Optical Activity: The Rosenfeld Polarizability

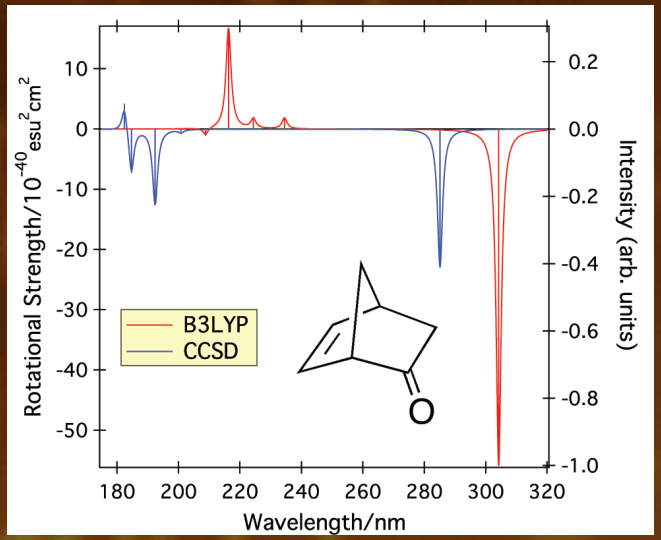
A quantum mechanical description of optical rotation may be obtained from second-order time-dependent perturbation theory, which shows that the dipole moment induced by a plane-polarized wave depends on two terms:

$$\langle \mu \rangle = \alpha \mathbf{E} + \frac{1}{\omega} \mathbf{G}' \frac{\partial \mathbf{B}}{\partial t}$$

where

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

The trace of this tensor is related to **optical rotatory dispersion (ORD)** and its residues to the **circular dichroism (CD)** spectrum for comparison to experimental data.



L. Rosenfeld, *Z. Physik* **52**, 161 (1928).

L. D. Barron, *Molecular Light Scattering and Optical Activity,* 2nd Ed., Cambridge University Press, 2004.

T.D. Crawford, *Theo. Chem. Acc.* **115**, 227-245 (2006).

Coupled Cluster Response Theory

The linear response function for perturbation operators *C* and *D* at frequency ω is:

$$\langle\langle C;D\rangle\rangle_\omega = \frac{1}{2}\hat{C}^{\pm\omega}P\left[C(-\omega),D(+\omega)\right]\left[\langle 0|\Lambda[\bar{C},X^D_\omega]|0\rangle + \frac{1}{2}\langle 0|\Lambda[[\bar{H},X^C_{-\omega}],X^D_\omega]|0\rangle\right]$$

where the overbar denotes coupled cluster similarity-transformed operators, e.g.:

$$\bar{H} = e^{-\hat{T}}He^{\hat{T}}$$

the symbol Λ denotes the coupled cluster left-hand ground-state wave function, and the permutation operators $C^{\pm\omega}$ and *P* ensure symmetry with respect to complex conjugation and sign reversal. The perturbed wave functions are determined by solving the appropriate systems of linear equations:

$$\sum_\nu \langle\mu|\left(\bar{H}-\omega\right)|\nu\rangle\langle\nu|X^D_\omega|0\rangle = -\langle\nu|\bar{D}|0\rangle$$

H. Monkhorst, Int. J. Quantum Chem. Symp. **11,** 421 (1977); H. Koch and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990); J. F. Stanton and R. J. Bartlett, J. Chem. Phys. 98, 7029 (1993) ; T. B. Pedersen and H. Koch, J. Chem. Phys. **106**, 8059 (1997); H. Sekino and R.J. Bartlett, Adv. Quantum Chem. 35, 149 (1999).

Coupled Cluster Response Theory

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"We prefer the denotation Coupled-Clutter Method (CCM) since it suggests most vividly the central features..."

H.J. Monkhorst, Int. J. Quantum Chem. Symp. **11**, 421 (1977)

$$\sum_\nu \langle\mu|\left(\bar{H} - \omega\right)|\nu\rangle\langle\nu|X^D_\omega|0\rangle = -\langle\nu|\bar{D}|0\rangle$$

H. Monkhorst, Int. J. Quantum Chem. Symp. **11,** 421 (1977); H. Koch and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990); J. F. Stanton and R. J. Bartlett, J. Chem. Phys. 98, 7029 (1993) ; T. B. Pedersen and H. Koch, J. Chem. Phys. **106**, 8059 (1997); H. Sekino and R.J. Bartlett, Adv. Quantum Chem. 35, 149 (1999).

The PSI3 Quantum Chemistry Suite

- Arbitrarily high angular momentum in integrals and derivative integrals
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- Analytic energy gradients for CCSD and CCSD(T) methods.
- Excitation energy methods, including RPA, CIS(D), EOM-CCSD, CC2, and CC3.
- Coupled cluster linear response for dipole polarizabilities and optical rotation.
- Determinant-based CI methods, including CASSCF, RASSCF, RAS-CI, Full CI.
- Integral direct SCF, MP2, and MP2-R12 energies.
- Diagonal Born-Oppenheimer correction for SCF and CI wave functions.
- Written in the C and C++ programming languages.

T. Daniel Crawford, C. David Sherrill, Edward F. Valeev, Justin T. Fermann, Rollin A. King, Matthew L. Leininger, Shawn T. Brown, Curtis L. Janssen, Edward T. Seidl, Joseph P. Kenny, and Wesley D. Allen,

J. Comp. Chem. **28**, 1610-1617 (2007).

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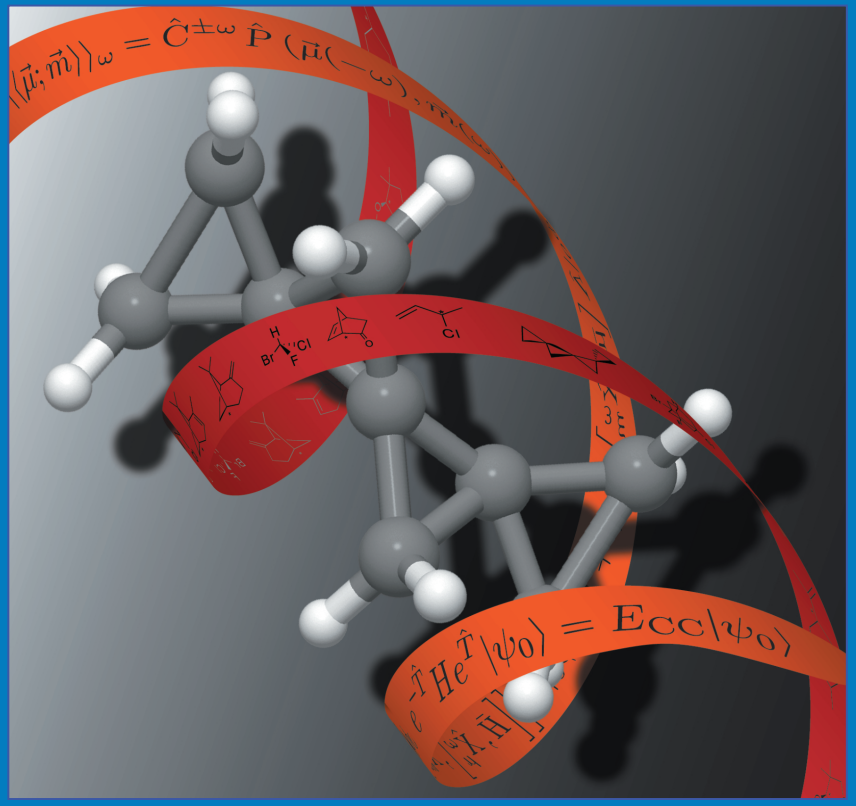
THE JOURNAL OF PHYSICAL CHEMISTRY A



(*P*)-(4)Triangulane and Helical Ribbons Depicting Paradigmatic Chiral Molecules and the Coupled-Cluster Chiroptical Response Equations (see page 5A)

DYNAMICS, KINETICS, ENVIRONMENTAL CHEMISTRY, SPECTROSCOPY, STRUCTURE, THEORY

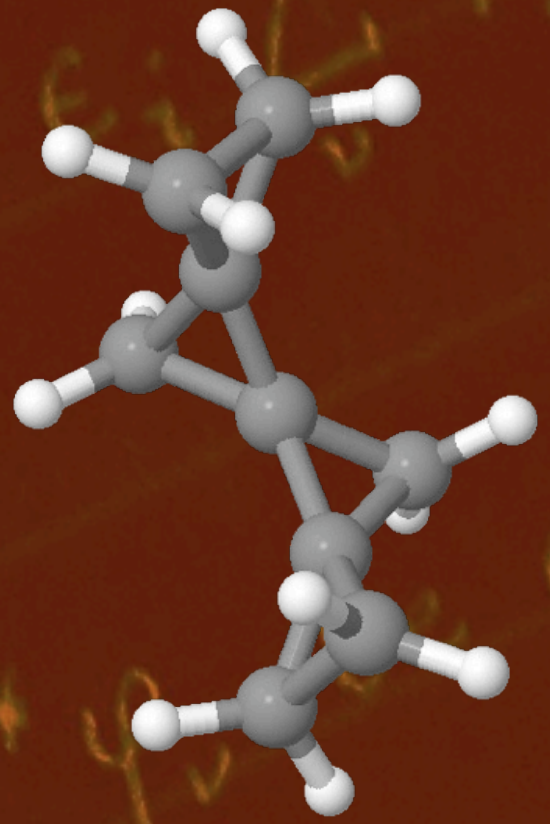
T. D. Crawford, M. C. Tam, M. L. Abrams, *J. Phys. Chem. A* **111**, 12057 (2007)

PUBLISHED WEEKLY BY THE AMERICAN CHEMICAL SOCIETY

(*P*)-(+)-[4]triangulane[a]

T. D. Crawford, L. S. Owens, M. C. Tam, P. R. Schreiner, and H. Koch, *J. Am. Chem. Soc.* **127**, 1368 (2005).

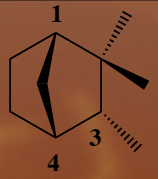
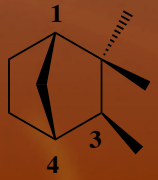
Wavelength (nm)	B3LYP aug-cc-pVDZ	CCSD aug-cc-pVDZ	Expt.[b]
589	221.5	**196.0**	192.7
578	231.4	**204.5**	201.3
546	264.3	**232.9**	229.7
436	460.7	**398.7**	400.2
365	752.2	**635.4**	648.2



[a] Specific rotation in deg/[dm (g/mL)] computed at the B3LYP/6-31G* optimized geometry.

[b] Measured in $CHCl_3$: A. de Meijere, A. F. Khlebnikov, S. I. Kozhushkov, R. R. Kostikov, P. R. Schreiner, A. Wittkopp, C. Rinderspacher, H. Menzel, D. S. Yufit, and J. A. K. Howard, *Chem. Eur. J.* **8**, 828-842 (2002).

Performance of Theory for $[\alpha]_D$: Alkanes

Molecule	B3LYP	CCSD	Expt.
 (*1R,2S,5R*)-*cis*-pinane	+17.9	+8.8	+23.3
 (*1S,2S,5S*)-*trans*-pinane	+3.6	+0.0	-15.9
 (*1S,3R,4R*)-endo-isocamphane	-11.1	-13.1	+6.6
 (*1S,3S,4R*)-exo-isocamphane	+4.1	+6.5	+15.8

T. D. Crawford and P. J. Stephens, *J. Phys. Chem. A* **112**, 1339-1345 (2008).

Specific rotations in deg/[dm (g/mL)].

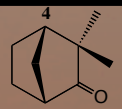
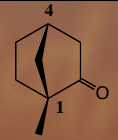
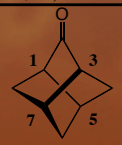
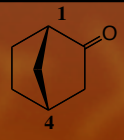
Performance of Theory for $[\alpha]_D$: Alkenes

Molecule	B3LYP	CCSD	Expt.
 (*1R*,*5R*)-α-pinene	+42.4	+53.7	+51.6
 (*1R*,*5R*)-β-pinene	-26.1	-2.0	+23.1

T. D. Crawford and P. J. Stephens, *J. Phys. Chem. A* **112**, 1339-1345 (2008).

Specific rotations in deg/[dm (g/mL)].

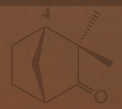
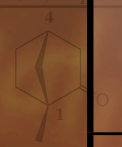
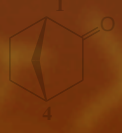
Performance of Theory for $[\alpha]_D$: Ketones

Molecule	B3LYP	CCSD	Expt.
 (*1R,4S*)-camphenilone	-56.7	-69.6	-72.3
 (*1R,5S*)-nopinone	-10.9	-8.7	+39.9
 (*1R,4S*)-1-methylnorbornanone	-28.9	-33.3	-45.5
 (*1R,3S,6S,7R*)-2-brendanone	+32.8	+47.8	+46.6
 (*1R,3R,5R,7R*)-bisnoradamantan-2-one	+13.2	+50.2	-78.4
 (*1S,4R*)-norbornanone	-10.4	+5.0	+29.8

T. D. Crawford and P. J. Stephens, *J. Phys. Chem. A* **112**, 1339-1345 (2008).

Specific rotations in deg/[dm (g/mL)].

Performance of Theory for $[\alpha]_D$: Ketones

Molecule	B3LYP	CCSD	Expt.
 (*1R,4S*)-camphenone	-56.7	-69.6	-72.3
 (*1R,5S*)-norcamphenone	-10.9	-8.7	+39.9
 (*1R,4S*)-1-methylnorbornanone	-28.9	-33.3	-45.5
 (*1R,3S,6S,7R*)-2-brendanone	+32.8	+47.8	+46.6
 (*1R,3R,5R,7R*)-bisnoradamantan-2-one			
 (*1S,4R*)-norbornanone	-10.4	+5.0	+29.8

Mean Absolute Deviations from Experiment:	
B3LYP	28.4
CCSD	25.4

All experimental data are from liquid-phase measurements

T. D. Crawford and P. J. Stephens, *J. Phys. Chem. A* **112**, 1339-1345 (2008).

Specific rotations in deg/[dm (g/mL)].