Chemically Accurate 0−0 Energies with Not-so-Accurate Excited State Geometries

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Ⓢ *Supporting Information*

ABSTRACT: Using a series of increasingly refined wave function methods able to tackle electronic excited states, namely ADC(2), CC2, CCSD, CCSDR(3), and CC3, we investigate the interplay between geometries and 0−0 energies. We show that, due to a strong and nearly systematic error cancelation between the vertical transition and geometrical reorganization energies, CC2 and CCSD structures can be used to obtain chemically accurate 0−0 energies, though the underlying geometries are rather far from the reference ones and would deliver significant errors for several chemical and physical properties. This indicates that obtaining 0−0 energies matching experiment does not demonstrate the quality of the underlying geometrical parameters. By computing CC3 total energies on CCSD structures, we model a large set of compounds (including radicals) and electronic transitions (including singlet−triplet excitations) and successfully reach chemical accuracy in a near systematic way. Indeed, for this particular set, we obtain a mean absolute error as small as 0.032 eV, chemical accuracy (error smaller than 1 kcal·mol^{-1} or 0.043 eV) being obtained in 80% of the cases. In only three cases out of more than 100 examples, the error exceeds 0.15 eV which is of the order of the typical error provided by TD-DFT or second-order wave function methods for 0−0 energies. The present composite approach seems therefore effective, at least for low-lying states, despite the fact that the geometries may not be considered as very accurate.
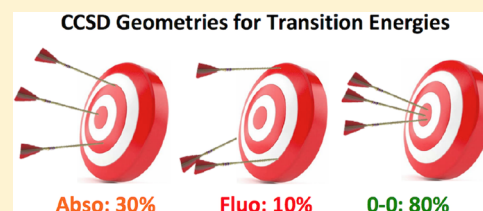
1. INTRODUCTION

The accurate modeling of phenomena occurring in electronic excited states (ESs) is often required to attain an in-depth understanding of experimental observations made in, e.g., solar cells and light emitting diodes. However, for such materials, a straightforward relationship between measured and computed ES properties is often hampered by the complexity of the chemical system (surrounding environment, nonadiabatic processes, dynamical effects...). This limits both the quality of the theory that one can apply and the experimental result precision. Therefore, when one is interested in direct theory-experiment comparisons, the most valuable target property probably remains the 0−0 energy (E^{0-0}) because E^{0-0} (often denoted T_{00} or "band origin" experimentally) (i) has been measured for many molecules in gas phase with uncertainty typically smaller than 1 cm^{-1} and (ii) is a well-defined theoretical quantity which corresponds to the difference between the ES and ground-state (GS) energies taken at their respective geometrical minimum (the adiabatic energy, E^{adia}), corrected by their corresponding zero-point vibrational energies (ZPVEs) (see Figure 1). This contrasts with many other ES properties, such as experimental bond lengths and dipole moments that are often obtained indirectly and therefore come with significant error bars. Another example is vertical transition energies which can be easily computed but have no clear experimental counterpart. In short, from the
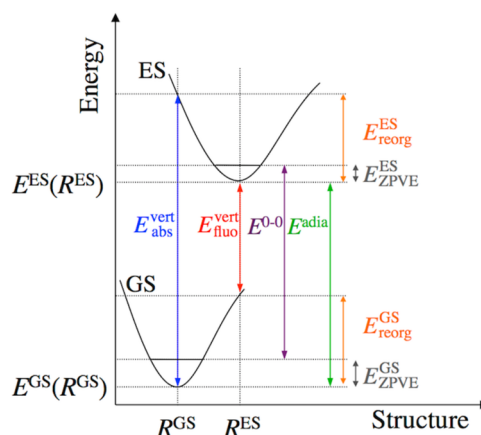

Figure 1. Representation of transition energies and energy differences discussed in the present work. E_{abs}^{vert} (blue) and E_{fluo}^{vert} (red) are the (vertical) absorption and emission/fluorescence energies, while E_{reorg}^{GS} and E_{reorg}^{ES} (orange) are the (geometrical) reorganization energies of the GS and ES states, respectively. The adiabatic and 0−0 energies are represented in green and purple, respectively. All these energies are defined as positive quantities.

theoretical point of view, E^{0-0} offers a nice opportunity to assess the accuracy of theoretical methods.

Given that E^{0-0} offers a meaningful comparison between theory and experiment, it is not surprising that many benchmarks have been devoted to their modeling.[1−14] These benchmarks have been performed considering either gas-phase molecules, for which theory−experiment comparisons are straightforward,[1−5,7,9,11,13,14] or solvated dyes, for which the measured absorption-fluorescence crossing point (AFCP) can be taken as a reference.[2,6,8,10,12] The second approach allows tackling larger compounds, of higher interest for practical applications, but at the cost of additional challenges originating, as mentioned above, from the modeling of the surrounding environment. Irrespectively of the set of compounds, the vast majority of these benchmarks has been carried out with time-dependent density functional theory (TD-DFT)[15] or correlated wave function approaches (partially) including contributions from double excitations, i.e., the configuration interaction singles with perturbative doubles [CIS(D)],[16] the second-order algebraic diagrammatic construction [ADC(2)],[17] and the second-order coupled-cluster-based CC2 method.[18] Although the corresponding results are unsurprisingly dependent on both the theoretical protocol and the selected set of molecules, the overall accuracy of the final theoretical estimates, as measured by the mean absolute error (MAE) with respect to experiment, typically falls in the 0.10−0.30 eV window, i.e., far from the desired "chemical accuracy" (1.0 kcal·mol^{-1} or 0.043 eV error).

Very recently, we proposed a protocol reaching, for organic compounds, such accuracy on an almost systematic basis.[14] Given that the vibrational correction is known to be relatively insensitive to the selected method,[8,9,19] the protocol described in ref 14 mainly focuses on the accurate calculation of adiabatic energies. To this end, high-level coupled-cluster methods including contributions from the triples, i.e., CCSDR(3)/def2-TZVPP and CC3/aug-cc-pVTZ, have been respectively applied to obtain the geometrical parameters and the total GS and ES energies. This led to a MAE of 0.018 eV for a set of 35 singlet−singlet valence states of small organic molecules, well below the chemical accuracy threshold.[14] However, in the same previous work,[14] we also showed that computing E^{adia} at a high level of theory, i.e., all-electron CC3 calculations in our case, is required to achieve a small MAE. Indeed, computing E^{adia} at the CCSDR(3), CCSD, and CC2 levels with the same CCSDR(3) geometries led to MAEs of 0.046, 0.207, and 0.078 eV, respectively, whereas freezing the core electrons during the CC3 calculations was enough to double the MAE to 0.045 eV.[14]

In the present contribution, we do assess the impact of the geometries on theoretical E^{0-0} values and, in particular, on E^{adia}. This question arises because the calculation of CCSDR(3)/def2-TZVPP geometries was the clear computational bottleneck of our original protocol as described in ref 14. Indeed, this method not only includes perturbative corrections for the triples, as CCSD(T) for the GS, which comes with a nonfavorable scaling with system size, but, in addition, does not have analytic gradients implemented which means that the gradient minimization process had to be carried out purely numerically. It would be undoubtedly much more advantageous to be able to use CCSD, CC2, or ADC(2) structures, as this would both decrease the scaling with system size and also allow taking advantage of analytical gradients. While the potential benefit was clear, hope was dim! To understand why,

let us first consider two exact formulations of the adiabatic energy:[8]

$$E^{adia} = E^{ES}(R^{ES}) - E^{GS}(R^{GS}) \tag{1a}$$

$$= \frac{E^{vert}_{abs} + E^{vert}_{fluo}}{2} + \frac{E^{GS}_{reorg} - E^{ES}_{reorg}}{2} \tag{1b}$$

The first equation gives the standard minimum-to-minimum energy difference definition of E^{adia}. However, as one can see in eq 1b, E^{adia} can be also expressed as the average of the absorption and fluorescence vertical energies corrected by half of the *difference* between the GS and ES geometrical reorganization energies (see also Figure 1). While this second definition does not offer a more efficient expression for practical calculations, it helps analyzing methodological trends. Indeed, except for compounds exhibiting important differences in ground and excited state potential energy surfaces, one can expect that the first contribution in eq 1b largely dominates, so that

$$E^{adia} \simeq \frac{E^{vert}_{abs} + E^{vert}_{fluo}}{2} \tag{2}$$

is a reasonable approximation.[8] Second, let us consider the results of a recent work,[20] in which we compared the vertical absorption and fluorescence energies obtained on a series of increasingly accurate geometries. For 24 compounds, we found that selecting second-order Møller−Plesset (MP2) [the GS equivalent of ADC(2)], CC2, and CCSD geometries in lieu of CCSDR(3) structures would yield average deviations of −0.01, −0.06, and +0.05 eV for E^{vert}_{abs}, respectively. For E^{vert}_{fluo}, the corresponding deviations are significantly larger: −0.03, −0.08 and +0.15 eV with ADC(2), CC2, and CCSD ES geometries, respectively. This illustrates that the ES structures are very sensitive to the selected electronic structure method.[19] As can be seen, the errors obtained with CCSD geometries largely exceed the chemical accuracy threshold for fluorescence. This left us rather circumspect before starting the present study. Indeed, one would need these errors to be almost canceled out by the reorganization energy difference, a much smaller term, in order to reach chemically accurate E^{adia} values with CCSD structures. Of course, this can happen if the two potential energy surfaces represented in Figure 1 are shifted strictly parallel to the horizontal axis: this would strongly modify the vertical energies without altering the adiabatic energies. However, we have also shown that[19,20] (i) CCSD [CC2 and ADC(2)] has a tendency to provide too localized [delocalized] ES geometries, e.g., the bond length alternation in a π-conjugated system tends to be too large [small] with CCSD [CC2 and ADC(2)]; (ii) these methods yield significantly larger errors in the ES than in the GS, with, e.g., CCSD [CC2] mean errors of −0.021 and −0.007 [0.030 and 0.009] Å for the ES and GS C=O bond lengths, respectively; and (iii) the accuracy of the various methods significantly depends on the nature of the bonding. This hints that the quality of the geometries might significantly influence the quality of the corresponding E^{0-0} values.

In the present work, we aim at multiple goals: (i) investigating the impact of geometries on the computed E^{0-0} values; (ii) determining, whether or not, the protocol of ref 14 can be made computationally lighter; (iii) estimating if the CC3 geometries would yield significant improvements over their CCSDR(3) counterparts; and (iv) extending the previous
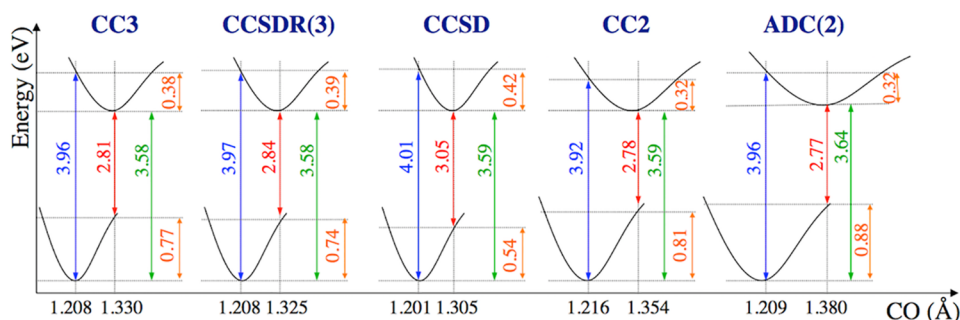
Figure 2. Representation of the CC3/*aug*-cc-pVTZ transition energies of formaldehyde computed with, from left to right, the CC3, CCSDR(3), CCSD, CC2, and ADC(2) optimized geometries. The absorption, fluorescence, adiabatic, and reorganization energies are represented in blue, red, green, and orange, respectively. On the horizontal axis, we provide the optimal C=O bond lengths for each geometry.

benchmark set, notably by considering radical species as well as singlet–triplet excitations.

2. COMPUTATIONAL DETAILS

We have used a variety of programs to determine the optimal GS and ES geometries as well as the transition energies. In every case, all the electrons are correlated, i.e., the frozen-core (FC) approximation was never applied during these optimizations. The ADC(2) and CC2 optimizations have been performed with the Turbomole package,[21] selecting the *def*2-TZVPP atomic basis set and applying the resolution-of-identity approximation. During these calculations, the self-consistent field Hartree–Fock (HF), second-order, and geometry optimization thresholds were all tightened compared to default values by selecting values of 10^{-9}, 10^{-7}, and 10^{-5} au, respectively. ADC(2) and CC2 numerical frequency calculations were systematically performed with the same atomic basis set. The (EOM-)CCSD optimizations and frequency calculations of the singlet and doublet states have been performed with Gaussian16[22] and Psi4[23] using the same *def*2-TZVPP basis set. The geometry convergence threshold was systematically tightened, with a requested residual mean force smaller than 10^{-5} au, whereas the CCSD (EOM-CCSD) energy convergence threshold was set to, at least, 10^{-8} (10^{-7}) au in Gaussian16 in order to obtain accurate analytical gradients and, consequently, accurate numerical frequencies. The U-CCSD optimizations of the lowest triplet state were achieved with Gaussian16 using the same basis set. The same program was used to determine the vibrational frequencies of these triplet geometries at the same level of theory, whereas the EOM-CCSD optimizations of the triplet excited state were performed with Psi4, starting with the U-CCSD structures and using an initial UHF guess. No triplet instability issues were detected during these calculations. The CCSDR(3) and CC3 optimizations were performed with the Dalton package[24] using the same basis set as for the other CC models. These optimizations used the default convergence thresholds of Dalton. We underline that analytical gradients are not available for these two levels of theory, so that the CCSDR(3) and CC3 minimizations were based on numerical differentiations of the total energies. Several geometries used here can be found in earlier contributions.[14,19,20,25,26] Unless otherwise stated, all total and transition energies reported herein have been determined at the CC3/*aug*-cc-pVTZ level (no frozen-core except when noted) with the Dalton[24] and Psi4[23] packages using default algorithms and parameters. A basis set study was performed and is detailed in Section 3.2. CC3 is the *de facto*

gold standard for ES calculations and has recently been shown to deliver very small errors with respect to full CI estimates for small compounds.[26−29] Finally, the B3LYP calculations performed to obtain (TD-)DFT/6-31+G(d) ZPVE were achieved with Gaussian16,[22] using the *ultrafine* quadrature grid.

3. RESULTS AND DISCUSSION

3.1. Formaldehyde: A Representative Example. For illustrative purposes, we qualitatively represent, in Figure 2, CC3 potential energy surfaces obtained using five different geometries for formaldehyde, a molecule undergoing significant structural changes after its hallmark $n \rightarrow \pi^*$ excitation. Although such a one-dimensional representation does not provide the overall picture (e.g., the puckering angle in the ES differs significantly from one method to another),[19] it allows to qualitatively capture, for a given method, the main energetic and geometrical effects, taking the CC3 geometry as a reference. For this geometry, E^{adia} = 3.580 eV, a value that is, as expected (see Introduction), rather close to the average between vertical absorption and emission energies (3.385 eV). In formaldehyde, the planar GS is significantly stiffer than the puckered ES, and one logically finds that $E_{\text{reorg}}^{\text{GS}}$ (0.77 eV) > $E_{\text{reorg}}^{\text{ES}}$ (0.38 eV).

Let us now turn toward less accurate geometries. As the CCSDR(3) structures are very similar to the CC3 ones,[19] their transition energies are very similar to each other as well (Figure 2), which is consistent with the fact that CCSDR(3) geometries were found good enough to deliver chemically accurate E^{0-0}.[14] Using CCSD—a method known to underestimate the GS-to-ES geometrical changes in small organic compounds—the C=O bond length in the ES becomes significantly shorter. Consequently, the two vertical transition energies increase, the Stokes shift ($\Delta^{\text{SS}} = E_{\text{abs}}^{\text{vert}} - E_{\text{fluo}}^{\text{vert}}$) decreases, and the GS and ES reorganization energies become nearly equal. However, as one can see, E^{adia} remains almost unchanged. The opposite scenario is found with CC2: the elongation of the C=O bond after excitation is exaggerated inducing an underestimation of the vertical transition energies, but vastly different GS and ES reorganization energies, with an overall negligible impact on E^{adia}. Finally, considering ADC(2) which delivers a poor ES geometry for formaldehyde, the difference between $E_{\text{reorg}}^{\text{GS}}$ and $E_{\text{reorg}}^{\text{ES}}$ is even more pronounced, but the adiabatic energy still only moderately deviates from the CC3 reference value. In short, there is a clear error compensation mechanism between the two terms in the rhs of eq 1b. Indeed, their magnitude significantly differ from one
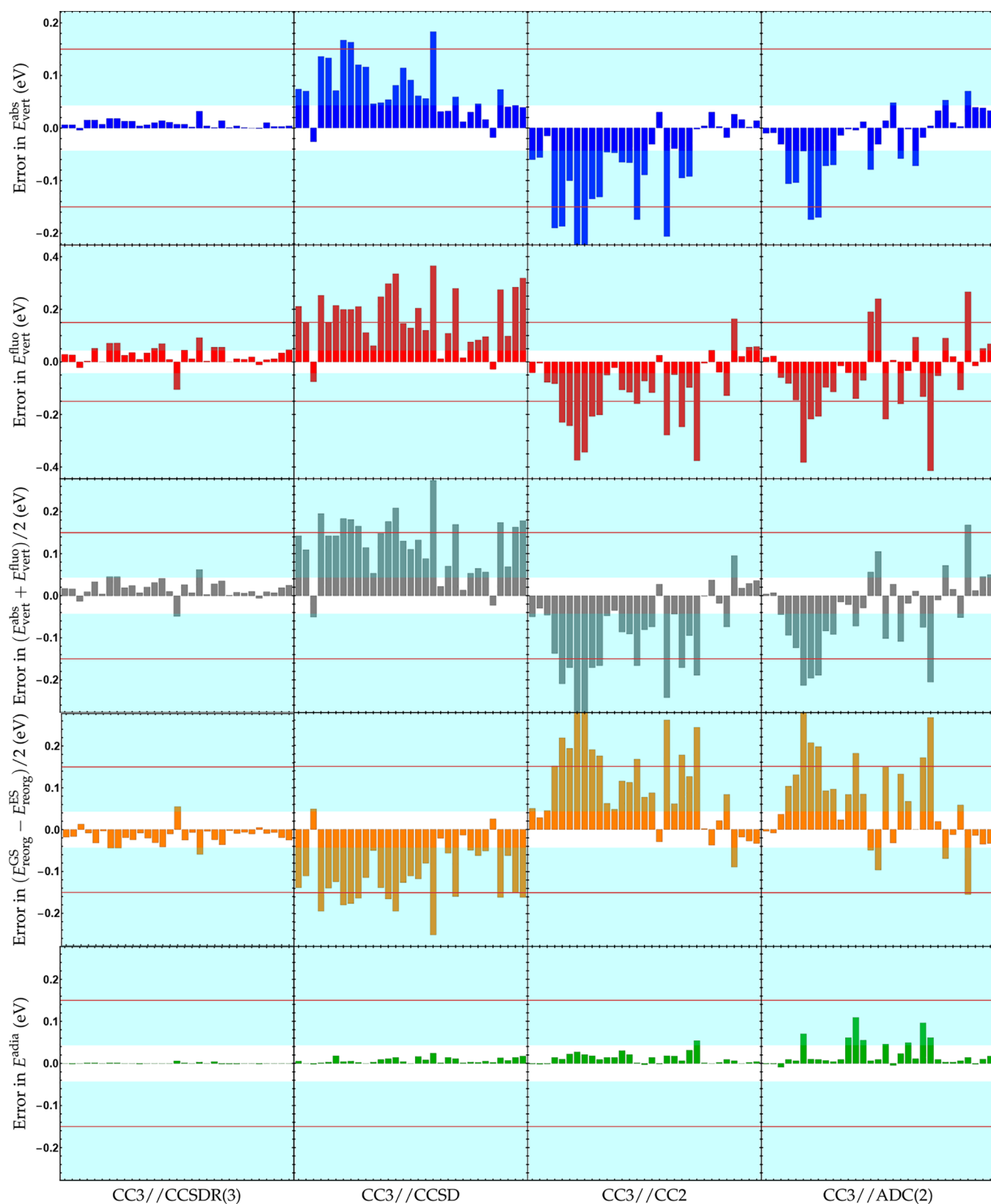
Figure 3. Bar charts of the error (in eV) made with various geometries for 31 singlet−singlet transitions using CC3/aug-cc-pVTZ//CC3/$def2$-TZVPP values as references. From left to right, the CCSDR(3), CCSD, CC2, and ADC(2) methods are selected for the geometry optimizations while retaining CC3 for the computation of transition energies. From top to bottom, the order is as follows: E_{abs}^{vert}, E_{fluo}^{vert}, $(E_{abs}^{vert}+E_{fluo}^{vert})/2$, $(E_{reorg}^{GS}-E_{reorg}^{ES})/2$, and E^{adia}. The white regions indicate chemical accuracy (with respect to the CC3 reference values); the horizontal red lines indicate errors of ±0.15 eV. Note the difference in vertical scales for some quantities. The transitions are ordered as given in Section S-1.1 in the SI.

Table 1. Statistical Analysis of the Impact of the Selected Method for the Geometry Optimization on the Computed CC3/*aug*-cc-pVTZ Transition Energies for 31 Representative Organic Compounds[a]

geometry	property	MSE	MAE	RMS	%CA	%AE
CCSDR(3)	E_{abs}^{vert}	0.008	0.008	0.011	100	100
	E_{fluo}^{vert}	0.024	0.033	0.043	65	100
	$(E_{abs}^{vert}+E_{fluo}^{vert})/2$	0.016	0.020	0.026	87	100
	$(E_{reorg}^{GS}-E_{reorg}^{ES})/2$	−0.016	0.020	0.026	87	100
	E^{adia}	0.000	0.001	0.001	100	100
CCSD	E_{abs}^{vert}	0.070	0.073	0.086	32	90
	E_{fluo}^{vert}	0.166	0.173	0.198	10	48
	$(E_{abs}^{vert}+E_{fluo}^{vert})/2$	0.118	0.123	0.138	10	65
	$(E_{reorg}^{GS}-E_{reorg}^{ES})/2$	−0.111	0.116	0.130	10	68
	E^{adia}	0.007	0.007	0.010	100	100
CC2	E_{abs}^{vert}	−0.074	0.082	0.114	42	81
	E_{fluo}^{vert}	−0.107	0.130	0.169	23	65
	$(E_{abs}^{vert}+E_{fluo}^{vert})/2$	−0.090	0.106	0.136	29	68
	$(E_{reorg}^{GS}-E_{reorg}^{ES})/2$	0.102	0.117	0.149	26	65
	E^{adia}	0.011	0.012	0.017	97	100
ADC(2)	E_{abs}^{vert}	−0.023	0.046	0.064	58	94
	E_{fluo}^{vert}	−0.053	0.122	0.159	26	71
	$(E_{abs}^{vert}+E_{fluo}^{vert})/2$	−0.038	0.075	0.097	36	84
	$(E_{reorg}^{GS}-E_{reorg}^{ES})/2$	0.060	0.093	0.120	36	77
	E^{adia}	0.022	0.024	0.037	74	100

[a]CC3 structures are systematically used as references. MSE, MAE, and RMS are given in eV, and they correspond to the mean signed, mean absolute, and root mean square errors, respectively. %CA and %AE are the percentage of cases reaching "chemical accuracy" (absolute error < 0.043 eV) and "acceptable error" (absolute error < 0.150 eV), respectively.

geometry to another with values of 3.385, 3.405, 3.533, 3.350, and 3.364 eV for the first term and 0.195, 0.175, 0.057, 0.244, and 0.278 eV for the latter when using CC3, CCSDR(3), CCSD, CC2, and ADC(2) geometries, respectively. Nevertheless, their sum, given by E^{adia}, is remarkably stable: 3.580, 3.580, 3.589, 3.594, and 3.642 eV for CC3, CCSDR(3), CCSD, CC2, and ADC(2), respectively.

As discussed in detail below, this compensation phenomenon is rather general. The adiabatic energies are significantly less sensitive to the quality of the selected geometry than the vertical absorption and fluorescence energies. On the bright side, this means that one can indeed use a cheaper method than CCSDR(3) in order to get ES structures, yet reaching accurate 0−0 energies. On the dark side, this indicates that matching experiment for E^{0-0} is not a proof that the underlying GS and ES structures are accurate.

3.2. Error Compensation Pattern. We obtained CC3 E^{adia} for 31 ES using geometries determined at the CC3/*def*2-TZVPP level (see the SI for details about states, compounds, and total energies). First we perform a basis set investigation and compare the CC3 E^{adia} values obtained with *aug*-cc-pVTZ, *aug*-cc-pCVTZ, d-*aug*-cc-pVTZ, *aug*-cc-pVQZ, d-*aug*-cc-pCVTZ, and d-*aug*-cc-pCVQZ. (The results are detailed in Section 1 of the SI.) Taking d-*aug*-cc-pCVQZ results as reference, one finds that the mean absolute error (MAE) obtained with *aug*-cc-pVTZ is 0.022 eV only for the 24 cases in which the calculations with the largest basis were technically possible. The largest deviations are obtained for HPO and isocyanogen, two quite "exotic" compounds, for which the *aug*-cc-pVTZ E^{adia} values are, respectively, 0.070 eV too small and 0.099 eV too large. Turning our attention to the other bases, we notice that the addition of core polarization functions slightly decreases the *aug*-cc-pVTZ E^{adia} values by an average of −0.023 eV, whereas going to the quadruple-ζ basis leads to a small increase of E^{adia}, on average by 0.010 eV. There is

globally a small error compensation between these two effects, explaining the overall accuracy of *aug*-cc-pVTZ, the basis set we have selected for the remaining of this study. Another important aspect is whether or not the FC approximation should be applied. In the vast majority of CC calculations the FC approximation is applied. This choice is justified as it has been shown that using FC significantly decreases the computational effort without affecting the vertical absorption energies; the typical variations are of the order of 0.010 eV only.[30] Although the *aug*-cc-pVXZ basis set family is not supposed to be applied while correlating core electrons (one should consider, e.g., the *aug*-cc-pCVXZ family for such purpose), we have found above relatively small differences between the *aug*-cc-pVTZ and d-*aug*-cc-pCVQZ results, possibly partly due to some error compensations. We have therefore performed here *aug*-cc-pVTZ calculations with and without FC approximation, and our results are listed in Table S-3 of the SI for both E_{fluo}^{vert} and E^{adia}. For the former vertical property, one finds a conclusion consistent with the literature, i.e., the impact of the FC approximation is negligible for all molecules (except for HPS) with a mean absolute difference (MAD) of 0.007 eV. In contrast, the FC approximation tends to significantly decrease E^{adia} (by an average of −0.030 eV), with a MAD compared to the "full" calculation as large as 0.043 eV. These findings are in line with our recent work,[14] and we have therefore correlated both the core and valence electrons in all our calculations reported below, except when noted.

Using the CC3/*aug*-cc-pVTZ//CC3/*def*2-TZVPP values as references, we can estimate the errors made while selecting a lighter level of theory for the geometry optimizations, while conserving CC3/*aug*-cc-pVTZ for the transition energies. The results are displayed in Figure 3, and a statistical analysis is provided in Table 1.

Table 2. Statistical Data Obtained by Comparing Experimental and Theoretical E^{0-0} Values for Singlet−Singlet Transitions[a]

geometry	ZPVE	count	MSE	MAE	RMS	%CA	%AE
CC3	CCSD	41	−0.011	0.027	0.036	81	100
	B3LYP	41	−0.011	0.024	0.035	85	100
CCSDR(3)	CCSD	53	−0.008	0.027	0.036	19	100
	B3LYP	53	−0.009	0.024	0.035	83	100
CCSD	CCSD	69	0.006	0.028	0.036	81	100
	CC2	60	−0.001	0.026	0.034	78	100
	ADC(2)	60	−0.004	0.029	0.037	78	100
	B3LYP	69	0.001	0.025	0.032	86	100
CC2	CC2	60	0.006	0.032	0.044	78	98
	ADC(2)	60	0.004	0.033	0.047	75	98
	B3LYP	60	0.007	0.030	0.041	80	98
ADC(2)	ADC(2)	60	0.021	0.046	0.061	63	98
	B3LYP	60	0.025	0.046	0.062	68	97

[a]The transition energies are systematically computed at the CC3/*aug*-cc-pVTZ level using different geometries and ZPVE corrections. The latter term was computed at the *def*2-TZVPP basis set for all methods, except for B3LYP for which the more compact 6-31+G(d) basis set was applied. "Count" refers to the number of transitions in each group. %CA and %AE are the percentage of cases reaching "chemical accuracy" (absolute error < 0.043 eV) and "acceptable error" (absolute error < 0.150 eV), respectively.

The bar chart of the error patterns obtained for the vertical absorption and fluorescence is displayed in the top two rows of Figure 3. Although the set of compounds considered here is significantly larger than the previously studied one,[20] the major trends and conclusions pertain. For a given method, the errors tend to be significantly larger for $E_{\text{fluo}}^{\text{vert}}$ than for $E_{\text{abs}}^{\text{vert}}$. This unsurprising observation is due to the higher methodological sensitivity of the ES geometries compared to their GS counterparts.[19] This is particularly striking with CCSDR(3) that systematically delivers chemically accurate $E_{\text{abs}}^{\text{vert}}$ as compared to CC3 but attains this goal in "only" 64.5% of the cases for $E_{\text{fluo}}^{\text{vert}}$. For a given molecule, one notices a general (but not systematic) correlation between the errors made for the two kinds of vertical transition energies: if a molecular GS structure is sensitive to the selected method, the same will hold for its ES geometry. Turning now to the comparison of the four methods [CCSDR(3), CCSD, CC2, and ADC(2)], it is obvious that CCSD geometries yield almost systematically too large absorption and fluorescence energies, with respective MSE of 0.070 and 0.166 eV. Qualitatively, these positive MSE confirm that CCSD provides an overlocalized picture of the system (in other words, too close from the HF picture), which is consistent with previous works.[19,20,31] With CC2 geometries, the errors go in the opposite direction, but their magnitudes are similar to the one obtained with CCSD (MSE of −0.074 and −0.107 eV for $E_{\text{abs}}^{\text{vert}}$ and $E_{\text{fluo}}^{\text{vert}}$, respectively). In other words, CC2 yields a too delocalized picture for the geometries of organic compounds,[19,20] that is, a description with the same error sign as a LDA or GGA functional in the DFT framework. The introduction of perturbative triples allows for correction of most of the CCSD error, consistently with previous works.[20,32] Finally, ADC(2) geometries give a more erratic error pattern but provide a MAE slightly smaller than with CC2 structures for $E_{\text{abs}}^{\text{vert}}$, consistent with the well-known quality of MP2 GS geometries.

Let us now turn our attention to E^{adia} and its two contributions as given in eq 1b (bottom three rows of Figure 3). It is certainly unsurprising that the error patterns obtained for the average of the absorption and emission energies (middle row of Figure 3) show the same trends as the one described above for absorption and fluorescence, i.e., a limited overestimation with CCSDR(3), a strong overshooting with

CCSD, a strong underestimation with CC2, and a less clear pattern with ADC(2). For $(E_{\text{abs}}^{\text{vert}}+E_{\text{fluo}}^{\text{vert}})/2$, chemical accuracy (as compared to CC3 structures) is reached in 87% of the cases with CCSDR(3) but only for 10%, 29%, and 35% of the transitions with CCSD, CC2 and ADC(2), respectively (Table 1). With the three latter methods, there is also a significant share of the cases with errors exceeding 0.15 eV, a large discrepancy given that it solely originates from the structures. Undoubtedly, it is striking that these large deviations are nearly exactly compensated by the errors made for the average difference of reorganization energies (penultimate row of Figure 3). Indeed, the third and fourth rows of Figure 3 are almost perfect mirror images of each other: while CCSD provides too large transition energies, its overlocalized description induces a significant underestimation of the reorganization energies. The same phenomenon holds for the other methods, and what was noticed for formaldehyde in the previous Section is therefore a very solid trend. Overall, very small errors are obtained for the adiabatic energies, with trifling MAEs of 0.001, 0.007, and 0.012 eV with CCSDR(3), CCSD, and CC2 geometries, respectively. Particularly astonishing is the success of CCSD for E^{adia} (bottom row of Figure 3): chemical accuracy is systematically reached, although this is almost never the case for the two components of eq 1b. In addition, the error magnitude in E^{adia} now follows the expected accuracy ladder: the more refined the method, the smaller the average error, which was not necessarily the case for the other properties.

3.3. Comparisons with Experiment for Singlet States.
Having performed a theory versus theory analysis, let us now turn to comparisons with experimental E^{0-0} values. We have built a statistically significant list of states for which we have determined CC3 transition energies on various geometries. The set encompasses 69 singlet−singlet transitions, significantly extending our previous set and including more challenging cases.[14] It is worth stressing that this set of transitions is mostly constituted of valence transitions and that the considered ES is often the lowest on the energy scale. These limitations are inherent to the experimental availability of accurate 0−0 energies and are typical of theory-experiment comparisons for this property.[1−3,7−9,12] The full list of data, including experimental references and symmetries of all states,

is available in the SI. We note that, in a few cases, the ZPVE could not be determined with all levels of theory, typically because some geometry optimizations in a given symmetry failed to converge (see Section S-1.2 in the SI for details). These cases are not statistically relevant for our purposes.

Before getting to the statistics, let us briefly discuss one interesting example, the first electronic transition in pyrazine. With ADC(2) and CC2, the geometry of the lowest ES belongs to the C_i point group, which is consistent with a previous investigation performed with these methods.[9] The deformation compared to the D_{2h} symmetry is significant with nonequal CN bond lengths attaining 1.288 and 1.368 Å with ADC(2) and 1.294 and 1.373 Å with CC2. B3LYP/6-31+G(d) foresees a C_{2h} point group, with, similarly, unequal CN distances (1.300 and 1.373 Å). In contrast, CCSD provides a D_{2h} ES geometry — all CN bonds being 1.338 Å long — which is consistent with higher levels of theory. For example, the CCSDR(3) optimization starting from the B3LYP minimum returns to a D_{2h} structure with CN distances of 1.346 Å. Despite these rather divergent descriptions of the ES geometries, the CC3 0−0 energies are always accurate with deviations of 0.031, 0.023, 0.036, and 0.038 eV compared to experiment when using the ADC(2), CC2, CCSD, and CCSDR(3) optimized structures, respectively. In other words, a chemically accurate E^{0-0} can be obtained even with an incorrect point group symmetry for the ES geometry. As discussed in our recent work,[14] changing the level of theory for computing E^{adia} is much more deleterious, e.g., the CCSD//CCSD E^{0-0} value is 0.157 eV off the experimental one.

Table 2 reports statistical results obtained for the set of considered compounds, combining various levels of theory for the geometry optimization and the calculation of the ΔE^{ZPVE} correction term. With the most refined level of theory, that is, selecting CC3 geometries and CCSD ZPVE, one obtains a MAE of 0.027 eV and a RMS of 0.036 eV, both below the chemical accuracy threshold. This approach also delivers errors smaller than 0.15 eV for all compounds and reaches chemical accuracy in 81% of the cases, a success slightly less impressive than in our previous contribution,[26] but the present set contains several "exotic" species, such as HPO, HPS, and $H_2C=Si$. For instance, the CC3//CC3 E^{0-0} value comes with a significant error of −0.102 eV compared to experiment for HPS, but even the CAS/MRCI+D/aug-cc-pV(5+d)Z method suffers from a (relatively) large error (0.073 eV) for this compound.[33] It is worth noting that applying the FC approximation during the calculation of the CC3 adiabatic energies would have significantly degraded the results. Indeed, with both CCSD or B3LYP ΔE^{ZPVE}, the MAE would have increased to 0.049 eV, with only 56% of the cases in which chemical accuracy would be attained (FC data are available in the SI). In addition, for the 24 states for which CC3/aug-cc-pCVQZ calculations were technically feasible (vide supra), we obtain a MAE of 0.031 (0.027) eV with the aug-cc-pVTZ (d-aug-cc-pCVQZ) basis set selecting CCSD ZPVE and CC3 geometries. Therefore, the improvement with the larger basis is rather limited, though noticeably smaller deviations are noticed for HPO and HPS, and a significantly larger error is obtained for isocyanogen. As one can see in Table 2, using B3LYP ΔE^{ZPVE} corrections instead of the CCSD essentially induces no change. This conclusion is well in line with the analysis of Winter and co-workers who demonstrated the small impact of the level of theory used for determining the vibrational correction.[9] When using CCSDR(3) or CCSD geometries, one

also notices very small changes of the statistical values, the CCSD geometries delivering results as accurate as the ones obtained with CC3 geometries, with a chemical accuracy rate reaching an astonishing 86% with the B3LYP ZPVE, close to the one we reported earlier.[26] As stated above,[19] the CCSD ES geometries are certainly not extremely accurate for all molecules, so this illustrates that a very nice match between experimental and theoretical E^{0-0} values can be reached even with not-so-accurate structures. When one climbs down the accuracy scale to CC2 geometries, the results remain very acceptable with a RMS close to chemical accuracy, whereas using ADC(2) for the geometry optimizations further degrades the results. Eventually, using CCSD geometries and B3LYP ZPVE, we obtain MAE of 0.021 and 0.027 eV for the 35 $n \rightarrow \pi^*$ and 26 $\pi \rightarrow \pi^*$ transitions considered here, respectively. This indicates that the approach seems equally efficient for both types of transitions. Whether or not this accuracy is maintained for Rydberg states is hard to judge due to the small number of such states in our set.

3.4. Triplet Excited States. For the triplet transitions, several methodological choices can be made. First, given the above results, we consider CCSD geometries only and we compute the ΔE^{ZPVE} corrections at this level as well as with B3LYP. In addition, as the collected experimental data nearly systematically focus on the lowest triplet state of a given symmetry, we optimize the corresponding geometries at both the U-CCSD/def2-TZVPP and EOM-CCSD/def2-TZVPP levels, the former scheme offering a more computationally appealing approach. For the adiabatic energies, we test both the LR-CC3/aug-cc-pVTZ approach implemented in Dalton[24] and the restricted open-shell "ground state" implementation available in Psi4.[23] In this latter approach the initial ROHF reference orbitals are transformed into semicanonical UHF orbitals during the calculation. Thirty singlet−triplet transitions have been considered in total. As above, details regarding total and transition energies, symmetries, and experimental references can be found in the SI.

First, as can be deduced from Tables S-23−S-25, the differences in E^{adia} obtained by selecting U-CCSD or EOM-CCSD structures or by using LR-CC3 or RO-CC3 energies are generally insignificant. Indeed, for the full set of compounds, the LR-CC3 E^{adia} values obtained on the EOM-CCSD and U-CCSD structures are very similar with a mean absolute difference of 0.011 eV and a maximal difference as small as 0.037 eV (oxalyl chloride, for which the EOM-CCSD and U-CCSD ES geometries have different symmetries). In contrast, when comparing the vertical phosphorescence energies determined with these two geometries, we obtain a MAD of 0.108 eV and a maximal deviation of 0.454 eV (oxalyl chloride). This result is perfectly in line with our previous conclusions that vertical transition energies are much more sensitive to the selected geometry than their adiabatic and 0−0 counterparts. The MAD determined when comparing the LR-CC3 and RO-CC3 adiabatic energies determined on the U-CCSD structures is as small as 0.027 eV. There are, however, two cases in which significant changes are noticed when going from LR-CC3 to RO-CC3 energies: acetylene (+0.060 eV) and cyanogen (+0.300 eV). Although there is no obvious rationale for these larger discrepancies, we note that these two outliers correspond to $\pi \rightarrow \pi^*$ rather than $n \rightarrow \pi^*$ excitations that constitute the majority of the considered cases in this Section. Next, several molecules are worth further discussion. The first is CHCl, for which we computed a negative vertical

Table 3. Statistical Data Obtained by Comparing Experimental and Theoretical E^{0-0} Values for Singlet−Triplet Transitions[a]

geometry	E^{adia}	ZPVE	count	MSE	MAE	RMS	%CA	%AE
U-CCSD	LR-CC3	U-CCSD	30	−0.028	0.040	0.055	70	97
	LR-CC3	U-B3LYP	30	−0.036	0.041	0.058	70	97
	RO-CC3	U-CCSD	28	−0.013	0.040	0.065	82	93
	RO-CC3	U-B3LYP	28	−0.021	0.042	0.067	75	93
EOM-CCSD	LR-CC3	U-CCSD	29	−0.020	0.033	0.050	76	97
	LR-CC3	U-B3LYP	29	−0.028	0.037	0.054	76	97

[a]The transition energies are systematically computed at the CC3/*aug*-cc-pVTZ level using different protocols and ZPVE corrections. The latter term was computed at the *def*2-TZVPP basis set (CCSD) or 6-31+G(d) (B3LYP) level. "Count" refers to the number of transitions in each group. %CA and %AE are the percentage of cases reaching "chemical accuracy" (absolute error < 0.043 eV) and "acceptable error" (absolute error < 0.150 eV), respectively.

phosphorescence energy. This unsettling feature is due to a crossing between the S_0 and T_1 potential energy surfaces, i.e., for the GS S_0 geometry, S_0 is, of course, the most stable state, whereas for the optimal triplet geometry, the lowest triplet indeed becomes energetically favored compared to the singlet. We note that the computed E^{0-0} is chemically accurate for that compound irrespective of the selected protocol. The second molecule is acetylene, for which our theoretical E^{0-0} estimates (3.752−3.814 eV) deviate substantially from a rather recent experimental value of 3.584 eV[34] but fit very well previous MR-AQCC values (3.84 eV)[35] or theoretical best estimates (3.81 eV).[36] Consistently with the detailed analyses carried out by Sherrill, Head-Gordon, Schaefer, and their co-workers,[36,37] we therefore conclude that the experimental value is inaccurate, and we discard acetylene from our statistics. Third, there is SO_2 for which the errors are abnormally large, e.g., −0.218 eV with LR-CC3. Given previous studies on this molecule showing unusually large basis set effects, e.g., see ref 38 and references therein, we performed LR-CC3/d-*aug*-cc-pVQZ calculations, which allowed halving the error (−0.109 eV). For the sake of consistency, we have nevertheless kept the original *aug*-cc-pVTZ result in our statistics.

The statistical data obtained for the singlet−triplet transitions are given in Table 3. As can be seen, the six tested protocols provide similar deviations, and there is no advantage nor disadvantage (in terms of accuracy) of using RO-CC3 instead of LR-CC3 or selecting U-CCSD instead of EOM-CCSD geometries, whereas the improvement brought by using CCSD ZPVE corrections instead of their B3LYP counterparts is very small, which probably does not justify the associated increase in computational cost. The MSEs are negative, and there is indeed a clear tendency to (slightly) underestimate the experimental value for singlet−triplet transitions. The MAEs are larger than for the singlet−singlet transitions, but this is mainly due to SO_2. Indeed, removing it from the set would decrease the LR-CC3//U-CCSD MAE from 0.040 to 0.033 eV, closer to the 0.027 eV value obtained in the previous Section with an equivalent approach. Chemical accuracy is reached in ca. 70−82% of the cases depending on the protocol which is certainly a very pleasant outcome for spin-flip transitions.

3.5. Radicals. Let us now turn toward the calculation of E^{0-0} for radical species. Open-shell molecules are more challenging for theoretical methods than their closed-shell counterparts, and this certainly holds for ES properties. In particular, DFT and TD-DFT are known to be less effective for radicals, or at the very least, the "optimal" functional for E^{0-0} is different for open- and closed-shell molecules.[2] We nevertheless computed ΔE^{ZPVE} with B3LYP/6-31+G(d) when

technically feasible (a few cases did not converge, see the SI). As for triplets, we use the unrestricted formalism during the geometry optimization, i.e., the GS and ES structures are obtained at the U-CCSD/*def*2-TZVPP and U-EOM-CCSD/*def*2-TZVPP levels, respectively. For the calculations of the CC3 transition energies, we apply the restricted open-shell protocol implemented in Psi4.[23] All the total and transition energies as well as geometries are available in the SI.

In contrast to the previous cases, the ΔE^{ZPVE} term is not systematically negative for radicals, and it can be very close to zero (F_2BO) or even significantly positive (NO_3, vinyl...). We obtain a very reasonable agreement between theory and experiment for most radicals (*vide infra*), except for two cases (CNO and FS_2) for which the deviations exceed 0.150 eV. For the former compound, a previous MRCI+Q/cc-pVQZ investigation reported a smaller error for E^{0-0} with respect to experiment.[39] This suggests that our basis set is too small and/or that multireference effects are involved. Having obtained a similar E^{0-0} value with CC3/*aug*-cc-pVQZ (instead of the triple-ζ basis set), we can safely conclude that multireference effects are probably significant for CNO. Interestingly, for the NCO isomer, our approach is chemically accurate. For FS_2, we did not found any high-level multireference results in the literature to compare with, so that the origin of the theory/experiment discrepancy could not be clarified. We suspect here large basis set effects as those noted for SO_2, though it was technically beyond reach to ascertain this claim.

As expected for these more challenging compounds, the average deviations are larger than for the closed-shell species (see Table 4). Nevertheless the MAE remains close to chemical accuracy, and the theoretical prediction matches the target accuracy in two-thirds of the cases, with only two compounds out of 20 for which the error exceeds 0.150 eV, the typical average error of standard ES approaches (see the Introduction).

Table 4. Statistical Data Obtained by Comparing Experimental and Theoretical E^{0-0} Values in Radicals[a]

geometry	ZPVE	count	MSE	MAE	RMS	%CA	%AE
U-CCSD	U-CCSD	20	0.023	0.043	0.063	65	90
	U-B3LYP	20	0.018	0.041	0.062	70	90

[a]The transition energies are systematically computed at the LR-RO-CC3/*aug*-cc-pVTZ level using two different ZPVE corrections. The latter term was computed at the *def*2-TZVPP basis set (CCSD) or 6-31+G(d) (B3LYP) level. "Count" refers to the number of transitions in each group. %CA and %AE are the percentage of cases reaching "chemical accuracy" (absolute error < 0.043 eV) and "acceptable error" (absolute error < 0.150 eV), respectively.

4. CONCLUSIONS

We have computed more than 100 0−0 energies associated with low-lying valence states using a panel of increasingly accurate wave function approaches. In contrast to previous benchmark studies devoted to E^{0-0}, our focus was set on the level of theory used to determine the ground and excited state geometries as well as the zero-point vibrational corrections, rather than the transition energies. For the latter, we systematically applied the CC3/aug-cc-pVTZ level, correlating all electrons to provide a uniform description. For the ZPVE correction term, ΔE^{ZPVE}, we found a very good agreement between the various levels of theory, so that one can safely use a computationally lighter approach to compute such a quantity. For instance, for the 112 cases in which both B3LYP/6-31+G(d) and CCSD/def2-TZVPP ZPVE values could be obtained, we found a mean absolute deviation between the two as small as 0.012 eV. Also, the correlation between the two sets of data is obvious, with only one case for which the deviation exceeds 0.050 eV (see Figure 4). The influence of the
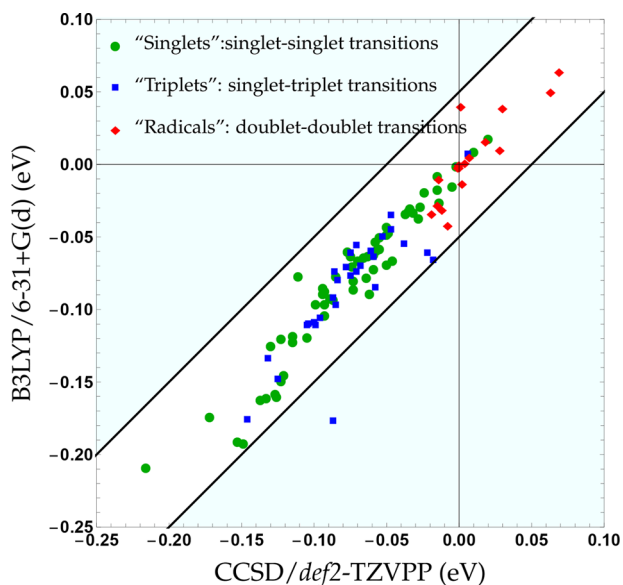

Figure 4. Comparisons of ΔE^{ZPVE} (eV) computed with B3LYP/6-31+G(d) and CCSD/def2-TZVPP for the three subsets of compounds: "singlets" (green dots), "triplets" (blue squares), and "radicals" (red diamonds). The white zone delimited by the two black lines indicates an absolute deviation smaller than 0.05 eV.

geometry on the 0−0 energies is rather small as well. Using CC3, CCSDR(3) or CCSD geometries essentially yields the same statistical deviations, a very small drop in accuracy being noticed for the CC2 structures and a more substantial one for the ADC(2) geometries. Likewise, using U-CCSD or EOM-CCSD structures for the lowest triplet state has also a very small impact on E^{0-0}. These results strongly contrast with the vertical transition energies that show a much larger geometrical dependence. By comparing the experimental and theoretical 0−0 energies obtained by combining (i) CC3 adiabatic energies, (ii) (U-)CCSD geometries, and (iii) B3LYP ZPVE corrections, we could reach chemical accuracy in 79.7% of the cases with a trifling MSE of −0.006 eV and a MAE of 0.032 eV. As highlighted in Figure 5, it is probably even more striking that this success is obtained for E^{0-0} values covering a wide range of energies. Even though this computational approach is
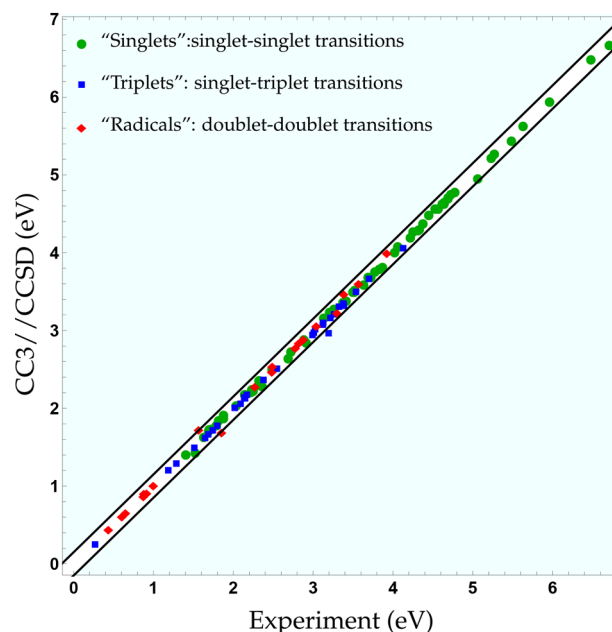

Figure 5. Comparison between experimental and theoretical 0−0 energies for the three subsets of compounds: "singlets" (green dots), "triplets" (blue squares), and "radicals" (red diamonds). The white zone delimited by the two black lines indicates an absolute deviation smaller than 0.15 eV.

limited to single-reference methods and a triple-ζ basis set, only three cases (out of 118) were found having a theory-experiment discrepancy exceeding 0.15 eV (the lowest triplet of SO_2 and the doublet−doublet transitions in CNO and FS_2). Whether the present approach would be as effective for Rydberg states or larger molecules remains to be determined. A key observation of the present study is that this unexpected success is a direct consequence of a strong and systematic error cancelation between the vertical transition energies and the CCSD geometry reorganization energies. It was indeed found previously that the CCSD geometries show significant deviations compared to the reference values obtained with higher levels of theory for polar bonds.[19] Consequently, the vertical emission energies computed on these structures differ significantly from the ones obtained on CC3 geometries.[20] Therefore, while one can rely on this error compensation phenomenon to determine chemically accurate E^{0-0} with "cheap" geometries, the drawback is that a close match between experiment and theory is no proof of the geometry accuracy.

To sum up, while we confirm our previous conclusions that chemical accuracy can be reached using CC3 to compute E^{adia},[14] we additionally demonstrate that this does not necessarily require very accurate geometries as generally thought.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.8b01103.

> List of total and transition energies for all compounds, list of experimental values and references, CCSD ground and excited state geometries (PDF)

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Notes

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