State-to-state rate constants calculations for the reactions C^++H_2 and S^++H_2

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Interaction astrochemistry - molecular physics

- **Spectroscopy**

Determination of present species in ISM

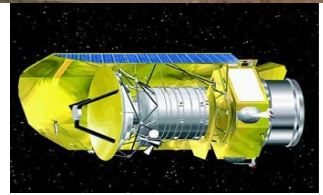Benchmark molecule to estimate temperature of observed region

- **Gas phase kinetics**

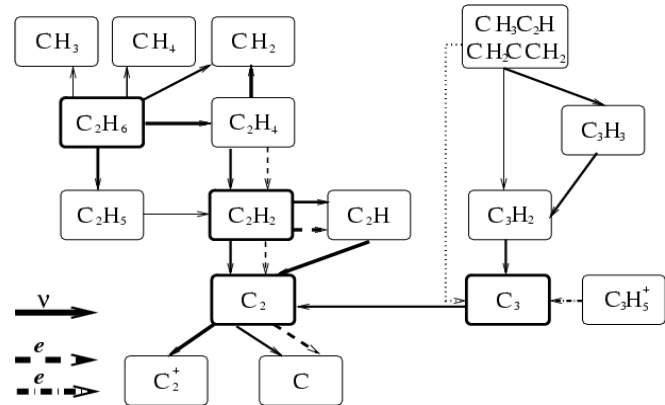Complex kinetic models to reproduce species abundance observations

→ information on physical properties of the region

→ which chemical complexity can be achieve in ISM ?

→ **Need rate constants**

Alma and Herschel

Carbon chemistry diagram

atom-diatom reactive collisions : first chemical reactions

ions-H_2 reaction

→ reaction with barrier, generally endothermic

→ light hydrides recently detected by Herschel

→ H_2 most abundant molecule

→ rovibrational excitation may enhance reactivity

→ experimental results available → benchmark

$$C^+ + H_2 \rightarrow CH^+ + H \qquad\qquad S^+ + H_2 \rightarrow SH^+ + H$$
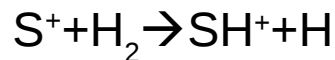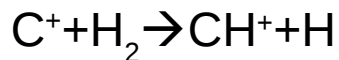
Theoretical approach

Solve Schrödinger equation :
$$\hat{\mathbf{H}}_{\mathrm{mol}}\Psi = E\Psi$$

$$\hat{\mathbf{H}}_{\mathrm{mol}} = \hat{\mathbf{T}}_{\mathrm{el}} + \hat{\mathbf{V}}_{\mathrm{el-el}} + \hat{\mathbf{T}}_{\mathrm{nuc}} + \hat{\mathbf{V}}_{\mathrm{nuc-nuc}} + \hat{\mathbf{V}}_{\mathrm{el-nuc}}$$
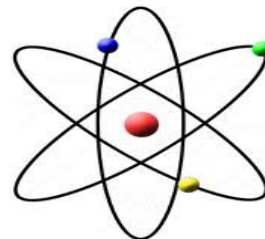
$$\hat{\mathbf{T}}_{\mathrm{nuc}} = \sum_{j=1}^{N_{\mathrm{nuc}}} \frac{P_j^2}{2M_j} \qquad \hat{\mathbf{T}}_{\mathrm{el}} = \sum_{j=1}^{N_{\mathrm{el}}} \frac{p_j^2}{2m_e} \qquad \hat{\mathbf{V}}_{\mathrm{el-el}} = \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

$$\hat{\mathbf{V}}_{\mathrm{nuc-nuc}} = \frac{1}{2}\sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} \qquad \hat{\mathbf{V}}_{\mathrm{el-nuc}} = -\sum_{i,j} \frac{Z_j e^2}{|r_i - R_j|}$$
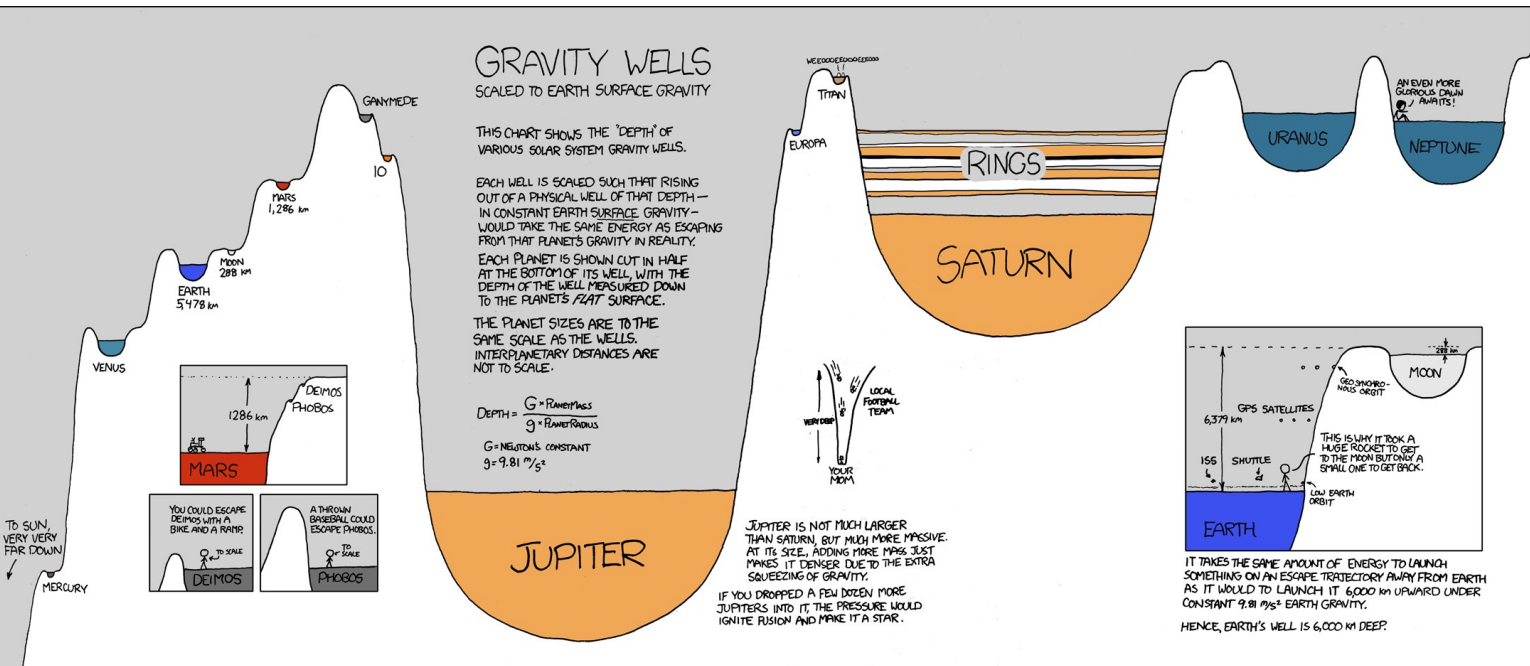
Method

Born-Oppenheimer approximation :

$$M \gg m \quad \rightarrow \quad \Psi(\boldsymbol{R}, \boldsymbol{r}) = \Psi(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})$$

→ The nuclei move in a electrostatic potential due to electrons

→ 2 steps to treat reaction :

- calculate the electronic Potential Energy Surface (PES)

- calculate the reaction dynamics using the PES

http://xkcd.com

Reaction dynamics

Quantum approach

→ **Time Dependant Wave Packet**

- Exact calculations (require a lot of cpu resource + time)
- for a given rovibrational state (v,j), computes all (v',j') of the S-matrix

Classical approach

→ **Quasi Classical Trajectories**

- Approximate calculations (cheap calculation, fast if potential is fast)
- initial conditions can follow a thermal distribution

C$^+$+H$_2$
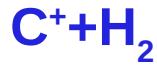
Surprising observation (Hershel) of "hot" CH$^+$ in some regions that cannot be simulated by standard heating mechanism :
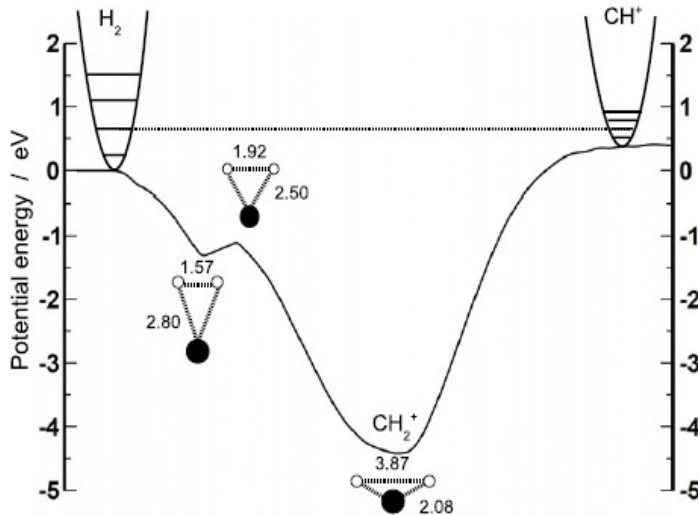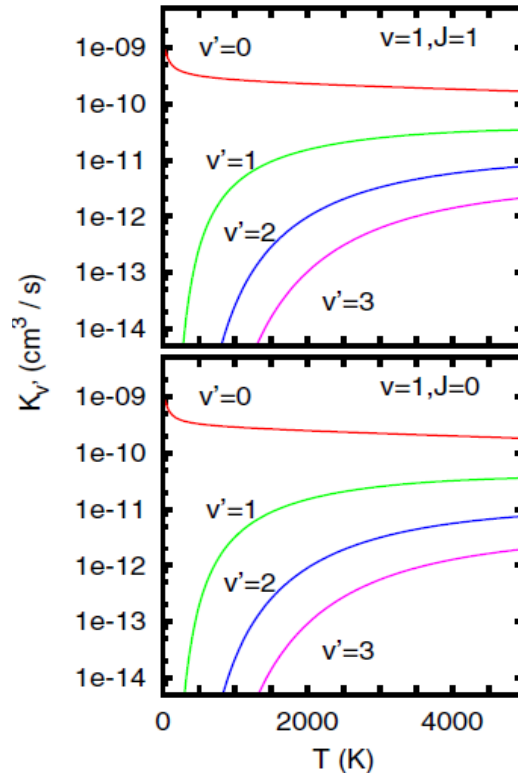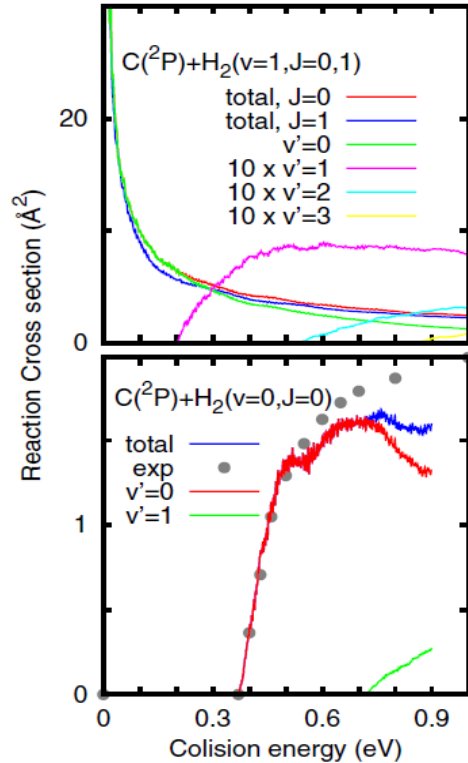→ chemical pumping ?

Figure 1. Minimum energy path for the C$^+$+H$_2$ reaction obtained using the PES of Stoecklin & Halvick (2005).

- PES from Stoecklin & Halvick

- **stable** CH$_2^+$ well (~ -4.5 eV) T-geometry
- no barrier to reach the well

- CH$^+$+H channel endothermic +0.36eV for v=0 → open when v=1

→ need state to state (v,j → v',j') rate constant to understand

→ use of time dependant wavepaquet method (quantum)

C⁺+H₂

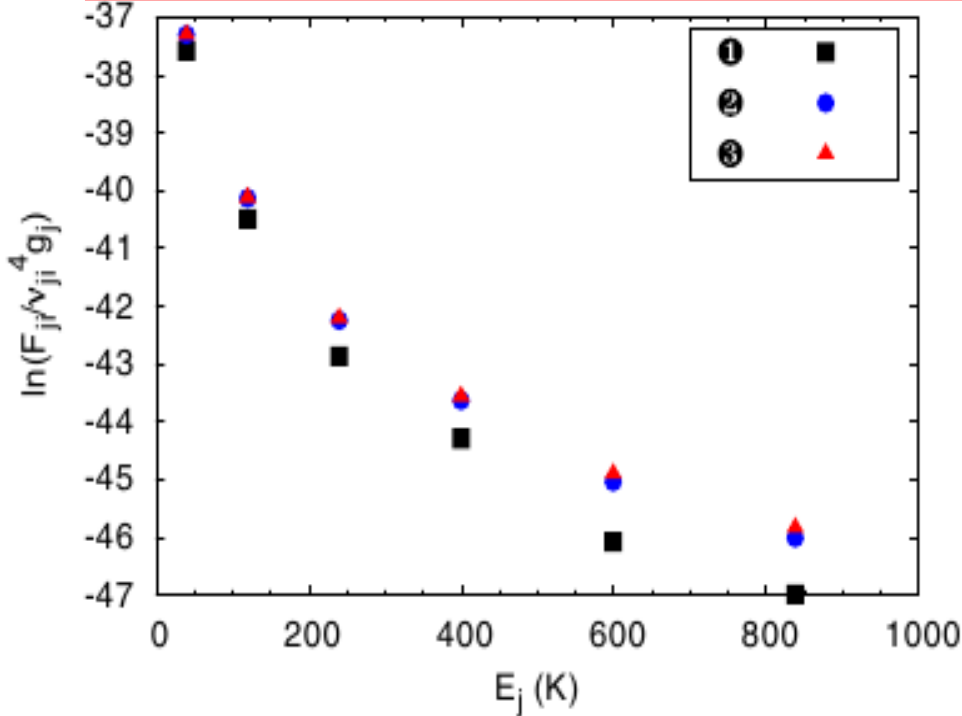- v=1 → typical cross section of barrierless exothermic reaction

- fast rate constant (>10^{-10} cm³/s)

- product vibrational distribution exhibits statistical behavior.

C⁺+H₂

$\ln(F_{ji}/v_{ji}^4 g_j)$ vs E_j (K)

Legend:
1 ■ (black square)
2 ● (blue circle)
3 ▲ (red triangle)

CH+ rotation diagram in the Orion Bar PDR predicted by the MADEX excitation code. (1)inelastic collision heating, (2)chemical pumping (Boltzman dist.) and (3) state-to-state.

Fji is the line flux in (W m⁻²) and vj i is the frequency of the transition in THz, and gj is the statistical weight of the upper level j.

- reduce discrepancy with observation (observation still "hotter")
→ higher rotational states of H2 have to be explicitly taken in account.
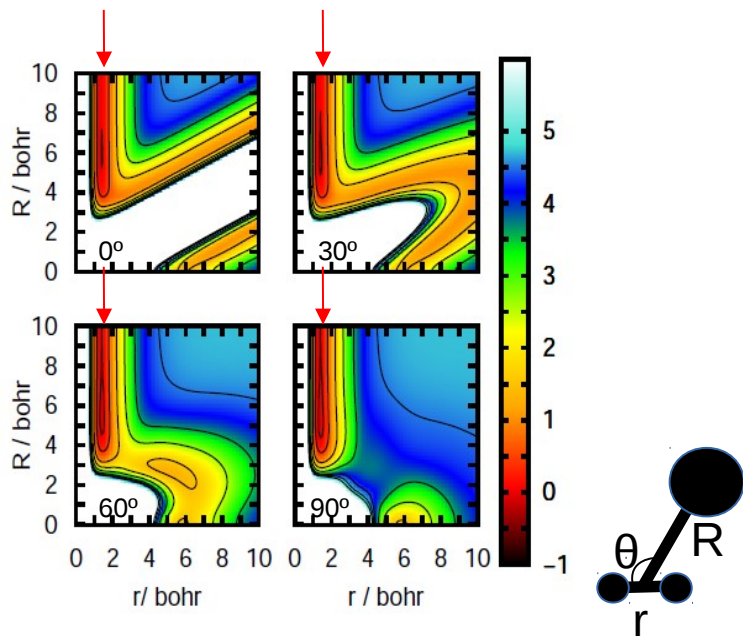→ coupling with excited el. state ??

- chemical pumping important in heating mechanism

- state-to-state effect increase with T

S⁺+H₂

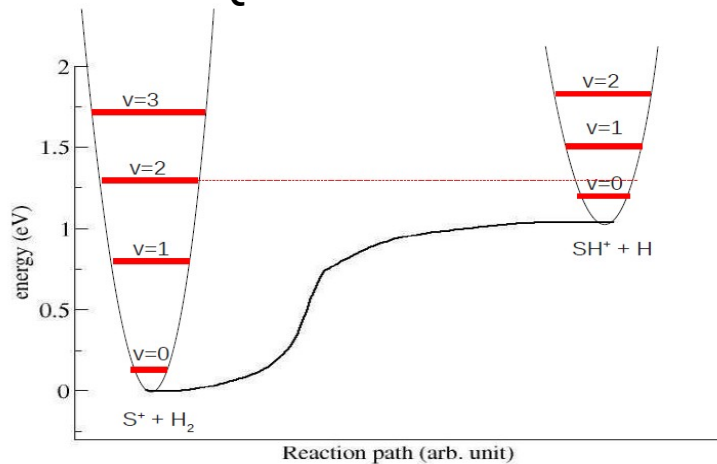-SH⁺ detected in 2010 (Hershel)

→ contribution of $S^+ + H_2$?

- endothermic reaction (+0.89 eV) for v=0 → open for v=2

- no well in quartet state

→ need vibrational specific thermal rate constants

→ use of QCT method

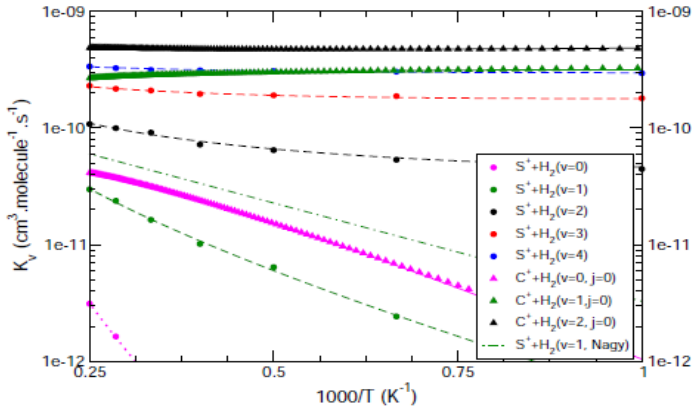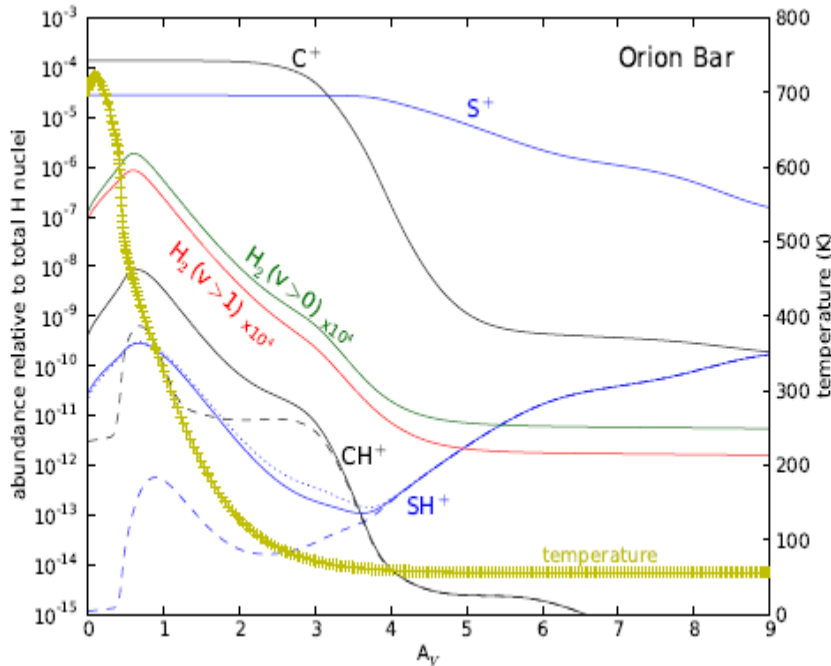Contour plot (Jacobi) for θ=0º, 30º,60º & 90º

S⁺+H₂
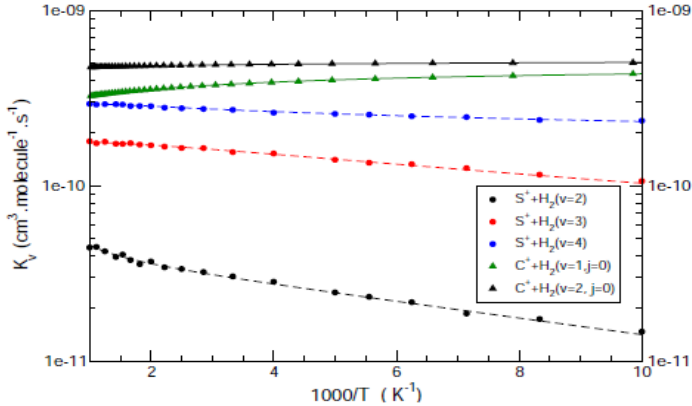
- high rate constant v>1
(~ 10^{-11}-10^{-10})
increase of several
order of magnitude
compared for v=0,1

- rate constants lower
than for C^+
   → no well
   → more endothermic

Abundance model

Model for the Orion Bar of the relative abundances of SH+, S+, CH+, C+, H2(v >0), and H2(v > 1) as a function of the depth in the cloud (expressed in visual extinction AV)

- $S^+ + H_2$ reaction important for production of SH^+

→ relative increase of the predicted abundances of SH^+ and CH^+ (5 and 3 order of magnitude respectively)

- concentration of CH+ and SH+ still underestimated compared to observations

→ effects of spin-orbit and non-adiabatic couplings ?

→ contribution from other reactions ?

Conclusion

- Prolific interaction between astrophysics and molecular physics

- rovibrational excitation of H_2 may enhance greatly reactivity

- thermal rate constants cannot always explain observations :
  vibrational specific or state to state rate constants may be required

   → any way to include them in KIDA ?

- standard equation often fails to fit rates in wide temperature range

   → any way to upload directly *ascii* file with numerical data ?

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