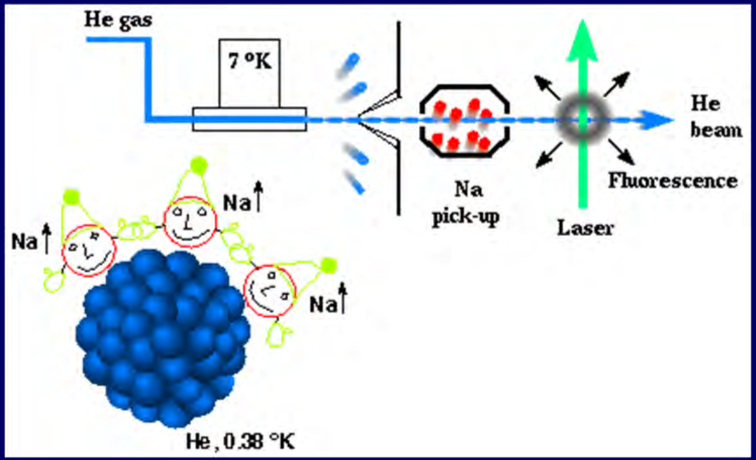
Shell Models for Alkali Metal Trimers:
Electronic Level Structure and Magnetic Properties from Experimental and Theoretical Investigations

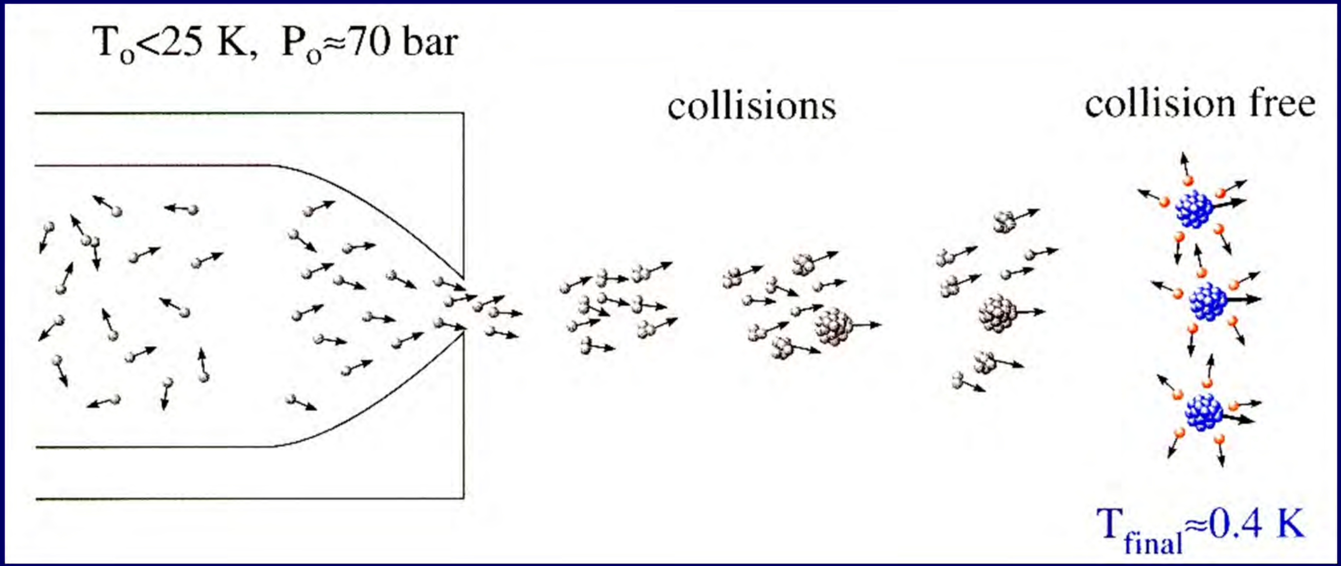
Lecture II



- introduction: helium droplets, doping with foreign species, spectroscopy
- alkali atoms and molecules on helium droplets
- spectra, absorption and magnetic circular dichroism
- identification of high spin trimers
- *ab initio* K_3 and Rb_3, K_2Rb and KRb_2 quartet states
- quartet state shell structure, harmonic oscillator states
- the ultimate resolution: electron spin resonance

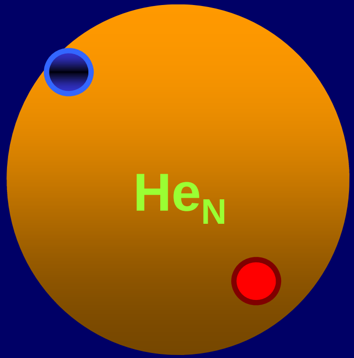
Wolfgang E. Ernst

Helium nanodroplets



cooling (adiabatic expansion) — **clusters grow** — **evaporative cooling**

- Excellent cryostat, at T~0.4K
- Weak interactions
- Liquid (in fact superfluid)
- Confinement (r = 20-100 Å)
- "Natural selection" of weakly bound species

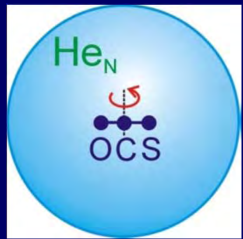


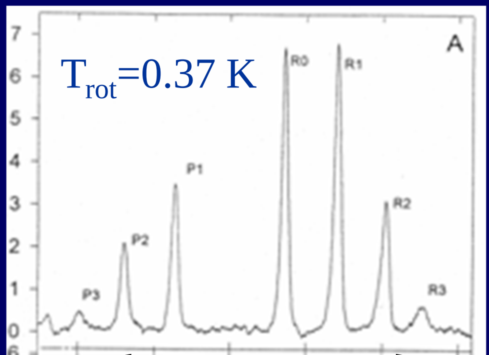
Superfluid helium droplets as nanocryostat

Spectroscopic linewidths?

Rotational (microwave) and vibrational (infrared) excitation of a dopant in a superfluid

No friction, only inertia



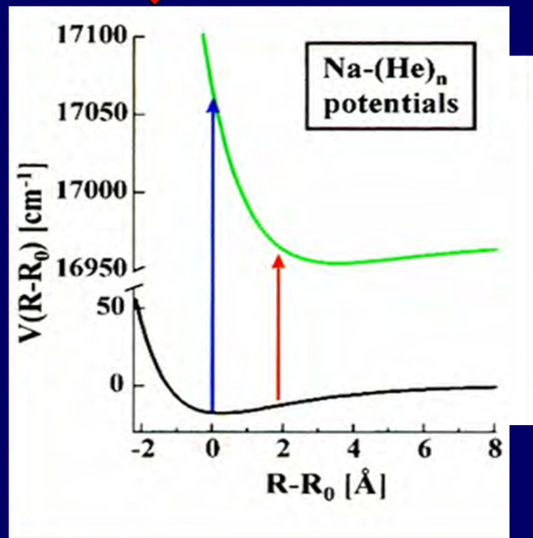


1 cm^{-1}

Grebenev, Toennies, Vilesov *(Science 1998)*

Electronic excitation (visible or UV) of a dopant

Electron repulsion by helium

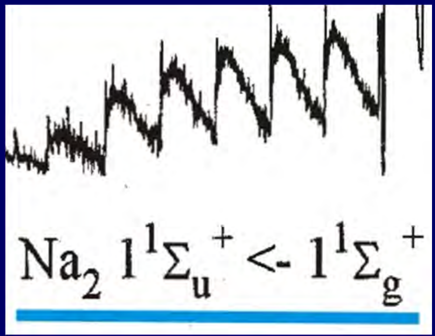


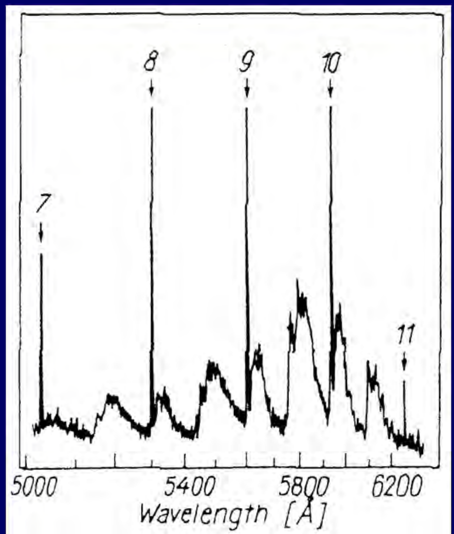
Broadened and blue-shifted

Details: C. Callegari and W. E. Ernst in: Handbook of High Resolution Spectroscopy, eds. F. Merkt and M. Quack, Wiley 2010

Superfluid helium droplets as nanocryostat

Spectroscopic linewidths?

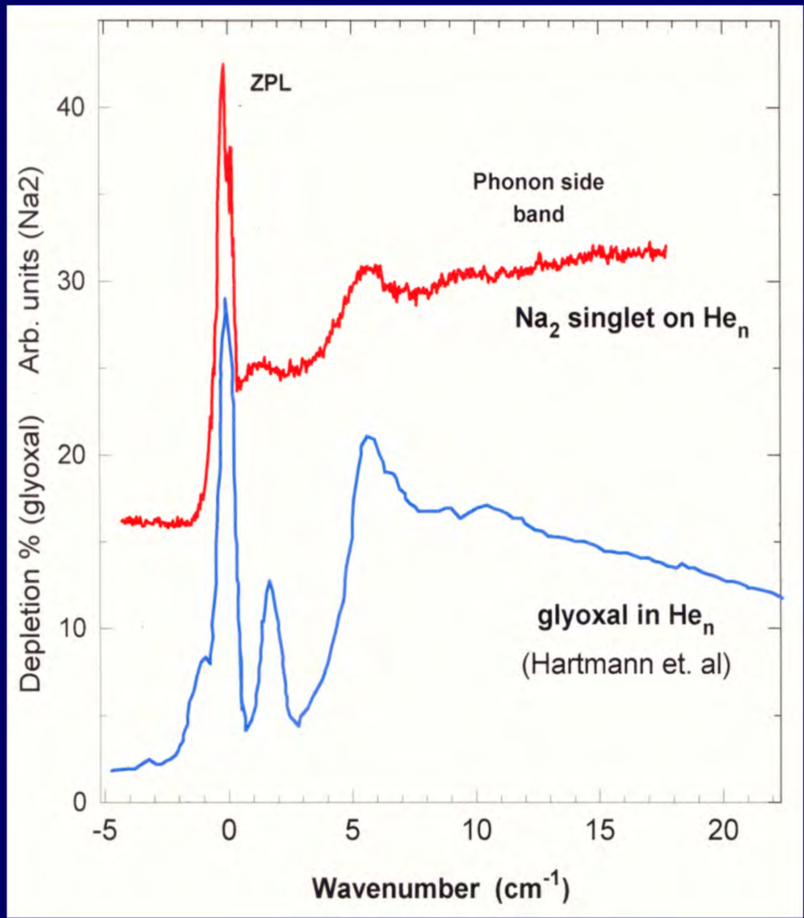




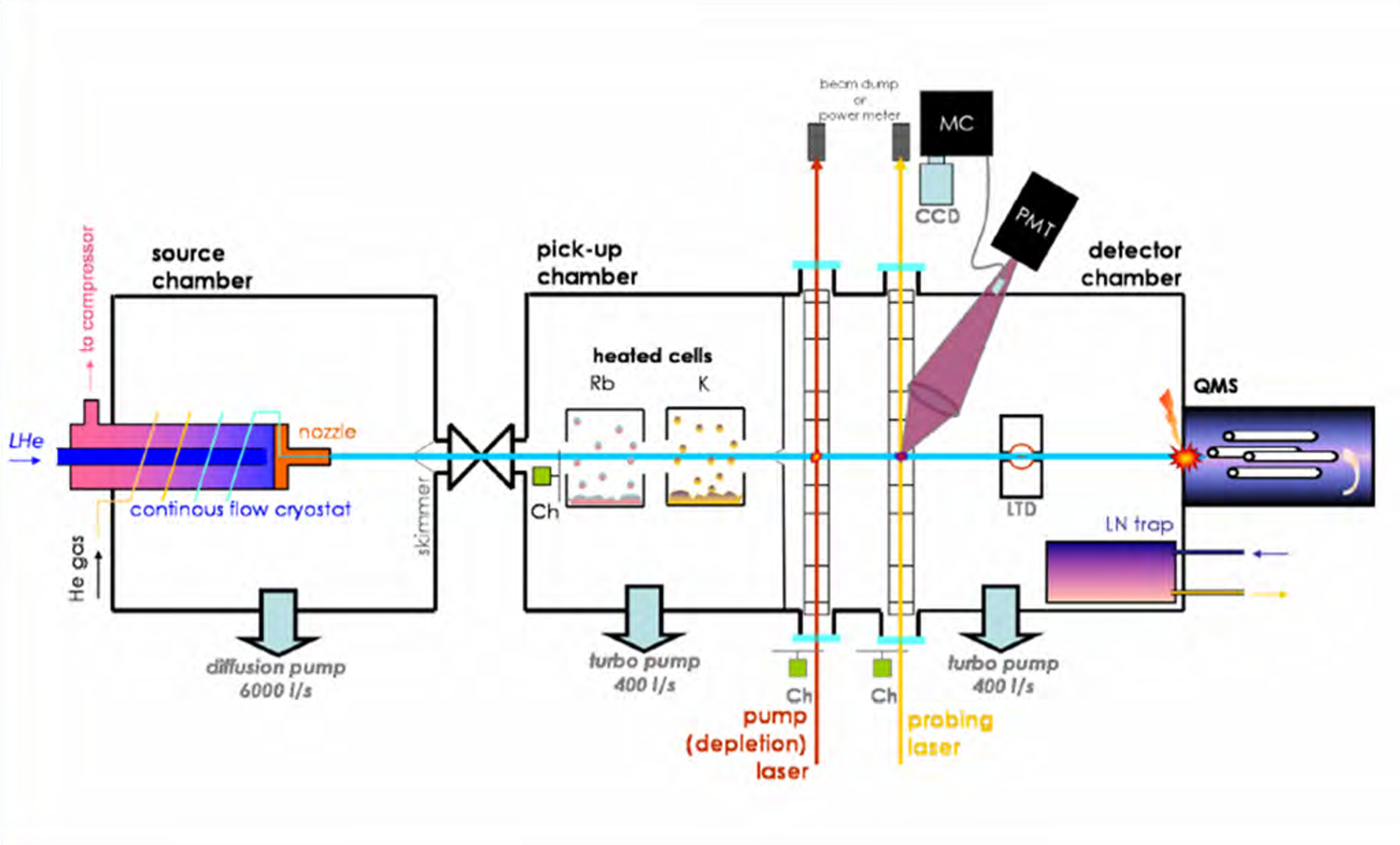
$KCl:O_2^-$ luminescence spectrum at 4.2K.

From: Freiberg & Rebane in „Zero-Phonon Lines"
(eds. Sild & Haller (Springer))

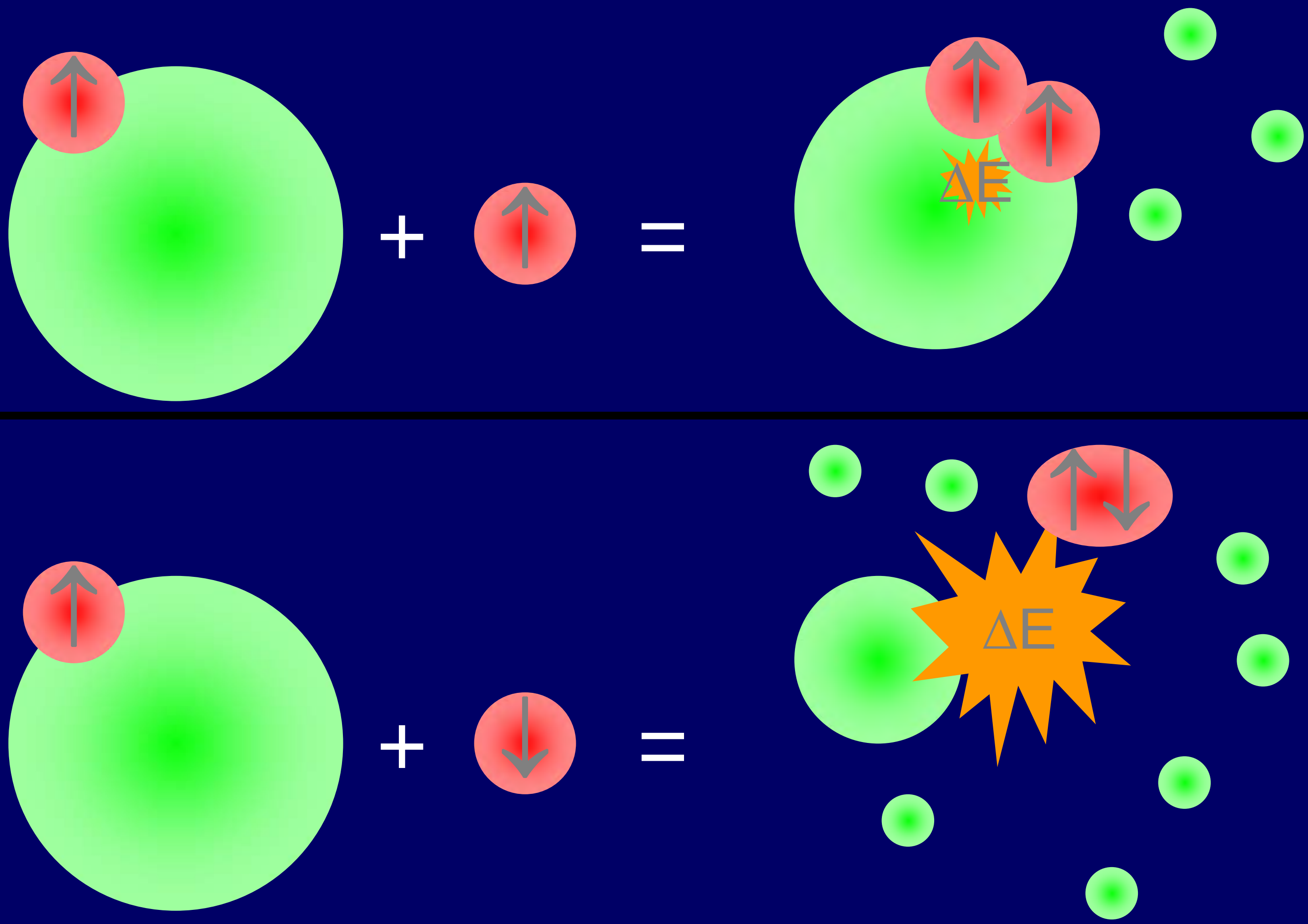
Comparison of LIF spectra of dopants on/in helium nanodroplets (Na_2 singlet vs. glyoxal):



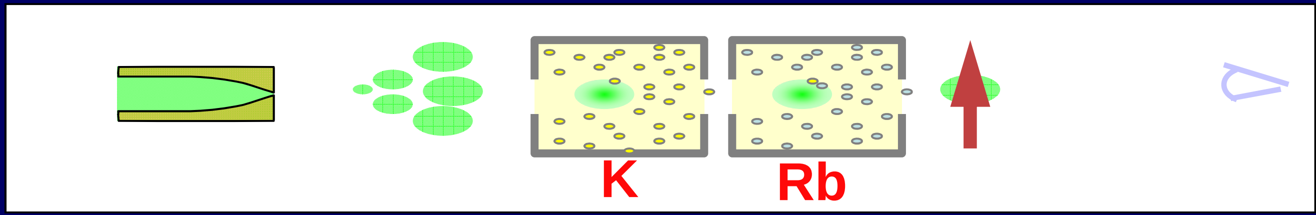
Experiment


beam dump
or
power meter
MC
CCD
PMT
source
chamber
to compressor
pick-up
chamber
detector
chamber
heated cells
Rb
K
QMS
LHe
nozzle
continous flow cryostat
skimmer
Ch
LTD
LN trap
He gas
diffusion pump
6000 l/s
turbo pump
400 l/s
Ch
Ch
turbo pump
400 l/s
pump
(depletion)
laser
probing
laser

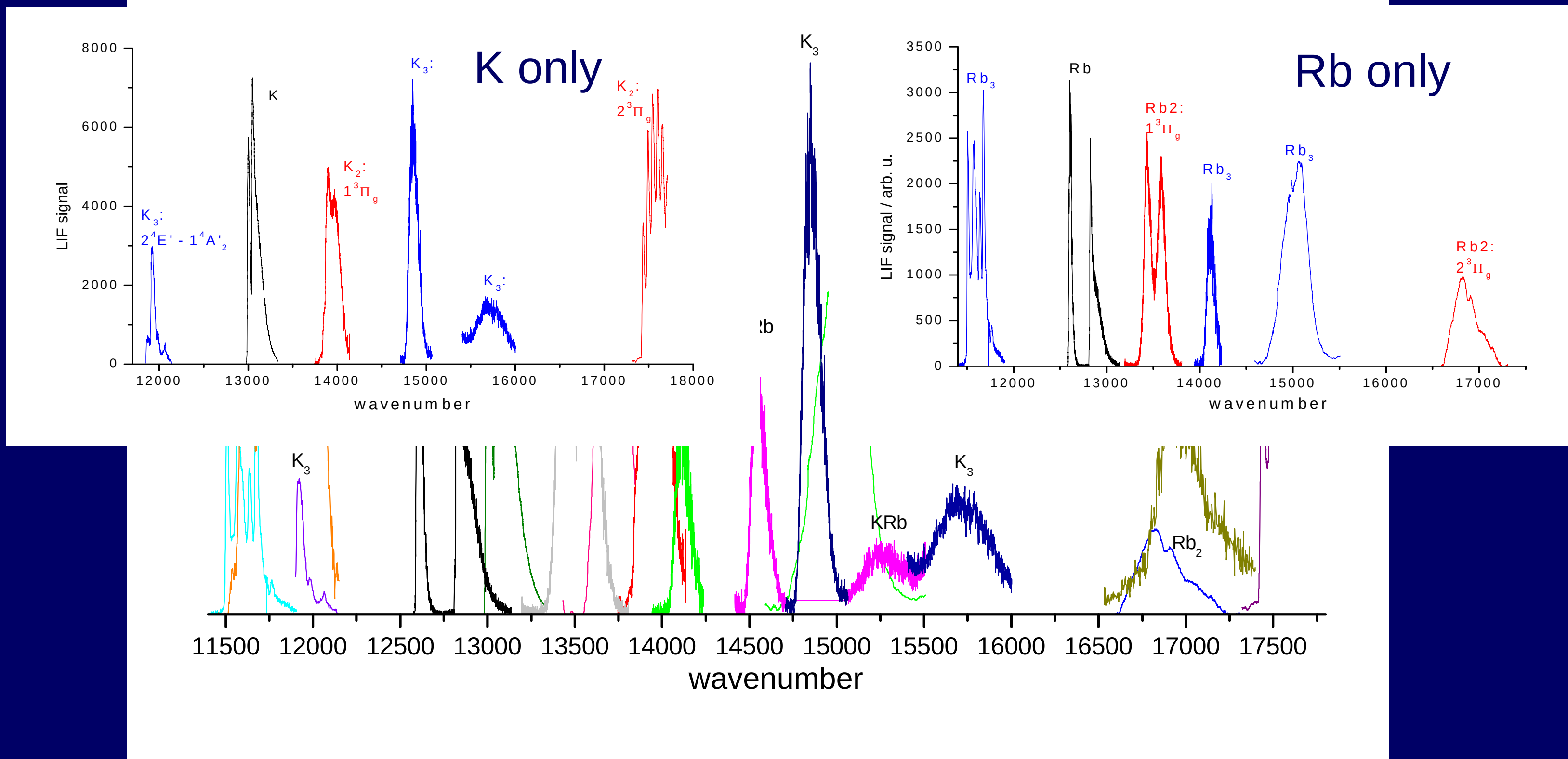
Alkali *n*-mers on He$_N$: High-spin selectivity



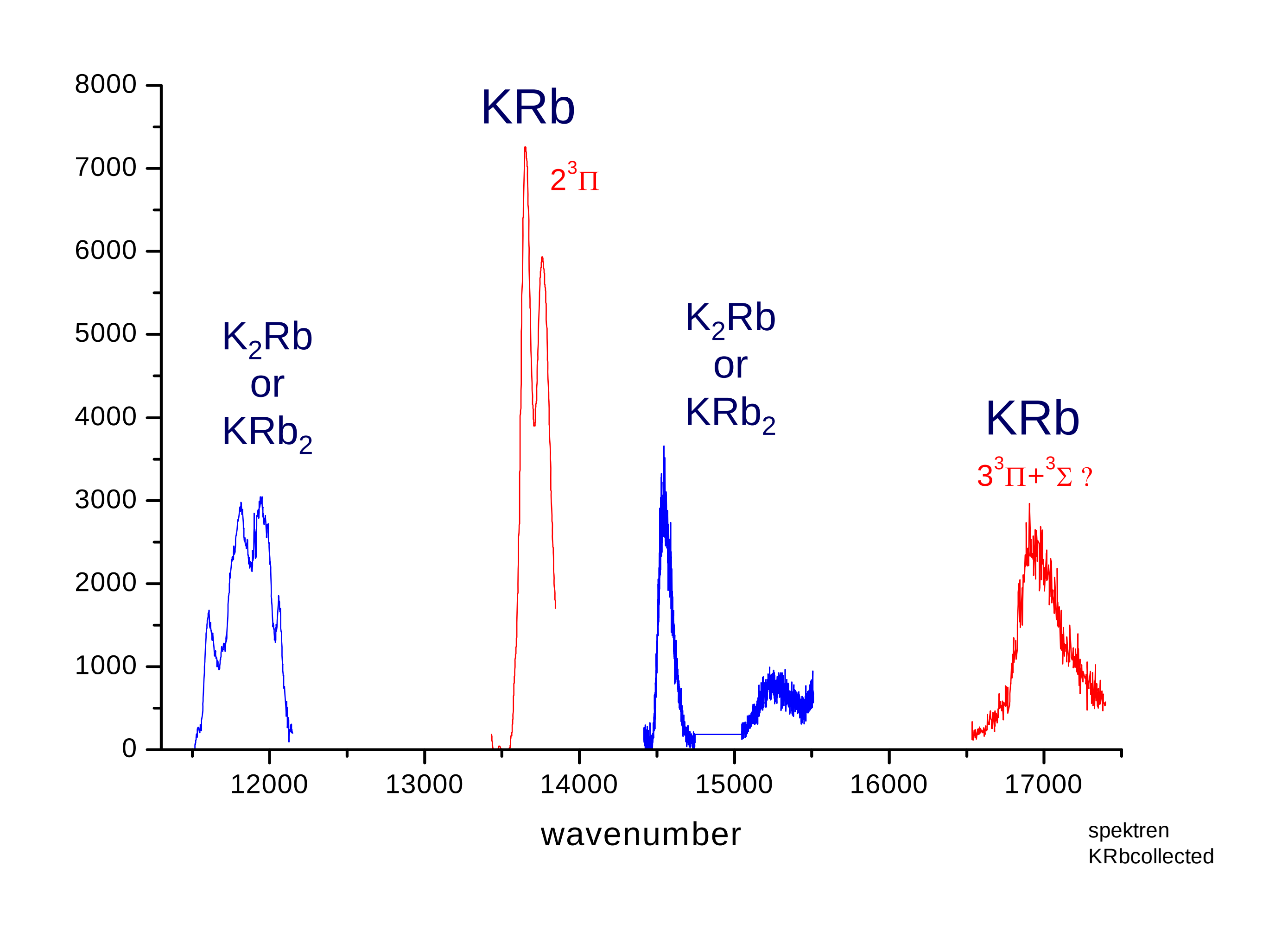
Homonuclear & heteronuclear alkali molecules



LIF spectra of K + Rb attached to He nanodroplets

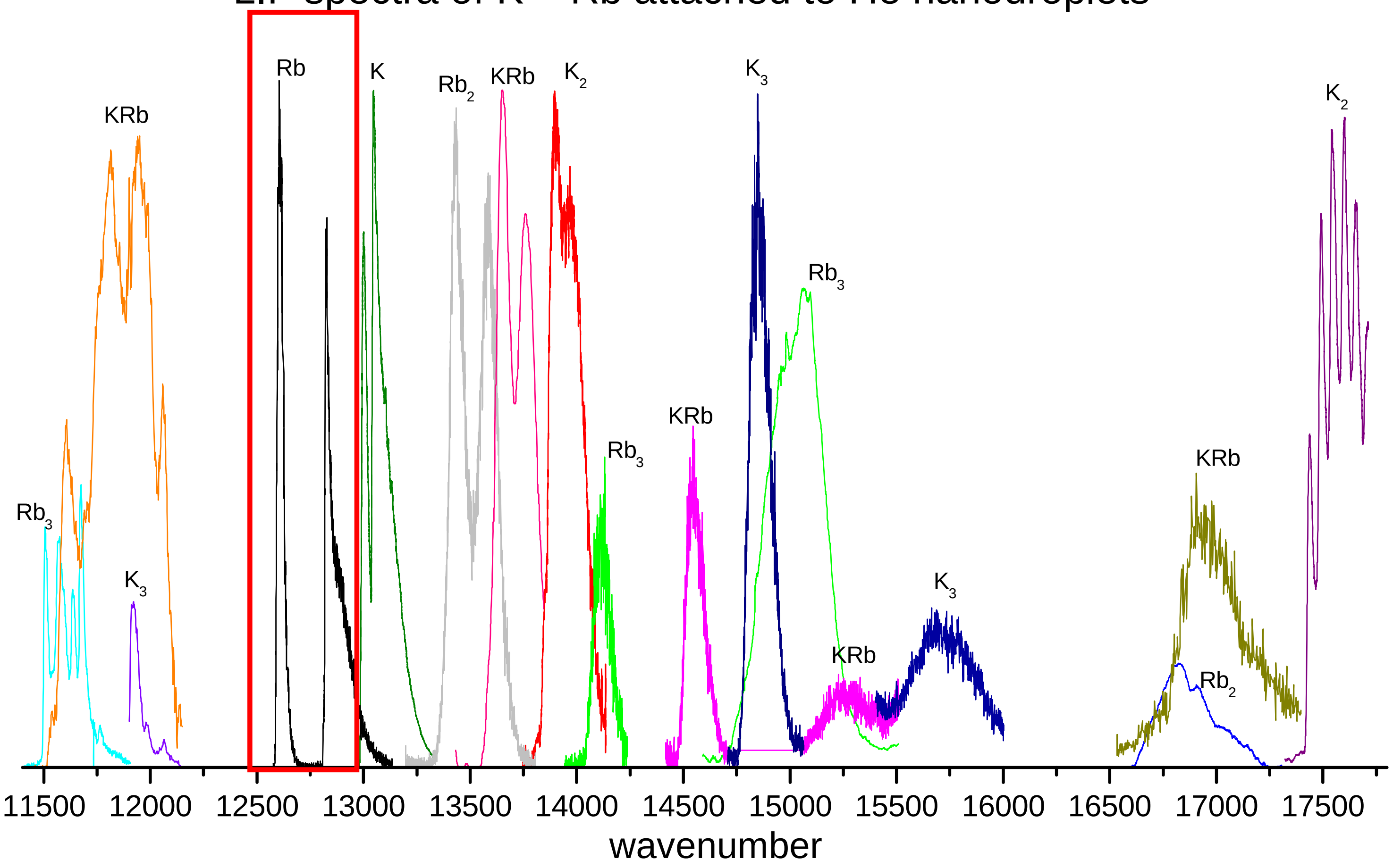


heteronuclear alkali molecules

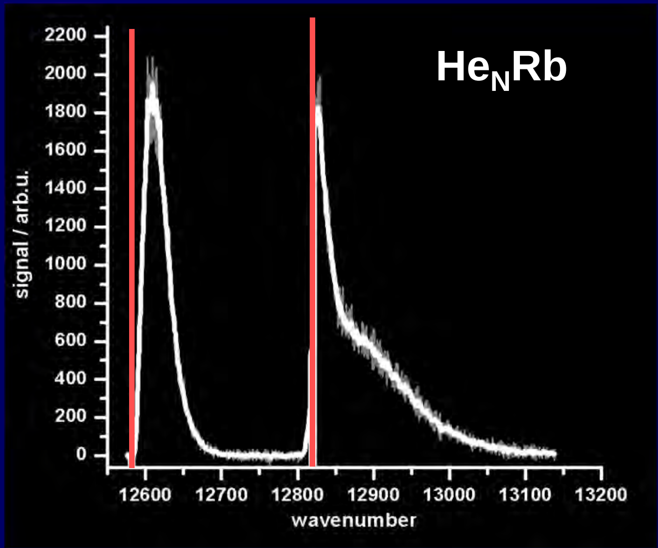


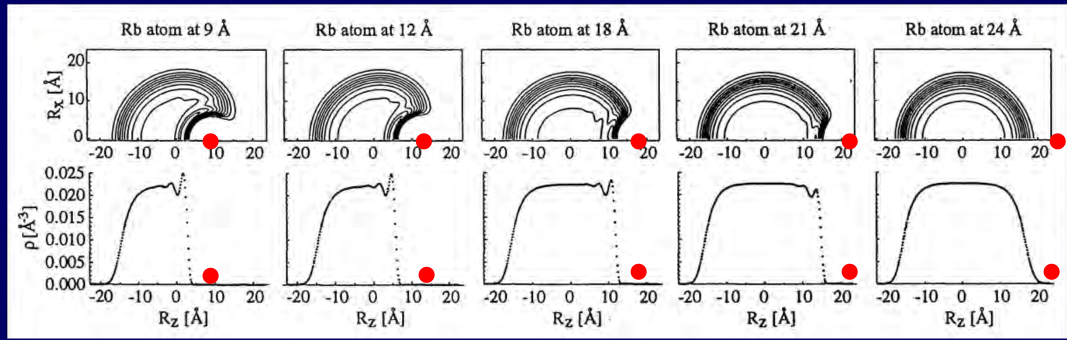
Johann Nagl and Carlo Callegari

LIF spectra of K + Rb attached to He nanodroplets

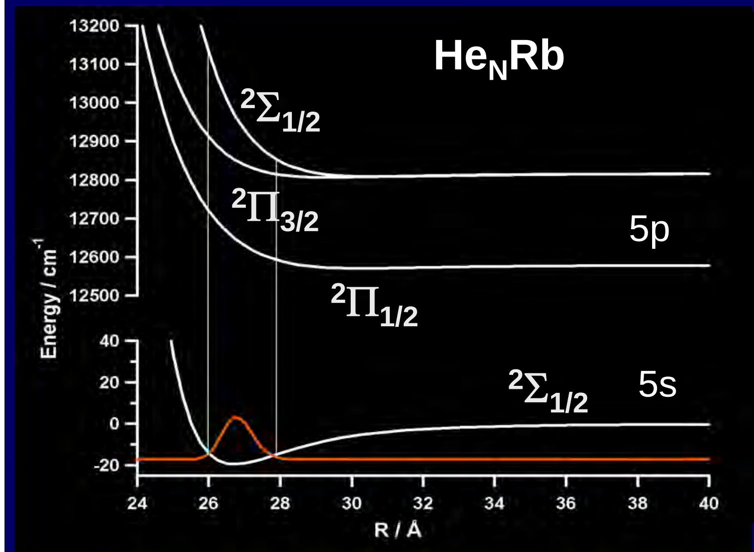


Alkali-He_N pseudo diatomic: atomic excitation ns-np

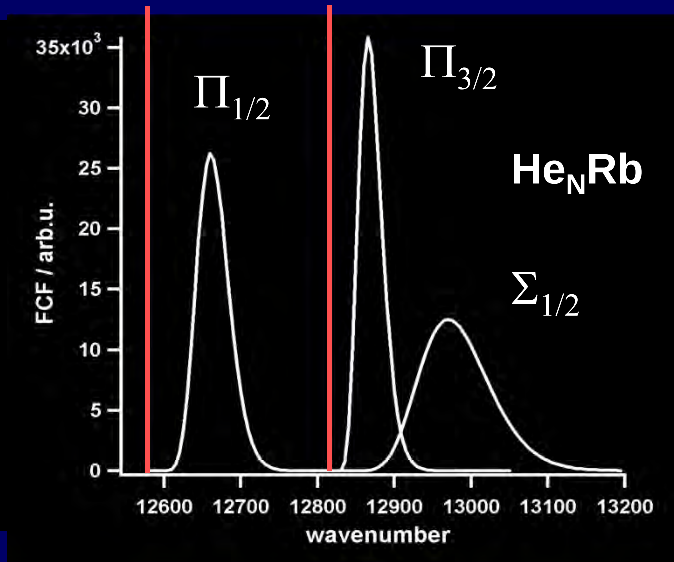




Rb 5s on He_N surface,
DFT calculation (help by F. Toigo) in:
Brühl, Trasca, Ernst JCP 115, 10220 (2001)

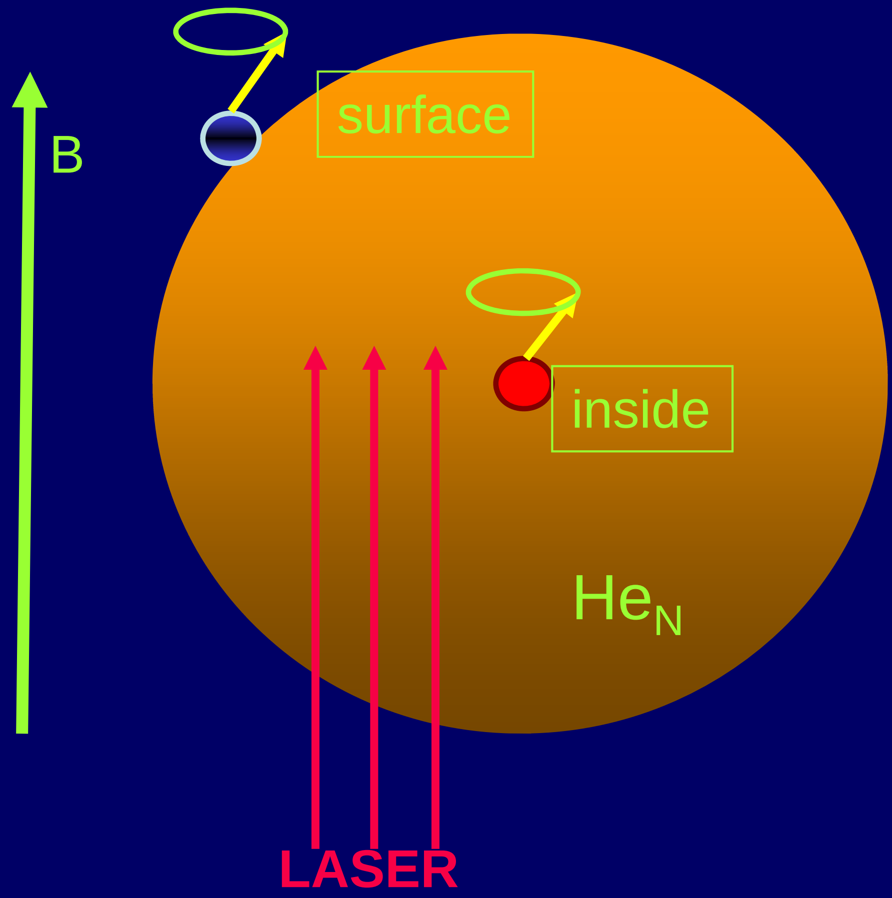


Treat He droplet as a giant
closed-shell atom
Calculate (vdW) molecular potential
by integrating vdW pair potentials
over He density
Approximate spectrum with F-C Factors



Key questions

Dopants with spin in external B-field



Carlo Callegari

Create spin precession:

Spin relaxation due to helium environment?

For atoms?

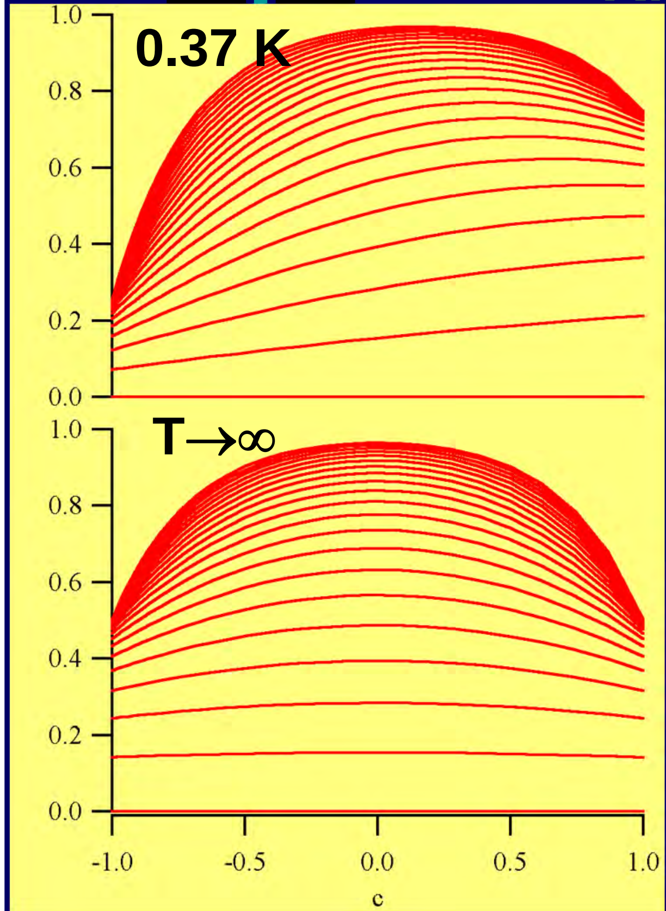
For molecules?

Related topic: helium buffer gas cooling of oriented atoms or molecules

Add magnetic field and exploit dichroism:

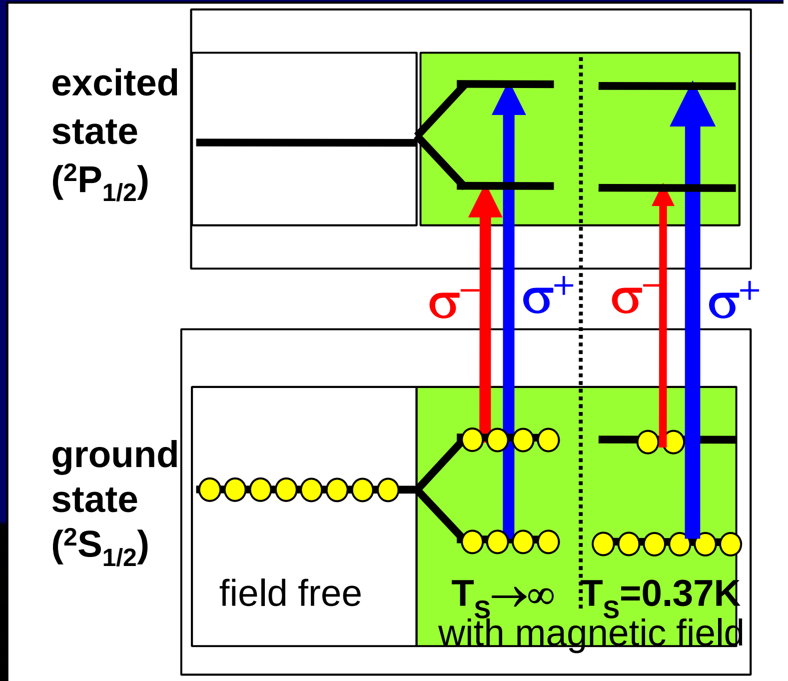
Spin temperature

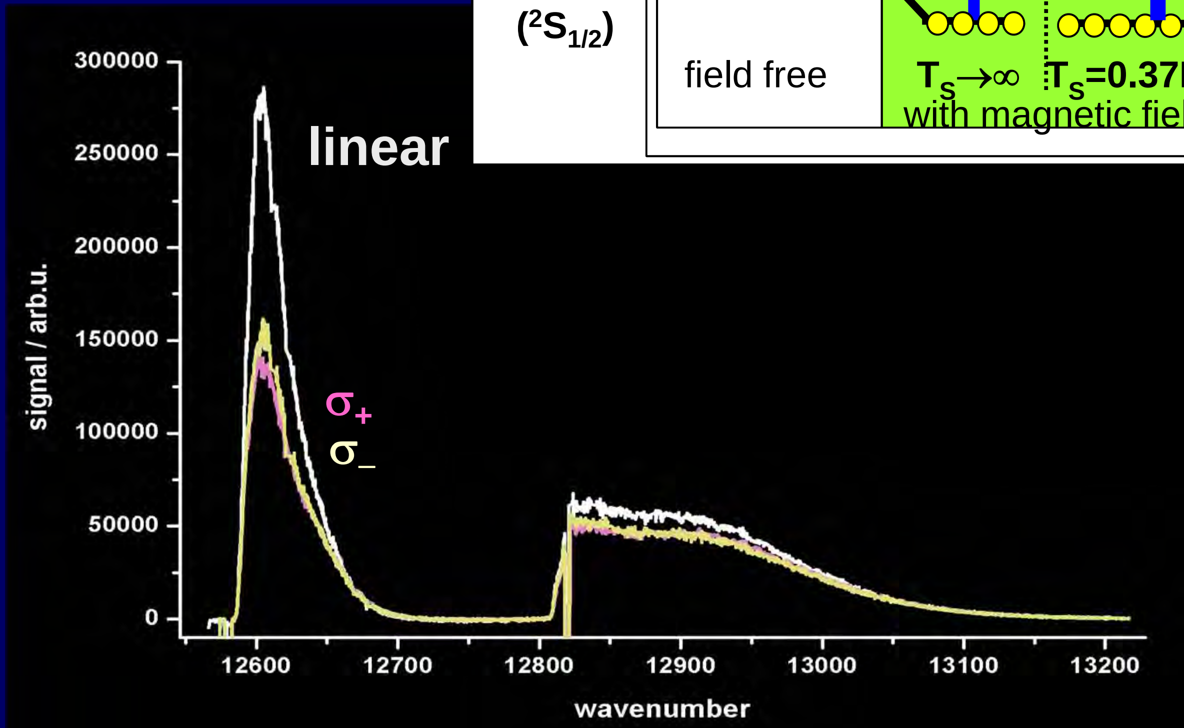
Rb 5s-5p



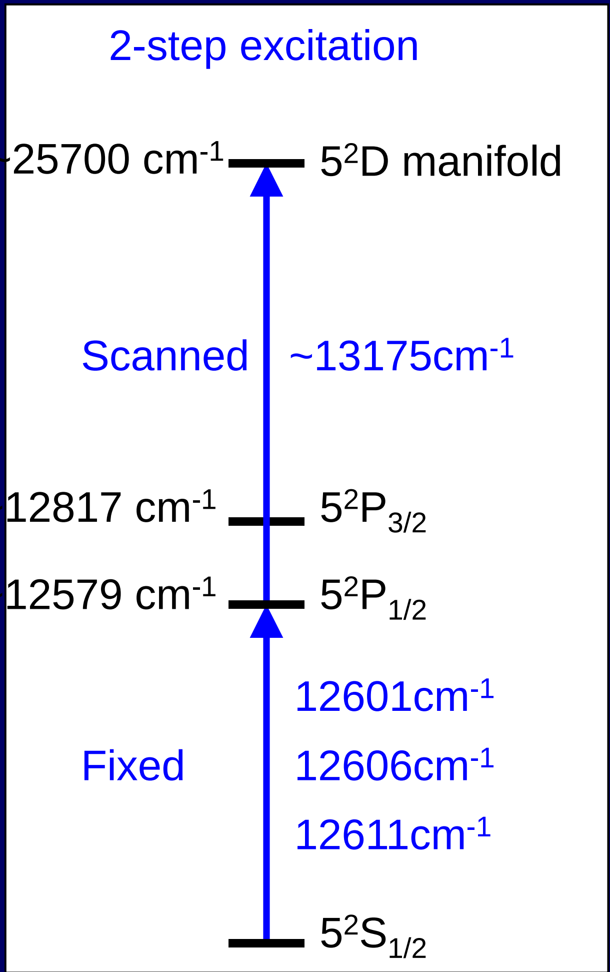
σ - ⟶ linear ⟶ σ +

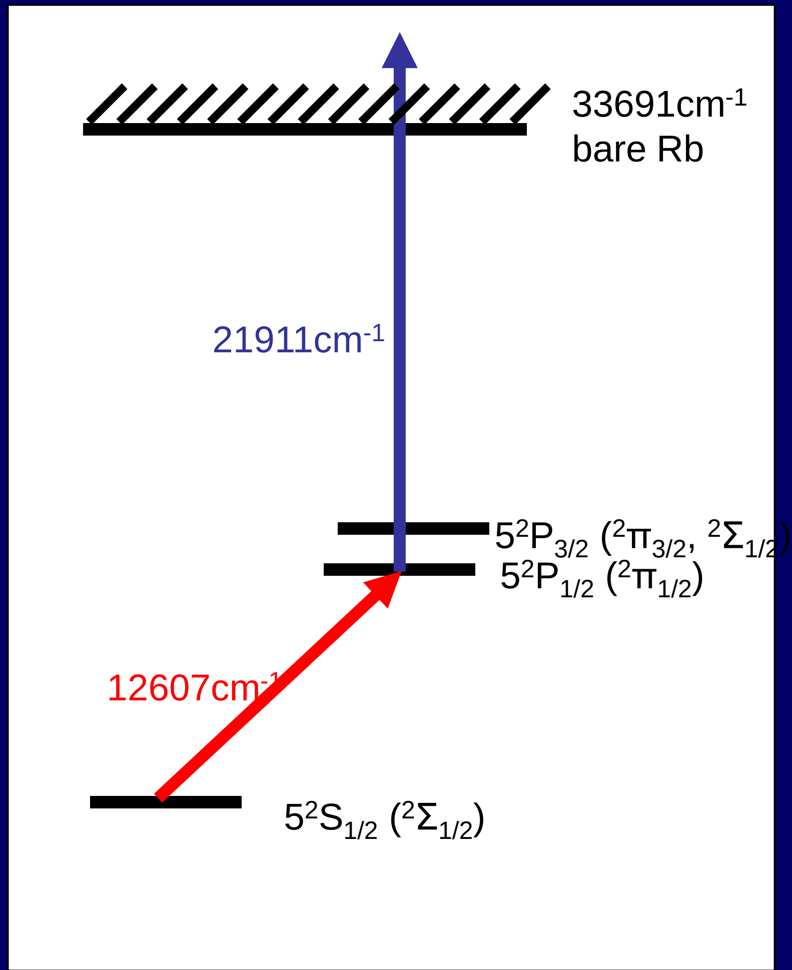
Phys. Rev. Lett. 98, 075301-1-4 (2007)



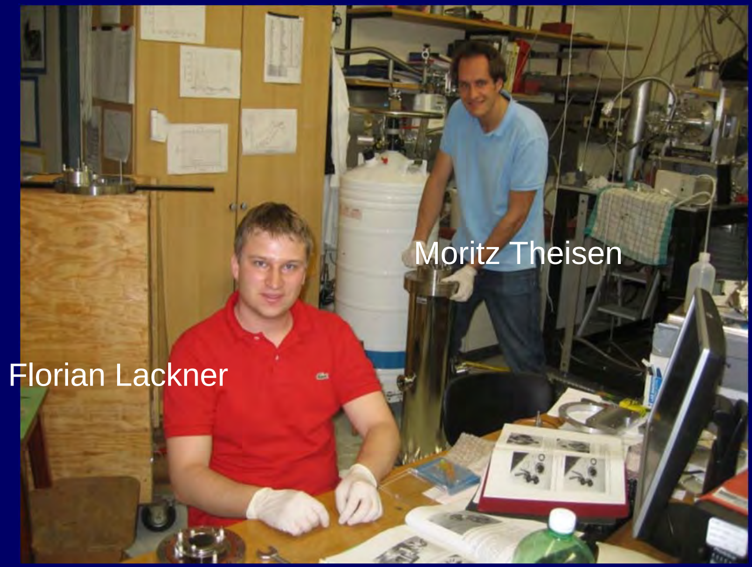


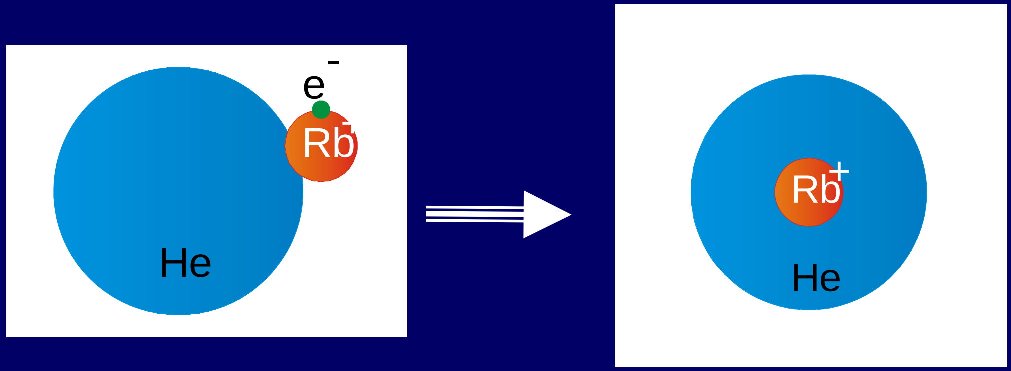
Highly excited states and ionization of atoms
For example: two step processes in He_N-Rb



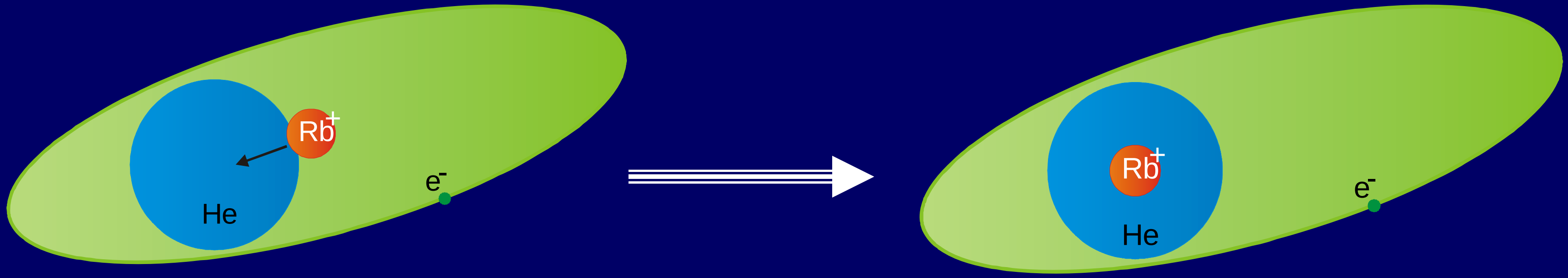


Moritz Theisen and Florian Lackner

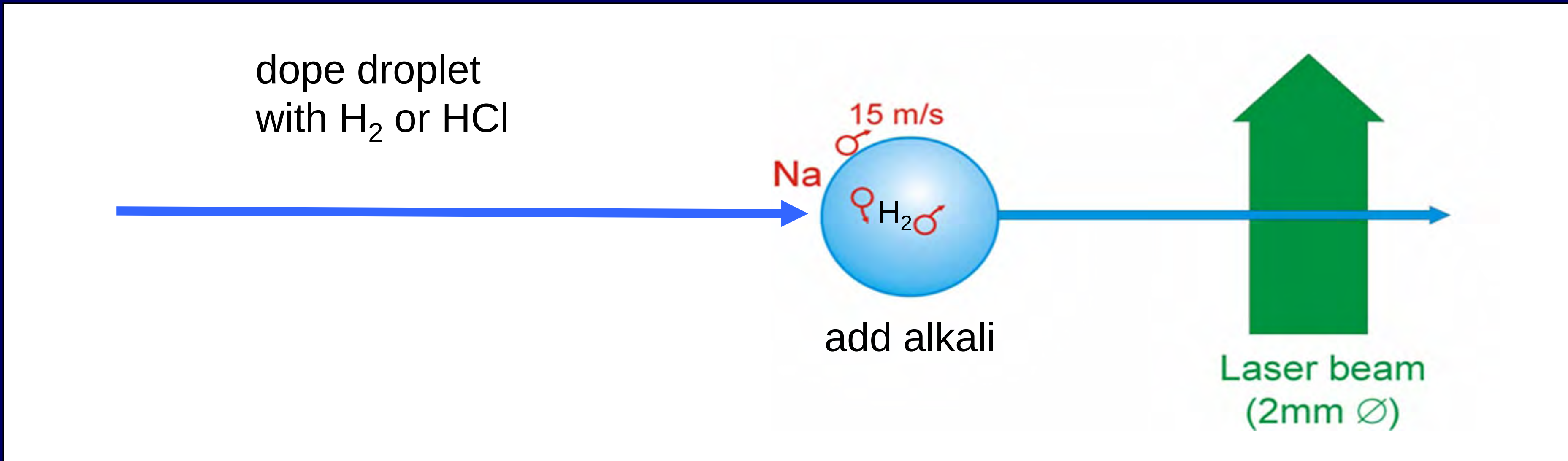




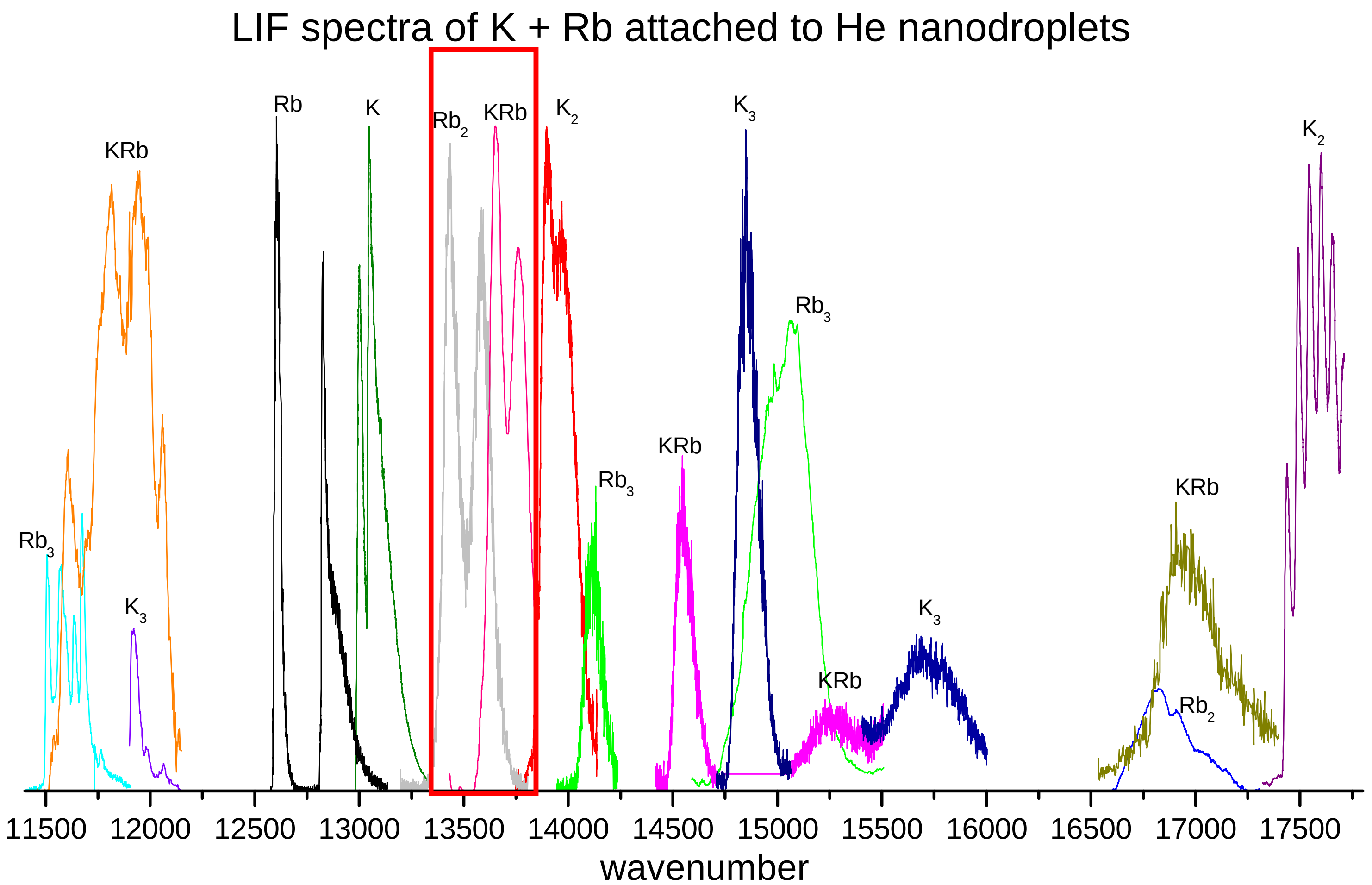
Goal: **High-lying Rydberg state**



Cold chemistry in confinement

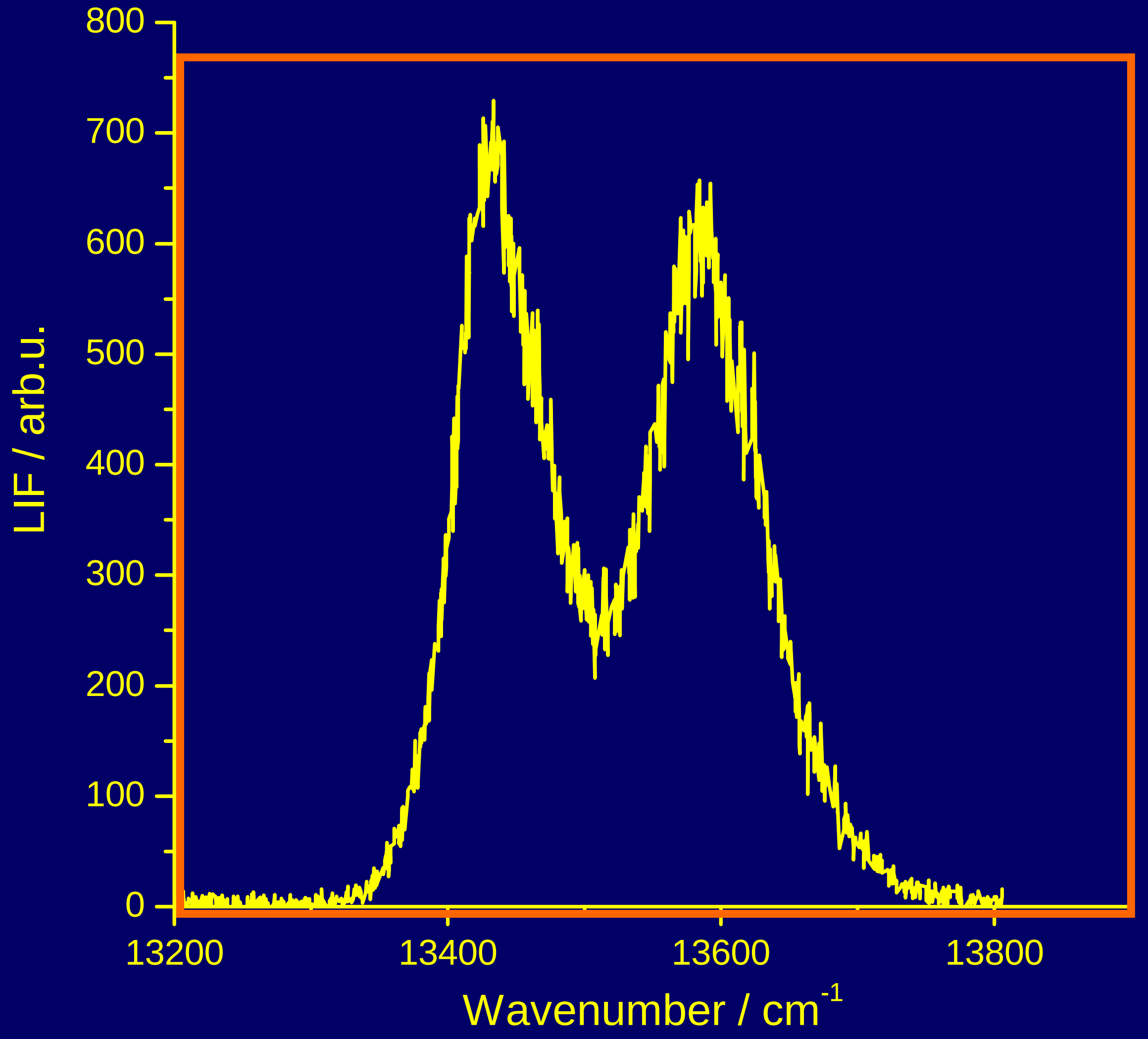


initiate reactions with laser excited atoms, e.g. Cs 7p + H_2



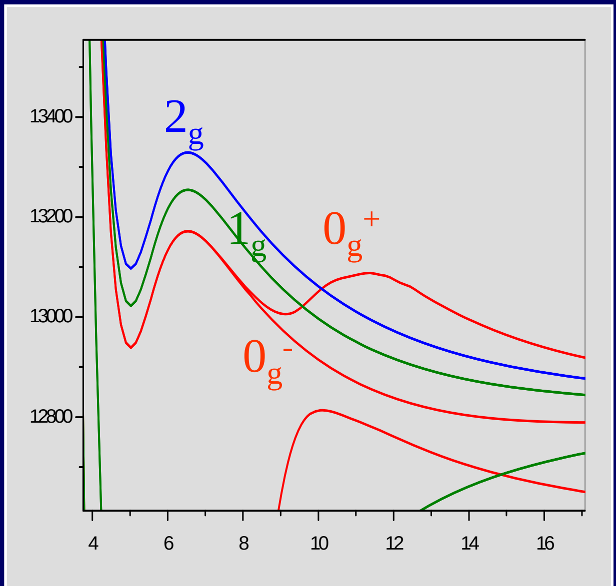
LIF spectra of K + Rb attached to He nanodroplets
Rb
K
Rb_2
KRb
K_2
K_3
KRb
Rb_3
K_3
Rb_3
KRb
Rb_3
KRb
K_3
KRb
Rb_2
K_2
11500
12000
12500
13000
13500
14000
14500
15000
15500
16000
16500
17000
17500
wavenumber

Rb on He nanodroplets: Rb_2 $1\ ^3\Pi_g \leftarrow 1\ ^3\Sigma_u^+$

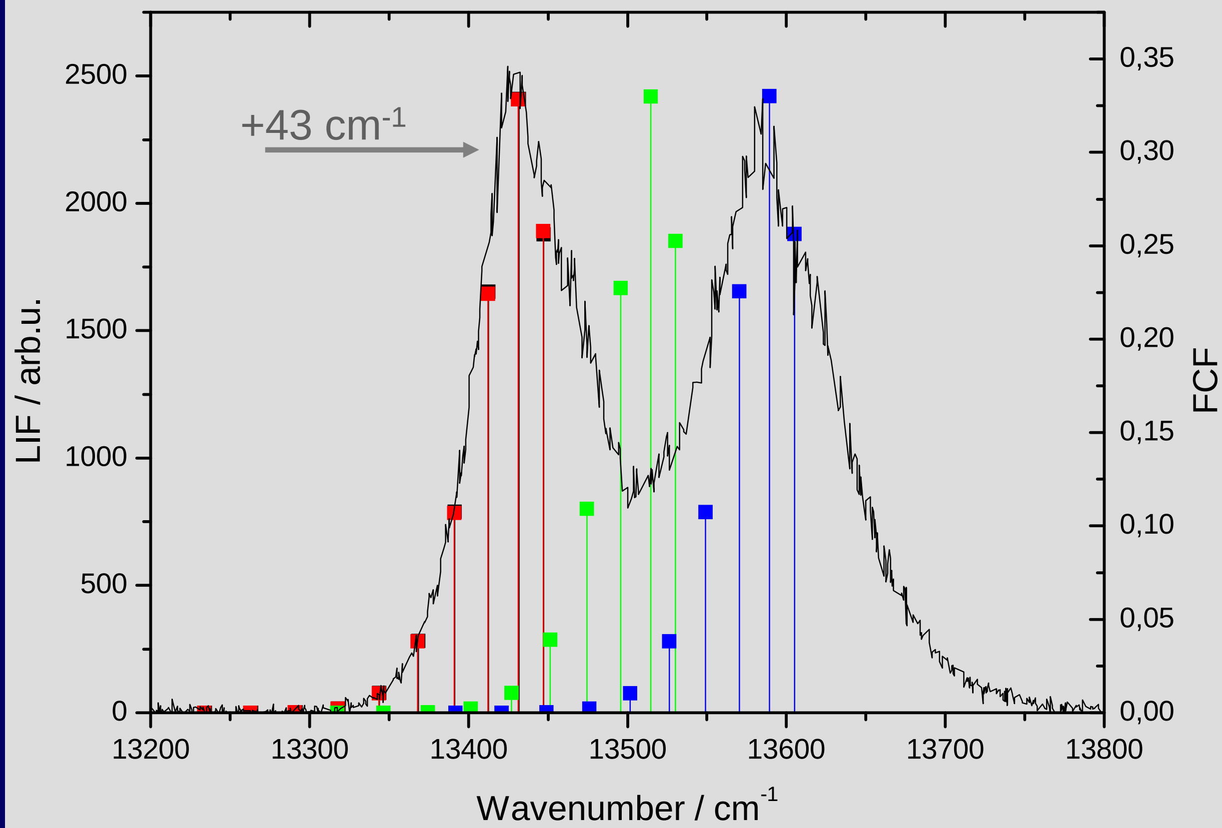


Comparison of Frank-Condon factors to LIF spectrum

ab-initio potential energy curves from O. Dulieu (Orsay)

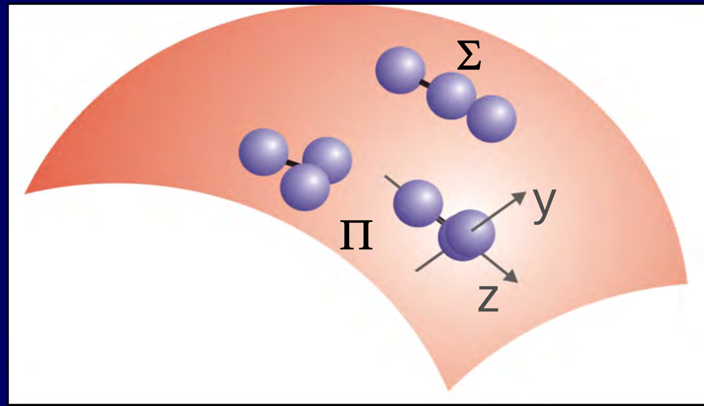


ground state: only v” = 0 populated
excited state v’=0–9 for each SO substate



Spin-orbit coupling: alkali $^3\Pi$ on helium

$$H = H_{mol} + H_d + H_{SO}$$



Basis: Eigenstates of H_{mol}
components of angular momenta along z: $|\Lambda\Sigma\rangle$
H_d interaction with helium
(determined by integrating alkali-He pair potentials (Pascale) weighted by the helium density distribution)

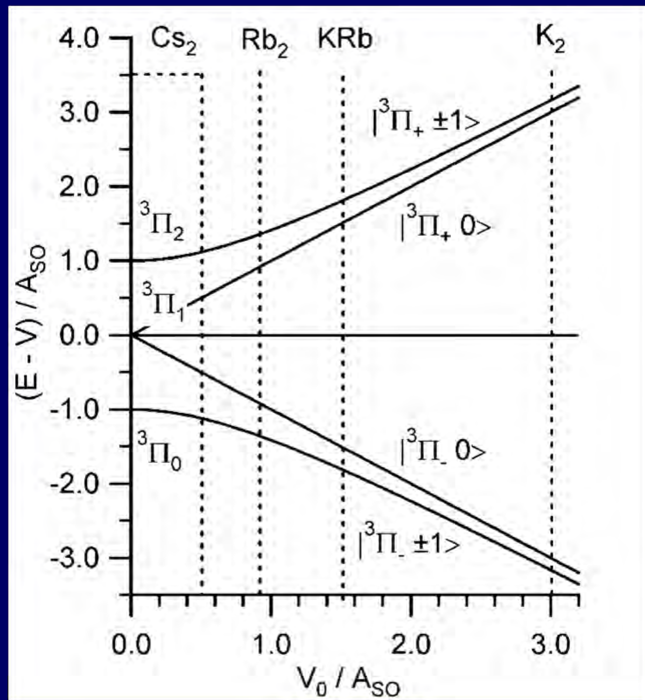
H_{SO}: Well known spin orbit Hamiltonian in $|\Lambda\Sigma\rangle$ basis (approximated R independent)

In general: 12x12 matrix

Gerald Auböck

Tendencies:
Cs_2 at left end,
others between
1 and 3 on horizontal scale

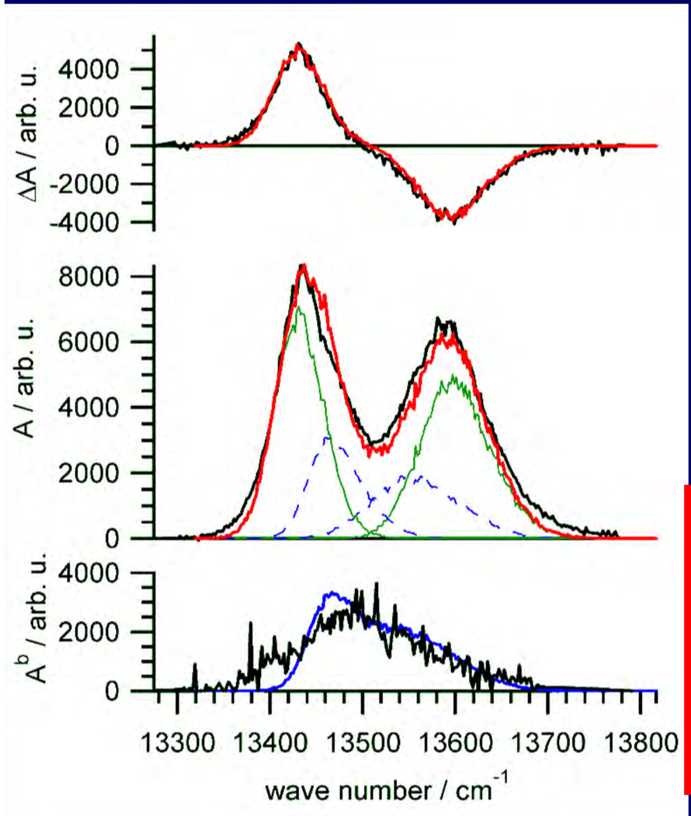
J. Phys. Chem. A111, 7404 (2007),
in memory of Roger Miller



Our model incl. Zeeman effect

(G. Auböck, J. Nagl, C. Callegari, and W.E. Ernst, J. Phys. Chem. A, 2007)

Rb_2: LIF, MCD with Simulation

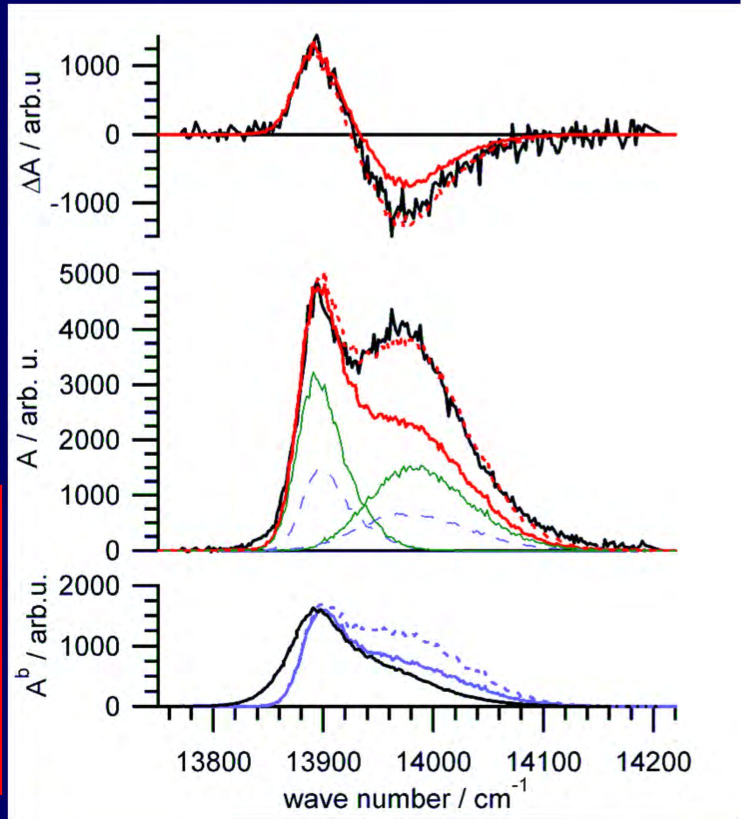


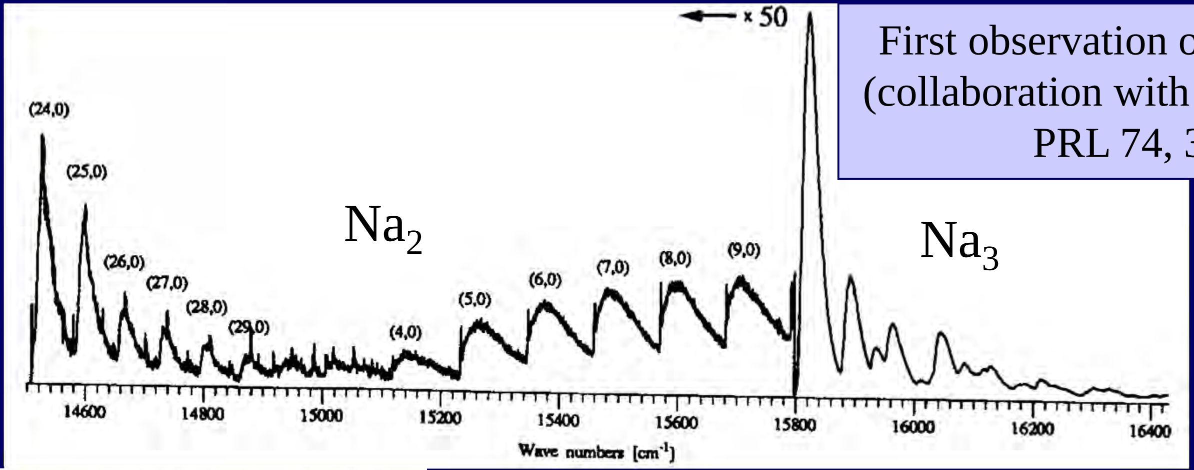
Zeeman populations correspond to 0.37 K temperature, i.e the same as inside the droplet.

τ<40μs

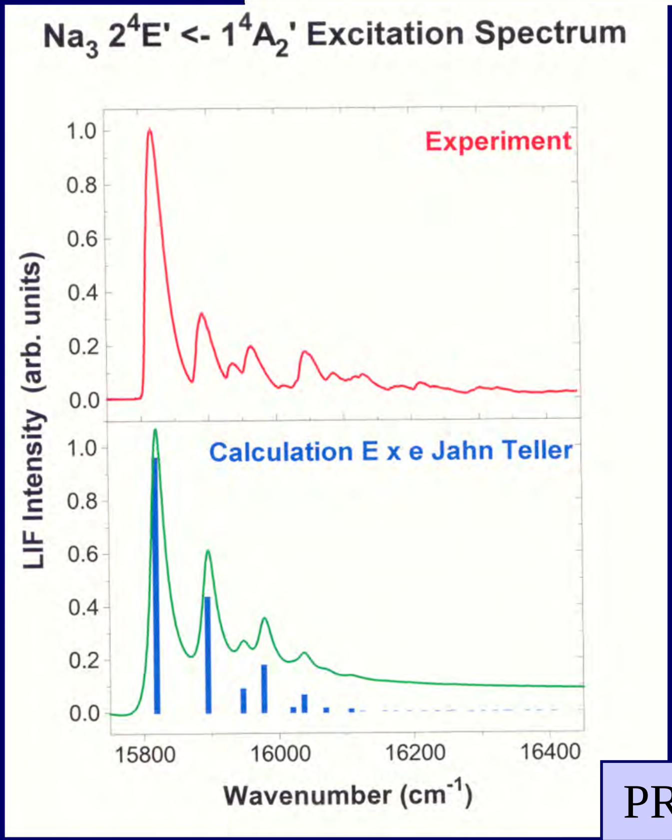
First measurement of the surface temperature of the droplet

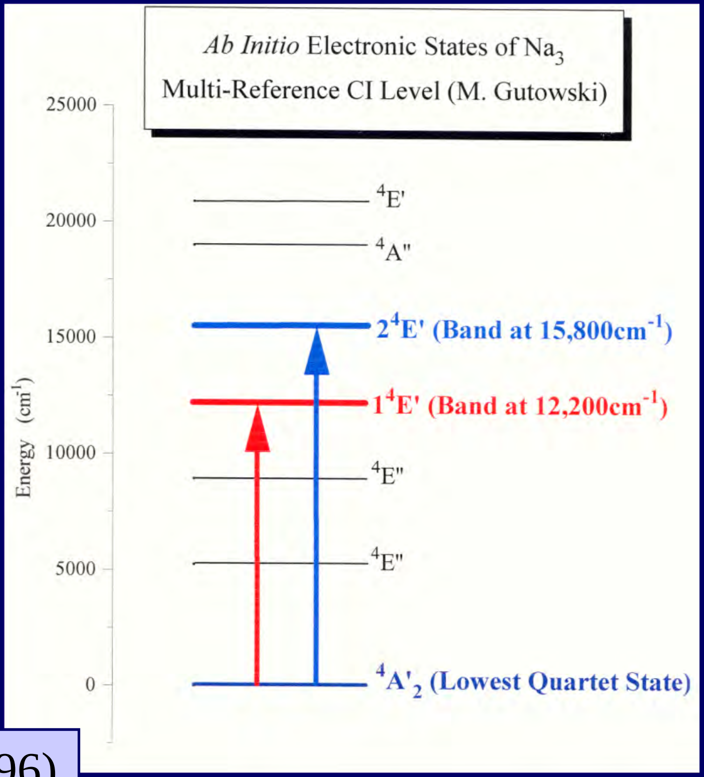
K_2: LIF, MCD with Simulation



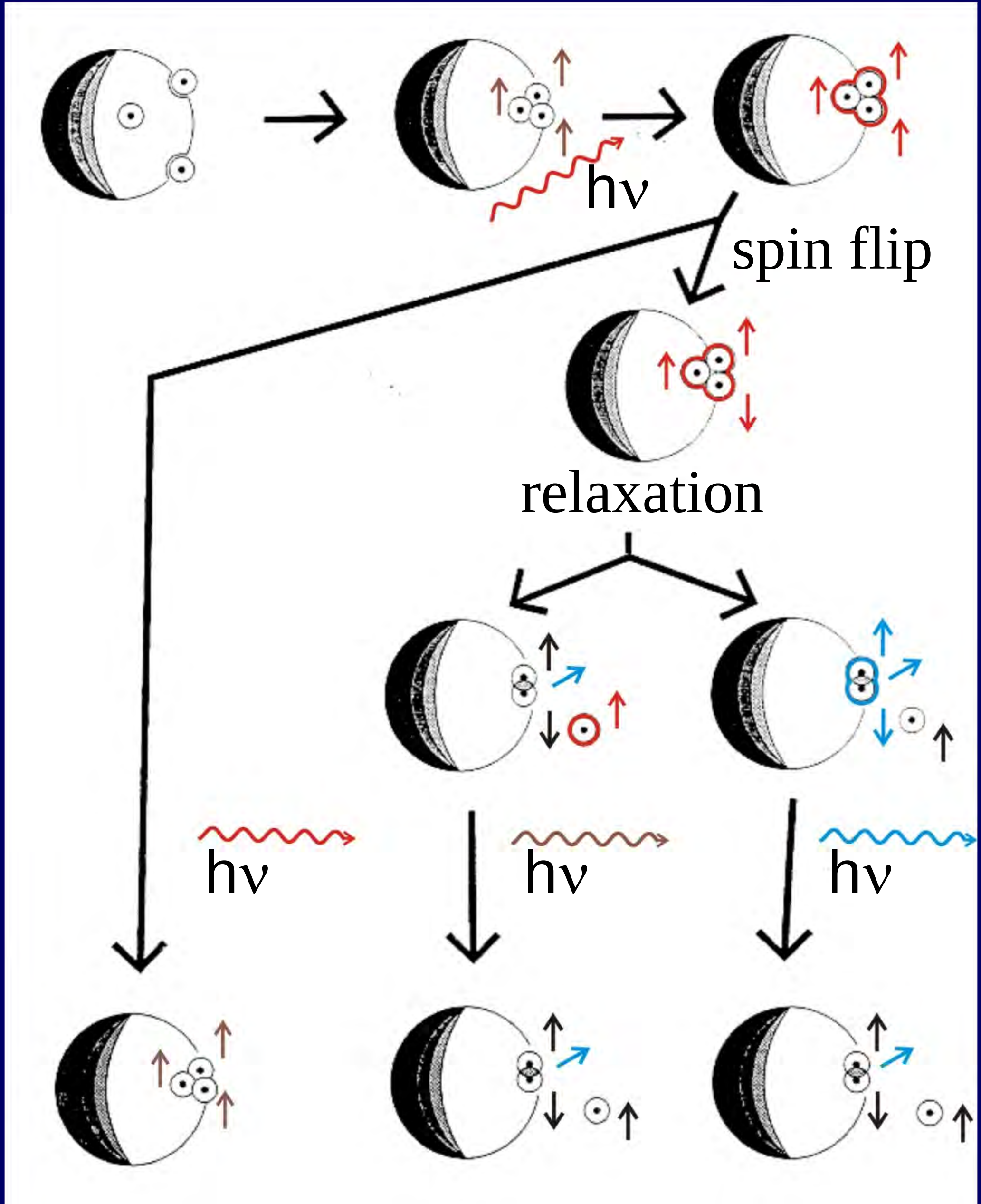


First observation of trimers on droplets
(collaboration with G. Scoles, Princeton)
PRL 74, 3592 (1995)





PRL 77,4532 (1996)



spinpolarized

trimer

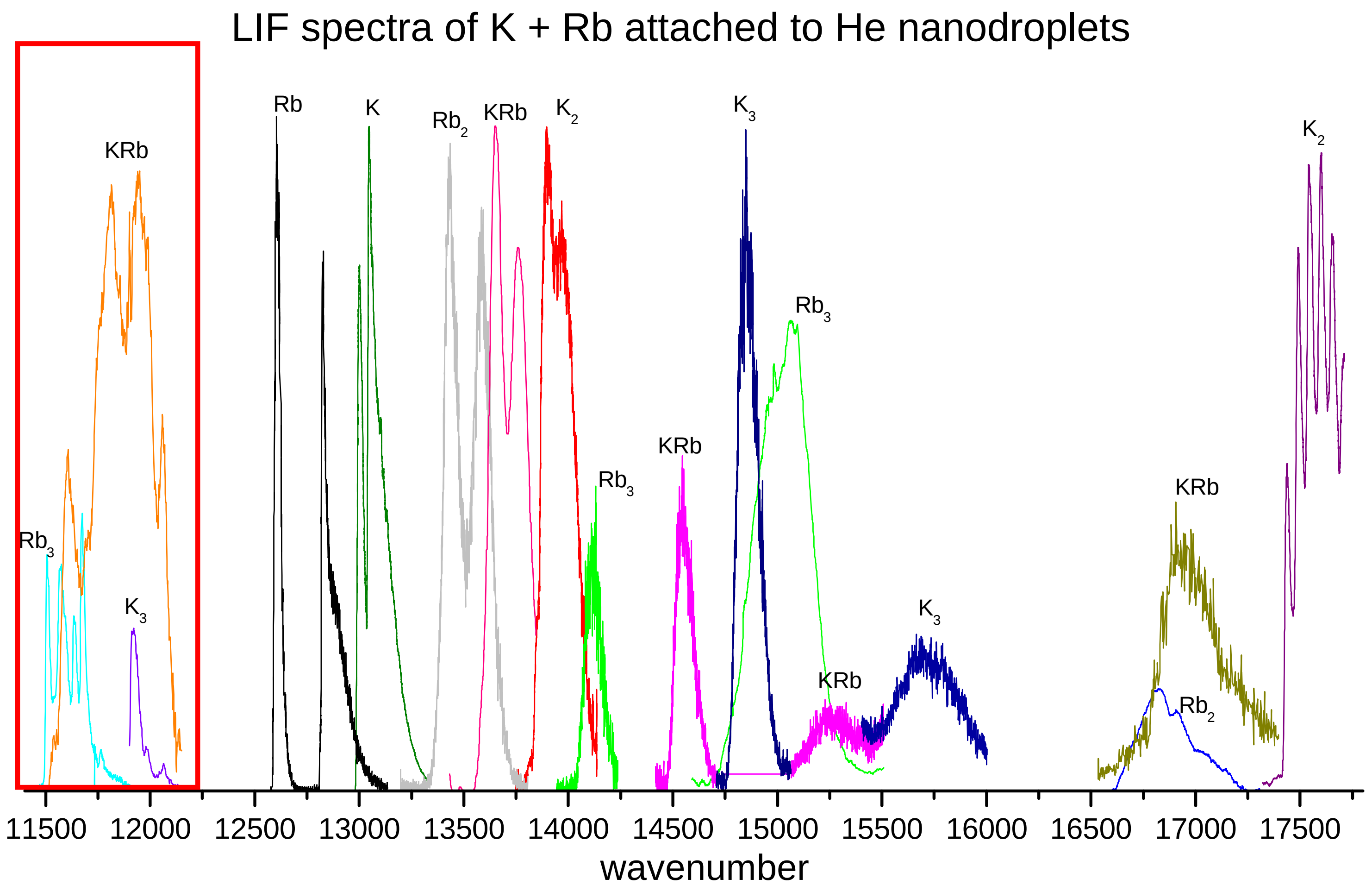
$E_{bind} \approx 850 cm^{-1}$

4.4 Å

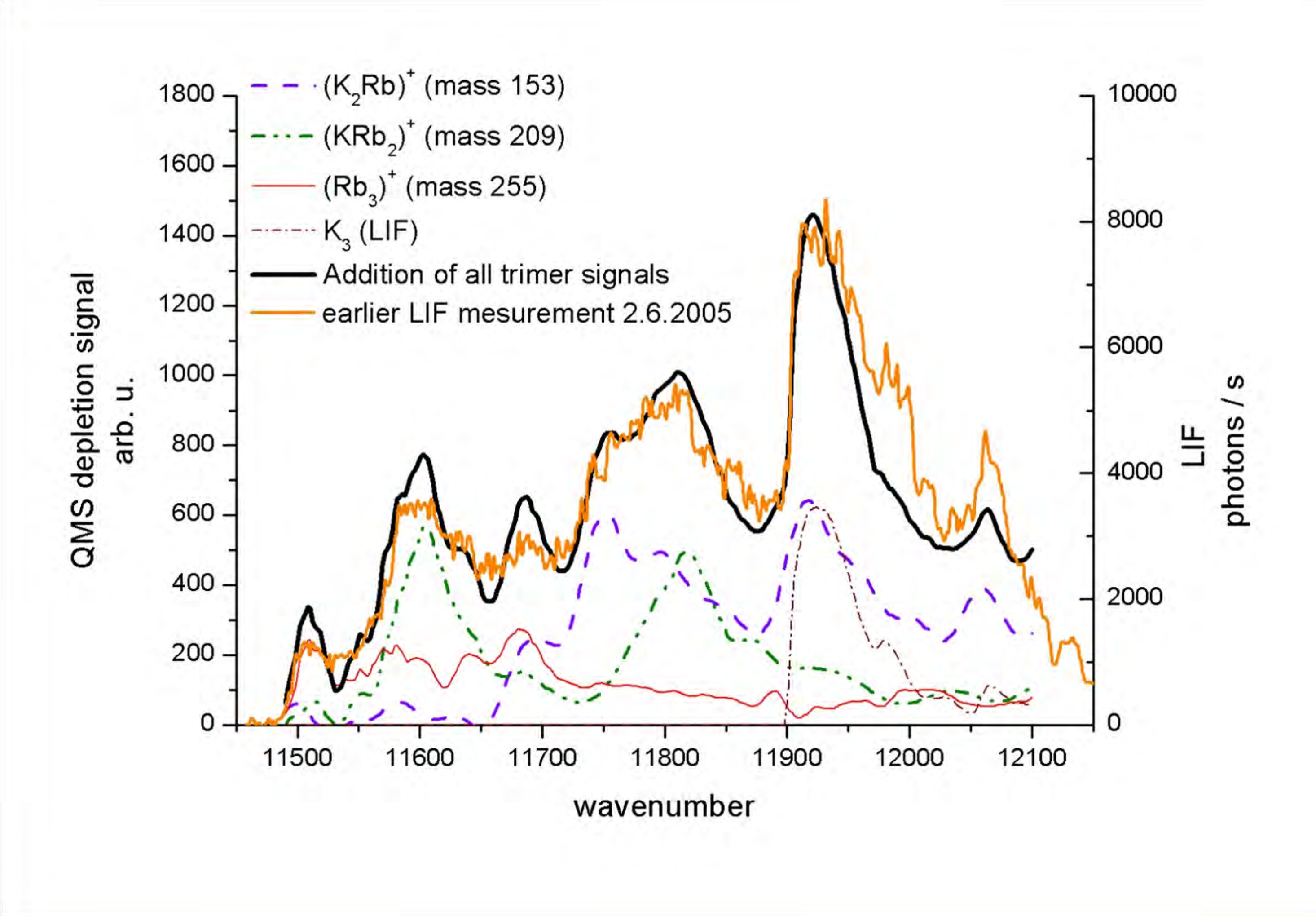
(~ 700 cm^{-1}
three-body int.)

Photoinduced
Spin Dynamics

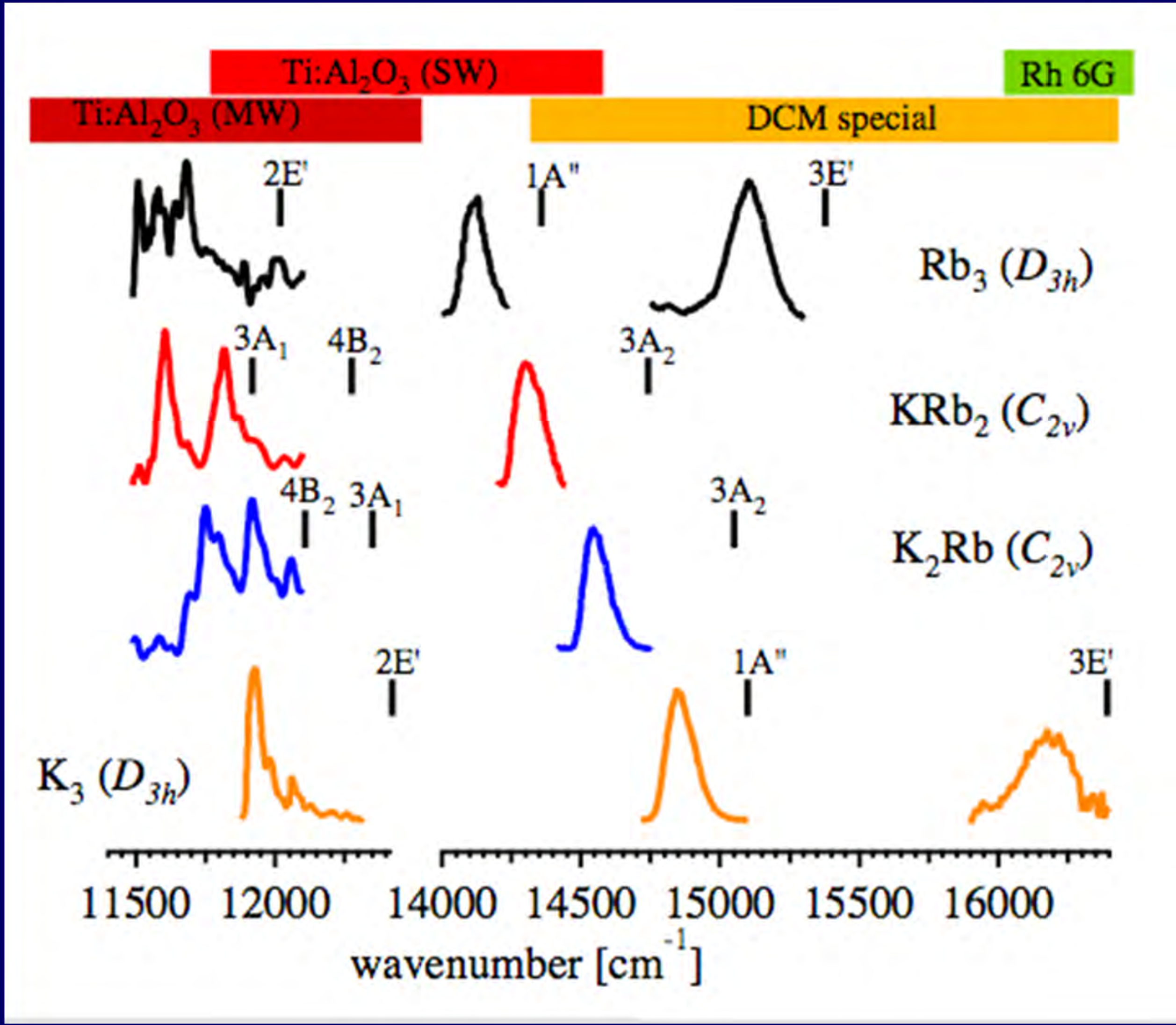
Science 273, 629 (1996)


LIF spectra of K + Rb attached to He nanodroplets
Rb
K
Rb2
KRb
K2
K3
K2
KRb
Rb3
Rb3
KRb
K3
KRb
K3
KRb
Rb2
Rb3
11500 12000 12500 13000 13500 14000 14500 15000 15500 16000 16500 17000 17500
wavenumber

Depletion spectra with mass selective detection
(use quadrupole mass spectrometer)



Alkali trimer quartet state excitations



(Phys. Rev. Lett. 100, 063001-1-4 (2008))

Calculations:

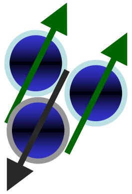
MOLPRO,
Complete Active Space
Self Consistent Field
(CASSCF) & CASPT2

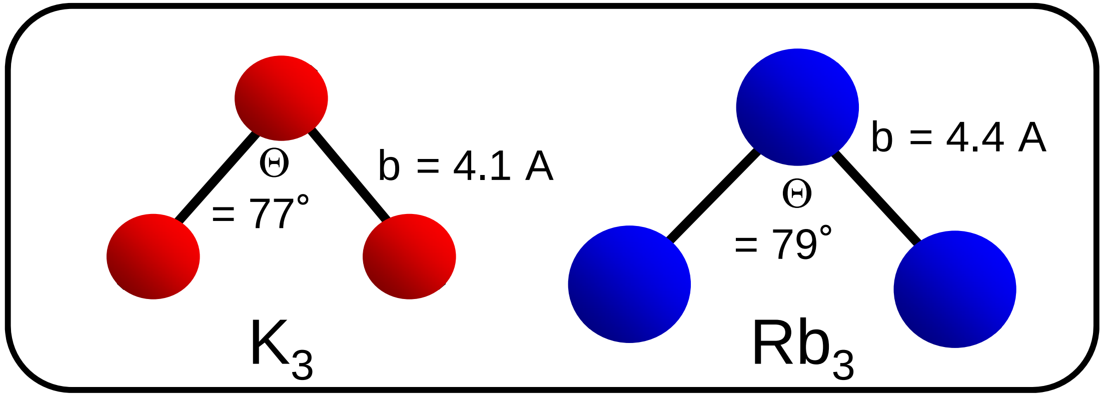
Andreas W. Hauser

Quartet trimers: Electronic structure

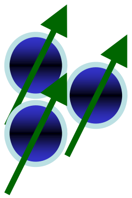
Homonuclear Alkali Trimers K_3 and Rb_3

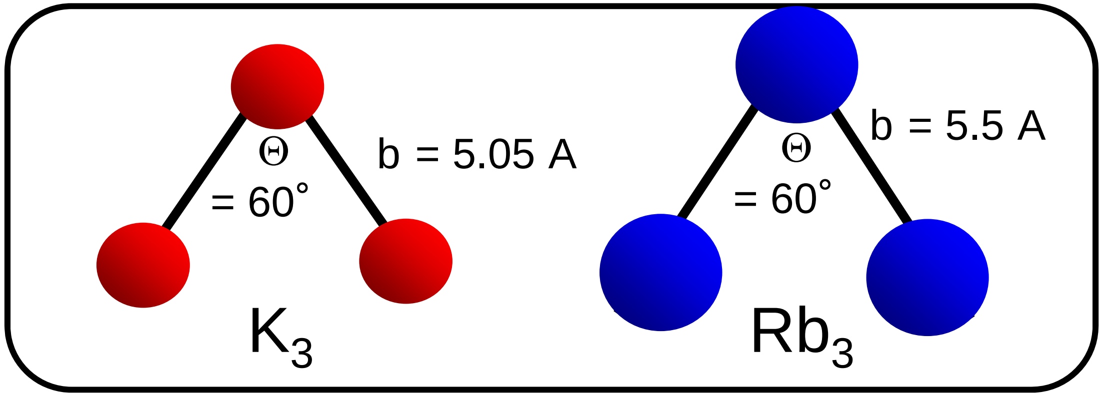
strongly bound
low-spin
$^2E'$ ground state



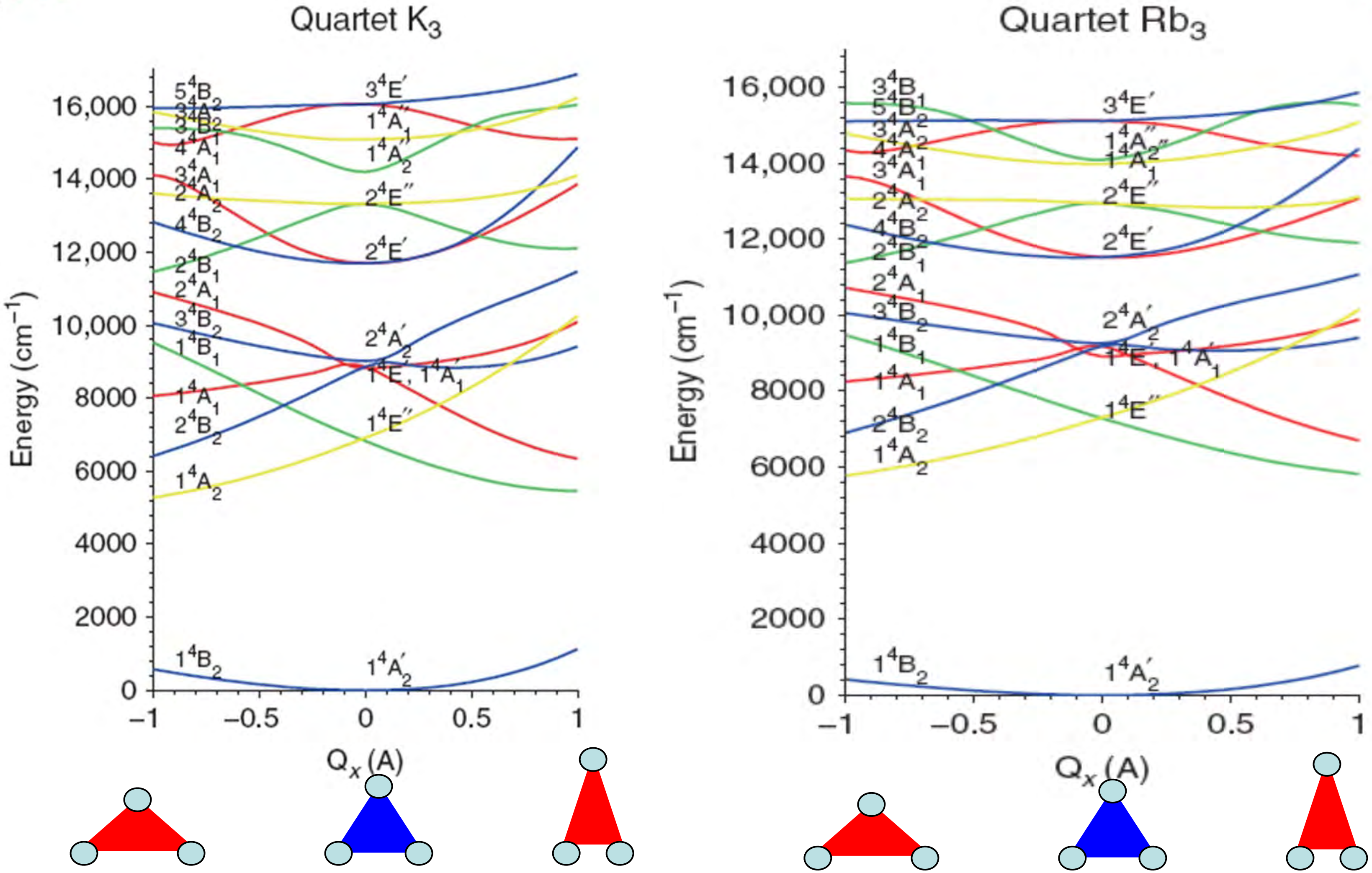


More weakly bound
(van der Waals) high-spin
$^4A_2'$ ground state





Geometry optimization at the RHF-CCSD(T) level of theory



Geometry optimization at the RHF-CCSD(T) level of theory

Introduction of normal coordinates

Scan over Qx coordinate

A shell model for the quartet states

A borrowed approximation: harmonic oscillator eigenfunctions

Does a single-electron approximation hold? ✓

Check CI vectors

yes, but not as good as for doublet

How localized are the MOs? ✓

Make density plots of canonical MOs

MOs are delocalized and show typical s,p,d character

Is the state pattern comparable to atomic s,p,d energies? ✗

No, it is more complicated

We observe a close similarity with the energy ordering of a harmonic oscillator

Fit MO energies with 5-parameter formula
including anharmonicity and cross terms

Compare the harmonic osci eigenenergies
with the observed bands of the ab inito calculation

This model offers a qualitative description of state energies

A shell model for the quartet states

Time-independend Schrödinger equation in N dimensions:

$$\left[-\frac{\hbar^2}{2m} \nabla_N^2 + V_N \right] \psi = E \psi$$

dimension !

Choose isotropic harmonic oscillator potential:

$$V(r) = \tfrac{1}{2} m \omega^2 r^2$$

Apply factorization method:

$$\psi = R_{n,L}^{(N)}(r) Y_L^M(\theta_i)$$

Solutions:

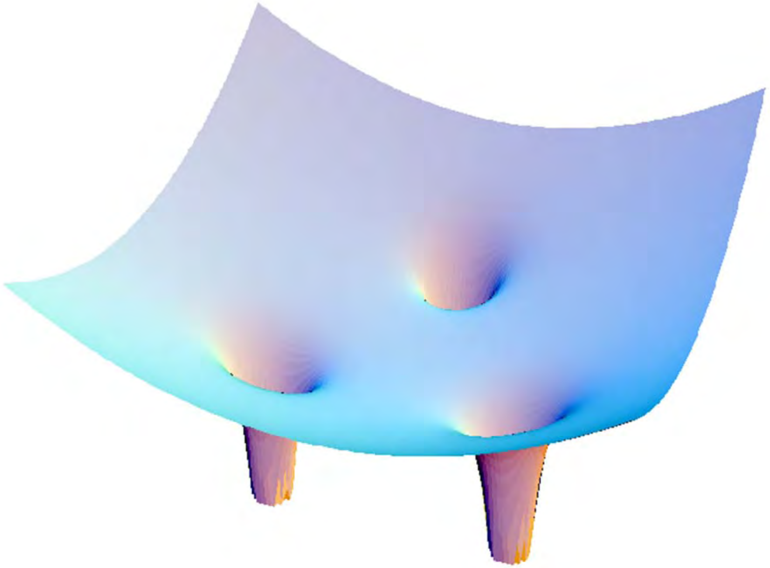
$$R_{n,L}^{(N)}(r) = \left[\frac{2n!}{\Gamma(n+L+N/2)} \right]^{1/2} r^L L_n^{L+N/2-1}(\omega r^2) \times \exp(-\tfrac{1}{2}\omega r^2)$$

$$E_{n,L}^{(N)} = (2n+L+N/2)\omega$$

→ $\mathcal{N}=2$ (x,y)

→ $\mathcal{N}=1$ (z)

A shell model for the quartet states



(x,y)

$$hc\tilde{\nu}_\rho(2n + |\ell| + 1) \equiv hc\tilde{\nu}_\rho(n_\rho + 1)$$

(z)

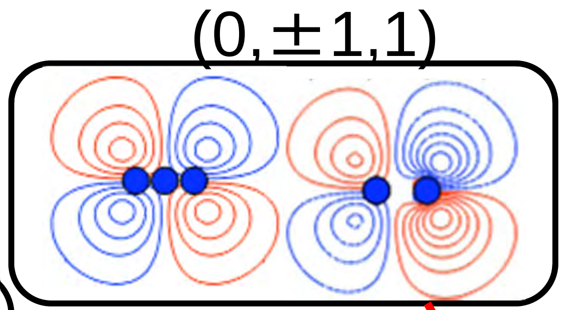
$$hc\tilde{\nu}_z(n_z + 1/2)$$

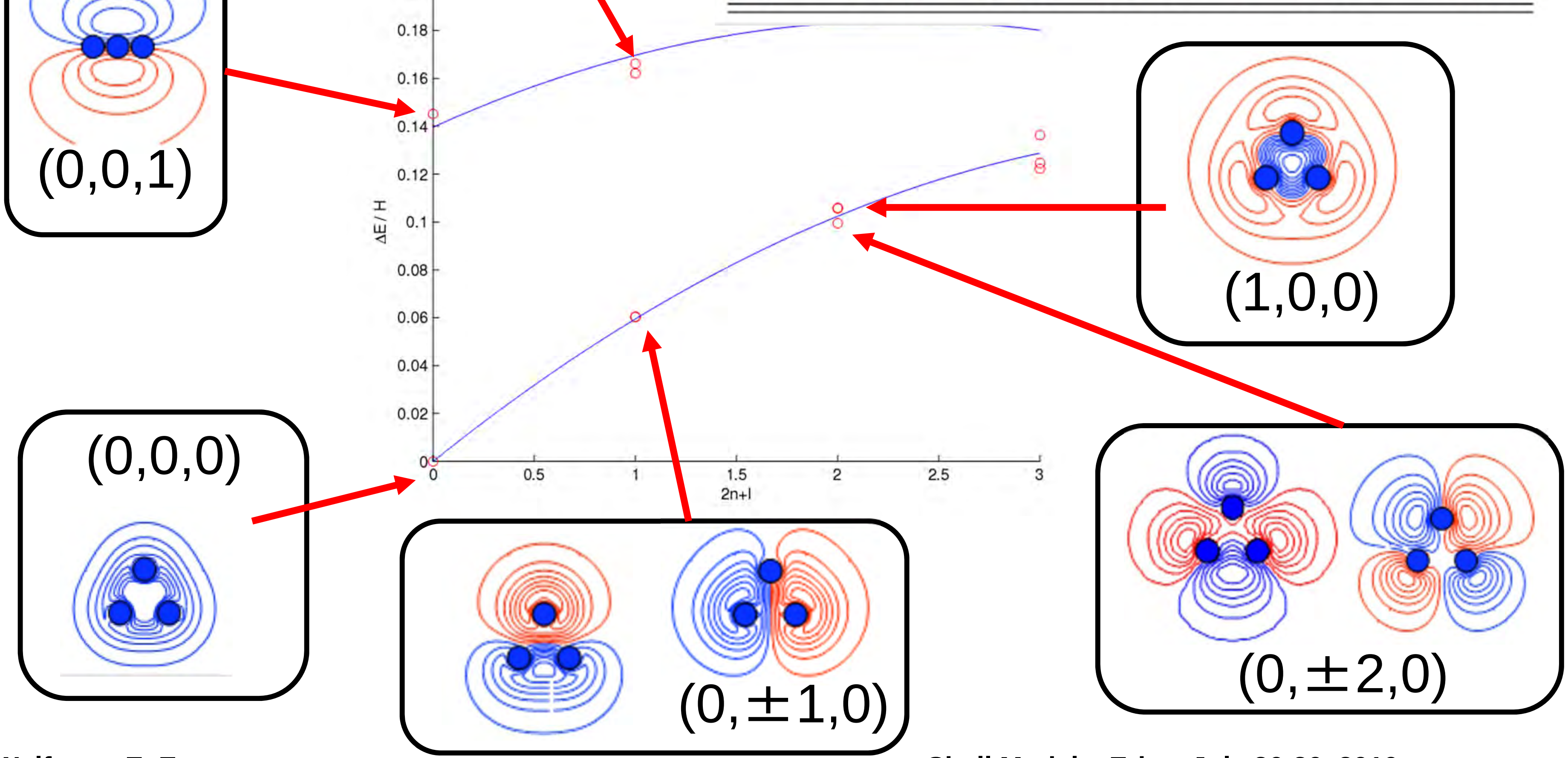
$$\Delta E/hc = n_\rho\tilde{\nu}_\rho + n_z\tilde{\nu}_z - x_\rho n_\rho^2\tilde{\nu}_\rho - x_z n_z^2\tilde{\nu}_z - x_{\rho z}n_\rho n_z\sqrt{\tilde{\nu}_\rho\tilde{\nu}_z}$$

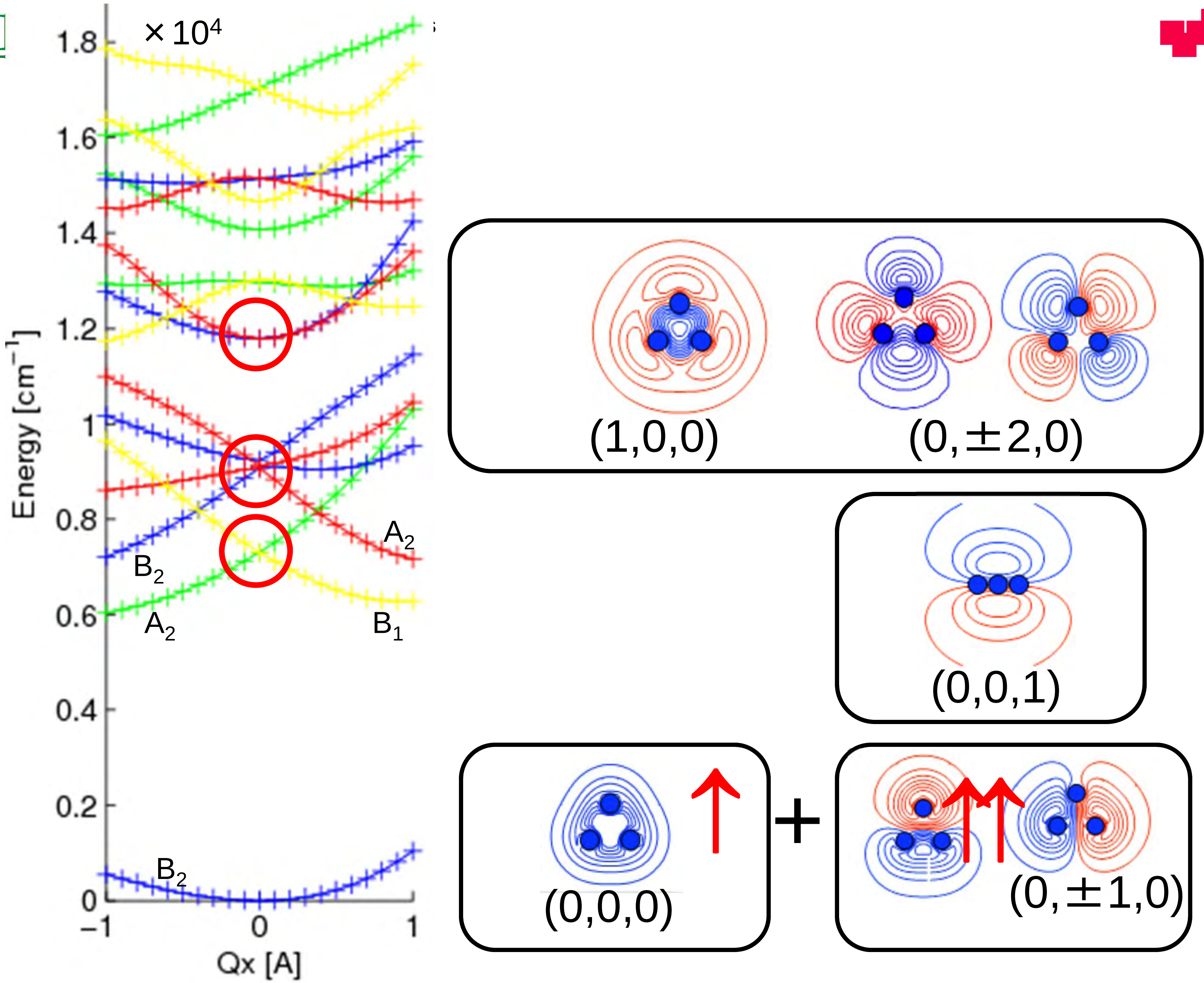
A shell model for the quartet states

$$E = h\nu_\rho(2n+l) + h\nu_z n_z + \text{anharm.}$$

	$\tilde{\nu}_\rho$ (cm^{-1})	$\tilde{\nu}_z$ (cm^{-1})	x_ρ	x_z	$x_{\rho z}$	Res. rms (cm^{-1})
K_3	14 963	19 589	0.1237	0	0.3571	930
K_2Rb	14 269	18 747	0.1201	0	0.3353	1100
KRb_2	13 975	18 104	0.1161	0	0.2963	1210
Rb_3	13 312	17 329	0.1136	0	0.2754	1070

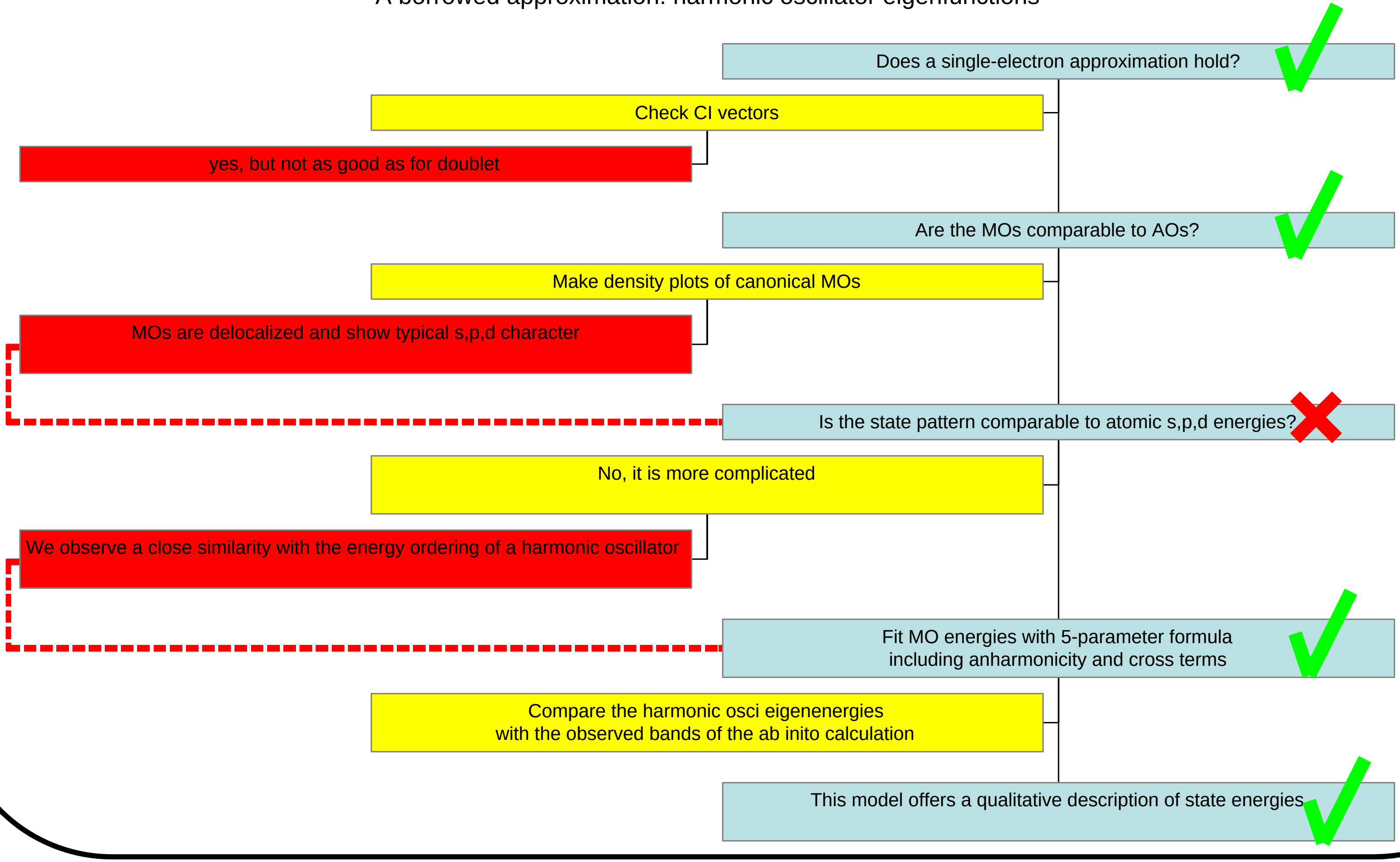





× 10^4
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Energy [cm^-1]
−1
0
1
Qx [A]
A2
B2
A2
B1
B2
(1,0,0)
(0,±2,0)
(0,0,1)
(0,0,0)
+
(0,±1,0)

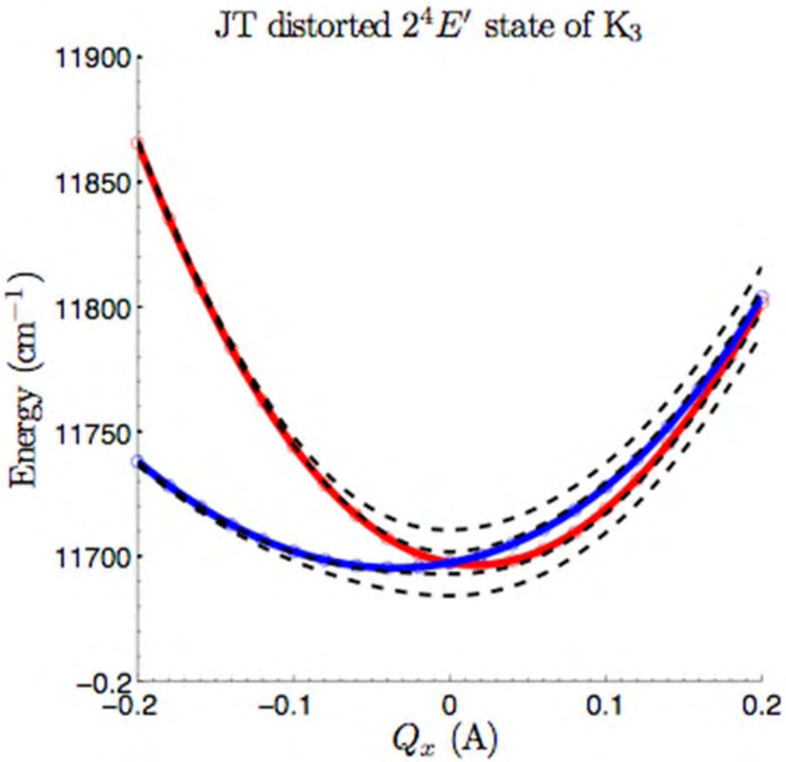
A shell model for the quartet states

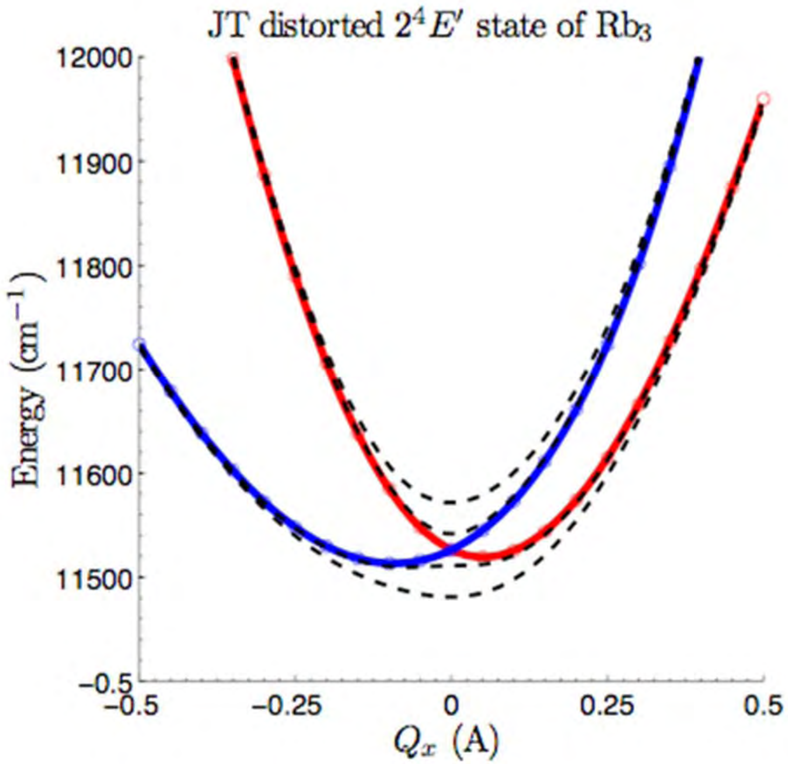
A borrowed approximation: harmonic oscillator eigenfunctions



Vibronic spectra

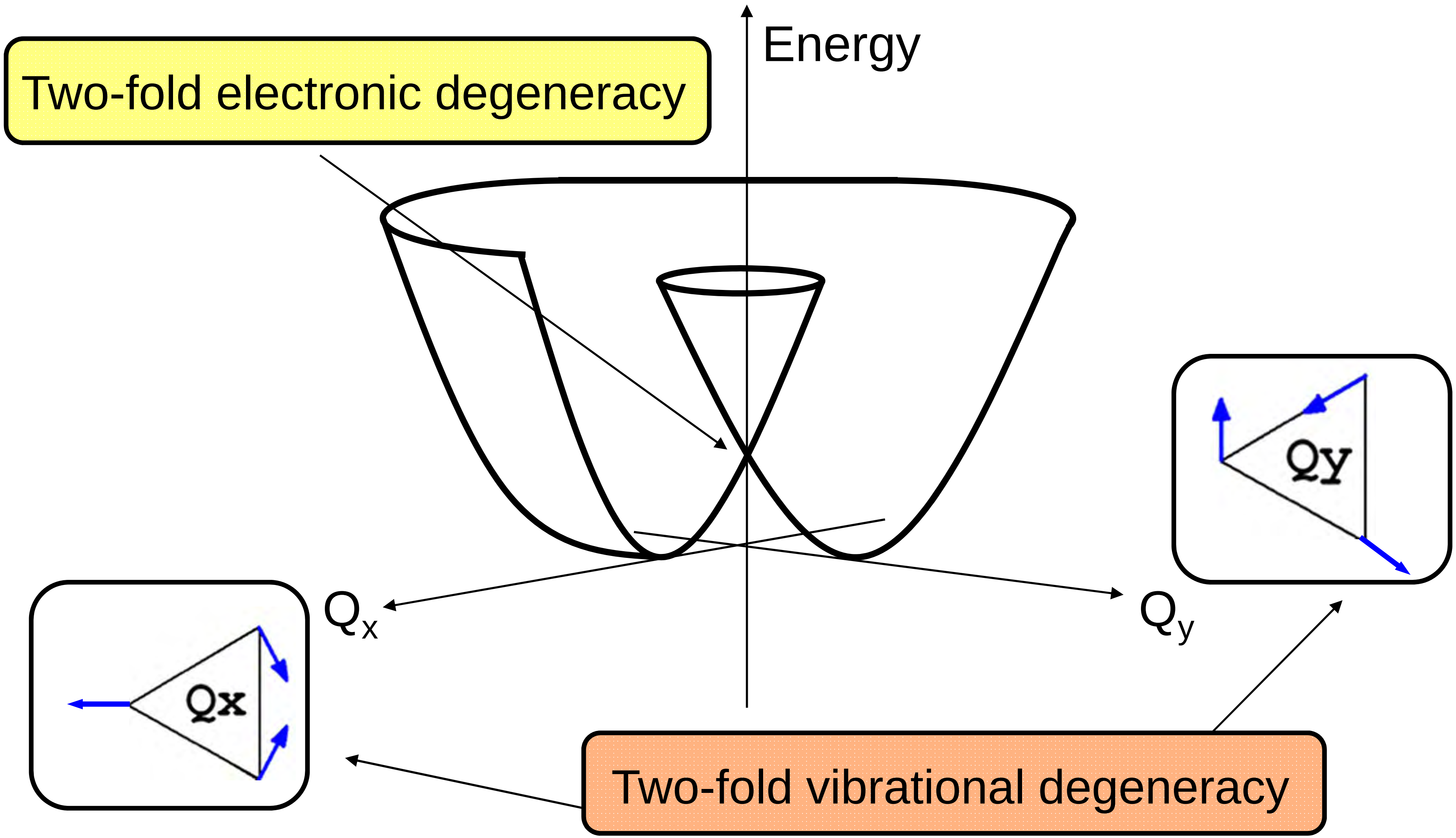
Further refinement: SO-coupling





CASPT2 + ECP-LS

Jahn-Teller effect theory



Relativistic Jahn-Teller effect theory

Adiabatic energy surfaces are obtained by diagonalization of $H_e + H_{SO}$:

2×2 potential surfaces !

Linear JT parameter

Harmonic force term

$= f(Qx, Qy)$

SO splitting

Quadratic JT parameter

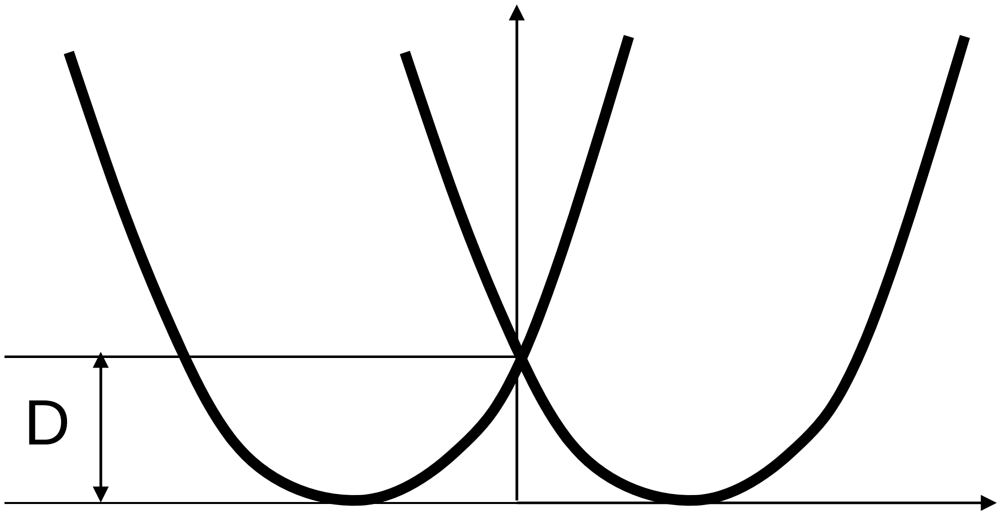
$$\epsilon_{\frac{1}{2}\pm} = \frac{1}{2}r^2 \pm \left[\Delta'^2 + k^2r^2 + kg\cos(3\phi)r^3 + \frac{g^2}{4}r^4\right]^{\frac{1}{2}}$$

$$\epsilon_{\frac{3}{2}\pm} = \frac{1}{2}r^2 \pm \left[(3\Delta')^2 + k^2r^2 + kg\cos(3\phi)r^3 + \frac{g^2}{4}r^4\right]^{\frac{1}{2}}$$

Jahn-Teller parameters

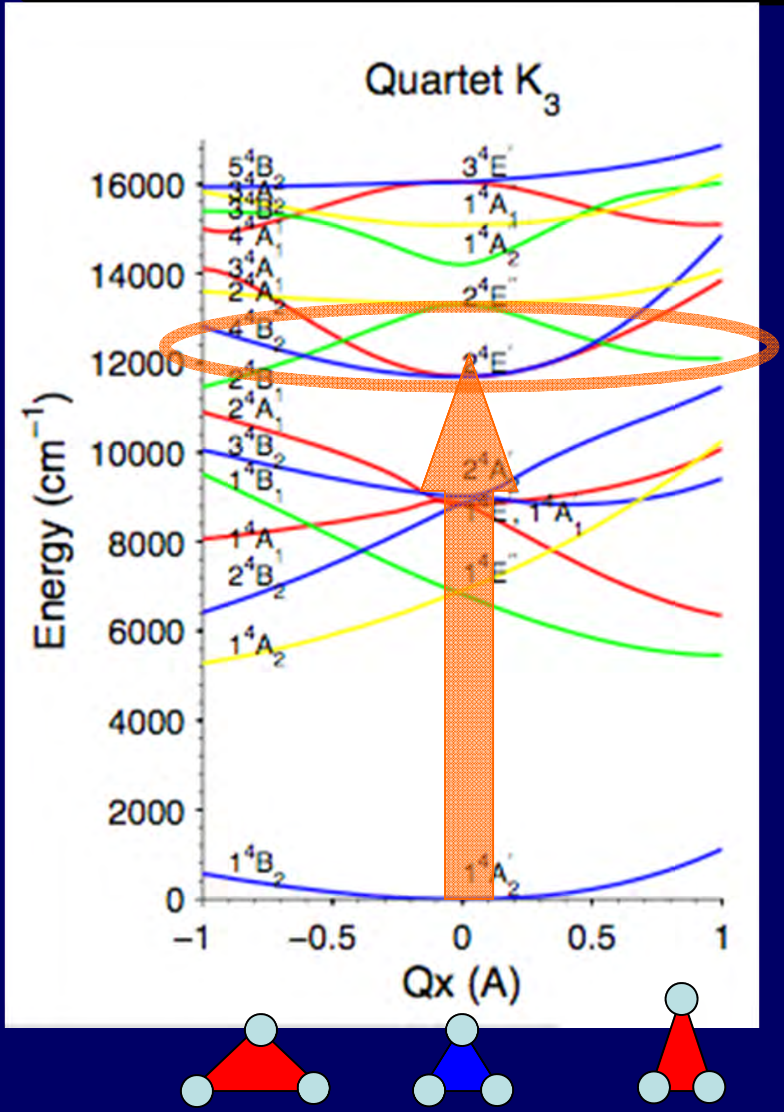
Parameters in dimensionless units:

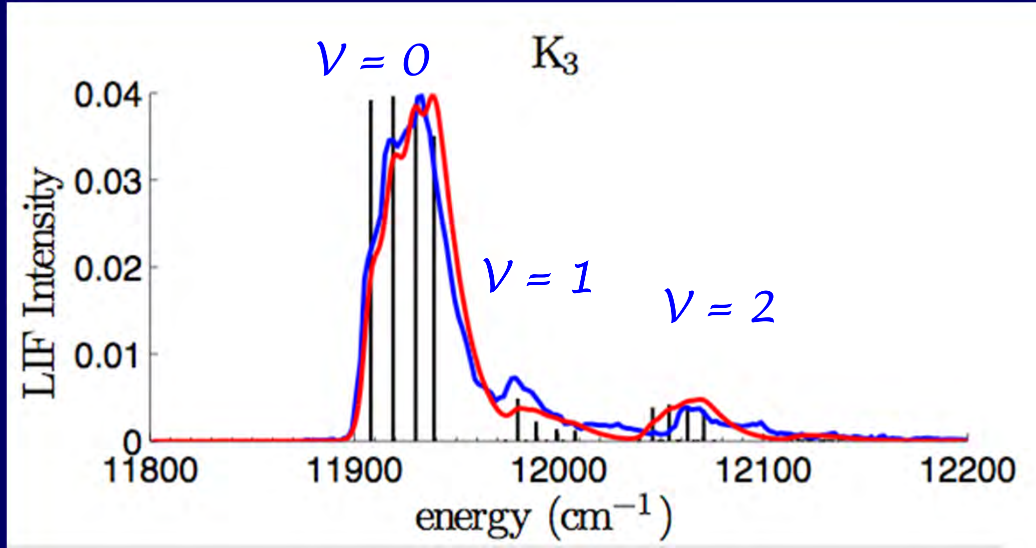
trimer	D	k	g	Δ'	ω (cm^{-1})
K_3	0.0202	0.2010	-0.3110	0.0656	67.1
Rb_3	0.2500	0.7071	-0.1774	0.3578	42.2

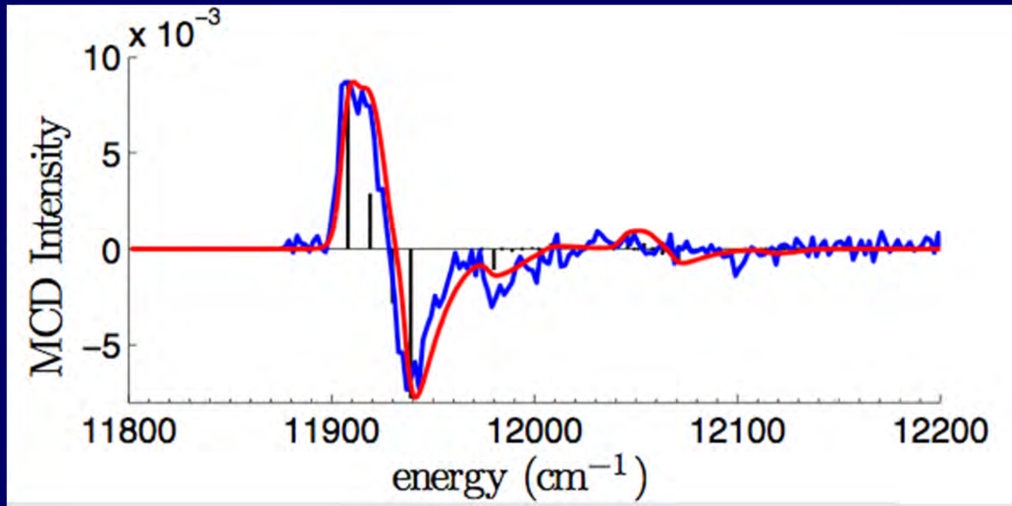


$$E_{JT}/(\hbar\omega) = k^2/2 = D$$

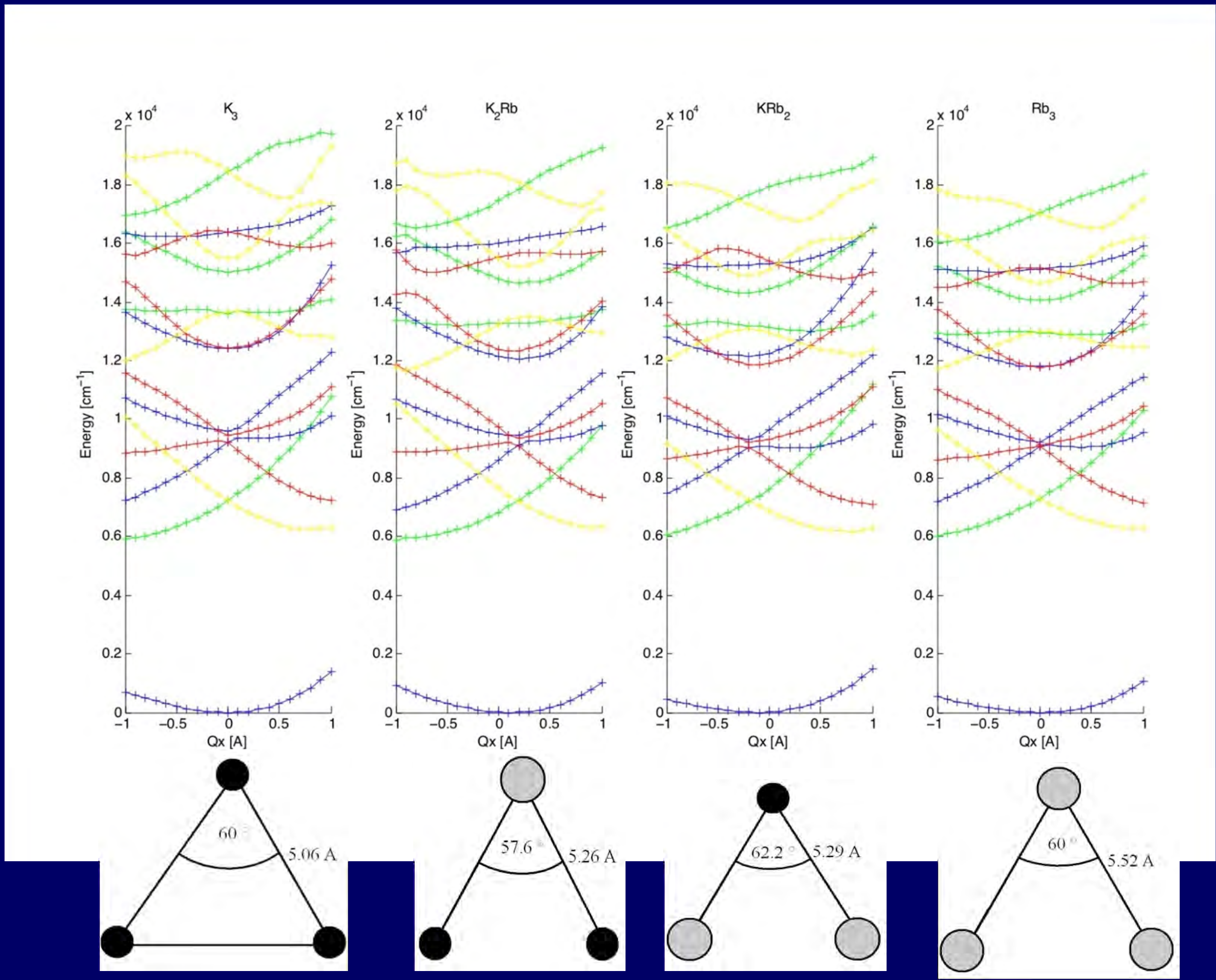
Vibronic spectra: the $1^4A_2' \rightarrow 2^4E'$ transition







Alkali trimer quartet state excitations



K_3 and Rb_3

(quartet):
Hauser, Auböck, Callegari, Ernst, J. Chem.Phys. **132**, 164310 (2010)

(doublet):
Hauser, Callegari, Soldan, Ernst, J. Chem. Phys. **129**, 044307 (2008)
and
spectral predictions:
Chem.Phys.
(in print)

heteronuclear:
in preparation

Level Structure and Magnetic Properties from One-Electron Atoms to Clusters with Delocalized Electronic Orbitals: Shell Models for Alkali Trimers

by **A.W. Hauser, C. Callegari, W.E. Ernst**

in: P. Piecuch et al. (eds.), *Advances in the Theory of Atomic and Molecular Systems*, Progress in Theoretical Chemistry and Physics 20, DOI 10.1007/978-90-481-2985-0 30, Springer Science+Business Media B.V. 2009

Doublet states:
Electronic shell model,

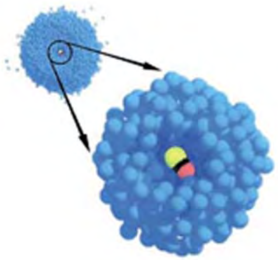
See e.g. Cocchini, Upton, Andreoni, J. Chem. Phys. 1989

Quartet states:
Our model relating the electronic structure to the eigenstates of the harmonic oscillator, cf. single particle states in quantum dots

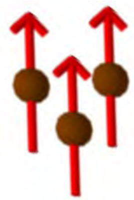
Magnetic Resonance

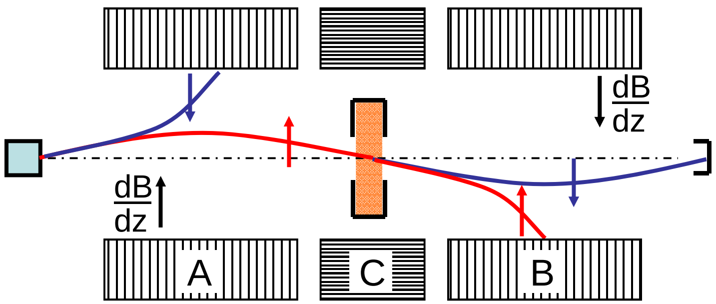
Superfluid helium nanodroplets

a cold container for single particles (0.38 K)



study exotic, 'unstable' species (e.g. K_3, Rb_3)

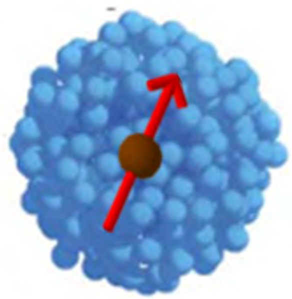




preparation

probing

manipulation



single atoms → long spin lifetime
→ create spin polarization

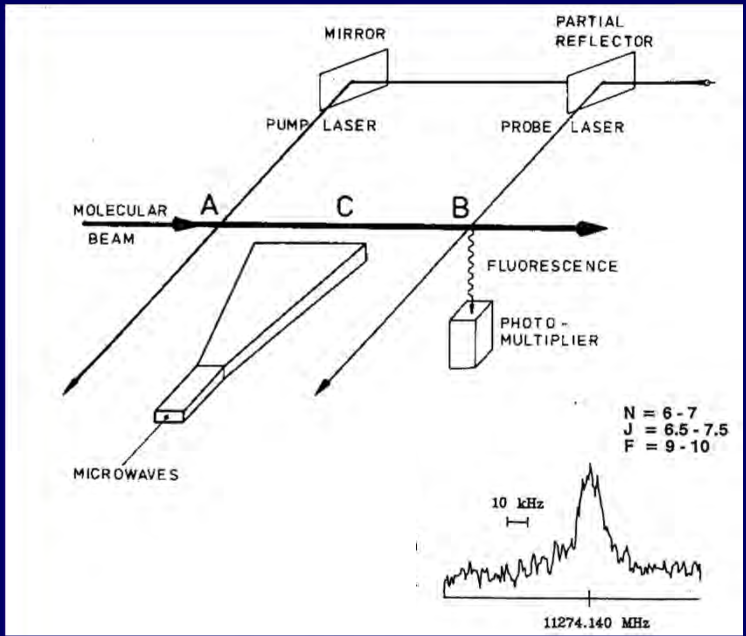
low optical density → indirect detection

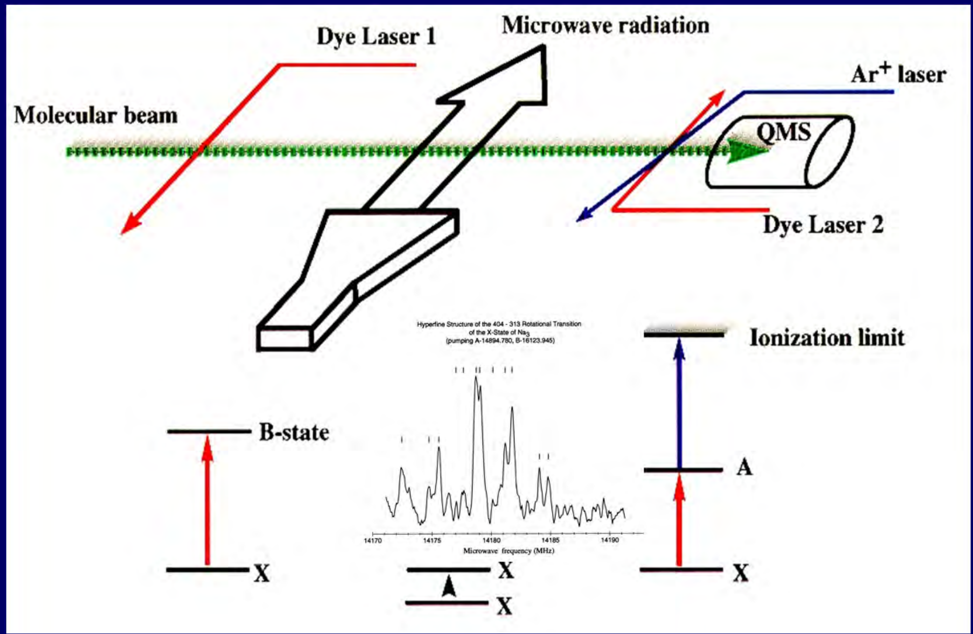
Rabi: spatial separation

High resolution mw or rf spectroscopy?

LIF Detection of Microwave Absorption e.g.
W. E. Ernst, S. Kindt, and T. Törring,
Phys. Rev. Lett. 51, 979(1983)

RTPI Detection of Microwave Absorption
Na_3, W.E. Ernst and O. Golonzka (1999)





W. E. Ernst, J. Kändler, C. Noda, J. S. McKillop and R. N. Zare,
Hyperfine Structure of BaI, J. Chem. Phys. 85, 3735-3743 (1986).

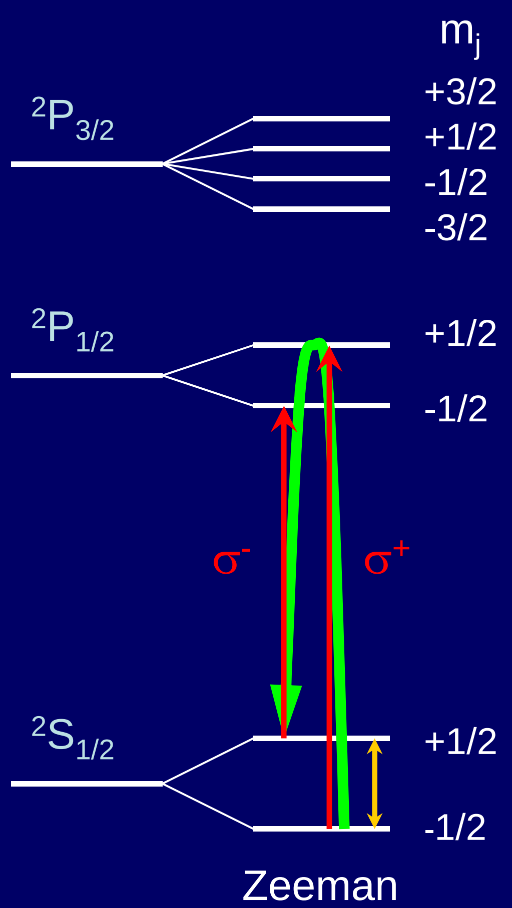
Molecules in/on helium droplets:

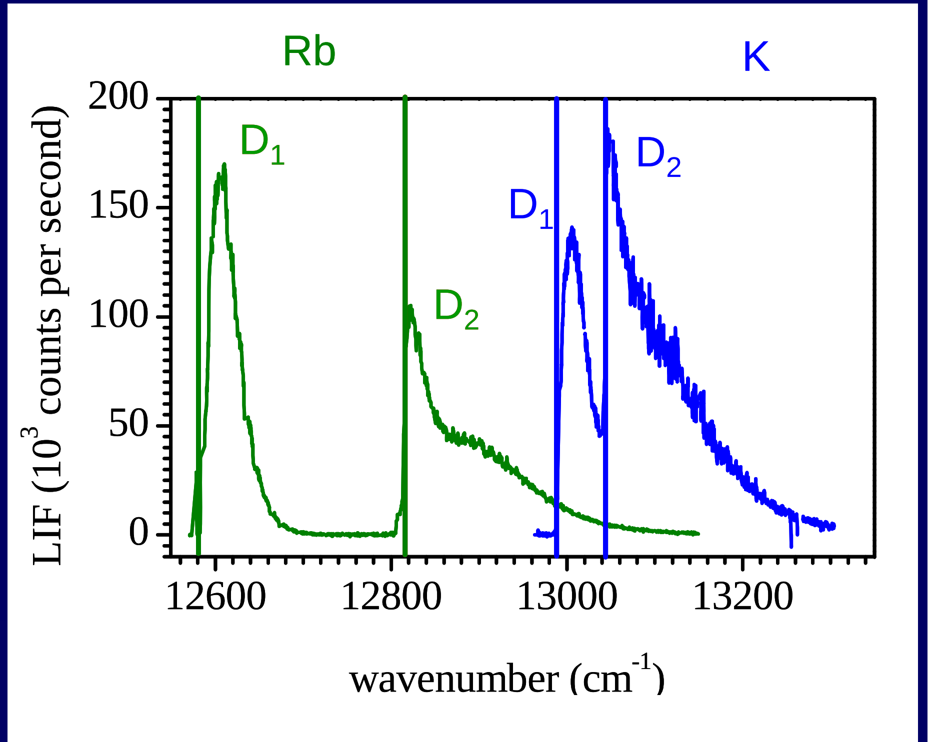
- Narrow linewidth on mw and IR transitions ☺
- Large linewidth on optical transitions ☹

How about polarization methods?

Pumping and probing

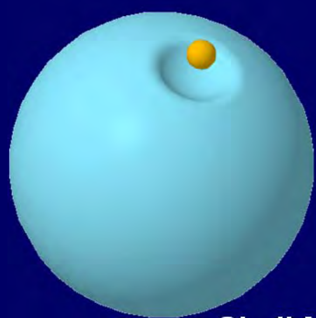
The optical $^2S_{1/2} \rightarrow {}^2P_{1/2}$ transitions can be used to manipulate and probe spin states





Rb can be spin polarized by optical pumping

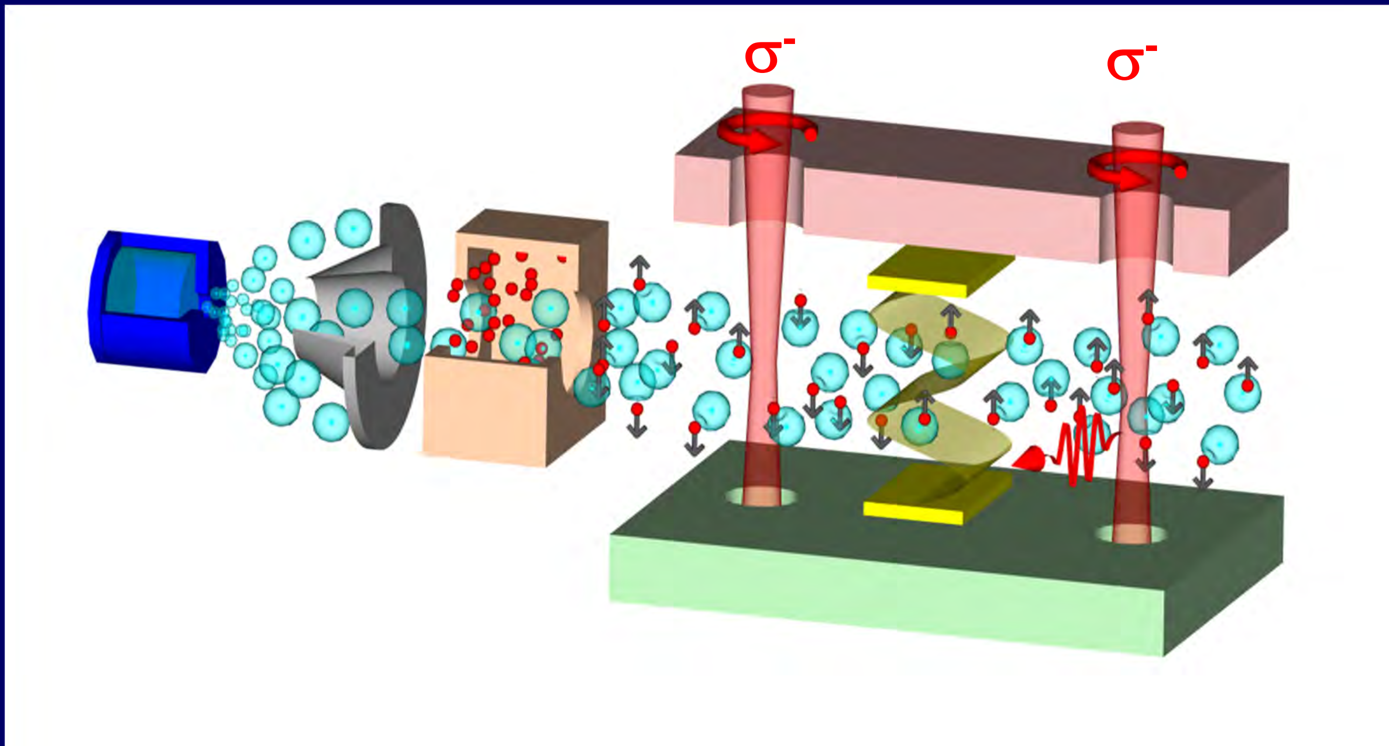
K can be spin polarized by depletion



G. Auböck, J. Nagl, C. Callegari, and W. E. Ernst
PRL 98, 075301(2007)
PRL 101, 035301(2008)

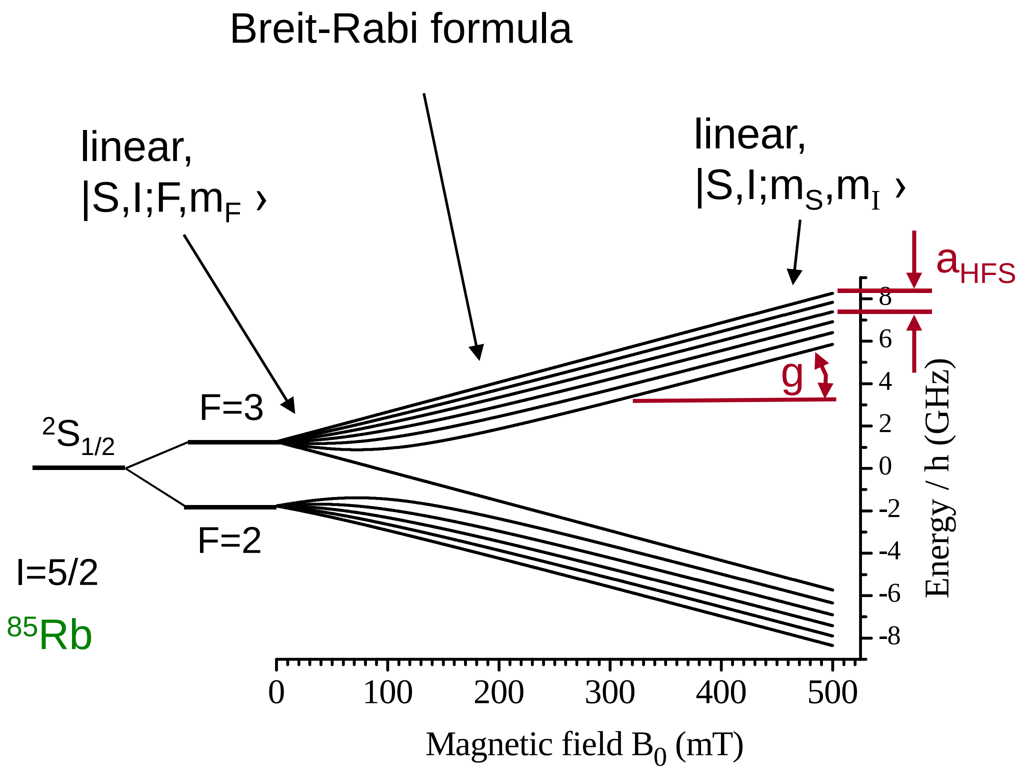
Optically Detected ESR

A pump | **C** mw | **B** probe

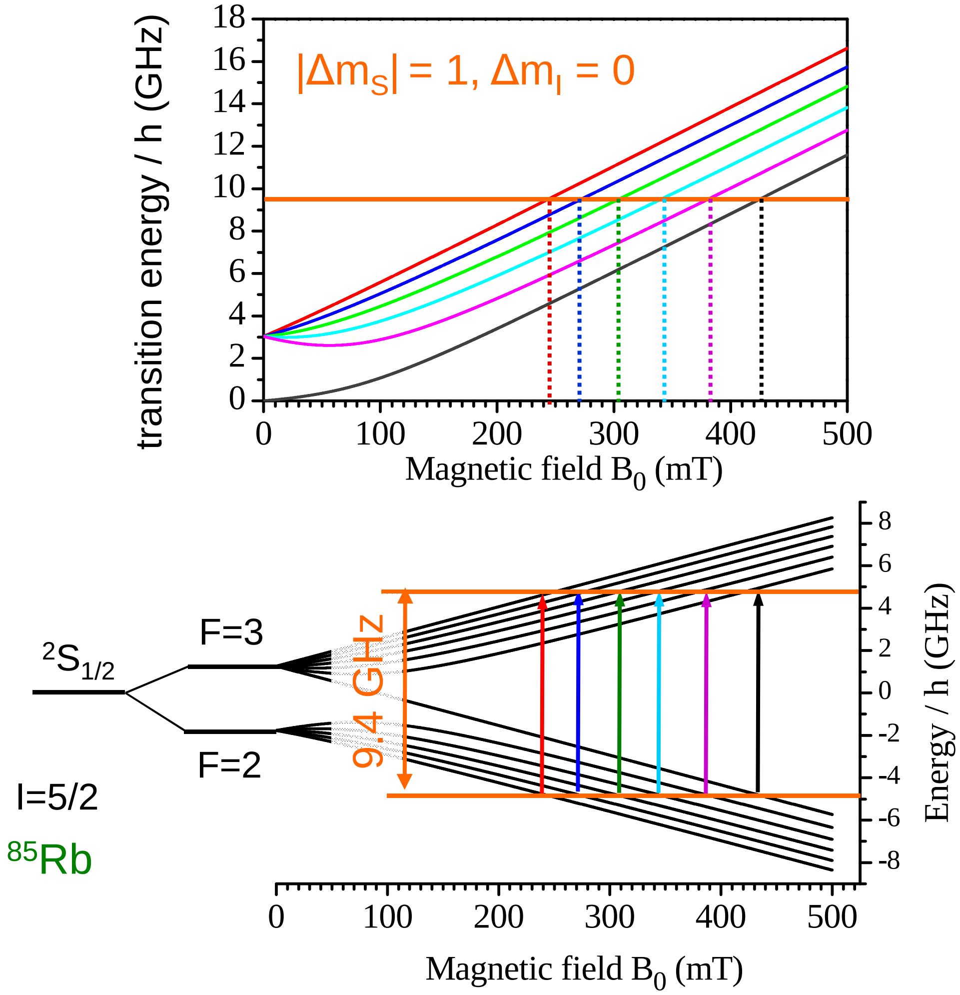


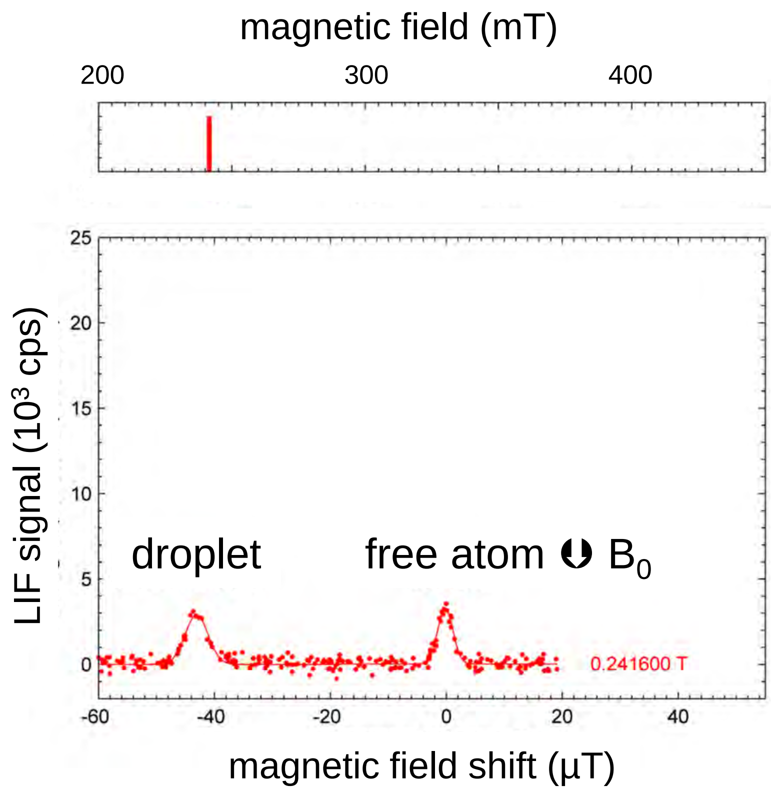
Markus Koch

ESR on helium droplets

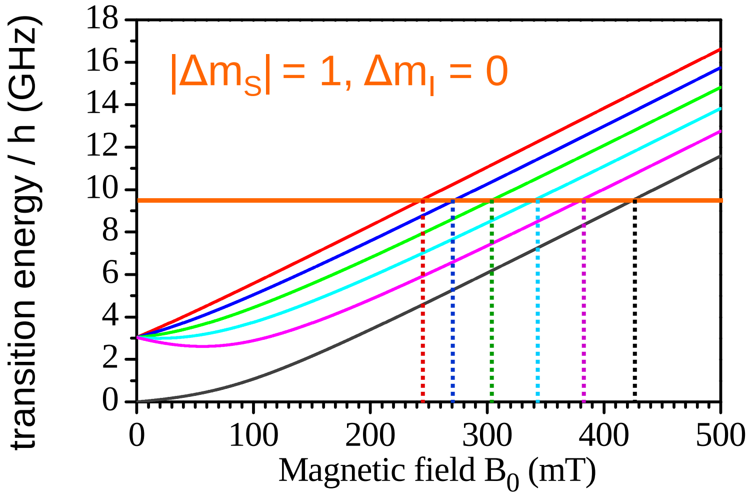


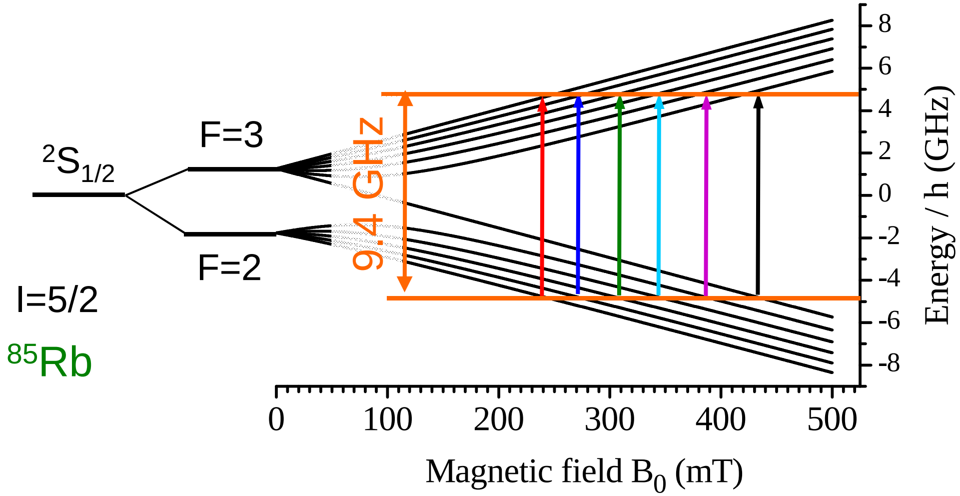
ESR on helium droplets

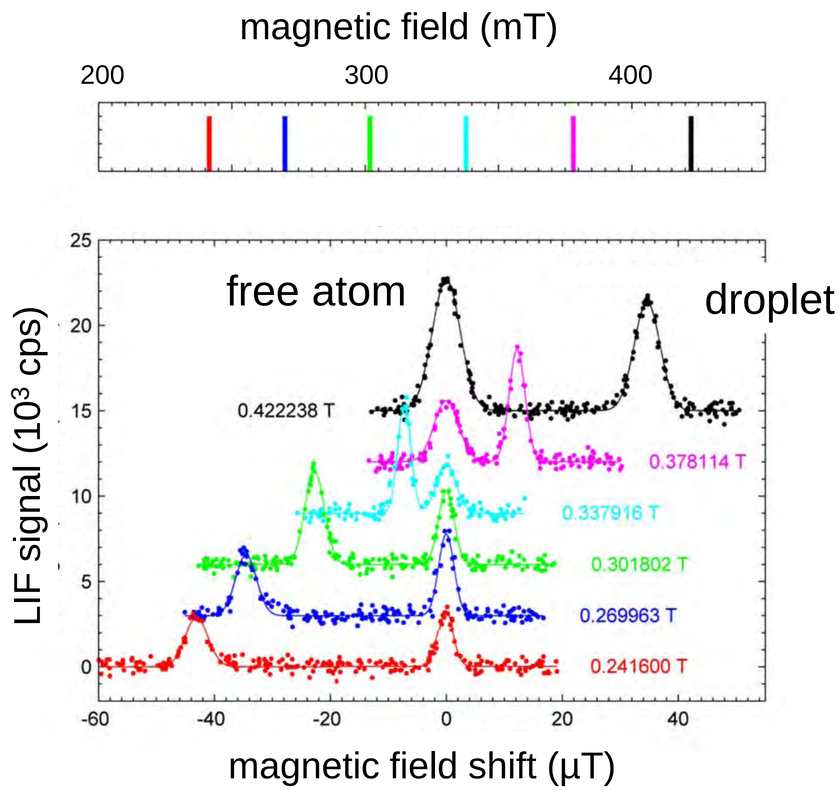




ESR on helium droplets





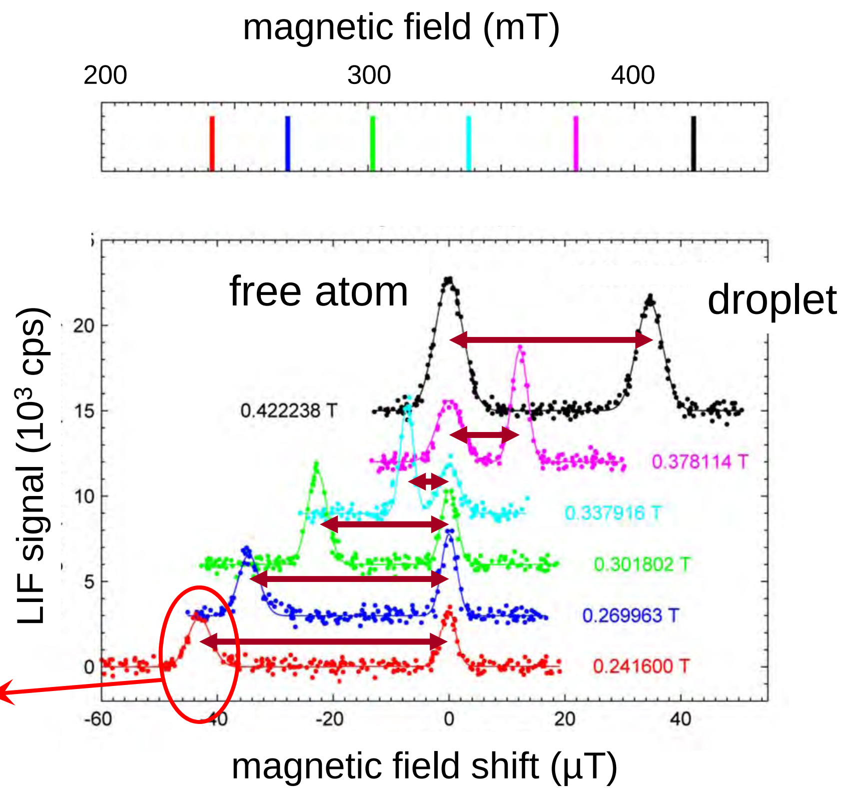


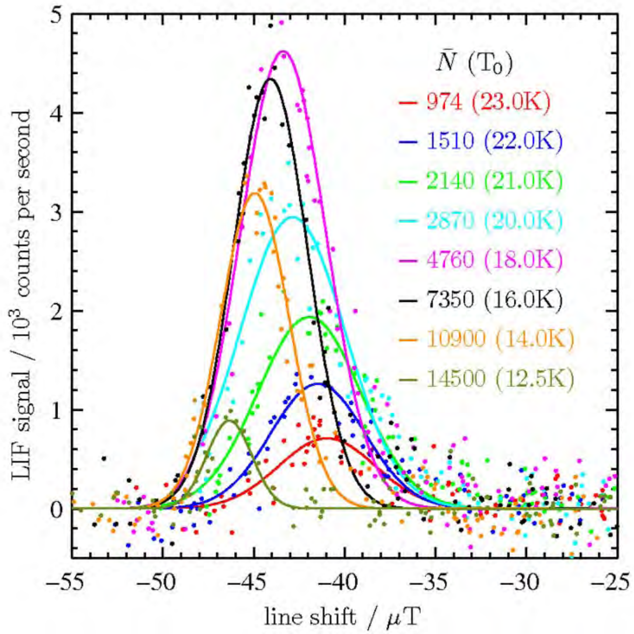
ESR on helium droplets

Modeling: Breit-Rabi formula

- droplet: variations δa_{HFS}, δg_S free parameters
- ^{39}K: $\delta a_{HFS}/a_{HFS}$ = 325 ± 40 ppm, $\delta g_S/g_S$ = 0 ± 3 ppm
- ^{85}Rb: $\delta a_{HFS}/a_{HFS}$ = 412 ± 8 ppm, $\delta g_S/g_S$ = 0 ± 3 ppm
- $\delta a_{HFS}/a_{HFS} = \delta|\psi_0|^2/|\psi_0|^2$

varies with droplet size!





M. Koch, J. Lanzersdorfer, C. Callegari, J.S. Muenter, and W. E. Ernst
J. Phys. Chem. A 113, 13347-13356(2009)

M. Koch, G. Auböck, C. Callegari and W. E. Ernst
Phys. Rev. Lett. 103, 035302-1-4(2009)

Electron spin density at alkali nucleus

Following Adrian [J. Chem. Phys. 32 (4), 972–981 (1960)], the relative change of hfs consists of two parts:

$$\left.\frac{\delta a_{\mathrm{HFS}}}{a_{\mathrm{HFS}}}\right|_{\mathrm{Pauli}} = \frac{|\Psi'_{n'00}(R_{\mathrm{A}},0,\theta)|^2}{|\Psi_{n00}(0,\theta)|^2} - 1 \qquad (1)$$

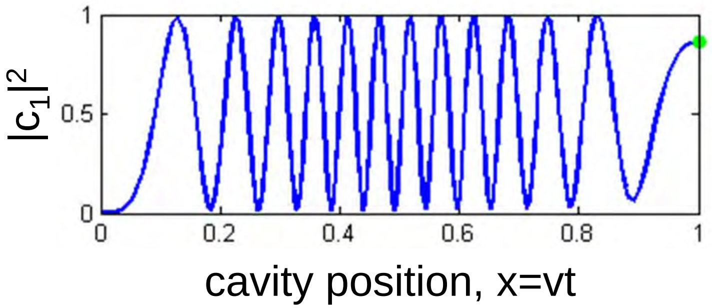
$$\left.\frac{\delta a_{\mathrm{HFS}}}{a_{\mathrm{HFS}}}\right|_{\mathrm{vdW}} = -\left(\frac{2}{E_{\mathrm{A}}} + \frac{1}{E_{\mathrm{A}}+E_{\mathrm{He}}}\right)\int_V \frac{f_6(|\vec{R}_A-\vec{R}|)C_6\;\rho_0(\vec{R})}{|\vec{R}_A-\vec{R}|^6}\mathrm{d}\vec{R} \qquad (2)$$

Relative change of electron spin density at alkali nucleus in ppm for He_N droplet

N	Pauli	van der Waals	Pauli + van der Waals
		K	
500	+1630	−1294	+336
1000	+1831	−1464	+367
2000	+1928	−1558	+370
		Rb	
500	+1838	−1446	+392
1000	+2151	−1698	+453
2000	+2270	−1812	+458

see M.Koch, C. Callegari, and W. E. Ernst, Mol. Phys. **108** (7), 1005 (2010), issue in honor of R. N. Zare

Rabi oscillations



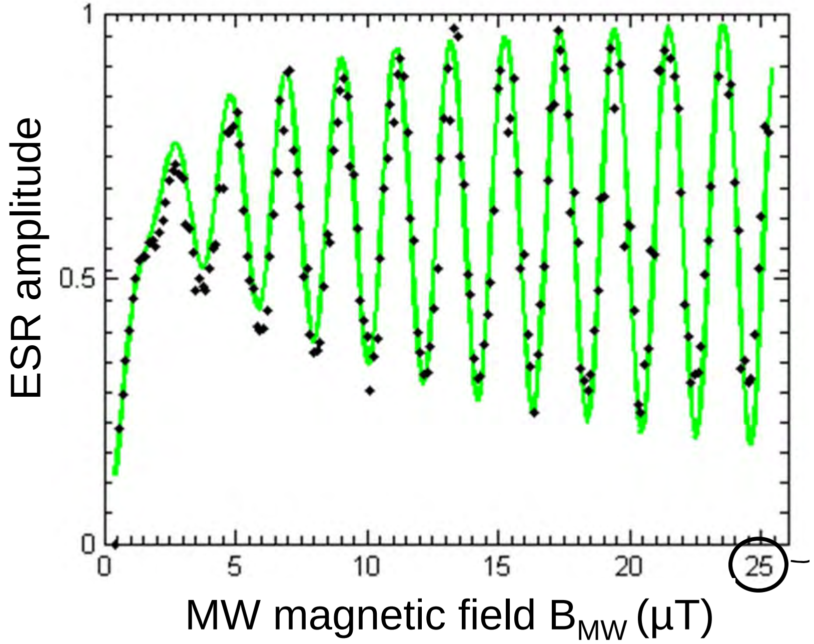
$$|\Psi(t)\rangle = C_1(t)|\psi_1\rangle + C_2(t)|\psi_2\rangle$$

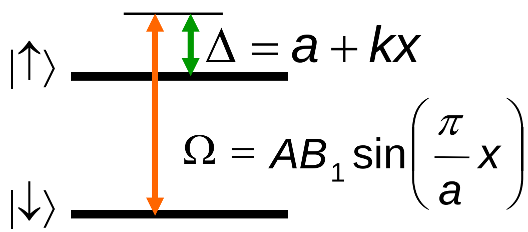
$$P_n(t) = |C_n(t)|^2, \quad \text{with } |C_1(t)|^2 + |C_2(t)|^2 = 1$$

$$\frac{\partial}{\partial t}\begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = -\frac{i}{2}\begin{bmatrix} -\Delta & \Omega \\ \Omega & \Delta \end{bmatrix}\begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}$$

$\Delta = \omega_0 - \omega$ … detuning

Ω … Rabi frequency

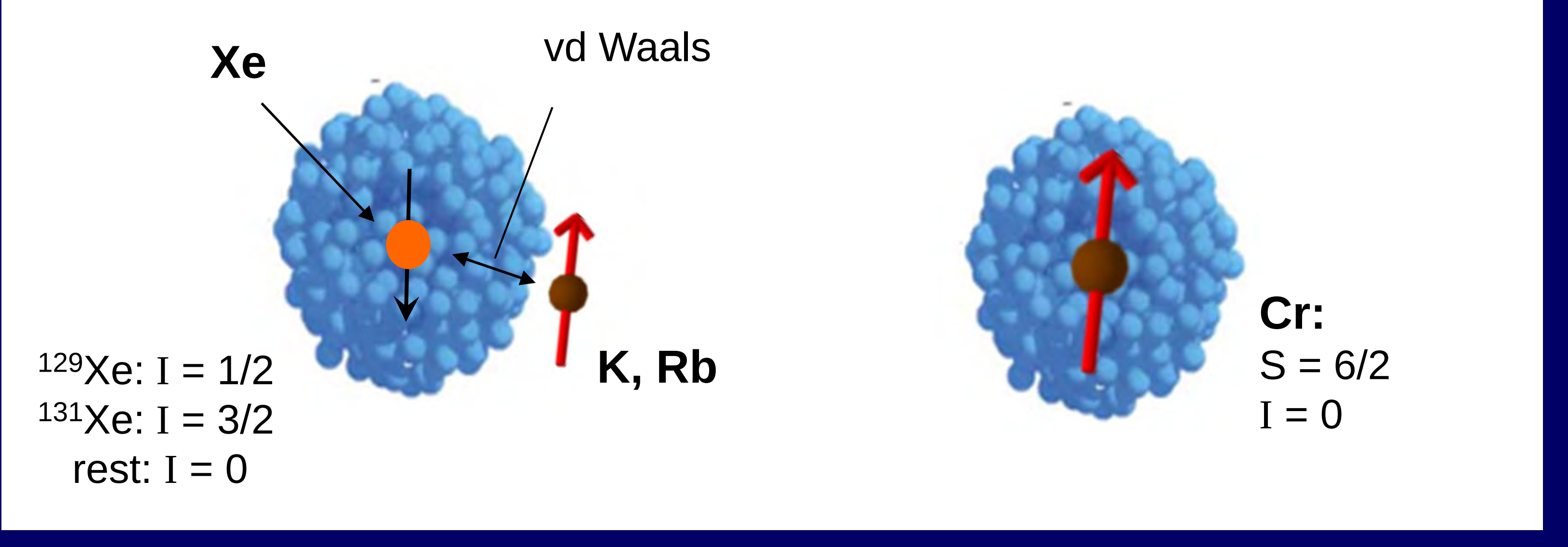




ESR on droplets: conclusions & future

- first demonstration of MR (ESR) on doped He_N
- hyperfine resolved ESR spectrum of ^{39}K, ^{85}Rb
- shifts (~400 ppm), droplet-size dependent: Fermi contact term
- coherent population transfer: Rabi oscillations

Currently in progress:



Poster by Martin Ratschek and Markus Koch (yesterday)

The HeDrop Team

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Fonds zur Förderung der wissenschaftlichen Forschung

& EU Network „Cold Molecules“

WE-Heraeus-Seminar No. 482

Helium Nanodroplets
– Confinement for Cold Molecules and Cold Chemistry

Physikzentrum Bad Honnef, Germany
May 29 to June 1, 2011

Scientific Organizers

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THE END