Millimeter wave spectroscopy 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

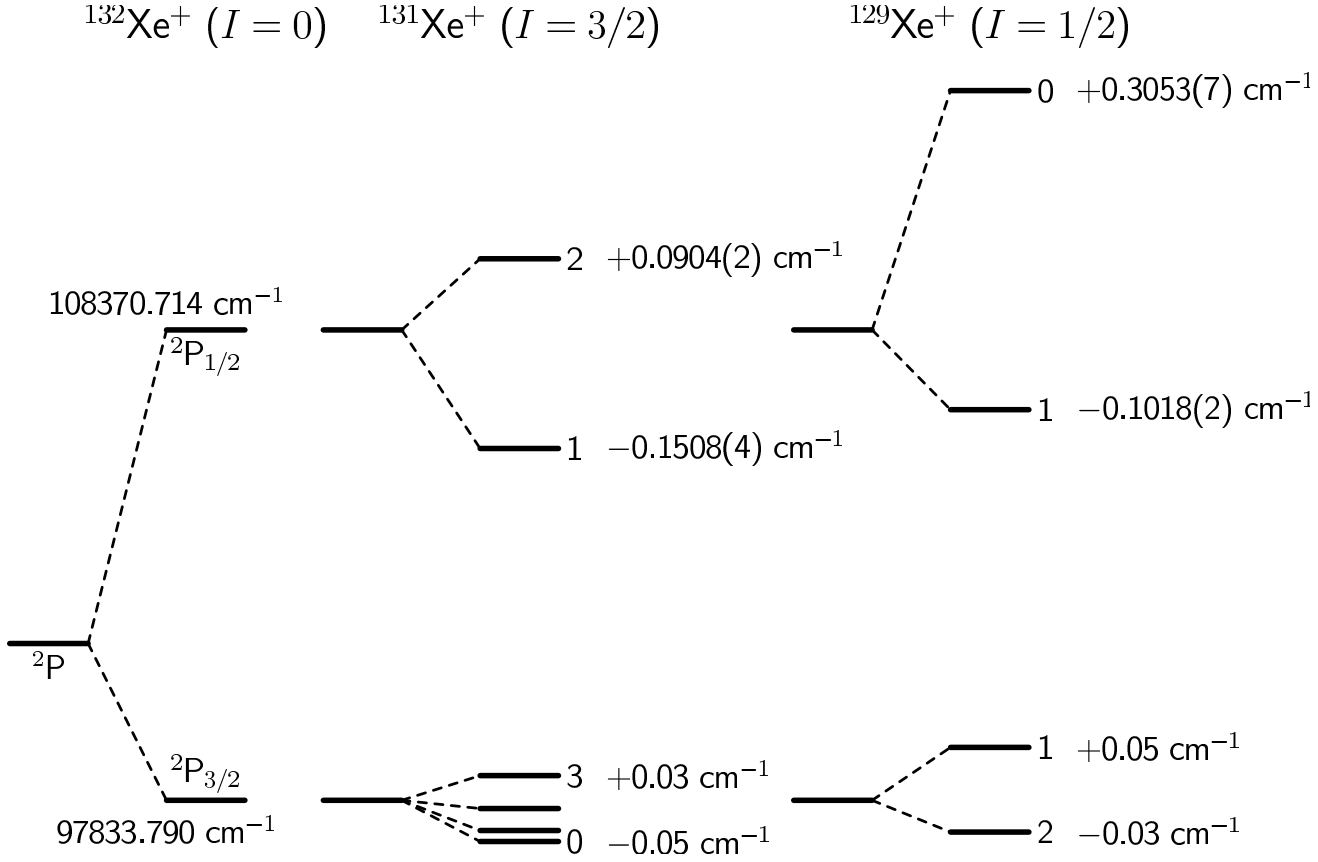
Rydberg states

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

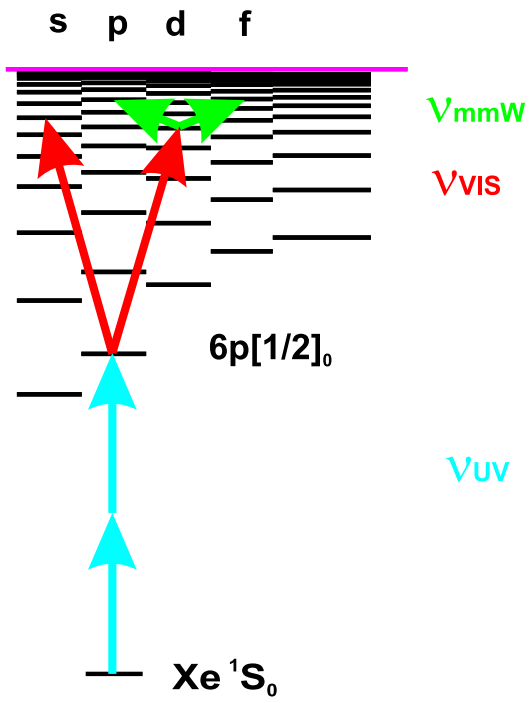
	Xe $(5p)^5[^2P_{3/2}]$ 54s $(n^* \approx 50.0)$	C_6H_6 $[C_6H_5CN]$
# particles	1 nucleus + 54 electrons	12 nuclei + 42 electrons
mass	131.29 u	78.11 u
radius	$\langle r\rangle \approx 1.5(n^*)^2 a_0$ $\approx 3750 a_0 = 198$ nm	$r_{\text{vdW}} \approx 0.35$ nm
level spacing	$E_{n+1} - E_n \approx 2R(n^*+0.5)^{-3}$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

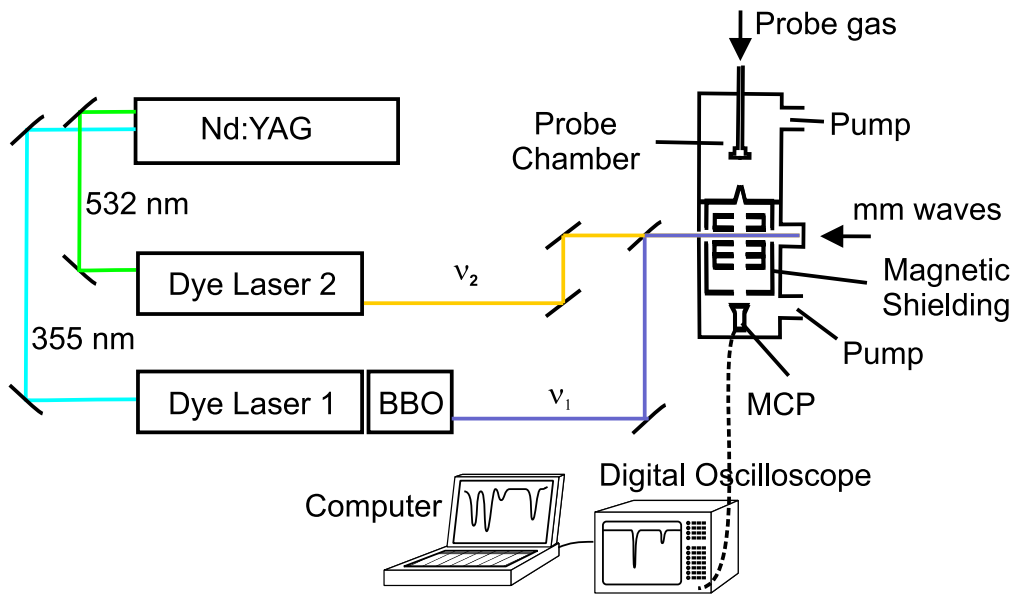
Hyperfine structure of ^{129}Xe$^+$ and ^{131}Xe$^+$

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



Millimeter wave experiments

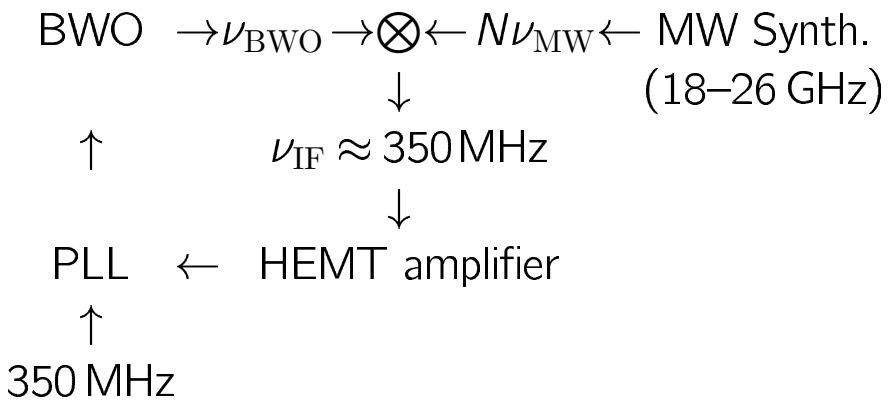


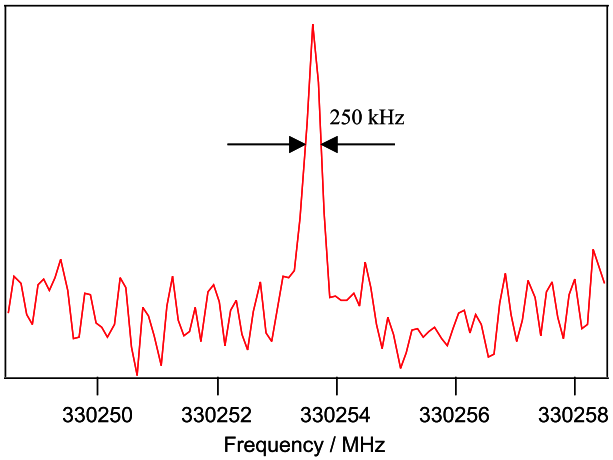


Millimeter wave system

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

Stabilisation:





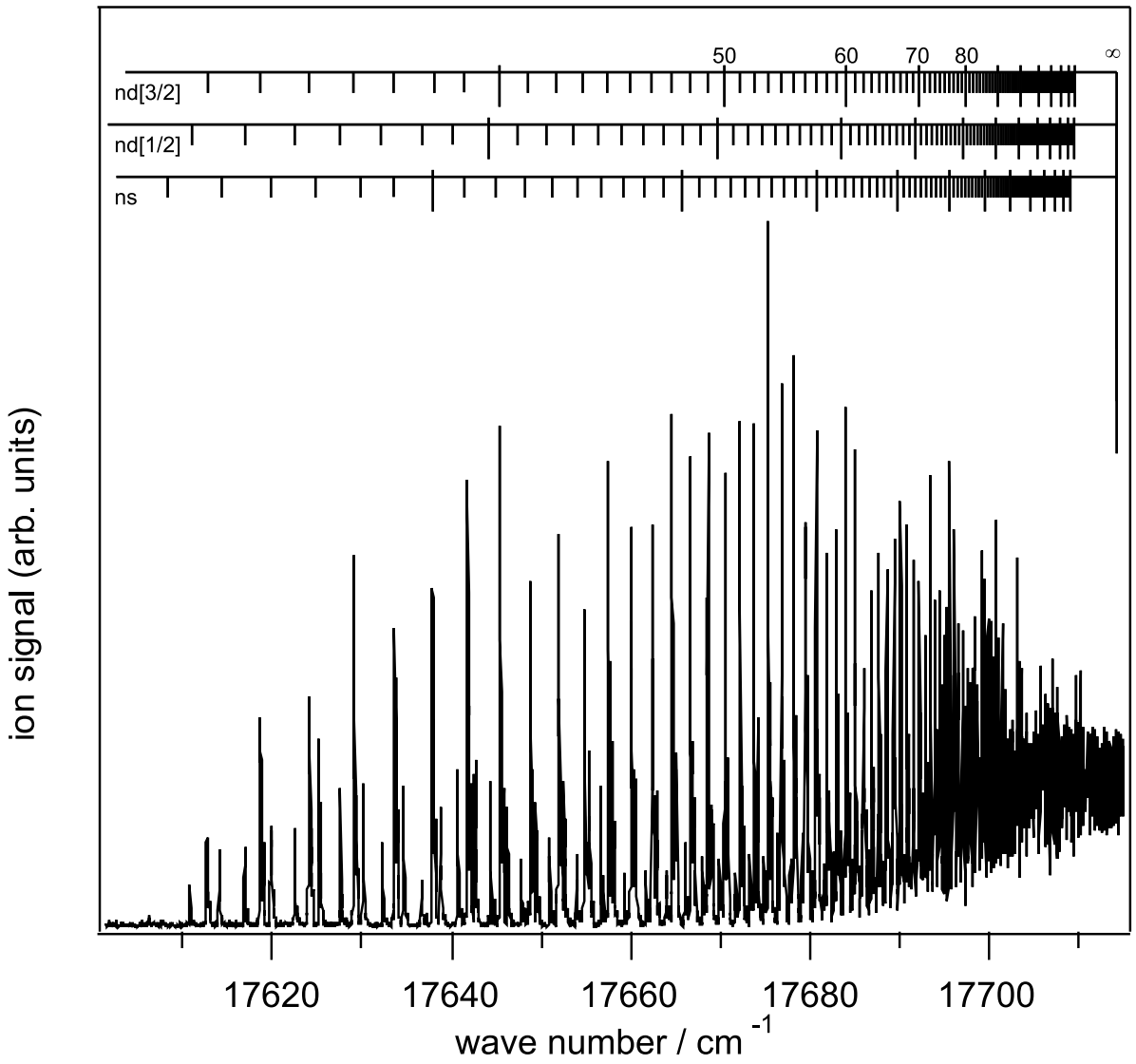
^{132}Xe: 61p $[5/2]_2 \leftarrow$ 52d $[3/2]_1$

Accuracy of the transition frequencies: <1 MHz

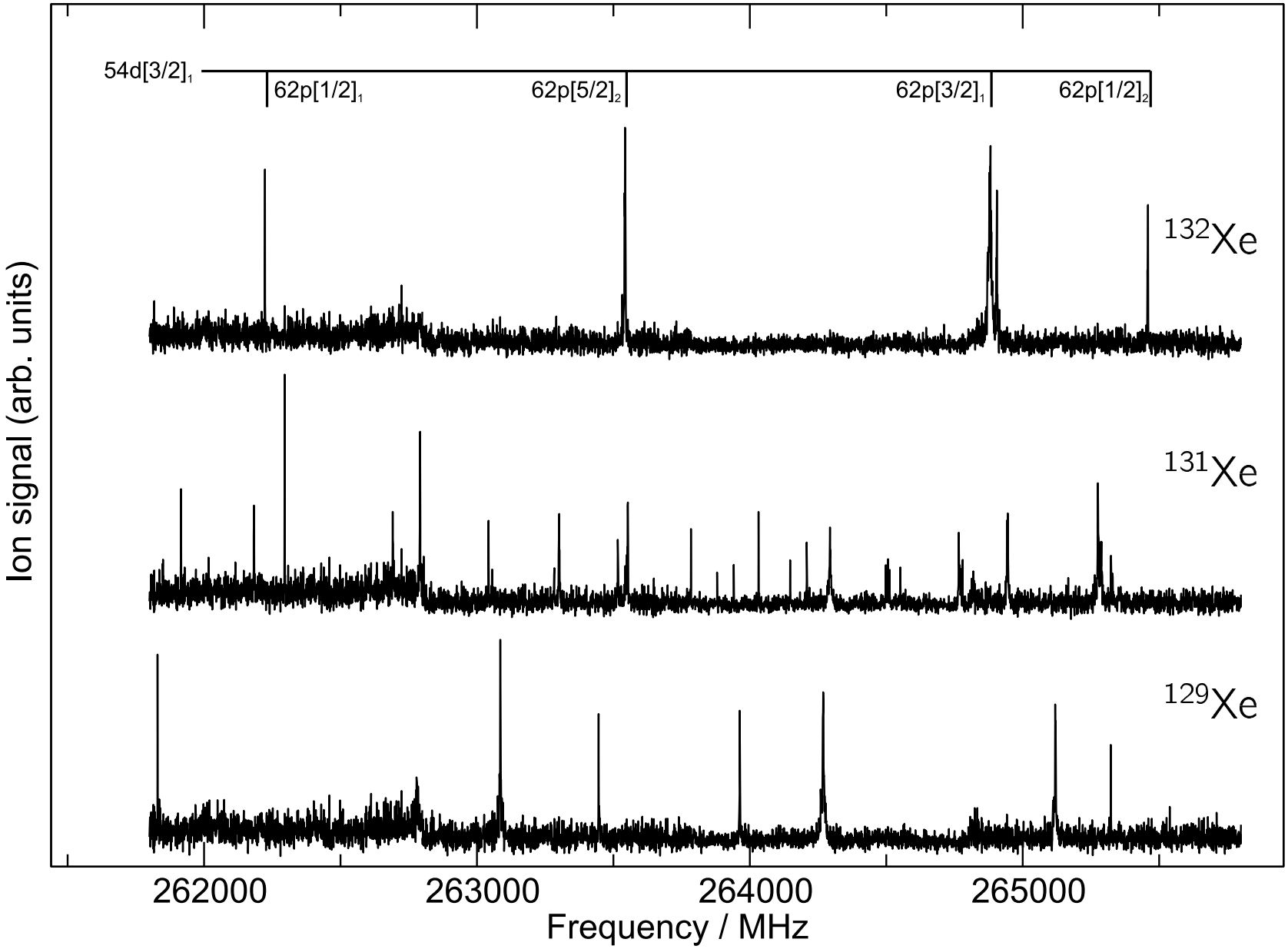
Harmonic mixer, HEMT amplifier: Univ. Köln
Phase lock loop: ETH Zurich

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

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



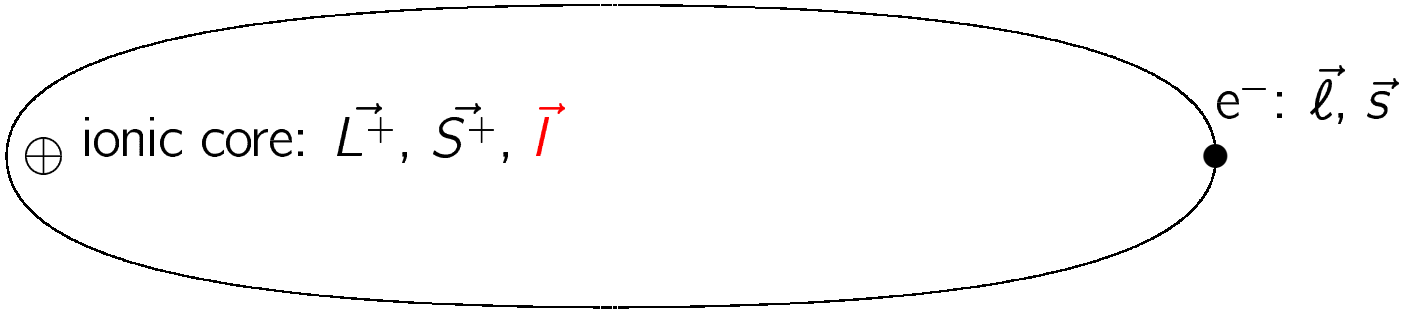
Photoionization laser spectrum of ^{136}Xe excited via the $6p\,[1/2]_0$ state (80118.9839 cm^{-1} above the $^1S_0$ ground state)


54d[3/2]1
62p[1/2]1
62p[5/2]2
62p[3/2]1
62p[1/2]2
132Xe
131Xe
129Xe
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:

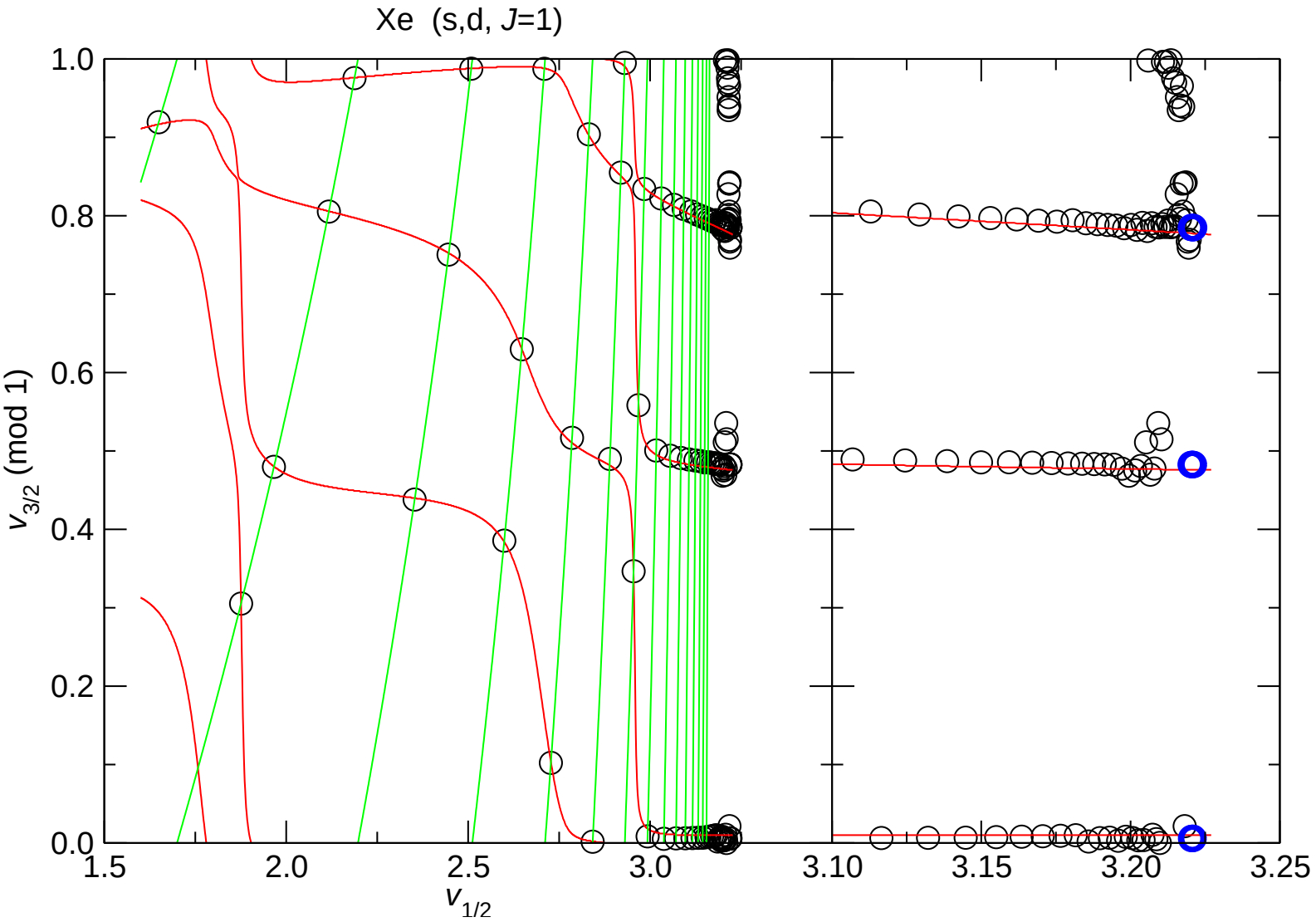
$$\det\left|U_{i_{(F)}\alpha}\sin[\pi(\mu_\alpha+\nu_{i_{(F)}})]\right|=0$$

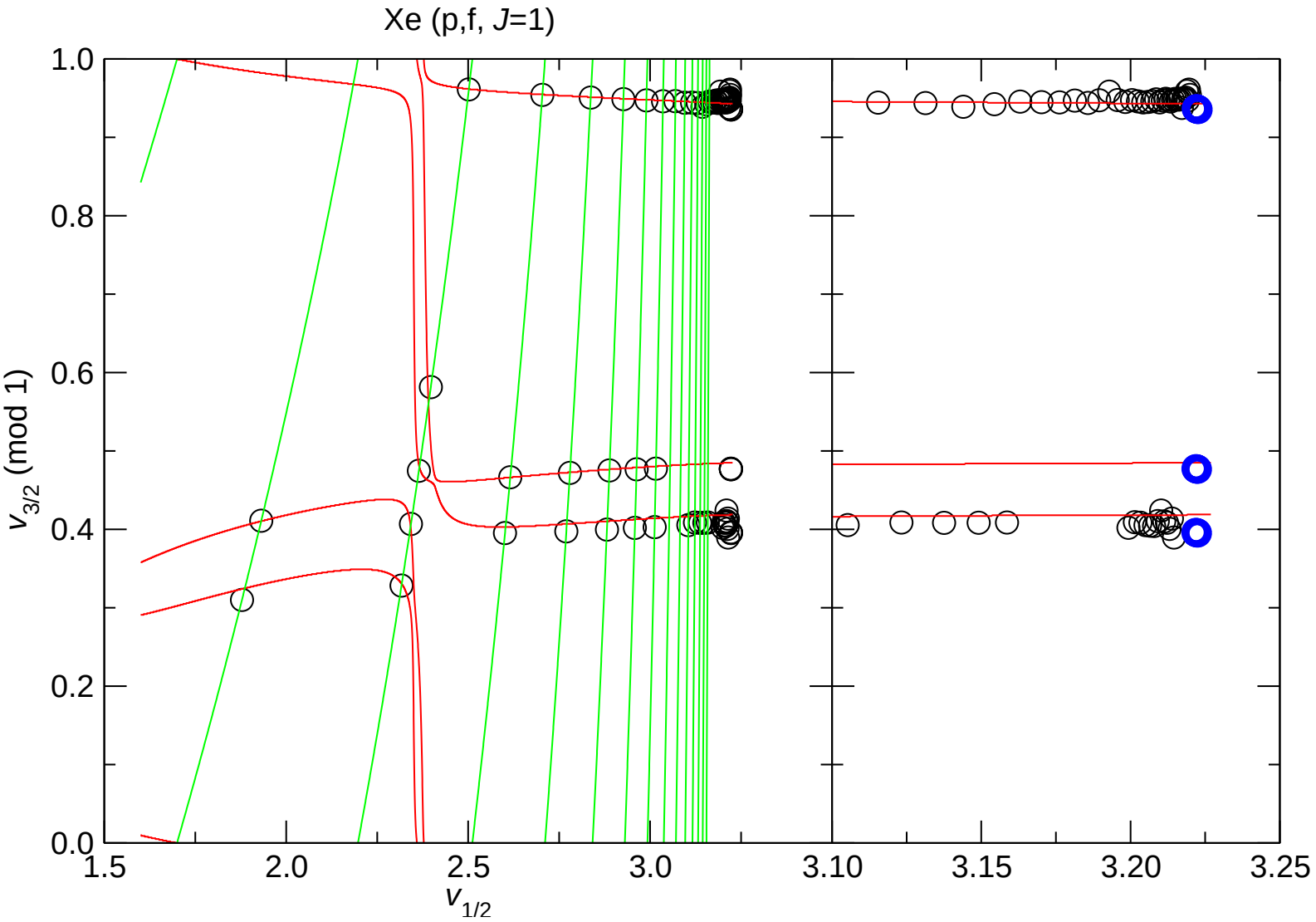
- eigen quantum defects μ_α: $\mu_\alpha=\mu_\alpha^{(0)}+\epsilon\mu_\alpha^{(1)}$ with $\epsilon=[E-E(^2\mathrm{P}_{J^+})]/R_M$
- transformation matrix $U_{i_{(F)}\alpha}$ between close-coupling eigenchannels α and dissociation channels i

  $$U_{i_{(F)}\alpha}=\sum_{\bar\alpha}U_{i_{(F)}\bar\alpha}V_{\bar\alpha\alpha}$$

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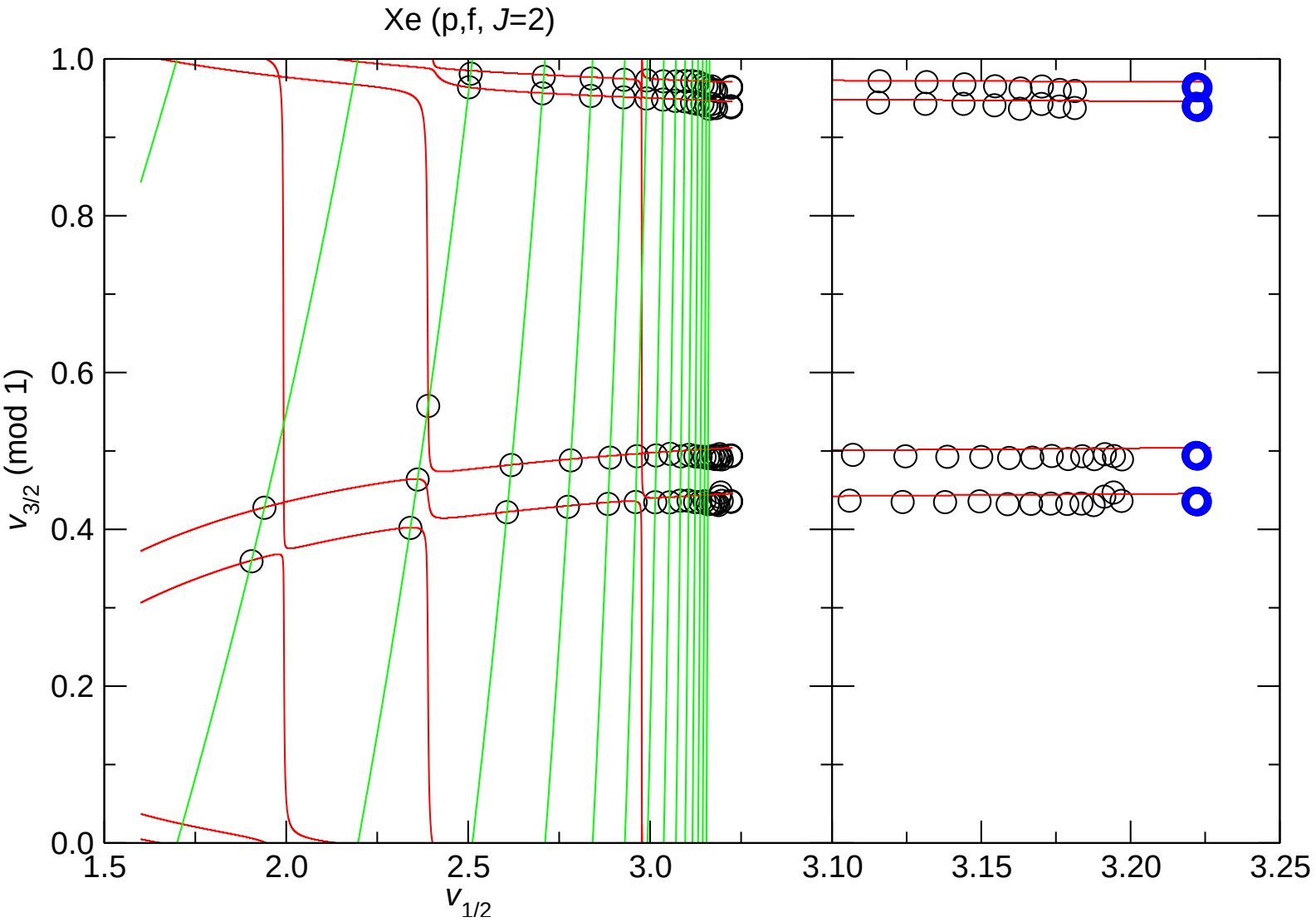
Xe (p,f, J=2)
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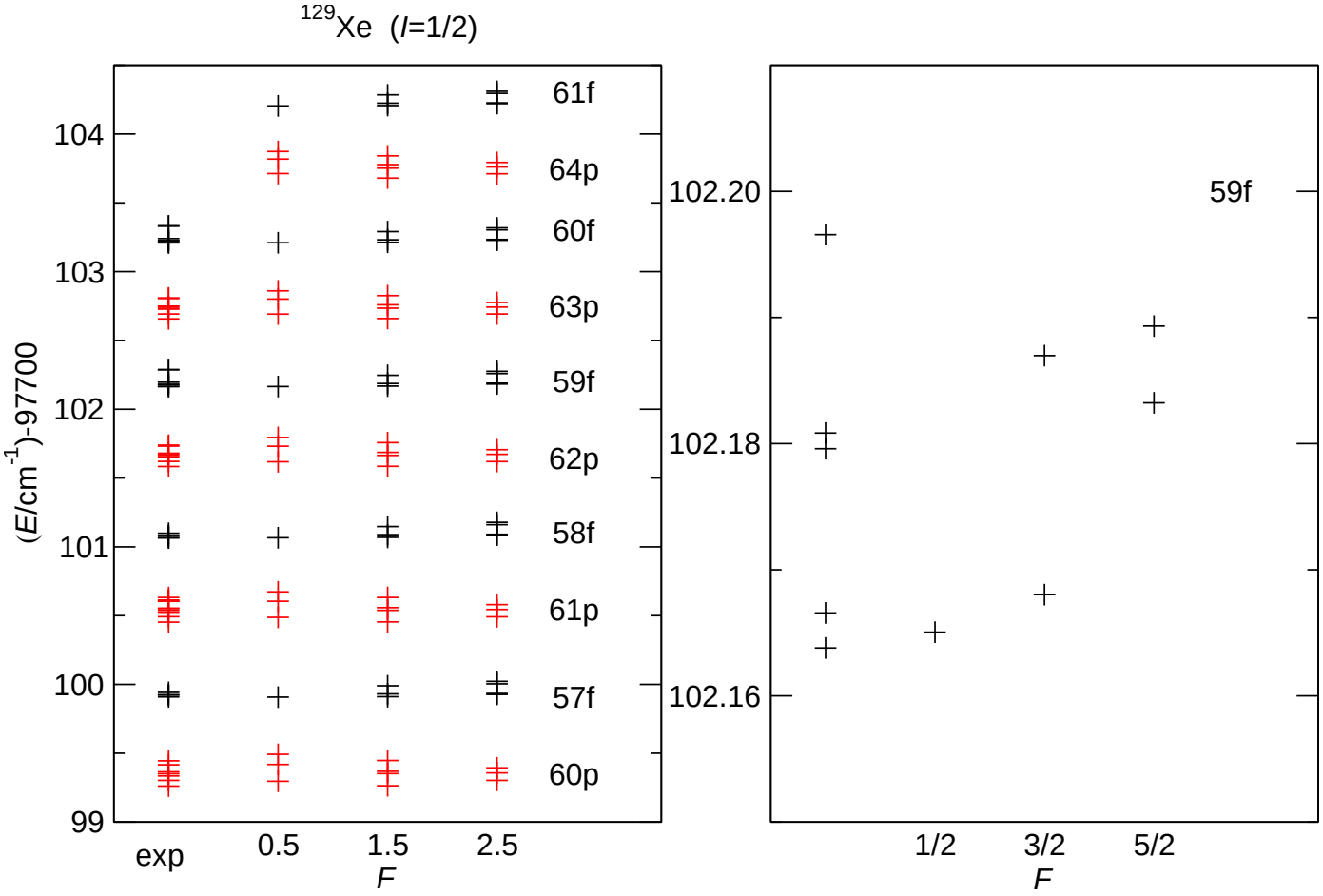
0.8
0.6
0.4
0.2
0.0
ν3/2 (mod 1)
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
ν1/2

	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

Hyperfine structure of ^{129}Xe



Analysis and MQDT Calculations

Rydberg series of even Xe isotopes ($I = 0$):

$n\ell[K]_J = (5\mathrm{p})^5\,[^2\mathrm{P}_{3/2}]\; n\ell[K]_J \qquad \ell = 0, 1, 2, 3, \ldots$ (s,p,d,f,...)
$n\ell'[K]_J = (5\mathrm{p})^5\,[^2\mathrm{P}_{1/2}]\; n\ell[K]_J \qquad K = |J^+ - \ell|, \ldots, J^+ + \ell, \;\; J = K \pm 1/2$

e.g., 10 np series: np $[1/2]_{0,1}$, np $[3/2]_{1,2}$, np $[5/2]_{2,3}$, np′ $[1/2]_{0,1}$, np′ $[3/2]_{1,2}$

Rydberg formula: $E_{n\ell K J} = E(^2\mathrm{P}_{J^+}) - \dfrac{R_M}{(n - \delta_{\ell K J})^2} = E(^2\mathrm{P}_{J^+}) - \dfrac{R_M}{(\nu_{J^+})^2}$

effective principal quantum number $\nu_{J^+}(E) = \left[\dfrac{R_M}{E(^2\mathrm{P}_{J^+}) - E}\right]^{1/2}$

^{132}Xe: $E(^2\mathrm{P}_{3/2}) = 97\,833.790\,\mathrm{cm}^{-1}$, $E(^2\mathrm{P}_{1/2}) = 108\,370.714\,\mathrm{cm}^{-1}$,
$R_M = 109\,736.8593\,\mathrm{cm}^{-1}$

Series	n					$\delta_{\ell KJ}$
nf $[5/2]_2$	57	58	59	60	61	0.03018(12)
nf $[3/2]_2$	57	58	59	60	61	0.05509(12)
nf $[3/2]_1$	57	58	59	60	61	0.05804(12)
np $[3/2]_2$	60	61	62	63		3.50050(12)
np $[3/2]_1$	60	61	62	63		3.51734(12)
	60	61	62	63		3.51807(12)
np $[5/2]_2$	60	61	62	63		3.55872(12)
np $[1/2]_1$	60	61	62	63		3.59870(12)
ns $[3/2]_1$	54	55	56			3.99423(8)
nd $[3/2]_1$	52	53	54	55		2.21505(8)
nd $[1/2]_1$	52	53	54	55		2.51732(8)

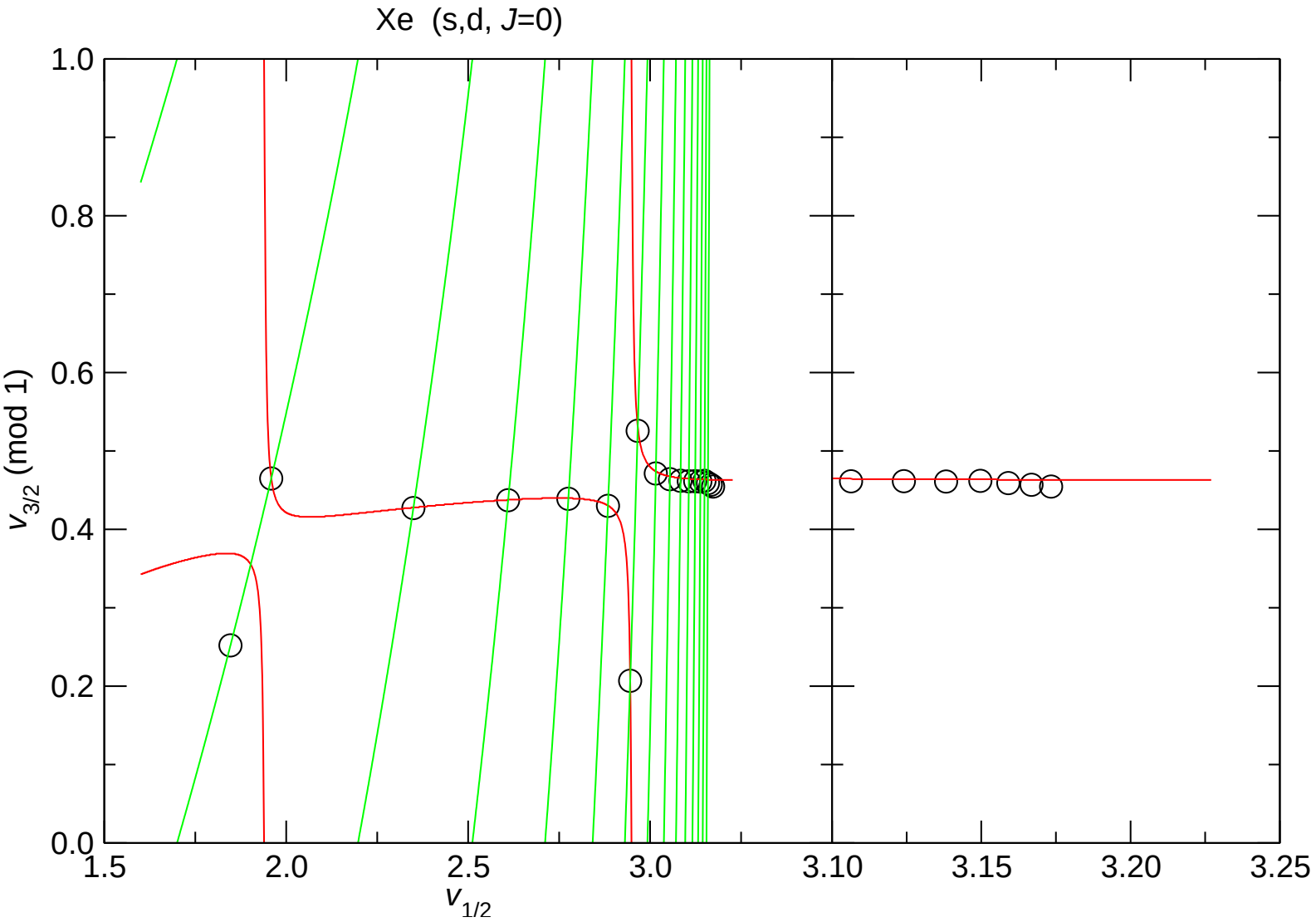
Hyperfine structure of the ion:

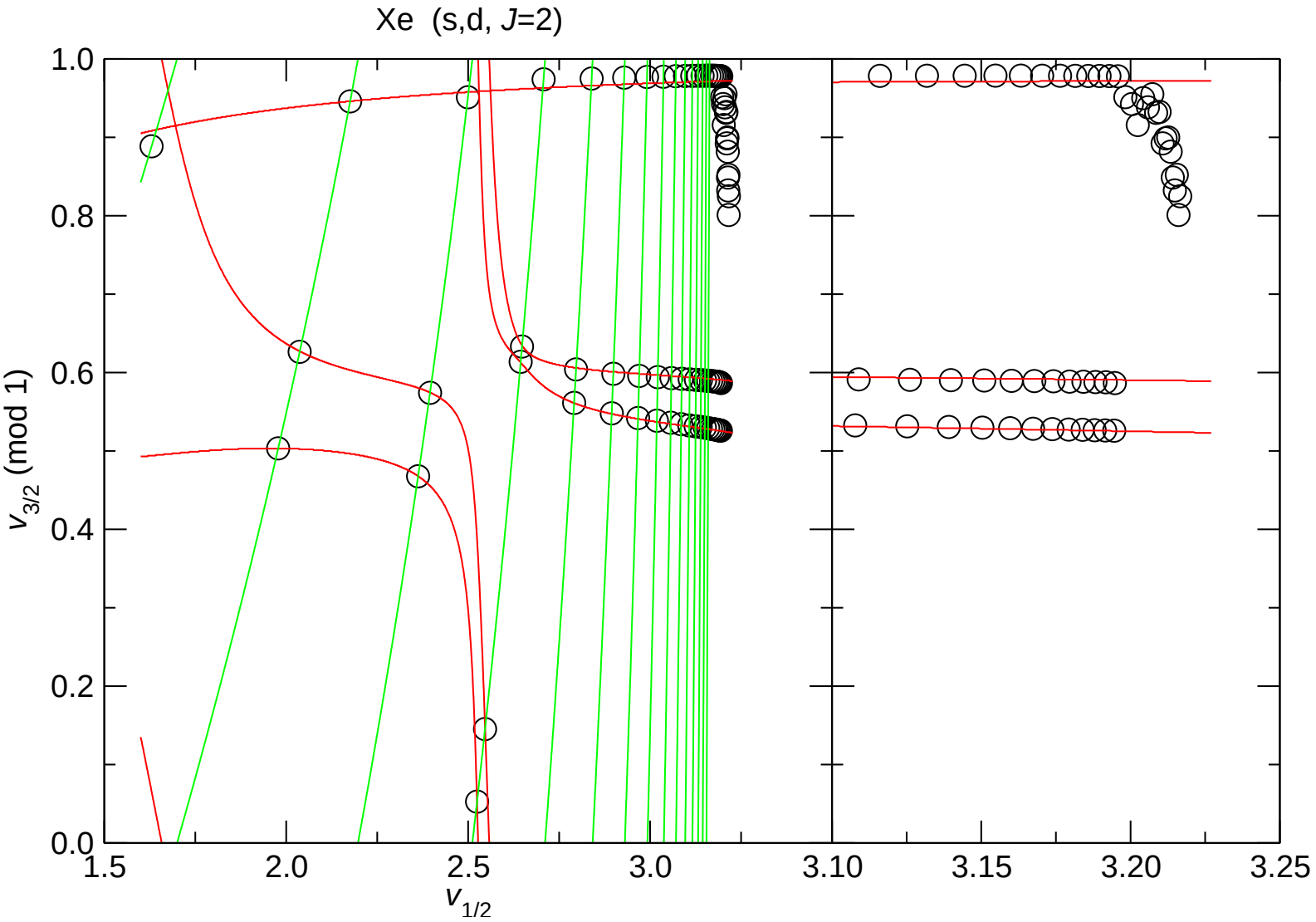
$$E(J^+,F^+) = E(J^+) + A_{J^+}\frac{C^+}{2} + B_{J^+}\frac{\frac{3}{4}C^+(C^+ +1) - I(I+1)J^+(J^+ +1)}{2I(2I-1)J^+(2J^+ -1)}$$

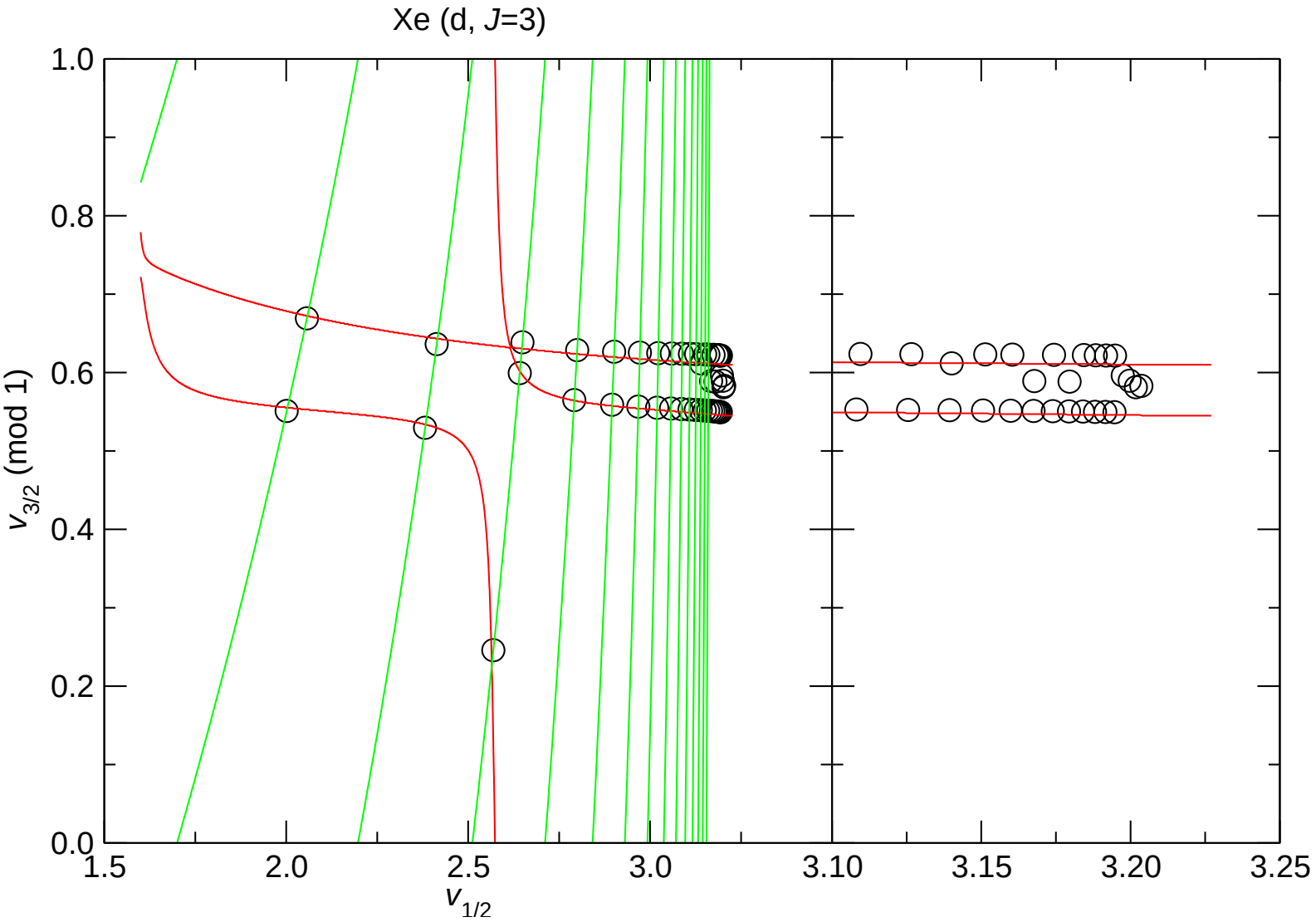
where $C^+ = F^+(F^+ +1) - I(I+1) - J^+(J^+ +1)$
and $B_{J^+} = 0$ for $J^+ < 1$ or $I < 1$
(A_{J^+}, B_{J^+}: magnetic dipole and electric quadrupole hyperfine parameter of the ion)

	^{129}Xe	^{131}Xe
$A(^2\mathrm{P}_{3/2})$ / cm^{-1}	$\approx -0.054(15)$ cm^{-1}	$\approx 0.014(5)$ cm^{-1}
$B(^2\mathrm{P}_{3/2})$ / cm^{-1}	—	$\approx 0.006(5)$ cm^{-1}
$A(^2\mathrm{P}_{1/2})$ / cm^{-1}	$-0.4071(9)$ cm^{-1}	$0.1206(3)$ cm^{-1}

H. J. Wörner *et al.*, Phys. Rev. A **71**, 052504 (2005).


Xe (s,d, J=0)
1.0
0.8
0.6
0.4
0.2
0.0
ν3/2 (mod 1)
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
ν1/2


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


Xe (d, J=3)
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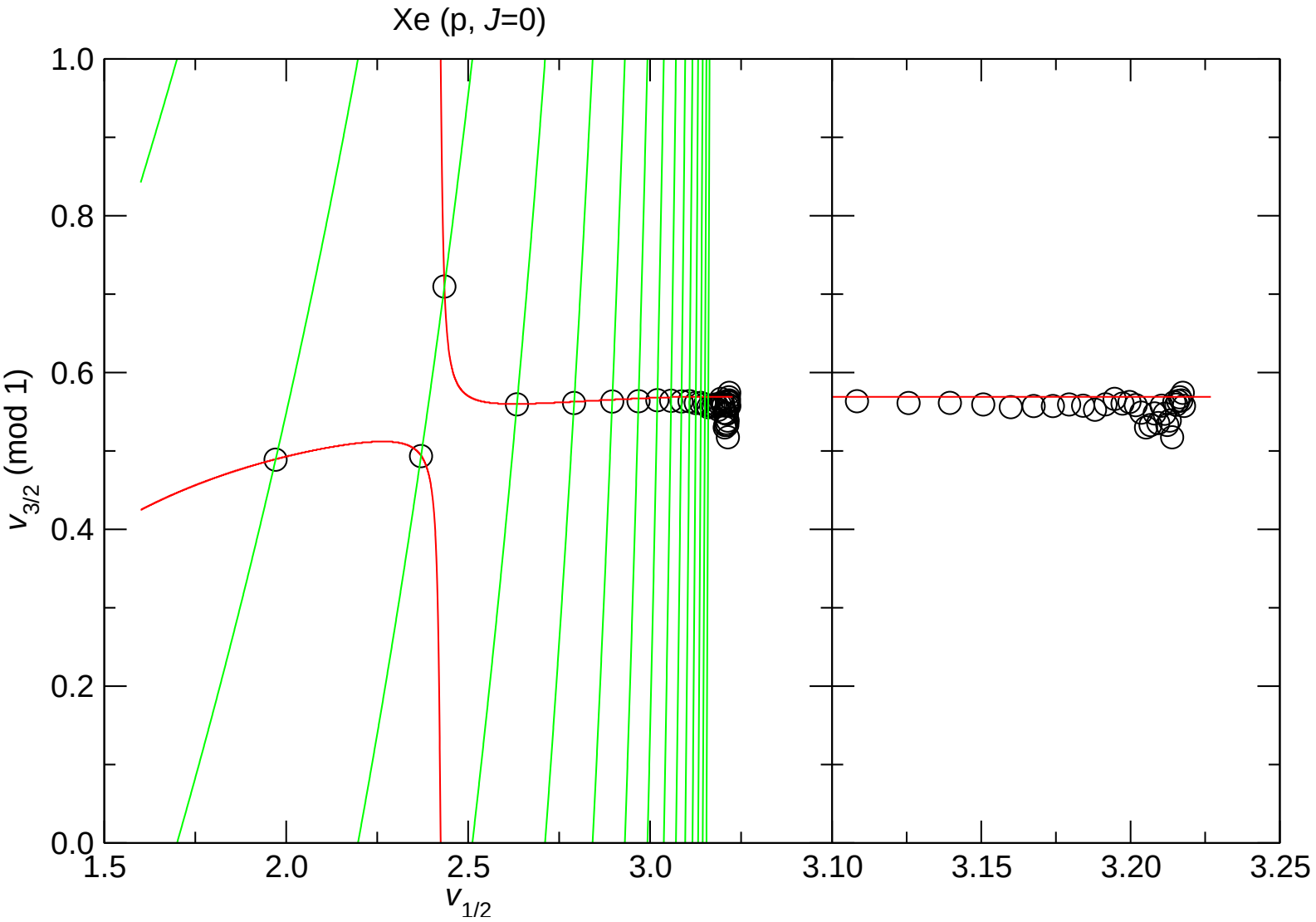
0.6
0.4
0.2
0.0
ν3/2 (mod 1)
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
ν1/2


Xe (p, J=0)
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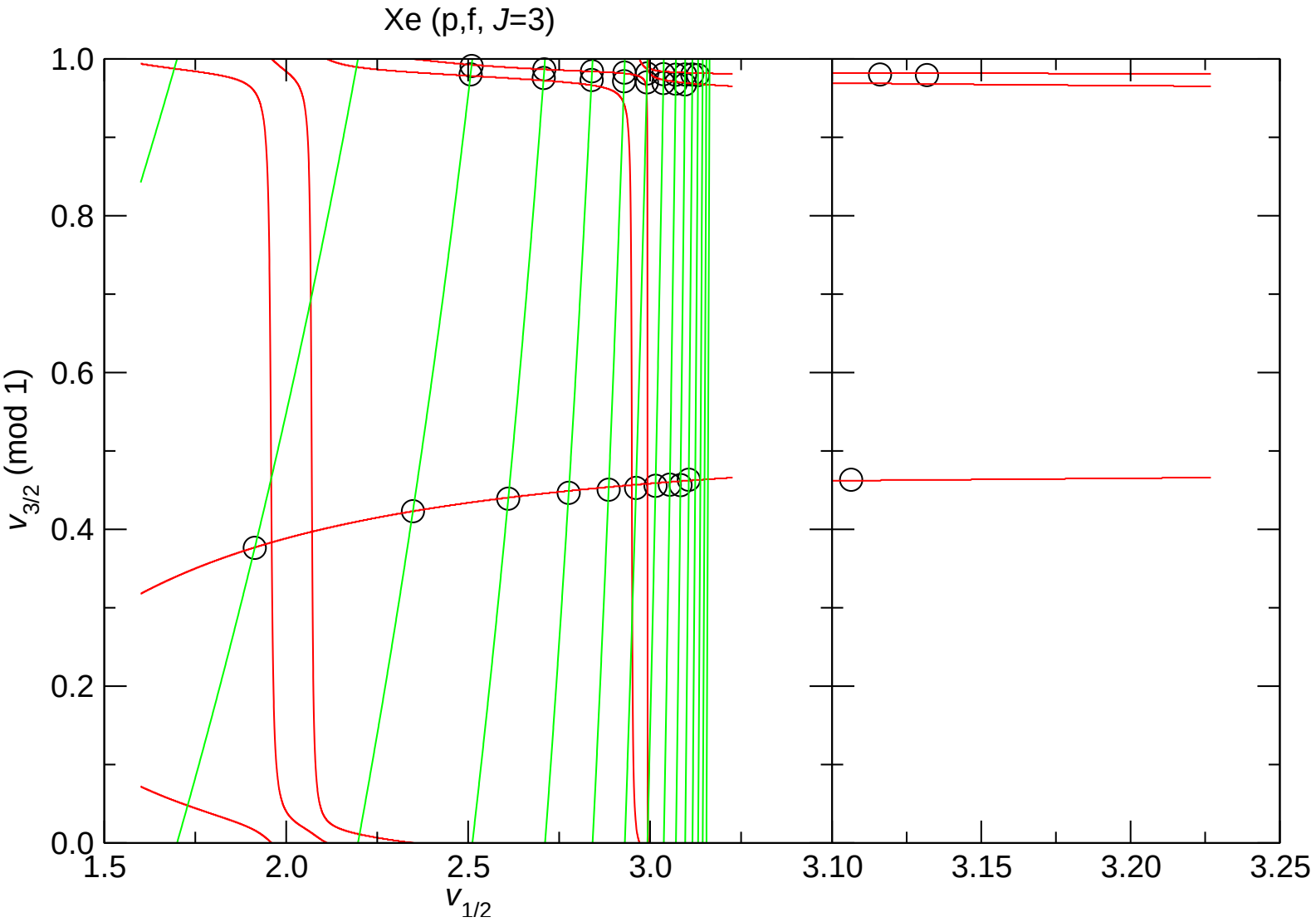
0.8
0.6
0.4
0.2
0.0
ν3/2 (mod 1)
1.5
2.0
2.5
3.0
3.10
3.15
3.20
3.25
ν1/2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