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

M. Thomas, B. Kirchner, *J. Chem. Phys. Lett.* **2016**, *7*, 509–513

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Vibrational circular dichroism spectroscopy

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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.

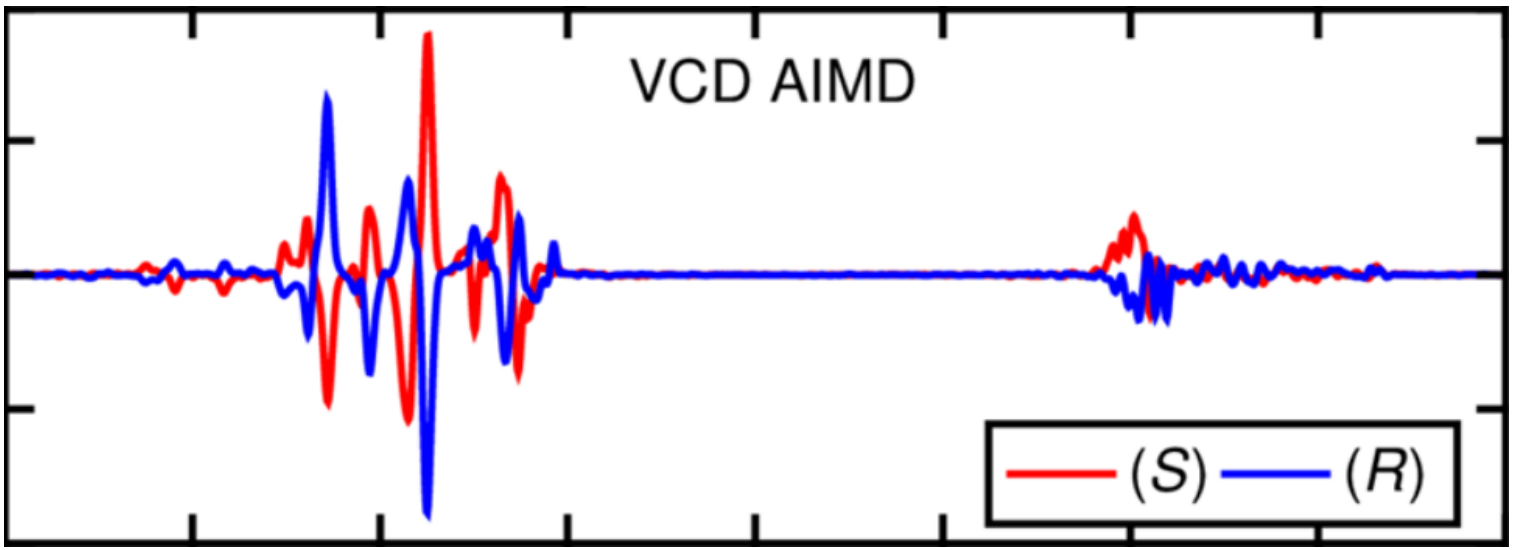

Figure 1: Computed VCD spectra of *(S),(R)*-2-butanol.

What's new?

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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 inito* MD simulations
  - AIMD: Forces are computed by electronic structure method
- Gas and bulk phase
- Allows for dynamic effects

Theory

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

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

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

$$\mu_k = \int r \cdot \rho(r)\mathrm{d}r \quad k = 1, \ldots, N \quad (2)$$

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

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

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

Results I

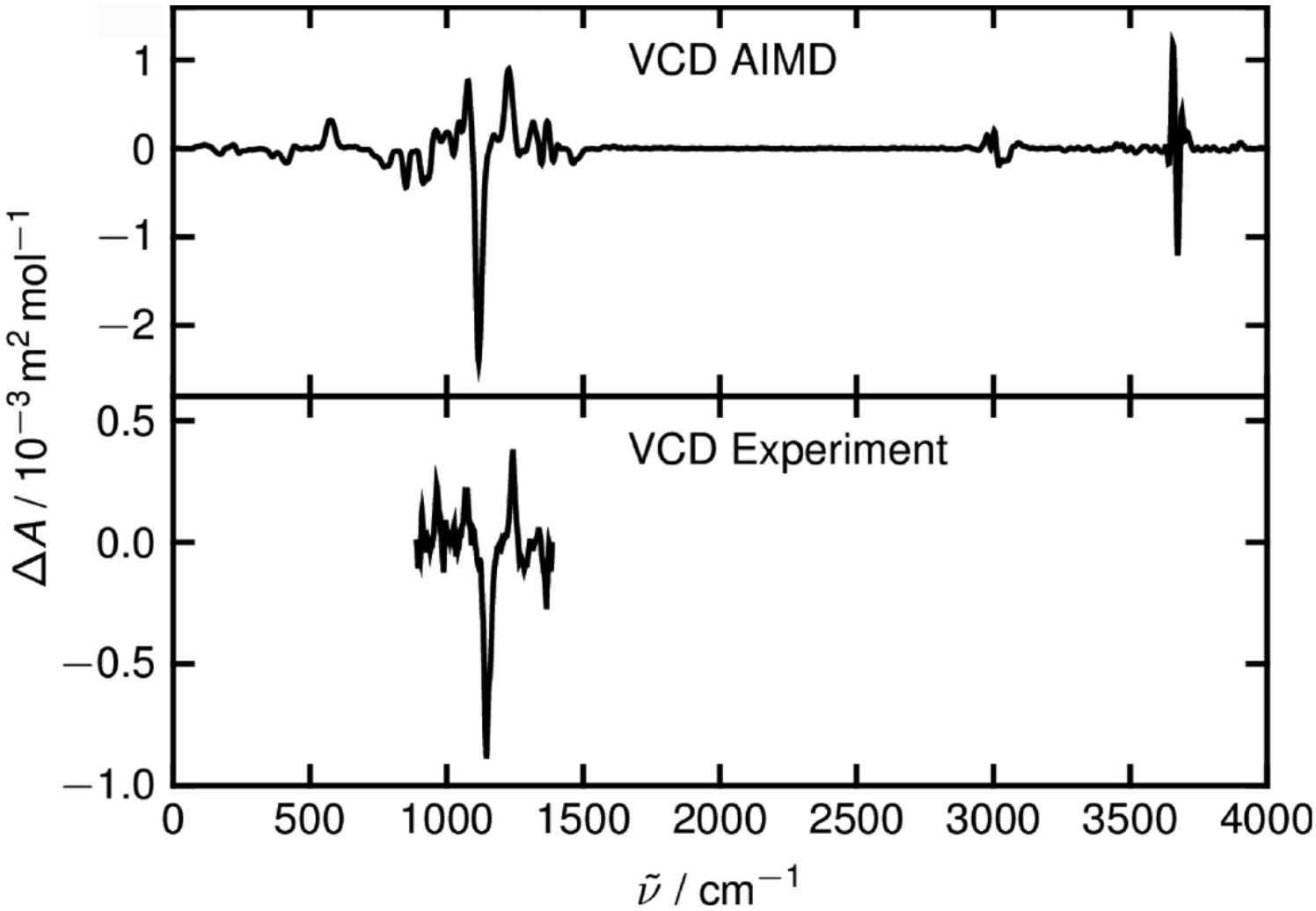

Figure 2: Gas Phase VCD spectra of *(R)*-2-butanol. AIMD: BLYP/DZ

Results II

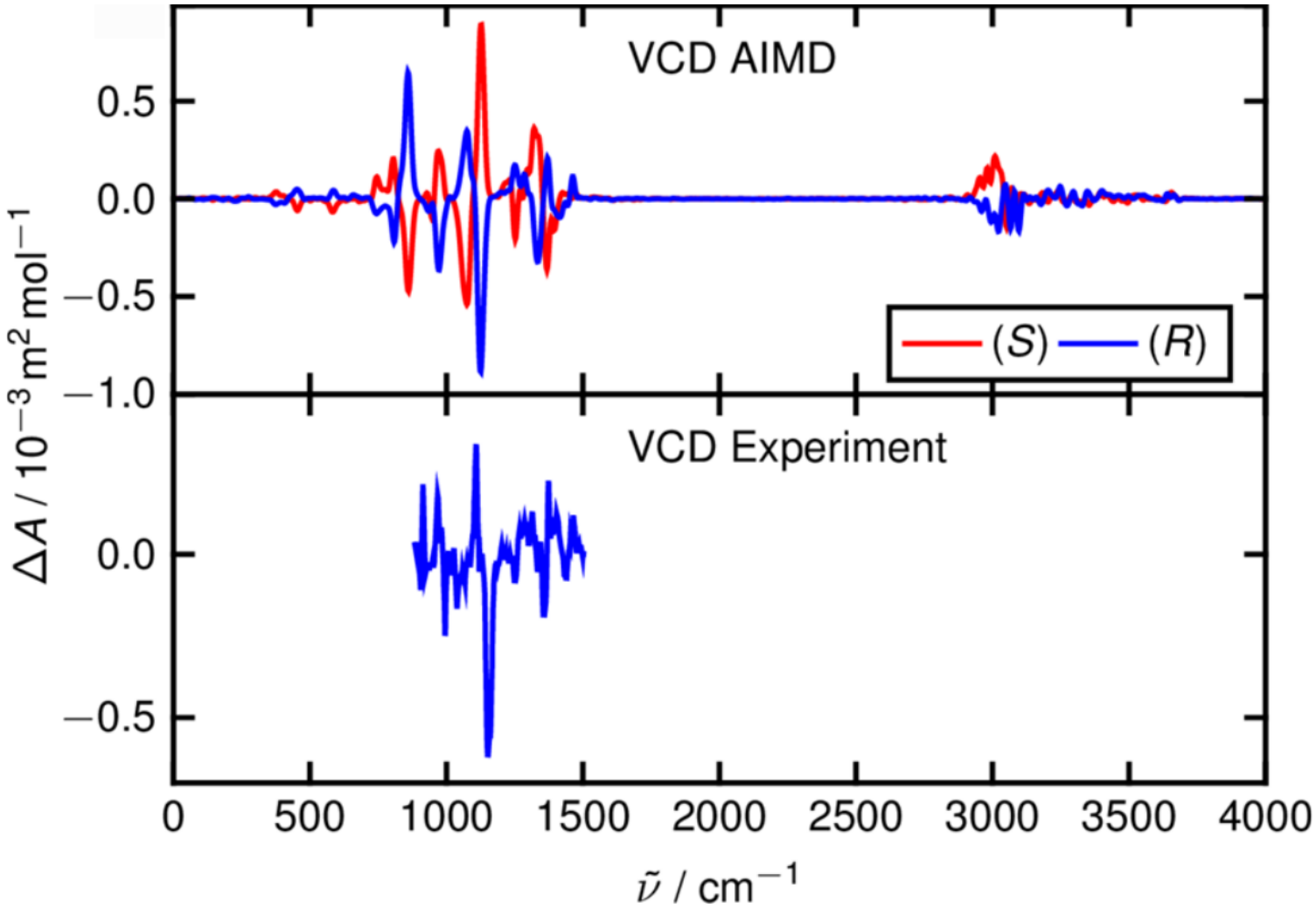

Figure 3: Bulk Phase VCD spectra of *(S),(R)*-2-butanol. AIMD: BLYP/DZ

Summary

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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