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Probing the Interstate Coupling near a Conical Intersection by Optical Spectroscopy

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S Supporting Information

ABSTRACT: Conical intersections are points where adiabatic potential energy surfaces cross. The interstate coupling between the potential energy surfaces plays a crucial role in many processes associated with conical intersections. Still no method exists to measure this coupling driving the chemical reactions between the potential energy surfaces involved. In this Letter, using a generic model for photoisomerization, we propose a novel experimental approach to estimate the coupling that mixes the electronic states near a conical intersection. The approach is based on analyzing the vibrational wavepacket of the reactant in the adiabatic ground and excited electronic states. The nuclear wavepacket dynamics are extracted from linear absorption and two-dimensional electronic spectroscopy. Comparing the frequencies of the coupling mode in the adiabatic ground and excited states from models with and without coupling between the potential energy surfaces suggests an experimental tool to determine the interstate coupling.

Conical intersections (CIs) play a crucial role in photochemistry, photophysics, and many chemical reactions.^{1–6} A CI is a point of crossing between two adiabatic potential energy surfaces (PESs).^{7,8} Near the CI, the electronic and nuclear degrees of freedom are strongly coupled, leading to a breakdown of the Born–Oppenheimer approximation.^{9,10} CIs are believed to be ubiquitous in organic^{11–15} and bio-organic^{16–25} chromophores and play a major part in charge and energy transfer processes. The crossing point provides a funnel for ultrafast (femtosecond) radiationless decay from an excited state. As a result, the detectable fluorescence is negligible (Kasha’s rule).²⁶ In experiments, this characteristic feature is considered strong evidence for the presence of a CI.⁷ Quantum chemical computation, on the other hand, allows for the determination of the ground- and excited-state PESs and identification of a CI to support the interpretation of the experimental results.^{27–31} Although different experimental methods have been developed to gain insight into CIs, no method exists to measure the coupling between the electronic states involved.

In the adiabatic picture, the nonadiabatic coupling is provided by nuclear momentum-like operators,³² which are nonlocal and depend on the derivative coupling vector $\langle \phi_i | \nabla \hat{H}_{el} | \phi_j \rangle / (E_j - E_i)$ for $i \neq j$, where $\hat{H}_{el}$ is the electronic Hamiltonian operator, ϕ_i and ϕ_j are the electronic wave functions, and E_i and E_j are the energy eigenvalues.^{7,10} The derivative coupling diverges at a CI, which makes it impossible to use this coupling to describe the quantum dynamics at the crossing point. This problem may be circumvented by switching to the diabatic picture in which the coupling between the electronic states is

provided by potential-like operators.^{7,10,32,33} In the diabatic picture, the derivative coupling is named interstate coupling and is expressed as off-diagonal matrix elements of the diabatic potential, $\langle \chi_i | \frac{\partial \hat{H}_{el}}{\partial R_a} | \chi_j \rangle R_a$, where χ_i and χ_j denote the diabatic electronic wave functions and R_a is the nuclear coordinate of interest.^{7,8,10} This coupling results in mixing of the electronic states and is responsible for the radiationless decay and many other important processes associated with CIs. Here, using a generic model for nonadiabatic photoisomerization, we introduce a novel way to experimentally determine the interstate coupling near a CI.

Nuclear wavepacket motion is sensitive to PES crossing,^{2,34,35} and therefore, the evolution of nuclear wavepackets has attracted widespread interest in fields such as Raman and time-resolved optical spectroscopy^{36–48} to elucidate non-adiabatic photochemical reactions. In such experiments, comparing nuclear coherences before and after the passage through the CI allows one to uncover the coherent wavepacket motion associated with the electronic surface crossing. However, using these results to measure the coupling between the electronic states in a CI system remains unresolved. A previous study used two-dimensional femtosecond stimulated Raman spectroscopy to identify the tuning and coupling modes in a system with a CI.⁴⁹ The authors of ref 49 were able to determine the anharmonic coupling between the tuning and coupling modes in the excited state by following the spectral

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peak positions of the two modes as a function of time delay, but the coupling between the electronic states could not be obtained. A recent study of ultrafast extreme ultraviolet spectroscopy investigated the dynamics of an electron hole pair between σ and π orbitals created near a CI in CO₂ molecules.⁵⁰ By analyzing the coherent oscillations generated from the electron hole pair density, the diabatic-to-adiabatic mixing angle was determined, which gives indirect information about the coupling between the vibronic states.

This Letter presents a novel scheme to determine the interstate coupling between two electronic states near a CI driving a photoisomerization reaction by capturing the vibrational coherences for the reactant in the adiabatic ground and excited states. Photoisomerization reactions play a crucial role in many photochemical and photobiological processes. We use a generic two-state model for cis–trans isomerization and calculate the linear absorption (1D) and two-dimensional electronic (2DES) spectra in both the presence (CI model) and absence (noCI model) of the interstate coupling. We then propose an analytical expression that can be used to estimate the interstate coupling from the differences in vibrational frequencies obtained in the adiabatic ground and excited states of the reactant.

The CI model employed here has frequently been applied to study light-induced cis–trans isomerization.^{51–59} This model generalizes common vibronic coupling Hamiltonians and assumes that the CI occurs near the Franck–Condon point.^{2,10,50,51,60,61} Specifically, our model describes two diabatic electronic states $|S_0\rangle$ (ground state) and $|S_1\rangle$ (excited state), respectively, coupled to two intramolecular nuclear modes. One of these modes is torsional, described by the angle θ , and the other is vibrational, described by the coordinate q . This is the simplest model for the study of nonadiabatic photoisomerization reactions^{62,63} and an ideal starting point for this study in which nonadiabatic effects play an important role. The Hamiltonian is given by ($\hbar = 1$)

$$\hat{H}_S = \sum_{n=0}^1 \sum_{m=0}^1 |S_n\rangle (\hat{T}\delta_{nm} + \hat{V}_{nm}) \langle S_m| \quad (1a)$$

$$\hat{T} = -\frac{1}{2I} \frac{\partial^2}{\partial \theta^2} - \frac{\omega}{2} \frac{\partial^2}{\partial \hat{q}^2} \quad (1b)$$

$$\hat{V}_{00} = E_0 + \frac{1}{2} W_0 (1 - \cos \theta) + \frac{1}{2} \omega \hat{q}^2 \quad (1c)$$

$$\hat{V}_{11} = E_1 - \frac{1}{2} W_1 (1 - \cos \theta) + \frac{1}{2} \omega \hat{q}^2 + \kappa \hat{q} \quad (1d)$$

$$\hat{V}_{01} = \hat{V}_{10} = \lambda \hat{q} \quad (1e)$$

Here, I denotes the moment of inertia for the torsional mode, ω is the frequency of the coupling mode q , and the displacement of the excited-state potential well of the coupling mode is described by the Huang–Rhys factor $\frac{(\kappa/\omega)^2}{2}$. E_0 and E_1 are the energy eigenvalues for $q = 0$ (i.e., the ground-state equilibrium geometry, which is the Franck–Condon point), and the constants W_0 and W_1 determine the size of the barrier for rotation of the torsional mode. The corresponding adiabatic PES of the model is illustrated by Figure 1a.

The interstate coupling $\hat{V}_{10} = \lambda \hat{q}$ between both diabatic states governs the isomerization reaction, and the main aim of this Letter is to show that the coupling constant λ may be

Figure 1. (a) Two adiabatic PESs, ground and excited states, in the two-dimensional nuclear coordinate space. (b) Linear absorption spectrum in the frequency domain with inhomogeneous line width $\Gamma = 354 \text{ cm}^{-1}$ and homogeneous line width $\Lambda = 106 \text{ cm}^{-1}$ and (c) the absolute linear response function, $|R(t)|$, in the time domain.

determined from spectroscopic experiments, in particular, by probing the effective frequency of the coupling mode in the adiabatic ground and excited states, respectively, of the molecule in the cis conformation. To this end, we calculate the vibrational wavepacket motion and 1D and 2DES spectra predicted by this model with (CI model) and without (noCI model) this coupling term. Furthermore, in order to assess the contribution of the torsional mode to the wavepacket motion, we also consider a harmonic oscillator (HO) model where this mode is neglected. The above assumption that the CI occurs close to the Franck–Condon region is important as this ensures that the dynamics near the crossing point and the Franck–Condon region are governed by the same effective Hamiltonian, specifically by the same value for λ .

Throughout this Letter, we use the parameters presented in Table 1. In the part of the paper where we present a more detailed study of the dependence on λ , this parameter is left free (Figure 4b and corresponding text) but all other parameters are kept at their values of Table 1. It is to be noted that a different value for E_1 is used for the CI, noCI, and HO models, so as to keep the vertical excitation energy at $q = 0$ fixed. To obtain the vibrational wavepacket motion, we numerically integrated the Schrödinger equation to obtain the wave function $\Psi(\theta, q, t)$, which in turn was used to calculate the spectra. Details are presented in the Supporting Information (SI).

Table 1. Parameters of the CI, noCI, and HO Models^a

		CI model	noCI model	HO model
torsional mode θ	Γ^{-1}	28.06×10^{-4}	28.06×10^{-4}	
	W_0	3.56	3.56	
	W_1	1.19	1.22	
	E_0	0.0	0.0	0.0
	E_1	2.58	2.61	2.48
coupling mode q	ω	0.19	0.19	0.19
	κ	0.19	0.19	0.19
	λ	0.19	0.00	0.00

^aAll quantities are given in eV.

We begin by analyzing the coherent wavepacket generated in the adiabatic excited-state PES reflected in 1D spectroscopy. Figure 1b shows the 1D spectra for the CI, noCI, and HO models. As is observed, the spectra are dominated by the Franck–Condon vibrational progression of the coupling mode q . This can be seen when comparing the spectra obtained from the HO model with those obtained from the CI and noCI models. However, Figure 1b reveals a notable difference in the distance between the peaks; the CI model shows a peak progression of 1669 cm^{-1} , while for the noCI and HO models this quantity is 1532 cm^{-1} ; the latter equals the bare frequency ω of the coupling mode (0.19 eV).

To get deeper insight into the observed progressions in the spectra, we analyze the time-dependent linear response function $R(t)$ ^{64,65} (Figure 1c) and the expectation value for the coordinate of the coupling mode (Figure 2) after impulsive

Figure 2. Time evolution of the expectation value of the position for the coupling mode in the excited-state PES. The expectation value is computed as $\langle \hat{q} \rangle = \langle \Psi(\theta, q, t) | \hat{q} | \Psi(\theta, q, t) \rangle$.

excitation to $|S_1\rangle$ at $t = 0$. Figure 1c shows that the linear response in the time domain decays to zero within 30 fs in all cases. During this time, in both the CI and noCI models, 100% of the electronic state population is in the adiabatic excited state and the whole system is still in the cis conformation (see SI Figure S1). In addition, up to 30 fs, the probability densities along the torsional mode are identical for these models (SI Figure S2). The concordance between the results for the CI and noCI models during the first 30 fs confirms that the wavepacket in the CI model does not pass through the CI during that time yet. In Figure 2, we display the expectation value of the coupling mode position $\langle \hat{q} \rangle$, which monitors the coherence of the vibrational motion.^{34,51} It is apparent from Figure 2 that in the noCI model the expectation value of $\hat{q}$ oscillates periodically with constant amplitude. By contrast, in the CI model, it is damped, which is a result of the vibrational dephasing process.^{7,34} The coherent oscillation in Figure 2 is

fitted to the sinusoid function $A \sin(Bt + \phi) + P$, where A , B , ϕ , and P are the free parameters of the fit (see SI Table S1). In the noCI model, the oscillations yield a constant period of 21.77 fs (1532 cm^{-1}), in accordance with the bare frequency ω of the coupling mode. However, in the CI model, the oscillation period of the coupling mode before reaching the CI region (0–30 fs) is different from that obtained after the system passes through the CI (40–85 fs). Here, we focus on analyzing the wavepacket before passing through the CI because after passing through the CI, part of the wavepacket goes to the trans conformation and part goes to the cis conformation of the adiabatic ground state. Thus, on this longer time scale, the oscillations show complex behavior. Before passing through the CI, the oscillation has a frequency of 1656 cm^{-1} , which closely matches the vibrational progression of 1669 cm^{-1} observed in the 1D spectra. We conclude that the peak progression observed in Figure 1b reflects the vibrational coherence of the coupling mode in the adiabatic excited state of the cis conformation.

We next turn to identifying the vibrational coherence associated with the cis conformation in the adiabatic ground state. To this end, we study the 2DES as a function of the population (delay) time t_2 . In a system with two electronic states and a CI, the 2D spectrum at early delay times is dominated by the ground-state bleach (GB) and stimulated emission (SE). Because the SE overlaps with the GB, it is difficult to extract the GB from the full 2DES at this time scale. After the system passes through the CI, the 2D spectrum has GB and photoinduced absorption (PA) contributions. The latter arises from the formation of the photoproduct in the ground state^{66–68} (i.e., the trans conformation) and is separated from the GB signal. This allows one to extract the GB signal, which carries information about the vibrational coherence in the adiabatic ground state of the cis conformation, from the full 2DES. Figure 3a displays the 2DES for the CI model at $t_2 = 60$ fs (i.e., after the isomerization). We observe negative features corresponding to characteristic absorption bands of the trans isomer and positive features related to the bleaching of the ground-state absorption of the cis isomer. Figure 3b shows the intensity of the diagonal and lower off-diagonal peaks as a function of t_2 . The quantum beat signal in Figure 3b was analyzed by fitting the data to the sinusoid function $A \sin(Bt + \phi) + P$ (see SI Table S2). We found that in the CI model the oscillations have an average period of 22.7 ± 0.2 fs ($1468.9 \pm 12.3\text{ cm}^{-1}$). This value is red-shifted compared to the value of 1669 cm^{-1} obtained from the 1D spectra. Analyzing the peak dynamics of the rephasing and nonrephasing GB spectra (Figure 3c,d), it turns out that these have oscillations with a period of 23.0 ± 0.8 fs ($1448.1 \pm 45.5\text{ cm}^{-1}$). This period agrees with the one obtained from the full 2DES, thereby strongly suggesting that the oscillations observed in Figure 3b reflect the vibrational coherences of the cis isomer in the adiabatic ground state. In the noCI model, however, the peak dynamics deduced from the GB spectra turns out to have a period of 21.77 fs (1532 cm^{-1}), which is identical to that generated from the 1D spectra.

To reveal the source of the frequency change in the CI model between the ground and excited states, we analyze the adiabatic PES. In the CI model, the PES is obtained by diagonalizing the diabatic Hamiltonian numerically. For simplicity, we consider $\theta = 0$ and fit the adiabatic PES of the coupling mode to the HO form $\frac{\omega}{2}(q + a)^2 + Y$, where ω , a , Y

Figure 3. (a) Calculated 2DES at $t_2 = 60$ fs; the rectangles define the diagonal and lower off-diagonal peaks. (b) Intensity of the diagonal and lower off-diagonal peaks as a function of waiting time. (c) Rephasing contribution to the GB spectra. (d) Nonrephasing contribution to the GB spectra. The waiting time was probed with 5 fs intervals, and the coherence times (t_1, t_3) were sampled using 0.5 fs intervals. The solid curves are the numerical results, while the dashed curves represent the fits to a sinusoid function.

are free parameters of the fit. In the noCI model, the frequency of the coupling mode in both the ground and excited state is the same at 1532 cm^{-1} , which is in line with the above results. In the CI model, the frequency of the coupling mode in the adiabatic ground state is 1316 cm^{-1} , and in the excited state, it is 1749 cm^{-1} . Given the fact that we assumed $\theta = 0$ and neglected anharmonic terms, these values agree quite well with those obtained from the 2DES ($1468.9 \pm 12.3\text{ cm}^{-1}$) and the 1D spectra (1669 cm^{-1}). These results confirm that the interstate coupling distorts the PES connected with the

coupling mode, resulting in different vibrational frequencies for this mode on the two electronic PESs involved.

It is easy to see that the interstate coupling term, $V_{01} = V_{10} = \lambda q$, causes the observed frequency shifts by changing the curvatures of the ground- and excited-state PESs in opposite ways. To this end, consider the PES schematically drawn in Figure 4a. For every q , the interstate coupling between the

Figure 4. (a) Adiabatic ground- and excited-state PESs of the coupling mode illustrating the changes of the potential surface. The solid curves are the PESs for the case where the interstate coupling $V_{01} = \lambda q$ is included, while the dashed–dotted curves are the PESs when this coupling is ignored. (b) Effective frequencies of the coupling mode in the electronic ground and excited states of the reactant as a function of the interstate coupling constant, λ . The red dashed–dotted curves indicate the analytical results obtained for $\theta = 0$. The blue dashed curves are the results obtained from the fitted PES assuming $\theta = 0$. The black dot and diamond represent, respectively, the frequencies obtained from the calculated linear absorption spectrum and 2DES for the λ value used in Figures 1–3.

ground and excited state mixes both electronic terms and repels them, like in a coupled two-level system. Because the coupling magnitude increases with q (i.e., away from the minima), also the coupling-induced level repulsion increases away from the minima. Thus, the ground-state PES flattens (i.e., gets a smaller curvature), while the excited-state potential gets steeper. This qualitatively explains the opposite shifts in the vibrational frequencies for the ground and excited states in the CI model.

The above suggests that the frequency difference of the coupling mode in the adiabatic ground and excited states of the reactant should provide information about the interstate coupling constant, λ . To confirm this, we investigate the dependence of the frequency difference on λ . Assuming that $\theta = 0$, the adiabatic PES in the CI model can be derived analytically, which basically boils down to solving the above-mentioned coupled two-level system with the particular shapes of the PES and the particular interstate coupling chosen here. This is done in the SI section 4, where an analytical solution is obtained by making the harmonic approximation. We find that the adiabatic PES can be written as

$$\varepsilon_- = E_0 + \left[\omega - \frac{2\lambda^2}{E_1 - E_0} \right] \frac{\hat{q}^2}{2} \quad (2a)$$

$$\varepsilon_+ = E_1 + \kappa\hat{q} + \left[\omega + \frac{2\lambda^2}{E_1 - E_0} \right] \frac{\hat{q}^2}{2} \quad (2b)$$

Accordingly, the frequency difference between the coupling mode in the adiabatic ground state ($\omega_{\text{gs}}^{\text{vib}}$) and that in the adiabatic excited state ($\omega_{\text{ex}}^{\text{vib}}$) reads

$$\omega_{\text{ex}}^{\text{vib}} - \omega_{\text{gs}}^{\text{vib}} = \frac{4\lambda^2}{E_1 - E_0} \quad (3)$$

For our model parameters, the frequencies derived from eq 2 (1307, 1758 cm^{-1}) are in good agreement with those obtained from the fitted adiabatic PES of the coupling mode assuming $\theta = 0$ (1316, 1749 cm^{-1}). Figure 4b shows the comparison between the analytical result, eq 2, (red dashed-dotted curves), and results obtained from fitting the numerically calculated PES for $\theta = 0$ (blue dashed curves). The two are in good agreement, confirming the validity of the approximations made to derive the analytical results. The two black symbols denote the results obtained from our full simulation of the 1D and 2DES spectra. We observe that the analytical results for the simplified model with $\theta = 0$ predict shifts with the correct sign and of the right order of magnitude. Evidently, the vibrational frequencies are very sensitive to the interstate coupling term. This is in line with a previous theoretical study of the resonance Raman spectrum of pyrazine.^{69,70} Here, we find that by measuring the vibrational frequencies of the reactant in the adiabatic ground and excited states as well as the electronic excitation energy, we can qualitatively estimate the value of the coupling constant λ between the electronic states using eq 3. Quantitative determination of λ requires explicit numerical simulations of the spectra as performed here. Then, by comparing the nuclear coherences obtained from the numerical simulations with those measured experimentally, one can determine the value of λ that matches the vibrational coherences observed in the experiment.

Our results call for experiments where the vibrational frequency is measured in the electronic ground and excited states of the reactant in a photoisomerization process. Currently, we are not aware of such experiments. An example that comes close are experiments on Rhodopsin (Rh), where the frequency of the local ethylenic stretching mode in the retinal, the coupling mode, was measured in the excited state of the reactant (Rh) and the ground state of the product (Batho-Rh).^{19,45,46} As we show in section 5 of the SI, an analogue of eq 3, which assumes that the fundamental frequency of the coupling mode is identical for Rh and Batho-Rh, then yields $\lambda = 0.03$ eV. This result should be considered with caution as we are aware that this assumption at best is approximate.^{28,62}

In conclusion, by employing model calculations, we have presented a new tool to estimate the interstate coupling in a system with cis–trans isomerization. By using a simple two-state model and assuming that the Franck–Condon point is near the CI, we have shown that the interstate coupling can be determined from the difference in the effective frequency of the vibrational coupling mode between the adiabatic ground and excited states in the cis (reactant) conformation. This difference may be detected by using a combination of linear and 2D spectroscopy, as we have considered; on the other hand, alternative experimental techniques, such as Raman,^{19,47,49,70} and pump–probe^{14,45,46,48,71,72} spectroscopy may be used

equally well. We found that the vibrational frequency difference between the ground and excited states can be used to qualitatively estimate the interstate coupling strength using a simple analytical formula. To get a quantitative value, explicit quantum simulations of the experiment as performed here will be required. The potential to determine the interstate coupling from experiment will provide critical information to test accurate ab initio based models for CIs, where the coupling term is key to the PES shape.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01463.

Computational details, expressions for the population dynamics and the linear and two-dimensional spectra, analysis of the cross-peak dynamics of the noCI model, analytical derivation of the adiabatic potential energy surface, and tables with all fitted parameters (PDF)

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Notes

The authors declare no competing financial interest.

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