Hyperfine excitation of OH⁺ by H

François Lique

Laboratoire Ondes et Milieux Complexes
Université du Havre, France
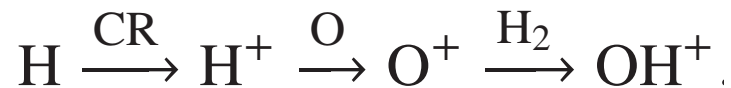
Le Havre (Normandie):
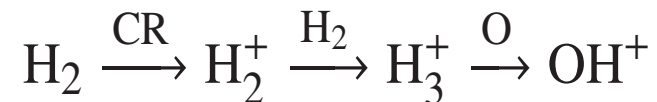*UNESCO world heritage site*

OH$^+$ in astrophysical media

- ✓ First detection of OH$^+$ in absorption in 2010

- ✓ OH$^+$ has been observed in absorption and emission in **a variety of interstellar environments** including diffuse ISM, hot and dense PDRs, the nuclei of active galaxies, planetary nebulae, …

- ✓ The OH$^+$ ions play **an important role in the interstellar chemistry** as they act as precursors to the H$_2$O molecule.

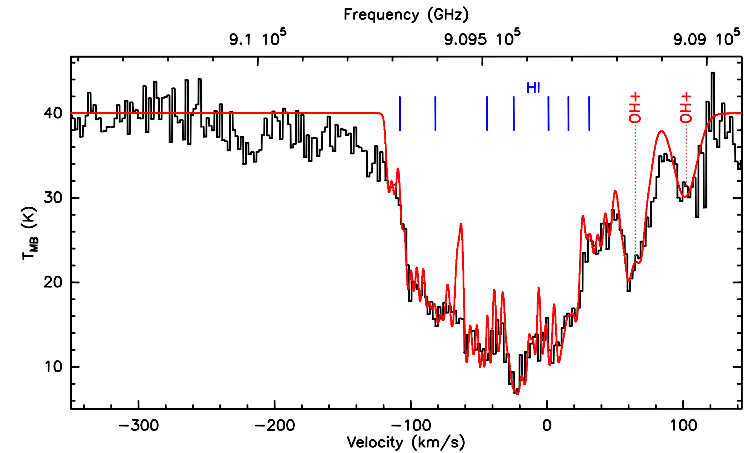- ✓ The chemistry of OH$^+$ is rather well understood

Fig. 2. Observed OH$^+$ spectrum towards Sgr B2(M) in black with the velocity scale referred to the stronger hyperfine line of OH$^+$. Frequencies for the two HFS lines at a velocity of 64 km s^{-1} local to Sgr B2(M) are indicated. Also velocities of the HI components from Garwood & Dickey (1989) are marked.

H I regions:

$$H \xrightarrow{CR} H^+ \xrightarrow{O} O^+ \xrightarrow{H_2} OH^+$$

Molecular clouds:

$$H_2 \xrightarrow{CR} H_2^+ \xrightarrow{H_2} H_3^+ \xrightarrow{O} OH^+$$

- ✓ OH$^+$ is a **probe of cosmic ray and X-ray ionization rates and molecular hydrogen fractions** in molecular clouds
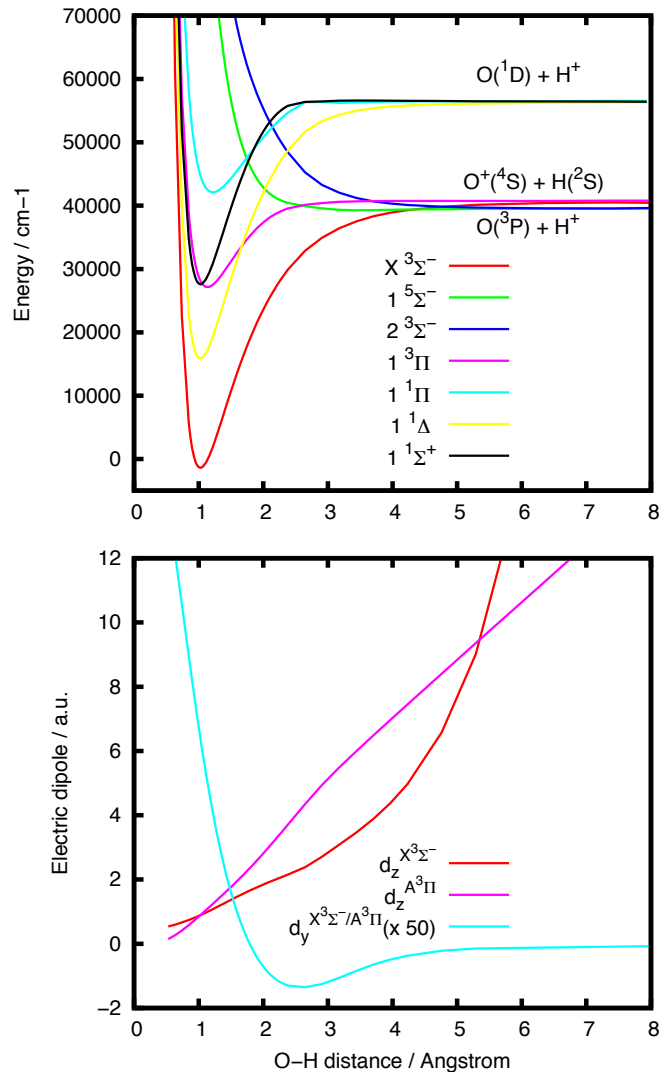
The excitation of OH⁺

✓ Since OH⁺ is very reactive and rapidly destroyed after its formation, its **rotational populations is expected to be out of LTE** and driven by the chemical state-to-state pumping mechanism of the $O^+ + H_2 \rightarrow OH^+ + H$ reaction.

✓ Gomez-Carrasco et al. (2014) computed state-to-state rate coefficients for the **chemical pumping mechanism**, OH⁺ radiative **Einstein coefficients** for infrared and UV together with the **inelastic collisional rates** for OH⁺-He collisions and introduced them in radiative transfer models to simulate the rotational emission of OH⁺ from PDRs.

✓ The state-to-state rate coefficients for the $O^+(^4S) + H_2(v, j) \rightarrow OH^+(X^3\Sigma^-) + H$ reaction were calculated from a time-dependent quantum method (so-called WP).
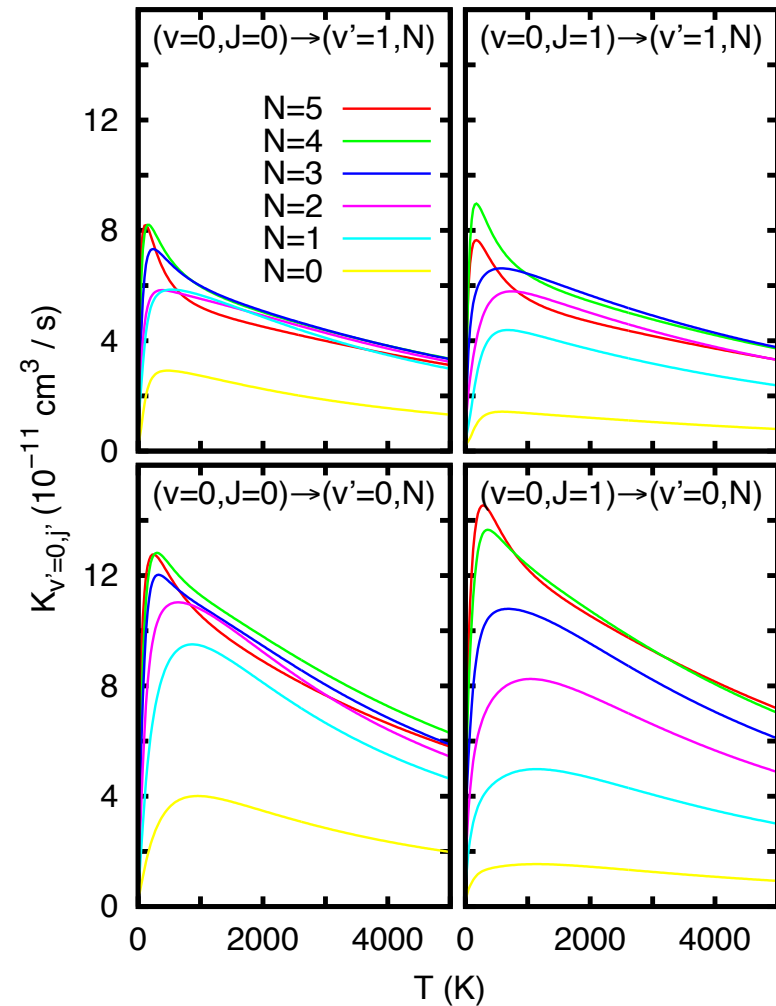
State-to-state rate coefficients for the $O^+ + H_2(v=0,j=0,1) \rightarrow OH^+(v'=0,1,N) + H$ reaction

The excitation of OH$^+$

✓ Radiative pumping of the vibrational and electronic levels of OH$^+$ by infrared and UV photons.

✓ Excitation of OH$^+$ by inelastic collisions with He.
He results are used as a model for H and H$_2$

*Top: Electronic states of the OH$^+$ cation. Bottom: Dipole moments and transition dipole moments*
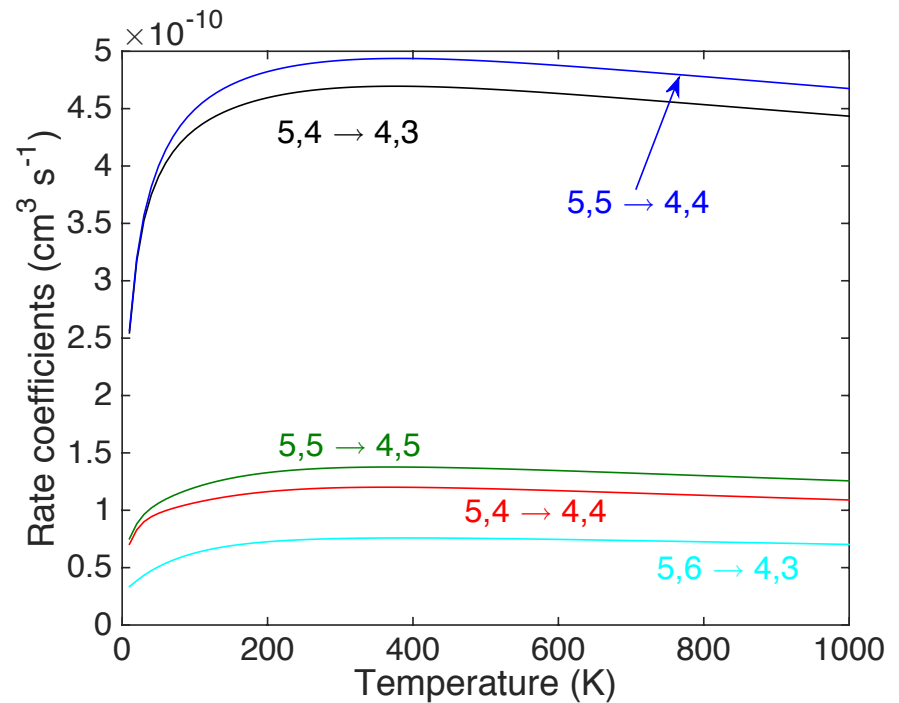
Temperature variation of the ine resolved OH$^+$-He rate coefficients. The numbers correspond to the $N, j \rightarrow N', j'$ quantum numbers.
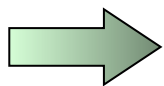
The excitation of OH⁺

Modeling OH⁺ emission of hot and dense PDRs *(using the Meudon PDR)*

✓ Visual extinction : $A_{V,max} = 10$
$n(H_2) = 10^4$ cm^{-3}
Cosmic ray ionization rate $\zeta = 3\ 10^{-16}$ s^{-1}

✓ 3 differents approaches :

(a) Only the excitation by nonreactive collisions

(b) Including chemical pumping assuming that the probability to form OH⁺ in an excited level follows a Boltzmann distribution at a formation temperature of 2000 K (as done by van der Tak et al. 2013)

(c) Adopting the branching ratios obtained with our quantum calculations
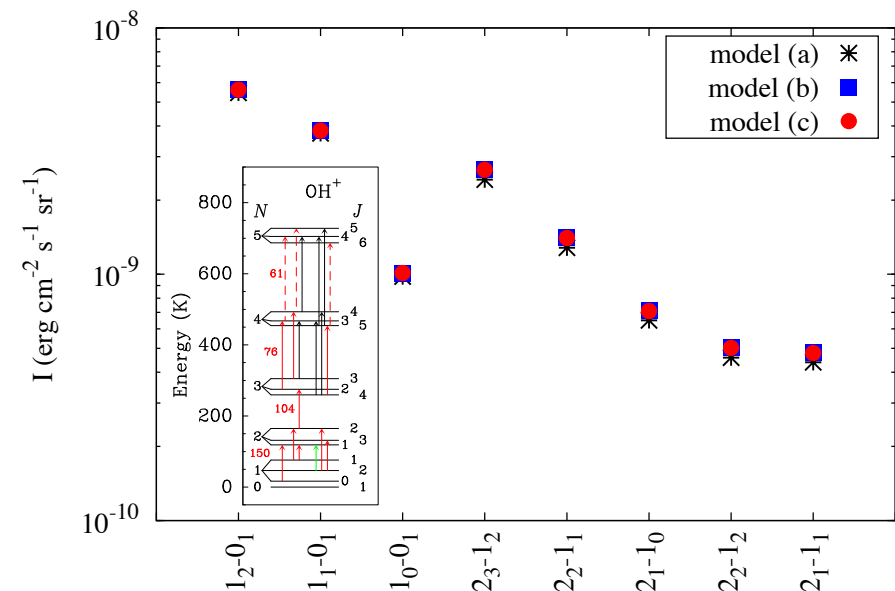
Intensities of the first rotational lines of OH⁺ in the direction perpendicular to the slab for the models (a), (b), and (c). Each $N_J - N'_{J'}$ line is labeled on the x-axis.
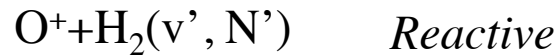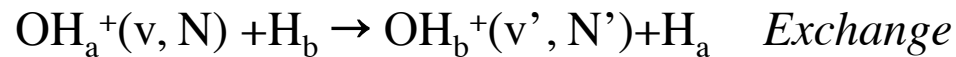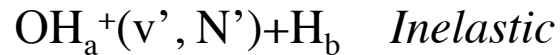
➡ **Inelastic collisions dominate over the chemical pumping for determining the emission from low rotational states of OH⁺ (in particular H collisions)**

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

$$OH_a^+(v, N) + H_b \rightarrow \begin{cases} OH_a^+(v', N') + H_b & \textit{Inelastic} \\ OH_b^+(v', N') + H_a & \textit{Exchange} \\ O^+ + H_2(v', N') & \textit{Reactive} \end{cases}$$

Reactive channels are endothermic by 0.5 eV
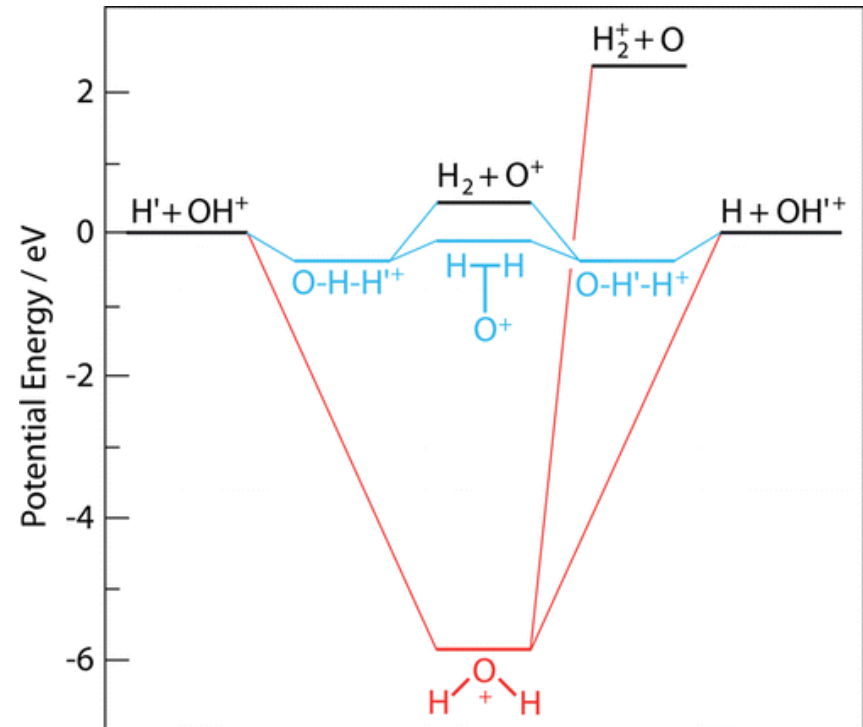
Accurate calculations for rotational excitation
have to include the reactive channels
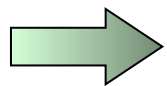
✓ 2 PES correlate to the OH$^+$ + H reactants:
^{4}A'' (insertion well ≈ 4 000 cm^{-1})
^{2}A'' (insertion well ≈ 50 000 cm^{-1})

✓ Close coupling approach cannot be used since
H$_2$O$^+$ well depth is larger than OH$^+$ well depth

*Schematic diagram of the doublet PES (red) and
quadruplet PES (blue). The reactants and products
are indicated in black (Stoecklin et al. 2015).*

**Study of the collisions from quantum time-dependent wave packet (WP)
calculations including both the inelastic and exchange processes**
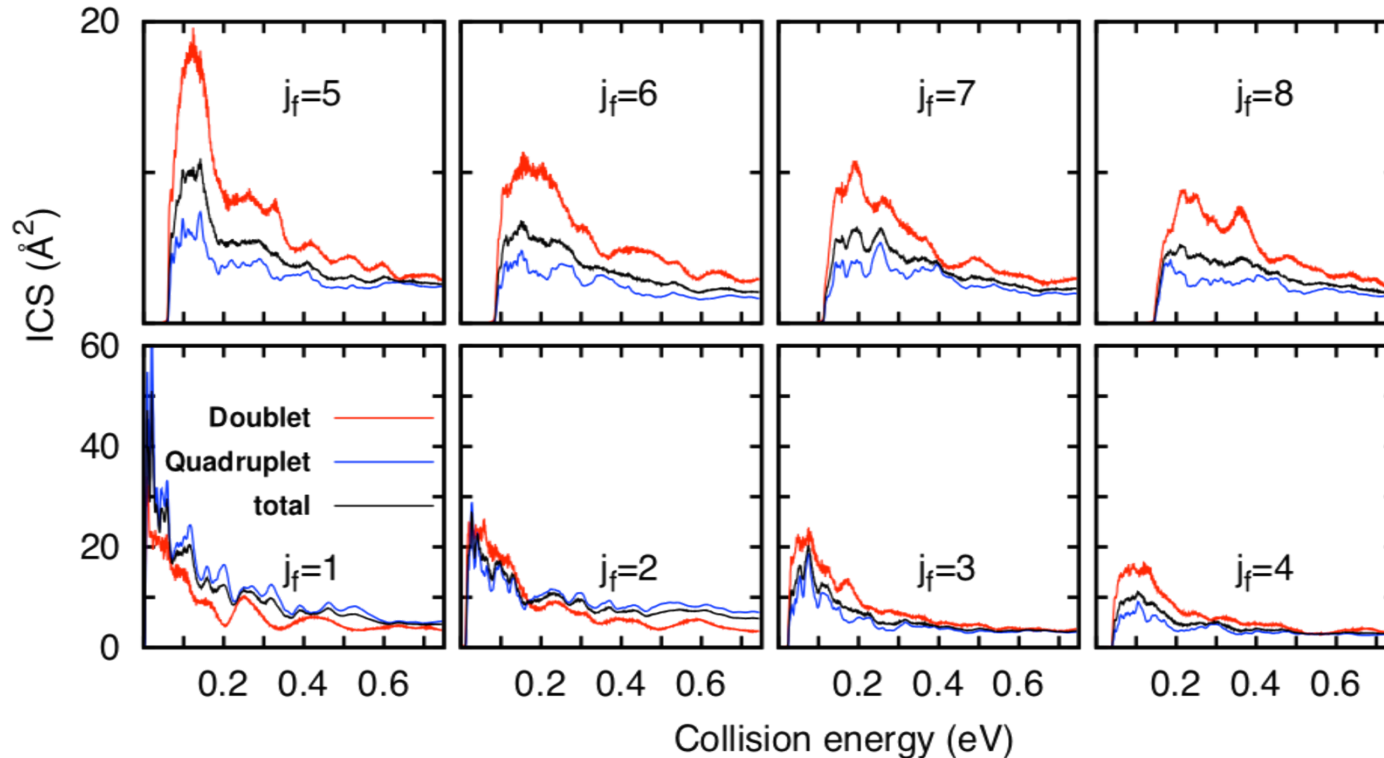
State-to-state cross sections

✓ The **exchange cross section is 10-20 times lower than the inelastic one** for all the final j'. This inelastic/exchange ratio decreases with the decreasing of collision energy.

✓ Rigid-rotor (RR) time independent approach (i.e. fixing the internuclear distance of the OH⁺ reactant) were also performed

✓ **RR and WP results agree relatively well** for the excitation on the quartet PES / larger differences are seen on the doublet PES
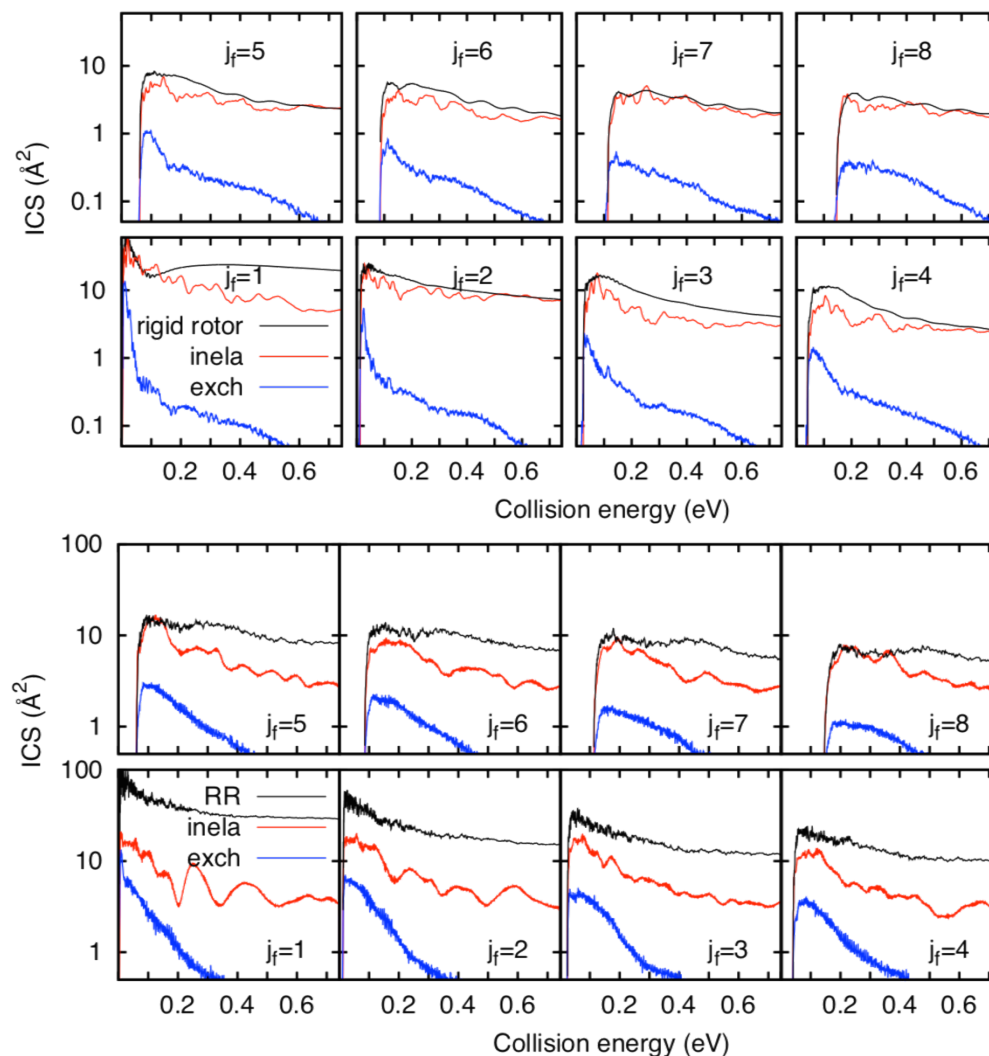
State-to-state integral cross section for the H+OH⁺(v=0,N=0) → OH⁺(v'=0,N') + H in the quartet (upper) and doublet (lower) state
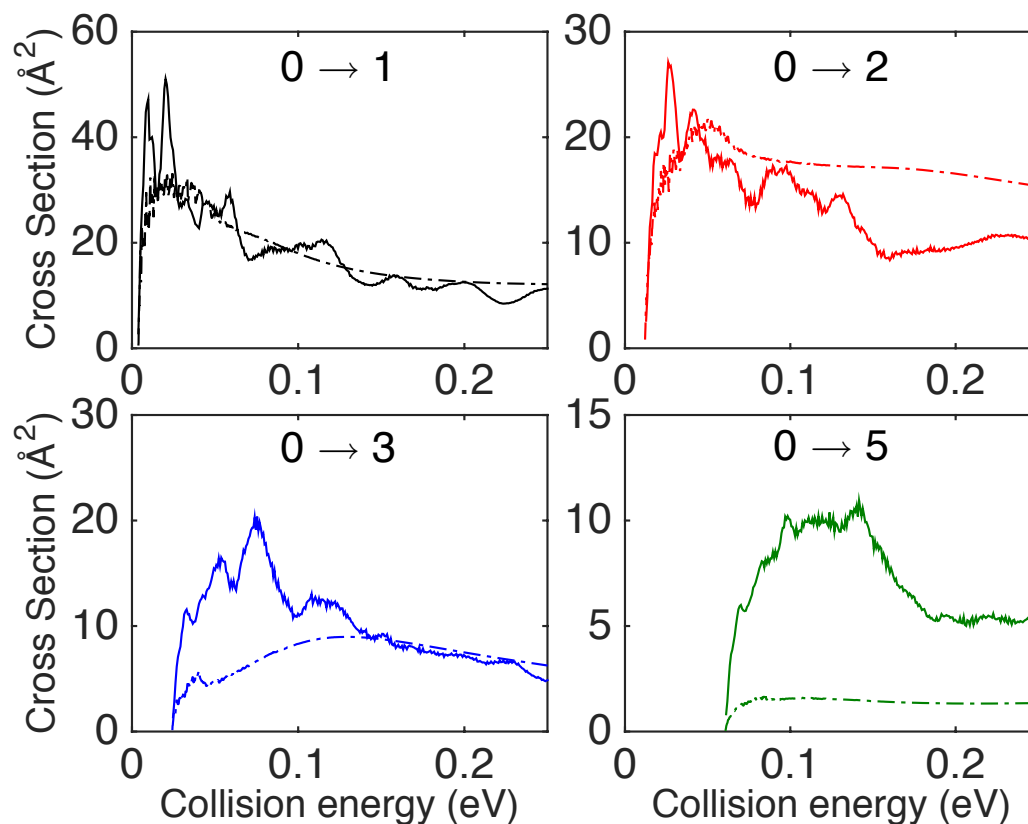
State-to-state cross sections

State-to-state cross sections, summed over inelastic and exchange channels, for H +
OH⁺(v=0, j=0) → OH⁺(v=0,j') + H for the doublet (red) and quartet (blue) states.

✓ For $\Delta N=1$, the cross sections for the quartet is larger. For higher $\Delta N=2$ and 3, the cross sections obtained for the two electronic states are very similar, whereas for $\Delta N > 4$ the ICS for the doublet is larger by a factor of ≈ 2–3.

✓ Using the electronic partition function is 2/6 for the doublet and 4/6 for the quartet, we found that **state-to-state cross sections could be well approximated by that of the quartet**.

Comparison with He results

✓ The **agreement between the two sets of cross sections is quite good** for small ΔN transitions.

✓ For transition with larger ΔN, significant differences appear.

✓ The differences can be explained by the relatively weak well depth of the OH⁺-He that does not favor transitions with large ΔN.

✓ From this comparison, we can see that **OH⁺-He collisional data can hardly be a template for OH⁺-H ones**. This fully justify the necessity of computing real OH⁺–H data.


State-to-state cross sections for H + OH⁺(v=0, N=0) → H + OH⁺(v'=0, N') (solid line) and He + OH⁺(v=0, N=0) → He + OH⁺(v'=0, N') (dashed line) collisions.

Through the computation of fine and hyperfine resolved data

✓ Due to the presence of deep potential wells, the exact calculations were **restricted to low rotational states, $N = 0$**, since the cost grows as $2N + 1$

✓ It is **not possible to include the fine and hyperfine structure of OH⁺** in the quantum dynamical calculations, whereas they are resolved in the astronomical observations
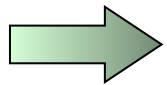
➡️ **Generate a full set of data that can be used for astrophysical modelling**

Using the IOS approximation, rotational rate coefficients are (Faure & Lique 2012) :

$$k^{\text{IOS}}_{N \to N'}(T) = (2N' + 1) \sum_L \begin{pmatrix} N' & N & L \\ 0 & 0 & 0 \end{pmatrix}^2 \boxed{k_{0 \to L}(T)}$$

WP rate coefficients

Fine structure rate coefficients:

$$k^{\text{IOS}}_{Nj \to N'j'}(T) = (2N + 1)(2N' + 1)(2j' + 1) \sum_L$$

$$\times \begin{pmatrix} N' & N & L \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} N & N' & L \\ j' & j & S \end{Bmatrix}^2 \times k_{0 \to L}(T)$$
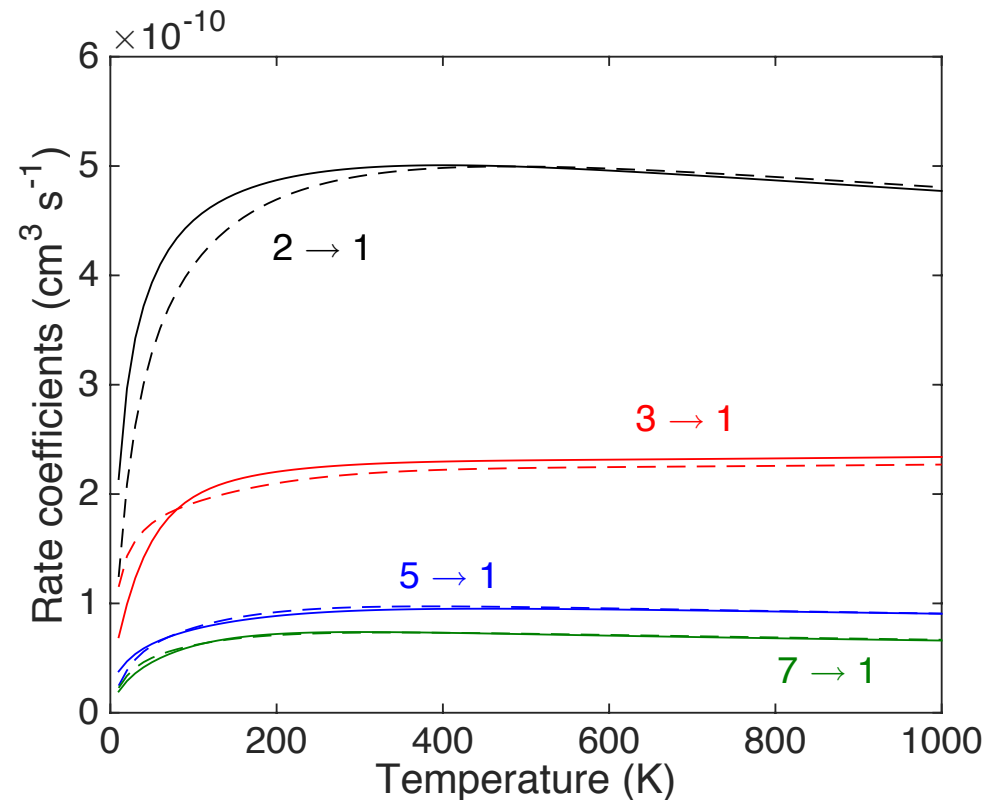
Hyperfine structure rate coefficients:

$$k^{\text{IOS}}_{Nj \to N'j'}(T) = (2N + 1)(2N' + 1)(2j + 1)(2j' + 1)$$

$$\times (2F' + 1) \sum_L \begin{pmatrix} N' & N & L \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \begin{Bmatrix} N & N' & L \\ j' & j & S \end{Bmatrix}^2 \begin{Bmatrix} j & j' & L \\ F' & F & I \end{Bmatrix}^2 \times k_{0 \to L}(T)$$

Validation of the IOS approach

✓ The **agreement between the two sets of data is very encouraging**. Both the magnitude and the temperature variation of the rate coefficients is very similar for all transitions.

✓ Mean deviations between the two sets of data occur at low temperature where the accuracy of the IOS approach is expected to be moderate.

✓ IOS sets of rate coefficients are accurate enough for astrophysical purpose and **can be used with confidence** to analyse OH⁺ emission spectra from warm environment where atomic hydrogen is abundant.

Comparison between IOS (solid lines) and WP (dashed lines) rate coefficients for the N → N' = 1 transitions of OH⁺ due to H collisions on the quartet PES.
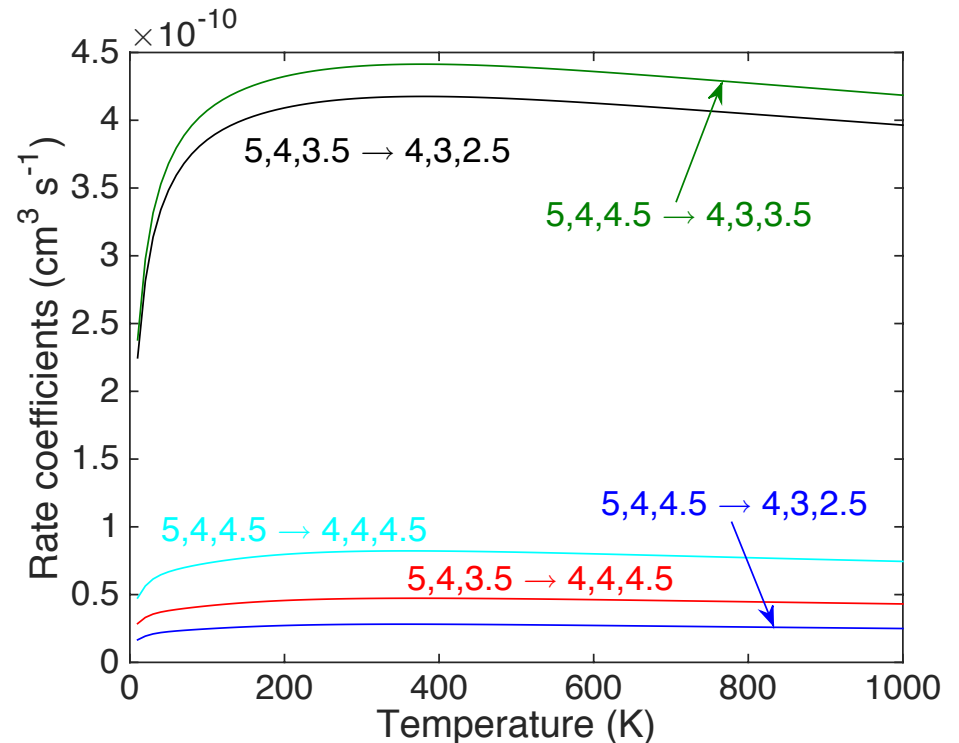
Fine structure excitation
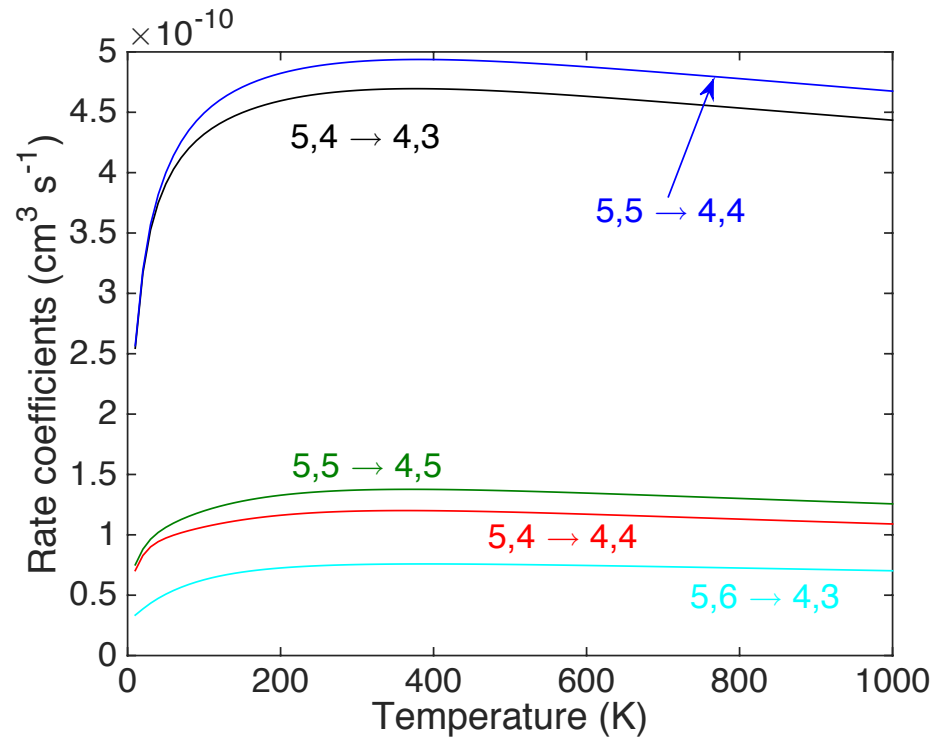
Typical fine structure resolved de-excitation rate coefficients for the OH⁺ molecule in collision with H as a function of the temperature.

Hyperfine structure excitation

Typical hyperfine resolved de-excitation rate coefficients for the OH⁺ molecule in collision with H as a function of the temperature.

Propensity rules: $\Delta j = \Delta N$

Propensity rules: $\Delta F = \Delta j$

Large magnitude of the rate coefficients ($k(T) > 10^{-10}$ cm³ s⁻¹)

III – Conclusion

The rotational, fine and hyperfine excitation of OH$^+$ by H have been investigated.

- ✓ We have obtained **fine- and hyperfine-resolved rate coefficients** for transitions involving the lowest levels of OH$^+$ for temperatures ranging from 10 to 1000 K

- ✓ The He and H data display the same propensity rules in favour of $\Delta j = \Delta N$ and $\Delta j = \Delta F$ transitions. However, the **H rate coefficients are much larger than the He ones** (even corrected by the ratio of the reduced mass)

- ✓ Set up a **methodology for studying the collisional excitation of reactive species**

Octavio Roncero

Susana Gomez-Carrasco (Salamanca)

Benjamin Godard (Obs. Paris)

Jacek Klos (Maryland)

Alfredo Aguado, Javier Aoiz, Jesus Castillo, Javier Goicoechea, Mireya Etxaluze, José Cernicharo (Madrid)

Niyazi Bulut

hYdRiDeS

Programme de physique et Chimie du milieu interstellaire

pcmi

Le Havre

Claude Monet

Thanks for your attention !

14