Two-dimensional optical spectroscopy: Two-color photon echoes of electronically coupled phthalocyanine dimers

Bradley S. Prall, Dilworth Y. Parkinson, and Graham R. Fleming
Department of Chemistry, University of California, Berkeley and Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Mino Yang
Department of Chemistry and Institute for Basic Sciences Research, Chungbuk National University, Cheongju 361-763, South Korea

Naoto Ishikawa
Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

(Received 6 November 2003; accepted 9 December 2003)

Two-color photon echo peak shift spectroscopy was used to study electronic coupling in a phthalocyanine homodimer. Two optical parametric amplifiers were used to produce pulses to excite the split lower states of LuPc$_2^-$. The existence of a two-color peak shift indicates the existence of correlation between these two dipole-allowed states. The nature of this correlation is discussed based on theoretical predictions of the interactions between exciton and charge resonance states.

Multidimensional infrared spectroscopy is being increasingly recognized as an important tool for obtaining structural and dynamical information regarding the nuclei of complex systems such as peptides and proteins in solution.\cite{1,2,3,4} Multidimensional optical spectroscopy\cite{5} of electronic transitions opens the possibility of obtaining information about the electronic structure and dynamics of complex multichromophoric molecular aggregates such as photosynthetic light harvesting complexes and synthetic assemblies for photonic devices.\cite{6,7,8,9}

Two-dimensional optical spectroscopy using three pulses with identical spectra has been achieved, most notably by Jonas and co-workers.\cite{10} In such a degenerate four-wave mixing experiment all the transitions of interest must lie within the bandwidth of a single laser pulse, which can be a restrictive requirement. An alternative to requiring that all pulses be resonant with all transitions of interest is to make some pulses resonant with one transition and some resonant with a second transition. An early example of this was the two color stimulated echoes performed by Duppen \textit{et al.} on low temperature pentacene doped crystals to study vibrational relaxation on the picosecond time scale.\cite{11,12} We report here the implementation of such an electronic multidimensional experiment: two-color, three pulse photon echo peak shift spectroscopy (2C3PEPS) on a bichromophoric system, lutetium bisphthalocyanine (LuPc$_2$)$_2$. Yang and Fleming (YF) proposed 2C3PEPS in 1999 as a probe of electronic coupling in molecular complexes,\cite{13} and we show here that, while the LuPc$_2$ system is more complicated than the theoretical model studied by YF, the straightforward analysis of experimental data they suggested does give a good first approximation to the electronic mixing between the coupled monomers. The experiment involves three input pulses; one dimension is controlled by the time delay between the first and second pulses and the second dimension is controlled by the color of the third pulse. The experiment can be viewed as a type of spectroscopy carried out on a cross peak in the two-dimensional spectral representation. The power and generality of the technique lie in its ability to determine electronic mixing parameters without prior knowledge of the original site energies of the chromophores.

An important experimental simplification of our method as compared to two-dimensional optical spectroscopy in a degenerate configuration\cite{10} is that 2C3PEPS is a homodyne-detected technique and does not require that any delays be interferometrically controlled. This in turn means that the two colors can be simply and reliably generated from two independent optical parametric amplifiers (OPAs). The method focuses specifically on correlations between electronic states: if there is no correlation there will be no peak shift, although even in the absence of correlated energies there may be some nondegenerate four-wave mixing signal when the two excited states share a common ground state.

The third-order nonlinear response for a four level exciton system based on the Frenkel exciton Hamiltonian was derived by Meier \textit{et al.}\cite{14} Their results were used by YF to study two-color photon echoes for electronically coupled dimers.\cite{13} YF treated the excitation fields as impulsive and controlled the inclusion of different response functions to differentiate between the one-color and two-color responses. They treated a dimer with equilibrium individual chromophore energies $e_A^q$ and $e_B^q$ and electronic coupling $J$. For an excitonically coupled dimer,

$$\tan(2\theta) = \frac{2J}{e_A^q - e_B^q}.$$ 

(1)
where $\theta$ denotes the degree of mixing between the two localized states creating the two eigenstates of the dimer, $|\mu\rangle$ and $|\nu\rangle$.

By assuming that all of the chromophores are coupled to independent baths but follow identical dynamics, YF found that $C_{\mu\nu}$, the renormalization coefficient for the line broadening function, was a critical parameter in describing the coupling between the two chromophores and could be related directly to $\theta$ by

$$C_{\mu\nu} = C_{\nu\mu} = 2 \cdot \sin^2 \theta \cos^2 \theta.$$  

YF showed that in the impulsive limit the two-color peak shift divided by the sum of the two-color and one-color peak shifts, $C_{\pi\pi}(T)$, approximately matched the value of $C_{\mu\nu}$

$$C_{\mu\nu} \approx C_{\pi\pi}(T) = \frac{\tau_{two}(T)}{\tau_{two}(T) + \tau_{one}(T)},$$  

where $\tau^*$ is the peak shift for the one- or two-color experiment. The electronic coupling between the states induces a correlation in their transition frequencies because any fluctuation localized on one chromophore shifts both exciton state energies to some degree, depending on the strength of the coupling. Motivated by the similarity of the calculated $C_{\pi\pi}(T)$ to the theoretically important $C_{\mu\nu}$, we measured one-color and two-color peak shifts for the bichromophic phthalocyanine dimer LuPc$_2^2$.

In the LuPc$_2$ dimer, 0.26 nm separates the two Pc faces and they are twisted with respect to each other by 45°. Figure 1 shows the absorption spectra for the monomer, LuPcAc, and the dimer, LuPc$_2^2$, and the structure of the dimer. The splitting between the dimer’s two excited states is $\sim 2000 \text{ cm}^{-1}$, but they are not split symmetrically around the monomer’s excited state and the splitting is not due to a simple excitonic interaction. The simplest description of the electronic structure of the dimer LuPc$_2^2$ involves four transitions with respect to monomers A and B. Two are localized excitations on a single chromophore, $|6e_{g}^A - 2a_{1u}^A\rangle$ and $|6e_{g}^B - 2a_{1u}^B\rangle$, and two are charge transfer excitations between the chromophores, $|6e_{g}^A - 2a_{1u}^B\rangle$ and $|6e_{g}^B - 2a_{1u}^A\rangle$. The two localized excitations interact with coupling $J_{EX}$ to generate two excited states and the two charge transfer states interact with coupling $J_{CR}$ to form two charge resonance states. This creates a six-level system: the ground state, two excited states, two charge-resonance states, and a doubly excited state. This model would only have one dipole-allowed transition, from the ground state to the upper exciton state; however, a third coupling, $J_{EX-CR}$, between the upper exciton state and the upper charge resonance state yields two states with dipole-allowed transitions from the ground state. The lowest, $1E_1$, has as its main component a charge resonance transition, $\{|6e_{g}^B - 2a_{1u}^A\rangle + |6e_{g}^A - 2a_{1u}^B\rangle\}/$ $\sqrt{2} = |CR\rangle$, while the second transition, $2E_1$, has an excitation component as the largest contribution, $\{|6e_{g}^A - 2a_{1u}^A\rangle + |6e_{g}^B - 2a_{1u}^B\rangle\}/\sqrt{2} = |EX\rangle$. Both transitions have contributions corresponding to the dominant component of the other transition.

Experiments were performed with laser pulses from a home built Ti:sapphire oscillator and regenerative amplifier. The 400 μJ/pulse output of the amplifier is split and 6 mW is sent into each of two optical parametric amplifiers (Coherent 9450), which are tunable between 500 and 750 nm and produce pulses of spectral FWHM of $\sim 15$ nm. The output of one OPA was centered at 620 nm and the output of the other was centered at 700 nm. A pair of F2 prisms was used after each OPA so that the final pulse duration was $\sim 40$ fs (nearly transform limited). The pulse energies at the sample were approximately 3 nJ. The monomer LuPc and the dimer LuPc$_2^2$ (Refs. 16, 22) were dissolved in ethanol and flowed through a room temperature 200 μm quartz cell.

In the two-color photon echo interferometer the three pulses are arranged in an equilateral triangle geometry and focused onto the sample with a 20 cm focal length achromatic lens. Briefly, three pulses with momentum vectors $k_1$, $k_2$, and $k_3$ interact with the sample. There are three time periods: an initial coherence ($\hat{\tau}$), a population ($T$), and a final coherence ($\hat{\tau}$). Time integrated echo profiles are measured as a function of the coherence time (the period between pulses 1 and 2) for fixed values of the population time (the period between pulses 2 and 3). The peak shift at a given population time is the coherence time that yields the greatest integrated echo signal.

The one- and two-color photon echo peak shifts are shown in Fig. 2. The data shown are for the one-color experiment on the lower state (700 nm pulses) and the two-color experiment with the first two pulses interacting with the upper state (620, 620, and 700 nm pulses). Characteristic features of both signals are a rapid decay on the order of 50 fs and a single strongly coupled vibration with a frequency of $\sim 160$ cm$^{-1}$. While the vibration, which appears in both signals, has a similar frequency, it appears with a phase shift between the two signals of approximately $\pi$. The one-color peak shift shows an additional slower response, on the order of picoseconds, not seen in the two-color data. The existence of a two-color peak shift indicates that some correlation ex-
exists between the two transition frequencies. Using the insight gained from calculations on the simple four-level exciton system, it is possible to examine the nature of this correlation.

Figure 3(a) shows the experimental $C_{\gamma\tau}(T)$ derived from the one- and two-color peak shifts. In an excitonic homodimer four-level system, $\lambda_{EX}^0 = \lambda_{CR}^0$ and thus $C_{\mu\nu} = 0.5$. Given the complexity of the LuPc$_2$ states described above, it is not clear how precisely $C_{\gamma\tau}(T)$ should be expected to approach this value in this case. The experimental $C_{\gamma\tau}(T)$ begins slightly higher than 0.5 and after an initial decay remains fairly constant at around 0.45 until 100 fs. It then decreases in the region of the peak shift data dominated by oscillations which are out of phase in the one- and two-color experiments. Thus, $C_{\gamma\tau}(T)$ drops quickly and the minimum appears at what would be the first round trip of the wave packet. It then rises to approximately 0.4 following this dip. Figure 3(b) shows the $C_{\gamma\tau}(T)$ calculated for the four-state excitonic system using simulations in the impulsive limit for several values of $C_{\mu\nu}$. The simulated $C_{\gamma\tau}(T)$ starts below $C_{\mu\nu}$, then approaches a value slightly above it as a limiting value. The calculations were performed using the same methods as YF, except that no static inhomogeneity was introduced; the line broadening function, $g(t)$, was constructed using a 175 cm$^{-1}$, 100 fs Gaussian component and a 100 cm$^{-1}$, 1 ps exponential component; no vibrational components were included.

Lutetium bisphthalocyanine is expected to differ from a homodimer model because of the electronic structure of the two split states. Maximum correspondence between the LuPc$_2$ electronic structure and the four-level exciton model is achieved by concentrating on the coupling between

FIG. 2. Filled circles: one-color three pulse photon echo peak shift for the dimer LuPc$_2$, with all three pulses resonant with the lower state (700 nm). Open circles: two-color peak shift of LuPc$_2$, where the first two pulses are resonant with the upper state and the third pulse is resonant with the lower state (620, 620, and 700 nm).

FIG. 3. Experimental (a) and simulated (b) values of $C_{\gamma\tau}(T)$ determined using Eq. (5). Simulations were carried out for three values of $C_{\mu\nu}$: 0.1 (triangles), 0.25 (open circles), and 0.45 (closed circles). See text for details.

$|CR+\rangle$ and $|EX+\rangle$, labeled $J_{EX-CR}$. The eigenstates of the dimer can be recast as

$$|2E_i\rangle = \left(\cos(\theta) \cdot B_{EX+}^{+} + \sin(\theta) \cdot B_{CR+}^{+}\right) |0\rangle = B_{2E_i}^{+} |0\rangle,$$

$$|1E_i\rangle = \left(-\sin(\theta) \cdot B_{EX+}^{+} + \cos(\theta) \cdot B_{CR+}^{+}\right) |0\rangle = B_{1E_i}^{+} |0\rangle,$$

where $B_{EX+}^{+}$ and $B_{CR+}^{+}$ are the creation operators for upper exciton and charge resonance states. It is then possible to estimate $\theta$ based on wave function coefficients calculated by Ishikawa and co-workers$^{19,20}$ or by comparing the strengths of the two transitions in the absorption spectrum. The wave-function coefficients yield a value of $\theta$ near 0.55 radians. Assuming that all the transition dipole strength comes from the $|EX+\rangle$ contribution, the ratio of the absorption intensities would yield tan$^2(\theta)$. Ignoring the slight differences in line widths between the two states, this analysis yields a ratio of the absorption intensities of approximately 0.45, which corresponds to a value of $\theta$ near 0.59 radians. Assuming that Eq. (3) still holds for expressing the renormalization coeffi-
cient of the line broadening function between $1E_1$ and $2E_1$, $C_{1E2E}$, in terms of $\theta$, then values of $\theta$ of 0.55 and 0.59 yield $C_{1E2E}$ of approximately 0.40 and 0.43. Both of these values are very close to 0.45, the experimental value of $C_{\tau s}(T)$ approached after the ultrafast decay on a timescale similar to the pulse durations.

This analysis oversimplifies the differences between the LuPc$_2$ system and the four-level exciton system. Because the two states used to create the mixed states in Eqs. (4) and (5) have very different character, it is not likely that they have identical line broadening functions. A more advanced theory for the nature of these multistate line broadening functions is necessary to accurately simulate these complex systems.\(^{26}\)

The nature of the doubly excited state could also play an important role in 2C3PEPS. However, without knowing the position of the doubly excited state it is impossible to determine how strongly it interacts with the excitation pulses. Because the various signal pathways interact on the field level in these four wave mixing experiments, even if the double excitation state is only weakly excited it can have a major effect on the signal through interference with the dominant pathways.\(^{27,28}\) Examining the signal at the electric field level using heterodyne detection could better separate the ground state bleach and stimulated emission responses from the excited state absorption response because it provides additional temporal and phase information.

In summary, two-color photon echo peak shift experiments were performed on LuPc$_2$. The existence of a finite 2C3PEPS indicates a correlation in transition frequencies between the $1E_1$ and $2E_1$ states. The value of $C_{\tau s}(T)$ determined experimentally using two-color photon echoes was $\sim 0.45$, close to the value of 0.5 expected for an excitonically coupled homodimer. It is also very similar to the value of 0.4–0.43 expected from a simple extrapolation of the exciton model that takes into account the more complicated electronic structure of LuPc$_2$, showing that this technique is sensitive to the interaction between the two chromophores. Further refinement of the technique via experiments on heterodimers and multimers should result in a powerful tool for studying complex multichromophoric systems. For example, heterodyne detection with diffractive optics could allow the determination of the full third order response of a system over a broad spectral range.\(^{10}\)

This work was supported by a grant from NSF.