Freezing molecules with light: How long can one maintain a non-equilibrium molecular geometry by strong light-matter coupling?

Eric R. Bittner,† Rayvn A. Malatesta, Gabrielle D. Olinger, and Carlos Silva-Acuña
1) Department of Chemistry, University of Houston, Houston, TX 77204
2) School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta, GA 30332
3) Department of Physics, University of Houston, Houston, TX 77204
4) School of Physics, Georgia Institute of Technology, 837 State Street, Atlanta, GA 30332

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In molecular photochemistry, the non-equilibrium character and subsequent ultrafast relaxation dynamics of photoexcitations near the Franck-Condon region limit the control of their chemical reactivity. We address how to harness strong light-matter coupling in optical microcavities to isolate and preferentially select specific reaction pathways out of the myriad of possibilities present in large-scale complex systems. Using Fermi’s Golden Rule and realistic molecular parameters, we estimate the extent to which molecular configurations can be “locked” into non-equilibrium excited state configurations for timescales well beyond their natural relaxation times. For upper polaritons—which are largely excitonic in character, molecular systems can be locked into their ground state geometries for tens to thousands of picoseconds and varies with the strength of the exciton/phonon coupling (Huang-Rhys parameter). On the other hand, relaxed LP lifetimes are nearly uniformly distributed between 2.1 – 2.4 ps and are nearly independent of the Huang-Rhys parameter.

I. INTRODUCTION

The past few years has seen a remarkable surge in the use and application of photonic optical cavities to induce, manipulate, and modify chemical processes through strong coupling between quantized cavity photons and molecular states to form polaritons. Cavity polaritons arise from non-perturbative coupling between the strongly quantized modes of the electromagnetic fields in the optical cavity and the optical transitions of the molecular species within the cavity. These transitions can be vibrational or vibronic depending upon the tuning of the cavity.

In the absence of a cavity, the electronic transitions can described within a Franck-Condon description whereby optical transitions from the ground state to the excited state occur within a fixed nuclear frame; this is followed by relaxation/reorganization on the excited state potential to some new local minimum energy geometry and then fluorescence or non-radiative decay carries the system back to the ground state. Generally, the reorganization occurs on a timescale on the order of ps, fluorescence occurs on the order of ns, and non-radiative decay occurs on timescales the order of ns to ms. As a result, fluorescence occurs according to Kasha’s rule from the lowest lying vibronic state of the excited state potential to the ground state potential that gives rise to the vibronic fine structure readily observed these systems. There may also be other important intersystem processes competing with this, such as charge-transfer and other photophysical processes that are initiated by the relaxation from the Franck-Condon point.

FIG. 1. Energy level diagram depicting the electronic and photon excitations in the microcavity.

In a microcavity, this picture needs to be modified in number of important ways. First, the correct quantum mechanics basis includes the quantized radiation field states into the atomic or molecular basis. We denote these as |φ; n⟩ where φ denotes the material (atomic, molecular, etc.) state while n denotes the number of quanta (photons) in the k-th mode of the radiation field. Thus, a molecule in the ground state with a cavity devoid of photons would be denoted as |g; 0⟩ with energy $E_g + \hbar \omega_k$. This is depicted in Fig. 2 in which to a first approximation the electronic potential surfaces are vertically shifted in energy by $\hbar \omega_k n_k$. For clarity, we show the case for a single mode cavity with frequency $\omega_c$. If the cavity is resonant or nearly resonant with the optical transition frequency, $\omega_c$, the adiabatic potential for the |g; n⟩ (i.e. molecular ground state + n cavity photons)
base electronic states with uniform spacing \( \delta \). Here, integer \( n \) \( \in \mathbb{N} \) indexes the quasi-continuum states with uniform spacing \( \delta \). Our final results will require \( \delta \to 0 \).

We write \( \hat{W} \) as the coupling between the internal (cavity) and external states. An initially prepared interior (cavity) state will decay exponentially into the quasi-continuum of external states with time constant \( \Gamma_\phi \) as per Fermi’s golden rule (FGR)

\[
\Gamma_\phi = \frac{2\pi}{\hbar} |\langle \psi_\mu | \hat{W} | \phi \rangle|^2 \frac{1}{\delta}
\]

where \( \delta \to 0 \) is the spacing between the quasi-continuum states exterior to the cavity.

Ordinarily, the UP and LP decay rates are “inherited” from the properties of the cavity and can be written as a weighted sum of the exciton decay rate and the cavity leakage rate

\[
\Gamma_{LP} = |s_k|^2 \Gamma_{ex} + |c_k|^2 \Gamma_{cav}
\]

This implies that the lower polariton lifetime is set by the fastest decaying component which is generally the lifetime of a photon in the cavity. However, experimental studies of organic microcavity systems suggest that their polariton states are much longer lived. This can be explained within the exciton bath-model developed by Lidsey et al, the kinetics of populating the lower (emissive) polariton state is slow compared to its emission rate. Furthermore, the observed emission rates are not angle dependent, suggesting that there is sufficient thermalization of the cavity states.

Of central concern of this paper is the cavity induced (or suppressed) dynamics of the molecular species on the UL and LP adiabatic potentials and importantly, the non-adiabatic coupling between the two. Vibrational and nuclear motions about and away from this point introduce coupling between the UP and LP states. In other words, the light-matter coupling introduces a non-adiabatic coupling between UP and LP adiabatic potentials. This non-adiabatic coupling affects the lifetime of molecular polaritons. The relaxed exciton is decoupled from the cavity and population in this state serves as a “dark reservior”.

In this paper we use Fermi’s golden rule (FGR) to compute the both UP and LP lifetimes using a vibronic coupling model. First, we will work with a exciton/phonon model that incorporates on- and off-diagonal couplings between the electronic terms and the internal vibrational modes of the molecular system. We append to this the coupling between the electronic terms and the internal vibrational modes within the Tavis-Cummings model. We use this as the starting point for computing the non-adiabatic coupling between the UP and LP polariton adiabatic potentials due to the vibronic motions of the molecule on these potentials. We arrive at simple expressions based upon the molecular vibronic couplings and frequencies and use this to estimate UP to LP conversion times for a wide range of molecular chromophore systems.
II. VIBRONIC COUPLING BETWEEN POLARITON BRANCHES

To frame our discussion, we use the following exciton/phonon model Hamiltonian

\[
H_{ex} = \sum_i \epsilon_i \langle i | \hat{d}^+_i \hat{d}_i \rangle + \sum_{ijq} g_{ijq} \langle i | \hat{b}^+_j \hat{b}_q \rangle \langle j | \hat{b}^+_q \hat{b}_i \rangle + \sum_q \hbar \omega_q \hat{b}^+_q \hat{b}_q \tag{5}
\]

where \(\epsilon_i\) are the electronic energies referenced to common molecular geometry (e.g. the ground state, \(i = 0\), and excited states \(i > 0\)); \(g_{ijq}\) are the diagonal and off-diagonal derivatives of the potential at this geometry, and \([\hat{b}_q, \hat{b}^+_q'] = \delta_{qq'}\) are boson operators for vibrational phonon modes with frequency \(\omega_q\). Each of these parameters can be determined by quantum chemical means.\textsuperscript{14,27} Importantly, the \(\epsilon_i\) energies correspond to the electronic eigenenergies defined at some local energy minimum. Correspondingly, the phonon normal modes, frequencies \(\hbar \omega_q\), and coupling forces \(g_{ijq}\) are similarly defined relative to this configuration. We append to this the radiation modes of a microcavity and couplings within the Tavis/Cummings model.\textsuperscript{28}

\[
\hat{V}_{cav} = \sum_k \hbar \Omega_{k,cav} \hat{a}^+_k \hat{a}_k + \sum_{k,i>0} \mu_{i0} \epsilon_k \langle 0 | \hat{d}^+_i \hat{d}_k + | i \rangle \langle i | \hat{a}^+_k \rangle \tag{6}
\]

where we take \(\mu_{i0} \epsilon_k\) to be the projection of the transition moment between the ground and excited states onto the electric field in the cavity. We assume the cavity has a single mode that is nearly resonant with a single electronic transition and work within a dressed-atom basis and write |0\rangle = |g, 1_k\rangle as the electronic ground-state with 1_k cavity photons and |1\rangle = |e, 0_k\rangle as the first exciton state with 0_k cavity photons. Fig.2 is a sketch of the adiabatic potentials for molecular motions in the UP and LP eigenbasis. The dashed (adiabatic) potentials correspond to the diabatic potentials for the ground and excited molecular states; however, the ground state potential is shifted up by the energy of a single cavity photon. In the scenario shown here, the cavity is resonant with the absorption frequency of the molecule. Vibrational wavepacket dynamics then follow the lower (orange) adiabatic potential away from the Franck-Condon point. As the molecule distorts along coordinate \(q\), the resulting polariton state evolves from being a 1:1 linear combination of a cavity photon and molecular excitation to being purely excitonic by the time it has relaxed.

Transforming to the UP/LP basis and assuming the cavity contains a single excitation, the cavity Hamiltonian takes the form

\[
\hat{H}_{cav} = H_{ex} + V_{cav} = \left( \begin{array}{cc} \hat{L}_k & U_k^\dagger \\ \hat{U}_k & \hat{L}_k^\dagger \end{array} \right) \left[ \begin{array}{c} \hbar \Omega_{L,k} + (s_k^2 g_1 - 2 c_k s_k g_0) \cdot X \langle g_0 | (c_k^2 - s_k^2) - c_k s_k g_1 \rangle \cdot X \hbar \Omega_{U,k} + (c_k^2 g_1 + 2 c_k s_k g_0) \cdot X \end{array} \right] \left( \begin{array}{c} \hat{L}_k \\ \hat{U}_k \end{array} \right) + \hbar \Omega \hat{B}^\dagger \hat{B} + \hbar \Omega \hat{B}_c \hat{B}_c^\dagger \tag{7}
\]

where the coefficients \(G_L, G_U, G_{UL}\) contain contributions from both the cavity and the original (cavity free) electron/phonon coupling. The \(G_L\) and \(G_U\) will introduce a reorganization energy to both the UP and LP potential surfaces while the \(G_{UL}\) and \(G_{LU}\) terms couple the UP and LP polariton branches via both diagonal and off-diagonal exciton/phonon coupling terms. This generalized model can be parameterized from \textit{ab initio} calculations.

A. Reduced Model

To analyse the interplay between the internal degrees of freedom and the cavity, we consider a far simpler model of a two-electronic state molecule with a single vibrational degree of freedom with frequency \(\omega\)

\[
H_{ex} = \epsilon_g |g\rangle \langle g| + |e\rangle \langle e| \left( \epsilon_e + \hbar \omega S(b^\dagger + b) \right)
+ g_{eg} \langle |g\rangle \langle e| + |e\rangle \langle g| \rangle (b^\dagger + b) + \hbar \omega b^\dagger b. \tag{8}
\]

Here, \(S\) is a dimensionless (Huang-Rhys) parameter that determines the relative shift between the ground state potential and the excited state diabatic potentials. Under this simplified model,

\[
G_L = \sin(\eta)^2 \hbar \omega S - 2 g_{eg} \sin(2\eta) \tag{9}
\]
\[
G_U = \cos(\eta)^2 \hbar \omega S + 2 g_{eg} \sin(2\eta) \tag{10}
\]
\[
G_{LU} = g_{eg} \cos(2\eta) - \hbar \omega S \sin(2\eta)/2 \tag{11}
\]
where
\[
\frac{1}{2} \tan(2\eta) = -\frac{\lambda_{eg}}{(\epsilon_e - \epsilon_g) - \hbar \Omega_{cav}}
\]
defines the mixing between the electronic transition between \(|g\rangle\) and \(|e\rangle\) and the photon mode of the cavity and \(\lambda_{eg} = \mu_{eg} E_\epsilon \sqrt{n_k}\) includes the molecular transition moment, field, and mode occupancy \(n_k\).

**B. Embedding into the continuum**

Thus far, we have neglected the dressing of the cavity states (i.e., the UP and LP polaritons) by their coupling \(\hat{W}\) to the photon states which are external to the cavity. For this, we apply the approach developed in Ref. [12] whereby we write \(|\psi_\mu\rangle\) as a solution of the full cavity + continuum Schrödinger equation
\[
(\hat{H}_\text{cav} + H_\text{ext} + \hat{W})|\psi_\mu\rangle = E_\mu|\psi_\mu\rangle
\]
Accordingly, we define the following matrix elements:
\[
v_n = \langle n|\hat{W}|LP\rangle = v
\]
\[
v_n' = \langle n|\hat{W}|UP\rangle = v'
\]
\[
0 = \langle n|\hat{W}|n'\rangle = \langle n|H_\text{ext}|LP\rangle = \langle n|H_\text{ext}|UP\rangle
\]
Direct (phonon mediated) coupling between the UP and LP is mediated by the off-diagonal terms in Eq. [7] and Eq. [8]. For compactness in notation and to parallel the development in Ref. [12] we shall write
\[
\hat{w} = G_{LU}(b^\dagger + b)
\]
and recognize that we will need to average over the initial vibrational states to obtain our final expressions.

**C. Why Eq. [4] is incomplete**

The assumption that the polariton decay is dictated by the cavity lifetime can be analyzed using the FGR approach. However, rather than using the vibronic coupling (as suggested above) as the perturbation, we take the light-matter interaction as the perturbation and consider the decay of the molecular excitation \(|e; 0\rangle\) into the quasi-continuum. The FGR rate for the exciton decay is then given by
\[
\Gamma_{ex} = \frac{2\pi}{\hbar} |\langle \psi_\mu|\hat{W}|e; 0\rangle|^2 \frac{1}{\delta}.
\]
If we assume that the decay of \(|e; 0\rangle\) is via \(|g; 1\rangle\), which in turn can decay to \(|g; 0\rangle\) by photon leakage from the cavity, then the coupling between the exciton and the continuum is given by
\[
\langle \psi_\mu|\hat{W}|e; 0\rangle = \langle \psi_\mu|g; 1\rangle \langle g; 1|\hat{W}|e; 0\rangle
\]
Thus, the rate depends upon the cavity detuning.
\[
\Gamma_{ex} = |\lambda_{eg}|^2 \frac{\Gamma_{cav}}{(\hbar \Gamma_{cav}/2)^2 + (\epsilon_e - \hbar \omega_{cav})^2}.
\]
For strongly detuned cavities in which \(|\epsilon_e - \hbar \omega_{cav}| \gg \hbar \Gamma_{cav}\), the exciton can not decay by radiating into the continuum. For a resonant cavity, on the other hand,
\[
\Gamma_{ex, res} = \frac{\Omega_{\text{Rabi}}^2}{\Gamma_{cav}}.
\]
However, this expression is not valid if the Rabi frequency is large compared to \(\Gamma_{cav}\), which is the energy width over which the coupling between the exciton and the continuum is significant. That is to say, that the cavity lifetime must be significantly longer than the Rabi oscillation period in order for Eq. [4] to be valid.

**D. UP Decay**

The probability amplitude that a continuum state \(|\psi_\mu\rangle\) will be excited from the UP is proportional to the square of the following matrix element:
\[
\langle \psi_\mu|\hat{W}|UP\rangle = \frac{\hat{w}v + v' \sum_n v_n^2/(E_\mu - E_n)}{(v^2 + (\hbar \Gamma_{cav}/2)^2 + E_\mu^2)^{1/2}}
\]
\[
= \frac{\hat{w}v + v'E_\mu}{(v^2 + (\hbar \Gamma_{cav}/2)^2 + E_\mu^2)^{1/2}}.
\]
where we recall that \(\hat{w}\) is the phonon-mediated UP/LP coupling, and \(v\) and \(v'\) are the couplings between the LP and UP polaritons to the external photon states, respectively. The FGR expression is obtained by taking the trace over the vibrational degrees of freedom, and gives an expression of the form
\[
\Gamma_U = \Gamma_{U, direct} + \Gamma_{U, seq}
\]
The first term gives the direct rate resulting from the decay of the UP directly into the continuum via the \(v'\) coupling
\[
\Gamma_{U, direct} = \frac{2\pi}{\hbar} \frac{(v')^2}{\delta} \frac{E_\mu^2}{v^2 + (\hbar \Gamma_{cav}/2)^2 + E_\mu^2}
\]
which reduces to Eqs. [20] and [21] upon taking \(\delta \to 0\) and setting \(v' = v\). The second term arises from the fact that the UP can first decay to the LP, which in turn is also embedded in the continuum via the sequential pathway
\[
|UP\rangle \xrightarrow{\delta} |LP\rangle \xrightarrow{\delta} |k\rangle
\]
If assume that the sequential path dominates so that the relaxation is sequential, the matrix element between \(UP\) and the continuum states factors into
\[
\langle \psi_\mu|\hat{W}|UP\rangle = \langle \psi_\mu|LP\rangle \langle LP|\hat{W}|UP\rangle = \langle \psi_\mu|LP\rangle \hat{w}.
\]
This gives a FGR expression

$$\Gamma_{U,seq} = \langle \dot{w}^2 \rangle_{th} \frac{\Gamma_{cav}}{(h\Gamma_{cav}/2)^2 + (h\Omega_{Rabi})^2}$$  \hspace{1cm} (27)

The matrix element $\langle \dot{w}^2 \rangle_{th}$ contains contribution from both the cavity and the internal vibronic coupling. If we average over a distribution of initial vibronic states

$$\langle \dot{w}^2 \rangle_{th} \approx g_2^2 \langle \cos^2(2\eta) \rangle_{th} + \frac{(h\omega_S/\pi)^2}{\pi^2}$$  \hspace{1cm} (28)

For a resonant cavity, the mixing between the cavity and optical transition takes its maximum value with $\eta = \pi/4$. Furthermore, for a mixing angle of $\eta = \pi/4$, the contribution to $G_{LU}$ from the internal non-adiabatic coupling is exactly equal to zero and is expected to be small compared to the reorganization energy $h\omega_S$. However, we can expand this about $X = 0$ at the crossing point, take the thermal average over the vibrational degrees of freedom, and use $2\lambda_{eg} = h\Omega_{Rabi}$ to describe the coupling to between the cavity and the molecule. Expanding the mixing angle terms for small values of the nuclear displacement

$$\langle \dot{w}^2 \rangle_{th} \approx \left( \frac{h\omega_S/\pi}{2} \right)^2 \left( 1 + \frac{(n_{th} + 1)}{2\Omega_{Rabi}^2} \right) + \cdots$$  \hspace{1cm} (29)

where we have summed over a thermal distribution of initial vibronic states and evaluated the density of states at the UP/LP energy gap.

The treatment is valid for sufficiently small coupling such that $h\omega_S/2$ is small compared to the cavity linewidth $h\Gamma_{cav}$. This means that the lifetime of the initial state UP is much longer than the lifetime for a cavity photon to decay into the continuum. This can be understood in terms of the period of a single Rabi oscillation between the two states, which is on the order of $(\omega_S)^{-1}$, and the time-scale for the decay of the LP state into the continuum, which is $\Gamma_{cav}^{-1}$. If the LP state decays rapidly to the continuum, the system initially in UP will decay immediately to the continuum once it passes through the LP state and have a vanishingly small likelihood of returning to the UP at the end of the first Rabi oscillation. Consequently, the lower limit of the UP lifetime is set by the radiative decay of the cavity.

E. Decay of the relaxed LP state

We now consider the decay from the relaxed LP state shown in Fig. 2. In this scenario, we assume the LP can undergo vibronic relaxation from the Franck-Condon point to the lower energy geometry as depicted in Fig. 2. As the system moves away from the Franck-Condon point, the UP and LP states resolve back towards being purely cavity photon-like ($|g; 1\rangle$) and purely molecular exciton-like ($|e; 0\rangle$), respectively.

The analysis for the decay rate proceeds as above, except that the vibronic contribution is from the shifted state and that the density of states contribution is evaluated at the UP-LP gap at the relaxed geometry, i.e. $2h\omega_S$. Only if $2h\omega_S$ is small compared to the natural line-width of the cavity $h\Gamma_{cav}$ will this state be able to decay into the continuum. Consequently, systems with large reorganization energies are more likely to form long-lived molecular excitons, held at their relaxed excited state geometries.

F. Molecular estimates

We can use the FGR expressions to provide estimates of the UP and LP lifetimes for a wide range of systems based upon their Huang-Rhys factors, $S$ and vibronic frequencies. Data for selected molecules are labeled on each plot and a complete data table including references and structures for each system is provided as Supplemental Material.

![FIG. 3. Golden Rule estimates of UP (red) and LP (blue) lifetimes for various molecular systems based upon their Huang-Rhys factors, $S$ and vibronic frequencies. Data for selected molecules are labeled on each plot and a complete data table including references and structures for each system is provided as Supplemental Material.](image)
ally, conjugated molecular systems have Huang-Rhys factors of \( S \approx 0.1 \) – 0.8 and vibronic coupling is dominated by C=C stretching modes which are typically around \( h\omega = 200 \text{ meV} \). Aside from the cavity couplings, all parameters for our model can be directly extracted from linear absorption/emission spectra of a molecular system.

We calculated reduced Huang-Rhys factors from spectral data freely available as part of the PhotochemCAD™ program and database for a variety of organic chromophores. Out of the 339 compounds included in the PhotochemCAD™ database, we identified a subset of compounds with 1) absorption and emission spectra available and 2) an identifiable vibronic structure. Using the peak position tool built into the PhotochemCAD™ program, we determined the vibrational energy, \( \hbar \omega_c \), from the energy difference between adjacent vibronic peaks.

Following the guidelines of de Jong et al. for determining \( S \) from experimental spectra, we then converted each spectrum to an energy scale. Next we converted the absorbance and emission to transition moment squared, \( W(E) \), using the relations \( \langle A(E) \rangle \propto WE(E) \) and \( \phi(E) \propto E^2W(E) \), where \( A(E) \) is the absorbance and \( \phi(E) \) is the photon flux per unit of energy. We then calculated the barycenter of the baseline-corrected absorbance and emission spectra by evaluating

\[
E_{bc} = \frac{\int W(E)E\,dE}{\int W(E)\,dE} \tag{30}
\]

using Simpson’s rule for each spectrum. Finally, for each compound we calculated the reduced Huang-Rhys parameter with the relation \( \Delta E_{bc} = 2S \), where \( \Delta E_{bc} \) is the difference between the barycenters of the absorption and emission spectra. A complete list of the couplings and sources is given in the SI. From this data, we report estimated UP and LP decay times for a variety of common compounds in Fig. 3(a,b).

Fig.3(a) , the model predicts a broad range of UP lifetimes ranging from 100ps to less than 500 fs, largely determined by the variation in Huang-Rhys factors. Small Huang-Rhys factors imply very weak vibronic coupling and small distortion of the molecule in its excited electronic state. Consequently, the system remains in the UP state near the avoided crossing region for long time. The LP lifetime spans a much narrower range than the UP lifetime. It is also surprisingly predicted to be shorter than the UP lifetime. This lifetime is entirely dominated by the fact that the relaxed LP is almost entirely excitonic-like (\( |c;0\rangle \)) rather than photon-like (\( |g;1\rangle \)). Consequently, relaxation from this state via cavity emission is an activated process with \( 2\hbar \omega S \approx \hbar \Omega_{\text{Rabi}} \).

III. DISCUSSION

The polariton lifetime dictates any eventual “polariton chemistry” that might be induced or manipulated via coupling to the cavity. Here, we consider the the lifetime for polaritons in resonant cavities, where we anticipate the strongest coupling between the molecular and photon degrees of freedom. The long-lifetimes of these states predicted by our model is directly related to the fact that we prepare the system in a light-matter eigenstate. We also assume that the cavities themselves are of sufficiently high-quality that strong-coupling can be achieved in the sense that Rabi splitting between UP and LP branches is larger than the emission linewidths of the polaritons. These are reasonable assumptions that are consistent with contemporary experimental conditions.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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### IV. DATA TABLE

| Compound          | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|-------------------|--------------------|-------------|-----------------|-----------------|------------|
| benzene          | 0.11               | 0.34        | 2.1             | 45              | [30],[31]  |
| toluene          | 0.12               | 0.44        | 2.1             | 24              | [30]       |
| o-xylene         | 0.14               | 0.27        | 2.1             | 46              | [32],[33]  |
| m-oxyylene       | 0.14               | 0.25        | 2.1             | 55              | [30],[33]  |
| p-xylene         | 0.10               | 0.23        | 2.1             | 115             | [30],[33]  |
| mesitylene       | 0.12               | 0.25        | 2.1             | 68              | [33],[34]  |
| durene           | 0.15               | 0.22        | 2.1             | 58              | [33],[34]  |
| pentamethylbenzene | 0.08               | 0.24        | 2.1             | 158             | [33],[34]  |
| phenol           | 0.10               | 0.25        | 2.1             | 99              | [30],[35]  |

Continued on next page
| Compound | $\hbar \omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|----------|-------------------|-------------|-----------------|----------------|------------|
| anisole  | 0.12              | 0.22        | 2.1             | 96             | [36]       |
| benzonitrile | 0.12            | 0.22        | 2.1             | 96             | [36], [37] |
| chlorobenzene | 0.12            | 0.28        | 2.1             | 58             | [38], [39] |
| 1,4-diethynylbenzene | 0.23            | 0.37        | 2.1             | 9.5            | [40]       |
| 1,2,4,5-tetracyanobenzene | 0.15           | 0.16        | 2.1             | 107            | [41]       |
| biphenyl | 0.16              | 0.61        | 2.1             | 7.3            | [30]       |
| p-terphenyl | 0.16             | 0.46        | 2.1             | 11.6           | [30]       |
| p-quaterphenyl | 0.14           | 0.44        | 2.1             | 16.5           | [30]       |
| 2,5-diphenyloxazole [PPO] | 0.19           | 0.38        | 2.1             | 13.0           | [30]       |
| 1,4-Bis(5-phenyl-2-oxazolyl)benzene, [POPOP] | 0.18           | 0.26        | 2.1             | 29.1           | [30]       |
| naphthalene | 0.17            | 0.38        | 2.1             | 15454          | [30]       |
| Compound                        | $\hbar \omega$ (eV) | $S$ (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|--------------------------------|----------------------|----------------|------------------|------------------|------------|
| anthracene                     | 0.18                 | 0.23           | 2.1              | 37.2             | [30]       |
| tetracene                      | 0.18                 | 0.18           | 2.1              | 62.7             | [30, 42]   |
| pyrene                         | 0.17                 | 0.34           | 2.1              | 19.0             | [30]       |
| 9,10-diphenylanthracene        | 0.18                 | 0.23           | 2.1              | 40.7             | [30]       |
| 9,10-Bis(phenylethynyl)anthracene | 0.12               | 0.18           | 2.1              | 136              | [30]       |
| rubrene                        | 0.17                 | 0.19           | 2.1              | 64.7             | [30, 43]   |
| 1,8-naphthalic anhydride       | 0.11                 | 0.29           | 2.1              | 61.3             | [44]       |

Continued on next page
| Compound                                      | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|----------------------------------------------|--------------------|-------------|------------------|------------------|------------|
| 1,4,5,8-naphthalenetetracarboxylic dianhydride | 0.19               | 0.21        | 2.1              | 42.0             | [45]       |
| 1,4-diphenylbutadiene                        | 0.19               | 0.32        | 2.1              | 17.9             | [46, 47]   |
| 1,6-diphenylhexatriene                       | 0.18               | 0.43        | 2.1              | 11.2             | [47]       |
| L-phenylalanine                              | 0.10               | 0.27        | 2.1              | 88.4             | [48, 49]   |
| L-tryptophan                                 | 0.15               | 0.58        | 2.1              | 9.31             | [45, 49]   |
| acridine                                     | 0.14               | 0.32        | 2.1              | 30.6             | [50, 51]   |
| acridone                                     | 0.16               | 0.34        | 2.1              | 22.0             | [51, 52]   |
| 1,1'-diethyl-2,2'-carbocyanine iodide        | 0.15               | 0.10        | 2.2              | 280              | [53]       |
| 1,1'-diethyl-2,2'-dicarbocyanine iodide      | 0.15               | 0.06        | 2.2              | 761              | [51]       |
| 1,1'-diethyl-3,3',3'-tetramethylindocarbocyanine iodide | 0.14               | 0.13        | 2.1              | 211              | [55, 56]   |

Continued on next page
| Compound     | $\hbar \omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|--------------|---------------------|-------------|------------------|------------------|------------|
| perylene     | 0.19                | 0.17        | 2.1              | 61.0             | [50]       |
| perylene, PMI| 0.14                | 0.21        | 2.1              | 70.0             | [57]       |
| perylene, PDI| 0.18                | 0.13        | 2.1              | 130              | [58, 59]   |
| phloxine B   | 0.16                | 0.09        | 2.2              | 324              | [60]       |
| rose bengal  | 0.17                | 0.08        | 2.2              | 315              | [61]       |
| Compound          | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|------------------|-------------------|-------------|------------------|------------------|------------|
| sulforhodamine 101 | 0.14              | 0.08        | 2.2              | 552              | 62, 63     |
| MgOEP            | 0.14              | 0.10        | 2.2              | 324              | 64        |
| ZnOEP            | 0.15              | 0.09        | 2.2              | 401              | 65, 66     |
| MgTPP            | 0.14              | 0.12        | 2.2              | 242              | 67, 68     |
| ZnOEP            |                    |             |                  |                  |            |

Continued on next page
| Compound             | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|----------------------|---------------------|-------------|------------------|------------------|------------|
| ZnTPP                | 0.16                | 0.15        | 2.1              | 120              | 69, 68     |
| MgTMP                | 0.15                | 0.13        | 2.1              | 165              | 70, 71     |
| (ODC)H2P             | 0.31                | 0.29        | 2.1              | 8.29             | 72, 70     |
| C6F5-H2P             | 0.32                | 0.29        | 2.1              | 8.18             | 73         |
| tetrabenzoporphine   | 0.17                | 0.09        | 2.2              | 256              | 74, 75     |

Continued on next page
| Compound                  | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|--------------------------|---------------------|-------------|------------------|------------------|------------|
| H$_2$TBP(CO$_2$Bu)       | 0.14                | 0.11        | 2.1              | 296              | 76         |
| ZnTBP(CO$_2$Bu)          | 0.16                | 0.04        | 2.3              | 1760             | 76         |
| H$_2$TBP(CO$_2$Me)Ph     | 0.16                | 0.16        | 2.1              | 103              | 77         |

Continued on next page
| Compound                  | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|--------------------------|--------------------|-------------|------------------|------------------|------------|
| ZnTBP(CO$_2$Me)Ph        | 0.13               | 0.07        | 2.2              | 738              | 78         |
| ZnTBP(CO$_2$Bu)Ph        | 0.13               | 0.07        | 2.2              | 709              | 76         |
| PdTBP(CO$_2$Bu)Ph        | 0.16               | 0.21        | 2.2              | 55.7             | 76         |
| C$_6$F$_5$-Corrole       | 0.16               | 0.16        | 2.2              | 98.1             | 78, 79     |
| H$_2$Pc                  | 0.09               | 0.06        | 2.3              | 1797             | 80, 81     |

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| Compound         | $\hbar \omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|------------------|----------------------|-------------|------------------|------------------|------------|
| H$_2$Pc(tBu)     | 0.10                 | 0.06        | 2.3              | 1565             | [82]       |
| chlorophyll a    | 0.14                 | 0.06        | 2.2              | 900              | [83] [84]  |
| chlorophyll b    | 0.16                 | 0.03        | 2.3              | 2081             | [84] [85]  |
| pheophorbide a   | 0.17                 | 0.04        | 2.3              | 1438             | [86]       |
| Compound                  | $h\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|---------------------------|---------------|-------------|------------------|------------------|------------|
| pyropheophorbide a        | 0.17          | 0.04        | 2.3              | 1669             | [87] [88]  |
| pyropheophorbide a methyl ester | 0.18          | 0.04        | 2.3              | 1,292            | [89] [90]  |
| chlorin e6                | 0.17          | 0.03        | 2.4              | 3017934          | [91] [92]  |
| purpurin 18               | 0.16          | 0.03        | 2.4              | 2,588            | [93] [94]  |
| Compound | $\hbar \omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|----------|------------------|-------------|-------------------|-----------------|------------|
| H2TPC    | 0.17             | 0.03        | 2.4               | 2.556           | [95] [96]  |

Continued on next page
| Compound     | $\hbar\omega$ (eV) | S (reduced) | $\tau_{LP}$ (ps) | $\tau_{UP}$ (ps) | References |
|--------------|--------------------|-------------|------------------|------------------|------------|
| H2C-1        | 0.17               | 0.03        | 2.3              | 2.241            | [97, 98]   |
| H2COxo-1     | 0.19               | 0.05        | 2.2              | 860              | [98]       |
| MgCOxo-1     | 0.18               | 0.09        | 2.2              | 279              | [98]       |
| ZnCOxo-1     | 0.17               | 0.06        | 2.2              | 676              | [98]       |