Spectroscopy of polyatomic molecules cooled by collisions with a buffer gas in a cryogenic cell

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## Precision measurements with molecules

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

<table>
<thead>
<tr>
<th>Measure</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{m_e}{m_p} ) (Schiller, Hilico/Karr, Ubachs, Koelemeij – HD(^{(+)}), ( \text{H}_2 )^{(+)})</td>
<td></td>
</tr>
<tr>
<td>( k_B ) (Gianfrani, ( \text{H}_2^{18})O, ( \text{CO}_2 ), ( \text{C}_2\text{H}_2 ) - LPL, ( \text{NH}_3 ))...</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measure</th>
<th>Their variations in time</th>
</tr>
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<tbody>
<tr>
<td>( \alpha ) (J. Ye, OH) - ( \frac{m_e}{m_p} ) (Hinds/Tarbutt, CH - Inouye, KRb - LPL, SF(_6))</td>
<td></td>
</tr>
</tbody>
</table>

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<tr>
<th>Test</th>
<th>Fundamental symmetries</th>
</tr>
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<tbody>
<tr>
<td>Parity &amp; time-reversal symmetry (eEDM): Hinds/Tarbutt (YbF), Cornell/Ye (( \text{HfH}^+ )), DeMille/Doyle/Gabrielse (ThO)</td>
<td></td>
</tr>
<tr>
<td>Parity symmetry: D. DeMille (BaF), Budker, Patterson &amp; LPL (chiral species)</td>
<td></td>
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</tbody>
</table>

| QED tests, 5\(^{th}\) force | Schiller, Hilico/Karr, Ubachs, Koelemeij – HD\(^{(+)}\), \( \text{H}_2 \)^{(+)} |

| Test the symmetrization postulate | Tino, De Natale,... (\( \text{O}_3 \), \( \text{CO}_2 \), \( \text{NH}_3 \),...) |

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

→ Require **advanced manipulation techniques** (already demonstrated in atomic physics):

- **control/cool** internal & external degrees of freedom
- Individual internal **states addressability**
- State-selective high **detection-sensitivity** and -rate
- Long **coherence times**
- Chemical stability...
Cold polyatomic molecules for fundamental physics...

Precision measurement of time-reversal symmetry violation with laser-cooled polyatomic molecules
Kozyryev & Hutzler, Phys Rev Lett (2017)

A stringent limit on a drifting proton-to-electron mass ratio from alcohol in the early universe
Bagdonaitė et al., Science (2013)

Tests of fundamental physics

Electron EDM

A new experiment to test the parity symmetry in cold chiral molecules using vibrational spectroscopy
Cournoël et al., Quantum Electron. (2019)

Drifting constants

Parity violation (PV)
Cold polyatomic molecules for fundamental physics...

Tests of fundamental physics

Drifting constants

Parity violation (PV)

Electron EDM

A new experiment to test the parity symmetry in cold chiral molecules using vibrational spectroscopy

Cournolet al, Quantum Electron. (2019)

M: Ru, Ir, Os

Δν_{PV} = |ν_L - ν_R| \neq 0 mHz to Hz
Buffer-gas cooling to $\sim K$

molecules of interest

1) Capillary loading
2) Beam loading
3) Laser ablation
4) Matrix-assisted desorption
5) Laser-induced acoustic desorption

well suited to solid state species
Buffer-gas cooling to ~K

Spectroscopy in the cell
narrower lines
stronger signals
simplified spectra

Buffer-gas-cooled molecular beams
collision-free
high flux (supersonic x 10) → more signal
low velocity (supersonic / 10) → better resolution
most intense cold molecular beam to date for diatomics and light radicals

extend to new complex polyatomic species

Internationally advocated for precision measurements:
D. DeMille, De Natale, J. Doyle, M Tarbutt, D Patterson, G. Rempe, J. Ye,...
(crucial precursor step to laser cooling or trapping)
Buffer-gas cooling of MTO

Collaboration with Mike Tarbutt at Imperial College
we’ve taken one of our QCL to London
tests in one of their cryogenic chamber

MTO: methyltrioxorhenium

→ precursor of chiral candidate species for a PV test
→ ideal achiral test molecule
Buffer-gas cooling of MTO

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MTO:
methyltrioxorhenium

→ precursor of chiral candidate species for a PV test
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Buffer-gas cooling of MTO

Ablation laser, YAG

QCL beam for spectroscopy

He inlet

MTO target

After one ablation pulse

MTO spectrum

Antisymmetric Re=O stretching Q branch

Antisymmetric Re=O stretch of MTO

- 1st organo-metallic species buffer-gas-cooled
- survives laser ablation
- $T_{\text{rot}} = 6 \pm 3 \text{ K}$

8 MHz resolution (combination of frequency noise, Doppler and collisions)
A novel spectroscopic tool in itself

Rotation and hyperfine-resolved spectroscopy

~8 MHz resolution, ~30 MHz accuracy → already allows for precision measurements:
Examples of $^3P(J,K)$ rovibrational transition of the $^{187}$Re=O antisymmetric stretching mode

**hyperfine structure partially resolved**

→ fit to a symmetric top hyperfine hamiltonian
→ hyperfine parameters in the $v = 1$ excited state

quadrupole coupling constant: $eQq^{\text{exc}} = 716$ (3) MHz
$\Delta eQq \ll 1$ → little variation with vibration

→ unprecedented for such a complex molecule

Buffer-gas cooling of trioxane

potential sources of formaldehyde in cometary comae → relevant prebiotic chemistry

solid at room temperature, with high vapour pressure (4 mbar) → can be loaded directly into the cell toward beam production

\[
(\text{CH}_2\text{O})_3 \rightarrow 12 \text{ atoms}
\]

\[
\nu_5 \text{ vibrational mode around } 977 \text{ cm}^{-1} \rightarrow \text{ probed using the QCL}
\]
1,3,5-trioxane: Q branch of the $\nu_5$ band

$\Delta J = 0$
$\Delta K = 0$

Linear absorption spectroscopy
- frequency modulation, harmonic 1
- $T < 15$ K
- 7.5 MHz resolution (combination of frequency noise, Doppler and collisions)
1,3,5-trioxane: Q branch of the $\nu_5$ band

**Saturated absorption spectroscopy**
- first time in the fingerprint mid-infrared region
- Sub-Doppler resolution (<1MHz) in buffer-gas cell

largest species for which saturated abs. spectroscopy has been demonstrated
3rd generation setup under construction at LPL

- Cryocooler
- 40 K shield
- TO BE INTEGRATED (already designed and machined)
  - Cryogenic cell
  - He inlet
  - 4 K shield (AVAILABLE)
Outlook

Buffer-gas cooling of **chiral species** of interest for a **PV test**:

- **Ru**: $\Delta v_{PV} \sim 100 \text{ mHz } (10^{-15})$
- **Os**: $\Delta v_{PV} \sim 1 \text{ Hz } (10^{-14})$

- intense C-O stretch @ 6.5 $\mu$m

Buffer-gas cooling of new polyatomic species of **atmospheric/astrophysical interest**:

Polyaromatic hydrocarbons (PAHs) and related species

*Fiechter et al, arXiv (2021)*

Demonstration of **buffer-gas-cooled molecular beams**

Doppler spectroscopy with free-running QCLs
Precise spectroscopic measurements:

⇒ using the **sub-Hz metrology-grade QCLs** available in the lab

10 µm, 6.4 µm, 17 µm...

⇒ **sub-Doppler** spectroscopy in a **cold cell** or in a **beam**

⇒ **10^{-10} - 10^{-12} uncertainty** (100 Hz - 10 kHz) on vibrational frequencies

⇒ enriching **molecular databases**

• Build **Ramsey interferometry** machine for reaching record **10^{-15} (sub-Hz)** vibrational frequency uncertainties ⇒ **tests of fundamental physics**

People involved

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Imperial College London
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M.R. Tarbutt

former membres
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R. Hendricks (postdoc)
T. Wall (postdoc)

Sponsors