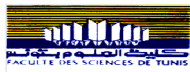


# Multichannel quantum defect study of ${}^3\Pi_u$ and ${}^3\Sigma_u^+$ states of $H_2$ : rovibronic energy levels



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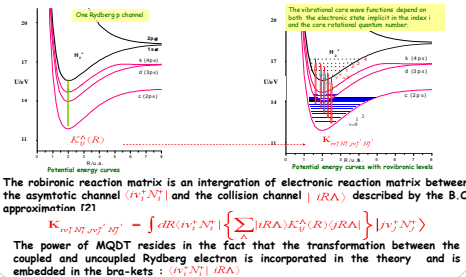
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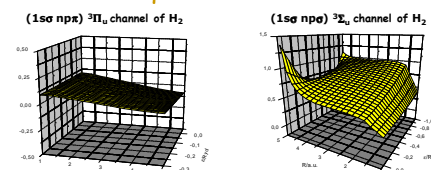
## Introduction

Multichannel quantum defect theory is applied to calculate the rovibronic energy levels of the  ${}^3\Pi_u$  and  ${}^3\Sigma_u^+$  states of  $H_2$ . First, a compilation of the best available experimental term values for these levels was prepared [1,4]. Second R-dependent quantum defect matrices for the  ${}^3\Pi_u$  and  ${}^3\Sigma_u^+$  were obtained from *ab initio* potential energy curves and used in an *ab initio* MQDT calculation. The rovibronic MQDT calculation are defined in new manner such as implemented in [7,8]. Thirdly we use the frame transformation method combined to the multichannel quantum defect theory [2] to calculate the rovibronic reaction matrix. The results obtained in this study provide for the first time a fully *ab initio* characterization for all measured rovibronic bound level energies of the  ${}^3\Pi_u^+$ ,  ${}^3\Sigma_u^+$  and  ${}^3\Sigma_g^+$  states of  $H_2$ . The agreement with the best available experimental levels [5] and previous theoretical calculations (where available) ([2,3]) is good. The quantum defect matrices thus obtained are also used to describe :  
 \* The predissociation of the  $2p\pi$   ${}^3\Pi_u$  state by the low-lying  $2p\pi$   ${}^3\Sigma_u^+$  state.  
 \* The fine structure and hyperfine structure of the  $c$   ${}^3\Pi_u$  state.  
 \* To calculate the transition dipole moments (d, k)  ${}^3\Pi_u \rightarrow a$   ${}^3\Sigma_g^+$  and (e, f)  ${}^3\Sigma_u^+ \rightarrow a$   ${}^3\Sigma_g^+$ .

## The rovibronic frame transformation method



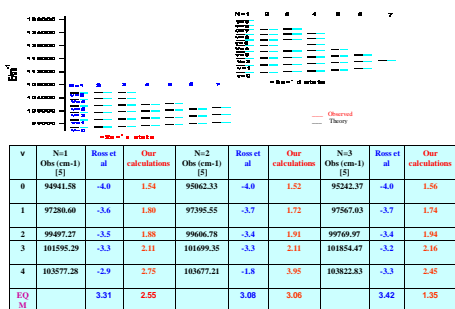
## Energy- and geometry-dependent quantum defects



### $\mu$ - quantum defects

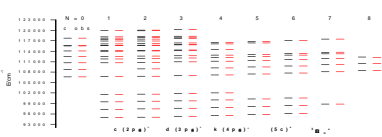
To avoid the appearance of the unphysical solutions with the  $\mu$  quantum defect (s and c Coulomb functions) and the energy dependence problem in  $H_2$  using  $\eta$ -defect (f and h Coulomb functions) [4], a new approach is implemented giving Coulomb functions ( $\xi$  and  $\zeta$ ) and associated quantum defects  $\mu$  which are found to have smooth R- and energy-dependences [7,8].

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



Comparison of observed [5] and calculated term values for c- (2pπ) state

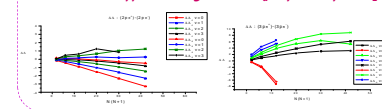
## Comparison of observed and calculated rovibronic energies levels of ${}^3\Pi_u^+$ and ${}^3\Sigma_u^+$ states of $H_2$



v	N=1 Obs (cm-1) [5]	Our calculations	N=2 Obs (cm-1) [5]	Our calculations	N=3 Obs (cm-1) [5]	Our calculations
0	94941.72	1.825	95962.46	2.899	95242.41	2.580
1	97280.60	-3.6	97395.55	-3.7	97567.03	-3.7
2	99497.27	-3.5	99606.78	-3.4	99769.97	-3.4
3	101595.29	-3.3	101699.35	-3.3	101854.47	-3.2

Comparison of observed [5] and calculated term values for c' (2pπ) state

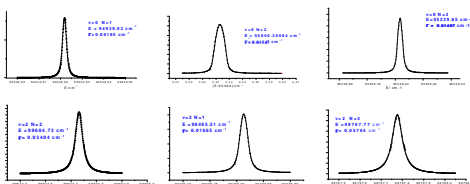
## Lambda - type doubling in the ${}^3\Pi_u^+$ symmetry of $H_2$



v	N=1 Obs (cm-1) [5]	Our calculations	N=2 Obs (cm-1) [5]	Our calculations	N=3 Obs (cm-1) [5]	Our calculations
0	106682.010	-0.845	106735.13	-0.929	106840.90	-1.182
1	108744.710	-0.593	108718.92	-0.282	108894.49	-0.906
2	110671.990	-0.174	112585.08	0.318	110812.46	-0.484
3	112461.150	0.424	114146.98	1.049	112592.62	0.109
4	114104.720	0.527	115623.69	1.487	114230.49	0.834
5	115581.82	0.964	116917.27	-5.658	115699.54	1.542

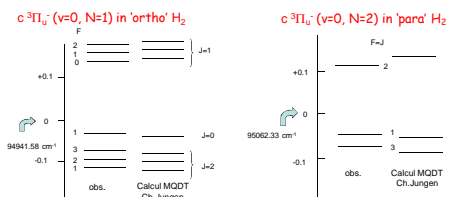
Comparison of observed [5] and calculated term values for e (3pσ) state

## Calculation of the lifetimes of predissociative level c' (2pπ) ${}^3\Pi_u^+$ of $H_2$



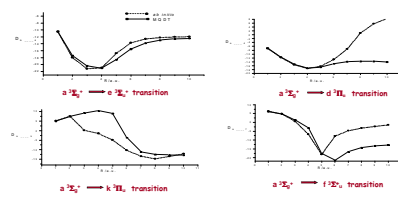
The rovibronic levels obtained for triplet symmetries ( ${}^3\Pi_u$  and  ${}^3\Sigma_u^+$ ) of  $H_2$  with the frame transformation method are used to calculate the first predissociative lifetimes of the rovibronic levels of c'  ${}^3\Pi_u$  state by the dissociative state  $b^3\Sigma_u^+$ .

## Fine and hyperfine structure of the ungerade triplet states of $H_2$ (n=2 and 3)



The fine structure and hyperfine structure of the N=1 (of orthohydrogen) and the N=2 (of parahydrogen) rotational levels of the c  ${}^3\Pi_u$  state will be compared to the experimental energy levels of Lichten [8].

## The transition dipole moments in the Coulomb approximation as a function of the internuclear distance R



Dipole transition moment D as a function of the internuclear distance R : our results (solid line) and *ab initio* computations of Ref [6] (dashed line). These calculations of transition moments, by using the Coulomb approximation, will be useful for the diagnosis of plasma of hydrogen.

## Conclusion

The quantum defects used in this work are defined in a new manner, extending the approach implemented in [7], they are characterized by smooth R- and energy dependences, a feature which is important for the rovibronic frame transformation in a full rovibronic MQDT [2]. We have performed for the first time a fully *ab initio* characterization for all measured rovibronic bound level energies of the  ${}^3\Pi_u$  and  ${}^3\Sigma_u^+$  channels. We have used the *ab initio* quantum defects and the frame-transformation technique to calculate rovibronic energy levels. The quantum defect matrices thus obtained are also used to calculate the transition dipole moments (d, k)  ${}^3\Pi_u \rightarrow a$   ${}^3\Sigma_g^+$  and (e, f)  ${}^3\Sigma_u^+ \rightarrow a$   ${}^3\Sigma_g^+$  in the Coulomb approximation as a function of the internuclear distance R.

- \* Further developments in progress involve:
- \* The first predissociative lifetimes of the rovibronic levels of c'  ${}^3\Pi_u$  state.
- \* The fine structure and hyperfine structure of the N=1 (of orthohydrogen) and the N=2 (of parahydrogen) rotational levels of the c  ${}^3\Pi_u$  state will be compared to the experimental energy levels of Lichten [8]
- \* Dipole transition moment D as a function of the internuclear distance R.

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