

Observation of combination bands involving intermolecular vibrations of CO₂- , N₂- and OCS-N₂O complexes using an external cavity quantum cascade laser

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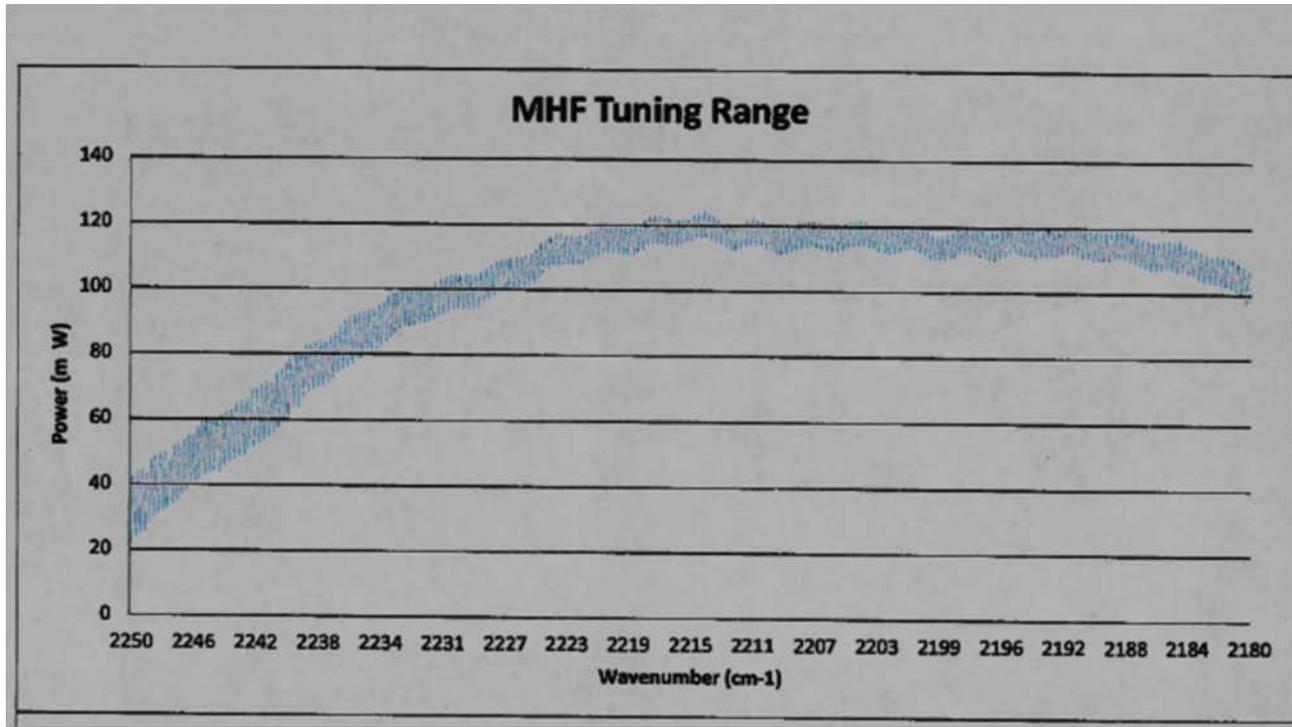
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National Research Council of Canada



External Cavity Quantum Cascade Laser



External Cavity design

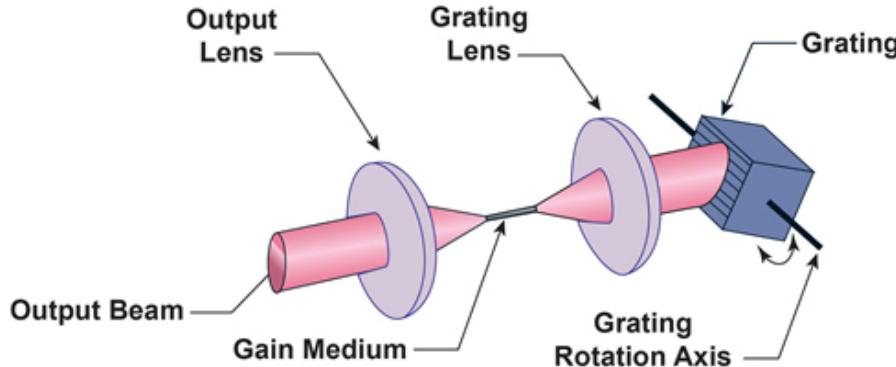
Linewidth: 45 MHz

Power: 20-120 mW

Full tuning range: 2140-2265 cm⁻¹

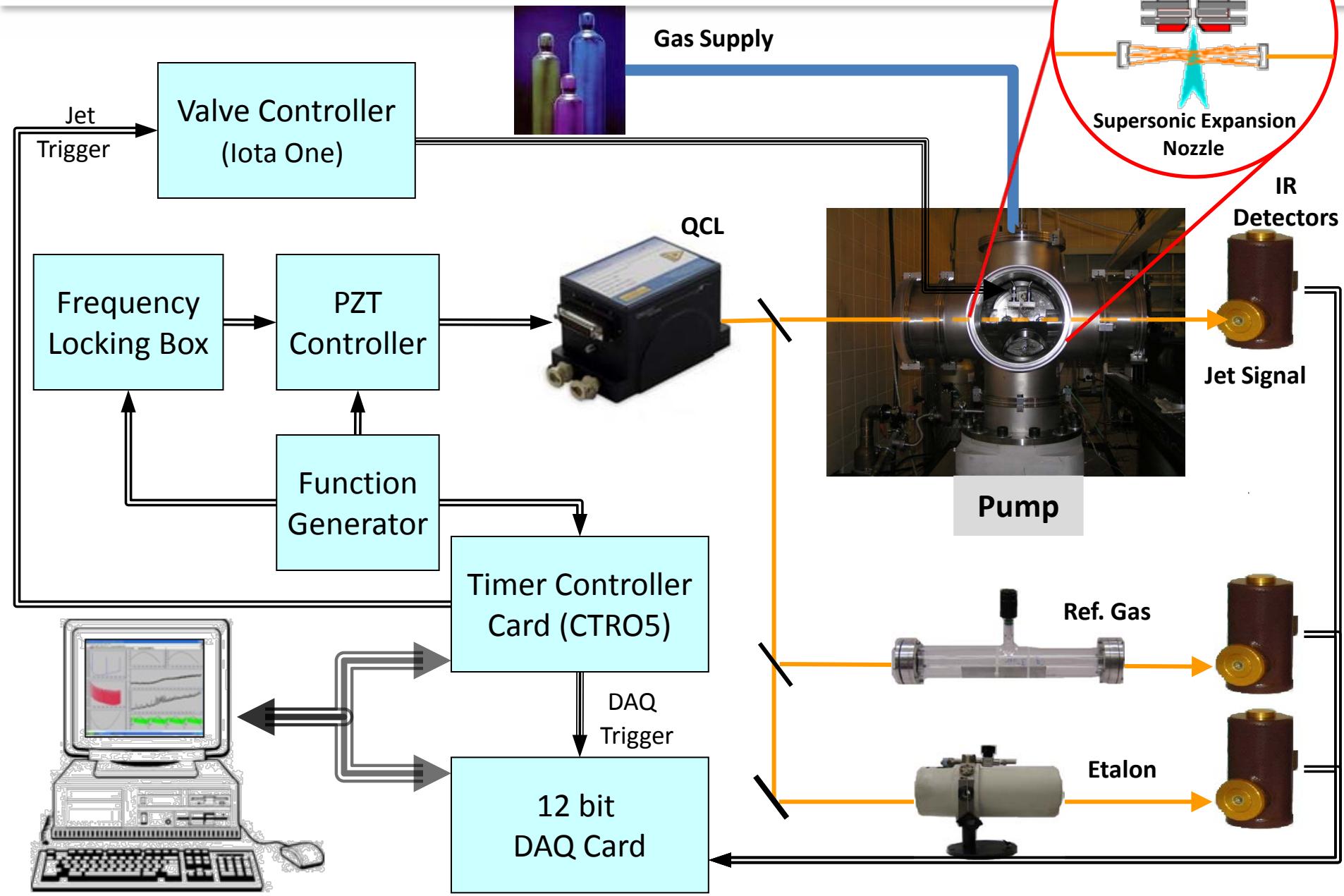
Mode Hop Free range: 2180-2250 cm⁻¹

External cavity quantum cascade laser

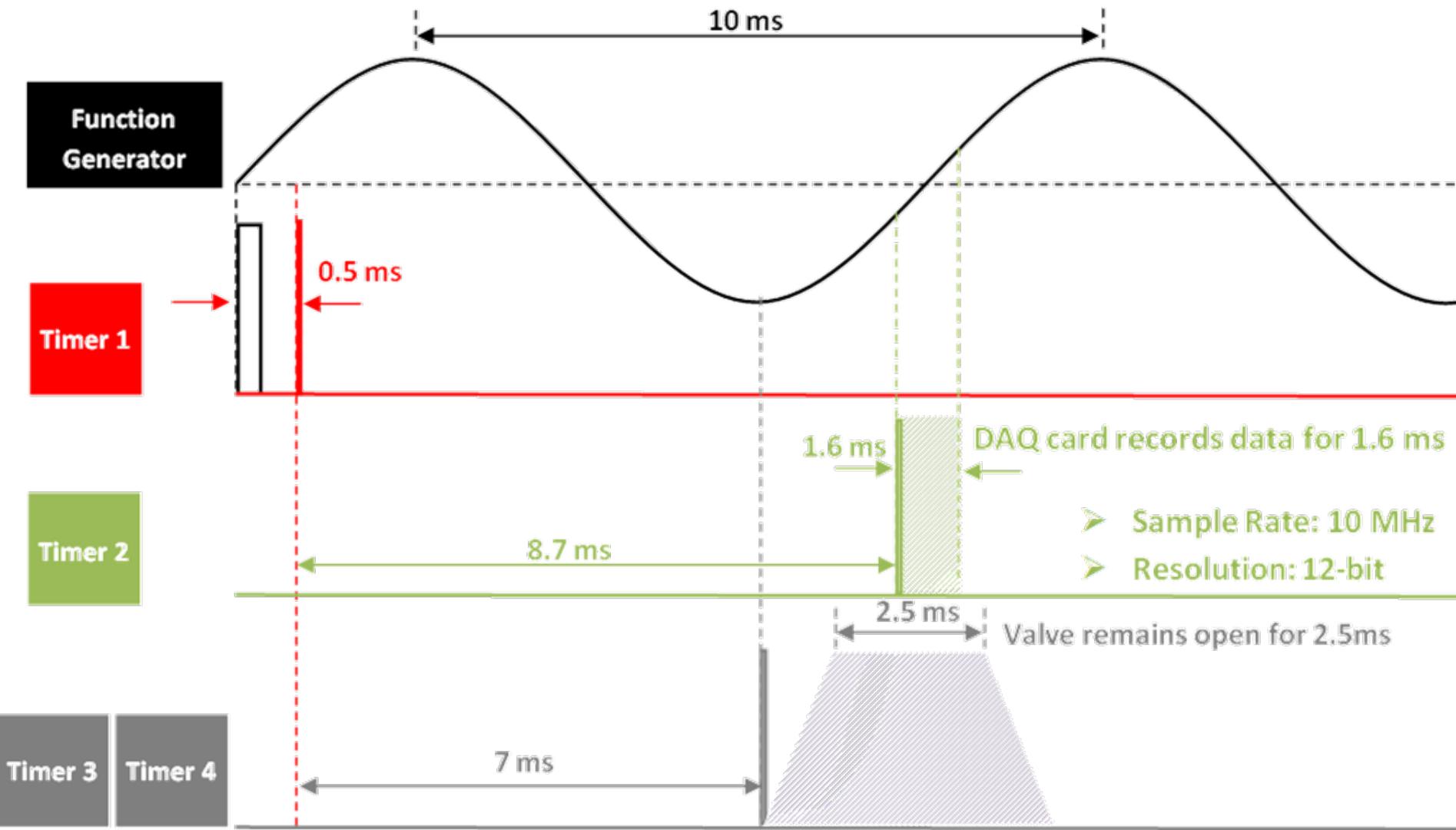


- No need for cryogenic cooling
- High power (10-200 mW)
- Better reproducibility
- Wide tuning range ($\sim 100 \text{ cm}^{-1}$)
- Mechanically tuned by PZT attached to grating
- Prone to mechanical noise
- Wavenumber agility is less than that of a diode laser. Higher $1/f$ noise

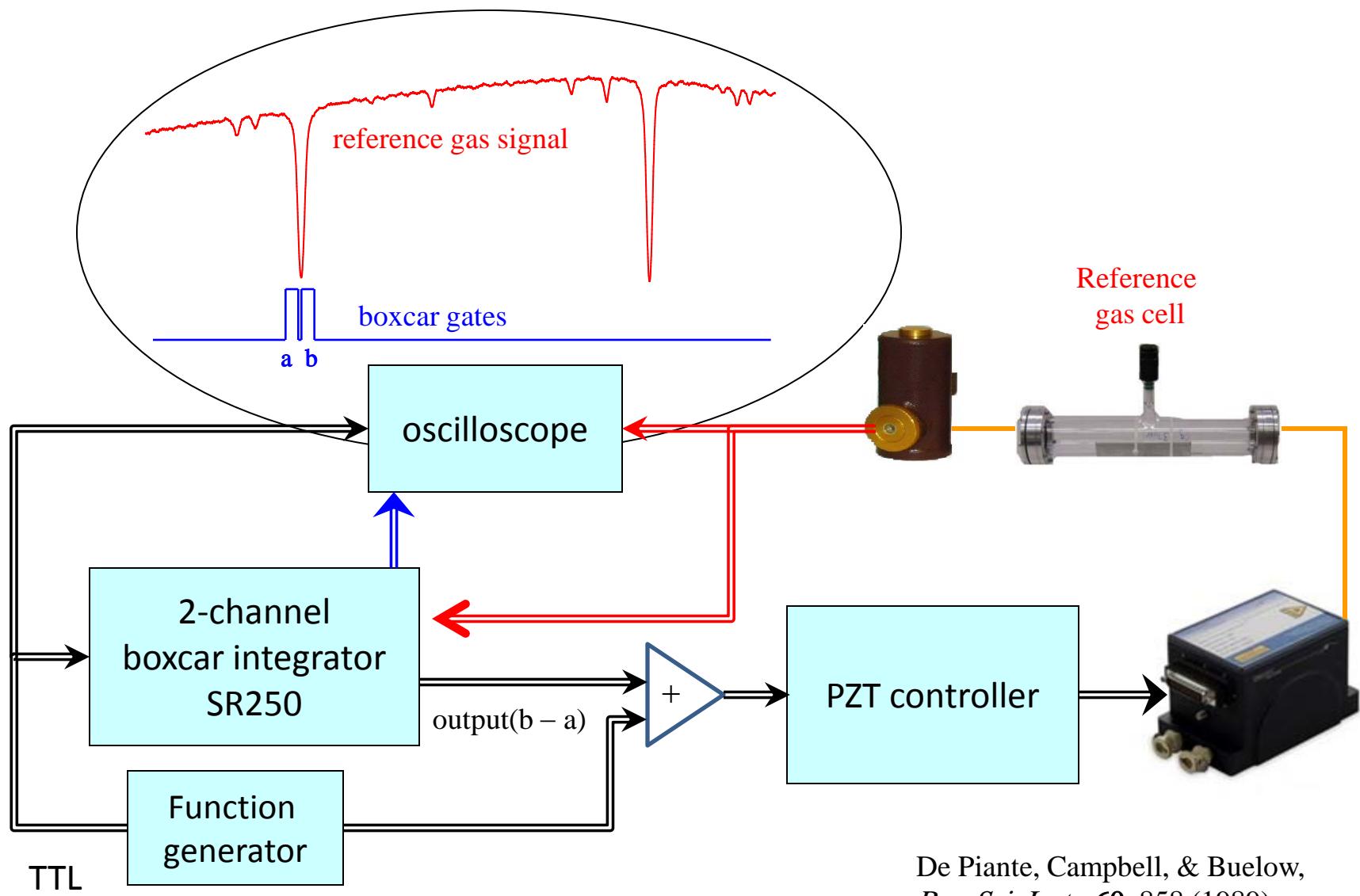
Experimental setup: Supersonic jet with a QCL probe



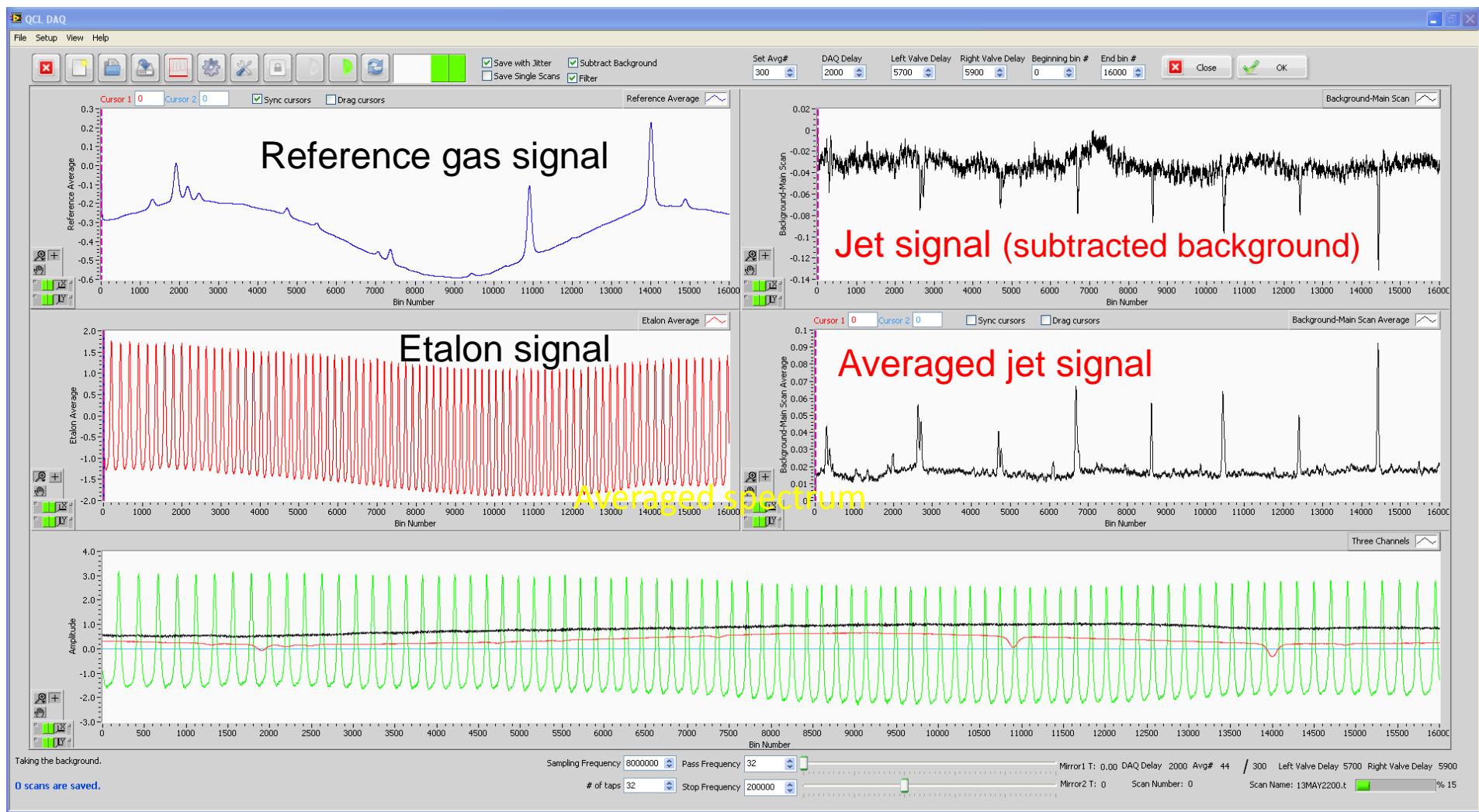
Time sequence for data acquisition (QCL)



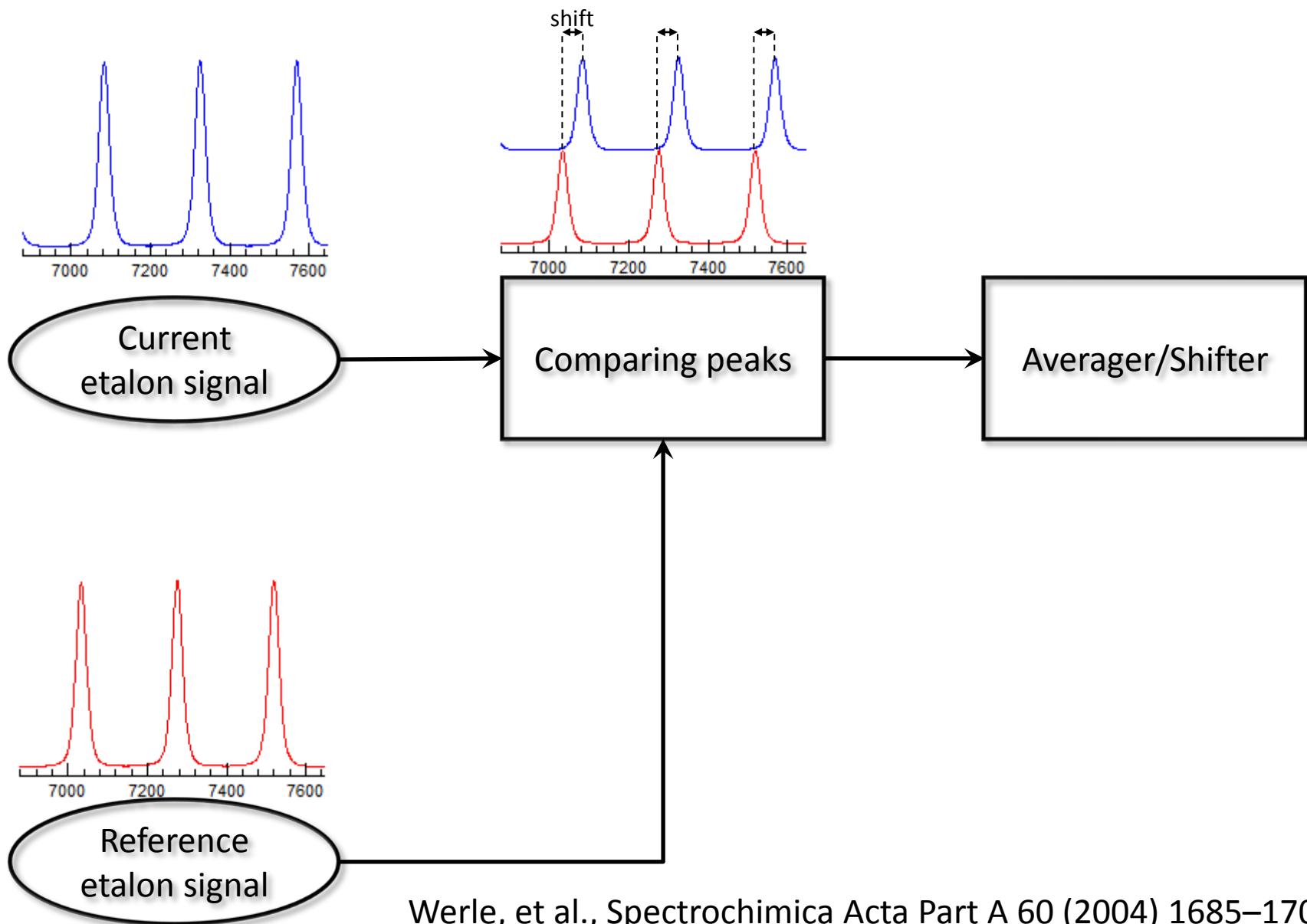
Sweep stabilization using 2-channel boxcar



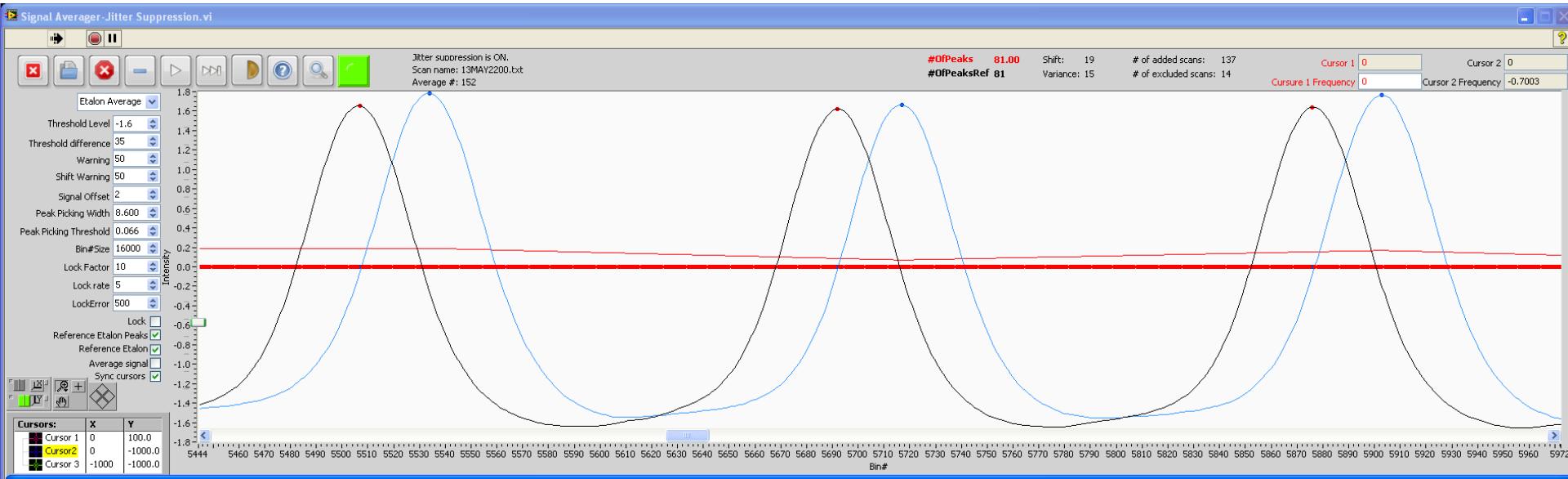
Snapshot of the computer screen during data acquisition



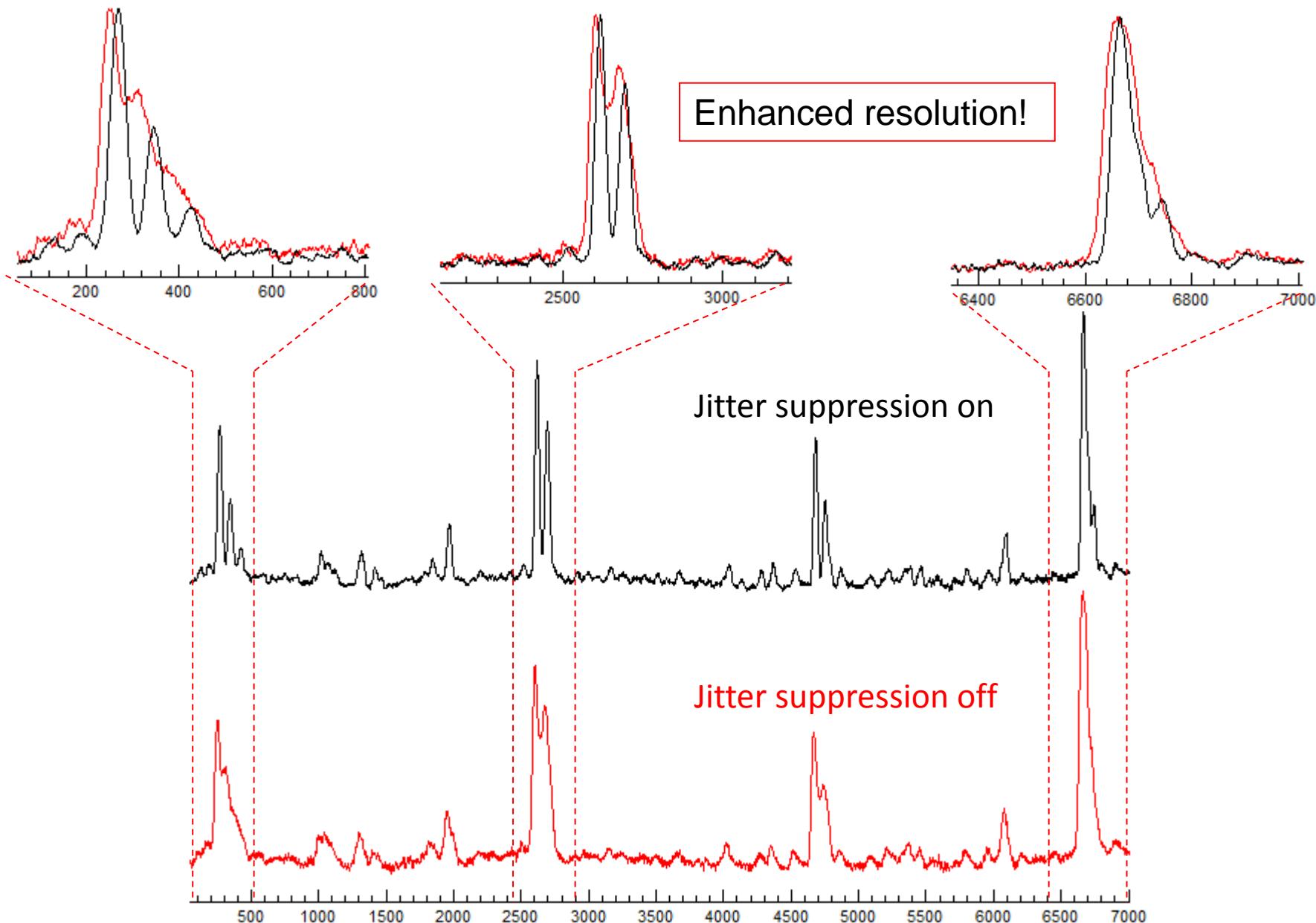
Jitter suppression



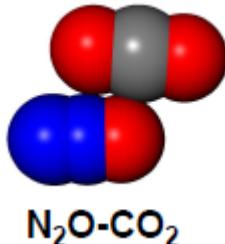
jitter suppression



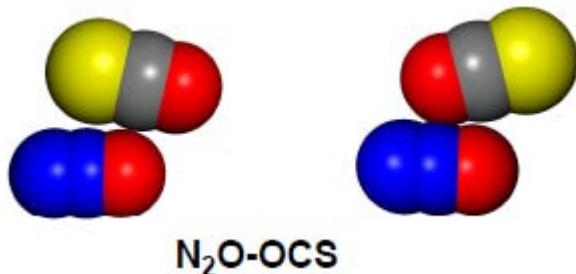
Enhanced resolution and improved SNR



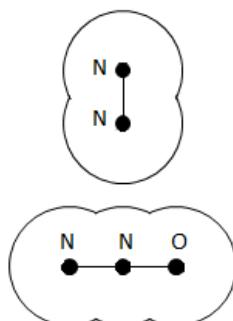
$\text{N}_2\text{O-CO}_2$, $\text{N}_2\text{O-OCS}$ and $\text{N}_2\text{O-N}_2$



Slipped parallel structure for $\text{CO}_2\text{-N}_2\text{O}$ dimer
Dutton *et al.*, J. Phys. Chem., 100 (1996) 17772.

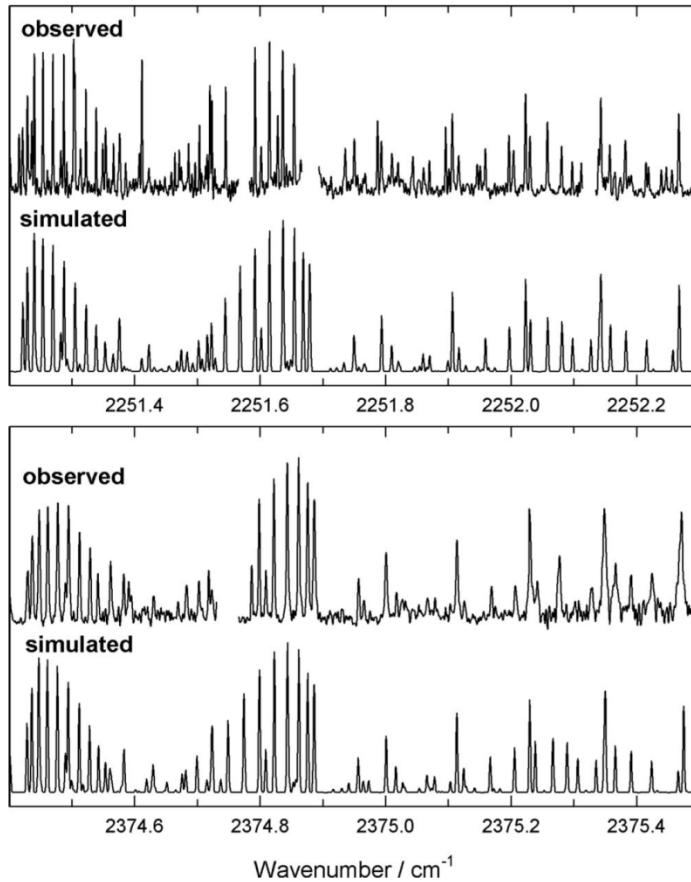


Two isomers of the $\text{OCS-N}_2\text{O}$ complex
H.O. Leung et al., 114 (2001) 4829.
M. Afshari et al., CPL 489 (2010) 30.



T-shaped structure for $\text{N}_2\text{-N}_2\text{O}$ dimer
Howard *et al.*, Faraday Discuss. Chem. SOC., 86 (1988), 21.

Torsional combination bands for N₂O-CO₂

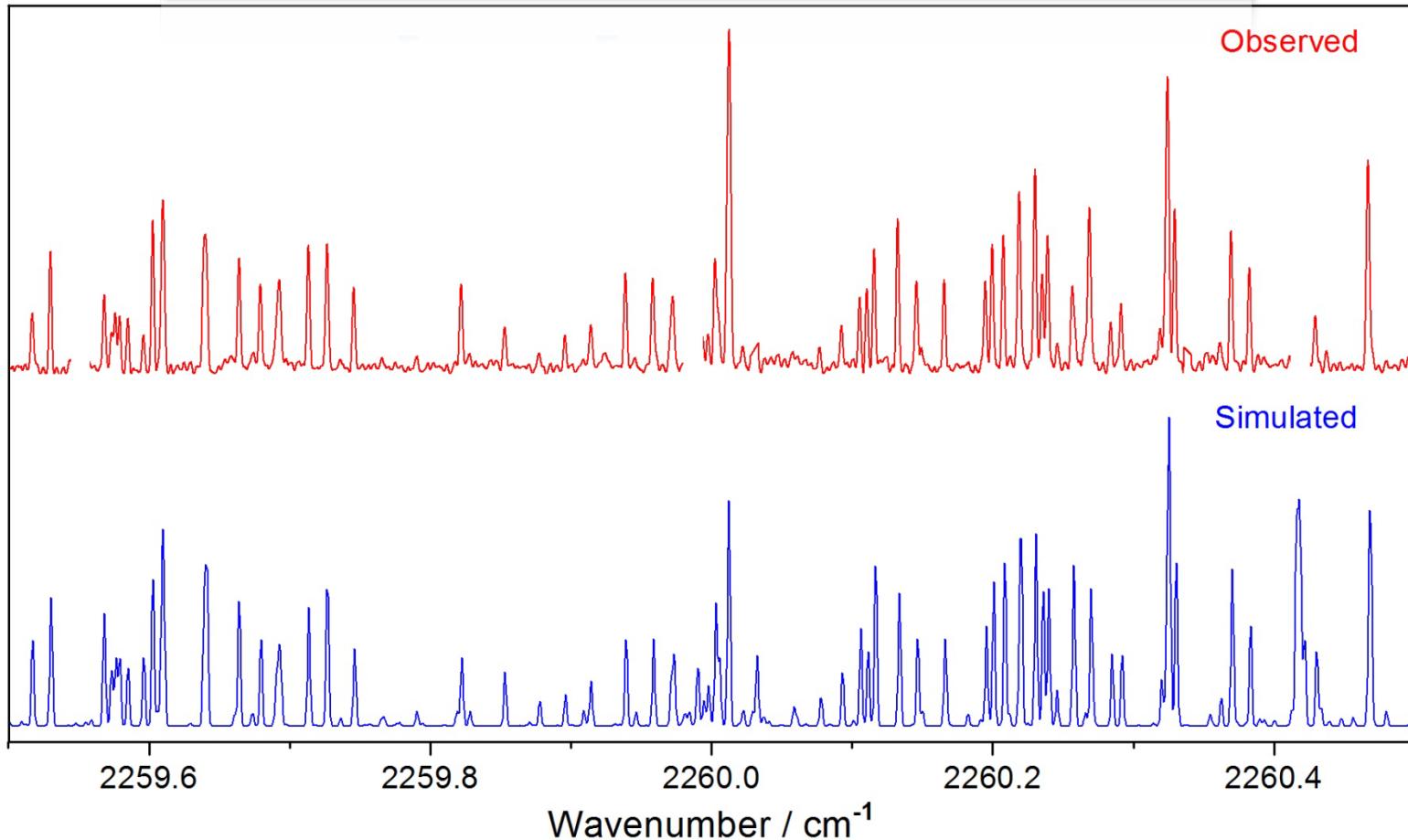


M. Afshri et al., JCP 129 (2008)
074314

Monomer vibration	Shift of the fundamental CO ₂ -N ₂ O band origin	Torsional frequency of CO ₂ -N ₂ O
CO ₂ ν_3	-0.278	25.802
N ₂ O ν_1	+1.996	25.707
N ₂ O ν_3	-5.319	...

Intermolecular modes do not depend strongly on the intramolecular vibrations in the weakly bound van der Waals complexes.

New N₂O-CO₂ combination band



Resulting intermolecular frequency

34.18 cm⁻¹

We used the PGopher computer program for assignment, simulation, and fitting of the spectra. (<http://pgopher.chm.bris.ac.uk/>)

Theoretical studies of the CO₂–N₂O van der Waals complex: *Ab initio* potential energy surface, intermolecular vibrations, and rotational transition frequencies

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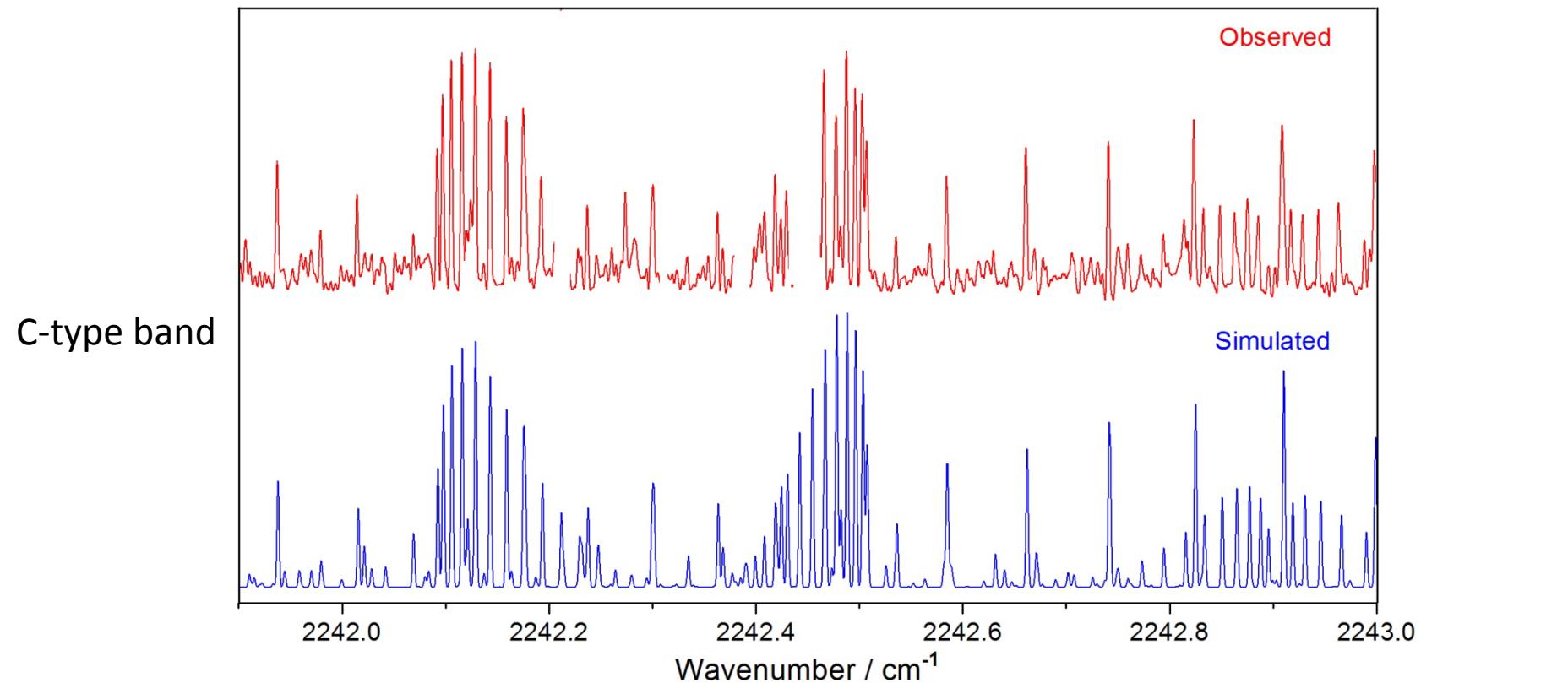
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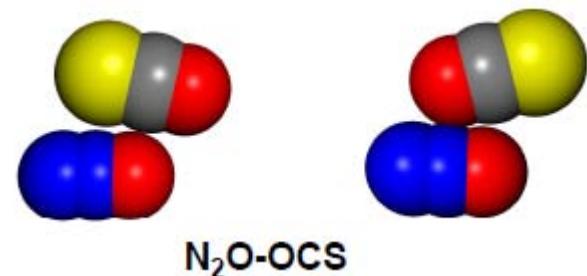
	Bound state			
	HF/6-311G* ^a	MP2/aug-cc-pVTZ ^b	Calc.	Expt. ^c
Slipped parallel isomer				
Torsion	32.01	27.38	25.760	25.8
Disrotation	29.06	38.58	32.450	 34.176 cm ⁻¹
Dissociation	45.59	58.60	44.612	
Conrotation	110.55	108.37	96.401	
T-shaped isomer				
Torsion		17.66	17.642	
Disrotation		8.68	8.261	
Dissociation		64.25		
Conrotation		74.41		

$\text{N}_2\text{O}-\text{OCS}$ torsional combination band

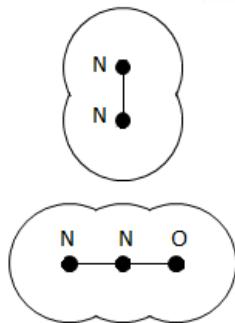


Torsional frequency for isomer b 17.11 cm^{-1}

$\text{CO}_2\text{-OCS}$ isomer a $18.73, 18.93 \text{ cm}^{-1}$
 $\text{CO}_2\text{-OCS}$ isomer b 15.9 cm^{-1}



$\text{N}_2\text{-N}_2\text{O}$ fundamental band



T-shaped structure for $\text{N}_2\text{-N}_2\text{O}$ dimer

Howard *et al.*, Faraday Discuss. Chem. SOC., 86 (1988), 21

b-type band

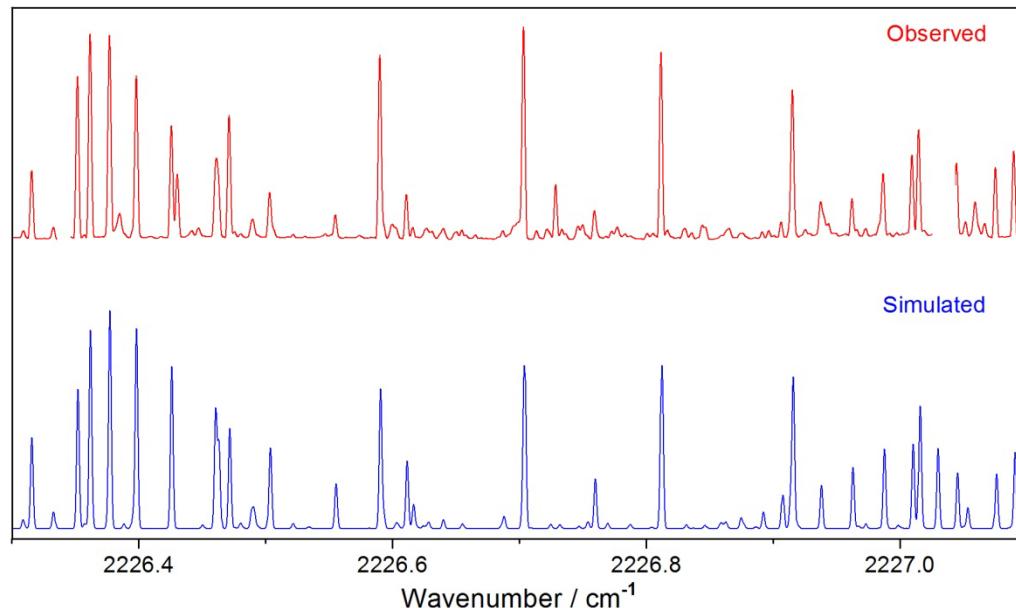
A potential based on distributed multiple and distributed dispersion model

H.O. Leung, JCP 110 (1999) 4394.

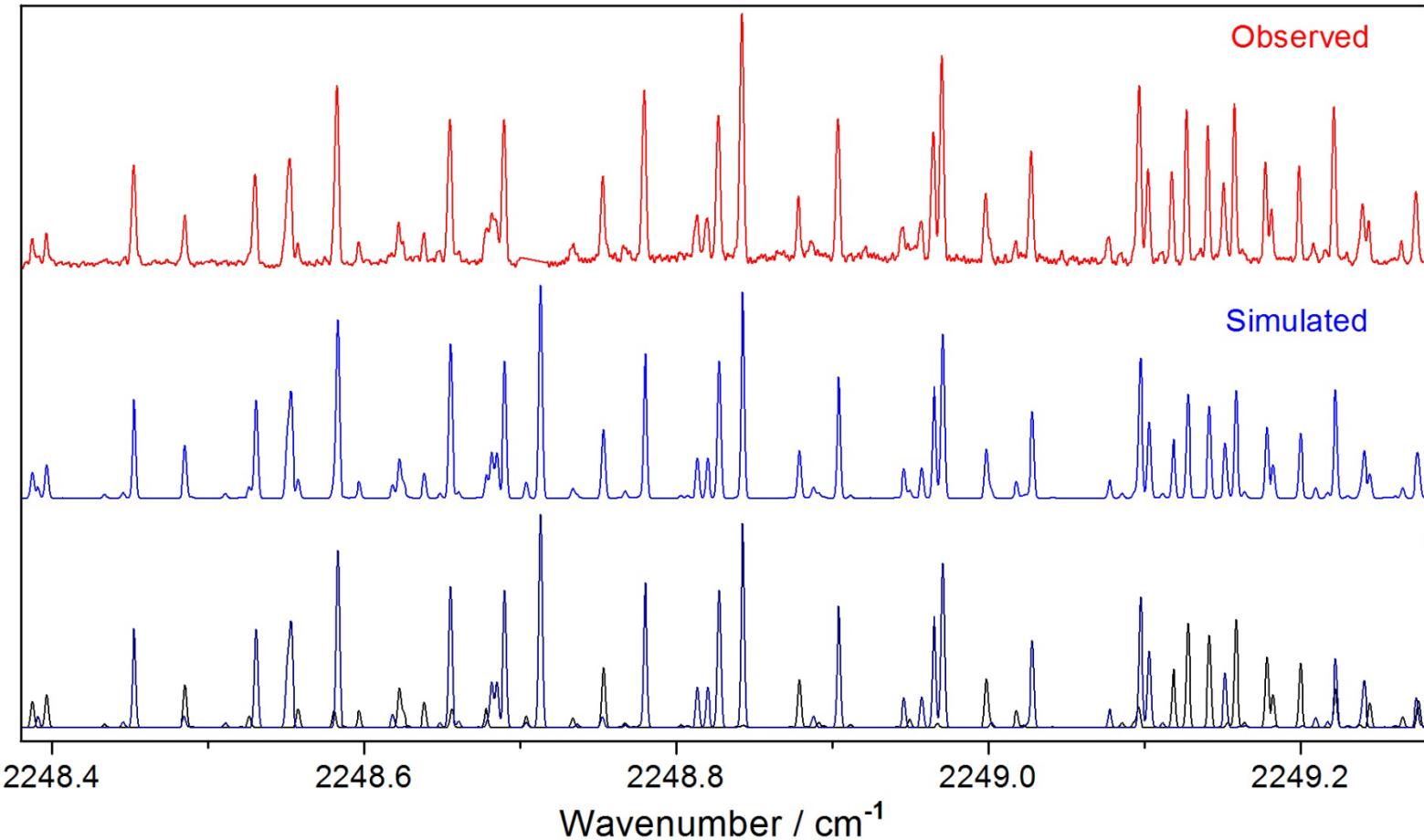
Mw observation of $^{15}\text{N}_2\text{-N}_2\text{O}$

The $^{15}\text{N}_2$ axis and the N_2O axis make an angle of 13° and 81° with the intermolecular axis, respectively.

a/b-type band with a weak a-type component



$\text{N}_2\text{-N}_2\text{O}$ combination band



a/b-type band with a weak b-type component

An in-plane intermolecular vibration and definitely not out-of-plane torsion.

Intermolecular vibrational frequency of 22.334 cm^{-1}

Summary

- ❑ Successful implementation of a CW-EC QCL in our apparatus with
 - ❑ Rapid-scan signal averaging technique
 - ❑ Continuous background subtraction
 - ❑ Laser frequency locking to reduce long term drifts
 - ❑ Post detection signal processing to reduce laser jitters
- ❑ Observation of combination bands of CO₂- , OCS- and N₂-N₂O
(in ν_1 fundamental region of N₂O).