

**Resonant effects in photoionization and dissociative recombination of hydrogen species of astrochemical** interest

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## Introduction

Diatomic molecular hydrogen is the most abundant molecule in interstellar molecular clouds. The modeling of these environments relies on accurate cross sections for the various relevant processes. Among them, photoionization plays a major role. The recent discovery of vibrationally excited molecular hydrogen in extragalactic environments [1] suggests that photoionization of molecular hydrogen arising from vibrationally excited levels by photons of 13.6 eV or less is possible and should be introduced in the modeling of interstellar photon dominated regions.

Only a limited amount of theoretical work on photoionization from vibrationally excited molecular hydrogen has been carried out, mainly in the late 70s. These early results are still used by the astrophysical community when photoionization needs to be included in the kinetic models.

# **Results**

In the present work [3] we address the topic of calculating photoionization cross sections for excitation from excited vibrational levels of the ground state by taking into account of the full manifold of Rydberg states and their interactions with the electronic continuum. We exemplify the importance of resonances with two particular cases of the Q(N' = N'' = 1) transition originating from the v'' = 1, 5 ground state levels.

$10^{-10}$		3 4		:8   :9 : 	10':11:12:13
$ \underbrace{\begin{array}{c} 3 \\ 6 \end{array}}_{10^{-25}} 10^{-25} $		a)			
$\frac{1}{27}$		b)	H(1)+H(3)		n=3-6
<b>A</b> (10	- - -				



The Dissociative Recombination (DR) of molecular cations with electrons is an other major elementary process in the kinetics and in the energy balance of astrophysical ionized media (supernovae, interstellar molecular clouds, planetary ionospheres).

## **Photoexcitation, spontaneous emission, photoionization**

 $\mathbf{H}_{2}(N'',v'') + h\nu \rightarrow \begin{cases} \mathbf{H}_{2}(N',v') & photoabsorption \\ \mathbf{H}_{2}^{+}(N',v') + e^{-} & photoionization \end{cases}$ 

The relevant potential energy curves of the H<sub>2</sub> molecule used in the calculations and the scheme of the studied processes:



#### Theory

We are using a method based on the multichannel quantum defect theory (MQDT) combined with the frame transformation [2], where the radiative transitions are treated as half-collisions and the photon-molecule interaction is represented by the dipole operator. The major steps:

Figure 2: Cross sections and line intensities for the Q(1) transitions from the vibrationally excited levels (left: v'' = 1 and right: v'' = 5) of the  $X^1 \Sigma_a^+$ ground state of the H<sub>2</sub> molecule.

The cross section is dominated by the presence of resonance structures corresponding to excitation of various vibrational levels of quasi-bound electronic states which lie above the ionization thresholds. These autoionizing resonances produce a major fraction of the averaged cross section.

			ionization		absorption			ioniz	ation	absorption	
upper	number of	$\mathbf{v}^{\prime\prime}$	overall	total vs.	overall	total vs.	$\mathbf{v}^{\prime\prime}$	overall	total vs.	overall	total vs.
state	resonances		contrib.	backgr.	contrib.	backgr.		contrib.	backgr.	contrib.	backgr.
$\overline{3p\pi D}$	11		0.01		0.16			0.01		0.17	
$4p\pi D'$	14	1	0.23	6.2	0.10	8.1	5	0.14	4.6	0.13	5.6
$5p\pi D''$	15		0.12		0.06			0.17		0.14	
$6p\pi D''$	" 12		0.08		0.04			0.07		0.06	
			44%		36%	-		39%		50%	

The overall contributions of the lowest lying (n = 3 - 6) four excited electronic states are more than one-third of the total photoionization/photoabsorption cross sections.

## **Dissociative Recombination**

The same Rydberg resonances occur in the Dissociative Recombination (DR) of

• The manifold of  $\Pi_u$  excited states of  $H_2$  represents a single unperturbed  $np\pi$ Rydberg series converging to the  $X^2\Sigma_a^+$  ground state of  $H_2^+$ .

• The energy dependent quantum defects,  $\mu(\epsilon, R)$ , and dipole moments,  $d(\epsilon, R)$ , are extracted directly from the clamped-nuclei (Born-Oppenheimer) potential energy curves using the Rydberg-equation.

• Frame-transformation: Energy dependent rovibronic quantum defects,  $\mu_{v^+N^+,v^{+\prime}N^{+\prime}}(\overline{\epsilon})$ , and dipole moments,  $d_{v^+N^+,v''N''}(\overline{\epsilon})$ .

• Reaction matrix:  $\mathbf{K} = SC^{-1}$ , where  $S = \mathbf{U} \sin \pi \mu \mathbf{U}^{\mathrm{T}}$  and  $C = \mathbf{U} \cos \pi \mu \mathbf{U}^{\mathrm{T}}$ .

• Applying the correct asymptotic boundary condition on the total wave function:

$$\mathbf{\Gamma}\mathbf{B} = \tan\beta\mathbf{\Lambda}\mathbf{B} \quad \text{where} \begin{cases} \Gamma_{ii'} = \sin\beta_i \mathcal{C}_{ii'} + \cos\beta_i \mathcal{S}_{ii'} & i \in closed \\ \Lambda_{ii'} = 0 & i \in closed \\ \Gamma_{ii'} = \mathcal{S}_{ii'} & i \in open \\ \Lambda_{ii'} = \mathcal{C}_{ii'} & i \in open \\ \beta_i = -\pi\nu_i & i \in closed \\ \beta_i = +\pi\tau_i & i \in open \end{cases}.$$

• The numerical solution for closed channels only gives the energy levels,  $E_{N'v'}$ , transition energies, mixing coefficients,  $B_{i'}$ , channel transition moments and Einstein coefficients.

$$A_{n \to v''N''} = \frac{4mc^2 \alpha^5}{t} \left(\frac{1}{2N'' + 1}\right) \left(\frac{E_n - E_{v''N''}}{2m'}\right)^3 \left|\frac{D_n}{2m'}\right|^2,$$

molecular cations with electrons:

$$AB^+(v_e^+) + e^-(\varepsilon) \longrightarrow AB^{**} \Leftrightarrow AB^* \longrightarrow [A+B]_{(\epsilon)}.$$



Figure 3: Rate coefficients for the dissociative recombination of HD<sup>+</sup> and  $H_3^+$ . On the left reduced rate coefficient for the DR of HD<sup>+</sup> ( $^{2}\Sigma_{a}^{+}, v_{i}^{+} = 0$ ) [4]. On the lower right DR of ground state  $H_3^+$  ion into ground state  $H_3$ . Upper right figure shows the scheme for the simplified three channel model [5].

# **Future plans**

- Photoionization of H<sub>2</sub>: R(N)(N = 0 4) and P(N)(N = 1 4) transitions
- Photodissociation, the photofragmentation of H<sub>2</sub> induced by two photons, and the

#### $\hbar \quad \langle 2N' + 1 \rangle \langle 2\mathcal{R}hc \rangle \mid a_0 \mid$

• By considering the open ionization channels in addition to their closed counterparts, the quantization condition will lead to open-channel ionization eigenphase and channel mixing coefficients, dipole amplitudes and finally to total photoabsorption/photoionization cross sections

$$\sigma_a(E) = \frac{4\pi^2 \alpha}{2N'' + 1} \left( E - E_{v^+ N^+}^+ \right) \left[ D(E) \right]^2.$$

• The calculated theoretical photoabsorption spectrum has to be corrected for the competing dissociation and fluorescence processes in order to get the *true* photoionization cross section.

role of the Rydberg states in the photoabsorption of diatomic molecules in multiphoton processes

#### • DR with spectroscopic accuracy

## Acknowledgments

The authors acknowledges support from ANR-SUMOSTAI project.

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