High-Resolution cw-CRDS of the $v_8$ Band of Methylene Bromide

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Overview

- Introduction
- Motivation for spectroscopy of CH$_2$Br$_2$
- Experimental
  - CH$_2$Br$_2$
    - General details
    - Spectra/simulations
- Conclusions
Why CH$_2$Br$_2$?

- Needed temperature probe of supersonic expansion for C$_{60}$ project
- Requirements
  - Need an accessible vibrational band
    - $\sim$1185-1198 cm$^{-1}$ (~8.5 µm)
  - The band should cover a reasonably small window in frequency space $\sim$5 cm$^{-1}$
  - A relatively simple molecule that is liquid or gas phase at room temperature.
- Only $\nu_8$ band of CH$_2$Br$_2$ reasonably fit the requirements
  - Band center $\nu_0 \sim 1195 \pm (1-3)$ cm$^{-1}$
  - Strong band
  - No high-resolution spectrum available

1194 cm$^{-1}$ (CD$_3$)$_2$HfD$_2$
1194 cm$^{-1}$ ZnZnD
1194 cm$^{-1}$ F$_2$C=C=C=O
1194 cm$^{-1}$ F$_2$C=C=CFCF:
1195 cm$^{-1}$ Boron dicarbide
1195 cm$^{-1}$ CuCuD-
1195 cm$^{-1}$ (N)$_2$(cyc-C$_3$N$_3$)N$_3$
1195 cm$^{-1}$ p-C$_6$H$_4$CINH$_2$+
1195 cm$^{-1}$ NSO
1195 cm$^{-1}$ DCF
1195 cm$^{-1}$ Ga$_2$H$_6$
1195 cm$^{-1}$ Methylamine
1195 cm$^{-1}$ Methane, dibromo-
1195 cm$^{-1}$ (CH$_3$)$_2$Ge
1195 cm$^{-1}$ C$_2$H$_5$IO
1195 cm$^{-1}$ CCl$_2$+
1196 cm$^{-1}$ ZnZnD
1196 cm$^{-1}$ Cl$_3$TiOCD$_3$
1196 cm$^{-1}$ 1,3-Butadiene-d$_6$
1196 cm$^{-1}$ 1,3-Butadiene
1196 cm$^{-1}$ 1,2,4-Trioxolane
1196 cm$^{-1}$ C$_6$F$_6$+
1196 cm$^{-1}$ HCOOH+
1196 cm$^{-1}$ HCCIBr
1196 cm$^{-1}$ CH$_3$CCCBr

Nist Chemistry WebBook. webbook.nist.gov/chemistry/
Experimental Overview

Cryostat with QCL

Mode-matching optics

Aspheric Lens

N₂O Reference cell

Reference Detector

AOM

High finesse cavity

Focusing optics & detector
Experimental: Laser

- Limited commercial availability ~8 µm
- Quantum cascade laser
  - Multi-quantum well design - Like a particle in a box
  - Wavelength coverage not as strongly tied to band-gap of materials
  - ~80 mW attainable cw output power
Laser Visual

Bias Voltage

Common Ground

5-7 Lasers Per Chip
Laser Housing/Mounting

- Laser Mount
- Cold Plate (77 K)
- Copper Ribbon for Thermal Conductivity but Mechanical Isolation
- "Sample Mount"
- Armature for Mechanical Rigidity
- On Reverse: Heater & Temp. Sensor

Janis VPF-100
Laser Tuning

Frequency tuning carried out by manipulating I and T of laser
cw-CRDS

- cw-light coupled into cavity
- Resonance-light intensity in cavity builds up
- Threshold-source uncoupled via AOM deflection
- Exponential decay of light from cavity measured
- Rate of decay depends on:
  - Mirror losses
  - Absorbing species present
- Can back out absorption coefficient

\[ I_{\text{CRD}}(t) \propto I_0 \exp\left[ -\frac{t}{\tau(\nu)} \right] \]

\[ \tau(\nu) = \frac{d}{c[(1 - R) + \sigma(\nu)Nd]} \]
Supersonic Expansion

- Rotational/Vibrational cooling of sample carried out in a supersonic expansion.
  - 0.7 mm pinhole expansion source
  - Normal experimental pressures $P_0/P_1 \sim 1.7 \times 10^4$
  - Sample delivery by bubbling Ar carrier gas through liquid CH$_2$Br$_2$

CH$_2$Br$_2$ + Ar
CH$_2$Br$_2$ General Details

- % Abundance of $^{79}$Br and $^{81}$Br is 50/50
- Three isotopomers present in sample
  - $\Rightarrow$ spectral congestion
- Low symmetry $\Rightarrow$ weak dependence of intensity w.r.t. nuclear spin statistics of CH$_2^{79}$Br$_2$ and CH$_2^{81}$Br$_2$

<table>
<thead>
<tr>
<th>Point Group Symmetry</th>
<th>CH$_2^{79}$Br$_2$</th>
<th>CH$_2^{79}$Br$^{81}$Br</th>
<th>CH$_2^{81}$Br$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Sample</td>
<td>25%</td>
<td>50%</td>
<td>25%</td>
</tr>
</tbody>
</table>

$C_{2v}$ $C_s$ $C_{2v}$
CH$_2$Br$_2$ Ground Rotational Constants

- Microwave work exists for all three isotopomers
- Ray’s Asymmetry Parameter:
  \[ K = \frac{2B - A - C}{A - C} \]
- Near prolate top
  - Spectral simplification

<table>
<thead>
<tr>
<th>Rotational Constant</th>
<th>CH$_2^{79}$Br$_2$*</th>
<th>CH$<em>2^{79}$Br$</em>{81}$Br**</th>
<th>CH$_2^{81}$Br$_2$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A” (MHz)</td>
<td>26031.314</td>
<td>26007.570</td>
<td>25984.704</td>
</tr>
<tr>
<td>B” (MHz)</td>
<td>1238.5367</td>
<td>1223.2946</td>
<td>1208.0839</td>
</tr>
<tr>
<td>C” (MHz)</td>
<td>1190.9420</td>
<td>1176.7957</td>
<td>1162.6650</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>-0.99617</td>
<td>-0.99625</td>
<td>-0.99634</td>
</tr>
</tbody>
</table>

**Niide et al. J. Mol. Spec. 139, 11-29 (1990)
**CH$_2$Br$_2$ Rovibrational Details**

- $\nu_8$ -CH$_2$ wag rovibrational band characteristics:
  - Vibrational band (Q-branch expected)
  - 3 distinct band-centers for each isotopomer $\sim$1197 cm$^{-1}$
  - a-type transitions
    - Selection Rules: $\Delta J=0, \pm 1$; $\Delta K_a=0$; $\Delta K_c=\pm 1$
CH$_2$Br$_2$ Spectra

Calibrated 1195.81 cm$^{-1}$ to 1196.96 cm$^{-1}$

Laser Frequency Step: 50 MHz
Spectra Compared To 15K Simulation

A' = 25890 MHz  B' = 1208 MHz  C' = 1178 MHz  $\nu_0 = 1196.98 \text{ cm}^{-1}$
Spectra Compared To 35K Simulation

A' = 25890 MHz  B' = 1208 MHz  C' = 1178 MHz  ν₀ = 1196.98 cm⁻¹
Conclusions

- High resolution spectroscopy of the methylene bromide $v_8$ band has been carried out.
- Preliminary work has provided a tentative assignment for the Q-branch of the CH$_2^{79}$Br$^{81}$Br isotopomer.
- Assessment of Q-branch features provides a rough diagnostic for the temperature of our supersonic expansion.
- More scanning needs to be done:
  - Beyond 1197 cm$^{-1}$ encompass a sufficient portion of the R branch.
  - At 35 MHz step size.
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