J|A|C|S
ARTICLES

Coupled Cluster and Density Functional Theory Studies of the Vibrational Contribution to the Optical Rotation of (*S*)-Propylene Oxide

Jacob Kongsted,[*,†] Thomas Bondo Pedersen,[‡] Lasse Jensen,[§]
Aage E. Hansen,[‖,⊥] and Kurt V. Mikkelsen[‖]

Contribution from the Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark, Department of Theoretical Chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden, Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, and Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Received September 27, 2005; E-mail: kongsted@chem.au.dk

Abstract: In a previous study (*Chemical Physics Letters* **2005**, *401* , 385) we computed the optical rotatory dispersion of (*S*)-propylene oxide in gas phase and solution using the hierarchy of coupled cluster models CCS, CC2, CCSD, and CC3. Even for the highly correlated CC3 model combined with a flexible basis set, the theoretical gas-phase specific rotation at 355 nm was found to be negative in contrast to the experimental result. We argued that vibrational contributions could be crucial for obtaining a complete understanding of the experimental result. Here, we show that this indeed is the case by using coupled cluster models and density functional theory methods to calculate the vibrational contributions to the gas-phase specific rotation at 355, 589.3, and 633 nm. While density functional theory (B3LYP and SAOP functionals) overestimates the specific rotation at 355 nm by approximately 1 order of magnitude and yields an incorrect sign at 589.3 and 633 nm, the coupled cluster results are in excellent agreement with the experimentally measured optical rotations. We find that all vibrational modes contribute significantly to the optical rotation and that temperature effects must be taken into account.

I. Introduction

The increasing interest in quantum chemical calculations of optical rotation (OR) stems from the prospect of easy and reliable determination of the absolute configuration of chiral molecules, see, e.g., refs 1−22. Evidently, determination of absolute configurations from a comparison of experimental and theoretical OR requires that the latter gives sufficiently accurate results; i.e., both sign and magnitude must be reliably predicted. While coupled cluster (CC) electronic structure theory is generally considered more accurate and therefore more reliable than density functional theory (DFT), the latter is considerably less demanding in terms of computational effort and may thus be applied to larger molecules. A number of theoretical studies have been dedicated to the assessment of the accuracy of DFT relative to coupled cluster singles and doubles (CCSD) as well as experimental results; see for example refs 13, 21, where the performance of the popular B3LYP exchange-correlation functional is investigated for small-angle (absolute value less than approximately 100 deg $[\mathrm{dm\ g/cm^3}]^{-1}$) OR. These studies have compared purely electronic OR computed at the equilibrium geometry to experimental results obtained in solution. Although useful guidelines for the statistical reliability of B3LYP results are deduced in ref 21, one has to recall that the potentially crucial

---

[†] University of Aarhus.

[‡] University of Lund.

[§] Northwestern University.

[‖] University of Copenhagen.

[⊥] Permanent address: Holmebjerg 5, Trørød DK-2950 Vedbæk, Denmark.

(1) Polavarapu, P. L. *Mol. Phys.* **1997**, *91*, 551.
(2) Kondru, R. K.; Wipf, P.; Beratan, D. N. *Science* **1998**, *282*, 2247.
(3) Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Stephens, P. J. *J. Phys. Chem. A* **2000**, *104*, 1039.
(4) Stephens, P. J.; Devlin, F. J.; Cheeseman, J. R.; Frisch, M. J. *J. Phys. Chem. A* **2001**, *105*, 5356.
(5) Ruud, K.; Taylor, P. R.; Åstrand, P. O. *Chem. Phys. Lett.* **2001**, *337*, 217.
(6) Grimme, S. *Chem. Phys. Lett.* **2001**, *339*, 380.
(7) Polavarapu, P. L. *Chirality* **2002**, *14*, 768.
(8) Ruud, K.; Helgaker, T. *Chem. Phys. Lett.* **2002**, *352*, 533.
(9) Mennucci, B.; Tomasi, J.; Cammi, R.; Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Gabrial, S.; Stephens, P. J. *J. Phys. Chem. A* **2002**, *106*, 6102.
(10) Autschbach, J.; Patchkovskii, S.; Ziegler, T.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys.* **2002**, *117*, 581.
(11) Polavarapu, P. L. *Chirality* **2003**, *15*, 284.
(12) Giorgio, E.; Rosini, C.; Viglione, R. G.; Zanasi, R. *Chem. Phys. Lett.* **2003**, *376*, 452.
(13) Ruud, K.; Stephens, P. J.; Devlin, F. J.; Taylor, P. R.; Cheeseman, J. R.; Frisch, M. J. *Chem. Phys. Lett.* **2003**, *373*, 606.
(14) Pedersen, T. B.; Sánchez de Merás, A. M. J.; Koch, H. *J. Chem. Phys.* **2004**, *120*, 8887.
(15) Pedersen, T. B.; Koch, H.; Boman, L.; Sánchez de Merás, A. M. J. *Chem. Phys. Lett.* **2004**, *393*, 319.
(16) Tam, M. C.; Russ, N. J.; Crawford, T. D. *J. Chem. Phys.* **2004**, *121*, 3550.
(17) McCann, D. M.; Stephens, P. J.; Cheeseman, J. R. *J. Org. Chem.* **2004**, *69*, 8709.
(18) Stephens, P. J.; McCann, D. M.; Devlin, F. J.; Cheeseman, J. R.; Frisch, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 7514.
(19) Kongsted, J.; Pedersen, T. B.; Strange, M.; Osted, A.; Hansen, Aa. E.; Mikkelsen, K. V.; Pawlowski, F.; Jørgensen, P.; Hättig, C. *Chem. Phys. Lett.* **2005**, *401*, 385.
(20) Ruud, K.; Zanasi, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3594.
(21) Stephens, P. J.; McCann, D. M.; Cheeseman, J. R.; Frisch, M. J. *Chirality* **2005**, *17*, S52.
(22) Mort, B. C.; Autschbach, J. *J. Phys. Chem A* **2005**, *109*, 8617.

10.1021/ja056611e CCC: $33.50

effects of solvation and of molecular vibrations have been completely disregarded. While solvent effects on OR are difficult to calculate accurately,[9,19] vibrational effects can in principle be straightforwardly computed, albeit at an increased computational cost.[5,20,22]

In the past few years the specific optical rotation of propylene oxide (also known as methyl oxirane) has been the subject of numerous theoretical studies.[2−6,9,10,12,15,16,19−22] The 355 nm OR of propylene oxide in the gas phase has turned out to be particularly challenging. Experimentally, Müller, Wiberg, and Vaccaro[23] reported the first gas-phase measurement of the specific rotation of (*S*)-propylene oxide at 355 nm to be 10.2 ± 2.9 deg [dm g/cm^3]$^{-1}$, later refined by Wilson et al.[24] to 7.49 ± 0.30 deg [dm g/cm^3]$^{-1}$, in contrast to the (extrapolated) cyclohexane solution rotation[23] of −26.4 deg [dm g/cm^3]$^{-1}$. Using DFT with the widely used B3LYP functional, Giorgio et al.[12] subsequently obtained 21 deg [dm g/cm^3]$^{-1}$ in reasonable agreement with the gas-phase experimental result. However, also using B3LYP, Stephens and co-workers[21] have demonstrated that calculations of small-angle ORs cannot generally be trusted for assigning absolute configuration; i.e., the sign of the OR is questionable, in particular for conformationally flexible molecules. Although this conclusion was reached by comparing to experimental results measured in solution, we believe that the discrepancy is largely ascribable to the neglect of vibrational contributions. Recently, Ruud and Zanasi[20] computed the OR at 355 nm including zero-point vibrational (ZPV) corrections with the B3LYP functional and a large atomic orbital basis set and reported the total OR to be 75.6 deg [dm g/cm^3]$^{-1}$. Although the sign is correct, the magnitude is clearly overestimated.

Recent theoretical studies using highly correlated CC wave functions have shown beyond dispute that, at the equilibrium geometry, the purely electronic contribution to the OR at 355 nm is negative.[15,16,19] Simply adding the B3LYP vibrational contributions yields positive OR. The CC studies of refs 16, 19 revealed a pronounced sensitivity to the nuclear conformation, corroborating that vibrational contributions are of decisive importance in accounting for the experimental result. Including vibrational effects along the lines of ref 20, the purpose of the present work is to test whether CC theory can reproduce the experimental result.

It is well established[16,19] that B3LYP yields an equilibrium geometry of (*S*)-propylene oxide in close agreement with more elaborate electronic structure models, notably the highly correlated CCSD model including perturbative triples (CCSD(T)) used in ref 16. We combine in this work DFT and CC to estimate the vibrational effects, using B3LYP for calculating the potential energy surface (and vibrational wave functions) and CC for computing the electronic OR surface.

Tam, Russ, and Crawford[16] argued that the good agreement between experiment and the B3LYP result of Giorgio et al.[12] is fortuitous: as the lowest-lying excited electronic states of (*S*)-propylene oxide are Rydberg states and as B3LYP is known to be inaccurate for transitions to such states, the positive OR at 355 nm is simply an artifact of the lowest B3LYP excitation energy being too low (i.e., at too long wavelength). On the other hand, using the SAOP functional,[25−27] Autschbach et al.[28] were able to compute the four lowest excitation energies with high accuracy compared to experiment. Hence, we have also performed calculations of the vibrational effects on the OR of (*S*)-propylene oxide using the B3LYP potential energy surface and SAOP for the OR surface.

II. Theoretical Background

The OR of a sample of chiral molecules may be calculated using the expression

$$[\alpha]_{\tilde{\nu}} = 28800\pi^2 N_{\mathrm{A}} a_0{}^4 \frac{\tilde{\nu}^2 \beta'(\omega)}{M} \tag{1}$$

where N_{A} is Avogadro's number, a_0 is the bohr radius in cm, $\tilde{\nu}$ is the frequency in cm^{-1}, M is the molecular weight in g/mol, and $\beta'(\omega)$ (in atomic units, $a_0{}^4$) is given as

$$\beta'(\omega) = -\mathrm{Im}\frac{\mathrm{Tr}\langle\langle \boldsymbol{\mu},\mathbf{m}\rangle\rangle_{\omega}}{3\omega} \tag{2}$$

i.e., in terms of of the trace of the frequency-dependent electric dipole-magnetic dipole polarizability tensor $\langle\langle \boldsymbol{\mu},\mathbf{m}\rangle\rangle_{\omega}$ in the length gauge formulation. In eq 2, the vector $\boldsymbol{\mu}(\mathbf{m})$ is the electric (magnetic) dipole operator. The disadvantage in using eq 2 directly in the calculation of OR is due to the origin-dependence of the length gauge formulation of $\beta'(\omega)$. However, this expression may be transformed to the inherently origin invariant velocity gauge.[15] Thus, we obtain for $\beta'(\omega)$ in the velocity gauge

$$\beta'(\omega) = \mathrm{Re}\frac{(\mathrm{Tr}\langle\langle \mathbf{p},\mathbf{m}\rangle\rangle_{\omega} - \mathrm{Tr}\langle\langle \mathbf{p},\mathbf{m}\rangle\rangle_{0})}{3\omega^2} \tag{3}$$

where ($\mathbf{p}$) is the electronic momentum operator. As advocated in ref 15, we have in eq 3 subtracted the unphysical static limit from the conventional velocity gauge expression, thus obtaining the so-called modified velocity gauge formulation.

Expanding the specific rotation in a Taylor series in the normal modes (Q_a) about a reference point (usually the equilibrium geometry) and keeping only the harmonic terms leads to

$$\langle[\alpha]_{\tilde{\nu}}\rangle = [\alpha]^{0}_{\tilde{\nu}} + \frac{1}{2}\sum_{a}\left(\frac{\partial^2[\alpha]_{\tilde{\nu}}}{\partial Q_a \partial Q_a}\right)\langle Q_a^2\rangle = [\alpha]^{0}_{\tilde{\nu}} + [\alpha]^{\mathrm{har}}_{\tilde{\nu}} \tag{4}$$

where $\langle[\alpha]_{\tilde{\nu}}\rangle$ is the vibrationally averaged specific rotation and where we have made use of the properties of the harmonic oscillator wave functions. Effects of anharmonicity are often important, and eq 4 is therefore not expected to give results of high accuracy in general (see for example the discussion in ref 22). However, as shown in refs 5, 29−31, the harmonic approximation may be valid provided the expansion point is

---

(23) Müller, T.; Wiberg, K. B.; Vaccaro, P. H. *J. Phys. Chem. A* **2000**, *104*, 5959.

(24) Wilson, S. M.; Wiberg, K. B.; Cheeseman, J. R.; Frisch, M. J.; Vaccaro, P. H. *J. Phys. Chem. A* **2005**, *109*, 11752−11764.

(25) Schipper, P. R. T.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys.* **2000**, *112*, 1344.

(26) Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. *Chem. Phys. Lett.* **1999**, *302*, 199.

(27) Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. *Int. J. Quantum Chem.* **2000**, *76*, 407.

(28) Autschbach, J.; Ziegler, T.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys.* **2002**, *116*, 6930.

(29) Åstrand, P. O.; Ruud, K.; Sundholm, D. *Theor. Chem. Acc.* **2000**, *103*, 365.

(30) Åstrand, P. O.; Ruud, K.; Taylor, P. R. *J. Chem. Phys.* **2000**, *112*, 2655.

(31) Ruud, K.; Åstrand, P. O.; Taylor, P. R. *J. Chem. Phys.* **2000**, *112*, 2668.

chosen as the so-called effective geometry, which is defined by minimization of the electronic plus zero-point vibrational (ZPV) energy. The effects of anharmonicity are then automatically included and can be quantified by the OR difference between the effective and equilibrium geometries as

$$[\alpha]_{\tilde{\nu}}^{\mathrm{anh}} = [\alpha]_{\tilde{\nu}}^{\mathrm{eff}} - [\alpha]_{\tilde{\nu}}^{\mathrm{eq}} \qquad (5)$$

where eff (eq) refers to the effective (equilibrium) geometry. Combining eqs 4 and 5 we finally arrive at

$$\langle[\alpha]_{\tilde{\nu}}\rangle = [\alpha]_{\tilde{\nu}}^{\mathrm{eq}} + [\alpha]_{\tilde{\nu}}^{\mathrm{har}} + [\alpha]_{\tilde{\nu}}^{\mathrm{anh}} \qquad (6)$$

which will be used in the calculations.

Based on the partition function for the quantum harmonic oscillator as well as the properties of the harmonic oscillator wave functions, the $\langle Q_a^2\rangle$ part of the harmonic contribution may be evaluated as

$$\langle Q_a^2\rangle = \frac{1}{2\omega_a}\coth\left(\frac{\omega_a}{2kT}\right) \qquad (7)$$

where ω_a is the ath harmonic vibrational frequency. This expression includes temperature effects in an approximate fashion, neglecting the temperature-dependence of the anharmonic contribution. In case of zero temperature, eq 7 reduces to the well-known expression $\langle Q_a^2\rangle$ $(T = 0) = (2\omega_a)^{-1}$.

III. Computational Details

The evaluation of the vibrational contribution to the OR relies on the determination of the harmonic potential at the effective geometry using DFT. Here we use the equilibrium and effective geometries, normal coordinates, and harmonic vibrational frequencies computed in ref 20 at the B3LYP/aug-cc-pVTZ level. To calculate the property Hessian by numerical differentiation we form the appropriate displacements along these normal coordinates. The diagonal elements of the property Hessian, $[\alpha]_{\tilde{\nu}}^{(2)}$, are calculated from the expression

$$([\alpha]_{\tilde{\nu}})_{aa}^{(2)} = \left(\frac{[\alpha]_{\tilde{\nu}}^{+\delta_a} - 2[\alpha]_{\tilde{\nu}} + [\alpha]_{\tilde{\nu}}^{-\delta_a}}{\delta_a^2}\right) \qquad (8)$$

where a is the index for the normal mode and δ_a is the displacement (stepsize) along the particular normal mode. The displacements have been determined according to $D_a\delta_a = s$ where D_a is the norm of the (unnormalized) Cartesian displacement vector corresponding to mode a and $s = 0.0050$ au. In this way the δ's are different for each mode such that small (large) stepsizes are automatically chosen for modes corresponding to overall large (small) atomic displacements. The choice $s = 0.0050$ au is based on a series of calculations, varying s in the interval 0.0001 to 0.005 au. For the CC response calculations, carried out by means of the Dalton program,[32] we use the A basis set of ref 19 consisting of the aug-cc-pVDZ[33,34] basis set for carbon, the aug-cc-pVTZ[33,34] basis set for oxygen, and the d-aug-cc-pVDZ[33,34] basis set for hydrogen.

In addition to the CC property calculations we perform an analogous series of OR calculations using the SAOP functional[25−27] implemented in the ADF program.[35] In contrast to Dalton, ADF has been designed for Slater orbitals, prohibiting the use of the A basis set (which consists of Gaussian functions) for the SAOP calculations. Instead, we use the even-tempered QZ3P-1DIFFUSE basis set, which is a quadruple-ζ quality basis set with three polarization functions and additional diffuse functions, adopted from the ADF basis set library.

IV. Results and Discussion

A. Torsional Effects Induced by the Methyl Group. As an initial investigation of the vibrational effects we study the dependence of the OR on the dihedral angle formed by the methyl group and the backbone structure of propylene oxide. In a series of papers Wiberg et al.[36−38] have studied conformational effects of the OR of small organic molecules and find that, in general, large-amplitude torsional motions have a significant influence on the OR. Thus, we expect that the OR of propylene oxide is quite dependent on the dihedral angle. For propylene oxide, the lowest harmonic vibrational frequency (corresponding to the torsional motion of the methyl group) is found to be approximately 206 cm^{-1}, i.e., comparable to kT at room temperature. Thus, the torsional motion is likely to play a crucial role in turning the negative electronic contribution into a positive total OR.

In Figure 1 we have plotted the relative energy (in kJ/mol) as a function of the change in the dihedral angle relative to the equilibrium geometry in which the methyl group hydrogens are found in a staggered conformation relative to the hydrogen directly bonded to the backbone structure. We observe that the B3LYP and CCSD potentials are in quite good agreement, thus justifying the use of the former to compute the potential energy surface. In Figure 1 we have also plotted the gas-phase OR (in deg $[\mathrm{dm\ g/cm^3}]^{-1}$) as a function of the change in the dihedral angle at 355, 589.3, and 633 nm. We observe that the trends for the OR at the three wavelengths are largely the same. However, the changes in the magnitude of the response at 355 nm are much more pronounced than those at the longer wavelengths. This is in line with the results found in refs 16, 19 using different molecular equilibrium structures obtained from different levels of theory. Of special interest is the observation that the OR actually changes sign for all wavelengths as a function of the change in the dihedral angle. For the 355 nm response, the sign of the OR changes (from negative to positive) when the dihedral angle is changed approximately 8° relative to the equilibrium geometry. Thus, even a small inaccuracy in the equilibrium geometry can lead to a sign change of the OR at 355 nm.

It is reasonable to expect that the significant variation of the OR as a function of the dihedral angle is accompanied by a change in the (presumably) most significant lower-lying electronic excitation energies and associated rotatory strengths. The location of the lowest electronic excitation energy is expected to be very important for the OR, especially if the frequency of the external perturbation is in the vicinity of this electronic transition. For propylene oxide, the lowest vertical electronic transition ($n_\mathrm{O} \rightarrow 3s$) is located near 175 nm[16,19,28] at the equilibrium geometry. However, as seen from Figures 2−4, the lower-lying excitation energies and oscillator and rotatory

---

[32] Dalton, a molecular electronic structure program, release 2.0, 2005; see http://www.kjemi.uio.no/software/dalton/dalton.html.
[33] Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
[34] Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J *J. Chem. Phys.* **1992**, *96*, 6769.
[35] ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands; see http://www.scm.com.
[36] Wiberg, K. B.; Wang, Y.; Vaccaro, P. H.; Cheeseman, J. R.; Trucks, G.; Frisch, M. J. *J. Phys. Chem. A* **2004**, *108*, 32.
[37] Wiberg, K. B.; Vaccaro, P. H.; Cheeseman, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 1888.
[38] Wiberg, K. B.; Wang, Y.; Vaccaro, P. H.; Cheeseman, J. R.; Luderer, M. R. *J. Phys. Chem. A* **2005**, *109*, 3405.

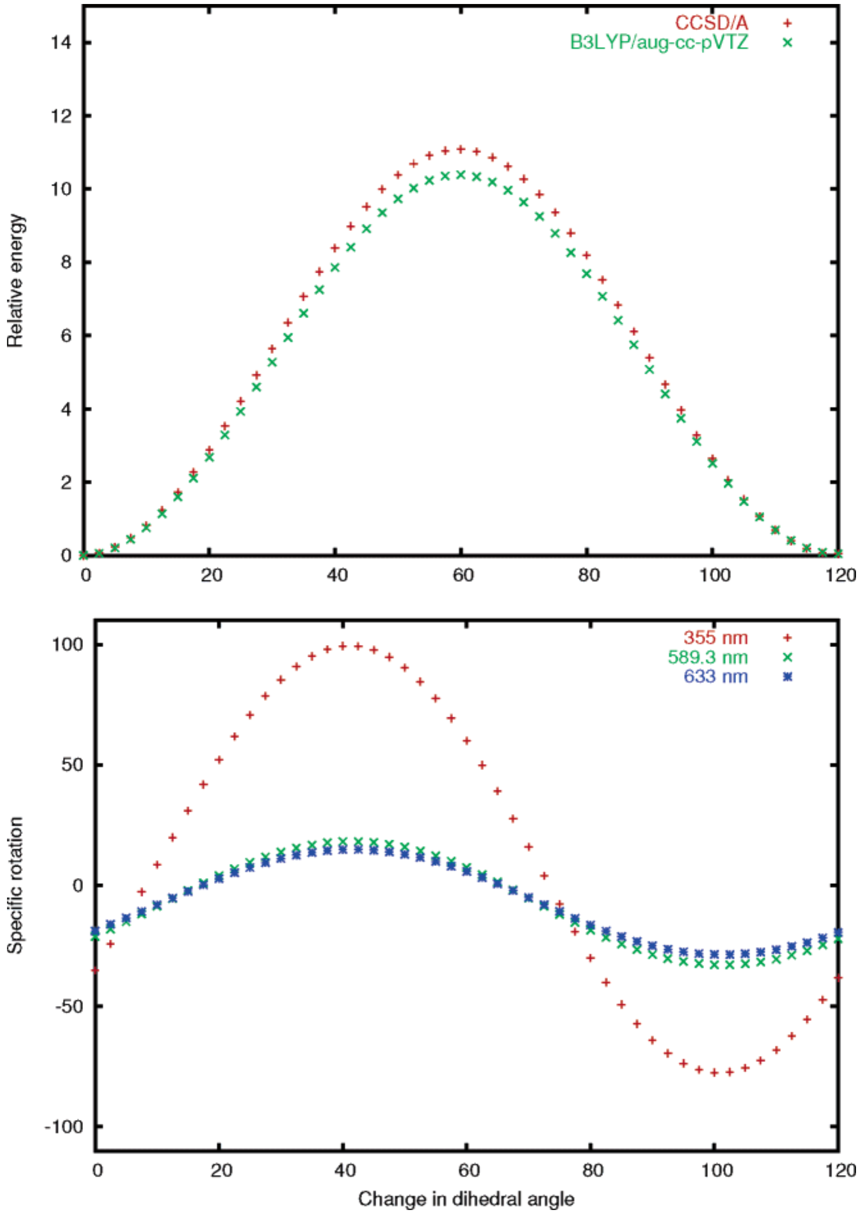

Figure 1. Relative energy (in kJ/mol) and 355, 589.3, and 633 nm specific rotation (CCSD/A; in deg [dm g/cm^3]$^{-1}$) as a function of the change in the dihedral angle formed by the methyl group and the backbone structure of (*S*)-propylene oxide.

strengths are largely unaffected by the change in dihedral angle. Thus, the significant changes in OR must be due to changes in the higher-lying states. We note that the lowest electronic transitions are to states of Rydberg character, and the states which are primarily responsible for the significant changes in the OR as a function of the dihedral angle are probably very diffuse and therefore difficult to characterize.

A simple procedure to account for the conformational effects is to compute the (classical) Boltzmann average over the OR curves in Figure 1. At 298.15 K, this procedure yields optical rotations equal to −24.6 deg [dm g/cm^3]$^{-1}$ at 355 nm, −18.0 deg [dm g/cm^3]$^{-1}$ at 589.3 nm, and −16.0 deg [dm g/cm^3]$^{-1}$ at 633 nm. Thus, although the correction is positive, the total OR at 355 nm is still negative. Consequently, we must take into consideration the vibrational states of all modes and calculate the quantum mechanical average.

B. Vibrational Effects. Table 1 presents the gas-phase OR for (*S*)-propylene oxide at 355, 589.3, and 633 nm. First, note that the electronic components of the CCSD OR are slightly different from our previously published results.[19] This is due to a (very small) difference in geometry: in ref 19 we used the equilibrium geometry obtained from B3LYP/cc-pVTZ, while here we use that obtained from B3LYP/aug-cc-pVTZ. Second, note that the experimental OR at 589.3 nm quoted in Table 1 was estimated from a measurement in cyclohexane solution by Kumata et al.[39] using the Lorentz local field factor to model the solvent effect. Therefore, this value is not strictly comparable to our theoretical results. However, CCSD calculations using a dielectric continuum model to account for solvent effects indicate that the 589.3 nm OR becomes slightly more negative in cyclohexane solution,[19] in agreement with the estimate of Kumata et al.[39] Thus, we believe that the theoretical and experimentally deduced results at 589.3 nm in Table 1 can be compared.

---

(39) Kumata, Y.; Furukawa, J.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3920.

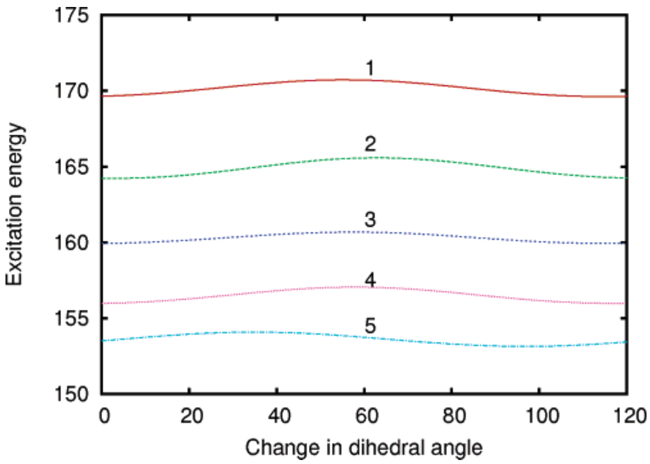

Figure 2. The five lowest vertical electronic excitation energies (in nm) as a function of the change in the dihedral angle formed by the methyl group and the backbone structure of (*S*)-propylene oxide computed at the CCSD/A level.

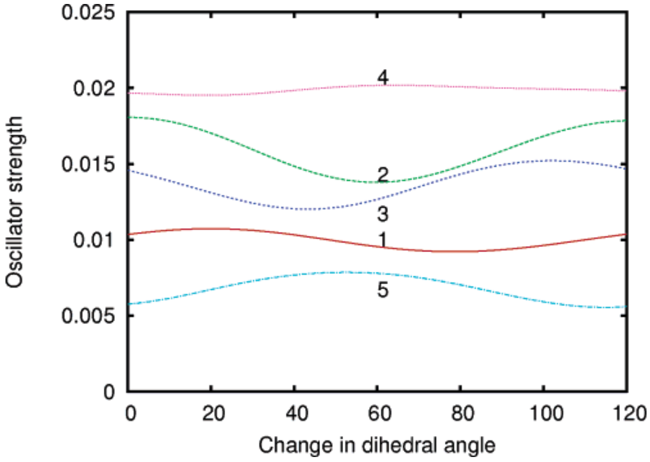

Figure 3. The velocity gauge oscillator strength corresponding to the five lowest vertical electronic excitation energies as a function of the change in the dihedral angle formed by the methyl group and the backbone structure of (S)-propylene oxide computed at the CCSD/A level.

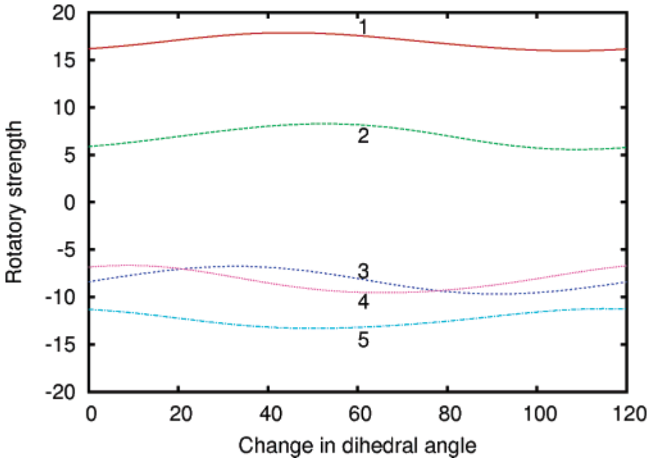

Figure 4. The velocity gauge rotatory strength (in 10^{-40} cgs) corresponding to the five lowest vertical electronic excitation energies as a function of the change in the dihedral angle formed by the methyl group and the backbone structure of (*S*)-propylene oxide computed at the CCSD/A level.

Table 1. Specific Rotation of (*S*)-Propylene Oxide in Units of deg [dm g/cm^3]$^{-1}$

λ (nm)	model	T (K)	$[\alpha]^{eq}_{eq}$	$[\alpha]^{har}$	$[\alpha]^{anh}$	$\langle[\alpha]\rangle$	$[\alpha]^{exp}$
355.0	CCSD	0	−36.29	18.17	12.84	−5.28	
		298.15		27.46		4.01	7.49 ± 0.30[b]
	DFT/SAOP	0	29.05	35.42	18.71	83.18	
		298.15		53.08		100.84	
	DFT/B3LYP[c]	0	27.5	28.1	20.0	75.6	
589.3	CCSD	0	−21.50	3.69	3.56	−14.25	
		298.15		6.22		−11.72	−11.9[d]
	DFT/SAOP	0	−3.12	7.70	5.43	10.01	
		298.15		12.21		14.52	
	DFT/B3LYP[c]	0	−7.7	5.5	5.2	3.0	
633.0	CCSD	0	−18.99	3.05	3.02	−12.92	
		298.15		5.19		−10.78	−8.38 ± 0.20[b]
	DFT/SAOP	0	−3.30	6.45	4.63	7.78	
		298.15		10.28		11.61	

[a] In all coupled cluster calculations we use the A basis set (ref 19) and the frozen core approximation. The specific rotations are given in the modified velocity gauge formulation for CCSD, in the length gauge with London orbitals (GIAOs) for B3LYP, and in the length gauge for SAOP [b] Gas phase, ref 24. [c] Reference 20. [d] Deduced from a measurement in cyclohexane solution, ref 39.

As discussed above, the anharmonic contribution can be viewed as the difference in OR between the effective and equilibrium structures. The most significant difference between the effective and equilibrium geometries of (*S*)-propylene oxide is a twist of 3.25° in the dihedral angle formed by the methyl group and the backbone structure.[20] As seen from Figure 1, such a change in the dihedral angle amounts to a change in the 355 nm specific rotation of about 14.3 deg [dm g/cm^3]$^{-1}$, i.e., approximately the anharmonicity reported in Table 1.

Regardless of the level of theory deployed, vibrational effects are singularly important for the OR of (*S*)-propylene oxide at all wavelengths: the magnitude of the vibrational contribution is comparable to or even larger than the electronic component. Moreover, all methods agree that the vibrational corrections are positive, although the DFT-based corrections are somewhat larger than those obtained from CCSD. As the vibrational wave functions (i.e., normal coordinates) were in all cases obtained from the B3LYP/aug-cc-pVTZ potential energy surface, we may conclude that B3LYP, SAOP, and CCSD qualitatively agree on the shape of the OR surface. Thus, the rather poor agreement between the DFT models and experiment can be traced back to an erroneous prediction of the electronic OR at the equilibrium geometry.

Although ZPV effects considerably improve the CCSD results, the OR at 355 nm remains negative at 0 K. At 298 K, on the other hand, the CCSD 355 nm OR is positive and in excellent agreement with experiment. It should be noted, however, that higher-order electron correlations might increase the result further: in ref 19 we estimated these effects to be +6.6 deg [dm g/cm^3]$^{-1}$ and +1.5 deg [dm g/cm^3]$^{-1}$ at 355 and 589.3 nm, respectively, using the CC3 method.[40,41] Adding these values to the CCSD results at 298 K from Table 1 leads to a total OR of 10.6 deg [dm g/cm^3]$^{-1}$ at 355 nm and −10.2 deg [dm g/cm^3]$^{-1}$ at 589.3 nm. Inarguably speculative, these estimates are nevertheless in quite good agreement with experimental findings. It should be stressed that another and perhaps more important source of error is the complete neglect of temperature-dependence in the anharmonic vibrational contribution.

---

(40) Christiansen, O.; Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1995**, *103*, 7429.
(41) Hald, K.; Pawlowski, F.; Jørgensen, P.; Hättig, C. *J. Chem. Phys.* **2003**, *118*, 1292.

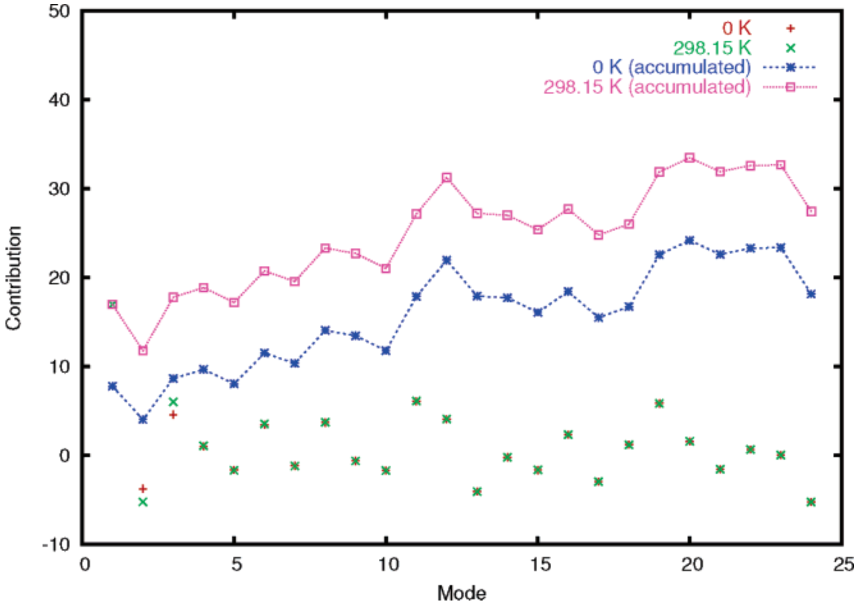

Figure 5. Individual and accumulated vibrational contributions to the 355 nm OR (in deg [dm g/cm^3]$^{-1}$) for each mode computed at the CCSD/A level.

As mentioned above, it has been argued that B3LYP produces an incorrect OR dispersion curve, in particular around 355 nm, as the lowest-lying excitation energy is predicted to be located at a too long wavelength.[16] On the other hand, the SAOP functional does yield the four lowest-lying excitation energies in good agreement with experiment.[28] Thus, it might be expected that SAOP would be capable of correctly describing the OR dispersion. As Table 1 clearly shows, however, this is not the case and we may ascribe this deficiency to a poor description of the rotatory strengths. More precisely, as the computed oscillator strengths are in line with experimental data,[28] the error must originate from the magnetic transition moments. This might perhaps have been anticipated, since the SAOP functional was constructed with the purpose of computing purely electric (dipole) properties.[25−27] We note that also in the long-wavelength region (589.3 and 633 nm) B3LYP and SAOP yield a positive OR, while CCSD and experiment find a negative OR. In absolute terms, the error is not large. In fact, the error cannot be large, since the OR in the static limit (infinite wavelength) must vanish identically. Neither the B3LYP nor the SAOP dispersion curve passes through zero, as required by the experimental observations. The CCSD model, in contrast, correctly reproduces this trend.

For CCSD, the distribution among the harmonic normal modes of vibrational contributions to the 355 nm OR is depicted in Figure 5. Only the three lowest modes show an appreciable variation in this temperature range, and among these the torsional motion is by far the most sensitive mode. In this sense, the torsional mode is the reason that the observed 355 nm OR is positive. However, it is important to realize that *all* the vibrational modes contribute significantly to the total OR. Note, for example, that the second and last modes contribute by about the same amount despite the energy difference between them (they are located at 376 and 3115 cm^{-1}, respectively).

V. Summary and Concluding Remarks

As suggested previously,[16,19] vibrational effects have a decisive impact on the OR of (*S*)-propylene oxide. The main contributor to the vibrational effects is the strongly anharmonic torsional motion of the methyl group: at 355 nm, the OR varies between −80 and +100 deg [dm g/cm^3]$^{-1}$ during a full 120° hindered rotation. As the barrier of the hindered rotation is 11.1 kJ/mol and the vibrational frequency is low, temperature effects are important. Unfortunately, a relatively simple classical Boltzmann averaging is insufficient, and a quantum mechanical procedure that takes into account all vibrational modes and includes anharmonicities must be employed.

The vibrational contributions have been shown by Ruud and Zanasi[20] to increase the discrepancy between the theoretical OR at the B3LYP level and experiment. We demonstrate that the SAOP functional yields comparable errors, despite the fact that SAOP describes the low-lying Rydberg states in accordance with experiment.[28] We find that the DFT models predict the OR dispersion incorrectly, failing to reproduce an experimental sign change between 355 and 589.3 nm. In contrast, the CCSD model reproduces both sign and magnitude of the experimental OR at the three wavelengths investigated here (355, 589.3, and 633 nm).

Our main conclusion is that theoretical calculations of OR can be used also for small-angle rotations provided that sufficiently high level electron correlation (CCSD in this case) is employed and that vibrational effects are properly accounted for, in particular if the molecule contains conformationally flexible groups. Our results clearly show that vibrational effects (along with potential solvent effects) must be considered, when single-point calculations of specific optical rotations are used together with experimentally determined specific optical rotations in order to resolve the stereochemistry of chemical compounds with small-angle optical rotations. Since most chiral molecules of practical interest are significantly larger than (*S*)-propylene oxide, our results emphasize the need for developing computational techniques to treat larger molecules with highly accurate ab initio methods such as CCSD or, even better, CC3.

Comparing almost exclusively to gas-phase experimental results in this work, we have had no reason to address the delicate problem of calculating solvent effects. However, the need for accurate solvation models is in fact stressed by the case of (*S*)-propylene oxide: in cyclohexane solution the (extrapolated) experimental 355 nm OR is[23] −26.4 deg [dm g/cm^3]$^{-1}$; i.e., the magnitude of the solvent effect is about the same as the electronic and vibrational contributions in the gas phase. From the investigations in this paper we expect that the sign change is primarily due to the solvent effect on the torsional mode combined with a difference in equilibrium geometry. In addition, the dispersion might be altered in the presence of the solvent through changes in the low-lying Rydberg states.

Acknowledgment. We are grateful to Prof. K. Ruud (University of Tromsø) for very helpful discussions and for providing us with the equilibrium and effective geometries of (*S*)-propylene oxide. We are also grateful to Prof. P. H. Vaccaro (Yale University) for supplying the refined experimental results of ref 24 prior to publication. K.V.M. thanks FNU, DCSC, and the EU network NANOQUANT for support.

JA056611E