

Insights for an Accurate Comparison of Computational Data to Experimental Absorption and Emission Spectra: Beyond the Vertical Transition Approximation

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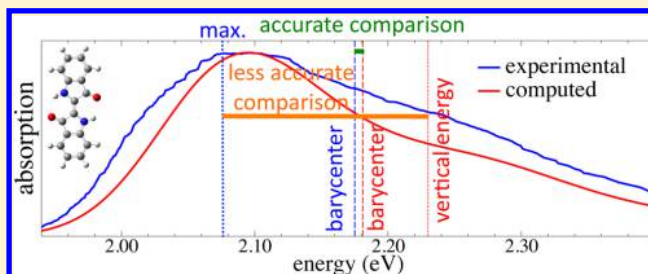
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S Supporting Information

ABSTRACT: In this work we carefully investigate the relationship between computed data and experimental electronic spectra. To that end, we compare both vertical transition energies, E_V , and characteristic frequencies of the spectrum like the maximum, ν^{\max} , and the center of gravity, M^1 , taking advantage of an analytical expression of M^1 in terms of the parameters of the initial- and final-state potential energy surfaces. After pointing out that, for an accurate comparison, experimental spectra should be preliminarily mapped from wavelength to frequency domain and transformed to normalized lineshapes, we simulate the absorption and emission spectra of several prototypical chromophores, obtaining lineshapes in very good agreement with experimental data. Our results indicate that the customary comparison of experimental ν^{\max} and computational E_V , without taking into account vibrational effects, is not an adequate measure of the performance of an electronic method. In fact, it introduces systematic errors that, in the investigated systems, are on the order of 0.1–0.3 eV, i.e., values comparable to the expected accuracy of the most accurate computational methods. On the contrary, a comparison of experimental and computed M^1 and/or 0–0 transition frequencies provides more robust results. Some rules of thumbs are proposed to help rationalize which kind of correction one should expect when comparing E_V , M^1 , and ν^{\max} .



1. INTRODUCTION

The comparison between experimental absorption and emission spectra and related computational values is likely one of the best examples of fruitful interaction between experimental and theoretical studies.^{1,2} Actually, the development of methods in quantum chemistry owes much to the comparison with spectroscopic data while, on the other hand, computations have always been profitably used to assign and interpret experimental spectra, even when they were limited to empirical or semiempirical methods. More recently, remarkable advances in the development of computational methods for the study of medium/large size molecules in their electronically excited states, and new functionals for TD-DFT, have been paralleled by several studies (too many to exhaustively review here) comparing computed and experimental spectra or, more precisely, quantities derived from the experimental spectra and computed values.^{3–8} Most of these studies were simply based on a comparison of the computed vertical excitation energy (E_V) with experimental absorption maxima (ν^{\max}). Although

they have provided very useful general methodological information, experiments provide spectra with their frequency-dependent line shape, and not single numbers. Even if E_V is correlated with ν^{\max} , the two quantities are not formally equivalent. In practice, as we also show in the following, deviations of a few tenths of an electronvolt are possible.^{9–27} Additional difficulties arise from the fact that most of the calculations are performed in the gas phase at 0 K, whereas experiments are in many cases available only in the condensed phase and at finite temperature.

These difficulties have been clearly highlighted by several recent studies, where much more precise procedures have been devised in order to assess the accuracy of the computational methods.^{11–16} They usually rely on the comparison between the computed 0–0 transition energy ν_{00} (i.e., between the ground vibrational states of the two electronic states) and the

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origin of the fluorescence spectrum, or the crossing point between absorption and emission spectra.^{12–15} On the other hand, for many compounds, sufficiently well resolved fluorescence spectra are not available, and in most of the studies in the literature, the accuracy of the computations is still judged on the basis of the agreement of E_V with the experimental ν^{\max} ; conversely, experimental bands are assigned on the ground of computed E_V (and oscillator strengths).

We therefore decided to investigate in detail the effective relation between E_V and spectral parameters, exploiting recent advances in the computation of vibrationally resolved spectra.^{9,10,17–30} Although it is now indeed possible, even for large-size semirigid molecules, to compute optical spectra that can directly be compared with experiments, both in the gas phase and in solution, it is interesting to highlight some general guidelines and a caveat for the comparison between computed E_V and absorption spectra, looking for the existence of simple rules of thumb to be used, for example, when the computation of vibrationally resolved spectra is not easily amenable.

In this contribution, we compute the absorption spectra (and for one test case the emission spectrum), in the gas phase and solution, of several prototypical compounds, chosen among those for which sufficiently resolved experimental spectra and/or high-level computational studies are available in the literature, and we compare their line shape, first moment (i.e., the center of gravity of the spectrum, M^1), and ν^{\max} with experimental data. The results are analyzed also on the grounds of simple relations that can be derived between E_V and M^1 of the spectrum.^{31–33} Our investigation also faces another point often overlooked, i.e., the necessity to carefully elaborate the experimental spectra in order to get a fully meaningful comparison with computational data.

2. COMPUTATIONAL DETAILS

DFT calculations have been employed to compute ground state minima and vibrational frequencies, whereas for the excited states (we focused on lowest-energy bright singlet states), we resorted to time-dependent (TD) DFT calculations, for which analytical gradients are available, followed by numerical calculation of the Hessian.³⁴ Most of our analysis has been performed by using PBE0 hybrid functional PBE0 (25% of HF exchange),³⁵ which has already been shown to provide spectral lineshapes in nice agreement with experimental data on a number of prototypical systems, including coumarin C153, free-base porphyrin, and *trans*-stilbene.^{16–21} We have however checked the possible dependence of our conclusions on the choice of the functional by performing test calculations on anthracene by employing three other functionals, namely, the gradient corrected BLYP functional,^{36,37} the hybrid functional B3LYP,^{37,38} and the long-range-corrected CAM-B3LYP functional.³⁹ We have used three different basis sets, from the minimal 6-31G(d) (used in most of our analysis) to the 6-311+G(2d,2p) basis set.

Bulk solvent effects have been included by the PCM model,⁴⁰ using the standard implementation of PCM/TD-DFT, based on the linear response theory (LR-PCM/TD-DFT),^{41,42} for which analytical gradients are available.³⁴

Fully converged vibrationally resolved spectra have been computed in harmonic approximation including the possible differences of ground and excited state normal modes and frequencies (Duschinsky effect),^{43–45} adopting both time-independent (TI) and time-dependent (TD) strategies. Different effective TI methods have been proposed in the

literature.^{27–30} The one we use here (now implemented also in Gaussian 09)^{24,25} is based on a partition of the possible vibronic transitions in classes C_n depending on the number n of simultaneously excited modes in the final state and on a prescreening technique to individuate the important contributions of classes C_n based on the analysis of the contributions of lower-order classes C_m ($m < n$).^{17–23} In one of the studied systems (namely *trans*-azobenzene), we have investigated also the effect of temperature on the spectral shape. In that case, to ensure the full-convergence necessary to reproduce M^1 , and to speed up the calculations, we adopted an effective TD approach based on an analytical expression of the finite-temperature time-correlation function χ , whose Fourier transform gives the spectrum line shape. A number of derivations of χ have been proposed in the literature^{47–54} and shown to be equivalent;⁵¹ we follow here the one given by Pollack and colleagues.^{48,49} TD methods are also the most suitable choice in the case of strong nonadiabatic couplings.^{55,56}

Since the relation between M^1 and E_V becomes more loose when Herzberg–Teller (HT) effects are relevant (see ref 33), we investigated here only bright transitions where Franck–Condon (FC) approximation is adequate. The harmonic potential energy surface (PES) of the final state has been modeled by using both the Vertical Hessian (VH) and Adiabatic Hessian (AH) approaches.⁴⁶ All the spectra calculations with either TI or TD strategies were performed by a development version of our code *FCclasses*.²⁶ Electronic calculations have been performed by using the Gaussian 09 program.⁵⁷

3. THEORETICAL BACKGROUND

A general TI expression including both absorption and emission spectra can be written as $S(\nu)$

$$S(\nu) = C\nu^p \sum_{\mathbf{w}, \mathbf{w}'} \rho_{\mathbf{w}'}(T) |\langle \mathbf{w}' | \mu_e | \mathbf{w} \rangle|^2 \delta(E_{\mathbf{w}'} - E_{\mathbf{w}} + h\nu) \quad (1)$$

where ν is the absorbed/emitted frequency, the sum is taken over the initial and final states, $|\mathbf{w}'\rangle$ and $|\mathbf{w}\rangle$ respectively, $E_{\mathbf{w}'}$ and $E_{\mathbf{w}}$ are their energies, $\rho_{\mathbf{w}'}(T)$ is the Boltzmann population of the initial states $|\mathbf{w}'\rangle$, and $p = 1$ and 3 for absorption and emission (if the spectrum is given as number of emitted photons per frequency and time units), respectively. In FC approximation, the electronic transition dipole moment μ_e , i.e., the off-matrix element of the dipole moment between the initial and final electronic states, is taken independently of the nuclear coordinates. $S(\nu)$ is usually convoluted with a proper normalized line shape function $g(\nu)$ (either a Lorentzian or a Gaussian depending on which, between homogeneous and inhomogeneous broadening, is dominant). Fluorescence is usually reported as the quantum distribution of emitted photons in arbitrary units (sometimes known as $\Phi(\nu)$), while an expression for molar absorptivity $\varepsilon(\nu)$ directly comparable to experimental spectra is

$$\varepsilon(\nu) = \frac{4\pi^2 \nu N_A}{3000 \times \ln(10) \times \hbar c_0 4\pi \varepsilon_0} \times \sum_{\mathbf{w}'} \rho_{\mathbf{w}'}(T) |\langle \mathbf{w}' | \mu_e | \mathbf{w} \rangle|^2 g(\nu, \nu_{\mathbf{w}\mathbf{w}'}) \quad (2)$$

where $\nu_{\mathbf{w}\mathbf{w}'} = h^{-1}(E_{\mathbf{w}} - E_{\mathbf{w}'})$, N_A is Avogadro's number, c_0 is the speed of light in vacuo, and ε_0 is the vacuum permittivity.

We assume an harmonic model for the initial and final electronic state PES. The initial state PES is simply

$$V'(\mathbf{Q}') = E_0' + \frac{1}{2} \mathbf{Q}'^T \Omega'^2 \mathbf{Q}' \quad (3)$$

where $E_0' = V'(\mathbf{Q}' = \mathbf{0})$, \mathbf{Q}' is the vector of the initial-state normal coordinates, and Ω' is the diagonal matrix of their frequencies. As schematically depicted in Figure 1, two choices

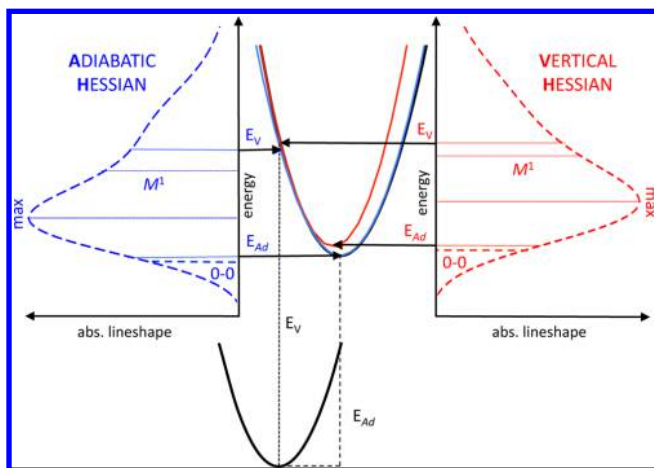


Figure 1. A schematic picture of the differences in VH and AH models for absorption. An anharmonic potential for the final state (black solid line) and its harmonic approximations through a second-order expansion at the final-state (AH, blue) and initial-state (VH, red) equilibrium geometries. VH (AH) potential coincides with the anharmonic one at the ground-state (excited) geometry, while it approximates it at the excited (ground) geometry. Consequently, AH and VH models may show differences in the equilibrium geometries for the final state and in the E_V , E_{Ad} , ν_{00} , and M^1 parameters. Close AH and VH predictions support the validity of harmonic approximation in the coordinate space relevant for the spectrum calculation.

are available for representing the final-state PES, V . In the VH approach, V is built from a second-order expansion around the initial-state equilibrium geometry ($\mathbf{Q}' = \mathbf{0}$)

$$V(\mathbf{Q}') = E_0' + \mathbf{g}^T \mathbf{Q}' + \frac{1}{2} \mathbf{Q}'^T \mathbf{F} \mathbf{Q}' \quad (4)$$

where $E_0' = V(\mathbf{Q}' = \mathbf{0})$, \mathbf{g} is the gradient of the final state PES, and \mathbf{F} is its force constant matrix.⁴⁶ The vertical excitation energy is defined as $E_V = |E_0' - E_0|$. According to the AH approach, on the contrary, the final state PES is expanded around its own equilibrium geometry

$$\mathbf{Q}' = \mathbf{J} \mathbf{Q} + \mathbf{K} \quad (5)$$

$$V(\mathbf{Q}') = E_0 + \frac{1}{2} \mathbf{K}^T \mathbf{J} \Omega^2 \mathbf{J}^T \mathbf{K} - \mathbf{K}^T \mathbf{J} \Omega^2 \mathbf{J}^T \mathbf{Q}' + \frac{1}{2} \mathbf{Q}'^T \mathbf{J} \Omega^2 \mathbf{J}^T \mathbf{Q}' \quad (6)$$

where the first equation reports the well-known linear relation between initial \mathbf{Q}' and final \mathbf{Q} state normal coordinates through the Duschinsky matrix \mathbf{J} and the vector of the equilibrium geometry displacements \mathbf{K} , Ω is the diagonal matrix of the final state frequencies and $E_0 = V(\mathbf{Q} = \mathbf{0})$. The difference of the energy of the two minima, called the adiabatic energy difference, is $E_{Ad} = |E_0 - E_0'|$. Comparing eqs 4 and 6, we have AH estimates for vertical data, $\mathbf{g}^{(AH)} = -\mathbf{J} \Omega^2 \mathbf{J}^T \mathbf{K}$, $\mathbf{F}^{(AH)} = \mathbf{J} \Omega^2 \mathbf{J}^T$, and $E_0^{(AH)} = E_0 + 1/2 \mathbf{K}^T \mathbf{F}^{(AH)} \mathbf{K}$; they are approximated

since they are extrapolated from data obtained at the final-state geometry assuming a harmonic final-state PES.⁴⁶ Consequently, also the AH value of E_V , $E_V^{(AH)}$ is approximated $E_V^{(AH)} = |E_0^{(AH)} - E_0'|$ (see Figure 1 for a schematic illustration for an absorption spectrum). Analogously, in the VH model, $E_{Ad}^{(VH)}$, the final-state frequencies $\Omega^{(VH)}$, and the displacement vector $\mathbf{K}^{(VH)}$ are approximated since they are extrapolated from data obtained at the initial-state geometry (see Figure 1).⁴⁶

It is not possible to establish a straightforward expression giving the maximum of the electronic spectrum as a function of molecular parameters, because the former depends on the photon frequency (see eq 1) and varies with the resolution of the experimental spectrum. On the contrary, it is possible to obtain analytical expressions for the first-moment M^1 of the normalized absorption/emission line shape $L(\nu)$, where $L(\nu) = NS(\nu)/\nu^p$ and N is the normalization factor. M^1 represents the average transition frequency, i.e., the center of gravity of the spectral line shape, and is defined as

$$M^1 = \int_{-\infty}^{\infty} \nu L(\nu) d\nu \quad (7)$$

Theoretically, it has a simple expression that, in FC approximation, is^{31–33}

$$M_{FC}^1 = \pm \sum_{\mathbf{w}'} \rho_{\mathbf{w}'}(T) |\langle \mathbf{w}' | (V(\mathbf{Q}') - V'(\mathbf{Q}')) | \mathbf{w}' \rangle|^2 \quad (8)$$

where the plus and the minus are for absorption and emission, respectively. Assuming the harmonic approximation (eq 3 for V' and eqs 4 or 6 for V), we straightforwardly get^{31–33}

$$M_{FC}^{1,abs} = E_V + \sum_r \frac{\hbar}{4\Omega_r'} (F_{rr} - \Omega_r'^2) \coth\left(\frac{\hbar\Omega_r'}{2k_B T}\right) \quad (9)$$

for absorption, and

$$M_{FC}^{1,emi} = E_V - \sum_r \frac{\hbar}{4\Omega_r'} (F_{rr} - \Omega_r'^2) \coth\left(\frac{\hbar\Omega_r'}{2k_B T}\right) \quad (10)$$

for emission. Notice that E_V is different for absorption and emission. The prime indicates the ground state for absorption and the excited state for emission, and \mathbf{F} is the force constant matrix of the excited (ground) state along the normal coordinates of the ground (excited) state for absorption (emission).

These equations show that there is a formal connection between M_{FC}^1 and E_V but also that they only coincide when the diagonal force constants of the final state PES, along initial-state normal coordinates, are identical to the square of the corresponding initial-state frequencies (see Figure 1). For weak transitions, where HT effects are remarkable, M^1 also depends explicitly on the transition dipole derivatives and the off-diagonal elements of the force constant matrix \mathbf{F} (non-vanishing when a Duschinsky effect exists).³³

VH approach is thus in principle best suited to compare vibronic M_{FC}^1 values and the E_V electronic data, since eqs 9 and 10 show that they exactly coincide if the ground and excited states have the same Hessian (Vertical Gradient model, VG).⁴⁶ On the other hand, the VH approach requires that the final state Hessian is evaluated at the initial state geometry, being possibly biased by the existence of imaginary frequencies,⁴⁶ and therefore making the application of AH models more straightforward. In the following, we have computed the spectra adopting both VH and AH approaches, showing that

Table 1. Experimental and Theoretical Spectral Parameters of the Absorption Lineshapes of Anthracene, Naphthalene, *trans*-Azobenzene (*trans*-Azobz), and *trans*-Indigo in the Gas Phase and in Solution

	experimental			theoretical				
	$\nu^{\max}(\lambda)^a$	ν^{\max}	M^1		E_V	$\nu_{\text{cmp}}^{\max b}$	$M_{\text{cmp}}^1 c$	$M_{\text{cmp}}^1(T)^d$
anthracene	3.412 ^e	3.412	3.669 ^h	gas phase				
				AH	3.369	3.066	3.294 (−1)	3.287
	3.480 ^f	3.480	3.547 ^h	VH	3.375	3.076	3.304 (0)	3.299
				cyclohexane				
<i>trans</i> -azobz	4.100 ^g	4.100	4.197 ^h	AH	3.330	3.021	3.254 (0)	3.248
				VH	3.336	3.029	3.263 (0)	3.259
	3.885 ^g	3.885	4.030 ^h	gas phase				
				AH	3.863	3.685	3.811(−3)	3.950
				VH	3.892	3.752	3.849(−2)	4.121
				CCl ₄				
naphthalene	4.624 ^e	4.622	4.740 ^h	AH	3.758	3.690	3.730(−10)	3.889
				VH	3.736	3.885	3.703(−2)	3.923
	4.508 ^f	4.508	4.618 ^h	gas phase				
				AH	4.566	4.358	4.458(−1)	4.449
<i>trans</i> -indigo	2.076 ⁱ	2.076	2.175	VH	4.581	4.372	4.471 (0)	4.461
				cyclohexane				
	1.948 ⁱ (1.951) ^j	1.936	1.841	AH	4.528	4.313	4.420 (0)	4.412
				VH	4.544	4.314	4.425 (−1)	4.414
	2.076 ⁱ	2.076	2.175	gas phase				
				AH	2.381	2.227	2.319(−1)	2.355
emission	1.948 ⁱ (1.951) ^j	1.936	1.841	VH	2.377	2.223	2.303(−3)	2.323
				sym-EtCl ₂				
	1.948 ⁱ (1.951) ^j	1.936	1.841	AH	2.230	2.130	2.181 (−1)	2.195
				VH	2.227	2.128	2.179 (−1)	2.188

^a $\nu^{\max}(\lambda)$ represents the data obtained by experimental spectrum in the wavelength domain; ν^{\max} represents those obtained from the lineshape in the frequency domain (see text). ^b ν_{cmp}^{\max} for the spectra computed at 0 K and convoluted with a Gaussian with HWHM reported in the figures' captions. ^c M_{cmp}^1 values at 0 K calculated from the analytical expressions in eq 9 and 10. In parentheses, we give the error (in meV) of the M_{cmp}^1 computed numerically (num) from the calculated spectrum with respect to the analytical one ($M_{\text{cmp}}^1(\text{num}) - M_{\text{cmp}}^1$). The very small values prove the very good convergence of the TI computations of the spectra with respect to the sum over all the possible final vibronic states. ^d $T = 300$ K except for the gas phase spectra of *trans*-azobenzene ($T = 373$ K). ^eFrom ref 61. ^fFrom ref 62. ^gFrom ref 63. ^hNotice this datum might be slightly underestimated because of the truncation of the experimental spectrum (see Figure 3 as an example). ⁱFrom ref 64. ^jIn parentheses, the value obtained from the quantum distribution of photons as a function of frequency (see text).

they deliver always very similar results, a support to the reliability of harmonic approximation of final state PES.

As a final comment, we remind that anharmonicities can clearly affect M_{FC}^1 . On the other hand, their contribution is not expected to be very large, since by symmetry the lowest-order anharmonicities affecting M_{FC}^1 are quartic terms.⁵⁸

4. RESULTS

4.1. Manipulating the Experimental Spectrum. Experimental spectra and their band maxima reported in the literature are usually tabulated on a wavelength scale ($S_i(\lambda)$). A meaningful comparison of the computed spectra with the experimental data require that the latter are properly mapped in the frequency domain ($S_i(\lambda) \rightarrow S_i(\nu)$).^{59,60} Let us consider an emission spectrum expressed as a quantum distribution of photons (Φ). We can easily recognize that the integral of Φ , i.e., the total number of emitted photons per unit of time, cannot depend on whether it is expressed as a function of λ or ν

$$\int_0^\infty \Phi_\nu(\nu) d\nu = \int_0^\infty \Phi_\lambda(\lambda) d\lambda \quad (11)$$

$$\Phi_\nu(\nu) = c_0 \frac{\Phi_\lambda(\lambda)}{\nu^2} \quad (12)$$

where the second equation is obtained from the first after changing the integration variable in the right-hand side $\lambda \rightarrow \nu$, $d\lambda = -c_0 \nu^{-2} d\nu$. Therefore, a proper transformation $\Phi(\lambda)$ vs $\Phi(\nu)$ requires that the ν^2 factor of eq 12 be considered. Such a correction alters the spectrum shape and, as a consequence, naming $\lambda_{\text{emi}}^{\max}$ and ν_{emi}^{\max} the maxima in the wavelength and frequency domain, respectively, in principle $\nu_{\text{emi}}^{\max} \neq c_0/\lambda_{\text{emi}}^{\max}$. Similar arguments do not apply to absorption spectra, because the molar absorptivity is defined as the logarithm of the ratio between the transmitted and incident intensity for unit length and molar concentration of the sample cell; its integral is therefore the same if one computes it both in the wavelength and in the frequency scale.⁶⁰

A further manipulation of the experimental spectrum is necessary before the computed E_V can be meaningfully compared with it. In fact, as we pointed out in eqs 9 and 10, E_V is formally correlated with the first moment of the spectrum line shape $L(\nu)$ and not with those of molar absorptivity (absorption) or of the quantum distribution of photons (emission). Therefore, before comparison, the experimental spectra must be transformed to the line shape functions [$L_{\text{abs}}(\nu) = \mathcal{N}\nu^{-1}\epsilon(\nu)$ and $L_{\text{emi}}(\nu) = \mathcal{N}\nu^{-3}\Phi_\nu(\nu) = \mathcal{N}\nu^{-5}\Phi_\lambda(\lambda)$],

In conclusion, maxima of experimental spectra cannot be in principle directly compared with calculations, but the following preliminary transformations are necessary:

$$\nu^{\max}(\varepsilon(\lambda)) \leftrightarrow \nu^{\max}(\varepsilon(\nu)) \xrightarrow{\nu} \nu^{\max}(L_{\text{abs}}(\nu)) \equiv \nu^{\max} \quad (13)$$

for absorption spectra and

$$\nu_{\text{emi}}^{\max}(\Phi(\lambda)) \xrightarrow{\nu^2} \nu_{\text{emi}}^{\max}(\Phi(\nu)) \xrightarrow{\nu^3} \nu_{\text{emi}}^{\max}(I_{\text{emi}}(\nu)) \equiv \nu_{\text{emi}}^{\max} \quad (14)$$

for emission spectra. In the following, as $\nu^{\max}(\varepsilon(\lambda))$ and $\nu_{\text{emi}}^{\max}(\Phi(\lambda))$, or shortly as $\nu^{\max}(\lambda)$, we label the quantities obtained directly by the spectra in the wavelength domain, while as ν^{\max} and ν_{emi}^{\max} , the “corrected” values to be compared with their computational counterpart. Once the spectra have been properly transformed, the experimental first moment M^1 can be computed numerically applying eq 7. It is important to remind that truncated spectra or overlapping contributions from different electronic states might bias the estimate of M^1 . Furthermore, also an accurate evaluation of the ν_{00} transition energy, when estimated by the crossing point between absorption and emission spectra,^{12–15} requires that the experimental spectra are properly transformed, and since transformations include normalization, also in this case the utilization of complete (i.e., not-truncated) spectra is recommended, and the cases of overlapping transitions should be handled with care. Finally, for what concerns our study, some inaccuracy could have been introduced by the fact that the original data were not available, and we have simply digitalized the published spectra.

The values obtained by manipulating, according to eqs 13 and 14, the experimental spectra of the four examined compounds in the gas phase and different solvents are reported in Table 1 (since now on we adopt eV units and, when needed, the computed values are distinguished by the experimental ones with a subscript cmp). As discussed more in detail in the SI, the transformation in the investigated cases does not significantly affect the position of the maxima. However, it noticeably changes the spectral line shape (see Figures 2–6), modulating the relative height of the different vibronic peaks. Especially for emission spectra (where a ν^5 factor is involved), an accurate

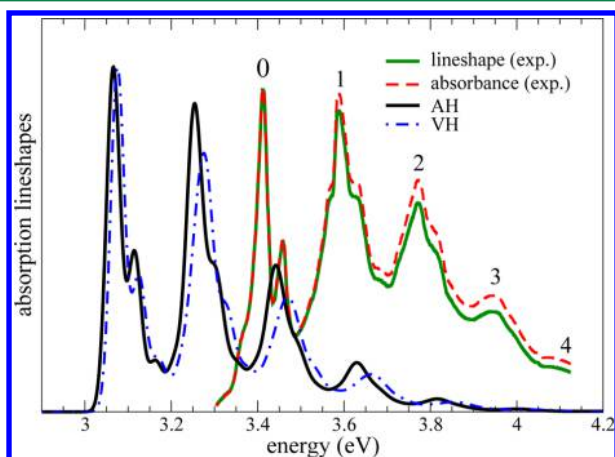


Figure 2. Anthracene gas phase absorption spectra computed with FCI AH and FCIVH models and convoluted with a Gaussian with HWHM = 160 cm⁻¹. The experimental gas phase (GP) spectrum taken from ref 61 is also shown. All spectra are given as normalized lineshapes.

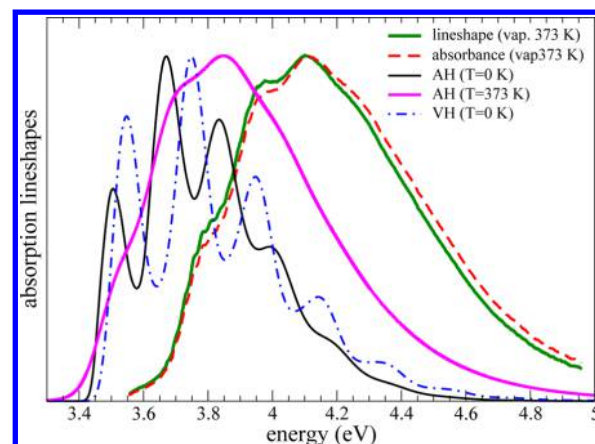


Figure 3. *trans*-Azobenzene gas phase absorption spectra computed with FCI AH (0 and 373 K) and FCIVH (0 K) models, convoluted with a Gaussian with HWHM = 160 cm⁻¹. The experimental spectrum taken from ref 63 is shown.

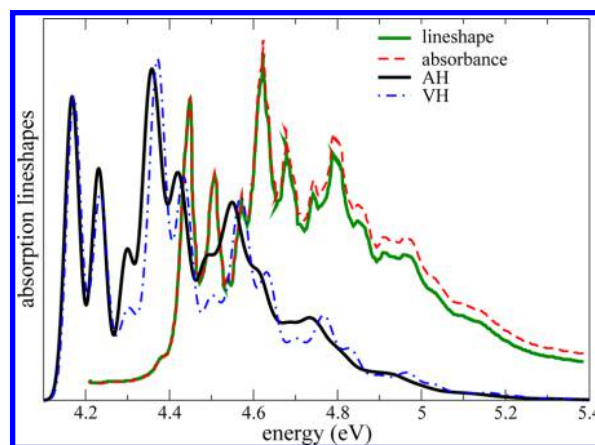


Figure 4. Naphtalene gas phase absorption spectra computed with FCI AH and FCIVH models, convoluted with a Gaussian with HWHM = 160 cm⁻¹. The experimental spectrum taken from ref 61 is shown.

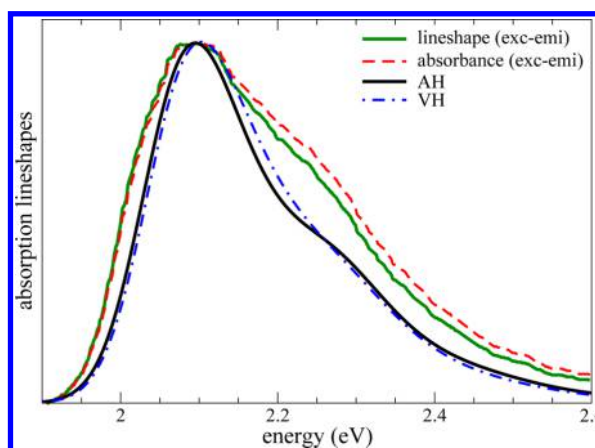


Figure 5. *trans*-Indigo absorption spectra in sym-EtCl₂ computed with FCI AH and FCIVH models, convoluted with a Gaussian with HWHM = 480 cm⁻¹. The experimental spectrum taken from ref 64 is also shown.

comparison with the experiments thus requires that the experimental spectra are properly transformed.

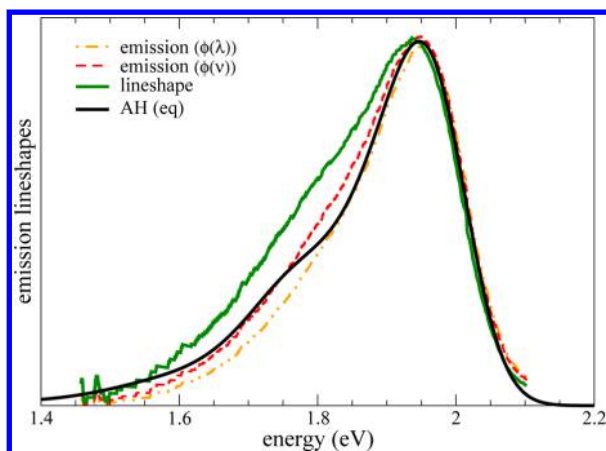


Figure 6. *trans*-Indigo emission spectrum in sym-EtCl₂ computed with FCI/AH, convoluted with a Gaussian with HWHM = 480 cm⁻¹. The experimental spectrum taken from ref 64 is also shown.

4.2. Spectra Simulations. We computed the spectra according to both VH and AH models. Table 1 in the SI shows that most of the VH calculations we performed (except for *trans*-indigo in solvent) are biased by the existence of low imaginary frequencies that were arbitrarily turned to real numbers to compute the spectra.⁴⁶ In practice, however, Table 1 shows that AH and VH predictions for computed $\nu_{\text{cmp}}^{\text{max}}$ and M_{cmp}^1 are very similar, strengthening the robustness of our results. This is not surprising also because, for all the analyzed systems, the AH error on E_V is always very small (within 0.03 eV, Table 1). Because of these facts, AH and VH results can be regarded as equivalent, most of all if one considers the expected

accuracy of the adopted electronic methods, and in the following, when not stated differently, we focus the discussion on AH data.

4.2.1. Anthracene. The shape of the computed spectrum of anthracene, obtained at the PBE0/6-31G(d) level of theory, is very close to the experimental one, both in the gas phase (see Figure 2) and in cyclohexane (Figure 1 in the SI): the lowest-energy (0) peak in the gas phase is the most intense; the spacing between the different peaks is nicely reproduced. Even finer details, as the appearance of a secondary peak at ~0.05 eV on the blue with respect to the 0 peak, are correctly caught by our calculations.

We have selected anthracene as a test case in order to verify whether our conclusions depend on the choice of the functional and of the basis set. The SI shows that the extension of the basis set leads to a moderate red shift of E_V and of the overall spectrum, with a small effect on the spectrum line shape. On the other hand, E_V strongly depends on the functional, but also in this case the predicted spectral line shape is very similar for different functionals and fully consistent with the experimental spectrum. In short, B3LYP and PBE0 better reproduce the relative intensity of the peaks, while CAM-B3LYP remarkably improves its position. The pure BLYP functional gives instead the worst performance.

Table 1 shows that at the PBE0/6-31G(d) level, E_V is noticeably blue-shifted with respect to the computed $\nu_{\text{cmp}}^{\text{max}}$ ($\Delta_{V-\text{max}} = E_V - \nu_{\text{cmp}}^{\text{max}} \sim 0.3$ eV) and more similar to M_{cmp}^1 (from now on, the FC subscript is skipped for brevity), even if a blue-shift is still appreciable ($\Delta_{V-M_1} = E_V - M_{\text{cmp}}^1 \sim 0.08$ eV). These conclusions are valid for all the compared functionals and basis sets. In fact, the SI shows that $\Delta_{V-\text{max}}$ and Δ_{V-M_1}

Table 2. Errors of the Different Methods Estimated from Their Prediction for E_V and the $\Delta_{V-\text{max}}$ and Δ_{V-M_1} Vibrational Corrections Computed at the PBE0/6-31G(d) Level of Theory According to the VH Model^a

		anthracene	<i>trans</i> -azobenzene	naphthalene	<i>trans</i> -indigo
exptl.	ν^{max}	3.41	4.10	4.62	2.08
	M^1	3.67	4.20	4.74	2.18
PBE0 ^b	E_V	3.37	3.86	4.57	2.23
	ν^{maxc}	3.07	3.69 [3.82] ^h	4.36	2.13
CAM-B3LYP ^b	$M^1(T)^d$	3.29	3.95	4.45	2.20
	E_V	3.70	4.11	4.80	2.44
	ν^{maxc}	3.40	4.07 ^h	4.59	2.34
	$M^1(T)^d$	3.62	4.20	4.68	2.41
CASPT2	E_V		4.23 ⁱ	4.33 ^j	1.81 ^l [1.66] ⁿ
	ν^{maxc}		4.19 ^h	4.12	1.71 [1.56]
	$M^1(T)^d$		4.32	4.21	1.78 [1.63]
CC	E_V	3.85 ^e		4.42 ^k	2.34 ^m [2.19] ⁿ
	ν^{maxc}	3.55		4.21	2.24 [2.09]
	$M^1(T)^d$	3.77		4.30	2.31 [2.16]
DFT-MRCI	E_V	3.51 ^f			
	ν^{maxc}	3.21			
	$M^1(T)^d$	3.43			
EOM-CCSD(T)	E_V	3.69 ^g			
	ν^{maxc}	3.39			
	$M^1(T)^d$	3.61			

^aThe PBE0/6-31G(d) results listed and adopted to estimate the $\Delta_{V-\text{max}}$ and Δ_{V-M_1} corrections are computed according to the AH model. Vertical VH results are very similar. ^bThis work; 6-31G(d) basis set. ^cValues at $T = 0$ K except for *trans*-azobenzene ($T = 377$ K). ^d $T = 0$ K except for *trans*-azobenzene ($T = 377$ K). ^eCCSDR(3)/ANO results.⁶⁵ ^fDFT-MRCI/TZVP results.⁶ ^gEOM-CCSD(T) results.⁶⁸ ^hAt 373 K. ⁱCASPT2/CASSCF(12,14)/6-31G(d) results.⁷⁰ ^jMSCASPT2/aug-cc-pVTZ results.⁷ ^kCC2/aug-cc-pVTZ results.⁷ ^lCASPT2/CASSCF(12,14)/(ANO-S C,N,O [3s2p] / H [2s]) results.⁷⁴ ^mCASPT2/CASSCF(14,14)/cc-pVDZ results.⁷⁵ ⁿIncluding the correction to E_V from the gas phase to sym-EtCl₂ computed at the LR-PCM/6-31G(d) level of theory.

always fall in the ranges 0.19–0.3 eV and 0.03–0.08 eV, respectively. Δ_{V-M_1} is positive as a result of the differences in the Hessian of initial and final states (eq 9), differences that are neglected in simpler VG and AS (Adiabatic Shift) models.⁴⁶ On the other hand, the remarkable values of $\Delta_{V-\max}$ are due to the intrinsic asymmetry of the FC progressions and of the resulting absorption band shape, and thus $\Delta_{V-\max}$ provides an estimate of the effect of the inclusion of vibrational effects on the predicted absorption maximum.

The SI also highlights the formal difference of Δ_{V-M_1} and Δ_{zpe} , i.e., the difference between the S_0 and the S_1 vibrational zero-point energies (zpe), discussing why, in the investigated cases, the two quantities end up with very similar values.

On the grounds of the above discussion, in the following we base our analysis on the computationally “cheap” PBE0/6-31G(d) level of theory, which, however, also according to previous studies,^{16–21} can provide a reliable basis for the simulation of optical line shape in medium/large size molecules.

The number of high-level ab initio calculations on anthracene is not very large.^{65–68} CCSDR(3) results⁶⁵ provide $E_V = 3.85$ eV. At the DFT-MRCI level, E_V is 3.51 eV.⁶ EOM-CCSD(T) calculations⁶⁸ predict that $E_V = 3.69$ eV. Table 2 shows that, considering corrections $\Delta_{V-\max}$ or Δ_{V-M_1} , equal to what is computed at the PBE0/6-31G(d) level (~ 0.3 eV and ~ 0.08 , respectively) would lead to predicted EOM-CCSD(T) absorption ν_{cmp}^{\max} and M_{cmp}^1 in very nice agreement (within 0.02 and 0.06 eV respectively) with the experiment. The performance of CAM-B3LYP is even slightly better.

The absorption spectrum of anthracene in cyclohexane solution (see the SI) is very similar to that measured in the gas phase,⁶⁹ but for an overall uniform red-shift (~ 0.1 eV). Our calculation well reproduces the optical line shape and the fact that a red-shift exists, even if its extent is underestimated. As reported in Table 1, in cyclohexane, E_V is blue-shifted by ~ 0.3 eV with respect to ν_{cmp}^{\max} and by only ~ 0.07 eV with respect to M_{cmp}^1 , fully confirming the results obtained in the gas phase and showing that the picture is not affected by solvent effect.

4.2.2. trans-Azobenzene. For *trans*-azobenzene, experimental⁶³ and computed absorption lineshapes are in striking agreement, both in the gas phase (see Figure 3) and in CCl_4 solution (see Figure 4 in the SI). For this system, we explicitly accounted for temperature effect on the spectrum, computing it within the TD approach according to the AH model at 0 K and at 373 K (in the gas phase) or 300 K (in CCl_4 , see the SI). Inclusion of temperature has a remarkable impact on the spectrum, clearly improving the comparison with experimental data by shifting ν_{cmp}^{\max} and M_{cmp}^1 by ~ 0.14 eV and inducing a sensible broadening. While broadening effects might be simulated with a larger HWHM of the convoluting Gaussian (see Figure 4 in the SI), the shift can be reproduced only by a proper accounting of temperature effects.

Comparing E_V and the experimental ν_{cmp}^{\max} at 373 K, one deduces that E_V is red-shifted by 0.24 eV, a value very similar to what was obtained comparing the experimental M^1 and M_{cmp}^1 (≈ 0.25 eV). However, the accuracy of the estimate of the electronic calculation based on the difference between E_V and ν_{cmp}^{\max} is accidental and due to the compensation of a number of neglected factors (depending on vibrational and temperature effects, see discussion in the SI). At the PBE0/6-31G(d) level, E_V is very close to ν_{cmp}^{\max} at 373 K, $\Delta_{V-\max}(373 \text{ K}) = 0.04$ eV; using such a correction for other methods, the CASPT2/

CASSCF(12,14)/6-31G(d) E_V value⁷⁰ 4.23 eV is confirmed to be in good agreement with the experiment. CAM-B3LYP/6-31G(d) results are practically on top of it (see Table 2).

4.2.3. Naphthalene. Figure 4 compares the experimental and computed absorption spectra of naphthalene in the gas phase for the bright excited state that, at the PBE0/6-31G(d) level, corresponds to S_1 (B_{2u} symmetry). Spectra recorded in a supersonic jet⁷¹ indicate the existence of a weak state (B_{1u} symmetry) with an origin at 3.97 eV, below the bright state, coupled to the bright state. However, as discussed more extensively in the SI, the first-moment M^1 of the spectrum is not remarkably affected by the B_{2u}/B_{1u} vibronic coupling.^{56,72,73}

The spectral line shape in Figure 4 is very well reproduced, suggesting that B_{2u}/B_{1u} coupling does not modulate the low-/intermediate-resolution line shape. However, ν_{cmp}^{\max} is ~ 0.26 eV red-shifted with respect to experimental ν_{cmp}^{\max} , i.e. a similar difference to that (~ 0.28 eV) between M^1 and M_{cmp}^1 (see Table 1). Comparison of E_V with the experimental ν_{cmp}^{\max} would have instead led to the erroneous conclusion that PBE0/6-31G(d) predictions were in perfect agreement with experiments.

As shown in the SI, computed and experimental spectra in cyclohexane are similar too, indicating that also for naphthalene our calculations provide a reliable basis to discuss vibrational effects on the absorption spectrum.

Confirming the same trend found for anthracene, E_V is significantly blue-shifted with respect to ν_{cmp}^{\max} ($\Delta_{V-\max} \sim 0.2$ eV) and to M_{cmp}^1 ($\Delta_{V-M_1} \sim 0.1$ eV). The difference between ν_{cmp}^{\max} and M_{cmp}^1 is smaller than for anthracene, since for naphthalene the ν_{cmp}^{\max} corresponds to an excited band, and it is more similar to M^1 , with a band shape more symmetric.

Naphthalene excited states have been thoroughly investigated by several post-SCF ab initio methods (see ref 7 for a review). According to Thiel et al.,⁷ in the gas phase the best theoretical estimate for E_V is 4.42 eV (CC/aug-cc-pVTZ results), while at the MSCASPT2/aug-cc-pVTZ level, $E_V = 4.33$ eV. These estimates are further red-shifted with respect to the PBE0/6-31G(d) E_V , 4.57 eV. As a consequence, correcting CASPT2 results with the $\Delta_{V-\max}$ value computed at the PBE0 level (see Table 2), we obtain a predicted absorption maximum in the gas phase at ~ 4.12 eV, significantly red-shifted with respect to the experiments (4.62,⁶¹ in the vapor phase). Also in this case, CAM-B3LYP results appear to be the closest to experimental data.

4.2.4. trans-Indigo. Absorption. We did not succeed in finding the experimental gas phase spectra for *trans*-indigo; therefore our analysis is mainly based on the spectra obtained in symEtCl₂ (sym-dichloro-ethane). Both in the gas phase and in solution, we obtain the same trend already discussed: E_V is noticeably blue-shifted with respect to ν_{cmp}^{\max} ($\Delta_{V-\max} = 0.16$ eV in the gas phase and 0.10 eV in symEtCl₂), while the difference between E_V and M_{cmp}^1 is smaller, $\Delta_{V-M_1} \approx 0.05$ eV. When accounting for $\Delta_{V-\max}$, PBE0/6-31G(d) predictions are much closer to the experimental data than one would have guessed simply comparing E_V to the experimental ν_{cmp}^{\max} . In fact, the real error of ν_{cmp}^{\max} is ~ 0.05 eV, and M_{cmp}^1 virtually coincides with the experimental M^1 .

Several post-HF studies have analyzed the *trans*-indigo excited states in the gas phase. CASPT2 studies provide E_V values of 1.96 eV (CASPT2/CASSCF(12/14))⁷⁴ or 1.81 eV (CASPT2/CASSCF(14/14)/cc-pVDZ),⁷⁵ while a larger value, $E_V = 2.34$ is predicted at the CC2/cc-pVDZ level of theory.⁷⁵ In this case, Table 2 shows that $\Delta_{V-\max}$ correction makes the

CASPT2 $\nu_{\text{cmp}}^{\text{max}}$ significantly red-shifted with respect to the experiments, considering that the solvent effect also causes an additional red-shift (see PBE0 results in Table 1); CC2/cc-pVDZ $\nu_{\text{cmp}}^{\text{max}}$ would instead be closer to the experimental one.

Emission. The ν^5 correction in eq 14 should have a deeper effect on the spectrum shape when the emitted photons are at low energy.⁷⁶ Therefore, the emission of *trans*-indigo, whose ν^{max} in symEtCl₂ is 1.94 eV,⁶⁴ is a good example to illustrate the impact of such a transformation. The emission spectrum in symEtCl₂, reported in Figure 6, has been simulated adopting the AH model and describing the solvent in the equilibrium regime with the excited state (the effects due to the nonequilibrium solvation of the ground state have been neglected).^{20,77} As expected, the spectral line shape is noticeably affected by the transformation described in the section 4.1. Just to make an example, the intensity of the broad shoulder at ~ 0.2 eV on the red-side with respect to ν^{max} is significantly more intense in the “line shape” spectrum. The computed line shape is in good agreement with the experimental one, the position and the relative intensity of the red-wing shoulder being nicely reproduced. In line with eq 10, $\nu_{\text{cmp}}^{\text{max}}$ is blue-shifted by ~ 0.1 eV with respect to M_{cmp}^1 , i.e., exhibiting the opposite behavior to that found for the absorption spectrum. The fluorescence quantum yield of *trans*-indigo is very small, $\sim 10^{-3}$, probably as a consequence of a fast S_1/S_0 internal conversion that follows from an excited-state intramolecular proton transfer (ESIPT) between the nitrogen atoms and the carbonyl oxygens.⁷⁸ The good agreement of the computed and experimental spectra support the thesis that the small, yet detectable, emission originates from the tautomer that is stable in the ground state, i.e. before the ESIPT takes place.

5. DISCUSSION

Table 1 analyzes the experimental data and shows that ν^{max} is systematically red-shifted in absorption and blue-shifted in emission with respect to M^1 by an average value of 0.13 eV (values between 0.07 and 0.25 eV). Interestingly, the lowest and highest values in this interval correspond to anthracene in the gas phase and cyclohexane, respectively. In these two environments, small changes in FC factors make the band maximum shift (by ~ 0.2 eV) from the 0 peak (gas phase) to the 1 peak (cyclohexane).

The trend observed in the experimental data is perfectly mirrored by our computational results: M_{cmp}^1 at 0 K is systematically larger than $\nu_{\text{cmp}}^{\text{max}}$ in absorption and smaller in emission (its average difference from ν_{00} is ~ 0.2 eV). Although E_V is correlated with M_{cmp}^1 of the spectrum line shape, our analysis clarifies that they do not coincide. M_{cmp}^1 is red-shifted for absorption and blue-shifted for emission, due to the fact that excited-state frequencies are generally lower than ground-state ones (eqs 9 and 10). Calculating the average of the difference of the computed E_V and M_{cmp}^1 for all the cases reported in Table 1, we find that, on average, E_V is larger than M_{cmp}^1 by 0.07 eV at 0 K and by 0.03 eV if the effect of temperature is considered. With the same procedure, we notice that the computed ν^{max} at 0 K reported in Table 1 is, on average, red-shifted by 0.2 eV with respect to E_V , by 0.13 eV with respect to M_{cmp}^1 at 0 K, and by 0.17 eV with respect to M_{cmp}^1 computed including the temperature effect. This highlights that the dependence on the temperature constitutes another uncontrolled source of error when comparing the experimental ν^{max} (usually obtained at room temperature) with E_V , that is intrinsically a 0 K value.

The comparison of experimental ν^{max} to E_V (or to M_{cmp}^1) is prone to errors due to the intrinsic dependence of ν^{max} on the spectra resolution. As discussed more in detail in the SI, M^1 or ν_{00} are better “reference values” than ν^{max} , especially in the case of well distinguished vibronic structures, when ν^{max} can strongly vary for tiny changes of experimental conditions or level of theory. For low-resolution spectra, measurements and computations of ν^{max} are more robust.

According to our analysis, estimating the performance of an electronic method by simply comparing E_V and the experimental ν^{max} can systematically bias the conclusions. As an example (see Table 1), the mean unsigned and signed errors of E_V computed at the PBE0/6-31G(d) level with respect to the experimental ν^{max} are 0.10 and -0.06 eV, respectively.⁷⁹ These values would suggest that the PBE0/6-31G(d) predictions almost perfectly agree with experiments, but for a small tendency to underestimate E_V . On the contrary, the mean unsigned and signed errors of $M^1(T)$ with respect to the experimental M^1 are 0.210 and -0.206 eV, pointing out a more accentuated (and systematic) tendency to underestimate the spectrum position (and therefore E_V).⁷⁹

The PBE0/6-31G(d) absorption lineshapes are very close to their experimental counterparts for all the examined systems, supporting the reliability of the simulated vibrational structure of the spectra. By adopting $\Delta_{V-\text{max}}$ and Δ_{V-M_1} data computed at the PBE0/6-31G(d) level, in Table 2 we have verified that the inclusion of vibrational corrections can sensibly alter the conclusions on the relative performance of the different electronic methods. In the cases analyzed here, ‘vibrationally corrected’ CASPT2 predictions are, for example, in general red-shifted with respect to experiment, as we found for PBE0 (but this latter method exhibits smaller absolute errors). CAM-B3LYP and methods of the coupled cluster family give instead estimates very close to experiments.

6. CONCLUSIONS

In this study, we have examined some key questions concerning the comparison between experimental and computed absorption and emission spectra, based on the analytical formulation of M^1 , on its dependence on molecular parameters and temperature, and on the analysis of some representative test cases. As a preliminary point, we highlighted that an accurate comparison between computed and experimental spectra requires that these latter ones are properly mapped from λ to the ν domain and then transformed to lineshapes. The effect of this transformation is expected to be rather small for ν^{max} , causing a shift of a few hundredths of an electronvolt, but it can be as large as ~ 0.2 eV for well resolved spectra with almost equal peaks, where the maximum can flip between adjacent peaks. However the transformation remarkably changes the lineshapes, especially for emission.

On the computational side, a thorough comparison of the computed absorption spectra shows that our conclusions are not affected by the density functional, the basis set, or the vibrational model (AH or VH) used in the calculations but reflect intrinsic molecular features.

The ν^{max} value depends on the underlying vibrational structure, on the spectrum resolution, and on the temperature, and it is not possible to write a simple equation connecting it to the vertical excitation energy E_V . More importantly, a systematic 0.1–0.3 eV shift has to be expected when comparing E_V and ν^{max} (the latter being lower than the former in

absorption and the opposite in emission), and the difference is the larger, the more asymmetric the spectrum line shape appears. Since several computational methods are claimed, mainly on the grounds of the comparison of computed E_V with experimental ν^{\max} , to be accurate within 0.2–0.3 eV, the concept of “expected” accuracy of a given method should be more carefully reconsidered. Due to the limited number of cases studied here, it is not possible to give a statistically reliable assessment of the accuracy of the different methods, and this was not the aim of the present study. However, our results indicate that methods that are considered, on the average, to overestimate absorption transition energies, i.e. for which E_V is usually larger than the experimental absorption ν^{\max} , might actually reveal to be more accurate than methods for which E_V and experimental ν^{\max} are closer.

An accurate comparison between theory and experiment should consider the full lineshapes of the measured and simulated spectra. However, it is often useful to have a synthetic descriptor of the quality of the computed data. In this perspective, M^1 does not depend on the resolution of the spectrum and is therefore a much more robust parameter to work with than ν^{\max} . Moreover, it can be in principle extracted both from intermediate- and low-resolution experimental spectra. Therefore, in all the cases where the experimental M^1 can be actually obtained (see discussion in section 4.1) it is recommendable to use it to compare with the corresponding M^1_{comp} . It is noteworthy that this latter can be obtained without explicitly computing the spectrum line shape from eqs 9 and 10, i.e., with the same information needed to compute ν_{00} .

For statistical comparisons on extended sets of molecules, where calculation of the ground and excited state frequencies necessary to compute M^1 (or ν_{00}) can be impractical, the computed E_V can be roughly compared with the experimental M^1 and ν^{\max} values. In several cases, M^1 is expected to be red-shifted by ~ 0.1 eV and ν^{\max} red-shifted in the range ~ 0.1 – 0.3 eV, with respect to E_V . The comparison of experimental and theoretical ν_{00} provides an accurate and complementary option, in particular when the high-resolution experimental spectrum is available. Remarkably, taking anthracene as an example, in the SI we show that M^1 and ν_{00} descriptors deliver very similar estimates of the accuracy of the computed method.

■ ASSOCIATED CONTENT

■ Supporting Information

Excited-state imaginary frequencies (if any) and ν_{00} values. Further analysis of the results. Figures and Tables comparing computed spectra of anthracene in gas phase with different basis sets and functionals, and computed and experimental spectra of anthracene and naphthalene in cyclohexane, and trans-azobenzene in CCl_4 . Experimental spectra (taken from literature) of trans-azobenzene in benzene and trans-indigo in CHCl_3 and EtOH, with the analysis of their ν^{\max} , $\nu^{\max}(\lambda)$ and M^1 parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

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over all the different systems/solvents. In an analogous way we obtained the signed and unsigned errors of the computed $M_{\text{comp}}^{\text{I}}(T)$ with respect to the experimental M^{I} .