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Computational Simulation of Vibrationally-Resolved Spectra for Spin-Forbidden Transitions

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Abstract

In this computational study, we illustrate a method for computing phosphorescence and circularly polarized phosphorescence (CPP) spectra of molecular systems, which takes into account vibronic effects including both Franck-Condon and Herzberg-Teller contributions. The singlet and triplet states involved in the phosphorescent emission are described within the harmonic approximation and the method fully takes mode-mixing effects into account when evaluating Franck-Condon integrals. Spin-orbit couplings, which are responsible for these otherwise forbidden phenomena, are accounted for by means of a relativistic two-component time-dependent density functional theory method. The model is applied to two types of chiral systems: camphorquinone, a rigid organic system which allows for an extensive benchmark, and some members of a class of iridium complexes. The merits and shortcomings of the methods are discussed, and some perspectives for future developments are offered.

1 Introduction

Phosphorescent materials, particularly those containing transition metal complexes, have found application in several fields and have been the object of extensive studies in recent years, thanks in part to their applicability in electroluminescent devices such as OLEDs, sensors, and probes.[1–4] In particular, chiral emitting systems are especially appealing because of their possible application in data storage, directional backlight 3D displays and LCDs, as spin sources in optical spintronics and information carriers in quantum computing.[5–12]

Phosphorescence spectroscopy is the method of choice for the study of phosphorescent materials, however the characterization of chiral systems would require a chiral spectroscopy, an example of which is circularly polarized luminescence (CPL), probing the differential emission of left and right circularly polarized light. When associated to triplet-singlet transitions, this technique is also known as circularly polarized phosphorescence

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(CPP). Although less common, in particular because of their high sensitivity and low signal strengths, CPL and CPP are emerging as powerful techniques to complement electronic circular dichroism (ECD) and provide more extensive characterizations of excited electronic states.[8]

Combining multiple spectroscopic techniques can indeed help understanding experimental data and the physical-chemical properties of the system(s) under study. Of course, this requires that the theoretical models adopted to interpret those data match the complexity of the observed processes. With large molecules, the support from computations becomes indispensable. In this context, methods rooted in the density functional theory (DFT), coupled to its time-dependent extension (TD-DFT) for the study of excited electronic states, have become very popular thanks to their good balance between computational cost and accuracy. However, electronic spectroscopies are often still simulated from pure electronic structure calculations, by simply broadening the peaks obtained from the electronic transition energies and moments of the properties of interest. This is often insufficient, in particular for sensitive, chiroptical spectroscopies, since experimental band-shapes actually have a vibrational structure, which may be well visible or partially hidden depending on the quality of the measurements. In recent years, methods of various levels of sophistication have been developed and implemented in standalone or general-purpose computational chemistry packages to include this information and simulate more reliable, vibrationally resolved electronic spectra, also called vibronic spectra.[13–19]

In this context, some of us have developed a general computational tool for the simulation of different kinds of one-photon spectroscopies;[20] this tool is based on the harmonic approximation supporting both internal and Cartesian coordinates with the possible inclusion of mode-mixings, as well as Franck-Condon (FC) and Herzberg-Teller (HT) effects.[20–23]

From a computational point of view, the calculation of a chiral transition property involves the evaluation of transition electric and magnetic dipole moments between the initial and final electronic states. For one-photon phosphorescence (OPP) and CPP, an additional difficulty is that the two states involved in the transition have different spin multiplicities, so spin-orbit couplings need to be taken into account to obtain non-vanishing transition moments. Such couplings are generally missing in standard electronic structure calculations and vibronic calculations are then done at the FC level, where the transition moment is assumed to be a constant, which acts as a scaling factor of the overall band-shape intensity. While such an approximation can be sufficient for one-photon absorption and emission spectra, provided the target transition is fully-allowed, it is generally insufficient for chiroptical spectroscopies where HT terms are often needed as well.[24, 25] In this case, a correct treatment of spin-orbit couplings to obtain the actual transition moments of the properties of interest is essential.

In this contribution we present calculations of phosphorescence and CPP spectra of both organic and inorganic molecular systems, shown in Figure 1, based on two-component density functional theory with the inclusion of vibronic effects, going whenever possible beyond the simple FC approximation. First we will focus our attention on camphorquinone,

a relatively small and rather rigid organic molecule. As second case study, we have selected some Ir(III) complexes as prototypes of the widely employed class of the orthometalated iridium complexes.

2 Theory

2.1 Spin-Orbit Couplings

Phenomena like phosphorescence or inter-system crossing are forbidden within non-relativistic quantum mechanics, and only become weakly allowed when spin-orbit couplings (SOC) are included in the Hamiltonian. Formally, SOC operators arise from the relativistic Dirac equation[26] but can also be employed within non-relativistic calculations as *ad hoc* coupling operators. Several methods have been described to accurately treat these types of interactions,[27–29] based on both perturbation theory or variational methods. In this contribution we choose to rely on the latter approach, with the spin-orbit interaction based on a two-component Hamiltonian.[30–41] This Hamiltonian can be used within the framework of density functional theory provided the functional dependence is adapted to accommodate the fact that two-component densities can in general be non-collinear, i.e. the orientation of the spin magnetization vector may vary with the position in space.[42–46] Transition densities and properties can be then calculated by performing a two-component time-dependent DFT (2c-TDDFT) calculation starting from the single-determinant 2c-DFT reference[40, 46] or, as an alternative, through a real-time propagation of the two-component Hamiltonian.[47] Here, we choose the first option, from which we can determine the singlet-to-triplet transition densities by solving the response equation through an iterative Davidson algorithm as previously described.[40, 46]

Given the computed transition density $\mathbf{X}$ in the atomic orbital (AO) basis, the transition electric and magnetic dipole moments between the singlet $|S\rangle$ and the triplet $|T\rangle$ can be evaluated as:

$$\langle S | \vec{\mu} | T \rangle = \text{tr} \mathbf{X} \vec{\mu} \quad ; \quad \langle S | \vec{m} | T \rangle = \text{tr} \mathbf{X} \vec{m} \quad (1)$$

Where the electric and magnetic dipole integral matrices are given by:

$$\vec{\mu}_{\mu\nu} = -e \langle \chi_\mu | \vec{r} | \chi_\nu \rangle \quad ; \quad \vec{m}_{\mu\nu} = -\frac{e}{2m_e c} \langle \chi_\mu | \vec{r} \times \vec{p} | \chi_\nu \rangle \quad (2)$$

Where χ denotes the AO functions, e is the elementary charge, c the speed of light, and m_e is the electron mass. The electric dipole moment can also be cast in the velocity form,[48–51] where the position operator is replaced by the momentum operator, so that the scalar product between the electric and magnetic dipole moments is independent of the gauge origin, as we did in this work when computing CPP intensities. Finally, it has been pointed out[52–55] that the calculation of molecular properties in two-component relativistic methods requires the inclusion of picture-change effects, i.e. the operators themselves should also be transformed using the two-component unitary transformation. Since the

transformation of the magnetic dipole operator is not trivial, in this contribution we choose to avoid this step and reserve such developments to future works.

The calculation of transition dipole moments performed on a molecule at the optimized geometry of the triplet state is sufficient to simulate a phosphorescence or CPP spectrum at the Franck-Condon (FC) level of theory, provided the vibrational analyses of both singlet and triplet states, or at least one of the states for simplified vibronic models, have been performed. In order to include Herzberg-Teller (HT) effects, the derivatives of transition moments must be computed too. In this work we performed a two-point numerical differentiation along each Cartesian coordinate for each atom of the molecule in order to evaluate such derivatives. The derivatives are then converted from Cartesian to normal coordinates before being used in vibronic calculations.

There is a problem that must be addressed when evaluating numerical derivatives of two-component transition quantities: given the fact that our two-component method relies on complex algebra, each transition vector carries an arbitrary complex phase factor. This phase factor cancels out when computing any physical observable since both phosphorescence and CPP intensities can be written as scalar products of two transition dipole moments. However, it is not possible to ascertain that the phase factor will be the same between the two differentiation points used for the evaluation of each numerical derivative. To fix this problem, we arbitrarily choose to fix the phase of each component of the transition electric dipole moment so that it is a real positive number, and use the same phase factor for the magnetic dipole moment. In this way, calculations remain consistent along the numerical differentiation paths, allowing us to extract derivatives that do not contain spurious terms. Note that in principle each of the three Cartesian components of the dipole should not be multiplied by different phase factors. However, in the present case this does not cause problems because we only need the *diagonal* components of the tensor product between two dipole moments for phosphorescence and CPP intensities. If we were to compute the phosphorescence of a spatially oriented sample such as a liquid crystal, we would also need cross terms between different Cartesian components (e.g. terms of the type $\mu_x^* \mu_y$), therefore the two arbitrary phase factors would not cancel out, forcing us to employ the same phase factor for all dipole components. Implementation of analytical derivatives would fix this problem since the phase would then carry over to all derivative terms.

2.2 Vibronic Calculations

Simulation of vibronic spectra is carried out using models based on the Franck-Condon principle, a good framework to describe transitions of semi-rigid systems, which do not undergo significant structural changes upon the electronic transition. Herein, the band-shape can be generated as a sum of individual transitions between vibrational states of the initial and final electronic states in the so-called time-independent (TI) approach (details can be found in Refs. [16, 56]). For OPP and CPP, the spectrum intensity is computed as,

$$I_{\text{OPP}}(\omega) = \frac{2\mathcal{N}_A}{3\epsilon_0 c^3} \omega^4 \sum_{i,f} \rho_i \text{Re} \left\{ \vec{\mu}_{if} \cdot \vec{\mu}_{if}^* \right\} \delta(\Delta \omega_{if} - \omega) \quad (3)$$

$$I_{\text{CPP}}(\omega) = \frac{8\mathcal{N}_A}{3\epsilon_0 c^4} \omega^4 \sum_{i,f} \rho_i \text{Im} \{ \vec{\mu}_{if} \cdot \vec{m}_{if}^* \} \delta(\Delta \omega_{if} - \omega) \quad (4)$$

where $\vec{\mu}_{if}$ and $\vec{m}_{if}$ are the transition integrals between the initial $|\bar{\psi}_i^v\rangle$ and final $|\bar{\psi}_f^v\rangle$ vibrational states, $\vec{\mu}_{if} = \langle \bar{\psi}_i^v | \vec{\mu} | \bar{\psi}_f^v \rangle$ and $\vec{m}_{if} = \langle \bar{\psi}_i^v | \vec{m} | \bar{\psi}_f^v \rangle$, $\mathcal{N}_A$ is Avogadro's number, ϵ_0 the vacuum permittivity, c the speed of light, and ω the angular frequency of the emitted radiation. Finally, ρ_i is the Boltzmann population of the initial state i at the chosen temperature, and ω_{if} is the frequency difference between states i and f . The double summation is in theory infinite but can be truncated using appropriate schemes. First, if temperature effects are neglected, then only the initial vibrational ground state is populated, avoiding the summation over i . Otherwise, only initial excited states having a population above a given fraction of the ground state can be included in the treatment. The summation over the final state can be reduced by using prescreening schemes to select *a priori* the most intense transitions. Here, the *class*-based scheme[14, 56–58] will be used. To compute the transition integrals, the vibrational frequencies and normal modes of each electronic states are needed. Without going into detail, we will just mention that those quantities are calculated about the minimum of each potential energy surface (PES), which correspond to the so-called adiabatic Hessian (AH) model, using the harmonic approximation. The two sets of normal coordinates (one per electronic state) can then be expressed with respect to one another through a affine relation, referred to as the Duschinsky transformation. It should be noted that most of the computational cost is due to the frequency calculations step, in particular for the excited state. Thanks to the recent developments, analytic frequencies are now available at the TD-DFT level but the cost is still higher than for DFT. For this reason, a common simplification is to assume the curvatures of the PESs of both states to be equal, so that only one set of frequencies and normal modes is needed, generally from the lower state. This approximation will be referred to in the following as Adiabatic shift (AS). A final practical difficulty is that the dependence of the transition moments obtained from the electronic structure calculation with respect to the nuclear coordinates, and so the normal coordinates, is not known analytically. In practice, the transition moments are expanded as Taylor series about the equilibrium geometry of one of the electronic states, giving raise to the Franck-Condon and Herzberg-Teller terms, corresponding respectively to the zeroth-order and first-order terms of the expansion. In the following, the acronym FCHT will be used to represent the inclusion of both terms in the calculations.

As mentioned above, the underlying framework is suitable to describe transitions accompanied by small structural changes, and can fail otherwise. Depending on the flexibility of the system and the magnitude of the deformations, an explicit simulation of the dynamics of the process, either at a quantum or classical level, may be necessary. However, in many cases, the impact is rather localized and affects only one or a few degrees of freedom, referred to as large amplitude motions (LAMs). Under those conditions, hybrid schemes, where the vibrational modes are divided in several classes, and each class is treated at a specific level of theory, are particularly appealing. For systems characterized by

localized deformations, the modes can be divided into two classes. The first one corresponds to a small number of LAMs, which require an *ad hoc*, anharmonic treatment. The second set of coordinates contains the remaining small-amplitude modes (SAMs), which are treated at the harmonic level.[59] From a practical perspective, the reliability of such hybrid schemes depend on the magnitude of the couplings between the two sets of coordinates. In fact, only by employing an appropriate set of coordinates, where those couplings are negligible, can the coordinates belonging to different classes be reliably treated at different levels of theory. Such a condition can be extremely challenging to meet with Cartesian-based normal coordinates, even for the simplest deformations due to the presence of strong couplings between LAMs and the other modes. An alternative solution relies on curvilinear, internal coordinates, which provide a more reliable description of molecular vibrations also for relatively strong deformations from the equilibrium position. Unfortunately, the use of internal coordinates is not as straightforward as for the Cartesian case. First, internal coordinates are non-linear functions of the Cartesian ones, thus making the calculation of harmonic and anharmonic force field more difficult. Furthermore, the definition of the internal coordinates is not unique for a given molecular topology, and can greatly affect the quality of the simulations. As a brief overview, a two-step procedure is usually employed to build internal coordinates. First, a set of redundant coordinates (*i.e.* whose number is larger than the vibrational degrees of freedom of the molecule) is built from the molecular topology. The most standard redundant set is based on the so-called primitive internal coordinates (PICs),[60] comprising all bonds distances, valence and dihedral angles. PICs can be complemented by special coordinates, such as out-of-planes, ring-puckering and linear bending coordinates. In this work, valence and dihedral angles corresponding to linear chains will be replaced by linear bending coordinates, whose definition can be found in Refs. [61–63]. The identification of linear chains is done following the algorithm presented in Ref. [20]. The resulting set of redundant internal coordinates will be referred to as generalized internal coordinates (GICs).

A direct use of redundant internal coordinates (either PICs or GICs) in actual calculations is not practical, since it leads to rectangular, non-invertible matrices. Even if spectroscopic models based on a direct use of redundant internal coordinates have been proposed in the recent years,[64, 65] it is convenient to define a non-redundant subset of the redundant internal coordinates before performing the calculations. Various algorithms have been proposed for such a task in the literature and applied to geometry optimization.[66–68] Here, the so-called delocalized internal coordinates (DICs),[69] which are obtained through a Singular Value Decomposition (SVD) of the Wilson **B** matrix, will be employed. As already discussed in our previous works,[20, 70] DICs provide an efficient reduction of mode-couplings also for non-trivial LAMs, as well as for systems characterized by complex topologies, especially in comparison with the widely used Z-matrix internal coordinates (ZICs).

When internal coordinates are employed, a different, non-orthogonal transformation matrix between internal and normal coordinates is built and used to define the Duschinsky transformation.[20, 70] For simulations carried out at the FC level, the rest of the theoretical framework can be kept unchanged, provided that the Duschinsky matrix was not assumed to

be orthogonal, as it is the case for Cartesian coordinates but not for the internal ones. For FCHT calculations, also the derivatives of the transition dipole moments must be converted to the internal-coordinates representation.[20]

3 Computational Details

All geometry optimizations and frequency calculations have been carried out with a development version of the Gaussian suite of quantum chemical programs.[15] The two-component relativistic Hamiltonian was built following the exact two-component (X2C) method,[30–38, 40] relying on the diagonalization of the one-electron Dirac Hamiltonian. Two-electron spin-orbit effects have been accounted for by using a scheme based on the scaling of the one-electron interactions depending on the nuclear charges and angular momenta.[71] In relativistic calculations, nuclei are not point-like, but modeled using *s*-type functions.[72, 73] Vibronic spectra were obtained using the time-independent (TI) algorithm, and each vibronic peak was broadened using Gaussian functions with half-width at half-maximum (HWHM) of 200 cm⁻¹ for camphorquinone and 500 cm⁻¹ for iridium complexes. Internal coordinates were used for all vibronic calculations, unless otherwise specified.[20] The molecular topology was built by defining two atoms X and Y as bonded if their distance is shorter than 130 % of their average XY bond length, taken from B3LYP/6-31G(d) results.[74] A threshold of 10⁻⁵ on the absolute value of the singular values of **B** has been used to select the non-redundant singular vectors. The following parameters of the class-based integral prescreening scheme have been used: $C_1^{\max} = 100$, $C_2^{\max} = 50$, $N_I^{\max} = 10^9$ where $N_I^{\max}$ is the maximum number of FC integrals to be computed in each class, $C_1^{\max}$ and $C_2^{\max}$ are the maximum number of quanta reachable by each excited mode in a given class (overtones, C_1 and 2-modes combinations C_2). For the electronic structure benchmarks, five hybrid exchange-correlation functionals have been employed: B3LYP[75, 76], CAM-B3LYP[77], PBE0[78], M06-2X[79], ω B97X-D[80]. The cc-pVDZ[81] basis set was used for camphorquinone in all calculations, whereas the 6-31G*[82, 83]/Lanl2DZ[84] basis set with pseudopotential on iridium was used for Ir complexes. sRGB colors have been calculated by the color utility present in VMS.[85, 86] Cube files visualization and manipulation have been performed with Caffeine.[87]

4 Result and Discussion

4.1 Benchmark

A first critical step in the setup of a reliable computational protocol is the definition of the most suitable electronic structure method and for DFT, this includes the choice of the exchange-correlation functional. A phosphorescence or CPP vibronic spectral calculation involves several steps, which can be affected differently by this choice. First the singlet and triplet geometries must be optimized, and the harmonic frequencies calculated in order to generate a model for each potential energy surface. Then, the transition dipole moments (and possibly their Cartesian derivatives) must be obtained by performing relativistic calculations on the system in the triplet geometry. The spectrum can then be generated using the vibronic model described above. The absolute position of the emission bands can depend quite

strongly upon the chosen functional, and in some cases, DFT is unable to provide accurate excitation energies. Nevertheless, when experimental data are available the calculated spectrum can be simply shifted to match the position of the 0-0 vibronic transition, between the vibrational ground states of the two electronic states involved in the transition. The most important factors determining the shape of the spectrum are instead the normal modes and frequencies obtained from the vibrational analyses, and again different functionals can in general give diverging results. The same is true for the transition dipole moments as well, with a direct impact on the absolute intensities for FC or the relative intensity of each band for FCHT. All these different effects can be studied separately to assess the quality of the different functionals.

In order to verify the reliability of the description of the PES, we performed a small benchmark with five commonly used hybrid and range-separated functionals: B3LYP, PBE0, M06-2X, CAM-B3LYP, and ω B97X-D. In Figure 2 the simulated vibronic phosphorescence spectra of camphorquinone and $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ obtained with the five functionals at the AH|FC level of theory are plotted against the experimental ones. Since we are interested in the description of the vibronic band-shapes rather than the absolute positions of the bands, the theoretical spectra were shifted to match the experimental one and in particular the intense band at about 2.21 eV. Moreover, all spectra have been renormalized. For camphorquinone, the M06-2X functional gives the less satisfactory results, with a nearly featureless band-shape while the other four functionals give similar results and reproduce qualitatively the general shape observed experimentally, albeit underestimating the shoulder at about 580 nm and more importantly the second band at 625 nm, only represented as a shoulder in the calculations (*vide infra*). The B3LYP functional shows the best performance and therefore has been used for this molecule in all subsequent calculations.

Moving to the Ir complexes, and considering for the moment just $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ for now (Figure 2b), only the B3LYP and PBE0 functionals provided vibronic spectra with shapes comparable to the experimental ones. In particular, results obtained with the other three functionals resulted in an insufficient spectrum convergence and a strong shift of some normal modes. Therefore, the spectra in Figure 2b had to be generated by removing the most problematic modes, in order to improve the overall convergence. As can be seen in Figure 2b, even after these modes have been removed, and the spectrum convergence has increased, the overall band-shape remains very different from the experimental one. PBE0 performs better in the reproduction of the two PESs for this organometallic system, moreover it has proved to provide good results in different applications dealing with organometallic compounds,[88] thus it has been employed in all further calculations on those systems.

4.2 Camphorquinone

The first system we analyzed is camphorquinone, a small organic chiral molecule for which experimental phosphorescence spectra are available.[89] The relatively small size of this system allows for a thorough comparison of the different levels of approximation available for the setup of the computational model.

We start our analysis by comparing the spectra in Figure 3a, obtained with the FC approximation. As an introductory remark, camphorquinone is rather rigid and does not

undergo significant changes between the triplet and singlet states, as can be noted from the superposition of the two equilibrium geometries shown in figure 5a. This is confirmed by the small values of the shift vector in Figure 5b. As a result, no large amplitude motions are expected and a full vibronic treatment within the FC approximation can be performed. As mentioned in the theoretical section, the emitting triplet is constituted by an ensemble of three degenerate states with a different projection of the spin angular momentum, and in the high-temperature limit these states are equally populated and therefore each can contribute to the overall spectral signal. In this case, the three states contribute to the overall signal in very different proportions, with one being dominant over the other two. At the FC level, the transition dipole moments being simply scaling factors, the overall spectral shape is the same in all three cases. At this level of approximation, we see a strong contribution from the 0-0 transition as the first peak, while other vibronic transitions (particularly those involving the second normal mode, i.e. the wagging motion of the carbonyl groups) contribute to a much lesser degree to the tail of the spectrum. Figure 3b shows that at the FCHT level the three spectra look strikingly different. There is the evident emergence of a strong shoulder at lower energy in the spectrum, which for the second triplet state even overpowers the strength of the 0-0 transition. This result can be ascribed to vibronic transitions involving two vibrational modes of similar energies: the symmetric and antisymmetric CO stretching motions of the carbonyl groups. The total spectra at the FC and FCHT levels are compared in Figure 4 with the experimental data.[89] The overall spectral shape is well reproduced by the theoretical model, however it can also be seen that while the FC spectrum lacks the low-energy band, the FCHT spectrum overestimates its intensity. A number of reasons can be invoked to explain this discrepancy, such as the lack of solvation effects or the fact that the spectrum is formally computed at zero temperature. Temperature effects can be included by populating excited vibrational states in the triplet PES as shown in equation 3, with a considerable increase in computational cost. A possible solution to this problem could be to resort to a time-dependent implementation[90, 91] though the implementation in this case is not trivial given the fact that in phosphorescence and CPP spectroscopy the transition dipole moments may be complex. Nevertheless, the present calculation still allows to successfully describe the origin of the spectral shape in terms of the vibrational modes of the molecule involved in the vibronic transition.

Switching now to CPP, the chiral equivalent of phosphorescence, we first look at the different contributions due to each triplet state and at the effect of the inclusion of HT terms. At the FC level, shown in Figure 6a, one state has a negligible rotational strength while the other two give significant contributions but with opposite signs. As before and for the same reason, only the total intensities and their signs change, but the spectral shape is the same. By including HT effects, shown in Figure 6b, significant changes in the intensities can be observed. The state that had a negligible intensity at the FC level now gives a significant positive contribution close to the 0-0 transition. For the other two states, though the spectrum for each state has the same sign as in the FC case, an inversion occurs due to the contributions from the two CO stretching motions. The sum spectra can be observed in Figures 6c and 6d. While the overall spectrum has a negative sign at the FC level, the FCHT spectrum presents two sign changes, having a negative sign close to the 0-0 transition, then a positive sign throughout the main vibronic sequence, and again a negative sign when the

final state falls within the region of excitation for the higher energy stretching modes. These results show that for a sensitive property such as CPP, relying on the FC approximation could be misleading, even in the case where one is only interested in the sign of the property rather than in the overall spectral shape. Regarding the g -values obtained from our calculations we observe that, for each triplet state, the electronic values are of the order of 10^{-3} . We also computed the electronic g value for the S_1 state obtaining a value of order 10^{-2} , which is consistent with those observed by Steinberg et al.[89] This analysis, however, remains preliminary since several effects are omitted with respect to the experimental data. In particular, solvent effects which are here neglected can have a significant impact as shown in the experimental study.[89]

4.3 Ir Complexes

Complexes of Iridium are known to exhibit intense phosphorescence emission[1, 2, 92–97], we therefore sought to analyze their triplet emission to test our computational method on such systems, both larger and more complex (due to the presence of the transition metal) than the previously studied organic molecule. Chiral complexes of Ir have also been described and can be obtained thanks to ligands such as 2-phenylpyridine (ppy), which can organize themselves around the metal center to give the complex a helical structure. Most strategies employed in the tuning of the photophysical properties of the phenylpyridine-based iridium compounds have involved the substitution of the donor/acceptor groups on the ppy and the substitution of the ancillary ligands.[1, 97] Here, we compare the results for some complexes in this class. Figure 7 shows the simulated spectra of the prototype $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ complex and three possible substitutions aimed at tuning the emission.

All complexes present rigid structures with relatively small geometric changes between the two states, with the exception of $[\text{Ir}(\text{ppy})_2(\text{NCO})_2]^-$. If we look at $[\text{Ir}(\text{ppy})_2(\text{NCO})_2]^-$, we see in Figure 8a, that there is a large distortion between the equilibrium geometries of the singlet and the triplet involving changes in the dihedral angle between the two phenylpyridine ligands and a linearization of the bond angle of the NCO^- ligands. Under such circumstances we expect that the use of internal coordinates for vibronic calculations can strongly improve the spectral convergence. As already noted in the theoretical section, in presence of linear angles a specific definition of the redundant set of internal coordinates is required. For $[\text{Ir}(\text{ppy})_2(\text{NCO})_2]^-$, GICs, where valence angles and dihedral angles associated to linear chains are substituted with two appropriate linear bending coordinates, have been used instead of the standard PICs. The experimental[93] phosphorescence spectrum can be seen in Figure 9, along with the vibronic spectra computed using Cartesian and internal coordinates. It can be immediately seen that there is a significant improvement in the agreement between theory and experiment upon switching to internal coordinates for this system, which gives a different band-shape and vibronic progression. These differences can be further understood by looking at Figure 10, which shows the Sharp and Rosenstock matrix $\mathbf{C}$ [98] and the shift vector $\mathbf{K}$ from the Duschinsky transformation.[99] In the time-independent framework used to simulate the spectral band-shape, each vibronic transition is treated individually. The most efficient way is to compute the intensity through recursion formulas relating the overlap integral for a given transition to those between states with lower numbers of quanta.[100] In practice, a direct consequence is that only the transition

between the vibrational ground states need to be known analytically and is used as starting point. In this condition, and ignoring temperature effects, off-diagonal elements of $\mathbf{C}$ are directly responsible for the intensity of combination bands, while the diagonal elements contribute to the vibrational progression, i.e. the overtones, of each mode. The larger off-diagonal terms obtained in Cartesian coordinates hint as a major contribution of combination bands to the overall band-shape, and consequently to its broadening, with respect to internal coordinates. The shift vectors are nearly equal in both cases, with two strongly shifted modes, specifically modes 2 and 7 depicted in Figure 8 that involve the dihedral angles of the ancillary ligands. However, those vibrations are more localized in DICS and thus do not contribute in any significant way to the transition involving higher-energy modes, contrary to Cartesian coordinates, as can be seen again from the shape of $\mathbf{C}$.

We finally select one simple complex, with two cyanide ligands, to perform a more extensive analysis. Indeed, the computational treatment of such systems can be quite prohibitive depending on the size of the ligands, both in terms of basis functions that are added to the system and, if numerical derivatives must be performed, in terms of the overall number of atoms. Therefore we select a relatively smaller system of the family of the ortho-metalated Ir(III) complexes, with two small cyanide substituents as prototype. These anionic iridium complexes are known for their high quantum yield [93] and have been recently employed in soft-salt systems with interesting results.[101]

The results can be seen in Figure 11a. At this level of approximation the overall spectral signal is due to only one of the three degenerated triplets of T_1 . The most intense transition in the spectra corresponds to the 0-0 transition, followed by a less intense peak originating from the vibronic transitions involving the CN bending and a series of carbon-carbon stretchings in the phenylpyridine ring. In spite of a small underestimation of the second peak, the overall shape of the spectrum is well reproduced, including the shoulder at 600 nm. In analogy with the case of camphorquinone, discussed above, we can speculate that the lack in intensity can be due to the absence of the HT contribution.

Because of their photochemical properties, Ir complexes have been widely studied in industry, in particular in the field of light emitting devices. In addition to their high quantum yield, an interesting feature is that they can be easily tuned by substituting or modifying the ligands, for instance to change the emission wavelength of the molecule, and so its color. This opens a broad range of possibilities to build devices purposely tailored for a given application. However, finding interesting configurations can be extremely time consuming and expensive experimentally, and calculations can help to select the best candidates provided that the level of theory is adequate to the physical-chemical problem. A quite demanding property is the color emitted by a molecule, which depends on the overall shape of the emission spectrum rather just on the vertical energy difference and so provides an immediate and visual assessment of the quality of the theoretical model with respect to experiment. A direct consequence is that, when using theory to screen a range of complexes, a series of purely electronic calculations would be insufficient for the purpose of determining the expected color of the system. Figure 12 shows the real phosphorescence color along with the one calculated at the AH|FC level of theory, placed within the $CIE_{x,y}$ color space. It can be seen that the predicted color is green whereas the observed one is

cyan. This is mostly due to the error in the singlet-triplet energy difference predicted by DFT. If the computed spectrum is shifted to match the position of the 0-0 transition then the prediction becomes much more accurate, giving the same qualitative result. Moreover, in Figure 12 the colors obtained with the AS|FC level of theory, that is by ignoring the mode mixing, as commonly done in vibronic simulations, have been also reported. The small differences between them and the AH|FC result testify a low contribution of the mode-mixing to the overall band-shape in this system.

We finally look at the CPP spectrum of this complex to examine its chiral response. Experimental spectra are not available, however the CPP sign is expected to be negative in Λ complexes and positive for the Σ configurations, while the magnitude of the dissymmetry factor g should be around 10^{-3} . [8, 102–104] Calculated g values for different functionals can be seen in Table 1. From these results, a remarkable difference between standard and range-separated functionals can be noted, with the latter yielding the expected sign. This trend might be related to the fact that the triplet-to-singlet transition for this molecule is a metal-to-ligand charge-transfer (MLCT). This can be seen in Figure 13 where the density difference for four complexes are shown. In the cyanide complexes there is a significant density difference on one of the phenylpyridine rings, whereas with the cyanate and thiocyanate complexes, the difference density is more localized on the metal.

5 Conclusion

We have presented a computational methodology to compute vibrationally resolved phosphorescence spectra and their chiral equivalent CPP based on relativistic two-component DFT calculations. Vibronic spectra were computed by modeling both singlet and triplet PESs using the harmonic approximation, and by employing an expansion of the transition dipole moments including Herzberg-Teller terms. The effect of the choice of functional on the different components of the calculation, as well as the role of the HT extension, has been discussed. By including all relevant contributions to the calculation, we were able to obtain calculated spectra in good accord with available experimental data.

The results on the Iridium complexes revealed that a simulation of a phosphorescence or CPP spectrum is rather delicate and the choice of the computational method is critical, depending on the nature of the ligands and the nature of, the singlet and triplet states. Different functionals can often provide very different results for the various steps involved in the calculation, from the modeling of the electronic states to the accurate prediction of the harmonic potential energy surfaces and hence the vibronic spectra. Much more work is required in this case to compile benchmarks that would select the best method for the different steps for these types of systems, and the need to go beyond the simple analysis of the electronic transition energy and rotatory or dipole strengths is evident.

Notwithstanding all the present developments, much work remains to be done. The development of an analytical formulation for 2c-TDDFT derivatives would provide significant computational savings expanding the set of systems which can be treated at the HT level of theory, as well as address problems regarding the stability of the phase of the computed properties. In addition, all the results presented in this work have been computed

for isolated molecules, though most experiments are carried out in the condensed phase, typically in solution. Solvent effects can significantly affect the relative energy of the initial and final state, as well as the vibrational modes and thus the vibronic band shape. The inclusion of solvent effects can be performed by relying on either continuum or discrete models, which would need to be coupled to the relativistic two-component description.

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(1*R*)-Camphorquinone Λ -[Ir(Rppy)₂(L)₂]⁻

- 1: R=F; L=CN⁻
 2: R=H; L=CN⁻
 3: R=H; L=NCO⁻
 4: R=H; L=NCS⁻

Figure 1.
Molecular structures of the systems studied.

Figure 2.

Simulated phosphorescence spectra of camphorquinone and $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$. For the latter molecule, in order to achieve reasonable convergence in TI vibronic calculations, modes 1,3,5 and 7 have been removed for the CAM-B3LYP and $\omega\text{B97X-D}$ functionals, whereas all modes up to 11 have been removed for M06-2X.

(a) FC

(b) FCHT

Figure 3. Vibronic FC and FCHT phosphorescence spectra of camphorquinone for each triplet substate.

Figure 4. Calculated FC, FCHT, and experimental[89], phosphorescence spectra of camphorquinone. Intensities in arbitrary units.

(a) Geometries

(b) Shift vector

Figure 5.

First panel: structural changes between the initial T_1 (light blue) and the final S_0 (deep red) electronic states of camphorquinone. Second panel: shift vector between the triplet and singlet states, red bars indicate a positive sign, blue bars indicate a negative sign.

Figure 6.

Calculated FC and FCHT CPP sum spectra of (1R)-camphorquinone. The spectra in panels (a) and (b) show the contribution due to each triplet state, panels (c) and (d) show the sum spectra. Intensities in arbitrary units.

Figure 7.
Vibronic spectra of [Ir(ppy)₂(CN)₂]⁻ prototype molecule and three substituted complexes.
(a) Non-normalized and (b) normalized spectra.

Figure 8.

(b) Structural changes between the initial (light blue) and the final electronic state (deep red) of [Ir(ppy)₂(NCO)₂]⁻; Normal modes 2 (a) and 7 (c) of the final states.

Figure 9. Experimental[93] (dashed black) and calculated phosphorescence spectra of $[\text{Ir}(\text{ppy})_2(\text{NCO})_2]^-$. The calculated spectra were obtained using either Cartesian (orange) or internal (blue) coordinates.

Figure 10.

Left: Cartesian Coordinates, Right: Generalized Internal Coordinates (GIC) Upper Panels: Graphical representation of the Sharp and Rosenstock **C** matrix for the $S_0 \leftarrow T_1$ transition of the $[\text{Ir}(\text{ppy})_2(\text{NCO})_2]^-$ complexes at AH/FC level of theory. Normalizing factor:0.3 Lower Panels: Graphical representation of the shift vector **K**, positive shifts are represented with red bars, whereas negative with blue bars

Figure 11.

(a) FC phosphorescence spectra of $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ for each triplet state; (b) comparison with the experimental[101] spectra.

Figure 12.

CIE 1931 coordinates of CN complex calculated on the simulated spectra obtained with different approaches.

Figure 13.

Triplet-to-singlet self-consistent field (SCF) electron density difference at the T_1 geometry. Red isosurfaces represent regions of electron depletion, blue isosurfaces represent regions of electron accumulation. (isodensity surfaces at ± 0.05 e/bohr³)

Table 1

Dissymmetry factor g of $\Lambda - [\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ calculated using different DFT functionals.

Functionals	B3LYP	CAM-B3LYP	M06-2X	PBE0	ω B97X-D
$10^3 g$	1.70	-2.98	3.36	5.46	-3.68