Fine structure of metastable $^4\text{He}_2$ using Zeeman-decelerated molecular-beam resonance spectroscopy

L. Semeria, P. Jansen, J. A. Agner, H. Schmutz and F. Merkt

Laboratory of Physical Chemistry
ETH Zurich, Switzerland
Introduction

Metastable $^4\text{He}_2$ in the $a^3\Sigma^+_u$ state ($\text{He}_2^*$) is a four-electron molecule and its properties can be calculated *ab initio* with high accuracy [1].

The **fine-structure** intervals of the $N = 1, 3, 5, 7 - 11$ and $25 - 29$ rotational states of $\text{He}_2^*$ were measured by radio frequency (RF) spectroscopy [2, 3, 4, 5].

**Experimental goals**

- Investigate the **fine structure** of the $a^3\Sigma^+_u$ ($v = 0, 1$) state of $\text{He}_2$ ($\text{He}_2^*$) using magnetic-resonance spectroscopy in a Zeeman-decelerated molecular-beam.
- Improve the resolution by recording **transit-time-limited** RF transitions.

Molecular-beam resonance experiments

Molecular-resonance spectroscopy in a **magnetic field**


Molecular-resonance spectroscopy in an **electric field**


Molecular beam spectrometer and oscillator

![Molecular beam spectrometer and oscillator](image1)

Hyperfine spectrum of the 3,3 inversion line of NH₃

![Hyperfine spectrum of NH₃](image2)
Fine structure of $\text{He}_2^*$

The metastable $a^3\Sigma^+_u$ state of $^4\text{He}_2$

- lifetime of 18 s
- magnetic moment of two Bohr magneton
- rotational and fine structure described by the effective Hamiltonian

$$\hat{H} = B_0 \hat{N}^2 - D_0 \hat{N}^4 + H_0 \hat{N}^6 + \frac{2}{3} \lambda_0 (3 \hat{S}_z^2 - \hat{S}^2) + \gamma_0 \hat{S} \cdot \hat{N}$$

Schlapp's formulas

$$F_1(J = N + 1) \simeq (2N + 3)B_\nu - \lambda_\nu - \sqrt{(2N + 3)^2 B_\nu^2 + \lambda_\nu^2 - 2\lambda_\nu B_\nu + \gamma_\nu (N + 1)}$$

$$F_2(J = N) \simeq 0$$

$$F_3(J = N - 1) \simeq -(2N - 1)B_\nu - \lambda_\nu + \sqrt{(2N - 1)^2 B_\nu^2 + \lambda_\nu^2 - 2\lambda_\nu B_\nu - \gamma_\nu N}$$
He\(^{2}\) and He\(^{3}\) detection

Detection procedure

- \(J = N \pm 1 \rightarrow N\) RF transitions in the \(a 3\Sigma^+_u\) state of He\(^2\)
- Excitation to Rydberg states converging to the \(X^+ 2\Sigma^+_u\) state of He\(^2\)
- Detection of He\(^{3}\) by pulse-field ionization
Experimental setup
Working principle of the Zeeman decelerator

\[ \hat{H}_z = -\frac{g_e \mu_B}{\hbar} \hat{S} \cdot \hat{B} - \frac{g_F \mu_B}{\hbar} \hat{N} \cdot \hat{B} \]

\[ \vec{F} = -\nabla W_z = \vec{\mu}_B \cdot \nabla \vec{B} \]

RF Repopulation

**Undecelerated** (black trace) and **decelerated** (blue trace) Rydberg spectra in the $(0, 1) \rightarrow 49p(0, 1_1)$ region

---

**RF Repopulation procedure**

- The uv-laser frequency is locked in **resonance** with a transition from the $J = N$ fine structure component to a Rydberg state (grey area)
- The Zeeman decelerator is turned on and eliminates the $J = N$ component
- A **RF pulse** is used to repopulate the $J = N$ component from the $J = N \pm 1$ components
Precision Measurements

$0 \rightarrow 1$ transition corresponding to a final velocity of $v_f = 136 \text{ ms}^{-1}$

$\nu_0 = 2199971.47(29) \text{ kHz}$

Residual magnetic field: 10.7 mG
**Transit-time-limited** measurements of $0 \rightarrow 1$ transition

---

- $v_f = 265 \text{ m s}^{-1}$
- $v_f = 136 \text{ m s}^{-1}$

---

**Frequency spectra**

- FWHM = 6 kHz
- FWHM = 3 kHz
Microwave spectra of the $J = N \pm 1 \rightarrow J = N$ ($v = 0$) transitions for $N = 7, 15, 19$ in comparison with the simulation.
Results for the fine-structure constants

- The **spin-spin** and **spin-rotation constants** for the $a^3\Sigma_u^+$ ($v=0,1$) states of $^4\text{He}_2$ have been obtained in a global-fit analysis of all measured transitions

$$\gamma_v(N) = \sum_{k=0}^{2} \gamma_k [N(N + 1)]^k$$

$$\lambda_v(N) = \sum_{k=0}^{3} \lambda_k [N(N + 1)]^k$$

All values are in MHz

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work</th>
<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v = 0$</td>
<td>$v = 1$</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$-2.42224(6)$</td>
<td>$-2.28050(17)$</td>
</tr>
<tr>
<td>$\gamma_1 \cdot 10^4$</td>
<td>$6.856(10)$</td>
<td>$6.507(6)$</td>
</tr>
<tr>
<td>$\gamma_2 \cdot 10^8$</td>
<td>$-6.03(14)$</td>
<td>$-5.34(6)$</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>$-1099.17016(12)$</td>
<td>$-1037.3945(5)$</td>
</tr>
<tr>
<td>$\lambda_1$</td>
<td>$0.19748(5)$</td>
<td>$0.20143(8)$</td>
</tr>
<tr>
<td>$\lambda_2 \cdot 10^6$</td>
<td>$-4.68(24)$</td>
<td>$-4.31(22)$</td>
</tr>
<tr>
<td>$\lambda_3 \cdot 10^9$</td>
<td>$1.35(23)$</td>
<td>$1.67(16)$</td>
</tr>
</tbody>
</table>

$^a$ Fixed
Conclusions

- A Zeeman decelerator was used to produce spin-polarized $\text{He}_2^*$ beams with final velocities down to $v_f = 100 \text{ ms}^{-1}$.

- RF transitions were recorded at a transit-time-limited resolution of 2.8 kHz. Their frequencies were determined with 300 Hz precision.

- The spin-spin and spin-rotation constants for the $a \, ^3\Sigma_u^+$ $(v = 0, 1)$ state of $^4\text{He}_2$ were determined.

- The method is applicable to any paramagnetic species.
Thank you for your attention!

Financial support

- Swiss National Science Foundation
- ERC advanced grant programme
- Supported by SCNAT and SCS through a «Chemistry Travel Award»
By considering the binding energy of a Rydberg state \( B = R_M/(n - \delta_l)^2 \) and the fact that a pulsed electric field causes ionization of Rydberg states located within

\[
\frac{\Delta E_I}{hc \cdot cm^{-1}} = C \sqrt{\frac{\varepsilon}{V/cm}}
\]

it is possible to determine the lowest-\( n \) state that can be resolved.

Typical values for prepulse and extraction field

- \( V_{\text{prepulse}} = -4 \)
- \( V, n_{\text{limit}} \approx 183 \)
- \( V_{\text{prepulse}} = 1500 \text{ V}, n_{\text{limit}} \approx 42 \)
RF transitions are recorded between spin-rotational components of the same \( N'' \) rotational level of the \( a^3\Sigma_u^+ \) state of He\(_2\).
Microwave spectra at $v_f = 300 \text{ m s}^{-1}$

$15 \leftarrow 14 \ (v = 0)$ transition
RF repopulation: \( \Delta t_{RF} = \frac{d_{laser}}{\nu_f} \)

0-\(1\) transitions, uv on \(J''=N''\) of \((0,1)\rightarrow49p(0,1)\)

- \(\Delta t_{RF} = 495 \mu s, d_{laser} = 68 \text{ mm}, P = -22 \text{ dB}_m\)
- \(\Delta t_{RF} = 450 \mu s, d_{laser} = 60.5 \text{ mm}, P = -25 \text{ dB}_m\)
- \(\Delta t_{RF} = 350 \mu s, d_{laser} = 47.6 \text{ mm}, P = -10 \text{ dB}_m\)
- \(\Delta t_{RF} = 295 \mu s, d_{laser} = 40.8 \text{ mm}, P = -5 \text{ dB}_m\)
The **first step** is to determine a set of **fine-structure constants** from the fit:

- Calculate the fine-structure splitting with the constants from [1]
- Minimize the residuals \( r_{i,\pm} = \frac{[\nu(N_i \pm 1 \leftarrow N_i) - \hat{\nu}_{x_{\text{Lit}}}(N_i \pm 1 \leftarrow N_i)]}{w_i} \) in a **weighted fit**
- Determine the constants \( x' \) from the 1st fit

The **second step** is to perform the **bootstrap** and determine the **uncertainties**:

- Calculate the new residuals on which the bootstrap will be performed
  - In a loop for \( i = 1 \) to \( n_{\text{boot}} \)
    - Bootstrap the residuals \( r'_{i,\pm} \rightarrow \tilde{r}_{i,\pm} \)
    - Perform the minimization
    - Determine the constants \( x_{i_{\text{boot}}} \)
  - Obtain the final value for the **fine-structure constants**

\[
x \pm \sigma_x = \sum_{i} \frac{x_{i_{\text{boot}}}}{n_{\text{boot}}} \pm \left( \frac{\sum_i (x - x_{i_{\text{boot}}})^2}{N - 1} \right)^{1/2}
\]

Global-fit residuals