Molecular Spectroscopy at JPL

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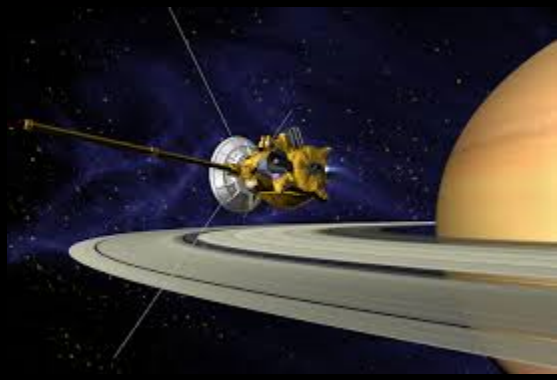
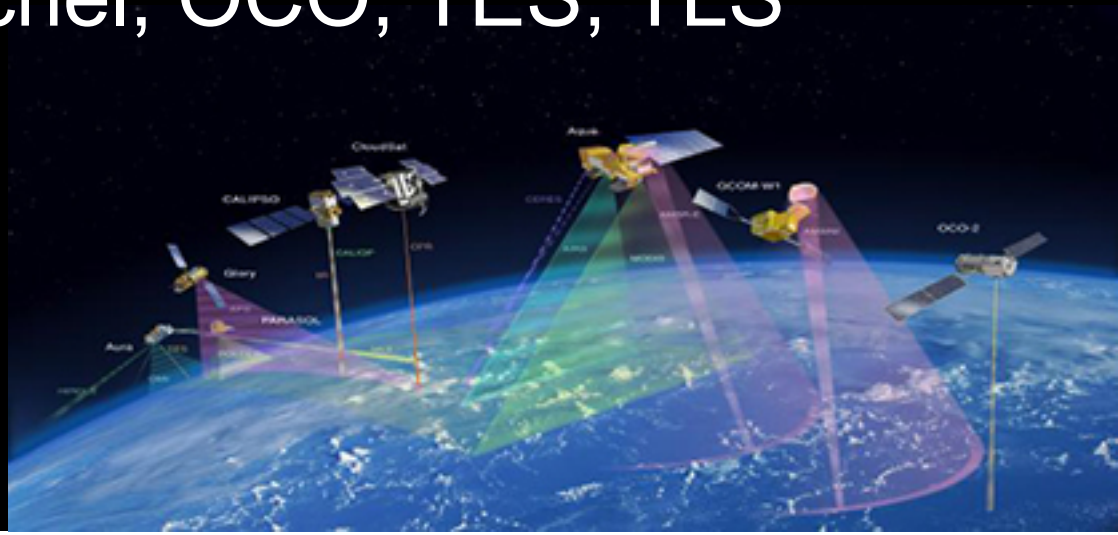
Space-based spectrometers

Heterodyne, FTS and Grating Spectrometry, In-situ Sensing

Coming Attractions:
PREFIRE and Vesper!



- MLS, Herschel, OCO, TES, TLS



Atmosphere — JPL Capabilities, Facilities, Instruments & Missions for Earth

Databases/Standards: BIPM; HITRAN (Harvard CfA/International Effort); JPL Spectral Line Catalog; GPS

Facilities: TMF/MLO; CLARS; SWAT Laboratory / Near-field antenna range; JPL Molecular Spectroscopy Laboratory

Cal/Val

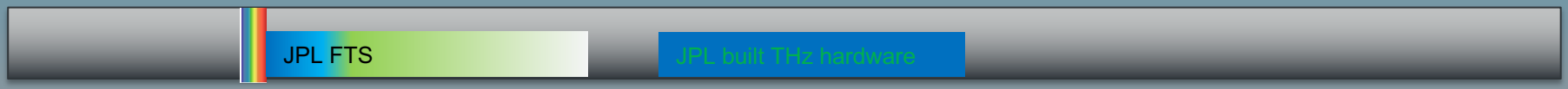
Instrumentation

DIAL, FTUVS; MSPI, MSPI –II; MISR, *MAIA*; TCCON, Mk IV, CLARS-FTS, UAS-TLS; OCO-2, *OCO-3*, *CIRAS*; CIRAS, AIRS, TES; SLS, *CAMLS*, *SWITCH, MASC*, *TEMPEST*, MLS; HAMSR, CloudSat, *RainCube*; APR-2,3; GPS-RO

Science

O_3,OH,BrO comp.; Aerosol; Airmass, SIF; CO_2, CH_4 comp.; O_3, CO_2, trace comp.; O_3, trace comp.; Clouds, precipitation; H_2O comp.

10^{16} 10^{14} 10^{12} 10^{10} 10^{8} Hz



10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} m

Science: Ground truth, land use; biodiversity; Plant health, Volcanoes, Ecosystem, Fires; Ocean Salinity, Winds, Altimetry, Topography; Ground motion, Hydrology Soil Moisture

Instrumentation: ASTER; *EcoSTRESS*; AVIRIS, PRISM, AVIRIS-NG, UCIS; HyTES, PhyTIR; Aquarius, GRACE, NISAR, QuikScat, RapidScat, JASON, COWVR, SMAP, *GRACE-FO,SWOT*

Cal/Val: AirSWOT, DopplerScat, GLISTEN-A, AVSAR,AirMOSS, WISE

Facilities: MISR IS; LW IS; JPL spectral GSE for TVAC; ARIA; ECCO; JPL antenna range / Large Aperture test rig

Databases / Standards: ASTER/Spectralon; GPS

Solid Earth/Ocean

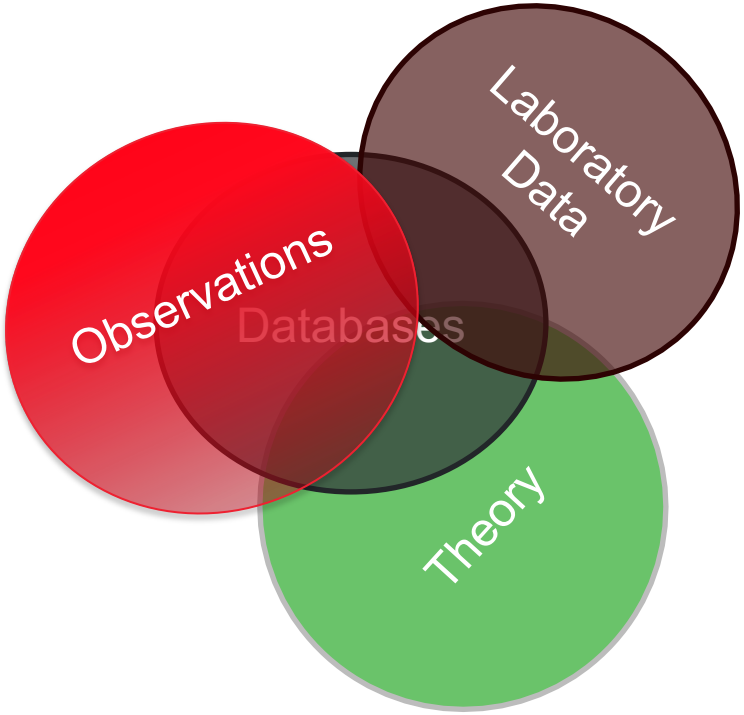
July 2017, draft

Legend: operational, *in development* ↔ spectral coverage ←- - -→ w/ partners

Molecular Spectroscopy Lab

Lab Measurements/Analysis/Databases/Remote & In Situ Sensing

- **<u>How we support composition science:</u>**
- Recording High resolution Laboratory spectra
- Analyzing data with thermodynamic and quantum mechanical models
- Comparing results with other laboratories and theory
- Cataloging/merging results into public databases
- Working with observers on formulation, algorithms, uncertainty quantification and discovery science



Molecular Spectroscopy Laboratory

Laboratory capabilities / Analysis Capabilities / Database Repository

- High resolution millimeter and submillimeter (THz) spectroscopy
  - Tunable, monochromatic local oscillators
    - Static cells 3m (< 1.2 THz), 1m (all THz)
    - Plasma cells for radicals and ions
  - FTmmW Cavity systems
- High resolution infrared spectroscopy
  - Bruker IFS125HR (FTIR) 16-17,800 cm^{-1}
  - M-squared Ti:Sapphire system, 4600-14,900 cm^{-1}

- Quantum Mechanics
  - SPFIT/SPCAT
  - SMAP
- Statistical Mechanical
  - Labfit (Brown)
  - Labfit (Benner)

- Isolated gases
  - JPL Catalog
  - CDMS
- Perturbed gases
  - HITRAN
  - GEISA

High Resolution mm & submm (THz) spectroscopy

Laboratory Capabilities: Tunable, monochromatic local oscillators (1)

Coverage spans 0.06 to 2.7 THz,

REVIEW OF SCIENTIFIC INSTRUMENTS **76**, 093113 (2005)

Application of cascaded frequency multiplication to molecular spectroscopy

Brian J. Drouin,[a] Frank W. Maiwald, and John C. Pearson
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Device	Multiplier	Range (THz)	Maximum power (μW)	Typical power (μW)	Harmonic content
AMC-15	4	0.05–0.07	4000	2000	<−30 dB
AMC-10	6	0.07–0.11	3000	1000	<−30 dB
Agilent 83558A	6	0.07–0.12	2000	1000	<−30 dB
MUT-05	3	0.14–0.22	400	50	<−30 dB
MUT-04	3	0.18–0.27	120	40	<−30 dB
VDI 1.9×5	5	0.40–0.60	40	10	−20 dB×6, ×7
VDI 1.5×6	6	0.60–0.75	100	30	−20 dB×4
VDI 1.2×5	10	0.77–0.85	50	10	<−30 dB
JPL ×2×2×2	8	0.70–0.83	800	50	···
JPL ×2×2×3	12	0.84–0.95	400	50	−23 dB×8
JPL ×2×2×3	12	1.05–1.28	100	30	−26 dB×16
JPL ×2×3×3	18	1.55–1.65	12	4	···
JPL ×2	2	1.65–1.75	<0.1	≪0.1	−10 dB×3
JPL ×3	3	2.57–2.65	<0.01	≪0.01	10 db×2

'workhorse' system:
Turn-key operation
- always locked (to standard)

Reproducible performance
- optical mounts with each chain
- quick band changes

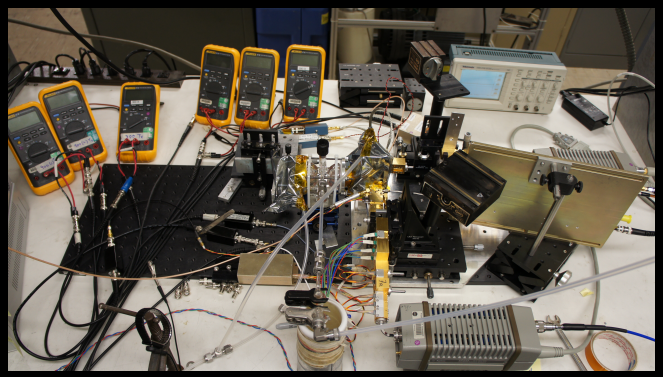
Fully programmable
- long, deep scans
- adjustable conditions macros

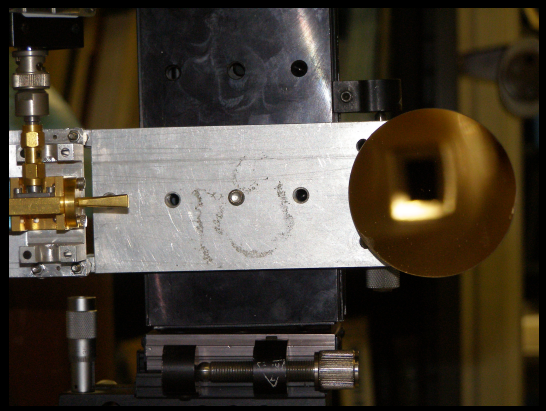
Most reliable component in plasma experime

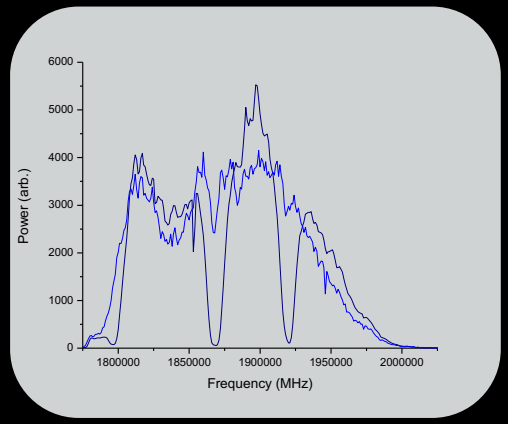
Upgrade to low phase noise synthesizers
- no filtering necessary
- lamb-dips as desired

High Resolution mm & submm (THz) spectroscopy

Laboratory Capabilities: Tunable, monochromatic local oscillators (2)







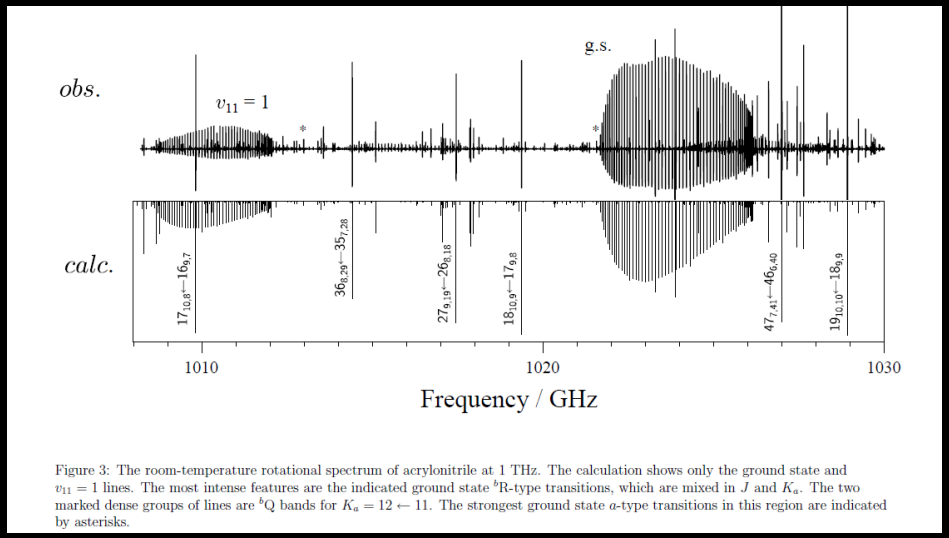
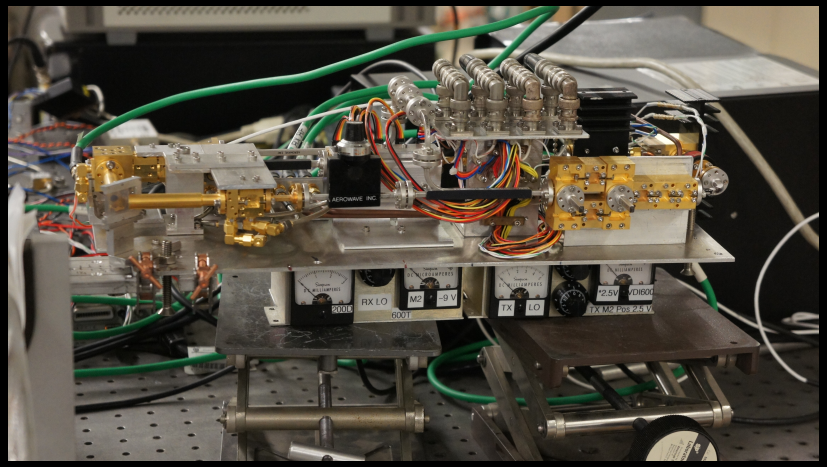


Figure 3: The room-temperature rotational spectrum of acrylonitrile at 1 THz. The calculation shows only the ground state and $v_{11} = 1$ lines. The most intense features are the indicated ground state ^{b}R-type transitions, which are mixed in J and K_a. The two marked dense groups of lines are ^{b}Q bands for $K_a = 12 \leftarrow 11$. The strongest ground state a-type transitions in this region are indicated by asterisks.



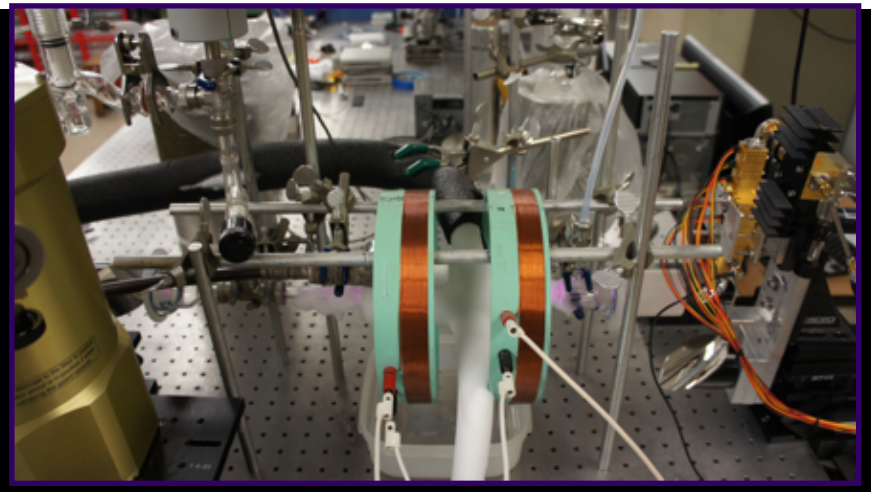
Zero-Field detection of HCl+

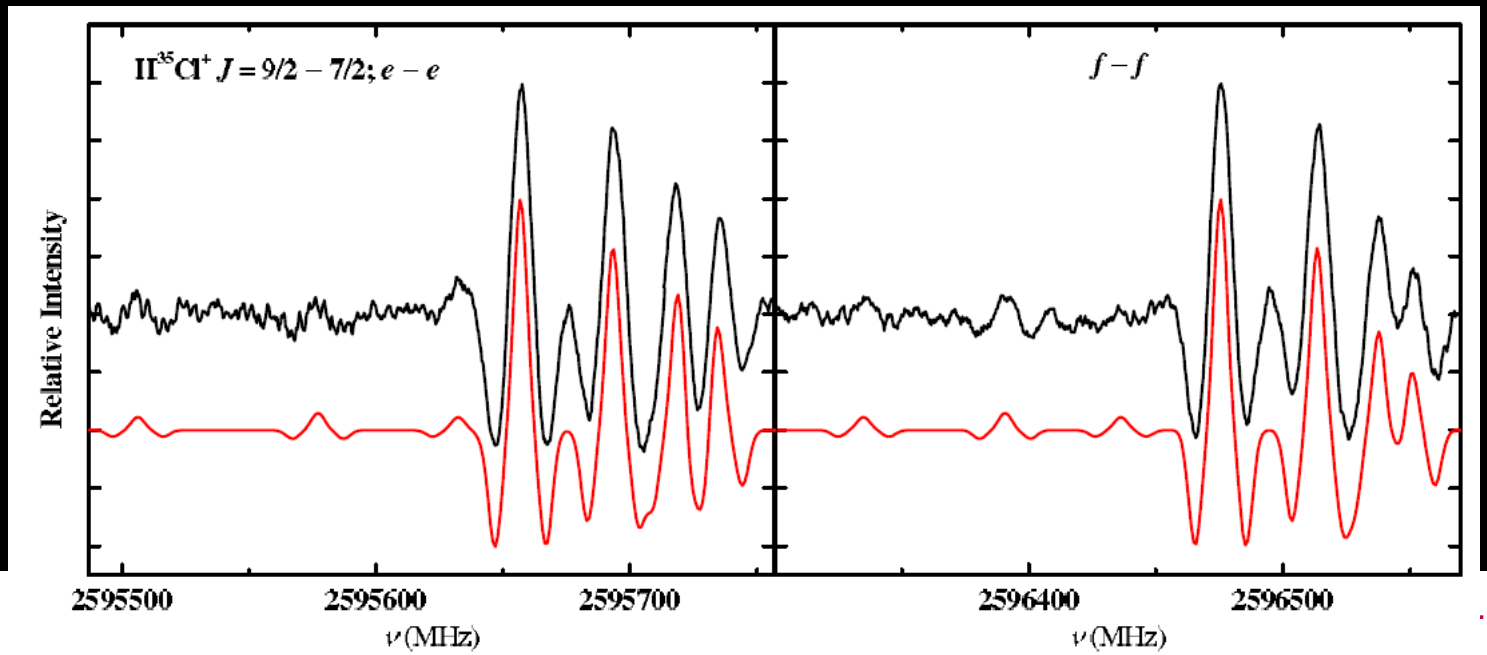
Laboratory Capabilities: Tunable, monochromatic local oscillators (X)

Complex Experiment
- reactive plasma

Complex Spectrum
- $^2\Pi_i$ with fine and hyperfine

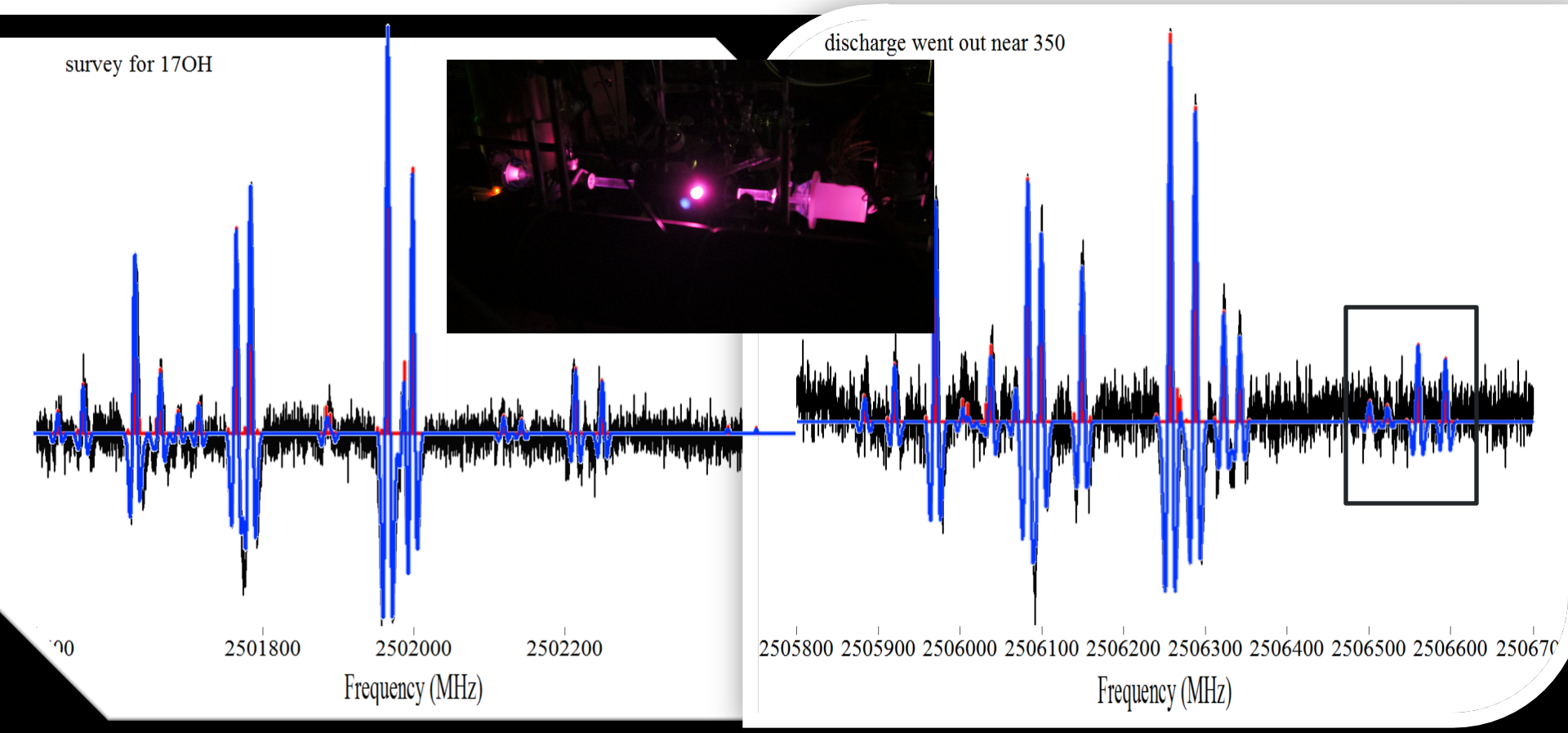
Interstellar Detection with HIFI
- DeLuca et al. Ap.J. 2012





1st look for ^{17}OH $^2\Pi_{3/2}$

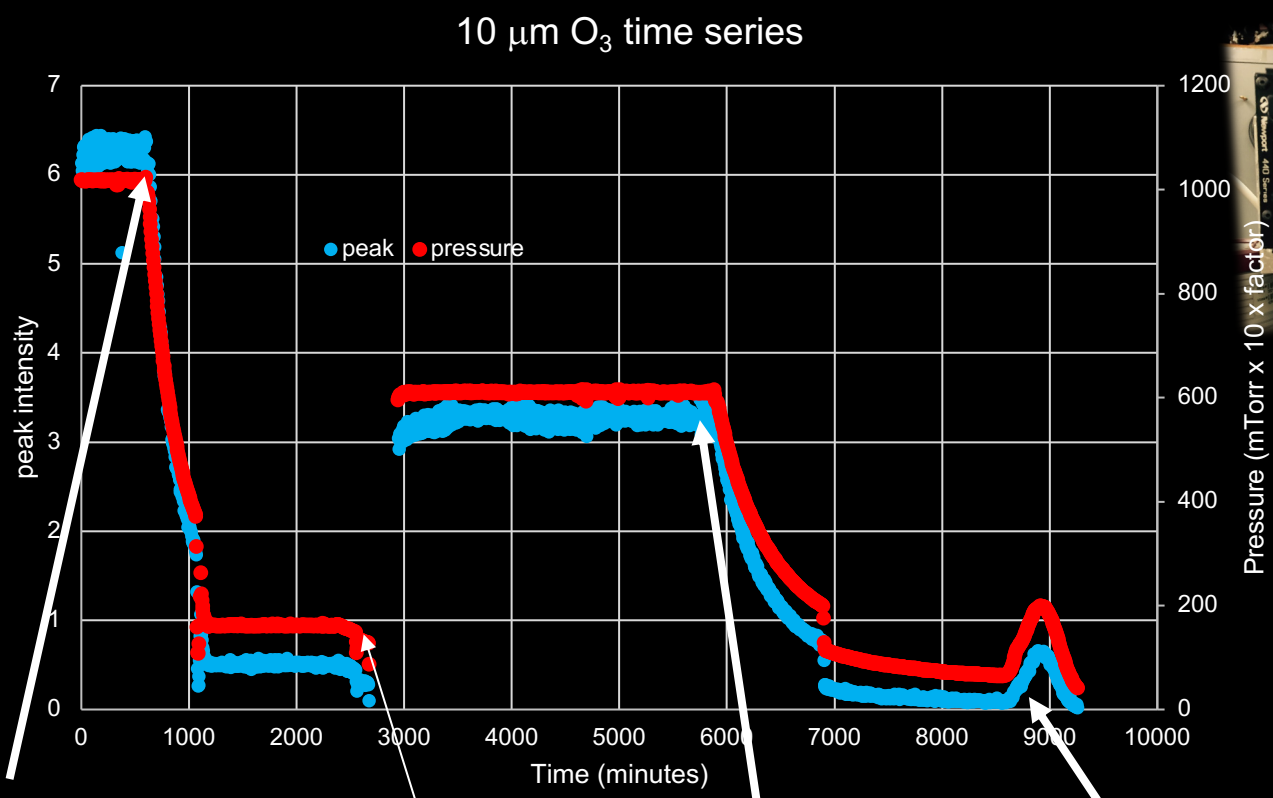
Laboratory Capabilities: Tunable, monochromatic local oscillators (X)

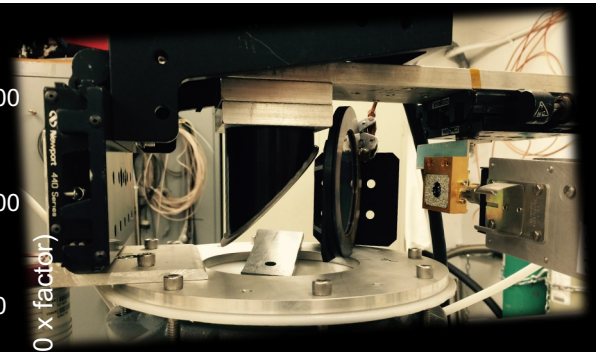


- *e* - *e* and *f* - *f* show splittings from
- $I = {}^5/_2$ for ^{17}O and $I = ½$ for ^1H

Monitoring Concentration

Laboratory Capabilities: Tunable, monochromatic local oscillators (X)





Drouin *et al.* JQSRT 2017 "Validation of ozone intensities at 10 μm with THz spectrometry"

Birk *et al.* JQSRT 2019 "Ozone intensities in the rotational bands"

Adjust set point & flow rate

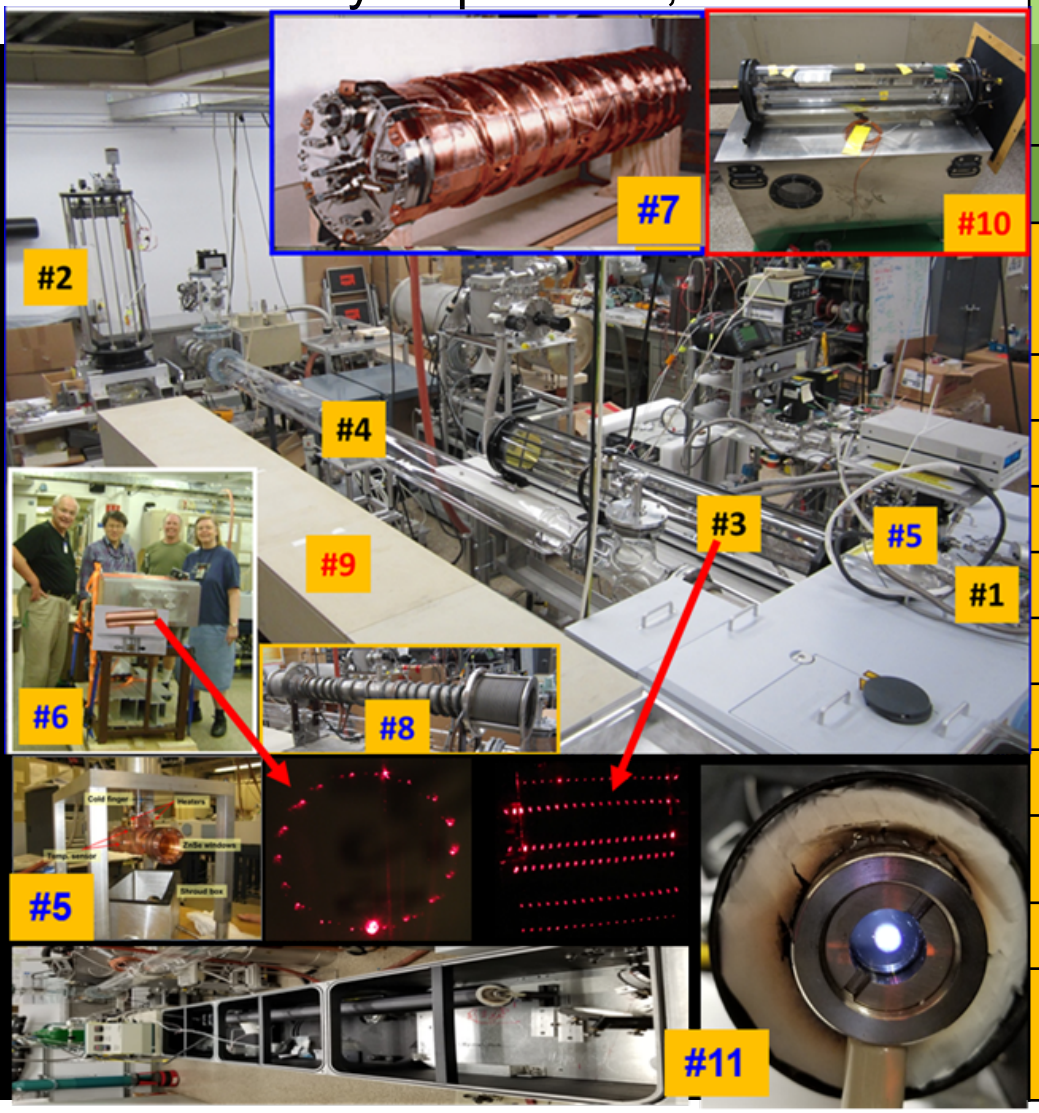
Adjust set point again

Stop regulating

Warm up O_3 trap

High Resolution Infrared Spectroscopy

Laboratory Capabilities, Bruker IFS 125HR



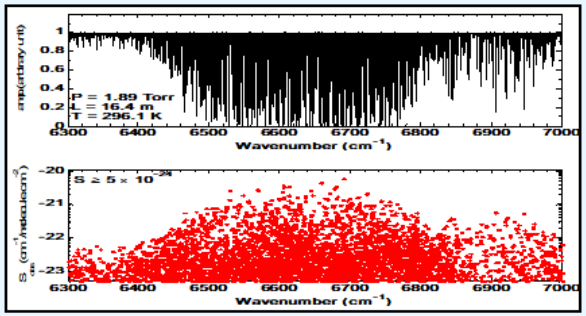
Various gas absorption cells configured to the FT-IR			
#	path (m)	T(K)	range
1	Short cells (0.005, 0.02, 0.06, 0.15, 0.2, 0.25) at room temperature		
2	6.6 – 32.5	296	0.7 – 50 µm
3	20 – 180	296	0.7 – 1.6 µm
4	0.76 and	296	IR *and* MW
5	0.204	80 – 296	1.6 – 15 µm
6	21	30 – 250	1.6 – 8 µm
7	4 – 52	20 – 296	15 – 500 µm
8	0.8	180–296	0.7 – 18 µm
9	vac. chamber (~2 m)		0.7 – 5 µm
10	2.2 – 22	296–420	0.7 – 8 µm
11	1.00 P=150 bars	296–530	0.6 – 2.5 µm

High Resolution Infrared Spectroscopy

Molecular Studies to Support NASA Missions: *(Published or In Progress)*

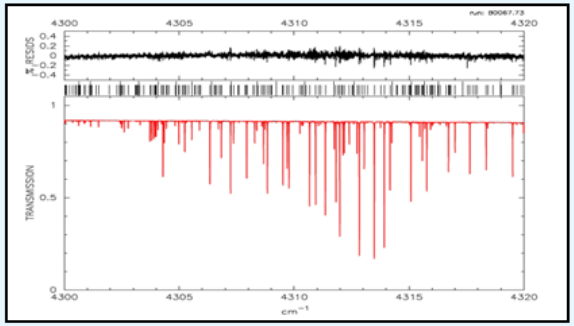
a) NH_3: 1.5µm *for Exoplanets*

***Experimental** lists for intractable regions: Pos., Str., Lower states E.*

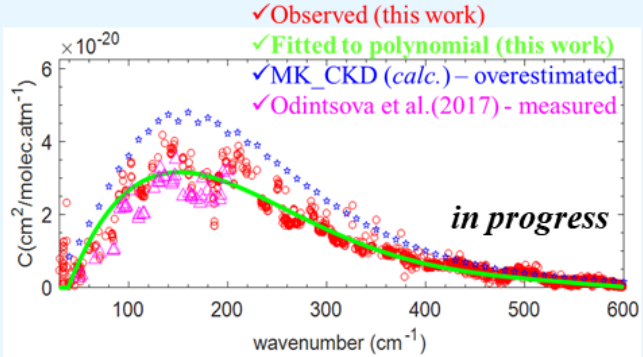


b) CH_3D: 2.4µm *for Earth+*

Line–by–line intensities (oscillator strengths) for theoretical modeling

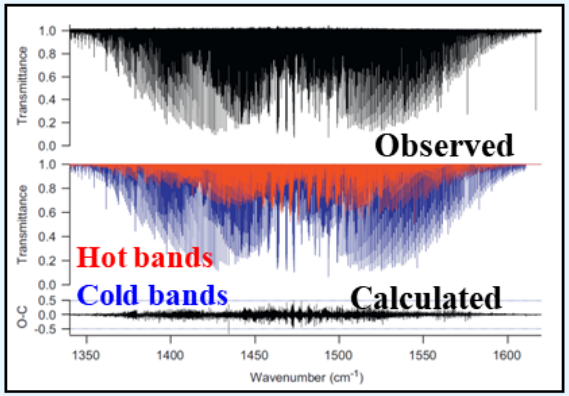


e) FIR H_2O continuum *for Earth*



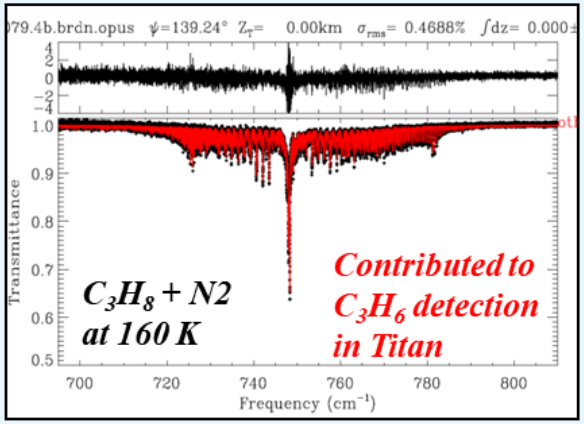
c) C_2H_6: 7µm *Outer planets*

Freq. and Assignments to produce calculated line parameters for databases



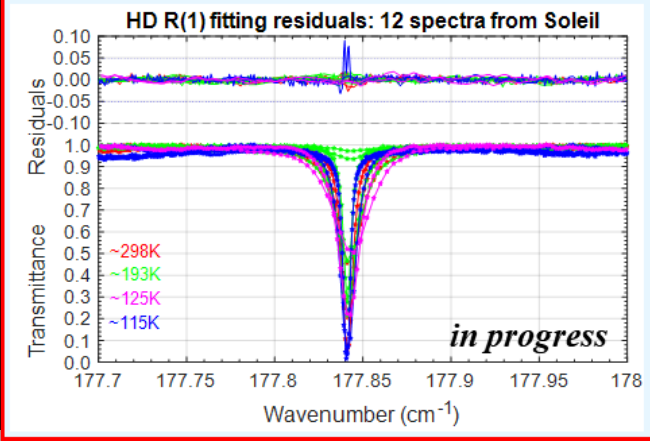
d) C_3H_8: 13 µm *for Titan*

Experimental Xsec vs Temperature



f) HD in the FIR: *for Saturn*

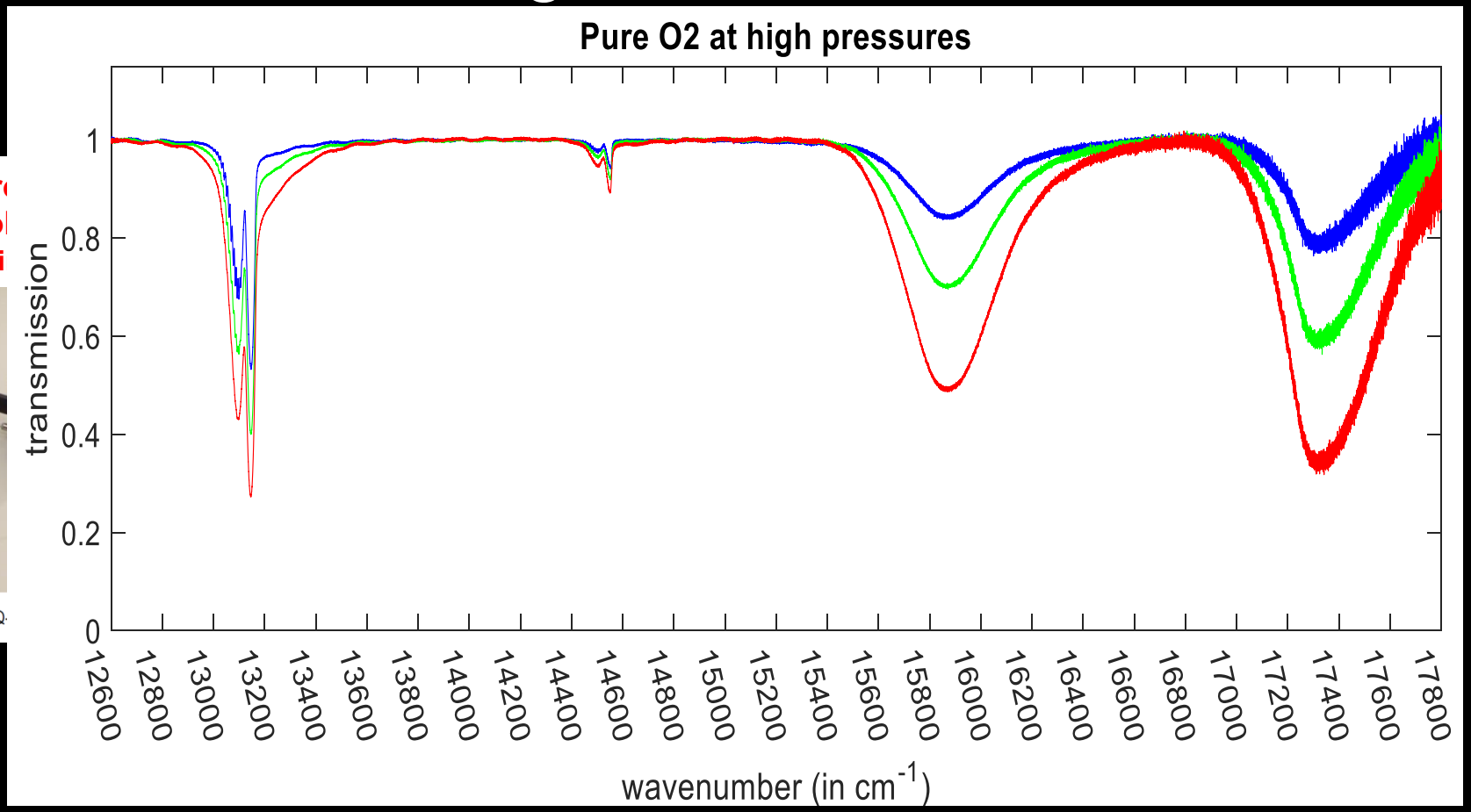
Determination of line shape parameters



Recent Upgrades to Bruker

Laboratory Capabilities: Bruker IFS 125 HR

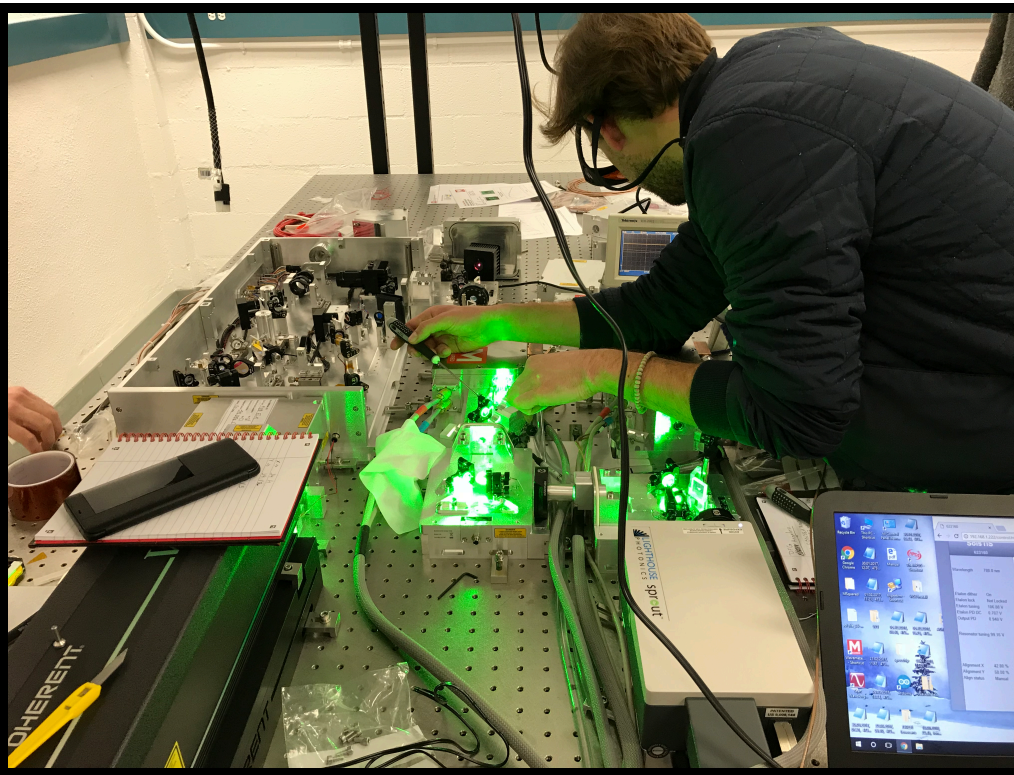
- Laser Driven Light Source
-



High Resolution Infrared Spectroscopy

M-Squared Laser System: installation

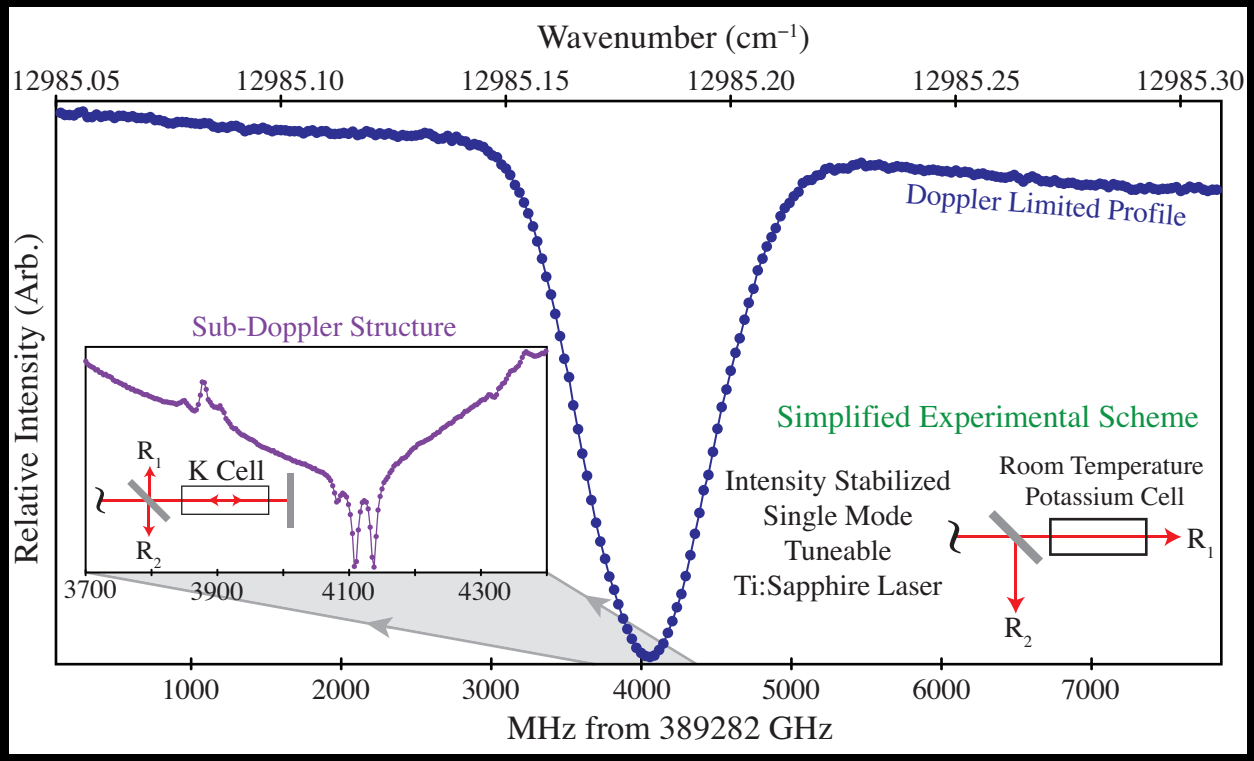
- Titanium Sapphire Systems
  - Standard unit tunable 700-1000nm
  - Additional unit 670-700nm
  - Lock to a WS-8 wavemeter (2 MHz precision)
  - Several Watts of output power
- Difference frequency module
  - Two PPLN crystals 1100-1400nm, 1400-2200nm



High Resolution Infrared Spectroscopy

M-Squared Laser System: 1st light

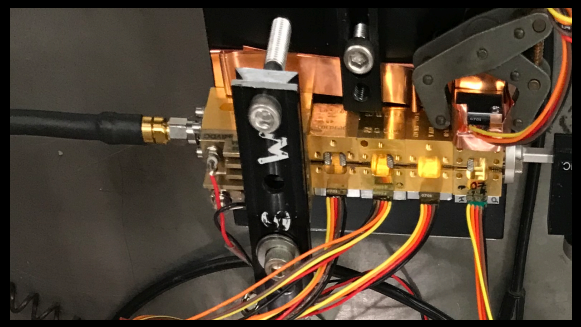
- Stabilized scanning frequency with Wavemeter
- Stabilized intensity with pre-cell detector
- Doppler-limited potassium in single pass
- Sub-Doppler features in double pass
- Goal is to use potassium as reference using slaved Sacher laser



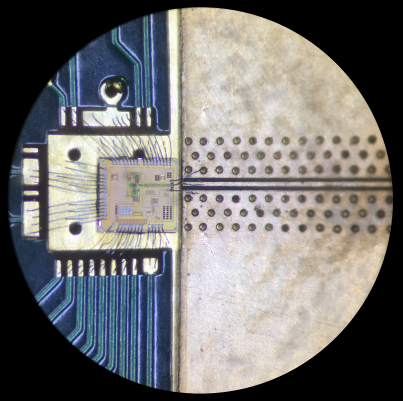
Common Developments with Remote Sensing

Emission Spectroscopy

- GaAs devices
  - MLS and Herschel Local Oscillators
  - VDI
- GaAs, GaN, InP devices
  - Low noise amplifiers
  - Power amplifiers
- Silicon devices (CMOS)
  - System on Chip Receivers



1W @
100 GHz
20cmx5cm
20W

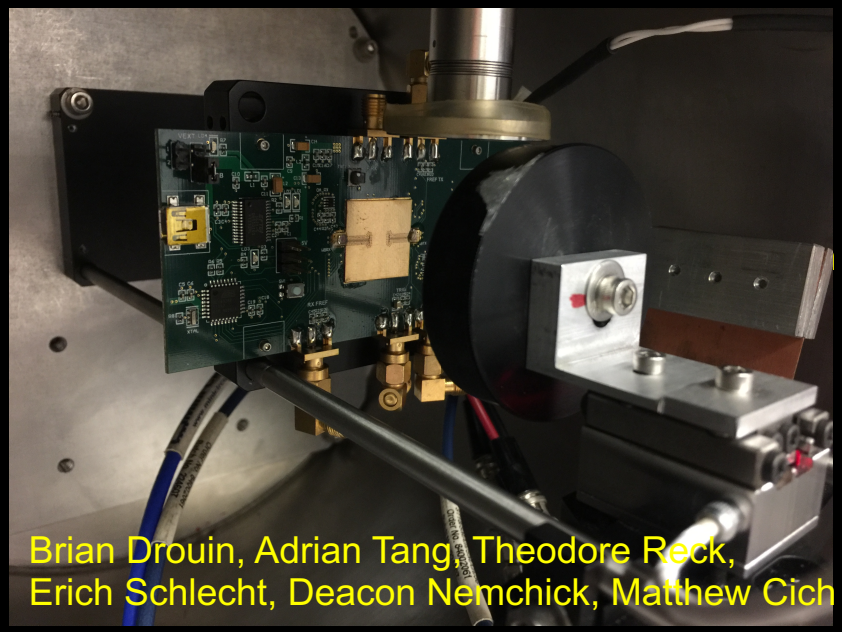


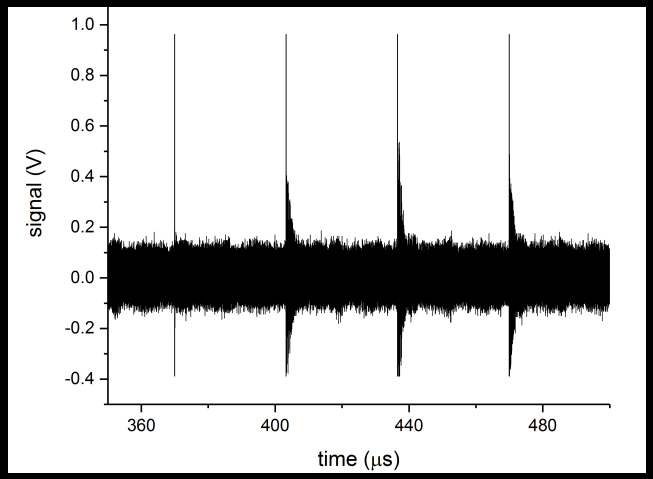
1mW @
100 GHz
1.2mmx1mm
0.3 W

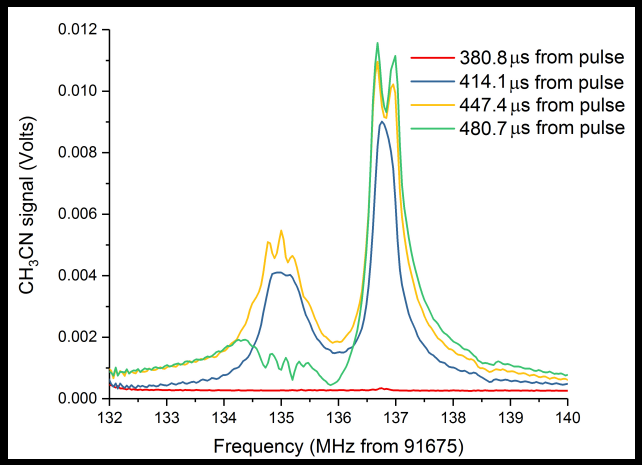
The Spectrometer on a Chip

Laboratory Capabilities: FTmmW Cavity Systems

Based on Flygare-Balle spectrometer design modified for *semi*-confocal cavity. Radiation injected in / detected from sides of planar mirror

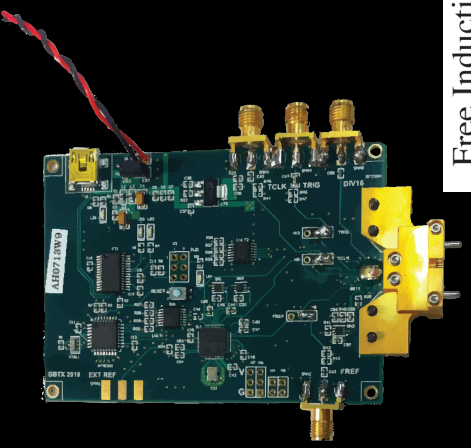


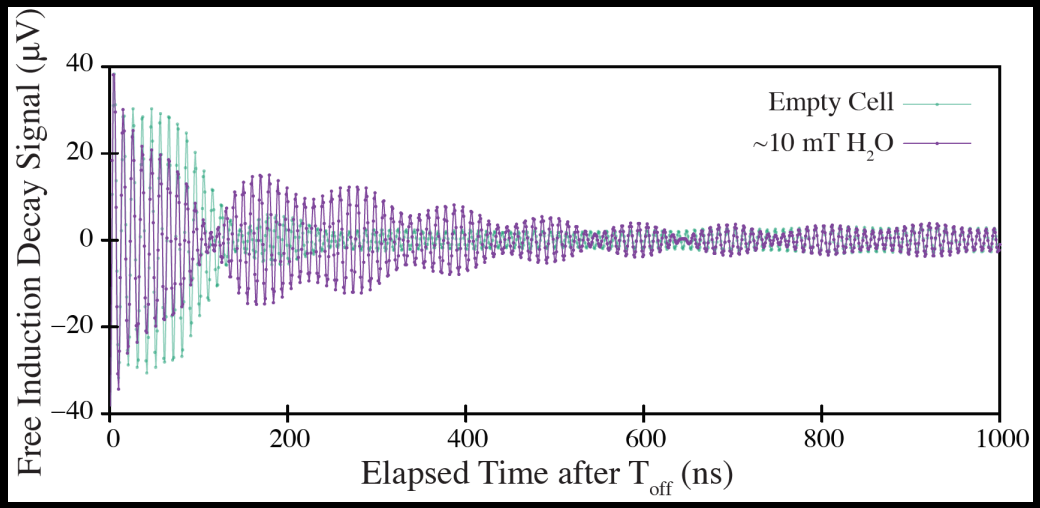


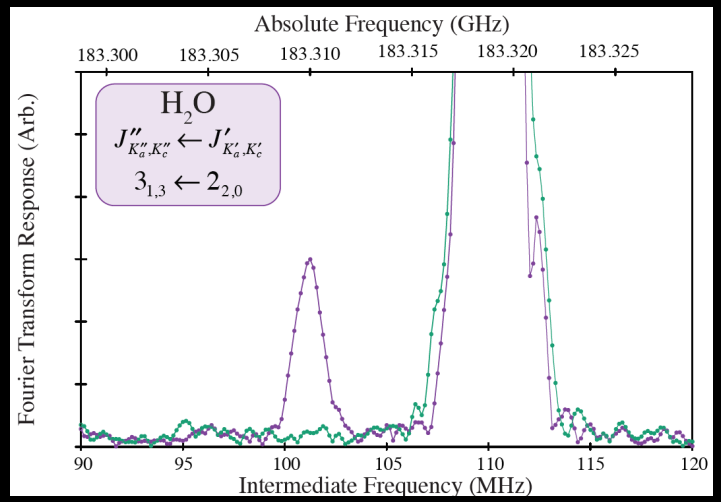


The Spectrometer on a Chip ^ 2

Laboratory Capabilities: G-band Transceiver system

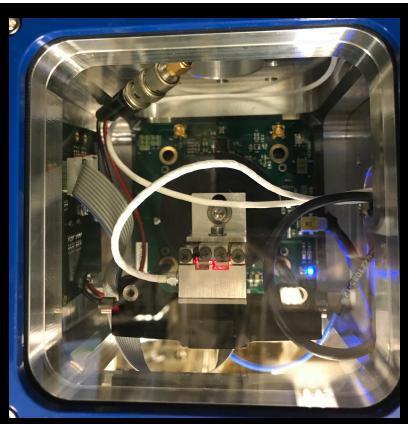


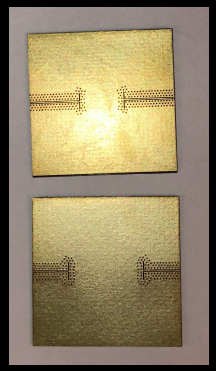


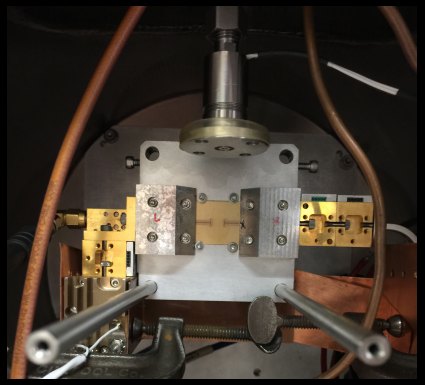


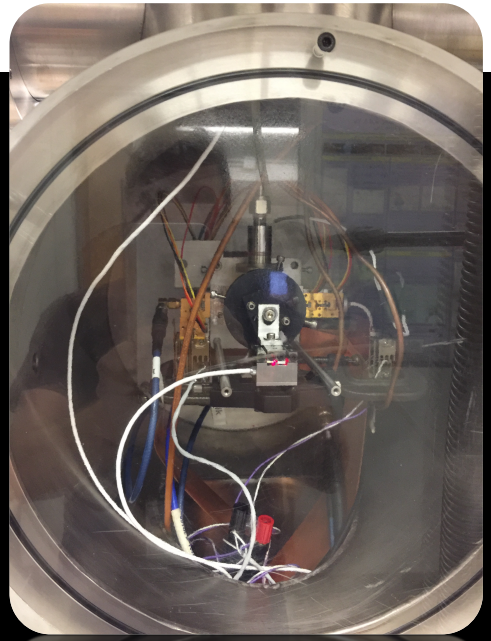
Modular Version of Cavity Spectrometer

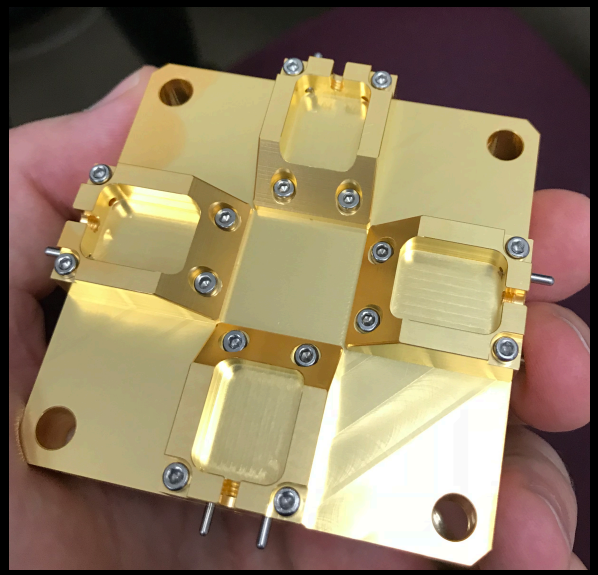
Laboratory Capabilities: FTmmW Cavity Systems





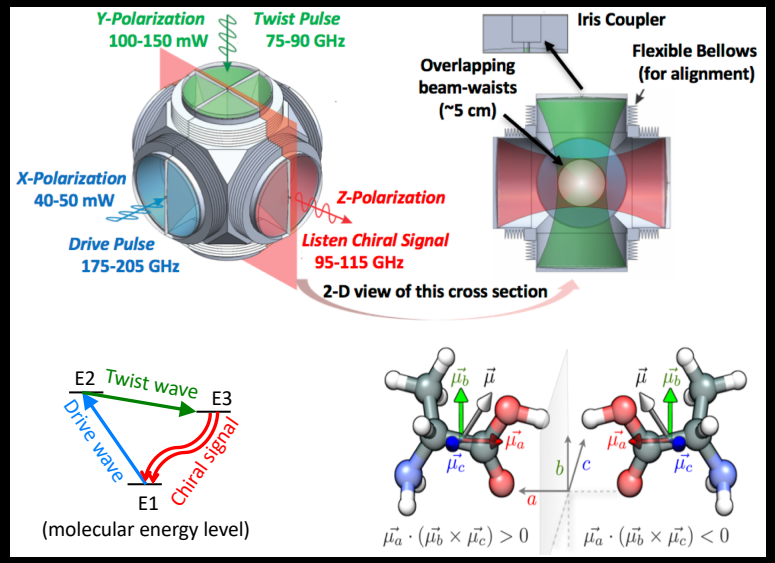


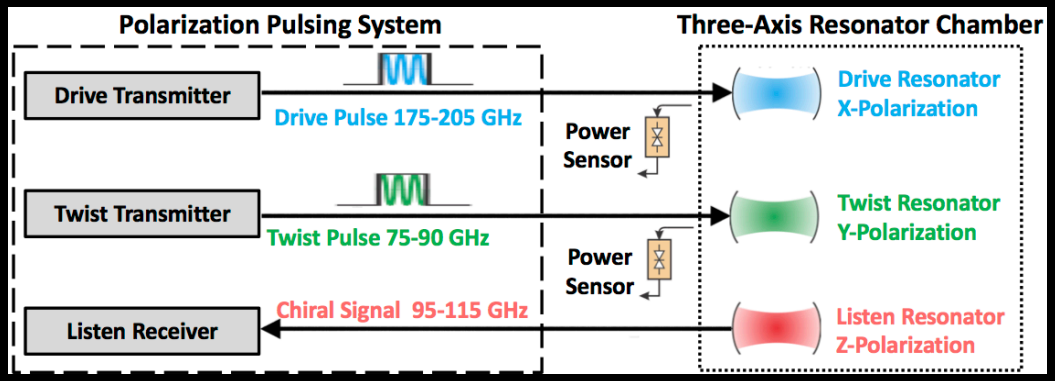




mm-wave chirality spectrometer (ChiralSpec)

Laboratory Capabilities: Chiral gas detection





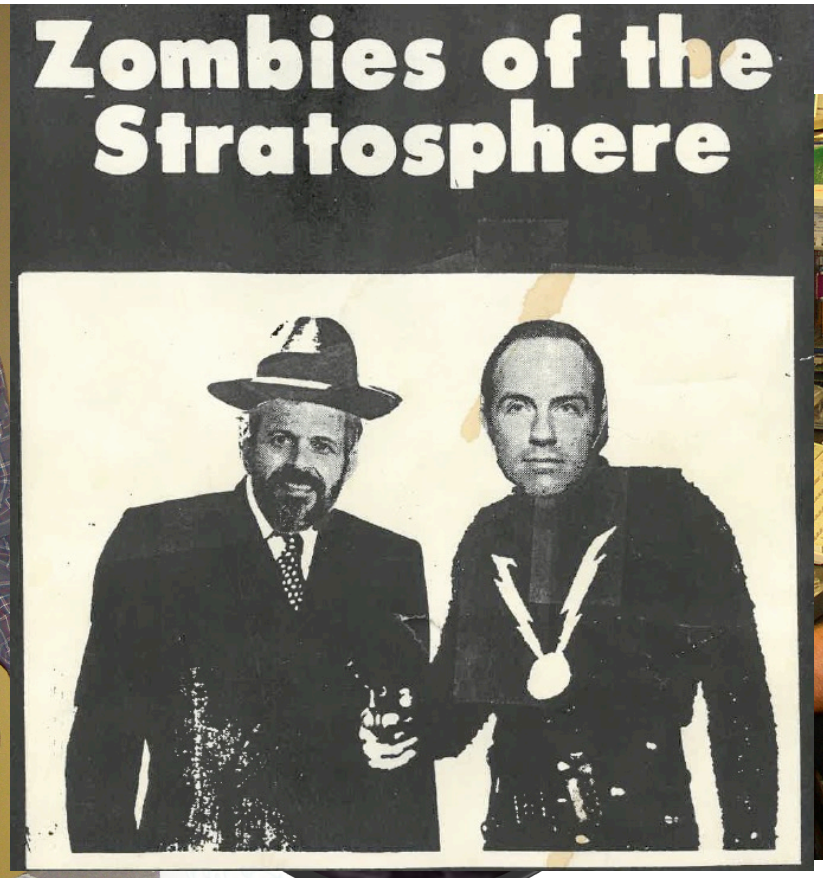
Science:

- Search for life
- Existence of habitats beyond Earth
- History of organics

A mm-wave 3-axis cavity resonator. It generates a time-domain chiral emission signal via exciting target species with two linearly polarized pulses called Drive and Twist. **Enantiomeric pair's chiral signals have the same frequency but 180° phase difference.** Its chirality resolution utilizes enantiomers' property of opposite sign of dipole moment product. It uses a cycle of three transitions involving the a, b and c dipoles.

Herbert M. Pickett, Edward A. Cohen

Mentors, Quantum Zombies



Jet Propulsion Laboratory
California Institute of Technology

specjpl.nasa.gov

Optical Oscilloscope

Modulating and measuring a laser at 100+ GHz

- GaN 1W amp from THz dev.
- Applications in optical communications or optoelectronics

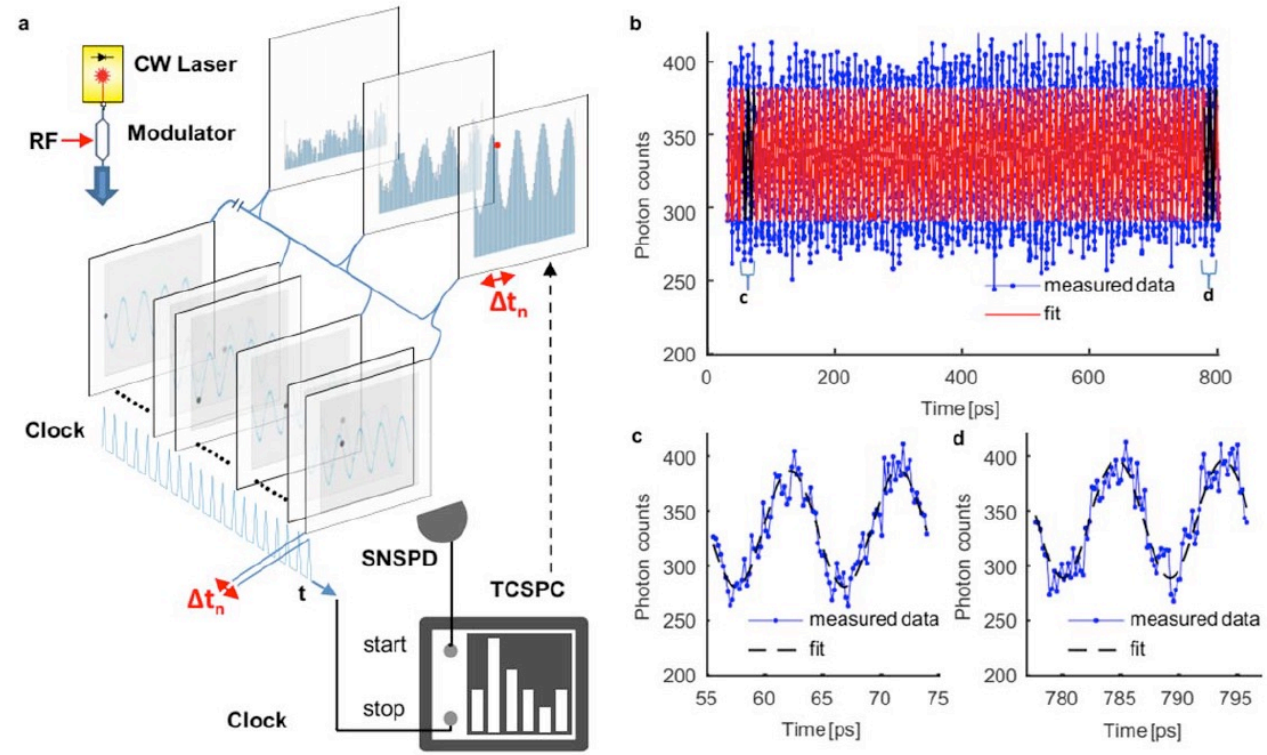
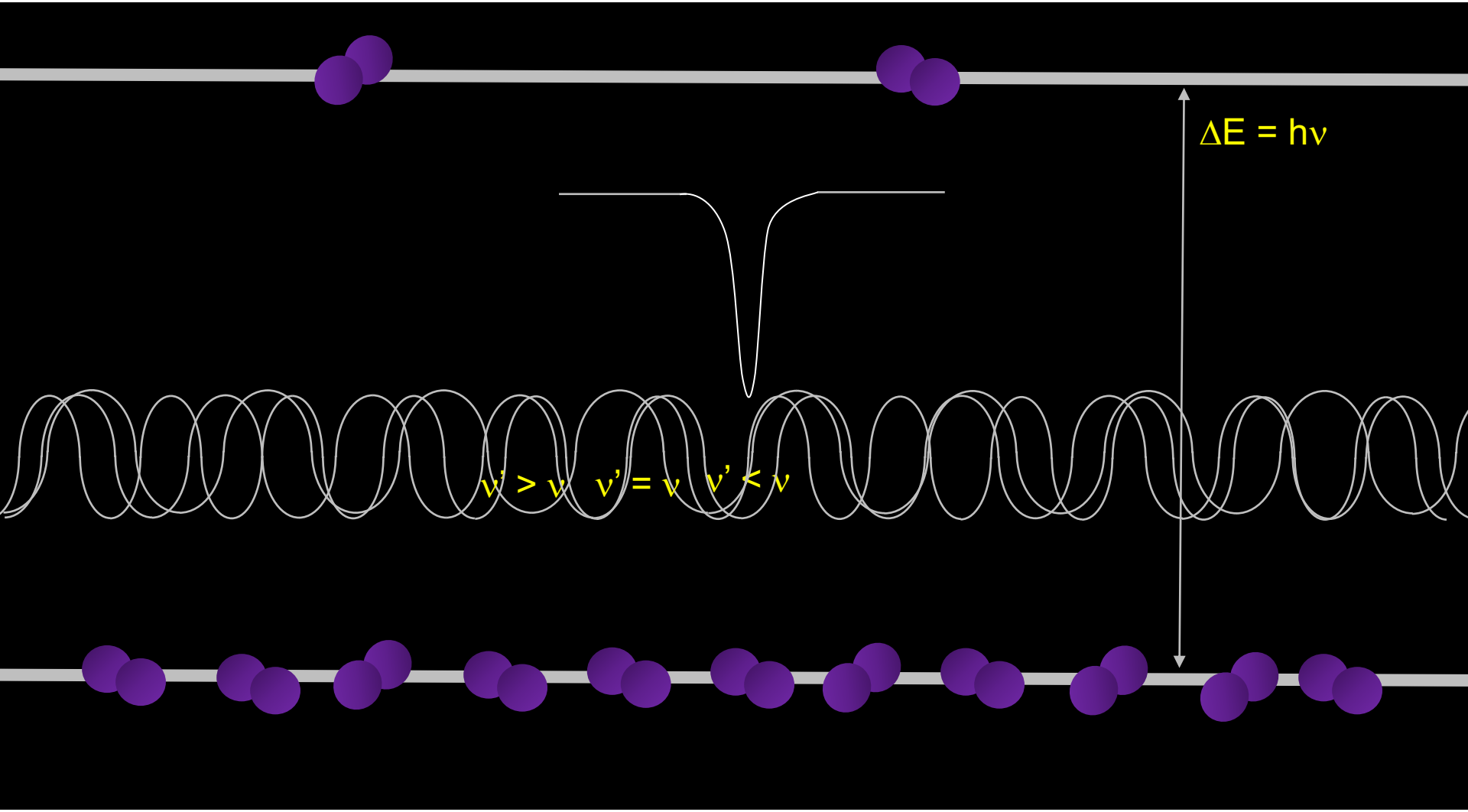


Figure 1 | Oscilloscope concept and measurement sequence. a, Experimental setup and

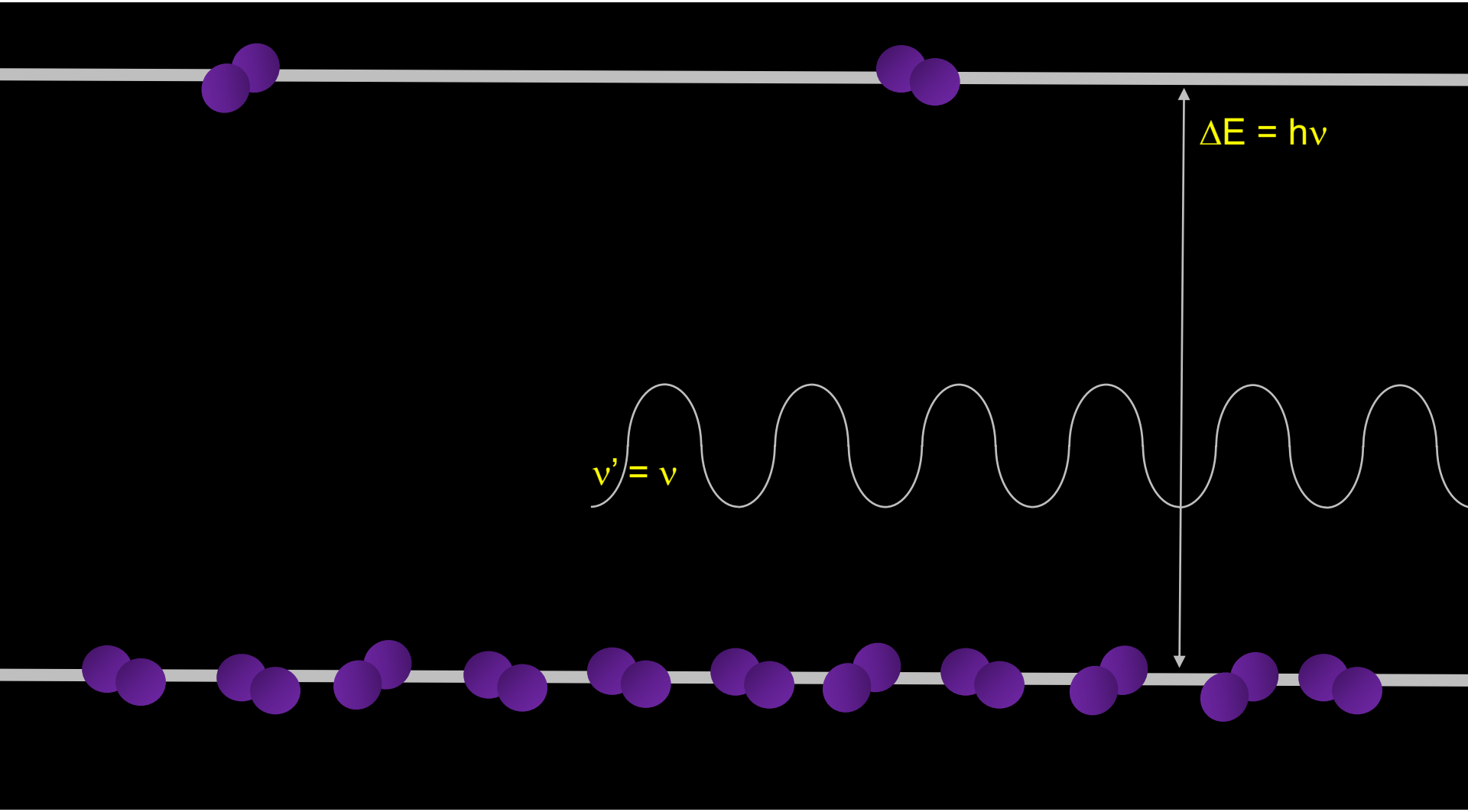
Atom/molecule: Two Level System

absorption



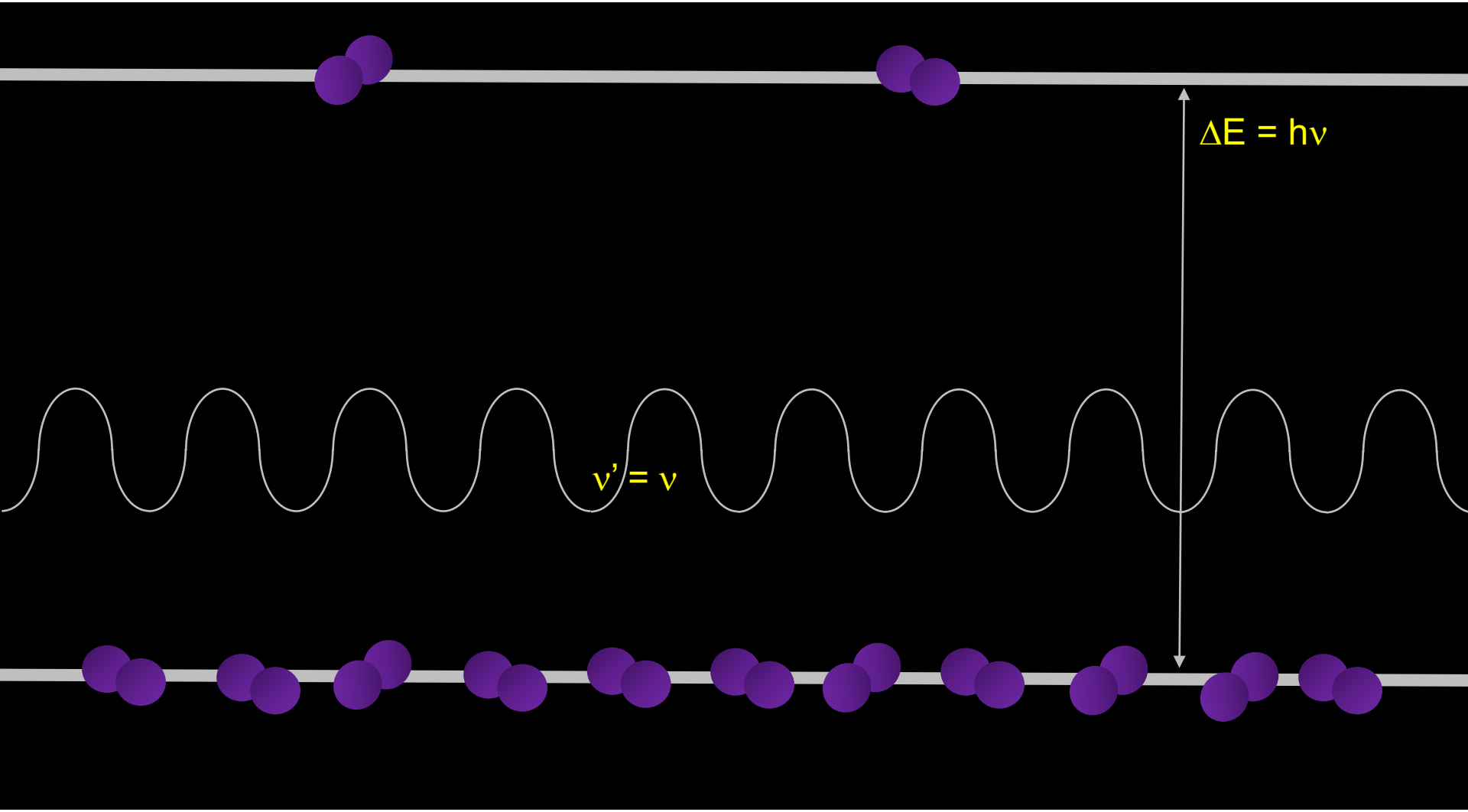
Atom/molecule: Two Level System

Emission



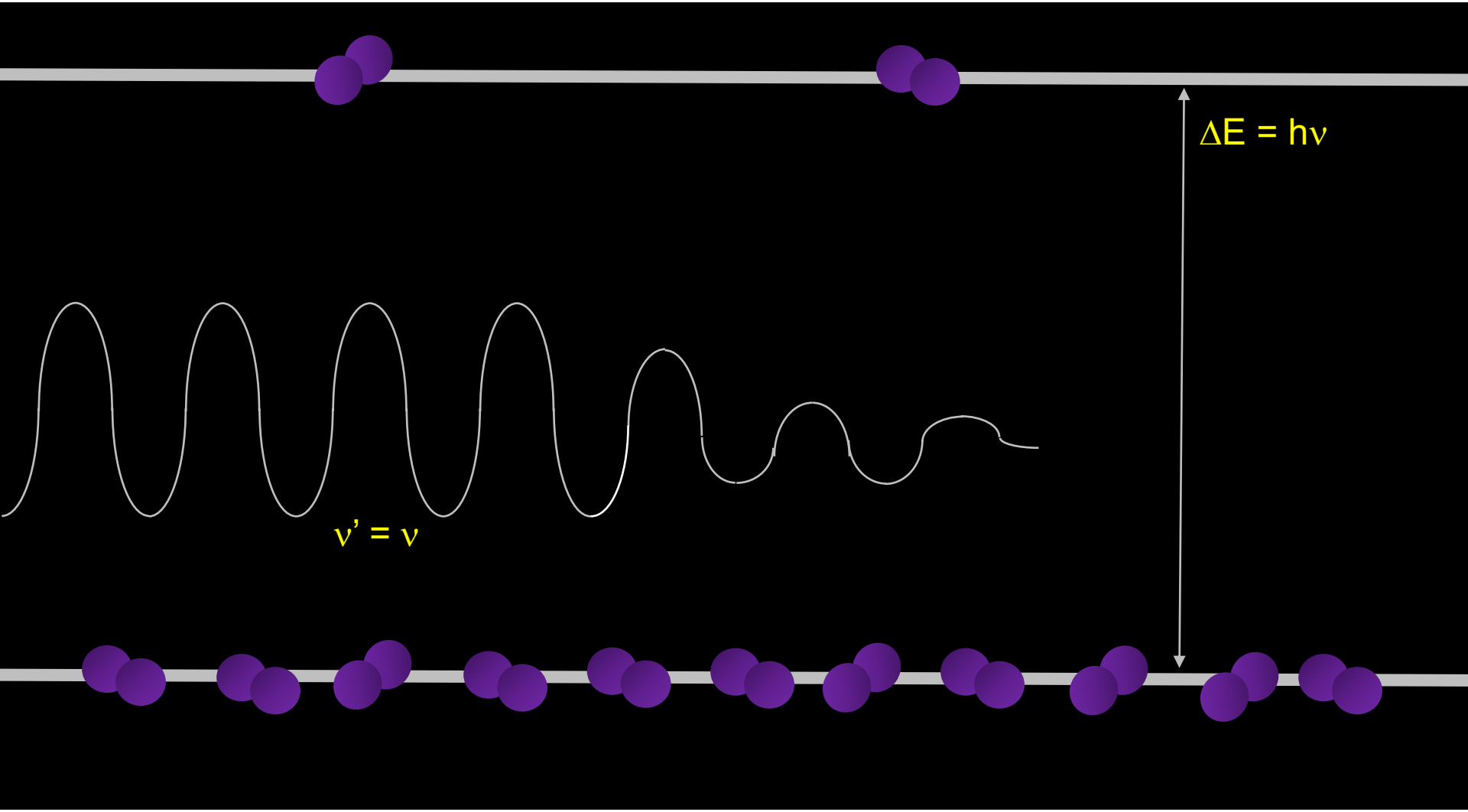
Atom/molecule: Two Level System

Saturated absorption



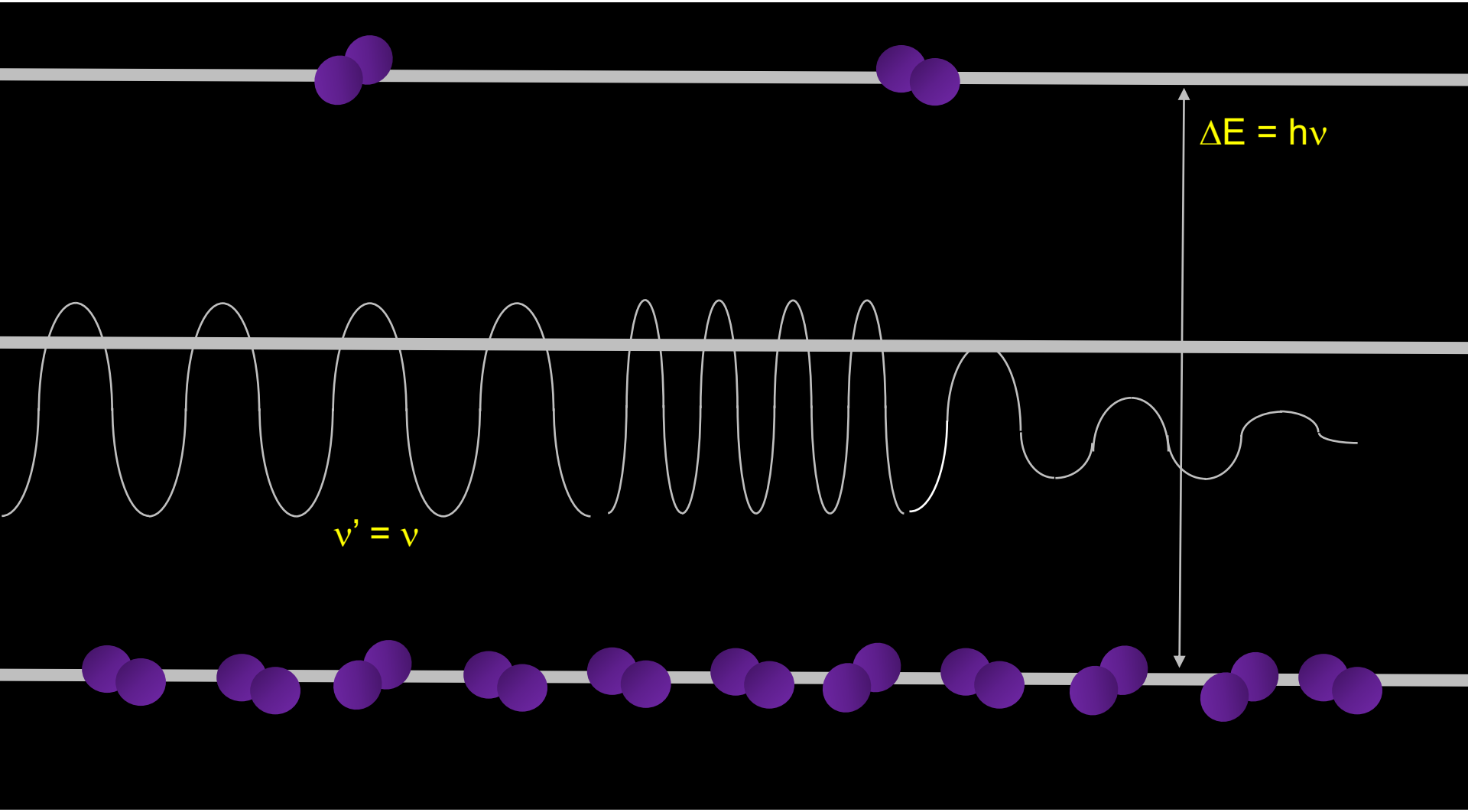
Atom/molecule: Two Level System

Saturated absorption, Spontaneous Emission



Atom/molecule: Three Level System

Saturated absorption, Driven Population Spontaneous Emission

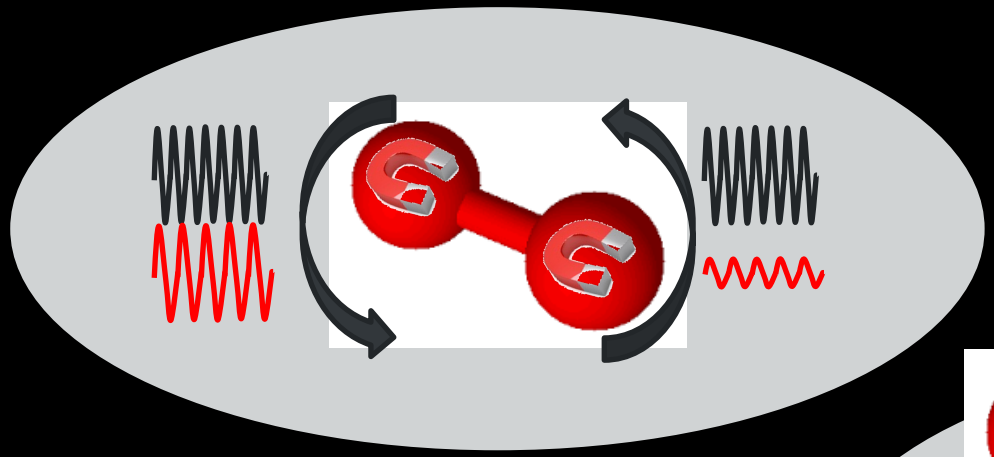


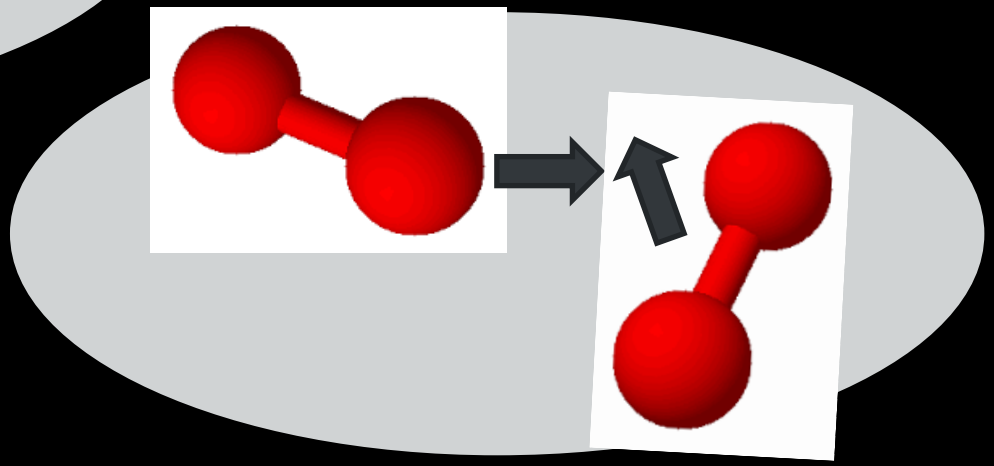
High Resolution Spectroscopy

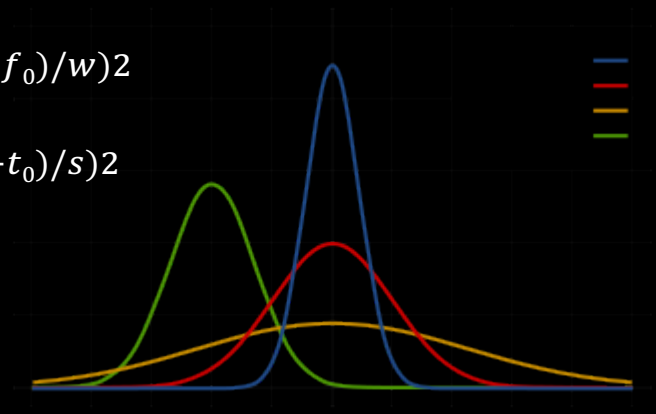
Gas-phase Lineshapes background

$$\frac{Iw}{(f-f_0)^2-w^2}$$

$$He^{-(t-t_0)/s}$$





$$Ie^{-((f-f_0)/w)2}$$

$$He^{-((t-t_0)/s)2}$$