Chirality Aspects in the Dimerization of Vicinal Diols

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2. Experimental Techniques

3. Comparison of ED and CD
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   - Energetic Predictions
   - Experimental Spectra
   - Comparison of Experiment and Theory

4. Summary and Outlook
Motivation

What sparked this Project?

- 1,2-Ethanediol (ED) studied experimentally and theoretically
- transiently chiral
  
  ![Molecule Diagram]

- energetic preference for hetero chiral dimers
- formation of homo dimers uncertain

What am I doing?

- trans-1,2-Cyclohexanediol (CD) studied experimentally and theoretically
- permanently chiral

- (R,R)
  
  ![Molecule Diagram]

- (S,S)
  
  ![Molecule Diagram]

- lack of interconversion could help understanding the formation of homo dimers in ED

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Experimental Techniques

Experimental Setups

- FTIR- and Raman-jet-setup
- resolution of ca. 1 – 2 cm$^{-1}$
- no restrictions regarding compounds besides vapor pressure
  ⇒ If we can get it in the gase phase we can measure it!

Advantages of Jet-Spectroscopy

- cooling of the rotational and vibrational levels
- better comparability with quantum chemical calculations
- relaxation of less stable conformers (barriers > 5 kJ mol$^{-1}$ cannot be overcome)
- reduced Doppler broadening
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Comparison of ED and CD

Nomenclature and Comparison of the Monomers

- **M**
  - $0.0 \text{ kJ mol}^{-1}$
  - $\angle \text{OCCO} - 62.2^\circ$
  - $\angle \text{O}_D \text{O}_A \text{H}_A 140.4^\circ > 120^\circ$

- **M'**
  - $1.3 \text{ kJ mol}^{-1}$
  - $\angle \text{OCCO} - 57.5^\circ$
  - $\angle \text{O}_D \text{O}_A \text{H}_A 109.0^\circ < 120^\circ$

- **M**
  - $0.0 \text{ kJ mol}^{-1}$
  - $\angle \text{OCCO} - 60.1^\circ$
  - $\angle \text{O}_D \text{O}_A \text{H}_A 144.8^\circ > 120^\circ$

- **M'**
  - $1.0 \text{ kJ mol}^{-1}$
  - $\angle \text{OCCO} - 55.9^\circ$
  - $\angle \text{O}_D \text{O}_A \text{H}_A 110.2^\circ < 120^\circ$
Comparison of ED and CD

Energetic Predictions of the Dimers

- B3LYP-D3(BJ,abc)/def2-QZVP
- zero point corrected
- double harmonic approximation

**CD het4 : hom3' : hom3'' : hom2''**
\[ \Rightarrow 3 : 1 : 1 : 1 \]

**ED het4 : hom3' : hom3'' : hom3a**
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Comparison of ED and CD

Energetic Predictions of the Dimers

- B3LYP-D3(BJ,abc)/def2-QZVP
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For CD:
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For ED:
- het4 : hom3’ : hom3’’ : hom3a
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Experimental Spectra

**Experimental Raman Spectra**
- Wavenumber range: 3700 to 3300 cm\(^{-1}\)
- Peaks at 28 cm\(^{-1}\) (M and M')
- Racemic 1,2-Cyclohexanediol

**Experimental IR Spectra**
- Wavenumber range: 3700 to 3300 cm\(^{-1}\)
- Peaks at 19 cm\(^{-1}\) (M and M')
- Racemic 1,2-Cyclohexanediol

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Experimental Spectra

Experimental Raman Spectra

Experimental IR Spectra

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Comparison of Experiment and Theory

Ethanediol

Cyclohexanediol

![Graphs showing harmonic wavenumber differences for Ethanediol and Cyclohexanediol.](image)

- difference relative to free OH mode of M
Summary

- ED and CD both exhibit energetic chirality recognition
- Dimers are structurally very similar
- Dimers form statistically "missing" ED homo-dimers due to shared population among multiple conformers
- Dispersion interactions are crucial for chiral discrimination

Outlook

- Tuning the hetero↔homo energy gap by chemical substitution
  - Transiently chiral systems
    - Pinacol
    - Ethanediamine
  - Permanently chiral systems
    - Cyclopentanediol
  - Mixed systems
    - Propanediol
- Perform dispersion interaction density analysis
Thank you for your attention!
Experimental Setup²

CD Monomer Relaxation Study

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ED Dilution

[Graph showing relative intensity counts per second versus wave number (cm$^{-1}$). Peaks are labeled M, M', and T.]
Simulated Spectra

Raman Spectra

IR Spectra

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