Where atomic spectra are dense and complex: Millimeter wave spectroscopy and MQDT analysis of high Rydberg states of xenon

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Introduction

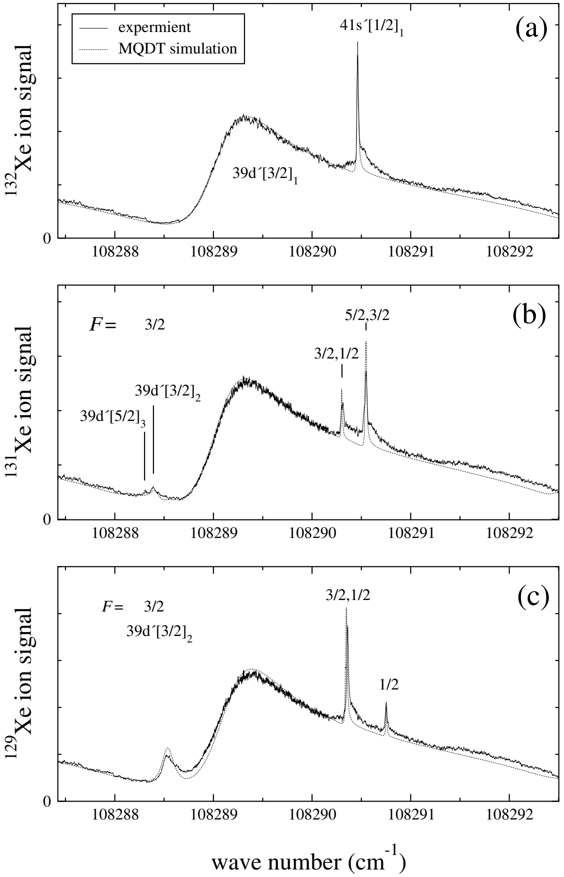
Goal: Study the role of nuclear spins in photoionization of atoms and molecules

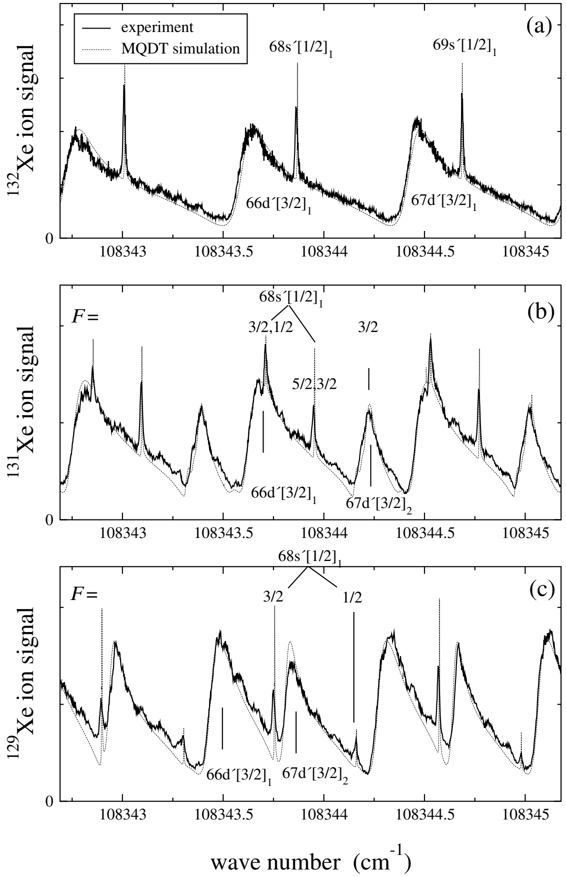
Strategy: Characterize the dynamics of photoionization channels by studying Rydberg states at ultra-high resolution

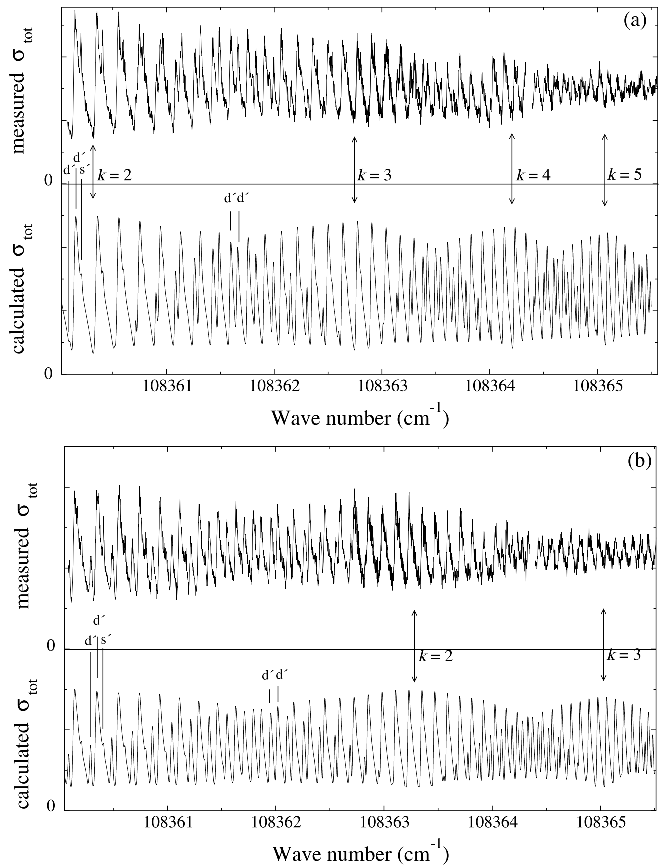
Example: Hyperfine structure of high Rydberg levels of ^{83}Kr ($\rightarrow$ hf structure of ^{83}Kr^{+})
H. J. Wörner, U. Hollenstein, F. Merkt, Phys. Rev. A **68**, 032510 (2003)
M. Schäfer, F. Merkt, Phys. Rev. A **74**, 062506 (2006)
Th. A. Paul, J. Liu, F. Merkt, $\rightarrow$RI01

Hyperfine structure of ^{129}Xe$^+$ and ^{131}Xe$^+$

H. J. Wörner, M. Grütter, E. Vliegen, F. Merkt, Phys. Rev. A **71**, 052504 (2005).







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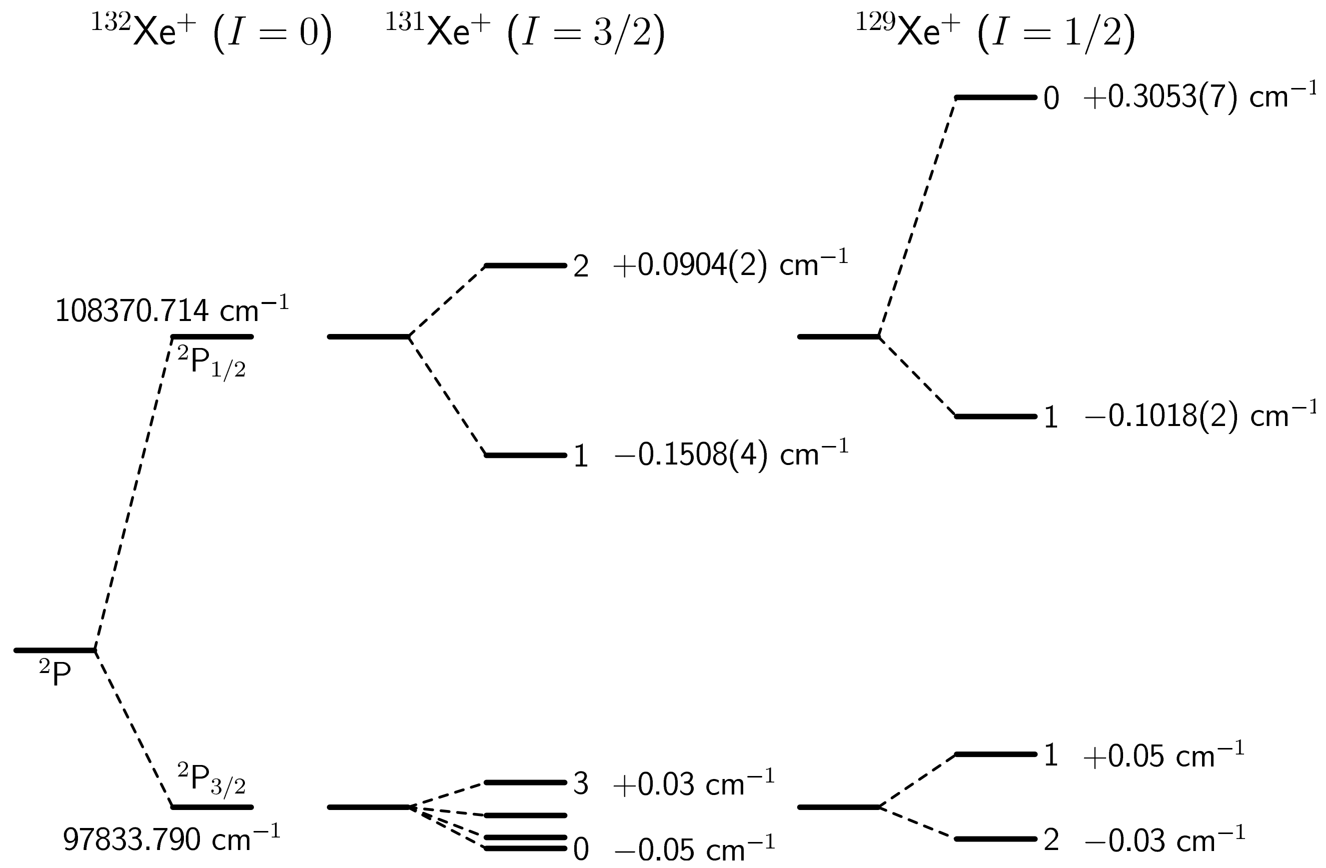
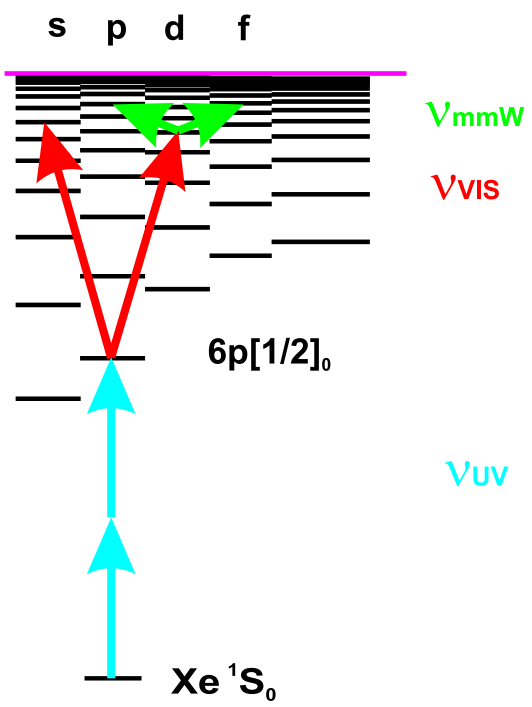
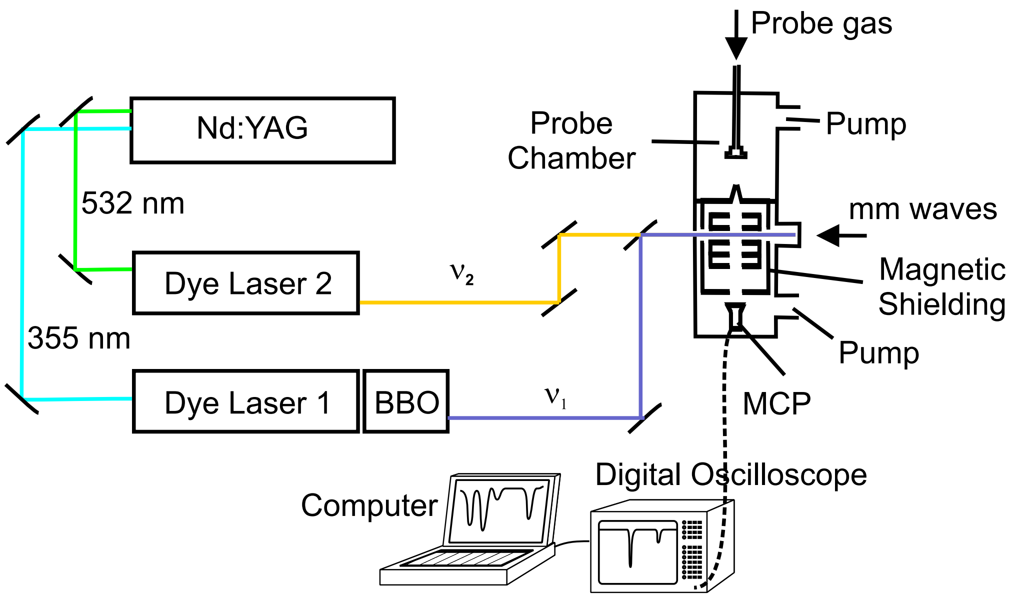


Millimeter wave experiments





Millimeter wave system

Source: 240–390 GHz Backward Wave Oscillator OB-65 (ISTOK, Russia), 20–40 mW output power

Stabilization:

BWO $\rightarrow \nu_{\mathrm{BWO}} \rightarrow \otimes \leftarrow N\nu_{\mathrm{MW}} \leftarrow$ MW Synth.

$\downarrow$ (18–26 GHz)

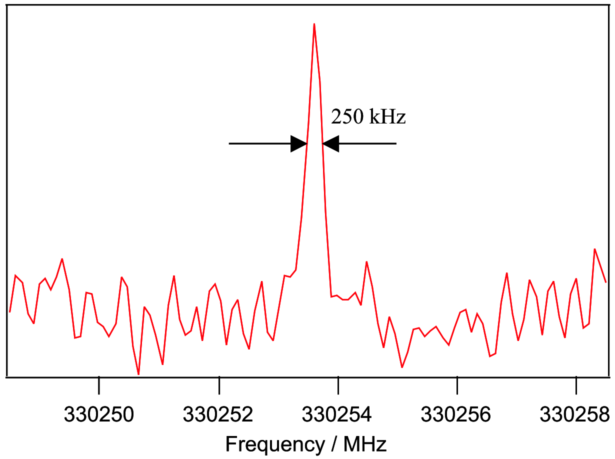
$\uparrow$ $\nu_{\mathrm{IF}} \approx 350\,\mathrm{MHz}$

$\downarrow$

PLL $\leftarrow$ HEMT amplifier

$\uparrow$

350 MHz



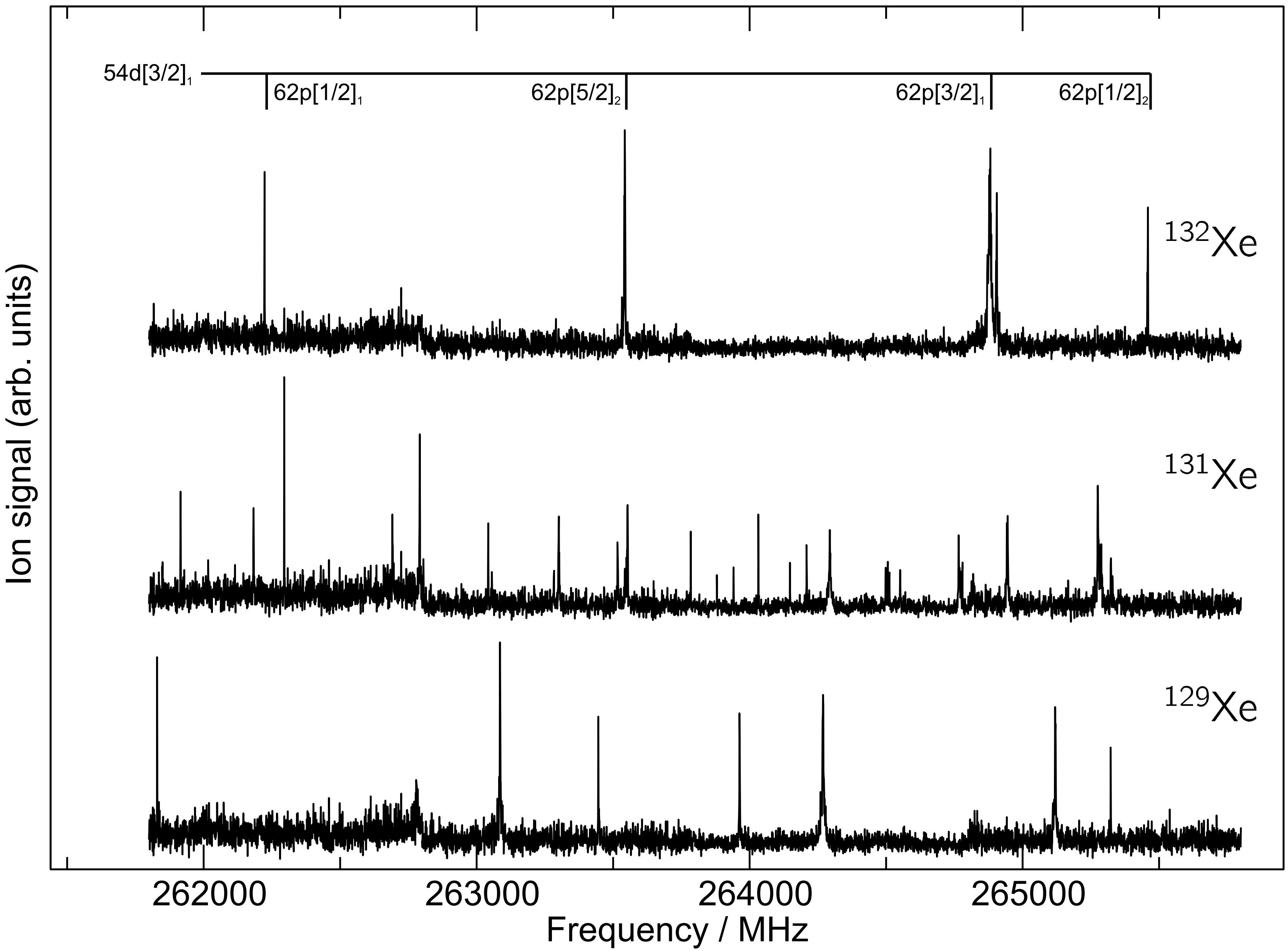
^{132}Xe: 61p $[5/2]_2 \leftarrow$ 52d $[3/2]_1$

Accuracy of the transition frequencies: <1 MHz

Harmonic mixer, HEMT amplifier: Univ. Köln
Phase lock loop: ETH Zurich

F. Lewen *et al.*, Rev. Sci. Instrum. **69**, 32 (1998).

M. Schäfer *et al.*, J. Phys. B, **39** 831 (2006).

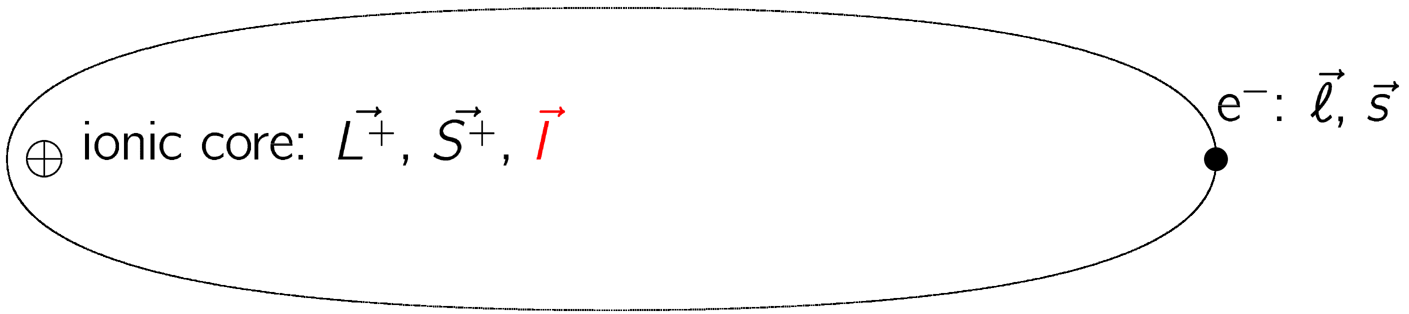


54d[3/2]$_1$
62p[1/2]$_1$
62p[5/2]$_2$
62p[3/2]$_1$
62p[1/2]$_2$
^{132}Xe
^{131}Xe
^{129}Xe
Ion signal (arb. units)
262000
263000
264000
265000
Frequency / MHz

Multichannel quantum defect theory (MQDT)

MQDT: Ham; Seaton; Fano. Xe: K. T. Lu, Phys. Rev. A **4**, 579 (1971).

hf structure (^{83}Kr): H. J. Wörner, U. Hollenstein, F. Merkt, Phys. Rev. A **68**, 032510 (2003)



close-coupling region:
strong ion core–electron interaction
(exchange, spin–orbit interaction)
LS coupling
$\vec{L}^+ + \vec{\ell} = \vec{L}$, $\vec{S}^+ + \vec{s} = \vec{S}$,
$\vec{L} + \vec{S} = \vec{J}$, $\vec{J} + \vec{I} = \vec{F}$
close-coupling eigenchannels α

angular momentum
frame transformation
←→

long-range region:
Coulomb field, ion energy levels
(incl. hyperfine interaction)
jj coupling
$\vec{L}^+ + \vec{S}^+ = \vec{J}^+$, $\vec{J}^+ + \vec{I} = \vec{F}^+$,
$\vec{\ell} + \vec{s} = \vec{j}$, $\vec{F}^+ + \vec{j} = \vec{F}$
dissociation channels i

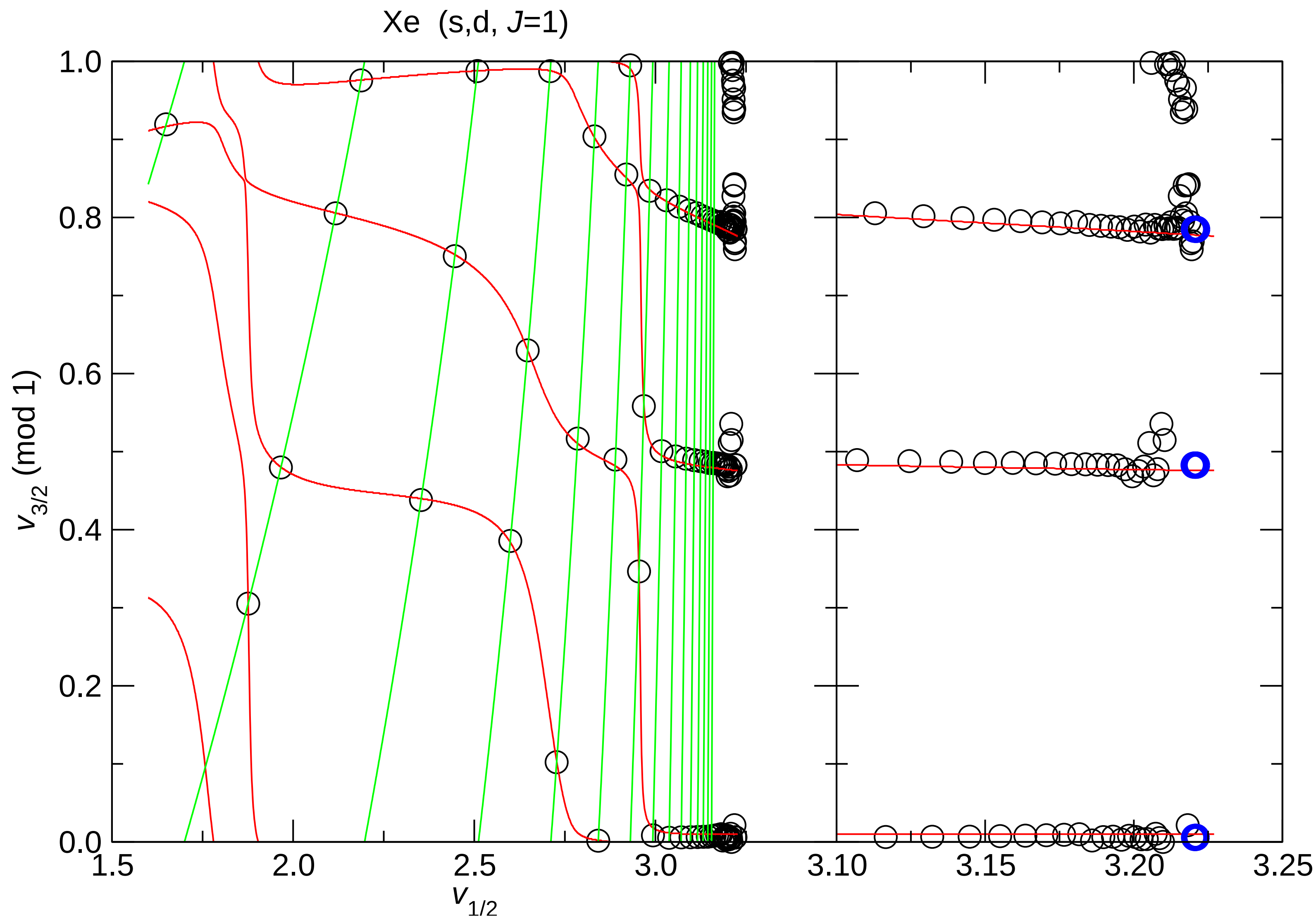
Rydberg states: jK coupling $\vec{L}^+ + \vec{S}^+ = \vec{J}^+$, $\vec{J}^+ + \vec{\ell} = \vec{K}$, $\vec{K} + \vec{s} = \vec{J}$, $\vec{J} + \vec{I} = \vec{F}$

Each bound level E is determined by:

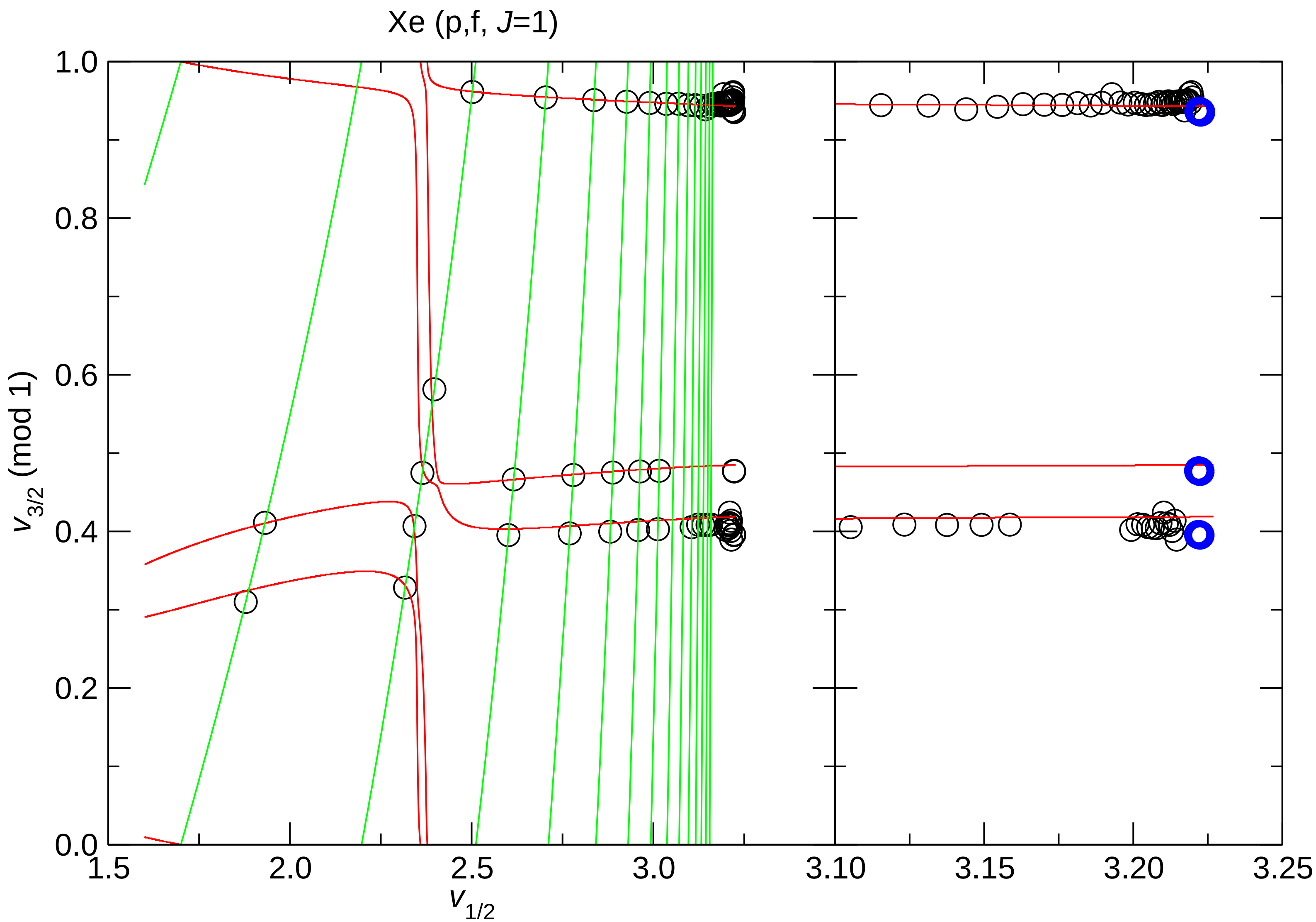
$$\det|U_{i_{(F)}\alpha}\sin[\pi(\mu_\alpha+\nu_{i_{(F)}})]|=0$$

- eigen quantum defects μ_α: $\mu_\alpha=\mu_\alpha^{(0)}+\epsilon\mu_\alpha^{(1)}$ with $\epsilon=[E-E(^2\mathrm{P}_{J^+})]/R_M$
- transformation matrix $U_{i_{(F)}\alpha}$ between close-coupling eigenchannels α and dissociation channels i
$$U_{i_{(F)}\alpha}=\sum_{\bar{\alpha}}U_{i_{(F)}\bar{\alpha}}V_{\bar{\alpha}\alpha}$$
where $U_{i\bar{\alpha}}=\langle LSJ|J^+jJ\rangle$ or $U_{i_F\bar{\alpha}}=\langle LSJF|J^+F^+jF\rangle$, $V_{\bar{\alpha}\alpha}$ accounts for the small departure of the close-coupling eigenchannels from pure LS coupling (where no s-d or p-f interaction occurs): $\mathbf{V}=\prod_{i,j>i}^{N}\mathbf{R}(\theta_{ij})$
- positions of the ionization thresholds $E(^2\mathrm{P}_{J^+(F^+)})$ (incl. hyperfine structure)

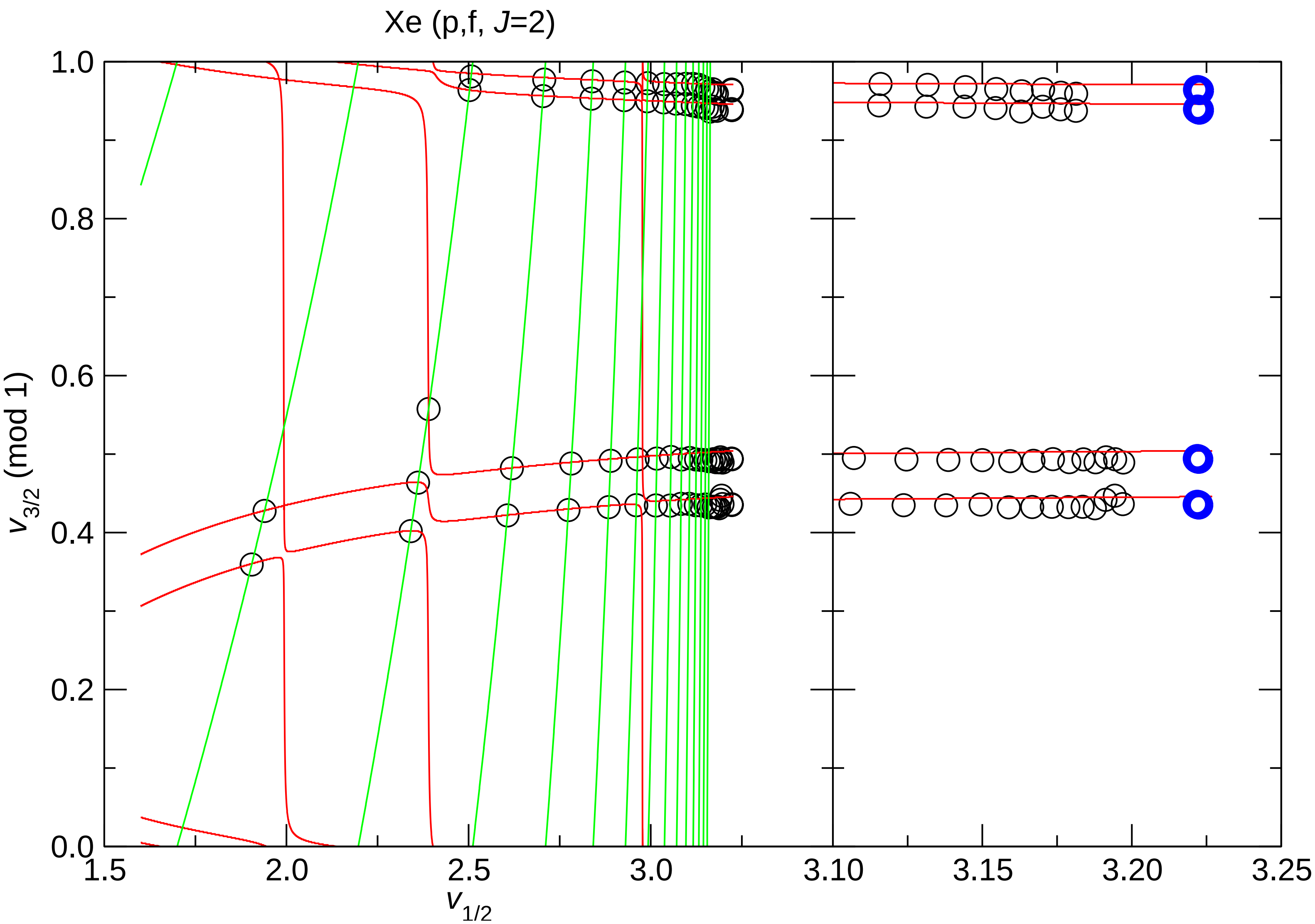
$$\nu_{i_{(F)}}\equiv\nu_{J^+F^+}(E)=\sqrt{R_M/(E(^2\mathrm{P}_{J^+(F^+)})-E)}$$



Xe (s,d, J=1)
1.0
0.8
0.6
0.4
0.2
0.0
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
ν3/2 (mod 1)
ν1/2



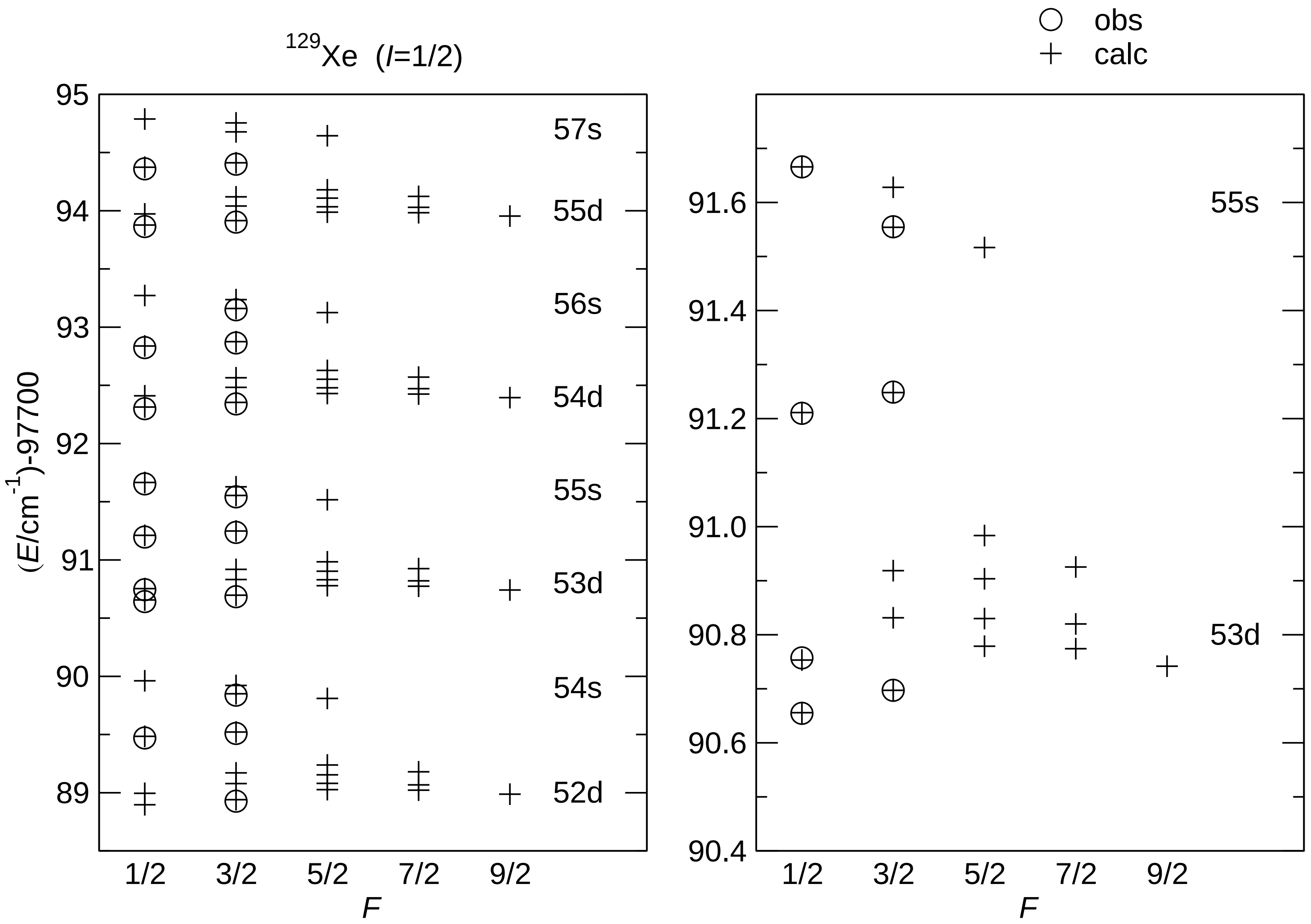
Xe (p,f, J=1)
1.0
0.8
0.6
0.4
0.2
0.0
$v_{3/2}$ (mod 1)
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
$v_{1/2}$



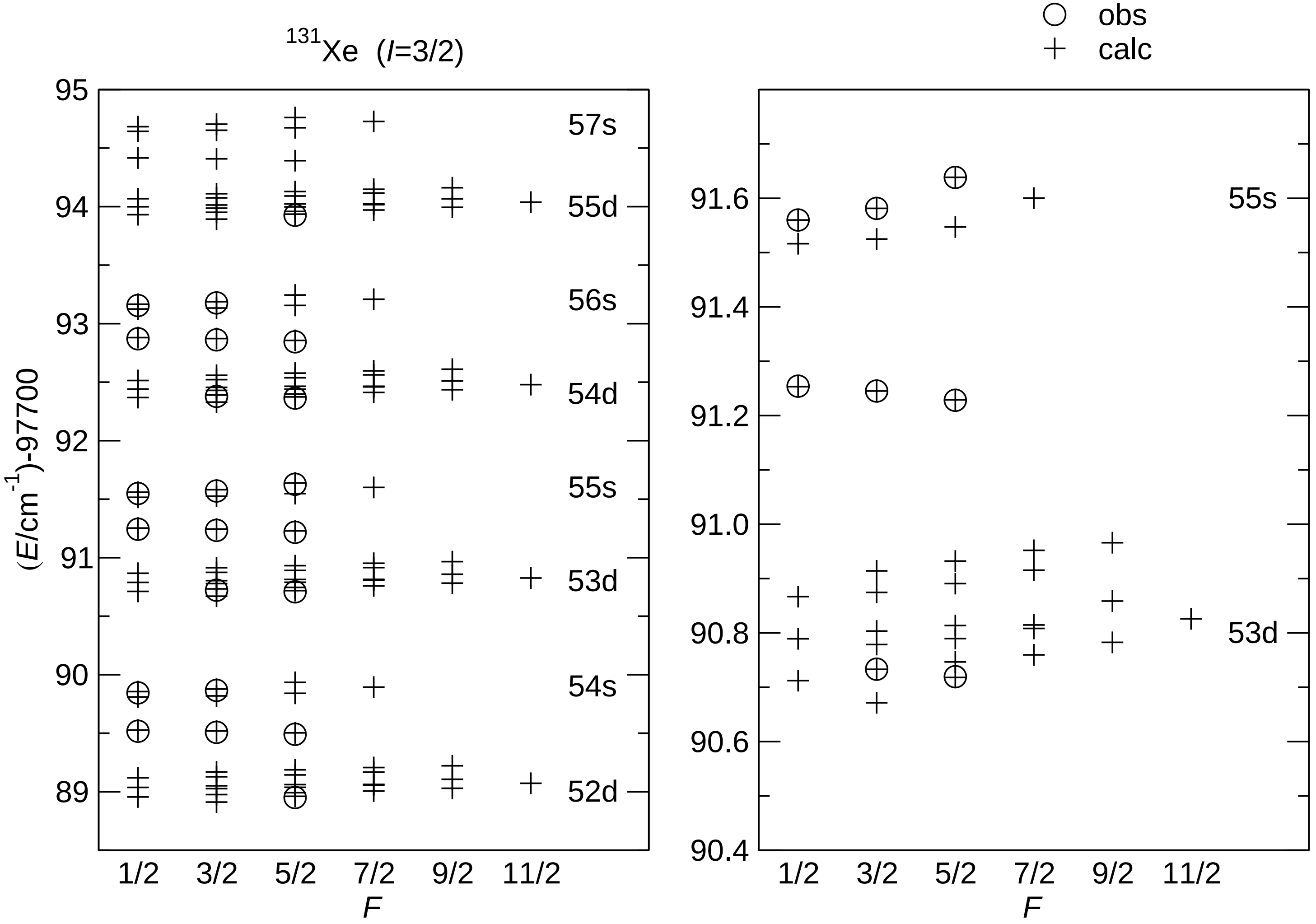
Xe (p,f, J=2)
1.0
0.8
0.6
0.4
0.2
0.0
$v_{3/2}$ (mod 1)
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
$v_{1/2}$

	μ_α		μ_α		μ_α		μ_α
s $^1P_1$	−0.0173	p $^1S_0$	0.4089	d $^1P_1$	0.1234	f $^1D_2$	0.0359
s $^3P_0$	0.0491	p $^3S_1$	0.5501	d $^3P_0$	0.5409	f $^3D_1$	0.0558
s $^3P_1$	0.0385	p $^1P_1$	0.6073	d $^3P_1$	0.5457	f $^3D_2$	0.0531
s $^3P_2$	0.0282	p $^3P_0$	0.5562	d $^3P_2$	0.5383	f $^3D_3$	0.0106
		p $^3P_1$	0.5092	d $^1D_2$	0.3553	f $^1F_3$	0.0681
		p $^3P_2$	0.4951	d $^3D_1$	0.3909	f $^3F_2$	0.0190
		p $^1D_2$	0.5496	d $^3D_2$	0.3974	f $^3F_3$	0.0162
		p $^3D_1$	0.6135	d $^3D_3$	0.3319	f $^3F_4$	0.0452
		p $^3D_2$	0.5782	d $^1F_3$	0.3816	f $^1G_4$	0.0206
		p $^3D_3$	0.5630	d $^3F_2$	0.4946	f $^3G_3$	−0.0219
				d $^3F_3$	0.5019	f $^3G_4$	0.0193
				d $^3F_4$	0.4797	f $^3G_5$	0.0460

uncertainties of fitted eigen quantum defects: ∼0.003

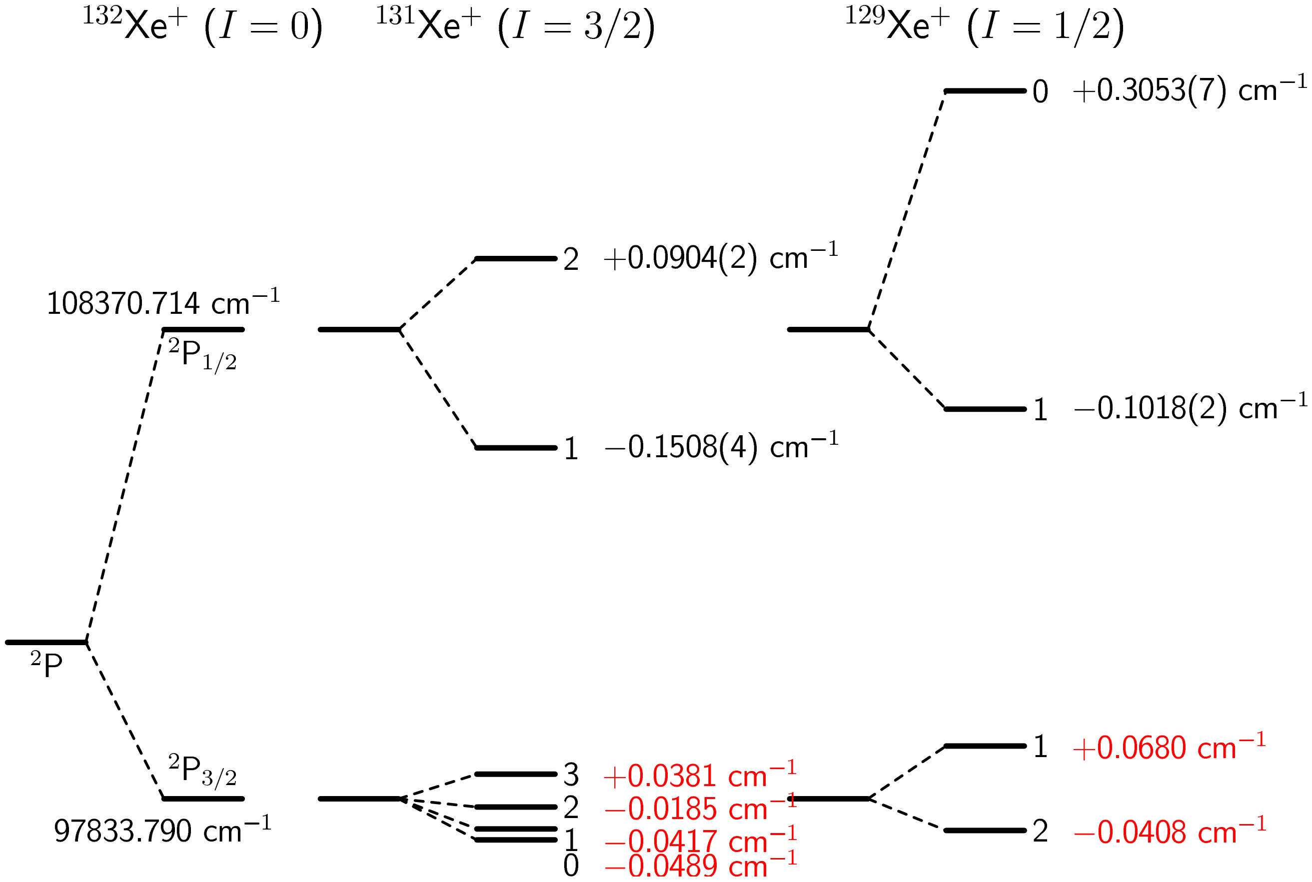


129Xe (I=1/2)
obs
calc
(E/cm-1)-97700
95
94
93
92
91
90
89
57s
55d
56s
54d
55s
53d
54s
52d
1/2
3/2
5/2
7/2
9/2
F
91.6
91.4
91.2
91.0
90.8
90.6
90.4
55s
53d
1/2
3/2
5/2
7/2
9/2
F



131Xe (I=3/2)
obs
calc
(E/cm-1)-97700
95
94
93
92
91
90
89
57s
55d
56s
54d
55s
53d
54s
52d
1/2
3/2
5/2
7/2
9/2
11/2
F
91.6
91.4
91.2
91.0
90.8
90.6
90.4
55s
53d
1/2
3/2
5/2
7/2
9/2
11/2
F

Hyperfine structure of ^{129}Xe$^+$ and ^{131}Xe$^+$

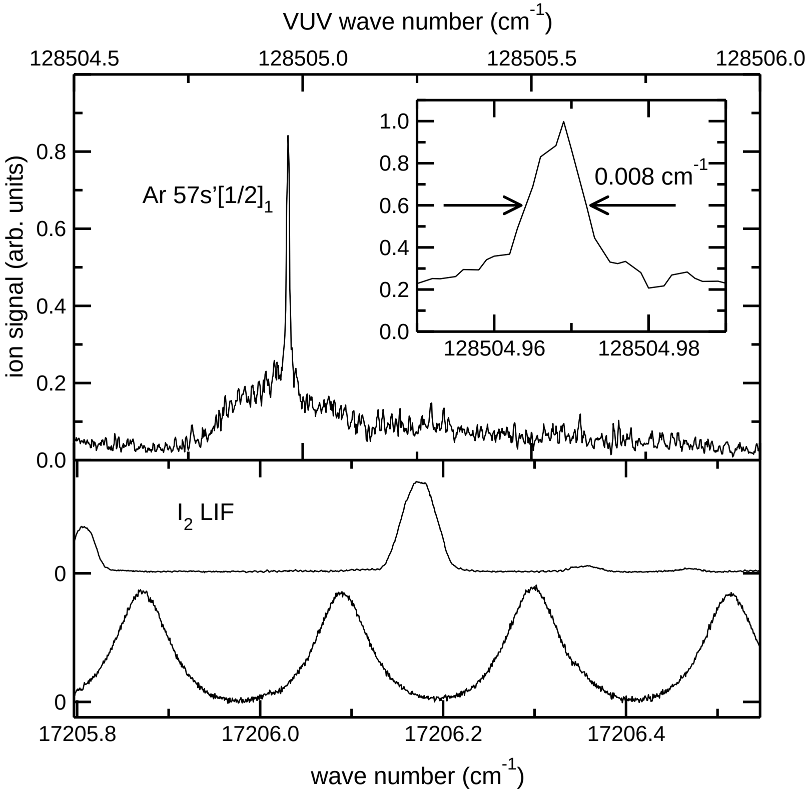


Rydberg states

Rydberg states = ion + Rydberg el. (n,ℓ): $E_{n\ell\alpha} = E_{\text{ion}} - \frac{R_M}{(n-\delta_{\ell\alpha})^2} = E_{\text{ion}} - \frac{R_M}{(n^*)^2}$

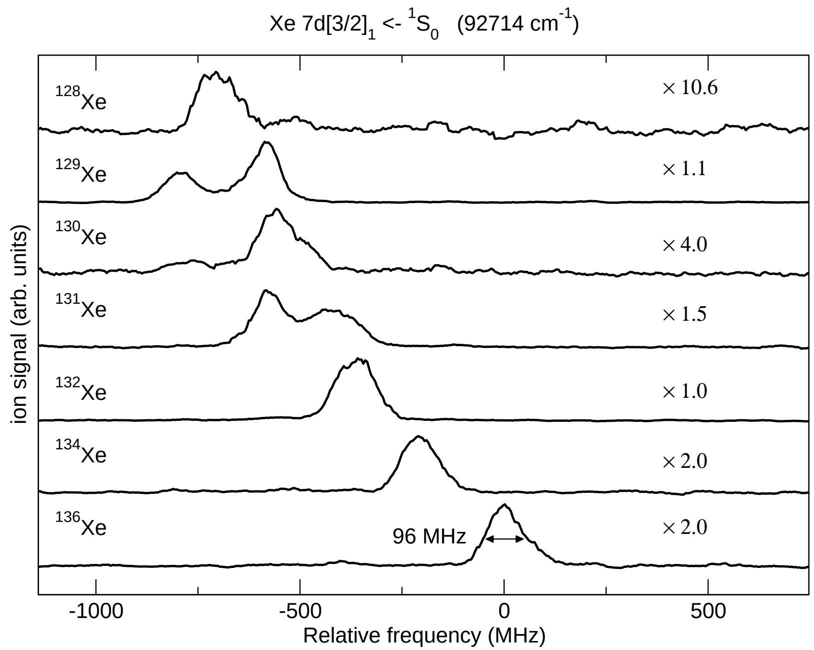
	Xe $(5p)^5[^2P_{3/2}]$ 54s ($n^* \approx 50.0$)	C_6H_6 [C_6H_5CN]
# particles	1 nucleus + 54 electrons	12 nuclei + 42 electrons
mass	131.29 u	78.11 u
radius	$\langle r \rangle \approx 1.5(n^*)^2 a_0$ $\approx 3750 a_0 = 198$ nm	$r_{\text{vdW}} \approx 0.35$ nm
level spacing	$E_{n+1} - E_n \approx 2R(n^* + 0.5)^{-3}$ ≈ 51.1 GHz	$E_{J+1,K} - E_{J,K} \approx 2B(J+1)$ $\approx (J+1) \cdot 11.4$ GHz
(trans.) dipole m.	$\langle n\ell \vert \mu \vert n\ell+1 \rangle \propto (n^*)^2 e a_0$ $\approx 6.4 \cdot 10^3$ D	[$\mu_a = 4.48$ D]

High-resolution VUV laser systems



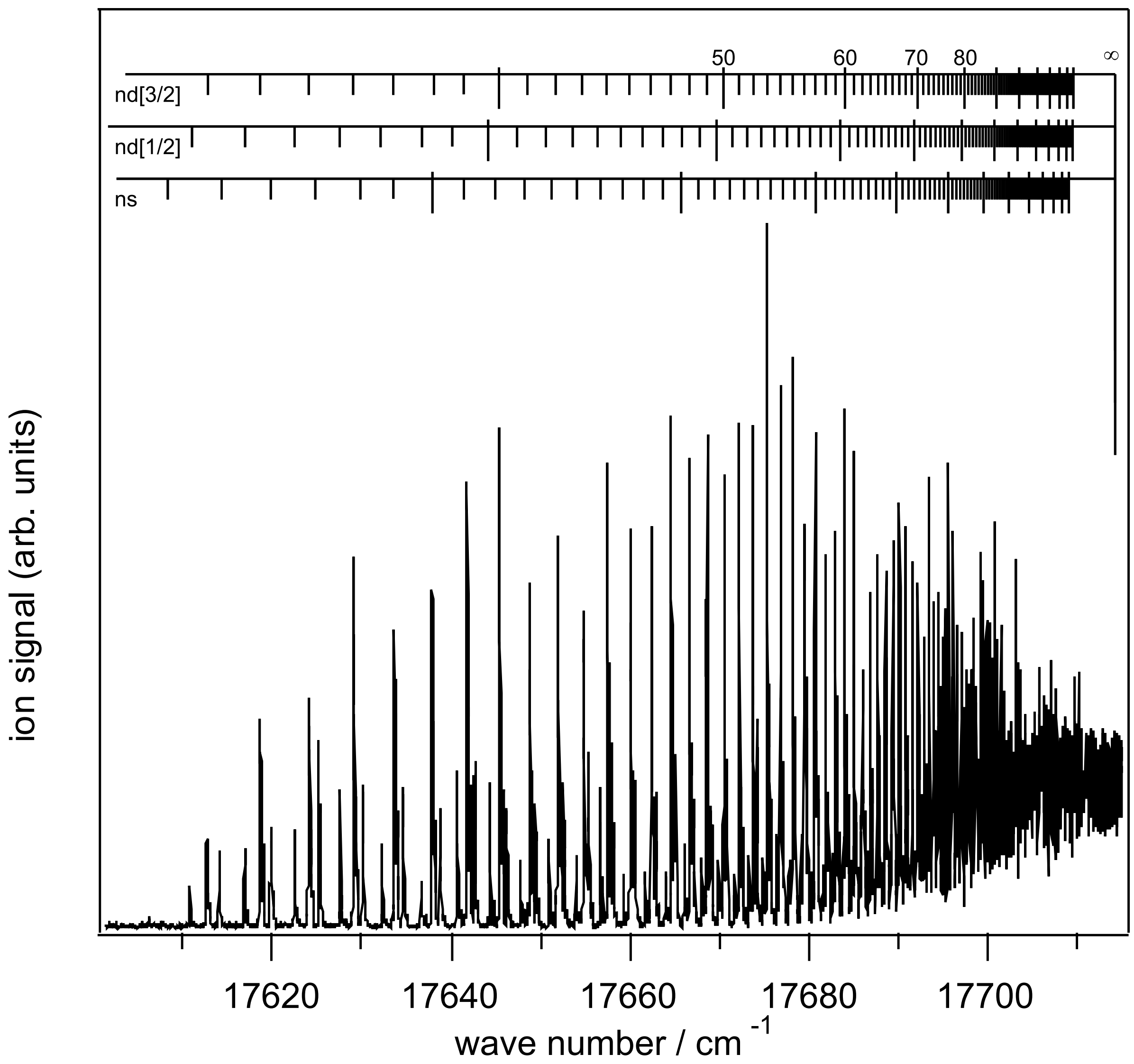
U. Hollenstein, H. Palm, F. Merkt, Rev. Sci. Instr. **71**, 4023 (2000)

resolution: 1 μeV @ 15.9 eV



Th. A. Paul, F. Merkt, J. Phys. B **38**, 4145 (2005)

resolution: 0.4 μeV @ 11.5 eV



Photoionization laser spectrum of ^{136}Xe excited via the $6p\,[1/2]_0$ state ($80118.9839\ \mathrm{cm}^{-1}$ above the $^1S_0$ ground state)