State-to-state molecular collisions: progresses and prospects

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I – Introduction

➢ **ALMA and HERSCHEL**

➢ Study of chemical composition and evolution of the ISM

➢ **Spectral lines analysis**

→ Interstellar **molecules identification**

⇨ **Spectroscopic data**

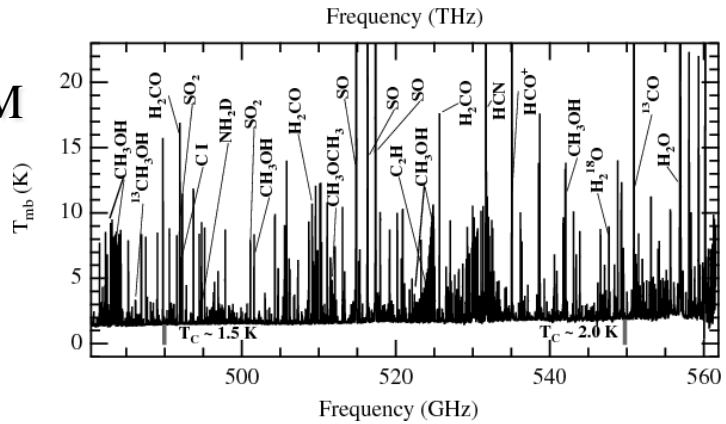
→ **Physical conditions**: Temperature, molecular abundance, gas density …

⇨ **Collisional rate coefficients**

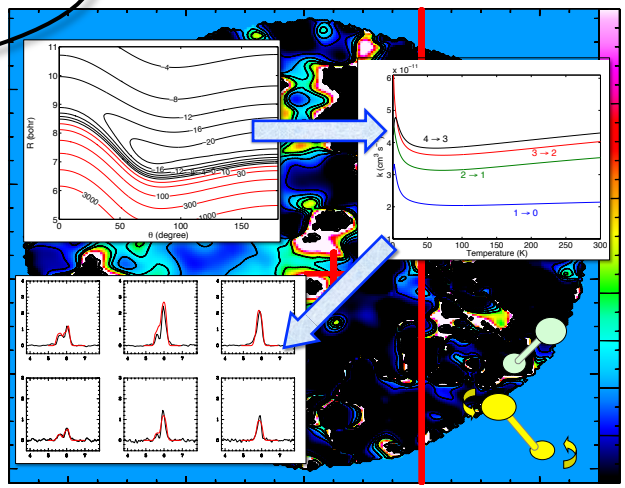
➢ **Evolution of interstellar matter**

→ Formation of **interstellar molecules**

⇨ **Reactive rate constants**

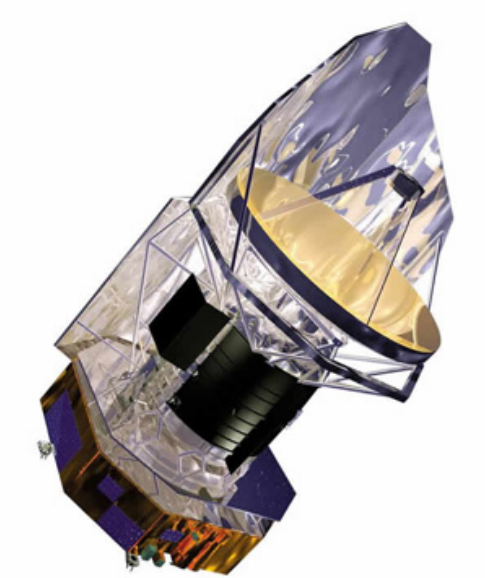


HIFI spectral scan of Orion (Bergin et al. 2010)



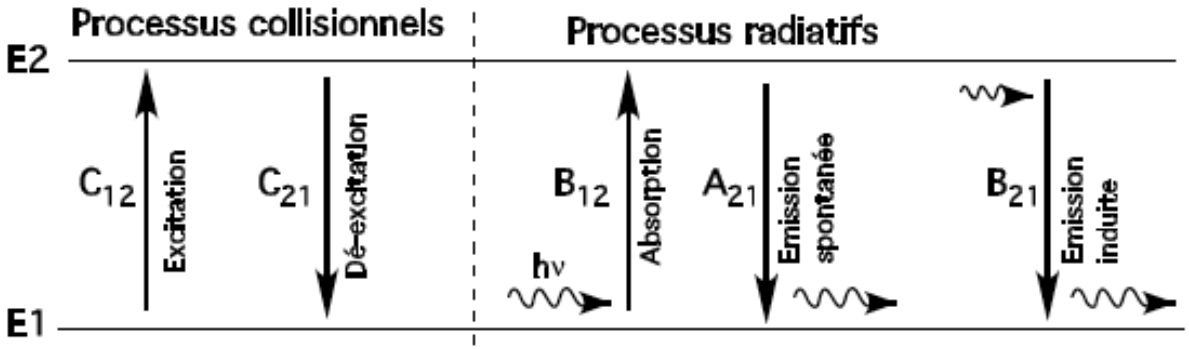
Roueff & Lique, Chem. Rev. ***113*** *(2013)*

I – Introduction



Modeling observational spectra → Molecular abundance
Gaz Density $n(H_2)$
Temperature

Knowledge of the population of the energy levels of molecules



C_{12} et C_{21} : Rate coefficients B_{12}, B_{21} et A_{12} : Einstein coefficients

Rate coefficients: Boltzmann average of the cross sections

→ **Calculation of rate coefficients for interstellar molecules in collision with He, H and H_2**

I – Introduction

2000 – 2010: - Data for collisions between the most abundant interstellar (closed shell) molecules with He and/or H_2: H_2, HD, CO, HCO^+, H_2O, SiS, NH_3, HF, …
- Data for collisions between the open-shell molecules with He : CN, SO, OH, O_2, NH, …

CHEMICAL REVIEWS

Review

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Molecular Excitation in the Interstellar Medium: Recent Advances in Collisional, Radiative, and Chemical Processes

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I – Introduction

2000 – 2010: - Data for collisions between the most abundant interstellar (closed shell) molecules with He and/or H_2: H_2, HD, CO, HCO^+, H_2O, SiS, NH_3, HF, …
- Data for collisions between the open-shell molecules with He : CN, SO, OH, O_2, NH, …

Presently: - **PCMI:** Collisions moléculaires inélastiques: nouvelles perspectives théoriques
Grenoble, Meudon, Marne La Vallée, Montpellier, Le Havre
Excitation of complex organic molecules: H_2CO, CH_3COOH
Excitation of open-shell molecules by H_2: CN, O_2, C_2H
New methodologies: HCl, N_2H^+
Data production: HCO^+, SiO, C_2H^-, CN^-, Metal cyanides …

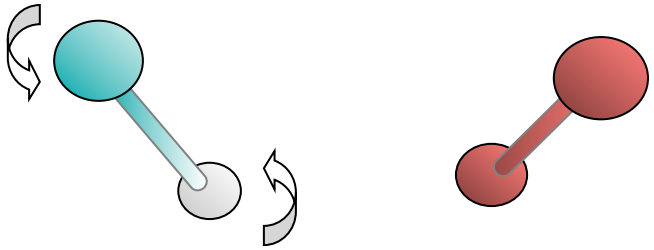
- **ANR Hydrides:** Understanding the excitation and chemistry of hydrides
Grenoble, Rennes, Bordeaux, Le Havre
Excitation of interstellar hydrides: HCl, OH, CH, NH_3
Competition between inelastic and reactive processes: OH^+
Experimental studies: CO, OH, CH

Poster of Alexandre Faure

- **ASTRONET**
Bordeaux, Meudon
Excitation of bending modes of interstellar molecules: C_3, HCN

II – Collisional excitation: Theory

Born-oppenheimer approximation (1927)



2 stages :

ab initio calculation of the potential energy surface between particules

Study of the dynamical of the nuclei

Quantum chemistry
Semi-empirical methods

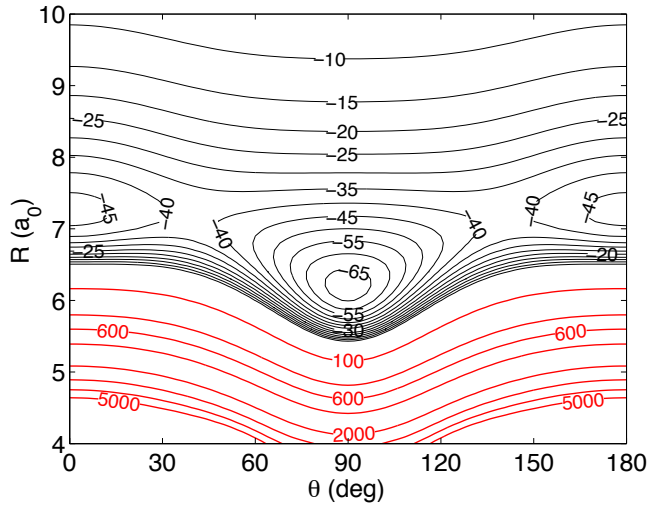
Quantum Methods (TI et TD)
Classical methods

Collisional cross sections calculations: $\sigma_{ij}(E_k)$

Accuracy

- **Close Coupling** (Exact calculations; CPU time : (Channel number)^3)
- **Coupled states** (Neglect coupling between rotational momentum and angular momentum)
- **IOS** (Neglect rotation of the molecule during collision)

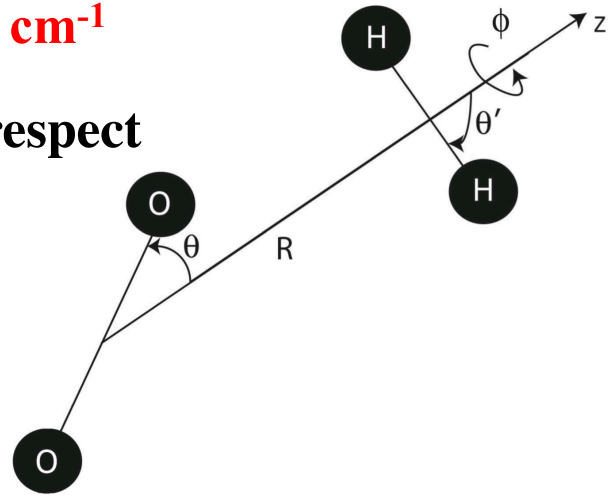
III – PCMI Project: O_2-H_2



Cut of the 4D O_2-H_2 PES for θ' =90° and ϕ = 0°

Potentiel well ~ 67.69 cm^{-1}

Weak anisotropy with respect to θ' and ϕ angles



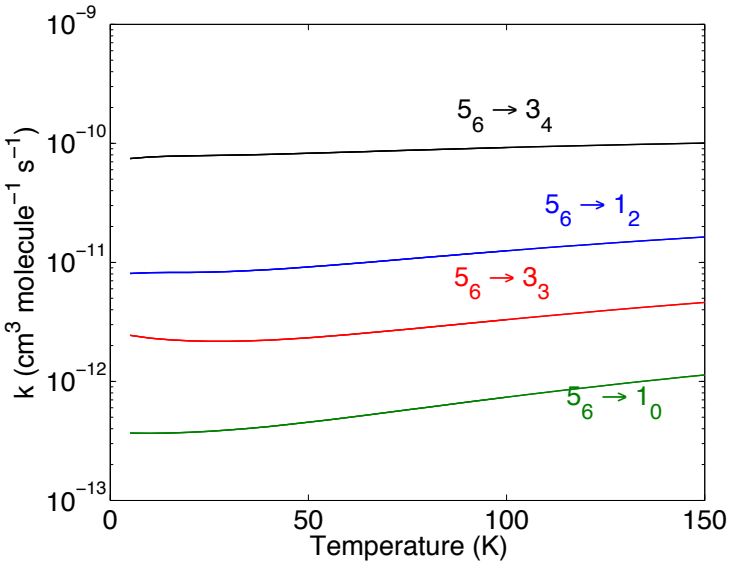
➢ Computation of Close Coupling cross sections for fine structure excitation of O_2 by H_2

Intermediate coupling scheme :

Diagonalisation of $\hat{H}_{rot} + \hat{H}_{S-N} + \hat{H}_{S-S}$ in the $|NSjm\rangle$ pure hund case (b) basis

$$\mathbf{j} = \mathbf{N} + \mathbf{S}$$

total **rotation** **spin**



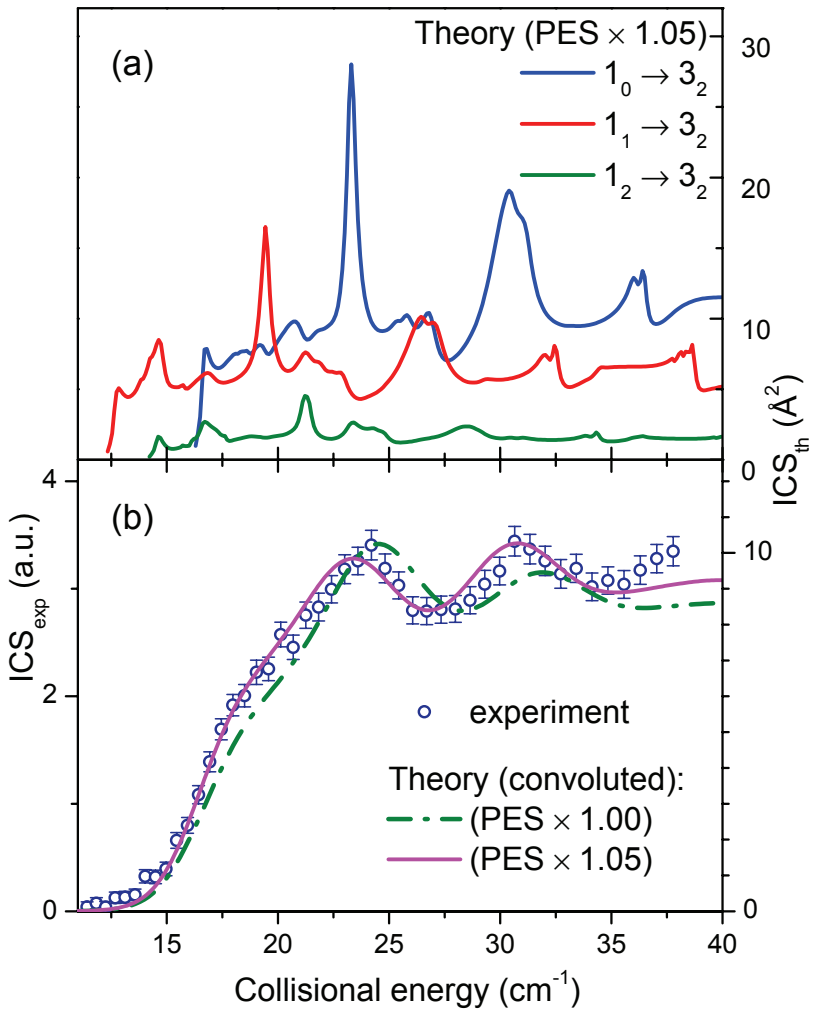
O_2—H_2 rate coefficients out of 5_6 state

*Kalugina et al. PCCP **14**, 16458 (2012)*

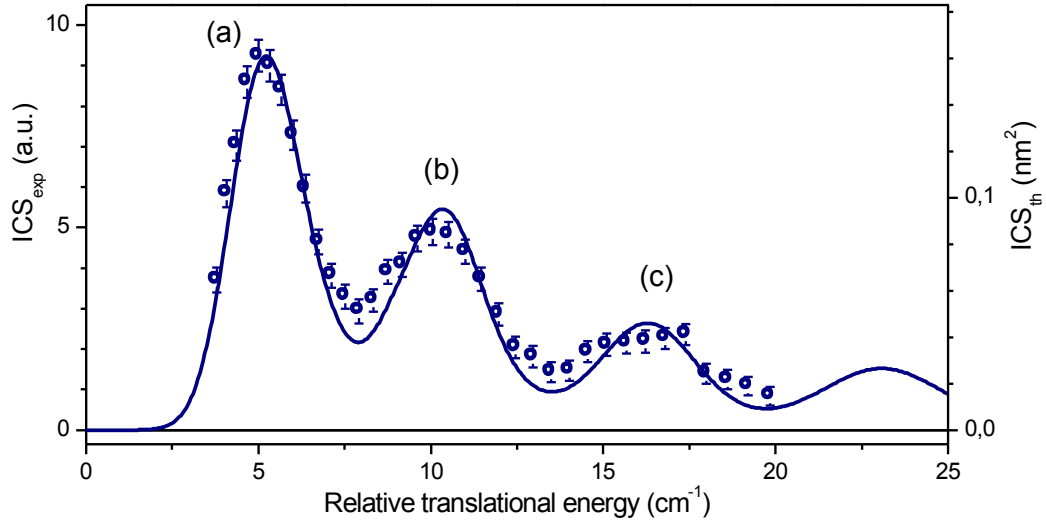
*Lique et al., A&A **567**, A22 (2014)*

III – PCMI Project: O_2-H_2

Comparison with crossed-beam experiments (Bordeaux)



$O_2(N=1, j=0)$ + p-H_2 → $O_2(N=3, j=2)$ n-H_2 ICS: Experiments (open circles); theory (solid line)

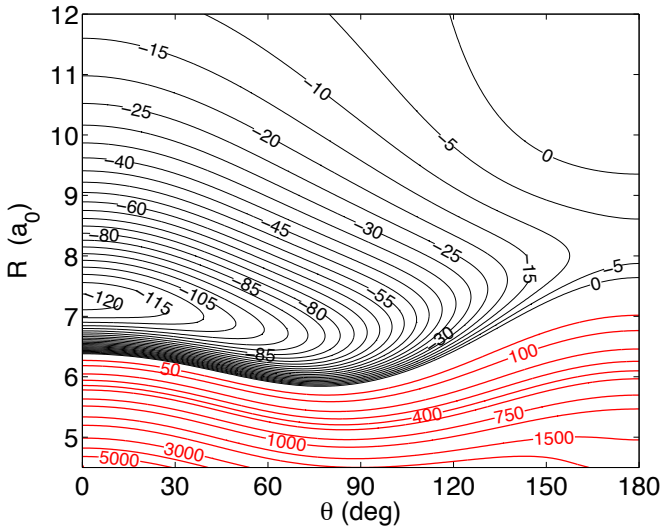


$O_2(N=1, j=0)$ + p-H_2 → $O_2(N=1, j=1)$ p-H_2 ICS: Experiments (open circles); theory (solid line)

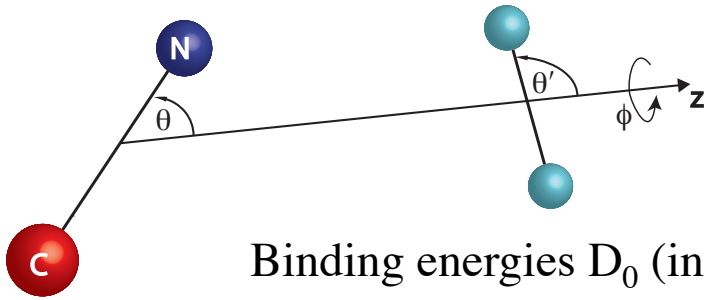
- ➢ Excellent between experiments and theory
- ➢ Theory reproduces well the position and width of the 3 peaks ($1_0 \rightarrow 1_1$ transition)
- ➢ Pure quantum nature of the inelastic collision process

*Chefdeville et al. Science **341**, 1094 (2013)*
*Lique et al., A&A **567**, A22 (2014)*

III – PCMI Project: CN-H_2

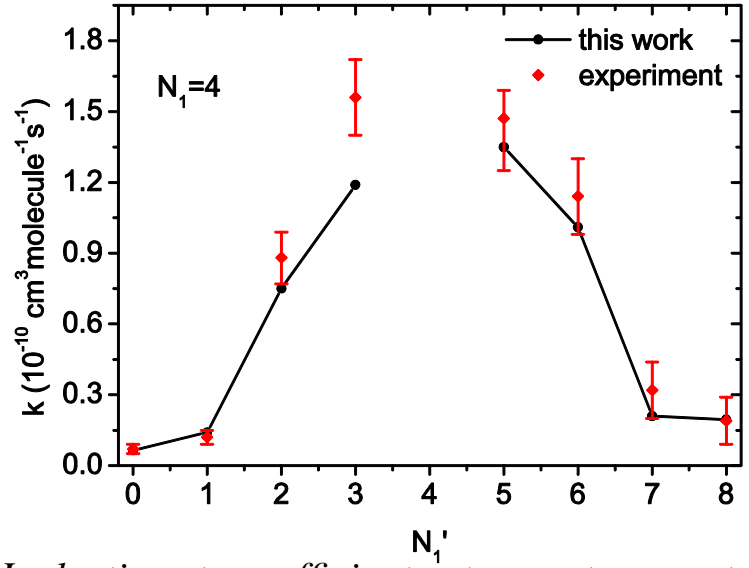


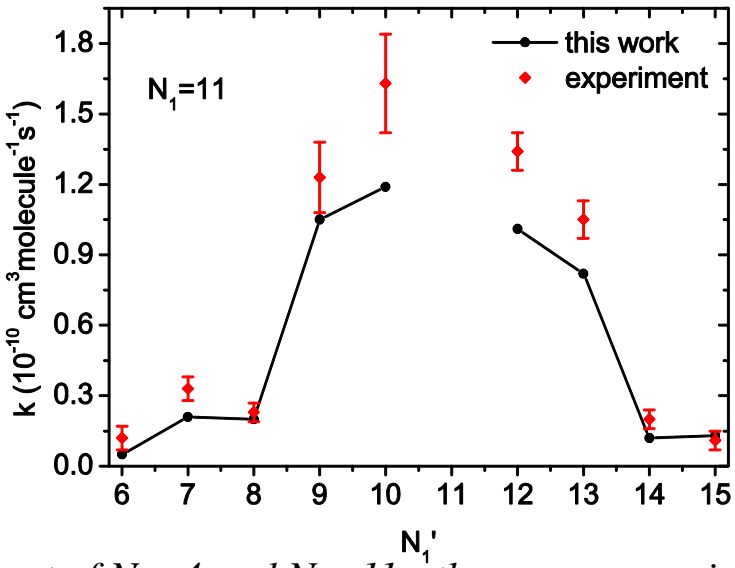
Cut of the 4D CN-H_2 PES for θ' =0° and ϕ = 0°



Binding energies D_0 (in cm^{-1}) of CN-H_2

Species	Exp.[1]	Our	Ref.[2]
p-H2		27.73	15.4
o-H2	38±1	38.75	26.3





Inelastic rate coefficients at room temperature out of N_1=4 and N_1=11 : theory vs. experiments

Exp.: Brunet et al. J. Chem. Phys. ***116****, 3617 (2002)* *Kalugina et al., J. Chem. Phys.* ***139****, 074301 (2013)*

III – PCMI Project: CN-H_2

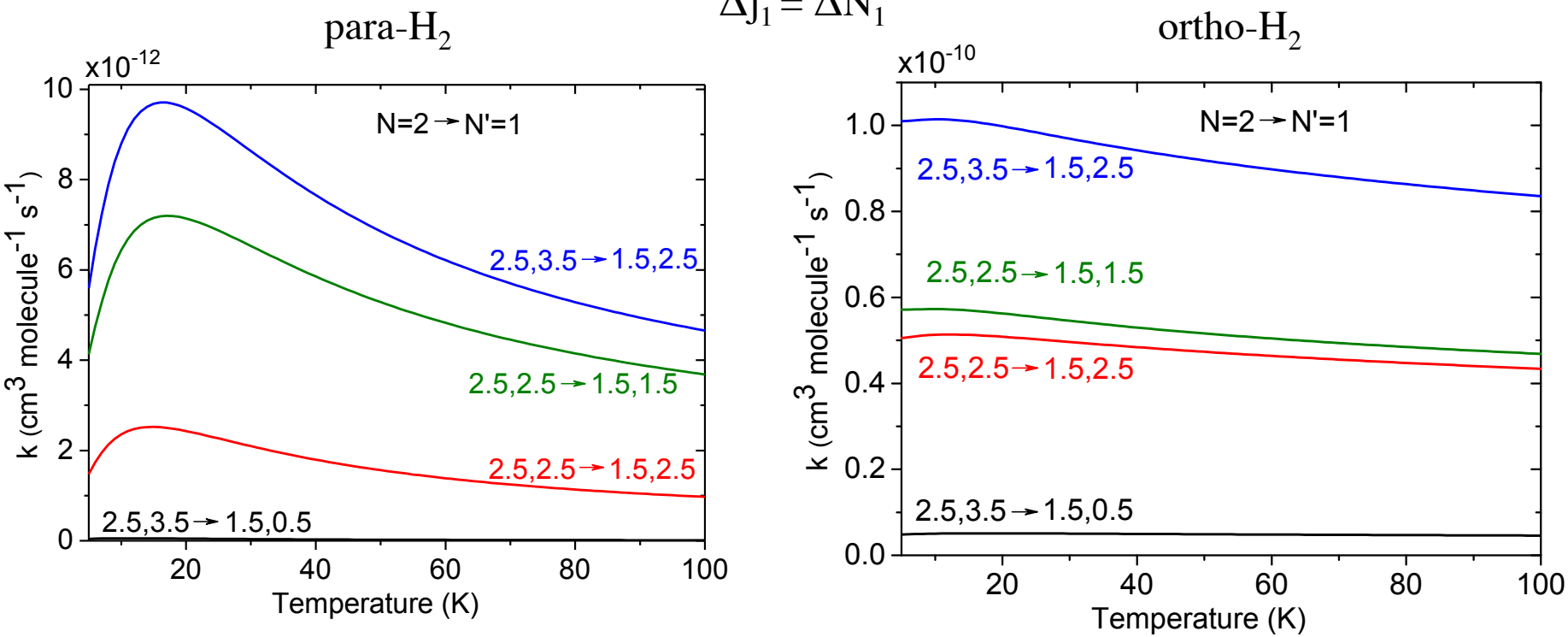
Need for fine / hyperfine structure resolved rate coefficients

⇩

Double recoupling on S-matrices

Hyperfine levels of CN: $N_1\ j_1\ F_1$ **$j_1 = N_1 + S_1$** **$F_1 = j_1 + I_1$**

$\Delta j_1 = \Delta N_1$



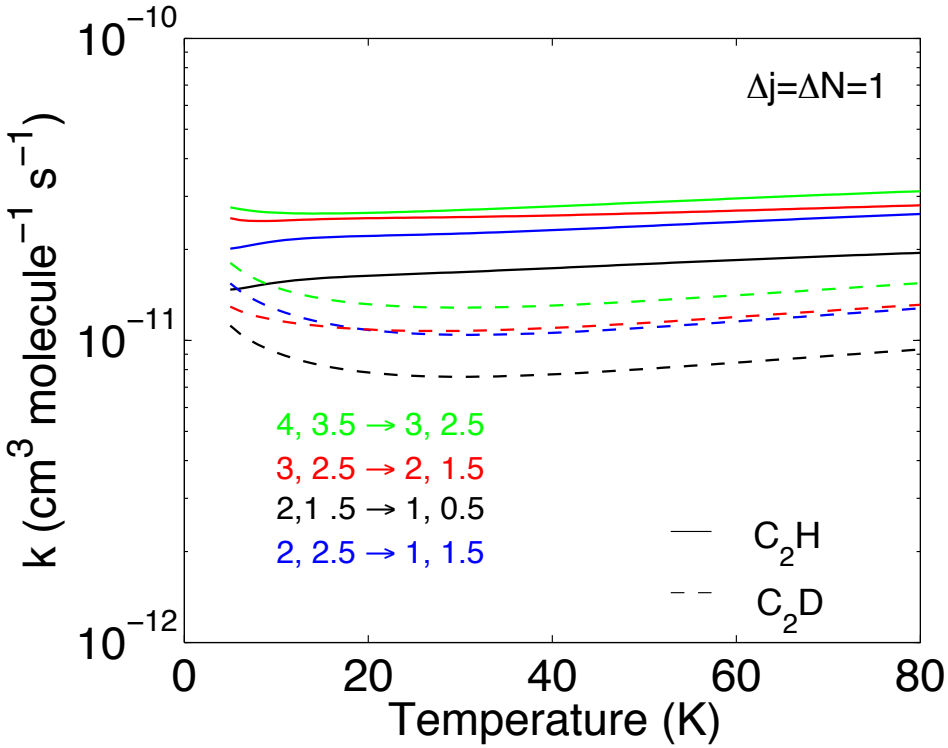
Temperature dependence of hyperfine structure resolved de-exitation rate coefficients of CN by H_2

Kalugina & Lique, MNRAS (2014)

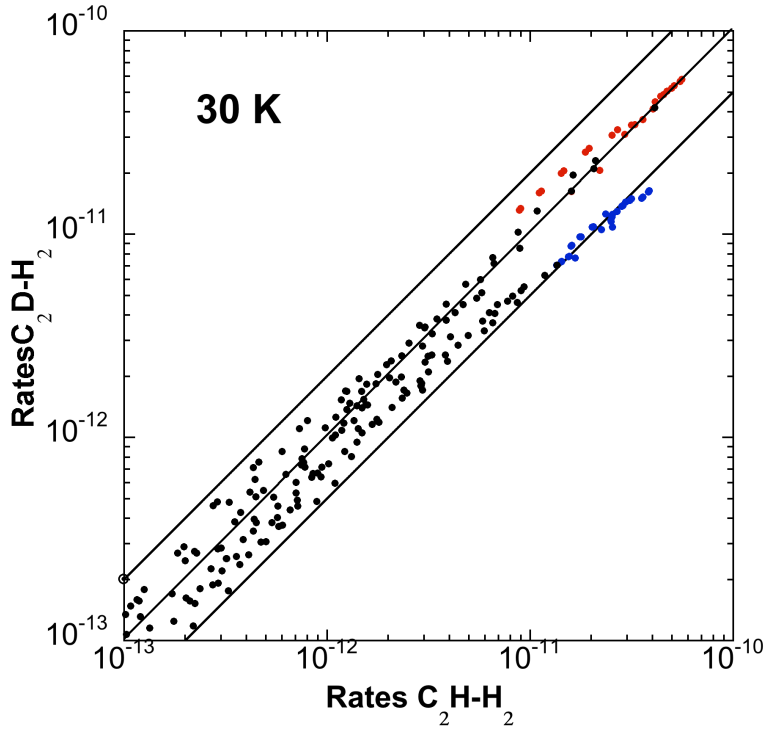
Propensity rules: $\Delta F_1 = \Delta j_1$

III – PCMI Project: C_2H-H_2

First hyperfine C_2H-H_2 and C_2D-H_2 rate coefficients



Temperature variation of C_2H-pH_2 and C_2D-pH_2 rate coefficients



C_2H vs C_2D: all Δj and ΔN at 30K

Significant differences between C_2H and C_2D rate coefficients → **Need of specific rate coefficients for all isotopologues**

Poster of Fabien Dumouchel

III – PCMI Project: CH_3COOH-He

Collisional excitation of methyl formate by He

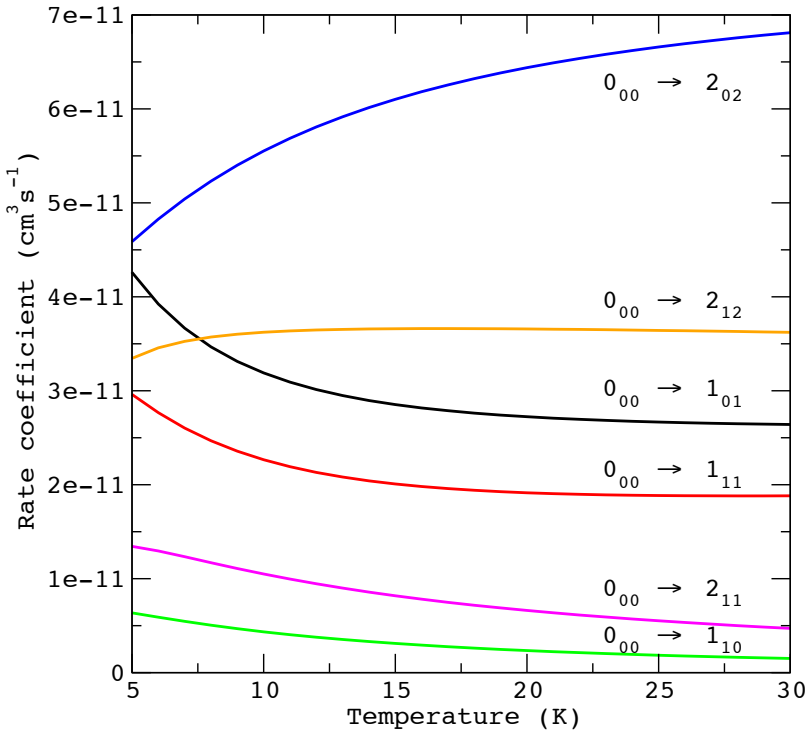


Fig. 2.— Rate coefficients for rotational excitation out of the ground rotational state (0_{00}) of A-$HCOOCH_3$ as a function of temperature.

Faure et al., ApJ ***783*** *72 (2014)*

Observations modeling of CH3COOH emission from Sagitarius B2

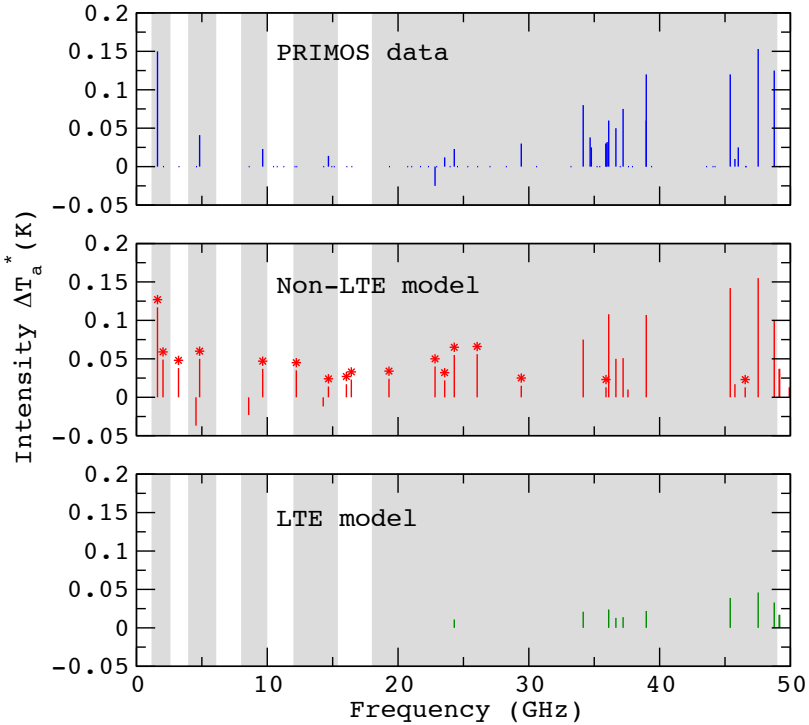
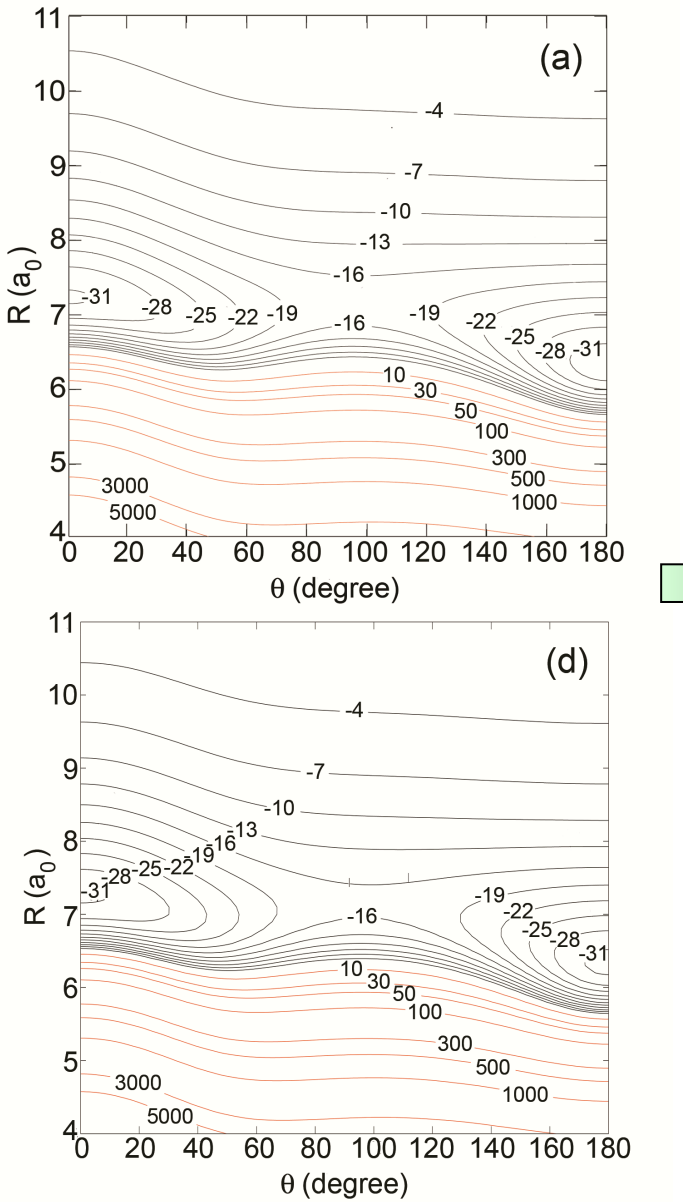


Fig. 5.— Intensity (ΔT_a^* in K) of A-methyl formate rotational transitions in the frequency range 0-50 GHz. PRIMOS data are plotted in the upper panel. Our best fit non-LTE results are represented in the middle panel. All lines marked with an asterisk are weak masers amplifying the continuum of Sgr B2(N). The bottom panel gives LTE results. The shaded areas show the observing passbands in the PRIMOS survey.

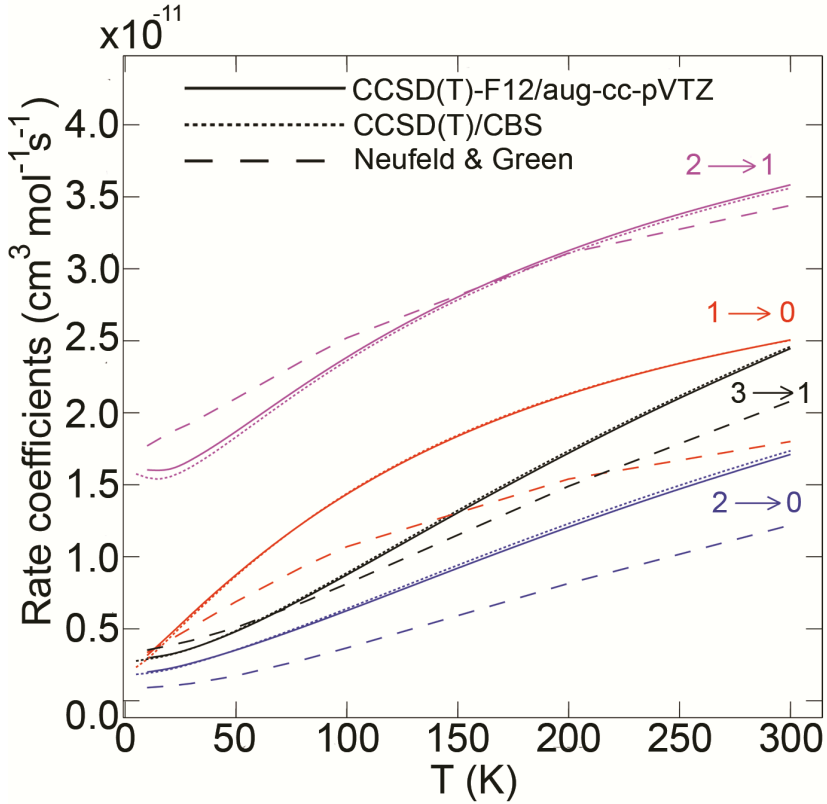
Crucial importance of non-LTE effects in the rotational spectra of complex organic molecules at centimetre wavelengths

III – PCMI Project: New methodologies



CCSD(T)-F12 and CCSD(T) HCl-He PES

Ajili et al., PCCP ***15****, 10062 (2013)*



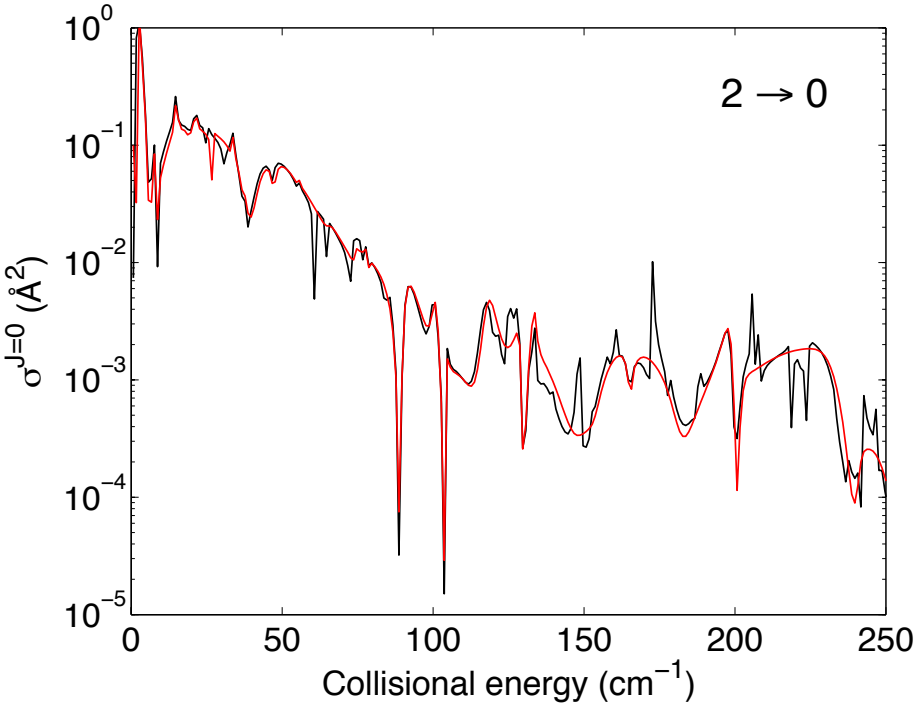
Temperature variation of HCl-He rate coeffcients obtained from different PES

Validation of PES obtained using explicitly correlated approaches

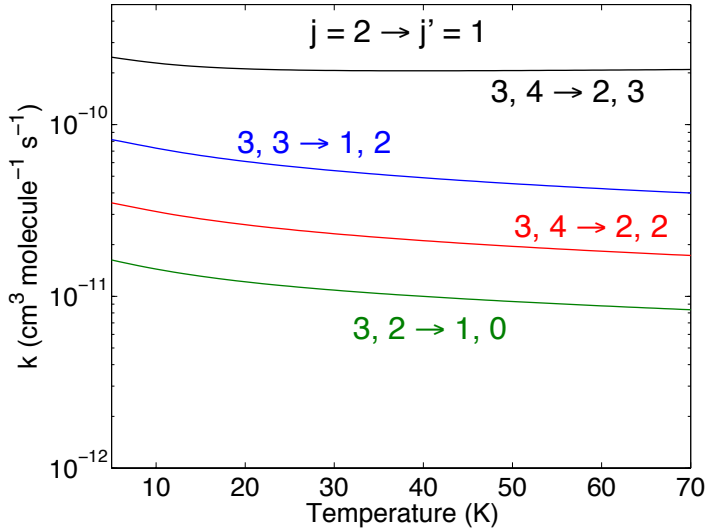
III – PCMI Project: New methodologies

Development of an adiabatic approach to reduce the dimension of collision equations

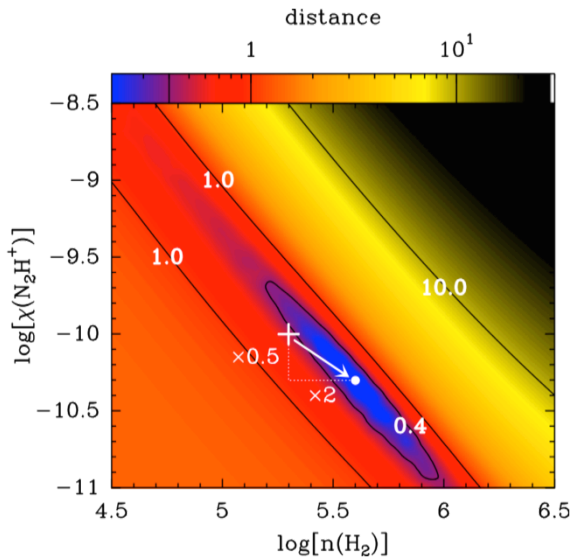
Y. Scribano



N_2H^+-p-H_2 cross sections : black : 4D ; red : 2D



N_2H^+-p-H_2 rate coefficients



Comparison of the intensities predicted with the H_2 and He rate coefficients

Validation of the reduced dimensional approach and application to the N_2H^+-H_2 collisional system

Lique et al., MNRAS (2014)

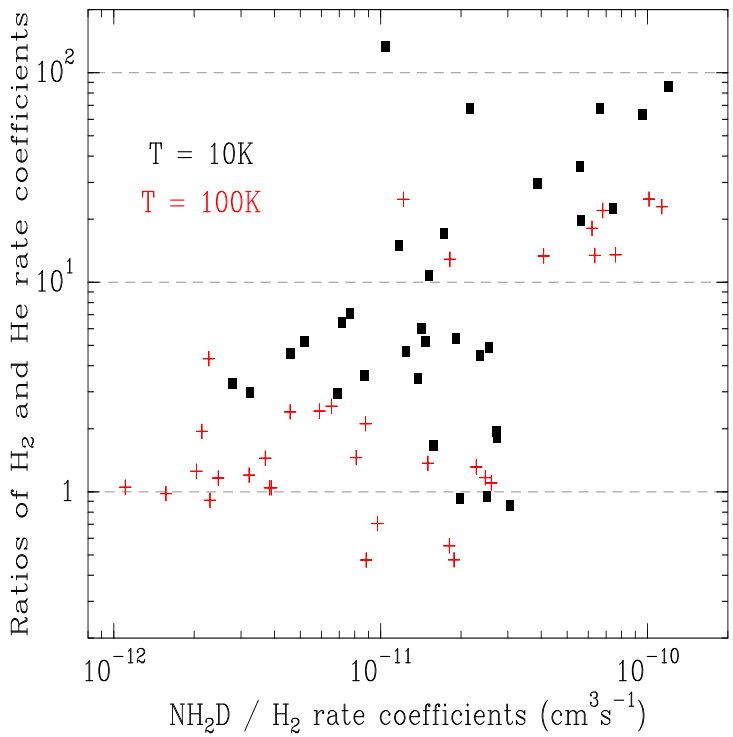
IV – ANR hydrides: NH_3-H_2

New rate coefficients for ammonia and its isotopologues:

- Calculations for both p- and o-H_2

Poster of Claire Rist

ND_2H-H_2



Comparison between NH_2D- H_2 and NH_2D – He rate coefficients (Machin et al. 2006)

NH_2D-H_2

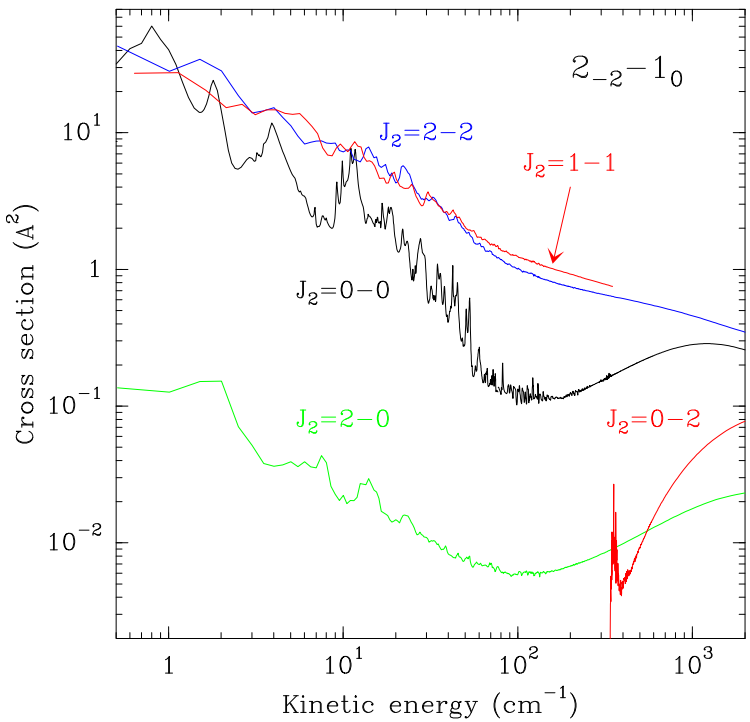


Figure 5. Cross sections associated to the $2_{-2} \rightarrow 1_0$ NH_2D transition and corresponding to the various $J_2 \rightarrow J_2'$ H_2 transitions with para–H_2 either in its fundamental state ($J_2 = 0$) or first excited state ($J_2 = 2$). The cross section with ortho–H_2 ($J_2 = 1 - 1$) is also indicated, for a reduced range of kinetic energies.

Significant differences with He

*Daniel et al., MNRAS **444**, 2544 (2014)*

IV – ANR hydrides: OH^+

Collisional excitation of OH^+ by H :
Competition between inelastic and reactive processes

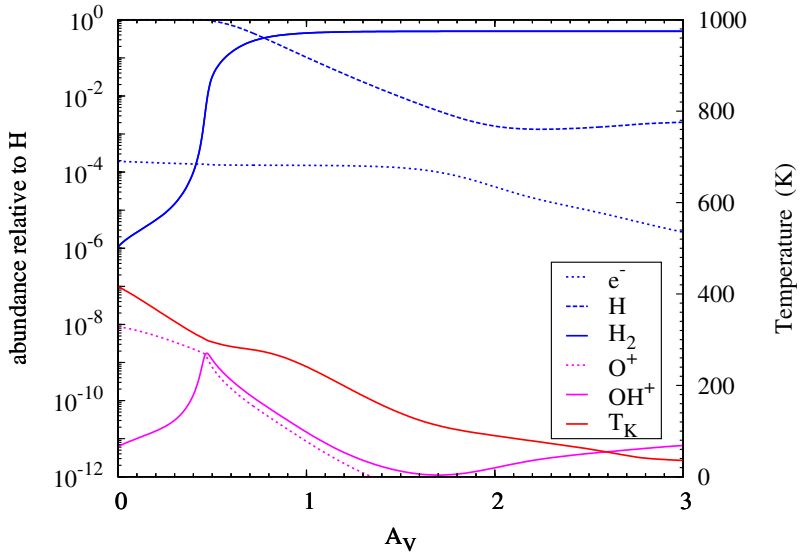


Figure 9. Kinetic temperature and abundances relative to total hydrogen density of H, H_2, O^+, OH^+, and e^- computed with the Meudon PDR code as functions of the visual extinction from the ionization front across a prototypical hot and dense PDR ($\chi = 10^4$ and $n = 10^4$ cm^{-3}).

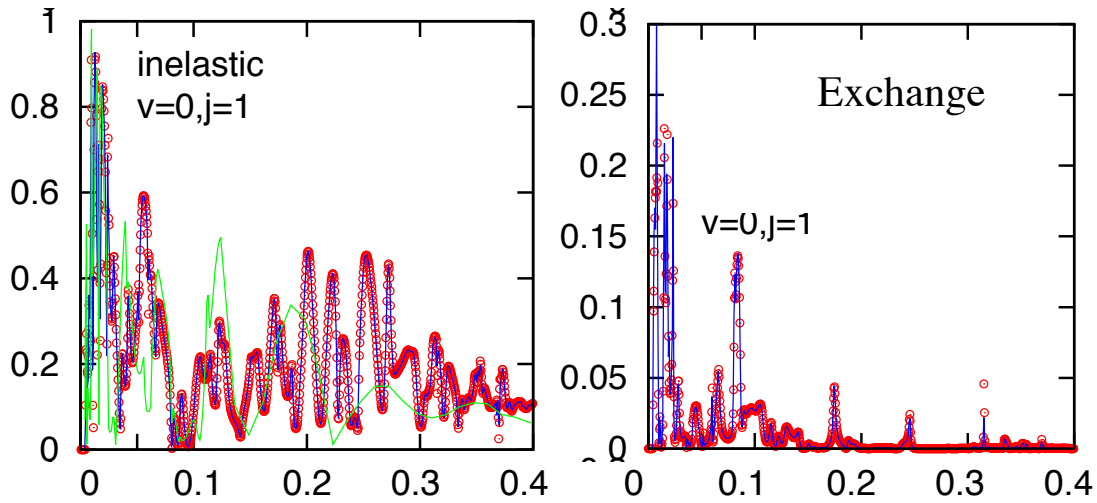
Gomez-Carrasco et al., ApJ 794, 33 (2014)

$OH_a^+(v', N') + H_b$ *Inelastic*

$OH_a^+(v, N) + H_b \rightarrow OH_b^+(v', N') + H_a$ *Exchange*

$O^+ + H_2(v', N')$ *Reactive*

Reactive channels are endothermic by 0.5 eV



Inelastic and exchange probabilities for the OH^+ - H collisions :
WP : blue ; CC : red ; 2D CC green

Accurate calculations for rotational excitation have to include the reactive channels (even if closed at low energies)

IV – ANR hydrides: Experiments

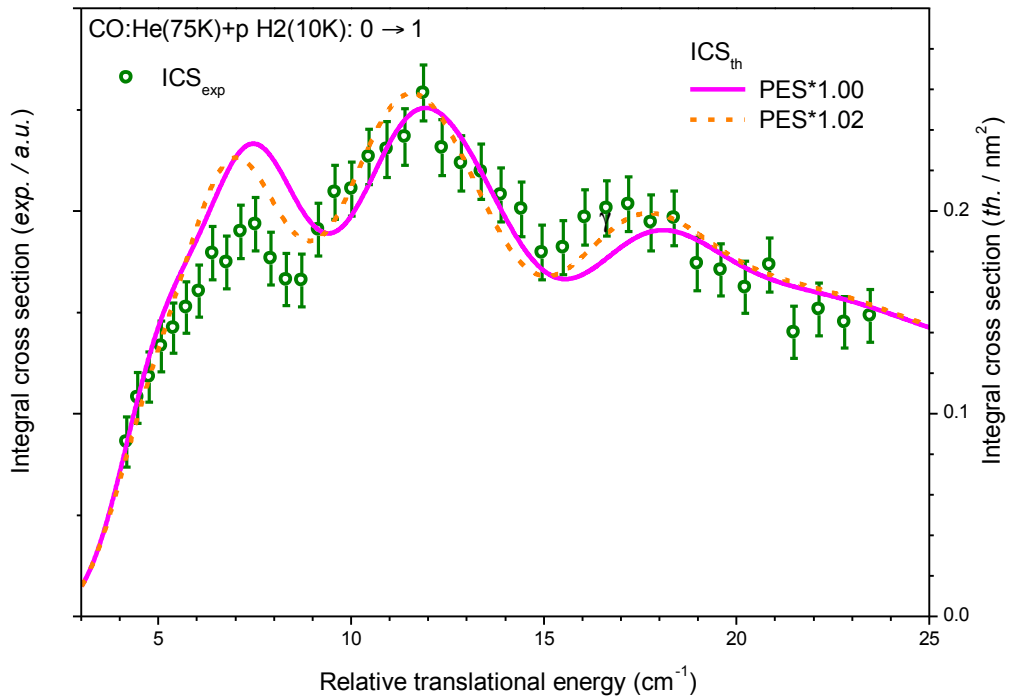
New study of CO-H_2 collisions

Experiment:
Molecular crossed beams :
ICS corrected from mean interaction time, <d*t*>: $ICS_{exp} = I_{REMPI} / (v_r <dt>)$, where I_{REMPI} stands for the observed signal and v_r the relative velocity.

Theory:
Close coupling calculations with PES from Jankowski et al., *Science* **336** (2012) 1147.

➢ **Very good** agreement between theory and experiments

➢ Theory reproduces well the position of the resonances

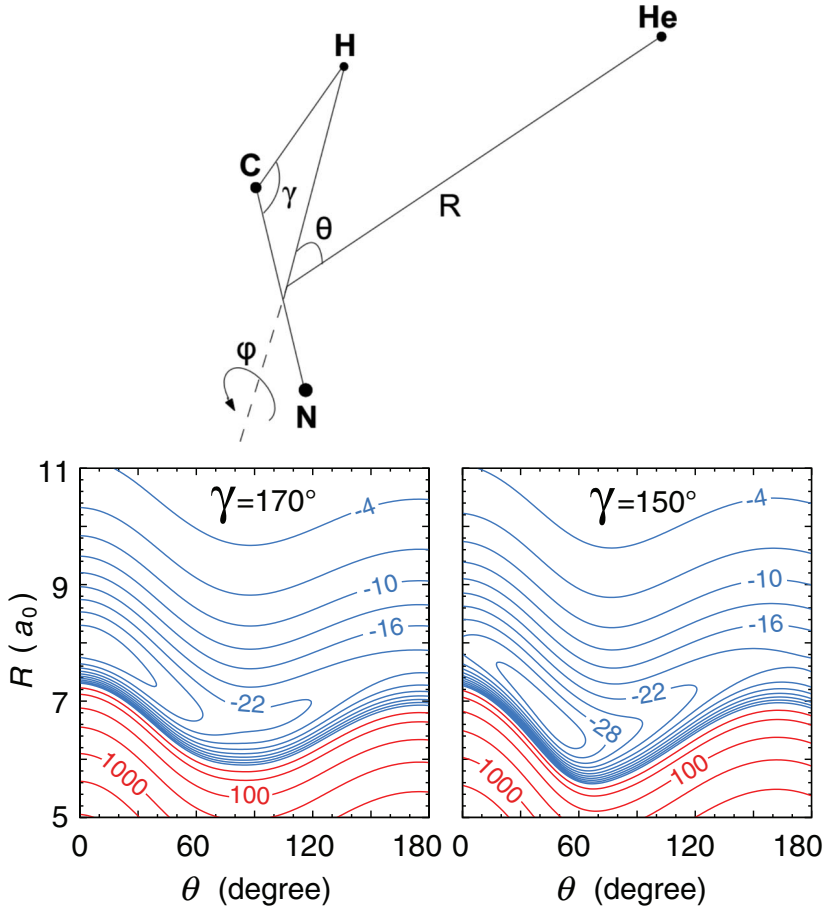


CO(j=0) + p-H_2 → CO(j=1) p-H_2 ICS:
Experiments (open circles); theory (solid line)

Validation of both theoretical and experimental approaches

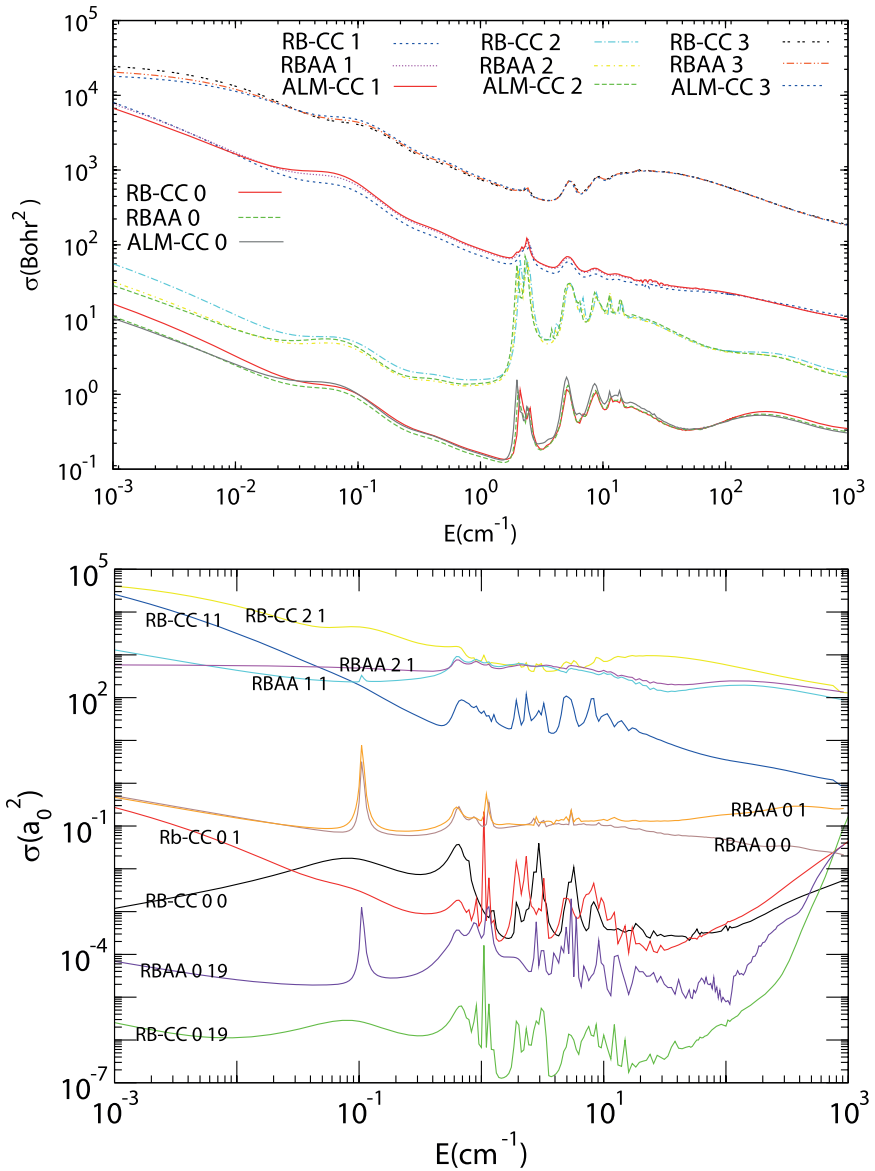
Poster of Astrid Bergeat

V – Astronet: HCN-He



Contour plot of the interaction energy for selected values of γ and for φ = 180°

Rigid rotor approach can be used for pure rotational excitation
Exact calculations are needed for ro-vibrational excitation



HCN-He cross sections for vibrationally elastic and inelastic transitions : Methods comparison

VI – Conclusions

- Computation of inelastic rate coefficients for about 30 molecules (more than 50 publications – many of them in collaboration between two or more groups)

- Fruitful collaborations with astronomers (HCN/HNC, CH_3COOH, HCl, N_2H^+ …)

- Future project :
  - ANR Cos Chem (Rennes, Bordeaux, Le Havre) : Anions excitation
  - PCMI « relaxation des niveaux de structure fine dans les atomes interstellaires (Le Havre, Rennes, Bordeaux) : Theory and experiments
  - PCMI « Excitation of complex organic molecules » (Grenoble, Montpellier Marne la Vallée)
  - …

Grenoble:	A. Faure, L. Wiesenfeld, C. Rist and F. Daniel
Bordeaux:	T. Stoecklin, P. Halvick, O. Denis Alpizar, C. Naulin, M. Costes, A. Bergeat and S. Chefdeville
Meudon:	N. Feautrier, C. Balança, A. Spielfiedel, F. Dayou and M.-L. Dubernet
Marne la Vallée:	M. Hochlaf and Y. Ajili
Le Havre:	F. Lique, F. Dumouchel, Y. Kalugina, M. Lanza and M. Hernandez Vera
Rennes:	S. Le Picard, I. Sims, M. Fournier
Montpellier:	Y. Scribano

Thanks for your attention !