

On the magnetic circular dichroism of benzene. A density-functional study

Jakub Kaminský, Jan Kříž, and Petr Bouř

Citation: *The Journal of Chemical Physics* **146**, 144301 (2017); doi: 10.1063/1.4979570

View online: <http://dx.doi.org/10.1063/1.4979570>

View Table of Contents: <http://aip.scitation.org/toc/jcp/146/14>

Published by the [American Institute of Physics](#)

Articles you may be interested in

[Long-range interactions from the many-pair expansion: A different avenue to dispersion in DFT](#)
The Journal of Chemical Physics **146**, 024111024111 (2017); 10.1063/1.4973728

[Announcement: Top reviewers for The Journal of Chemical Physics 2016](#)
The Journal of Chemical Physics **146**, 100201100201 (2017); 10.1063/1.4978399

[Excited states from modified coupled cluster methods: Are they any better than EOM CCSD?](#)
The Journal of Chemical Physics **146**, 144104144104 (2017); 10.1063/1.4979078

[Benchmark study of the structural and spectroscopic parameters of the hydroxymethyl peroxy \(HOCH₂OO\) radical and its decomposition reaction to HO₂ and H₂CO](#)
The Journal of Chemical Physics **146**, 144303144303 (2017); 10.1063/1.4979573

[Screening methods for linear-scaling short-range hybrid calculations on CPU and GPU architectures](#)
The Journal of Chemical Physics **146**, 144108144108 (2017); 10.1063/1.4978476

[CC2 oscillator strengths within the local framework for calculating excitation energies \(LoFEx\)](#)
The Journal of Chemical Physics **146**, 144107144107 (2017); 10.1063/1.4979713



**COMPLETELY
REDESIGNED!**

**PHYSICS
TODAY**

Physics Today Buyer's Guide
Search with a purpose.

On the magnetic circular dichroism of benzene. A density-functional study

Jakub Kaminský, Jan Kříž, and Petr Bouř^{a)}

Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo náměstí 2, 16610 Prague, Czech Republic

(Received 7 February 2017; accepted 21 March 2017; published online 10 April 2017)

Spectroscopy of magnetic circular dichroism (MCD) provides enhanced information on molecular structure and a more reliable assignment of spectral bands than absorption alone. Theoretical modeling can significantly enhance the information obtained from experimental spectra. In the present study, the time dependent density functional theory is employed to model the lowest-energy benzene transitions, in particular to investigate the role of the Rydberg states and vibrational interference in spectral intensities. The effect of solvent is explored on model benzene-methane clusters. For the lowest-energy excitation, the vibrational sub-structure of absorption and MCD spectra is modeled within the harmonic approximation, providing a very good agreement with the experiment. The simulations demonstrate that the Rydberg states have a much stronger effect on the MCD intensities than on the absorption, and a very diffuse basis set must be used to obtain reliable results. The modeling also indicates that the Rydberg-like states and associated transitions may persist in solutions. Continuum-like solvent models are thus not suitable for their modeling; solvent-solute clusters appear to be more appropriate, providing they are large enough. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4979570>]

I. INTRODUCTION

Magnetic circular dichroism (MCD) of aromatic compounds has been attracting attention because the spectra are very sensitive to the molecular structure and offer the possibility to identify degenerate excited electronic states.^{1–7} This also holds for the vibrational spectral region.⁸ Unlike for plain absorption, MCD spectral bands can be both positive and negative, which often makes it possible to resolve overlapping electronic transitions.

For benzene, MCD is relatively well documented. High-quality spectra of the liquid phase date back to 1960s and 1970s^{4,9} when it was necessary to calibrate the Stephens' canonical MCD theory.^{10,11} Vapor spectra were published later,¹² same as the gas phase MCD measured using synchrotron radiation.^{13,14} The MCD spectroscopy thus tremendously facilitated the absorption studies aimed at the assignment of electronic transitions, as confirmed by subsequent computational works.^{4,15–19} A rich vibrational sub-structure of some electronic bands^{13,14,20} appears to be a common feature of similar aromatic systems.²¹

Early assignments of benzene electronic transitions were based on simplified models^{4,15} that failed to explain some spectral features.⁹ Later, rigorous quantum-chemical approaches yielded better results,^{16–18,22,23} although a sufficiently large basis set allowing for full spatial extent of the Rydberg states had to be used. It is worth noting that the Rydberg states are present throughout the entire spectrum; quantum numbers as high as $n = 75$ have been reported.²⁴ Interestingly, basis sets with incomplete diffuse functions gave worse transition

energies than those lacking them altogether.¹⁶ Very accurate transition energies, including Rydberg and double-excitation states, were obtained by the multireference Møller-Plesset perturbation (MRMP) method.¹⁷

In larger systems including biologically relevant molecules the Rydberg states are omnipresent as well.²⁵ Yet for computational modeling to be feasible it is desirable to investigate computationally less demanding methods. Semiempirical models such as CNDO (complete neglect of differential overlap) cannot be readily used to describe the Rydberg states,¹⁵ but the Rydberg parameters were incorporated into the Zerner's INDO/S (spectral extension of the intermediate neglect of differential overlap) method.²⁶ Nowadays, time-dependent density functional theory (TDDFT) represents a more reasonable compromise in computational speed and accuracy, as shown earlier for benzene and its transition energies. However, spectral shapes were not modeled and only a limited basis set was used.¹⁹

In the present study, we analyze the performance of TDDFT in terms of its capability to reproduce the MCD intensities, including the lowest-energy Rydberg transitions. For simulations of the vibrationally split lowest-energy (non-Rydberg) band, the “integrated approach” of Barone *et al.*^{27,28} that includes the differences in ground and excited state geometry and vibrational harmonic frequencies is used. We find testing of the theory important because while the TDDFT is increasingly used to interpret MCD spectra of a wide range of aromatic compounds^{29–32} larger molecules do not allow for extensive tuning of the methodology. Although it is not yet possible to fully model the liquid phase, the benzene/methane and to a limited extent also benzene/water clusters helped us to estimate the fate of the Rydberg orbitals in solutions. The results suggest that solutions may support Rydberg-like transitions

^{a)}Electronic address: bour@uochb.cas.cz

and that the MCD technique is sensitive enough to identify them.

Modern TDDFT implementations represent an efficient way of MCD intensity simulations.³³ In general, they follow the Stephens' MCD formalism,^{10,11} e.g., directly implemented within the response theory^{34–37} or via the complex polarization propagator.³⁸ Quite interesting is also the MCD implementation exploring real-time propagation of the TDDFT wave function.³⁹ We are using the sum over state (SOS) method⁴⁰ employing efficient TDDFT implementations⁴¹ and making it possible to include a large number of excited electronic states.

TDDFT has sometimes been found to provide inaccurate energies of the Rydberg states, although the reasons vary and in some parameters the inaccuracy is not greater than for other states.^{42–44} Charge-transfer corrections of simpler functionals often do not provide better results^{45,46} and approaches such as constrained-variational DFT thus may be more suitable.⁴⁷ Exact analyses have so far been confined to rather small systems, such as helium atom.⁴⁸ Specifically for benzene, we use the B3LYP⁴⁹ and CAM-B3LYP⁵⁰ functionals because their energies compare reasonably well with both high-level wavefunction computations and the experiment.

II. METHODS

Experimental MCD and absorption benzene spectra in *n*-hexane solutions were obtained on a JASCO J-815 (Japan) spectrometer equipped with a permanent magnet (1.5 T). The spectra were measured in 1 cm and 1 mm quartz cells at 0.01M and 5×10^{-4} M concentrations, for the 185–220 nm and 220–300 nm spectral range, respectively. Scanning speed was set to 20 nm/min, temperature 20 °C, and accumulation time 4 s/point; averages of three scans are shown.

Benzene geometry was optimized at the B3LYP/6-311++G** level of theory, and TDDFT computations of electronic transition energies and intensities (also with other basis sets and functionals) were performed with the Gaussian program.⁵¹ The GUVUDE program^{40,52} interfaced to Gaussian was employed to compute the MCD spectral intensities. The origin-independent “LORG” (localized orbital/local origin) sum over state formula⁵² was used for the Faraday B-term. Note, nevertheless, that the origin dependence is not a critical factor for molecules close to the coordinate origin.⁵² The contribution of an $n \rightarrow j$ transition is (in atomic units)

$$B_{LORG} = \text{Im} \mu_{nj,\alpha} \varepsilon_{\alpha\beta\gamma} T_{nj,\beta\gamma}. \quad (1)$$

The “electronic transition tensor”³² \mathbf{T}_{nj} , or the “MCD tensor,” can be written within the LORG formalism⁵² as

$$T_{nj,\beta\gamma} = \sum_{k \neq n} \frac{\mu_{jk,\beta} m_{kn,\gamma}}{E_{kn}} + \sum_{k \neq j} \frac{\mu_{kn,\beta} m_{jk,\gamma}}{E_{kj}} - \frac{i\varepsilon_{\gamma\delta\varepsilon}}{4N_e} \left[\sum_{k \neq n} \mu_{jk,\beta} \left(\sum_{l \neq n} \frac{\mu_{kl,\delta} \nabla_{l,n,\varepsilon}}{E_{ln}} + \sum_{l \neq k} \frac{\mu_{l,n,\delta} \nabla_{kl,\varepsilon}}{E_{kl}} \right) + \mu_{kn,\beta} \sum_{k \neq j} \left(\sum_{l \neq k} \frac{\mu_{jl,\delta} \nabla_{lk,\varepsilon}}{E_{kl}} + \sum_{l \neq j} \frac{\mu_{lk,\delta} \nabla_{jl,\varepsilon}}{E_{lj}} \right) \right], \quad (2)$$

$\mu_{nj,\alpha} = \langle n | \mu_{\alpha} | j \rangle$ is the α -coordinate of the transition dipole moment element, similarly for the magnetic dipole moment \mathbf{m} and the gradient operator ∇ , $\varepsilon_{\alpha\beta\gamma}$ is the anti-symmetric tensor, $E_{kn} = E_k - E_n$ is a difference of electronic energies, and N_e is the number of electrons. Einstein summation convention is followed, i.e., Cartesian coordinate index occurring twice in a product is summed over. Degenerate electronic levels (Faraday A-terms) were also included, as a limit of close-lying states.⁵³

The Kaufmann's basis set optimized to represent Rydberg states⁵⁴ was placed at the center of benzene molecule; by default, orbitals up to the main quantum number (n) of 7 and the orbital quantum number (l) of 1 were taken. We indicate this by the letter “R,” e.g., B3LYP/6-311++G**/R (or just B3LYP/R) calculation was performed with the standard 6-311++G** basis set augmented by the diffuse functions. An extended DFT integration grid of 350 radial and 974 Lebedev angular points was used. By default, 500 excited electronic states were considered. Although the MCD tensor depends on electronic states also outside the investigated spectral region, contribution of the higher-energetic states quickly diminishes.³⁵ For the B3LYP/6-311++G**/R calculation, the dependence of the spectrum on the number of the electronic states is shown in Figure S1 (supplementary material).

To study solvation effects, benzene was placed in a (26 Å)³ cubic box filled with methane molecules to the density of liquid methane (0.656 g/ml). Methane was used as a model of non-polar solvents for its high hydrogen content; its addition increased the computational time less than solvents with similar chemical properties and with a higher ratio of heavy atoms. After an equilibration stage and 0.1 ns molecular dynamics (1 fs integration time, *NVT* ensemble, OPLSAA⁵⁵ force field) benzene/methane clusters were created by removing solvent molecules that were farther away than 6, 8, and 15 Å from benzene. Geometry of the cluster was partially optimized in vibrational normal modes coordinates⁵⁶ with the 300 cm⁻¹ threshold for vibrational frequencies,⁵⁷ and subjected to TDDFT computations as for the free molecule. An analogous computation was performed in benzene placed in a cubic box of water (37.12 Å box size, OPLSAA (benzene) and TIP3P⁵⁸ (water) force fields, 6 Å cluster size only). For water, however, the TDDFT computation provided unrealistic results because of the cluster surface effects; water excited states were interfering with those of benzene. A similar effect has been observed for smaller benzene-water clusters for the absorption spectra.⁵⁹ The B3LYP computation was not usable as calculated spectrum was dominated by water transitions, often centered at the surface of the cluster (cf. Figures S2 and S3 of the supplementary material). Thus results obtained at the CAM-B3LYP level that can be better related to benzene solutions in water are reported; for the other systems, no such problems with B3LYP were observed. For example, MCD and absorption benzene spectra generated by B3LYP and CAM-B3LYP are quite similar, except for a fairly systematic energy shift (Figure S4 of the supplementary material; a newer ω B97X⁶⁰ functional is added for comparison, too).

Vibrational substructure of the lowest-energy (B_{2u}) band⁹ was modeled within the harmonic approximation for the electronic ground and excited state vibrational potentials,^{61,62}

and expansions of the transition electric dipole moment²⁷ and MCD tensor³² to the first order. The dipole moment derivatives were calculated by the Gaussian, and MCD tensor derivatives were obtained within the origin-independent SOS approach^{40,52} by the GUVCD program. Following the convention of Barone *et al.*,²⁷ the transition dipole moments and the MCD tensor were thus expanded as functions of the vibrational normal mode coordinates Q_J of the electronic excited state,

$$X(\mathbf{Q}) = X(0) + \sum_J \frac{\partial X}{\partial Q_J} Q_J, \quad (3)$$

where $X = \mu_{nj,\alpha}$ or $X = T_{nj,\beta\gamma}$, $\frac{\partial X}{\partial Q_J} = \sum_{\alpha=1}^3 \sum_{\lambda=1}^{N_{at}} \frac{\partial X}{\partial R_{\lambda\alpha}} S_{\lambda\alpha}^J$, \mathbf{S} is the Cartesian-normal mode transformation matrix, and the Cartesian derivatives $\frac{\partial X}{\partial R_{\lambda\alpha}}$ were calculated numerically. Then we had to modify Eq. (1) to obtain contributions from all transitions between vibrational states ν_n of the electronic ground state and vibrational states ν_j of the electronic excited state,

$$B(\nu_n \rightarrow \nu_j) = \text{Im} \langle \nu_n | \mu_{nj,\alpha}(\mathbf{Q}) | \nu_j \rangle \varepsilon_{\alpha\beta\gamma} \langle \nu_n | T_{nj,\beta\gamma}(\mathbf{Q}) | \nu_j \rangle, \quad (4)$$

which could be calculated analytically within the harmonic approximation. As pointed out earlier,⁶³ this approach may not well describe some vibrational resonance phenomena, but otherwise it provides a very good basis for reproducing the MCD vibrational structure, including the Franck-Condon and Herzberg-Teller contributions.³²

III. RESULTS AND DISCUSSION

A. TDDFT performance

Table I shows benzene transition energies obtained in the present study and elsewhere, computations and the experiment. Apparently, the B3LYP results reasonably well match energies previously computed with the HCTH (Hamprecht, Cohen, Tozer and Handy's) functional.¹⁹ All approaches struggle to reproduce the ordering of the higher-energy transitions. Note that also the experiment may not be assigned reliably.²³ As expected, advanced wave function methods such as CCSD(T)

(coupled clusters with single, double and partially triplet excitations),²² CC2 (second order coupled cluster),¹⁶ or MRMP¹⁷ reproduce the experimental values better than TDDFT, at least in terms of the average error given at the last line of the table. Nevertheless, also the TDDFT approximation seems to well describe the overall character of benzene lowest-energy transitions, including the Rydberg states.

B. Basis set dependence

An extended basis set is obviously crucial to reproduce the Rydberg states. This is not quite clear from the calculated transition energies (Table I) where the basis set extension often exerts only a minor effect and is obscured by the inaccuracy of the theoretical methods. For example, augmenting the 6-311++G** basis set by the Kaufmann's Rydberg-optimized one shifts the B3LYP energy of the second transition only slightly (6.09 \rightarrow 6.00 eV), and in fact away from the experimental value of 6.33 eV. The first and third "non-Rydberg" transitions are not at all affected by the basis set variations at the two digit precision.

On the other hand, absorption and MCD spectral intensities (Fig. 1) are more dependent on the basis set size. The "non-Rydberg" 6-311++G** (174 basis functions) and aug-cc-pVTZ (414 b.f.) basis sets provide rather similar absorption shapes, although the latter basis set is much larger and qualitatively advanced, namely, containing f functions on carbon atoms. The MCD patterns differ mainly in the band around 180 nm, which is negative for 6-311++G** and positive for aug-cc-pVTZ. More substantial intensity change is caused by augmenting the basis set by the Kaufmann's diffuse functions. An extra absorption band appears at 185 nm, and the signal below 160 nm is split. We also see that the " $(n=7, l=1)$ " functions (as related to the main and orbital quantum numbers, respectively⁵⁴) appear to be sufficient as further expansions to $n=9$ or $l=2$ ("d-orbitals") do not significantly change the absorption and MCD intensities in the investigated wavelength range. The last three computations with the Rydberg basis sets reproduce the measured intensities rather well (dashed line in Fig. 1, only a part of the spectrum is accessible by the spectrometer), including the MCD sign. The computed positions of the absorption bands at 185 nm (~ 6.71 eV, transition number

TABLE I. Lowest-energy transition energies (in eV) in benzene.

Transition ^a	B3LYP/6-311++G**	B3LYP/aug-cc-pVTZ	B3LYP/R	CAM-B3LYP/R	Experiment	HCTH ¹⁹	CCSD(T) ²²	CC2 ¹⁶	MRMP ¹⁷
1 B_{2u}	5.39	5.38	5.39	5.48	4.90 ⁶⁴	5.42	4.74	5.23	4.70
2 E_{1g}	6.09	6.03	6.00	6.43	6.33 ⁶⁵	6.10	6.25	6.45	6.52
3 B_{1u}	6.05	6.02	6.05	6.16	6.20 ⁶⁴	6.22	6.17	6.46	6.21
4 A_{2u}	6.61	6.53	6.47	6.90	6.93 ⁶⁶	6.81	6.80	6.97	6.99
5 E_{2u}	6.63	6.55	6.49	7.00	6.95 ⁶⁶	7.78	6.88	7.03	7.06
6 A_{1u}	6.69	6.61	6.54	7.11	...	6.81	6.97	7.12	6.93 ⁶⁷
7 E_{1u}	6.96	6.91	6.71	7.01	6.94 ⁶⁴	7.00	6.99	7.07	6.93
8 E_{1g}	7.28	7.16	6.90	7.63	7.54 ⁶⁸	7.49	...	7.56	7.12
9 E_{1u}	7.93	7.50	6.94	7.28	7.41 ⁶⁶	7.35	...	7.32	7.29
10 A_{2u}	6.63	7.69	6.95	7.00	...	7.17
δ^b	0.33	0.32	0.43	0.22	0.00	0.36	0.10	0.17	0.19

^aRydberg transitions in bold.

^bMean square deviation.

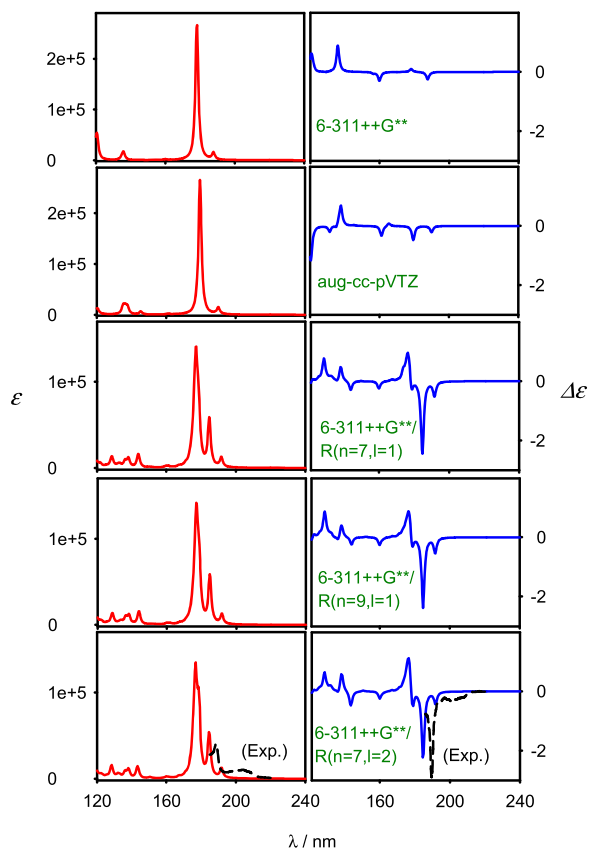


FIG. 1. Absorption (left) and MCD (right) benzene spectra calculated with five different basis sets and the B3LYP functional. The experiment is indicated by dashed line, intensities are in $\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$, and MCD is normalized to the magnetic field of 1 T.

6, E_{1u} , in Table I) and 192 nm (~ 6.47 eV, transition number 4, A_{2u}) are slightly shifted compared to the experimental values of 189 and 204 nm, respectively.

The basis set dependence is consistent with the orbital analysis of the excited states. The spatial extent of the dominant orbitals (Table II, column 3) indicates a Rydberg character for most of the lowest-energy excited states, with a

TABLE II. Spatial extent^a of excited states in benzene and its clusters with methane and water.

	C_6H_6^b		$\text{C}_6\text{H}_6@CH_4^b$		$\text{C}_6\text{H}_6@H_2O^c$	
	E	$\langle r \rangle$	E	$\langle r \rangle$	E	$\langle r \rangle$
1	5.39	4	5.30	6	4.30	16
2	6.00	10	5.74	15	4.88	18
3	6.05	4	5.95	6	5.07	16
4	6.47	26	5.99	17	5.13	16
5	6.49	26	6.05	17	5.26	16
6	6.54	26	6.08	17	5.29	18
7	6.71	66	6.48	67	5.33	9
8	6.90	65	6.62	73	5.39	16
9	6.94	63	6.64	74	5.47	37
10	6.95	27	6.65	73	5.55	18

^aDefined as a square root of the quadrupole moment, $\langle r \rangle = \sqrt{\langle \varphi | r^2 | \varphi \rangle}$, in a.u., where φ is the dominant orbital, energies E in eV, for 10 lowest-energy transitions. Note that in some works the “spatial extent” may be defined differently, e.g., for the all-electron wavefunction.

^bB3LYP/R.

^cCAM-B3LYP/R.

maximum of 66 bohrs for the 7th transition, which is impossible to model with the standard 6-311++G** or aug-cc-pVTZ basis set, where the most diffuse coefficients correspond to a typical distance of about 1-5 bohrs only (see the basis set structure at <https://bse.pnl.gov/bse/portal>). An example of Rydberg low-energy virtual p-orbitals is plotted in Fig. 2(A), for isodensity of 0.002 a.u.

C. Solvent dependence

Experimental absorption and MCD spectra of benzene in the liquid phase and vapor are very similar,^{12,69,70} suggesting that the Rydberg-like character of some transitions must be conserved in some way. Indeed, this is confirmed by the cluster models. As exemplified in Fig. 2, the shapes of the diffuse virtual orbitals involved in the electronic transitions are quite similar in methane and vacuum. Large variations in orbital shapes occur in the benzene/water cluster, although also here the diffuse character of the orbitals is obvious as well (cf. Table II). The outcome of the benzene/methane calculation without the diffuse basis set is very interesting, because the Rydberg benzene states could be modeled as well. Here, the solute electrons could be excited into the 3-21+G atomic orbitals of the solvent (Fig. 2(D)).

The orbital extent (Table II, Fig. 2) may be somewhat misleading, because in the clusters the solvent shields the solute charge of the excited benzene molecule, which sometimes leads to very diffuse states. Nevertheless, the “survival” of the Rydberg excitations is visible also in the absorption and MCD spectra simulated for small (6 Å radius) and large (8 Å) benzene/methane clusters; these are plotted together with the vacuum results in Fig. 3. Within 160-220 nm, in vacuum (left panel), the standard basis set fails to reproduce the strong MCD signal obtained with the diffuse basis set. On the contrary, the spectra simulated with and without the diffuse basis set become more similar in the clusters (middle and right panels). This is consistent with the orbital analysis (Fig. 2) suggesting that Rydberg-like orbitals may be formed from a solvent-centered basis set. Below 160 nm, the results are obscured by the methane excited states. As expected, implicit polarizable continuum solvent models⁷¹ with the standard basis set provided results almost identical to vacuum (not shown) and are thus not suitable for reliable modeling of MCD intensities that are due to the diffuse transitions.

D. Vibrational structure of the $A_{1g} \rightarrow B_{2u}$ transition

The lowest-energy transition does not have a Rydberg character, but is interesting because of its well-developed vibrational structure. In addition, it is nearly forbidden (the transition dipole moment is very small), and absorption and MCD intensities originate almost entirely in the vibrational motion. The first excited state was predicted to have a geometry with the same D_{6h} symmetry as the ground state; the bond lengths calculated at different levels are listed in Table III. The simulated (B3LYP/6-311++G**) and experimental MCD and absorption spectra are plotted in Fig. 4. Overall, there is a very good agreement between the calculated and experimental spectral shapes, although the calculated absolute intensities are higher than in the experiment. A systematic error of 20.6 nm (~ 0.4 eV) is acceptable and explicable by the

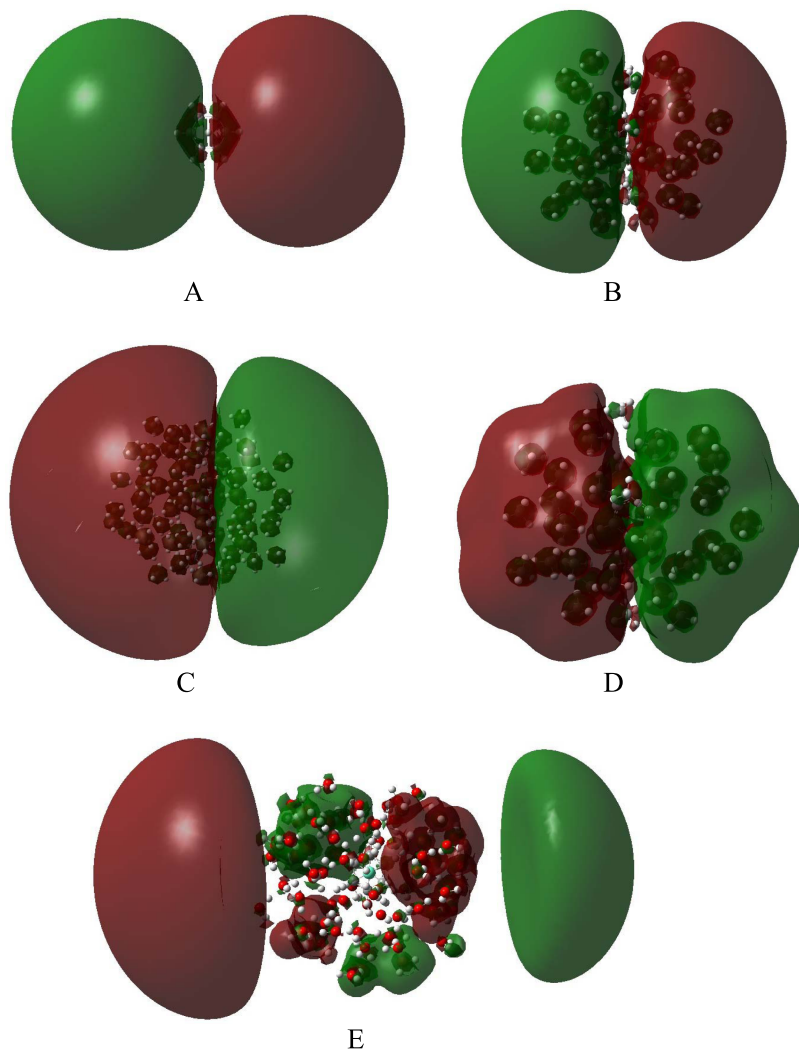


FIG. 2. Low-energy p-like Rydberg benzene orbitals calculated in vacuum (a), for 6 Å ((b) and (d)) and 8 Å (c) clusters with methane, and for a 6 Å water cluster (e). The B3LYP/R (CAM-B3LYP for water) level was used, with 3-21G basis set for the solvent, case D was computed at the B3LYP/6-311++G** (benzene)/3-21+G(methane) level, i.e., without the diffuse basis set.

imperfection of the B3LYP functional. The experimental absorption bands are nearly equidistant; the increment (6 nm \sim 900 cm^{-1}) approximately corresponds to the vibrational frequency of the breathing mode (number 12 in Fig. 4). Although combined with other modes, vibrational mode number 12 dominates the vibrational progression because its normal mode displacement very well connects the geometries of the ground and excited states (both symmetric). The 267 nm experimental band is not predicted.

In the wavenumber scale (cm^{-1}), calculated and experimental positions of the most intense vibrational sub-bands of the $A_{1g} \rightarrow B_{2u}$ transition are listed in Table IV. A closer look at Figure 4 or Table IV reveals that in the longer-wavelengths region the theoretical spacing between the major bands is larger than in the experiment. The opposite is true for shorter wavelengths. For example, for the band pair experimentally at 261/255 nm (i.e., separated by 902 cm^{-1}), the B3LYP separation is 42 608–41 632 = 976 cm^{-1} . For the pair

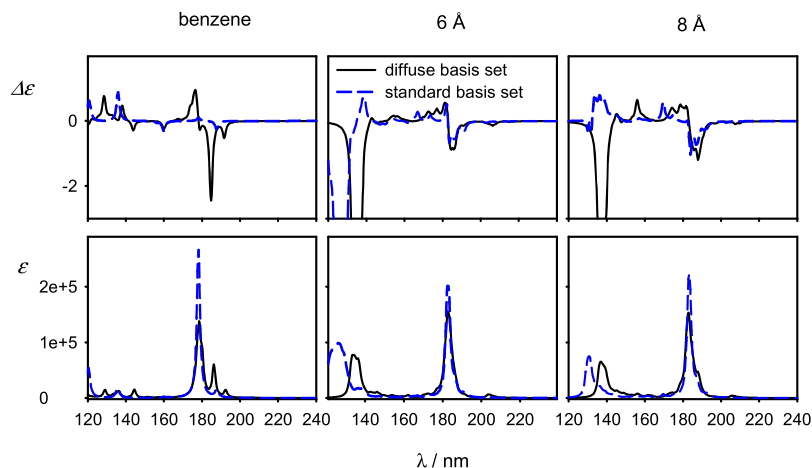


FIG. 3. MCD (top) and absorption (bottom) spectra simulated for benzene and the 6 Å and 8 Å benzene/methane clusters. The diffuse basis set comprised the 6-311++G**/R (benzene) and 3-21G (CH_4) functions vs. the standard 6-311++G** (benzene) and 3-21G (CH_4) basis sets.

TABLE III. Calculated bond lengths in the ground and first singlet excited states.

State		d_{CH} (Å)	d_{CC} (Å)
S_0	B3LYP/6-311++G**	1.084	1.394
	B3LYP/aug-cc-pVTZ	1.082	1.391
	CAM-B3LYP/6-311++G**	1.084	1.389
S_1	B3LYP/6-311++G**	1.082	1.425
	B3LYP/aug-cc-pVTZ	1.080	1.421
	CAM-B3LYP/6-311++G**	1.082	1.419

experimentally at 249/242 nm (separated by 1162 cm^{-1}), the B3LYP distance is 1010 cm^{-1} . The increasing separation between the vibrational sub-bands can be most likely attributed to anharmonic effects, not included in the simulation. Only small changes can be explained at the harmonic level. In our example, the calculated change was $1010 - 976 = 34\text{ cm}^{-1}$ against the observed $1162 - 902 = 260\text{ cm}^{-1}$. The band distance itself is obviously close to the frequency of the dominating mode number 12 (954 cm^{-1} , Fig. 4).

The vibrational pattern is not too dependent on the approximation in the electronic calculation. In Fig. 5, high-resolution absorption pattern calculated by two functionals is compared to a higher-resolution experiment.²⁰ A closer look, however, reveals that the B3LYP functional provides somewhat better relative intensities than CAM-B3LYP. Related to the CAM-B3LYP wavelength scale, within 205–22 nm and around 225 nm the CAM-B3LYP intensities are too weak, and intensities of the two weaker bands around 230 nm are similar for CAM-B3LYP, while an $\sim 2:1$ ratio better corresponding to the experiment is obtained by B3LYP.

The basis set change (6-311++G** \rightarrow aug-cc-pVTZ) has a much smaller effect than the functional variation. It is

TABLE IV. Calculated and experimental frequencies (cm^{-1}) of strong vibrational bands of the $A_{1g} \rightarrow B_{2u}$ transition.

Band	B3LYP	CAM-B3LYP	Expt.	Dominating vibrational state
1	41 632	42 937	38 314	$4^1 5^1$
2	42 301	43 630	39 063	18^1
3	42 608	43 898	39 216	$4^1 12^1$
4	43 234	44 603	40 000	$12^1 18^1$
5	43 573	44 883	40 161	$12^1 23^1$
6	44 195	45 662	40 816	$12^2 17^1$
7	44 583	45 872	41 322	$12^2 23^1$

interesting to note that although the ground and excited states are symmetrical (A_{1g}), a number of modes of different symmetries contribute to the absorption and MCD intensities as well, as indicated in Fig. 4. All of them are polarized in the benzene plane. If we transform the MCD tensor to a vector \mathbf{t} , $t_{nj,\alpha} = \epsilon_{\alpha\beta\gamma} T_{nj,\beta\gamma}$, then (see Eq. (4)) the MCD intensity $B = \text{Im}\langle v_n | \mathbf{t}_{nj} | v_j \rangle \bullet \langle v_n | \mathbf{t}_{nj} | v_j \rangle$, which is a similar expression to rotational strength describing the natural optical activity. Formally, the MCD vector takes the role of the transition magnetic dipole moment. In benzene, positive contributions to MCD bands are obtained when the transition dipole moment and the MCD vector are parallel, while anti-parallel cases give a negative signal.

Finally, we point out that the calculation of the vibrational splitting helps to correct/aide the assignment of some bands and makes it possible to more objectively compare the experimental and theoretical results. For example, the vertical excitation energy of the first transition calculated at the B3LYP/6-311++G**/R level (5.39 eV, Table I) is different from the long-wavelength absorption threshold of the vibrationally resolved pattern (240 nm \sim 5.17 eV, experimentally

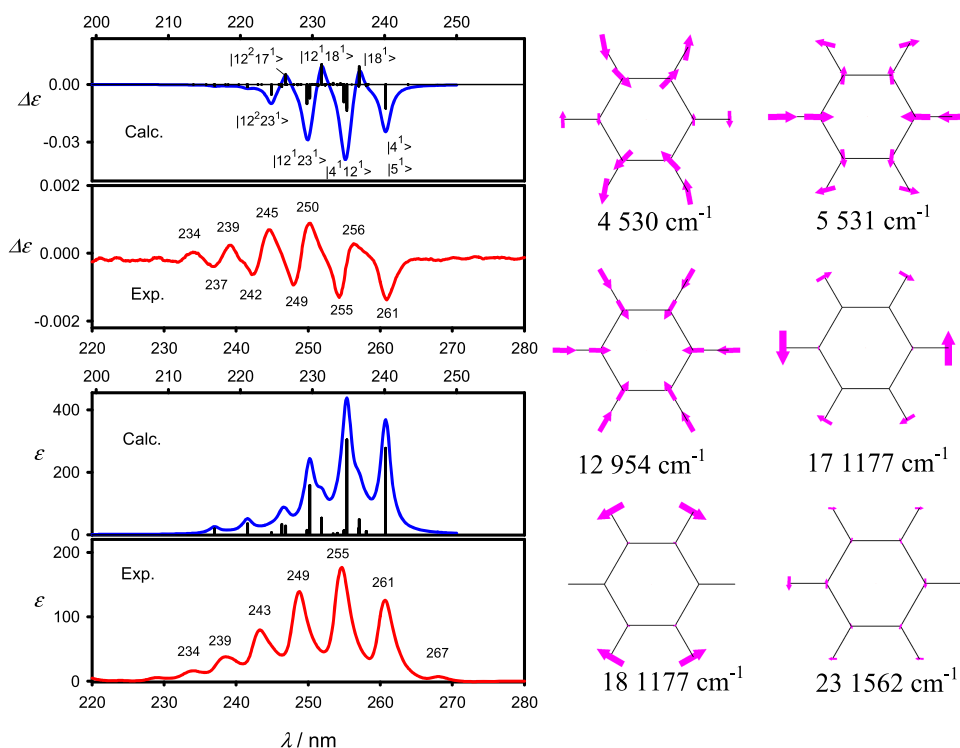


FIG. 4. Calculated (B3LYP/6-311++G**) and experimental MCD and absorption benzene spectra of the $A_{1g} \rightarrow B_{2u}$ transition exhibiting vibrational splitting. (Note that the calculated and experimental spectra are shifted relative to each other by 20 nm.) Dominant vibrational states are indicated, e.g., $12^2 17^1$ denotes a state with two excitations in mode 12 and one excitation in mode 17. For six most significant normal modes the Cartesian displacement is plotted on the right, the number and fundamental frequency in the electronically excited state are indicated.

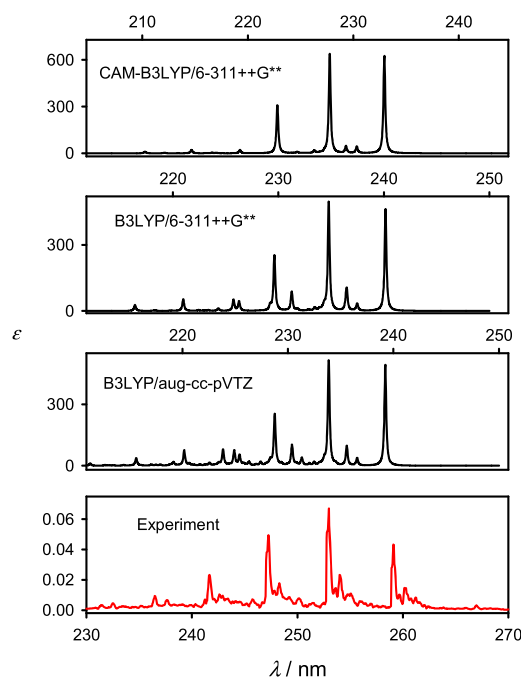


FIG. 5. Calculated and high-resolution experimental absorption patterns of the B_{2u} band. The experiment is redrawn from Ref. 20.

261 nm \sim 4.75 eV), which is again different from the apparent center of the entire B_{2u} band (about 233 nm \sim 5.30 eV, experimentally 4.90 eV). This “vibrational correction” of 5.39 – 5.30 = 0.09 eV improves the results of all the electronic methods listed in Table I, except MRMP.

IV. CONCLUSIONS

We have used a combined (TDDFT, MD, SOS, and vibrational) approach to better understand the MCD spectra of benzene as a model aromatic compound. The TDDFT computations of the Rydberg states required a large grid for numerical integration and revealed an interesting dependence of theoretical absorption and MCD spectral intensities on the diffuse character of the basis set. The relatively affordable TDDFT methodology also enabled a limited mimicking of the solvent environment by model clusters, which revealed, rather surprisingly, that the Rydberg-like excitations may persist also in solutions. The lowest-energy transition exhibits a clear vibrational structure, which could be modeled at the TDDFT level as well. Most of the observed MCD and absorption vibrational features could be explained at the harmonic approximation; the theory thus opens a way to study the potential energy surfaces of aromatic compounds, including their excited electronic states. Because of the ever increasing power of computational chemistry and high information contents of MCD spectra, the presented approach is likely to shed more light on structure and interactions of benzene and similar aromatic molecules.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the dependence of MCD on the number of included states, functional, and details on the water cluster computations.

ACKNOWLEDGMENTS

The work was supported by the Grant Agency of the Czech Republic (Grant Nos. 13-03978S and 16-05935S) We thank Dr. Radek Pelc for the discussion on the text.

- ¹G. H. Weeks *et al.*, “A probe for substituent hyperconjugative power: MCD (magnetic circular dichroism) of the benzene L_b band,” *Pure Appl. Chem.* **58**, 39 (1986).
- ²J. Michl, “Magnetic circular dichroism of aromatic molecules,” *Tetrahedron* **40**, 3845 (1984).
- ³J. Michl, “Magnetic circular-dichroism of cyclic pi-electron systems. I. Algebraic-solution of perimeter model for A-terms and B-terms of high-symmetry systems with a $(4n+2)$ -electron[N] annulene perimeter,” *J. Am. Chem. Soc.* **100**, 6801 (1978).
- ⁴P. J. Stephens *et al.*, “Magnetic circular dichroism of benzene, triphenylene, and coronene,” *J. Chem. Phys.* **48**, 132 (1968).
- ⁵J. Waluk *et al.*, “The electronic spectrum of benz[*a*]anthracene, linear and magnetic circular dichroism and fluorescence polarization studies,” *Chem. Phys.* **116**, 411 (1987).
- ⁶M. R. Whipple, M. Vařák, and J. Michl, “Magnetic circular dichroism of cyclic π -electron systems. 8. Derivatives of naphthalene,” *J. Am. Chem. Soc.* **100**, 6844 (1978).
- ⁷A. Tajiri and M. Hatano, “MCD studies of azulene and naphthalene,” *Chem. Phys. Lett.* **34**, 29 (1975).
- ⁸T. R. Devine and T. A. Keiderling, “Magnetic vibrational circular dichroism of benzene and 1,3,5-trisubstituted derivatives,” *J. Phys. Chem.* **88**, 390 (1984).
- ⁹D. J. Shieh, S. H. Lin, and H. Eyring, “Magnetic circular dichroism of molecules in dense media. I. Theory,” *J. Phys. Chem.* **76**, 1844 (1972).
- ¹⁰P. J. Stephens, “Theory of magnetic circular dichroism,” *J. Chem. Phys.* **52**, 3489 (1970).
- ¹¹P. J. Stephens, “Magnetic circular dichroism,” *Annu. Rev. Phys. Chem.* **25**, 201 (1974).
- ¹²S. D. Allen *et al.*, “The magnetic circular dichroism spectrum of benzene and toluene and the magnetic moment of the $^1E_{1u}$ state,” *Chem. Phys. Lett.* **30**, 140 (1975).
- ¹³R. Vitenberg, B. Katz, and B. Scharf, “The assignment of the benzene first-ionization rydberg spectrum via J-T splittings involving linearly inactive modes,” *Chem. Phys. Lett.* **71**, 187 (1980).
- ¹⁴P. A. Snyder *et al.*, “Magnetic circular dichroism (MCD) of the Rydberg transitions in benzene using synchrotron radiation,” *Chem. Phys. Lett.* **82**, 546 (1981).
- ¹⁵J. H. Obbink and A. M. F. Hezemans, “CNDO-S calculations of magnetic circular-dichroism of some monosubstituted benzenes using complete angular momentum operator,” *Theor. Chim. Acta* **43**, 75 (1976).
- ¹⁶O. Christiansen *et al.*, “Integral direct calculation of CC2 excitation energies: Singlet excited states of benzene,” *Chem. Phys. Lett.* **263**, 530 (1996).
- ¹⁷T. Hashimoto, H. Nakano, and K. Hirao, “Theoretical study of valence and Rydberg excited states of benzene revisited,” *J. Mol. Struct.: THEOCHEM* **451**, 25 (1998).
- ¹⁸H. H. Falden *et al.*, “Benchmarking second order methods for the calculation of vertical electronic excitation energies: Valence and Rydberg states in polycyclic aromatic hydrocarbons,” *J. Phys. Chem. A* **113**, 11995 (2009).
- ¹⁹N. C. Handy, and D. J. Tozer, “Excitation energies of benzene from Kohn-Sham theory,” *J. Comput. Chem.* **20**, 106 (1998).
- ²⁰E. Pantos, J. Philis, and A. Bolovinos, “The extinction coefficient of benzene vapor in the region 4.6 to 36 eV,” *J. Mol. Spectrosc.* **72**, 36 (1978).
- ²¹M. H. Palmer *et al.*, “Combined theoretical and experimental study of the valence, Rydberg and ionic states of fluorobenzene,” *J. Chem. Phys.* **144**, 204305 (2016).
- ²²J. E. Del Bene, J. D. Watts, and R. J. Bartlett, “Coupled-cluster calculations of the excitation energies of benzene and the azabenzenes,” *J. Chem. Phys.* **106**, 6051 (1997).
- ²³J. Lorentzon *et al.*, “A CASPT2 study of the valence and lowest Rydberg electronic states of benzene and phenol,” *Theor. Chim. Acta* **91**, 91 (1995).
- ²⁴K. Siglow and H. J. Neusser, “Photo- versus pulsed field-ionization of individual high n ($n \lesssim 57$) Rydberg states: Resolved d,g series of benzene,” *J. Chem. Phys.* **112**, 647 (2000).
- ²⁵H. Basch, M. B. Robin, and N. A. Kuebler, “Electronic states of the amide group,” *J. Chem. Phys.* **47**, 1201 (1967).

- ²⁶J. D. Head, "Inclusion of Rydberg orbitals in semiempirical calculations on excited states?," *Int. J. Quantum Chem.* **95**, 580 (2003).
- ²⁷V. Barone *et al.*, "Fully integrated approach to compute vibrationally resolved optical spectra: From small molecules to macrosystems," *J. Chem. Theory Comput.* **5**, 540 (2009).
- ²⁸F. Santoro and V. Barone, "Computational approach to the study of the lineshape of absorption and electronic circular dichroism spectra," *Int. J. Quantum Chem.* **110**, 476 (2010).
- ²⁹P. Štěpánek *et al.*, "Magnetic circular dichroism of chlorofullerenes: Experimental and computational study," *Chem. Phys. Lett.* **647**, 117 (2016).
- ³⁰P. Štěpánek *et al.*, "Fullerene resolution by the magnetic circular dichroism," *J. Chem. Phys.* **138**, 151103 (2013).
- ³¹P. Štěpánek *et al.*, "Porphyrin protonation studied by magnetic circular dichroism," *J. Phys. Chem. A* **116**, 778 (2012).
- ³²N. Lin *et al.*, "First principles studies of the vibrationally resolved magnetic circular dichroism spectra of biphenylene," *J. Chem. Theory Comput.* **9**, 1557 (2013).
- ³³T. Kjergaard, S. Coriani, and K. Ruud, "Ab initio calculation of magnetic circular dichroism," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 443 (2012).
- ³⁴M. Seth, T. Ziegler, and J. Autschbach, "Ab initio calculation of the C/D ratio of magnetic circular dichroism," *J. Chem. Phys.* **122**, 094112 (2005).
- ³⁵H. Solheim *et al.*, "The A and B Terms of magnetic circular dichroism revisited," *J. Phys. Chem. A* **112**, 9615 (2008).
- ³⁶M. Seth *et al.*, "Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism. II. Calculation of A terms," *J. Chem. Phys.* **128**, 234102 (2008).
- ³⁷M. Seth and T. Ziegler, in *Advances in Inorganic Chemistry* edited by R. VanEldik and J. Harley (Elsevier Academic Press, Inc., San Diego, 2010), p. 41.
- ³⁸H. Solheim *et al.*, "Complex polarization propagator calculations of magnetic circular dichroism spectra," *J. Chem. Phys.* **128**, 094103 (2008).
- ³⁹K. M. Lee, K. Yabana, and G. F. Bertsch, "Magnetic circular dichroism in real-time time-dependent density functional theory," *J. Chem. Phys.* **134**, 144106 (2011).
- ⁴⁰P. Štěpánek and P. Bouř, "Computation of magnetic circular dichroism by sum over states summations," *J. Comput. Chem.* **34**, 1531 (2013).
- ⁴¹F. Furche, and R. Ahlrichs, "Adiabatic time-dependent density functional methods for excited state properties," *J. Chem. Phys.* **117**, 7433 (2002).
- ⁴²M. E. Casida and M. Huix-Rotllant, "Progress in time-dependent density functional theory," *Annu. Rev. Phys. Chem.* **63**, 287 (2012).
- ⁴³S. L. Li and D. G. Truhlar, "Testing time-dependent density functional theory with depopulated molecular orbitals for predicting electronic excitation energies of valence, Rydberg, and charge-transfer states and potential energies near a conical intersection," *J. Chem. Phys.* **141**, 104106 (2014).
- ⁴⁴K. Yang *et al.*, "Density functional study of multiplicity-changing valence and Rydberg excitations of p-block elements: Delta self-consistent field, collinear spin-flip time-dependent density functional theory (DFT), and conventional time-dependent DFT," *J. Chem. Phys.* **135**, 044118 (2011).
- ⁴⁵C. Hu and O. Sugino, "Modified linear response for time-dependent density-functional theory: Application to Rydberg and charge-transfer excitations," *Phys. Rev. A* **74**, 032508 (2006).
- ⁴⁶C. Hu and O. Sugino, "Average excitation energies from time-dependent density functional theory," *J. Chem. Phys.* **126**, 074112 (2007).
- ⁴⁷T. Ziegler and M. Krykunov, "On the calculation of charge transfer transitions with standard density functionals using constrained variational density functional theory," *J. Chem. Phys.* **133**, 074104 (2010).
- ⁴⁸A. Wasserman, N. T. Maitra, and K. Burke, "Accurate Rydberg excitations from the local density approximation," *Phys. Rev. Lett.* **91**, 263001 (2003).
- ⁴⁹A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648 (1993).
- ⁵⁰T. Yanai, D. Tew, and N. C. Handy, "A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP)," *Chem. Phys. Lett.* **393**, 51 (2004).
- ⁵¹M. J. Frisch *et al.*, GAUSSIAN REVISION D01 (Gaussian, Inc., Wallingford, CT, USA, 2009).
- ⁵²P. Štěpánek and P. Bouř, "Origin-independent sum over states simulations of magnetic and electronic circular dichroism spectra via the localized orbital/local origin method," *J. Comput. Chem.* **36**, 723 (2015).
- ⁵³P. Štěpánek *et al.*, "Resolving electronic transitions in synthetic fluorescent protein chromophores by magnetic circular dichroism," *ChemPhysChem* **17**, 2348 (2016).
- ⁵⁴K. Kaufmann, W. Baumeister, and M. Jungen, "Universal Gaussian basis sets for an optimum representation of Rydberg and continuum wavefunctions," *J. Phys. B: At., Mol. Opt. Phys.* **22**, 2223 (1989).
- ⁵⁵G. A. Kaminski *et al.*, "Evaluation and reparametrization of the OPLS-AA force field for proteins via comparison with accurate quantum chemical calculations on peptides," *J. Phys. Chem. B* **105**, 6474 (2001).
- ⁵⁶P. Bouř and T. A. Keiderling, "Partial optimization of molecular geometry in normal coordinates and use as a tool for simulation of vibrational spectra," *J. Chem. Phys.* **117**, 4126 (2002).
- ⁵⁷J. Hudcová, K. H. Hopmann, and P. Bouř, "Correction of vibrational broadening in molecular dynamics clusters with the normal mode optimization method," *J. Phys. Chem. B* **116**, 336 (2012).
- ⁵⁸W. L. Jorgensen, J. Chandrasekhar, and J. D. Madura, "Comparison of simple potential functions for simulating liquid water," *J. Chem. Phys.* **79**, 926 (1983).
- ⁵⁹D. Sharma and M. J. Paterson, "The structure and UV spectroscopy of benzene-water (Bz-W₆) clusters using time-dependent density functional theory," *Photochem. Photobiol. Sci.* **13**, 1549 (2014).
- ⁶⁰J. D. Chai and M. Head-Gordon, "Systematic optimization of long-range corrected hybrid density functionals," *J. Chem. Phys.* **128**, 084106 (2008).
- ⁶¹T. E. Sharp and H. M. Rosenstock, "Franck-Condon factors for polyatomic molecules," *J. Chem. Phys.* **41**, 3453 (1964).
- ⁶²F. Santoro *et al.*, "Effective method to compute Franck-Condon integrals for optical spectra of large molecules in solution," *J. Chem. Phys.* **126**, 084509 (2006).
- ⁶³M. Z. Zgierski, "Vibronic structure of MCD spectra. I. Non-Condon effects in molecules with nondegenerate electronic states," *J. Chem. Phys.* **83**, 2170 (1985).
- ⁶⁴A. Hiraya and K. Shobatake, "Direct absorption spectra of jet-cooled benzene in 130–260 nm," *J. Chem. Phys.* **94**, 7700 (1991).
- ⁶⁵P. M. Johnson, "The multiphoton ionization spectrum of benzene," *J. Chem. Phys.* **64**, 4143 (1976).
- ⁶⁶P. M. Johnson and G. M. Korenowski, "The discovery of a 3p Rydberg state in benzene by three-photon resonant multiphoton ionization spectroscopy," *Chem. Phys. Lett.* **97**, 53 (1983).
- ⁶⁷K. Hirao, H. Nakano, and T. Hashimoto, "Multireference Møller-Plesset perturbation treatment for valence and Rydberg excited states of benzene," *Chem. Phys. Lett.* **235**, 430 (1995).
- ⁶⁸R. L. Whetten, K. J. Fu, and E. R. Grant, "Ultraviolet 2-photon spectroscopy of benzene - a new gerade Rydberg series and evidence for the ¹E_{2g} valence state," *J. Chem. Phys.* **79**, 2626 (1983).
- ⁶⁹W. R. Mason, *A Practical Guide to Magnetic Circular Dichroism Spectroscopy* (Wiley-Interscience, Portland, 2007).
- ⁷⁰I. N. Douglas, R. Grinter, and A. J. Thomson, "The magnetic circular dichroism spectrum of the ¹B_{2u} ← ¹A_{1g} transition of benzene in the vapour phase," *Mol. Phys.* **26**, 1257 (1973).
- ⁷¹E. Cancès, B. Mennucci, and J. Tomasi, "A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics," *J. Chem. Phys.* **107**, 3032 (1997).