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# Analysis of the $S_2 \leftarrow S_0$ vibronic spectrum of the *ortho*-cyanophenol dimer using a multimode vibronic coupling approach

Sabine Kopec,<sup>1</sup> Philipp Ottiger,<sup>2</sup> Samuel Leutwyler,<sup>2</sup> and Horst Köppel<sup>1</sup>

<sup>1</sup>Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

<sup>2</sup>Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

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The  $S_2 \leftarrow S_0$  vibronic spectrum of the *ortho*-cyanophenol dimer (oCP)<sub>2</sub> is analyzed in a joint experimental and theoretical investigation. Vibronic excitation energies up to 750 cm<sup>-1</sup> are covered, which extends our previous analysis of the quenching of the excitonic splitting in this and related species [Kopec *et al.*, J. Chem. Phys. **137**, 184312 (2012)]. As we demonstrate, this necessitates an extension of the coupling model. Accordingly, we compute the potential energy surfaces of the *ortho*-cyanophenol dimer (oCP)<sub>2</sub> along all relevant normal modes using the approximate second-order coupled cluster method RI-CC2 and extract the corresponding coupling constants using the linear and quadratic vibronic coupling scheme. These serve as the basis to calculate the vibronic spectrum. The theoretical results are found to be in good agreement with the experimental highly resolved resonant two-photon ionization spectrum. This allows to interpret key features of the excitonic and vibronic interactions in terms of nodal patterns of the underlying vibronic wave functions. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4913363>]

## I. INTRODUCTION

Hydrogen-bonded molecular dimers represent a relevant class of excitonically coupled aggregates which are important constituents of very different systems such as conjugated polymers, molecular crystals, and photobiological complexes.<sup>1-5</sup> These dimers offer the advantage of being representative for larger systems but are still small enough to allow detailed experimental and theoretical investigations. These help to unravel the underlying microscopic mechanisms responsible for their properties of interest. In one of our groups, efforts have been undertaken for more than a decade to exploit this feature and study the excitonic energy splittings and vibrational excitations accompanying the  $S_2/S_1 \leftarrow S_0$  electronic transition in such systems using resonant-two photon-ionization (R2PI) spectra. The examples chosen were typically doubly H-bonded aromatic and heteroaromatic species, most notably the 2-aminopyridine (2AP)<sub>2</sub>, *ortho*-cyanophenol (oCP)<sub>2</sub>, 2-pyridone (2PY)<sub>2</sub>, and related molecular dimers.<sup>6-11</sup> The systems all show similar excitonic splitting schemes, with a (mostly) forbidden  $S_1 \leftarrow S_0$  transition, that becomes slightly allowed upon asymmetric isotopic substitution.

More recently, we have focussed on the interplay between excitonic and vibronic couplings and have shown this to have a drastic impact on the magnitude of the excitonic energy splittings, reducing them by a factor of 10-40 compared to the purely electronic (Davydov) splittings.<sup>7,12,13</sup> This “quenching of the excitonic splitting” has been obtained based on a combination of model Hamiltonians well-known in excitonic coupling theory<sup>14-16</sup> and modern *ab initio* calculations for all the relevant vibronic coupling constants entering the

description. Very satisfactory agreement with the observed  $S_1/S_2$  energy splittings could be obtained,<sup>6,7,12</sup> thus reconciling the large discrepancy between *ab initio* theory and experiment that existed before.<sup>8</sup> We have adopted and compared two different approaches using Förster perturbation theory and an effective mode *ansatz* that yielded a complementary description of the phenomenon.<sup>12,13</sup> We furthermore analysed the quenching in terms of a nonadiabatic tunneling splitting on the lower adiabatic potential energy surface (PES). This interpretation has been adopted by other groups.<sup>17,18</sup>

In the present work, we augment the range and scope of the analysis presented in Refs. 7 and 12. While earlier mostly the origins of the  $S_1 \leftarrow S_0$  and/or  $S_2 \leftarrow S_0$  electronic transition have been considered, we now address the spectral energy range up to typically 300-700 cm<sup>-1</sup> excitation energy and elucidate the importance of the vibronic couplings from a more general perspective. Not surprisingly, this more extended scope of investigation necessitates more advanced theoretical approaches. Whereas earlier the traditional Fulton-Gouterman (FG) Hamiltonian<sup>14,15</sup> and Förster perturbation theory<sup>16</sup> have been used and found appropriate, these turn out to be not sufficiently accurate for our present purposes, see below. Therefore, we rely instead on the more general so-called linear vibronic coupling (LVC) approach<sup>19</sup> which has proven successful in a wide range of applications that are not primarily related to excitonic coupling systems.<sup>20,21</sup> As prominent examples, we mention the successful analysis of complex spectral structures in the photoelectron and absorption spectra of systems ranging from triatomics such as NO<sub>2</sub> (Ref. 22) and SO<sub>2</sub> (Ref. 23) to the benzene cation and its fluoro derivatives.<sup>24,25</sup> From the systematic point of view, the phenomenon of vibronic intensity borrowing could be treated

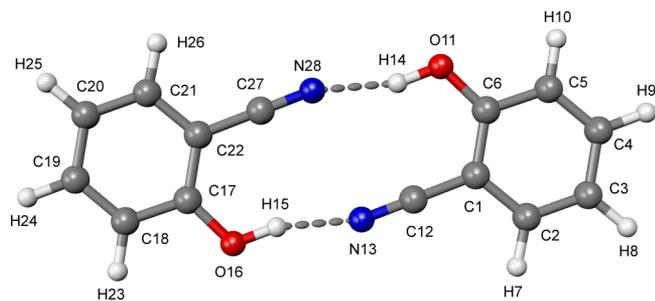


FIG. 1. Optimized ground state geometry of  $(\text{oCP})_2$  (RI-CC2/aug-cc-pVTZ) with atom labels.

on an equal footing with strong non-Born-Oppenheimer effects.<sup>19–21</sup> All these aspects will be seen to play a role also for the present investigation. Although the basic methodological ingredients like Taylor series expansion and diabatic electronic states are similar, in the FG approach and in the LVC approach, the latter naturally allows to relax certain constraints between coupling constants which exist within the FG formalism. Moreover, and more importantly, it offers a natural framework for including also the *intermonomer* vibrational modes in the description. These are often important and have already been introduced in a more *ad hoc*<sup>7</sup> or a specialized<sup>26,27</sup> manner. The LVC approach is used here for the dimer as a whole, and thus the intermonomer modes enter the description naturally.

As a representative example, we focus on the *ortho*-cyanophenol dimer  $(\text{oCP})_2$ , see Fig. 1. The monomers are bound by two antiparallel O–H···N hydrogen bonds to form a centrosymmetric ( $C_{2h}$ ) dimer. Since the oCP chromophore has a planar geometry in the ground and excited states of both the monomer and dimer, this simplifies the theoretical investigations of the vibronic spectrum. In the energy range from 32 850 to 33 600  $\text{cm}^{-1}$ , the spectrum is dominated by the presence of the  $S_1$  ( $A_g$ ) and  $S_2$  ( $B_u$ ) excited electronic states. Only the  $S_2 \leftarrow S_0$  transition is dipole-allowed while the  $S_1 \leftarrow S_0$  transition is forbidden by dipole selection rules in  $C_{2h}$ . We compare our theoretical results for this energy range to the experimental R2PI spectrum that has been measured in one of our groups. The  $(\text{oCP})_2$  system has been investigated previously by Zehnacker-Rentien *et al.*<sup>28</sup> They performed quantum chemical calculations at the density functional level with the B3LYP functional using the cc-pVTZ basis and discussed fluorescence excitation and dispersed fluorescence as well as ground state IR spectra. Our previous comparison of experimental and calculated, quenched excitonic splittings for  $(\text{oCP})_2$  showed a good agreement within  $\approx 20\%$ .<sup>12</sup>

This contribution is organized as follows: Sec. II starts with a short summary of the Fulton-Gouterman model, followed by an introduction to the general vibronic coupling treatment and an overview of the dynamical methods employed for this work. In Sec. III, we outline the computational details of the quantum chemical as well as dynamical calculations and describe the experimental techniques employed. Results for the optimized geometries, coupling constants, and spectra are presented in Sec. IV. The conclusions are given in Sec. V.

## II. THEORETICAL FRAMEWORK

### A. Fulton-Gouterman model

Vibronic coupling in molecular homodimers is often described by a model Hamiltonian originally introduced by Witkowski and Moffitt<sup>29</sup> and subsequently elaborated (and simplified) by Fulton and Gouterman.<sup>14,15</sup> Following frequent use in the literature, we refer to this Hamiltonian as FG model below. Here, the nuclear vibrational motion is given by identical harmonic oscillators in each monomer  $A, B$  with frequency  $\omega$ , normal mode coordinates  $Q_A$  and  $Q_B$ , and linear coupling  $l$  occurring upon electronic excitation. The coupling parameters for both monomers are equal, since the monomers are taken to be identical. The electronic excitonic coupling  $V_{AB}$  is assumed to be independent of the nuclear coordinate. The corresponding Hamiltonian for the simplified case of a single pair of modes is given by<sup>14,15,30</sup>

$$\mathcal{H}_{FG} = \left( E_{exc} + \frac{P_A^2}{2\mu} + \frac{\mu\omega^2}{2} Q_A^2 + \frac{P_B^2}{2\mu} + \frac{\mu\omega^2}{2} Q_B^2 \right) \mathbf{1} + \begin{pmatrix} lQ_A & V_{AB} \\ V_{AB} & lQ_B \end{pmatrix}, \quad (1)$$

where  $\mathbf{1}$  is the unit matrix and  $E_{exc}$  is the vertical excitation energy in the monomer.

Transformation to a delocalized electronic and vibrational basis, where the latter is denoted by  $Q_{\pm} = \sqrt{\mu\omega/2\hbar}(Q_A \pm Q_B)$ , and introducing the reduced linear coupling parameter  $b = l\sqrt{\hbar/2\mu\omega}$  yields

$$\mathcal{H}_{deloc} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \mathcal{H}_{FG} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \left( E_{exc} + \frac{\hbar\omega}{2} (P_+^2 + Q_+^2 + P_-^2 + Q_-^2) \right) \mathbf{1} + \begin{pmatrix} V_{AB} + bQ_+ & bQ_- \\ bQ_- & -V_{AB} + bQ_+ \end{pmatrix}. \quad (2)$$

Due to the simple approximations embodied in the FG model, the coupling constants for both  $Q_+$  and  $Q_-$  are identical. Furthermore, the FG model in its original sense only accounts for intramonomer modes. For a more detailed description, we refer to the original publications<sup>14,15</sup> or to our recent work.<sup>7,12,13</sup>

### B. General vibronic coupling model

#### 1. Hamiltonian

In the present work, we study the structure of the vibronic spectrum of  $(\text{oCP})_2$  in the framework of a multimode vibronic coupling model as described, for example, in Ref. 19. Like in Eqs. (1) and (3), the Hamiltonian relies on a diabatic electronic basis where the nuclear kinetic energy operator  $T_N$  is diagonal and the coupling matrix  $\mathbf{W}$  arises from the potential energy part

$$\mathcal{H} = T_N \mathbf{1} + \mathbf{W}(\mathbf{Q}). \quad (4)$$

The elements of  $\mathbf{W}$  in Eq. (4) are given in terms of dimensionless normal coordinates  $Q$  and are expanded in a

Taylor series around a chosen reference geometry  $Q_0 = 0$  which is taken as the ground state equilibrium geometry of the dimer. Truncation of the expansion after the first and second order terms leads to the linear and quadratic vibronic coupling models (LVC and QVC, respectively).<sup>19</sup>

The LVC Hamiltonian reads<sup>19</sup>

$$\mathbf{W}^{(1)}(Q_g, Q_u) = V_0(Q_g, Q_u)\mathbf{1} + \begin{pmatrix} E_1 + \sum_i k_i^{(1)} Q_{gi} & \sum_j \lambda_j Q_{uj} \\ \sum_j \lambda_j Q_{uj} & E_2 + \sum_i k_i^{(2)} Q_{gi} \end{pmatrix}, \quad (5)$$

with the ground state potentials  $V_0(Q_g, Q_u) = \sum_{i,j} \frac{\hbar\omega_{gi}}{2} Q_{gi}^2 + \frac{\hbar\omega_{uj}}{2} Q_{uj}^2$ .

Only symmetry selection rules are used to provide restrictions on the coupling constants and on the vibrational modes which are relevant to the diagonal and off-diagonal elements of the coupling matrix.<sup>19</sup> For  $\mathbf{W}^{(1)}$ , they read

$$\Gamma_1 \otimes \Gamma_Q \otimes \Gamma_2 \supset \Gamma_{A_g}. \quad (6)$$

Equation (6) states that a vibrational mode with symmetry  $\Gamma_Q$  can couple electronic states with symmetries  $\Gamma_1$  and  $\Gamma_2$  only if their direct product comprises the totally symmetric irreducible representation  $\Gamma_{A_g}$  of the point group of the molecule. Therefore, the totally symmetric modes  $g$  always lead to intrastate couplings with elements in the diagonal of the coupling matrix  $\mathbf{W}$  whereas the off-diagonal elements (index  $u$ , interstate couplings) depend on the symmetry of the system in question. The corresponding modes are referred to as coupling modes and are normally different (for  $\Gamma_1 \neq \Gamma_2$ ) from the totally symmetric modes appearing in the diagonal of  $\mathbf{W}$ . The coupling modes cause a repulsion of the PES, and for large interstate coupling constants this leads to a double-well shape of the lower electronic surface along the respective (non-totally symmetric) normal mode coordinate. The totally symmetric modes, called tuning modes, modulate the energy separation between the coupled electronic states.<sup>19</sup>

For brevity, the extension to quadratic coupling terms is only given for a single coupling mode  $Q_u$  and a single tuning mode  $Q_g$ ,

$$\mathbf{W}(Q_g, Q_u) = V_0(Q_g, Q_u)\mathbf{1} + \begin{pmatrix} E_1 + k^{(1)} Q_g + \frac{1}{2} \gamma_g^{(1)} Q_g^2 + \frac{1}{2} \gamma_u^{(1)} Q_u^2 & \lambda Q_u + \frac{1}{2} \mu_{gu} Q_g Q_u \\ \lambda Q_u + \frac{1}{2} \mu_{gu} Q_g Q_u & E_2 + k^{(2)} Q_g + \frac{1}{2} \gamma_g^{(2)} Q_g^2 + \frac{1}{2} \gamma_u^{(2)} Q_u^2 \end{pmatrix}, \quad (7)$$

with  $\gamma_g$  and  $\gamma_u$  as quadratic coupling constants and  $\mu_{gu}$  as the mixed quadratic coupling.

## 2. Vibronic eigenfunctions

Vibronic eigenfunctions for interacting PESs involve products of an electronic and a vibrational factor (it is only due to integration over the electronic coordinates that the Hamiltonian of Eq. (4) appears as a matrix in electronic function space and the eigenfunctions as vectors in the same space). Without that integration, the vibronic eigenfunctions for two coupled states generally appear as

$$\Psi(\mathbf{r}, \mathbf{Q}) = \phi_1(\mathbf{r})\chi_1(\mathbf{Q}) + \phi_2(\mathbf{r})\chi_2(\mathbf{Q}). \quad (8)$$

In the presence of a symmetry and for two vibrational modes as in Eq. (7), this expression reads more explicitly,

$$\Psi_{A_g}(\mathbf{r}, Q_g, Q_u) = \phi_{A_g}(\mathbf{r})\chi_g(Q_g, Q_u) + \phi_{B_u}(\mathbf{r})\chi_u(Q_g, Q_u), \quad (9)$$

$$\Psi_{B_u}(\mathbf{r}, Q_g, Q_u) = \phi_{A_g}(\mathbf{r})\chi_u(Q_g, Q_u) + \phi_{B_u}(\mathbf{r})\chi_g(Q_g, Q_u). \quad (10)$$

For later reference, we have already introduced the symmetry labels  $A_g$  and  $B_u$  appropriate to the point group  $C_{2h}$  of (oCP)<sub>2</sub>. The labels  $g$  and  $u$  (gerade and ungerade) denote the symmetry of the vibrational wave function (WF)  $\chi$  under the sign change operation of the non-totally symmetric coordinate  $Q_u$  only, see Eq. (7). In a power series expansion, this implies that the  $\chi_g(Q_g, Q_u)/\chi_u(Q_g, Q_u)$  contain only even/odd powers of the coupling mode coordinate  $Q_u$ .

## 3. Adiabatic potential energy surfaces

The adiabatic PESs are generally obtained by diagonalization of the diabatic coupling matrix  $\mathbf{W}(\mathbf{Q})$  of Eq. (4), i.e., taking the nuclear coordinates as parameters. For the specific case of Eq. (7), we get

$$V_{1,2}(Q_g) = \frac{\hbar\omega_g}{2} Q_g^2 + \frac{\gamma^{(1,2)}}{2} Q_g^2 + k^{(1,2)} Q_g + E_{1,2}, \quad (11)$$

$$V_{1,2}(Q_u) = \frac{\hbar\omega_u}{2} Q_u^2 + \frac{E_1 + E_2}{2} + \frac{\gamma_u^{(1)} + \gamma_u^{(2)}}{4} Q_u^2 \pm \sqrt{\left(\frac{E_2 - E_1}{2} + \frac{\gamma_u^{(2)} - \gamma_u^{(1)}}{4} Q_u^2\right)^2 + (\lambda Q_u)^2}, \quad (12)$$

where we have put the other coordinate ( $Q_u$  or  $Q_g$ ) to zero for simplicity. Equations (11) and (12) immediately show how the linear and quadratic coupling constants can be determined from the adiabatic PES. For the totally symmetric modes, the intrastate linear coupling constant for the state  $i$  is<sup>19</sup>

$$k_i = \left. \frac{\partial V_i(Q)}{\partial Q_g} \right|_{Q=0} \quad (i = 1, 2). \quad (13)$$

From the difference of the adiabatic PES, one obtains the interstate coupling constant

$$\lambda = \sqrt{\frac{1}{8} \left. \frac{\partial^2 (V_2 - V_1)^2}{\partial Q_u^2} \right|_{Q=0}}. \quad (14)$$

For sufficiently large coupling constants  $\lambda$ , the PESs along the coupling modes show the aforementioned double-minimum structure. This effect is intensified in the multi-mode case.<sup>19</sup> For  $\Delta < L$ , the corresponding stabilization energy upon symmetry lowering through the coupling modes is given by

$$E_{stab} = \frac{(\Delta - L)^2}{2L}, \quad \text{with } L = \sum_i \frac{\lambda_i^2}{\hbar\omega_i} \quad \text{and } \Delta = \frac{E_2 - E_1}{2}. \quad (15)$$

Note that, even in the linear coupling approximation ( $\gamma = \mu = 0$ ), the Hamiltonian of Eq. (7) generalizes the FG-Hamiltonian widely used in the literature to treat excitonically coupled systems.<sup>19,31–34</sup> This is easily seen from the delocalized FG Hamiltonian of Eq. (3). This transformed Hamiltonian shows the analogy between the FG and the general LVC model, where the relation between the coupling parameters is  $\lambda = k^{(1)} = k^{(2)} = b$ ,  $\omega_g = \omega_u$ .

### C. Dynamical calculations

In quantum dynamical calculations, vibronic spectra are often obtained via wave-packet propagation. The spectral intensity distribution  $P(E)$  is thereby calculated as the Fourier transform of the autocorrelation function  $C(t)$ ,

$$P(E) \propto \int e^{iEt} C(t) dt, \quad \text{with } C(t) = \langle \Psi(0) | \Psi(t) \rangle. \quad (16)$$

$C(t)$  is also known as the survival amplitude, that is, a measure for the probability that the wave function at time  $t$  is equal to the initial wave function  $\Psi(t=0)$ . The wave-packet propagation is done using the powerful multiconfigurational time-dependent Hartree (MCTDH) method developed in the Heidelberg group.<sup>35–37</sup> The basis of this method is the use of a multiconfigurational wave function that is a weighted sum over Hartree products of optimized time-dependent basis functions  $\varphi$  for each degree of freedom  $f$ ,

$$\Psi(Q_1, \dots, Q_f, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}(t) \varphi_{j_1}^{(1)}(Q_1, t) \cdots \varphi_{j_f}^{(f)}(Q_f, t). \quad (17)$$

The latter are expanded in a primitive basis set. To increase the computational efficiency, several degrees of freedom are combined (mode combination) and treated as a single particle, thus increasing to the so-called MCTDH contraction effect. Equations of motions for the expansion coefficients and single-particle functions are derived through the Dirac-Frenkel variational principle.<sup>35–37</sup>

## III. COMPUTATIONAL AND EXPERIMENTAL METHODS

### A. Computational details

In its electronic ground state, the oCP dimer has a planar equilibrium structure corresponding to the  $C_{2h}$  symmetry group (see also below). Its 78 vibrational degrees of freedom

TABLE I. Number of primitive basis functions (PBFs) as well as of time-dependent single-particle functions (SPF) used in the MCTDH calculation. The vibrational modes (degrees of freedom, DOF) combined to particles are given in the first column. The second column denotes the number of primitive harmonic oscillator functions for each DOF. The numbers of SPFs are listed in column three.

Modes	PBF basis	SPF basis
( $\nu_4, \nu_5$ )	20, 28	19
$\nu_7$	20	8
( $\nu_9, \nu_{10}$ )	18, 15	12
$\nu_{13}$	13	4
( $\nu_{17}, \nu_{18}$ )	20, 18	10
$\nu_{24}$	10	2

transform as follows:

$$\Gamma_Q = 27a_g \oplus 26b_u \oplus 13a_u \oplus 12b_g. \quad (18)$$

As a first step in the investigation, geometry optimizations for the ground and first two excited singlet states were carried out. This was followed by frequency calculations, where the harmonic frequencies were obtained numerically.

The adiabatic PESs for the  $S_0$ ,  $S_1$ , and  $S_2$  states were determined by single-point calculations at normal mode displacements  $Q_i = \pm 0.5, \pm 1.0, \pm 2.0$ , and  $\pm 3.0$  for a given mode. The linear and quadratic vibronic coupling constants were obtained by least squares fits to the electronic excitation energies (see below for more details). All electronic structure calculations of (oCP)<sub>2</sub> were performed at the RI-CC2/aug-cc-pVTZ level, of the oCP monomer at the RI-CC2/cc-pVTZ level, both employing the TURBOMOLE program package Version 6.0.<sup>38</sup>

The vibronic spectra were computed using the MCTDH program suite.<sup>39</sup> The propagation calculations were performed using a basis of single-particle-functions and a product of harmonic oscillator functions as initial wave function. The basis set details used in the subsequent calculation are given in Table I. The contraction effect caused by the shorter length of the single-particle vector compared to the number of primitive basis functions is  $\approx 10^6$ . The line spectra for the 2-mode cases reported in Sec. IV D were obtained using the Lanczos algorithm as implemented in the MCTDH package.<sup>39</sup> The corresponding vibronic eigenfunctions for the 2-mode case are accessible through relaxation calculations using so-called single-set block-improved relaxation.<sup>40</sup> The adiabatic spectra shown for comparison were generated with the aid of the POTFIT routine<sup>41,42</sup> available in the MCTDH package.

### B. Experimental techniques

The experimental setup has been discussed in detail previously.<sup>6,9</sup> The vibrationally cold oCP complexes were synthesized in a supersonic jet-expansion. The oCP sample (Aldrich, 99%) was placed in a home-built, magnetically actuated nozzle and heated to 80 °C. Neon was used as a carrier gas with a backing pressure of 1.2 bars. The skimmed molecular beam was overlapped spatially and temporally with an excitation and an ionization laser in the source of a 1 m time-of-flight mass spectrometer. Molecular ions were

produced according to the R2PI scheme where the complexes are excited from the vibrationally cold electronic ground state to the vibrational levels of an electronically excited state that is accessible by one-photon excitation and are subsequently ionized by a second laser pulse at 228 nm. The resulting, singly charged ions were detected using a microchannel plate detector (MCP).

The output of a Radiant-Dyes NarrowScan dye laser (Sulforhodamine B), pumped by the 532 nm output of a Nd:YAG laser was used for excitation ( $\sim 50 \mu\text{J}/\text{pulse}$ , UV-bandwidth  $\sim 0.09 \text{ cm}^{-1}$ ). The spectra were calibrated by measuring the fundamental frequency with a HighFinesse Angstrom WS6 high precision wavemeter. The 228 nm ionization laser pulses ( $200 \mu\text{J}$ ) were produced by sum-frequency mixing of the 640 nm output of a dye-laser (DCM), pumped by the 532 nm output of an Nd:YAG laser, with the 355 nm output of the same pump laser. Nozzle and lasers were operated at a repetition rate of 20 Hz.

## IV. RESULTS AND DISCUSSION

### A. Equilibrium geometries and vibrational analysis

The optimized ground state structure and the atom numbering scheme are shown in Fig. 1. The  $S_1$  and  $S_2$  excited electronic states transform as  $A_g$  and  $B_u$ , respectively, in the  $C_{2h}$  point group. With calculated vertical excitation energies of  $35\,693 \text{ cm}^{-1}$  and  $36\,001 \text{ cm}^{-1}$  (see Table II), they are separated by only  $308 \text{ cm}^{-1}$  and are therefore subject to vibronic coupling. This gives rise to the LVC scheme adopted in Eq. (5), the coupling and tuning modes being of  $b_u$  and  $a_g$  symmetry.

A list of bond lengths and angles of the  $S_0$  equilibrium structure, the  $S_1$  state structure both at the  $C_{2h}$  symmetry-restricted (first order) saddle point and at its  $C_s$  symmetric equilibrium geometry, and the  $S_2$  state at its  $C_{2h}$  symmetric structure is given in the supplementary material (Tables SI and SII).<sup>43</sup>

For comparison, the monomer structure parameters are included to the supplementary material as well (Table SIII).<sup>43</sup> It is seen there that upon dimerization, the intramonomeric hydrogen bond becomes wider, while the intermonomeric hydrogen bond is formed. The dimerization does not have an effect on the CH bond lengths, and only a very minor one on the aromatic CC bond lengths and the angles not located at the functional groups. Due to the dimeric hydrogen bonds, the angle at the hydroxy group  $\angle \text{H14-O11-C6}$  is widened from the typical  $109.2^\circ$  to  $114.9^\circ$ , while the cyano-angle  $\angle \text{C1-C12-N13}$  is widened by  $5.5^\circ$  to be almost linear in the dimer. Therefore, the intramonomeric hydrogen bond H14-N13 becomes  $0.35 \text{ \AA}$  longer, i.e., it virtually disappears

TABLE II. Vertical and adiabatic  $S_1$  and  $S_2$  excitation energies of (oCP)<sub>2</sub> at the RI-CC2/aug-cc-pVTZ level (in  $\text{cm}^{-1}$ ).

	$S_1 (C_s)$	$S_1 (C_{2h})$	$S_2 (C_{2h})$
vertical	-	35 693	36 001
adiabatic	33 846	34 575	35 003

in the dimer. These changes also have small effects on the neighboring bond lengths and angles.

Tables SI and SII<sup>43</sup> also give evidence of the geometrical changes occurring upon electronic excitation. Upon a  $C_{2h}$  restricted geometry optimization in the  $S_1$  state, the intermolecular hydrogen-bond is shortened by  $0.135 \text{ \AA}$ . The aromatic bond lengths are all slightly increased, while there is no effect on the corresponding angles. Only the lengths and angles at the two functional groups show deviations up to  $0.03 \text{ \AA}$  and  $2.2^\circ$ . The equilibrium structure of the second excited state is similar to this despite a somewhat shorter (by  $\approx 0.015 \text{ \AA}$ ) hydrogen bond. Full relaxation in the  $S_1$  state leads to the loss of the equivalence of the two monomers resulting in a  $C_s$  symmetric structure. Apart from minor deviations, the  $C_{2h}$  restricted  $S_1$  structure is the average of those of the left and right monomers in the dimeric  $C_s$  structure.

A complete list of all dimer normal modes is given in the supplementary material, Table SIV.<sup>43</sup> The numbering of the modes follows the ground state vibrational frequency in ascending order, irrespective of symmetries. The same holds for the monomer modes. For a complete list of  $a'$  monomer modes, see Ref. 13 (supplementary material).

We show the displacement vectors for a selected set of in-plane monomer and dimer modes in Figs. 2 and 3. The comparison of monomer modes (Fig. 2) with dimer modes (Fig. 3) shows similarities and differences in the relation between monomer and dimer vibrations. From model considerations, the dimer modes are expected to be positive and negative linear combinations of monomer modes, differing only by a few wavenumbers in energy. This is true, for example, for the in-plane dimer modes  $\nu_{17}$  and  $\nu_{18}$  that have their origin in  $\nu_7^{\text{mono}}$ . This mode-pair also occurs in the 2-aminopyridine dimer and has been previously discussed in detail.<sup>7</sup> Another pair of dimer modes is  $\nu_9$  and  $\nu_{10}$ . Here,  $\nu_9$  is a negative combination of  $\nu_1^{\text{mono}}$ , with an energy difference of  $41.1 \text{ cm}^{-1}$ . However,  $\nu_{10}$  clearly shows admixing of a rotational

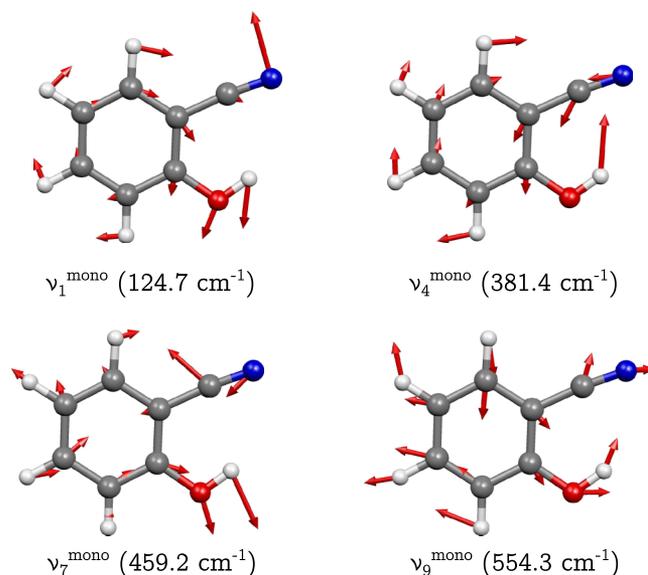


FIG. 2. Displacement vectors for the lowest-frequency totally symmetric ( $a'$ ) *o*-cyanophenol monomer modes.

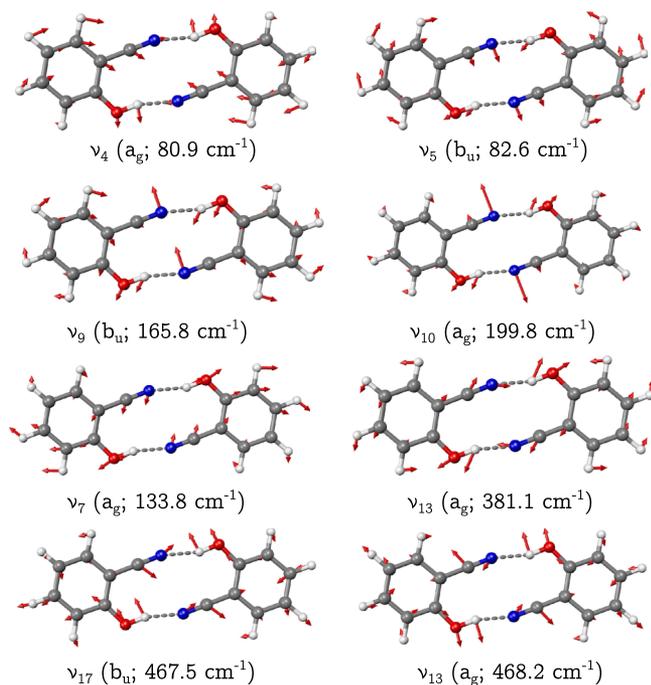


FIG. 3. Displacement vectors for some important low-frequency in-plane ( $a_g$ ,  $b_u$ ) (*o*-cyanophenol)<sub>2</sub> dimer modes.

motion, since the displacement vectors at the benzyl ring are significantly smaller than for  $\nu_1^{mono}$ . The frequency shift of  $74.8\text{ cm}^{-1}$  supports this observation. The deviation between monomer and dimer modes is most pronounced for modes that involve a stretching or bending of the hydrogen bond. A different example for the latter is the mode pair  $\nu_{31}$ ,  $\nu_{32}$  ( $b_g$ ,  $a_u$ ) that represents an out-of-plane CCOH torsional motion with a frequency of about  $740\text{ cm}^{-1}$ . The corresponding  $a''$  monomeric mode  $\nu_6^{mono}$  has a frequency of only  $447\text{ cm}^{-1}$ .

The intermonomeric modes ( $\nu_1 - \nu_5$  and  $\nu_7$ ) play a special role. They have very low frequencies, between 10 and  $150\text{ cm}^{-1}$ , and are composed of monomer translations and rotations. Of these, only the mode pair  $\nu_4$ ,  $\nu_5$  (H-bond shearing and cogwheel) with frequencies of  $80.9$  and  $82.5\text{ cm}^{-1}$  and mode  $\nu_7$  (H-bond stretch with admixture of rotation,  $133\text{ cm}^{-1}$ ) have the proper  $a_g$  and  $b_u$  symmetries to enter the LVC description for the  $S_1$  and  $S_2$  excited states. We will show later that these are the most important modes for the analysis of the vibronic spectrum.

## B. Determination and discussion of coupling parameters of (oCP)<sub>2</sub>

The monomer coupling parameters were taken from Ref. 12. There they were obtained by least squares fits to the excited state PES using the shifted harmonic oscillator model. Only the  $S_1$  state of oCP was considered, since the energy difference to the second excited state is  $1.26\text{ eV}$  and the Born-Oppenheimer separation is expected to be valid. The coupling parameters for modes with frequencies up to  $800\text{ cm}^{-1}$  are collected in Table III.

The dimer coupling constants have been obtained by least squares fits of the QVC model to the *ab initio* calculated

TABLE III. Coupling parameters of the totally symmetric oCP monomer vibrational modes (RI-CC2/cc-pVTZ) up to  $800\text{ cm}^{-1}$ , obtained by harmonic least squares fits to the PESs. Parameters are taken from Ref. 13. All modes included in the calculation of the spectrum are marked with an asterisk.

Mode	$\omega_{GS}$ ( $\text{cm}^{-1}$ )	$b$ ( $\text{cm}^{-1}$ )	$b^2/\omega_{GS}$ ( $\text{cm}^{-1}$ )	$b^2/\omega_{GS}^2$
1*	124.7	92.7	68.9	0.552
4*	381.4	-105.5	29.2	0.077
7*	459.2	-350.3	267.2	0.582
9*	554.3	-47.4	4.0	0.007
11	591.6	151.7	38.9	0.066
13	730.2	268.3	98.6	0.135

adiabatic PESs (see Eqs. (11) and (12)). For the totally symmetric modes in the framework of linear (quadratic) couplings, the PESs are shifted harmonic oscillators (including a frequency change).

Anharmonicity along single-mode coordinates in the ground state of hydrogen-bonded systems is a well-known phenomenon and has been the subject of extensive studies.<sup>44</sup> As an example, for the (oCP)<sub>2</sub> system, Fig. 4(a) shows the ground state potentials along the totally symmetric normal mode  $\nu_{10}$  including the harmonic ground state potential and the anharmonic fit to the *ab initio* single-point energies calculated along  $Q_{10}$ . The harmonic model is clearly not in good agreement with the *ab initio* energies. To analyse the impact of the ground state anharmonicity on the excited state PESs, we compare the coupling constants resulting from harmonic fits to the excitation energies with those resulting from harmonic fits to the PESs. For mode  $\nu_{10}$ , the first one is depicted in Fig. 4(b) and is of very satisfactory quality. The second fit is shown as a dotted line in Fig. 4(c). The solid line in Fig. 4(c) is obtained by adding the anharmonic fit to the ground state potential from Fig. 4(a) and the harmonic fit to the excitation energy from Fig. 4(b). The comparison of the solid and dotted lines in Fig. 4(c) clearly demonstrates that the fully harmonic fit does not well reproduce the excited state PES. For mode  $\nu_{10}$ , e.g., the values for the linear coupling constant in the first excited state in the two approaches are  $45.3\text{ cm}^{-1}$  and  $91.4\text{ cm}^{-1}$ . This leads to a difference in the Huang-Rhys factor (also called Poisson parameter in the literature)  $S = k^2/2\omega^2$  of a factor of 4. Therefore, the vibrational excitation is negligible in one case and clearly visible in the other. For all modes considered, the fit to the excitation energy nicely confirms the quadratic vibronic coupling model. The anharmonic character of the PES of the  $S_1$  and  $S_2$  excited states is “inherited” from the ground state.

Since the experimental spectrum is of high resolution and also the observed quenched excitonic splitting is rather small, very small inaccuracies in the coupling constants have a rather large impact on the quality of the theoretical results. Therefore, we obtained all coupling constants through least squares fits to the excitation energies rather than to the PESs to eliminate the ground state anharmonicity from the fit. The corresponding coupling constants for the  $a_g$  modes up to  $800\text{ cm}^{-1}$  are compiled in Table IV. Therein, the frequency  $\omega_{GS}$  is the RI-CC2 harmonic frequency. For both excited states,  $k$  is the linear and  $\gamma$  the quadratic vibronic coupling constant

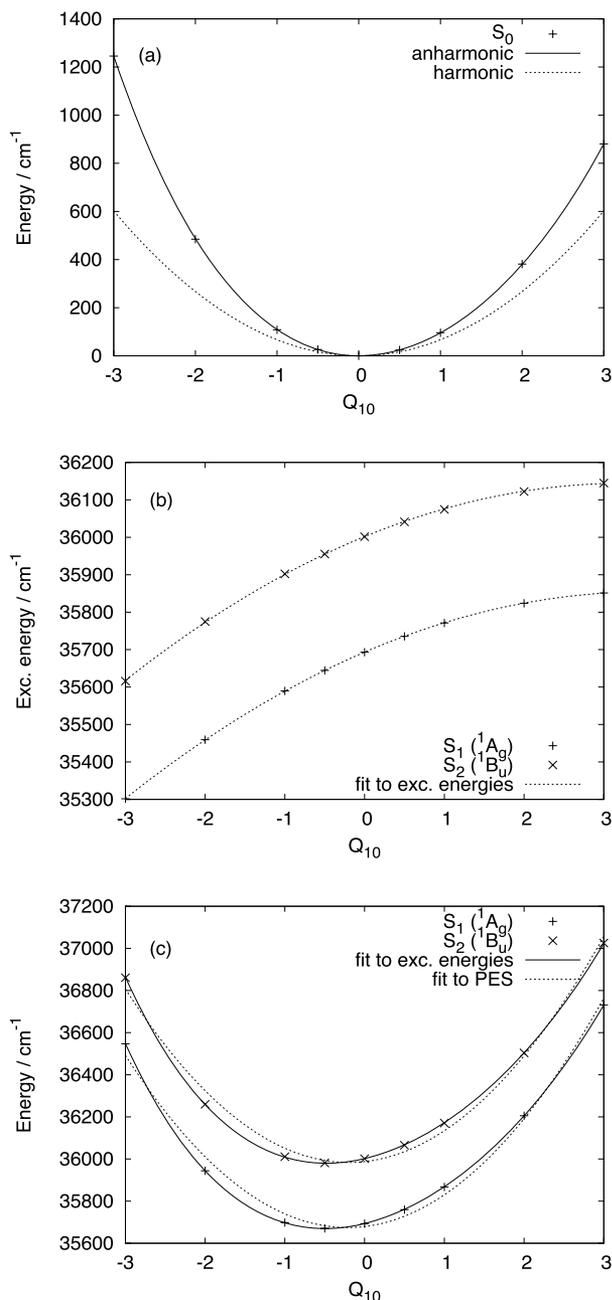


FIG. 4. Determination of coupling constants for mode  $\nu_{10}$  ( $a_g$ ). (a) Comparison between anharmonic and harmonic ground state potentials. The energy at the ground state equilibrium geometry ( $Q=0$ ) is set to zero. (b) QVC fit to the excitation energies. The negative curvatures indicate a frequency lowering upon excitation. (c) Comparison between different QVC fits to the excited state PES. The dashed line gives the results when fitting directly to the PES of the excited state, the solid line results from fitting to the excitation energy of the central panel. In the latter case, the plotted data are obtained by adding the anharmonic ground state potential of panel (a).

obtained through least squares fits; the first corresponds to a shift relative to the ground state potential minimum and the latter to a frequency change in the electronically excited state. The sum of the harmonic ground state frequency and the quadratic coupling constant  $\gamma$  therefore is an approximation to the excited-state frequency. Additionally, the Huang-Rhys factor for each mode is given. The modes that are explicitly treated in the subsequent calculation of the spectra are marked

with an asterisk. Fig. 5 shows the agreement between the *ab initio* data and the fit to the excitation energies along these modes ( $\nu_4$ ,  $\nu_7$ ,  $\nu_{13}$ , and  $\nu_{18}$ ). The negative curvatures are due to a frequency lowering upon excitation (i.e., negative values of  $\gamma$ ).

For the 1D-cuts along the  $b_u$  coupling modes, a least squares fit to the squared difference of the interacting surfaces yields the linear interstate coupling constant  $\lambda$  as well as the difference in the quadratic coupling constants (see Eq. (12)). The sum of the quadratic coupling constants is determined from the sum of the excitation energies. The values obtained are collected in Table V for modes with frequencies up to  $800 \text{ cm}^{-1}$ . Besides the harmonic ground state frequency  $\omega_{GS}$ , the linear and the quadratic coupling constants  $\gamma$  for both excited states (obtained from both the difference and the sum of the excitation energies) are given, together with the Huang-Rhys factor for each mode. The modes that are explicitly considered in the subsequent calculation of the spectra are marked with an asterisk. Fig. 6 displays the least squares fit functions to the sum (solid) and difference (dotted) of the excitation energies along these modes ( $\nu_5$ ,  $\nu_9$ , and  $\nu_{17}$ ). For graphical reasons, the difference is given as a negative quantity. The negative curvature of the sum of the excitation energies indicates a frequency lowering. The fits of the model are seen to be in good agreement with the *ab initio* data.

Key energetic quantities for the first two excited states are given in Table II. It lists the vertical excitation energies for the  $S_1$  and  $S_2$  excited states and compares them with energies obtained under  $C_{2h}$ -constrained and fully relaxed structural optimizations. The energy gain due to the geometry relaxation in the  $S_1$  state of  $1847 \text{ cm}^{-1}$  ( $=35693 \text{ cm}^{-1} - 33846 \text{ cm}^{-1}$ ) can be decomposed into the  $C_{2h}$  symmetry-constrained structural relaxation ( $1118 \text{ cm}^{-1} = 35693 \text{ cm}^{-1} - 34575 \text{ cm}^{-1}$ ) and the asymmetric in-plane distortion ( $729 \text{ cm}^{-1} = 34575 \text{ cm}^{-1} - 33846 \text{ cm}^{-1}$ ). In earlier work,<sup>13</sup> we related these findings to the FG model and found for the  $C_{2h}$ -constrained structural relaxation  $1281 \text{ cm}^{-1}$  and for the asymmetric distortion a stabilization energy of  $1131 \text{ cm}^{-1}$ . The deviations are approximately 15% and 35%, respectively.<sup>13</sup> We are now able to compare with the predictions of the present coupling model. The structural relaxation can be assigned to the  $a_g$  modes in the  $S_1$ -state, in which the energy gain amounts to  $1064 \text{ cm}^{-1}$ . The symmetry-lowering through coupling modes is given by the stabilization energy in the multi-mode case (see Eq. (15)) and amounts to  $E_{stab} = 729 \text{ cm}^{-1}$ . The results obtained using the linear vibronic coupling model are in excellent agreement with the full (i.e., model-independent) *ab initio* calculations.

For the quantum dynamical analysis discussed below, only the most relevant modes are included in the vibronic Hamiltonian. These are determined by their frequencies and the size of the Huang-Rhys factor. However, from our previous work,<sup>7,12,13</sup> it is clear that all vibrational modes contribute to quenching the energy gap between the excited states. To account for this feature, we introduce a “prequenched” excitonic splitting as an effective energy difference between the two coupled surfaces. This is taken to represent the vibronic quenching by the higher-frequency modes, not included below, and is in some cases chosen

TABLE IV. Coupling parameters of the totally symmetric ( $\text{oCP}$ )<sub>2</sub> modes (RI-CC2/aug-cc-pVTZ) up to 800 cm<sup>-1</sup>, obtained by least squares fits to the excitation energies. All modes included in the calculation of the spectrum are marked with an asterisk.

Mode	$\omega_{GS}$ (cm <sup>-1</sup> )	$k^{(1)}$ (cm <sup>-1</sup> )	$k^{(2)}$ (cm <sup>-1</sup> )	$\gamma^{(1)}$ (cm <sup>-1</sup> )	$\gamma^{(2)}$ (cm <sup>-1</sup> )	$(k^{(1)})^2/2\omega_{GS}^2$	$(k^{(2)})^2/2\omega_{GS}^2$
4*	80.9	-67.4	-50.0	-33.8	-32.5	0.347	0.191
7*	133.8	127.4	85.2	-20.2	-16.2	0.453	0.203
10*	199.5	91.4	87.6	-25.9	-27.0	0.105	0.096
13*	381.1	-170.7	-152.4	-21.8	-22.6	0.100	0.080
18*	468.2	371.4	362.6	-26.7	-27.4	0.315	0.300
24*	570.1	153.9	148.7	-31.6	-34.8	0.036	0.034
25	594.4	107.0	104.7	-9.3	-10.3	0.016	0.016
30	729.8	-267.0	-270.1	-33.9	-35.8	0.067	0.068

phenomenologically such that the computed, quenched excitonic splitting, obtained as the difference between the first lines in the calculated  $S_1$  and  $S_2$  spectra, well approximates the experimentally observed splitting. The prequenching only has a minor impact on the shape of the spectrum but leads to an enormous difference in the final quenched excitonic splitting. Moreover, we will see in Sec. V that the prequenching splitting can be well estimated from the treatments of Refs. 12 and 13.

### C. Analysis of spectra

The experimental spectrum has been measured up to 750 cm<sup>-1</sup> above the  $S_2$  vibronic origin. Also the computed spectrum has been restricted to this region. The experimental spectrum is dominated by the  $S_2(^1B_u) \leftarrow S_0(^1A_g)$  transition

and its associated  $a_g$  vibrational excitations, which are fully allowed. As will be shown below, vibrational  $b_u$  excitations of the  $S_1(^1A_g)$  state also become allowed via vibronic coupling.

#### 1. Fulton-Gouterman model

As a starting point, we compare the calculated spectrum based on the FG model with the experimental 2C-R2PI spectrum in Fig. 7. Diagonalization of the original FG Hamiltonian (Eq. (1)) yields the spectra for both locally excited states. For comparison with the experimental spectrum, restriction to the symmetry-allowed  $S_2 \leftarrow S_0$  transition is achieved by employing the FG Hamiltonian in the electronically and vibrationally delocalized basis (see Eq. (3)). Therefore, in the spectrum, the modes appear as positive

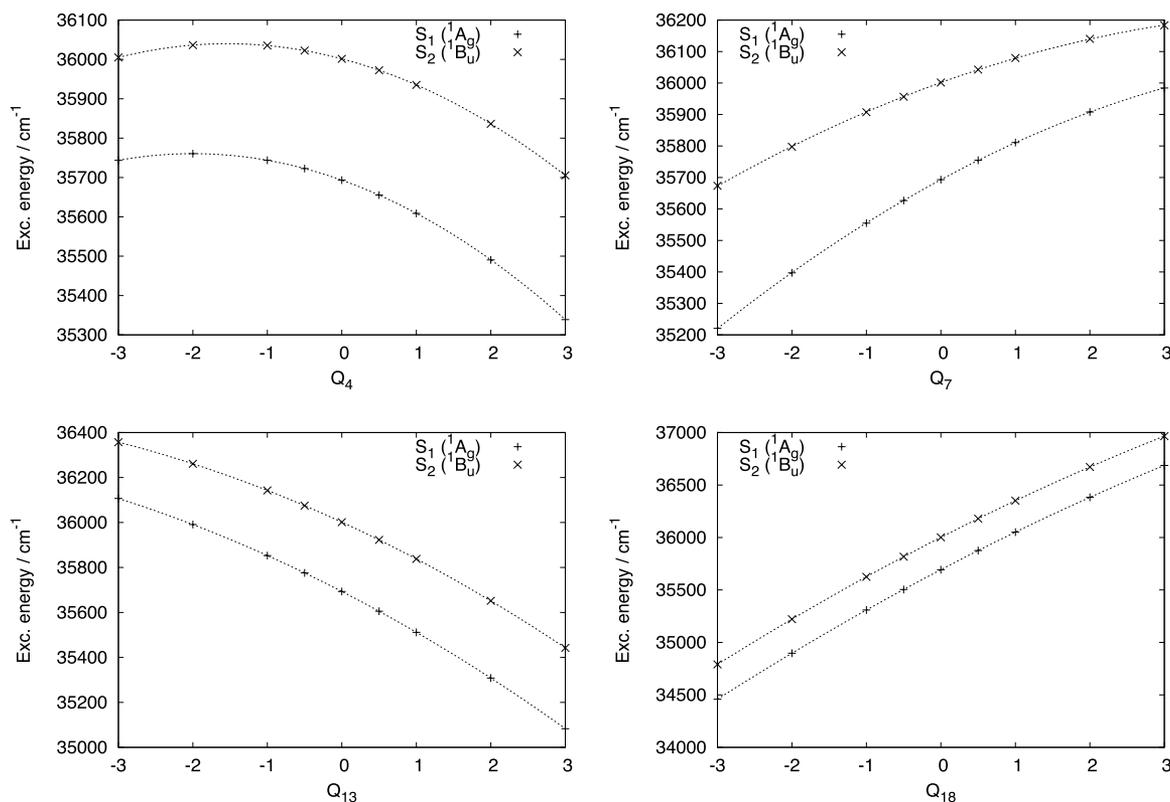


FIG. 5. Least squares fits (dashed lines) to the excitation energies of the  $S_1(^1A_g)$  and  $S_2(^1B_u)$  excited states along the  $a_g$  modes 4, 7, 13, and 18. + and  $\times$  display the *ab initio* data points.

TABLE V. Coupling parameters of the  $b_u$ -symmetric (oCP)<sub>2</sub> modes (RI-CC2/aug-cc-pVTZ) up to 800 cm<sup>-1</sup>, obtained by least squares fits to the sum and difference of the excitation energies (compare Eq. (12)). All modes included in the calculation of the spectrum are marked with an asterisk.

Mode	$\omega_{GS}$ (cm <sup>-1</sup> )	$\gamma^{(1)}$ (cm <sup>-1</sup> )	$\gamma^{(2)}$ (cm <sup>-1</sup> )	$\lambda$ (cm <sup>-1</sup> )	$\lambda^2/2\omega_{GS}^2$
5*	82.6	-36.5	-36.5	71.1	0.370
9*	165.8	-50.4	-21.5	67.8	0.084
16	407.0	-25.3	-25.3	12.5	$5 \times 10^{-4}$
17*	467.5	-35.6	-24.2	373.5	0.319
23	559.2	-28.9	-28.9	80.2	0.010
26	596.0	-8.8	-8.8	150.5	0.032
29	724.3	-37.7	-37.7	216.2	0.045

and negative combinations  $Q_+$  and  $Q_-$  of the monomeric modes. The vibrations considered for the calculation are the four lowest-frequency totally symmetric modes of the oCP-monomer ( $\nu_1^{mono}$ ,  $\nu_4^{mono}$ ,  $\nu_7^{mono}$ ,  $\nu_9^{mono}$ , see Table III and Fig. 2) in the energy range up to 560 cm<sup>-1</sup>. To account for the effect of the higher-frequency modes, we introduce a prequenched excitonic splitting of 69.5 cm<sup>-1</sup>. The corresponding quenching (or reduction) factor  $\Gamma$  is determined in a non-phenomenological way by applying Förster's perturbation theory expression<sup>16</sup>  $\Gamma = \prod_i \exp -b_i^2/(\hbar\omega_i)^2$  to all the higher-frequency modes starting from mode  $\nu_{11}^{mono}$ . For more details, we refer to Ref. 13 from which also the coupling constants are taken. The spectra are shifted to a common origin.

In the calculated FG spectrum of Fig. 7(b), the line at 117 cm<sup>-1</sup> represents an excited state with a roughly equal mixture of one and two quanta of the monomer mode  $\nu_1^{mono}$  in

its negative linear combination, i.e., levels  $1_-^1$  and  $1_-^2$ . In line with the symmetry considerations of Sec. II B 2, the former (latter) component is associated with the  $A_g$  ( $B_u$ ) symmetric electronic wave function. The following line at 125 cm<sup>-1</sup> corresponds to a single-quantum excitation of the positive linear combination of  $\nu_1^{mono}$  ( $1_+^1$ ). The three lines at 235, 242, and 250 cm<sup>-1</sup> are higher quanta of mode  $\nu_1^{mono}$ , namely,  $1_+^3$ ,  $1_+^1 1_-^2$ , and  $1_+^2$ . Even a third series of lines is visible at 363 cm<sup>-1</sup>, namely,  $1_+^1 1_+^3$ ,  $1_+^2 1_-^2$ , and  $1_-^4$ . Note that lines with an even number of quanta in  $1_-$  are always associated with the  $B_u$ -symmetric electronic wave function (as already stated above), whereas odd quanta come with the  $A_g$ -symmetric electronic wave function. Somewhat separated is the first excitation of mode  $\nu_4^{mono}$  at 382 cm<sup>-1</sup>, with a rather small relative intensity of 0.04, reflecting the small Huang-Rhys factor of 0.08. The excitations of mode  $\nu_7^{mono}$  follow at 454 and 459 cm<sup>-1</sup>, also as a single quantum  $7_+^1$  and one or two quanta  $7_-^1$  and  $7_-^2$ . This is

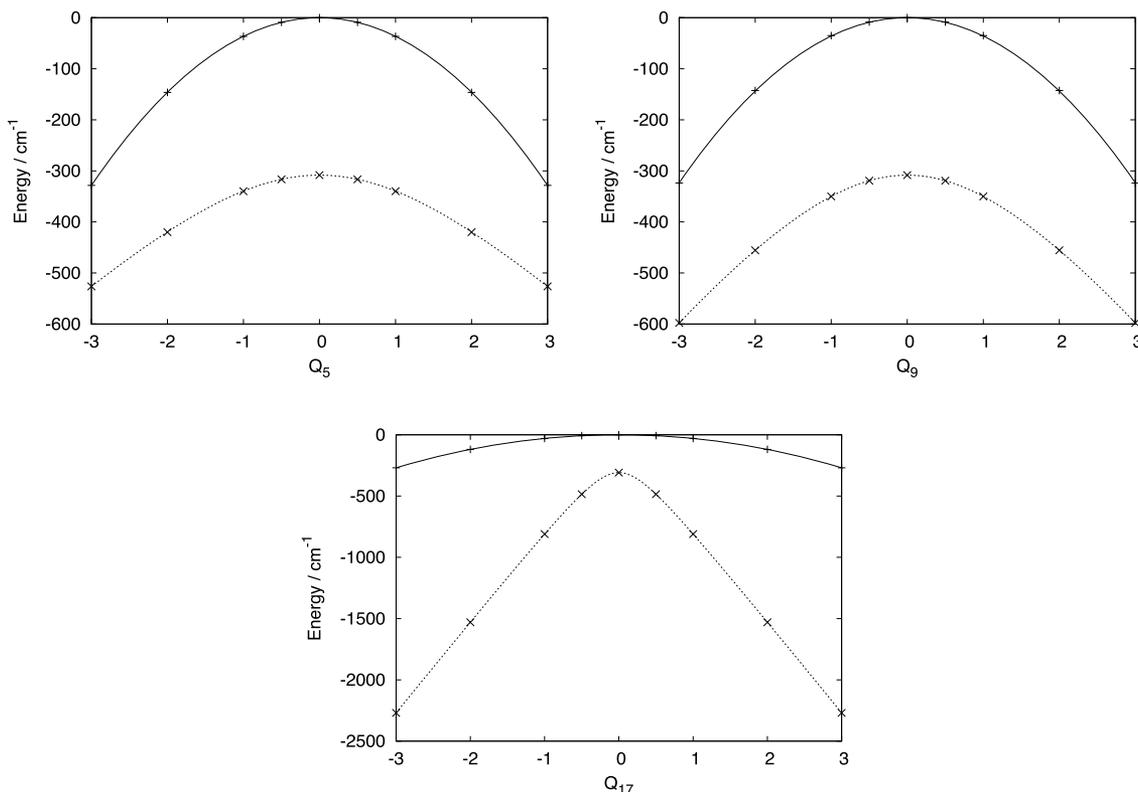


FIG. 6. Least squares fit to the sum (solid) and difference (dashed) of the excitation energies along  $b_u$  modes 5, 9, and 17. The sum at  $Q = 0$  is set to zero. + and x display the sum and the difference of the *ab initio* calculated energies (in cm<sup>-1</sup>) of the  $S_1$  and  $S_2$  states, respectively.

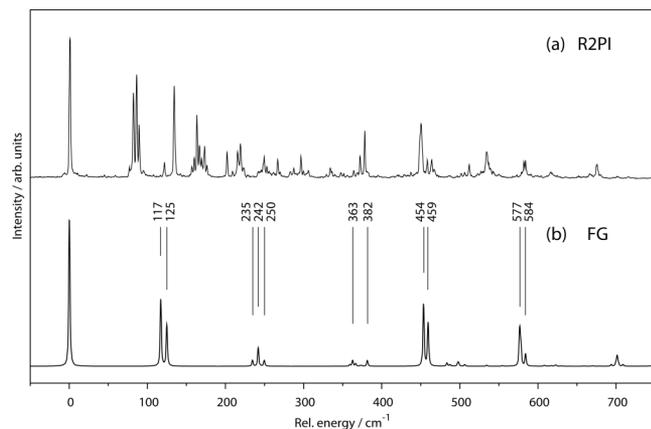


FIG. 7. Comparison of the experimental R2PI spectrum (a) with a 4-mode spectrum (b) calculated in the framework of the Fulton-Gouterman model, employing only monomer vibrational modes. In panel (b), the labels of several weaker lines have been omitted for clarity.

again similar to mode  $\nu_1^{mono}$ . More details will be discussed in Sec. IV D. The combined excitations of  $\nu_1^{mono}$  and  $\nu_7^{mono}$  are seen at 577 and 584  $\text{cm}^{-1}$ . All assignments of the calculated FG spectrum are summarized in Table VI.

The experimental and theoretical spectra are in acceptable agreement for the energy range of mode  $\nu_7^{mono}$ . This is due to the similarity of  $\nu_7^{mono}$  with the corresponding dimer modes  $\nu_{17}$  and  $\nu_{18}$  (see Sec. IV A). The FG model is sufficient in this case. The deviations between theory and experiment are most obvious in the low-frequency range. The dimer vibrations  $\nu_9$  and  $\nu_{10}$  that correspond to the monomer mode  $\nu_1^{mono}$  are 40 to 75  $\text{cm}^{-1}$  higher in energy and the lines are therefore expected to be shifted to higher energy (see Fig. 8). Instead, the experimental spectrum shows the excitation of low-frequency intermonomeric modes at about 80  $\text{cm}^{-1}$ , which are not accounted for in the FG spectrum due to the limitation of the model.

In previous related work on the 2-aminopyridine dimer, the FG model has been extended in an *ad hoc* way by including also intermonomer modes with empirically fitted values of the coupling constants.<sup>7</sup> Here, we aim for a more rigorous approach with parameters computed *ab initio*

TABLE VI. Assignment of spectral features of the  $S_2 \leftarrow S_0$  transition of the *ortho*-cyanophenol dimer calculated within the FG approach, see Fig. 7. All frequencies in  $\text{cm}^{-1}$ .

Mode	FG
$1_2^-$	117
$1_+^1$	125
$1_3^3$	235
$1_+^1 1_2^-$	242
$1_+^2$	250
$1_+^2 1_2^-$	363
$4_+^1$	382
$7_2^-$	454
$7_1^1$	459
$1^1 7^1$	577
$1^1 7^1$	584

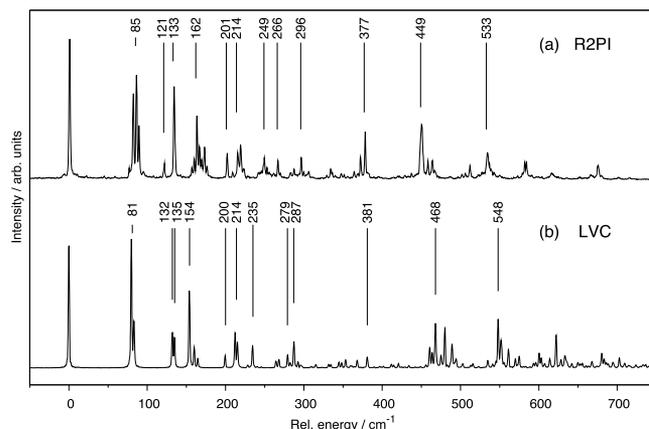


FIG. 8. Comparison of the experimental R2PI spectrum (a) with a 9-mode spectrum (b) calculated in the framework of the LVC model.

and therefore proceed by using a more general vibronic Hamiltonian (Eq. (5)) for the analysis of the spectrum.

## 2. Linear vibronic coupling scheme

Fig. 8 shows a comparison between the experimental R2PI spectrum and the calculated 9-mode LVC spectrum. Both spectra are shifted to a common origin. The 2C-R2PI spectrum of (oCP)<sub>2</sub> is measured over the 32 850–33 600  $\text{cm}^{-1}$  range. The first band in the experimental spectrum in Fig. 8(a) is assigned to the  $0_0^0$  band, which lies at 32 855  $\text{cm}^{-1}$ . The vibronic Hamiltonian comprises the  $a_g$ -symmetric modes  $\nu_4$ ,  $\nu_7$ ,  $\nu_{10}$ ,  $\nu_{13}$ ,  $\nu_{18}$ , and  $\nu_{24}$ , as well as the  $b_u$ -symmetric modes  $\nu_5$ ,  $\nu_9$ , and  $\nu_{17}$ . Their frequencies are all in the energy range of interest. The coupling constants are taken from Tables IV and V. The phenomenological, prequenched excitonic splitting used is 105.8  $\text{cm}^{-1}$ , see also Sec. V.

All assignments of the experimental and calculated spectra are summarized in Table VII. For the LVC spectrum, they are based on energetic considerations, together with the calculated nodal properties of the vibronic levels, computed as indicated in Sec. III A.

TABLE VII. Comparison of experimental (R2PI) and theoretical (LVC) spectral features of the  $S_2 \leftarrow S_0$  transition (see Fig. 8) of (oCP)<sub>2</sub>. All frequencies in  $\text{cm}^{-1}$ .

Mode	R2PI	LVC
$\nu_4^1$	85.3	{79.8, 83.2}
$\nu_5^2$	121.2	132.1
$\nu_7^1$	133.4	134.8
$\nu_4^2$	162.5	153.8
$\nu_{10}^1$	201.2	199.5
$\nu_4^1 \nu_7^1$	{214.4, 218.2}	{212.2, 215.0}
$\nu_4^3$	-	234.5
$\nu_4^1 \nu_{10}^1$	266.0	279.3
$\nu_4^2 \nu_7^1$	295.8	287.3
$\nu_{13}^1$	377.4	380.9
$\nu_{18}^1$	449.3	468.0
$\nu_4^1 \nu_{18}^1$	533.4	548.0

The first detail that stands out in the computed spectrum, Fig. 8(b), in comparison to the FG spectrum in Fig. 7(b) is the pair of low-frequency lines near  $80\text{ cm}^{-1}$ . They correspond to the intermonomeric mode  $\nu_4$  (H-bond shearing, see Fig. 3). The experimental spectrum shows a band multiplet, while the LVC spectrum shows a doublet of lines with similar intensity. For further discussion of the calculated doublet structure, we refer to Sec. IV D. In the following, we address possible explanations for the experimentally observed multiplet structure.

From comparative calculations including the low-frequency  $b_g$  symmetric mode  $\nu_3$  ( $40.4\text{ cm}^{-1}$ ), we consider it unlikely that a double excitation of mode  $\nu_3$  (within the QVC scheme) is responsible for one of these extra lines. Also the inclusion of quadratic couplings in modes  $\nu_4$  or  $\nu_5$  as well as their mixed coupling does not result in further lines in this region of the spectrum. We suspect that the experimentally observed multiplet is due to couplings of vibrations  $\nu_4$  and  $\nu_5$  with the very low-frequency modes  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  that appear between  $10$  and  $50\text{ cm}^{-1}$ , see the list of frequencies (Table SIV in the supplementary material.<sup>43</sup>) As an indication, we point out that also all higher quanta of mode  $\nu_4$  show a similar multiplet structure. These putative couplings have not been analyzed in detail, since the methods employed in this work rely on rectilinear Cartesian displacement coordinates that are not suited for the description of the out-of-plane low-frequency modes  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ .

The line at  $135\text{ cm}^{-1}$  can be assigned to the totally symmetric intermonomeric mode  $\nu_7$  (see Fig. 3). The experimental spectrum shows a line at  $121\text{ cm}^{-1}$  that does not appear in the LVC spectrum. Due to symmetry constraints, we can exclude an excitation of the  $b_g$ -symmetric mode  $\nu_6$  (calculated at  $121.6\text{ cm}^{-1}$ ). Instead, we assign it as the double excitation of mode  $\nu_5$ , which appears as the line at  $132\text{ cm}^{-1}$  in the calculated spectrum. A series of lines for the double excitation of mode  $\nu_4$  appears at  $154\text{ cm}^{-1}$  about  $8\text{ cm}^{-1}$  lower than in the experimental spectrum. The following lines in the LVC spectrum (Fig. 8(b)) can be assigned to mode  $\nu_{10}$  ( $200\text{ cm}^{-1}$ ), a combination of modes  $\nu_4$  and  $\nu_7$  ( $214\text{ cm}^{-1}$ ) and a triple excitation of mode  $\nu_4$  ( $235\text{ cm}^{-1}$ ). We further assign the line at  $279\text{ cm}^{-1}$  to a combined excitation of modes  $\nu_4$  and  $\nu_{10}$  and that at  $287\text{ cm}^{-1}$  to a combined excitation of two quanta in mode  $\nu_4$  and one quantum in mode  $\nu_7$ . The corresponding lines in the experimental spectrum occur at  $266\text{ cm}^{-1}$  and at  $296\text{ cm}^{-1}$ .

The intensity of the  $a_g$  mode  $\nu_{13}$  at  $381\text{ cm}^{-1}$  is significantly underestimated by the LVC model. Since its ground state PES shows a harmonic behaviour and the quadratic fit to the excitation energies works well (see Fig. 5), the deviations cannot be caused by anharmonicity. Also the inclusion of quadratic coupling parameters for mode  $\nu_{13}$  does not improve the relative intensity (see Table IV). The small intensity is therefore probably due to an underestimation of the linear coupling along this mode by the *ab initio* calculation. At  $468\text{ cm}^{-1}$  appears the excitation of mode  $\nu_{18}$ . The shift relative to experiment is  $19\text{ cm}^{-1}$ . The higher-frequency region in the experimental spectrum shows combined excitations of mode  $\nu_{18}$  with either mode  $\nu_4$  or mode  $\nu_7$ . Here, the assignment in the calculated spectrum is not unique.

Despite some deviations, the spectra are in good overall agreement. We recall that all frequencies and coupling constants are computed purely *ab initio* without any empirical adjustment. Clearly, the results obtained using the LVC model are superior to the FG model.

#### D. Assignment of low-dimensional spectra and wave functions

For a more detailed insight into the vibronic coupling phenomenon, we analyze a two-mode spectrum including only the two low-frequency intermonomeric vibrations  $\nu_4$  ( $a_g$ ) and  $\nu_5$  ( $b_u$ ), see Fig. 3. As before, we introduce a phenomenological, prequenched splitting between the electronically excited states. Due to the suppression of more modes than in the spectrum of Fig. 8, the prequenched excitonic splitting is reduced to  $40\text{ cm}^{-1}$ . The spectra are shown in Fig. 9 together with the numbering of the vibronic lines. The blue (upward) lines belong to states of  $B_u$  vibronic symmetry (symmetry-allowed transitions), while the red (downward) lines indicate  $A_g$  vibronic symmetry (forbidden transitions; not relevant for comparing with experiment, but included for the discussion). Due to the reduced dimensionality of the calculations, the spectral range is reduced to  $200\text{ cm}^{-1}$ . The first line in the  $B_u$  spectrum is set to zero energy. We present the vibronic WFs corresponding to the vibronic levels according to their symmetry as contour lines employing a colouring scheme to indicate their sign. They are collected in Fig. 10 for the states that appear in the  $A_g$  spectrum and Fig. 11 for those in the  $B_u$  spectrum. The left columns contain the electronic part of the WF corresponding to the lower  $A_g$ -symmetric ( $S_1$ ) electronic state, whereas the right columns show the  $B_u$ -symmetric ( $S_2$ ) electronic WF component, see also Eq. (10). In accordance with symmetry considerations, the  $A_g$ -symmetric electronic WF component for the  $A_g$ -symmetric vibronic lines shows an even number of nodes in the coupling mode  $\nu_5$ , whereas for the  $B_u$ -symmetric electronic WF component, the number of nodes is odd (see

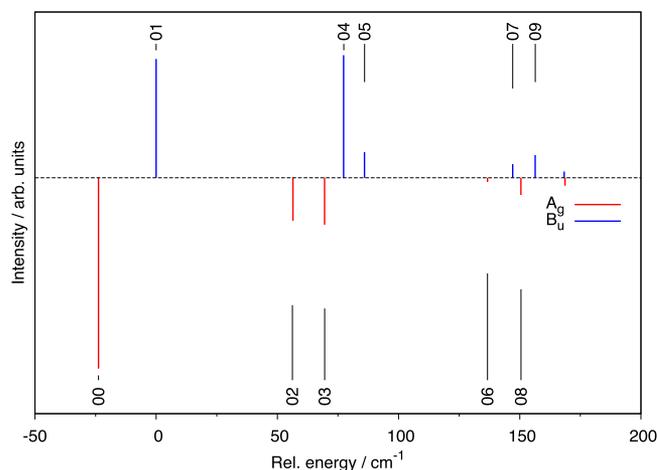


FIG. 9. LVC model 2-mode spectrum of  $A_g$  (red, downward) and  $B_u$  (blue, upward) vibronic symmetry corresponding to Fig. 8. Only  $Q_4$  and  $Q_5$  are retained with an effective, prequenched energy gap of  $40\text{ cm}^{-1}$ . The associated excited-state vibronic wave functions are shown in Figs. 10 and 11.

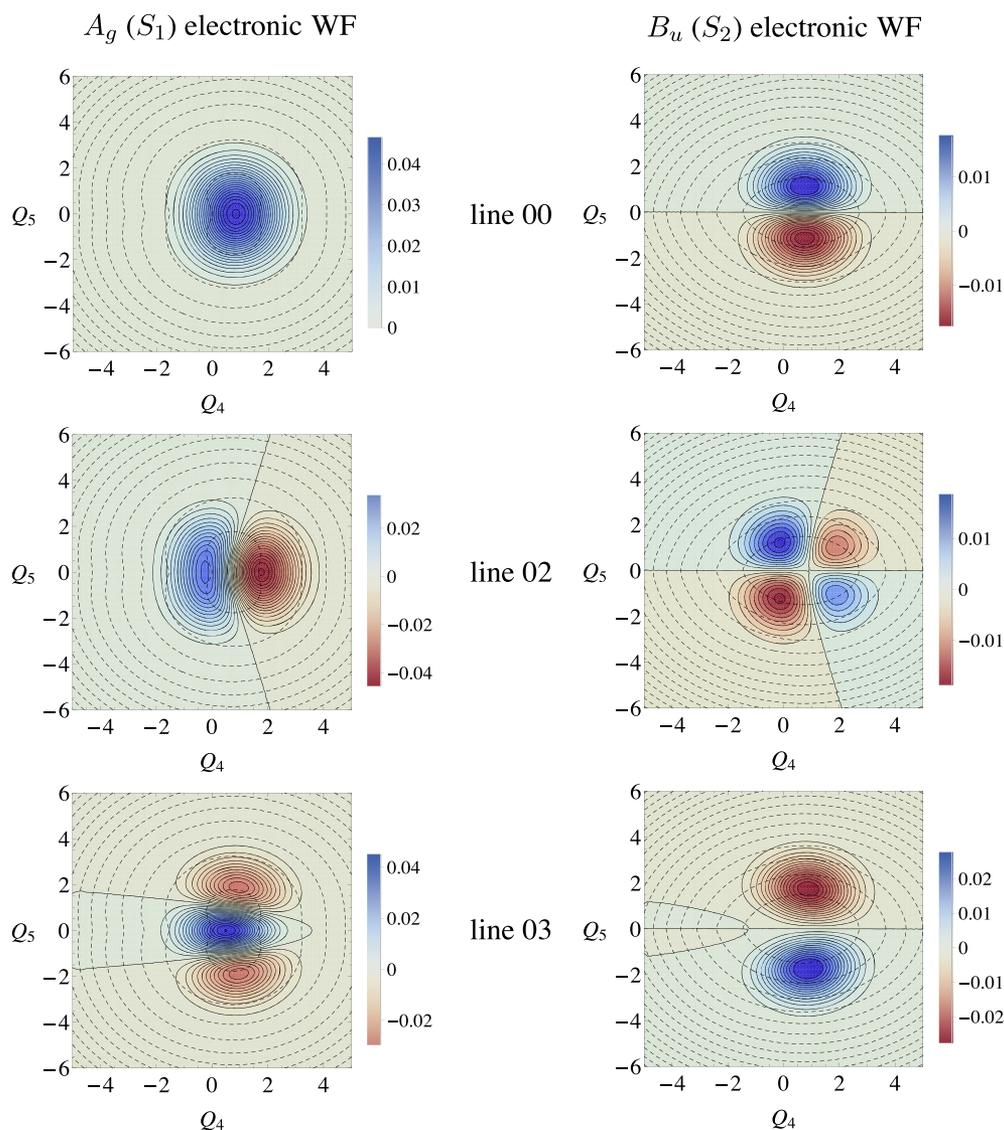


FIG. 10. Wave functions (solid, colored lines) and potential energy surfaces (dashed lines) for  $A_g$  vibronic symmetry states of the 2-mode spectrum (red, downward in Fig. 9, forbidden transitions). The different wave function amplitude scales to the right of each sub-figure reflect the different weights of the electronic wave function as listed in Table VIII.

Fig. 10). For the  $B_u$  vibronic states, even and odd nodes are interchanged (see Fig. 11). All subfigures of Fig. 10 and Fig. 11 include the adiabatic PESs for the  $S_1$  and  $S_2$  states as dashed contour lines. The assignments of the vibronic lines together with the weights of the respective WFs are collected in Table VIII.

The 00 line in Fig. 9 corresponds to an excitation with a nodeless WF in the  $S_1$  state with a contribution of 86.2%, corresponding to the optically forbidden vibronic  $S_1$  origin. The remaining 13.8% of the vibronic WF corresponds to the fundamental of mode  $\nu_5$  in the  $S_2$  ( $B_u$ ) electronic state. The first  $B_u$  vibronic state 01 amounts to a single excitation of the intermonomeric mode  $\nu_5$  in the  $A_g$  electronic state (weight 46.1%) and a broad nodeless wave function in the  $B_u$  electronic state (53.9%). The WF components for the vibronic states 00 and 01 are interchanged relative to each other. However, state 00 clearly is the vibronic origin of the  $S_1$  ( $A_g$ ) state, whereas the contributions from the  $S_1$  and  $S_2$  states for 01 are almost equally mixed.

Of the following two  $A_g$ -symmetric vibronic states 02 and 03, the first consists of a fundamental excitation of mode  $\nu_4$  with a contribution of 84.4%, and a combination of single quanta of modes  $\nu_4$  and  $\nu_5$  with a contribution of 15.6%. The vibronic state 03 is a mixture of a double excitation of mode  $\nu_5$  (64.9%) with the fundamental of mode  $\nu_5$  (35.1%). Although the  $A_g$ -symmetric electronic contribution to the vibronic WF is clearly dominant, the contribution from the second excited electronic state increases with increasing vibronic energy as is seen from the weights in Table VIII. This increased mixing of the two states is expected, as the vibronic energies approach and move up in the energy range of the  $S_2$  electronic state.

The lines 04 and 05 are symmetry-allowed ( $B_u$ ) vibronic excitations of both  $\nu_4$  and  $\nu_5$  in the  $A_g$ -symmetric electronic state (40.7% and 36.8%, respectively) and are approximate mirror images of each other. The same holds for the corresponding  $B_u$  electronic components. They both appear as one node in  $Q_4$  and a combination of zero and two nodes in  $Q_5$

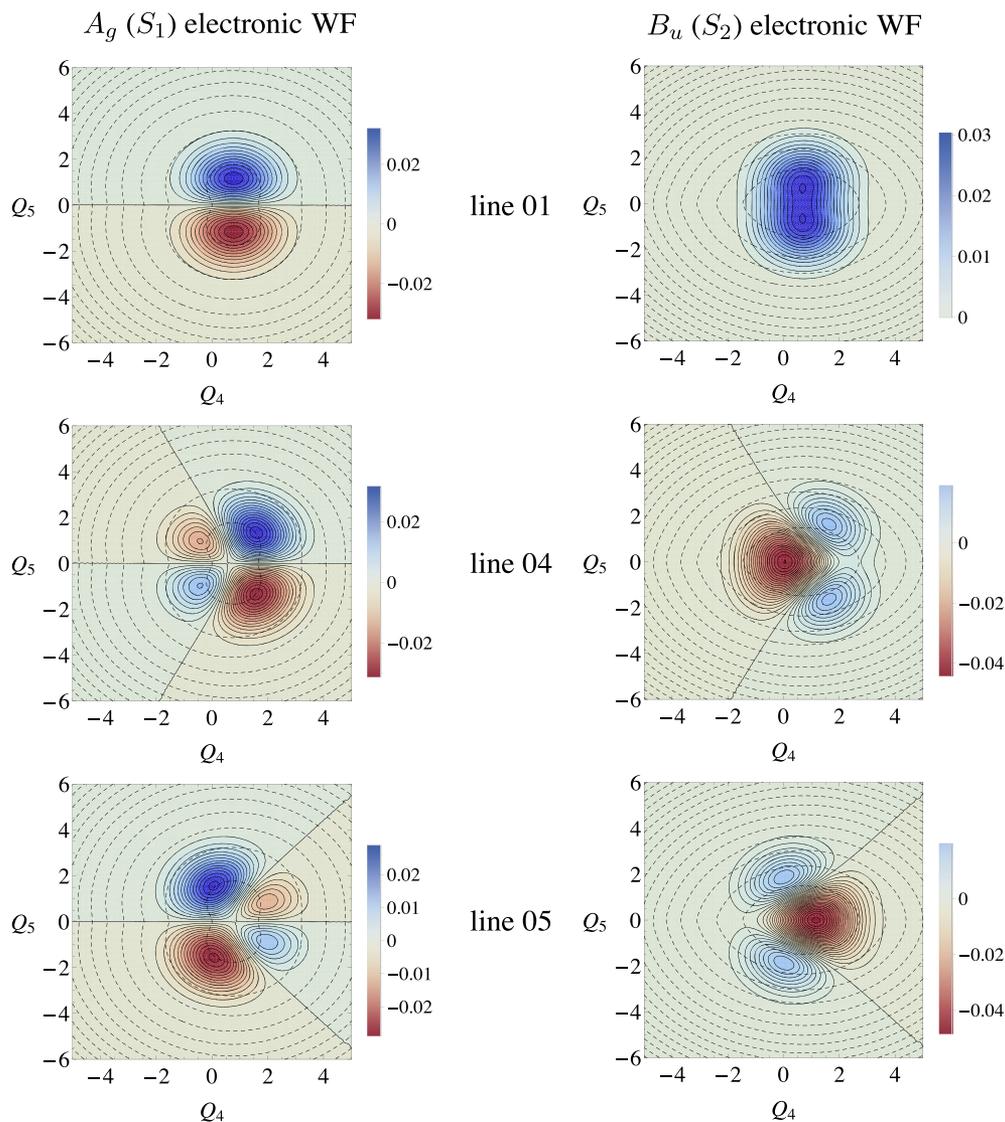


FIG. 11. Same as Fig. 10, for  $B_u$  vibronic symmetry states of the 2-mode spectrum (blue, upward in Fig. 9, allowed transitions).

(59.3% and 63.2%, respectively). The two lines are separated by  $8.6 \text{ cm}^{-1}$ . This is slightly more than the separation of  $3.4 \text{ cm}^{-1}$  for the doublet in the 9-mode LVC spectrum near  $80 \text{ cm}^{-1}$  (Fig. 8); the difference is, however, not significant. One might expect one of the lines to be the excitation of the totally symmetric mode  $\nu_4$  on the  $B_u$  electronic state, and the other one to be the excitation of the coupling mode  $\nu_5$

TABLE VIII. Assignment of the vibronic lines in the 2-mode spectrum of Fig. 9. Energies are given in  $\text{cm}^{-1}$ . The weights given in % refer to the electronic wave function given in the table heading.

Line	Energy	$A_g (S_1)$		$B_u (S_2)$	
00 (red)	-23.8	$0_0^0$	86.2%	$4_0^0 5_0^1$	13.8%
01 (blue)	0.0	$4_0^0 5_0^1$	46.1%	$0_0^0$	53.9%
02 (red)	56.2	$4_0^1 5_0^0$	84.4%	$4_0^1 5_0^1$	15.6%
03 (red)	69.5	$4_0^0 5_0^2$	64.9%	$4_0^0 5_0^1$	35.1%
04 (blue)	77.4	$4_0^1 5_0^1$	40.7%	$4_0^1 5_0^0 + 4_0^0 5_0^2$	59.3%
05 (blue)	86.0	$4_0^1 5_0^1$	36.8%	$4_0^1 5_0^0 + 4_0^0 5_0^2$	63.2%

on the  $A_g$  electronic surface due to intensity borrowing.<sup>19,45</sup> The doublet structure in both spectra is associated with the mirror images of peculiar nodal patterns displayed in Fig. 11.

For the  $B_u$ -symmetric vibronic states, the mixing of the two electronic states is in general more pronounced than for the  $A_g$ -symmetric states. Clearly, the effects observed are not solely due to intensity borrowing from the  $A_g$ -symmetric electronic state. For further insight, we neglect nonadiabatic effects and compare the LVC 2-mode spectra with spectra computed for uncoupled adiabatic PESs.<sup>19</sup>

In Fig. 12, we display the 2-mode spectra on the  $S_1$  adiabatic surface (red, down) and the  $S_2$  adiabatic surface (blue, up) using the same modes ( $\nu_4$  and  $\nu_5$ ) and parameters as for the LVC spectra of Fig. 9. The vibrational lines are denoted  $a, b, \dots, f$  for the first excited state and  $k, l, \dots, p$  for the second excited state. The corresponding six wave functions are collected in Figs. 13 and 14. In the  $A_g$  spectrum, only lines  $a$  ( $0.0 \text{ cm}^{-1}$ ,  $0^0$  origin),  $c$  ( $80.4 \text{ cm}^{-1}$ ,  $4^1$ ),  $d$  ( $109.8 \text{ cm}^{-1}$ ,  $5^2$ ), and  $f$  ( $160.9 \text{ cm}^{-1}$ ,  $4^2$ ) are visible. Lines

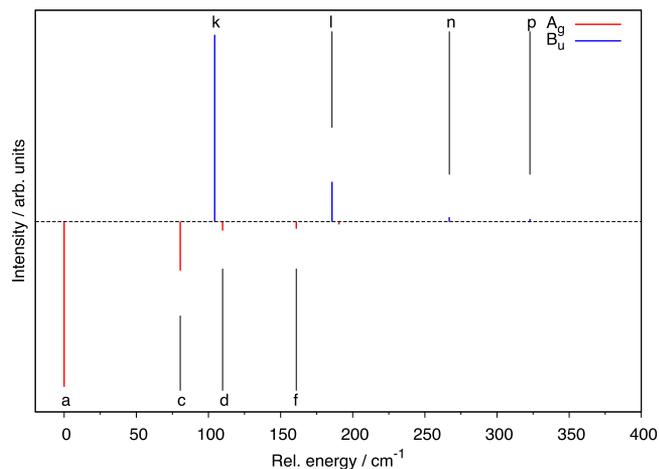


FIG. 12. Same spectrum as in Fig. 9 but recomputed in the adiabatic approximations.  $A_g$  symmetry corresponds to the lower adiabatic PES,  $B_u$  symmetry to the upper adiabatic PES. The underlying vibronic wave functions are shown in Figs. 13 and 14.

$b$  ( $46.3 \text{ cm}^{-1}$ ,  $5^1$ ) and  $e$  ( $126.8 \text{ cm}^{-1}$ ,  $4^1 5^1$ ) have vanishing intensity due to symmetry as they include a single excitation of the  $b_u$ -symmetric mode  $\nu_5$ . The relative energy for excitations of the  $a_g$ -symmetric mode  $\nu_4$  is as expected from the shifted

harmonic oscillator model close to the harmonic ground state frequency of  $80.9 \text{ cm}^{-1}$ . However, for the  $b_u$ -symmetric mode  $\nu_5$ , the computed adiabatic frequency is smaller by a factor of almost two, due to the repulsion of the electronically excited states, by which the lower surface is flattened.<sup>19</sup>

In the  $B_u$  spectrum, lines  $k$  ( $104.3 \text{ cm}^{-1}$ ,  $0^0$  origin),  $l$  ( $185.6 \text{ cm}^{-1}$ ,  $4^1$ ),  $n$  ( $266.9 \text{ cm}^{-1}$ ,  $4^2$ ), and  $p$  ( $322.8 \text{ cm}^{-1}$ ,  $5^2$ ) are visible. There, lines  $m$  ( $219.3 \text{ cm}^{-1}$ ,  $5^1$ ) and  $o$  ( $300.7 \text{ cm}^{-1}$ ,  $4^1 5^1$ ) have vanishing intensity. Herein, the frequency for mode  $\nu_4$  again matches the harmonic ground state frequency, whereas the frequency for mode  $\nu_5$  is almost 50% larger since the upper adiabatic surface is steeper along the coupling mode.

In contrast to the coupled LVC wave functions of Figs. 10 and 11, the WF for the uncoupled adiabatic surfaces leads to regular nodal structures along both the coupling and the tuning modes. The difference between the WFs computed in the LVC scheme and the adiabatic approximation demonstrates the large amount of nonadiabaticity that is present in the (oCP)<sub>2</sub> system, where some of the nodal patterns result from mixing of different numbers of vibrational quanta. A similar profound difference can be found in the spectra, in particular the doublet structure of the lines at  $80 \text{ cm}^{-1}$  in Fig. 9 can be ascribed to nonadiabatic effects.

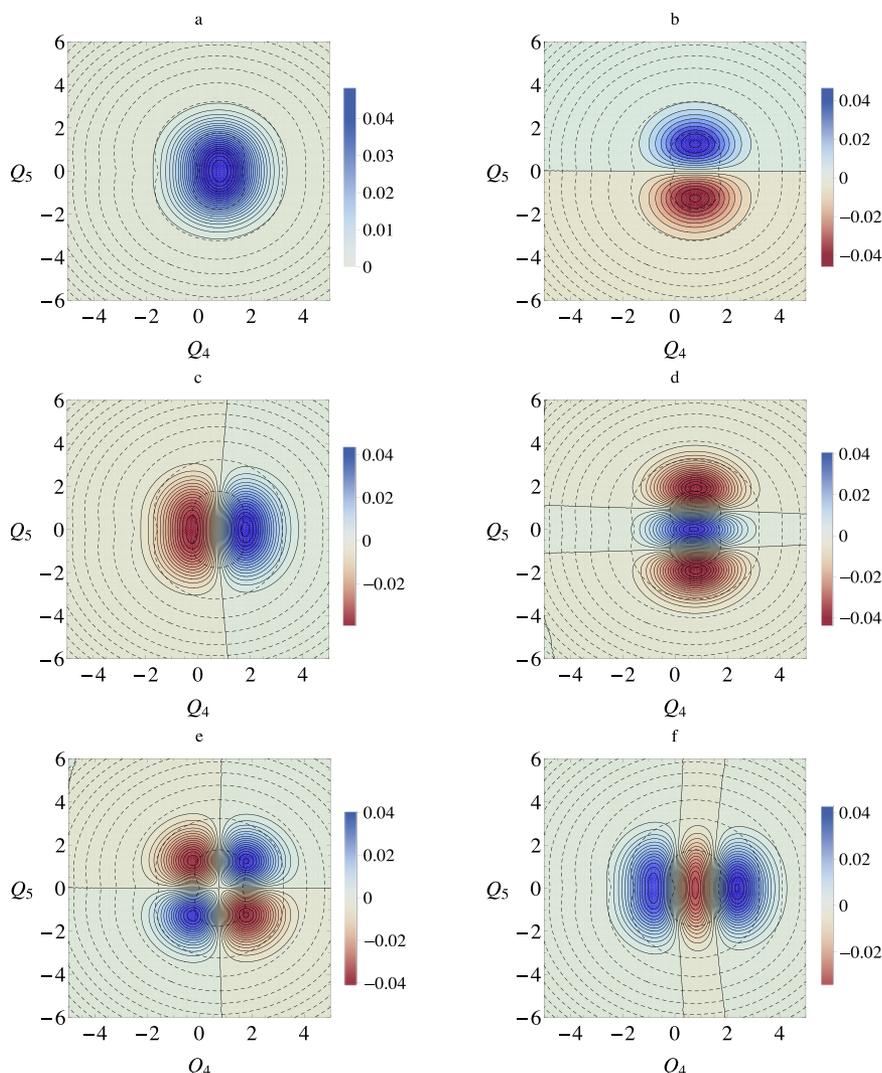


FIG. 13. Wave functions (solid, colored lines) and PESs (dashed lines) for  $A_g$  vibronic lines of the adiabatic 2-mode spectrum (red, downward in Fig. 12).

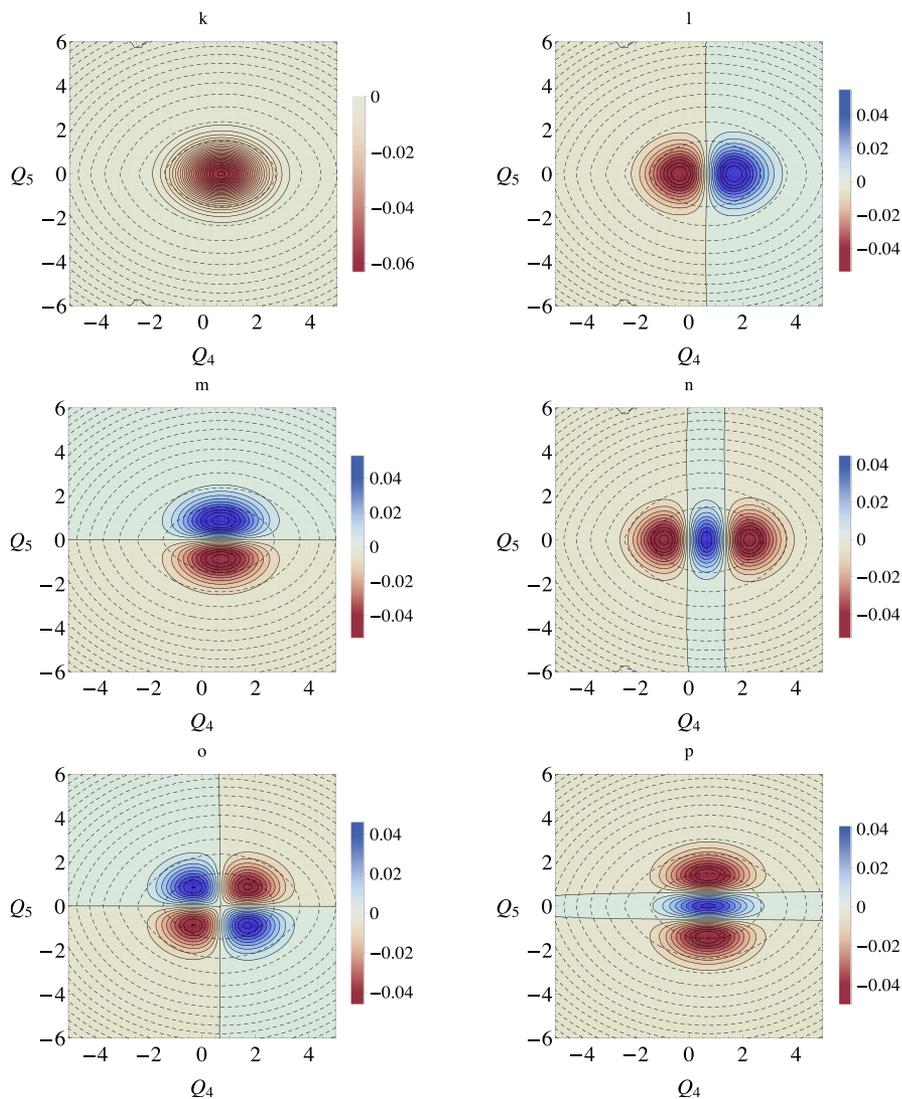


FIG. 14. Same as Fig. 10, for  $B_u$  vibronic symmetry states of the adiabatic 2-mode spectrum (blue, upward in Fig. 12).

## V. CONCLUSIONS

We first show that the experimental R2PI spectrum of the *ortho*-cyanophenol dimer cannot be satisfactorily reproduced within the scope of the Fulton-Gouterman model. Instead, one has to go beyond and use more general vibronic coupling schemes. We herein presented our results for the coupled  $S_1/S_2 \leftarrow S_0$  transitions of (oCP)<sub>2</sub> using the LVC approach and the MCTDH method. In contrast to the FG model, the spectrum is dominated by the intermonomer vibrations  $\nu_4$ ,  $\nu_5$ , and  $\nu_7$ , which illustrates the limitations of the FG model. We cannot explain the multiple splittings in the low frequency mode  $\nu_4$  as well as the underestimated intensity of mode  $\nu_{13}$ . However, the experimental and calculated spectra are in good overall agreement. This agreement is unprecedented for first-principles calculations like here, which rely almost exclusively on *ab initio* data for the system parameters. The present approach is relatively close to that of Nebgen *et al.*<sup>26,27</sup> who use a FG type of treatment for the intramonomer modes and a quadratic coupling scheme for the intermonomer modes. This latter work differs from ours also in the amount of parameter adjustment needed to reproduce experimental spectra.

From a low-dimensional analysis of the vibronic wave functions, we identify nodal properties of the wave functions which confirm the more tentative assignments based only on energetic considerations. All vibronic states (irrespective of symmetry) involve substantial mixing of the  $S_1$  ( $A_g$ ) and  $S_2$  ( $B_u$ ) *electronic* states (taken as diabatic in accordance with the matrix Hamiltonian of Eq. (5)). For the dipole-allowed  $S_2$  ( $B_u$ ) *vibronic* symmetry, the  $S_2$  electronic state is associated with an even number of nodes in the coupling mode coordinate, and for the  $S_1$  electronic state, this number is odd. For the dipole-forbidden  $S_1$  ( $A_g$ ) *vibronic* symmetry, “even” and “odd” are to be interchanged. We emphasize that this qualitative feature, as well as the nodal patterns of Figs. 10 and 11, remains the same in the 9-mode calculation of Fig. 8 as in the 2-mode calculation. From comparative calculations on the uncoupled adiabatic surfaces, we can identify most of the effects observed as nonadiabatic.

Except for the prequenched (“effective”) energy gap, all system parameters are obtained from *ab initio* data without any adjustment. Even for the energy gap, we can make contact with the theoretical treatment of Refs. 12 and 13, which can be used to compute a prequenched energy gap resulting from the

coupling to all the higher-frequency modes not included in the calculation of the spectrum. For the 9-mode spectrum of Fig. 8 and the 2-mode spectrum of Fig. 9, this leads to “prequenched” gaps of  $98.2\text{ cm}^{-1}$  and  $43.9\text{ cm}^{-1}$ , respectively (starting from a vertical excitonic splitting of  $308\text{ cm}^{-1}$ ).<sup>46</sup> These numbers are close to the values actually adopted for the calculation of the spectra, namely,  $105.8\text{ cm}^{-1}$  and  $40.0\text{ cm}^{-1}$  according to Secs. IV C 2 and IV D. Thus, even in this respect, the phenomenological adjustment amounts to a few  $\text{cm}^{-1}$  only. Efforts are underway to further improve the treatment and understanding of the prequenching effects.

The present approach is expected to pave the way for the analysis of related systems. It should also allow for a more detailed understanding of the time-dependence of the excitation energy transfer in all these cases. Work along these lines is ongoing in our groups.

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