Collisional excitation of interstellar molecules: towards reactive systems

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Context

- *Astrochemistry:* obtaining the **most accurate census of the molecular content** in the interstellar medium (ISM)

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How do the organic molecules form?

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  Key questions: *How do stars and planets form?*
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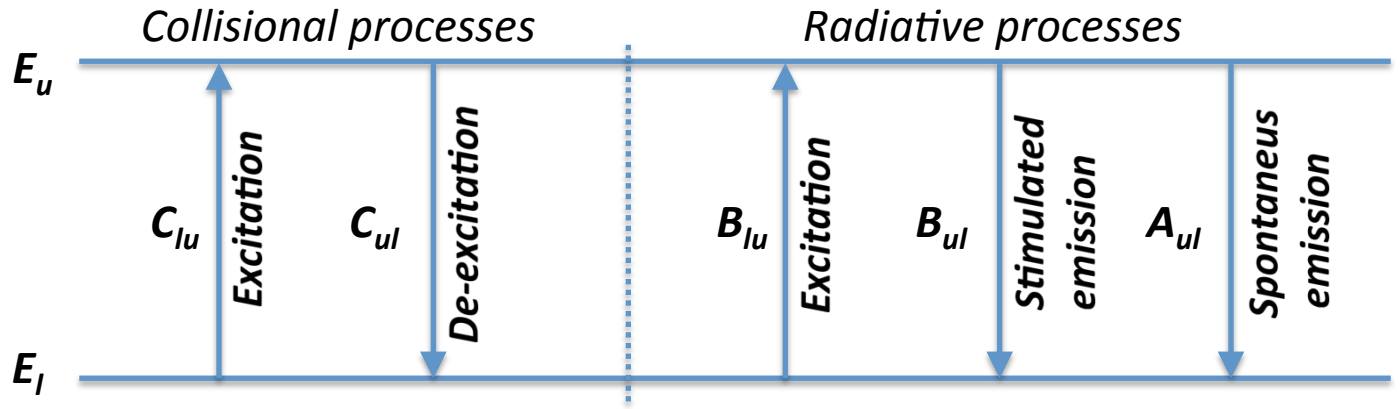
- Our knowledge about ISM relies on **molecular spectra**
- In the ISM, the low density cannot maintain local thermodynamic equilibrium (LTE)
- **Non-LTE analysis** of the observational spectra is required

Knowledge of population of energy levels of interstellar molecules



C_{lu} et C_{ul} : Rate coefficients

B_{lu}, B_{ul} et A_{ul} : Einstein coefficients

Studying collisional excitation of interstellar molecules by H and H_2

What has been done so far?

- Excitation studies of interstellar molecules **began in the 70's** (Dalgarno, Green, Flower,...)
- "**Molecular Universe**" RTN network (2004-2008): update for a number of key molecules
- Full **quantum calculations** feasible
- Theoretical calculations **rival the accuracy of experimental data**
- **Highly accurate data available** for ~50 molecules (over ~300 detected)
- **Precise determination of the molecular content** in molecular clouds

See the review by Roueff and Lique (2013)

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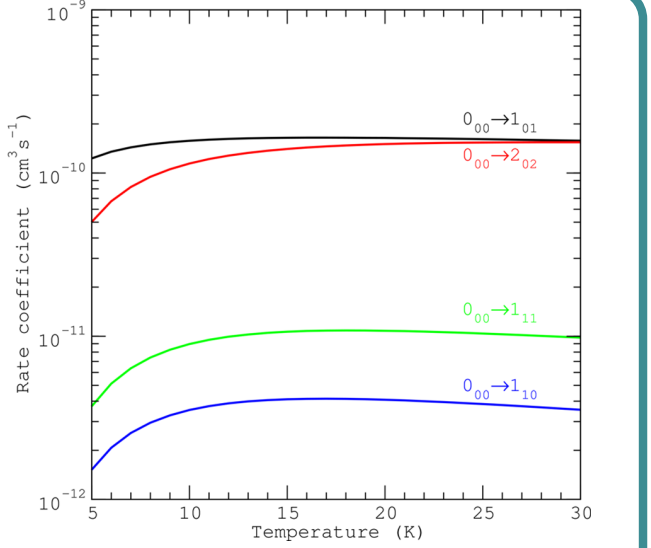
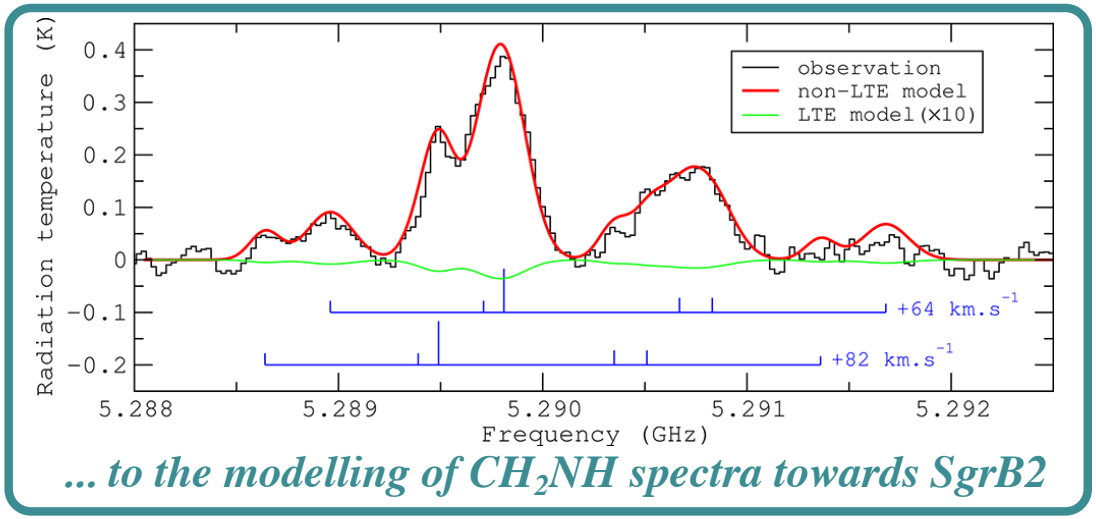


From excitation rate coefficients of CH_2NH by H_2 ...

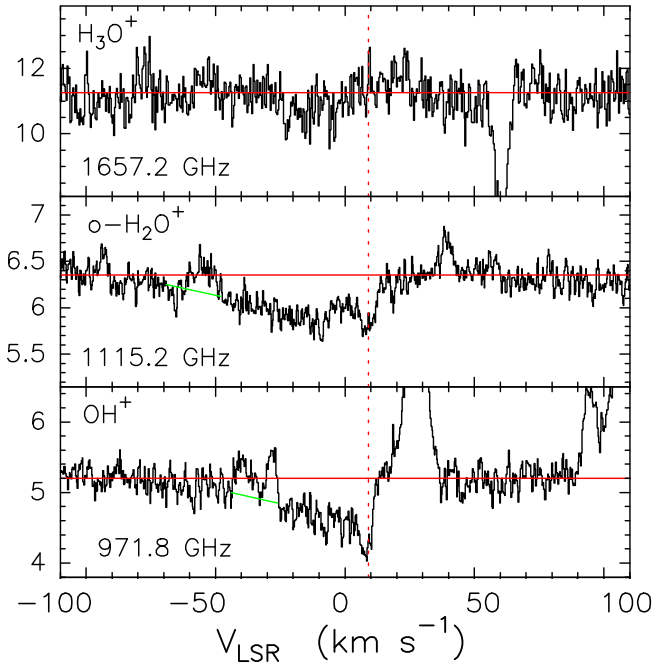


... to the modelling of CH_2NH spectra towards SgrB2

Faure, Lique and Remijan (2018)

Detection of new (reactive) molecules

- New telescopes allow **highly resolved observations**
- Detection of **reactive molecules** (H_2O^+, OH^+, CH HS...), i.e. **rapidly destroyed by** H, H_2 or e^- (Black 1998)
- **Key species** for astrochemistry
- Accurate analysis of the spectra is **hampered by the complete lack of collisional data**



OH^+, H_2O^+ and H_3O^+ towards Orion KL

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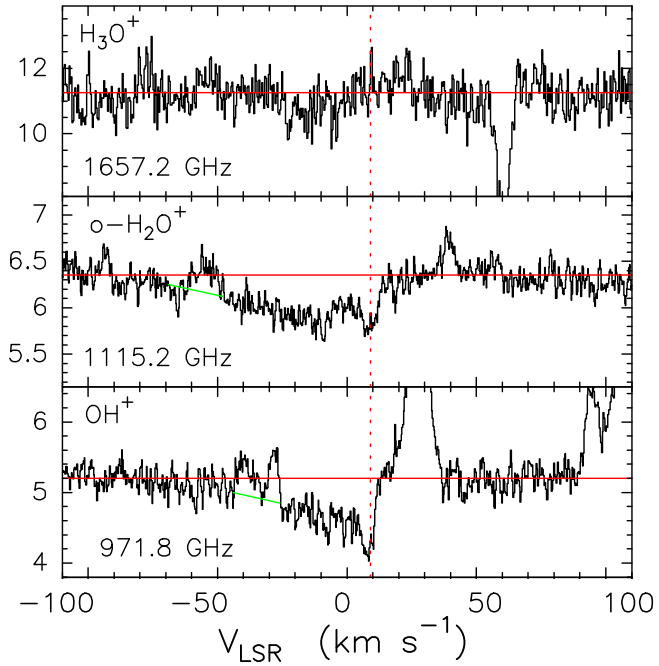


OH^+, H_2O^+ and H_3O^+ towards Orion KL

Problematic: *How can we get such collisional data?*

- Complex competition between inelastic and reactive processes

$$A(n_A) + B(n_B) \longrightarrow AB^* \longrightarrow \begin{cases} \text{Inelastic} \rightarrow A(n'_A) + B(n'_B) \\ \text{Reactive} \rightarrow C(n_C) + D(n_D) \end{cases}$$

n: quantum state

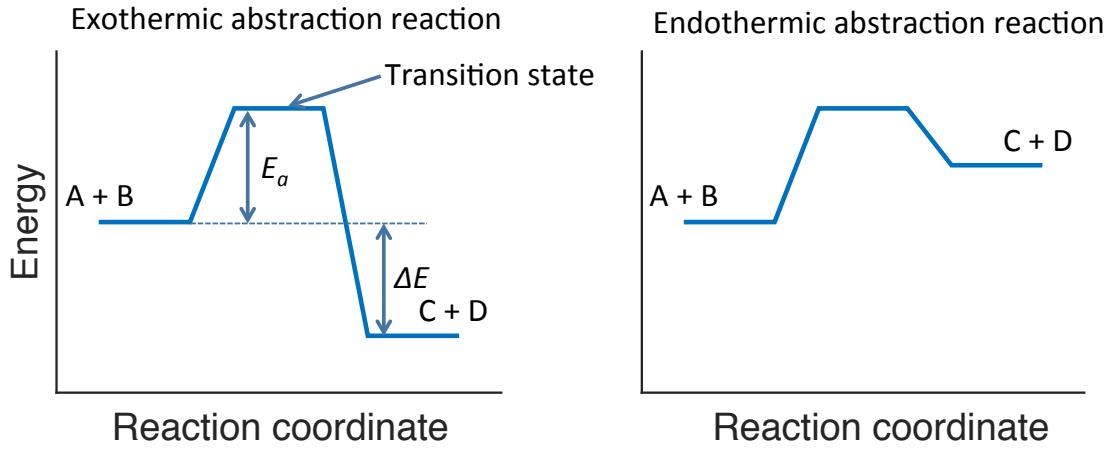
- **No available methods and codes** to take into account the reactivity at a **state-to-state level**

Development of new methods to provide collisional data for these molecules

Towards a method to fully consider the inelastic / reactive competition

Schematically, the dynamics of gas-phase reactive collisions are governed by two mechanisms:

Abstraction reaction:



- **Reduced dimension approaches** (neglecting the reaction process) may be reliable at ISM temperatures
- **Validity domain (if any) and accuracy** of these approaches

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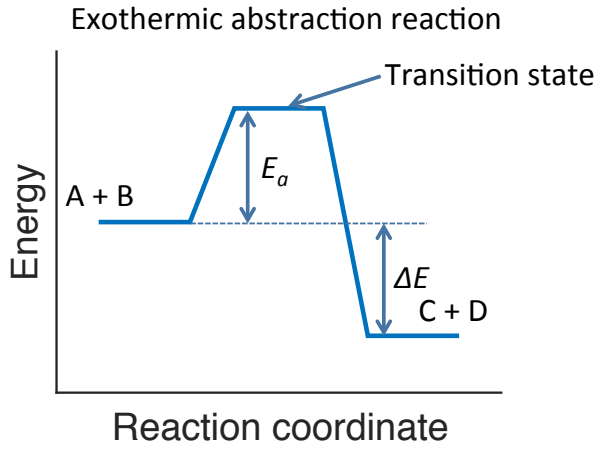

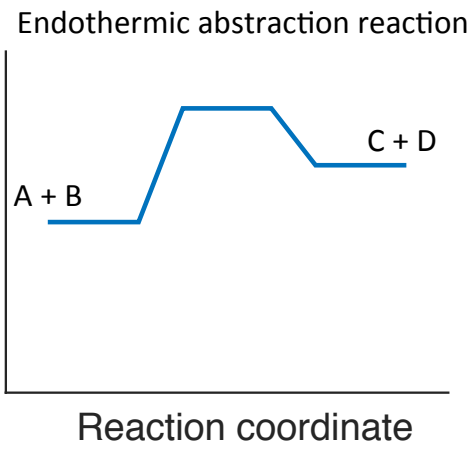

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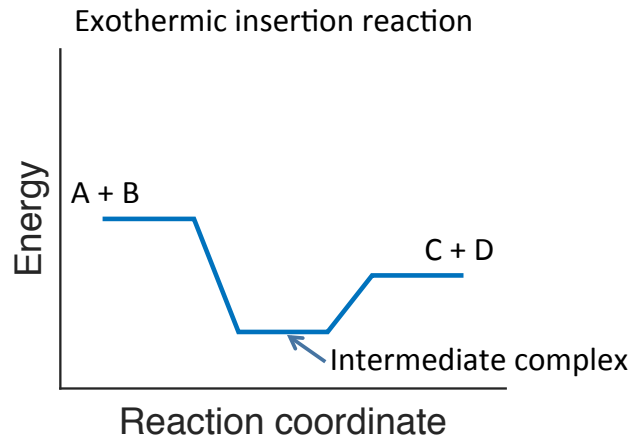
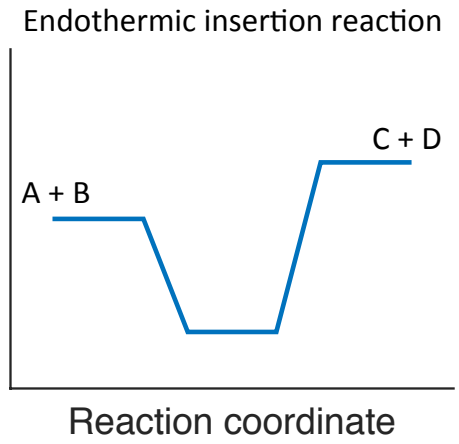
Insertion reaction:



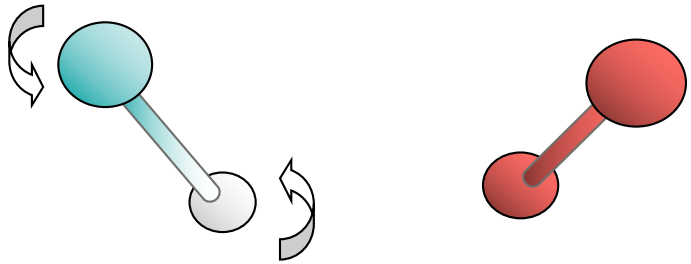


- **Reactive channels need a priori to be included** (especially for exothermic reactions)
- **Statistical quantum approaches*** can be used to generate accurate data for both collisional excitation and reactive processes

* *Formation of a long-lived intermediate complex: statistical distribution of the population of the energy levels*

Study of molecular systems

Born-oppenheimer approximation (1927)



2 stages :

ab initio calculation of the potential energy surface between particules

→ **Quantum chemistry**
Semi-empirical methods

Study of the dynamical of the nuclei

→ Quantum Methods (**TI** et TD)
(Quasi-)Classical methods
Statistical methods

Collisional cross sections calculations:

Accuracy ↓

- **Close Coupling** (CPU time = Channel number^3)
- **Coupled states** (Neglect centrifugal distorsion)
- **Quasi-Classical Trajectory**

↕ **- Statistical methods ?**

Reduced dimension approaches

Methods:

- Target: **rigid rotor** (internuclear distance fixed)
- **Reactive channels are closed**
- Equivalent to pure inelastic scattering

Questions:

- **Validity domain and accuracy**
- Strategy for computing the interaction potential

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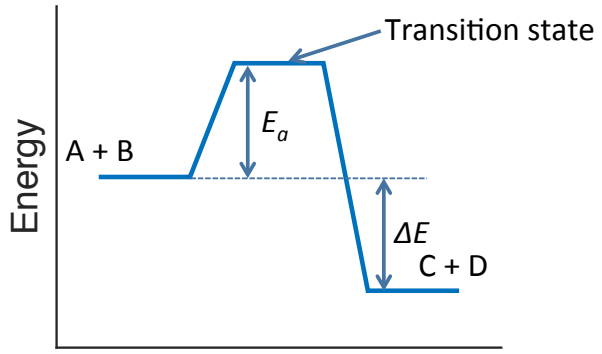

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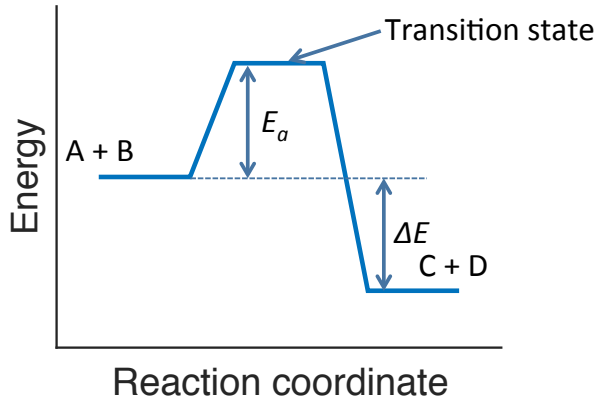
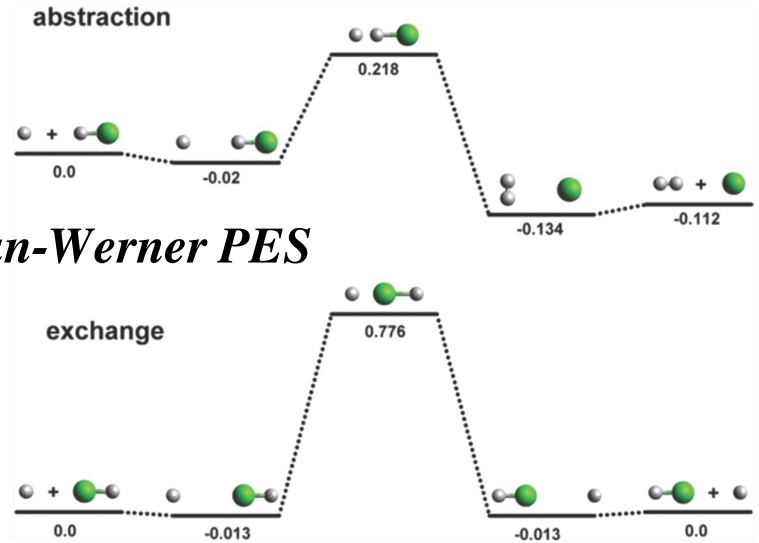


Rigid rotor vs. Reactive calculations



Bian-Werner PES

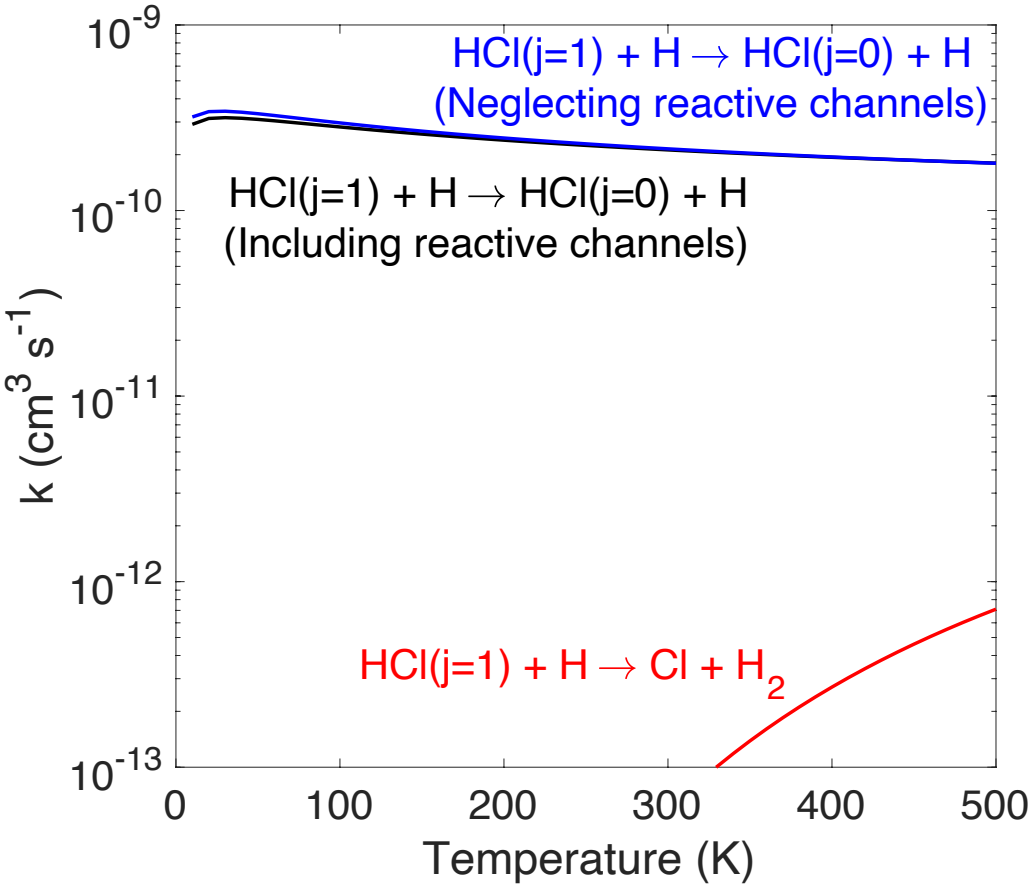
Schematic representation of HCl + H reaction

$$HX(v,j) + H' \rightarrow \begin{cases} HX(v',j') + H' & \textit{Inelastic} \\ H'X(v',j') + H & \textit{Exchange} \\ X + H_2(v',j') & \textit{Reactive} \end{cases}$$

Reactive channels are endo/exothermic

Influence of the reactive channels ?
(Reactive and exchange channels are inhibited by a large barrier)

Inelastic vs. reactive approaches for the excitation of HCl by H

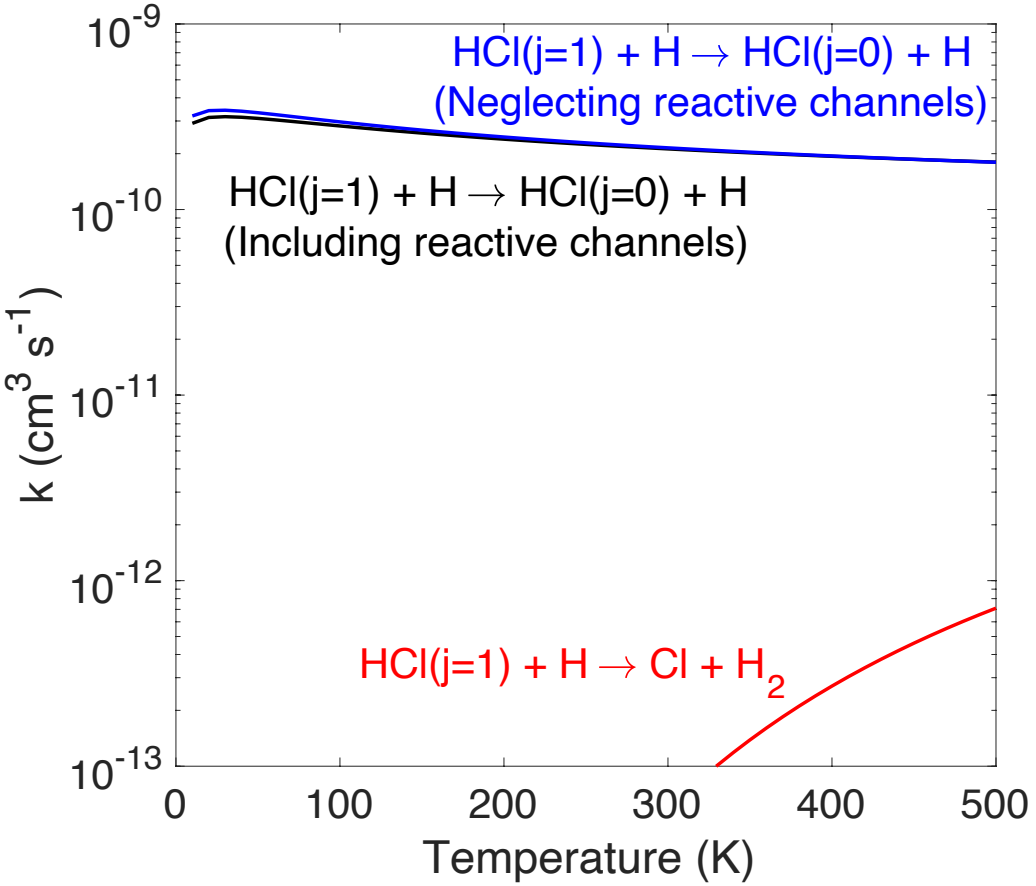


Rotational relaxation and destruction of HCl(j=1) induced by collisions with H

- Accurate description of the rotational excitation obtained using the rigid rotor approach

Reduced dimension approaches: HCl-H

Inelastic vs. reactive approaches for the excitation of HCl by H



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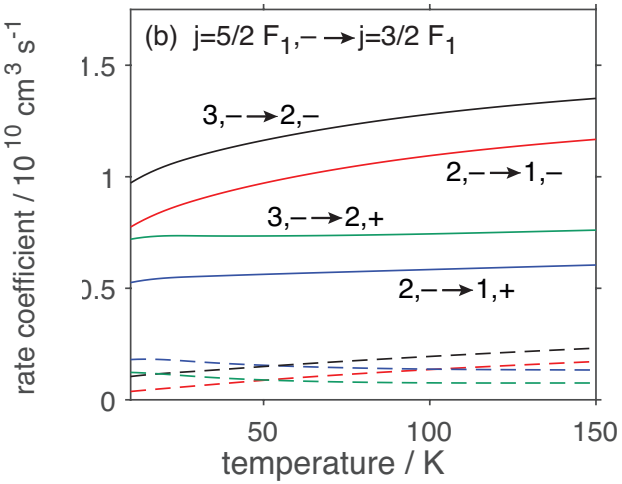
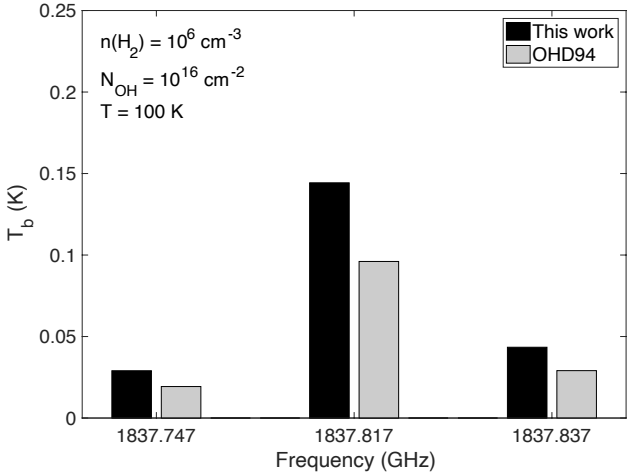
Validation of rigid rotor approaches for reactive systems with barrier

Reduced dimension approaches: Applications

Collisional excitation of OH by H_2





The new rate coefficients increase the line intensities by a factor ~1-2

OH-H_2 Hyperfine resolved rate coefficients and brightness temperature of some OH lines obtained with present and previous Offer et al. (1994) rate coefficients

Reduced dimension approaches: Applications

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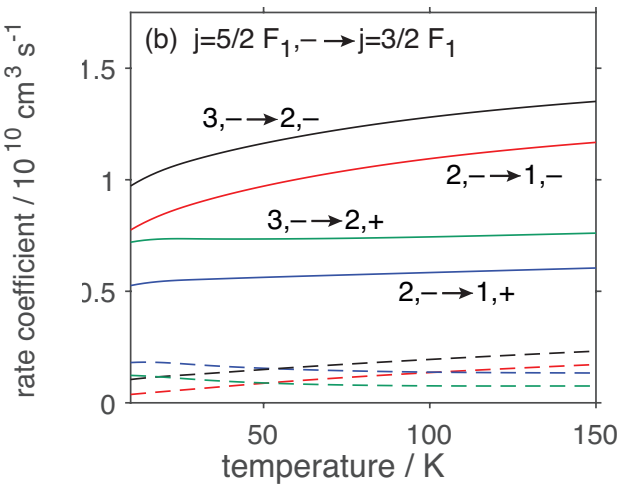

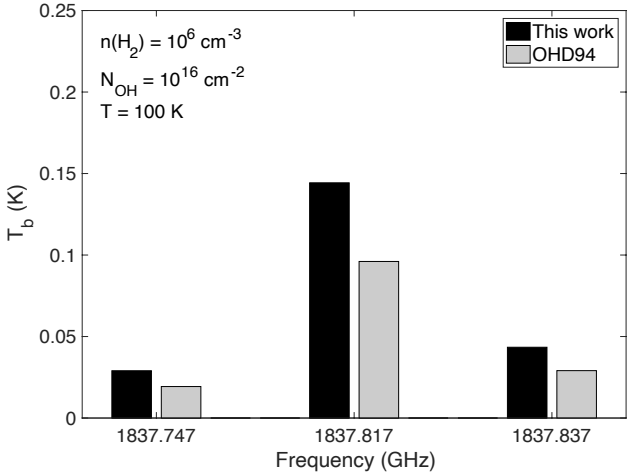

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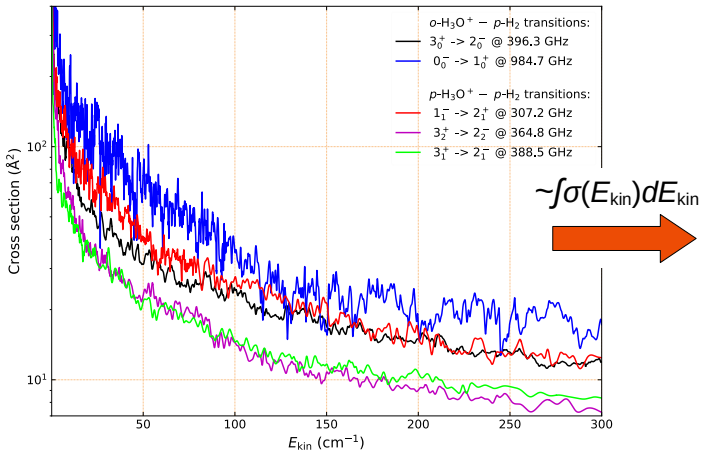
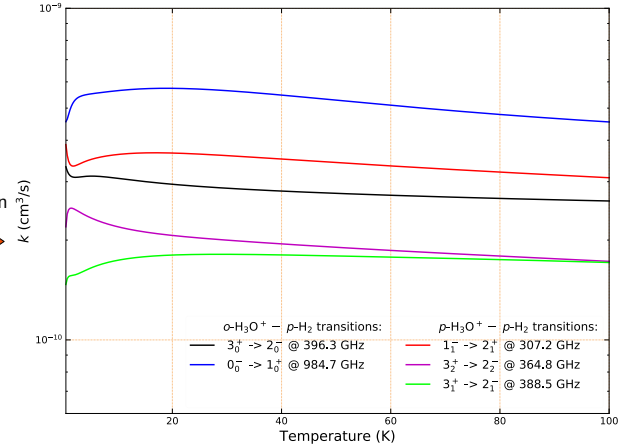


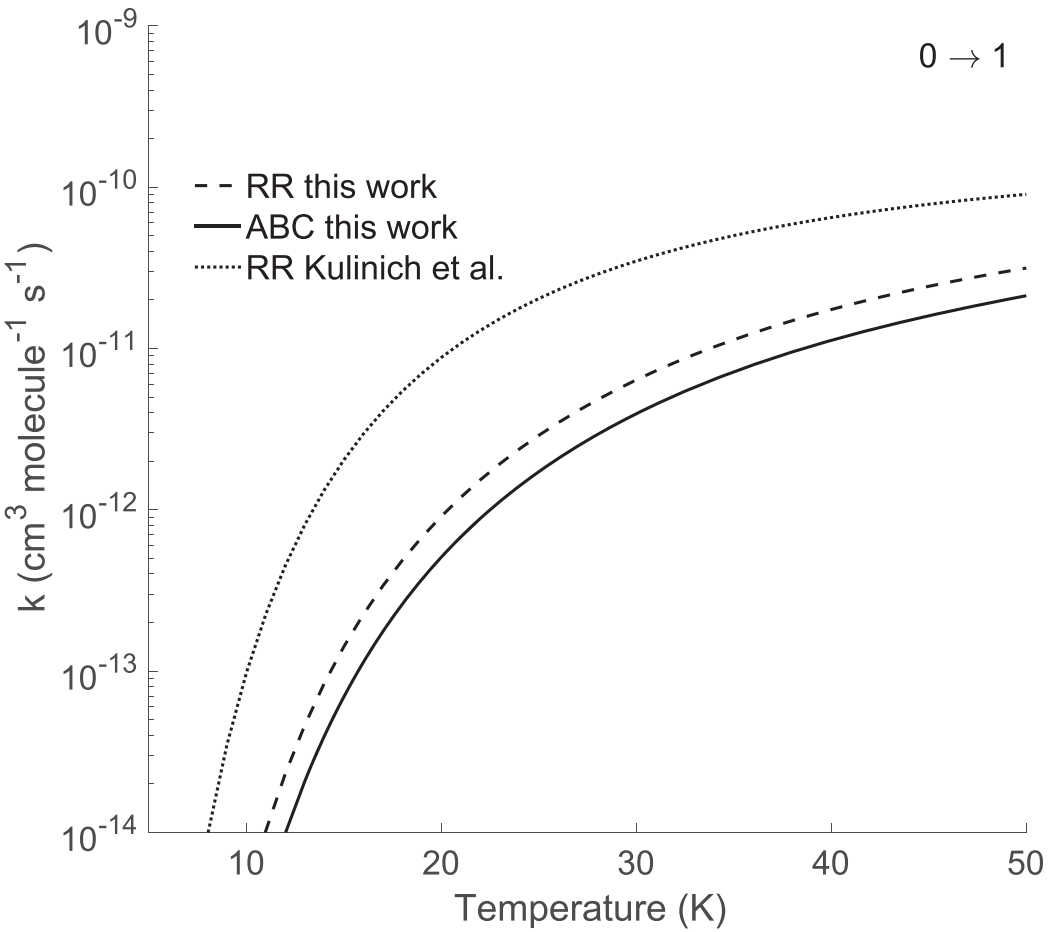


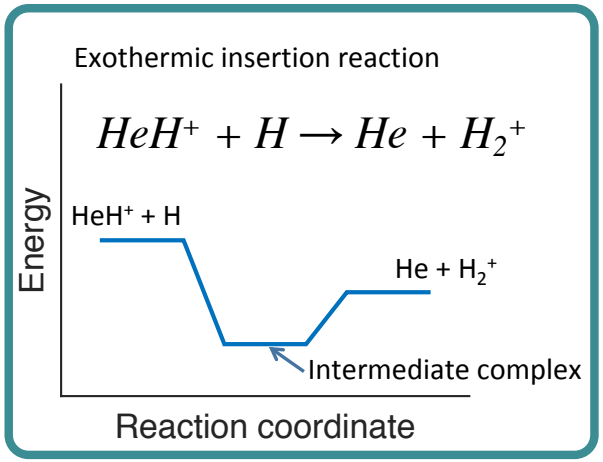
First state-to-state rate coefficients for the H_3O^+-H_2 collisional system

Cross sections and rate coefficients for transitions in H_3O^+ induced by $H_2(j=0)$

Reduced dimension approaches: limitations

Collisional excitation of HeH^+ by H





Rate coefficients for the rotational excitation of HeH^+ ($j = 0 \rightarrow j' = 1$) by H.
__ 3D reactive results; -- non reactive results; … Kulinich et al. (2020)

- Rigid rotors calculations overestimate the exact reactive ones
- Need of a **method considering the competition between inelastic and reactive collisions**

Reduced dimension approaches: limitations

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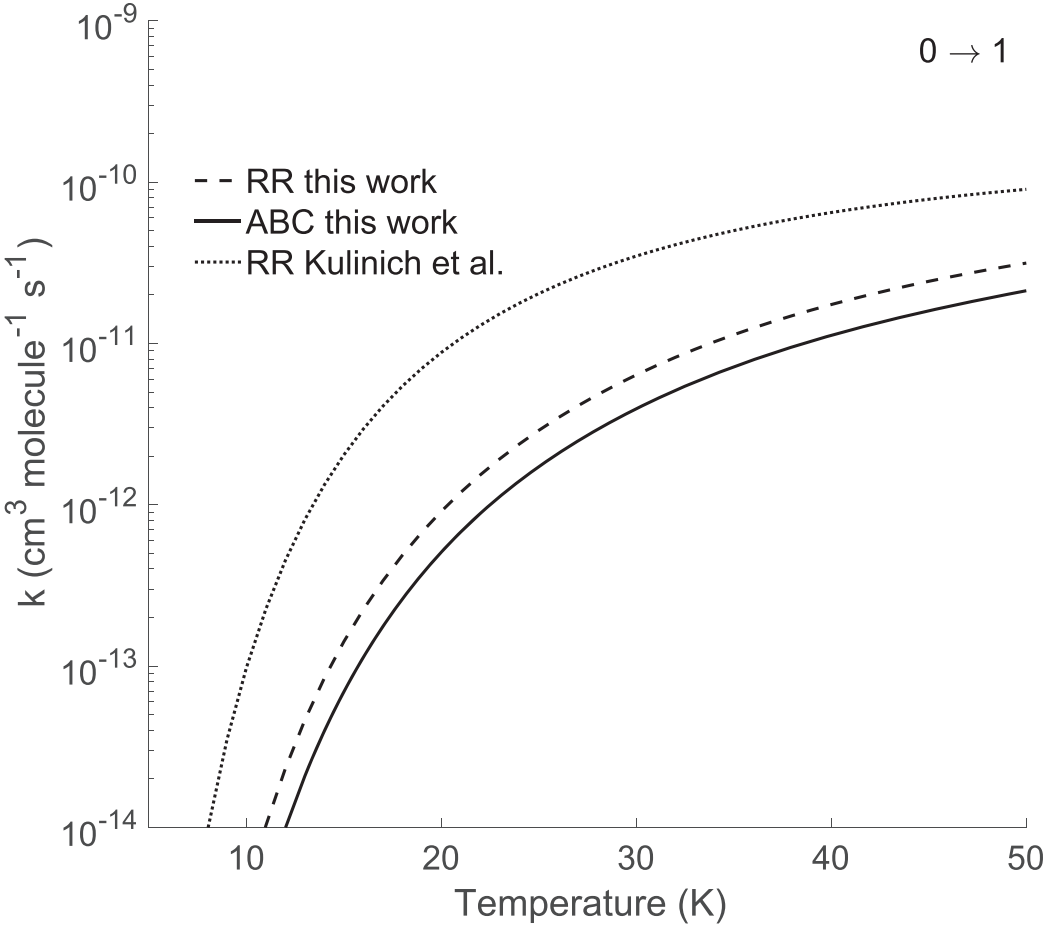

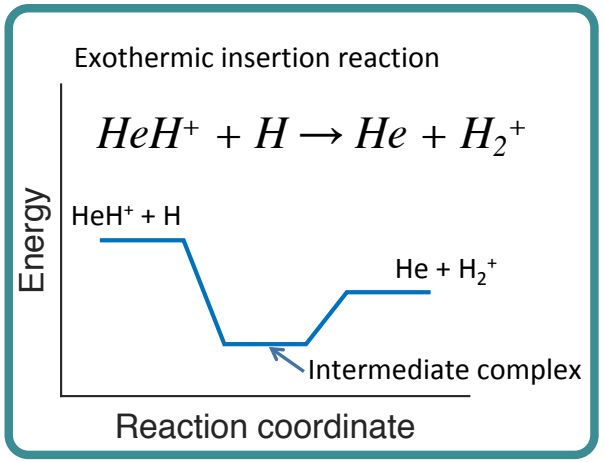

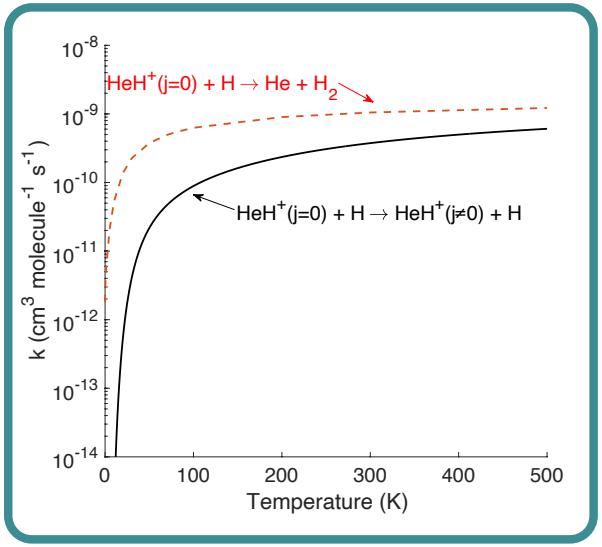

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Statistical approaches

Statistical adiabatic channels model (SACM; Quack & Troe 1974, Loreau et al. 2018)

Statistical approach - Adiabatic channels (*adiabats*) obtained by diagonalizing the Hamiltonian excluding the nuclear kinetic term for each *J:*

$$\langle \alpha' | H_{\text{int}} + V + \frac{\mathbf{L}^2}{2\mu R^2} | \alpha \rangle$$

α : angular functions of Ψ

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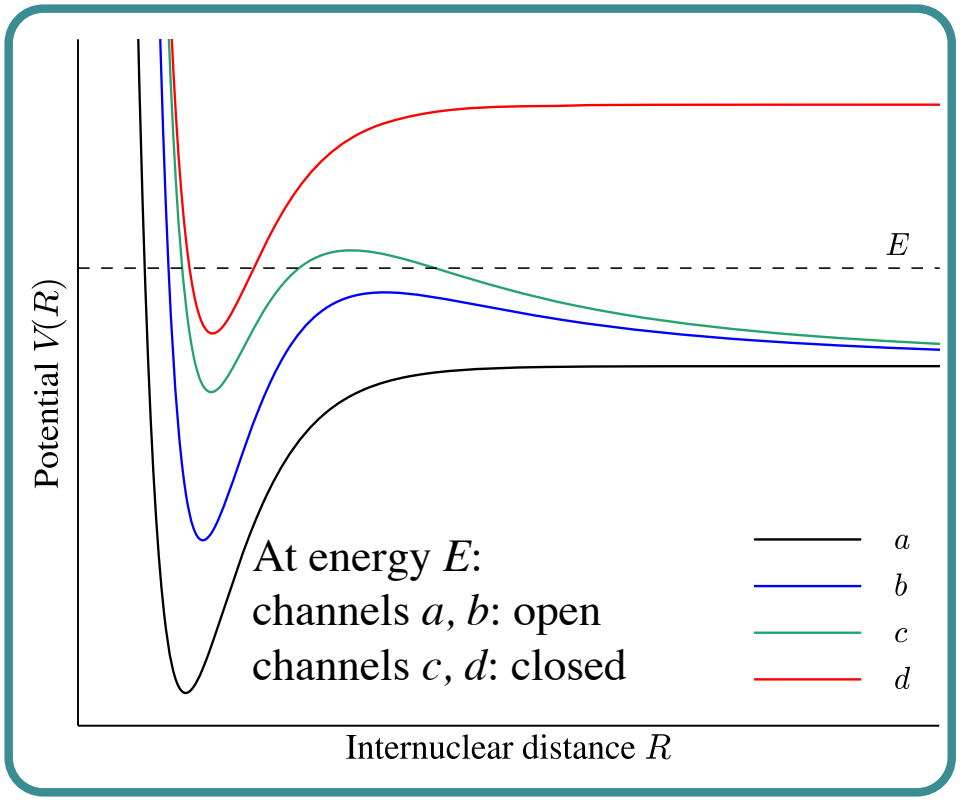

We assume that all open channels have the same probability $1/N(E,J)$, where $N(E,J)$ is the number of open channels at an energy E for a given J:

$$|S_{ij}(E,J)|^2 = \begin{cases} 1/N(E,J) & \textit{for open channels} \\ 0 & \textit{for closed channels} \end{cases}$$

$$\sigma_{if}(E) = \frac{\pi}{(2j_1+1)(2j_2+1)k^2} \sum_{J=0}^{\infty} (2J+1)|S_{if}(E,J)|^2.$$

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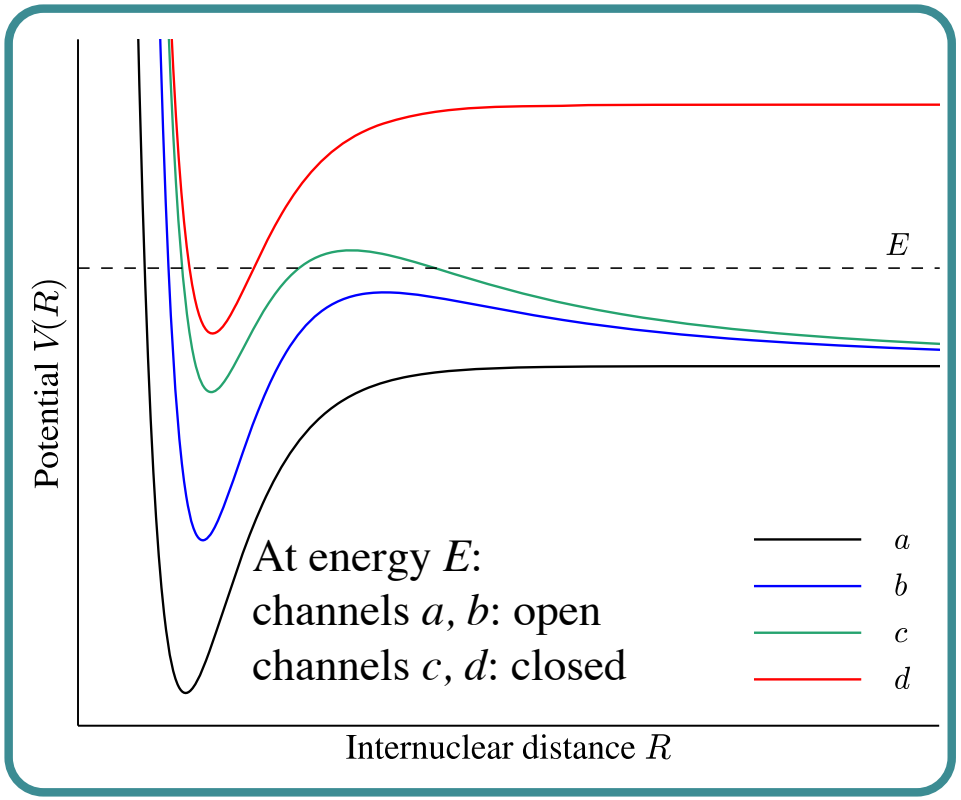

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- No need to include closed channels / The adiabatic curves are independant of energy
- Expected to be valid for collisional systems with a long-lived intermediate complex

Statistical approaches OH^+-H

Application to the OH^+ - H strongly bound (non reactive) system

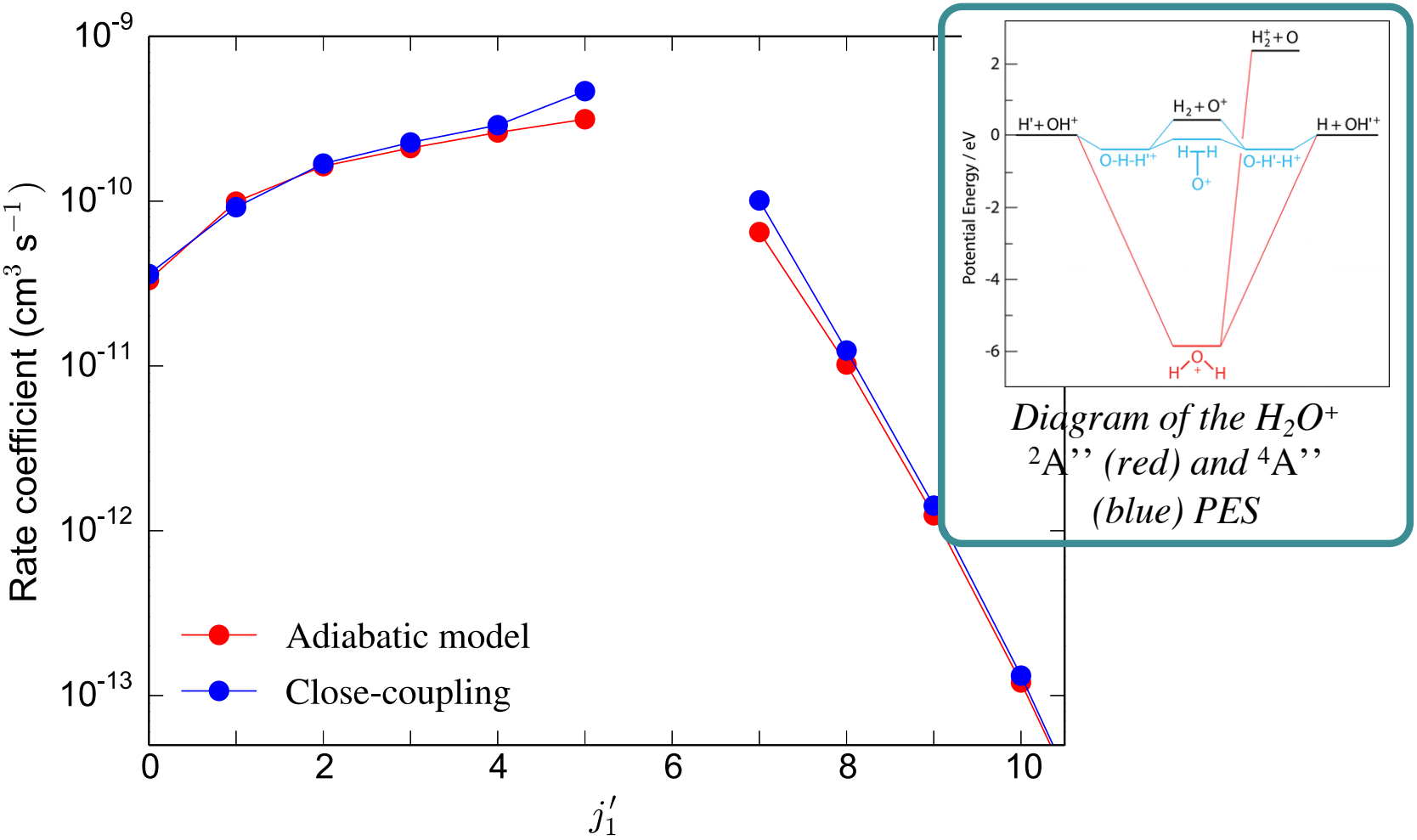


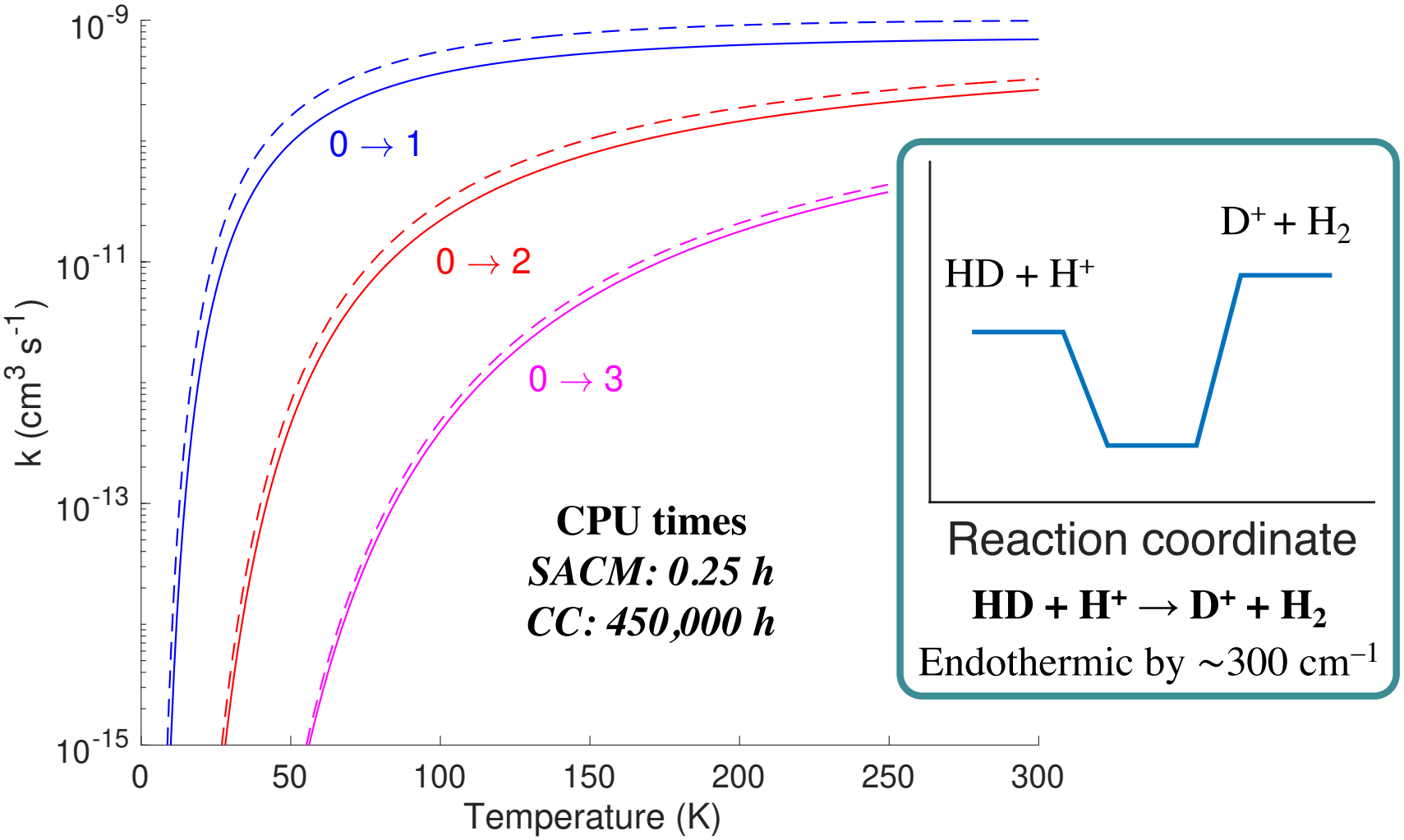
Diagram of the H_2O^+ $^2A''$ (red) and $^4A''$ (blue) PES

Rate coefficients for $OH^+(j_1 = 6) + H \rightarrow OH^+(j_1) + H$ as a function of j_1' at a temperature of 200 K.

- The SACM approach slightly underestimates the transitions with $\Delta j_1 = 1$ compared to the CC results, but all other transitions and **propensities are nicely reproduced**

Statistical approaches: HD-H$^+$

Application to the HD - H$^+$ reactive system

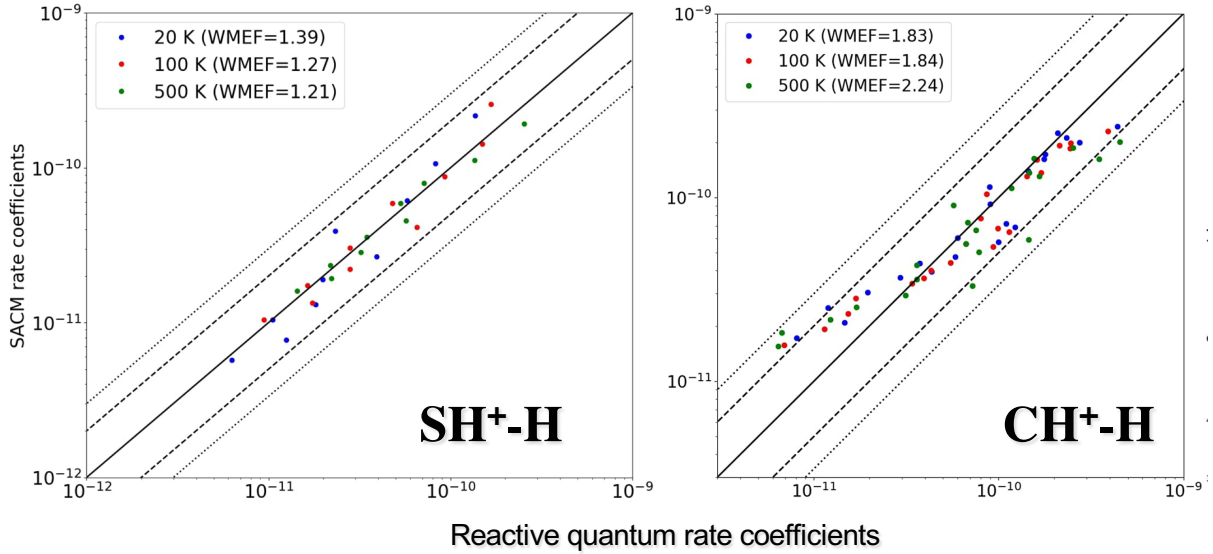


Rate coefficients for the rotational excitation of HD by H$^+$. CC (solid lines) vs. SACM (dashed lines)

- The two sets of data are in **very good agreement**, with differences lower than a factor of 1.5

Statistical approaches: applications

Collisional excitation of SH^+ and CH^+ by H



$$\mathrm{WMEF} = \frac{\sum_i k_i^{\mathrm{CC}} r_i}{\sum_i k_i^{\mathrm{CC}}},$$

SACM provides an interesting alternative to « almost »exact quantum calculations

Comparison at several temperatures of the SACM and the quantum rate coefficients

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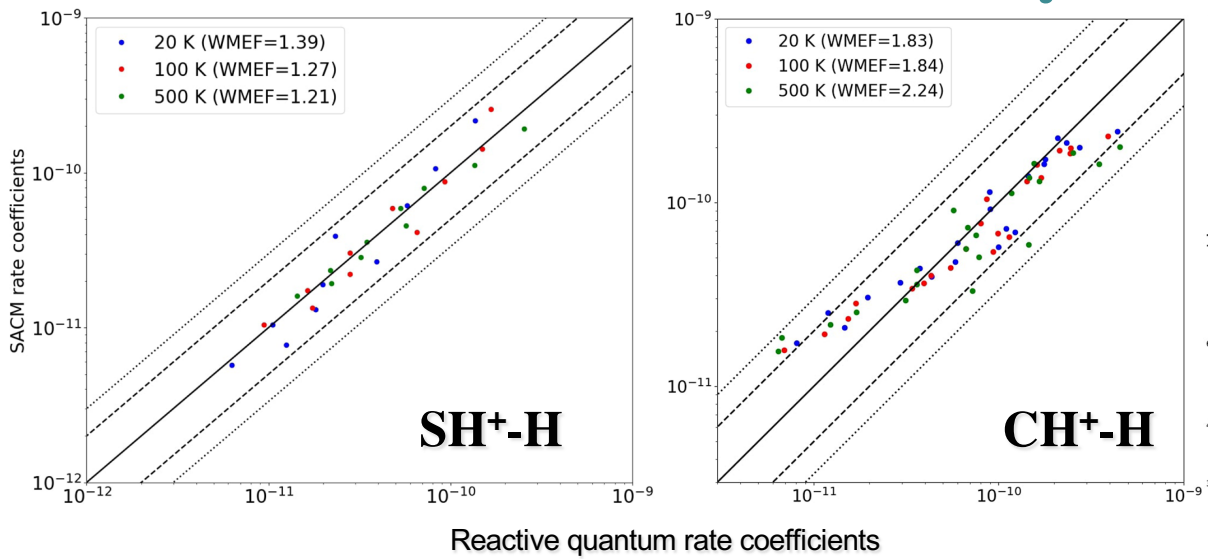

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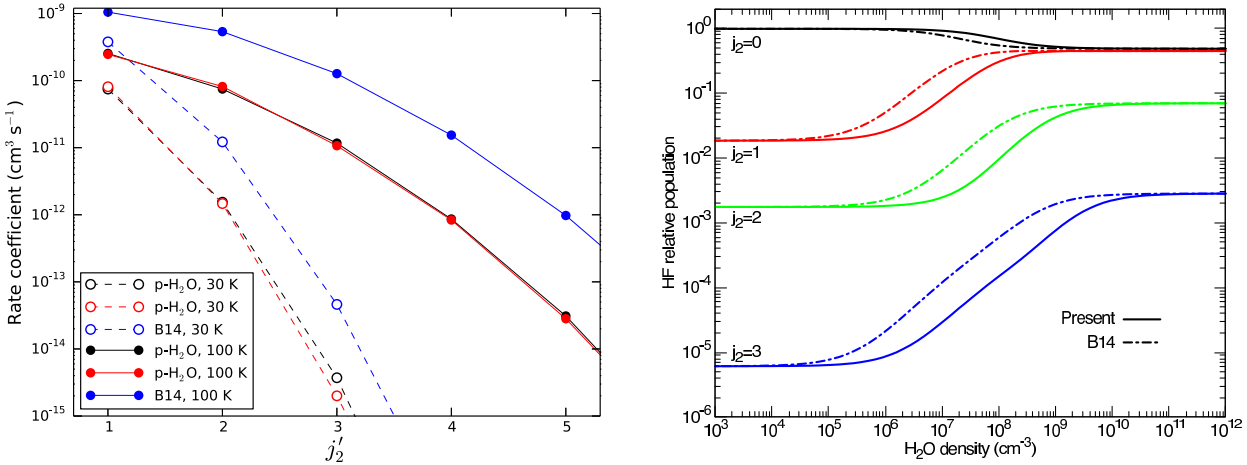
Collisional excitation of HF by H_2O



First state-to-state rate coefficients for the HF-H_2O collisional system

Left: Rate coefficients for the rotational excitation of HF (j_2=0 – j_2') by H_2O
Right : Level populations of HF(j_2 = 0–3) as functions of H_2O density in cometary comae model

Statistical approaches: limitations

Collisional excitation of HeH^+ by H

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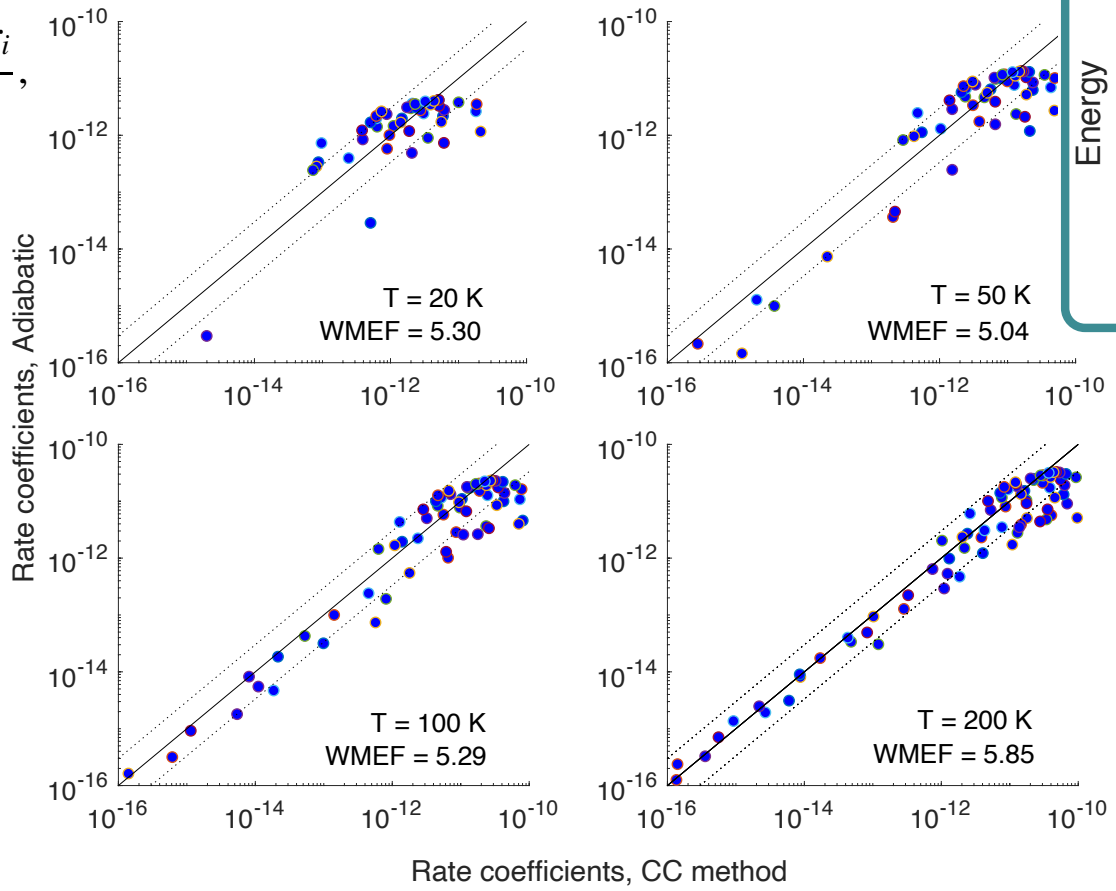

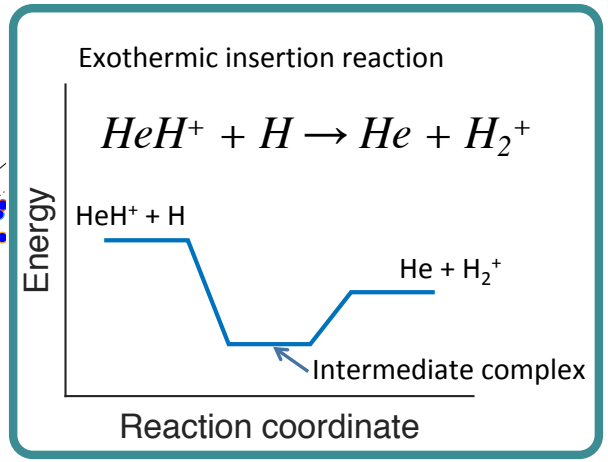

SACM and CC rate coefficients for $HeH^+(j)$ + H collisions

- SACM predicts the rate coefficients with a **reasonable accuracy.** Most rate coefficients are accurate to within a factor 2-3.
- Discrepancies attributed to a non favourable formation of the complex

Conclusion

- **Production of new collisional data for ions and radicals** (H_3O^+, CF^+, NS^+, C_2H, OH)
- **Validation of the statistical adiabatic channels models** for scattering calculations at low temperatures and for strongly bound and reactive systems
- Ongoing work:
  Generation of a SACM code to treat collisional excitation of ionic polyatomic systems
  Application to the OH^+ and H_2O^+ ions
- Accurate **determination of the abundance of reactive molecules** in the interstellar medium

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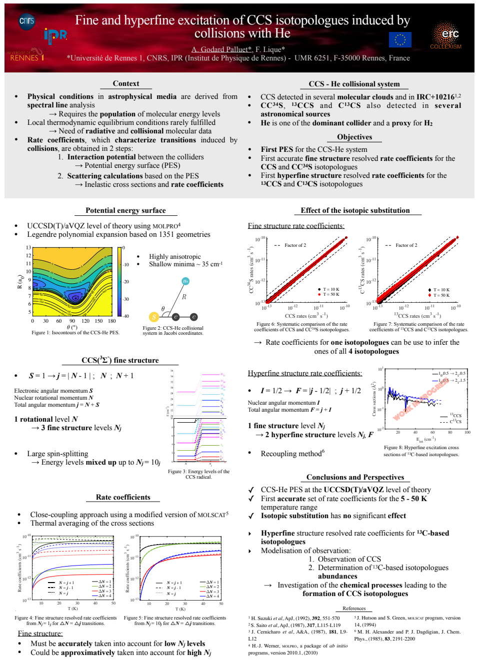

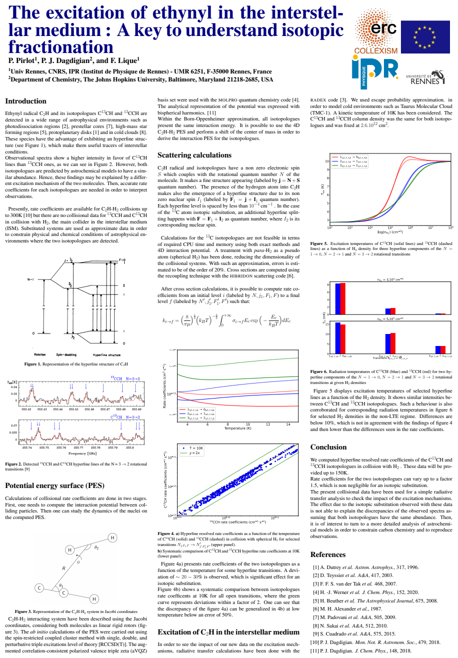

Thanks for your attention !