

# Development of a Novel Index for Analysis of Electronically Excited States

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Concerning the major factors in the context of excited states analyses, namely charge centroids of the orbitals involved in the excitations, the distance between orbital centroids, and overlap integrals, a new metric—the  $\Omega$  index—is proposed to assign the character and optical properties of electronically excited states. Using several molecules from different classes and also a well-studied standard database for time-dependent density functional theory (TD-DFT) studies as benchmark criteria, accountability of the developed index is numerically assessed for local, charge transfer, and Rydberg excitations. It is shown that the nature of excited states can be discriminated using

the  $\Omega$  index, where its superior performance for those situations in which the previous descriptors were not helpful is also unveiled. Relationships are also examined between the  $\Omega$  index and optical properties of some molecules under study in the framework of the sum-over-state approach. It is observed that there are correlations between the proposed index and computed hyperpolarizabilities based on the sum-over-state scheme. These findings offer the possibility of estimating excited-state properties of large systems from simple descriptors without explicitly performing calculations of high-order response functions.

## 1. Introduction

There has been a recent surge in the literature on the development, benchmarking, and application of time-dependent density functional theory (TD-DFT)<sup>[1–3]</sup> approximations for modeling excited-state properties in a wide variety of physical, chemical, and biochemical systems.<sup>[4–31]</sup> This success can be ascribed to the outstanding ratio of accuracy to computing time in TD-DFT calculations. Nevertheless, there are notoriously difficult problems for TD-DFT in its current form, leading to failures in situations involving charge-transfer (CT) excitations, excited states of extended  $\pi$ -conjugated systems, multiply excited states, and photoionization processes.<sup>[32–38]</sup> In an endeavor to address these drawbacks, we have recently faced a range of metrics to overcome the problems of TD-DFT in terms of performance of functionals. Some of these descriptors have been presented based on centroid distances and geometrical features, whereas for others different concepts such as molecular orbitals, electron densities, and a physical picture of exciton wave functions have been imposed.<sup>[39–49]</sup> Such metrics have pros and cons for individual problematic excitations, which in turn led to new measures being developed. Among others, and of particular relevance to the present work, the recently proposed descriptor by Guido et al.<sup>[41]</sup> is of interest. This index is based on the charge centroids of the orbitals involved in the excitations and can be interpreted in terms of the hole–electron distance. Despite the superior performance of this index in comparison to previous metrics as a diagnostic test of excit-

ed states within the framework of TD-DFT, it seems that there are also some problems in this respect. In the contribution described here, a new index incorporating important features of excited states analyses, such as charge centroids of the orbitals involved in the excitations, distance between the orbital centroids, and overlap integrals, is proposed for characterizing the short-range and long-range excitations. Moreover, in a recent investigation it has been shown that there are relationships between excited-state descriptors and nonlinear optical properties of push–pull systems.<sup>[50]</sup> Following on from that work, it would also be interesting to explore whether or not there exist such relationships between the proposed metric in this work and the response properties of excited states for some systems under study. We tried to answer this question during this study as well.

The present paper is organized as follows. We commence by providing theoretical considerations on the proposed index. Next, the details of our calculations and the systems considered as benchmark sets are explained. Then, we present the results of TD-DFT calculations based on the proposed diagnostic descriptor for the benchmarked sets. Finally, the main conclusions of the paper are summarized.

## 2. Theoretical Framework

In single-electron excitation processes an electron leaves one point and goes to another point, where these points are real space functions and can be considered as hole and electron, respectively. The hole–particle pair interactions are related to the distance covered during the excitation, and consequently, one possible descriptor can be derived as the ratio of average distance weighted in the function of the excitation coefficients

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[Eq. (1)]:

$$\frac{\sum_{ia} K_{ia}^2 |\langle \varphi_a | \mathbf{r} | \varphi_a \rangle - \langle \varphi_i | \mathbf{r} | \varphi_i \rangle|}{\sum_{ia} K_{ia}^2} \quad (1)$$

where  $K_{ia} = X_{ia} + Y_{ia}$  includes both excitation ( $X_{ia}$ ) and de-excitation ( $Y_{ia}$ ) coefficients and the subscripts of molecular orbitals ( $\varphi$ ) follow the usual conventions as  $i$  for occupied and  $a$  for virtual orbitals. In a recent paper, **the ratio defined in [Eq. (1)] which is denominated as  $Q$  henceforth has been proposed as a metric of CT excitations**<sup>[41]</sup> It has been suggested that the numerical values of this index [ $\text{\AA}$ ] have discrimination power to distinguish the short-range and long-range excitations, as  $Q \leq 1.5 \text{ \AA}$  for the former and  $Q \geq 2.0 \text{ \AA}$  for the latter. However, as will be discussed in the following, in some cases the predicted intervals for the  $Q$  index are not in agreement with those obtained from detailed analyses and visualization of the excitation under study. Accordingly, developing a new index and resolving the failures at a reasonable computational cost is desirable.

As two important factors in the context of excited states analyses, the overlap integral of hole–electron distribution,  $S$ , and the distance between the centroids of hole and electron involved in the excitation,  $D$ , are considered. The overlap integral of hole–electron distribution is a measure of spatial separation of hole and electron. On the other hand, the distance between centroids of hole and electron can be considered as a measure of CT length. In this way, the quantities  $S$  and  $D$  are expressed based on the density distribution of holes and electrons,  $\rho_{\text{hole}}(\mathbf{r})$  and  $\rho_{\text{electron}}(\mathbf{r})$ , respectively.<sup>[51]</sup>

The overlapping extent of hole and electron is as follows [Eq. (2)]:

$$S = \int \min [\rho_{\text{hole}}(\mathbf{r}), \rho_{\text{electron}}(\mathbf{r})] d\mathbf{r} \quad (2)$$

Based on the property of the definition of hole and electron distribution,  $\int \rho_{\text{hole}}(\mathbf{r}) d\mathbf{r} = 1$  and  $\int \rho_{\text{electron}}(\mathbf{r}) d\mathbf{r} = 1$ .

The distance between the two centroids as a measure of the CT length is expressed as [Eq. (3)]:

$$D_{\text{CT}} = [(D_{\text{CT},x})^2 + (D_{\text{CT},y})^2 + (D_{\text{CT},z})^2]^{1/2} \quad (3)$$

where [Eq. (4)–(6)]:

$$D_{\text{CT},x} = |X_{\text{electron}} - X_{\text{hole}}| \quad (4)$$

$$D_{\text{CT},y} = |Y_{\text{electron}} - Y_{\text{hole}}| \quad (5)$$

$$D_{\text{CT},z} = |Z_{\text{electron}} - Z_{\text{hole}}| \quad (6)$$

Here,  $X_{\text{electron}} = \int x \rho_{\text{electron}}(\mathbf{r}) d\mathbf{r}$  is the  $x$  coordinate of the centroid of the electron, and other coordinates for electron and also hole centroids can be expressed in the same way. Our numerical analyses show that (see below) the explicit inclusion of  $S$  and  $D$  for presenting a new descriptor leads to more reliable

results. After examining all the possible combinations of the three factors  $Q$ ,  $S$ , and  $D$  and considering their dimensions, we propose a new index called  $\Omega$  in which the sum of the charge centroids of the orbitals involved in the excitations and the distance between the centroids of hole and electron is weighted according to the overlap integral of hole–electron distribution [Eq. (7)]:

$$\Omega = \frac{Q + D}{S} \quad (7)$$

It is underlined here that the basic components of our proposed index, namely charge centroids of the orbitals involved in the excitations, distance between the orbital centroids, and overlap integrals are important and widely used concepts in quantum chemistry. The straightforward evaluation of the  $\Omega$  index at a reasonable computational cost should also be noted.

Besides dissecting the type of excited states using the new  $\Omega$  index, its relationship with linear and nonlinear optical properties of excited states was also explored. To this end, we used the sum-over-states (SOS) approach<sup>[52,53]</sup> to compute the polarizability  $\alpha$  and first hyperpolarizability $\beta$  of excited states [Eq. (8) and (9)]:

$$\alpha_{AB}(-\omega; \omega) = \hat{P}[A(-\omega), B(\omega)] \sum_{i \neq 0} \frac{\mu_{0i}^A \mu_{i0}^B}{\Delta_i - \omega} \quad (8)$$

$$\beta_{ABC}(-\omega_\sigma; \omega_1, \omega_2) = \hat{P}[A(-\omega_\sigma), B(\omega_1), C(\omega_2)] \sum_{i \neq 0} \sum_{j \neq 0} \frac{\mu_{0i}^A \mu_{ij}^B \mu_{j0}^C}{(\Delta_i - \omega_\sigma)(\Delta_j - \omega_2)} \quad (9)$$

where  $\mu_{ij}^A = \langle i | \hat{\mu}^A | j \rangle$ ,  $\bar{\mu}_{ij}^A = \mu_{ij}^A - \mu_{00}^A \delta_{ij}$ , and  $\omega_\sigma = \sum \omega_i$ . Here,  $A$ ,  $B$ , and  $C$  denote the directions  $x$ ,  $y$ , or  $z$ ,  $\omega$  is the energy of external fields (where  $\omega = 0$  refers to static electric field),  $\Delta_i$  is the excitation energy of state  $i$  with respect to the ground state 0,  $\hat{P}$  is the permutation operator,  $\hat{\mu}$  is the dipole moment operator, and  $\mu_{ij}^A$  is  $A$ th component of the transition dipole moment between states  $i$  and  $j$  (for  $i=j$  this term simply corresponds to electric dipole moment of state  $i$ ). More details on the formalism of the SOS scheme for calculating the dipole polarizabilities and first, second, or third hyperpolarizabilities of excited states can be found in Ref. [52].

## Computational Details

The first test set for analyzing the role of quantities  $S$ ,  $D$ , and  $Q$  to monitor the type of excitations includes molecules from various categories with different types of excitations. More specifically, we have considered examples of chromophores (coumarin and indole), nucleobases (adenine, cytosine, guanine, thymine, uracil), amino acids (tryptophan and tyrosine), substituted naphthalenes (1-chloronaphthalene and 1-methylnaphthalene), and a polycyclic aromatic hydrocarbon (tetraphene).<sup>[54]</sup> Moreover, for detailed analyses on the performance of the proposed index, one of the well-studied databases in the context of excited states investigations, namely the standard benchmark set of Peach et al.,<sup>[39]</sup> was also

used. This set contains a wide range of excitations, many of which have been shown to be a challenge for TD-DFT. For the TD-DFT calculations of excited states, three functionals of different rungs are used: PBE as a representative of the generalized gradient approximation (GGA),<sup>[55]</sup> B3LYP as a widely used hybrid functional with a fixed amount of exact exchange (20%),<sup>[56,57]</sup> and CAM-B3LYP as a long-range corrected functional containing 19% and 65% exact exchange at short and long range, respectively.<sup>[58]</sup> Following previous suggestions and for a straightforward comparison between the present results and earlier published data, the appropriate basis sets with the recommended geometries were used in our calculations.<sup>[39,54]</sup> In particular, all the computations use the cc-pVTZ basis set, whereas for N<sub>2</sub>, CO, and H<sub>2</sub>CO with the Rydberg character of some of the excitations, the *d*-aug-cc-pVTZ basis set has been used. All the TD-DFT calculations were carried out using the Gaussian 09 suite of programs.<sup>[59]</sup> Plus, computations of the proposed index and optical properties of excited states have been implemented in a multifunctional wave function analyzer program developed by Lu and Chen.<sup>[51]</sup>

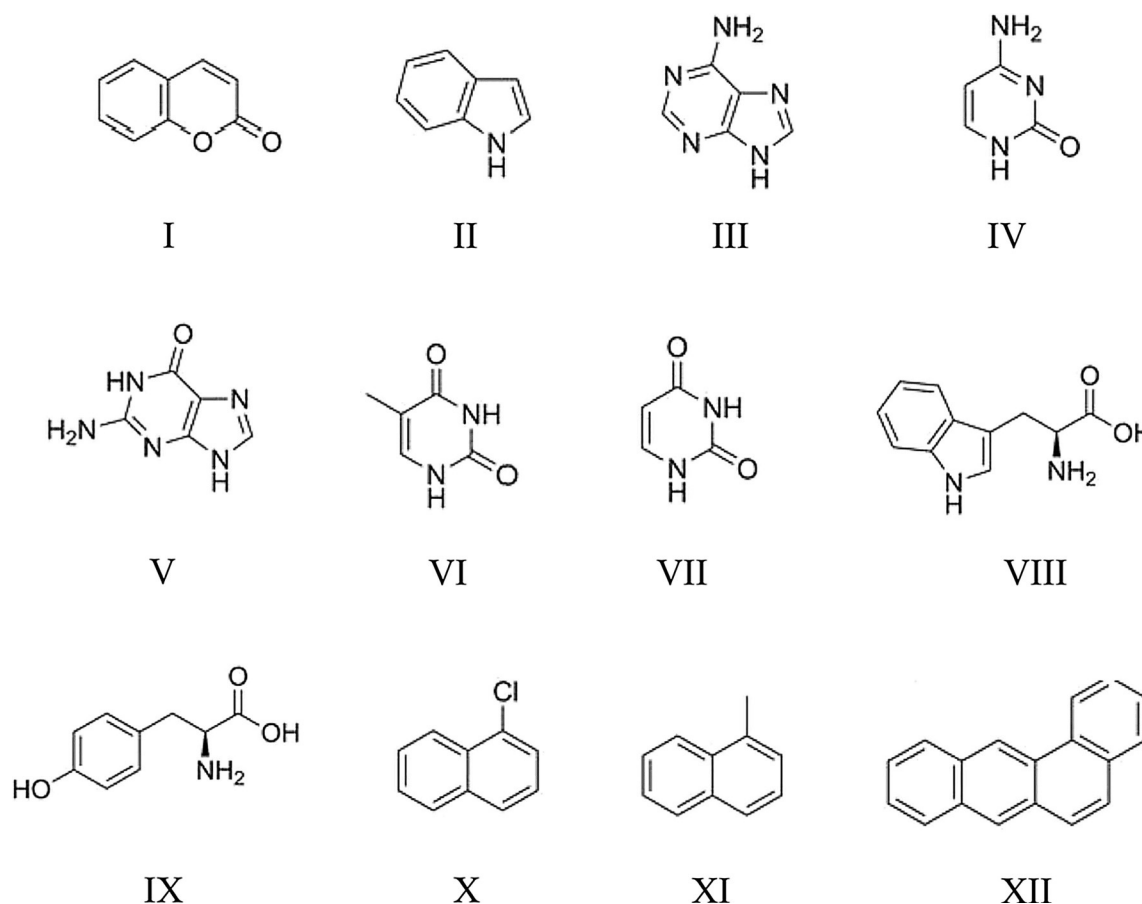
### 3. Results and Discussion

We first evaluated the performance of  $\Omega$  index defined in Equation (7) for various types of excitations in the first set of molecules. Figure 1 shows the structures along with their names for the corresponding molecules in this set. The CAM-B3LYP/cc-pVTZ-computed values of excitation energies, oscilla-

tor strengths, *S*, *D*, and *Q* quantities for the five lowest excited states of all the included molecules are collected in Table 1. Consider the role of the *S* and *D* quantities on the type of excited states. As expected from the definitions of various types of excitations, analyzing the values of *S* and *D* in detail along with visualization of the hole and electron distributions for the excitations under study, we arrived at the following classifications for local, CT, and Rydberg excitations (LE, CT, and R, respectively):

- 1) Large *S* and small *D* → Same spatial range of hole and electron distributions → LE
- 2) Small *S* and large *D* → Large spatial range between hole and electron distributions → CT
- 3) Small *S* and small *D* → Intermediate spatial range between hole and electron distributions → R

As illustrative examples of LE and CT excitations, consider the second and fifth excitations of 1-chloronaphthalene, respectively. Based on the values of *S* and *D* we anticipate that the second excitation ( $\Delta E = 4.54$  eV) with a small distance and consequently large overlap ( $D = 0.07$  Å and  $S = 0.74$ ) and the fifth excitation ( $\Delta E = 6.27$  eV) with a large distance and small overlap ( $D = 1.41$  Å and  $S = 0.28$ ) should be LE and CT, respectively. A simultaneous visualization of hole and electron distri-



**Figure 1.** Structures of the considered molecules in the first benchmark set: I (coumarin), II (indole), III (adenine), IV (cytosine), V (guanine), VI (thymine), VII (uracil), VIII (tryptophan), IX (tyrosine), X (1-chloronaphthalene), XI (1-methylnaphthalene), and XII (tetraphene).

**Table 1.** Computed values of excitation energies [eV], oscillator Strength,  $Q$  [Å],  $S$ ,  $D$  [Å], and  $\Omega$  index [Å] for the molecules in the first test set.

Molecule	$\Delta E^a$	$\Delta E$	$f$	$Q$	$S$	$D$	$\Omega$
coumarin	3.99	4.40	0.17	0.61	0.49	0.61	2.49
		4.90	0.00	2.64	0.22	1.68	19.64
	4.53	4.95	0.13	1.43	0.58	0.76	3.74
		5.89	0.04	0.81	0.63	0.35	1.84
		6.18	0.39	0.70	0.66	0.15	1.29
indole	4.37	5.02	0.36	0.47	0.64	0.25	1.13
	4.77	5.09	0.11	0.60	0.60	0.76	2.27
		6.20	0.00	2.84	0.13	2.52	41.23
		6.38	0.52	0.86	0.65	0.79	2.54
		6.65	0.39	0.56	0.65	0.66	1.88
adenine	5.37	0.00	1.11	0.21	0.51	7.71	
		5.37	0.26	0.45	0.53	0.46	1.72
	4.92	5.47	0.03	0.71	0.66	0.26	1.47
		5.96	0.00	0.38	0.25	0.64	4.08
		6.30	0.00	0.72	0.22	0.53	5.68
cytosine	4.28	4.97	0.06	1.01	0.43	0.89	4.42
		5.24	0.00	1.67	0.22	1.30	13.50
	5.90	0.00	1.72	0.19	1.85	18.79	
		5.98	0.12	1.47	0.42	1.29	6.57
		6.10	0.00	1.74	0.20	1.89	18.15
guanine	4.37	5.14	0.16	1.31	0.47	0.66	4.19
		5.56	0.00	1.50	0.23	1.17	11.61
	5.65	0.29	0.74	0.52	0.25	1.90	
		6.15	0.00	3.22	0.14	2.96	44.14
		6.37	0.00	1.11	0.23	0.48	6.91
thymine	5.10	0.00	1.66	0.22	1.31	13.50	
		4.95	5.28	0.18	0.46	0.45	0.48
	6.43	0.00	1.60	0.20	1.15	13.75	
		6.62	0.00	2.23	0.14	2.50	33.79
		6.67	0.06	1.72	0.25	1.64	13.44
uracil	5.06	0.00	1.75	0.21	1.39	14.95	
		5.08	5.45	0.17	0.45	0.47	0.46
	6.35	0.00	1.66	0.20	1.15	14.05	
		6.58	0.04	1.76	0.23	1.69	15.00
		6.81	0.00	2.11	0.15	1.85	26.40
tryptophan	4.43	4.92	0.08	0.81	0.53	0.89	3.21
		5.00	0.04	0.67	0.74	0.26	1.26
	5.58	0.01	1.53	0.26	0.62	8.27	
		6.10	0.00	3.82	0.15	2.35	41.13
		6.22	0.36	1.60	0.52	0.87	4.75
tyrosine	4.50	5.08	0.03	0.99	0.60	0.25	2.07
		5.66	0.00	2.12	0.25	0.65	11.08
	5.89	0.09	0.86	0.72	0.31	1.63	
		6.33	0.00	2.67	0.14	2.42	36.36
		6.42	0.00	3.10	0.15	3.10	41.33
1-chloronaphthalene	4.30	4.50	0.09	0.22	0.68	0.16	0.56
	4.50	4.54	0.02	0.23	0.74	0.07	0.41
		5.98	0.98	0.34	0.72	0.29	0.88
		6.13	0.19	0.63	0.62	0.52	1.85
		6.27	0.00	2.03	0.28	1.41	12.29
1-methylnaphthalene	4.33	4.55	0.05	0.20	0.67	0.16	0.54
	4.51	4.56	0.05	0.20	0.68	0.14	0.50
	5.80	6.00	1.09	0.22	0.76	0.32	0.71
		6.25	0.15	0.14	0.69	0.62	1.10

butions for the two considered excitations of 1-chloronaphthalene is shown in Figure 2. In agreement with the values of  $S$  and  $D$  quantities, the electron and hole regions exhibit LE and CT character for the second and fifth excitations, respectively. The values of the  $Q$  descriptor for these LE and CT excitations, 0.23 and 2.03 Å, respectively, are also consistent with those obtained from  $S$ ,  $D$ , and visualization analyses.

Overall, after a comprehensive examination of all the data, we found that the excited states analyses based on  $S$  and  $D$  values and the  $Q$  index confirm each other for predicting the CT type of excitations. In other words, for each excitation at  $Q \geq 2.0$  Å, there is a small value for  $S$  and a large value for  $D$ , leading to a CT excitation. However, in the case of LEs, although the results predicted from the  $Q$  values are validated by  $S$  and  $D$  quantities in some cases, such as the second excitation in 1-chloronaphthalene, this is not the case in general. In fact, in some cases there is no agreement between the suggested interval of the  $Q$  index for LEs and the analyses based on the  $S$  and  $D$  values. For instance, on the basis of the proposed interval for  $Q$  index the fourth and fifth excitations of adenine with  $Q=0.38$  and  $0.72$  Å ( $\leq 1.5$  Å) should be LE, whereas the small values of  $S$  (0.25 and 0.22) and large values of  $D$  (0.64 and 0.53 Å) for the two excitations show the CT character. It seems that the predictions of the  $Q$  descriptor do not reproduce the anticipated excitation types in such cases, leading in turn to propose a new descriptor (the  $\Omega$  index). The computed values of the new  $\Omega$  index [Eq. (7)] for all the molecules considered are listed in Table 1. Concerning the results of  $\Omega$  index, we find that not only for the two considered excitations of adenine with  $\Omega$  index values of 4.08 and 5.68 Å, but also in most cases for which CT excitations were incorrectly predicted as LE by  $Q$  the analysis based on  $\Omega$  index provides a satisfactory description. More importantly, the new  $\Omega$  index predicts the LE and CT excitations in such a way that its results are confirmed from intuition of  $S$  and  $D$  and visualization of the excitations under study.

Aside from the discussed results on the first test set, a new proposed index should further be benchmarked against a standard database. To this end, we relied on the benchmark set of Peach et al.<sup>[39]</sup> including a wide range of excitations (LE, CT, and R), to which its applicability has been extensively advocated. The corresponding molecules in this benchmark set, type of excitations, reference values of excitation energies, and deviations of the computed excitation energies using the PBE, B3LYP, and CAM-B3LYP functionals are gathered in Table S1 in the Supporting Information. Plotted in Figure 3 are the deviations in the computed excitation energies against the associated values of  $\Omega$  index for all the types of excitations. At first glance, we notice that the  $\Omega$  index can discriminate the description of short- and long-range excitations. Upon a closer inspection, it can be concluded that despite the different behavior of the various functionals for the modeling of various kinds of excited states, the type of LEs for which the degree of charge redistribution is small has  $\Omega$  index values below 20 Å, highlighting the point that the occupied and virtual orbitals involved in the excitation occupy similar regions of space. This range is distinguishable from those provided for CT excitations



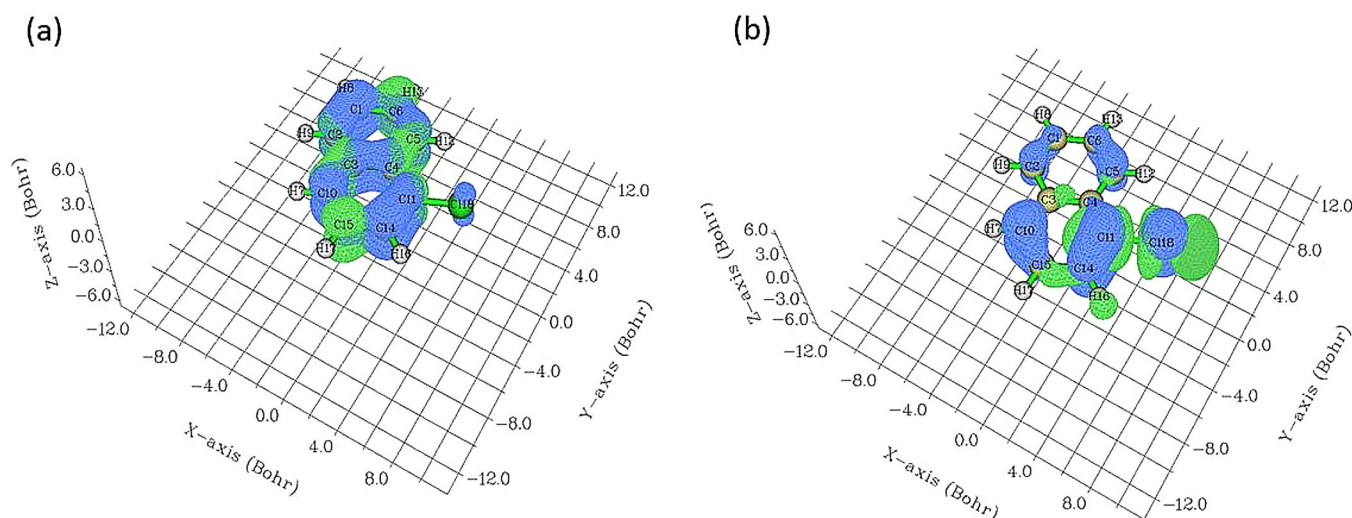
Table 1. (Continued)							
Molecule	$\Delta E^a$	$\Delta E$	$f$	$Q$	$S$	$D$	$\Omega$
tetraphene		6.37	0.17	0.15	0.71	0.66	1.14
	3.26	3.68	0.65	0.23	0.69	0.21	0.64
	3.53	3.85	0.00	1.41	0.80	0.10	1.89
		4.70	1.07	1.37	0.74	0.31	2.27
	4.36	4.87	0.00	0.74	0.78	0.09	1.06
		5.00	0.46	0.59	0.72	0.07	0.92

[a] Experimental data. For more details on the reference excitation energies of the considered molecules, see Refs. [60–66]

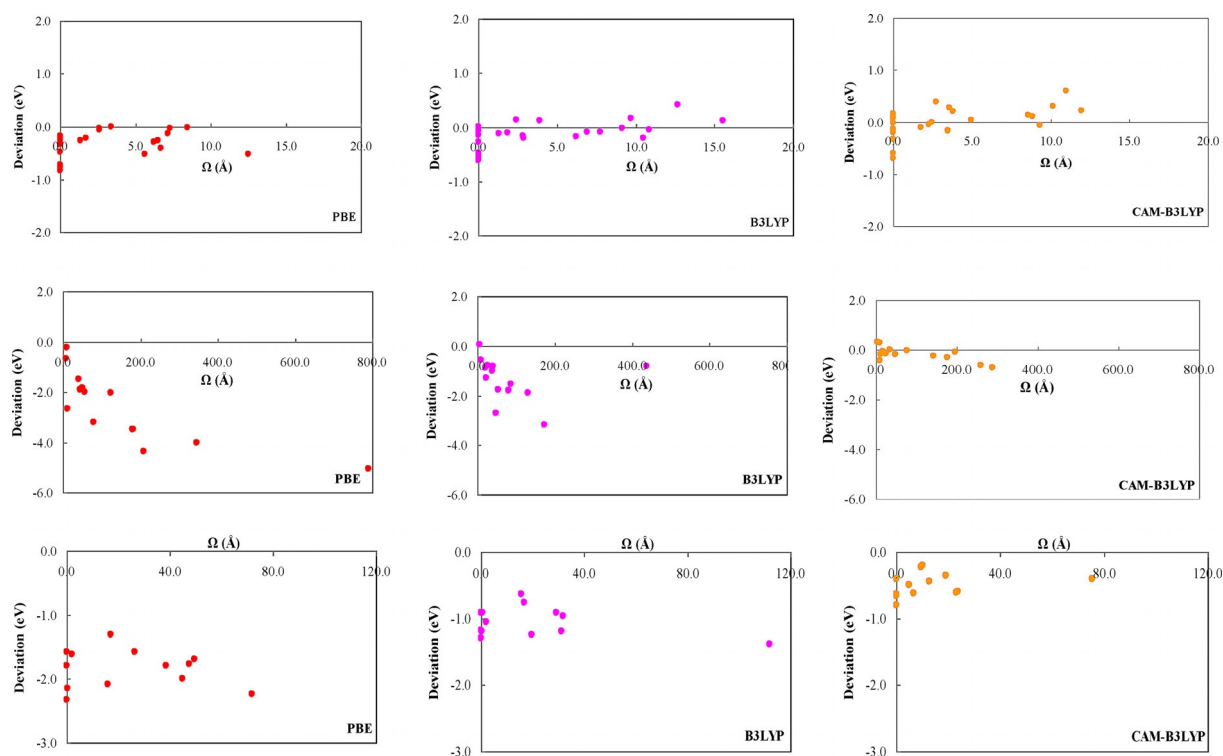
with smaller spatial overlap between the occupied and virtual orbitals than that of LEs. As a matter of fact, except for some outliers due to large distance and low overlap, the larger interval from 50 to 300 Å, with most values concentrated below 200 Å, is apparent for CT excitations, indicating the discriminatory power of  $\Omega$  index for LE and CT excitations. Such ranges are also expected in terms of the distance in the transitions, for which short distances characterize local excitations, whereas usually larger distances are found for CT excitations. For the R excitations, although there are some overlaps with those obtained for LEs with small values of  $\Omega$  index, most points have been scattered around the  $\Omega$  values larger than 20 Å and lower than 80 Å. Moreover, not only is there a systematic underestimation of excitation energies in the case of R excitations, but also their description is somewhat weaker compared to other types. It is noted however that the diffuse nature of the Rydberg orbitals and minimal spatial overlap between the orbitals involved in R excitations play a crucial role in this behavior. Putting all these findings together, it can be concluded that the largest values of our proposed index correspond to excitations that have CT character, whereas the states with intermediate values of  $\Omega$  can be considered as R excited states; finally, the smallest  $\Omega$  values are related to LE character.

From another perspective, the dependence of the metric of excited states to performance of functionals and their selection for TD-DFT calculations is of concern. It can be seen from Figure 3 that for each type of excitation, the excitation energy deviations are reduced upon going from PBE to B3LYP to CAM-B3LYP, with the latter being the best performer. The performance of DFT approximations in turn can be associated with their proficiency to provide balanced description of the quantities involved in deriving the  $\Omega$  index, that is,  $S$ ,  $D$ , and  $Q$ . On the other hand, consistent with earlier analyses in this respect,<sup>[42,46,49]</sup> we find from the corresponding plots of the CT and R excitations that in most cases the deviations in excitation energies show a roughly linear correlation with increasing the values of  $\Omega$ . It is noted here that in practice the large distances often imply large TD-DFT deviations, depending on the nature of the density functional used. Moreover, in agreement with our findings, it has also been shown that if using GGA functionals (such as PBE) and hybrid functionals with exact exchange contributions lower than approximately 35% (such as B3LYP), the deviations in CT excitation energies increase with the increasing of the distance covered during the excitation.<sup>[41]</sup> However, in cases for which the  $\Omega$  index values have larger intervals with respect to LEs, the use of a range-separated functional such as CAM-B3LYP is recommended. In this respect, similar conclusions have also been reached based on other excited states descriptors.<sup>[40,41]</sup> Finally, concerning the results of LE, CT, and R excitations using all the DFT methods tested, at least one approximate diagnostic test to comment on the reliability of a given excitation in connection to functionals performance emerges: consistent with those obtained from the results of other descriptors such as the  $\Delta$  index,<sup>[39]</sup> it seems that an excitation with large  $\Omega$  index likely shows a significant deviation.

Another advantage of using the  $\Omega$  index is its accountability for centrosymmetric molecules. In fact, according to the definition of  $Q$  in Equation (1), the value of this quantity is zero for systems with a center of inversion. However, even in such sit-



**Figure 2.** Visualization of electron (green) and hole (blue) distributions for the a) second and b) fifth excitations of 1-chloronaphthalene.

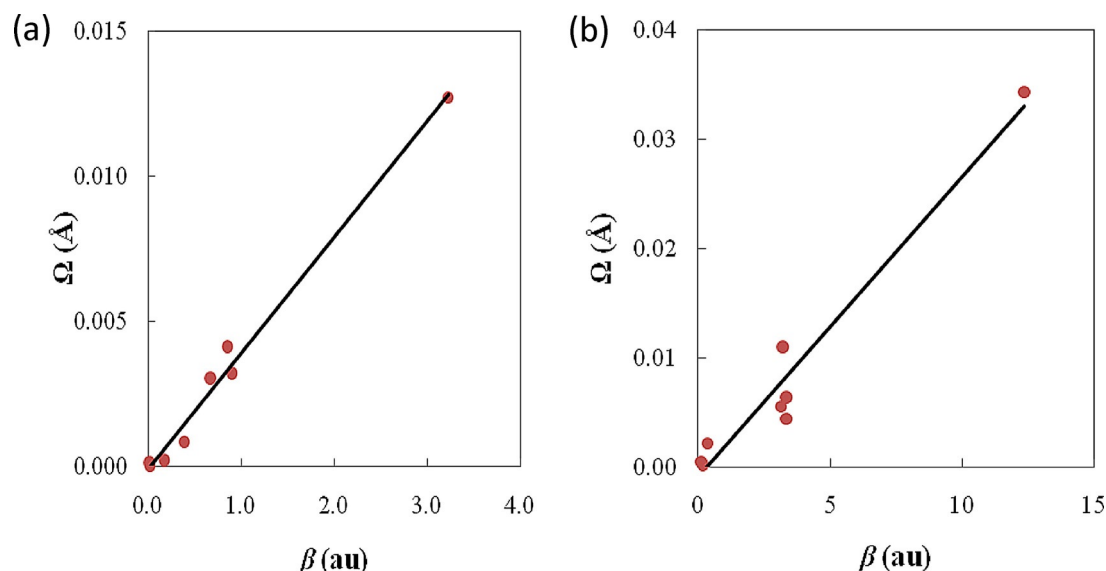


**Figure 3.** The deviations in excitation energies computed from PBE, B3LYP, and CAM-B3LYP functionals against the  $\Omega$  index for the considered benchmark set. Top: local excitations; middle: charge-transfer excitations; bottom: Rydberg excitations.

uations the value of the  $\Omega$  index would not vanish. Indeed, setting  $Q$  equal to zero in Equation (7), the  $\Omega$  index still gives the value of  $D/S$ . This enables us to analyze centrosymmetric molecules like those considered in the benchmark set, such as  $N_2$ , acenes, and so forth, which in turn include the  $\pi$ -conjugated systems as difficult cases for TD-DFT calculations. Regarding this issue, in a recent related work the root-mean-square deviation of the position operator has also been used to fix the problems of the  $Q$  index and extend its applicability.<sup>[42]</sup> Having confirmed the validity of  $\Omega$  index for excited states analyses of molecules with centers of inversion, it should also be mentioned that the results of the  $\Omega$  index might not be considered as an exact quantitative metric for excited states analyses of such systems and more efforts are still needed in this arena. Also, the easy access to a metric with reduced computational cost, as one of the important points in the field, should also be taken into account.

Lastly, some benefits of using the excited states metrics for estimation of optical properties of excited states are also presented. Most recently, List et al.<sup>[50]</sup> have shown that for some molecules such as conjugated systems containing electron-donating and electron-withdrawing groups, there are relationships between the metric of CT excitations and nonlinear optical properties. In fact, their findings have been based on the two-state model, comprising the ground state and the first excited state, which in turn provides useful information in the context of optical properties and excited states investigations.<sup>[67]</sup> Because the dipole moment difference between the two states as a key quantity in the two-state models is related

to hyperpolarizability and transition energy, it is thus possible that there exist relations between the excited state descriptors affected by dipole moment changes and excited-state optical properties. In more detail,  $\Delta E \propto \Omega$  and  $\Delta\mu$ , and therefore  $\Omega \propto \Delta\mu$ . On the other hand, the response properties of excited states such as first hyperpolarizabilities  $\beta$  are related to the dipole moment difference between the states,  $\beta \propto \Delta\mu$ . Putting all these observations together, it can be expected that  $\Omega \propto \beta$ . In this part, we intend to check such relationships for the  $\Omega$  index. Furthermore, it is also interesting to see whether or not such connections for conjugated systems without any substituents and also for linear optical properties. Hereby, we performed several analyses to explore the relationships of the  $\Omega$  index with isotropic and anisotropic polarizabilities and first hyperpolarizabilities of excited states of two acenes as conjugated systems without substituent groups. Figure 4 shows the relationship between  $\Omega$  index and first hyperpolarizability  $\beta$  for the two acenes (acene 2 and acene 3; noted in the Supporting Information) as illustrative examples. It can be seen that there are good correlations between  $\Omega$  index and first hyperpolarizability as a nonlinear optical property. Also, from such relationships among the descriptors of excited states and optical properties, we can also obtain the correlations between metrics of excited states and other properties related to hyperpolarizabilities such as two-photon absorption probability.<sup>[50]</sup> Additional analyses have also been carried out for another  $\pi$ -conjugated system of the benchmarked set, polyacetylenes, and the same conclusions were obtained. However, on the relationship between the  $\Omega$  index and isotropic/anisotropic polarizability, we



**Figure 4.** Correlation between  $\Omega$  index and first hyperpolarizability  $\beta$  of excited states for a) acene 2 and b) acene 3.

observed that the obtained correlations are not as strong as those provided between  $\Omega$  and  $\beta$ . This is, however, not surprising as based on the formula in the two-state model, we find explicit correlation between hyperpolarizabilities and transition energies, whereas there is no such analytical relation for linear polarizabilities. Nonetheless, what we would like to highlight the most here is that since obtaining the included parameters in our proposed index, those such as  $Q$  only require the evaluation of linear response eigenvectors, such correlations are encouraging and deserve more attention because they provide the possibility of estimating the excited-states properties, or at least predicting the trend in these properties, for large systems without expensive computations of high-order response functions.

To conclude, we are acutely aware that although the present index and earlier descriptors in this context can provide valuable information for excited states analyses, there is still room in the field. Subjects for future studies regarding our proposed index are as follows: reinforcing the discrimination power of the index using natural transition orbitals to simplify the chemical interpretation of the excited states in difficult cases, examining the effects of solvents and geometry relaxations, and improving the  $\Omega$  index for predicting various optical properties of excited states.

## 4. Conclusions

In short, in aiming to analyze the excited states characters, a new index called  $\Omega$  is presented in this work. The proposed index has been based on the three important factors for excited states analyses, that is, charge centroids of the orbitals involved in the excitations, their distances, and overlap integrals. Taking several molecules from different categories and also some molecules from another standard benchmark set, the applicability of the proposed descriptor has numerically been evaluated. We found that by using the  $\Omega$  index, various types

of excited states can be distinguished. Moreover, the superior performance of the  $\Omega$  index in cases for which the previous descriptors were not helpful has also been demonstrated. Using the proposed index in this work in combination with earlier descriptors with different theoretical bases not only provides some insights in the context of functionals benchmarking but also gives a reliable diagnostic test for TD-DFT transitions. Finally, we have also examined the relationships between the  $\Omega$  index and (hyper)polarizabilities of some molecules in the framework of sum-over-state approach in which good correlations between our proposed index and hyperpolarizabilities were found. We are convinced that the present work and recent efforts on the proposing of the metrics of excited states help us to further understand the physics of the problem and performance of functionals in TD-DFT calculations.

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- [1] E. Runge, E. K. Gross, *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
- [2] M. E. Casida in *Time-Dependent Density Functional Response Theory for Molecules in Recent Advances in Density Functional Methods* (Ed.: D. P. Chong), World Scientific, Singapore, **1995**, pp. 155–193.
- [3] A. Dreuw, M. Head-Gordon, *Chem. Rev.* **2005**, *105*, 4009–4037.
- [4] D. Jacquemin, E. A. Perpète, O. A. Vydrov, G. E. Scuseria, C. Adamo, *J. Chem. Phys.* **2007**, *127*, 094102–6.
- [5] I. Ciofini, C. Adamo, *J. Phys. Chem. A* **2007**, *111*, 5549–5556.
- [6] D. Jacquemin, E. A. Perpète, G. E. Scuseria, I. Ciofini, C. Adamo, *J. Chem. Theory Comput.* **2008**, *4*, 123–135.
- [7] M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer, W. Thiel, *J. Chem. Phys.* **2008**, *128*, 134110–25.
- [8] M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer, W. Thiel, *J. Chem. Phys.* **2008**, *129*, 104103.

- [9] S. P. A. Sauer, M. Schreiber, M. R. Silva-Junior, W. Thiel, *J. Chem. Theory Comput.* **2009**, *5*, 555–564.
- [10] D. Jacquemin, V. Wathelet, E. A. Perpète, C. Adamo, *J. Chem. Theory Comput.* **2009**, *5*, 2420–2435.
- [11] D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* **2010**, *6*, 2071–2085.
- [12] M. Caricato, G. W. Trucks, M. J. Frisch, K. B. Wiberg, *J. Chem. Theory Comput.* **2010**, *6*, 370–383.
- [13] M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer, W. Thiel, *J. Chem. Phys.* **2010**, *133*, 174318–13.
- [14] D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, *Theor. Chem. Acc.* **2011**, *128*, 127–136.
- [15] S. S. Leang, F. Zahariev, M. S. Gordon, *J. Chem. Phys.* **2012**, *136*, 104101.
- [16] A. Mohajeri, M. Alipour, *Theor. Chem. Acc.* **2012**, *131*, 1148–1157.
- [17] M. Isegawa, R. Peverati, D. G. Truhlar, *J. Chem. Phys.* **2012**, *137*, 244104.
- [18] M. Isegawa, D. G. Truhlar, *J. Chem. Phys.* **2013**, *138*, 134111.
- [19] D. Bousquet, R. Fukuda, P. Maitrad, D. Jacquemin, I. Ciofini, C. Adamo, M. Ehara, *J. Chem. Theory Comput.* **2013**, *9*, 2368–2379.
- [20] C. Adamo, D. Jacquemin, *Chem. Soc. Rev.* **2013**, *42*, 845–856.
- [21] A. D. Laurent, D. Jacquemin, *Int. J. Quantum Chem.* **2013**, *113*, 2019–2039.
- [22] M. Alipour, *J. Phys. Chem. A* **2014**, *118*, 1741–1747.
- [23] D. Escudero, W. Thiel, *J. Chem. Phys.* **2014**, *140*, 194105.
- [24] C. Fang, B. Oruganti, B. Durbeej, *J. Phys. Chem. A* **2014**, *118*, 4157–4171.
- [25] L. Barnes, S. Abdul-Ai, A. R. Allouche, *J. Phys. Chem. A* **2014**, *118*, 11033–11046.
- [26] M. Alipour, *Theor. Chem. Acc.* **2015**, *134*, 70.
- [27] C. Latouche, D. Skouteris, F. Palazzetti, V. Barone, *J. Chem. Theory Comput.* **2015**, *11*, 3281–3289.
- [28] D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **2015**, *11*, 5340–5359.
- [29] C. Adamo, T. Le Bahers, M. Savarese, L. Wilbraham, G. García, R. Fukuda, M. Ehara, N. Rega, I. Ciofini, *Coord. Chem. Rev.* **2015**, *304*, 166–178.
- [30] M. Alipour, *Theor. Chem. Acc.* **2016**, *135*, 67.
- [31] S. Budzák, A. D. Laurent, C. Laurence, M. Medved, D. Jacquemin, *J. Chem. Theory Comput.* **2016**, *12*, 1919–1929.
- [32] Z. L. Cai, K. Sendt, J. R. Reimers, *J. Chem. Phys.* **2002**, *117*, 5543–5549.
- [33] S. Grimme, M. Parac, *ChemPhysChem* **2003**, *4*, 292–295.
- [34] A. Dreuw, J. L. Weisman, M. Head-Gordon, *J. Chem. Phys.* **2003**, *119*, 2943–2946.
- [35] R. J. Cave, F. Zhang, N. T. Maitra, K. Burke, *Chem. Phys. Lett.* **2004**, *389*, 39–42.
- [36] A. Dreuw, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 4007–4016.
- [37] R. J. Magyar, S. Tretiak, *J. Chem. Theory Comput.* **2007**, *3*, 976–987.
- [38] N. T. Maitra, F. Zhang, R. J. Cave, K. Burke, *J. Chem. Phys.* **2004**, *120*, 5932–5937.
- [39] M. J. G. Peach, P. Benfield, T. Helgaker, D. J. Tozer, *J. Chem. Phys.* **2008**, *128*, 044118.
- [40] T. Le Bahers, C. Adamo, I. Ciofini, *J. Chem. Theory Comput.* **2011**, *7*, 2498–2506.
- [41] C. A. Guido, P. Cortona, B. Mennucci, C. Adamo, *J. Chem. Theory Comput.* **2013**, *9*, 3118–3126.
- [42] C. A. Guido, P. Cortona, C. Adamo, *J. Chem. Phys.* **2014**, *140*, 104101.
- [43] H. Ma, T. Qin, A. Troisi, *J. Chem. Theory Comput.* **2014**, *10*, 1272–1282.
- [44] F. Plasser, M. Wormit, A. Dreuw, *J. Chem. Phys.* **2014**, *141*, 024106.
- [45] T. Etienne, X. Assfeld, A. Monari, *J. Chem. Theory Comput.* **2014**, *10*, 3896–3905.
- [46] T. Etienne, X. Assfeld, A. Monari, *J. Chem. Theory Comput.* **2014**, *10*, 3906–3914.
- [47] T. Etienne, *J. Chem. Theory Comput.* **2015**, *11*, 1692–1699.
- [48] F. Plasser, B. Thomitzni, S. A. B  ppler, J. Wenzel, D. R. Rehn, M. Wormit, A. Dreuw, *J. Comput. Chem.* **2015**, *36*, 1609–1620.
- [49] S. A. Mewes, F. Plasser, A. Dreuw, *J. Chem. Phys.* **2015**, *143*, 171101.
- [50] N. H. List, R. Zalesny, N. A. Murugan, J. Kongsted, W. Bartkowiak, H.   gren, *J. Chem. Theory Comput.* **2015**, *11*, 4182–4188.
- [51] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.
- [52] F. Aiga, K. Sasagana, R. Itoh, *J. Chem. Phys.* **1993**, *99*, 3779–3789.
- [53] B. J. Orr, J. F. Ward, *Mol. Phys.* **1971**, *20*, 513–526.
- [54] R. Fukuda, M. Ehara, *J. Comput. Chem.* **2014**, *35*, 2163–2176.
- [55] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [56] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [57] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [58] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- [59] Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford, CT, **2009**.
- [60] K. V. Masrani, H. S. Rama, S. L. Bafna, *J. Appl. Chem. Biotechnol.* **1974**, *24*, 331–341.
- [61] L. Serrano-Andr  s, B. O. Roos, *J. Am. Chem. Soc.* **1996**, *118*, 185–195.
- [62] L. B. Clark, G. G. Peschel, I. Tinoco, Jr., *J. Phys. Chem.* **1965**, *69*, 3615–3618.
- [63] R. Abouaf, J. Pommier, H. Dunet, *Chem. Phys. Lett.* **2003**, *381*, 486–494.
- [64] D. Biermann, W. Schmidt, *J. Am. Chem. Soc.* **1980**, *102*, 3163–3173.
- [65] M. Suto, X. Wang, J. Shan, L. C. Lee, *J. Quant. Spectrosc. Radiat. Transfer* **1992**, *48*, 79–89.
- [66] M. W. Mackey, J. W. Daily, J. T. McKinnon, E. P. Riedel, *J. Photochem. Photobiol. A* **1997**, *105*, 1–6.
- [67] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664–2668.

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