The GHz and THz spectrum of mono-deuterated oxirane

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Oxirane (ethylene oxide)

- A highly strained three-membered heterocycle
- Isomeric of acetaldehyde and vinyl alcohol
- Determination of abundance can shed light on construction/destruction pathways towards the formation of more complex organic molecules
- Observation of deuterated species provides D/H ratio as an indicator of history of the cold prestellar phase in star-forming regions
- ~10% or above [XD]/[XH] is commonly found
mono-deuterated oxirane: isotopically chiral


For isotopic chirality and molecular parity violation
Parity violation: Energy difference in enantiomers of a chiral molecule

Traditional theory:
van’t Hoff 1887
\[ R \rightleftharpoons S \quad \Delta_R H_0^\theta = 0 \]
exactly by symmetry

Today:
electroweak parity violation
\[ \Delta_{PV} H_0^\theta = \Delta_{PV} E_0 \times N_A \]
\[ \approx 10^{-(11\pm2)} \text{ J/mol} \]

Example: CHBrClF
Spectroscopy of 1-d oxirane


- Aims:
  1) to extend the measurement of pure rotational transitions to the GHz and THz regions to support astronomical observations;

  2) further investigation of rovibrational levels based on this ground state study
GHz setup at ETH Zürich

Detector

2.5 m gaseous cell

Frequency multiplier
75-110 GHz

Lock-in amplifier
Second-harmonic lock-in detection

MW synthesizer
250kHz-20GHz

Overview spectra: 69-113 GHz

25 μbar
294 K
measured MW spectrum of D1-oxirane

Simulated MW spectrum of D1-oxirane
Spectroscopic parameters of the ground state of 1d-oxirane

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Previous MW¹</th>
<th>GHz this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (MHz)</td>
<td>24252.47(17)</td>
<td>24252.64843(23)</td>
</tr>
<tr>
<td>B (MHz)</td>
<td>19905.34(17)</td>
<td>19905.52198(19)</td>
</tr>
<tr>
<td>C (MHz)</td>
<td>13327.40(17)</td>
<td>13327.58408(16)</td>
</tr>
<tr>
<td>Δ₁ (kHz)</td>
<td></td>
<td>17.01001(37)</td>
</tr>
<tr>
<td>Δ₂ (kHz)</td>
<td></td>
<td>25.44301(72)</td>
</tr>
<tr>
<td>Δ₃ (kHz)</td>
<td></td>
<td>17.31528(86)</td>
</tr>
<tr>
<td>δ₁ (kHz)</td>
<td></td>
<td>13.17077(19)</td>
</tr>
<tr>
<td>δ₂ (kHz)</td>
<td></td>
<td>4.74440(16)</td>
</tr>
<tr>
<td>d₉ (kHz)</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>N</td>
<td>20</td>
<td>112</td>
</tr>
</tbody>
</table>

Synchrotron-based high resolution FTIR setup at the Swiss Light Source

Overview spectra: 25-80 cm\(^{-1}\) (0.75-2.4 THz)

FT THz spectrum of D1-oxirane with synchrotron radiation

Simulated THz spectrum of D1-oxirane
FT THz spectrum of D1-oxirane with synchrotron radiation

Simulated THz spectrum of D1-oxirane
FT THz spectrum of D1-oxirane with synchrotron radiation

Simulated THz spectrum of D1-oxirane
Impurities in the sample

FT THz spectrum of D1-oxirane with synchrotron radiation

Simulated THz spectrum of D1-oxirane

Simulated THz spectra of CH$_2^{35}$Cl$_2$
Impurities in the sample

FT THz spectrum of D1-oxirane with synchrotron radiation

Simulated THz spectrum of D1-oxirane

Simulated THz spectra of CH$_2^{35}$Cl$_2$
# Spectroscopic parameters of the ground state of 1d-oxirane

Watson's A-reduction, $I^r$-representation

<table>
<thead>
<tr>
<th></th>
<th>MW$^1$, GHz</th>
<th>MW, GHz, THz</th>
<th>CCSD(T)/cc-pVTZ$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A / cm$^{-1}$</td>
<td>0.808981247$^3$</td>
<td>0.808981247</td>
<td>0.810323354</td>
</tr>
<tr>
<td>B / cm$^{-1}$</td>
<td>0.663976719</td>
<td>0.663976719</td>
<td>0.664053797</td>
</tr>
<tr>
<td>C / cm$^{-1}$</td>
<td>0.444560261</td>
<td>0.444560261</td>
<td>0.444974269</td>
</tr>
<tr>
<td>Δ$J$ / 10$^{-6}$ cm$^{-1}$</td>
<td>0.5715(84)</td>
<td>0.56976 (26)</td>
<td>0.51125</td>
</tr>
<tr>
<td>Δ$K$ / 10$^{-6}$ cm$^{-1}$</td>
<td>0.8468(15)</td>
<td>0.84866 (82)</td>
<td>0.56639</td>
</tr>
<tr>
<td>Δ$JK$ / 10$^{-6}$ cm$^{-1}$</td>
<td>0.5798(17)</td>
<td>0.57729 (95)</td>
<td>0.70275</td>
</tr>
<tr>
<td>$δJ$ / 10$^{-6}$ cm$^{-1}$</td>
<td>0.15857(21)</td>
<td>0.15835 (10)</td>
<td>0.1349</td>
</tr>
<tr>
<td>$δK$ / 10$^{-6}$ cm$^{-1}$</td>
<td>0.4382(11)</td>
<td>0.44029 (67)</td>
<td>0.51125</td>
</tr>
<tr>
<td>$H_J$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>0.52 (19)</td>
<td>0.54</td>
</tr>
<tr>
<td>$H_{JK}$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>4.9 (11)</td>
<td>5.3937</td>
</tr>
<tr>
<td>$H_{KJ}$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>-25.7 (41)</td>
<td>-27.3523</td>
</tr>
<tr>
<td>$H_K$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>24.9 (31)</td>
<td>24.0967</td>
</tr>
<tr>
<td>$h_J$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>0.140 (81)</td>
<td>0.063</td>
</tr>
<tr>
<td>$h_{JK}$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>1.39 (64)</td>
<td>2.56</td>
</tr>
<tr>
<td>$h_K$ / 10$^{-12}$ cm$^{-1}$</td>
<td>-</td>
<td>1.18 (25)</td>
<td>1.69</td>
</tr>
<tr>
<td>$d_{rms}$ / cm$^{-1}$</td>
<td>0.0000035</td>
<td>0.000074</td>
<td></td>
</tr>
</tbody>
</table>

No. of distinct 132 530

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3 Values without parenthesis were held fixed to the respective values of the ground state obtained by fitting only transitions in the GHz region of this study.
Comparison between experiment and theory

$J'_{K_a'K_c'} - J''_{K_a'K_c''}$

Exp.

sim. Ref.[11]

Calc.

Calc. (scaled)

sim. this work
Conclusion

1d-oxirane has been measured in both GHz (79-113 GHz) and THz (0.75-2.4 Hz) regions.

The analysis of the pure rotational spectra is a success, allowing improved predictions for observation missions.

Future work

The rovibrational spectra of the lowest vibrational modes have been measured, the analysis is in part completed and in part still in progress.
Acknowledgement

- The group of Martin Quack at ETH Zürich: [www.ir.ETHz.ch](http://www.ir.ETHz.ch)