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

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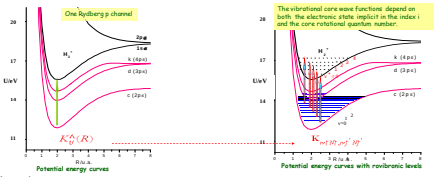
Introduction

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 rovironic 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 2pπ c $^3\Pi_u$ state by the low-lying 2pσ b $^3\Sigma_u^+$ 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

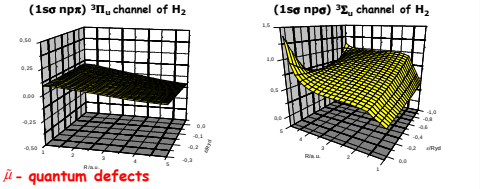


The robironic reaction matrix is an intergration of electronic reaction matrix between the asymtotic channel $\langle v_i^+ N_i^+ |$ and the collision channel $| iRA \rangle$ described by the B.O approximation [21

$$K_{v_i^+ N_i^+ v_j^+ N_j^+} = -\int dR \langle v_i^+ N_i^+ | \left\{ \sum_{\Lambda} |iRA\rangle K_{ij}^{\Lambda}(R) \langle jRA| \right\} | v_j^+ N_j^+ \rangle$$

The power of MQDT resides in the fact that the transformation between the coupled and uncoupled Rydberg electron is incorporated in the theory and is embedded in the bra-kets : $\langle v_i^+ N_i^+ | iRA \rangle$

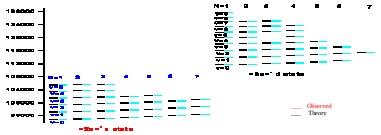
Energy- and geometry-dependent quantum defects



$\tilde{\mu}$ - quantum defects

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

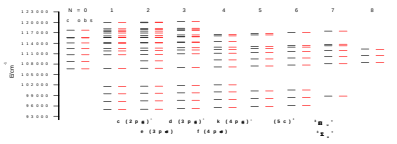
Comparison of observed and calculated rovibronic energies levels of $^3\Pi_u^-$ states of H_2



v	N=1 Obs (cm-1) [5]	Ross et al	Our calculations	N=2 Obs (cm-1) [5]	Ross et al	Our calculations	N=3 Obs (cm-1) [5]	Ross et al	Our calculations
0	94941.58	-4.0	1.54	95062.33	-4.0	1.52	95242.37	-4.0	1.56
1	97280.60	-3.6	1.80	97395.55	-3.7	1.72	97567.03	-3.7	1.74
2	99497.27	-3.5	1.88	99606.78	-3.4	1.91	99769.97	-3.4	1.94
3	101595.29	-3.3	2.11	101699.35	-3.3	2.11	101854.47	-3.2	2.16
4	103577.28	-2.9	2.75	103677.21	-1.8	3.95	103822.83	-3.3	2.45
EQM			3.31	2.55		3.08	3.06		3.42	1.35

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

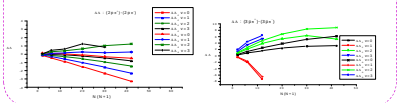
Comparison of observed and calculated rovibronic energies levels of $^3\Pi_u^+$ and $^3\Sigma_u^+$ states of H_2



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	95062.46	2.099	95242.41	2.500
1	97280.50	1.795	97395.64	2.090	97567.18	2.477
2	99497.28	1.937	99607.08	2.351	99770.37	2.643
3	101595.34	2.171	101699.82	2.612	101855.10	2.884

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

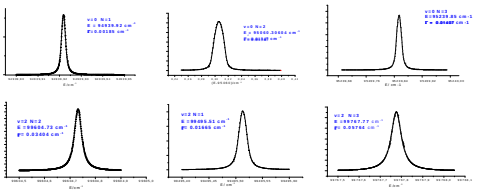
Lambda - type doubling in the $^3\Pi_u^{+-}$ symmetry of H_2



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	110718.92	-0.282	108894.49	-0.906
2	110671.990	-0.174	112505.08	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

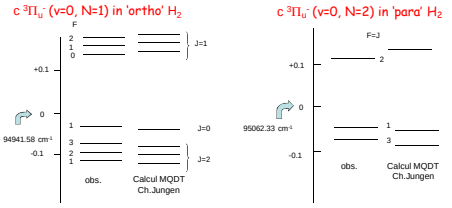
Comparison of observed [5] and calculated term values for e (3pσ) state

Calculation of the lifetimes of predissociative level c+ (2pπ) $^3\Pi^+_u$ of H_2



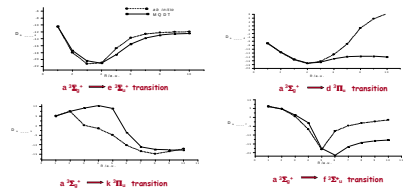
The rovibronic levels obtained for triplet symmetries ($^3\Pi_u$ and $^3\Sigma_u^+$) of H_2 with the frame transformation method are used to calculate the first predissociative lifetimes of the rovibronic levels of c+ $^3\Pi_u$ state by the dissociative state b$^3\Sigma_u^+$.

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 eneregy 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 defetcs and the frame-transformation technique to calculate ro-vibronic energy levels.
The quantum defect matrices thus obtained are also used to calculate the transition dipole moments (d, k) $^3\Pi_u \longrightarrow$ a $^3\Sigma^+_g$ and (e, f) $^3\Sigma_u \longrightarrow$ 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 eneregy levels of Lichten [8].
* Dipole transition moment D as a function of the internuclear distance R.

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