High-Resolution Spectroscopy Using
A New All-Solid-State VUV Laser System

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High-resolution electronic spectroscopy demands narrow-band VUV radiation (< 200 MHz, ns pulses).

Resolution of VUV laser sources is limited by

a) bandwidth of primary sources in the NIR, IR, VIS or UV.

b) FT-limit of VUV pulses, $\Gamma_v \Gamma_t = 4\ln(2)/\pi$ (10 ns $\equiv$ 88 MHz).

An all-solid-state VUV laser system with unprecedented resolution:

- broad and easy tunability.
Frequency upconversion

Commercial tunable NIR, IR, VIS or UV laser

Amplification of primary radiation

Frequency upconversion

Experiment

Bandwidth - is intrinsically restricted by the FT-limit

- may be augmented by adopting long pulses (ns - µs).
Realizing long seed pulses

+ NIR radiation bursts are generated by the pulsed diffraction side-band of an acousto-optic-modulator.
Amplifying pulses: Dye vs. Ti:Sa

Dye System

- dye (\(\tau < 1\) ns)
- 8 ns pump pulse
- Nd:YAG
- \(x \times 10^4\)

Ti:Sa System

- Ti:Sa crystal (\(\tau > 3\) \(\mu\)s)
- \(x 3\)

Time (ns) vs. Time (\(\mu\)s)

unamplified signal vs. amplified signal
High pulse energies are required.

Long lifetime of population inversion implies low amplification factors.

Pulsed seed beam, 25 Hz, 0.2 nJ/pulse

Nd:YAG 532 nm
pump beam, 25 Hz,
120 mJ/pulse

Ti:Sa crystal
7 x 7 x 10 mm³
Pulse shapes at different stages in the amplification process:

<table>
<thead>
<tr>
<th>Power (arb. Units)</th>
<th>Unamplified NIR pulses</th>
<th>NIR pulses after 9 passes</th>
<th>NIR pulses after 16 passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 nJ/pulse</td>
<td>0.2 nJ/pulse</td>
<td>2 μJ/pulse</td>
<td>0.6 mJ/pulse</td>
</tr>
<tr>
<td>1 nJ/pulse</td>
<td>1 nJ/pulse</td>
<td>20 μJ/pulse</td>
<td>3 mJ/pulse</td>
</tr>
<tr>
<td>2 nJ/pulse</td>
<td>2 nJ/pulse</td>
<td>40 μJ/pulse</td>
<td>4 mJ/pulse</td>
</tr>
<tr>
<td>4 nJ/pulse</td>
<td>4 nJ/pulse</td>
<td>90 μJ/pulse</td>
<td>6 mJ/pulse</td>
</tr>
</tbody>
</table>
VUV pulses

- VUV signal (arb. units)
- Time (ns)

17 ns pulse duration

40 ns pulse duration
Assessment of possible chirp

+ Frequency evolution during pulse:

\[ \omega = \omega_0 + \varphi(t) \]

Cause:

+ Time dependent changes in refractive index:

\[ n(\omega,t) = n_0(\omega) + n_1(t) \]

+ Extracting chirp from beat pattern with a slightly frequency detuned cw reference beam:

\[ I(t) = I_{cw} + I_p(t) + 2\sqrt{I_{cw}I_p(t)} \sin(\omega t) \]
The frequency evolution can be reconstructed from
- phase information obtained from frequency filtering the FT of the heterodyne signal and subsequent inverse FFT.

- No measurable frequency chirp and a constant frequency shift of (-5 ± 2) MHz exists.

- VUV pulses of 17 ns ↔ 50 MHz bandwidth.
Application to atomic VUV spectroscopy

\[(5p)^{6}S_{0} \rightarrow 5p^{5}(^{2}P_{3/2})7d[3/2](J=1)\] resonance by \((1_{\text{VUV}} + 1_{\text{VIS}})\) REMPI:

\[\begin{align*}
\text{Xe} \hspace{1cm} \text{VUV} \\
\v_{\text{VUV}} \\
\text{Xe}(^{1}S_{0}) \\
\v_{1} \\
3\v_{1} \\
\v_{2} \hspace{1cm} \text{Xe} \hspace{1cm} \text{VIS} \\
\text{Xe}(^{3}S_{0}) \\
Xe^{2}P_{1/2} \text{ threshold} \\
\v_{532} \hspace{1cm} \text{Xe} \hspace{1cm} \text{VIS} \\
5p^{5}(^{2}P_{3/2})7d[3/2](J=1) \text{ at } 92714.55 \text{ cm}^{-1} \\
\v_{\text{VUV}} \\
\end{align*}\]
Xe (5p)${}^{6}S_{0} \rightarrow 5p{}^{5}(^{2}P_{3/2})7d[3/2](J=1)$ at 92714.55 cm$^{-1}$

- FWHM = 96 MHz
- $^{128}$Xe
- $^{129}$Xe
- $^{130}$Xe
- $^{131}$Xe
- $^{132}$Xe
- $^{134}$Xe
- $^{136}$Xe

**Mass resolution of TOF:**

$m/\Delta m > 300$

**VUV bandwidth predicted from Doppler-free UV spectroscopy:**

50 MHz
Reducing Doppler-broadening by:
- use of small skimmer and nozzle.

Reducing power broadening by:
- moderate VUV intensities.

Lorentz fit

Gauss fit

Approaching the FT-limit
Application to molecular VUV spectroscopy

Hyperfine structure in Rydberg states of $\text{H}_2$ and $\text{D}_2$:

$\text{H}_2$ via R(1):
the nd$_1$ series

$1.3 \text{ GHz}$

$\text{Energy above } \text{H}_2 \ X \ ^1\Sigma_g^+ (v''=0, J''=0) \text{ ground state (cm}^{-1})$
Realization, characterization and application of a new high resolution (0.003 cm\(^{-1}\) at 93000 cm\(^{-1}\), Doppler-limited), tunable all-solid-state VUV system was presented.

Measurements of the \(^1\text{S}_0 \rightarrow \text{Xe } 5p^5(2\text{P}_{3/2})7d[3/2](J=1)\) resonance revealed, for the first time, the hyperfine splittings of the \(I \neq 0\) isotopes.

Measurements of the high lying nd Rydberg series of \(\text{H}_2\) and \(\text{D}_2\) have been performed revealing hyperfine structure.

The narrow bandwidth and wide tunability attainable will enable the exploration of the finest details in VUV photochemistry and photophysics.
Applications

High-resolution spectra of H₂ and D₂:

Bandwidth:

Ti:Sa (VUV): 100 MHz
PDA (UV): 125 MHz
Combined: <200 MHz