$^{-1}$, and 611.1 cm$^{-1}$.

It is important to note that the vibronic transitions to the intermolecular $\nu_4''$ and the intramolecular $\nu_{16}'$ and $\nu_{17}'$ states are not observed in any of the emission spectra of (2PY)$_2$–$h_2$ and (2PY)$_2$–$d_2$, because these states are $b_g$ in the centrosymmetric dimers. However, in the noncentrosymmetric (2PY)$_2$–$d_1$ they become totally symmetric ($a'$), the transitions are then vibrationally allowed and appear as strong bands in the fluorescence spectrum. One can see that the $S_1\rightarrow S_0$ electronic transition of (2PY)$_2$–$d_1$ retains some of its “forbidden” $A_g\rightarrow A_g$ character, because vibronic transitions which would be $A_g\rightarrow B_g$ in $C_{2h}$ are more intense than those that would be $A_g\rightarrow A_g$ transitions in $C_{2h}$. Hence, the transitions to $\nu_5''$, $\nu_{16}'$ and $\nu_{17}'$ which in the centrosymmetric dimers would be vibronically $B_g$ exhibit an enhanced overall transition moment, relative to the vibrations that would be $A_g$.

The ground state wave numbers of the three (2PY)$_2$ isotopomers are compiled and compared in Table V. For (2PY)$_2$–$^{13}$C no fluorescence spectra were recorded due to the relatively small signal contribution and the strong spectral overlap with the intense (2PY)$_2$–$h_2$ absorption bands.

**IV. DISCUSSION**

**A. Exciton splittings**

Introduction of a single H/D or $^{13}$C/$^{12}$C isotopic substitution changes the symmetry of the nuclear framework from $C_{2h}$ to $C_s$, thereby modifying the vibrational wave functions, frequencies and zero-point energy. Since the dimer structure changes only very slightly upon mono- and di-deuteration, the electronic wave functions remain very similar, but the $g\leftrightarrow u$ symmetry selection rule is removed by the symmetry lowering. Thus, the 2C–R2PI spectra of the asymmetrically isotope-substituted (2PY)$_2$–$^{13}$C and (2PY)$_2$–$d_1$ dimers both exhibit a weak $S_1\rightarrow S_0$ origin. The exciton splittings between these and the strong $S_2\rightarrow S_0$ origins can be directly measured and are 43.6 cm$^{-1}$ for (2PY)$_2$–$^{13}$C and 52.4 cm$^{-1}$ for (2PY)$_2$–$d_1$. The effect of the $^{13}$C isotope substitution on the dimer structure and vibrational wave numbers is very small; hence, we estimate the exciton splitting of the (2PY)$_2$–$h_2$ species to be also $\approx 43$ cm$^{-1}$, more than twice the 20 cm$^{-1}$ value estimated by Held and Pratt.

In Sec. II C the exciton splittings were estimated from the dipole–dipole interaction energy, $\Delta E = 2V_{AB} = 2V_{dd}$, using the calculated 2PY transition dipoles $|\mu|$ from the ab initio CIS/6-31G(d,p) calculations. Depending on the 2PY geometry chosen, $|\mu| = 1.17 \times 10^{-29}$ cm or 1.11...
\[ \times 10^{-29} \text{Cm}, \text{leading to exciton splittings of } \Delta E = 817 \text{ or } 726 \text{ cm}^{-1}, \text{see Sec. II.C.} \]

Conversely, experimental values for monomer-centered transition dipoles can be derived from the measured exciton splittings \( \Delta E = 52.4 \text{ cm}^{-1} \) and 43.6 cm\(^{-1} \). Assuming that \( \theta_A = \theta_B = 90^\circ \), \( \phi = 0^\circ \) and taking the \textit{ab initio} calculated center-of-mass separation, \( R_{AB} = 5.36 \text{ Å} \), one obtains \( |\mu| = \sqrt{2} \pi \varepsilon_0 \cdot \Delta E \cdot R_{AB} = 3.0 \times 10^{-30} \text{ Cm} \) for \((2PY)_2-d_1 \) and \( 2.7 \times 10^{-30} \text{ Cm} \) for \((2PY)_2-^{13}\text{C} \), being 23 and 26% of the CIS values, respectively. However, this procedure assumes the entire electronic oscillator strength to be concentrated into atomic linelike transitions and neglects its redistribution over many vibrational transitions. As a result, the purely electronic estimate of the exciton splitting is too high. In the weak-coupling dimer model treatment,\(^7\) each vibronic state \( v \) of the dimer is split by a reduced amount \( V_{AB} F_v \) into a pair of \([+\]+\) and \([-\]-\) excitonic states, where \( F_v \leq 1 \) is the Franck–Condon factor (FCF) of the \( 0^0 \) transition, and the total \( V_{AB} \) interaction is obtained by summing the \( V_{AB} F_v \) over all \( v \)'s in the excited state. If the FCF \( |\mu| \) values were correct, the observed \( \Delta E \) would imply a Franck–Condon factor for the electronic origin of \( F_v(0^0) = 5–7\% \). This is in qualitative agreement with the observed FCF of the \( 0^0 \) transition in the fluorescence spectrum.

**The coupling matrix element \( V_{AB} \):** As discussed in the Introduction, the exciton splitting \( \Delta E \) depends on the difference of the monomer exciton energies, \( V_{AA} - V_{BB} = \delta \) and the electronic coupling matrix element \( V_{AB} \), i.e., \( V_{AB} = \sqrt{\Delta E^2 - \delta^2}/2 \). The small isotopic shift for the \( ^{13}\text{C} \) isotopomer has a negligible influence on \( \Delta E \), so that the value measured for \((2PY)_2-^{13}\text{C} \) can be taken as the \( \Delta E \) for both \((2PY)_2-h_2 \) and \((2PY)_2-d_{2} \), for which \( \delta = 0 \text{ cm}^{-1} \). \( V_{AB} \) is then \( \Delta E/2 \), giving \( V_{AB} = 21.8 \text{ cm}^{-1} \).

Assuming that \( V_{AB} \) remains the same for the \((2PY)_2-d_1 \) heterodimer, one obtains \( \delta = 29.1 \text{ cm}^{-1} \), which should be equal to the measured H/D deuteration spectral shift of the \( S_1 \rightarrow S_0 \) electronic transition of free \( 2PY \).\(^4\)\(^2\)\(^5\) The resulting exciton splitting pattern is shown in Fig. 7(a), together with the splitting for \((2PY)_2-h_2 \) in Fig. 7(b). The comparison to experiment is not without problems.

1. The first electronic excitation of \( 2\text{-pyridone} \) \((2PY-h) \) exhibits two electronic origins,\(^4\)\(^2\)\(^5\) denoted \( A \) and \( B \), which lie 99.1 cm\(^{-1} \) apart.\(^3\) For \( 2PY-d \), the deuteration spectral shifts are to the blue, but are different, being \( \delta(A') - A = + 43.0 \text{ cm}^{-1} \) and \( \delta(B' - B) = + 25.4 \text{ cm}^{-1} \). This shows that there are deuteration-dependent zero-point vibrational effects on the \( A \) and \( B \) origin frequencies in the monomer.

2. It is not clear whether the \( \delta(A' - A) \) and \( \delta(B' - B) \) values of \( 2PY \) can be applied to \((2PY)_2 \). In \( 2PY-h \) and \( 2PY-d \), the \( A, B \) and \( A', B' \) bands originate in the same \( S_0 \) ground state with planar geometry, but terminate in two different \( S_1 \)-state levels with different nonplanar geometries. \( A_\text{II} \) et al. postulated that the two excited states are the zero-point levels of different conformers, involving pyramidal displacements at the \( N \) atom giving pseudooxial and pseudoequatorial directions of the \( N-H \) bond.\(^4\) On the other hand, the \( S_2 \) excited state geometry of all three isotopomeric \((2PY)_2 \) dimers is known to be planar,\(^2\) and hence the \( \delta \) value employed in the model calculation should be that of a hypothetical planar \( 2PY \) and not the experimental value for nonplanar \( 2PY \).

3. Using the values \( V_{AB} = 21.8 \text{ cm}^{-1} \) and \( \delta = 29.1 \text{ cm}^{-1} \) for \((2PY)_2-d_1 \) shifts its \( S_2 \rightarrow S_0 \) origin 19.0 cm\(^{-1} \) above that of \((2PY)_2-h_2 \), as indicated in the diagram in Fig. 7(a). However, the \textit{observed} blueshift is only +9.5 cm\(^{-1} \). Use of the same parameters for the exciton splitting of \((2PY)_2-d_2 \) would imply that its \( S_2 \rightarrow S_0 \) origin would lie 29.1 cm\(^{-1} \) above that of \((2PY)_2-h_2 \), whereas the observed shift is only +8.8 cm\(^{-1} \).

Obviously, the \( S_2 \rightarrow S_0 \) spectral shifts of \((2PY)_2-d_1 \) and \((2PY)_2-d_2 \) calculated with the model are not in agreement with observations.

**Modification of the exciton coupling matrix element \( V_{AB} \):** As an alternative, we assume that the \( V_{AB} \) coupling is slightly modified by the single H/D exchange, changing \( V_{AB} \) to \( V_{AB} + \varepsilon \). In Fig. 8 we plot the locus of all pairs \( (\delta, \varepsilon) \) that are consistent with the observed \( \Delta E = 52.4 \text{ cm}^{-1} \) of \((2PY)_2-d_1 \). The point marked (1) corresponds to the case \( \delta = 29.1 \text{ cm}^{-1}, \varepsilon = 0 \text{ cm}^{-1} \) just discussed. The point marked (2) corresponds to \( \delta = 10.2 \text{ cm}^{-1}, \varepsilon = 3.9 \text{ cm}^{-1} \) which reproduces both the observed \( \Delta E = 52.4 \text{ cm}^{-1} \) and the correct location of the \( S_2 \rightarrow S_0 \) and \( S_1 \rightarrow S_0 \) origins. The corresponding splitting pattern is shown in Fig. 7(c).

Applying these parameters \( \delta = 10.2 \text{ cm}^{-1}, \varepsilon = 3.9 \text{ cm}^{-1} \) to the doubly deuterated \((2PY)_2-d_2 \) yields the splitting pattern shown in Fig. 7(d): The predicted splitting is 51.4 cm\(^{-1} \). The predicted \( S_2 \rightarrow S_0 \) blueshift is +14.1 cm\(^{-1} \), which is closer to the observed +8.8 cm\(^{-1} \) shift. Thus, the modified Frenkel exciton model improves the agreement with experiment, but still cannot reproduce all the observed data quantitatively.

Can the 20% difference of \( V_{AB} + \varepsilon = 25.7 \text{ cm}^{-1} \) for \((2PY)_2-d_1 \) and \( V_{AB} = 21.8 \text{ cm}^{-1} \) for \((2PY)_2-^{13}\text{C} \) be inter-

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**FIG. 7.** Schematic representation of the observed exciton splittings and the \( S_1 \rightarrow S_0 \) and \( S_2 \rightarrow S_0 \) transition energies of (b) \((2PY)_2-h_2 \), (c) \((2PY)_2-d_1 \), and (d) \((2PY)_2-d_2 \), represented by thick horizontal lines. UV transition wave numbers are marked on the left. The observed exciton splittings and \( S_2 \rightarrow S_0 \) deuterium shifts are labeled with boldface numbers. UV and visible shift wavelengths are marked on the right.
strand of a nucleic acid to the other across double hydrogen bonds. Interstrand transfer rates in DNA cannot be directly measured, since in nucleic acids there is also rapid excitation transfer along each strand. The latter rate depends on the identity of the neighboring bases and also on the interbase stacking distances, the roll and twist angles, and hence on the helix conformation.

B. Comparison to previous measurements

Held and Pratt showed that the $S_2\rightarrow S_0$ electronic excitation of (2PY)$_2$ is delocalized over the 2PY subunits by measuring the number and relative intensities of $S_2\rightarrow S_0$ electronic origins of the (2PY)$_2$–$h_2$–$d_1$, and $d_2$ isomers for various H:D isotopic ratios in the beam.\(^1\) The observation of a single $0_0^*$ transition for (2PY)$_2$–$d_1$ indicates delocalization, since in the case of very weak or no delocalization, two equally intense origins ($d_0^+-d_0^-$) and ($d_0^-+d_1^-$) would be observed. Above, we confirmed our observation of a single electronic $S_2\rightarrow S_0$ transition by isotopically resolved 2C–R2PI spectroscopy of (2PY)$_2$–$d_1$. The spectrum in Fig. 3(c) also exhibits a weak feature at 30 778, 2 cm$^{-1}$, below the main $0_0^*$ transition. As discussed above, this is the electronic origin of the (2PY)$_2$–$h_3$–$^{13}$C isopomer which appears in the same mass channel. Thus, the $d_1$ and $d_0$ monomer subunits cannot be separately excited in the asymmetrically deuterated (2PY)$_2$–$d_1$ dimer, confirming Held and Pratt’s observation.

The benzene dimer and trimer exhibit very small exciton splittings on the $S_1\rightarrow S_0$ origin band which are of the order of 1.4 to 2.0 cm$^{-1}$,\(^11\),\(^26\) about 40 times smaller than the splittings observed for the (2PY)$_2$ isomers. The benzene dimer exciton splittings are also much smaller than any of the intermolecular vibrational frequencies which couple to the $S_1\rightarrow S_0$ excitation, which places this system in the weak-coupling limit, $V_{AB}\ll \hbar \nu$.\(^7\),\(^8\)

In contrast, the exciton splittings observed for (2PY)$_2$ are of the order of the lowest intermolecular frequencies, $V_{AB}\approx \hbar \nu'$, but are smaller than the higher intermolecular frequencies $\nu'_1$ to $\nu'_6$. This places (2PY)$_2$ in the weak to intermediate coupling regime, depending on the intermolecular vibration. A realistic model of the vibronic coupling for (2PY)$_2$ would involve at least the three intermolecular modes $\nu'_1$, $\nu'_3$, and $\nu'_6$, for which the observed Huang–Rhys factors are of the order of $S=0.1$–0.4; see Tables III, IV, and V. However, since the intermolecular vibrational structure can be clearly analyzed and behaves nearly harmonically, the frequency shifts induced by the vibronic coupling,\(^7\),\(^8\),\(^13\) relative to the uncoupled vibrational level positions, cannot be larger than $\approx 5\%$.

C. Morse potential model of the intermolecular stretching coordinate

The observed $\nu''_6$, $2\nu''_6$, and $3\nu''_6$ frequencies can be used to determine a one-dimensional (1D) anharmonic potential energy function for the $\nu''_6$ intermolecular stretching vibration. The $\nu''_6$ coordinate was modeled as a 1D motion and the 2-pyridone–$h$ or 2-pyridone–$d$ moieties were treated as pseudoatoms of mass 95.1 or 96.1 amu. The resulting 1D
vibrational Schrödinger equation was solved numerically and the three experimental spacings were fitted to an $S_0$ state Morse stretching potential, with well depth $D_e = -11.7$ kcal/mol (4092.1 cm$^{-1}$) and curvature parameter $a = 2.20$ Å$^{-1}$. The analogous calculations for (2PY)$_2$–$d_1$ and (2PY)$_2$–$d_2$ yielded identical potential parameters to within the stated accuracy. The excited state dissociation energy $D_0(S_2)$ was derived from $D_0(S_0) = -4008.2$ cm$^{-1}$, calculated from the above parameters, and reduced by the spectral blueshift +900 cm$^{-1}$. This value is the average of the spectral blueshifts of the dimer origin relative to the $A$ and $B$ origins of the 2PY monomer. The resulting $S_2$ state Morse potential has a well depth $D_e = -9.11$ kcal/mol (3187.2 cm$^{-1}$) and curvature parameter $a = 2.30$ Å$^{-1}$.

From the ratio of Franck–Condon factors (FCFs) observed in Fig. 4, I($0^0_0$)/I($6^0_1$) = 100:43:7, the relative displacement of the $S_0$ and $S_2$ state Morse potentials along the $v_6$ coordinate was derived by calculating the FCFs from the 1D anharmonic stretching wave functions, which gives $\pm 0.057$ (±0.005) Å. Since the $S_2$–$S_0$ electronic excitation leads to a decrease of $D_0$ by 900 cm$^{-1}$, we interpret the displacement as an increase of the intermolecular center-of-mass distance. This displacement of $+0.057$ (±0.005) Å is smaller than the increase in N–O hydrogen bond distance of $+0.100$ (±0.005) Å derived by Held and Pratt. However, the in-plane $v_4$ shear vibration also couples quite strongly to the $S_2$–$S_0$ electronic transition, see Figs. 3–5, indicating a sizable displacement along the $v_4$ coordinate, which may also increase the N–O distance.

V. CONCLUSIONS

In (2-pyridone)$_2$–$h_2$, the 2PY monomers are symmetry-equivalent centers for electronic excitation, the $S_1$–$S_0$ ($A_g$–$A_g$) transition is strictly forbidden and only the $S_2$–$S_0$ vibronic spectrum is observed. Introduction of a single N–H/N–D or $^{13}$C/$^{12}$C isotopic substitution changes the symmetry of the nuclear framework from $C_s$ to $C_1$ and modifies the selection rules. The two-color R2PI spectra of the asymmetrically isotopically substituted (2PY)$_2$–$^{13}$C and (2PY)$_2$–$d_1$ were found to exhibit a weak $S_1$–$S_0$ and a strong $S_2$–$S_0$ transition, allowing the $S_1$/$S_2$ state exciton splittings of $\Delta E = 43.6$ cm$^{-1}$ and 52.4 cm$^{-1}$ to be directly observed. They provide a quantitative measure for the delocalization of the lowest $S_1$–$S_0$ and $S_2$–$S_0$ electronic excitations in a doubly N–H–O hydrogen-bonded dimer which shows the same H bonding pattern as uracil. Double deuteration at the N–H bond in the (2PY)$_2$–$d_2$ dimer restores perfect $C_{2h}$ symmetry and leads to disappearance of the $S_1$–$S_0$ transition. The exciton splittings of (2PY)$_2$–$h_2$ and (2PY)$_2$–$d_2$ are expected to be very similar to $\Delta E = 43.6$ cm$^{-1}$.

A single deuteration at N shifts the $S_2$–$S_0$ origin by $+9.5$ cm$^{-1}$ to the blue relative to (2PY)$_2$–$h_2$. Double deuteration shifts by $+8.8$ cm$^{-1}$, and replacement of a single $^{13}$C atom by $^{13}$C by $+1.9$ cm$^{-1}$. The combined band on spectral blueshifts and $S_1$/$S_2$ state exciton splittings observed for (2PY)$_2$–$^{13}$C and (2PY)$_2$–$d_1$ could not be explained with the basic Frenkel exciton model. A deuteration-dependent modification of the coupling matrix element from $V_{AB} = 21.3$ cm$^{-1}$ to $V_{AB} + e = 25.7$ cm$^{-1}$ improves the agreement with the combined data. A more detailed treatment should involve multimode vibronic coupling to the intermolecular vibrations.

The $S_2$–$S_0$ spectra of (2PY)$_2$–$h_2$, (2PY)$_2$–$^{13}$C, (2PY)$_2$–$d_1$, and (2PY)$_2$–$d_2$ exhibit bands that cannot be explained in terms of $a_g$ symmetric intermolecular vibronic fundamentals. The observation that these bands have a nearly constant spacing from the $S_1$–$S_0$ origin of (2PY)$_2$–$d_1$ supports the assignment of these bands to the $b_u$ symmetry $v_3$ and $v_4 + v_5$ levels, built on the $S_1$ origin and appearing through vibronic coupling with the $S_2(B_u)$ state. These excitations act as false origins, on which totally symmetric intermolecular vibrations of the $S_2$ state are then built.

The analysis of the fluorescence spectra of (2PY)$_2$–$h_2$, (2PY)$_2$–$d_1$, and (2PY)$_2$–$d_2$ yield a nearly complete set of intermolecular ground state frequencies, given in Table VI. Both the absolute values and the deuteration shifts are in good agreement with the B3LYP/6-311+ (G(2d,2p)) calculations, see Table I. A fit of the $v_6''$ intermolecular stretching progression in terms of Morse potentials for the $S_0$ and $S_2$ states give a displacement along this coordinate of $+0.057$ (±0.005) Å upon $S_2$–$S_0$ excitation.

**TABLE VI. Experimental $S_0$ state intermolecular vibrational wave numbers of (2-pyridone)$_2$–$h_2$, –$d_1$, and –$d_2$ (in cm$^{-1}$).**

<table>
<thead>
<tr>
<th>Species</th>
<th>(2PY)$_2$–$h_2$ Freq.</th>
<th>(2PY)$_2$–$d_1$ Freq.</th>
<th>(2PY)$_2$–$d_2$ Freq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1'$</td>
<td>22.3$^a$</td>
<td>22.5$^a$</td>
<td></td>
</tr>
<tr>
<td>$v_2'$</td>
<td>59.6$^a$</td>
<td>59.2$^a$</td>
<td></td>
</tr>
<tr>
<td>$v_3'$</td>
<td>89.8$^a$</td>
<td>89.2$^a$</td>
<td></td>
</tr>
<tr>
<td>$v_4'$</td>
<td>98.0</td>
<td>98.2</td>
<td></td>
</tr>
<tr>
<td>$v_5'$</td>
<td>107.9</td>
<td>105.9</td>
<td></td>
</tr>
<tr>
<td>$v_6'$</td>
<td>162.6</td>
<td>162.7</td>
<td>162.4</td>
</tr>
</tbody>
</table>

$^a$From overtones and combination bands.

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12. V. May and O. Köhn, *Charge and Energy Transfer Dynamics in Molecules*.

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