

Classical Magnetic Dipole Moments for the Simulation of Vibrational Circular Dichroism by ab Initio Molecular Dynamics

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Vibrational circular dichroism spectroscopy

Measurement of the difference in absorption ΔA of left and right circularly polarized IR radiation.

- Important technique to analyze chiral molecules
- Enantiomers have mirrored spectra
- Powerful tool in combination with IR spectroscopy.

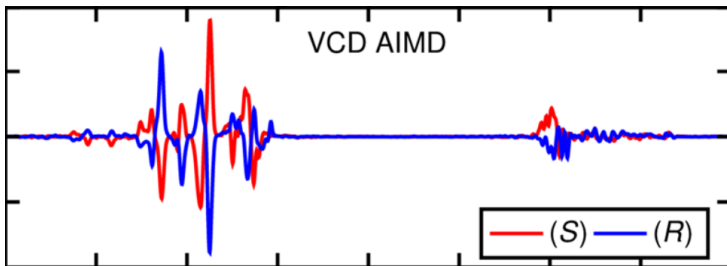


Figure 1: Computed VCD spectra of (S),(R)-2-butanol.

Computation of VCD spectra so far:

- Static quantum chemistry, based on
 - a) magnetic field perturbation theory, or
 - b) nuclear velocity perturbation theory
- Easy for gas phase
- Inclusion of bulk effects by implicit or explicit solvation models
- But: No dynamic effects

Newly introduced by this paper:

- VCD spectra from *ab initio* MD simulations
 - AIMD: Forces are computed by electronic structure method
- Gas and bulk phase
- Allows for dynamic effects

VCD spectrum can be obtained from FT of time cross-correlation function of electric dipole moment $\mu(t)$ and magnetic dipole moment $m(t)$.

$$\Delta A(\tilde{\nu}) \propto \int [\langle \dot{\mu}(\tau) \dot{m}(t + \tau) \rangle_{\tau} - \langle \dot{m}(\tau) \dot{\mu}(t + \tau) \rangle_{\tau}] \exp(-2\pi i c \tilde{\nu} t) dt \quad (1)$$

The electric dipole moment is obtained from Voronoi tessellation of the electron density ρ (fast).

$$\mu_k = \int r \cdot \rho(r) dr \quad k = 1, \dots, N \quad (2)$$

Key point: The magnetic dipole moment is obtained from the electric current density j and the continuity equation (computational bottleneck).

$$\frac{\partial \rho(r, t)}{\partial t} + \nabla j(r, t) = 0 \quad (3)$$

$$m = \frac{1}{2} \int r \cdot j(r) dr \quad (4)$$

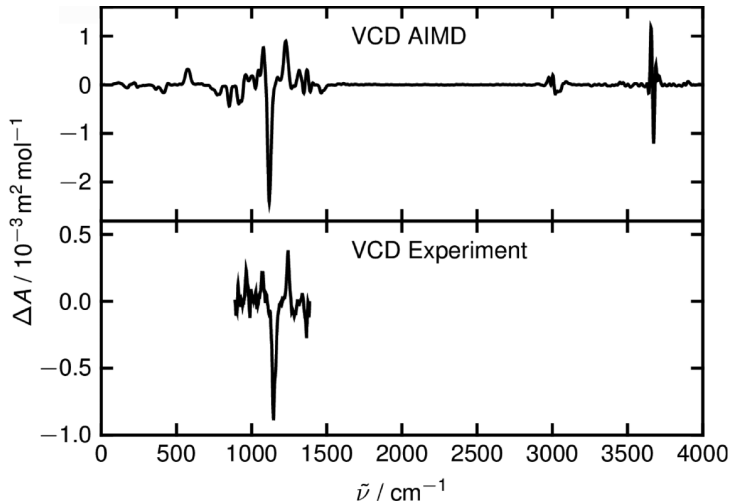


Figure 2: Gas Phase VCD spectra of (*R*)-2-butanol. AIMD: BLYP/DZ

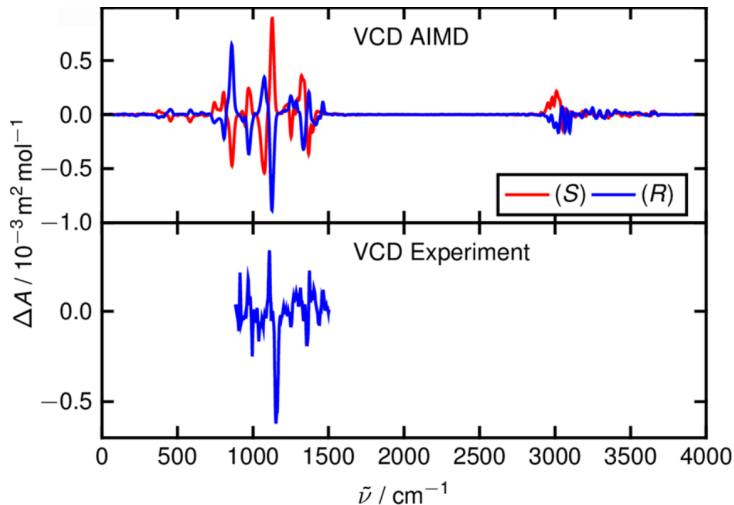


Figure 3: Bulk Phase VCD spectra of *(S),(R)*-2-butanol. AIMD: BLYP/DZ

VCD spectra from AIMD simulations:

- + Accurate
- + Allow for dynamics
- + Yield (all) different conformers and their spectra
- + Separate analysis of every molecule possible
- + Not restricted to any particular electronic structure method

- Much higher cost compared to static QC
- Highly accurate electronic structure methods often not affordable