Molecular Dynamics

The Importance of Molecular Vibrations: The Sign Change of the Optical Rotation of Methyloxirane**

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Since the publication of the first measurement of the optical rotation of (*S*)-methyloxirane in the gas phase by Müller et al.[1] there has been much theoretical interest in the optical rotation of this molecule. To a large extent, this is because it has proven very difficult to obtain the correct sign of the optical rotation of this molecule at the experimental wavelength of 355 nm in theoretical calculations.[2–4] Several coupled-cluster investigations,[3,4] such as the highly correlated CC3 approach which includes triple excitation corrections, all predict a negative optical rotation for (*S*)-methyloxirane at the experimental wavelength of 355 nm. The geometry dependence of the property is important, but the

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use of different geometries[4] has not been sufficient to reproduce the experimental sign of the optical rotation at 355 nm.

DFT/B3LYP calculations provided a positive optical rotation at 355 nm, in agreement with experiment.[2,3] However, Tam et al.[3] argue that this result is a consequence of the incorrect prediction by the B3LYP functional of the energy for the excitation to the lowest Rydberg state, which is too low compared to experimental values because of the well-known limitations of common density functionals in reproducing the correct asymptotic limit for diffuse excited states.[5,6] The too low excitation energy leads to an unphysically strong dispersion of the optical rotation in the vicinity of electronic excitations, which occurs at too long wavelengths, and thus incorrectly increases and changes the sign of the optical rotation calculated at the DFT/B3LYP level of theory.

It was suggested in the coupled-cluster studies that the observed discrepancy between theory and experiment may be a result of vibrational effects. There has only been one study of zero-point vibrational effects on optical rotation in the literature,[7] which also included an examination of the zero-point vibrational corrections to (*S*)-methyloxirane. It was shown that zero-point vibrational corrections could be quite sizeable in comparison to the electronic contribution. However, at 589 nm and at the Hartree–Fock level of theory, the calculated zero-point vibrational correction was only 3.6 deg$\,$dm$^{-1}\,$g$^{-1}\,$mL, which was not enough to change the sign of the calculated CCSD or CC3 optical rotation.

Herein, we present calculations of the zero-point vibrational corrections of the optical rotation of (*S*)-methyloxirane at the DFT/B3LYP level of theory, with both 589 and 355 nm as the wavelength for the incident light. The zero-point vibrational corrections are calculated by using a computational method described previously.[7–9] The use of the B3LYP functional should give us some understanding of the importance of electron correlation effects,[10] although we keep in mind the potential problems of B3LYP calculations at 355 nm that result from the too low excitation energy. Our results were obtained using the aug-cc-pVDZ and aug-cc-pVTZ basis sets,[11,12] and are collected in Table 1.

Notably, the dispersion is also very strong for the zero-point vibrational corrections to the optical rotation, and these corrections are 18.6 (48.1) and 2.1 (10.7) at 355 and 589 nm, respectively, when calculated using the aug-cc-pVDZ (aug-cc-pVTZ) basis set. There is also a large difference in the zero-point vibrational correction calculated at the double- (DZ) and triple-zeta (TZ) levels of theory, which is primarily a result of the change in sign of the anharmonic contribution. In our approach, the anharmonic contribution arises from a shift in the molecular geometry, and is related to the cubic force field of the molecule.[8,9] When going from the DZ to the TZ basis set, the changes in the cubic force lead to a change of direction of the rotation of the methyl group, and thus to a change of the sign of the anharmonic term. The DFT/B3LYP results at the aug-cc-pVDZ level are in good agreement with our previous Hartree–Fock results at 589 nm (3.6).[7]

Table 1: Calculated and experimental optical rotations of (*S*)-methyloxirane.[a]

λ [nm]	$[\alpha]_\lambda^{e}$	$[\alpha]_\lambda^{eff}-[\alpha]_\lambda^{e}$	$\langle[\alpha]_\lambda^{(2)}\rangle^{eff}$	$\langle[\alpha]_\lambda\rangle^{ZPV}$	$\langle[\alpha]_\lambda\rangle$	Exp.[1]
			aug-cc-pVDZ			
355	11.6	−24.0	42.6	18.6	30.1	10.2[b]
589.3	−14.9	−7.1	9.2	2.1	−12.8	−26.9[c]
			aug-cc-pVTZ			
355	27.5	20.0	28.1	48.1	75.6	10.2[b]
589.3	−7.7	5.5	5.2	10.7	3.0	−26.9[c]
			best theoretical estimates[d]			
355	−23.2			48.1	24.9	10.2[b]
589.3	−17.7			10.7	−7.0	−26.9[c]

[a] The optical rotation at the equilibrium geometry $[\alpha]_\lambda^{e}$, the anharmonic zero-point vibrational correction ($[\alpha]_\lambda^{eff}-[\alpha]_\lambda^{e}$), the harmonic vibrational correction $\langle[\alpha]_\lambda^{(2)}\rangle^{eff}$, the total zero-point vibrational correction $\langle[\alpha]_\lambda\rangle^{ZPV}$, and the vibrationally averaged optical rotation $\langle[\alpha]_\lambda\rangle$ were calculated at the B3LYP level of theory with two different basis sets. All results reported in units of deg$\,$dm$^{-1}\,$g$^{-1}\,$mL. [b] For the gas phase. [c] Cyclohexane solution. [d] Using the CC3 results[4] for the equilibrium-geometry optical rotation, and the B3LYP/aug-cc-pVTZ results reported herein for the vibrational correction.

The vibrationally averaged optical rotation calculated at the B3LYP/aug-cc-pVTZ level of theory now appears quite meaningless, as it is much too large at 355 nm and has the wrong sign at 589 nm. However, if we combine our zero-point vibrational corrections (obtained with the aug-cc-pVTZ basis set) with the best correlated data for the optical rotation (the CC3 results of Kongsted et al.[4]), we find that their value for the equilibrium-geometry optical rotation of −23.2 at 355 nm leads to a vibrationally averaged optical rotation of 24.9, whereas at 589 nm their equilibrium-geometry optical rotation of −17.7 leads to a vibrationally averaged optical rotation of −7.0 when combined with our calculated zero-point vibrational correction (see Table 1). The experimental data at 589 nm were obtained in solution and were extrapolated to −26.9 in the innocuous solvent cyclohexane. Calculations show that the effects of a dielectric medium are to make the optical rotation more negative.[4]

The sensitivity of our calculated vibrational corrections to the quality of the basis (and in practice to the quality of the anharmonic force field), and the rather dramatic consequence this has for the vibrational corrections to the optical rotation of methyloxirane, highlights the inadequacy of a local-mode approximation to such a freely rotating methyl group. We might therefore expect that our anharmonic contribution may be too large. Furthermore, although there is no strict correlation between the dispersion dependence of the vibrational correction and the electronic contribution to the property, the dependence on dispersion may be exaggerated in our vibrational corrections by the too low B3LYP excitation energies. Still, even if our vibrational corrections are somewhat large, we believe an even more accurate calculation of the vibrational correction will leave our conclusion unchanged and lead to an improved agreement with experiment.

In conclusion, the observed change of sign of the optical rotation of (*S*)-methyloxirane when going from a wavelength of 589 to 355 nm is a result of the vibrational corrections to these properties. Our approach has inherent limitations because of the too low excitation energies predicted by the DFT/B3LYP level of theory, and the inadequacy of a local-mode approximation in modeling the contributions to the optical rotation that result from the rotation of the methyl group. However, we believe that our results and conclusions will not be overturned by a more accurate calculation. The apparent success of DFT/B3LYP in obtaining the correct sign of the optical rotation at 355 nm[2,3] is shown to be fortuitous, in agreement with earlier observations.[3,4]

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