

Communications to the Editor

Ab Initio Predictions of Anomalous Optical Rotatory Dispersion

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Chemists have practiced the measurement of optical rotation as a function of wavelength (optical rotatory dispersion) for more than a century.^{1,2} The observed optical rotations were explained¹ initially using the Law of Inverse Squares (Biot's law), i.e., $\alpha = k/\lambda^2$, where α is the observed rotation, λ is the wavelength, and k is a constant. When the measured optical rotations follow this criterion, or more precisely the Lowry's condition¹ that α , $\partial\alpha/\partial\lambda$, and $\partial^2\alpha/\partial\lambda^2$ must remain constant in sign, then it is referred to as normal rotatory dispersion. Anomalous rotatory dispersion, deviating from the normal dispersion, can show optical rotation sign reversals with inflection points in the dispersion data. In such cases, the rotatory dispersion data are represented¹ by the Drude equation, $\alpha = \sum_m A_m/(\lambda^2 - \lambda_m^2)$, where A_m and λ_m are constants specific to the molecule under investigation. These empirical representations can be seen to have quantum mechanical counterparts as described below.

The theoretical quantity pertinent to calculating the optical rotation is the electric dipole–magnetic dipole polarizability tensor, given by the expression^{3–5}

$$G'_{\alpha\beta} = \frac{-4\pi}{h} \sum_{n \neq s} \frac{\omega}{\omega_{ns}^2 - \omega^2} \text{Im} \{ \langle \psi_s^0 | \hat{\mu}_\alpha | \psi_n^0 \rangle \langle \psi_n^0 | \hat{m}_\beta | \psi_s^0 \rangle \} \quad (1)$$

where $\hat{\mu}_\alpha$ and \hat{m}_β are respectively the electric dipole moment and magnetic dipole moment operators; ψ_s^0 and ψ_n^0 represent the ground and excited electronic state wave functions, respectively; $\omega_{ns} = 2\pi(E_n^0 - E_s^0)/h$, where E_n^0 and E_s^0 are the unperturbed energies of states n and s , respectively; and ω is the angular frequency of exciting radiation. The quantity

$$\beta = -\omega^{-1}(G'_{xx} + G'_{yy} + G'_{zz})/3 \quad (2)$$

is related to the optical rotation ϕ (in rad/cm) as⁶ $\phi = 4\pi N\beta\omega^2/(n^2 + 2)/3c^2$, where N represents the number of molecules per unit volume, n represents the refractive index of the medium, and $\omega^{-1}G'_{\alpha\alpha}$ are in CGS units. The experimental optical rotations are most commonly reported as specific rotation $[\alpha]$ in units of deg/[dm(g/cm³)]. The corresponding theoretical quantity is $[\alpha] = 3600\phi V_m/2\pi M$, where M and V_m are respectively the molar mass and molar volume. Using these definitions, a convenient expression for the specific rotation is given⁷ as

$$[\alpha] = (0.1343 \times 10^{-3})\beta\bar{\nu}^2(n^2 + 2)/3M \quad (3)$$

(1) Lowry, T. M. *Optical rotatory power*; Dover Publications: New York, 1964.

(2) Djerassi, C. *Optical rotatory dispersion: Applications to organic chemistry*; McGraw-Hill: New York, 1960.

(3) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.

(4) Buckingham, A. D.; Longuet-Higgins, H. C. *Mol. Phys.* **1968**, *14*, 63.

with β in units of (bohr)⁴, M in gm/mol, and $\bar{\nu}$ (wavenumber at which the optical rotation is measured) in cm⁻¹.

There are two approaches to evaluating eq 3: the static method and the dynamic method. In the static method, an explicit evaluation of the sum over excited states in eq 1 is avoided by noting that, when $\omega_{ns} \gg \omega$, eq 1 can be simplified as⁸

$$\omega^{-1}G'_{\alpha\beta} = -(h/\pi)\text{Im}\{ \langle (\partial\psi_s/\partial F_\alpha) | (\partial\psi_s/\partial B_\beta) \rangle \} \quad (4)$$

Amos developed⁸ and implemented⁹ an approach for evaluating eq 4 in the static limit ($\omega \rightarrow 0$) by calculating the derivatives $(\partial\psi_s/\partial F_\alpha)$ and $(\partial\psi_s/\partial B_\beta)$ using the coupled perturbed Hartree–Fock method.¹⁰ Equations 2 and 4 are obtained in the static limit, so they are independent of wavelength, and the optical rotations obtained via eqs 2–4 can be seen to follow Biot's law. The optical rotations obtained with the static method^{11–13} are suitable for comparison with the measurements at wavelengths far greater than that of the first electronic transition.

In the dynamic method, eq 1 is evaluated¹⁴ as a function of ω or λ . By substituting eqs 1 and 2 in eq 3, the resulting equation can be seen to have a functional form similar to that of Drude's equation. A method to evaluate eq 1 has been developed¹⁴ and implemented¹⁵ by Jorgensen and co-workers. This method was used earlier^{16,17} for calculating the optical rotations at 589.3 nm via eqs 1–3, but no attempts have been made for verifying anomalous optical rotatory dispersion. It is important to have dispersion data to avoid wrong conclusions that might be reached from optical rotation data at a single wavelength. In this paper we apply the dynamic method for predicting anomalous rotatory dispersion, for the first time, using (3R)-methylcyclohexanone as a test case.

All calculations were done using the DALTON program¹⁵ on a Pentium II (300 MHz) based PC with LINUX operating system. Both London and non-London orbitals were used for the evaluation of eq 1, but only the results obtained with London orbitals are presented here. Using the geometries of 3-methylcyclohexanone for the chair and boat conformations optimized with the

(5) Barron, L. D. *Molecular Light Scattering and Optical Activity*; Cambridge University Press: Cambridge, U.K., 1982.

(6) (a) Caldwell, D. J.; Eyring, H. *The Theory of Optical Activity*; Wiley-Interscience: New York, 1971. (b) Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; John Wiley: New York, 1944.

(7) Polavarapu, P. L. *Mol. Phys.* **1997**, *91*, 551.

(8) Amos, R. D. *Chem. Phys. Lett.* **1982**, *87*, 23.

(9) Amos, R. D.; Rice, J. E. *CADPAC: The Cambridge Analytic Derivative Package*, Issue 4.0, 1987.

(10) (a) Stevens, R. M.; Pitzer, R.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *38*, 550. (b) Gerratt, J.; Mills, I. M. *J. Chem. Phys.* **1968**, *49*, 1719. (c) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *13*, 225. (d) Yamaguchi, Y.; Osamura, Y.; Goddard, J. D.; Schaefer, H. F., III. *A new dimension to quantum chemistry*; Oxford University Press: Oxford, U.K., 1994.

(11) Polavarapu, P. L. *Tetrahedron: Asymmetry* **1997**, *8*, 3397.

(12) Polavarapu, P. L.; Chakraborty, D. K. *J. Am. Chem. Soc.* **1998**, *120*, 6160.

(13) Polavarapu, P. L.; Chakraborty, D. K. *Chem. Phys.*, in press.

(14) Olsen, J.; Jorgensen, P. In *Modern Electronic Structure Theory*, Part II; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995.

(15) Helgaker, T.; Jensen, H. J. Aa.; Jorgensen, P.; Olsen, J.; Ruud, K.; Agren, H.; Anderson, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalakov, E. K.; Enevoldsen, T.; Fernandez, B.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. *DALTON: An ab initio electronic structure program*, 1997, Release 1.0.

(16) Kondru, R. K.; Wipf, P.; Beratan, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 2204.

(17) Polavarapu, P. L.; Zhao, C. *Chem. Phys. Lett.* **1998**, *296*, 105.

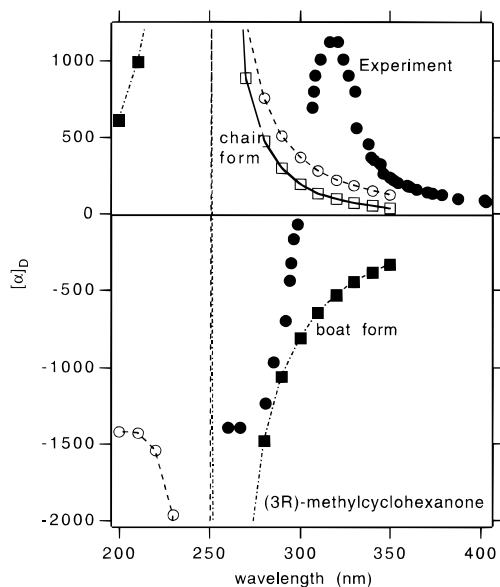


Figure 1. Comparison of experimental optical rotatory dispersion data^{21a} of (3*R*)-methylcyclohexanone in the 250–400 nm range (●) to those calculated with DZP basis set in the 200–350 nm range for the chair conformation (○) and boat conformation (■); the data were also obtained with a larger aug-cc-pVDZ basis set in the 260–350 nm range (□) for the chair conformation.

6-31G basis set,¹⁸ optical rotations were calculated with DZP¹⁹ basis set. For the chair conformation, optical rotations were also calculated with a larger aug-cc-pVDZ²⁰ basis set. The calculated optical rotatory dispersion data (without including any spectral broadening or dampening effects) for the (*R*)-configuration are compared with the corresponding experimental data^{21a} for (+)-enantiomer (in cyclohexane, at 0.827 M to 1.694 mM) in Figure 1. No differences were reported^{21b} for the optical rotatory dispersion data in methanol at 0.212 M.

For the chair conformation, starting at longer wavelengths, the magnitude of DZP-predicted optical rotation increases with decreasing wavelength, goes to a maximum, and reverses sign at 250.8 nm, which is the wavelength of the first electronic transition predicted with DZP basis set. With the aug-cc-pVDZ basis set, the first electronic transition of the chair conformation is predicted to occur at 252.1 nm, so with this basis, the inflection point occurs at 252.1 nm. Upon sign reversal, the magnitude of predicted

negative optical rotation decreases with decreasing wavelength. The experimental optical rotatory dispersion data for the (+)-enantiomer show a similar pattern, except for two differences: (a) the sign reversal in the experimental data²¹ occurs at 297 nm, so the predicted optical rotatory dispersion curve appears shifted toward shorter wavelengths in relation to the experimental curve, and (b) the peak rotations predicted at the inflection point (off-scale in Figure 1) are much greater than those observed.

Similar conclusions were also obtained from the comparison of calculated and experimental anomalous optical rotatory dispersion data for (+)-(3*R*)-methylcyclopentanone, indicating the generality of these predictions in this series of molecules.

The predicted optical rotatory dispersion data for the boat conformation of 3-methylcyclohexanone, with the same (*R*)-configuration, is opposite to that of the chair conformation (see Figure 1) and to that of experimental data for the (+)-enantiomer. This observation is in agreement with the well-established conclusion that the chair conformation is predominant for 3-methylcyclohexanone.

There are two limitations which can be improved in the future calculations: (1) The wavelength shift of the inflection point in the predicted optical rotatory dispersion data arises from a poor description of the excited states at the Hartree–Fock (HF) level of theory, as has been evident in the electronic circular dichroism calculations²² on methylcyclohexanone. That is, the energy gap between the ground and excited states is predicted to be much higher at the HF level of theory than that deduced from the experimental electronic spectra. The experimental data in cyclohexane^{21a} and methanol^{21b} solutions are similar, so the absence of solvent influence in the calculations might not be significant here. Then it is first necessary to have a balanced and high level of correlation in both ground and excited states in order for the wavelength of electronic transitions to be predicted correctly.²³ (2) Under resonance conditions (at $\omega = \omega_{ks}$) optical rotation is determined¹⁴ by the term $\langle \psi_s^0 | \hat{\mu}_\alpha | \psi_k^0 \rangle \langle \psi_k^0 | \hat{m}_\beta | \psi_s^0 \rangle$, so the prediction of peak magnitudes of optical rotation near resonance may also be improved by using the correlated wave functions. It may be necessary to use a dampening function to reduce the large predicted magnitudes near resonance. To determine the applicability and reliability of such dampening functions, the predictions obtained for optical rotatory dispersion involving multiple resonances must be compared with the corresponding experimental data.

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JA9828556

(18) Hariharan, P. C.; Pople, J. A., *Theor. Chim. Acta* **1973**, *28*, 213.

(19) Dunning, T. H. *Chem. Phys.* **1970**, *53*, 2823.

(20) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(21) (a) French, H. S.; Naps, M. *J. Am. Chem. Soc.* **1936**, *58*, 2303. (b) Djerassi, C.; Krakower, G. W. *J. Am. Chem. Soc.* **1959**, *81*, 237.

(22) Rauk, A.; Jarvie, J. O.; Ichimura, H.; Barriol, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 5656.

(23) Private discussion with Professor Arvi Rauk.