

Quantum Control of Ultrafast Internal Conversion using Nano-Confined Virtual Photons

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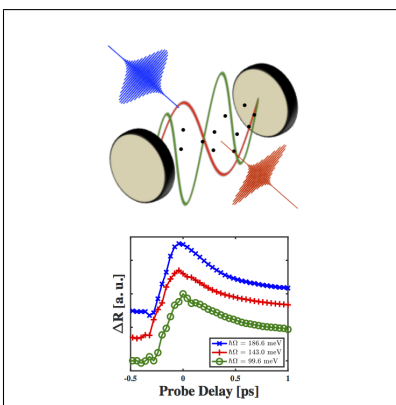
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Abstract

The rational control of non-radiative relaxation remains an unfulfilled goal for synthetic chemistry. In this study, we show strongly coupling an ensemble of molecules to the virtual photons of an electromagnetic cavity provides a rational handle over ultrafast, non-radiative dynamics. Specifically, we control the concentration of zinc tetraphenyl porphyrin molecules within nano-scale Fabry-Perot cavity structures to show a variable collective vacuum Rabi splitting between the polaritons coincides with changes in internal conversion rates. We find these changes obey a power law dependence on the collective vacuum Rabi splitting, but deviate from the predictions of so-called gap laws. We also show simple theories of structural changes caused by polariton formation cannot explain discrepancies between our results and established theoretical predictions. Our results demonstrate a mechanism by which cavity polariton formation controls the fundamental photo-physics of light harvesting and photocatalytic molecular moieties and the gap remaining in our fundamental understanding of these mechanisms.

Graphical TOC Entry



Introduction

Relaxation is the most important step in determining the utility of a light absorbing or emitting substance. The presence of insufficient non-radiative relaxation from a highly absorbing electronic state to a lower lying state more capable of forming a desired chemical product or emitting a desired photon can inhibit the applicability of specific molecules and materials for next generation photo-chemical and opto-electronic platforms. Given this reality, the ability to control non-radiative relaxation mechanisms remains a potentially transformative goal.

Despite the need to control relaxation processes, especially on ultrafast time scales, traditional chemical methods using solution or solid phase synthesis remain incapable of deterministically controlling these processes. In specific cases of metal-centered complexes designed for photocatalytic and opto-electronic technologies, studies show the rate of non-radiative relaxation can be controlled by modulating the gap between participating electronic states.¹⁻³ What remains unclear, however, are hard and fast rules quantitatively connecting synthetic principles, such as the Hammett parameter, with changes to these energy gaps. Since we lack the ability to accurately predict relationships between the structures and dynamics of specifically targeted molecules these connections do not exist. Furthermore, even with the clarification of these connections it is not clear synthetic methods have been developed to produce such molecular targets with sufficiently high yields. In the absence of traditional synthetic methods to control the energy flow between molecular states with deterministic precision we seek alternative strategies to manipulate ultrafast relaxation dynamics central to potentially transformative advances in photo-catalytic and opto-electronic applications.

The strong coupling of light to material electrons leads to the formation of hybrid light-matter states known as polaritons whose energies separate by a gap proportional to the coupling strength known as the vacuum Rabi splitting, $\hbar\Omega$.⁴ When one embeds molecules into a sufficiently high quality electromagnetic resonator, the molecular electrons can strongly couple to a quantum mechanically fluctuating, virtual photons within the resonator's shaped photonic density of states and form *cavity polaritons*. Despite being first demonstrated over 20 years ago,⁵ the effects of cav-

ity polariton formation on the ultrafast relaxation processes of complex molecules central to their potency in photochemical applications remain unclear.

The large transition dipole moment of the Soret transition of metalloporphyrins has made these systems ideal choices for light harvesting,⁶⁻⁸ electron and energy transfer,⁹ and artificial photosynthesis¹⁰⁻¹² whose primary physical processes include non-radiative relaxation on ultrafast time scales. However, an incomplete understanding of how polariton formation in nanoscale cavities affects these ultrafast relaxation processes inhibits the rational design of resonator structures to control photo-physical and photochemical processes of this well established class of molecules using quantized virtual photons. Most importantly, it still remains unclear whether cavity polariton formation changes the electronic and nuclear structure of strongly coupled molecules central to their photochemical reactivity, as predicted by theory.¹³⁻¹⁸ In this study we demonstrate polariton formation can be used to deterministically control ultrafast internal conversion rates between the excited singlet states of zinc tetraphenyl porphyrin (ZnTPP), a model system for light harvesting and energy transfer moieties. Moreover, these results do not conform with the canonical theory of non-radiative relaxation.

The collective coupling of the quantum mechanically fluctuating virtual photons of an electromagnetic resonator to cavity-embedded molecules provides a powerful handle over the vacuum Rabi splitting between the polariton states.⁴ Specifically, as one loads more molecules into the cavity structure, one can increase the vacuum Rabi splitting by a known amount for a given cavity length.⁵ For the case of ZnTPP, this increasing vacuum Rabi splitting will drive the energy of lower polariton closer to that of the first excited singlet state, S_1 . As we show below, this collective, quantum mechanical control over the energy gap between these states translates directly into control over the rate of ultrafast relaxation between them.

The left panel of Figure 1 compares the linear absorption spectrum of a ~ 200 nm poly(methyl methacrylate) (PMMA) film doped with ZnTPP to the transmission spectrum of Fabry-Perot cavity structure containing a ~ 140 nm, ZnTPP-doped PMMA film embedded within it. The cavity structure was fabricated as described in the Methods section below. For the case of Figure 1, the

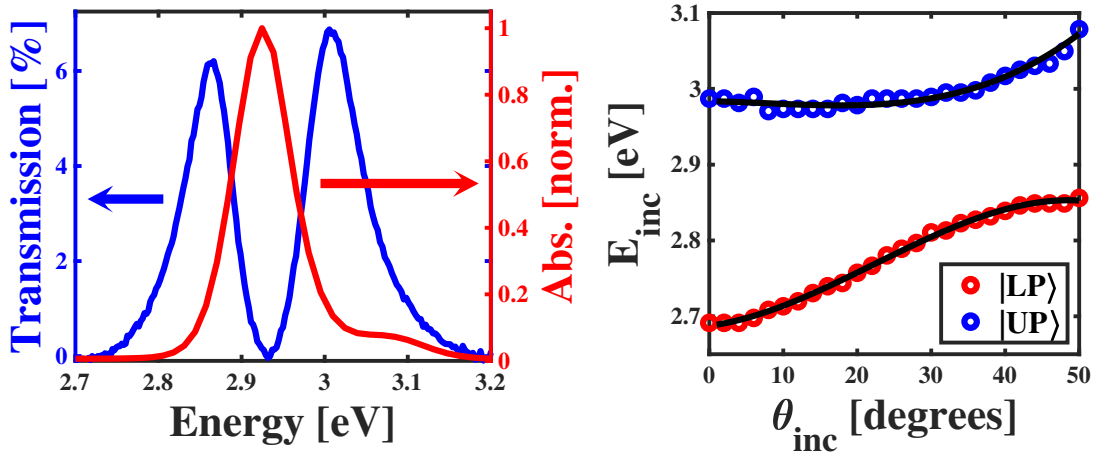


Figure 1: Left panel: comparison of the linear UV-vis absorption spectrum a PMMA film doped with ZnTPP in the region of the molecule’s Soret resonance (red) to the transmission of the Fabry-Perot cavity structure described in the text at 44° (blue) possessing a Rabi splitting energy of ~ 186.6 meV. Right panel: comparison of the dispersion of the energy of the lower polariton ($|LP\rangle$) to that of upper polariton ($|UP\rangle$) observed by changing the angle an incident beam makes with surface normal of the cavity structure.

incident beam makes an angle of 44° with respect to the cavity structure’s surface normal. Unlike the single, prominent Soret peak and small blue-shifted shoulder of the linear absorption spectrum of the free space film, Figure 1 shows the cavity transmission spectrum possesses two peaks corresponding to the upper and lower polaritons. The slightly higher intensity of upper polariton peak suggests we detuned the cavity to the blue side of the Soret resonance of ZnTPP at this incident angle. The right panel of Figure 1 shows the avoided crossing in the dispersion of the loaded cavity structure as we tune through different incident angles. At the angle shown in the left panel of Figure 1, we find the vacuum Rabi splitting energy between the polaritons is 186.6 meV. Figure S1 of the Supporting Information (SI) shows as we reduce the concentration of the ZnTPP in each cavity structure, the Rabi splitting also reduces. As shown in Figure S1, at a film concentration near 15 mM we can still resolve distinct cavity polariton peaks separated by a Rabi splitting of 99.6 meV.

To assess the ability of cavity polariton formation to control the ultrafast relaxation dynamics of strongly coupled ZnTPP molecules, we undertook measurements of the ultrafast dynamics of solution-phase molecules and cavity polariton samples. We pump both types of samples at 3.10 eV (400 nm) and compare their dynamical response at 1.970 ± 0.015 eV (630 ± 10 nm). Zewail

and co-workers observed a transient absorption signal in this spectral window whose initial decay matches that of the internal conversion from S_2 to S_1 in solution phase ZnTPP molecules, as established from their time-resolved photoluminescence measurements following 3.12 eV (397 nm) excitation.¹⁹ In the case of our cavity polariton measurements, the 3.1 eV pump pulse either directly excites the upper polariton for the largest values of the vacuum Rabi splitting we examine or excites the sample just above the upper polariton. Given previous studies, excitation above the upper polariton should engage the polariton dynamics.^{20,21} However, by probing an excited state absorption process off resonance with polaritonic transitions, we are not sensitive to intra-polariton relaxation processes and can instead focus our attention on how polariton formation affects ultrafast conversion into non-polaritonic states. This approach contrasts with previous studies. Lidzey and co-workers previously examined the dynamics of ZnTPP in similar cavity polariton samples,²² but they pumped the lower polariton only for a single vacuum Rabi splitting value and did not compare their results to those found from solution-phase measurements.

The data in Figure 2 show the ultrafast reflectivity of the cavity polaritons formed using ZnTPP depends not only polariton formation, but also on the strength of the coupling between the molecules' Soret resonance and the cavity's virtual photons. Specifically, Figure 2 shows as we increase the collective Rabi splitting by concentrating more ZnTPP in the cavity, the initial time scale of each kinetic trace reduces. The transient absorption we measured for solution phase ZnTPP molecules is shown in Figure S2 of the SI. To establish a quantitative trend between the ultrafast internal conversion time scale and the collective Rabi splitting of the cavity polariton we form, we fit each trace using a multiple exponential model after deconvolving the Gaussian intensity feature due to the temporal overlap of the pump and probe pulses. We shown comparisons between fits to these model functions and the experimentally measured kinetic traces in Figure S3 of the SI. Given the work of Zewail, we correlate the fastest time scale with the internal conversion from the optically excited state into the first excited state of ZnTPP, S_1 . Lidzey and co-workers show the intrapolariton relaxation should occur at significantly higher rates than those we find in this analysis,²³ which suggests we do not probe that relaxation process as expected from our

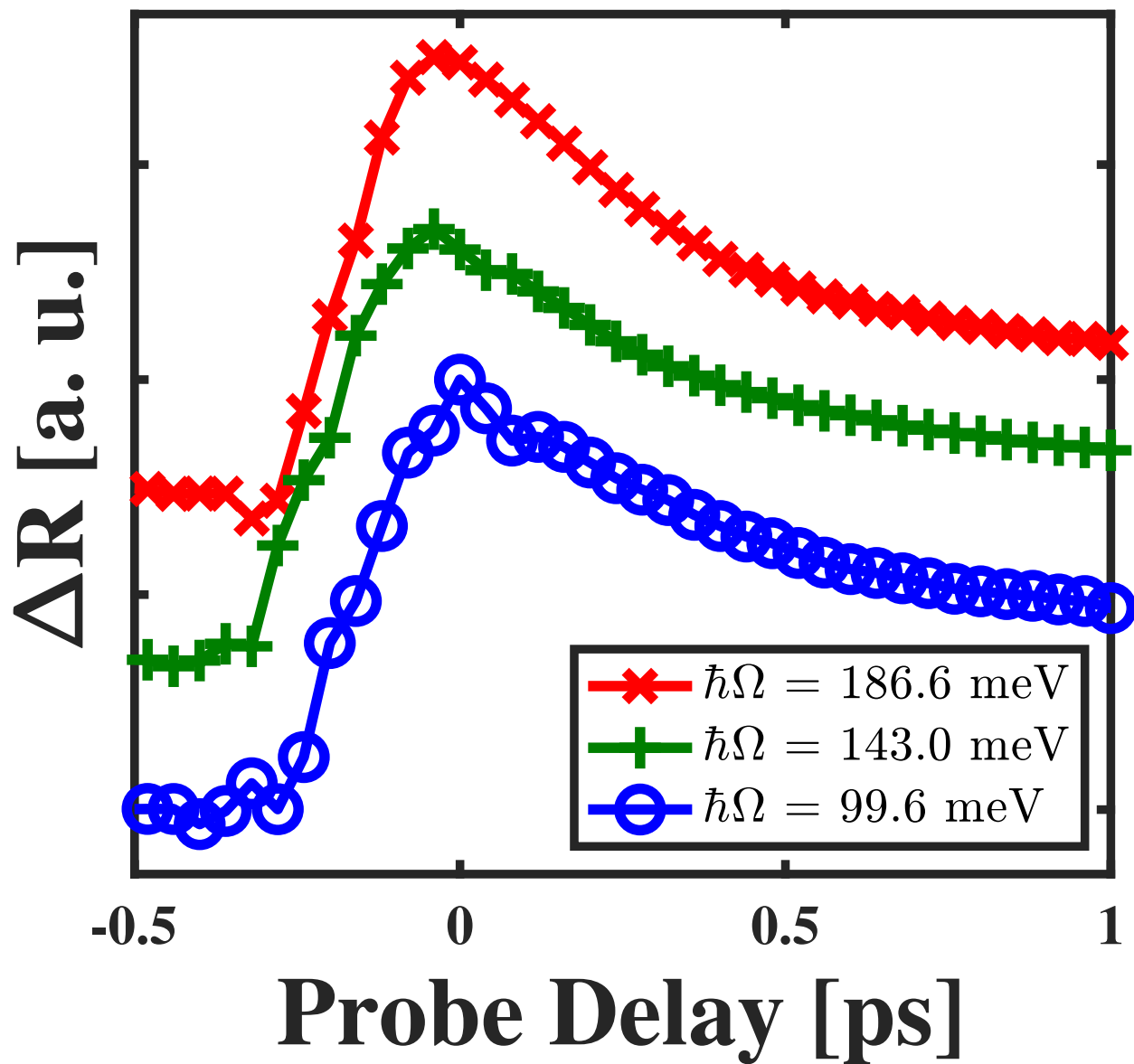


Figure 2: Comparison of the ultrafast transient reflectivity of the 1.970 ± 0.015 eV band of a white light continuum probe pulse from a zinc tetraphenyl porphyrin cavity polariton sample following 3.1 eV excitation for a Rabi splittings of 186.6 meV (blue), 143 meV (red), and 99.6 meV (green) for the probe delay window between -0.5 ps and 1 ps. The kinetic traces have been offset vertically to more easily compare them visually.

experimental design.

Figure 3 shows the results of our nonlinear regression analysis of measured transient reflectivity

traces schematically. In particular, we find an increase in the internal conversion rate as the energy gap between the collective lower polariton state and the S_1 state of individual ZnTPP molecules reduces. This increase in the internal conversion rate upon polariton formation can be modeled by assuming the total rate is the sum of two terms: one term due to relaxation of the free space molecules and another due to polariton formation using a test function of the vacuum Rabi splitting, $\hbar\Omega$, we write as,

$$k_{IC} = k_{IC}^{cp} \left(\frac{\hbar\Omega}{2E_0} \right)^P + k_{IC}^0. \quad (1)$$

In Eq. (1) k_{IC}^0 is the internal conversion rate of the free space molecules, which is determined from the nonlinear regression analysis detailed above, k_{IC}^{cp} is the rate of polariton-induced internal conversion and E_0 and P parametrize this additional decay channel. Figure 4 shows the results of modeling the observed internal conversion rates using Eq. (1) with the uncertainties in rate constants shown as error bars. Through this analysis we find model values of $k_{IC}^{cp}=0.3018 \text{ ps}^{-1}$, $E_0=0.05781 \text{ eV}$, and $P=3.449$.

Despite the sufficient fit of the model in Eq. (1) to the measured internal conversion decay rates shown in Figure 4, this model still lacks a basis in microscopic physics. Several authors developed theoretical descriptions of the dominant determinants of non-radiative relaxation between the electronic states of large molecules.²⁴⁻²⁹ In particular, Jortner and several co-authors developed theories explaining the rate of non-radiative relaxation between the excited electronic states of aromatic molecules, like metalloporphyrins.²⁷⁻²⁹ In their most prominent theory, these authors proposed the non-radiative rate obeys a relationship dependent on the energy gap between involved states, written as,

$$k_{IC} = \frac{C^2 \sqrt{\pi}}{\hbar \sqrt{\hbar\omega_\nu \Delta E}} \exp \left(-\Delta E / \hbar\omega_\nu \left\{ \log \left[\frac{2\Delta E}{\hbar\omega_\nu \Delta_\nu^2} \right] - 1 \right\} \right), \quad (2)$$

where the terms C is the non-adiabatic coupling between the electronic states due to the nuclear kinetic energy operator, ω_ν is the frequency of a vibration involved in the non-radiative transition,

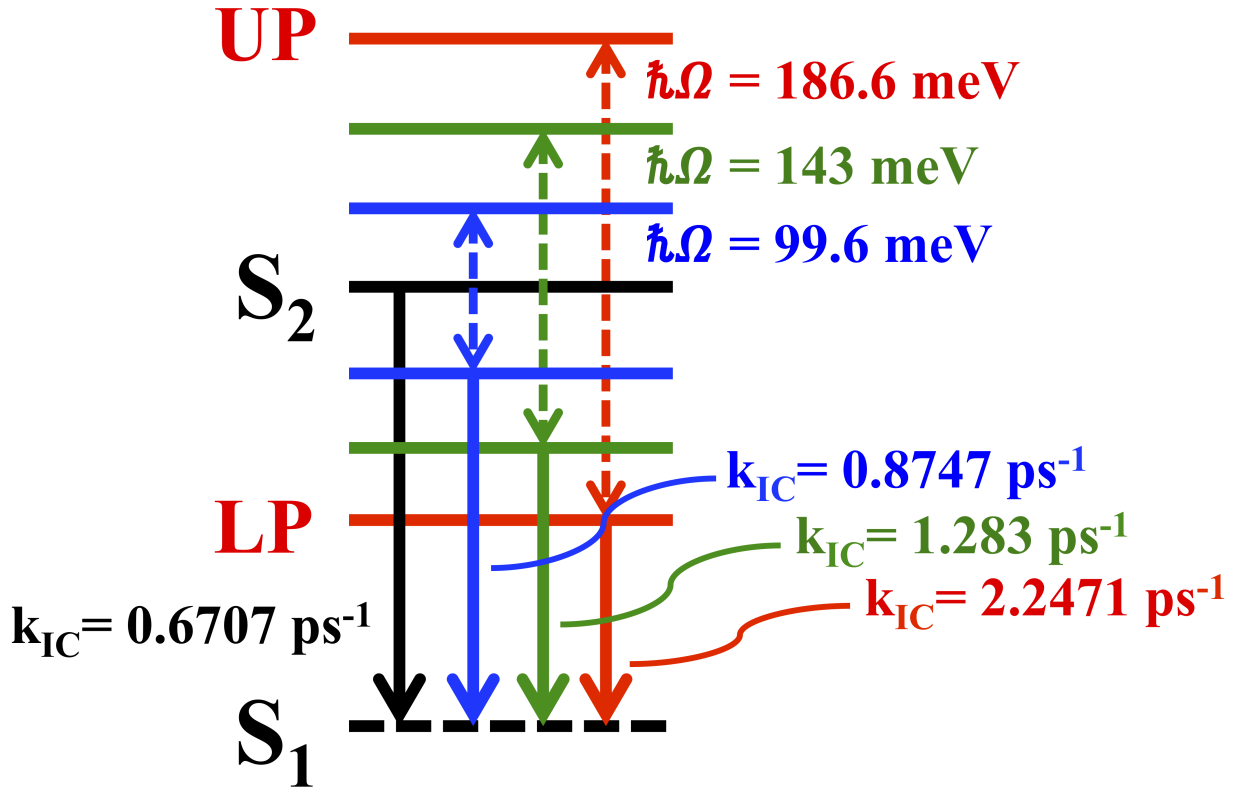


Figure 3: Schematic representation of the change in the ultrafast internal conversion decay rate, k_{IC} , as a function the value of the Rabi splitting between the energies of cavity polaritons formed using the Soret transition of zinc tetraphenyl porphyrin (ZnTPP) molecules. As we reduce the energy gap between the S_2 and S_1 states of solution phase ZnTPP molecules (black) with polaritons separated by 99.6 meV (blue), 143 meV (green), and 186.6 meV (red) k_{IC} increases to the color-coded values reported in the schematic.

Δ_ν is the dimensionless displacement between the two involved states along that vibration, and ΔE is the energy gap between the ground vibrational states of each respective electronic manifold.

In addition to its direct dependence on ΔE , Eq. (2) suggests the time constant of internal conversion stems from two separate, but related nuclear structural effects. First, since internal conversion must occur via the excited vibrational states of the lower lying electronic manifold, the overlap of the vibrational states, known as Franck-Condon factors, between the different manifolds also controls the time constant. In the case of large structural differences between the involved electronic states, significant Franck-Condon factors exist between the lowest lying vibrational state of relaxing electronic manifold and highly excited vibrational states of its electronic counterpart.

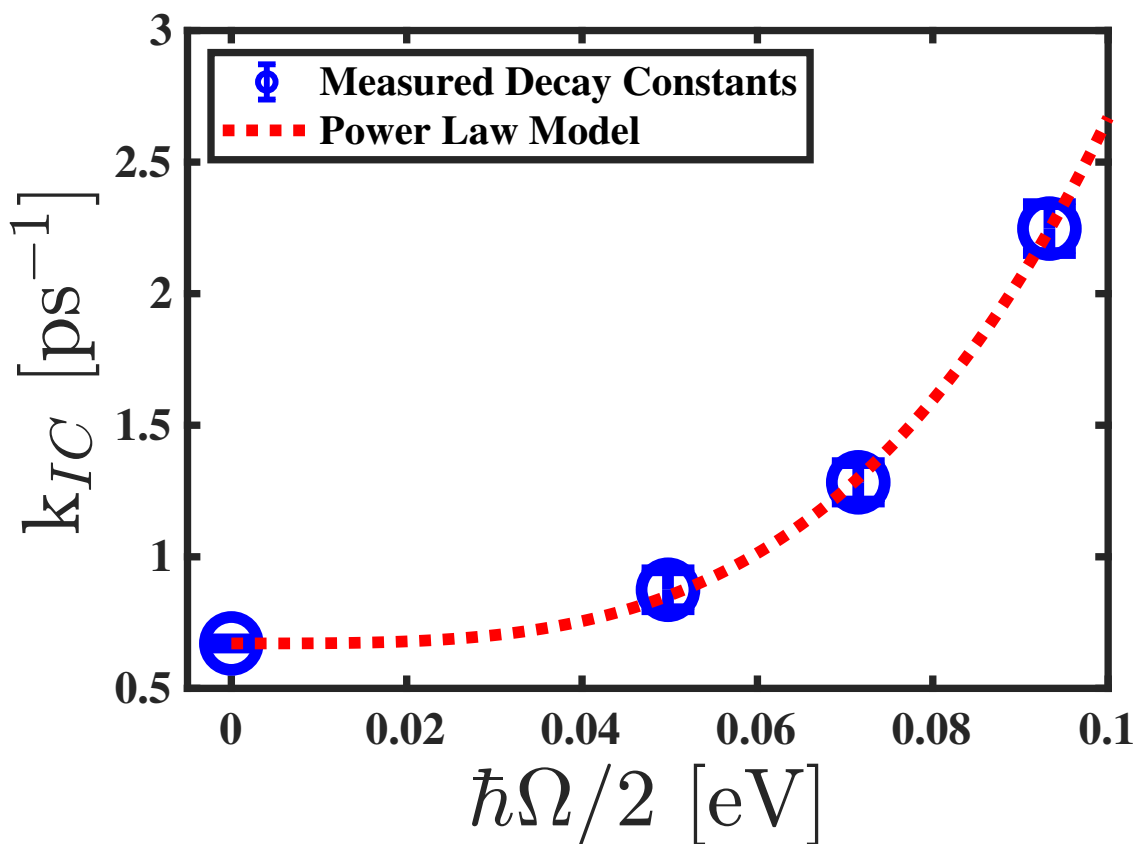


Figure 4: Comparison of the trend in measured internal conversion time constants for solution phase and strongly cavity-coupled ZnTPP molecules to a power law fit using Equation (1).

Second, internal conversion necessitates a coupling between electronic states mediated by a change in the nuclear structure of each state along a participating vibrational coordinate, as captured by the quantity C . For large changes in structure, states couple more strongly together via the Franck-Condon mechanism and the non-radiative relaxation process needs a smaller value of C to occur. For smaller changes in nuclear structure, the Franck-Condon factors are smaller and a larger value of C is needed to induce non-radiative relaxation. Despite the known importance of the dependence of the internal conversion time constant on these characteristics of the involved electronic states, their interdependence with the energy gap and their inaccurate prediction via ab initio methods inhibits using Eq. (2) as a guide towards controlling internal conversion time scales via traditional synthetic methods.

Since we seek to establish a fundamental physical understanding of how the quantum fluc-

tuations of cavity-confined photons affect ultrafast non-radiative relaxation, we also modeled the internal conversion time constants as a function of the energy gap between the S_1 state of ZnTPP and either the S_2 or the lower polariton, depending on the specific sample, as described in Eq. (2). In this model we presume the vibration of interest is a ring distortion possessing an effective frequency of 1190 cm^{-1} ($\hbar\omega_\nu = 0.1475\text{ eV}$), given the separation of the peaks of the linear absorption spectrum shown in the left panel of Figure 1. We also presume the energy of the S_1 state remains the same value relative to the molecule’s ground as we change the collective vacuum Rabi splitting. Figure 5 shows the results of this modeling. Through the modeling we find the time scales of each of our samples do not match the expected trend based on Eq. (2). In particular, we extract out values of 2.573 eV and 0.00881 for C and Δ_ν , respectively. Analysis of the UV-vis absorption spectrum of ZnTPP suggests S_2 possesses $\Delta_\nu = 0.1538$ relative to S_0 . Given many authors conclude the S_0 and S_1 states possess the same equilibrium structure, this displacement would also refer to that of the S_2 relative to S_1 , which is a factor of two larger than the value found from modeling the internal conversion rates with Eq. (2). When we consider the possibility internal conversion occurs via C-H stretching vibrations at 3300 cm^{-1} (0.41 eV), the values extracted from our model change to $C = 6.724\text{ eV}$ and $\Delta_\nu = 0.0003157$ with no significant improvement in the resulting fit to the measured data, as shown in Figure S4 of the SI.

The results of our analysis shown in Figure 5 suggest some physical parameter of cavity polariton formation besides the energy gap between the participating electronic states affects the internal conversion rate. Two facets of the effect of cavity polariton formation emerge as possible explanations for the deficiency of the standard theory based solely on energy gaps. First, it is possible the formation of cavity polaritons not only changes the energies of the polariton states themselves, but also the energies of closely lying electronic states of the strongly coupled molecules. To test this idea, we measured the steady-state fluorescence emitted by the S_1 state following excitation at 532 nm , as shown in Figure S5 of the SI. Given the lack of any significant shifts in the peak positions of these spectra, these results suggest cavity polariton formation does not affect the energy of the S_1 relative to that of the ground state, S_0 . Therefore, even though we systematically push the energy

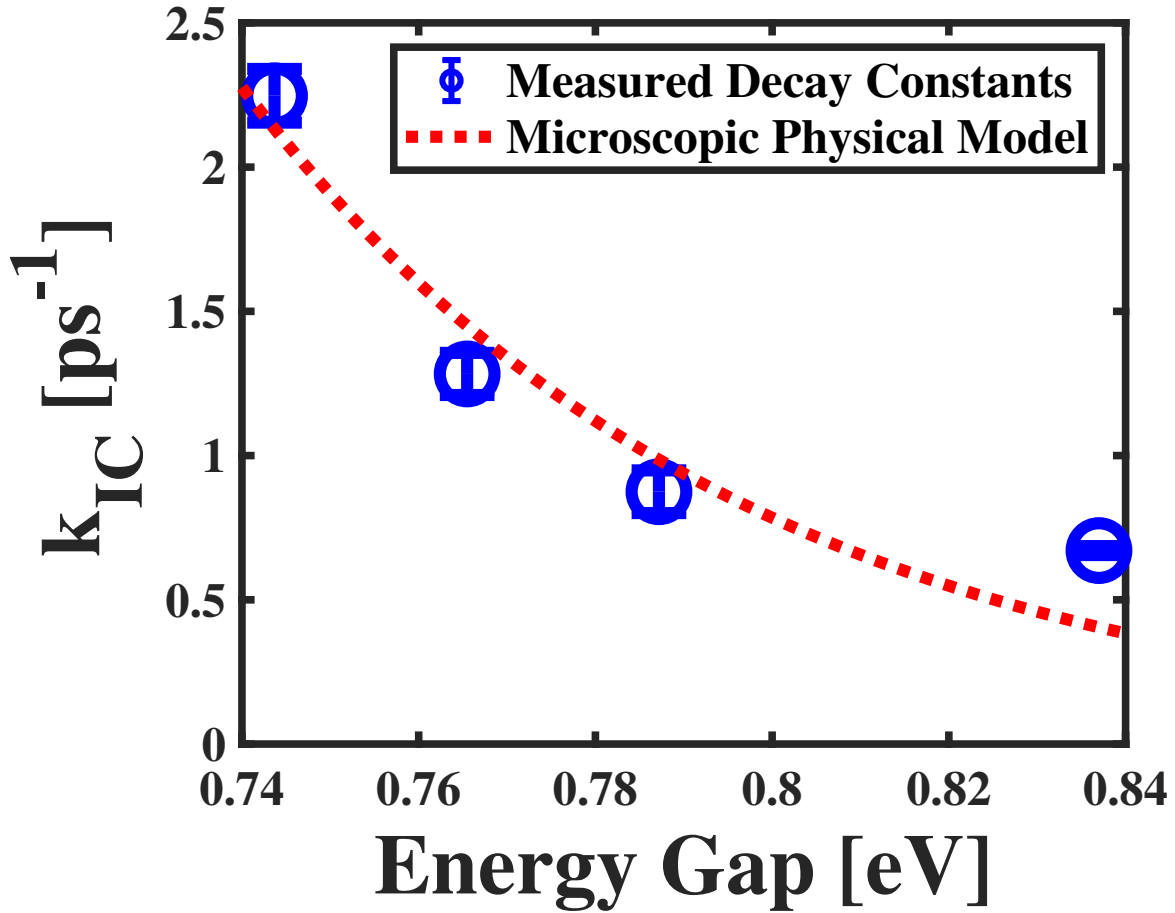


Figure 5: Comparison of the trend in measured internal conversion time constants for solution phase and strongly cavity-coupled ZnTPP molecules to a microscopic model developed by Jortner and co-workers, as described explicitly by Equation (2).

of the lower polariton state closer and closer to that of the S_1 , there does not seem to be evidence the S_1 energy changes as a function of the collective Rabi splitting.

Second, a fundamental interpretation of physical parameters in Eq. (2) suggests any changes induced in the equilibrium structure of a molecule induced by polariton formation could play a significant role in the observed dynamics. Specifically, the direct dependence of the internal conversion rate on the dimensionless displacement, Δ_ν , could be a route to polaritonic control of molecular dynamics based on the results of previous theoretical studies.^{13–18} To assess this idea, we phenomenologically investigated changes to Δ_ν of a single, harmonic mode induced by polariton formation within a framework proposed by Mukamel and co-workers¹⁷ we amend to consider

a polyatomic molecule.³⁰ Using this phenomenological model, we calculate how the S_2 potential energy surface changes upon polariton formation and how these changes affect Δ_ν of the lower polariton relative to the unaffected S_1 state. The parameters of these potential energy surfaces are determined from density functional theory calculations reported in our previous study.³⁰ As shown in Figure 6, this simple model does not predict a trend in Δ_ν for different collective vacuum Rabi splitting values consistent with the measured internal conversion rate constants. In particular, while our results indicate the internal conversion rates for $\hbar\Omega/2 = 0.05$ eV and 0.07 eV fall below the predictions of Jortner’s model, the Δ_ν values we find from our phenomenological model at similar collective vacuum Rabi splitting values should coincide with increases in the internal conversion rate. Based on this disagreement, we tentatively conclude structural changes like those predicted by proposed theories cannot adequately explain our experimental results. More advanced structural models of polariton formation must be developed.

In conclusion, we have demonstrated controlling concentrations of ZnTPP within electromagnetic resonator structures can be used to directly control the ultrafast internal conversion dynamics of ZnTPP molecules strongly coupled to the cavity’s virtual photons. Moreover, we showed this control depends on the energy gap between the lower cavity polariton and the S_1 state of ZnTPP. The changes in the measured ultrafast dynamics of the polaritons we form point to microscopic physics beyond the models typically used to explain non-radiative relaxation. In particular, the phenomenological model proposed by Englman and Jortner cannot adequately explain the trend in internal conversion as a function of the energy gap between the delocalized polaritonic states and localized molecular states. Given the prominence of non-adiabatic coupling mechanisms in the photophysics of metalloporphyrins, a specialized model appropriately accounting for frequency shifts and non-Condon vibronic coupling effects may be necessary to explain our results. These effects may emerge from more advanced ultrafast spectroscopic experimental in which one coherently modulates the structure of cavity-embedded molecules to directly assess how polaritonic PESs change relative to their free space counterparts.^{31–34} However, such a development is beyond the scope of the current study.

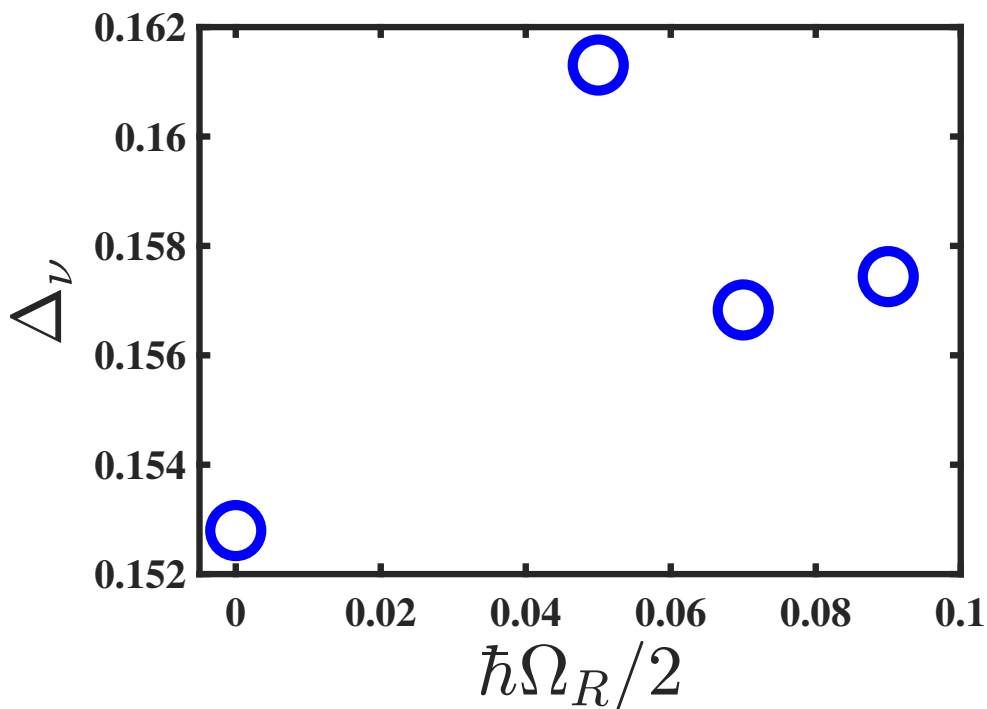


Figure 6: The numerically calculated dependence of the dimensionless displacement of the lower polaritonic potential energy surface relative to the S_1 state of zinc tetraphenylporphyrin found as a function of the collective vacuum Rabi splitting energy, $\hbar\Omega_R$. The trend found from these numerical calculations does not account for the discrepancies between our measured polaritonic internal conversion decay rates and the rates predicted by standard microscopic physical theories.

Our results indicate the ultrafast photophysics of metalloporphyrins can be controlled using cavity polariton formation and this mechanism provides unheard of precision in controlling the rates of non-radiative relaxation. Based on our straightforward approach detailed above, this control can be applied to enhance non-radiative rates in porphyrin-based nanomaterials for photocatalytic and opto-electronic applications. For example, cavity polariton formation using metalloporphyrin arrays could lead to deterministic control over the initial pathways to electron transfer and subsequent photo-catalytic activity, as pioneered by Holten *et al.*⁷

In addition to enabling control over the capabilities of porphyrin molecular moieties in materials science, cavity polariton formation can be used to disentangle the ultrafast mechanisms of energy transfer and charge separation in biologically relevant systems containing porphyrin or porphyrin-like molecular constituents such as light harvesting proteins. We envision fabricating

cavity structures similar to those we have studied here in which these biological systems are embedded with differing concentrations. The modulation of electronic energy gaps via control over the collective Rabi splitting could serve as a deterministic method to decipher the electronic states involved in non-radiative processes in tandem with methods like molecular mutations at specific sites of the biological material. With an additional handle capable of controlling the electronic structure of the light activated molecules, our results show researchers can use control over the collective vacuum Rabi splitting of cavity polariton states to enable better performance of porphyrin materials and a better understanding of porphyrins in biology.

Methods

Zinc tetraphenyl porphyrin (ZnTPP) was purchased from Sigma Aldrich and used without further purification. Thin films of poly methyl methacrylate (PMMA) were formed by spinning a commercially available solution containing the polymer (MicroChem) on the substrate of choice using a commercial spin coater (Laurell WS-650Mz-23NPPB) followed by annealing the resulting substrate/film system at 180 °C for 3 minutes to cure the film. ZnTPP was added to polymer solution prior to the spin coating process to appropriately dope the resulting film. To characterize the doped film linear absorption measurements were used, we made a 0.959 mM ZnTPP concentration PMMA solution and spun it on a clean microscope slide at 1900 rpm. The UV-vis absorption spectrum was then acquired with a Jasco-V-570 spectrophotometer.

A cavity polariton sample was formed by fabricating a custom designed distributed Bragg reflector (DBR) from alternating layers of SiO₂ and S₃N₄ on a cleaned, optical grade fused silica substrate using chemical vapor deposition. The stop band of the DBR structure was chosen to overlap with the Soret resonance of the ZnTPP, as established from UV-vis absorption measurements. We then spun samples of 1.989 mM, 0.988 mM, and 0.494 mM ZnTPP concentration PMMA solution at 5500 rpm on top of the DBR structure. Ellipsometry measurements show we form a ~140 nm film with these spin processing parameters. Following curing of the doped poly-

mer film, we deposited a ~ 15 nm film of Al over the film to form the Fabry-Perot cavity. We checked for the successful formation of cavity polaritons using angle resolved transmission measurements. The beam from a commercial halogen lamp (Thorlabs QTH10) was focused through the cavity structure at different incident angles, collected, and then detected in a fiber-coupled dispersive spectrometer (OceanOptics OceanFX).

Ultrafast transient reflectivity measurements were carried out using the 1.55 eV output of a regenerative amplified seed pulse from a Titanium-doped sapphire oscillator (Spectra Physics Solstice Ace). Part of the output was used to pump a frequency convertor to generate 3.1 eV pump pulses. Another part of the laser output was passed through a delay stage assembly, spatially filtered, and focused into a 3 mm thick sapphire plate to generate white light continuum. The white light continuum was then passed through a short pass filter with a 90% transmission edge at 1.65 eV (Thorlabs FESH0750) to reject residual intensity at 1.55 eV. The two beams were then steered to the sample and overlapped in space using a pinhole. The portion of the probe beam reflected from the sample was then steered to a Si photodiode affixed with a 30 meV wide bandpass filter centered at 1.97 eV. We angled the substrate surface to put the ZnTPP Soret transition and cavity mode in resonance when considering the pump incidence direction.

The authors declare no competing financial interests.

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