VCD SPECTROSCOPIC STUDIES ON INTERMOLECULAR INTERACTIONS:
LEARNING THE BASICS FROM NOBLE GAS MATRICES

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Chirality and chemistry

central chirality

helical chirality

axial chirality

planar chirality

"An object is chiral when it is not superimposable with its mirror image."
Vibrational Circular Dichroism (VCD)

\[ \Delta A = A_{\text{LCP}} - A_{\text{RCP}} \]

(1R)-\(\alpha\)-pinene

\[ \begin{align*}
\text{absorbance } A \\
\text{wavenumber / cm}^{-1}
\end{align*} \]
Research interests

solute-solvent interactions

chirality transfer and asymmetric catalysis

chiral materials

enantioselective interactions
The concept of matrix isolation

Trapping of molecules in inert noble gas matrix onto a spectroscopic window which is cooled below the melting point of the matrix gas (e.g. $T_m(Ar)=83.85$ K)

- Ratio of analyte to matrix gas determines separation
- Window temperature determines softness of matrix

Annealing (short warm-up of the matrix) can lead to a better ordering of the matrix crystal lattice.

Annealing or deposition at higher temperature can lead to aggregation of the analyte.
Matrix-isolation VCD

WHY THE HASSLE?

- self-aggregation under controlled conditions
- intermolecular hydrogen bonding of chiral molecules in clusters with solvent molecules
- chirality transfer to achiral molecules
- the VCD in the OH region which is typically very broad in solution measurements

Cool down: 1 hr
Deposition: 4-9 hrs
Measurement: 3x 4 hrs
Warm-up & pumping: 9 hrs
Each experiment: 2 days
MI-VCD of Propylene Oxide

PROPYLENE OXIDE

- small, so it's a perfect benchmark molecule
- many vibrational spectroscopic studies conducted incl. VCD
- PO shows chirality transfer to water molecules in concentrated aqueous solution

**EXPERIMENT**
- ratio ML / Ar = 1 : 500
- deposition: 10 K, 6 hrs @ 1.5sccm
- resolution: 2 cm⁻¹

**COMPUTATIONS**
- DFT b3lyp/6-311++G(3df,3pd)
- scaling 0.986 (FP) and 0.97 (CH)
- line width HWHH 2 cm⁻¹
MI-VCD of Propylene Oxide

MI-VCD of PO: Anharmonicity effects

Anharmonic contributions to IR and VCD intensities in collaboration with Gaussian developers

Dr. Julien Bloino
(National Research Council of Italy, Pisa)

Prof. Dr. Vincenzo Barone
(Scuola Normale Superiore, Pisa)

- EXPERIMENT
  ratio ML / Ar = 1 : 500
deposition: 10 K, 6 hrs @ 1.5 sccm
resolution: 2 and 0.5 cm\(^{-1}\)

- COMPUTATIONS
  DFT b3lyp/6-311++G(3df,3pd)
scaling 0.986 (FP) and 0.97 (CH)
line width HWHH 2 cm\(^{-1}\)

MI-VCD of 3-butyn-2-ol

A

$\Delta E = 1.96$ kcal/mol
Pop = 2.1%

B

$\Delta E = 0.19$ kcal/mol
Pop = 41.1%

C

$\Delta E = 0.00$ kcal/mol
Pop = 56.8%

EXPERIMENT
ratio Butynol/Argon = 1 : 360
deposition time: 6 hrs @ 1sccm
resolution: 2 cm$^{-1}$
* impurities

COMPUTATIONAL DETAILS
DFT b3pw91/6-311++G(2d,p)
harmonic frequencies scaled by 0.98
line width HWHH 4cm$^{-1}$
Matrix-warmup: Formation of dimers

- Diluted solution (0.1 M) shows the same positive VCD bands ($a$ and $b$), but dimer bands ($b'$ and $c'$) as well.
- Negative dimer band $a$ cancels out positive monomer band $a$.
- Presence of dimers in 0.1 M solution explains the lower intensity ratio of band $a$ compared to $b$. 
MI-VCD of methyl lactate (ML)

<table>
<thead>
<tr>
<th>Conf</th>
<th>[\Delta E]</th>
<th>Pop (%)</th>
<th>(\angle (\text{CCOH}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00 kcal/mol</td>
<td>95.2%</td>
<td>-36.8°</td>
</tr>
<tr>
<td>B</td>
<td>2.12 kcal/mol</td>
<td>2.6%</td>
<td>45.5°</td>
</tr>
<tr>
<td>C</td>
<td>2.24 kcal/mol</td>
<td>2.2%</td>
<td></td>
</tr>
</tbody>
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EXPERIMENTAL SPECTRA ARE NICELY REPRODUCED BY CALCULATIONS.

- **EXPERIMENT**
  - ratio ML / Ar = 1 : 500
  - deposition: 10 K, 3 hrs @ 1.5sccm
  - resolution: 2 cm\(^{-1}\)

- **COMPUTATIONS**
  - DFT b3lyp/6-311++G(2d,p)
  - frequencies scaled by 0.99
  - line width HWHH 4 cm\(^{-1}\)

Ammonia is an ideal candidate for chirality transfer studies:

- Small but strong acceptor
- Only few IR bands, so no overlap with chirality donor molecule:
  - NH stretching: 3500-3200 cm\(^{-1}\)
  - NH bending: 1680-1600 cm\(^{-1}\)
  - Deformation: 1050-950 cm\(^{-1}\)

EXPERIMENT
- Ratio ML / Ar = 1 : X : 500
- Deposition temperature: 30 K
- Resolution: 2 cm\(^{-1}\)

COMPUTATIONS
- DFT b3lyp/6-311++G(2d,p)
- Frequencies scaled by 0.99
- Line width HWHH 4 cm\(^{-1}\)
Concluding remarks

- VCD is a very powerful technique to study the conformations and interactions of chiral molecules not only in solution but also in cold rare-gas matrices.

- Can give insights into the solution structures which can hardly be accessed by other spectroscopic techniques.

- Applicable to a wide range of materials, from small molecules to polymers, from metal complexes and nanoparticles, from small sugars to carbohydrates and peptides.

... as long as they are soluble enough respectively as long as they can be sublimed.
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