Instrumental developments for measuring parity violation in cold chiral molecules using vibrational spectroscopy


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Precision measurements with molecules

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

| Measure constants | $m_e/m_p$ (Schiller, Hilico/Karr, Ubachs, Koelemeij – HD$^+$, H$_2^+$)  
|                   | $k_B$ (Gianfrani, H$_2^{18}$O, CO$_2$, C$_2$H$_2$ - LPL, NH$_3$),... |
| Measure their variations in time | $\alpha$ (J. Ye, OH) - $m_e/m_p$ (De Natale, Maddaloni, CF$_3$H - Bethlem, NH$_3$ - LPL, SF$_6$) |
| Test fundamental symmetries | parity & time-reversal symmetry (eEDM): Hinds (YbF), Cornell/Ye (HfH$^+$), DeMille/Doyle/Gabrielse (ThO)  
|                            | parity symmetry: D. DeMille (BaF), LPL (chiral species),... |
| QED tests, 5$^{th}$ force | W. Ubachs (H$_2$, HD$^+$),... |
| Test the symmetrization postulate | Tino, De Natale,... (O$_3$, CO$_2$, 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 and cooling of internal and external degrees of freedom
- individual hyperfine states addressability
- state-selective high detection-sensitivity and -rate
- high-resolution spectroscopy
- long coherence times
- chemical stability
Parity, a broken symmetry

the weak nuclear force violates parity

- predicted by Lee and Yang (1956)
- observed in nuclear and high-energy physics
- observed in atoms (Bouchiat, 1982; Wieman, 1997) - effect $\propto Z^3$

never observed in chiral molecules

- probe the Standard Model and physics beyond it in the low-energy regime
  - enhanced effects $\propto Z^5$
  - nuclear-spin dependent contributions, anapole moments, isotopic effects and neutron skin,...
- link to biomolecular homochirality
- evaluate relativistic quantum chemistry
- advanced manipulation techniques for polyatomic species

predicted in 1974
Parity violation in chiral molecules

several proposed experimental methods

• Lethokov’s proposal (1975): vibrational spectroscopy (~30 THz)

The attempts so far

<table>
<thead>
<tr>
<th>molecule</th>
<th>experimental sensitivity</th>
<th>$\Delta \nu_{PV}^{calc} / \nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>camphor</td>
<td>$10^{-8}$ (Oka, 1977)</td>
<td>$3 \times 10^{-19}$ (Schwerdtfeger, 2004)</td>
</tr>
<tr>
<td>CHFClBr</td>
<td>$2.5 \times 10^{-13}$ (Chardonnet, 2002)</td>
<td>$8 \times 10^{-17}$ (Schwerdtfeger, 2005)</td>
</tr>
</tbody>
</table>

→ produce samples of ‘better’ molecules
→ build a more sensitive machine
PV in chiral molecules: our strategy

Molecules with measurable PV:

- Rhenium, $Z_{Re} = 75$

- $100$ to $1000 \times$ bigger PV effect ($10^{-14}$ - $10^{-13}$) for rhenium complexes

- Synthesized but in solid form

PV in chiral molecules: our strategy

Molecules with measurable PV:

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Challenges when working with such complicated molecules:

1. solids $\rightarrow$ difficulty making intense sources in the gas phase (beams)
2. state-of-the-art CO$_2$ lasers typically used are not tuneable enough
3. direct detection of mid-IR laser absorption is not sensitive enough
A novel more sensitive machine

Develop an experiment comprising:

1: buffer-gas-cooled molecular beam
cold, slow, intense

2: quantum cascade laser (QCL) based Ramsey interferometer ⇔ primary frequency standardsremarkable tuneability and spectral purity

3: microwave (MW) detection and manipulation
high sensitivity, state- and enantiomer-selectivity

Frequency metrology approach:

- molecular beam Ramsey interferometry
- more than 100 × better expected sensitivity: < 10^{-15}
Buffer-gas-cooled molecular beam

**technique adapted to solid state species**

- cold (4K)
- high flux \((\text{supersonic} \times 10)\)
- low velocity \((\text{supersonic} \div 10)\)

→ increase in resolution

...extend to new complex chiral species

Internationally advocated for precision measurements: J. Doyle (Harvard), D. DeMille (Yale), Ed Hinds (Imperial College), De Natale (LENS), G. Rempe (MPQ), J. Ye (JILA),...
Buffer-gas cooling of MTO

- collaboration with M. Tarbutt and Ed Hinds at Imperial College
- we’ve taken a QCL to London
- tests in one of their cryogenic chamber

- **MTO**: methyltrioxorhenium achiral parent of chiral candidate species
- 1\textsuperscript{st} organo-metallic species buffer-gas-cooled
- survives laser ablation!
- $T_{\text{rot}} = 6 \pm 3$ K
- very promising for buffer-gas beams production

Buffer-gas cooling polyatomic species

Precise spectroscopic measurements already possible

**MTO**

\[
\text{CH}_3\text{ReO}_4
\]

**Trioxane**

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

**Saturated absorption spectroscopy in a buffer-gas cell**

→ 1st time in the *fingerprint* mid-IR region

→ highest resolution ever in a buffer-gas cell

**hyperfine structure partially resolved in isolated rovibrational transitions**

→ hyperfine parameters in the \(v=1\) excited state

\[eQq^{\text{exc}} = 716 (3) \text{ MHz}\]

→ unprecedented for such a complex species


QCL stabilization to a near-IR frequency reference

- Primary atomic clocks
  - Stability
  - Accuracy
  - Accuracy
    - $\sim 10^{-15}$ at 1 s
  - Ultrasable cavity
  - Accuracy
  - Optical fibre link
    - $\nu_{\text{ref}} \sim 1.54 \mu m$
  - Spatial transfer
  - Fibre phase-noise correction
  - Spectral transfer
  - Optical frequency comb
  - QCL

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

- Ultimate QCL stabilities (0.06 Hz) and accuracies (sub-Hz)
- Narrowest QCLs laser so far (0.2 Hz)

M Abgrall, Y Le Coq, R Le Targat, H Álvarez Martinez, W-K Lee, D Xu, P-E Pottie

Ultra-precise spectroscopy with QCLs: record frequency uncertainties

OsO$_4$ saturated absorption spectrum around 29 THz

\[ \nu_{\text{OsO}_4/R(14)} \]

\[ -0.10 \rightarrow -0.05 \rightarrow 0.00 \rightarrow 0.05 \rightarrow 0.10 \]

\[ 200 \text{ kHz} \]

\[ 5 \text{ MHz} \]

\~200 finesse 1.5-m long Fabry-Perot cavity

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

Methanol saturated absorption spectrum

\[ P(E_1,co,0,2,32) \text{ line, C-O stretch} \]

in a multipass cell

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

near-IR metrological level transferred to the mid-IR ⇒ ‘atomic physics’ types of precise measurements on molecules
QCL stabilization to a near-IR frequency reference

- **ultrastable 1.54 µm laser**
- 43 km fibre
- \( v_{\text{ref}} \approx 1.54 \mu m \)
- \( f_0 \)
- 1.82 µm
- 1.55 µm
- \( v_{\text{QCL}} \)
- 10.3 µm
- AgGaSe₂
- PLL
- Δ
- PD
- EOM
- 8-18 GHz
- laser diode
- \( v_{\text{LO}} \)
QCL stabilization to a near-IR frequency reference

- Ultrastable 1.54 μm laser
- 43 km fibre
- Microwave electro-optic modulator
  - Tunable from 8 to 18 GHz
- Home-made 8-18 GHz synthesizer:
  - $\rightarrow$ YIG oscillator
  - $\rightarrow$ Phase-jump free
  - $\rightarrow$ Phase-locked to a DDS

\[ v_{\text{ref}} \approx 1.54 \text{ μm} \]

Carrier

8-18 GHz 8-18 GHz

PLL

EOM

PD

Tunable source phase-locked to $v_{\text{ref}}$
Ultra-precise spect. with QCLs: spectral coverage/tuneability/resolution

~100 GHz covered, ~full QCL’s tuneability

~400 MHz, continuous tuning range (EOM)
Summary / Perspectives

• Development of a molecular beam setup for Ramsey interferometry of chiral species

• Molecule considered: organo-metallic species in the solid phase

• Buffer-gas-cooling of MTO/trioxane

• QCL based spectrometers with record stabilities and accuracies

- New techniques for measuring and controlling complex molecules
- Of interest to a wide community → testing physics with cold molecules, low temperature chemistry, spectroscopy, gas mixture analysis,…

• Perspectives: build the Ramsey interferometry machine,
⇒ buffer-gas-cooled beam, improve detection sensitivity using microwave detection (under progress), spectroscopy of chiral derivatives of MTO, the increase wavelength coverage, spectroscopy of other candidates, enantiomer-selective detection…
Former members: Clara Stoeffler, Bruno Chanteau
Visitors: Andrei Goncharov, Alexandre Shelkovnikov