Predicting Phosphorescence Rates of Light Organic Molecules Using Time-Dependent Density Functional Theory and the Path Integral Approach to Dynamics

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Supporting Information

ABSTRACT: In this work, we present a general method for predicting phosphorescence rates and spectra for molecules using time-dependent density functional theory (TD-DFT) and a path integral approach for the dynamics that relies on the harmonic oscillator approximation for the nuclear movement. We first discuss the theory involved in including spin–orbit coupling (SOC) among singlet and triplet excited states and then how to compute the corrected transition dipole moments and phosphorescence rates. We investigate the dependence of these rates on some TD-DFT parameters, such as the nature of the functional, the number of roots, and the Tamm–Dancoff approximation. After that, we evaluate the effect of different SOC integral schemes and show that our best method is applicable to a large number of systems with different excited state characters.

1. INTRODUCTION

Phosphorescent materials have been a major focus of research during the past few years, with applications in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells, photovoltaic cells, chemical sensors, and bioimaging. Because most molecular materials presenting this kind of long-lived emission contain heavy metals to increase spin–orbit coupling (SOC), the interest in purely organic molecules presenting triplet emission has also grown recently for economical and ecological reasons.

As they exhibit weak SOC, light organic molecules usually have rather slow phosphorescence rates, between 10^−3 and 10^3 s−1, and nonradiative pathways prevail at room temperature. Usually, these compounds become phosphorescent only at about 77 K, in organic glasses or as pure materials, when the intersystem crossing back to the ground state slows down, and the emission quantum yield then gets higher. Yet, some molecules do present high phosphorescence rates, even at room temperature, and these are currently under study for various applications.

The theoretical prediction of these rates is rather challenging since it must account for relativity to allow for singlet and triplet mixing. The rate for a radiative transition between an initial state Ψ_i and a final state Ψ_f can be calculated from Fermi’s Golden Rule as

\[ k(\omega)_\text{ff} = \frac{4\omega n^3}{3\hbar c} \langle [\mu_i, [\mu_f, \hat{H}]] \rangle^2 \delta(E_i - E_f \pm \hbar\omega) \]  

where \( \omega \) is the frequency of the photon, \( n \) is the refractive index of the medium, \( \hbar \) is the planck constant divided by \( 2\pi \), \( c \) is the speed of light, \( \mu \) is the dipole moment operator, and \( E \) is the energy of a given state. The rate thus depends on the transition dipole matrix element, and because nonrelativistic operators do not couple spin eigenstates, \( \langle \Psi_f \mid \mu_i \mid \Psi_i \rangle = 0 \) after spin integration and there can only be transitions between states of same multiplicity.

However, the rate is, in practice, nonzero due to the relativistic mixing of singlets and triplets. In nonrelativistic quantum mechanics, the SOC operator (\( \hat{H}_{\text{SOC}} \)) coupling states with different multiplicity can be added to the nonrelativistic Hamiltonian in an ad hoc manner. The SOC effects are usually accounted for in the literature by using first-order perturbation theory, with the perturbed triplet \( \langle \Psi_{\text{SOC} T_1} \rangle \) given by

\[ \langle \Psi_{\text{SOC} T_1} \rangle = \langle \Psi_{T_1} \rangle + \sum_n \frac{\langle \Psi_{\text{SOC} T_1} \mid \hat{H}_{\text{SOC}} \mid \Psi_n \rangle}{E(T_n) - E(S_n)} \]  

so that phosphorescence rates can be obtained from eq 1 under the Franck–Condon assumption that the transition dipole moment is independent of nuclear coordinates. As there are three spin sublevels for the triplets, the final observed rate \( k^\text{obs} \) is calculated considering the Boltzmann population of each state.

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molecular orbitals. In eq 5, the SOC integrals in the spherical basis are given by

\[
\begin{align*}
\zeta^{(0)} &= \zeta(c) \\
\zeta^{(+1)} &= - \frac{\left(\zeta^{(s)} + i\zeta^{(t)}\right)}{\sqrt{2}} \\
\zeta^{(-1)} &= \frac{\left(\zeta^{(s)} - i\zeta^{(t)}\right)}{\sqrt{2}}
\end{align*}
\]

These SOC matrix elements can be calculated using the Wigner–Eckart theorem for spherical tensor operators^{45,46} of rank 1,

\[
\langle \Psi^M | \hat{H}_{SOC} | \Psi^M' \rangle = \sum_{pq} \left( -1 \right)^m \left( S', M' \right) \left( S, M \right) \times \langle \Psi^M \rangle \sum_{pq} \langle \Psi^M \rangle \langle \Psi^M' \rangle
\]

(10)

The Clebsch–Gordan coefficients (CGC) in the brackets only couple states for which \( |S' - S| \) is at most 1 and \( M' + M = M \). The reduced matrix element can be calculated as

\[
\langle \Psi^M \rangle \sum_{pq} \langle \Psi^M \rangle \langle \Psi^M' \rangle = C_i \sum_{pq} \langle \Psi^M \rangle \langle \Psi^M' \rangle
\]

(11)

where \( \langle \Psi^M \rangle \) is at most one, depending on the states coupled, and \( C_i \) is a simple constant depending on \( S \) and \( M \) as determined as the inverse CGC for \( S = M \) and \( S' = M' = S - I \). Thus, it is only necessary to compute the SOC integrals \( \zeta \) and the transition spin density matrices on the right-hand side of the above equation.

In TD-DFT, assuming a closed shell reference, the spin adapted singlet and triplet state vectors can be calculated as single excitations

\[
\langle \Psi^M_{\alpha} \rangle = \sum_{ia} \langle \Psi^M_{\alpha} \rangle \langle \Psi^M_{\alpha} \rangle
\]

(12)

with \( \tilde{X}_{\alpha} \) being a general notation for the normalized versions of eqs 6, 7, and 8 for triplet excitations as well as for the singlet excitation operator obtained from

\[
\tilde{E}_{pq} = a_{p}^\dagger a_{q} + b_{p}^\dagger b_{q}
\]

(13)

after normalization so that \( \langle 0 \tilde{X}_{\alpha}^\dagger \tilde{X}_{\alpha} | 0 \rangle = 1 \). In effect, the operators in eqs 6, 7, and 8 are multiplied by \( \sqrt{2} \), while the one in eq 13 is divided by \( \sqrt{2} \). Here and in the following, the labels \( i, j, ... \) refer to occupied molecular orbitals and the labels \( a, b, ... \), to virtual molecular orbitals, as opposed to the general labels \( p, q, ... \) which may refer to either of these. The symbol \( \tilde{x}_{i}^\dagger \) in eq 12 is a generic notation for the amplitude corresponding to the excitation operator \( \tilde{X}_{\alpha} \).

For singlets, we will use the notation \( x_{i}^\dagger \) while for triplets the convention \( x_{i}^\dagger = t_{i}^\dagger \) will be preferred. Technically, the triplet equations are solved only once in TD-DFT/TDA since the three sublevels yield identical results so long as the Hamiltonian does not affect the spin functions. This result is then used to compute the reduced matrix elements from eq 11. Since only singlet and triplet states will be considered in the following, a new notation is introduced in which \( \langle 0 | \Psi_{\alpha}^{M} \rangle \) denotes the ground state and \( l_{\alpha} \equiv \Psi_{\alpha}^{M} \) and \( l_{\alpha}^{M} \equiv \Psi_{\alpha}^{M} \) denote the singlets and triplets, with \( s_{i}^\dagger \) and \( t_{i}^\dagger \) being the corresponding excitation amplitudes. Since the
SOC operator is Hermitian, it is enough to compute the matrix elements for which \( S' \leq S \). Then, the surviving transition densities can be written as

\[
\langle T^{\Gamma, (1)}_{pq} | 0 \rangle = \frac{1}{\sqrt{2}} \sum_{ia} \delta_{p_i} \delta_{q_j} \rho_{ia}^k
\]

(14)

\[
\langle T^{\Gamma, (1)}_{pq} | S_\nu \rangle = \frac{1}{2} \sum_{ia} \delta_{p_i} \delta_{q_j} \rho_{ia}^k - \frac{1}{2} \sum_{ia} \delta_{p_i} \delta_{q_j} \rho_{ia}^k
\]

(15)

\[
\langle T^{\Gamma, (0)}_{pq} | T_K^\nu \rangle = \frac{1}{2} \sum_{ia} \delta_{p_i} \delta_{q_j} \rho_{ia}^k + \frac{1}{2} \sum_{ia} \delta_{p_i} \delta_{q_j} \rho_{ia}^k
\]

(16)

The delta symbols in the above equations merely indicate which contributions survive for a specific choice of the generic labels \( p \) and \( q \). The only necessary coefficients \( C_i \) in eq 11 are then \( C_0 = 1 \) and \( C_0 = \sqrt{2} \). In full TD-DFT, the SOC matrix elements are computed from the renormalized \( X + Y \) vectors (such that \( X + X^* + Y = 1 \)), which are not necessarily normalized if hybrid functionals are used. Note that it is also possible to handle singly excited open shell systems in a spin adapted manner, as discussed elsewhere.

After the matrix for \( H_{\text{REL}} \) is built and diagonalized, we obtain the mixed single–triplet SOC states:

\[
|\Psi^{\Gamma}_{\text{SOC}}\rangle = C_0^{\Gamma, 0}(0) + \sum_n C_n^{\Gamma, 0}(S_\nu) + \sum M \sum_k D_{kM}(T_K^M)
\]

(17)

with the complex eigenvector coefficients \( C_i \), for singlets and \( D_{kM} \) for triplets. If solvent effects are to be included, one can use the linear response conductor-like polarizable continuum model (LR-CPCM) to approximately correct the energies of the TD-DFT states before constructing the \( H_{\text{REL}} \) matrix.

Finally, the transition dipole matrix elements can be computed. As the ground state only couples through SOC with the triplets, its SOC-corrected wave function is given by

\[
|\Psi^{\Gamma}_{\text{SOC}}\rangle = C_0^{\Gamma, 0}(0) + \sum M \sum_k D_{kM}(T_K^M)
\]

(18)

and the transition dipoles from ground to excited states can be obtained from

\[
\mu_{pq} \equiv \langle \Psi^{\Gamma}_{\text{SOC}}|\mu|\Psi^{\Gamma}_{\text{SOC}}\rangle = Tr(\Gamma \mu)
\]

(19)

where \( \mu_{pq} \) denotes the dipole integrals, while the SOC one body reduced density matrix \( \Gamma_{pq} \) is given by

\[
\Gamma_{pq} = (C_0^{\Gamma, 0} \times C_0^{\Gamma, 0}) + \sum_n (C_n^{\Gamma, 0} \times C_n^{\Gamma, 0}) + \sum M \sum n \sum k (D_{kM}^0 \times D_{kM}^0) + \sum M \sum n \sum k (D_{kM}^0 T^M_{pq})
\]

(20)

This in turn contains contributions from unmixed quantities, including the ground state density

\[
\gamma^{\Gamma, 0}_{pq} = 2 \sum_i \delta_{p_i} \delta_{q_j}
\]

(21)

and the triplet–triplet transition density

\[
\gamma^{\Gamma, 0}_{pq} = 2 \sum_{ia} \delta_{p_i} \delta_{q_j} \rho_{ia}^k
\]

(22)

keeping in mind that only transition densities between triplet states of the same \( M \) value will survive after spin integration and that these yield identical results independent of \( M \).

2.2. Path Integral Approach for the Rates. In order to compute the rates of phosphorescence, we solve eq 1 for the first three mixed (triplet dominated) excited states, according to our previously described method. This is based on the idea first explored by Lin in the 1970s that one can use the Fourier Transform (FT) representation of the delta function

\[
\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} dt
\]

(24)

to switch the problem from the energy to the time domain. The formulation was explored further by Tannor and Heller in the 80s, see refs 36 and 42 and references therein, and was recently revisited by Tatchen and Pollak38 and began to be applied in different contexts. Using this formulation, it is possible to calculate \( k_\phi \) from the FT of a correlation function \( \chi(t) \) that is computed from the path integral of the multidimensional harmonic oscillator:

\[
k_\phi(\omega) = 2\pi \Re \int_0^{+\infty} \chi(t)e^{-i\omega t} dt
\]

with \( \alpha \) being a collection of parameters. As we have shown, this formulation can be implemented very efficiently and yields as a result both the rate and the emission spectrum.

The correlation function itself depends on the electronic transition dipole \( \mu_\alpha \), which in the present case is calculated from eq 20 and its derivatives,

\[
\chi(t) = e^{\frac{\Delta E}{k_B T}} \left[ \langle \mu^2 \rangle \langle \rho^{FC} \rangle (t) + \sum_k \frac{\partial \mu^k}{\partial Q_k} \langle \rho^{HT/FC} \rangle (t) \right]
\]

(25)

as well as on the functions

\[
\rho^{FC} (t) = Tr(e^{-iHt} e^{-i\hat{R}t})
\]

(26)

\[
\rho^{HT/FC} (t) = Tr(\hat{Q}_k e^{-i\hat{R}t} e^{-i\hat{R}t})
\]

(27)

\[
\rho^{HT} (t) = Tr(\hat{Q}_k e^{-i\hat{R}t} \hat{Q}_k e^{-i\hat{R}t})
\]

(28)

which contain information on the vibrational coupling at the Franck–Condon (FC) and Herzberg–Teller (HT) levels. Here \( \hat{H} \) is the vibrational Hamiltonian, \( \hat{Q}_k \) is a normal coordinate, and the bar denotes the coordinates of the final state. The derivatives in eq 25 are calculated numerically, while the functions \( \rho \) are evaluated as discussed in our earlier work. These functions depend on the Dushinsky rotation and displacement matrices that connect initial and final normal coordinates, and they also account for temperature dependence which is introduced by summing over all initial states weighed by a Boltzmann factor.

Using this method to solve eq 1 together with the SOC-corrected transition dipole moment matrix elements, we can
now predict phosphorescence rates (and intrinsic lifetimes) including the solvent, Duschinsky, and the Herzberg–Teller effects.

3. COMPUTATIONAL DETAILS

All calculations were carried out using the development version of the ORCA software package. Structures were optimized using the B3LYP, BP86, or WB97X-D functionals and the def2-TZVP(F) basis set. For ground states, the optimization followed the restricted Kohn–Sham (KS) DFT process, while for excited state singlets, TD-DFT optimizations were carried out using the restricted KS determinant as reference. For triplet states, unrestricted KS ground state calculations were performed rather than computing the triplet excited states from TD-DFT with a restricted KS reference. In order to accelerate the computation of two electron integrals, the resolution of identity approximation was used for the Coulomb part (RI) and the chain of spheres algorithm for the exchange part (COSX), with the corresponding auxiliary basis and grid settings. The DFT grid was set to GRID5, and the COSX grid was GRIDXS, with all the other parameters chosen as default unless otherwise stated. When LR-CPCM was used, the solvent of choice was ethanol to be consistent with the reference data. Unless otherwise mentioned, the spin–orbit integrals were calculated using the RI-SOMF(1X) approximation.

For the excited states, TD-DFT with or without TDA was employed. The convergence criteria for both the SCF and geometry optimizations was set to TIGHT, with a convergence threshold of 10⁻⁸ Hartree in the former and 10⁻⁶ Hartree in the latter case. No optimized structure presented negative frequencies. It was assumed that the geometries and Hessians of the triplet sublevels were the same and, to calculate the rates, eq 3 was used although no significant zero-field splitting was encountered. During the calculation of SOC integrals using mean-field approaches, the KS ground state density was used when necessary.

The individual rates were calculated using the ORCA_ESD module recently developed, using default settings and Duschinsky mixing, including our automatic selection of parameters for the FT step and normal modes described in the previous sections. The SO integrals were calculated using mean-field approaches, the KS ground state density was used when necessary.

For the excited states, TD-DFT with or without TDA was employed. The convergence criteria for both the SCF and geometry optimizations was set to TIGHT, with a convergence threshold of 10⁻⁸ Hartree in the former and 10⁻⁶ Hartree in the latter case. No optimized structure presented negative frequencies. It was assumed that the geometries and Hessians of the triplet sublevels were the same and, to calculate the rates, eq 3 was used although no significant zero-field splitting was encountered. During the calculation of SOC integrals using mean-field approaches, the KS ground state density was used when necessary.

4. RESULTS AND DISCUSSION

For initial testing, a set of well studied molecules were chosen, which have different excited state characters, from purely π–π* to n–π* states. This set consists of anthracene (ANT), naphtalene (NAP), phenanthrene (PHE), carbazole (CAR), benzofuran (BFUR), quinoxaline (QNX), biacetyl (BIA), benzophenone (BZP), and anthrone (ATQ), all shown in Figure 1.

![Figure 1. Set of molecules chosen for testing the proposed method.](image)

These molecules present experimental rates varying from 0.01 to 340 s⁻¹ and are thus suitable for evaluating the range of applicability of our method. However, since the range is large and so are the errors in the predictions, we found that the ratio of experimental and theoretical rate was the most suitable quantity for comparison. Here, we define this ratio as 

$$R = \frac{k_{\text{theo}}}{k_{\text{exp}}},$$

where the subscripts “theo” and “exp” correspond to theoretical and experimental rates respectively. For the data in Figure 1, we found that the ratio varied from 0.01 to 100, indicating a wide range of accuracy.

4.1. Dependence on TD-DFT Parameters. All geometries for the S₀ and T₁ states of the test set were optimized using BP86, B3LYP, and WB97X-D functionals, and its rates were calculated using TD-DFT excited states with LR-CPCM energy corrections for the solvent. At first, the number of TD-DFT roots were varied from 10 to 25, in order to evaluate the effect of both the nature of the functionals and the number of roots necessary to converge the results. It was found that in all cases they converged after coupling the 20 lowest energy excited singlets and the 20 lowest energy triplets, so we decided to include the 25 lowest energy roots for each multiplicity as the default to ensure convergence. Thus, the final SOC matrix involves 101 states, including the ground state, 25 singlet states, and 75 triplet states (25 for each sublevel).

When comparing the effect of different functionals, we found that B3LYP was the one with the smallest error, with R = 1.98. For BP86, the error was determined to be R = 5.69 while R = 6.97 was found for the range-corrected WB97X-D3. In Figure
2, a comparison between the experimental and the calculated rates is presented, indicating the amount of the Herzberg–Teller effect for each molecule.

Table 1. Average Errors Obtained from Full TD-DFT, TDA, and Gas Phase Calculations for the Test Set Shown in Figure 14

| Method | Δ| MSRE | MURE |
|--------|---|------|------|
| TD-DFT | 1.98 | 68.7 | 91.2 |
| vacuum | 2.15 | 71.9 | 103 |
| TDA    | 4.76 | 362  | 374  |

“Mean signed relative errors (MSRE) and mean unsigned relative errors (MURE) are given as percentages.

be seen, the solvent effect was not important for these molecules, since there were almost no charge-transfer states involved and the CPCM correction was small. On the other hand, the effect of TDA was more dramatic. This was due in particular to large deviations for CAR and QNX with $R_{\text{CAR}} = 13.7$ and $R_{\text{QNX}} = 17.5$. Looking closely at these results, it is possible to determine that the differences are caused by large derivatives of transition dipole moments over certain modes that are not encountered when using full TD-DFT. It is known that TDA yields triplet energies closer to the experiment, while full TD-DFT is better for properties such as transition dipole moments and it is the latter which makes a difference here. If one considers only the other molecules in this set, there was no such error, the TDA approximation is actually the best, with an $R = 1.65$. Even so, full TD-DFT seems to be more robust in general and will be used from here on.

4.2. Effect of Different Schemes for SOC Integrals.

Since there are different approaches to compute the SOC integrals, we also investigated the effect of these on the overall rates. The SOC operator $H_{\text{SOC}}$ can be included in non-relativistic quantum mechanics using the Breit–Pauli (BP) approximation

$$H_{\text{SOC}} = H_{\text{SOC}}^{(1)} + H_{\text{SOC}}^{(2)}$$

where the SOC operator is composed of one electron terms ($H_{\text{SOC}}^{(1)}$) and two electron terms ($H_{\text{SOC}}^{(2)}$). In constructing a second quantized representation for these operators, it should be kept in mind that we are aiming for a one body description of the form shown in eq 5. Thus, the matrix elements $z_{pq}^{(-m)}$ consist of a sum, $z_{pq}^{(-m)} = z_{pq}^{(-m)} + g_{pq}^{(-m)}$, of a true one electron term $g_{pq}^{(-m)}$ and an effective one body term $g_{pq}^{(-m)}$ arising from $H_{\text{SOC}}^{(2)}$ under the mean field approximation. The explicit forms of these matrix elements are

$$h_{pq}^{(-m)} = (p|h_{pq}^{(-m)}|q)$$

$$g_{pq}^{(-m)} = \sum_i [2(pqg^{(-m)}|i) - 3(pqg^{(-m)}|q)]$$

where the complex integrals are labeled as $(1^*1|1^*2)|2^*2$ and $h^{(-m)}$ and $g^{(-m)}$ can be obtained following the recipe in eq 9 from the components of the Cartesian vector operators

$$h = \frac{a^2}{2} \sum_A Z_A I_{1A} \frac{I_{1A}}{r_{1A}^3}, \quad g = \frac{a^2}{2} \frac{I_{12}}{r_{12}^3}$$

Here, $α$ is the fine structure constant, 1 and 2 denote electronic spatial coordinates, $r_{1A} = |r_{1A}|$ and $r_{12} = |r_{12}|$ denote the distance between electron 1 and nucleus A and between electron 1 and 2, respectively. The angular momentum operators I are given as $I_{1A} = r_{1A} \times p_1$ and $I_{12} = r_{12} \times p_1$, where $p_1$ is the momentum operator belonging to electron 1. As we will treat SOC as a one electron property, the question remains in what precise form the two electron effects can be treated.

The simplest approximation for the BP SOC Hamiltonian is to use the one electron part and account for the other electrons through a shielding on the effective nuclear charge (i.e., replace $Z_A$ with some effective charges $Z_A^*$. Here, we use the charges from Koseki et al. and will refer to this approach as ZEFF. It is also possible to include the two electron terms approximately, using mean field approaches as in Hartree–Fock theory. We use the efficient mean field approach called RI-SOMF that makes use of the RI scheme to accelerate Coulomb integrals and another mean field approach named AMFI-A by Schimmelpfenning, that uses precomputed atomic densities and only accounts for one-center integrals. A fourth option is to compute the BP SOC integrals similarly to the SOMF but including local DFT exchange and correlation, here named VEFF-2X, which we will simply
refer to as VEFF in this study. The results for the test set are presented in Figure 3.

As it can be seen directly from Figure 3, the RI-SOMF and VEFF approaches as well as the simplest ZEFF approach yield results which agree well with each other and with experiment. The comparatively mild variation in the rates predicted by these three methods can be attributed to differences in the quality of the SOC matrix elements and their derivatives. For PHE and NAP, VEFF and RISOMF differ quite substantially, both as far as the transition dipoles and their derivatives are concerned. However, both methods yield results in the same order of magnitude. The relatively large deviation of the AMFI-A values from the other results is connected to the one-center approach, which should be avoided for the present purposes. In fact, if the RI-SOMF calculations are carried out using the one-center approximation, the results are very close to the AMFI-A values.

A well-balanced method should produce both accurate SOC matrix elements and reliable SOC derivatives, since the quality of the latter has a significant impact on the calculated phosphorescence rates. It seems that ZEFF, although only containing one electron terms, produces quite accurate rates, being even slightly more accurate than RI-SOMF with an $R_{ZEFF} = 1.56$. Even so, the mean field RI-SOMF approach should be more reliable if heavier atoms are also present and a better treatment of the two electron terms becomes necessary. In this sense, it is more general and it does not depend on the choice of the exchange-correlation functional or other empirical parameters either. We thus recommend RI-SOMF as the default approach, while retaining VEFF as a possibility and ZEFF as a cheaper alternative for weak coupling.

### 4.3. Results for a Larger Test Set.

Finally, having defined a suitable set of default choices for our method, B3LYP functional, full TD-TDF with LR-CPCM corrections, and RI-SOMF SOC integrals, we investigate the accuracy of this method on a larger set. In addition to the ones portrayed in Figure 1, we add the well-known molecules presented in Figure 4, which are pyrene (PYR), biphenyl (BIP), benzonitrile (BNT), adenine (ADE), xanthone (XAN), and anthraquinone (ATQ).

From these 15 molecules, 5 have only $\pi-\pi^*$ excited states with very weak SOC, 5 have well-defined $n-\pi^*$ states that give rise to larger SOC matrix elements, and 5 have some sort of mixed states. It can be seen in Figure 5 that these differences give rise to phosphorescence rates that are up to 4 orders apart, e.g., between anthracene (ATQ) and anthraquinone (ATQ), as expected from the usual theoretical background of molecular photophysics. Again, as in the previous case, most of these rates are due to vibronic coupling between the triplet and the ground state and would not be correct under the simpler FC assumption.

As explained in our previous work regarding fluorescence, the emission rates can be also related to the experimental spectrum, and in Figure 6, we show the comparison between the experimental and theoretical phosphorescence spectra of biacetyl. As can be seen, there is a good correspondence in both the intensity and the position of the bands. In this case, about 50% of the intensity is due to the HT effect and the associated theoretical rate is in excellent agreement with the experiment.

### 5. CONCLUSIONS

In this work, we have provided a derivation of the spin–orbit coupling between TD-DFT ground and excited states and the application of the corrected transition dipole moment matrix
elements for the computation of phosphorescence rates and spectra. In order to solve the relevant rate equations, we use our previously developed approach for fluorescence, based on the path integral solution of the multidimensional harmonic oscillator model, and investigated the effects of different parameters on the predicted rates.

From our results, we conclude that the functional B3LYP yielded the best predictions, when using the full TD-DFT equations, at least when compared with BP86 and WB97X. The results obtained using the TDA approximation were also very good but had a large deviation for two test cases and are thus less robust. For simple organic molecules such as those explored here, spin–orbital coupling is weak and the Franck–Condor approximation is not sufficient to give qualitatively correct predictions. To achieve this, the Herzberg–Teller effects must be accounted for; otherwise, the results deviate enormously from the experiment. In terms of the spin–orbit integrals, we conclude that the effective nuclear charges as developed by Koseki et al. and the mean-field integrals with or without local DFT contributions compare well to the experiment, at least for light organic molecules. We recommend the RI-SOMF method in particular and advise against using the one-center approximation for calculating phosphorescence rates.

We finally show that, under the use of these optimal parameters, phosphorescence rates can be predicted for a series of diverse molecules that span almost 4 orders of magnitude in terms of the phosphorescence rates. Using these results, emission spectra can also be predicted in good agreement with the experiment.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.8b00841.

Complementary information such as numerical data related to the figures and some intermediate results necessary for calculating the rate for ANT (PDF).

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Notes

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