High-Resolution cw-CRDS of the ν_8 Band of Methylene Bromide

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Overview

- Introduction
- Motivation for spectroscopy of CH_2Br_2
- Experimental
- CH_2Br_2
  - General details
  - Spectra/simulations
- Conclusions

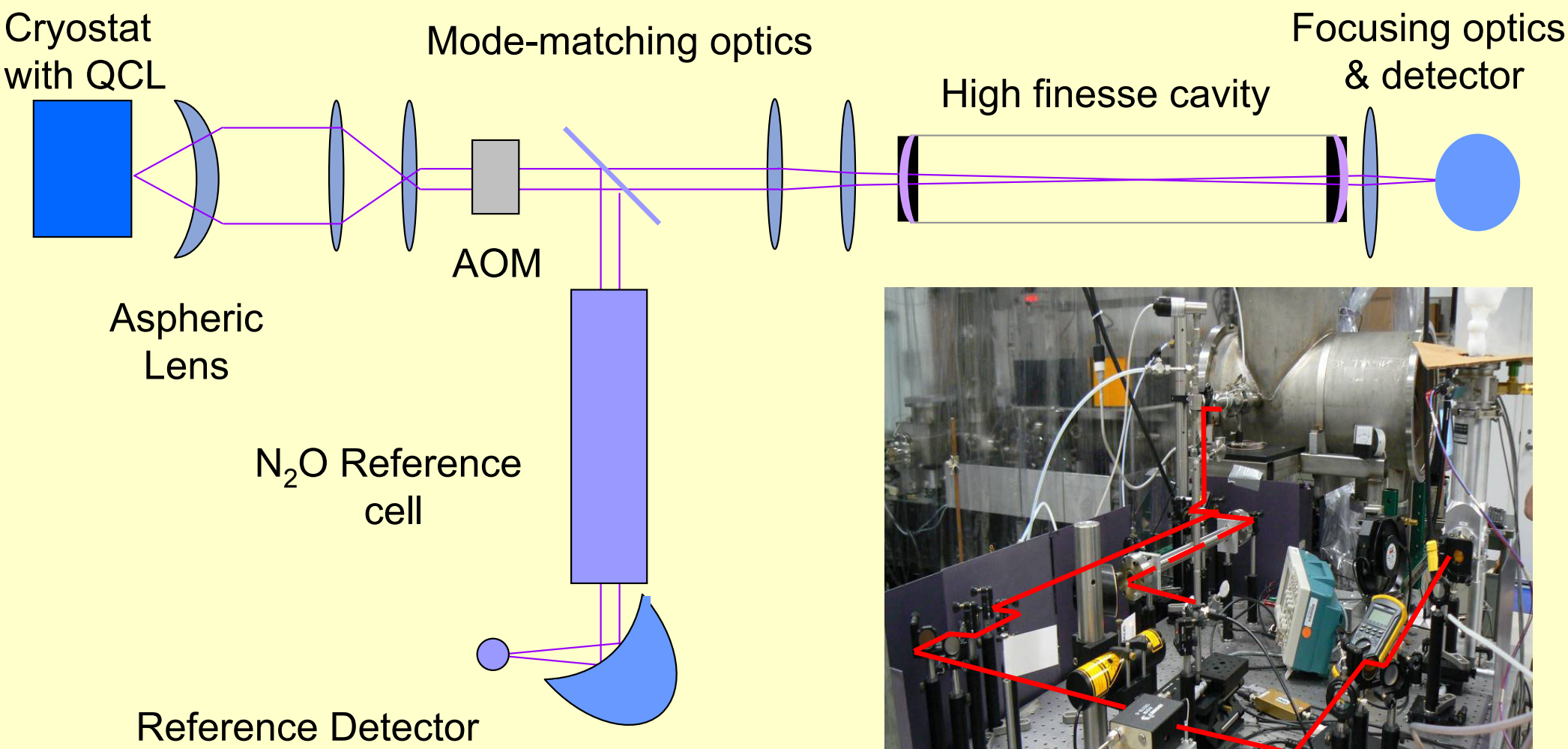
Why CH_2Br_2?

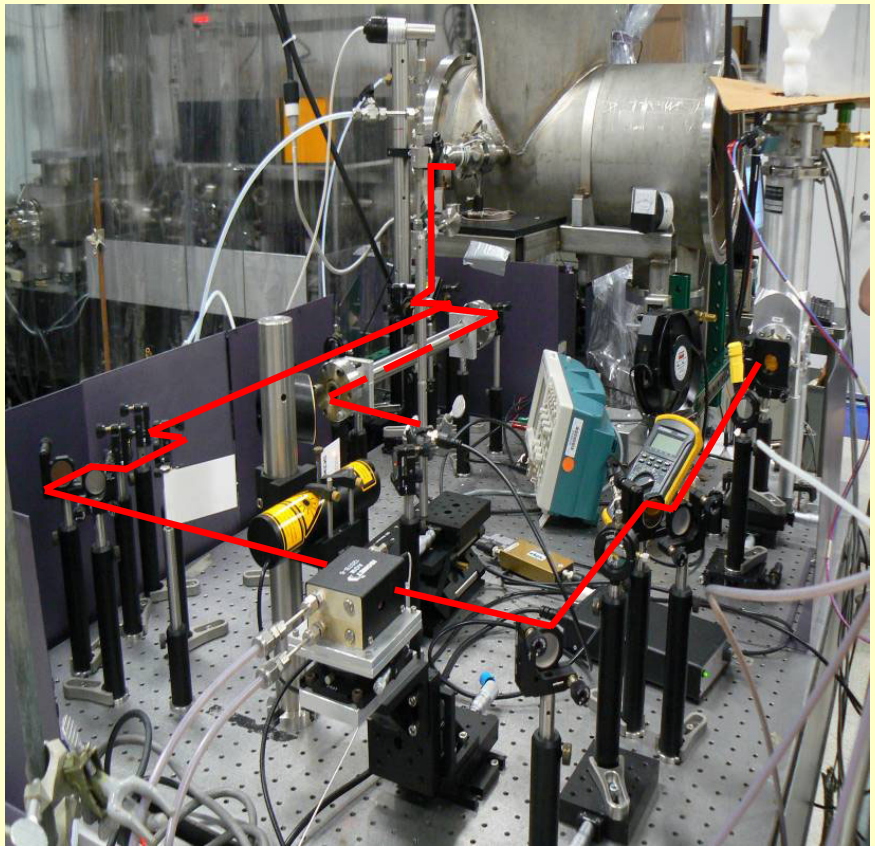
- Needed temperature probe of supersonic expansion for C_{60} project
- Requirements
  - Need an accessible vibrational band ~1185-1198 cm^{-1} (~8.5 μm)
  - The band should cover a reasonably small window in frequency space ~5 cm^{-1}
  - A relatively simple molecule that is liquid or gas phase at room temperature.
- Only v_8 band of CH_2Br_2 reasonably fit the requirements
  - Band center v_0~1195 ± (1-3) cm^{-1}
  - Strong band
  - No high-resolution spectrum available

1194 cm^{-1} (CD3)2HfD2
1194 cm^{-1} ZnZnD
1194 cm^{-1} F2C=C=C=O
1194 cm^{-1} F2C=C=CFCF:
1195 cm^{-1} Boron dicarbide
1195 cm^{-1} CuCuD-
1195 cm^{-1} (N)2(cyc-C3N3)N3
1195 cm^{-1} p-C6H4ClNH2+
1195 cm^{-1} NSO
1195 cm^{-1} DCF
1195 cm^{-1} Ga2H6
1195 cm^{-1} Methylamine
1195 cm^{-1} Methane, dibromo-
1195 cm^{-1} (CH3)2Ge
1195 cm^{-1} C2H5IO
1195 cm^{-1} CCl2+
1196 cm^{-1} ZnZnD
1196 cm^{-1} Cl3TiOCD3
1196 cm^{-1} 1,3-Butadiene-d6
1196 cm^{-1} 1,3-Butadiene
1196 cm^{-1} 1,2,4-Trioxolane
1196 cm^{-1} C6F6+
1196 cm^{-1} HCOOH+
1196 cm^{-1} HCClBr
1196 cm^{-1} CH3CCCl+

Nist Chemistry WebBook. **webbook**.**nist**.gov/**chemistry**/

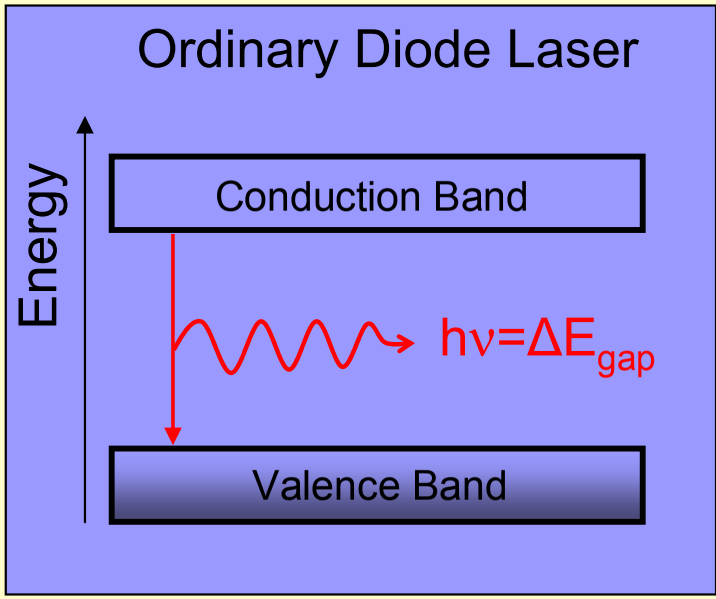
Experimental Overview

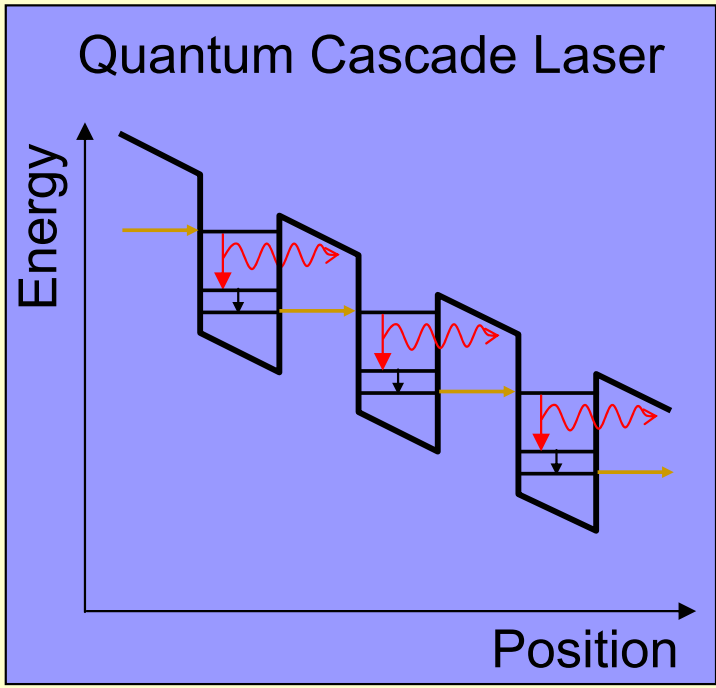




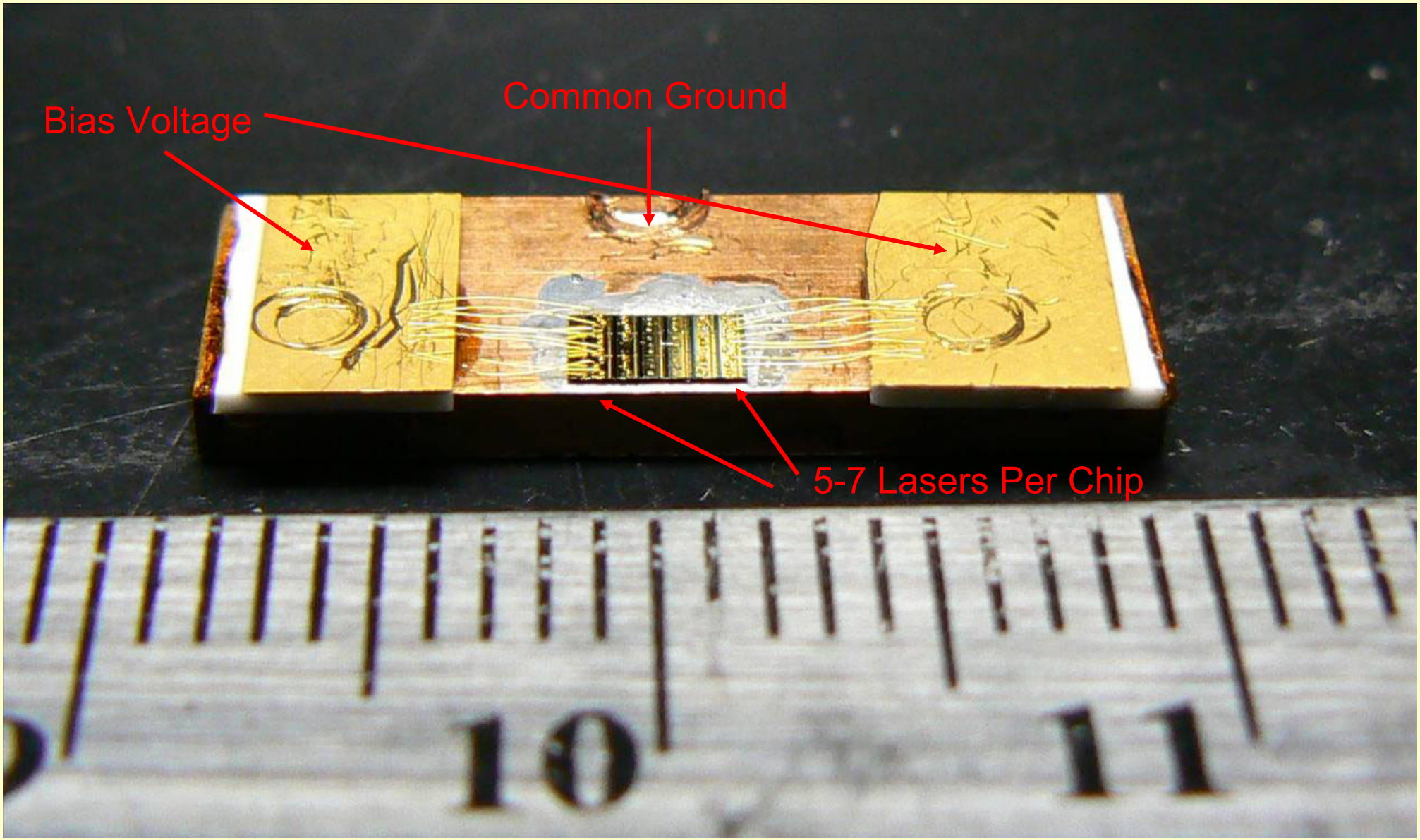
Experimental:Laser

- 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



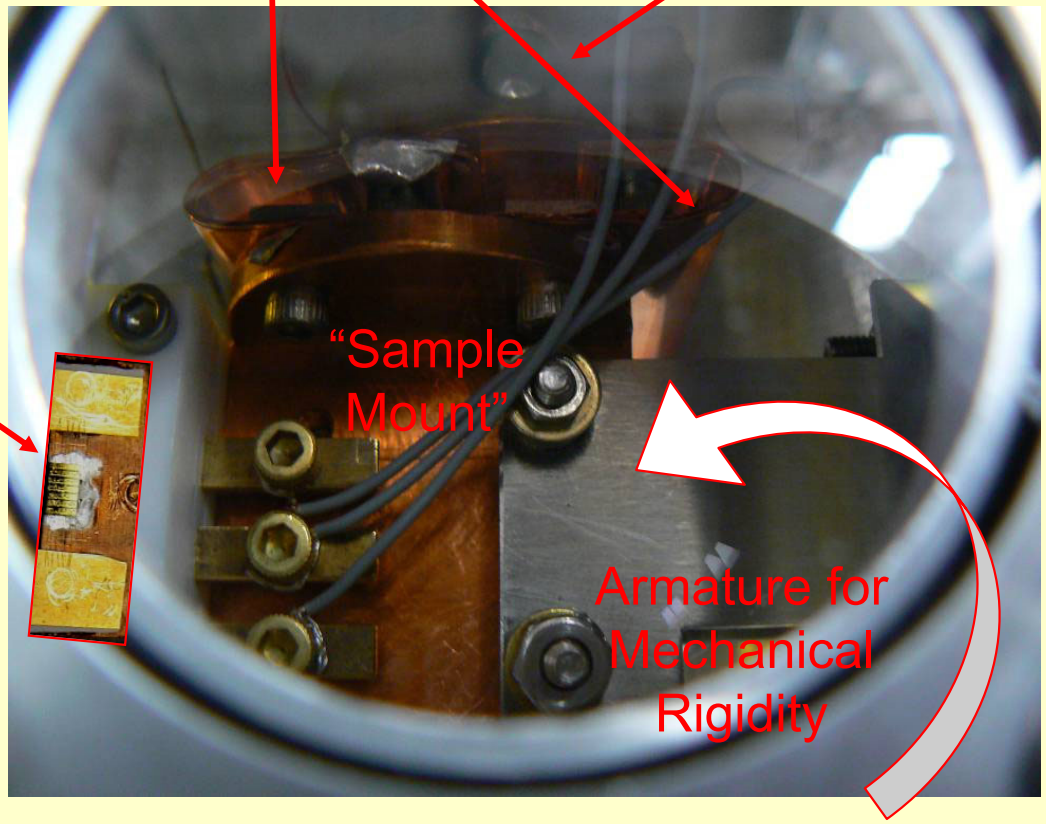
Laser Housing/Mounting

Janis VPF-100

Copper Ribbon for Thermal Conductivity but Mechanical Isolation

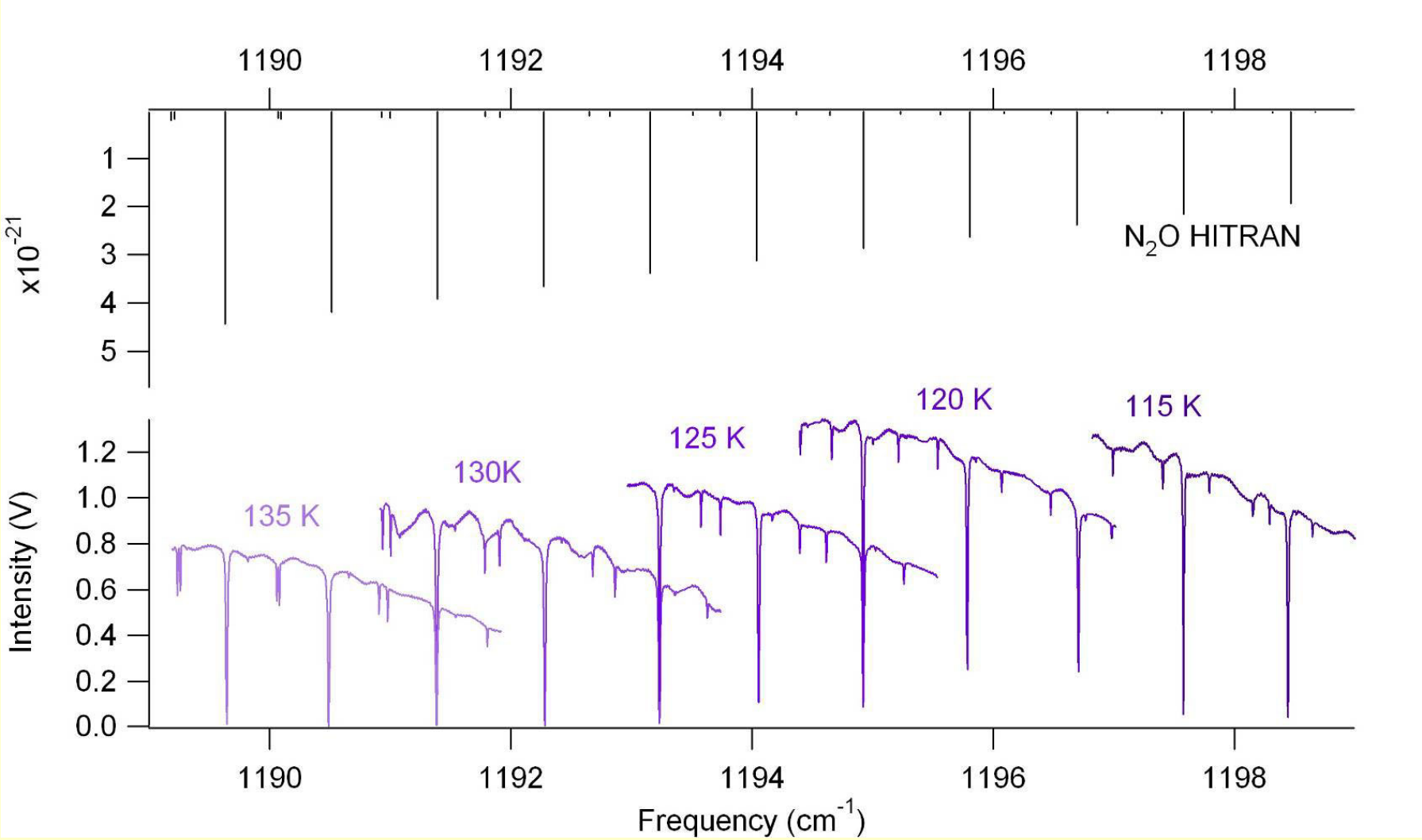
Cold Plate (77 K)

Laser Mount



On Reverse: Heater & Temp. Sensor

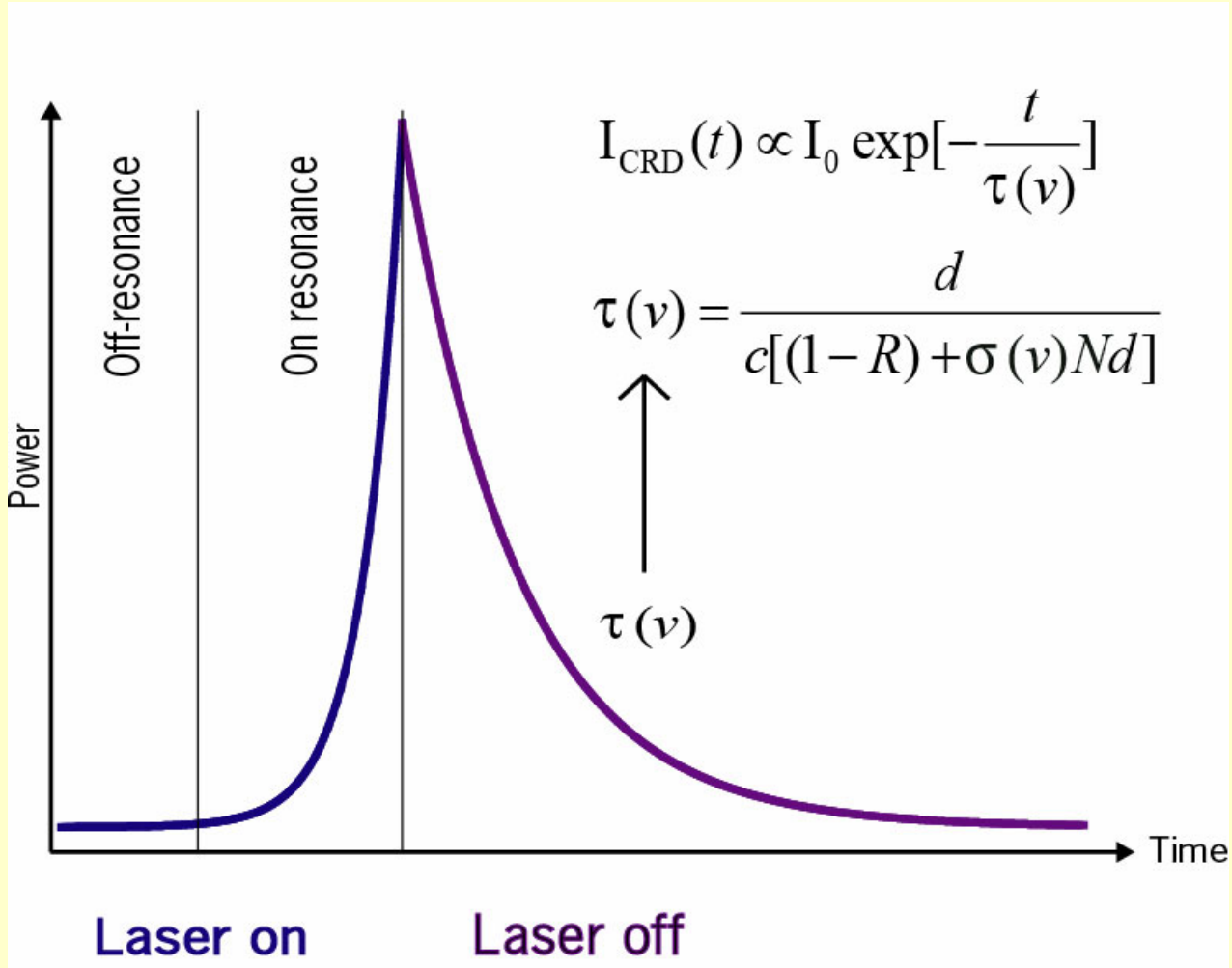
Laser Tuning



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



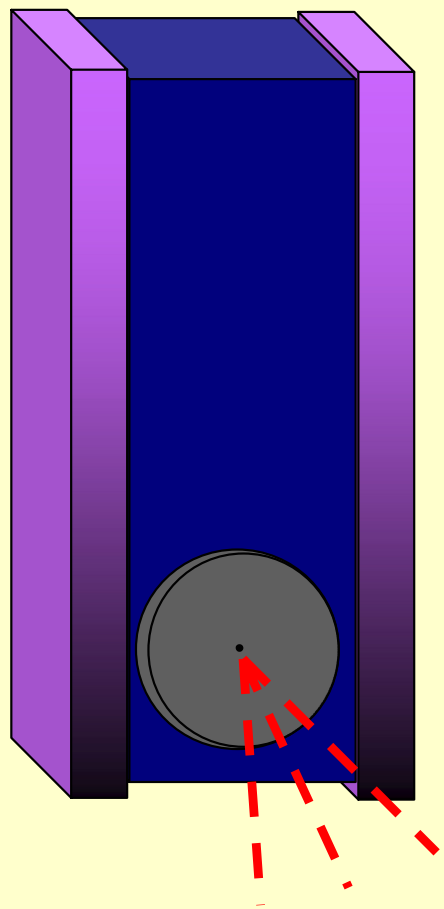
$$I_{CRD}(t) \propto I_0 \exp[-\frac{t}{\tau(v)}]$$

$$\tau(v) = \frac{d}{c[(1-R)+\sigma(v)Nd]}$$

$$\tau(v)$$

Supersonic Expansion

- Rotational/Vibrational cooling of sample carried out in a supersonic expansion.
  - 0.7 mm pinhole expansion source
  - Normal experimental pressures $P_o/P_1 \sim 1.7 \times 10^4$
  - Sample delivery by bubbling Ar carrier gas through liquid CH_2Br_2



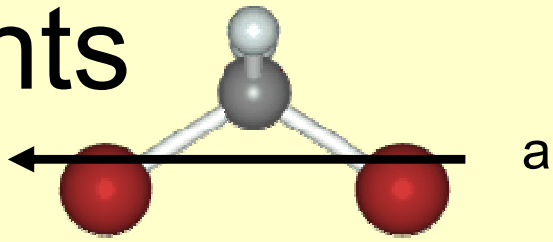
CH_2Br_2 + Ar

CH_2Br_2 General Details

- % Abundance of ^{79}Br and ^{81}Br is 50/50
- Three isotopomers present in sample
  - ➔spectral congestion
- Low symmetry ➔ weak dependence of intensity w.r.t. nuclear spin statistics of $CH_2{}^{79}Br_2$ and $CH_2{}^{81}Br_2$

	$CH_2{}^{79}Br_2$	$CH_2{}^{79}Br^{81}Br$	$CH_2{}^{81}Br_2$
% Sample	25%	50%	25%
Point Group Symmetry	C_{2v}	C_s	C_{2v}

CH_2Br_2 Ground Rotational Constants



- Microwave work exists for all three isotopomers
- Ray's Asymmetry Parameter:

$$\kappa = \frac{2B - A - C}{A - C}$$

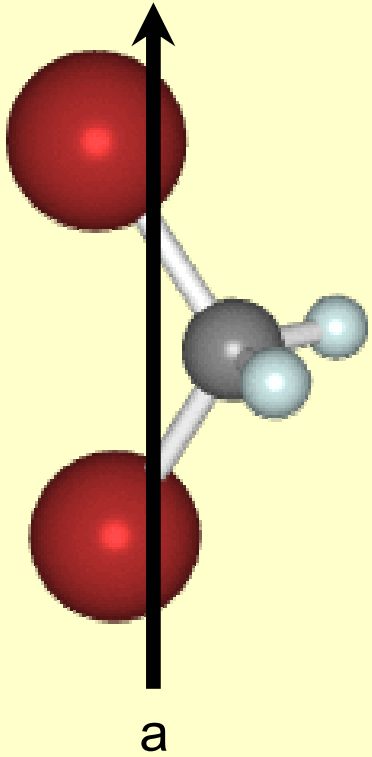
- Near prolate top
  - Spectral simplification

Rotational Constant	$CH_2{}^{79}Br_2{}^{*}$	$CH_2{}^{79}Br^{81}Br^{**}$	$CH_2{}^{81}Br_2{}^{*}$
A" (MHz)	26031.314	26007.570	25984.704
B" (MHz)	1238.5367	1223.2946	1208.0839
C" (MHz)	1190.9420	1176.7957	1162.6650
κ	-0.99617	-0.99625	-0.99634

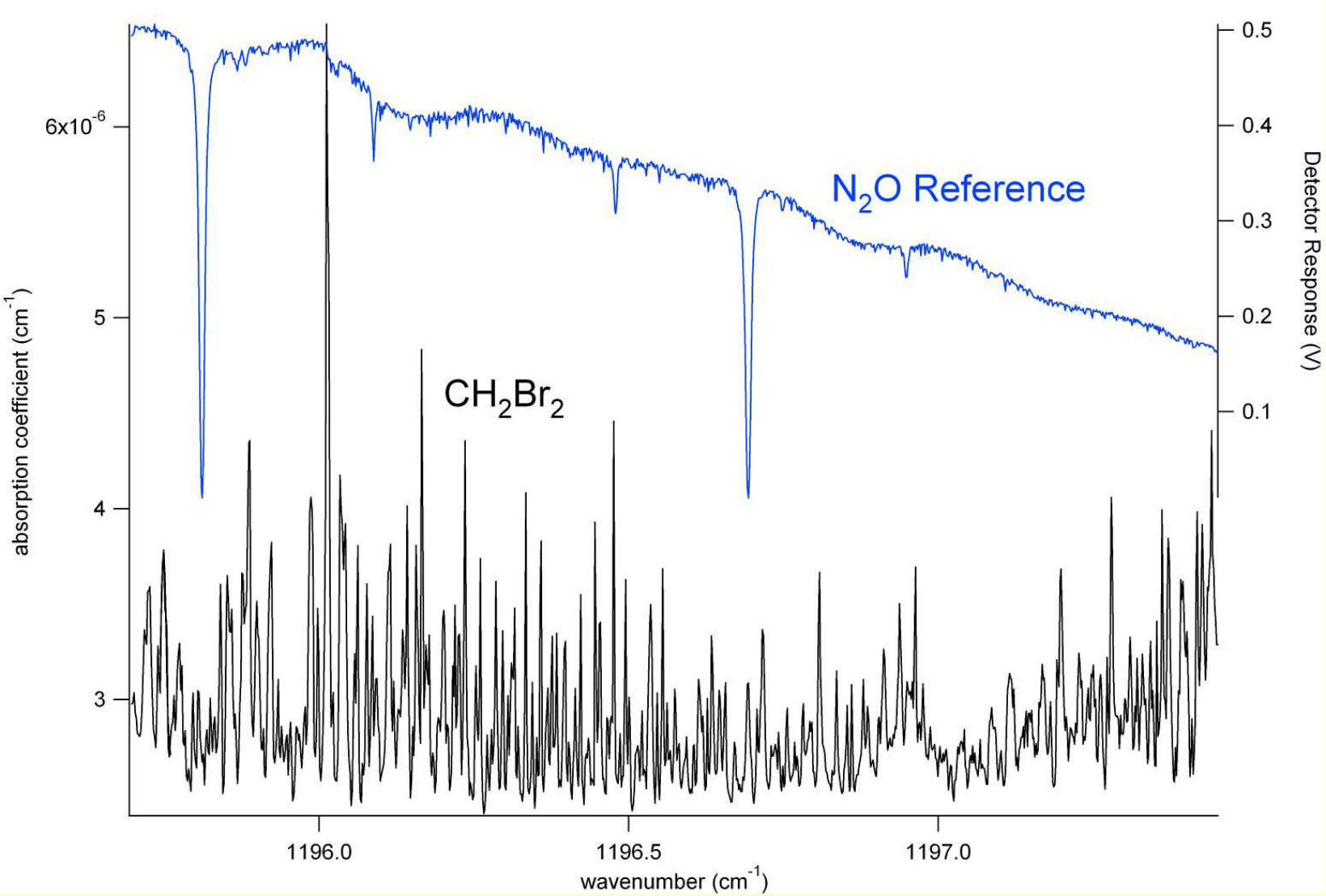
*Davis W.R. and Gerry M.C.L. J. Mol. Spec. **109**, 269-282 (1985)
Niide *et al*. J. Mol. Spec. **139, 11-29 (1990)

CH_2Br_2 Rovibrational Details

- v_8 -CH_2 wag rovibrational band characteristics:
  - ‖ vibrational band (Q-branch expected)
  - 3 distinct band-centers for each isotopomer ~1197 cm^{-1}
  - a-type transitions
    - Selection Rules: $\Delta J=0,\pm1$; $\Delta K_a=0$; $\Delta K_c=\pm1$



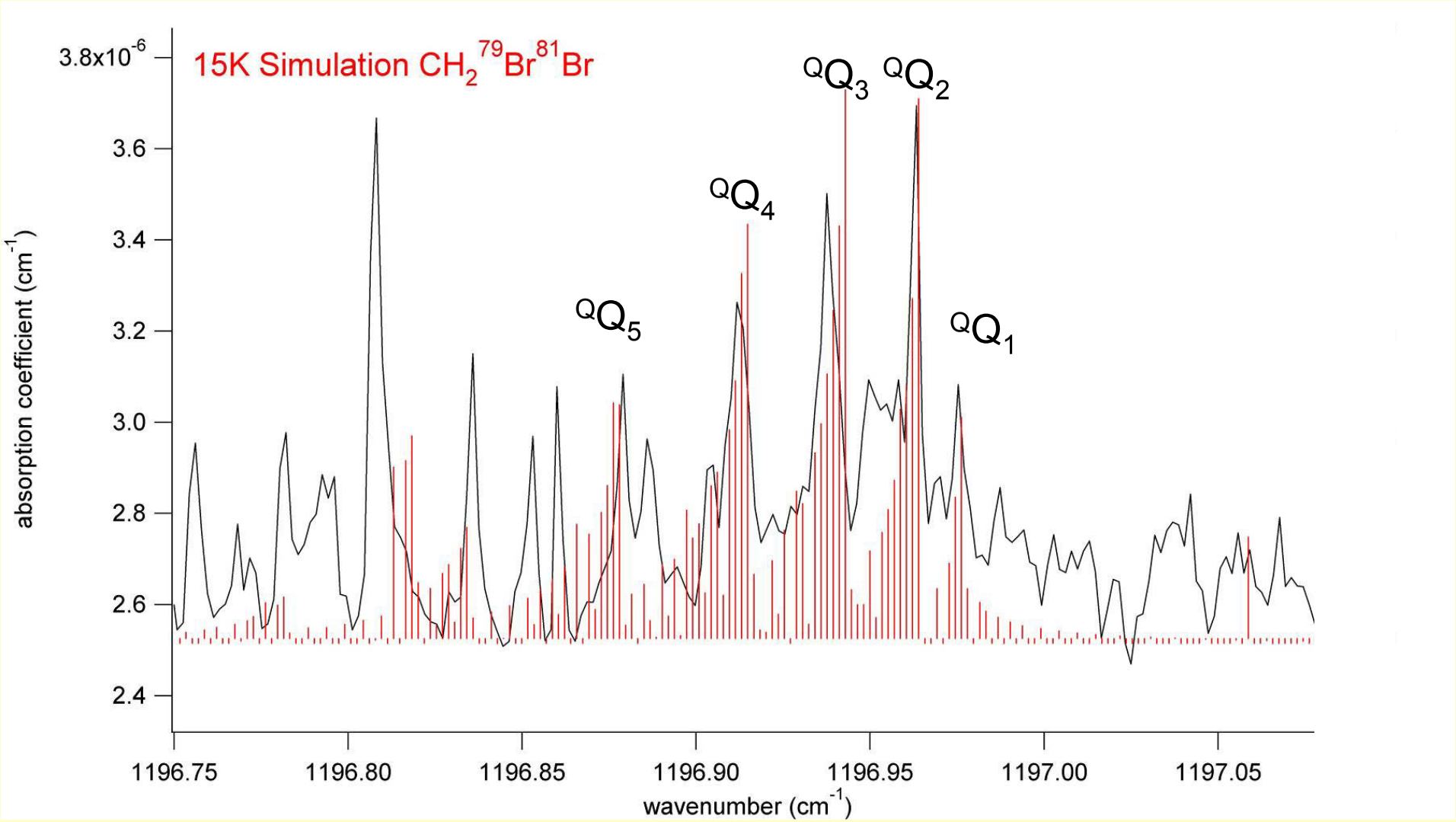
CH_2Br_2 Spectra



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

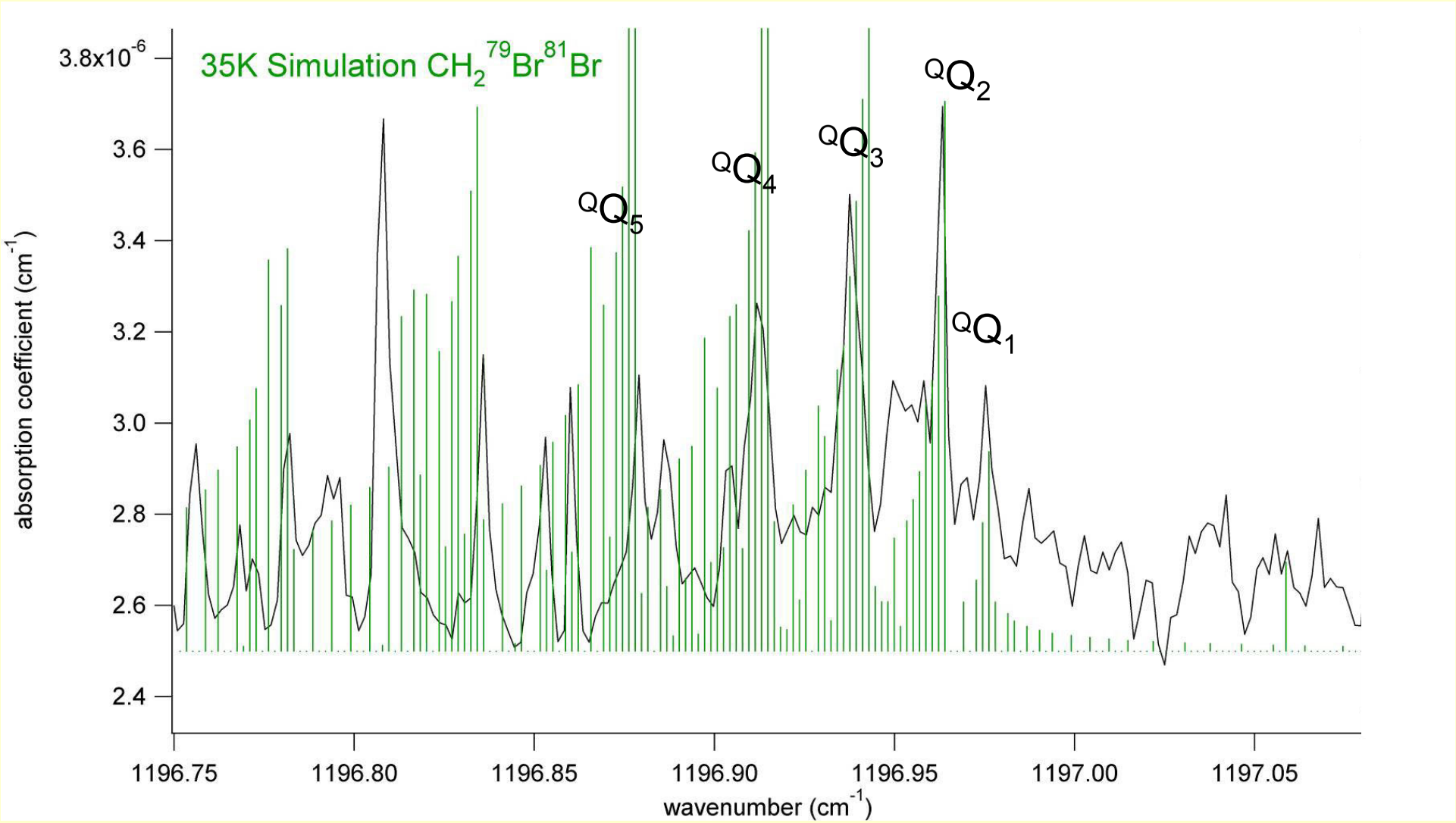
Laser Frequency Step: 50 MHz

Spectra Compared To 15K Simulation



A′=25890 MHz B′=1208 MHz C′=1178 MHz ν_0=1196.98 cm^{-1}

Spectra Compared To 35K Simulation

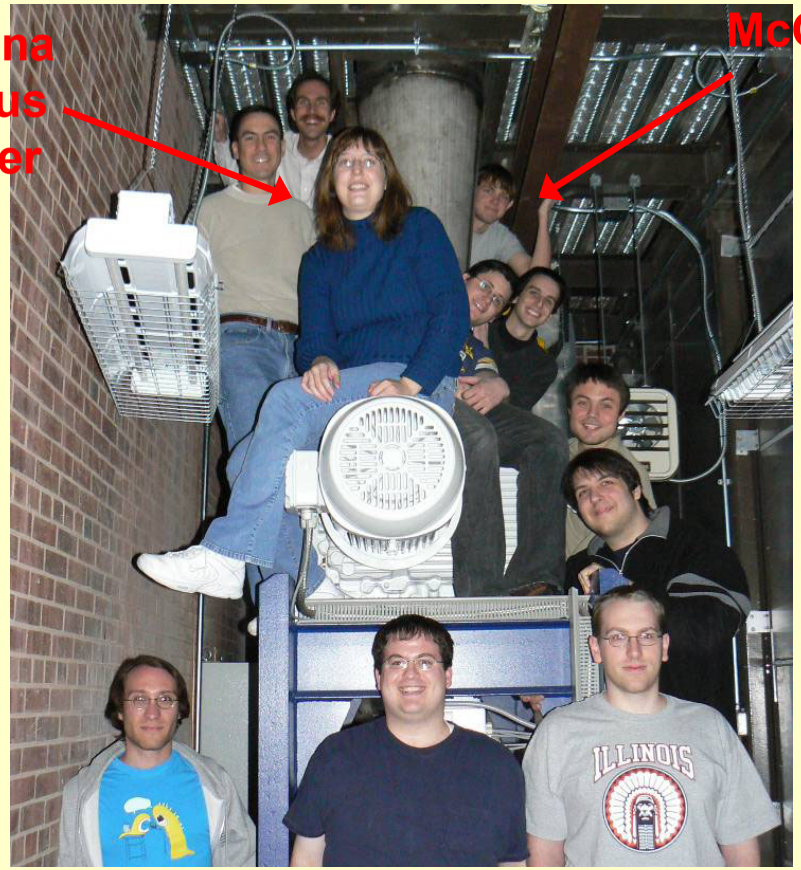


A′=25890 MHz B′=1208 MHz C′=1178 MHz ν_0=1196.98 cm^{-1}

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

Acknowledgements



Rich Saykally
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David Plusquellic-JB95 Fitting Package

David Woon-Vibration/Rotation Animations

NASA Laboratory Astrophysics

Dreyfus
UIUC