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Ab Initio Optical Rotatory Dispersion and Electronic Circular Dichroism Spectra of (*S*)-2-Chloropropionitrile

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Coupled-cluster and density-functional methods have been used to determine specific rotations and electronic circular dichroism (ECD) rotational strengths for (*S*)-2-chloropropionitrile. Coupled-cluster specific rotations using both the length- and velocity-gauge representations of the electric-dipole operator, computed with basis sets of triple-ζ quality containing up to 326 functions, compare very well with recently reported gas-phase cavity-ring-down polarimetry data. ECD rotational strengths for the six lowest-lying excited states are found to vary in sign, and the second excited state, which has a larger rotational strength than the first by a factor of 4, was found to yield a much larger contribution (by a factor of 10) to the overall negative specific rotation observed both experimentally and theoretically. However, both valence and Rydberg states appear to make substantial contributions to the total rotation, often of opposite sign from the converged/linear-response result. Furthermore, the sum-over-states approach was found to be inadequate for reproducing the specific rotations derived from the linear-response approach, even when 100 excited states (well beyond the estimated ionization limit) were included in the summation. Density-functional specific rotations using the B3LYP functional with basis sets of quadruple-ζ quality containing up to 588 functions are found to be too large compared to experiment by approximately a factor of 2. This error appears to be related to both the underestimation of the electronic excitation energies, as well as concomitant overestimation of the corresponding ECD rotational strengths. Although earlier studies reported good agreement between density-functional specific rotations and experiment when electric-field-dependent functions were used in conjunction with a double-ζ-quality basis set, the results reported here, which are near the basis-set limit, suggest that this agreement may be fortuitous.

1. Introduction

Enantiomeric pairs of chiral molecules exhibit distinct stereospecific responses to polarized light, whether in absorption, refraction, or scattering.[1] These responses may be used to determine the absolute configuration of an enantiomerically pure sample, provided sufficient information is available a priori about the corresponding circular dichroism, birefringence, or scattering intensity differences. Unfortunately, such information can often be obtained only following X-ray analysis of high-quality single-crystal samples or asymmetric/rational synthesis of the target enantiomer, a time-consuming task, especially for cases involving large numbers of possible stereoisomers.[2]

In recent years, state-of-the-art ab initio quantum chemical methods[3,4] have been extended to include calculations of chiro-optical properties such as optical rotation and circular dichroism spectra in the hope that such first-principles calculations might provide an alternative approach for the assignment of absolute configuration. The quantum mechanical foundations for such computations were laid more than 75 years ago by Rosenfeld, who demonstrated that the electric dipole moment of an isolated chiral molecule induced by a polarized electromagnetic field depends not only on the usual electric-dipole polarizability tensor, but also on the mixed electric-dipole/magnetic-dipole polarizability tensor,[5]

$$G'_{\alpha\beta}(\omega) = -\frac{2}{\hbar}\sum_{n\neq 0}\frac{\omega}{\omega_{n0}^2 - \omega^2} Im(\langle 0|\mu_\alpha|n\rangle\langle n|m_\beta|0\rangle) \quad (1)$$

where ω is the field angular frequency, $|0\rangle$ and $|n\rangle$ denote the ground and excited electronic states, respectively, $\mu = \Sigma_i e_i \boldsymbol{r}_i$ is the length-gauge representation of the electric-dipole operator and $\boldsymbol{m} = \Sigma_i e_i/2m_i \boldsymbol{r_i} \times \boldsymbol{p_i}$ is the magnetic-dipole operator. The trace of this tensor is related to the specific rotation—the optical rotation, normalized for path length and concentration—of nonoriented (i.e., liquid- or gas-phase) samples, and its residues provide the rotatory strength associated with electronic circular dichroism (ECD) spectra.

The first ab initio calculations of the Rosenfeld optical activity tensor were reported in 1986 by Lazzeretti and Zanasi using time-dependent Hartree−Fock theory for the water molecule (for which the off-diagonal elements of the tensor may be nonzero).[6] The first ab initio calculations of optical rotation were carried out at the Hartree−Fock level by Polavarapu in 1997[7] using a “static-limit” approximation to the Rosenfeld tensor developed by Amos in 1982.[8] The first such calculations of ECD rotatory strengths were reported some thirteen years earlier by Rauk using truncated configuration interaction models[9] and by Hansen and Bouman using time-dependent Hartree−Fock theory.[10] The current state-of-the-art in theoretical calculations of electronic chiro-optical properties includes both density-functional theory (DFT)[11] and coupled-cluster theory[12,13] for optical rotation[14−23] and ECD rotatory spectra.[24−29] Reviews of the theoretical underpinnings and history of ab initio chiro-

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optical techniques, as well as some recent important applications, may be found in refs 30−33.

One of the major obstacles in the development of accurate theoretical models of chiro-optical properties, however, is the problematic comparison with experimental data, due to the wide variety of conditions under which optical rotation angles and ECD spectra are obtained. It is well-known, for example, that solvent and temperature effects can be significant for specific rotation, even resulting in changes in the sign of the rotation between polar and nonpolar solvents for species such as methyloxirane.[20,22,34,35] Although theoretical models of solvation effects have advanced considerably in the past decade,[36,37] they are not yet capable of the level of accuracy needed for reliable predictions of chiro-optical properties.[22,38,39]

In 2000, Muller, Wiberg, and Vaccaro reported the first quantitative measurements of optical rotation of gas-phase samples using their newly developed technique of cavity ring-down polarimetry.[40] They have since applied this new experimental approach to a wide array of small molecules,[40−42] thus providing benchmark specific rotation data free of the "veil of solvation" that will likely prove to be invaluable in the development of new theoretical techniques.

This work focuses on the small, conformationally rigid molecule, (*S*)-2-chloropropionitrile, for which Wiberg et al. recently measured the gas-phase specific rotation at 633 and 355 nm, $[\alpha]_{633} = -6.8 \pm 2.3$ deg dm^{-1} (g/mL)$^{-1}$ and $[\alpha]_{355} = -37.9 \pm 2.9$ deg dm^{-1} (g/mL)$^{-1}$, as well as the neat-state specific rotation at the sodium D-line, $[\alpha]_{589} = -14.5$ deg dm^{-1} (g/mL)$^{-1}$.[41] They further noted that solvent effects were considerable in this case and reported $[\alpha]_{589}$ values ranging from -11.6 deg dm^{-1} (g/mL)$^{-1}$ in acetonitrile to -34.6 deg dm^{-1} (g/mL)$^{-1}$ in benzene, as compared to an interpolated gas-phase value of -8.3 deg dm^{-1} (g/mL)$^{-1}$. Comparison of these results with DFT-based optical rotation data (B3LYP) revealed significant basis-set effects: split-valence and correlation consistent basis sets up to the triple-ζ level produce specific rotations more than a factor of 2 larger than their experimental counterparts. However, Wiberg et al. further observed that the addition of electric-field-dependent (EFD) functions to the correlation-consistent double-ζ basis set, using the protocols developed by Darling and Schlegel,[43] reduced the computed rotations to within the experimental error bars.

In a recent study comparing high-level ab initio (coupled-cluster) and density-functional (B3LYP) specific rotation data to gas-phase results of Wilson et al. for the conformationally flexible chiral molecule epichlorohydrin, we found that the coupled-cluster singles and doubles method in conjunction with large one-electron basis sets was capable of reproducing the experimental rotations to within less than 1% using the length-gauge representation of the electric dipole operator and to within 6% using the modified velocity-gauge representation.[44] In addition, we found that, similarly to the work of Wiberg et al. for 2-chloropropionitrile, the B3LYP approach overestimated the rotations of the individual conformers as well as the Boltzmann-weighted rotation.

The present study seeks to answer several fundamental questions regarding the ability of quantum chemical models to reproduce the experimental gas-phase specific rotation of (*S*)-chloropropionitrile. First, are the DFT results of Wiberg et al. robust? That is, does the addition of EFDs serve to advance the B3LYP method more rapidly toward the complete-basis-set (CBS) limit? If not, what is the nature of the underlying problem in the DFT approach? Second, how do convergent coupled-cluster methods perform for this property, and is their basis-set convergence behavior similar to that of DFT? How do origin-independent velocity-gauge and origin-dependent length-gauge representations of the coupled-cluster Rosenfeld tensor (vide infra) compare? Is the basis-set dependence of coupled-cluster methods similar to that observed by Wiberg et al. for DFT? To address these questions, we have carried out a series of coupled-cluster and density-functional calculations of optical rotatory dispersion and electronic circular dichroism rotational strengths of (*S*)-chloropropionitrile with a hierarchy of correlation-consistent basis sets.

II. Computational Methods

Optical rotation calculations for several wavelengths were carried out for (*S*)-chloropropionitrile using coupled-cluster frequency-dependent linear-response theory[45,46] at both the CC2[47] and the singles and doubles (CCSD) levels of theory,[48,49] as well as with time-dependent density-functional theory (TD-DFT)[50,51] with the B3LYP functional.[14,52−54] For the coupled-cluster methods, two representations were used for the electric-dipole operator: the standard length-gauge approach, for which the specific rotation is inherently origin-dependent, and the velocity-gauge approach, which gives origin-independent results. For the former, center of mass was chosen as the origin, whereas for the latter, we report the "modified velocity-gauge" approach of Pedersen et al., for which the specific rotation computed at a given field frequency is shifted by its zero-frequency counterpart.[55] The B3LYP data were obtained using gauge-including atomic orbitals (GIAOs) and are thus origin independent.[14]

In addition, excitation energies and ECD rotational strengths for the six lowest-lying electronically excited states of (*S*)-2-chloropropionitrile were computed using equation-of-motion CC (EOM-CC)[56] theory and the corresponding TDDFT/B3LYP approach.[50,51] The excitation frequencies coincide with the positions of first-order poles in the specific rotation [cf. eq 1], whose sign and widths are related to the corresponding ECD rotational strengths (i.e., Cotton poles).[1] Rotational strengths are reported using both length- and velocity-gauge representations of the electric-dipole operator for all three levels of theory. The EOM-CC rotational strengths reported here have been determined using transition-strength expressions analogous to those described by Stanton and Bartlett.[56]

Several basis sets were used in this work, including the Sadlej triple-ζ basis set (174 functions), which was designed for electric-field-dependent properties such as dipole polarizabilities[57−59] and the correlation-consistent basis sets of Dunning and co-workers.[57,60−62] For the latter, with the coupled-cluster methods, we used the aug-cc-pVDZ basis set (155 functions), a "mixed" doubly augmented double-ζ basis set with d-aug-cc-pVDZ on C, N, and H and aug-cc-pVDZ on Cl, which we label d-aug-cc-pVDZ* (207 functions), and the aug-cc-pVTZ basis set (326 functions). B3LYP optical rotation calculations were carried out with these and larger basis sets, including a "mixed" doubly augmented triple-ζ basis set with d-aug-cc-pVTZ on C, N, and H and aug-cc-pVTZ on Cl, which we label d-aug-cc-pVTZ* (426 functions), as well as the aug-cc-pVQZ basis set (588 functions). These latter basis sets appear to be close to the complete basis-set limit for the B3LYP functional (vide infra).

Core orbitals (1s on C and N, and 1s, 2s, and 2p on Cl) were held frozen in all CC2 and CCSD calculations reported here. All coupled-cluster optical rotation, excitation-energy, and ECD calculations were carried out with the PSI3 program package,[63] whereas the corresponding B3LYP calculations, as well as all

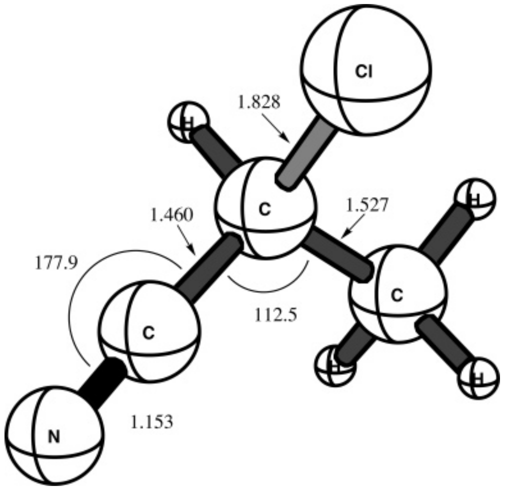

Figure 1. Key parameters of the B3LYP/6-311++G** optimized geometry of (*S*)-2-chloropropionitrile, which was used for all optical rotation and ECD calculations reported in this work. Bond lengths are given in Angstroms, and bond angles are given in degrees.

DFT geometry optimizations and harmonic vibrational frequency calculations were carried out with the Gaussian suite.[64]

III. Results and Discussion

The optimized geometry of (*S*)-2-chloropropionitrile (see Figure 1) was determined using analytic energy gradients at the B3LYP[11,52,53] level of theory with the split-valence 6-311++G** basis set,[57,65−67] which is the same level used by Wiberg et al.[41] This optimized structure was confirmed to be a minimum on the potential energy surface via harmonic vibrational frequency calculations, carried out using analytic energy second-derivative methods. The computed rotational constants compare to within 1.3% with those determined by Ogata et al. from the experimental microwave spectrum.[68] The corresponding theoretical structure agrees reasonably well with that inferred from the microwave data, with C−C bond distances reproduced to within a few thousandths of an Angstrom. However, the B3LYP/6-311++G** C−Cl bond distance of 1.828 Å is somewhat longer than its experimental counterpart of 1.791 Å, in agreement with earlier calculations.[41]

Tables 1 and 2 report the computed specific rotations of (*S*)-2-chloropropionitrile at the CC2 and CCSD levels of theory, respectively, at wavelengths of 633, 589, 436, and 355 nm. As expected, the rotations increase in magnitude—from −9.9 at 633 nm to −40.6 at 355 nm at the CCSD/aug-cc-pVTZ level of theory—as the wavelength decreases, indicating the onset of a Cotton pole as the field frequency approaches that of the lowest-lying excited states. CC2 and CCSD length-gauge rotations agree very well with one another in this case, differing by only 2.0 with the aug-cc-pVTZ basis set. The CC2 and CCSD velocity-gauge rotations differ more substantially, up to 12.1 at 355 nm with the d-aug-cc-pVDZ* and Sadlej-pVTZ basis sets.

Of particular interest, however, is the convergence of these methods with respect to basis set. The difference between the aug-cc-pVDZ and aug-cc-pVTZ rotations is relatively small for both CC2 and CCSD, with a maximum shift of 8.4 deg dm^{-1} (g/mL)$^{-1}$ at 355 nm. The shift between the aug-cc-pVDZ and d-aug-cc-pVDZ* basis sets is similar to that between the aug-cc-pVDZ and aug-cc-pVTZ sets, though a second set of diffuse functions on the triple-ζ basis will likely produce a much smaller incremental change from the aug-cc-pVTZ results in Tables 1 and 2 (vide infra). It is likely that the aug-cc-pVTZ results for both methods are within a few degrees of the basis set limit for both methods.

Both CC2 and CCSD also compare well to the experimental gas-phase rotations reported by Wiberg et al.[41] Indeed, at the CCSD level, the velocity-gauge CCSD/aug-cc-pVTZ result of −8.0 deg dm^{-1} (g/mL)$^{-1}$ lies within the experimental error bars

TABLE 1: CC2 Specific Rotation [In deg dm^{-1} (g/mL)$^{-1}$] for (*S*)-2-Chloropropionitrile[a]

λ (nm)	aug-cc-pVDZ	d-aug-cc-pVDZ*[c]	aug-cc-pVTZ	Sadlej-pVTZ	Experiment[d]
		Length gauge[b]			
633	−6.7	−9.4	−8.9	−10.0	−6.8 ± 2.3
589	−7.9	−11.1	−10.5	−11.7	
436	−16.8	−22.9	−21.8	−24.0	
355	−30.2	−40.0	−38.6	−41.6	−37.9 ± 2.9
		Modified velocity gauge			
633	−8.5	−11.5	−10.7	−11.4	−6.8 ± 2.3
589	−10.0	−13.5	−12.6	−13.4	
436	−20.8	−27.6	−25.9	−27.4	
355	−36.8	−47.4	−45.1	−47.3	−37.9 ± 2.9

[a] Computed at the B3LYP/6-311++G** optimized geometry. [b] The center of mass was used as the coordinate origin. [c] d-aug-cc-pVDZ(H,C,N) + aug-cc-pVDZ(Cl). [d] Ref 41.

TABLE 2: CCSD Specific Rotation [In deg dm^{-1} (g/mL)$^{-1}$] for (*S*)-2-Chloropropionitrile[a]

λ (nm)	aug-cc-pVDZ	d-aug-cc-pVDZ*[c]	aug-cc-pVTZ	Sadlej-pVTZ	experiment[d]
		Length gauge[b]			
633	−7.9	−10.3	−9.9	−11.0	−6.8 ± 2.3
589	−9.3	−12.1	−11.7	−12.9	
436	−19.0	−24.4	−23.6	−25.9	
355	−32.9	−41.6	−40.6	−43.9	−37.9 ± 2.9
		Modified velocity gauge			
633	−5.8	−8.5	−8.0	−8.4	−6.8 ± 2.3
589	−6.8	−10.0	−9.4	−9.9	
436	−14.4	−20.4	−19.5	−20.3	
355	−25.8	−35.3	−34.0	−35.2	−37.9 ± 2.9

[a] Computed at the B3LYP/6-311++G** optimized geometry. [b] The center of mass was used as the coordinate origin. [c] d-aug-cc-pVDZ(H,C,N) + aug-cc-pVDZ(Cl). [d] Ref 41.

TABLE 3: B3LYP Specific Rotation[a] [In deg dm^{-1} (g/mL)$^{-1}$] for (*S*)-2-Chloropropionitrile[b]

λ (nm)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	d-aug-cc-pVDZ*[c]	d-aug-cc-pVTZ*[d]	Sadlej-pVTZ	experiment[e]
633	−12.3	−15.7	−15.7	−16.0	−14.6	−14.0	−6.8 ± 2.3
589	−14.6	−18.5	−18.6	−18.9	−17.3	−16.5	
436	−31.7	−39.3	−39.5	−40.1	−37.0	−35.5	
355	−59.1	−71.6	−72.1	−72.9	−68.1	−65.5	−37.9 ± 2.9

[a] Using the origin-invariant GIAO-based approach with the length-gauge representation of the electric-dipole operator as described in ref 14. [b] Computed at the B3LYP/6-311++G** optimized geometry. [c] d-aug-cc-pVDZ(H,C,N) + aug-cc-pVDZ(Cl) [d] d-aug-cc-pVTZ(H,C,N) + aug-cc-pVTZ(Cl). [e] Ref 41.

for $[\alpha]_{633}$ of −6.8 ± 2.3, whereas the corresponding length-gauge results of −9.9 deg dm^{-1} (g/mL)$^{-1}$ lie slightly above these bounds. At the shortest wavelength, the length- and velocity-gauge CCSD/aug-cc-pVTZ results closely bracket the experimental value of $[\alpha]_{355}$ of −37.9 ± 2.9 deg dm^{-1} (g/mL)$^{-1}$ at values of −40.6 and −34.0 deg dm^{-1} (g/mL)$^{-1}$, respectively. We note that these errors are similar in magnitude and sign to those found for the length- and modified velocity-gauge CCSD approach for (*R*)-epichlorohydrin.[44]

The corresponding B3LYP specific rotations are reported in Table 3. The relatively low computational cost of DFT optical rotation calculations as compared to CC methods allows for the use of significantly larger basis sets, in this case up to d-aug-cc-pVTZ* (426 functions) and aug-cc-pVQZ (588 functions). As can be seen from Table 3, the difference between the triple-ζ and quadruple-ζ specific rotations are small, 0.5 deg dm^{-1} (g/mL)$^{-1}$ at most, whereas the doubly augmented basis sets at the double- and triple-ζ levels differ by up to 4.8 deg dm^{-1} (g/mL)$^{-1}$ at 355 nm. Furthermore, the addition of a second set of diffuse functions at the triple-ζ level (aug-cc-pVTZ to d-aug-cc-pVTZ*) decreases the computed rotation by 1.1 deg dm^{-1} (g/mL)$^{-1}$ at 633 nm and 3.5 deg dm^{-1} (g/mL)$^{-1}$ at 355 nm. These data suggest that further expansion of the basis set will have little effect, and the aug-cc-pVQZ and d-aug-cc-pVTZ* results are likely to be close to the B3LYP basis-set limit.

The B3LYP specific rotations compare poorly to the gas-phase experimental results, with errors in $[\alpha]_{633}$ and $[\alpha]_{355}$ just above and below a factor of 2, respectively, with the aug-cc-pVQZ and d-aug-cc-pVTZ* basis sets. Again, this pattern is essentially identical to that found for conformers of epichlorohydrin, with the B3LYP method consistently overestimating the specific rotation as compared to CCSD for all wavelengths.[44] Wiberg et al. reported that the addition of electric-field-dependent (EFD) functions to the aug-cc-pVDZ basis set yields specific rotations within the experimental error bars.[41] However, the data reported in Table 3 suggest that the addition of EFD functions to larger basis sets such as those described above would not improve the comparison with experiment, and the good agreement obtained by Wiberg et al. with the modest double-ζ basis may be fortuitous.

Table 4 reports excitation energies, oscillator strengths, length-gauge ECD rotational strengths, and the corresponding state-by-state optical rotation contributions computed at the B3LYP, CC2, and CCSD levels of theory using the aug-cc-pVDZ basis set for the six lowest-lying electronic states of (*S*)-2-chloropropionitrile. To the best of our knowledge, no experimental values for the lowest excitation energies of this molecule have been reported in the literature, but given the established accuracy of EOM-CC methods for singly excited states of closed-shell molecules (typically to within ca. 0.2 eV), the close correspondence of the CC2 and CCSD excitation energies (within 0.02 eV) suggests that higher levels of theory will offer little improvement. In addition, both methods agree reasonably well on the values of the ECD rotational strengths for the lowest two states, and the length-gauge data shown in the Table differ only slightly (a few hundredths of a cgs unit for the rotational strength and a few deg dm^{-1} (g/mL)$^{-1}$ for the specific-rotation contributions) from corresponding velocity-gauge results (not reported). However, the higher-lying states reveal more substantial differences between the CC2 and CCSD rotational strengths, including changes of sign. These differences appear to be related to the varying Rydberg vs valence character of the states, as described by the $\Delta\langle r^2\rangle$ values also reported in Table 4. As noted by Grimme, pure valence states (for second-row atoms) typically have $\Delta\langle r^2\rangle$ values < 10 a_0^2.[69] For example, the third excited state, for which the sign of the rotational strength changes between CC2 and CCSD, is described at the CC2 level as Rydberg-like, whereas CCSD suggests primarily valence character for this same state.

TABLE 4: Excitation Energies (eV), Oscillator Strengths (unitless), Rotational Strengths (10^{-40} esu^2 cm^2), $\Delta\langle r^2\rangle$ in (a_0^2), and Specific-Rotation Contributions [deg dm^{-1} (g/mL)$^{-1}$] of the Six Lowest Excited States of (*S*)-2-Chloropropionitrile[a]

					specific rotation contribution[b]			
state	excitation energy	oscillator strength	rotational strength[b]	$\Delta\langle r^2\rangle$	633 nm	589 nm	436 nm	355 nm
				B3LYP				
1	6.284	0.0004	0.4341	3	4.8	5.6	11.5	19.9
2	6.393	0.0104	−4.8203	3	−51.3	−60.2	−122.1	−210.7
3	6.947	0.0016	−1.7688	0	−15.7	−18.4	−36.6	−61.5
4	7.335	0.0379	0.6135	18	4.8	5.7	11.1	18.5
5	7.375	0.0155	−1.1053	24	−8.6	−10.1	−19.8	−32.8
6	7.448	0.0263	32.7099	11	249.7	291.7	573.4	947.1
				CC2				
1	6.966	0.0007	0.6107	3	5.4	6.3	12.5	21.1
2	7.037	0.0087	−3.8565	3	−33.3	−38.9	−77.3	−129.5
3	8.074	0.0095	6.5067	12	41.8	48.8	94.7	153.9
4	8.145	0.0330	9.1416	16	57.6	67.2	130.4	211.6
5	8.213	0.0284	7.9442	27	49.2	57.4	111.2	180.1
6	8.551	0.0659	3.5277	0	20.1	23.4	45.1	72.6
				CCSD				
1	6.947	0.0005	0.5696	3	5.1	5.9	11.8	19.8
2	7.022	0.0061	−3.2946	3	−28.6	−33.4	−66.4	−111.2
3	8.026	0.0003	−3.5944	1	−23.4	−27.3	−53.0	−86.2
4	8.245	0.0457	17.4927	24	107.5	125.3	242.6	393.0
5	8.330	0.0340	6.3411	23	38.1	44.4	85.9	138.9
6	8.497	0.0413	9.9141	4	57.2	66.6	128.5	207.0

[a] Computed at the B3LYP/6-311++G** optimized geometry using the aug-cc-pVDZ basis. [b] Rotational strengths and state-by-state specific rotation contributions were computed using the length-gauge representation of the electric dipole operator with the molecular center of mass chosen as the coordinate origin.

Table 4 also shows that B3LYP produces excitation energies lower than their EOM-CC counterparts by more than 0.6 eV. Although this result is to be expected of the B3LYP approach, particularly for states involving significant Rydberg character, we also note that this occurs for states with strong valence contributions, as illustrated by the $\Delta\langle r^2\rangle$ values in Table 4. This underestimation of the transition frequencies at least partially explains the overestimation by the TDDFT method of the values of $[\alpha]_\lambda$ described above: the divergence of eq 1 shifts to longer wavelengths with B3LYP than CC2 or CCSD, leading to an early onset of the corresponding Cotton pole. We note, however, that errors in the position of the pole provide only part of the picture and that overestimation of the ECD rotational strengths may also be a factor. This is observed in Table 4, particularly for the sixth excited state, which appears to be strongly overestimated relative to CCSD. We further note that even state-of-the-art functionals that produce correct excitation energies can still yield values of $[\alpha]_\lambda$ that are too large because of overestimation of the corresponding rotational strength. Recent results reported by Autschbach et al. and by Kongsted et al. with the SAOP functional for the problematic methyloxirane molecule provide a case in point: although SAOP excitation energies for the four lowest states agree well with experiment and with EOM-CCSD, the corresponding ECD rotational strengths are too large by a factor of 2−3,[70] and its optical rotation values at 355 nm are larger than experimental data by an order of magnitude.[35] As a counterexample, we note that B3LYP appears to perform superbly for (1*S*,4*S*)-norbornenone,[17] yielding a sodium D-line specfic rotation of −1216 deg dm^{-1} (g/mL)$^{-1}$ and a rotational strength of −55.6 cgs for the lowest excited state as compared to the liquid-phase experimental values of ca. −1150 deg dm^{-1} (g/mL)$^{-1}$ and −51 cgs, respectively. CCSD, on the other hand, compares very poorly, giving a value of $[\alpha]_D$ of −741 deg dm^{-1} (g/mL)$^{-1}$and a rotation strength of −23.1 cgs (length gauge). It is not yet clear if these results represent a fundamental failing of the CCSD model or if the liquid- and gas-phase rotations differ significantly for this molecule.

Table 4 also shows that the contribution of the six lowest excited states of 2-chloropropionitrile to the total specific rotation does not adequately account for the rotations reported in Tables 1−3. Indeed, although the second state clearly yields a much larger contribution to the total rotation than the first (by a factor of 4−5 for CC2 and CCSD and a factor of 10 for B3LYP), their sum does not approach the corresponding values in Tables 1−3. Indeed, for CCSD, the 355 nm individual rotational contributions from the second through sixth excited states are each larger than the total rotation—and five of these have the opposite sign of the converged/linear-response result.

To examine this point further, we also computed the first 100 B3LYP/aug-cc-pVDZ excited states of (*S*)-2-chloropropionitrile and their corresponding specific-rotation contributions and found that the resulting summation exceeds the aug-cc-pVDZ rotations reported in Table 3 by a factor of 3.5−4.75, depending on the choice of wavelength.[71] Furthermore, many of these states make contributions several times larger (and often of opposite sign) than the total rotation, e.g., the sixth excited state at 7.45 eV (well above the lowest excitation energy of 6.3 eV) makes a contribution of +947 deg dm^{-1} (g/mL)$^{-1}$ to the 355 nm rotation of −55.7 deg dm^{-1} (g/mL)$^{-1}$ (computing using a non-GIAO approach for direct comparison[71]). Even unphysical states beyond the (orbital-relaxed) B3LYP/aug-cc-pVDZ ionization limit of 11.4 eV make substantial contributions to the total rotation (e.g., the 98th excited state at 11.8 eV makes a contribution of −181 deg dm^{-1} (g/mL)$^{-1}$ to the 355 nm rotation).

Nevertheless, the available data suggest that the failure of B3LYP to reproduce the gas-phase experimental specific rotations can be partially explained by its underestimation of excitation energies and apparent overestimation of corresponding rotational strengths. Additional experimental estimates of high-resolution gas-phase ECD rotational strengths for (*S*)-2-chloropropionitrile would help to test this hypothesis.

Conclusions

We have reported coupled-cluster and density-functional specific rotations and ECD rotational strengths for (*S*)-2-chloropropionitrile. CC2 and CCSD specific rotations computed with large basis sets (up to 326 functions) in both length- and velocity-gauge representations compare very well with recently reported gas-phase experimental data by Wiberg et al.[41] In addition, we find that the six lowest-lying excited states yield ECD rotational strengths with varying signs, and that these are often larger than and of opposite sign to the total rotation computed from the linear-response formulation. This suggests that a sum-over-states approach to determining the total rotation is not viable for systems such as 2-chloropropionitrile. The remaining discrepancies between coupled-cluster theory and experiment may be attributed to several factors, including zero-point vibration and temperature effects, both of which have been shown to be significant for systems such as methyloxirane,[35,72] as well as to residual correlation effects. However, we note that Wiberg et al.[41] specifically considered the impact of vibrations on the specific rotation at 589 nm and found that a low-lying mode involving the methyl torsion was primarily responsible for the observed temperature effects. A detailed analysis of the vibrational contributions will be the focus of future work in this area.

B3LYP specific rotations with large basis sets (up to 588 functions) are too large compared to experiment by approximately a factor of 2, an error that may be partly explained by an apparent underestimation of the molecule's excitation energies and concomitant overestimation of the corresponding rotation strengths (as compared to coupled-cluster data). Although earlier work[41] reported good agreement between B3LYP and experimental specific rotations when EFD functions were used to further augment the standard aug-cc-pVDZ basis set, the near-CBS-limit results reported here suggest that this agreement may be fortuitous.

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