Submillimeter (THz) / Infrared Double Resonance: Regimes for molecular sensors

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Sensors for Broad Spectral Signatures

• **Broad spectral domain**: Atmospheric remote sensing and sensors for large molecules

• SubMM (THz) spectroscopy has absolute specificity at low pressures due to highly resolved rotational lines - great technique for sensing at low pressures for smaller molecules.

• Both of these scenarios share the challenge of spectral features that are broad resulting loss of sensitivity and specificity
  - Sensitivity: signature hard to separate from systematic effects
  - Specificity: fewer resolvable resolution elements

**Solution and strategy:**

Previous talk discussed one approach: Medium Resolution Cavity spectroscopy

In this talk we outline the second approach: **IR-THz Double resonance spectroscopy**
Double resonance spectroscopy Technique

Experimental setup

1. Choose suitable IR pump laser – absorption line coincidence
2. Monitor modulation of the linked rotational transitions (at THz frequencies) initiated by the IR pump laser
3. Establish a 3D specificity matrix (IR pump, THz probe, Time constant of the DR trace) with as many points as possible
   • to increase specificity for a particular molecule
   • dilutes spectroscopic signature in large molecules

Example $^{12}$CH$_3$F

Spectral and temporal features
Optimum regime for atmospheric pressure DR sensor

- The collisional relaxation rate at atmospheric pressure is ~ 100ps
- Saturate (or come as close as you can) in 100 ps
- Probe the directly pumped transitions before collisions equilibrate states
- => Linewidths of 10 GHz

CH$_3$F

V3=1
J12,K2

Probe frequencies

9P20 CO2 line, 100ps pulse

- 654.582 GHz
- 604.297 GHz
- 663.365 GHz
- 612.409 GHz
Experimental setup

CO₂ Hot Cell
OFID

~ 100ps

TEA CO₂ laser

Spectrometer

50ns
30 Hz
0.15 J

High speed
IR detector

THz source

Sample cell

DR signal

THz Heterodyne Receiver

6 GHz, 40 GS/s
Digitizing Oscilloscope

Fast Data acquisition system

100 ps pump laser system

Fast Data acquisition system

6 GHz, 40 GS/s
Digitizing Oscilloscope

DR signal

THz Heterodyne Receiver

100 ps pump laser system

Fast Data acquisition system
100 ps laser pulse generation: Optical free induction decay (OFID)

**Time domain**

- 100 ns
- ~10 ps
- 30 to 200 ps

**Spectral domain**

- 70 MHz
- ~100 GHz
- ~70 MHz

Diagram:
- Hybrid CO$_2$ Laser → Plasma Shutter → OFID Filter
100 ps Laser system – operational

TEA Laser (Source)  
Plasma shutter (Fast Switch)  
OFID filter

TEA Laser output  
50 ns HWHM

Plasma Switch output  
25 ns HWHM, ~ 10-20 ps falling edge

CO₂ Hot cell output  
< 100 ps HWHM
**Experimental Results – Phase 1 (nano-second pulse excitation)**

**Experiment Parameters**

- **Sample**: $^{12}$CH$_3$F (1 Torr of Gas)
- **Pressure range**: 1 - 760 T (air)  
  At 1 Torr there is 1 collision every 100 ns
- **Pump**: 9P20 Laser excitation (30 Hz rep rate, 600 mW Avg power)
- **Probe**: 654.582 GHz ($V_3=1$, J12,K2, Q branch)
- **Cell**: 1. 10 cm wide, 120 cm long cylindrical cell  
  2. 2mm x 4mm , 30 cm long rectangular waveguide cell
- **Oscilloscope**: 6 GHz Analog BW, 50 Ohm DC coupled, 5 GS/s Sampling rate

Rotational transition being monitored
Pump Laser pulse temporal shape: Nature of Double Resonance signature

TEA CO₂ Complex laser pulse structure

Corresponding Double resonance signature

% THz Probe power modulated by the laser

60% modulation

Shows pump saturation
Pump Saturation and the Rabi Frequency

Pump power: 600 mW Avg (~ 0.4 MW Peak power)
Cell diameter: 10 cm
Rabi Frequency: 1.2 GHz
Sample pressure: 20 mT

- Since the Rabi Frequency exceeds the collision rate at 20 mT, the pump will be broadened and neighboring K states are also pumped to saturation
- K = 0, 1, 2, 3, 4 are within the pump range
- K = 0 is not pumped because it has zero dipole matrix element for the transition and is a forbidden transition for Q branch

654.582 GHz (V₃=1, J12, K2, Q branch)
Pressure Dependence of Double Resonance Signal

- Pressure Dependence of Double Resonance Signal
- DR Signal at Atmospheric Pressure (1T of $^{12}\text{CH}_3\text{F}$ in 760 T Atmosphere)
- Graphs showing time (us) vs. pressure and time (us) vs. current (μA), with different pressures indicated (1T, 2T, 3T, 4T, 5T, 10T)
- Graphs demonstrating the variation of DR signal amplitude (V) with time (us) at atmospheric pressure
Pressure Dependence of Double resonance signature

Experimental Results

Small signal gain simulation
1. $J$ and $K$ levels relax within 1 - few gas kinetic collisions

2. Vibrational relaxation takes ~10000 collisions

3. We want to operate in a timeframe before the pumped $J$ levels relax,
   - At 1 T, before 100 ns
   - At 760 T, before 100 ps
DR Signal Amplitude (1 collision limit) degradation with pressure

At 1 Torr when Collision rate (~100 ns) is matched By the pump pulse width (100 ns) we see a very strong DR signal (500 times stronger) in the first few ns of the DR trace => when we move to 100 ps pump pulse at 760 T we should see a similar enhancement
Very high Sensitivity

Detection of 20 mT CH₃F in 760 T of atmospheric air

With 50 ns IR pump
Signal : noise = 10:1
Dilution = 20 mT in 760 T
Path length = ~ 1 feet

Extending the result to 100 m (300 ft) path
the sensitivity can be estimated to be:
(0.02/760)*(1/10)*(1/300) = 8.6 ppb

Sensitivity estimate: 8.6 ppb
IR –THz Double resonance Technique : Issues

• As outlined and demonstrated, this technique is very attractive and effective for application as sensors in broad spectral domain

• This technique has an issue: Spectral Sparcity of the Pump laser

• The TEA CO₂ laser provides discrete excitation frequencies, which limits its applicability to different molecules
Solution: Quantum Cascade Laser as the IR pump source

Example: $^{12}\text{CH}_3\text{F}$

TEA laser - Only one coincidence

QCL > 30 IR lines accessible
QCL Double Resonance at low pressure– Chirped Excitation

- **Sample**: $^{12}\text{CH}_3\text{F}$
- **IR Pump**: 1022 cm$^{-1}$ (9.78 μm)
  - Current modulation (10 KHz, 6 Vpp)
  - IR Pump Sweep Bandwidth: 1 GHz
  - Power: 10 mW

- **THz Probe**: CW @ 654.64 GHz (K=0)
- **Sample Cell**: Waveguide sample cell
  - Cross section: 5 mm by 3 mm
  - Length: 30 cm

V$^3$=1 Rotational THz spectrum
Experimental details:
1. QCL is swept $1022.6 \pm 0.05$ cm$^{-1}$ at 1 kHz repetition rate (bottom trace) to provide the pump pulse and overlap the J=12 vibrational transition.

2. THz system is consecutively tuned to detect $K=0$, $1$, $2$ rotational transitions of $v_3=1$ vibrational state.

3. THz signal enhancement induced by the IR pump is observed at appropriate time offsets from the beginning of the IR chirp.
Sensitivity Enhancement: Sample Cells with Smaller Cross Section

The absorption strength of the GS lines (~50%) suggests that if we fully saturated the IR transitions the expected gain in $v_3=1$ signal would be ~25%. The observed 4% gain is a factor 6 below optimal.

Reduction of cell size (ongoing) would raise Rabi frequency by a factor of 4, which would bring us closer to the optimum performance.
Summary

- IR –THz double resonance spectroscopy is an attractive technique for spectroscopy of scenarios where we encounter broad spectral features.

- 100 ns pump data looks very promising.

- **Part per billion** sensitivity demonstrated

- **100 ps pump laser is operational** and hence ps regime experiment is very close.

- Issue of spectral sparcity for the pump laser has been addressed by incorporating a QCL as a tunable chirped pulse IR pump and demonstrating that the technique works.
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