Goals:

-Provide an introduction on Rydberg atom and molecule optics

- Provide an overview of the properties of Rydberg atoms and molecules

- Present the instrumentation and methods used in spectroscopic studies of Rydberg states and in Rydberg optics exerpiments

- Describe methods to produce cold molecular samples in the gas phase

- Develop in the class the concept of a new experiment which should lead to the electrostatic trapping of CO molecules

Week 1:

Rydberg atoms and molecules

Supersonic beams as cold molecule sources

Rydberg stark deceleration and trapping

Week 2:

Coherent sources of short wavelength radiation

FT-limited pulsed radiation by pulsed amplification of cw radiation

Frequency calibration and stabilization

Multiphoton excitation schemes in molecules (polarization, optical layout)

Week 3:

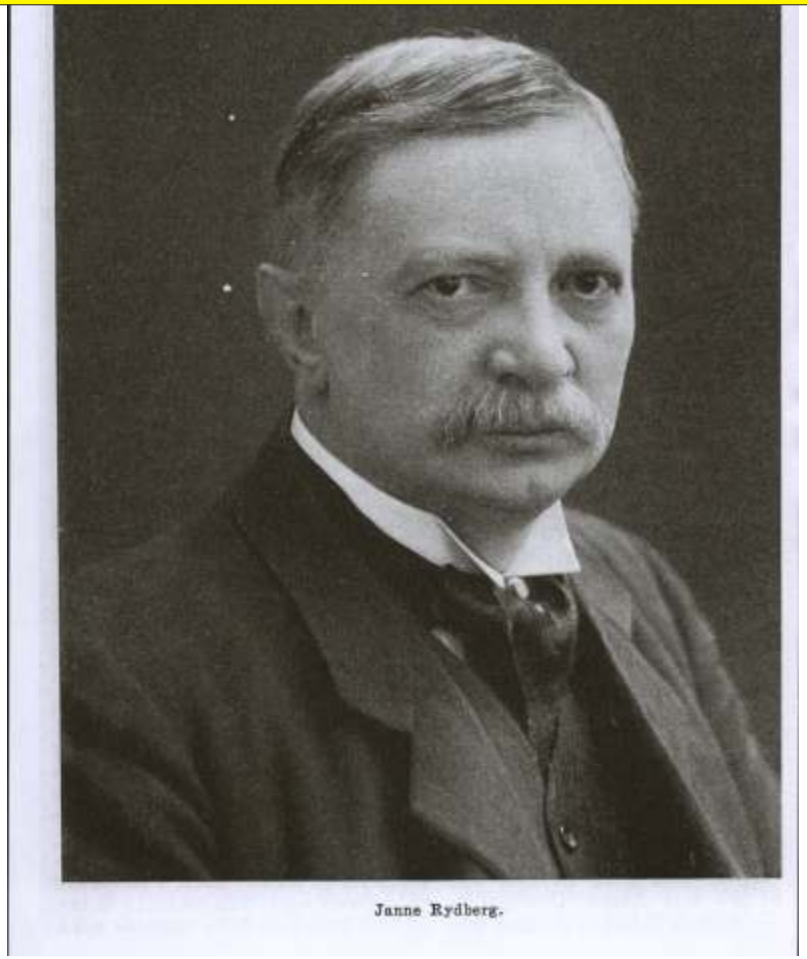
Sources of cold samples and detection techniques

Velocity map imaging

Generation of short electric and magnetic field pulses

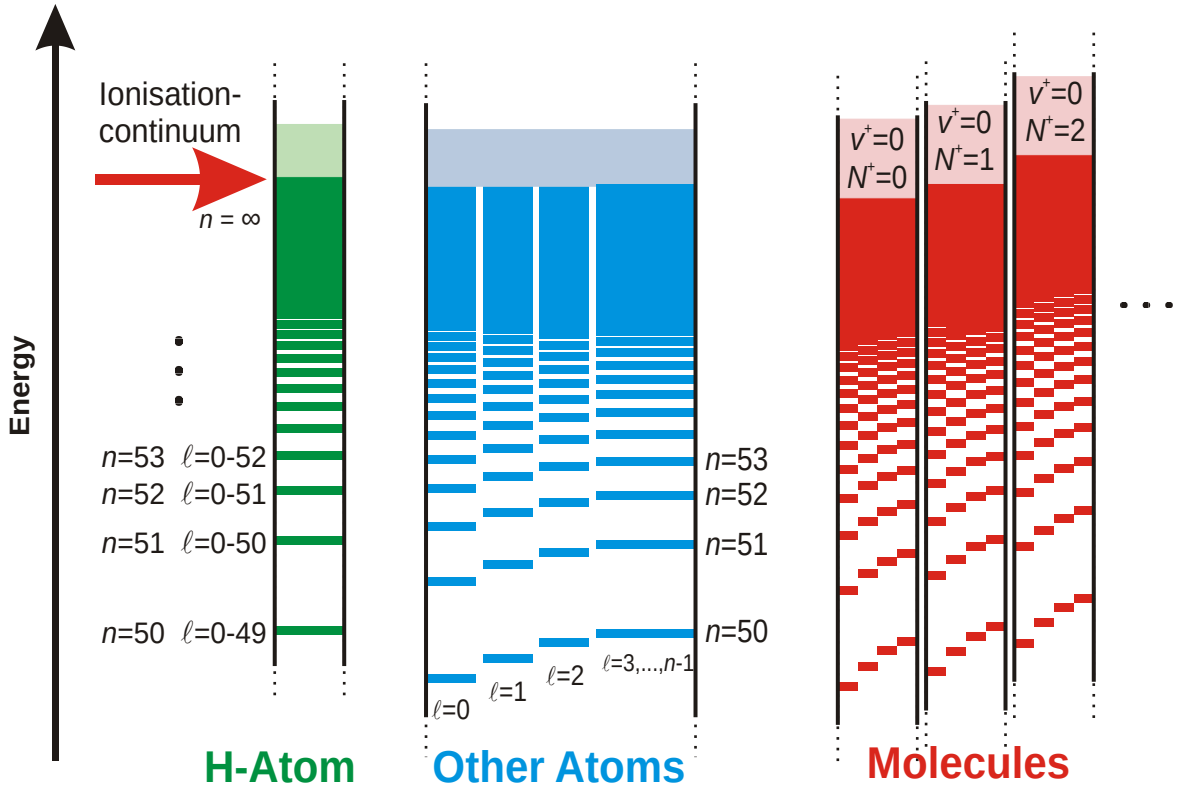
I. Introduction

Rydberg formula: $\tilde{\nu} = IP - \frac{R}{(n - \delta_\ell)^2}$



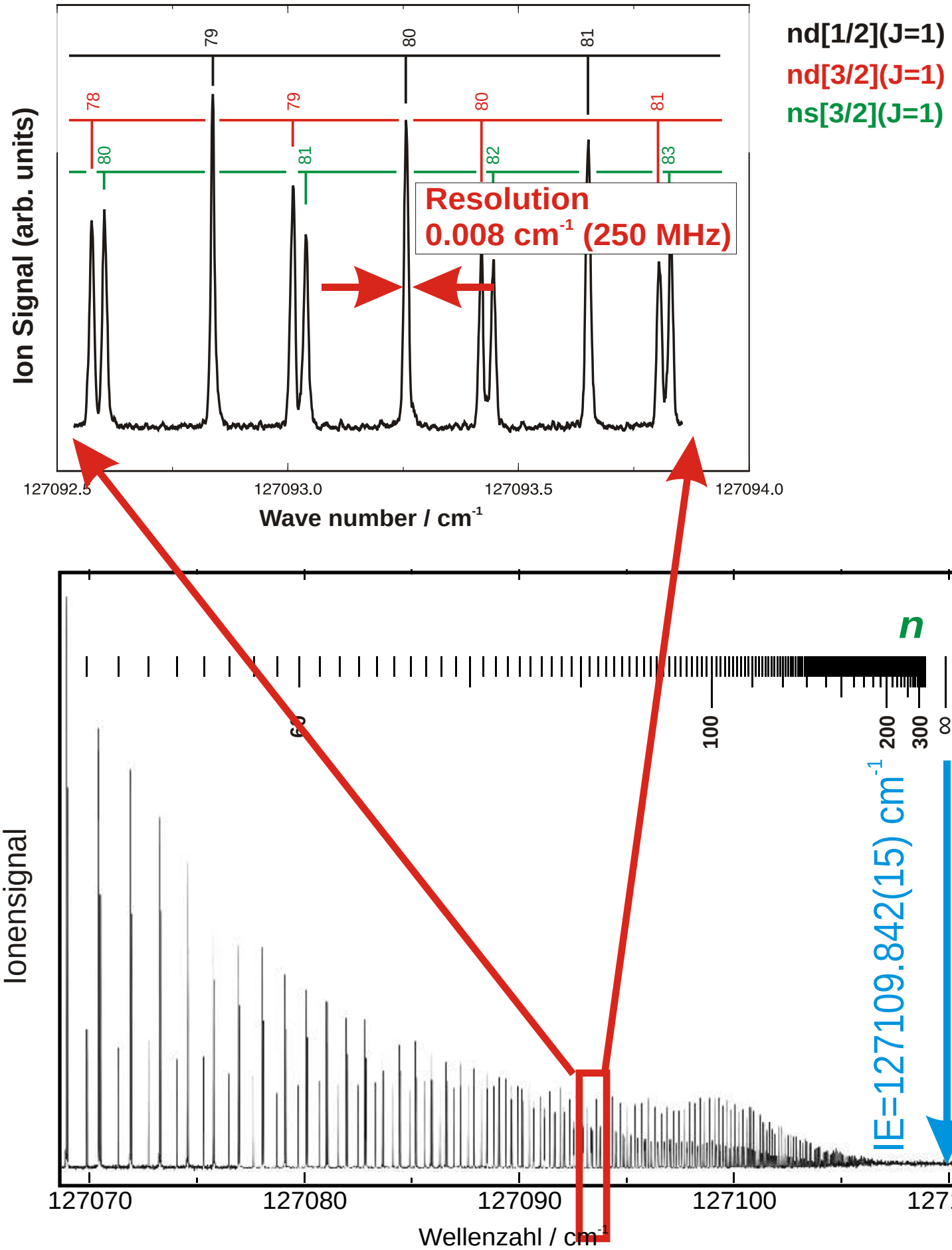
Mulliken, 1964: “Rydberg states are the stepping stones to ionization”

Rydberg states of atoms and molecules

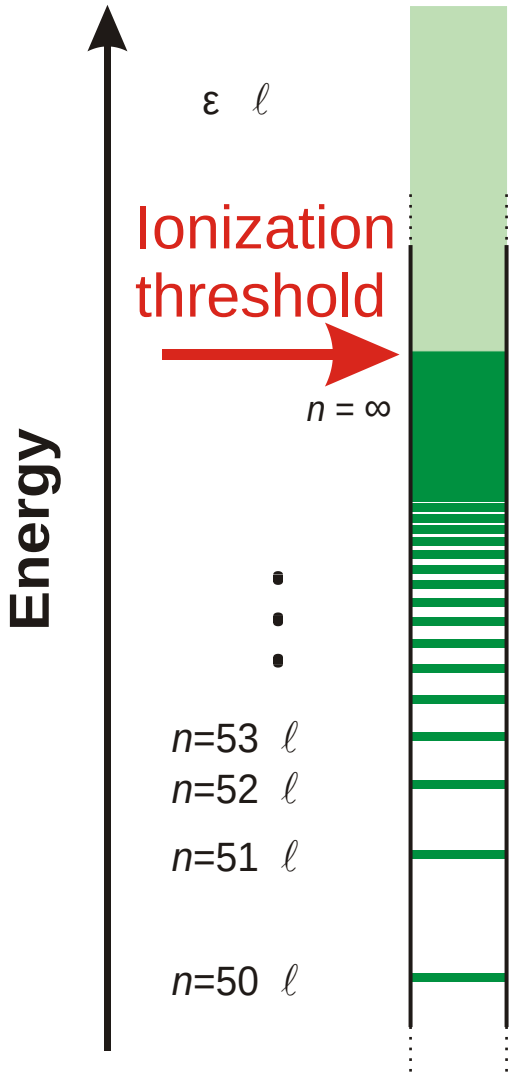


J. R. Rydberg, Z. Phys. Chem.(Leipzig) 5, 227 (1890)

Pulsed-field ionization spectrum of argon

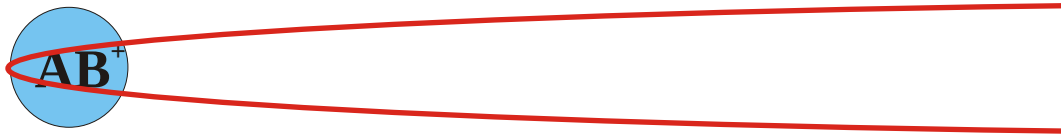


Ionization channel = Ion in well-defined (v^+, J^+) quantum state + electron of given orbital angular momentum ℓ



Ionization continuum (channel open)

Free electron colliding with AB^+



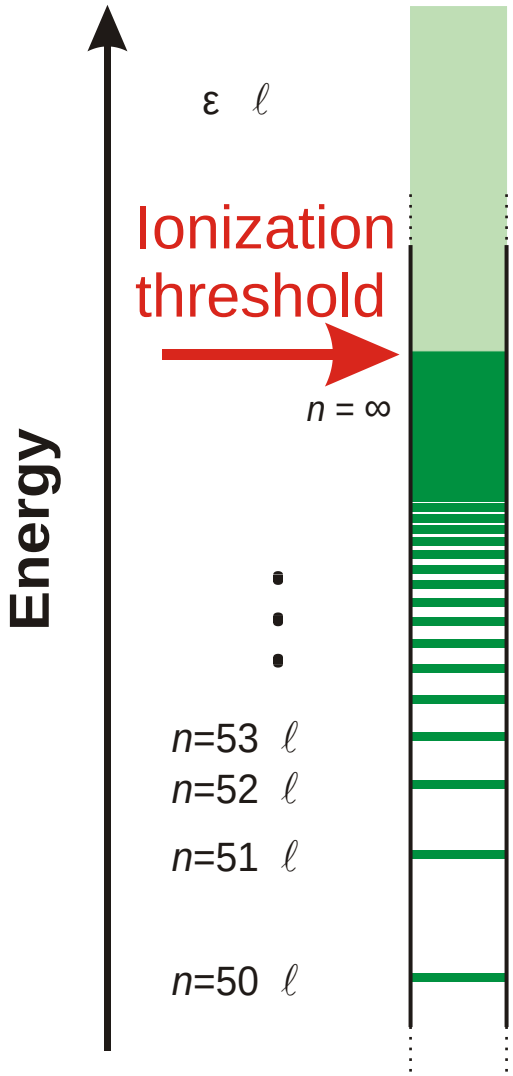
Collisional phase shift
$\delta = \pi\mu$

Bound levels (channel closed)

Electron in a Rydberg orbit

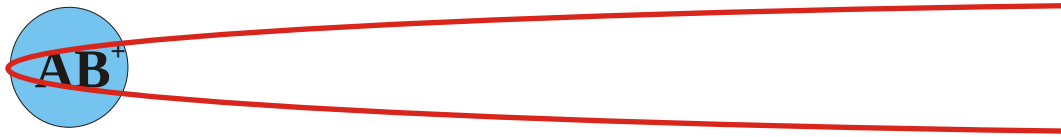
Quantum defect μ

Ionization channel = Ion in well-defined (v^+, J^+) quantum state + electron of given orbital angular momentum ℓ



Ionization continuum (channel open)

Free electron colliding with AB^+



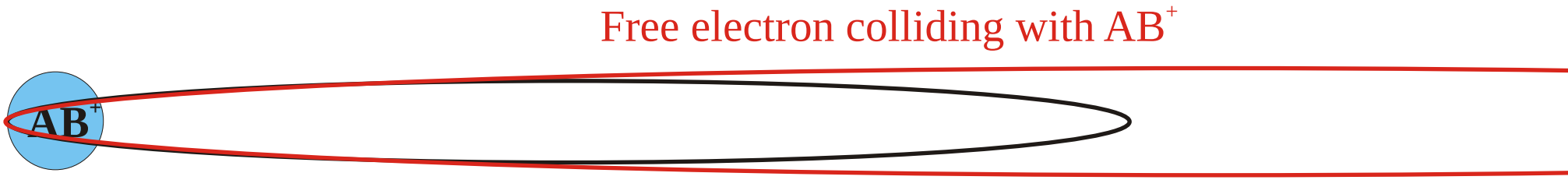
Same short-range collision physics

Different boundary conditions

Bound levels (channel closed)

Electron in a Rydberg orbit

Rydberg states, photoionization and reaction dynamics



$AB^* \longrightarrow AB^+ + e^-$	Autoionisation / inelastic scattering
$AB^* \longrightarrow A + B$	Predissociation / dissociative recombination
$AB^* \longrightarrow A^+ + B + e^-$	Dissociative ionisation / reactive scattering
$AB^* \longrightarrow A + B^+ + e^-$	
$AB^* \longrightarrow AB + h\nu$	Radiative decay / radiative recombination

Decay rates scale with n^{-3}

Study ion-electron collisions and photoionization dynamics
by high-resolution spectroscopy of high Rydberg states

Treat the Rydberg states theoretically as a collision
(Multichannel quantum defect theory (U. Fano, M. Seaton, Ch. Jungen))

PHYSICAL PROPERTIES OF RYDBERG STATES

Property	n-dependence	n=1	n=100	n=200	n=1000
Classical radius	$a_0 n^2$	0.5 Å	0.5 μm	2 μm	50 μm
Binding energy	$-R n^{-2}$	13 eV 109735 cm^{-1}	1.3 meV ~11 cm^{-1}	0.33 meV ~2.7 cm^{-1}	13 μeV ~0.1 cm^{-1}
Ionisation field (V/cm)	n^{-4}	$2.5 \cdot 10^{8}$	2.5	0.15	$2.5 \cdot 10^{-4}$
Period of the electronic motion	$n^3 \tau_1$	$1.5 \cdot 10^{-16}$s	$1.5 \cdot 10^{-10}$s	$1.2 \cdot 10^{-9}$s	$1.5 \cdot 10^{-7}$s
Spacing between adjacent Rydberg	$2 R n^{-3}$	~80000 cm^{-1} ~10 eV	~0.2 cm^{-1} ~7 GHz	~0.02 cm^{-1} ~0.8 GHz	~0.0002 cm^{-1} ~7 MHz

Further properties:

Lifetime: n^3

Resonant dipole-dipole interaction: n^4

Polarisability: n^7

Van der Waals interaction: n^{11}

Factors governing the n-dependence of the properties of Rydberg states:

1) The amplitude of the wave function in the ion core region

$$\Psi_{nlm}(R<Rc) \sim n^{-3/2}$$

2) The energetic distance to the nearest zero order state (perturbation theory)

$$\Delta E^{(0)} \sim n^{-3}$$

3) The size of the Rydberg orbit (geometric interpretation of cross-sections and transition moments)

$$\langle R \rangle \sim n^2$$

$$\langle nl|\mu|n'l' \rangle \sim n^2 \qquad (\text{for } n' \cong n)$$

Examples of n-scaling laws:

1) Properties derived from the amplitude of the wave function at short range

$$P(R<Rc) \sim n^{-3}$$

Lifetime $\sim n^3$

Absorption cross section from ground state $\sim n^{-3}$

2) Properties derived from the dimension of the Rydberg orbit:

Collisional cross section $\sim n^4$

Transition between neighboring states $I \sim \langle n,l \mid \mu \mid n',l' \rangle^2 \sim n^4$

3) Properties derived using perturbation theory:

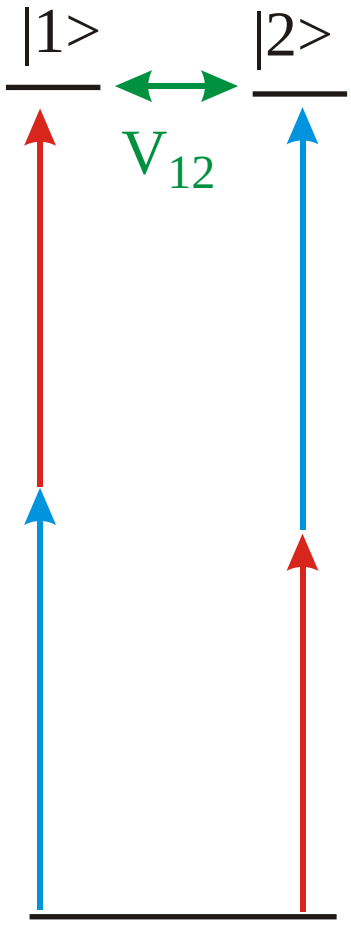
First-order Stark shift: $\Delta E^{(1)} \sim knF$ $(k=-n+|m|+1,...,n-|m|-1)$

Second order Stark shift: $\Delta E^{(2)} \sim \frac{1}{2} \alpha F^2$

Polarisability: $\alpha \sim n^7$

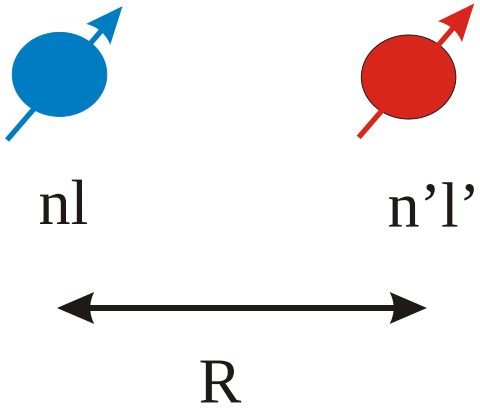
$\alpha \sim \Sigma \langle n,l \mid \mu \mid n',l' \rangle \langle n',l' \mid \mu \mid n,l \rangle / \Delta E^{(0)} \sim n^7$

Dipole-dipole interactions in Rydberg states

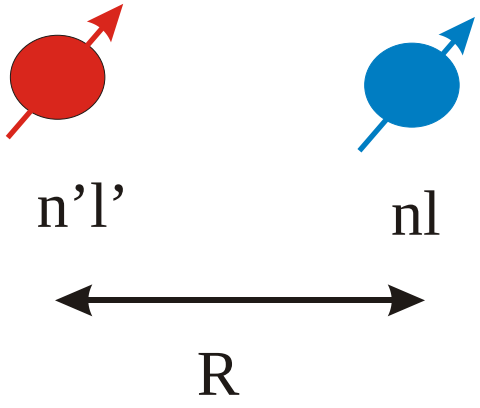


The resonant dipole-dipole interaction:

$|1\rangle = |nl\rangle|n'l'\rangle$ (**21s**,**20p**)



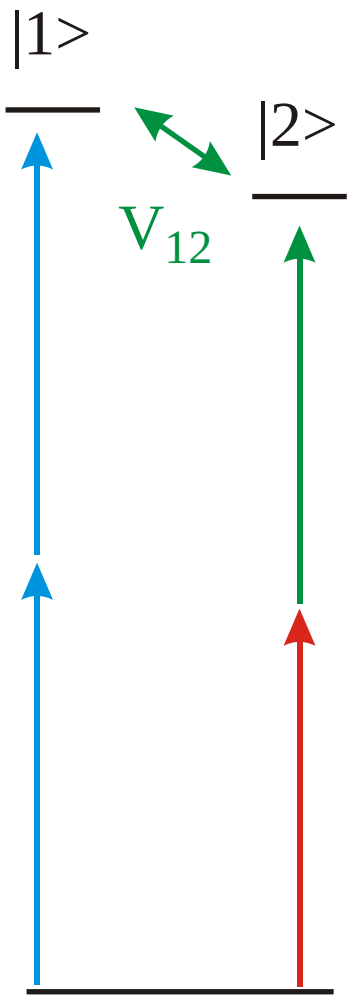
$2\rangle = |n'l'\rangle\,|nl\rangle$ (**20p**,**21s**)



$$V_{12} = \langle nl|\mu|n'l'\rangle \langle n'l'|\mu|nl\rangle / R^3 \sim n^4$$

$$E_1^{(0)} = E_2^{(0)} = E^{(0)} \qquad E = E^{(0)} +/- \Delta E^{(1)} \text{ with } \Delta E^{(1)} \sim n^4/R^3$$

The nonresonant dipole-dipole (van der Waals) interaction:



$|1\rangle = |nl\rangle|nl\rangle$ (**20p**,**20p**) $\quad 2\rangle = |n'l'\rangle\,|n''l''\rangle$ (**20d**,**21s**)

$$\Delta E^{(2)} \sim \sum\sum \frac{\langle nl|\mu|n'l'\rangle \langle nl|\mu|n''l''\rangle \langle n'l'|\mu|nl\rangle \langle n''l''|\mu|nl\rangle}{R^6\ \Delta E^{(0)}}$$

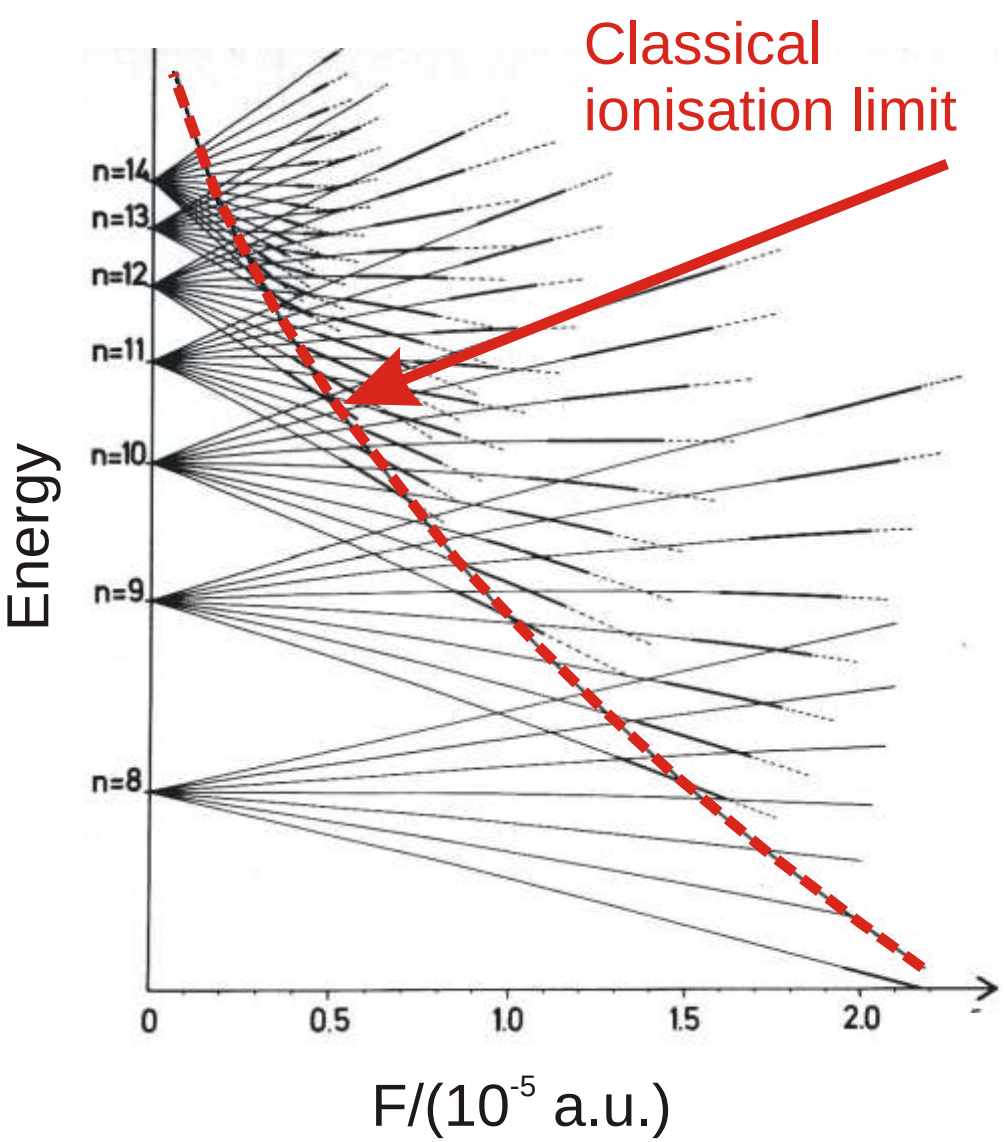
$$\sim\ n^{11}$$

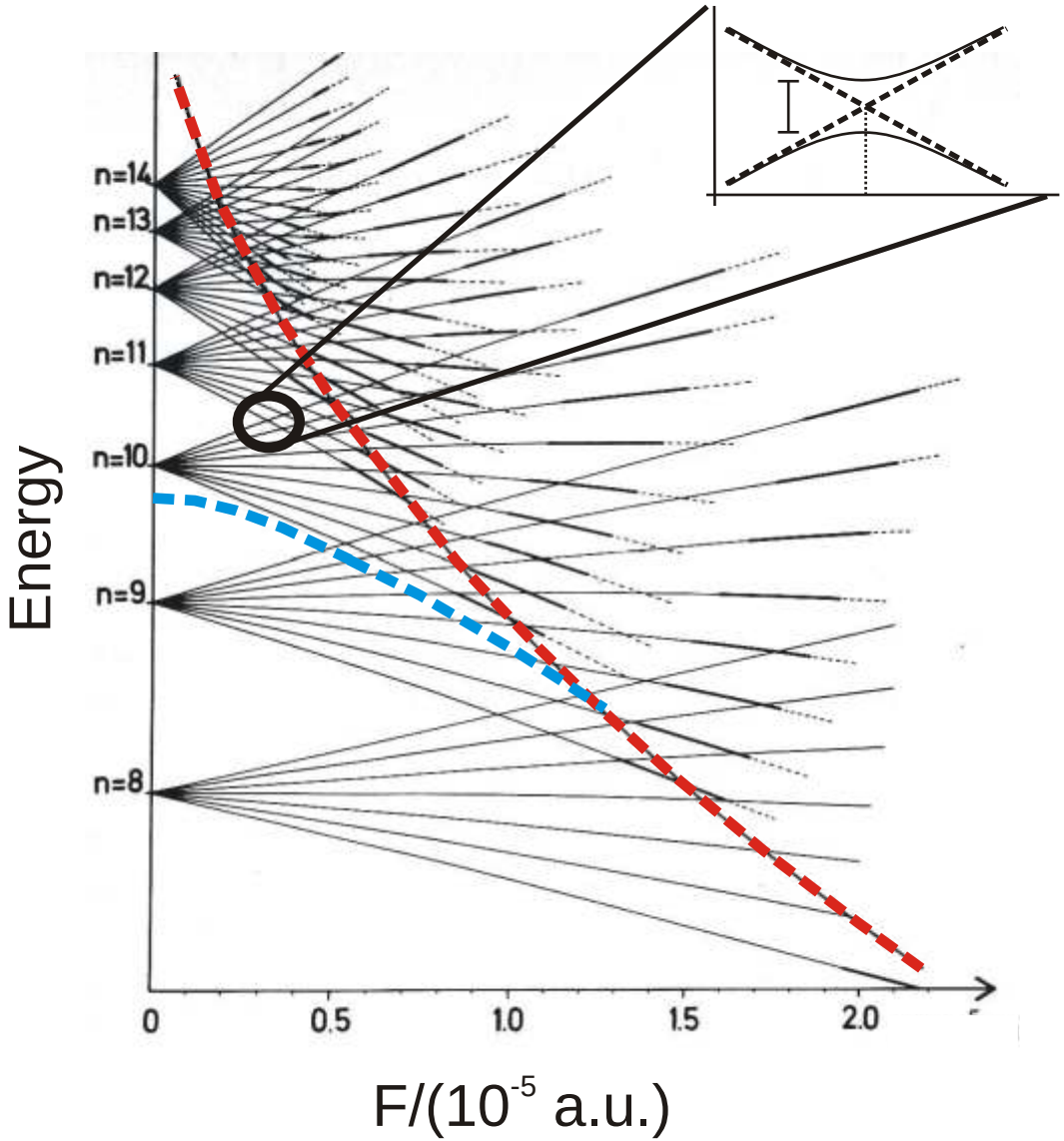
Rydberg states and electric fields

$H = H^o + eFz$

H atom

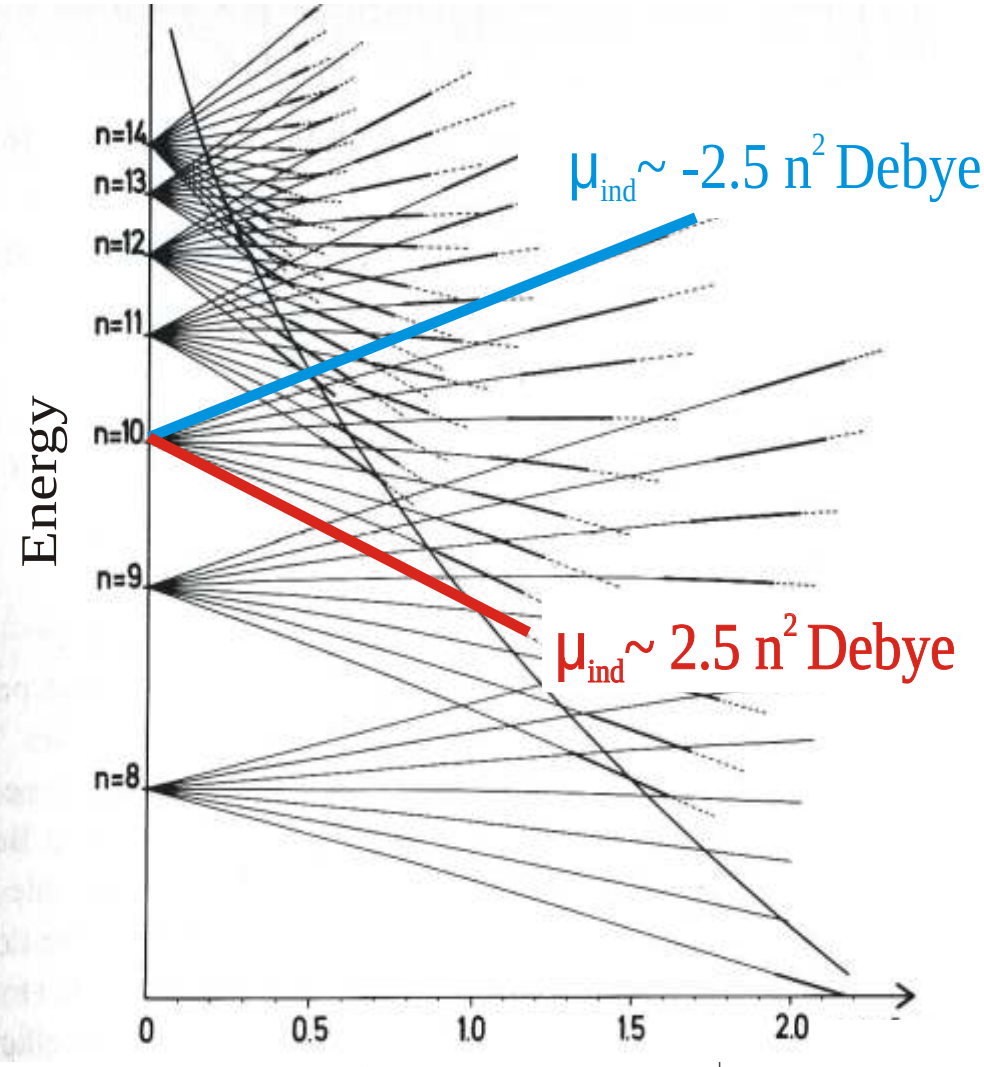
Other atoms





First-order Stark shift: $\Delta E^{(1)} \sim ea_o knF$ $(k=-n+|m|+1,...,n-|m|-1)$

Stark states and scaling laws:



Stark states are linear combinations of pure l states:

$$|n,k,m\rangle = c(nkm,nlm)\,|nlm\rangle$$

Stark states have an induced dipole moment

$$\mu_{ind} = e a_o\, kn$$

For the most blue and red shifted states:

$$\mu_{ind} = e a_o\, n^2$$

Only the low-l components are accessible from the ground or low-lying electronic states.

Absorption cross-section to Stark states ~ n^{-4}

The penetrating character of the Rydberg states is diluted by nonpenetrating high-l components:

Lifetime ~ n^4

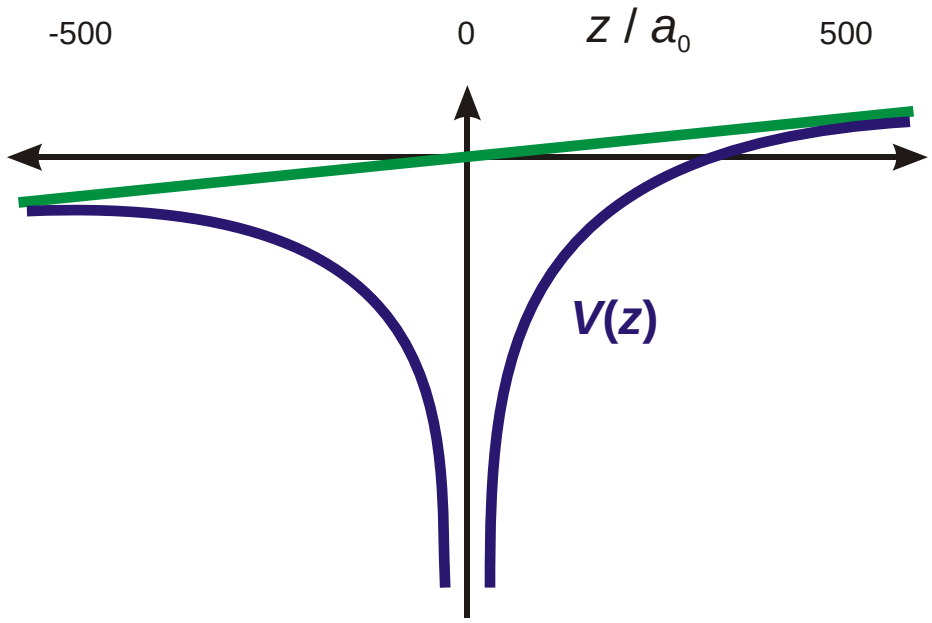
Electric field ionization of Rydberg states

Simple classical model:

homogeneous electric field induces a saddle point in the potential

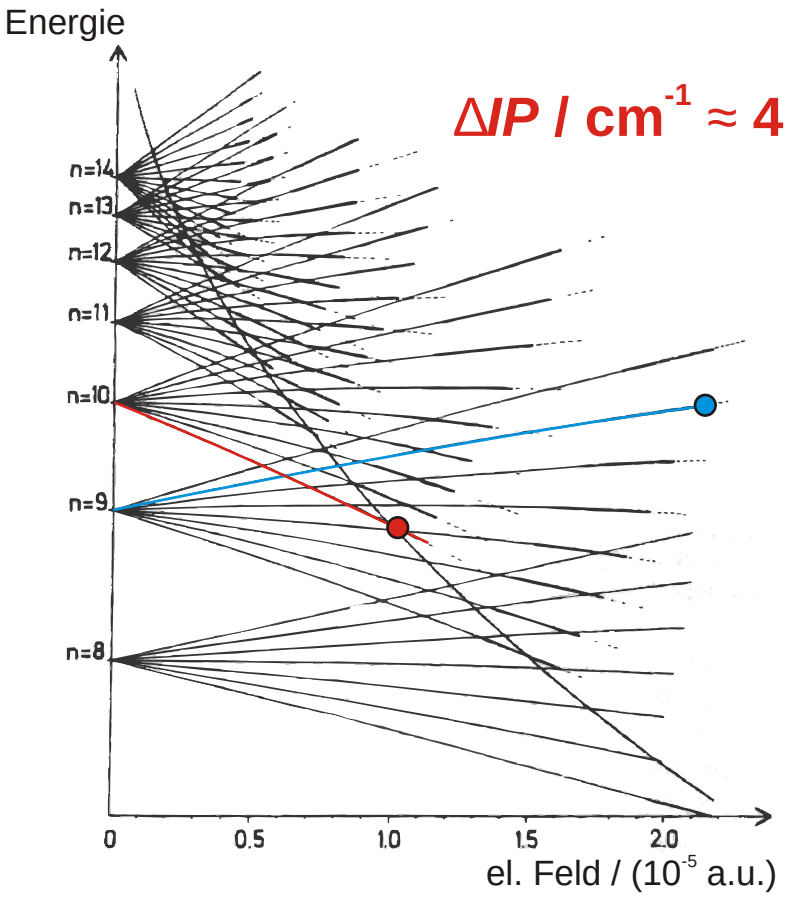
$$V = -1/r + eFz$$

$$\Delta IP \,/\, \mathrm{cm}^{-1} = 6.12\sqrt{F \,/\, (\mathrm{V/cm})}$$

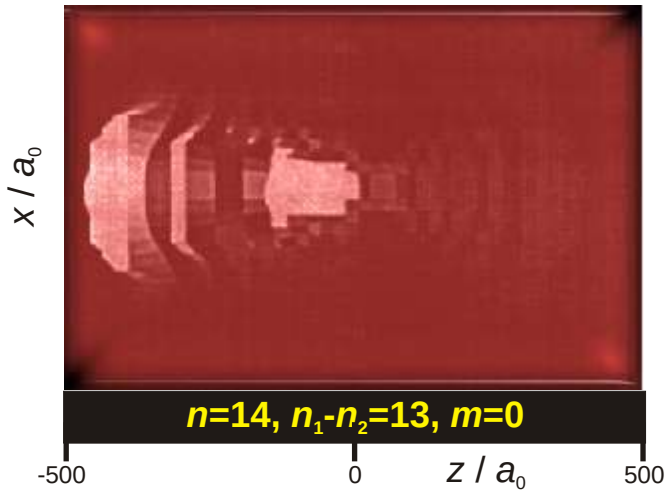


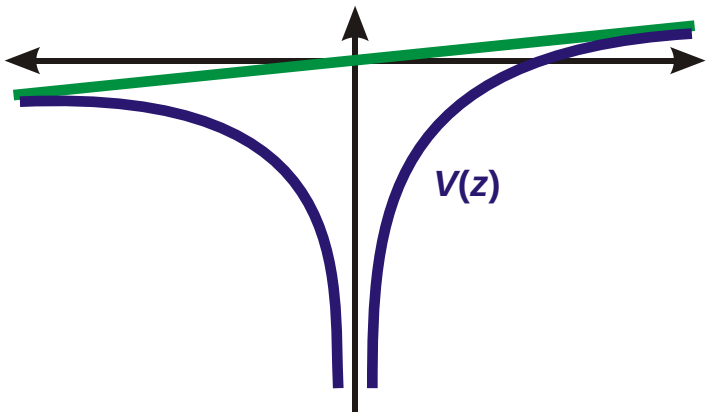
From $\Delta IP = R/n^2$ one obtains that the threshold field for field ionization is proportional n^{-4}

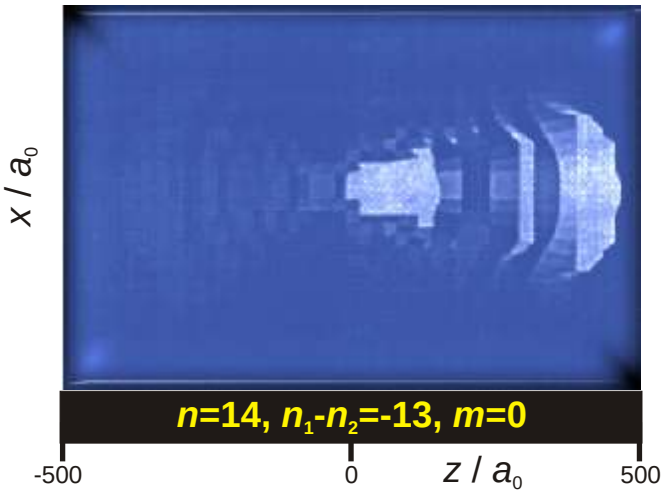
Hydrogenic (diabatic) field ionization

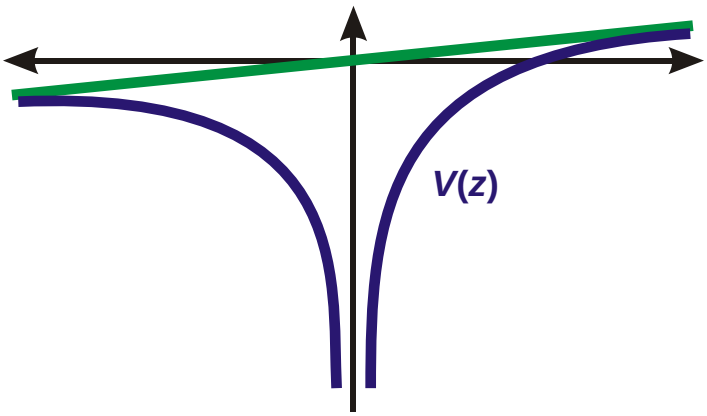


$$\Delta IP \,/\, \mathrm{cm}^{-1} \approx 4\sqrt{F \,/\, (\mathrm{V/cm})}$$

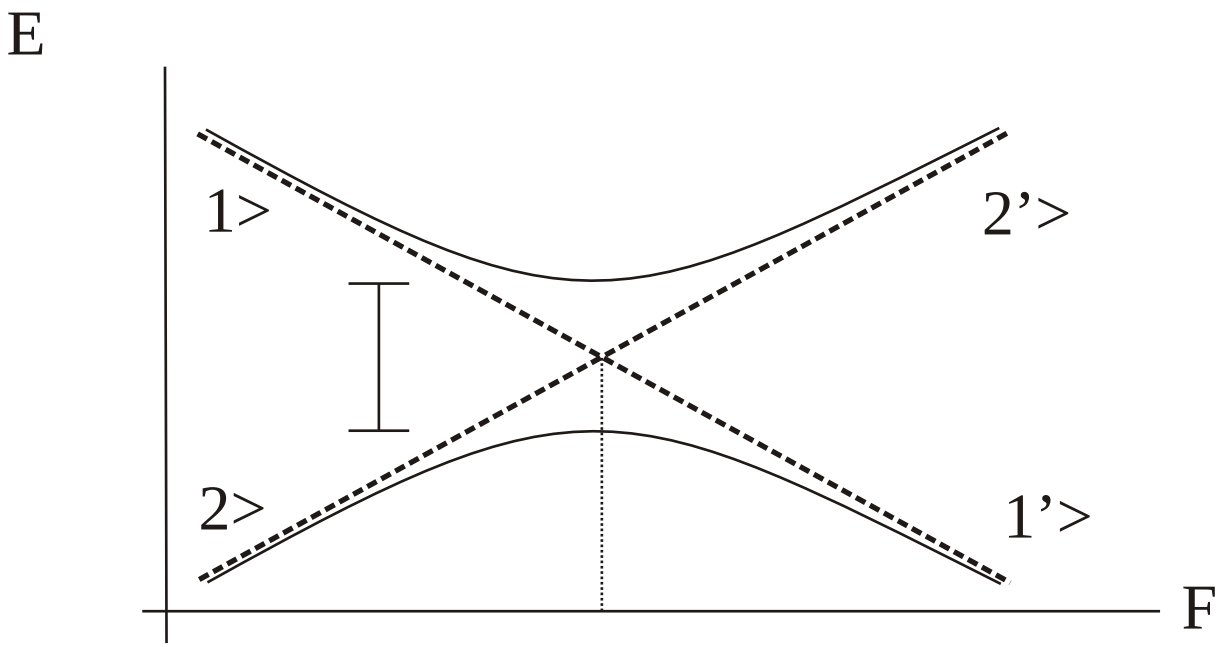








Landau-Zener dynamics at curve crossings:



$$\begin{bmatrix} E_1 & V_{12} \\ V_{12}^* & E_2 \end{bmatrix}$$

$$P_{diab} = \exp\{-2\pi|V_{12}|^2 / [\hbar(dW/dt)]\}$$

dW/dt: rate of change of the level separation.
In a field dW/dt = (dW/dF)(dF/dt), with (dF/dt) the slew rate

Diabatic traversal: $|1\rangle \longrightarrow |1'\rangle$
Adiabatic traversal: $|1\rangle \longrightarrow |2'\rangle$

High slew rates and small interactions favor diabatic processes

Rydberg states in chemistry and physics:

Physics:

Astrophysics: recombination lines

Plasma physics

Atom and molecule optics: control of motion with inhomogeneous fields

Quantum information processing: large atom-photon interaction
large dipole-dipole interaction

Antihydrogen: formed in high Rydberg states

Chemistry:

Model systems for studying chemical reactions

Ion spectroscopy

Ideal systems for studies by high-resolution spectroscopy

Experiments with Rydberg states

Experimental procedure:

a) Excitation from the neutral ground state:
Single-photon excitation with narrow bandwidth VUV laser
Multiphoton excitation schemes

b)Transitions between neighbouring Rydberg states:
Millimetre waves and microwaves

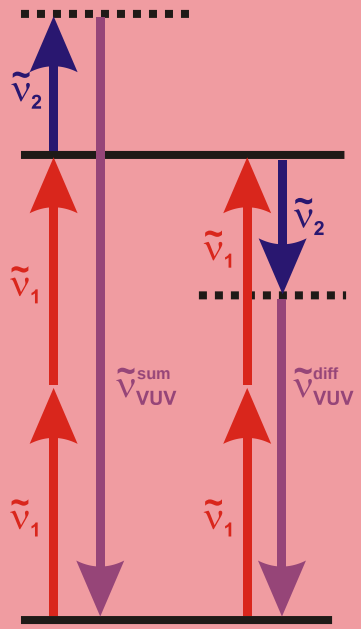
c) Detection of Rydberg states:
Selective field ionisation

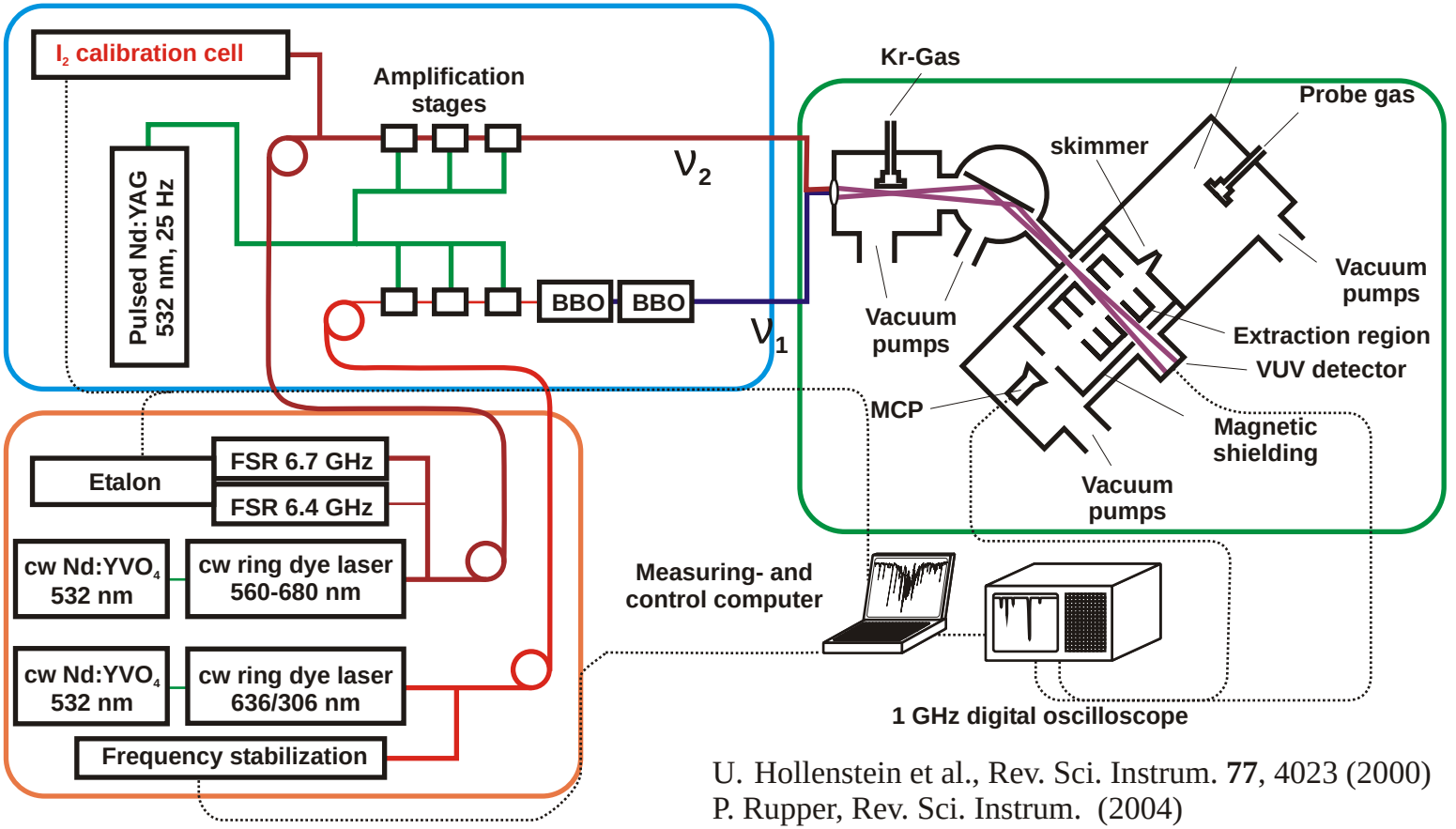
Magnetic shielding, control of stray electric fields,
low Rydberg/ion densities

Broadly tunable, narrow bandwidth VUV laser

Tunable range: 10-20 eV
Bandwidth: 250 MHz
10^{10} photons/pulse
Rep. Rate: 25 Hz

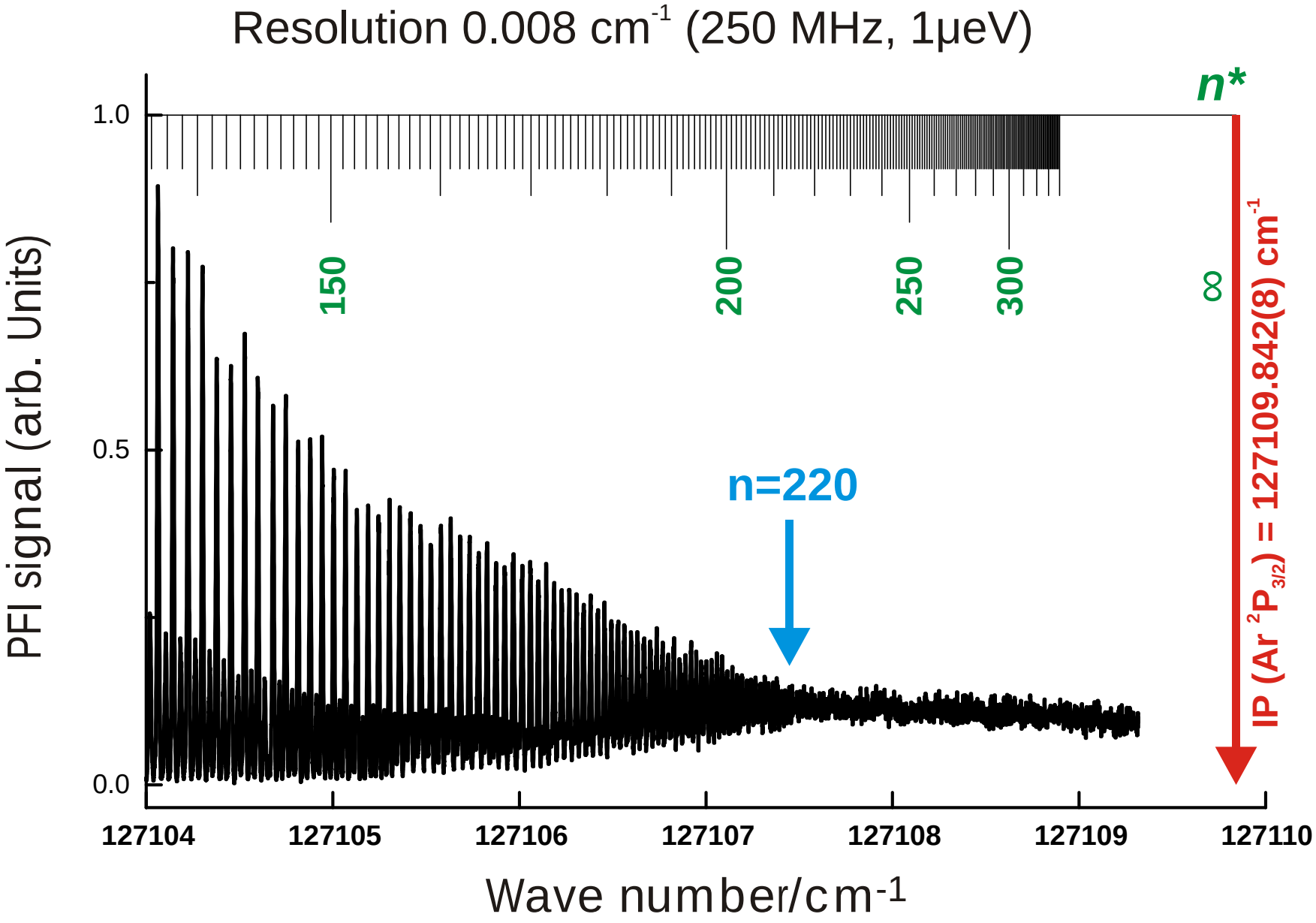
VUV generation by resonance-enhanced four-wave mixing in rare gases (Ar, Kr, Xe)



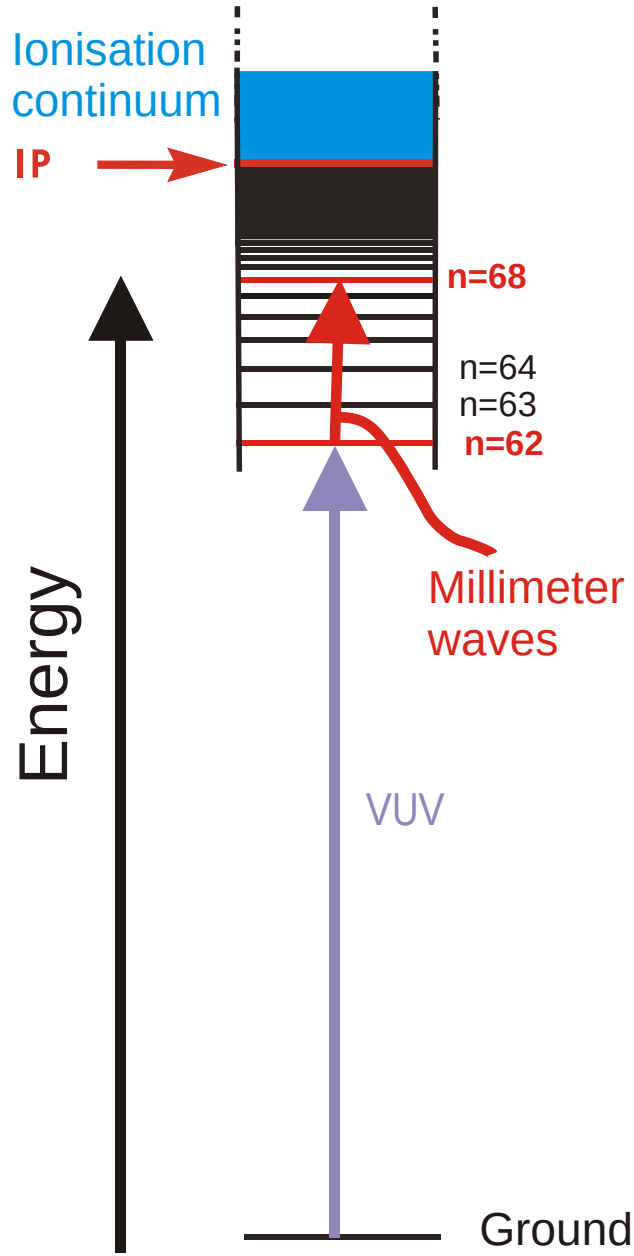


U. Hollenstein et al., Rev. Sci. Instrum. **77**, 4023 (2000)
P. Rupper, Rev. Sci. Instrum. (2004)

VUV laser spectroscopy of high Rydberg states argon



B) Millimeter wave spectroscopy

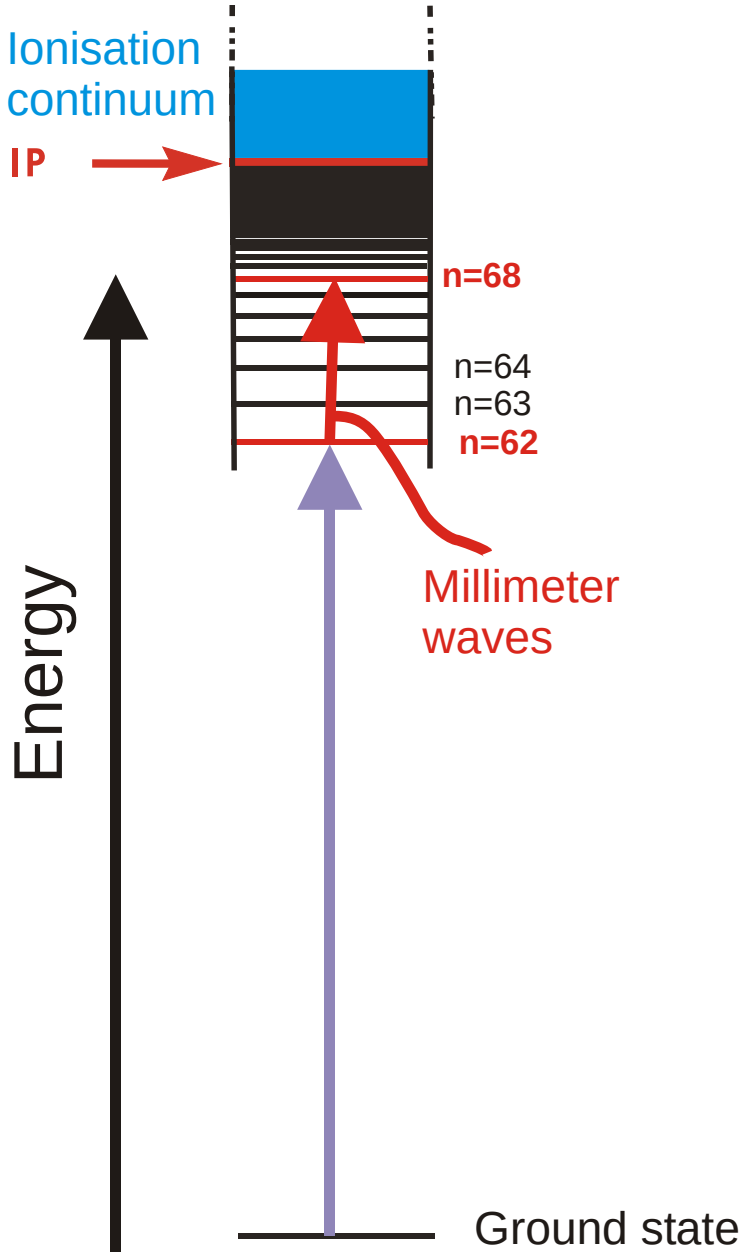


Advantages:

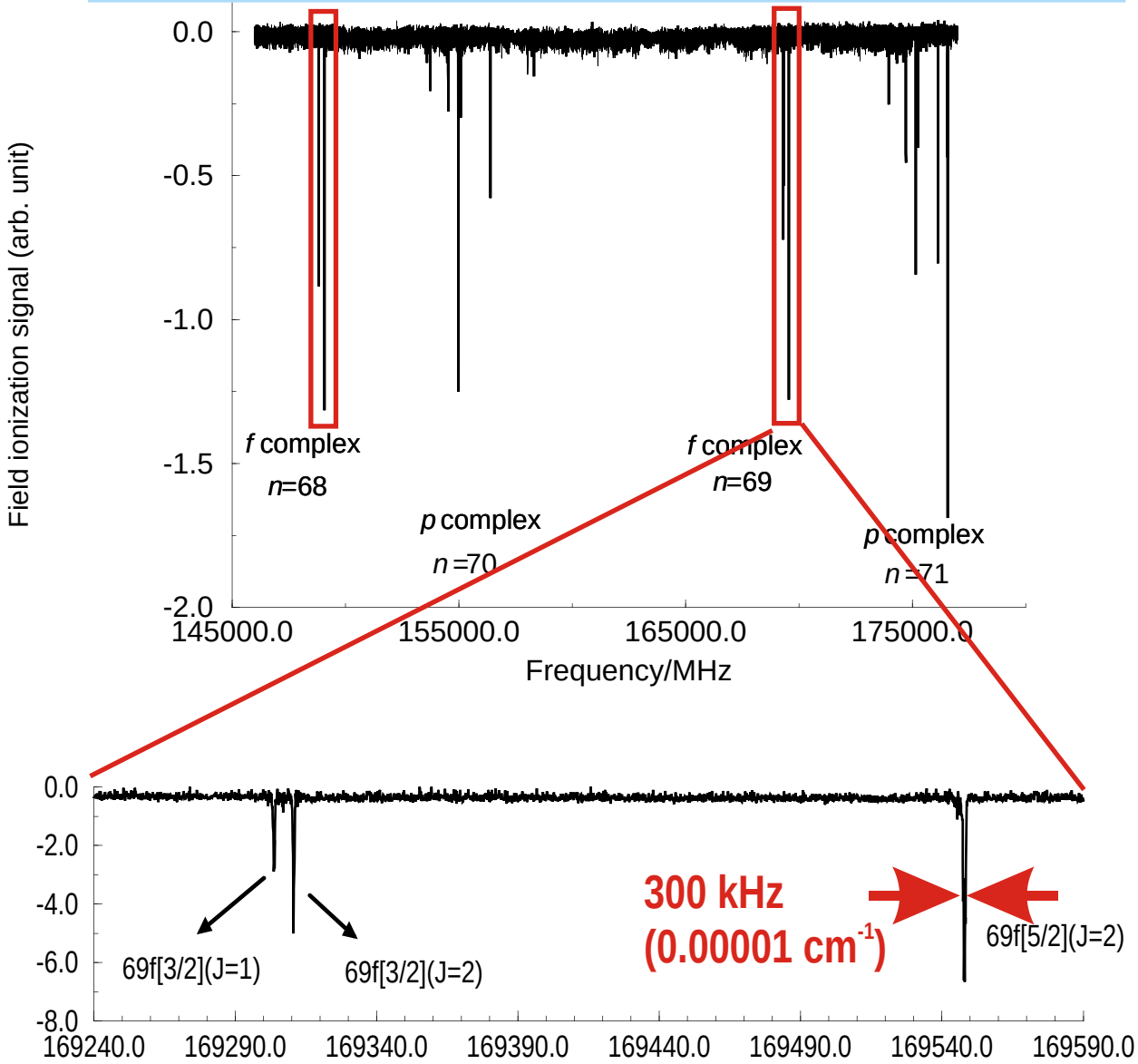
- cw excitation
- Narrow bandwidth
- Doppler broadening minimal
- Frequency stabilized
- large transition moments (~n^2)

Sources: 120-180 GHz BWO (AMC Chemnitz)
240-360 GHz BWO (developed with help of G. Winnewisser, Cologne)

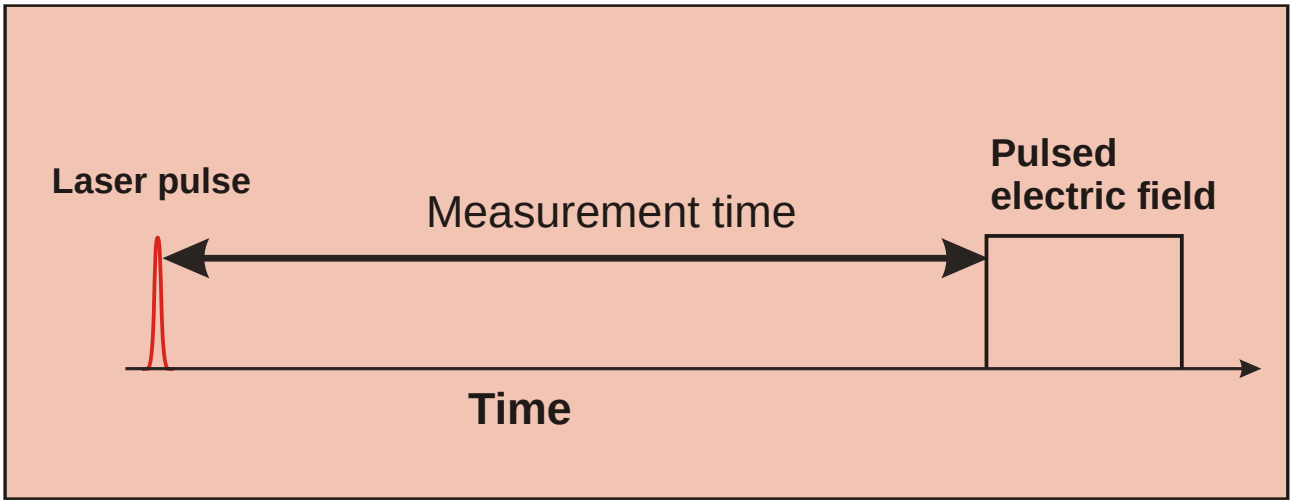
Millimetre wave spectroscopy of high Rydberg states



Millimetre wave spectrum recorded from the n=62 d[3/2](J=1) level of argon



Millimetre wave spectroscopy of high Rydberg states and resolution



60 kHz = 0.000002 cm^{-1} = 0.25 neV