Basis Set Recommendations for DFT Calculations of Gas-Phase Optical Rotation at Different Wavelengths

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S Supporting Information

ABSTRACT: Even for pure substances, the deduction of the absolute configuration is not always straightforward since there is no direct link between the magnitude and sign of the optical rotation and the absolute configuration. It would be very useful to use computations of the optical rotation to link experimentally measured optical rotations to an absolute configuration. Such electronic structure calculations of the optical rotation typically employ regular energy optimized basis sets from wave function theory, and especially the aug-cc-pVDZ basis set has been popular. Here, we have carried out extrapolation of the optical rotation to the basis set limits for nine small or medium sized molecules, using basis sets developed specifically for DFT and magnetic properties (aug-pcS-n series). We suggest that assignment of absolute configuration by comparisons between theoretical and experimental optical rotations may be improved by employing different wavelengths, and accordingly the optical rotation at two wavelengths (589.3 and 355.0 nm) has been investigated. Several fitting schemes were used to estimate the optical rotations at the basis set limit. It was found that use of the aug-cc-pVDZ basis set often leads to results that deviate significantly form the basis set limit results, especially at 355.0 nm but also at 589.3 nm. The double-ζ aug-pcS-1 basis set usually provides results which are closer to the limiting values. The basis set requirements are generally more severe at 355.0 nm, where also the aug-cc-pVTZ and 6-311++G(3fd,3dp) basis sets show significant deviations from the basis set limit results, while the aug-pcS-2 basis set always leads to results within an acceptable deviation.

■ INTRODUCTION

The most well-known property of a chiral molecule is probably its optical rotation, which refers to the nonresonant, distinct interaction of a molecule with a chiral electromagnetic field, e.g., left or right polarized light. The optical rotation is wavelength dependent and equal in magnitude, but opposite in sign for two enantiomers of a chiral compound. Measurements of optical rotation therefore offer a facile method for discriminating between the relative configuration of two enantionmers. Unfortunately, linking the absolute configuration of a chiral molecule to the sign and magnitude of its optical rotation is nontrivial. This link may be obtained by combining measurements of optical rotation with X-ray crystallography or total asymmetric synthesis. A crystal of the target molecules is a prerequisite for X-ray crystallography, and the data analysis is somewhat involved.[1] Total asymmetric synthesis can be laborious and costly, especially if a large number of substances are under investigation. Despite these potential issues in obtaining absolute configurations, this particular piece of information is often crucial. Prominent examples are asymmetric catalysis and biological transformations where enzymes often recognize a distinct stereoisomer of chiral substrates, leading to different reactivity for two enantiomers. In medicinal chemistry, the undesired stereoisomer can even have unwanted or harmful side effects.[2]

Determining absolute configurations by comparing calculated and measured optical rotations would clearly be a valuable tool. Several studies within the past decade have shown that first-principles calculations can be of great aid in such assignments.[3−6] The theoretical expression for optical rotation was first described by Rosenfield[7] using time-dependent perturbation theory. The dipole moment induced by an electromagnetic field with field vectors $E(r,t)$ and $B(r,t)$ was given by Rosenfield as[8]

$$\boldsymbol{\mu}_{\text{ind}} = \alpha E(r, t) + \frac{G'}{\omega} \frac{\partial B(r, t)}{\partial t}$$

(1)

where α is the electric dipole–dipole polarizability. The G' tensor is the central quantity for optical rotation, and assuming a ground state reference, ψ_0, it is defined according to

$$G'(\omega) = -\frac{2\omega}{\hbar}\text{Im} \sum_{n \neq 0} \frac{\langle \psi_0 | \hat{\boldsymbol{\mu}} | \psi_n \rangle \langle \psi_n | \hat{\mathbf{m}} | \psi_0 \rangle}{\omega_{n0}^2 - \omega^2}$$

(2)

where $\hat{\mathbf{m}} = \sum_i (q_i)/(2m_e)\mathbf{r} \times \mathbf{p}$ and $\boldsymbol{\mu} = \Sigma_i q_i \mathbf{r}_i$ describe the magnetic and electric dipole operators, respectively. ω_{n0} is the $\psi_n \leftarrow \psi_0$ excitation frequency and ω the frequency of the incident light. As always in these kinds of perturbation expressions, n runs over all excited states. The G' tensor is within a DFT framework (as used in this work) most efficiently calculated by means of a response function.[9] Instead of reporting the G' tensor, experimental studies usually report the specific rotation in deg/(dm g/mL), which is related to the trace of the G' tensor as[10]

$$[\alpha]_\omega = \frac{(72.0 \times 10^6)\hbar^2 N_A \omega}{c^2 m_e^2 M} \frac{1}{3}[\text{Tr}G']$$
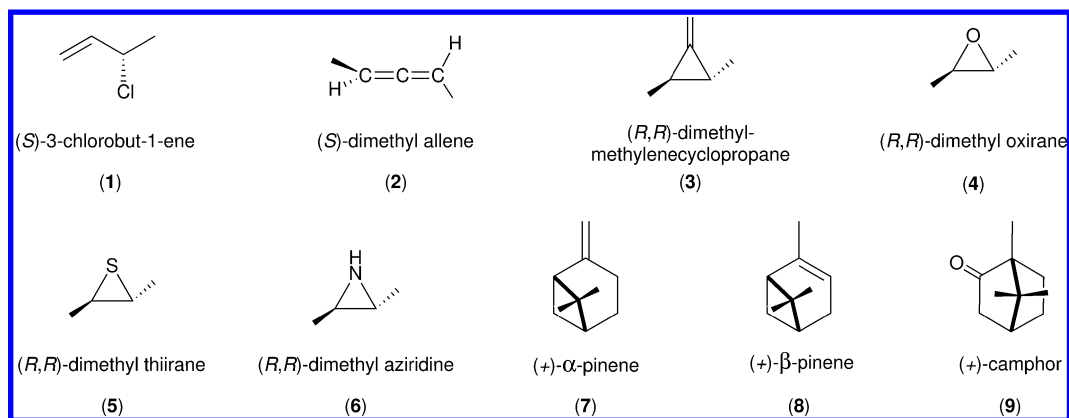
(3)

Figure 1. Molecules used in this study.

M being the molecular mass, N_A being Avogadro's number, c being the speed of light, and m_e being the electronic mass. The sodium D line (589.3 nm) is normally used as incident light, but occasionally measurements are performed at 633.0 or 355.0 nm. The use of the sodium D line has the advantage that most organic molecules do not absorb light at this frequency. From a computational point of view, the use of a frequency far from an excitation energy of the molecule is convenient as the response function diverges when ω approaches ω_{n0}.

Although advanced correlated wave function studies of optical rotation have begun to emerge,[8−14] most studies today use density functional theory, which often allows accuracy comparable to correlated wave function methods, but at a significantly reduced cost. Several TD-DFT benchmarks of optical rotations have been performed,[15−18] most recently by Mach and Crawford[13] and by Srebro et al.[19] In these studies, Dunning-[20,21] or Pople-style basis sets are usually applied. These basis sets are optimized for wave function methods. In this work, we investigate the basis set convergence of optical rotation using a series of modified polarization consistent basis sets[22] which have been optimized for DFT calculations of NMR shielding constants,[23] namely, the aug-pcS-n series of basis sets. Where most studies only investigate one or two basis sets within a basis set family (e.g., aug-cc-pVDZ and aug-cc-pVTZ), we have determined the basis set limit for a set consisting of nine molecules. The reason that the use of the aug-pcS-n basis sets may be advantageous is that the optical rotation is a mixed magnetic and electric property, and the $\hat{m}$ operator in eq 2 is intimately connected with the PSO operator used in calculating NMR shielding constants. The external field in NMR can also be a contributing factor to make the basis set dependence rather similar. The electric dipole operator is known to require diffuse basis functions for a good representation, and we thus focus on results using the aug-pcS-n basis sets. The aug-pcS-n basis sets contain an additional tight p function relative to the standard aug-pc-n basis sets and are slightly less contracted. We have also tested the aug-pcJ-n basis sets,[24] which contain additional tight functions relative to aug-pcS-n, and are even less contracted, but they gave results very similar to aug-pcS-n and will not be discussed further.

As initial studies showed that basis sets which are considered standard for calculating optical rotations in some cases give rise to different signs for the same compound, a more robust mean for linking absolute configuration to the optical rotation through computations would be to perform comparisons for more than one wavelength of incident light. This has also been

pointed out previously,[25] but little concern has been given to the fact that this requires basis sets which can deliver results of the same quality at different wavelengths. Consequently, two wavelengths of incident light have been employed in the present case. The optical rotations in the basis set limits are estimated and compared to results using Dunning- and Pople-type basis sets.

■ METHODS

The chiral molecules used for the basis set investigation are shown in Figure 1. All geometries have been optimized using the B3LYP functional[26−28] and the 6-311G(p,d) basis set using the Gaussian09 software package.[29] We thus use a subset of the molecules used in the recent benchmark by Srebro et al.[19] and the basis set extrapolation study by Campos et al.[30] The magnetic dipole operator in eq 2 depends on the choice of gauge origin; however the gauge dependence of the optical rotations is avoided by using London atomic orbitals.[31] While a recent implementation of optical rotation with time-dependent London orbitals has been presented,[32] we use here the implementation of Ruud and Helgaker[9] in the DALTON program,[33] which applies standard time-independent London orbitals. The optical rotation for molecules 1−6 was calculated using the aug-pcS-n basis sets,[23] from the simplest (unpolarized) double-ζ (n = 0) to pentuple-zeta (n = 4) basis sets. Although results based on the aug-cc-pVDZ, aug-cc-pVTZ, and 6-311G(3df,3pd) basis sets are available in the literature, we have here repeated these calculations to avoid issues concerning program and geometry differences. We have further extended these calculations, such that 1−6 have been calculated with the aug-cc-pVXZ series where X = D, T, Q, and 5 and with the Pople basis set 6-311++G(3d,3p). For molecules 3 and 4, optical rotations have further been calculated using the regular polarization consistent basis set series, aug-pc-n with n = 0−4. The medium sized molecules 7−9 are computationally expensive with the pentuple sized basis set, especially during the response calculation of the G′ tensor, and were only done up to the quadruple-ζ basis sets (n = 3; X = Q). A set of calculations were also performed for 1−6 with aug-pcS-2, stripped for diffuse f functions (aug-pcS-2′). The total number of (contracted) basis functions is for each molecule 1−9 and the basis set given in the Supporting Information. In all calculations of optical rotations, the standard B3LYP functional or the long-range corrected CAM-B3LYP functional[34] was applied, using wavelengths of incident light at either 589.3 nm (sodium D line) or at 355.0 nm.

Table 1. Optical Rotation Basis Set Limits (deg/(dm g/mL)) Calculated with B3LYP[a]

fit (eq.)	basis	n/X	nm	parameters	1	2	3	4	5	6
4	aug-pcS-n	2,3,4	355.0	B	935.4	308.7		124.7		286.2
				C	1.7	1.4		3.8		3.3
5	aug-pcS-n	2,3,4	355.0	B	935.6	308.8		124.7		286.2
				C	5.6	4.3		12.3		11.1
5	aug-pcS-n	2,3	355.0	B	937.9	309.3	−39.5	127.6	249.8	287.0
5	aug-pcS-n	3,4	355.0	B	936.2	309.0	−43.0	124.8	249.7	286.2
5	aug-cc-pVXZ	T,Q	355.0	B	937.3	307.4	−42.8	125.1	251.5	286.5
5	aug-cc-pVXZ	Q,5	355.0	B	940.9	306.8	−44.0	124.8	247.9	285.6
4	aug-pcS-n	2,3,4	589.3	B	204.9	135.1		60.4		91.2
				C	0.8	2.5		3.6		3.6
5	aug-pcS-n	2,3,4	589.3	B	205 0.1	135.1		60.4		91.2
				C	2.1	8.4		12.3		12.5
	aug-pcS-n	2,3	589.3	B	204.9	135.6	−4.9	61.4	128.0	91.6
5	aug-pcS-n	3,4	589.3	B	205.0	135.1	−6.2	60.4	127.5	91.2
5	aug-cc-pVXZ	T,Q	589.3	B	205.1	134.7	−6.3	60.4	128.3	91.2
5	aug-cc-pVXZ	Q,5	589.3	B	205.7	134.6	−6.6	60.4	127.9	91.0

[a]Parameters B and C are given in eqs 4 and 5. The definition of aug-pcS-2′ is given in the Methods section.

Table 2. Optical Rotation Basis Set Limits (deg/(dm g/mL)) Calculated with CAM-B3LYP[a]

fit (eq.)	basis	n/X	nm	parameters	1	2	3	4	5	6
4	aug-pcS-n	2,3,4	355.0	B	796.5	352.5		131.7		241.5
				C	0.7	3.2		3.3		4.9
5	aug-pcS-n	2,3,4	355.0	B	797.2	352.5		131.7		241.5
				C	1.8	3.2		11.4		17.0
5	aug-pcS-n	2,3	355.0	B	796.2	352.6	−11.8	134.4	344.7	242.8
5	aug-pcS-n	3,4	355.0	B	796.5	352.6	−14.9	131.8	343.1	241.6
5	aug-cc-pVXZ	T,Q	355.0	B	797.6	351.6	−15.0	131.9	343.9	241.5
5	aug-cc-pVXZ	Q,5	355.0	B	799.9	351.3	−15.9	131.9	341.2	240.9
4	aug-pcS-n	2,3,4	589.3	B		130.4		55.1		78.4
				C		6.3		3.2		4.1
5	aug-pcS-n	2,3,4	589.3	B		130.4		57.1		78.4
				C		3.2		10.9		14.2
5	aug-pcS-n	2,3	589.3	B	184.2	130.7	−1.2	58.0	135.3	78.9
5	aug-pcS-n	3,4	589.3	B	184.7	130.5	−2.3	57.1	134.5	78.4
5	aug-cc-pVXZ	T,Q	589.3	B	184.8	130.2	−2.4	57.1	135.1	78.4
5	aug-cc-pVXZ	Q,5	589.3	B	185.2	130.1	−2.7	57.1	134.8	78.2

[a]Parameters B and C are given in eqs 4 and 5. The definition of aug-pcS-2′ is given in the Methods section.

The optical rotations in the basis set limit can be estimated by several fitting schemes. At the SCF level, the energy with increasing basis set size is expected to converge exponentially as, e.g., given by the Fellers three parameter fit.[35,36]

$$Y = A \exp(-XC) + B \qquad (4)$$

with X defined as the cardinal number (L_{max}). To the best of our knowledge, eq 4 has not been used as an extrapolation scheme for optical rotation but was recently used to determine the basis set limit for NMR spin−spin coupling constants, using the B3LYP functional.[37−40] An alternative to the exponential fitting scheme in eq 4 is the power extrapolation scheme

$$Y = AX^{-C} + B \qquad (5)$$

which is devised after the detailed derivations by Schwartz,[41] showing that the correlation energy contribution of an atomic orbital with angular momentum l falls off asymptotically as $(l + 1/2)^{-4}$. Equations 4 and 5 are here employed with variable exponents. In addition, we have also employed eq 5 with C fixed to 3.0,[42] while Truhlar has employed power extrapolation schemes with an empirical exponent.[43] It should be emphasized

that these power extrapolation schemes are devised for extrapolation of the basis set limit *correlation energy*. Since DFT is a single-determinant SCF method, the extrapolation scheme in eq 4 seems at first glance most prudent from a theoretical point of view. However, since both eq 4 and eq 5 are derived with respect to energies, there is no rigorous theoretical justification for either of the two extrapolation schemes when applied to properties. Furthermore, a recent investigation for atomization energies has shown that none of the proposed extrapolation methods stand out as being uniquely best.[44] Accordingly, both types of schemes are here investigated. To avoid a three point fitting procedure, a two point extrapolation formula is frequently invoked.[45,46] This method has for instance been used with eq 5 for estimation of optical rotation basis set limits[30] using the AXZP basis sets.[47,48] The basis set limits have here also been calculated using a two-point extrapolation formula based on eq 5.

■ RESULTS AND DISCUSSION

We will first focus on the basis set limits and fits obtained with eqs 4 and 5. The next subsections consider basis economy and
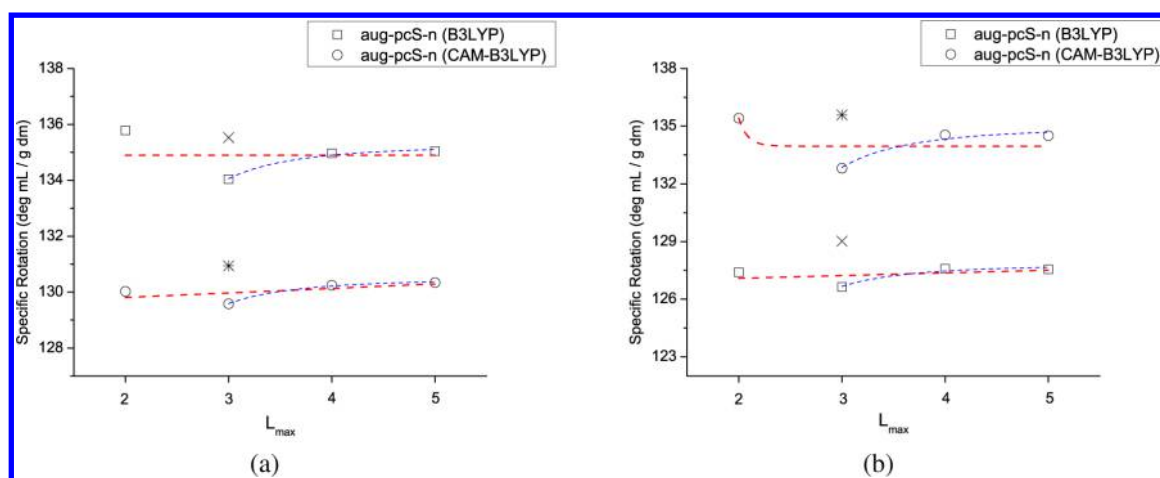
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Figure 2. aug-pcS-n basis set fits to eq 4 at 589.3 nm. The red line shows fits for n = 1, 2, 3, and 4 with eq 4. Fits for eq 5 using n = 2, 3, and 4 are shown in blue. (a) (S)-dimethyl allene (**2**) and (b) (R,R)-dimethyl thiirane (**5**). Results for the aug-pcS-2′ basis set (omitting diffuse f functions) are marked with (×) (B3LYP) and (∗) (CAM-B3LYP).

Table 3. B3LYP Optical Rotation (deg/(dm g/mL)) Calculated at 589.3 nm[a]

fit (eq.)	n/X	basis	1	2	3	4	5	6	MAD
	1	aug-pcS-1	199.1	135.8	−0.3	65.0	127.4	94.2	4.5
	2	aug-pcS-2	204.2	134.0	−7.8	58.9	126.6	90.6	1.4
	2	aug-pcS-2′	202.7	135.5	−4.6	60.3	129.0	92.6	1.2
5	1,2	aug-pcS-n	206.3	133.3	−11.0	56.3	126.5	89.1	2.6
5	1,2′	aug-pcS-n′	204.2	135.4	−6.4	58.3	129.7	91.9	1.1
5	3,4	aug-pcS-n	205.0	135.1	−6.2	60.4	127.5	91.2	0
5	T,Q	AXZP[b]		140.7	−5.8	43.9	131.3	92.5	(5.5)
	D	aug-cc-pVDZ[c]	200.2	131.2	13.6	75.8	165.8	102.7	15.6
	T	aug-cc-pVTZ[c]	199.5	134.3	−2.1	62.5	135.7	93.9	3.9
		6-311G++(3df,3pd)	199.3	124.9	−1.0	61.0	140.7	95.1	6.4
exptl.[d]				81.0	57.6	58.8	129.0	103.8	

[a]The definition of aug-pcS-2′ is given in the Methods section. [b]Study by Campos et al.[30] [c]The reported values are within 5 deg/(dm g/mL) of those reported by Stevens et al.[49] An exception is **3**, which has been reported to be sensitive to the specifications used under geometry optimization[19] [d]Experimental values are taken from refs 50−54.

the obtained basis set limits in relation to previous benchmarks for molecules **1−6**, and in relation to other basis set series. Finally, the medium sized molecules α-pinene (**7**), β-pinene (**8**), and camphor (**9**) are considered. It should be noted that while **2−6** are conformationally rigid molecules, **1** is conformationally flexible. The basis set convergence will most likely be similar in the different conformers, and only one conformer is considered here. But in order to compare directly with experimental results, several conformers would have to be considered.

Fitting Schemes. Since aug-pcS-0 is a double-ζ basis set without polarization functions, it is not expected to be capable of describing the electric dipole operator. Our results confirm this, and results and fits using aug-pcS-0 will not be discussed. Extrapolations using an exponential or a power form with the exponent, C, as a fitting parameter require three points for determining the fitting parameters and can only be done if the three points show a monotonic change in the calculated optical rotation. For the three largest members of the of the aug-pcS-n series (n = 2, 3, 4), the latter criterion is not fulfilled for molecules **3** and **5** for any of the used functionals and wavelengths of incident light, nor for molecule **1** with CAM-B3LYP at 589.3 nm of incident light. The power form with a fixed exponent is a two point fit and can be employed for any two results. We thus compare the basis set limit obtained by

either a three point exponential or power form with n = 2, 3, and 4 and by a two point power form with a fixed power of 3 for n = 3 and 4. These results are shown in Tables 1 (B3LYP) and 2 (CAM-B3LYP). The basis set limits for molecules **2−6** are in good agreement with the limits from ref 30. Selected fits are illustrated in Figure 2 for molecules **2** and **5**. While the optical rotation for these two molecules does not exhibit any dramatic basis set effect at 589.0 nm of incident light, this changes drastically at 355.0 nm (not shown in the figure). This drastic change is a general observation for molecules **1−6** and the aug-pcS-n basis set series (see Figures 1−6 in the Supporting Information). Another general observation is that the aug-pcS-3 and aug-pcS-4 results are very similar, which indicates that the aug-pcS-4 results are very close to the basis set limit. It appears that the change from aug-pcS-1 to aug-pcS-2 in most cases tends to slightly overestimate the remaining basis set error. The three point fits obtained with variable exponent C gives a wide spread in C values, which suggests that the fitting schemes should be viewed as mere fitting functions, at least for the small set of molecules investigated here. The results in Table 1 show that there is very little difference between using either extrapolation schemes, and we will in the following take the basis set limit as the value obtained by extrapolating the aug-pcS-3 and -4 results using eq 5 with C = 3.0. A final general observation that should be commented

Table 4. CAM-B3LYP Optical Rotation (deg/(dm g/mL)) Calculated at 589.3 nm[a]

fit (eq.)	n/X	basis	1	2	3	4	5	6	MAD
	1	aug-pcS-1	181.4	130.0	3.3	62.5	135.4	81.4	2.2
	2	aug-pcS-2	184.6	129.6	−3.6	55.7	132.8	77.7	1.1
	2	aug-pcS-2′	183.7	130.9	−1.0	57.0	135.6	79.5	0.9
5	1,2	aug-pcS-n	185.9	129.4	−6.4	52.8	132.4	76.2	1.1
5	1,2′	aug-pcS-n′	184.6	131.3	−2.8	54.6	135.6	78.7	1.2
5	3,4	aug-pcS-n	184.7	130.5	−2.3	57.1	134.5	78.4	0
	D	aug-cc-pVDZ[b]	182.3	126.5	15.5	71.0	169.2	87.0	13.6
	T	aug-cc-pVTZ[b]	180.7	130.0	1.5	58.7	140.8	80.1	6.3
		6-311G++(3fd,2dp)	178.6	122.0	2.8	58.0	144.8	82.5	10.3
exptl.[c]				81.0	57.6	58.8	129.0	103.8	

[a]The definition of aug-pcS-2′ is given in the Methods section. [b]The reported values are similar to those reported by Stevens et al.[49] [c]Experimental values are taken from refs 50−54.

Table 5. B3LYP Optical Rotation (deg/(dm g/mL)) Calculated at 355.0 nm[a]

fit (eq.)	n/X	basis	1	2	3	4	5	6	MAD
	1	aug-pcS-1	897.1	314.3	−18.1	139.04	277.8	299.7	20.8
	2	aug-pcS-2	929.6	307.0	−47.1	120.5	255.7	285.0	4.0
	2	aug-pcS-2′	924.2	311.5	−37.2	124.8	267.1	291.2	7.2
5	1,2	aug-pcS-n	943.2	303.9	−59.4	112.7	252.5	278.8	8.4
5	1,2′	aug-pcS-n′	935.6	310.3	−45.3	118.8	262.6	287.6	7.1
5	3,4	aug-pcS-n	936.2	309.0	−43.0	124.8	249.7	286.2	0
	D	aug-cc-pVDZ	904.4	291.8	30.4	170.8	411.7	328.7	62.2
	T	aug-cc-pVTZ	909.9	305.8	−26.0	132.3	298.3	298.8	9.2
		6-311G++(3fd,3dp)	916.4	279.5	−26.4	123.9	296.2	295.7	20.5

[a]The definition of aug-pcS-2′ is given in the Methods section.

upon in this subsection is that while the limiting values are very similar for the aug-cc-pVXZ and aug-pcS-n basis sets, the convergence is significantly faster with the aug-pcS-n basis sets, as will be discussed further in a following subsection.

Figure 2 shows that the use of the aug-cc-pcS-1 or aug-pcS-2 basis sets leads to results for the optical rotation on either side (overestimated/underestimated, respectively) of the basis set limits, and we have investigated the origin for this. Removal of the diffuse f function, thereby defining the aug-pcS-2′ basis set, removes the underestimation of the optical rotation and, excluding the $n = 1$ based results, leads to a monotonic convergence toward the basis set limit. Unfortunately, the results with the aug-pcS-2′ basis set are often worse than with the unmodified basis set.

The results obtained by a two point extrapolation using n = 2 and 3 or n = 3 and 4 differ only slightly from exponential or power regression fits with n = 2, 3, and 4. For large systems where the aug-pcS-4 basis set is computationally infeasible, the basis set limit can thus be estimated from aug-pcS-2 and -3 results. Extrapolation using aug-pcS-1 and -2′ results is not recommended, and as shown in the following, extrapolation using aug-pcS-1 and aug-pcS-2′ results appears to be inferior to raw aug-pcS-2 results, especially when both wavelengths of incident light are considered.

Basis Set Economy versus Accuracy at 589.3 nm for Molecules 1−6. The basis set limits for the six small molecules **1−6** have been compiled in Tables 3 (B3LYP results) and 4 (CAM-B3LYP results) along with results using the aug-pcS-n, aug-cc-pVDZ, aug-cc-pVTZ, and 6-311G++(3df,3pd) basis sets. Further, the experimental optical rotations (at 589.3 nm) are also given for molecules **2−6**. The performance is quantified by the mean absolute deviation (MAD) relative to the basis set limit results. The basis set

errors using the aug-cc-pVDZ basis set are in several cases quite significant; for example, the calculated optical rotation for (R,R)-dimethyl thiirane (**5**) is around 40 deg/(dm g/mL) too high compared to the basis set limit. The aug-cc-pVTZ basis set provides results closer to the basis set limit. The aug-pcS-1 basis set provides results better than or similar to all of the above three basis sets, despite being of similar size as the aug-cc-pVDZ (see Table 4 in the Supporting Information).

In the previous subsection, it was noted that the aug-pcS-2 basis set somewhat underestimated optical rotations with respect to the basis set limit, in severe cases leading to nonmonotonic convergence. In an attempt to at least obtain a more monotonic convergence, the most diffuse f function was removed from the aug-pcS-2 basis set, leading to the definition of the aug-pcS-2′ basis set. Extrapolations (1 and 2′ in Tables 3 and 4) using this basis set do in fact improve the extrapolated values (for the B3LYP results), albeit by only a small margin. However, we cannot recommend this procedure, and it is more consistent to use the full aug-pcS-2 basis set, which is more reliable for the lower wavelength (355.0 nm) of incident light, as shown in the following subsection.

Unfortunately, the good performance of the aug-pcS-n basis sets compared to aug-cc-pVDZ does not necessarily lead to an improved optical rotation with respect to experimental values. For instance, the B3LYP optical rotation in the case of (R,R)-dimethyl aziridine (**6**) with the aug-cc-pVDZ basis set leads to an optical rotation close to the experimental value, in contrast with the basis set limit. One of the more severe cases is (R,R)-dimethyl cyclo propane (**3**) where the gas-phase basis set limit does not even reproduce the experimental sign of the optical rotation, irrespective of whether the B3LYP or the long-range corrected CAM B3LYP functionals are used. Although still far from the experimental value, the aug-cc-pVDZ basis set

Table 6. CAM-B3LYP Optical Rotation (deg/(dm g/mL)) Calculated at 355.0 nm^a

fit (eq.)	n/X	basis	1	2	3	4	5	6	MAD
	1	aug-pcS-1	772.5	350.8	7.6	148.1	369.1	252.17	15.3
	2	aug-pcS-2	793.7	350.6	−17.9	127.7	344.1	239.60	1.5
	2	aug-pcS-2′	790.6	353.9	−10.1	131.4	356.2	245.1	4.9
5	1,2	aug-pcS-n	802.7	350.6	−28.7	119.1	333.6	234.3	7.4
5	1,2′	aug-pcS-n′	798.2	355.2	−17.6	124.4	350.8	242.1	6.0
5	3,4	aug-pcS-n	796.5	352.6	−14.9	131.8	343.1	241.6	0
	D	aug-cc-pVDZ	777.9	334.5	49.2	172.9	487.2	271.2	144.1
	T	aug-cc-pVTZ	778.4	349.7	−0.2	137.1	380.0	248.9	37.0
		6-311++G(3fd,3dp)	776.5	327.9	2.9	132.6	383.8	252.6	40.7

^{a}The definition of aug-pcS-2′ is given in the Methods section.
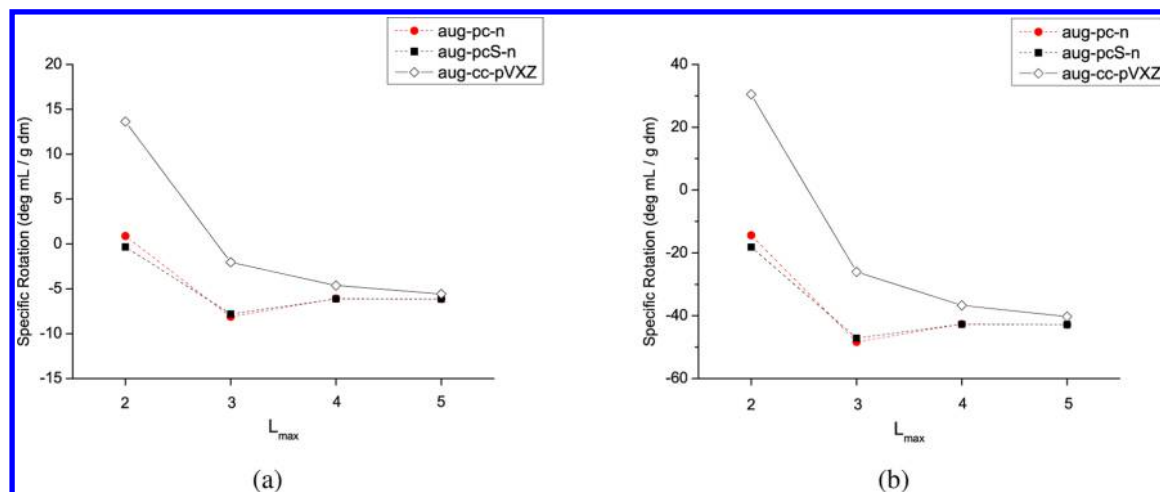

Figure 3. Basis set convergence (B3LYP results) for aug-pcS-n vs aug-pc-n and aug-cc-pVXZ at (a) 589.3 nm and (b) 355 nm for dimethylmethylene cyclopropane (**3**).

provides the correct sign. The results using larger basis sets show that the aug-cc-pVDZ basis set errors in these cases lead to fortuitous better agreements with experimental results.

It should be noted that all of the reported experimental values at 589.3 nm are from the condensed phase, while the computational results refer to gas phase conditions. Examples where the effect of solvation is substantial are known experimentally,[55] and the effect has been studied with a continuum solvent model, such as PCM.[56] Apart from inclusion of solvents, also ro-vibrational corrections have previously been shown to have substantial effects on optical rotations.[11,57−59] Finally, Boltzmann averaging is occasionally necessary for molecules with contributions from several possible conformers. This is for instance the case for (S)-3-chlorobut-1-ene (**1**).[11,60,61]

Basis Set Economy versus Accuracy at 355.0 nm for Molecules 1−6. To the best of our knowledge, extrapolations to the basis set limit have not been performed at 355.0 nm as both experimental and computational studies of optical rotation are usually carried out at the sodium D line (589.3 nm). From Tables 5 and 6, it is seen that the basis set requirements are more severe at 355.0 nm compared to 589.3 nm. The use of the aug-pcS-1 basis set is usually not sufficient to obtain an optical rotation within an acceptable margin of the converged result. Errors around 30 deg/(dm g/mL) are not uncommon for the molecules **1−6**. Occasionally, even the basis set of triple-ζ quality, aug-pcS-2, is a bit off the basis set limit. Even worse are the results for the aug-cc-pVDZ and aug-cc-pVTZ basis sets: The aug-cc-pVDZ basis set is for all of the molecules **1−6**

significantly off the basis set limit and in severe cases by over 150 deg/(dm g/mL). Some improvement is gained by moving to the aug-cc-pVTZ basis set, but the optical rotations with this basis set are still not satisfactory. The Pople-style basis set is intermediate between aug-cc-pVDZ and aug-cc-pVTZ in accuracy. Extrapolations using the aug-pcS-1 and aug-pcS-2 basis set results at 355.0 nm of incident light deteriorate the results relative to the raw aug-pcS-2. The aug-pcS-2′ basis set performs worse on average compared to aug-pcS-2, and extrapolations based on aug-pcS-1 and aug-pcS-2′ are also inferior to the aug-pcS-2 results.

Experimental results at 355.0 nm are scarce, and only results for (S)-3-chlorobut-1-ene (**1**) are available for the present set of molecules. The measured optical rotation of 259.4 deg/(dm g/mL) from ref 62 is far from the calculated basis set limiting values of 936 (B3LYP) and 797 (CAM-B3LYP). The disagreement is not surprising, as it has been shown by several authors that this molecule has several low-lying conformers, which contribute significantly to the measured optical rotation.[11,60,61]

Performance of the aug-pcS-n versus the aug-pc-n and aug-cc-pVXZ Series. The use of the aug-pcS-n basis sets is motivated by the form of the operators involved in calculating the optical rotation. However, for comparison purposes, we have also tested the full series of Dunning basis sets aug-cc-pVXZ (X = n + 1) for the molecules **1−6** and the regular aug-pc-n basis sets for (R,R)-dimethyl methylene cyclopropane (**3**) and (R,R)-dimethyl oxirane (**4**). The aug-pc-n and aug-pcS-n series converge very similarly for these two

Table 7. Optical Rotation (deg/(dm g/mL)) for Molecules 7−9 Calculated at 589.3 nm

fit (eq.)	n/X	basis	B3LYP			CAM-B3LYP		
			7	8	9	7	8	9
5	2,3	aug-pcS-n	43.6	−24.2	59.1	57.8	−4.3	42.6
	1	aug-pcS-1	45.0	−23.5	59.6	58.8	−4.0	43.1
	2	aug-pcS-2	44.2	−24.1	59.1	58.2	−3.9	42.7
5	T,Q	aug-cc-pVXZ	43.6	−23.8	59.2	57.8	−4.2	42.7
	D	aug-cc-pVDZ	44.3	−27.0	59.0	58.3	−6.5	42.5
	T	aug-cc-pVTZ	43.8	−23.9	58.9	58.1	−4.2	42.5
		6-311++G(3fd,2pd)	42.7	−22.8	58.2	56.9	−3.5	42.0
exptl.[a]			51	23.1	44.3	51	23.1	44.3

[a]Values reported by Grimme[15] and Stephens et al.[18]

Table 8. Optical Rotation (deg/(dm g/mL)) for Molecules 7−9 Calculated at 355.0 nm

fit (eq.)	n/X	basis	B3LYP			CAM-B3LYP		
			7	8	9	7	8	9
5	2,3	aug-pcS-n	100.5	−247.8	550.5	195.3	−111.4	344.7
	1	aug-pcS-1	102.4	−247.4	550.0	195.8	−110.4	346.8
	2	aug-pcS-2	102.7	−244.7	547.4	196.5	−109.7	343.9
5	T,Q	aug-cc-pVXZ	100.8	−246.0	550.0	195.2	−110.4	344.9
	D	aug-cc-pVDZ	97.4	−260.2	571.7	194.7	−120.0	358.7
	T	aug-cc-pVTZ	99.8	−248.1	546.9	195.6	−111.5	343.3
		6-311++G(3fd,2pd)	96.7	−243.8	546.3	192.1	−109.3	342.4
exptl.[a]			188.2	−69.7		188.2	−69.7	

[a]Taken from Wilson et al.[62]

cases (shown in Figure 3 for **3**). Whether this is a general feature will require a significantly larger test set of molecules. Since the aug-pcS-n basis sets are only marginally larger than the aug-pc-n, we recommend using the former.

As shown in the first section, the basis set limits for aug-cc-pVXZ and aug-pcS-n are very similar. However, as indicated by Figure 3, the aug-pcS-n basis sets converge faster, and aug-pcS-1 typically already provides quite reasonable values, compared to the basis set limit. This is the case for all of the molecules **1**−**6** (see Supporting Information). That the aug-cc-pVXZ basis sets are not always optimal for optical rotations has been shown previously by Baranowska et al.[63] These authors compared the aug-cc-pVXZ series up to high order using the nonexisting "chiral methane" in the basis set convergence studies

With respect to higher order ab initio methods, molecules **1**−**6** are within the reach of accurate couple cluster methods. The CCSD/aug-cc-pVDZ results for **4**, **5**, and **6** are 78.3, 156.0, and 93.5 deg/(dm g/mL),[64] which are in fair agreement with the present DFT results using the same basis set. A detailed investigation of the optical rotations from CCSD versus B3LYP with the aug-cc-pVTZ basis set has been done for 2-chloropropionitrile.[65] This showed that the optical rotation obtained from B3LYP was a factor of 2 too high. On the basis of the present results, it is likely that these CCSD results are not converged with respect to the basis set, and it is thus difficult to make a strict comparison between the performance of DFT and CCSD methods.

Basis Set Limits for Molecules 7−9 at 355.0 and 589.3 nm. The basis set limits of the optical rotations for the medium sized molecules **7**−**9** are presented at 589.3 nm (Table 7) and at 355.0 nm (Table 8) of incident light. As discussed previously, the extrapolated results for the optical rotation obtained by a two point extrapolation using $n = 2$ and 3 or $n = 3$ and 4 differ only slightly, and we will in the following estimate the basis set limit based on the aug-pcS-2 and -3 results. α-Pinene (**7**) is

generally not particularly sensitive to the choice of basis set, and the error introduced by using the aug-pcS-1 basis set is already quite small, even when considering the basis set limits at 355.0 nm. The aug-cc-pVTZ and the Pople-style basis sets also lead to results in reasonable agreement with the basis set limit at both wavelengths. β-Pinene (**8**) and camphor (**9**) are more sensitive to the choice of basis set, and at 355.0 nm the aug-cc-pVDZ basis set results are significantly off the basis set limit. The aug-pcS-1 basis set, on the other hand, is for both β-pinene and camphor much closer to the basis set limit at both wavelengths of incident light.

While condensed phase results only exist for **7**−**9** at 589.3 nm, gas-phase cavity ring-down polarimetry studies have been reported for **7** and **8** at 355.0 nm.[62] At 589.3 nm, both B3LYP and CAM-B3LYP give basis set limits in reasonable agreement with experimental results for α-pinene (**7**), while β-pinene (**8**) is more problematic at this wavelength, leading to the wrong sign, irrespective of the applied functional. At 355.0 nm, the long-range corrected functional leads to values quite close to experimental values for α-pinene (**7**), while β-pinene (**8**) again is somewhat problematic, although the correct sign is obtained for both of the functionals used. As emphasized in the previous subsections, a direct comparison between experimental results requires inclusion of ro-vibrational corrections (in absence of a solvent). Previous studies for α-pinene showed such corrections to be around 20 deg/(dm g/mL)[11] (aug-cc-pVDZ results).

■ CONCLUSION

The performance of the modified polarization consistent basis sets aug-pcS-n has been tested in calculations of optical rotation for nine small or medium sized molecules. The basis set limits have been estimated at the sodium D line (589.3 nm) and at 355 nm by an exponential (eq 4) and a power regression scheme (eq 5), as well as by simple two-point extrapolation

formulas. Two point extrapolations based on either n = 3 and 4 or n = 2 and 3 provide results very close to the basis set limit, while extrapolations based on n = 1 and 2 cannot be recommended. Use of the aug-pcS-1 basis set leads in most cases to results of sufficient quality at 589.3 nm, producing results which on average are 2−3 deg/(dm g/mL) from the basis set limit. A problematic case is (*R,R*)-dimethyl cyclopropane (**3**), where it already at 589.3 nm becomes necessary to move to the aug-pcS-2 basis sets in order to obtain a value close to the basis set limit. The present study further shows that the aug-pcS-1 basis set is to be preferred over aug-cc-pVDZ or the Pople-style basis sets, which often deviates significantly from the basis set limit. This is especially critical at 355.0 nm, where the basis set requirements are more severe. At this wavelength, it is recommended to use basis set of at least triple-ζ quality, as the aug-pcS-1 results can be up to 20% in error and the maximum deviation around 40 deg/(dm g/mL), while the aug-pcS-2 basis set yields optical rotations within 5% of the basis set limit. These considerations regarding different basis set requirements at different wavelengths become important for calculation of optical rotation in medium or large molecules, where the larger basis sets are not affordable. Furthermore, the different basis set behavior at different wavelengths is important when comparing computed optical rotations with experimental results. Since different basis sets for some molecules can lead to a change in sign of the optical rotation (*c.f.* **3** in Table 3), it is advisable to use a multifrequency approach when comparing measured and calculated optical rotations. For this comparison to make sense, the optical rotation must be described equally well at all frequencies, and the aug-pcS-2 basis set would appear to be suitable for this purpose. If the aug-pcS-2 is computationally infeasible, the aug-pcS-1 also performs reasonably, but at 355.0 nm its performance can lead to some errors. The higher sensitivity at 355.0 nm is presumably due to the fact that the manifold of excitation energies are more dense around this wavelength, thus making the response formalism more sensitive to basis set quality. The two employed exchange-correlation functionals display the same basis set convergence but result in different predictions for the optical rotations, and these often differ significantly from experimental values.

It is clear that the effects of different exchange-correlations functionals as well as solvent effects and ro-vibrational corrections should be taking into account before a strict comparison between calculated and experimental values is possible. On the basis of the present work, we suggest that the aug-pcS-1 or aug-pcS-2 basis sets may be suitable for such investigations. The advantage of being able to use smaller basis sets in such calculations is, apart from being able to investigate larger systems, that also using a series of snapshots from MD simulations combined with Boltzmann averaging procedures becomes tractable.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Table 1: Statistics over optical rotation calculations for molecules 1−6. Table 2: Results with the modified aug-pcS-3′ basis set versus the original aug-pcS-3 basis set (B3LYP). Table 3: Results with the modified aug-pcS-3′ basis set versus the original aug-pcS-3 basis set (CAM-B3LYP). Table 4: Number of basis set functions for molecules 1−9 with aug-cc-pVXZ and aug-pcS-n basis sets. Figures 1−6: Convergence of aug-cc-pVXZ basis sets versus aug-pcS-n. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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