

# Multichannel quantum defect theory of ${}^3\Pi_u$ and ${}^3\Sigma_u^+$ states of $H_2$ : rovibronic energy levels

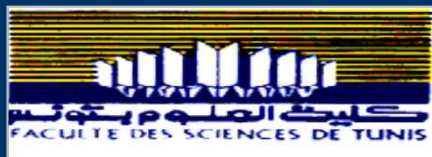
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# Frame transformation approach

Function describing the molecule in the Born-Oppenheimer region :

$$|iR \Lambda \rangle$$

Each molecular asymptotic channel function contain a factor :  $|iv_i^+ N_i^+ \rangle$

The transformation between these two this limits is embedded in the bra-kets :

$$U = {}^{JM} \langle iv_i^+ N_i^+ | iR \Lambda \rangle^{JM}$$

We then use the frame transformation technique , using the electronic quantum defect matrices, to calculate rovibronic reaction matrix and therefore the rovibronic energy levels :

$$K_{iv_i^+ N_i^+, jv_j^+ N_j^+} = \int dR {}^{JM} \langle iv_i^+ N_i^+ | \left\{ \sum_{\Lambda} |iR \Lambda \rangle^{JM} K_{ij}^{\Lambda}(R) {}^{JM} \langle jR \Lambda | \right\} | jv_j^+ N_j^+ \rangle^{JM}$$

# Frame transformation approach

The adiabatic potential energy curves of Rydberg states are obtained by solving the following secular equation :

$$\det \left| \tan(\beta_i) \delta_{ij} + K_{ij}(E) \right| = 0$$

where :

$$K_{ij} = \sum_{\alpha=1}^N U_{i\alpha} \tan \pi \mu_{\alpha} U_{\alpha j}^+$$

The full rovibronic reaction matrix leads to and accounts for all interactions between different rotational, vibrational, and electronic channels :

$$K_{iv_i^+ N_i^+, jv_j^+ N_j^+} = \int dR^{JM} \left[ U K_{ij}^{\Lambda}(R) U^+ \right]$$

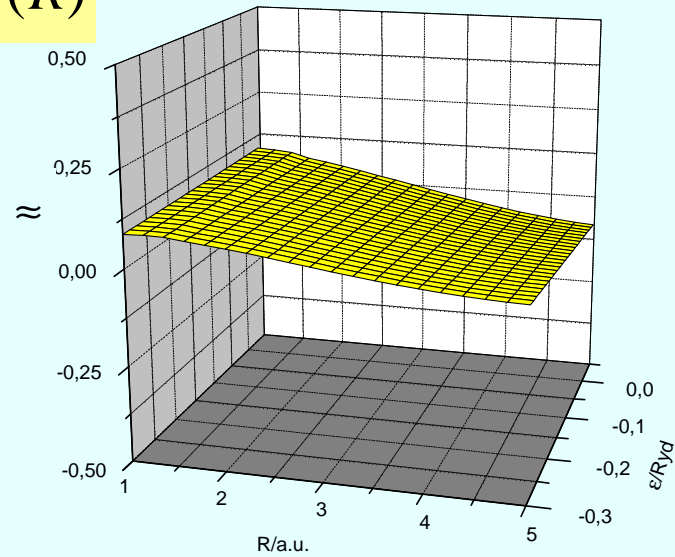
$$\langle iv_i^+ N_i^+ | iR\Lambda \rangle^{JM}$$

Smooth variation in  $R$

# Triplets levels with $p$ symmetry of $H_2$

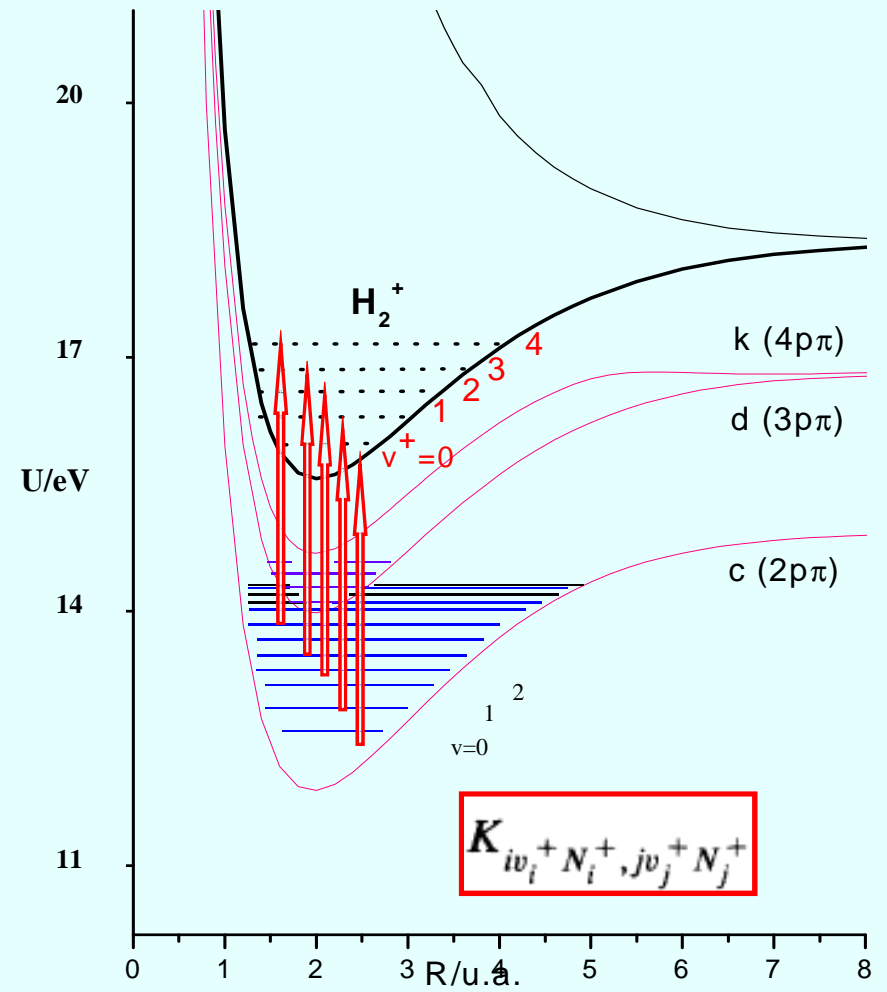
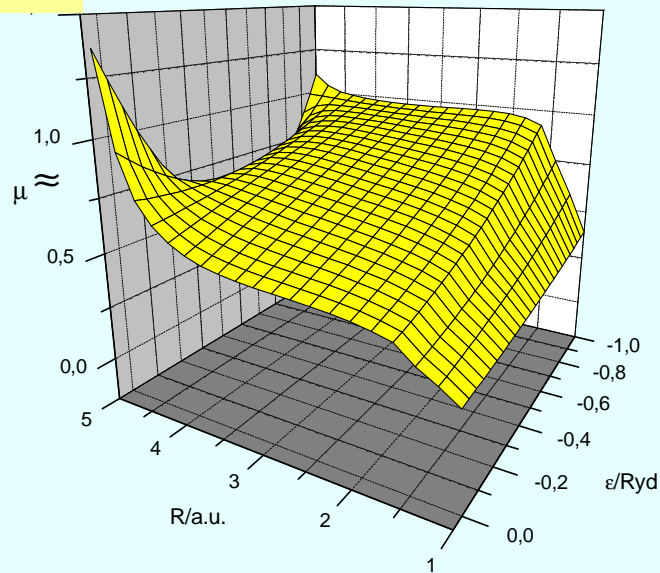
$$K_{ij}^{\Pi}(R)$$

${}^3\Pi_u$  symmetry of  $H_2$



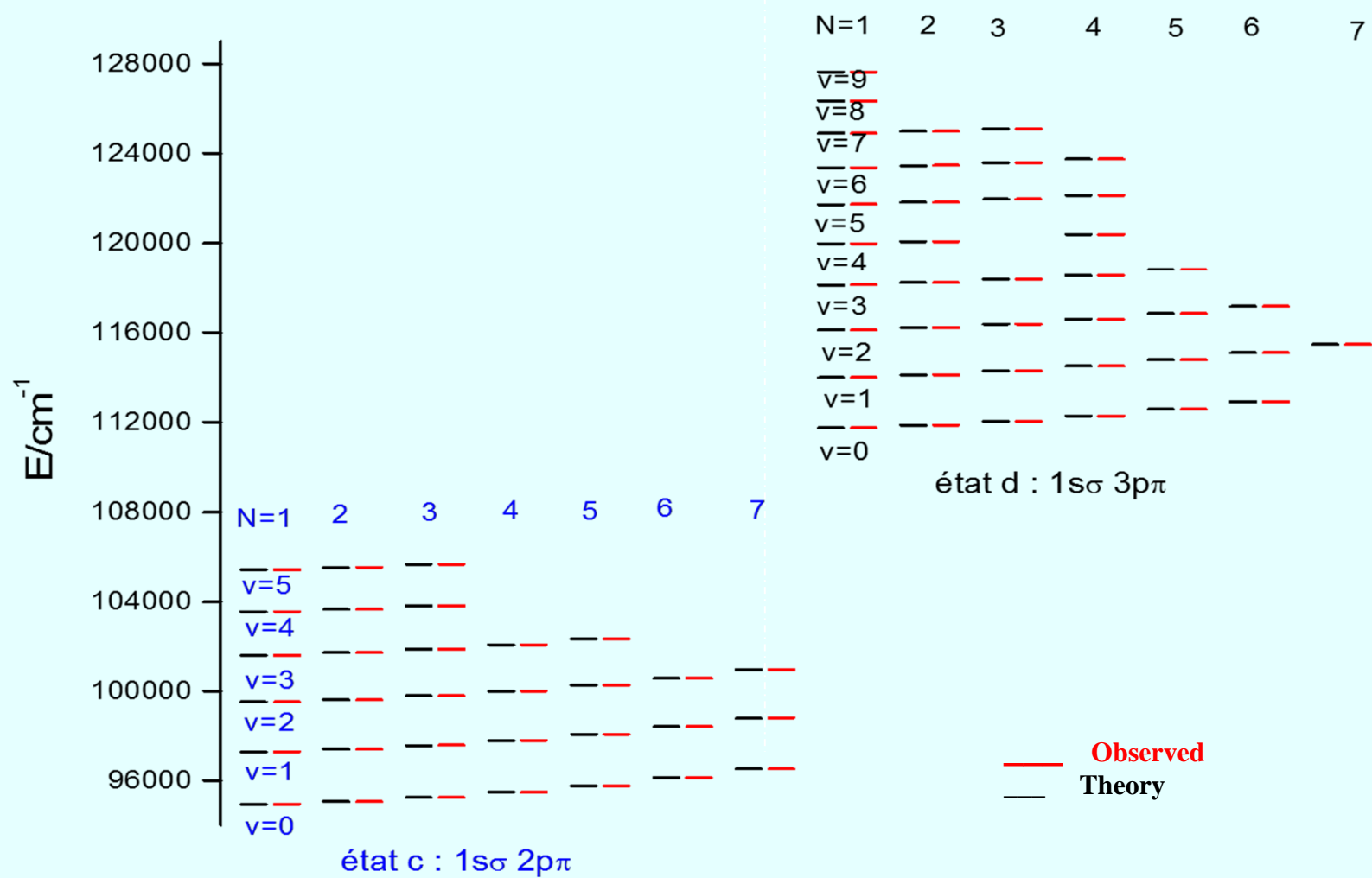
$$K_{ij}^{\Sigma}(R)$$

${}^3\Sigma_u$  symmetry of  $H_2$



Potential energy curves with rovibronic levels

# Comparison of observed and calculated rovibronic energies levels of ${}^3\Pi_u$ - states of $H_2$



## Comparison of observed and calculated term values for the : $c^- (2p\pi)$ state

<b>v</b>	<b>N=1 Exp (cm<sup>-1</sup>) [2]</b>	<b>Ross et al [1]</b>	<b>Our results</b>	<b>N=2 Exp (cm<sup>-1</sup>) [2]</b>	<b>Ross et al [1]</b>	<b>Our results</b>	<b>N=3 Exp (cm<sup>-1</sup>) [2]</b>	<b>Ross et al [1]</b>	<b>Our results</b>
<b>0</b>	94941.58	-4.0	1.54	95062.33	-4.0	1.52	95242.37	-4.0	1.56
<b>1</b>	97280.60	-3.6	1.80	97395.55	-3.7	1.72	97567.03	-3.7	1.74
<b>2</b>	99497.27	-3.5	1.88	99606.78	-3.4	1.91	99769.97	-3.4	1.94
<b>3</b>	101595.29	-3.3	2.11	101699.35	-3.3	2.11	101854.47	-3.2	2.16
<b>4</b>	103577.28	-2.9	2.75	103677.21	-1.8	3.95	103822.83	-3.3	2.45
<b>5</b>	105445.50	-2.3	4.26	105539.99	-1.3	5.25	105677.87	-2.8	3.84
<b>EQM</b>		<b>3.31</b>	<b>2.55</b>		<b>3.08</b>	<b>3.06</b>		<b>3.42</b>	<b>1.35</b>

[1] S.C.Ross, Ch.Jungen, and A.Matzkin, *Can. J. Phys.* 79. 561 (2001).  
 [2] H. M.Crosswhite, (Wiley, New York, 1972).



## Comparison of observed and calculated term values for the : $c^+ (2p\pi)$ state

v	N=1 Exp (cm <sup>-1</sup> ) [2]	<b>Our results</b>	N=2 Exp (cm <sup>-1</sup> ) [2]	<b>Our results</b>	N=3 Exp (cm <sup>-1</sup> ) [2]	<b>Our results</b>
0	94941.72	<b>1.825</b>	95062.46	<b>2.099</b>	95242.41	<b>2.500</b>
1	97280.50	<b>1.795</b>	97395.64	<b>2.090</b>	97567.18	<b>2.477</b>
2	99497.28	<b>1.937</b>	99607.08	<b>2.351</b>	99770.37	<b>2.643</b>
3	101595.34	<b>2.171</b>	101699.82	<b>2.612</b>	101855.10	<b>2.884</b>

## Comparison of observed and calculated term values for the : e (3ps) state

v	N=1 Exp (cm <sup>-1</sup> ) [2]	<b>Our results</b>	N=2 Exp (cm <sup>-1</sup> ) [2]	<b>Our results</b>	N=3 Exp (cm <sup>-1</sup> ) [2]	<b>Our results</b>
0	106682.010	<b>-0.845</b>	106735.13	<b>-0.929</b>	106840.90	<b>-1.182</b>
1	108744.710	<b>-0.593</b>	110718.92	<b>-0.282</b>	108894.49	<b>-0.906</b>
2	110671.990	<b>-0.174</b>	112505.08	<b>0.318</b>	110812.46	<b>-0.484</b>
3	112461.150	<b>0.424</b>	114146.98	<b>1.049</b>	112592.62	<b>0.109</b>
4	114104.720	<b>0.527</b>	115623.69	<b>1.487</b>	114230.49	<b>0.834</b>
5	115581.82	<b>0.964</b>	116917.27	<b>-5.658</b>	115699.54	<b>1.542</b>

[2] H. M. Crosswhite, (Wiley, New York, 1972).



# Work in progress and perspectives

- Calculation of the lifetimes of predissociative level  $c^+ (2p\pi) ^3\Pi_u^+$  of  $H_2$
- Fine and hyperfine structure of the ungerade triplet states of  $H_2$  (n=2 and 3)
- The transition dipole moments in the Coulomb approximation as a function of the internuclear distance R