

The *gerade* Rydberg states of H₂: VUV spectroscopy and MQDT analysis

Hans Jakob Wörner and Frédéric Merkt, ETH Zürich, Switzerland
Christian Jungen, Laboratoire Aimé Cotton, Orsay, France

- 1 MQDT model
- 2 Determination of quantum defect curves
- 3 Rovibronic calculations at low n
- 4 Prediction of photoionization spectra and comparison with experimental data
- 5 Hyperfine-resolved spectra of ortho-H₂
- 6 Conclusions and outlook

The *gerade* Rydberg states of hydrogen

Motivations

Test state-of-the-art MQDT calculations against ultrahigh resolution spectroscopy.
Success for the p and f (*ungerade*) states of H₂ at the level of 600 kHz

(Osterwalder et al., *J. Chem. Phys.* **121**, 11810 (2004))

Global analysis of the *gerade* manifold of H₂ from $n=2$ to across all ionization thresholds
Complete understanding of spin-rovibronic interactions in a prototypical molecule.

The gerade Rydberg states of hydrogen

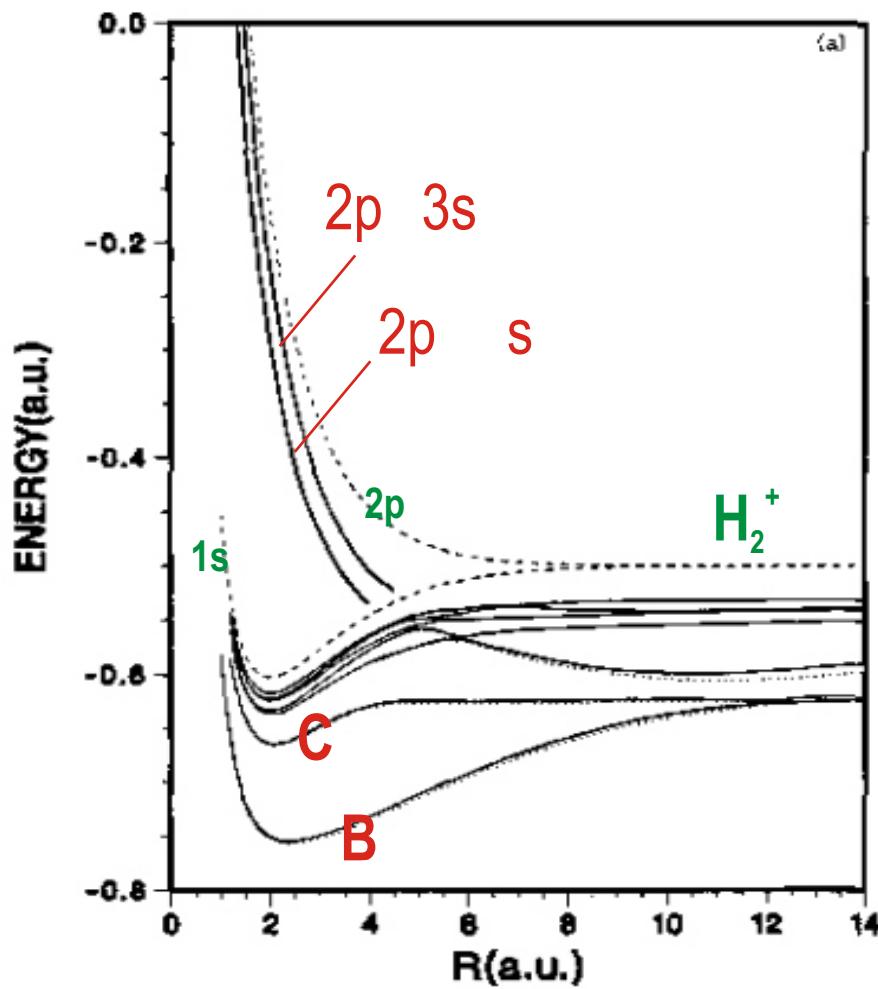
Motivations

A large body of spectroscopic data is available, but has never been analyzed:

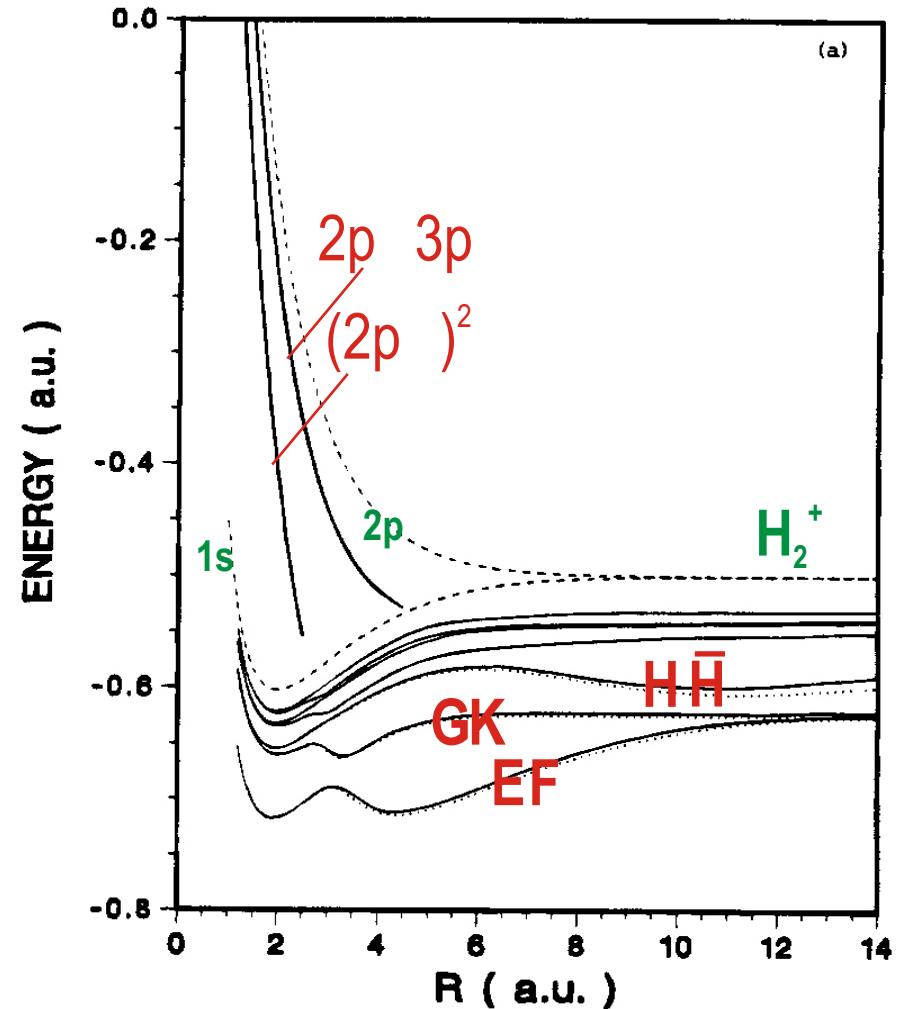
1. Accurate positions of EF, GK, H \bar{H} rovibronic levels (Herzberg, Jungen)
2. Rydberg spectra from $n=10$ to 50 converging on X $^2_g^+$, $v^+=0$, $N^+=0,1,2,3,4$:
Rottke, Welge (1992); Glab, Qin, Bistransin (1994); Osterwalder (2004);
3. Fine and hyperfine structure of triplet spin-rovibronic levels of the a,g,h,i,j states
Freund, Miller (1973-74); Ottinger, Rox (1994)
4. Fully resolved mmW spectra of $n = 51$ to 65 below $N^+=1$ (ortho) Osterwalder (2004);
5. Hyperfine resolved laser spectra $n = 35$ to 65 below $N^+=1$ (ortho) (this work)

Doubly excited states and adiabatic potential curves

Singlet ungerade manifold



Singlet gerade manifold



MQDT and scattering theory

(C. Greene and C. Jungen, Adv. At. Mol. Phys. 21, 51 (1985))

Scattering representation:



$$\sum_{i'} \hat{A}_i(v_i) v_i^{1/2} f_i(r) S_{ii'} - f_i(r) \delta_{ii'}$$

Parametrization in terms of reaction matrix K(NxN):

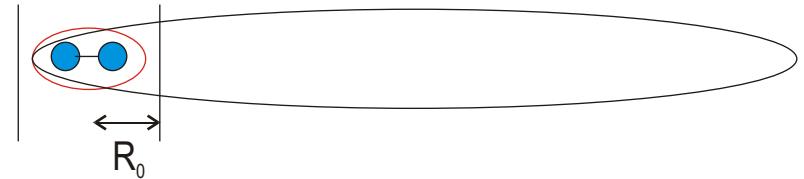
$$\hat{A}_i(E) = \sum_{i=1}^N g_i(r) K_{ii}$$

The representation that diagonalizes K is the basis of "eigenchannels":

$$K = U \tan(\theta) U^T$$

U transforms between eigen- and fragmentation channels:

$$U = (v | R)^{(N)} (N | \)^{(1J)}$$



MQDT and scattering theory

The eigenchannel wavefunctions have a common phase shift in the fragmentation channels.

For $R > R_0$:

$$(E) \quad \hat{\psi}_i(r) = U_i \psi_i(r) e^{i\phi_i} = f_i(r) \cos(\phi_i) + g_i(r) \sin(\phi_i)$$

Large R boundary conditions:

Bound states: The wave functions must decay exponentially.

Continuum states: The wavefunctions must have a common eigenphase shift ϕ_i .

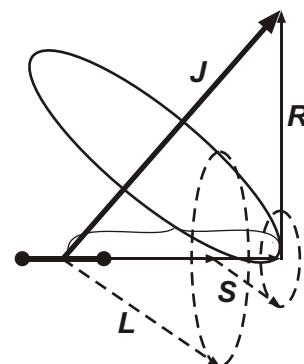
N

$$F_i(E) A_i(E) = 0$$

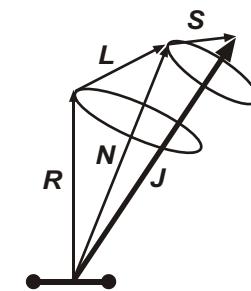
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$$F_i(E) = \begin{cases} U_i \sin(\phi_i) & (\text{closed channels}) \\ U_i \sin(\phi_i) & (\text{open channels}) \end{cases}$$

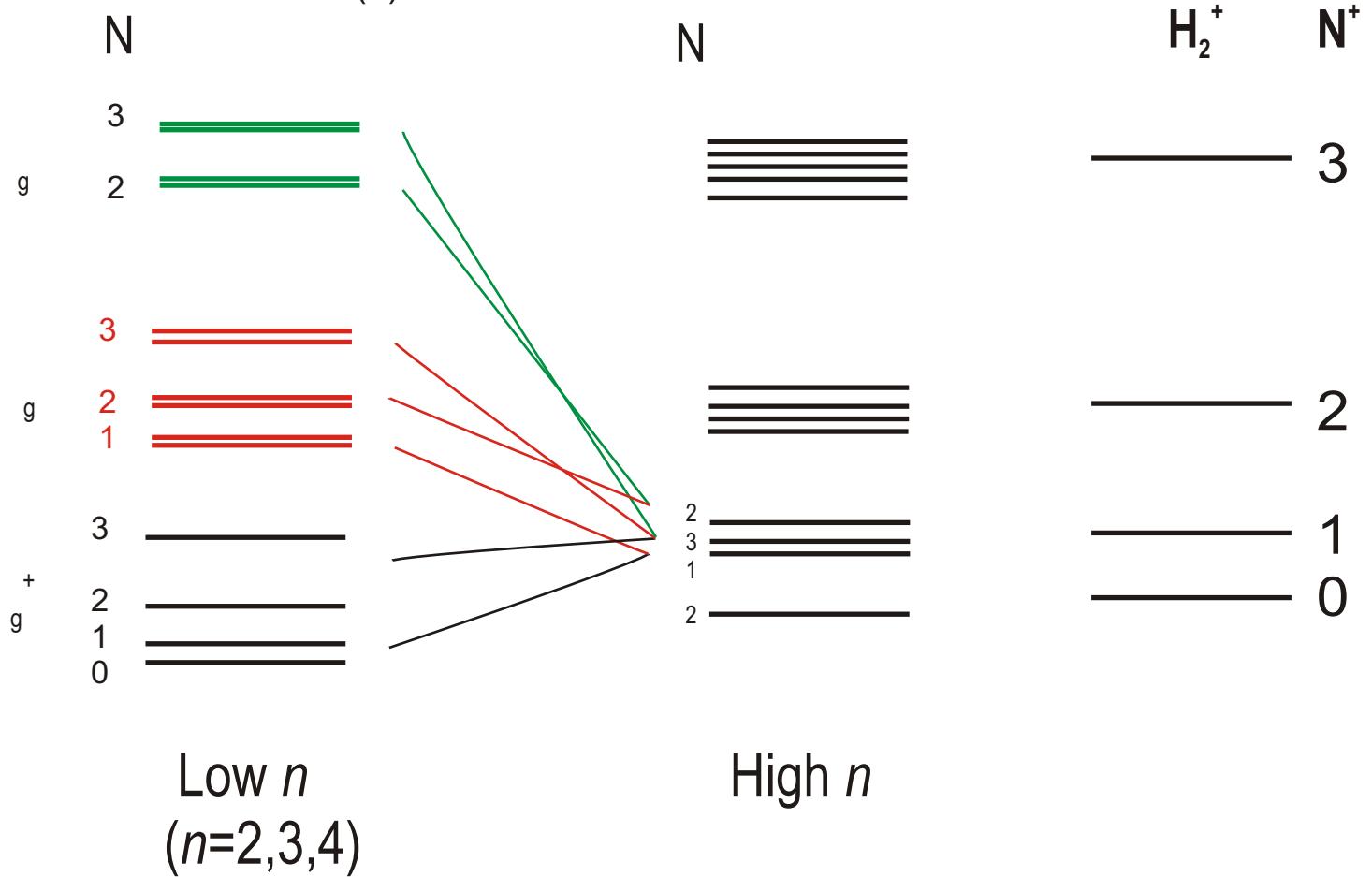
L-uncoupling in d states



Hund's case (a)

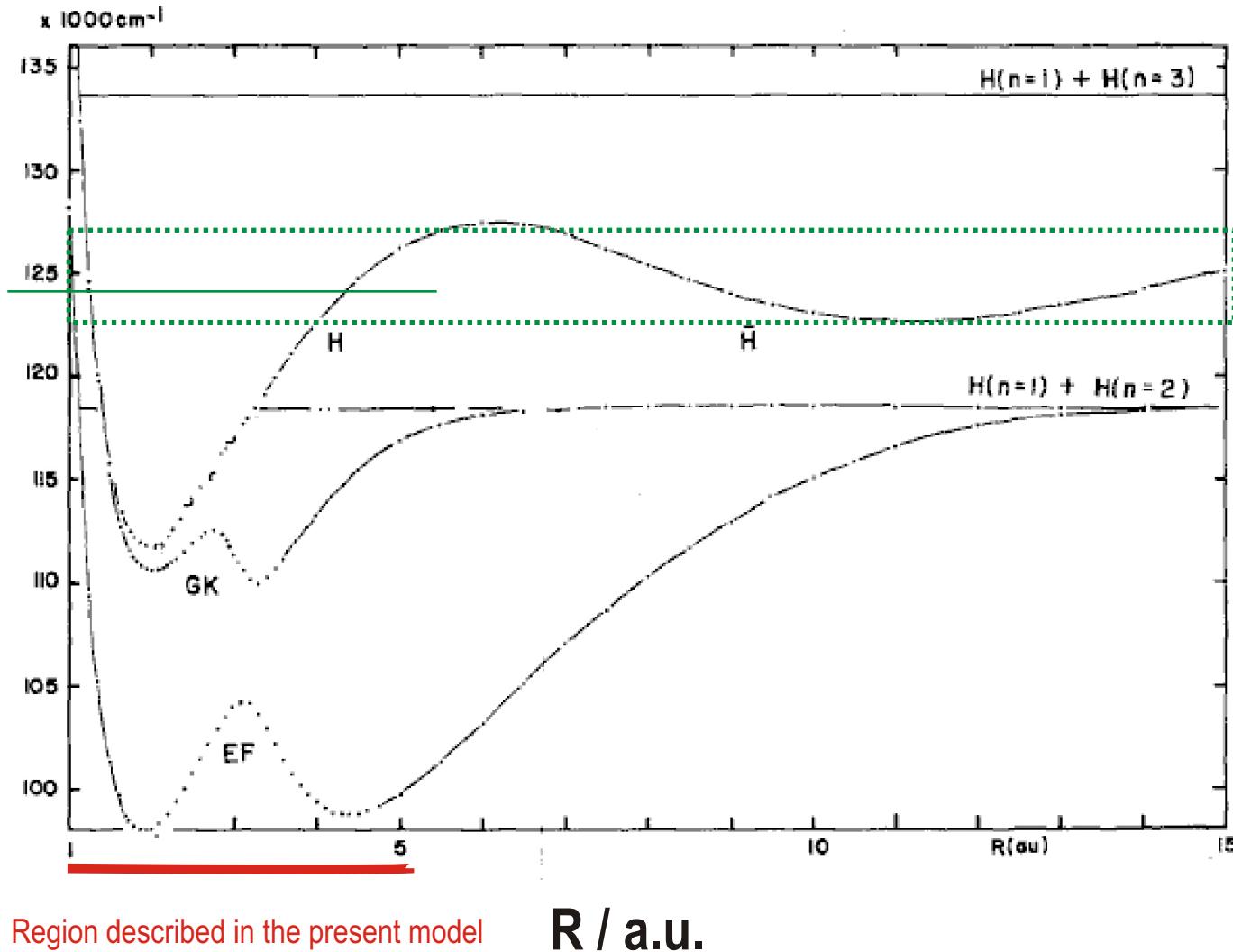


Hund's case (d)



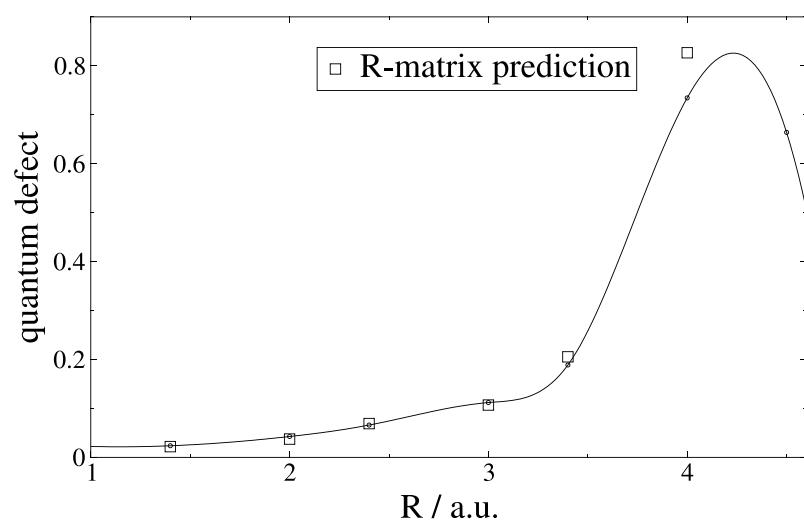
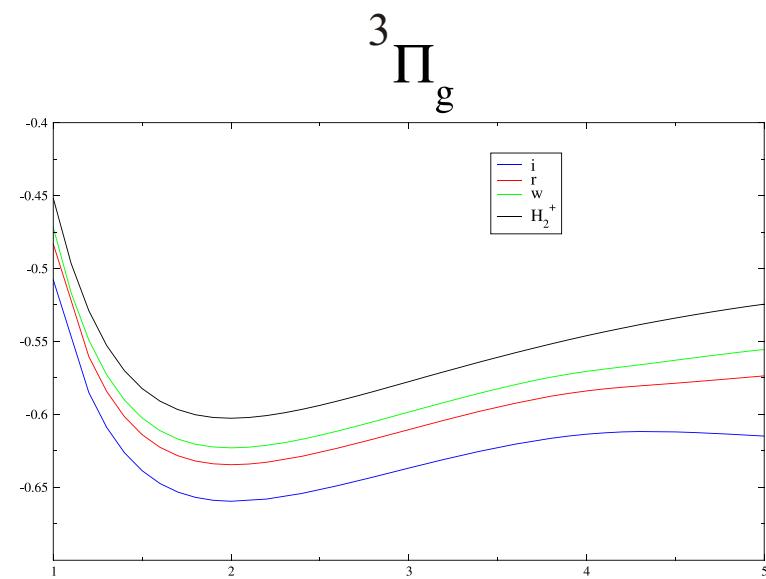
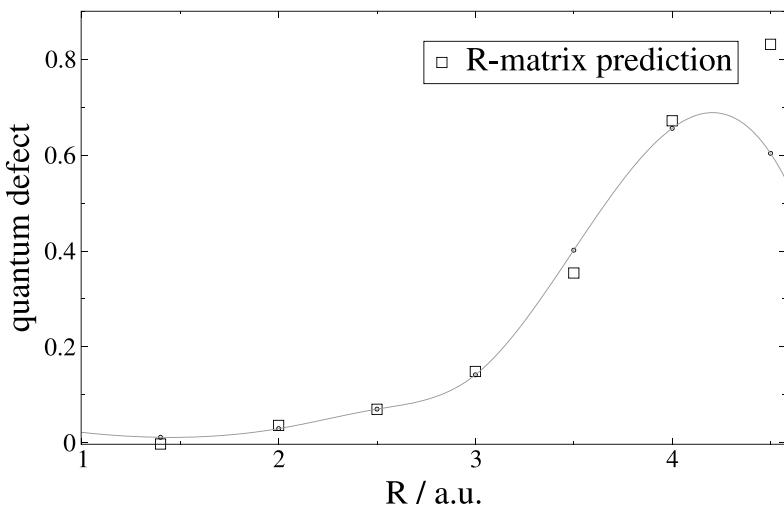
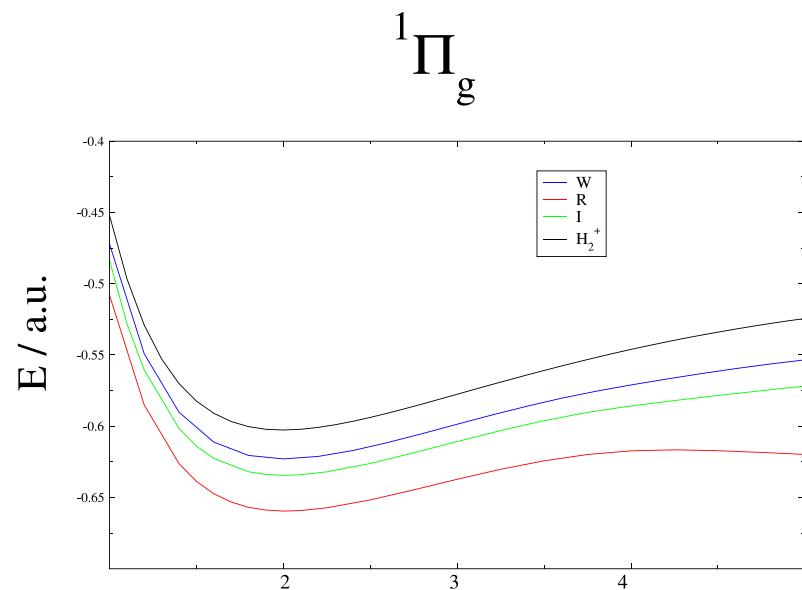
The ${}^1_g^+$ symmetry

$H_2^+, v^+ = 0, N^+ = 0$



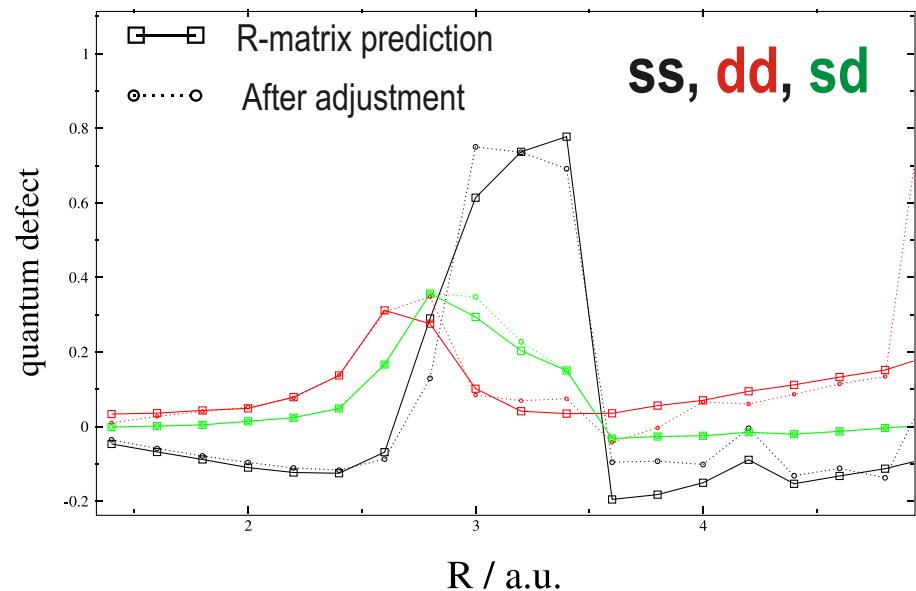
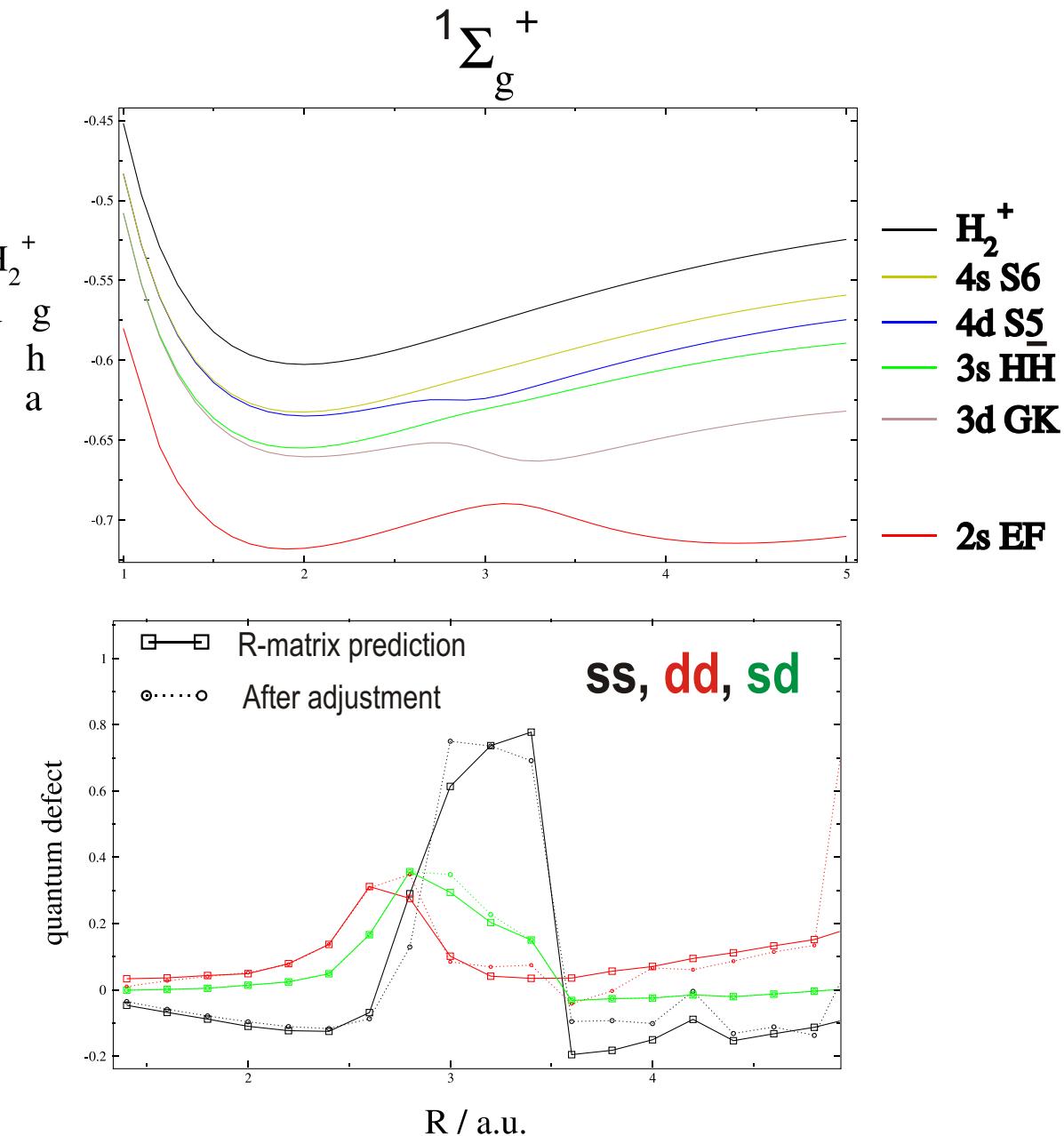
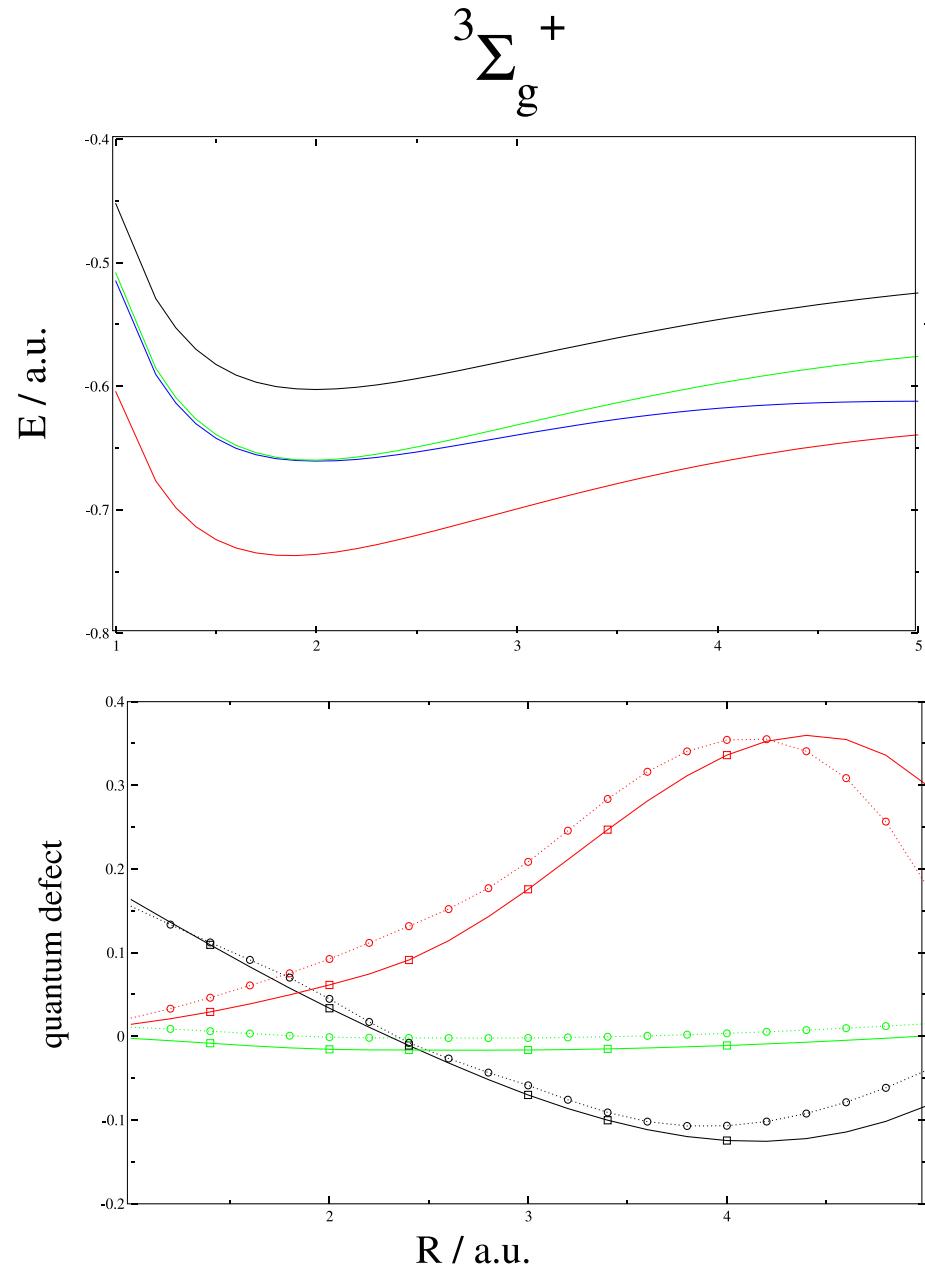
Available PFI and photoionization spectra

Derivation of quantum defect functions for the gerade states



Potential curves from Wolniewicz and Dressler

Derivation of quantum defect functions for the gerade states



State	V	N	OBS	CALC	CALC-OBS	State	V	N	OBS	CALC	CALC-OBS
I	0	1	112066.65	112065.62	-1.03	J	0	1	112072.89	112072.77	-0.12
		2	112140.82	112140.02	-0.8			2	112147.64	112147.77	0.13
		3	112264.88	112264.32	-0.56			3	112272.11	112272.46	0.35
		4	112441.77	112441.38	-0.39			4	112449.12	112449.69	0.57
J	0	2	112513.95	112513.49	-0.46	I	0	2	112525.97	112526.36	0.39
I	0	5	112671.67	112671.55	-0.12			5	112679.1	112679.88	0.78
J	0	3	112732.18	112731.49	-0.69			3	112743.57	112743.72	0.15
	4	4	113007.64	113006.63	-1.01			4	113018.39	113018.32	-0.07
	5	5	113336.26	113335.16	-1.1	I	1	1	113346.57	113346.35	-0.22
I	1	1	114179.22	114177.96	-1.26			2	114172.13	114171.03	-1.1
	2	2	114259.06	114257.96	-1.1			3	114252.86	114251.99	-0.87
	3	3	114384.38	114383.58	-0.8			4	114379.11	114378.39	-0.72
J	1	4	114557.69	114557.13	-0.56	J	1	2	114552.96	114552.4	-0.56
I	1	5	114779.65	114779.39	-0.26			3	114718.24	114717.7	-0.54
J	1	3	114904.61	114903.73	-0.88			4	114914.55	114913.75	-0.8
	4	4	115158.2	115157.11	-1.09			5	115166.62	115165.56	-1.06
	5	5	115463.46	115462.36	-1.1	I	2	1	115470.26	115469.22	-1.04
I	2	1	116145.57	116144.34	-1.23			2	116114.42	116111.88	-2.54
	2	2	116227.95	116226.68	-1.27			3	116197.52	116195.23	-2.29
	3	3	116353.23	116352.32	-0.91			4	116324.01	116321.86	-2.15
	4	4	116523.39	116522.42	-0.97	J	2	1	116494.72	116492.66	-2.06
	5	5	116737.95	116737.5	-0.45			2	116709.73	116708.02	-1.71
J	2	2	116776.23	116775.6	-0.63			3	116787.2	116786.59	-0.61
	3	3	116954.76	116954.01	-0.75			4	116963.16	116962.29	-0.87
	4	4	117186.46	117185.31	-1.15	R	0	1	117191.62	117190.48	-1.14
	5	5	117467.14	117466.08	-1.06			2	117589.25	117589.51	0.26
R	0	1	117587.66	117587.08	-0.58			3	117603.37	117603.77	0.4
	2	2	117599.44	117599.21	-0.23			4	117710.18	117710.6	0.42
	3	3	117706.1	117705.98	-0.12	S	0	1	117834.75	117834.88	0.13
S	0	2	117830.35	117829.88	-0.47			2	117878.14	117878.66	0.52
R	0	4	117874.13	117874.05	-0.08			3	117881.49	117879.54	-1.95
I	3	1	117958.86	117956.2	-2.66			4	117964.15	117962.31	-1.84
	2	2	118041.08	118038.55	-2.53	R	1	1	118071.35	118071.36	0.01
S	0	3	118067.15	118066.58	-0.57			2	118088.35	118086.67	-1.68
R	0	5	118099.26	118099.27	0.01			3	118103.25	118103.81	0.56
I	3	3	118164.91	118162.62	-2.29			4	118254.04	118252.61	-1.43
	4	4	118330.71	118328.64	-2.07	I	3	1	118356.84	118356.87	0.03
S	0	5	118352.97	118352.28	-0.69			2	118071.35	118071.36	0.01
I	3	5	118539.02	118536.72	-2.3			3	118088.35	118086.67	-1.68
J	3	2	118687.78					4	118254.04	118252.61	-1.43
	3	3	118725.16	118724.66	-0.5	S	0	1	118356.84	118356.87	0.03
	4	4	118885.31	118884.75	-0.56			2	118088.35	118086.67	-1.68
	5	5	119094.2	119093.57	-0.63			3	118103.25	118103.81	0.56
I	4	1	119348.28	119348.21	-0.07			4	118254.04	118252.61	-1.43
R	1	1	119675.7	119699.9		I	3	1	118356.84	118356.87	0.03
	2	2	119739.35	119737.25	-2.1			2	118088.35	118086.67	-1.68
I	4	3	119770.24	119768.88	-1.36			3	118103.25	118103.81	0.56
S	0	2	119873.14	119872.05	-1.09			4	118254.04	118252.61	-1.43

Rovibronic (+) levels : the triplet manifold

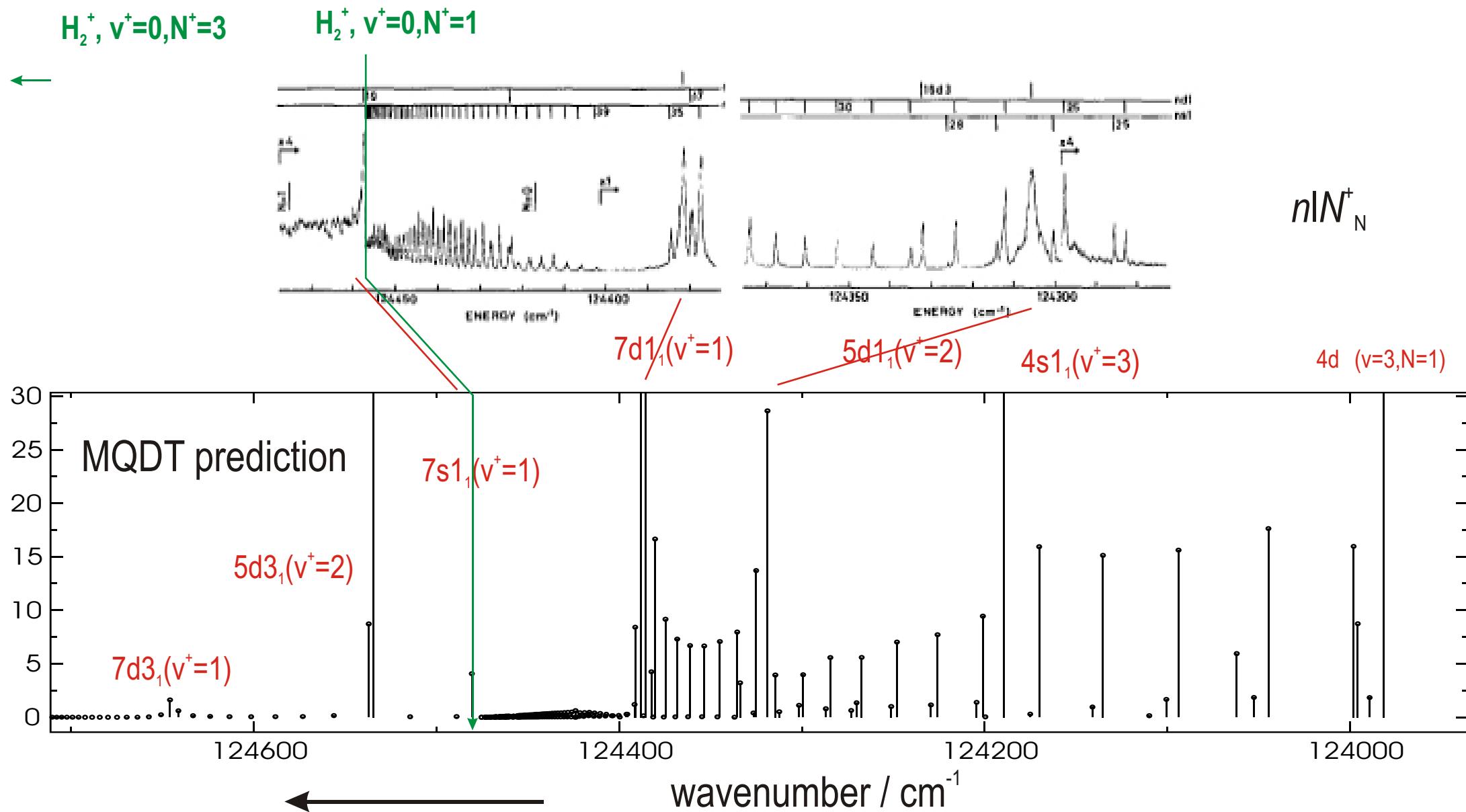
	N=0	Calc	Obs-calc	N=1	Calc	Obs-calc	N=2	Calc	Obs-calc	N=3	Calc	Obs-calc
A0	95076.3	95073.4	2.9	95142.98	95140.06	2.93	95275.79	95272.84	2.95	95473.73	95470.72	3.01
A1	97600.62	97596.79	3.83	97664.04	97660.12	3.93	97790.35	97786.27	4.08	97978.59	97974.24	4.35
A2	99989	99993.62	-4.62	100049.26	100053.87	-4.61	100169.29	100173.88	-4.59	100348.13	100352.72	-4.59
H0	111793.45			111948.16	111941.3	6.85	112050.12	112046.94	3.18	112223.28	112222.04	1.23
H1	111921.18			114198.05	114197.87	0.18	114312.11	114312.33	-0.22	114482.28	114482.5	-0.22
G0				111796.47	111803.74	-7.28	111826.5	111830.24	-3.75	111896.64	111898.65	-2.01
G1	113886.39	113890.5	-4.11	113883.81	113888.87	-5.06	113910.96	113914.48	-3.52	113980.42	113982.87	-2.45
G2	115784.97	115785.87	-0.9	115794.54	115795.18	-0.64	115829.4	115829.98	-0.58	115901.99	115902.42	-0.43
I0				112153.63	112150.99	2.64	112310.89	112308.5	2.39	112503.69	112501.62	2.07
I1				114269.16	114262.4	6.76	114419.39	114414.26	5.13	114614.15	114610.27	3.88
I2				116182.22	116180.63	1.59	116319.29	116317.55	1.74	116504.19	116501.96	2.23
J0				112529.55	112528.87	0.68	112779.41	112778.21	1.21			
J1				114712.08	114711.39	0.69	114924.7	114923.69	1.01			
J2				116777.92	116777.35	0.57	116962.18	116961.35	0.83			

Rovibronic (+) levels : the singlet manifold

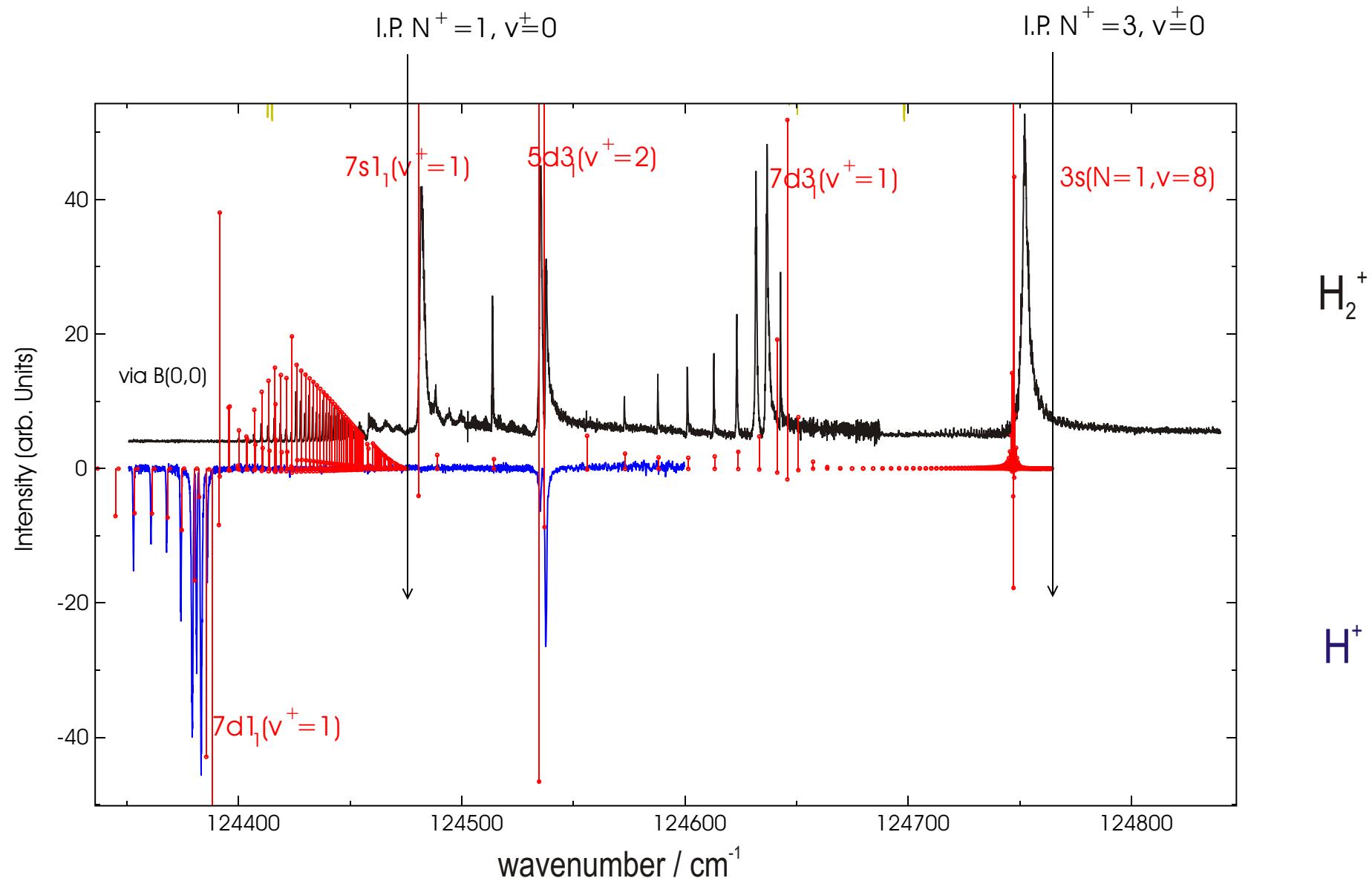
	N=1			N=2			N=3			N=4					
2s	E0	99228.21	99221.68	-6.53	99354.57	99348.16	-6.41	99542.78	99536.58	-6.19	99791.34	99785.45	-5.89		
	E1	101554.04	101548.1	-5.94	101671.65	101666.22	-5.43	101849.41	101842.02	-7.39	102081.05	102073.9	-7.15		
3d	J0				112536.77	112538.71	1.93	112774.61	112781.1	6.49	113078.22	113086.33	8.11		
	3s	H0	113016.73	113018.1	1.37	113134.08	113136.92	2.84	113303.44	113313.92	10.48	113548.77	113547.59	-1.18	
4d	4s	H2	117338.5	117340.57	2.07	117455.5	117447.86	-7.64	117590.25	117586.44	-3.81	117759.31	117775.03	15.72	
		P0	117411.08	117412.45	1.37	117391.59	117397.31	5.72	117453.99	117457.2	3.21	117567.98	117571.24	3.26	
R0			117690.54	117692.99	2.45	117936.39	117937.83	1.44	118202.52	118200.59	-1.93				
					117712.89	117714.21	1.32	117880.79	117882.34	1.55					
O0			117945.76	117945.01	-0.75	118068.94	118065.35	-3.59	118257.1	118259.92	2.82				

Photoionization spectra of ortho-H₂: excitation X(0,1) --> B(0,0) --> ns,nd ($N=1$)

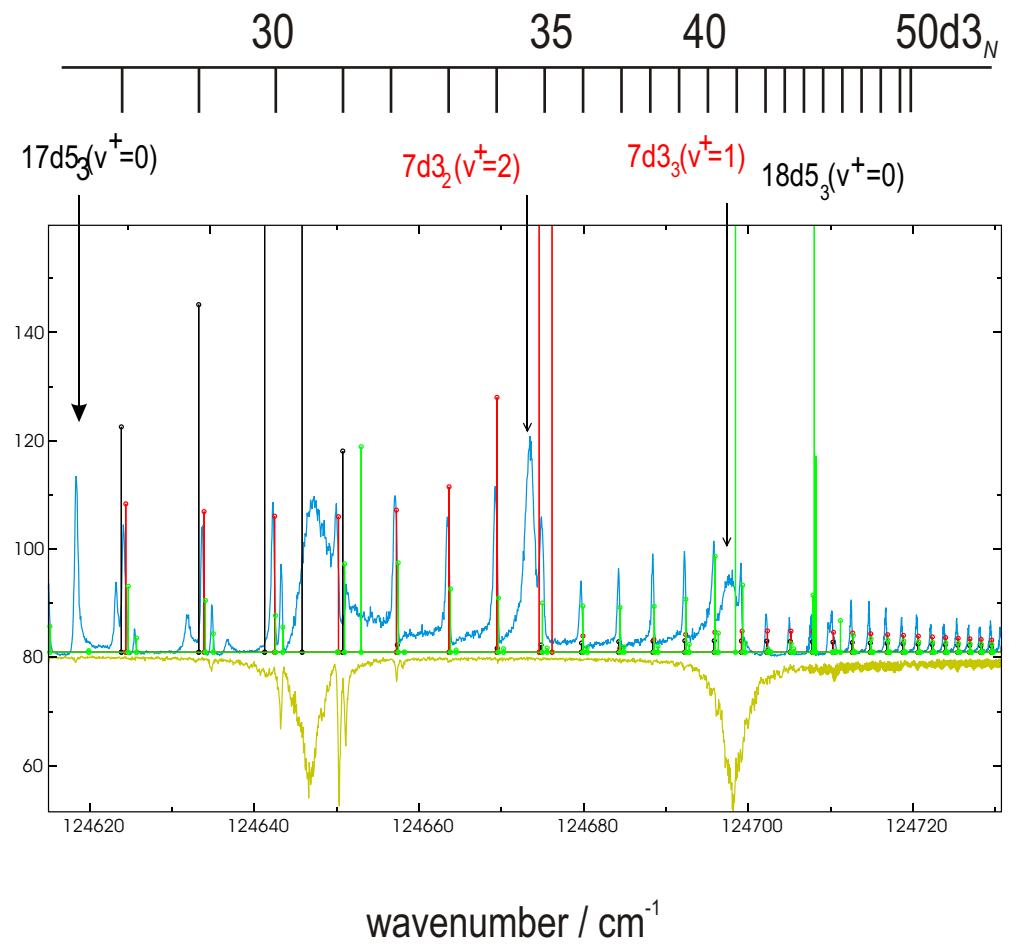
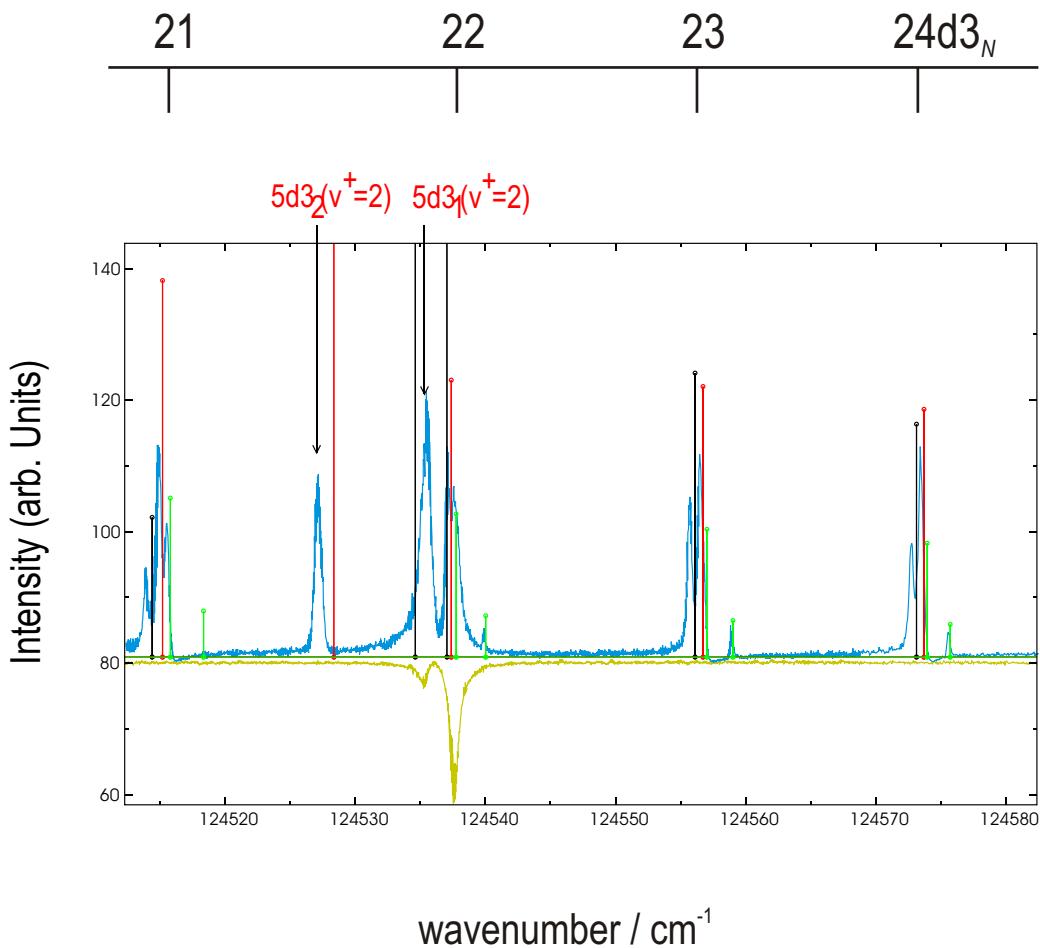
H. Rottke and K. Welge, J. Chem. Phys. 97, 908 (1992)



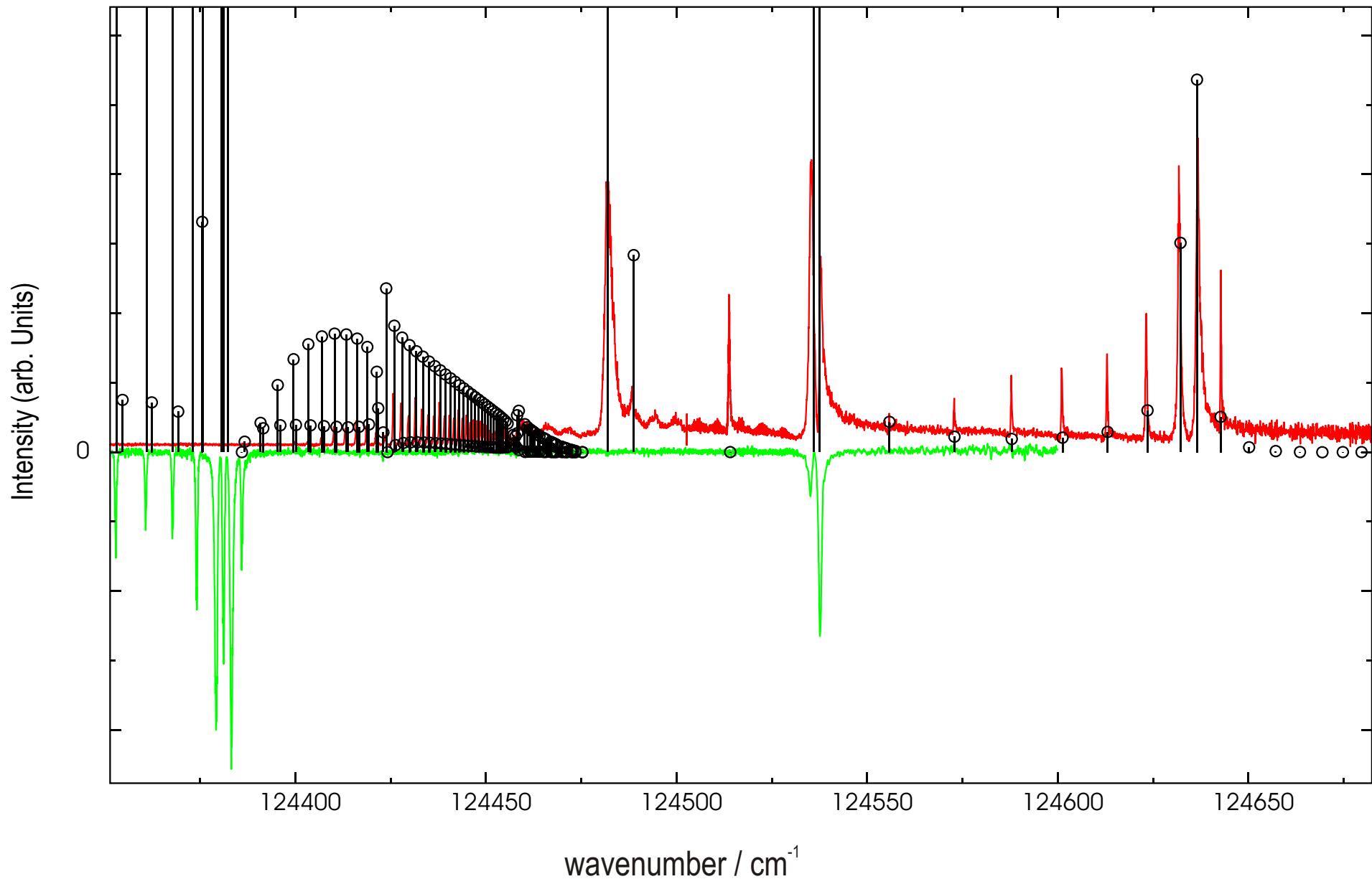
Photoionization spectra of ortho-H₂: excitation X(0,1) --> B(0,0) --> ns,nd (N=1)



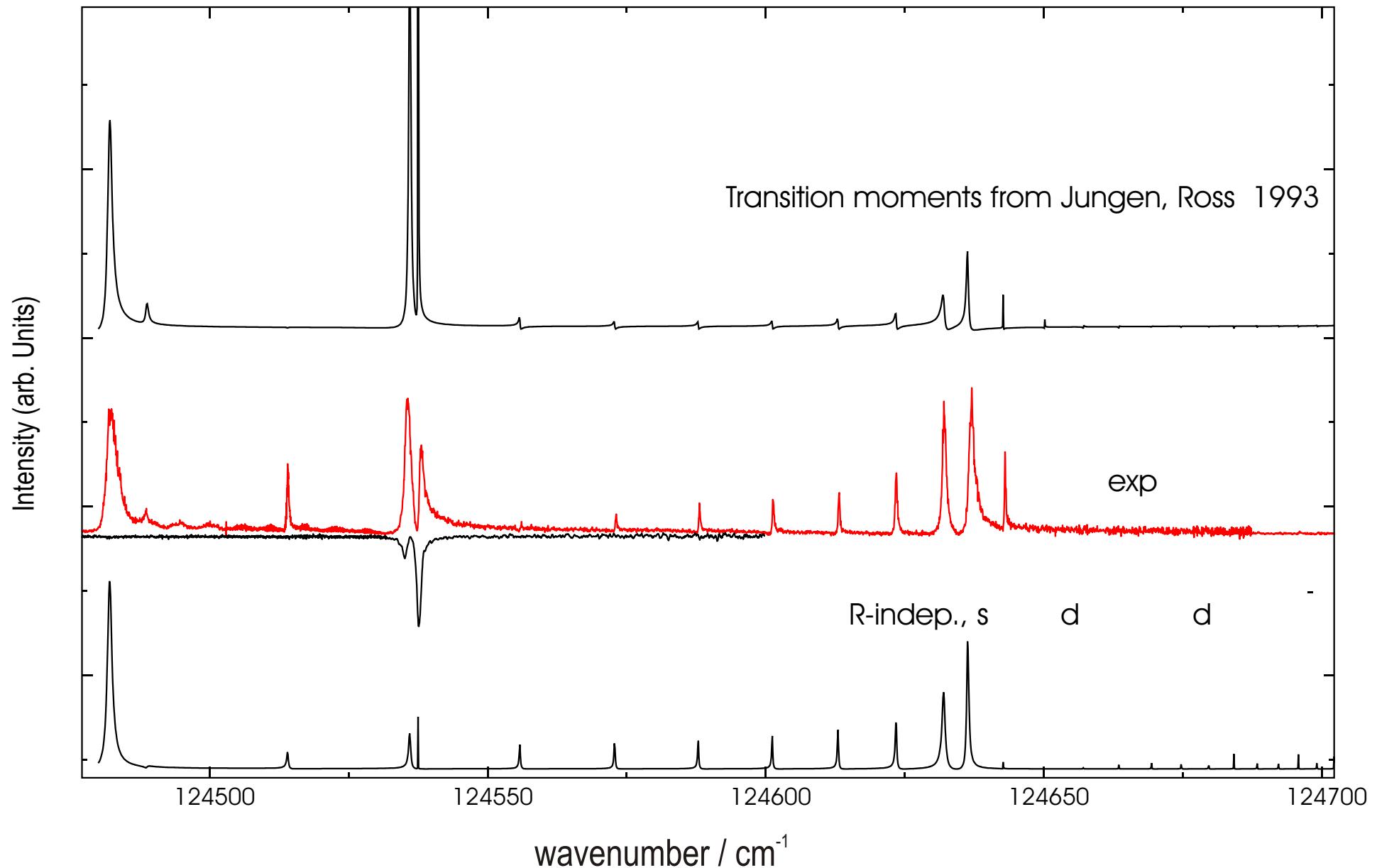
Spectra from : A. Osterwalder et al., J. Chem. Phys. 121, 11810 (2004)



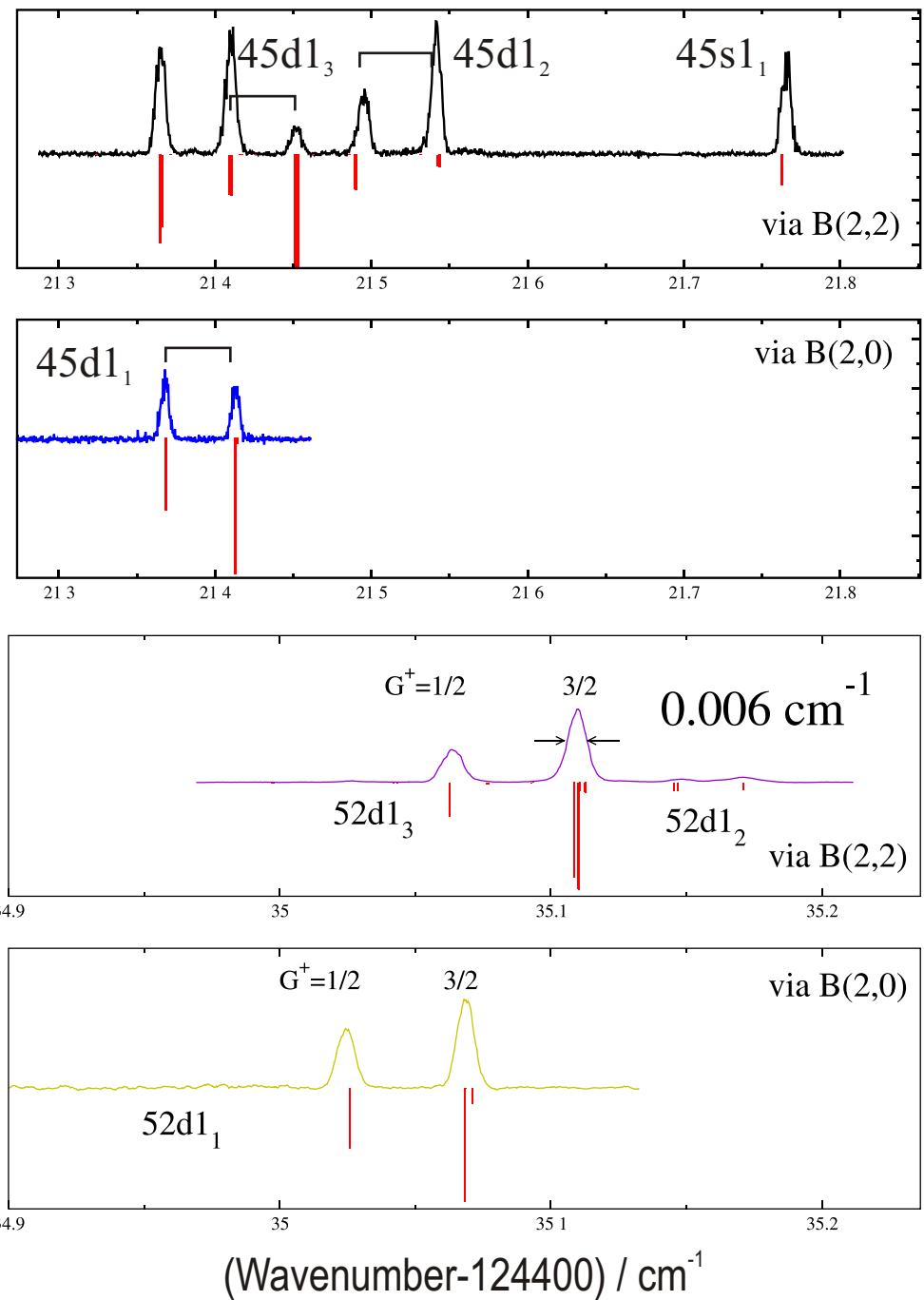
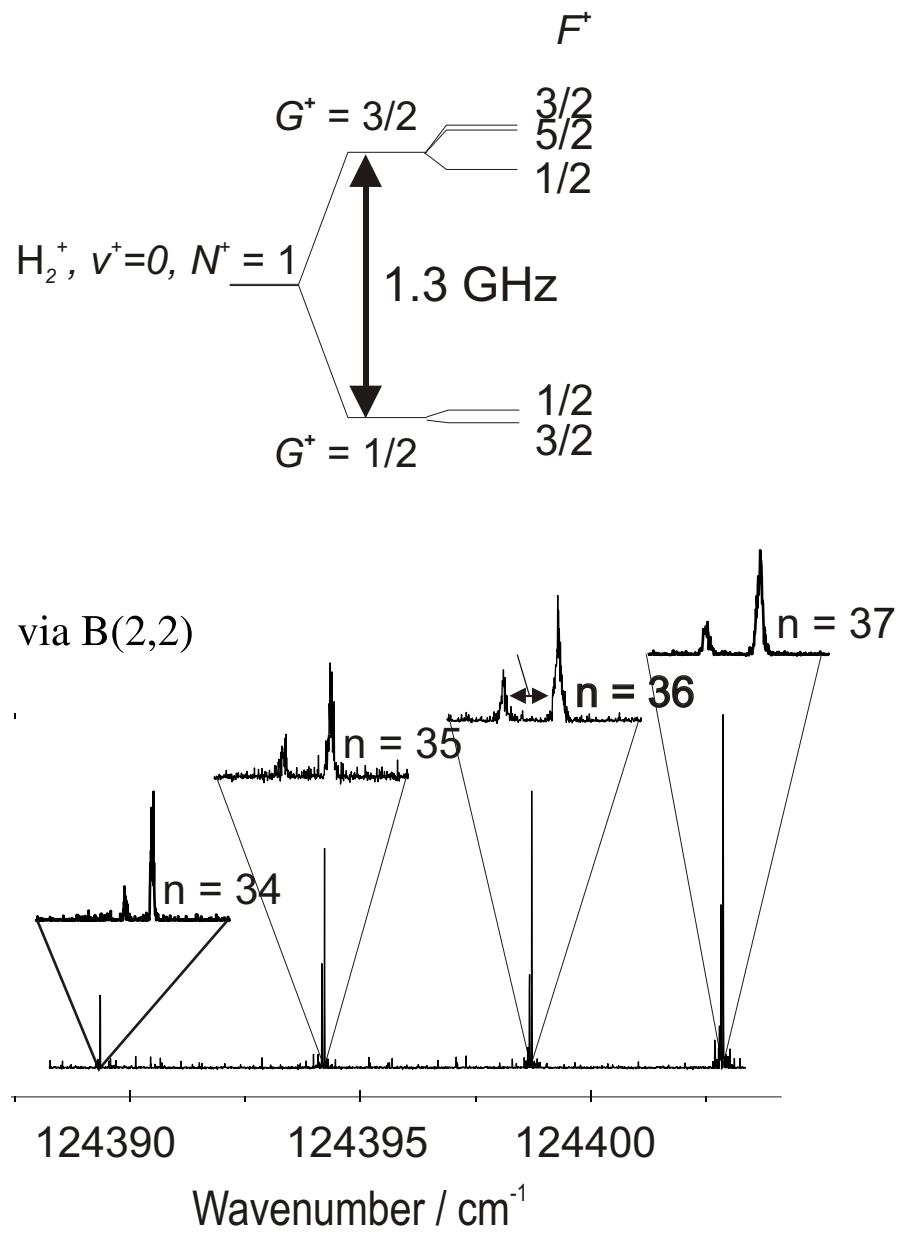
After a slight adjustment of the quantum defect curves... (-0.004, +0.005, unch.)



Intensities, line shapes and autoionization

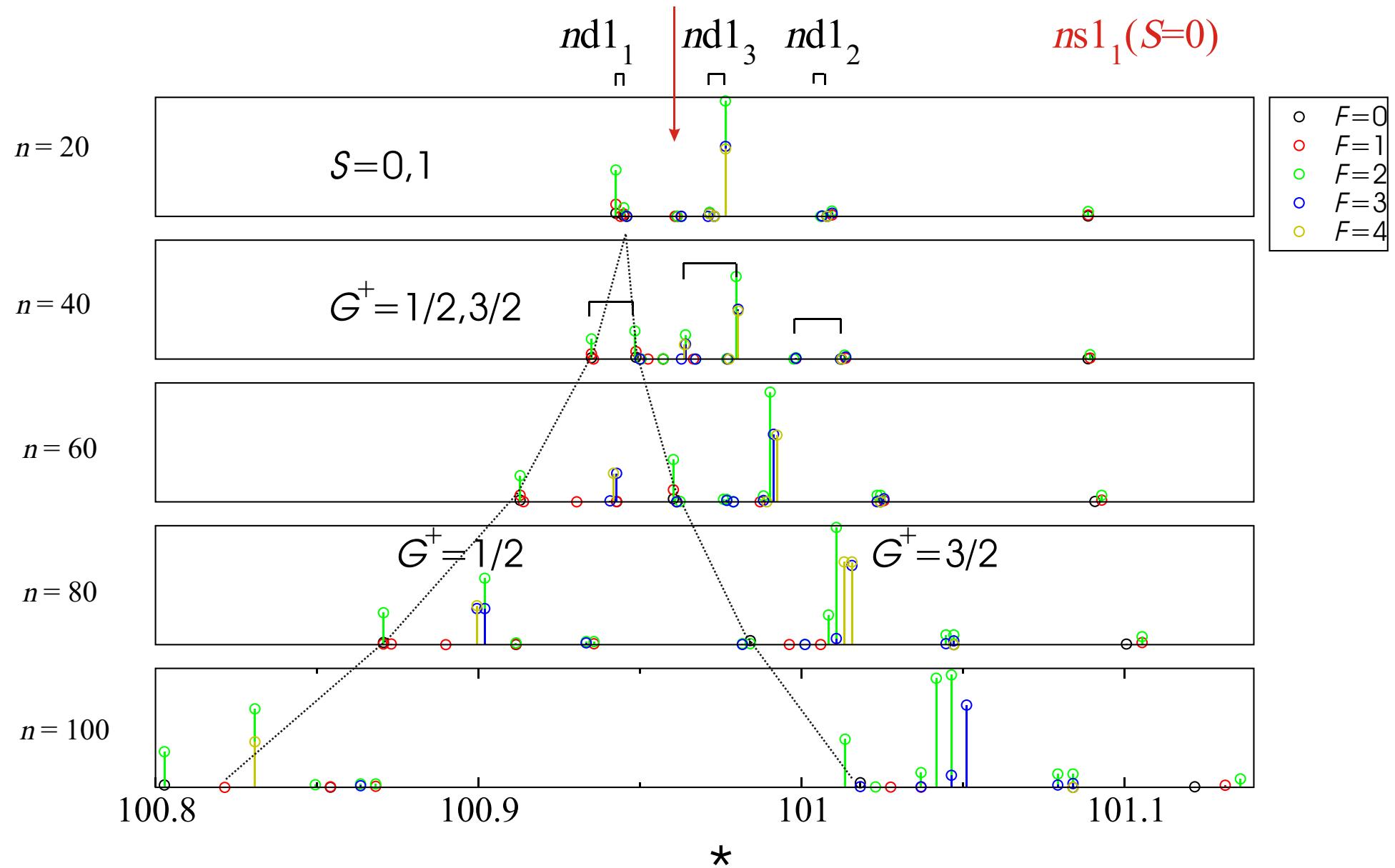


Hyperfine structure in the gerade states



Spin-decoupling

$ns1_1(S=1)$



Summary

1. Pure *ab initio* quantum defect curves have been obtained for H₂ that predict both the rovibronic structure of the low *n* excited *gerade* Rydberg states and the high *n* Rydberg states around the ionization thresholds to near spectroscopic accuracy.
2. The quantum defect curves can be adjusted to yield a quantitative agreement with experimental spectra.
3. Autoionization lineshapes and linewidths are in qualitative agreement with the experiment.
4. The hyperfine structure of the Rydberg states and the recoupling of electronic and nuclear spins are described accurately.

The present quantum defect curves provide a complete description of the spin-rovibronic interactions in the *gerade* states and the (autoionization) dynamics induced by these interactions.

Outlook

1. Study the hyperfine structure of autoionizing levels and the role of nuclear spin in photoionization.
2. Incorporate predissociation in MQDT model of *gerade* states.
3. Improve hyperfine structure parameters for H₂⁺.

