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Magnetic Circular Dichroism of Naphthalene Derivatives: A Coupled Cluster Singles and Approximate Doubles and Time-Dependent Density Functional Theory Study

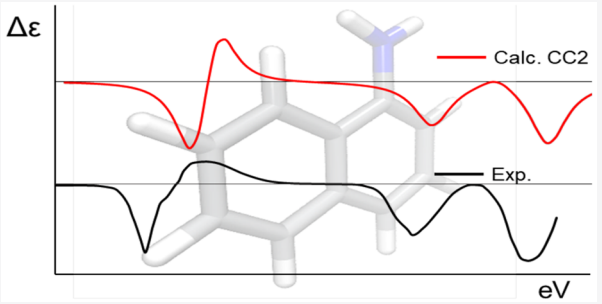
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ABSTRACT: The UV−vis absorption and magnetic circular dichroism spectra of naphthalene and some of its derivatives have been simulated at the Coupled Cluster Singles and Approximate Doubles (CC2) level of theory, and at the Time-Dependent Density Functional Theory (TD-DFT) level using the B3LYP and CAM-B3LYP functionals. DFT and CC2 predict in general opposite energetic ordering of the L_b and L_a transitions (in gas phase), as previously observed in adenine. The CC2 simulations of UV and MCD spectra show the best agreement with the experimental data. Analysis of the Cartesian components of the electric dipole transition strengths and the magnetic dipole transition moment between the excited states have been considered in the interpretation of the electronic transitions and the Faraday $\mathcal{B}$ term inversion among the naphthalene derivatives.



INTRODUCTION

The photoabsorption spectrum of naphthalene (and other polycyclic aromatic hydrocarbons in general) has been extensively investigated with several spectroscopic techniques, comprising magnetic circular dichroism (MCD) spectroscopy. It has been shown that MCD spectroscopy is complementary to UV−vis absorption spectroscopy, offering a better sensitivity to distinguish electronic transitions.[1] Foss and McCarville[2,3] observed a correlation between the sign of the Faraday $\mathcal{B}$ term and the direction of the electric transition dipole moment in the MCD spectra of toluene, naphthalene, anthracene, and tetracene. Further theoretical advancements in understanding the MCD response of polycyclic aromatic hydrocarbons were reported by Stephens[4] and Larkindale.[5]

In 1978, Michl published a series of papers where he proposed some general rules for a qualitative interpretation of the MCD spectra of $(4N + 2)$-electron $[n]$annulene (where N is the number of π-electrons).[6−8] According to the nomenclature proposed by Platt,[9] the first four excited states are labeled as L_b, L_a, B_b, and B_a. On the basis of the π-electron perimeter model and the Pariser−Parr−Pople (PPP) method, Michl was able to rationalize the sign of the Faraday $\mathcal{A}$ and $\mathcal{B}$ terms for the bands given by the transitions from the ground state to the L and B states. Even though, in Michl's approach, only $\pi\pi^*$ mixing was considered for the evaluation of the $\mathcal{B}$terms, the predicted results showed a good agreement with the experimental data (for this type of molecule, contributions from the magnetic $n\pi^*-\pi\pi^*$ mixing on the MCD signals are negligible).[10] This approach was also found to be useful for rationalizing contributions from substituents with inductive and mesomeric effects on the π-electron system by estimating the perturbation caused to HOMO and LUMO levels.[10] It was previously pointed out that the prediction of the correct energy ordering of the first two transitions, L_b and L_a, is not always obtained by simple TD-DFT calculations[11−13] unless a careful choice of functional is made.[14] Analogous problems have been found in substituted naphthalenes.[15] In this context, Coupled Cluster (CC) calculations have been reported, showing a significant improvement in the accurate prediction of L_b and L_a transitions.[11,15,16] Here, we present a Coupled Cluster Singles and Approximate Doubles (CC2) and TD-DFT study of the absorption and MCD spectra of naphthalene and three mesomeric derivatives and compare them with the experimental data and with previous interpretations.

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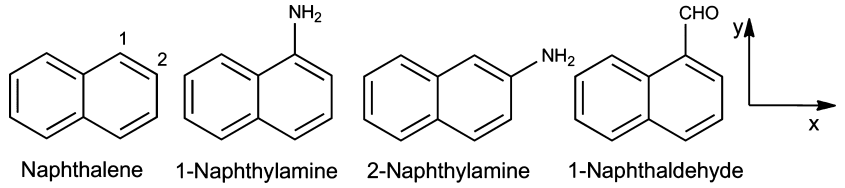


Figure 1. Structures of naphthalene and naphthalene derivatives. As indicated, the molecular plane is *xy*.

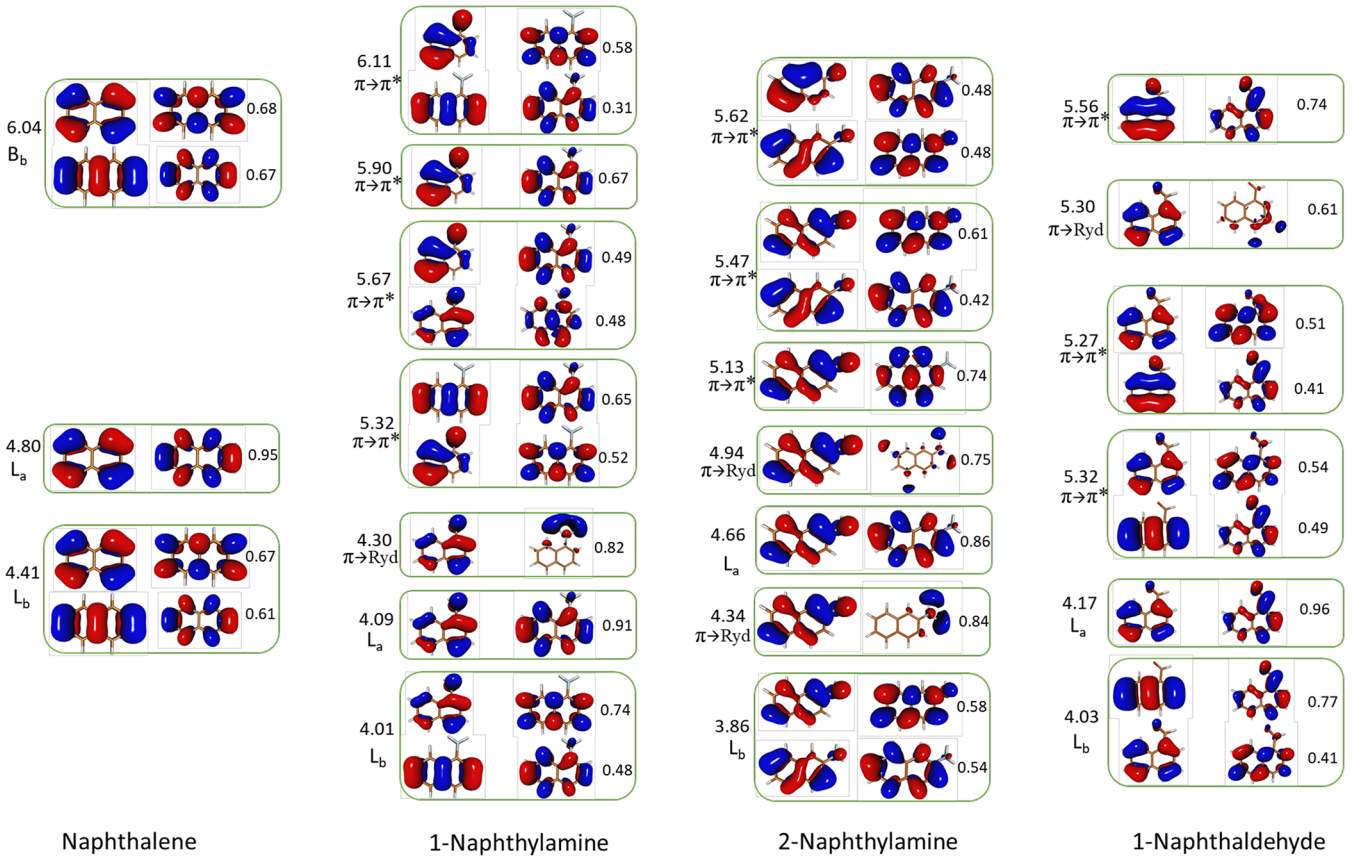


Figure 2. RI-CC2 calculated vertical excitation energies with the corresponding Natural Transition Orbital (NTO) composition and assignments for naphthalene and its derivatives. Pairs of occupied and virtual NTOs are given next to each other, with the occupied NTO on the left. If more than one NTO pair contributes substantially, the NTO pairs are stacked on top of each other. The numbers on the right of the NTO pairs indicate their weights in the eigenvector.

COMPUTATIONAL METHODOLOGY AND DETAILS

The ground state geometries of the molecules reported in Figure 1 were optimized, in vacuo, at the CC2 level of theory using the aug-cc-pVDZ[17] basis set. The excitation energies, oscillator strengths, and Faraday $\mathcal{B}$ terms were calculated within the response function formalism[16,18−21] at the CC2 level of theory with the resolution-of-the-identity (RI) approximation,[16] as implemented in Turbomole.[22,23] For the CC2 calculations the aug-cc-pVDZ orbital basis was used in combination with the corresponding optimized auxiliary basis set.[24] The excitation energies, oscillator strengths, and Faraday $\mathcal{B}$ terms were also computed within the TD-DFT formalism,[18,20,25,26] adopting the B3LYP[27] and CAM-B3LYP[28] functionals and the aug-cc-pVDZ basis set. The TD-DFT calculations were performed using the Dalton code.[29] For the calculations on 1-naphthylaldehyde, we focused, for the comparison of the three electronic structure methods, on the *Z* conformer, since, according to previous works, it represents around 80 % of the conformer population.[30,31] CC2 results for the *E* conformation (and the Boltzmann average of the two) are reported in the Supporting Information file. A Lorentzian line shape-function was chosen for the broadening of the MCD and absorption spectra (fwhm γ = 1000 cm^{-1}).[16,32] Experimental data have been redigitized[33] and adapted from the work of Michl and co-workers.[10] For ease of comparison, a vertical translation has been applied to all experimental spectra, so that they do not overlap with the computed ones.

We note that Michl's measurements were conducted in solution, specifically cyclohexane for naphthalene and 1-naphthaldehyde, and acetonitrile for 1-naphthylamine and 2-naphthylamine. In this study, we focused on the effect of substitution on the MCD spectrum. Since the program packages used for the DFT and CC2 calculations did not support identical solvent models, we carried out the calculations in the gas phase for better comparability. Moreover, both cyclohexane and acetonitrile are nonprotic solvents that do not form H-bridges with the solute. Thus, the solvent effects, in particular for naphthalene and 1-naphthaldehyde, which have been measured

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in cyclohexane, should be small compared to the substitution effects.

RESULTS AND DISCUSSION

A characterization (composition and assignments) of the relevant excited states for naphthalene and its derivatives on the basis of CC2 Natural Transition Orbitals (NTO) is shown in Figure 2. Consistent with previous work,[14,34−36] the L_b excited state of naphthalene involves the HOMO−1 → LUMO and HOMO → LUMO+1 transitions with similar weights. The L_a transition of naphthalene, on the other hand, is dominated by the HOMO → LUMO component. A similar behavior was observed for the three substituted naphthalenes studied here, as well as for other naphthalene derivatives as reported in the literature.[15,37]

In Table 1, the computed results for the spectral properties of naphthalene at TD-DFT and CC2 levels of theory are collected.

Table 1. Naphthalene Calculated Excitation Energies ΔE_j (eV), Oscillator Strengths (f) with the Cartesian Component of the Transition Strength (S) and Faraday $\mathcal{B}$ Term (au) for the Basis Set aug-cc-pVDZ

ΔE_j	$f(0 \rightarrow j)$	$\mathcal{B}(0 \rightarrow j)$
	RI-CC2	
4.41 (L_b)	4×10^{-5} ($S_x = 4 \times 10^{-4}$; $S_y = 0$)	−1.2
4.80 (L_a)	0.08 ($S_x = 0$; $S_y = 0.66$)	13.8
6.04 (B_b)	1.44 ($S_x = 9.7$; $S_y = 0$)	107.9
6.14	0.018 ($S_z = 0.12$)	−9.3
6.37	0.26 ($S_x = 0$; $S_y = 1.7$)	−95.2
6.41	0.019 ($S_z = 0.12$)	10.6
	B3LYP	
4.30 (L_a)	0.05 ($S_x = 0$; $S_y = 0.51$)	8.0
4.40 (L_b)	3×10^{-5} ($S_x = 0.004$; $S_y = 0$)	−1.3
5.80 (B_b)	1.25 ($S_x = 8.8$; $S_y = 0$)	123.3
5.91	0.02 ($S_z = 0.12$)	−2.5
6.01	0.18 ($S_x = 0$; $S_y = 1.21$)	−106.8
6.04	0.01 ($S_z = 0.1$)	6.1
	CAM-B3LYP	
4.55 (L_b)	5×10^{-6} ($S_x = 4 \times 10^{-5}$; $S_y = 0$)	−4.6
4.59 (L_a)	0.07 ($S_x = 0$; $S_y = 0.6$)	8.5
5.98 (B_b)	1.32 ($S_x = 9.06$; $S_y = 0$)	121.8
6.25	0.25 ($S_x = 0$; $S_y = 1.29$)	−100.6
6.38	0.03 ($S_z = 0.18$)	−6.9
6.59	0.01 ($S_z = 0.08$)	1.8

The calculated MCD and absorption spectra obtained for naphthalene are depicted in Figure 3, and compared with the corresponding experimental data.[10,38] The computed spectra have been shifted on the energy axis to align them to the experimental B band.

The experimental spectra of naphthalene, both UV and MCD, are characterized by vibronic components.[39−41] Looking at the experimental UV, reproduced in the bottom panel of Figure 3, the first transition (around 3.8−3.9 eV) has near zero strength and is almost all vibronic. It has been assigned to L_b. The second transition (roughly centered at 4.6 eV) has higher strength and it has been attributed to L_a. The strongest UV band is peaked at 5.6 eV and is assigned to B_b. For naphthalene and substituted naphthalene, the L_b state is lower in energy than the L_a state, both in the gas phase as well as in nonpolar/weakly polar solvents.[9,42−46] The CC2 calculations yield the correct energetic ordering,[11] $L_b < L_a$, for the first two transitions of naphthalene

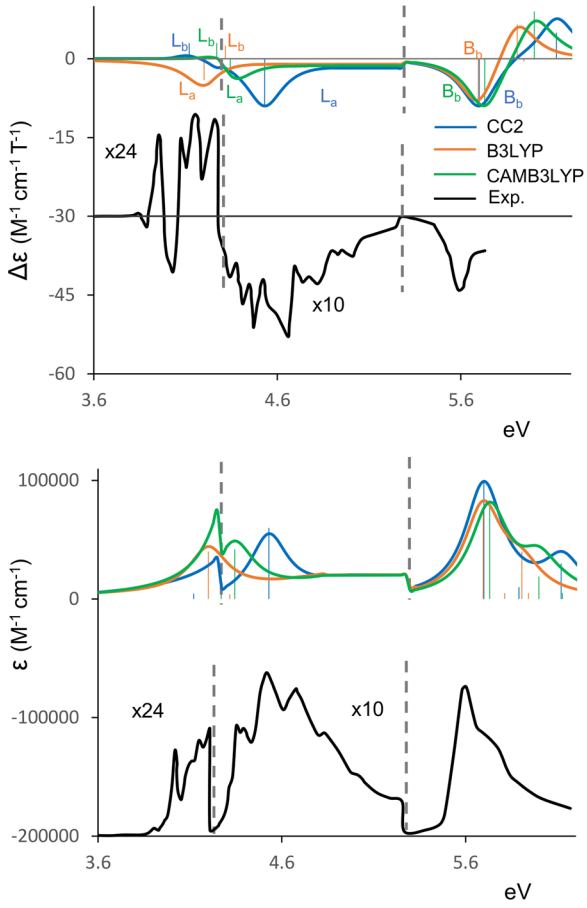


Figure 3. Naphthalene. Experimental[38] (recorded in cyclohexane, black lines) and calculated UV absorption (*bottom*) and MCD (*top*) spectra. A vertical translation was applied on the experimental spectra. The computed spectra have been shifted to align them with the experimental B_b peak at 5.6 eV. The CC2 and CAM-B3LYP spectra have been enhanced by the same scaling factors as experiment in the different frequency regions. For a coherent comparison, the B3LYP sticks of L_a have been scaled by 10 and those of L_b by 24. The sticks in the MCD spectrum correspond to $-\mathcal{B}$ values, according to the standard MCD convention. Horizontal shift applied: −0.25 eV for CC2 and CAM-B3LYP results; −0.2 eV for B3LYP results.

with a separation of 0.4 eV. The CAM-B3LYP calculations also correctly reproduce the energetic order of L_b and L_a,[36] but the separation between the two transition is only 0.04 eV. The B3LYP functional gives the inverted ordering, i.e. L_a at lower energy than L_b, as already discussed in previous works.[11−13,36] According to previous works,[47−49] the transition moment of L_b is directed along the long axis of the molecule (x axis in Figure 1). The transition moment of L_a is instead directed along the short axis (y axis in Figure 1). Our results are consistent with these studies.

The simulated UV absorption spectrum at the CC2 level is in good agreement with the experimental one and is consistent with the calculated spectra reported in previous studies.[41,50,51] Note that when simulating the spectra, we have scaled the intensities by the same factors as in experiment in Figure 3—that is, a factor 10 for L_a and a factor 24 for L_b. B3LYP also yields two bands in the UV spectrum, but the L_a band is much more separated from the B_b band and moves in the frequency region experimentally attributed to the L_b band.

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Both CC2 and TD-DFT yield a negative $\mathcal{B}$ term for the L_b band and a positive $\mathcal{B}$ term for the L_a band. As the $\mathcal{B}$ term of L_a is larger (roughly 1 order of magnitude for CC2 and B3LYP, and a factor 2 for CAM-B3LYP), it prevails in the MCD response in the spectral regions of the L states. The B_b state yields the largest (negative) MCD band. The MCD calculations thus reproduce the sign and the relative intensities of the experimental MCD bands, even though the vibronic effects are not included. A vibrational study of the MCD bands of naphthalene is reported in ref 41. It is worth noting that the inverted order of the L_b and L_a transitions with the B3LYP functional is not accompanied by a sign inversion of the associated $\mathcal{B}$ terms, as otherwise observed in adenine.[16,52] Sign inversion of the $\mathcal{B}$ terms of two energetically close states upon switching of their order happens if their $\mathcal{B}$ terms are dominated by the contribution from the magnetic dipole transition moments between them[16]

$$\mathcal{B}(0 \rightarrow 1) \approx \epsilon_{\alpha\beta\gamma}\frac{m_\alpha^{12} d_\beta^{01} d_\gamma^{20}}{\omega_2 - \omega_1} = -\epsilon_{\alpha\beta\gamma}\frac{m_\alpha^{21} d_\beta^{02} d_\gamma^{10}}{\omega_1 - \omega_2}$$
$$\approx -\mathcal{B}(0 \rightarrow 2) \quad (1)$$

In this case, the $\mathcal{B}$ terms of these two states give rise to a bisignate feature in the MCD spectrum which is invariant under inversion of the order of the two states. For naphthalene, the magnetic dipole transition moment between the L_b and L_a states contributes at the CC2 level with, respectively, −1.6 and +1.6 to their $\mathcal{B}$ terms. For L_b another significant contribution of +0.4 arises from the coupling to the B_a state, and for L_a the $\mathcal{B}$ term is dominated by the much larger contribution from the coupling to the B_b states which contributes with ≈+8. Because of the small ground to excited state electric transition strength of L_a, the couplings to the B and higher-lying states are thus (more) important than the L_a and L_b coupling. This explains why for naphthalene the $\mathcal{B}$ terms of the L states do not flip signs when their order switches from CC2 or CAM-B3LYP to B3LYP. Thus, the inverted state ordering has little effect on the appearance of the simulated MCD spectrum and the contribution of the positive $\mathcal{B}$ term (negative band) of L_a is predominant in any case.

The introduction of a substituent in the parent molecule brings changes in the chemical and physicochemical properties of the aromatic system, such as reactivity and electronic and magnetic properties.[53−57] Such changes are dependent on the nature and the position of the substituent.[53,55,56,58] Substitutions which affect the delocalization of the π electrons in a conjugated orbital system are referred to as mesomeric (M).[58] If the substituent carries an empty antibonding orbital, as in the case of the CHO group, it results in an electron-withdrawing (negative) mesomeric effect (−M).[8,58] If the substituent carries a filled bonding or nonbonding orbital of π-symmetry, as in the case of amino groups, the result is an electrons donation, corresponding in an electron-donating (positive) mesomeric effect (+ M).[8,58]

For naphthalene, as for other acenes, the substitution lowers the symmetry. Together, this can change the state ordering and the weights with which orbital transitions contribute to a transition.[12,13] UV−vis and MCD spectra for 1-naphthylamine and 1-naphthylaldehyde are shown in Figure 4 and 5, respectively. The spectra for 2-naphthylamine are shown in Figure 6. The computed spectra were obtained from the energies, oscillator strengths and $\mathcal{B}$ terms tabulated in Tables 2, 3, and 4. As observed for naphthalene, the CC2 method predicts the L_b transition at lower energy than L_a for all three substituted

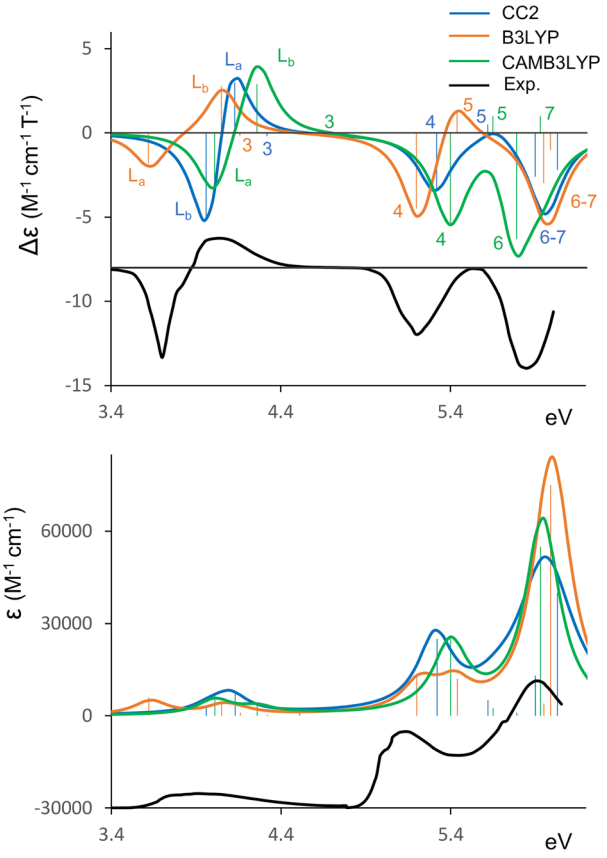


Figure 4. 1-Naphthylamine. Experimental[10] (recorded in acetonitrile, black lines) and calculated UV absorption (*bottom*) and MCD (*top*) spectra. A vertical translation was applied on the experimental spectra.

naphthalenes. Both, B3LYP and CAM-B3LYP, on the other hand, give $L_a < L_b$ for the three substituted cases;[15] see Tables 2, 4 and 3.

We start with the analysis of the effect of the naphthalene derivatives substituted in position 1, see Figures 4 and 5 and Tables 2 and 3.

The two different substituents significantly affect the electronic transitions of the two naphthalene derivatives. Experimentally, both amino and CHO group substitutions in position 1 move the L_a transition to lower energy with respect to the unsubstituted naphthalene, whereas the L_b transition is almost unchanged in energy, which results in an overlap of L_b and L_a bands in the 1-substituted naphthalene molecules.[43,59] For 1-naphthylamine, the transition moments of L_b and L_a are polarized almost perpendicular to each other, as in the unsubstituted naphthalene, whereas in 1-naphthaldehyde the angle between the two transition moments is significantly smaller (around 62 deg), mostly due to the rotation of the L_b transition moment (see Table 3).

The above trends are generally confirmed by the CC2 results: in 1-naphthylamine, the L_a excitation moves down by ≈0.7 to 4.09 eV (vs 4.80 eV in naphthalene), whereas the L_b transition moves by a more modest ≈0.4 to 4.01 eV, so the two transitions almost overlap. In 1-naphthaldehyde, L_b moves by ≈0.4 eV and L_a by 0.63 eV to the red, so their separation is ≈0.15 eV.

The two DFT functionals do not reflect the above trends: according to both the B3LYP and the CAM-B3LYP calculations, the L_a and L_b states of 1-naphthylamine move to lower energy

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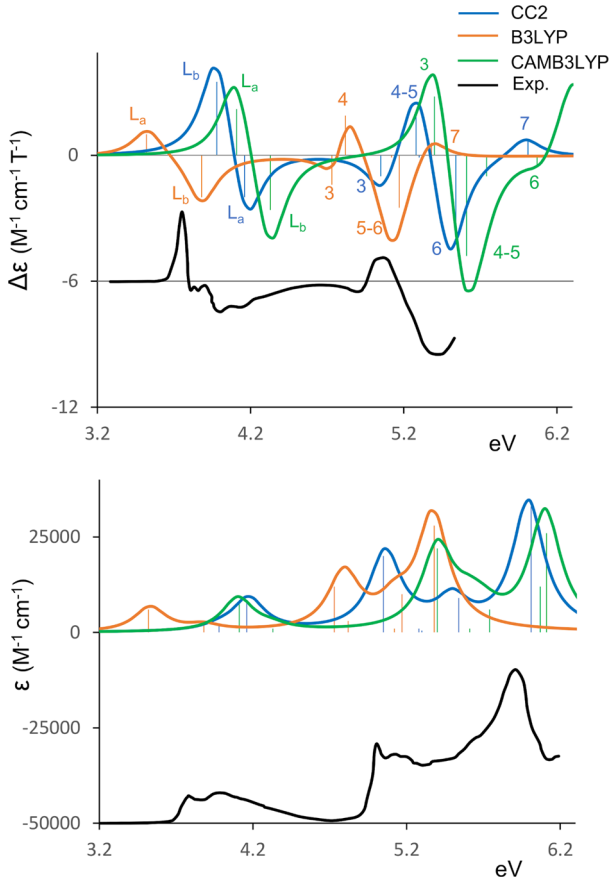


Figure 5. 1-Naphthaldehyde. Experimental[10] (recorded in cyclohexane, black lines) and calculated UV absorption (*bottom*) and MCD (*top*) and spectra. A vertical translation was applied on the experimental spectra.

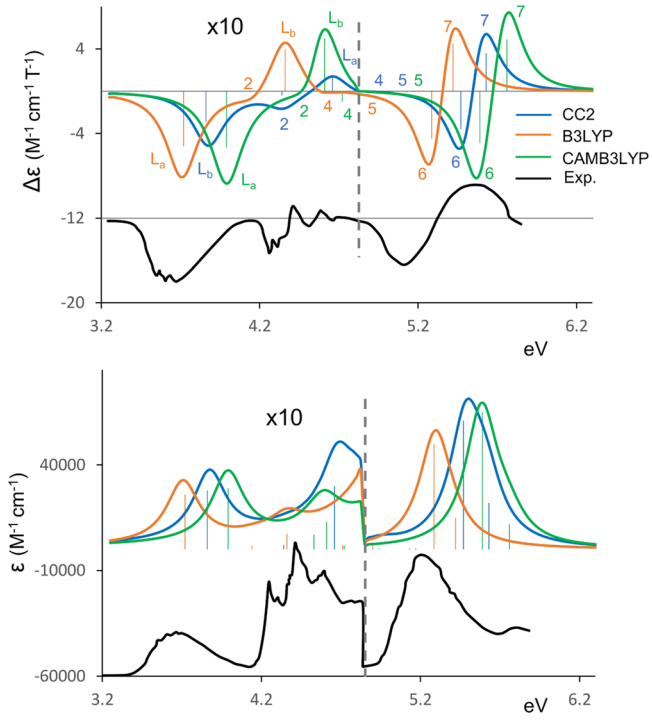


Figure 6. 2-Naphthylamine. Experimental (recorded in acetonitrile, black line) and calculated UV absorption (*bottom*) and MCD (*top*) spectra. A vertical translation was applied on the experimental spectra. The CC2 and TD-DFT calculations spectra have been enhanced by the same scaling factor as experiment.

compared to naphthalene, but their splittings also increases. A similar behavior is found for the 1-naphthaldehyde case.

MCD spectroscopy magnifies the differences compared to UV absorption due to the possibility to observe changes in sign in the bands. It was observed by Michl and co-workers that the amino substituent leads to a positive $\mathcal{B}$ term for the L_b transition and a negative $\mathcal{B}$ term for the L_a transition.[10] Opposite behavior was observed for the MCD spectrum of 1-naphthylaldehyde, where a negative $\mathcal{B}$ term was associated with the L_b transition and a positive $\mathcal{B}$ term was associated with the L_a one.[10] As a consequence, characteristic, and reasonably well resolved, asymmetric double signed spectral patterns emerge in correspondence of the two states L_a and L_b.

The CC2 results are in line with these observations. As pointed out earlier, the two DFT functionals yield reverse order of the L_a and L_b transitions compared to CC2. Yet, the L_a transitions always have positive $\mathcal{B}$ term for the amines and negative for the aldehyde, and vice versa for the L_b transitions. In other words, the TD-DFT L_a and L_b transitions have reversed energetic order compared to CC2, as well as opposite sign of the $\mathcal{B}$ terms, as also observed in gas phase for adenine.[16] For the substituted naphthalenes, both L states have sizable oscillator strengths and, thus, the coupling between the two states becomes much more important for their $\mathcal{B}$ terms and leads to bisignate profile which is invariant under inversion of the states' ordering. As a consequence, the appearance of a double signed L_a/L_b band is reproduced by the two TD-DFT functionals as

Table 2. 1-Naphthylamine Calculated Excitation Energies ΔE_j (eV), Oscillator Strengths (f) with the Cartesian Component of the Transition Strength (S), the Angle (α) between L_b and L_a State, and Faraday $\mathcal{B}$ Term (au) for the Basis Set aug-cc-pVDZ

ΔE_j	$f(0 \rightarrow j)$	α	$\mathcal{B}(0 \rightarrow j)$
	RI-CC2		
4.01 (L_b)	0.03 (S_x = 0.27; S_y = 4 × 10^{-4})	89.1	155.8
4.09 (L_a)	0.10 (S_x = 0.01; S_y = 1.08)		−146.9
4.30	0.01 (S_z = 0.09)		0.6
5.32	0.38 (S_x = 2.2; S_y = 0.02)		46.2
5.67	0.04 (S_x = 0.009; S_y = 0.3)		−19.2
5.90	0.03 (S_x = 0.03; S_y = 0.12)		35.1
6.11	0.62 (S_x = 3.1; S_y = 0.03)		29.3
	B3LYP		
3.69 (L_a)	0.07 (S_x = 0.13; S_y = 0.67)	72.6	109.2
4.05 (L_b)	0.05 (S_x = 0.45; S_y = 0.06)		−116.8
4.16	0.005 (S_z = 0.05)		1.6
5.18	0.23 (S_x = 1.37; S_y = 0.41)		99.5
5.41	0.17 (S_x = 1.28; S_y = 0.001)		−42.4
5.94	0.03 (S_x = 0.09; S_y = 0.15)		62.3
6.01	0.82 (S_x = 4.1; S_y = 0.11)		5.4
	CAM-B3LYP		
4.01 (L_a)	0.11 (S_x = 0.16; S_y = 0.92)	76.4	84.3
4.26 (L_b)	0.05 (S_x = 0.46; S_y = 0.03)		−77.8
4.51	0.006 (S_z = 0.05)		0.8
5.40	0.49 (S_x = 3.0; S_y = 0.4)		77.2
5.67	0.01 (S_x = 0.4; S_y = 0.09)		−30.7
5.76	0.004 (S_x = 0.06; S_y = 0.04)		100.4
5.99	0.63 (S_x = 3.7; S_y = 0.1)		30.2

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Table 3. 1-Naphthaldehyde Calculated Excitation Energies ΔE_j (eV), Oscillator Strengths (f) with the Cartesian Component of the Transition Strength (S), the Angle (α) between L_b and L_a, and Faraday $\mathcal{B}$ Term (au) for the Basis Set aug-cc-pVDZ

ΔE_j	$f(0 \rightarrow j)$	α	$\mathcal{B}(0 \rightarrow j)$
	RI-CC2		
4.03 (L_b)	0.02 (S_x = 0.16; S_y = 0.09)	61.9	−90.4
4.17 (L_a)	0.15 (S_x = 0.1; S_y = 1.4)		79.8
5.12	0.36 (S_x = 2.8; S_y = 0.001)		31.1
5.27	0.02 (S_x = 0.05; S_y = 0.02)		−70.4
5.30	0.01 (S_z = 0.08)		0.4
5.56	0.11 (S_x = 0.15; S_y = 0.85)		80.9
5.98	0.42 (S_x = 2.05; S_y = 0.33)		−10.6
	B3LYP		
3.51 (L_a)	0.11 (S_x = 0.29; S_y = 0.90)	39.8	−39.1
3.88 (L_b)	0.03 (S_x = 0.15; S_y = 0.12)		69.6
4.76	0.28 (S_x = 0.72; S_y = 1.02)		89.9
4.81	0.03 (S_x = 0.001; S_y = 0.26)		−107.
5.12	0.01 (S_z = 0.001)		0.3
5.27	0.10 (S_x = 0.42; S_y = 0.37)		75.6
5.38	0.39 (S_x = 1.92; S_y = 0.25)		−17.1
	CAM-B3LYP		
4.14 (L_a)	0.15 (S_x = 0.4; S_y = 1.12)	42.6	−70.1
4.33 (L_b)	0.02 (S_x = 0.14; S_y = 0.08)		77.6
5.40	0.38 (S_x = 1.01; S_y = 1.77)		−72.5
5.61	0.01 (S_x = 0.62; S_y = 0.14)		83.0
5.74	0.06 (S_z = 0.005)		20.7
6.10	0.11 (S_x = 0.86; S_y = 0.07)		10.1
6.23	0.41 (S_x = 2.06; S_y = 0.19)		−39.2

Table 4. 2-Naphthylamine Calculated Excitation Energies ΔE_j (eV), Oscillator Strengths (f) with the Cartesian Component of the Transition Strength (S), the Angle (α) between L_b and L_a, and Faraday $\mathcal{B}$ Term (au) for the Basis Set aug-cc-pVDZ

ΔE_j	$f(0 \rightarrow j)$	α	$\mathcal{B}(0 \rightarrow j)$
	RI-CC2		
3.86 (L_b)	0.051 (S_x = 0.3; S_y = 0.38)	19.8	16.1
4.34	0.005 (S_z = 0.04)		1.5
4.66 (L_a)	0.055 (S_x = 0.01; S_y = 0.47)		− 12.4
4.94	0.003 (S_z = 0.02)		0.1
5.13	0.002 (S_x = 0.02; S_y = 0.002)		1.7
5.47	0.99 (S_x = 7.1; S_y = 0.38)		158.3
5.62	0.23 (S_x = 0.83; S_y = 0.85)		−165.6
	B3LYP		
3.72 (L_a)	0.049 (S_x = 0.36; S_y = 0.17)	9.6	14.4
4.17	0.002 (S_z = 0.02)		1.2
4.36 (L_b)	0.015 (S_x = 0.1; S_y = 0.03)		−7.9
4.71	0.003 (S_z = 0.03)		0.9
4.90	0.03 (S_x = 0.02; S_y = 0.45)		1.2
5.29	0.95 (S_x = 7.1; S_y = 0.1)		160.7
5.40	0.14 (S_x = 0.74; S_y = 0.18)		−149.1
	CAM-B3LYP		
3.99 (L_a)	0.05 (S_x = 0.09; S_y = 0.14)	23.6	14.0
4.53	0.003 (S_z = 0.03)		0.7
4.59 (L_b)	0.03 (S_x = 0.14; S_y = 0.08)		−13.5
4.72	0.002(S_z = 0.02)		4.4
5.17	0.01 (S_x = 0.22; S_y = 0.001)		0.7
5.59	1.12 (S_x = 8.1; S_y = 0.17)		140.1
5.75	0.16 (S_x = 0.56; S_y = 0.60)		−129.0

well. It has been observed that the polarization of the transition moment for L_b and L_a bands of a substituted naphthalene varies depending on the mixing with other allowed transitions.[43,60]

Moving toward higher energies, several transitions contribute to the spectral region characteristic of the B bands. In 1-naphthylamine, both CC2 and CAM-B3LYP yield two relatively intense transitions plus two weaker ones, whereas B3LYP has three relatively intense transitions plus a weaker one. The sign pattern of the corresponding $\mathcal{B}$ terms is the same in all three methods, but the magnitudes of the $\mathcal{B}$ terms themselves are quite different. As a consequence, the B3LYP MCD spectrum in this region shows a positive band that is absent in the experiment. The calculated CC2 MCD spectrum is in excellent agreement with the experimental one. In 1-naphthaldehyde, all three electronic structure methods yield in absorption two intense and two weak electronic transitions, but with different sign patterns as far as the $\mathcal{B}$ terms are concerned. The $\mathcal{B}$ term of the first B band is positive both for CC2 and B3LYP, followed by a larger negative one. The opposite occurs for CAM-B3LYP. As a consequence, CAM-B3LYP does not reproduce the MCD negative/positive/negative spectral pattern in the experimental MCD spectrum in this frequency region. A comparison of the CC2 spectra for the Z conformation and the E conformation of 1-naphthaldehyde, as well as their Boltzmann average, is reported in Figure S4 of the Supporting Information. The averaging over the two conformers leads to a small red shift of the bands in the region around 5.2 eV, improving slightly the agreement with experiment, but the effect is below the intrinsic accuracy of CC2.

Considering the case of the amino group as substituent, we compare the effect of substitution at 1 and 2 positions. The substitution in 2 position shifts the L_b transition to lower energy with respect to both naphthalene and 1-naphthylamine, resulting in well-separated L_b and L_a bands.[43,59] In 2-naphthylamine, the transition moment of L_b is not directed parallel the long-axis of the molecule, but it is rotated toward the short-axis[10,60] (see Table 4). The MCD spectrum of 2-naphthylamine (Figure 6) shows a relevant difference from the MCD spectrum of 1-naphthylamine (Figure 4): the $\mathcal{B}$ term of the L_b transition of 2-naphthylamine is significantly weaker (about one-tenth) than the corresponding one of 1-naphthylamine. The $\mathcal{B}$ term of the L_a transition of 2-naphthylamine is weaker and opposite in sign with respect to the corresponding one in 1-naphthylamine. Other differences are also present for the transitions at higher energy (see Table 2 and Table 4). A direct comparison of experimental and calculated data between 1-naphthylamine and 2-naphthylamine is reported in Figure S5 of the Supporting Information. As for the previous cases, the CC2 spectra are in best agreement with the experimental spectra.

CONCLUSION

In conclusion, CC2 provides a good representation of all four aromatic systems, well reproducing their electronic transitions as UV absorption, confirmed by the accurate prediction of their MCD response. All trends upon introduction of a substituent in the naphthalene parent molecule discussed by Michl and co-workers[10] are confirmed by our CC2 calculations. On the other hand, both TD-B3LYP and TD-CAM-B3LYP fail to correctly reproduce some of the UV and MCD spectral features, and offer discording characterizations of the underlying electronic transitions. We attribute these problems to different mixing of the excited states induced by the substitutions which are not

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accurately reproduced by TD-DFT because of larger errors in the relative energies for different orbital transitions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c09669.

Geometrical parameters of the optimized structures of naphthalene and its derivatives and alternative renderings of the spectra (PDF)

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Notes

The authors declare no competing financial interest.

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