High-resolution spectroscopy of *n*p Rydberg states of He_2: Autoionization dynamics and MQDT calculations

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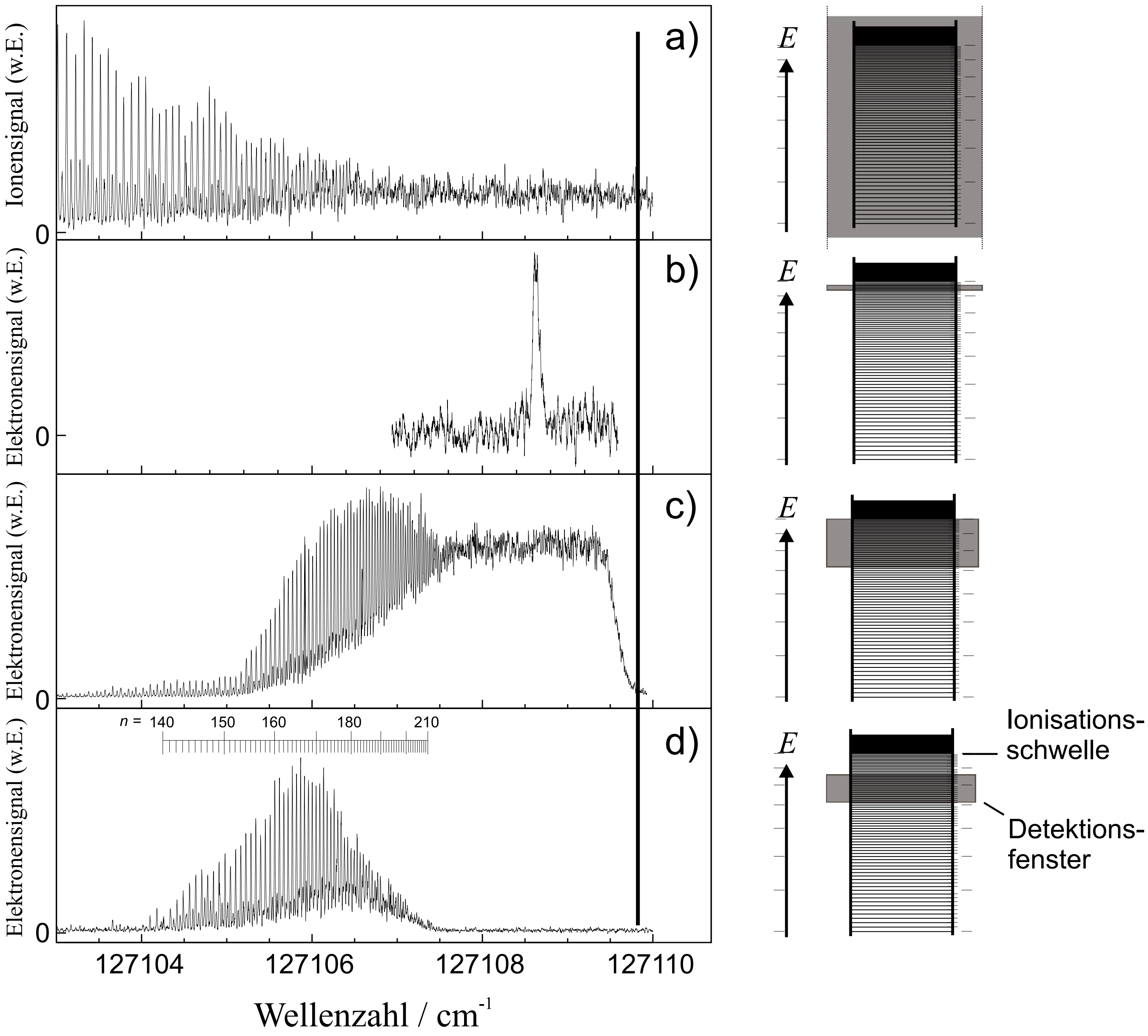
Motivation

- He_2 and He_2^+: "small" systems (4 and 3 e^- system)
- He_2: Rydberg molecule (electronic ground state very weakly bound)
- Experimental information about He_2^+ scarce:
  + high-v,J from A $^2\Sigma_g^+$ - X $^2\Sigma_u^+$ microwave transitions [1]
  + $v^+ = 1-0$ rovibrational spectrum of $^3He^4He^+$ [2]
- PFI-ZEKE-PES of metastable He_2^* a $^3\Sigma_u^+$:
  $\Rightarrow$ rovibrational structure of $^4He_2^+$ [3]
  $\Rightarrow$ autoionization dynamics of Rydberg states

[1] A. Carrington, C. H. Pyne, P. J. Knowles, J. Chem. Phys. **102** 5979 (1995)

[2] N. Yu, W. H. Wing, Phys. Rev. Lett. **59**, 2055 (1987), **60**, 2445 (1988)

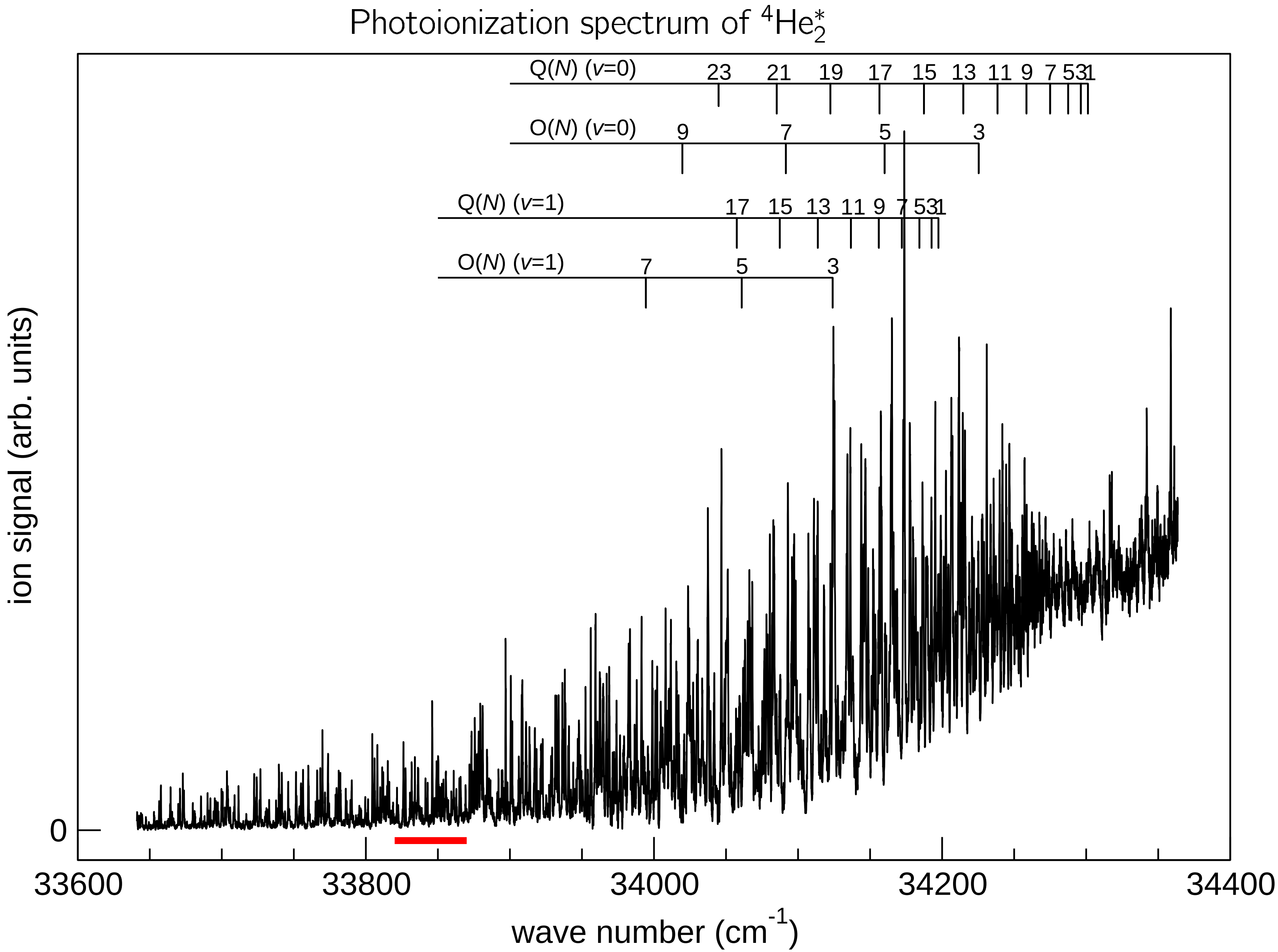
[3] M. Raunhardt, M. Schäfer, N. Vanhaecke, F. Merkt, J. Chem. Phys. **128**, 164310 (2008).

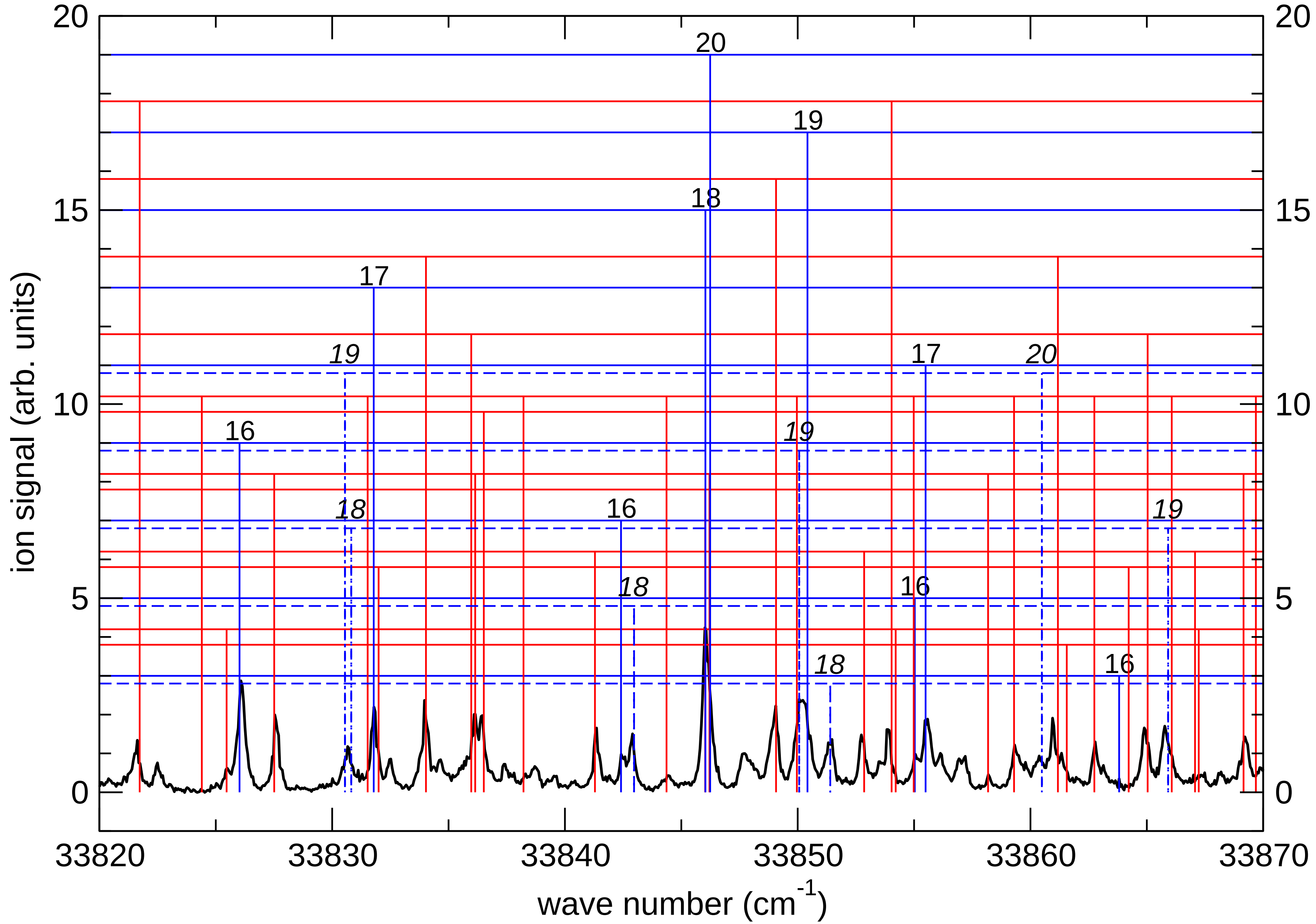


Photoionization spectrum

Pulsed-field-ionization
zero-kinetic-energy
photoelectron spectrum
(PFI-ZEKE-PES)

Rydberg-state-resolved
threshold-ionization
spectroscopy
(RSR-TIS)


Photoionization spectrum of $^4He_2^*$
Q(N) (v=0)
23 21 19 17 15 13 11 9 7 5 3 1
O(N) (v=0)
9 7 5 3
Q(N) (v=1)
17 15 13 11 9 7 5 3 1
O(N) (v=1)
7 5 3
ion signal (arb. units)
0
33600 33800 34000 34200 34400
wave number (cm^{-1})



ion signal (arb. units)
wave number (cm^{-1})
33820
33830
33840
33850
33860
33870
0
5
10
15
20
20
19
18
17
16
19
18
16
18
19
18
17
16
20
16
19

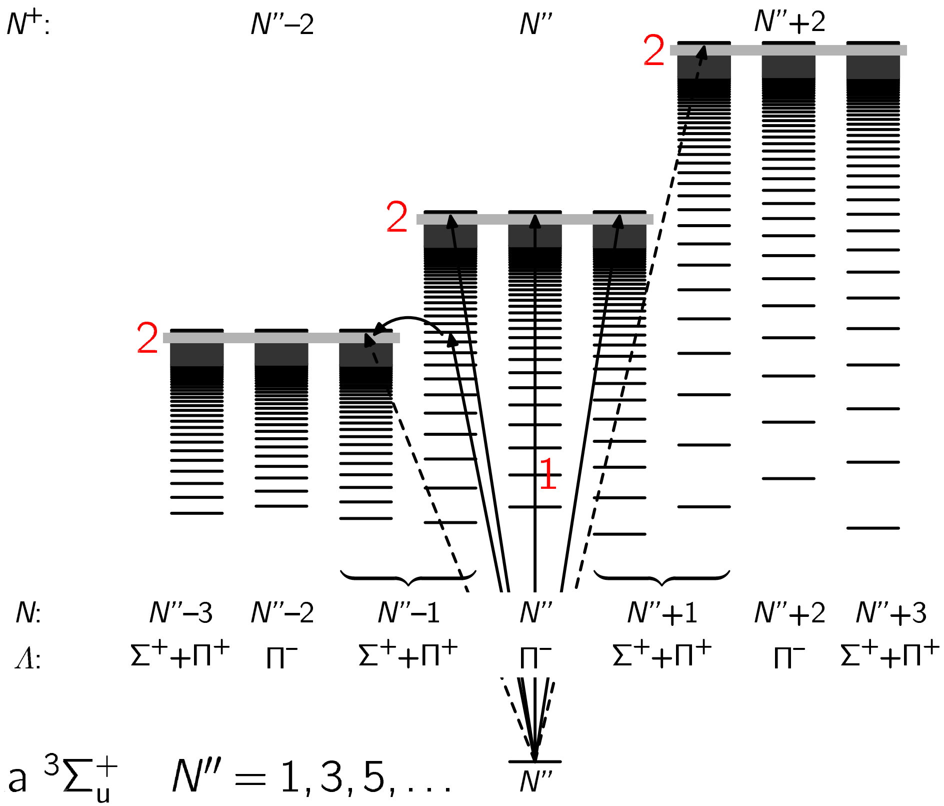
Pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy

1 Laser excitation to high-n
np Rydberg states
$N = N''$ $(np\pi\ ^3\Pi_g^-)$
$N = N'' \pm 1$ $(np\sigma\ ^3\Sigma_g^+,\ np\pi\ ^3\Pi_g^+)$

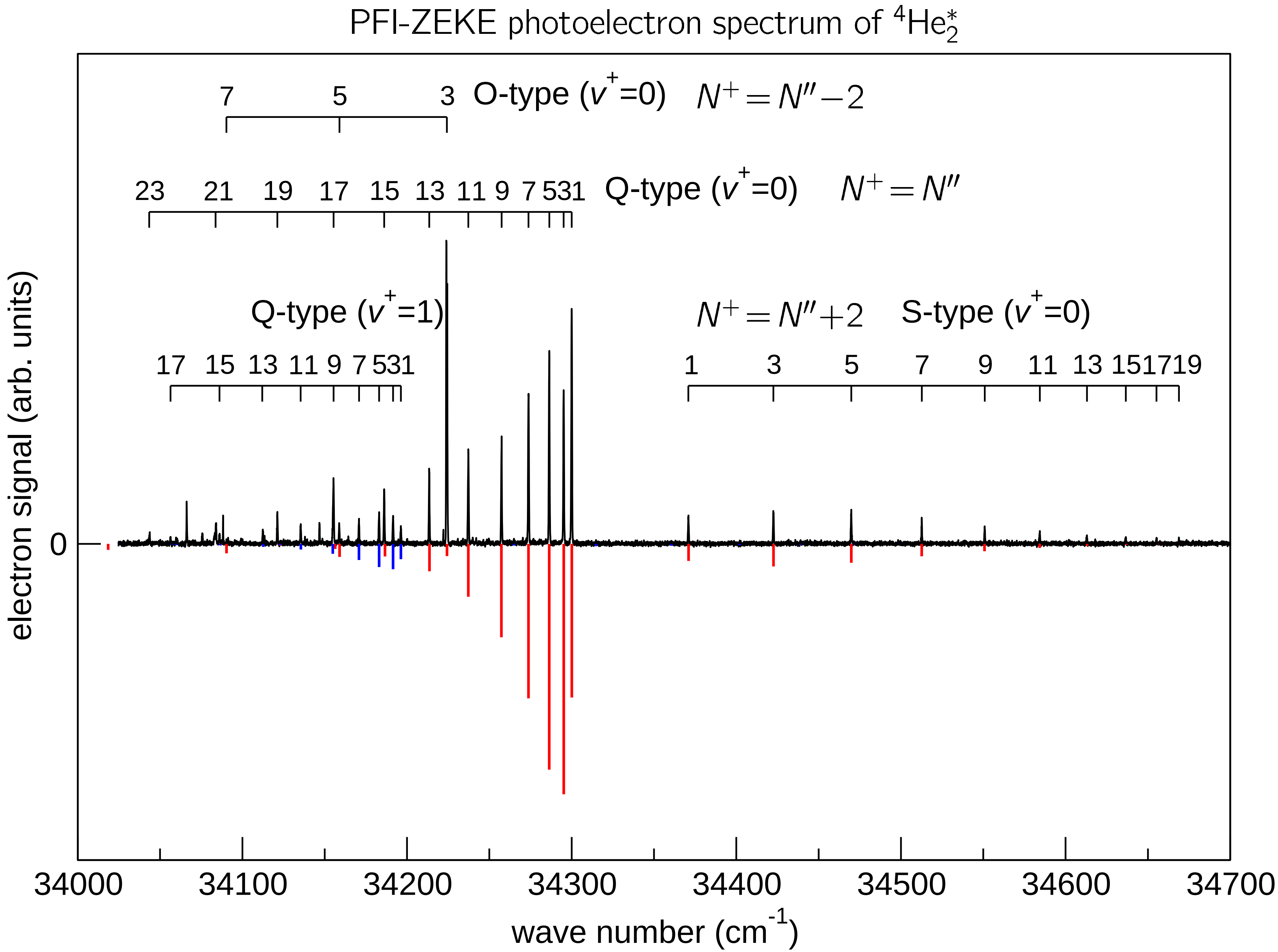
notation for high-n states:
$npN^+{}_N$ with $N = N^+, N^+ \pm 1$

2 Pulsed field ionization

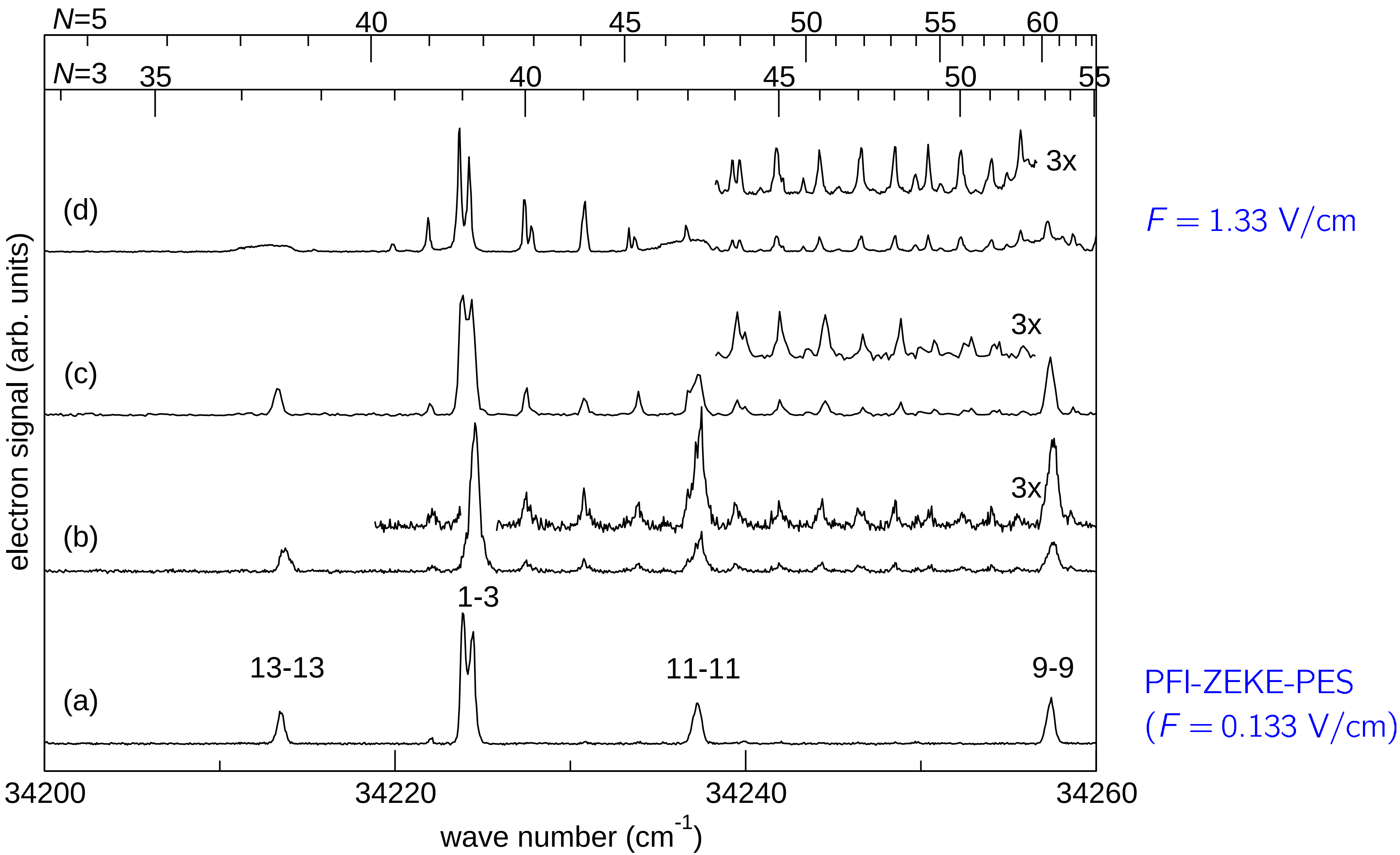
$^4He_2^+\ [(1\sigma_g)^2(1\sigma_u)]\ X^+\ ^2\Sigma_u^+ \quad N^+ = 1, 3, 5, \ldots$



$^4He_2\ [(1\sigma_g)^2(1\sigma_u)]2s\sigma_g\ a\ ^3\Sigma_u^+ \quad N'' = 1, 3, 5, \ldots$

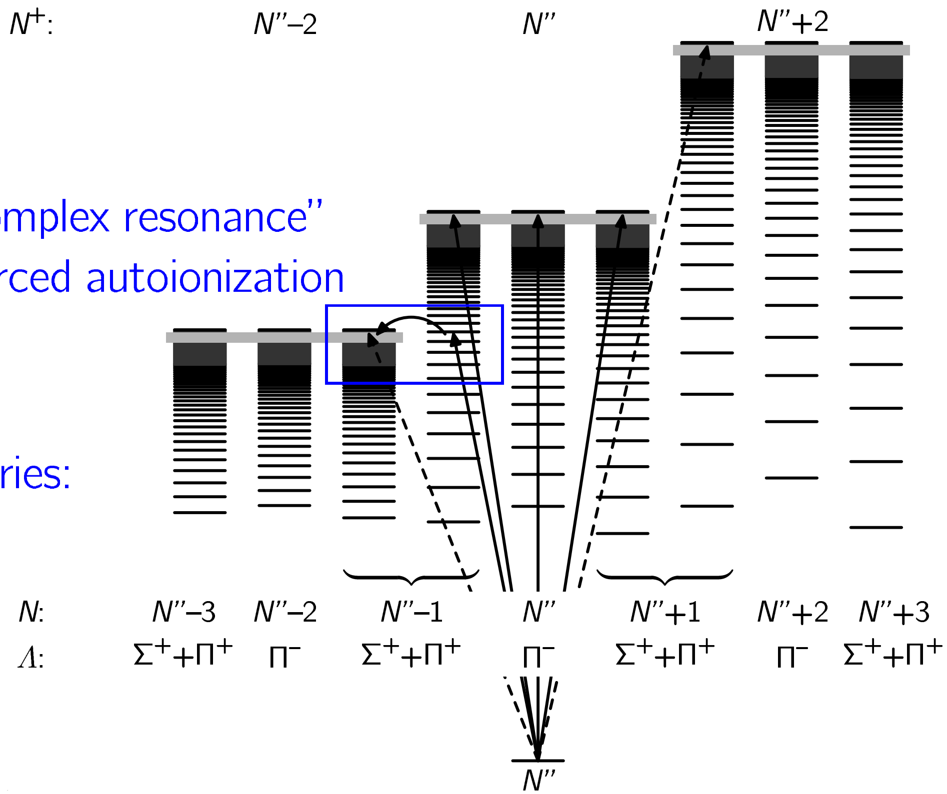


PFI-ZEKE photoelectron spectrum of $^4He_2^*$
7 5 3 O-type (v^+=0) $N^+ = N'' - 2$
23 21 19 17 15 13 11 9 7 5 3 1 Q-type (v^+=0) $N^+ = N''$
Q-type (v^+=1)
17 15 13 11 9 7 5 3 1
$N^+ = N'' + 2$ S-type (v^+=0)
1 3 5 7 9 11 13 15 17 19
electron signal (arb. units)
0
34000 34100 34200 34300 34400 34500 34600 34700
wave number (cm^{-1})


N=5
40
45
50
55
60
N=3
35
40
45
50
55
3x
(d)
F = 1.33 V/cm
3x
(c)
3x
(b)
1-3
13-13
11-11
9-9
(a)
PFI-ZEKE-PES
(F = 0.133 V/cm)
electron signal (arb. units)
34200
34220
34240
34260
wave number (cm-1)

Pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy

“complex resonance”
forced autoionization

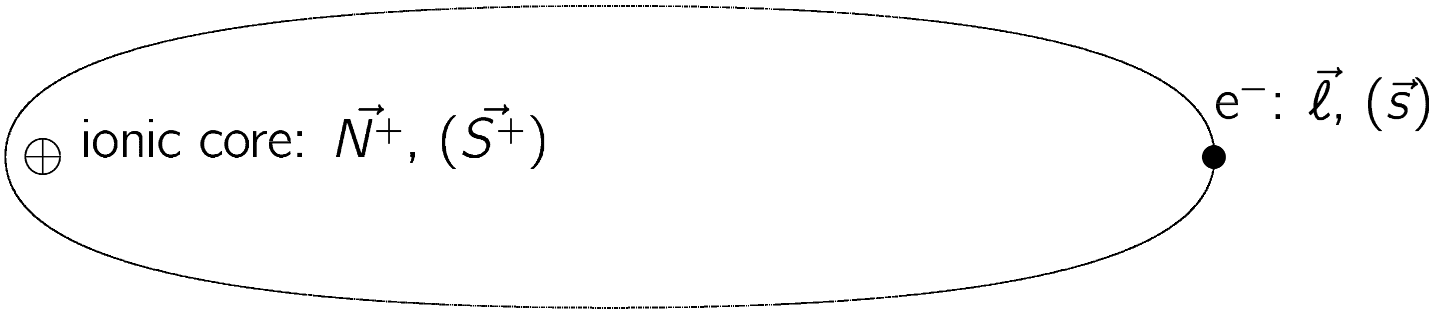


Calculation of interacting Rydberg series:
$\Longrightarrow$ MQDT

Multichannel quantum defect theory (MQDT)

developed for H_2: U. Fano, *Phys. Rev. A* **2**, 353 (1970); **15**, 817 (1977)
G. Herzberg, Ch. Jungen, *J. Mol. Spectrosc.* **41**, 425 (1972)

appl. to He_2 $np\lambda$: D.S. Ginter, M.L. Ginter, *J. Mol. Spectrosc.* **82**, 152 (1980)
D.S. Ginter, M.L. Ginter, C.M. Brown, *J. Chem. Phys.* **81**, 6013 (1984)



close-coupling region:
strong ion core–electron interaction
Hund's case (b) (N)
close-coupling eigenchannels α

angular momentum $\longleftrightarrow$ frame transformation

long-range region:
Coulomb field, ion energy levels
Hund's case (d) (N^+)
dissociation channels i

N	close-coupling channels	dissociation channels	
$1, 3, \ldots$	npπ ($^3\Pi_g^-$)	$N^+ = N$	1 channel (*)
$2, 4, \ldots$	npσ ($^3\Sigma_g^+$)	$N^+ = N - 1$	2 channels
	npπ ($^3\Pi_g^+$)	$N^+ = N + 1$	

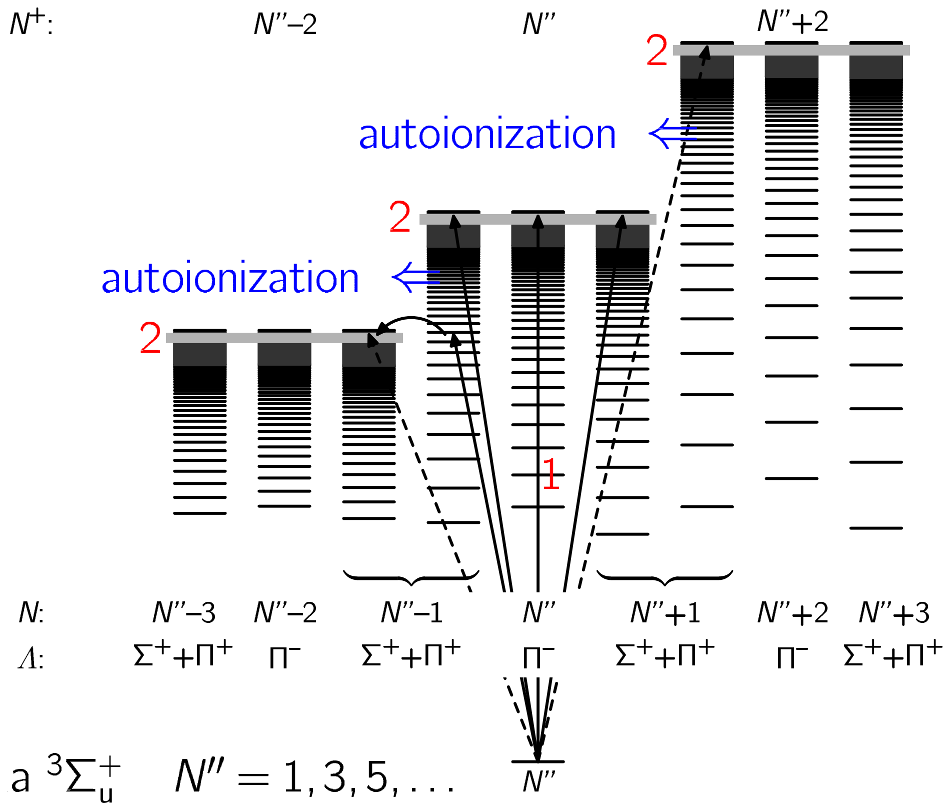
* Rydberg formula can be used

Rydberg-state-resolved threshold ionization spectroscopy

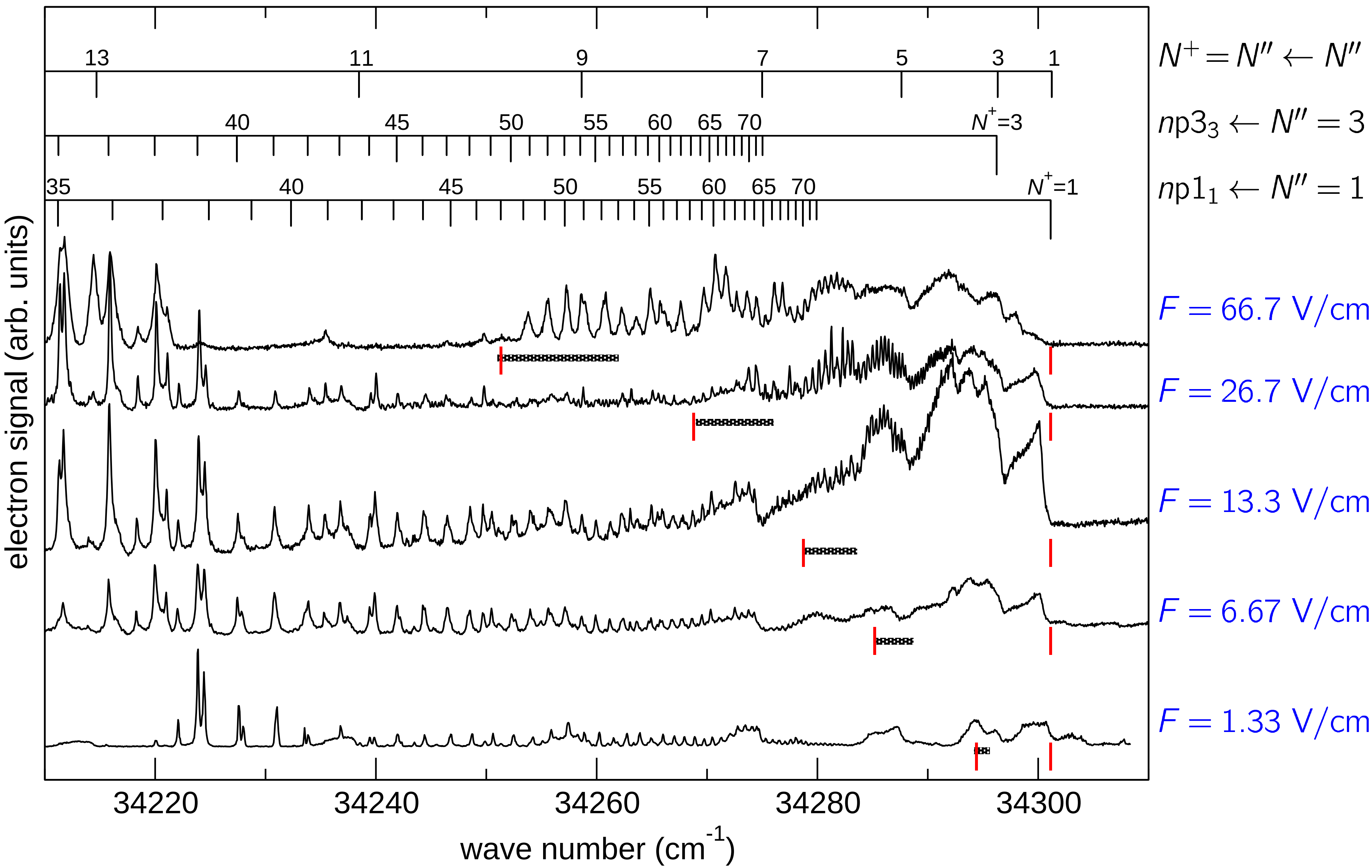
1 Laser excitation to high-n
np Rydberg states
$N = N''$
$N = N'' \pm 1$

2 Pulsed field ionization
$\Delta E_{\mathrm{PFI}} = -4.8\,\mathrm{cm}^{-1}\sqrt{F/\mathrm{V\,cm}^{-1}}$
$\Delta E_{\mathrm{dc}} = -6.1\,\mathrm{cm}^{-1}\sqrt{F/\mathrm{V\,cm}^{-1}}$

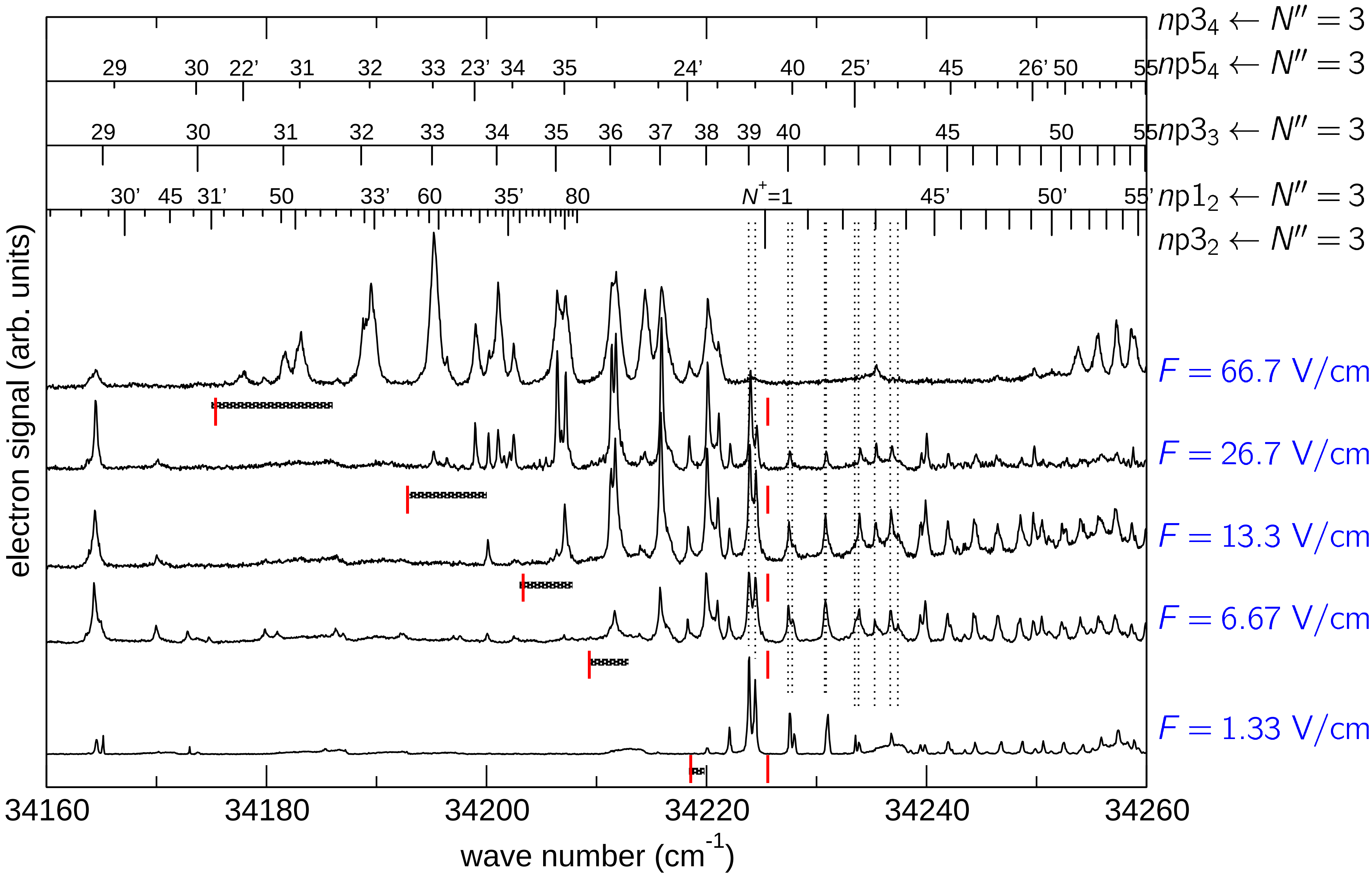
$F/\mathrm{V\,cm}^{-1}$	$\Delta E_{\mathrm{PFI}}/\mathrm{cm}^{-1}$	n
0.133	−1.75	250
1.33	−5.5	140
133	−55	45



$^4\mathrm{He}_2\ [(1\sigma_g)^2(1\sigma_u)]2s\sigma_g\ a\ ^3\Sigma_u^+\quad N'' = 1, 3, 5, \ldots$



$N^+ = N'' \leftarrow N''$
$n\mathrm{p}3_3 \leftarrow N'' = 3$
$n\mathrm{p}1_1 \leftarrow N'' = 1$
N^+=3
N^+=1
$F = 66.7$ V/cm
$F = 26.7$ V/cm
$F = 13.3$ V/cm
$F = 6.67$ V/cm
$F = 1.33$ V/cm
electron signal (arb. units)
wave number (cm^{-1})
34220
34240
34260
34280
34300

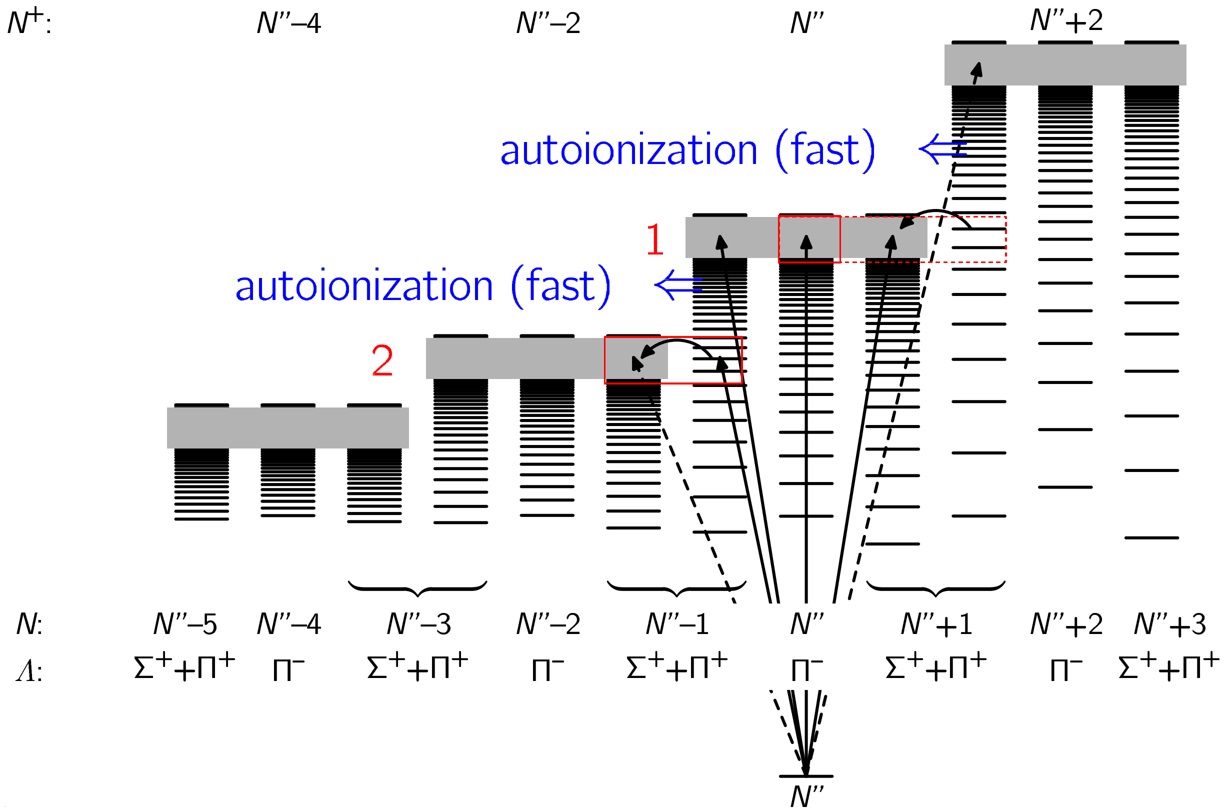


$np3_4 \leftarrow N'' = 3$
$np5_4 \leftarrow N'' = 3$
$np3_3 \leftarrow N'' = 3$
$np1_2 \leftarrow N'' = 3$
$np3_2 \leftarrow N'' = 3$
$N^+=1$
$F = 66.7$ V/cm
$F = 26.7$ V/cm
$F = 13.3$ V/cm
$F = 6.67$ V/cm
$F = 1.33$ V/cm
electron signal (arb. units)
wave number (cm^{-1})

Rydberg-state-resolved threshold ionization spectroscopy

1 $np N''_{N''} \leftarrow N''$ (resolved for $N''=1,3,5$)
$np1_2 \leftarrow 1$
below $N^+ = N''$ threshold

2 $npN''/(N''-2)_{N''-1} \leftarrow N''$
("complex resonance")
below $N^+ = N''-2$ threshold



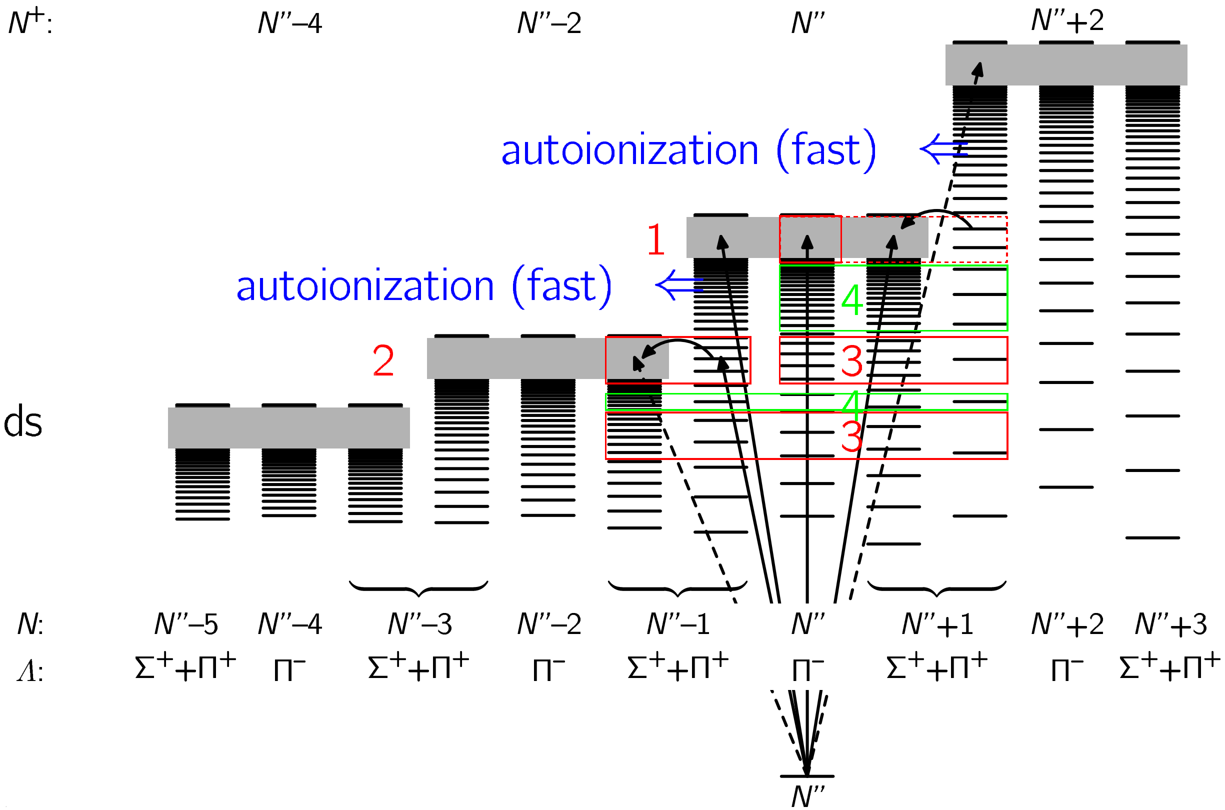
Rydberg-state-resolved threshold ionization spectroscopy

1 $np N''_{N''} \leftarrow N''$ (resolved for $N''=1,3,5$)
$np1_2 \leftarrow 1$
below $N^+ = N''$ threshold

2 $np N''/(N''-2)_{N''-1} \leftarrow N''$
("complex resonance")
below $N^+ = N''-2$ threshold

3 $np N^+{}_N \leftarrow N''$
below $N^+ = N''-2, 4, \ldots$ thresholds

4 $np N^+{}_N \leftarrow N''$
often weak or
stray-field dependent



Conclusion and outlook

- Combining high-resolution spectroscopy and multichannel quantum defect theory (MQDT) to explore high-n Rydberg states and their dynamics
- Observed forced rotational autoionization where N^+ is changing by up to 4
- Full analysis of high Rydberg states

Helium dimer (review)

^{4}He$_2$ X $^1\Sigma_g^+$: extremely weakly bound, only one quantum state ($v = 0$, $J = 0$) ($D_e = 7.650(3)$ cm^{-1}, $r_e = 2.968(6)$ Å, $D_0 = 0.00120(3)$ cm^{-1})

F. Luo, G. C. McBane, G. Kim, C. F. Giese, W. R. Gentry, J. Chem. Phys. **98**, 3564 (1993)

R. E. Grisenti, W. Schöllkopf, J. P. Toennies, G. C. Hegerfeldt, T. Köhler, M. Stoll, Phys. Rev. Lett. **85**, 2284 (2000)

M. Jeziorska, W. Cencek, K. Patkowski, B. Jeziorski, K. Szalewicz, J. Chem. Phys. **127** 124303 (2007)

and many more theoretical papers...

^{4}He$_2$ $[(1\sigma_g)^2(1\sigma_u)]2s\sigma_g$ a $^3\Sigma_u^+$: $T_e = 17.86$ eV, long lifetime (18 s) ($\omega_e = 1808.500(84)$ cm^{-1}, $B_e = 7.707364(67)$ cm^{-1}, $r_e = 1.0454158(45)$ Å, theory: $D_e = 15\,848$ cm^{-1} with barrier of 505 cm^{-1} at $r = 2.71$ Å)

C. M. Brown, M. L. Ginter, J. Mol. Spectrosc. **40**, 302 (1971)

C. Focsa, P. F. Bernath, R. Colin, J. Mol. Spectrosc. **191**, 209 (1998)

R. M. Jordan, H. R. Siddiqui, P. E. Siska, J. Chem. Phys. **84**, 6719 (1986)

N. Bierre, A. O. Mitrushenkov, P. Palmieri, P. Rosmus, Theor. Chem. Acc. **100**, 51 (1998)

^{4}He (1s)(2s) 2 $^3S_1$: $T = 159\,855.9726(15)$ cm^{-1} (19.820 eV), rad. lifetime 8000 s

$^4\mathrm{He}_2^+$ $(1\sigma_\mathrm{g})^2(1\sigma_\mathrm{u})$ $\mathrm{X}^+\ ^2\Sigma_\mathrm{u}^+$

extrapolation from He_2 Rydberg states ($v^+ = 0$: $N^+ \leq 21$, $v^+ = 1$: $N^+ \leq 15$):
$\omega_\mathrm{e} = 1698.6\ \mathrm{cm}^{-1}$, $B_\mathrm{e} = 7.211\ \mathrm{cm}^{-1}$, $r_\mathrm{e} = 1.0806$ Å;
$T_0 = 34302.3(10)\ \mathrm{cm}^{-1}$ (*wrt* He_2 a $^3\Sigma_\mathrm{u}^+$)

M. L. Ginter, D. S. Ginter, J. Chem. Phys. **48**, 2284 (1968)

D. S. Ginter, M. L. Ginter, J. Mol. Spectrosc. **82**, 152 (1980)

$v^+ = 1 - 0$ infrared spectrum of $^3\mathrm{He}^4\mathrm{He}^+$
$\omega_\mathrm{e} = 1832.7598(50)\ \mathrm{cm}^{-1}$, $B_\mathrm{e} = 8.3906(40)\ \mathrm{cm}^{-1}$, [$r_\mathrm{e} = 1.08096(26)$ Å]

N. Yu, W. H. Wing, Phys. Rev. Lett. **59**, 2055 (1987), **60**, 2445 (1988)

$\mathrm{A}^+\ ^2\Sigma_\mathrm{g}^+$ $(v' = 0, 1) \leftarrow \mathrm{X}^+\ ^2\Sigma_\mathrm{u}^+$ $(v'' = 22, 23)$ microwave spectrum of $^4\mathrm{He}_2^+$

A. Carrington, C. H. Pyne, P. J. Knowles, J. Chem. Phys. **102** 5979 (1995)

theory: $D_\mathrm{e} = 19\,945.82\ \mathrm{cm}^{-1}$, $r_\mathrm{e} = 1.0811(3)$ Å

J. Xie, B. Poirier, G. I. Gellene, J. Chem. Phys. **122**, 184310 (2005)

PFI-ZEKE: $\omega_\mathrm{e} = 1698.578(106)\ \mathrm{cm}^{-1}$, $B_\mathrm{e} = 7.20997(46)\ \mathrm{cm}^{-1}$, $r_\mathrm{e} = 1.08102(3)$ Å,
$T_0 = 34302.1(2)\ \mathrm{cm}^{-1}$

M. Raunhardt, M. Schäfer, N. Vanhaecke, F. Merkt, J. Chem. Phys. **128**, 164310 (2008).

		$^4He_2$		$^3He_2$
	$v, v^+ = 0$	$v, v^+ = 1$	$v, v^+ = 2$	$v, v^+ = 0$
T_v (cm^{-1})	0.0	1732.1615[a]	3386.5024[a]	0.0
B_v (cm^{-1})	7.58914[a]	7.34874[a]	7.10175[a]	10.0386(95)
D_v (10^{-4} cm^{-1})	5.6153[a]	5.6538[a]	5.7439[a]	9.90[b]
H_v (10^{-8} cm^{-1})	3.22[a]	2.84[a]	3.31[a]	
$T_v^+ - T_v$ (cm^{-1})	34302.236(20)	34198.390(24)	34102.102(46)	34292.298(27)
$T_v^+ - T_0^+$ (cm^{-1})	0.0	1628.416	3186.469	0.0
B_v^+ (cm^{-1})	7.09796(25)	6.87394(52)	6.6528(27)	9.3884(91)
D_v^+ (10^{-4} cm^{-1})	5.012(5)	5.094(18)	5.79(28)	9.051(94)

[a] Fixed to the values of C. Focsa, P. F. Bernath, R. Colin, J. Mol. Spectrosc. **191**, 209 (1998).

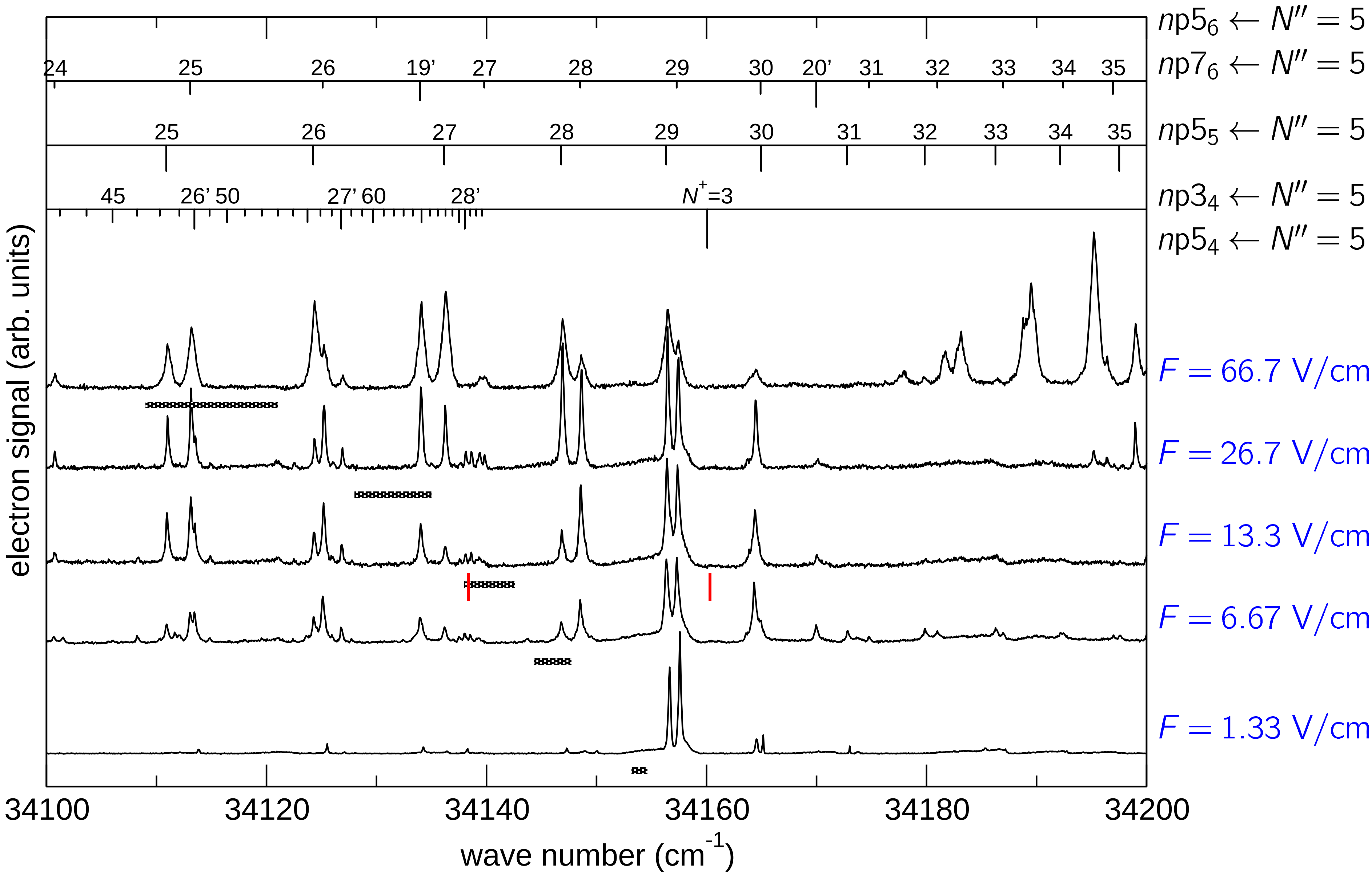
[b] Derived from the value of $^4He_2$.

$^4He_2^+$: $B_e = 7.20997(46)\ \mathrm{cm}^{-1}$, $r_e = 1.08102(3)$ Å [H_2^+: $r_e = 1.052$ Å]

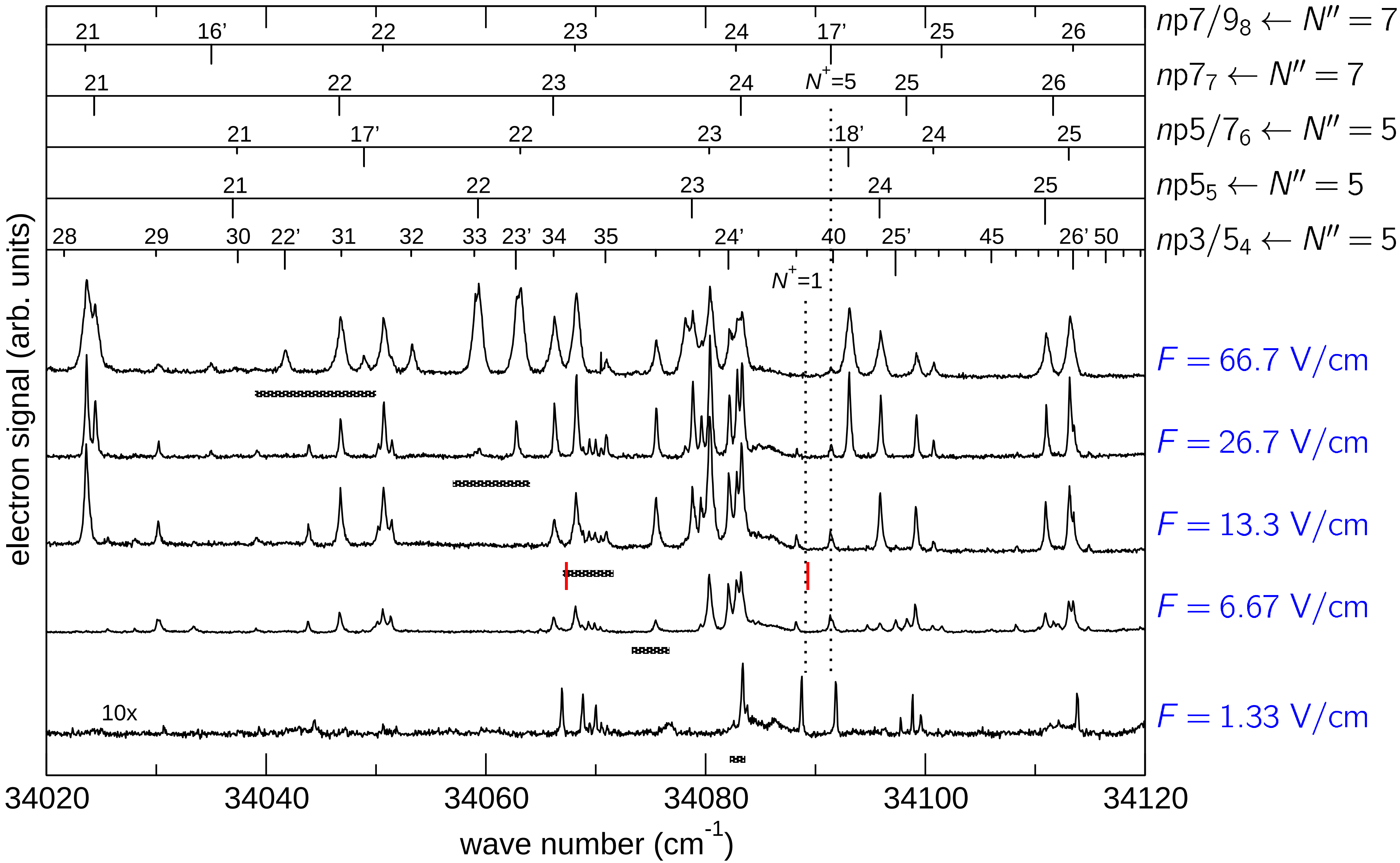
$\omega_e = 1698.578(106)\ \mathrm{cm}^{-1}$, $\omega_e x_e = 35.131(40)\ \mathrm{cm}^{-1}$, $k = 340\ \mathrm{N\,m}^{-1}$ [H_2^+: $k = 160\ \mathrm{N\,m}^{-1}$]

Lit.: $B_e = 7.211\ \mathrm{cm}^{-1}$, $r_e = 1.0806$ Å (theor.: 1.0811(3) Å)

$\omega_e = 1698.6\ \mathrm{cm}^{-1}$, $\omega_e x_e = 35.25\ \mathrm{cm}^{-1}$; $T_0^+ - T_0 = 34302.3(10)\ \mathrm{cm}^{-1}$



np$5_6 \leftarrow N'' = 5$
np$7_6 \leftarrow N'' = 5$
np$5_5 \leftarrow N'' = 5$
np$3_4 \leftarrow N'' = 5$
np$5_4 \leftarrow N'' = 5$
24 25 26 19' 27 28 29 30 20' 31 32 33 34 35
25 26 27 28 29 30 31 32 33 34 35
45 26' 50 27' 60 28' N^+=3
$F = 66.7$ V/cm
$F = 26.7$ V/cm
$F = 13.3$ V/cm
$F = 6.67$ V/cm
$F = 1.33$ V/cm
electron signal (arb. units)
34100 34120 34140 34160 34180 34200
wave number (cm^{-1})

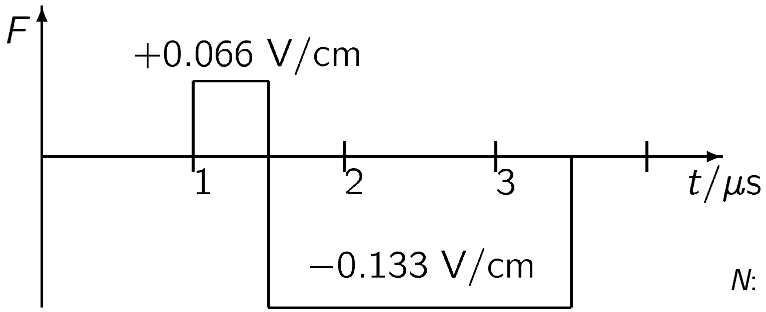


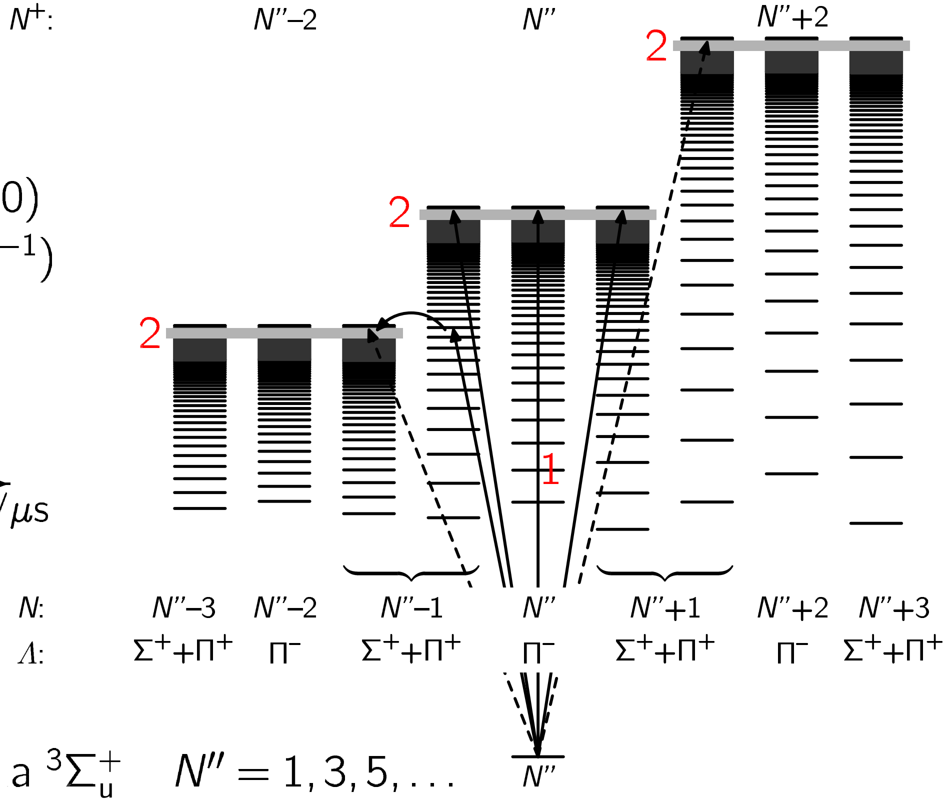
$np7/9_8 \leftarrow N'' = 7$
$np7_7 \leftarrow N'' = 7$
$np5/7_6 \leftarrow N'' = 5$
$np5_5 \leftarrow N'' = 5$
$np3/5_4 \leftarrow N'' = 5$
N^+=5
N^+=1
$F = 66.7$ V/cm
$F = 26.7$ V/cm
$F = 13.3$ V/cm
$F = 6.67$ V/cm
$F = 1.33$ V/cm
10x
electron signal (arb. units)
wave number (cm^{-1})
34020
34040
34060
34080
34100
34120

Pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy

1 Laser excitation to high-n
np Rydberg states
$np\pi\ ^3\Pi_g^-$ $(N = N'')$
$np\sigma\ ^3\Sigma_g^+$, $np\pi\ ^3\Pi_g^+$ $(N = N'' \pm 1)$

2 Pulsed field ionization $(250 < n < 300)$
$(\Gamma_{\mathrm{FWHM}} = 0.5\ \mathrm{cm}^{-1}$, shift $-1.20\ \mathrm{cm}^{-1})$





$^4He_2\ [(1\sigma_g)^2(1\sigma_u)]2s\sigma_g\ a\ ^3\Sigma_u^+ \quad N'' = 1, 3, 5, \ldots$

Symmetries and selection rules

$D_{\infty h}(M)$		E	(12)	E^*	$(12)^*$
Λ_g^+	$+s$	1	1	1	1
Λ_u^+	$+a$	1	-1	1	-1
Λ_g^-	$-a$	1	-1	-1	1
Λ_u^-	$-s$	1	1	-1	-1

$\Lambda = \Sigma, \Pi, \Delta, \ldots \qquad (\Gamma^* = \Sigma_u^-, -s)$

Γ_{Ryd}	$+s$	ℓ even
	$-s$	ℓ odd
Γ_{rot}	$+s$	N even
	$-a$	N odd
Γ_{nspin}	$+s$	$w = (2I+1)(I+1)$
	$+a$	$w = (2I+1)I$
Γ_{int}	$\pm s$	for bosonic nuclei
	$\pm a$	for fermionic nuclei

statistical weights:

$\Gamma_{\mathrm{rve}} \otimes \Gamma_{\mathrm{nspin}} \supset \Gamma_{\mathrm{int}}$

$\Gamma_{\mathrm{Ryd}} \otimes \Gamma_{\mathrm{rve}}^+ \otimes \Gamma_{\mathrm{nspin}} \supset \Gamma_{\mathrm{int}}$

		$^4He_2$		$^3He_2$	
	$N^{(+)}$:	e	o	e	o
$X^+ \ ^2\Sigma_u^+$	N^+	0	1	3	1
high Ryd	N^+	0	1	3	1
$np\sigma \ ^3\Sigma_g^+$	N	1	0	1	3
$np\pi \ ^3\Pi_g^+$	N	1	0	1	3
$np\pi \ ^3\Pi_g^-$	N	0	1	3	1
2s a $^3\Sigma_u^+$	N	0	1	3	1

Symmetries and selection rules

$D_{\infty h}(M)$		E	(12)	E*	(12)*
Λ_g^+	$+s$	1	1	1	1
Λ_u^+	$+a$	1	-1	1	-1
Λ_g^-	$-a$	1	-1	-1	1
Λ_u^-	$-s$	1	1	-1	-1

$\Lambda = \Sigma, \Pi, \Delta, \ldots \qquad (\Gamma^* = \Sigma_u^-, -s)$

Γ_{Ryd}	$+s$	ℓ even
	$-s$	ℓ odd
Γ_{rot}	$+s$	N even
	$-a$	N odd
Γ_{nspin}	$+s$	$w = (2I+1)(I+1)$
	$+a$	$w = (2I+1)I$
Γ_{int}	$\pm s$	for bosonic nuclei
	$\pm a$	for fermionic nuclei

electric dipole transitions: $(\Gamma'_{\mathrm{nspin}} = \Gamma''_{\mathrm{nspin}})$

$\Gamma'_{\mathrm{rve}} \otimes \Gamma''_{\mathrm{rve}} \supset -s$

photoionization:

$\Gamma^+_{\mathrm{rve}} \otimes \Gamma''_{\mathrm{rve}} \supset -s$ for ℓ even

$\Gamma^+_{\mathrm{rve}} \otimes \Gamma''_{\mathrm{rve}} \supset +s$ for ℓ odd

$+ \leftrightarrow -$	$+ \not\leftrightarrow +$	$- \not\leftrightarrow -$	ℓ even
$+ \leftrightarrow +$	$- \leftrightarrow -$	$+ \not\leftrightarrow -$	ℓ odd
$s \leftrightarrow s$	$a \leftrightarrow a$	$s \not\leftrightarrow a$	
$g \leftrightarrow u$	$g \not\leftrightarrow g$	$u \not\leftrightarrow u$	ℓ even
$g \leftrightarrow g$	$u \leftrightarrow u$	$g \not\leftrightarrow u$	ℓ odd

$2s\ a\ {}^3\Sigma_u^+ \rightarrow np\ {}^3\Pi_g^-$	$N' - N'' = 0$
$2s\ a\ {}^3\Sigma_u^+ \rightarrow np\ {}^3\Sigma_g^+, {}^3\Pi_g^+$	$N' - N'' = \pm 1$
$2s\ a\ {}^3\Sigma_u^+ \rightarrow X^+\ {}^2\Sigma_u^+$	$N^+ - N''$ even

(p photoelectron: $N^+ - N'' = 0, \pm 2$)

For each N block: $\det|U_{i\alpha}\sin[\pi(\mu_\alpha+\nu_i)]|=0$

where $\mu_\alpha=\mu_\alpha^{(0)}(1+\mu_\alpha^{(1)}\epsilon)(1+A_\alpha N(N+1))$ with $\epsilon=[E-E(^2\Sigma_u^+,N^+=0)]/R_M$

$\nu_i=[R_M/(E_i-E)]^{1/2}$

with $E_i=E(^2\Sigma_u^+,N^+=0)+B^+N^+(N^++1)-D^+[N^+(N^++1)]^2$ $(N^+=1,3,\ldots)$

$U_{i\alpha}$:		α:	1	2	3
		i	$np\sigma$ $(^3\Sigma_g^+)$	$np\pi$ $(^3\Pi_g^+)$	$np\pi$ $(^3\Pi_g^-)$
$N=2,4,\ldots$:	$N^+=N-1$	1	$\left[\frac{N}{2N+1}\right]^{1/2}$	$\left[\frac{N+1}{2N+1}\right]^{1/2}$	0
	$N^+=N+1$	2	$-\left[\frac{N+1}{2N+1}\right]^{1/2}$	$\left[\frac{N}{2N+1}\right]^{1/2}$	0
$N=1,3,\ldots$:	$N^+=N$	3	0	0	1

α	$np\sigma$ $(^3\Sigma_g^+)$	$np\pi$ $(^3\Pi_g^\pm)$
$\mu_\alpha^{(0)}$	0.770882(29)	0.070697(12)
$\mu_\alpha^{(1)}$	−0.39453(30)	−0.09476(65)
$A_\alpha\times10^4$	0.37739(49)	−1.0323(49)