High-precision mid-infrared spectroscopy with a widely tuneable SI-traceable optical-frequency-comb-stabilised QCL

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Outline

• Motivation: precise spectroscopic measurements with molecules
• QCL stabilization allowing wide tuneability
• High-precision spectroscopic measurements
• Summary / Perspectives
# Precision measurements with molecules

- Complementary to measurements in atoms for *precision tests of fundamental physics*:

| Measure constants | \( \frac{m_e}{m_p} \) (Schiller, Hilico, Ubachs – HD\(^{+}\), H\(_2\)\(^{+}\))
|                  | \( k_B \) (Gianfrani, \( H_2^{18}O \), CO\(_2\) - LPL, NH\(_3\)),... |
| Measure their variations in time | \( \alpha \) (Ye, OH) - \( \frac{m_e}{m_p} \) (Truppe/Hinds/Tarbutt, CH - Bethlehem, NH\(_3\) - LPL, SF\(_6\)) |
| Test fundamental symmetries | Parity & time-reversal symmetry (eEDM): Hinds (YbF), Cornell/Ye (HfH\(^{+}\)), DeMille/Doyle/Gabrielse (ThO)
|                           | Parity symmetry: DeMille (BaF), LPL (chiral species),... |
| QED tests, 5\(^{th}\) force | W. Ubachs (\( H_2, HD^{+}\)),... |
| Test the symmetrization postulate | Tino,... (\( O_3, CO_2, NH_3\),... |

- Many are based on *high-resolution spectroscopy*, often in the *mid-infrared* domain

- Frequency references for frequency metrology
  provide an almost continuous set of references throughout the MW, THz, IR, visible, UV

- Precision spectroscopy of polyatomic molecules for *physical chemistry* studies:
  atmospheric physics, astrophysics, collision physics, chemical dynamics and reaction, trace gas detection, breath analysis...
Precision measurements with molecules

- Need efficient mid-IR laser sources of well-controlled frequency

- Mid-IR quantum cascade lasers (QCLs) are promising
  - \(\text{cw, mW to W power levels}\)
  - \(3\text{-}25\ \mu\text{m range}\)
  - \(\text{tuneability } \sim 100\ \text{GHz or more}\)
  - \(\times\) free-running line width 10 kHz to few MHz → frequency stabilization needed

- Several frequency stabilization schemes developed in the last years
  → stable cavities, molecular lines, injection, combs,…

- **Challenges:**
  - most stable reference → near-IR ultra-stable lasers
  - traceability to a primary standard

→ ultra-stable optical fiber links
→ frequency comb to bridge the gap between near-IR and mid-IR
SI-traceable frequency-comb-stabilised QCL

- National metrology institute
- Ultrastable 1.54 µm laser
- Ultra-stable cavity
- Accuracy
- 43 km optical fibre link
- Spatial transfer
- Fibre phase-noise correction
- Spectral transfer
- Frequency comb
- High-resolution spectroscopy

\[ \nu_{QCL} = \frac{n}{N} (\nu_{\text{ref}} + \Delta_1) + \Delta_2 \]

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see also: Insero et al., *Sci. Rep.* (2017)
Optical fibre link for ultra-stable frequency transfer

- correction of the propagation noise
- added noise (transfer instability)
  - a few $10^{-16}$ after 1 s
  - $\sim 10^{-19}$ after $\sim$ a day
- frequency inaccuracy $< 10^{-19}$

Fractional frequency stability vs. Integration time, s

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QCL stabilization to a near-IR frequency reference

- Ultrastable 1.54 μm laser
- 43 km fibre

- Microwave electro-optic modulator tuneable from 8 to 18 GHz
- Home-made 8-18 GHz synthesizer:
  - → YIG oscillator
  - → phase-jump free
  - → phase-locked to a DDS

\[ \nu_{\text{ref}} \approx 1.54 \mu m \]

- PLL
- PD
- EOM
- \( \nu_{\text{LO}} \)
- 8-18 GHz

Tuneable source phase-locked to \( \nu_{\text{ref}} \)
QCL stabilization to a near-IR frequency reference

- ultrastable 1.54 µm laser
- 43 km fibre

$\nu_{\text{ref}} \approx 1.54 \mu m$

- laser diode
- EOM
- PLL
- PD
- 8-18 GHz

- optical frequency comb:
  - 2 outputs
  - both stabilized
  - tuneable
QCL stabilization to a near-IR frequency reference

- ultrastable 1.54 µm laser
- 43 km fibre
- sum frequency generation:
  \[ \Delta = (p-q) f_{\text{rep}} - v_{\text{QCL}} \]
- direct link from near-IR and mid-IR
- QCL tuneable over ~1.5 GHz

\[ v_{\text{ref}} \approx 1.54 \mu m \]

\[ \nu_{\text{QCL}} = 10.3 \mu m \]

\[ q f_{\text{rep}} + f_0 \]

\[ p f_{\text{rep}} + f_0 \]

\[ q f_{\text{rep}} + f_0 + v_{\text{QCL}} \]
Performances of the stabilized QCL


- ultimate QCL stabilities (0.06 Hz @ 1s) and accuracies (sub-Hz, 10 mHz potentially)
- narrowest QCL so far (0.1 Hz)

⇒ ‘atomic physics’ types of precision measurements on molecules
Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

saturated absorption spectroscopy
in a multi-pass cell or a Fabry-Perot cavity

20 cm

Multipass cell (Aerodyne)
182 paths – 36.4 m

0.1 to 10 Pa

Gas inlet
Gas outlet

G1
G2

BS3
M
pump

Probe

L2
L1

BS1

200 finesse, 1.5-m long cavity

PD

Lock-in Amplifier
Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

saturated absorption spectroscopy

OsO$_4$ around 29 THz

- ~25 kHz linewidth
- a few 10 Hz uncertainty
- state-of-the-art

in a 1.5-m long Fabry-Perot cavity

frequency modulation, 3$^{}\text{rd}$ harmonic

Methanol, P(E,co,0,2,32) line, C-O stretch

- ~400 kHz linewidth
- a few kHz uncertainty
- $10^2$-$10^4$ improvement compared to literature / HITRAN database

in a multipass cell

frequency modulation, 1$^{\text{st}}$ harmonic
Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

pressure broadening: 100.8 (0.2) kHz/Pa
Ultra-precise spectroscopy with quantum cascade lasers: record frequency uncertainties

<table>
<thead>
<tr>
<th>Systematics</th>
<th>Correction (kHz)</th>
<th>Uncertainty (kHz)</th>
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<td>line fitting</td>
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<td><strong>Total</strong></td>
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</tbody>
</table>

→ 7.4 kHz global uncertainty

~2000 improvement over previous measurements

Santagata et al, Optica (2019)
Ultra-precise spectroscopy with QCLs: spectral coverage/tuneability

\[ \sim 100 \text{ GHz covered, } \sim \text{full QCL's tuneability} \]

HITRAN simul

\[ P(E,co,0,2,33) \]


\[ \sim 400 \text{ MHz, continuous tuning range (EOM)} \]
Summary / Perspectives

• Precise and tuneable frequency control of a mid-IR QCL referenced to a comb
  → stability and accuracy transfer from 1.54 µm to 10 µm
  → direct link to primary frequency standards
  → record stabilities/accuracies:
    - 0.05 Hz ($2 \times 10^{-15}$) satbility @ 1 s
    - 0.1 Hz line width
    - 0.3 Hz ($10^{-14}$) accuracy, potentially 0.01 Hz ($3 \times 10^{-16}$)
  → anywhere in 5-20 µm region potentially, 1.5 GHz continuous tuning

• Saturated absorption spectroscopy of OsO$_4$, CH$_3$OH
  → uncertainty on central frequency from a few 10 Hz to a few kHz
  → unprecedented resolution: new lines and subtle patterns unreported so far

Allows the level of near-IR ultra-stable lasers to be transferred to the mid-IR
  ⇒ ‘atomic physics’ types of precision measurements on molecules
  ⇒ study of any species showing absorption between 3 and 25 µm

no longer constrained by CO$_2$ laser or any molecular reference
Summary / Perspectives

- Precise spectroscopic measurements of a variety of species
- Integration in a new generation molecular clock under construction

- Study of hyperfine structure of methanol
- me/mp time variation using CH$_3$OH or NH$_3$
- Measure the energy difference between the two enantiomers of a chiral molecule induced by the parity violation inherent in the weak interaction
