Pompage chimique de CH^+ et OH^+

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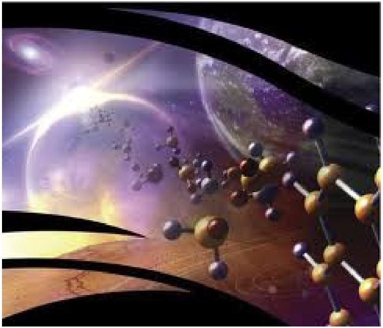
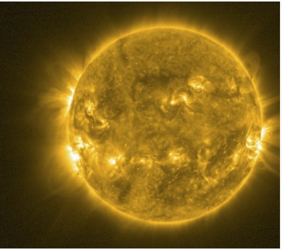
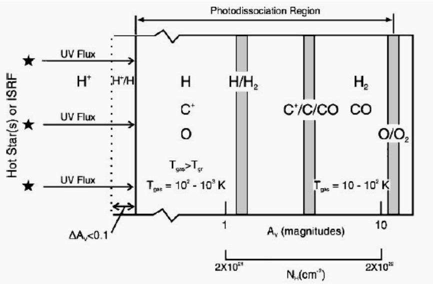


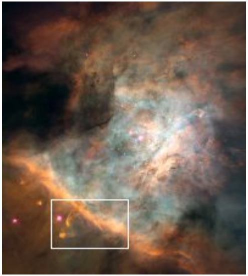
Outline

Molecular Universe

Hollenbach & Tielens, Annu. Rev. Astrophys. ('97)







<u>Stellar atmosphere:</u>
atomic lines
Atom+Atom collisions
Magnetic fields
Polarization of lines
Hanle effect

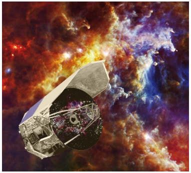
<u>PDR</u>
Formation of H_2
act as shield for other molecules

$$M^+ + H_2 \rightarrow MH^+ + H$$
$$M + H_3^+ \rightarrow MH^+ + H_2$$

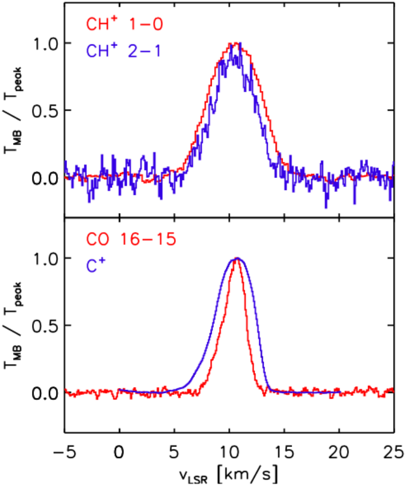
<u>Molecular clouds</u>
low temperatures
varying densities
formation of complex molecules

Molecules as probes

- Hydrogen is $> 70\,\%$ in mass
- The rest of elements detected in smaller fractions
- Detection of infrared-microwave individual transitions



CH, CH^+, OH^+, SH, SH^+, ...



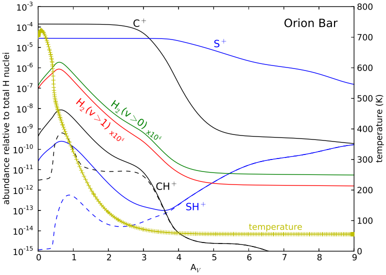
by Nagy, *et al.*, A & A (2013)

Molecules as probes

- Hydrogen is > 70 % in mass
- The rest of elements detected in smaller fractions
- Detection of infrared-microwave individual transitions
- Flux from different excitations

Beyond Maxwel-Boltzmann distributions for short-lived species

Need for final state formation rate



M. Agúndez, PDR model (Medon code)

Astrophysical conditions density, temperature, etc

Chemical pumping in molecular clouds and PDR's

- Exhothermic reactions of H_2 with atoms and ions

$$H_2(v=0) + O^+ \rightarrow OH^+(v',j') + H$$

Gómez-Carrasco, *et al.* ApJ,('14)

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- Chemistry of $H_2(v>0)$ in ISM

Agúndez, *et al.* ApJ, **713**,662 ('10)

Initial state dependent chemistry

$$H_2(v=1) + C^+ \rightarrow CH^+(v',j') + H$$ Zanchet, *et al.* ApJ,**766**,80 ('13)

$$H_2(v>1) + S^+ \rightarrow SH^+(v',j') + H$$ Zanchet, *et al.* AJ,**146**,125 ('13)

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- The most abundant ion is H_3^+

  - H_2^+ disappears in the exothermic $H_2 + H_2^+ \to H_3^+(v) + H$ reaction

    6D PES, Sanz-Sanz, *et al.* JCP,**139** , 184302 ('13)

  - However $H_2 + H_3^+ \to H_3^+ + H_2$ (ortho/para conversion, deuteration)

    9D PES, Aguado, *et al.* JCP,**133** , 024306('10)

    QCT biased statisitcal model, Gomez-Carrasco, *et al.* JCP,**137** , 094303 ('12)

  - H_3^+ is very reactive with other species: $H_3^+ + O \to H_2 + OH^+$

Outline and acknowledgements

- Reactive collisions: A+BC → AB+C

  - Endothermic from excited vibrational states C^++H_2(v)
    A. Zanchet, B. Godard, N. Bulut, P. Halvick and J. Cernicharo

  - Exothermic from excited vibrational states O^++H_2(v)
    S. Gómez-Carrasco, B. Godard, F. Lique, N. Bulut
    J. Kloss, A. Aguado, F.J. Aoiz, J. F. Castillo
    J. R. Goicoechea, M. Etxaluze and J. Cernicharo

- Inelastic vs. exchange collisions:

  - OH^+ + H → H + OH^+(v'J') in two PES's
    N. Bulut and F. Lique

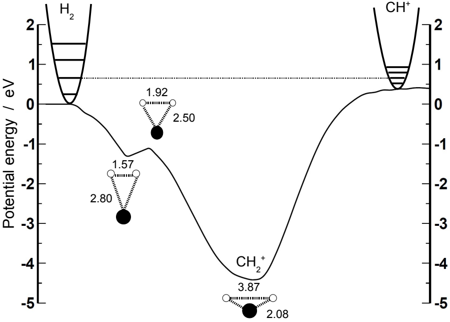
Outline

$C^+ + H_2$: PES

$$C^+(^2P) + H_2(v, j = 0) \rightarrow CH^+ + H$$

Ground state PES by
Stoeklin & Halvick, PCCP('05)

- Deep well ≈ 4.5 eV
- Endothermic by ≈ 0.38 eV
- No Quantum dynamical calculation.

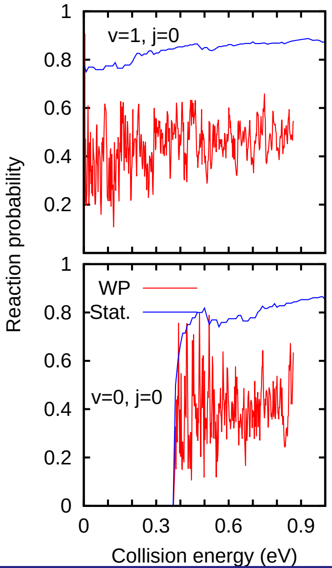


$C^+ + H_2$: Total Reaction Probabilities for J=0

$$C^+(^2P)+H_2(v=0,1,j=0) \rightarrow CH^+(v',j')+H$$

Full dim. Wave packet dynamics
reactant Jacobi coor. with MADWAVE3

- Dense grids: about 105 Mpoints (including hecility Ω)
- Many resonances: CH_2^+ complex
  long propagation times
- For H_2(v=0): threshold at $\approx$ 0.38 eV
- For H_2(v=1): no threshold
- Statistical model does not work properly



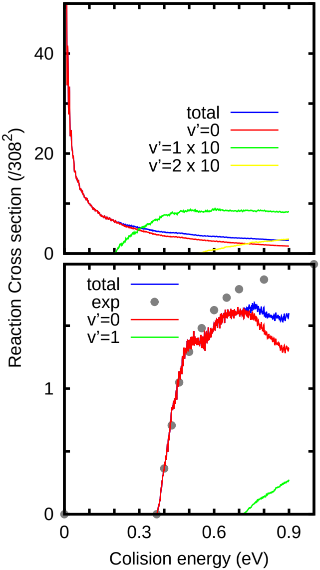
$C^+ + H_2$: Integral Reaction Cross section

$$C^+(^2P) + H_2(v=0,1,j=0) \rightarrow CH^+(v',j') + H$$

J=0,1,2,..., 20
J=20, 25, 30, ..., 50

J-shifting interpolation for $J > 20$

- Experimental data:
  Gerlich, Disch & S. Scherbarth, JCP ('87)
  in arbitrary units
- Inclusion of electronic partition function:
  0.407 at 300K
  with the $C^+(^2P_{1/2,3/2})$ spin-orbit splitting
  64 cm^{-1}



C$^+$ + H$_2$: State-to-state rate constants

$$C^+(^2P)+H_2(v=1,j=0) \rightarrow CH^+(v',j')+H$$

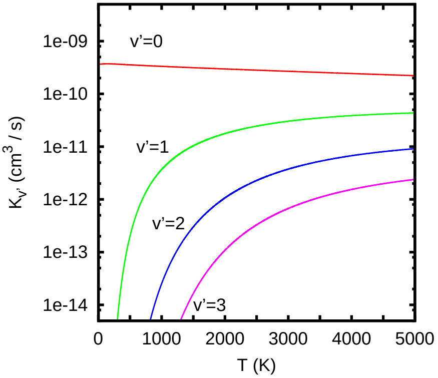
- No threshold for $j' < 8$

  Langevin extrapolation

  to avoid WP errors

- State-to-state coefficients

$$K_{vj\rightarrow v'j'}(T) = \sqrt{\frac{8}{\pi\mu\,(k_BT)^3}} \times \int_0^\infty EdE \quad \sigma_{vj\rightarrow v'j'}(E)\, e^{-E/k_BT}$$



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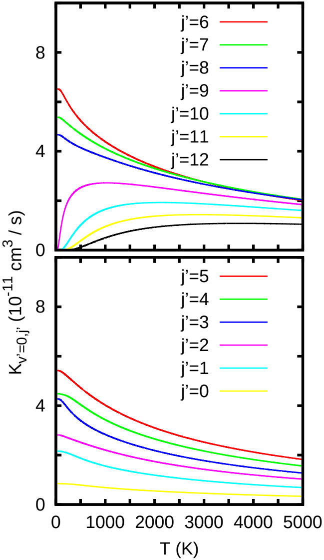


Astrophysical models

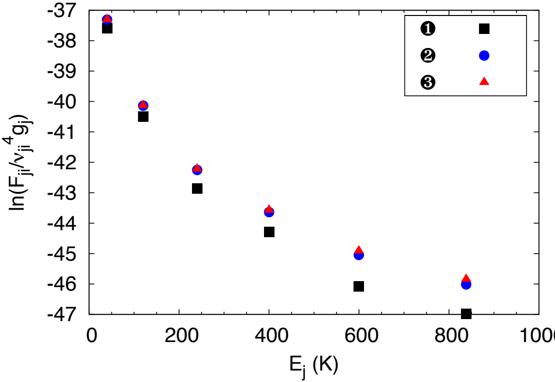
- PDR model of Orion bar (Madex code)

- Intensity of some lines of $CH^+(j' > 0)$

- Improves previous models

- Still discrepancies

Zanchet *et al.*, ApJ ('13) 766:88



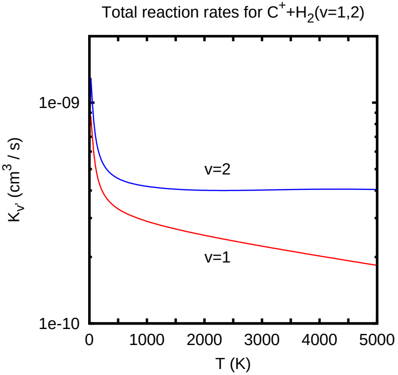
Chemical pumping increases flux from higher j's

Possible improvements

Zanchet *et al.*, AJ ('13) 146:125

also $S^+ + H_2(v > 2)$

- Higher $v > 1$ contributions still need to be included in PDR models

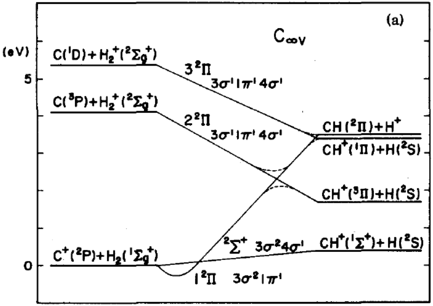


Possible improvements

- Higher $v > 1$ contributions still need to be included in PDR models
- Only $^2P_{1/2}$ reacts

$$Q_e(T) = \frac{2}{2 + 4e^{-91,2/T}}$$

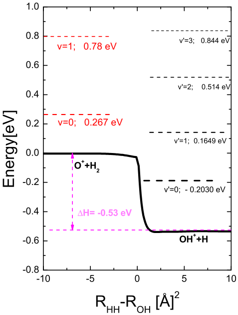
- Non-adiabatic and spin-orbit transitions



Outline

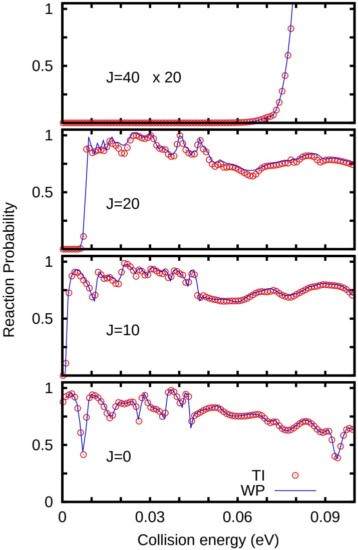
$H_2(v=0, j=0) + O^+(^4S) \rightarrow H + OH^+(v', j')$

PES: Martínez, *et al.*, JCP ('04)



$$P^J(E) = \sum_{v'j'} |S_{v,j\rightarrow v'j'}|^2 \rightarrow$$

Good agreement with TI-ABC
E≥ 0.1 meV !!



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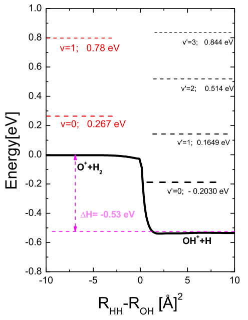

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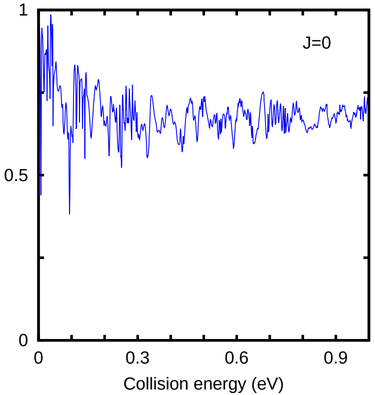

J-shifting approach

- J-shifting approach: Bowmann ('85)

$$P_J(E) = P_{J=0}(E^*) \quad \text{with} \quad E^* = E - BJ(J+1)$$

ovestimates reaction probabilities for $J >> 0$

- J-shifting interpolation:

$$P_J(E) = \frac{J - J_1}{J_2 - J_1} P_{J_1}(E_1) + \frac{J_2 - J}{J_2 - J_1} P_{J_2}(E_2) \quad \text{with} \quad J_1 < J < J_2$$

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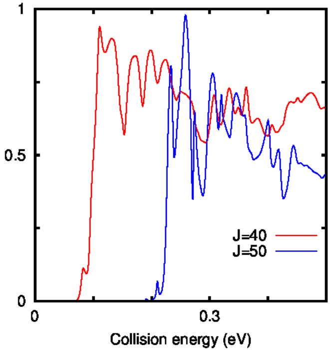

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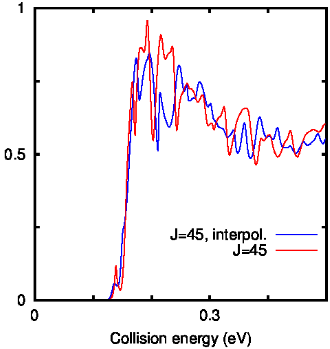


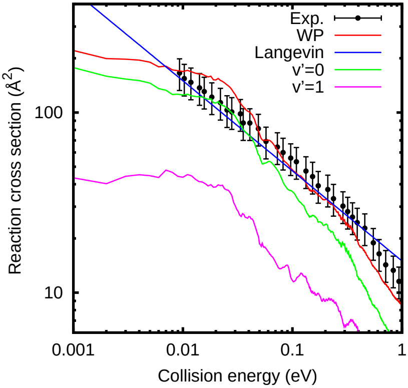
Cross section: $H_2(v=0, j=0) + O^+$

$$\sigma_{vj} = \frac{\pi}{k^2} \sum_J (2J+1) P^J(E)$$

Experiment:
Burley, Ervin, Armentrout, ('87)

Langevin model works for total σ_{vj}

but not for individual $\sigma_{vj \to v'j'}$!!

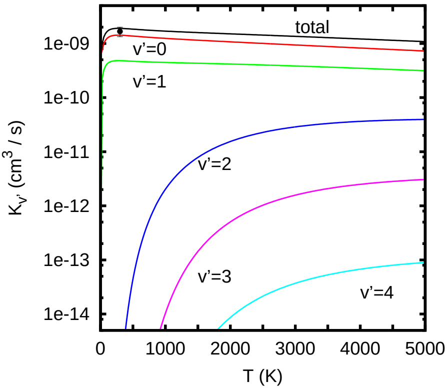


State-2-state rates: $H_2(v=0, j=0) + O^+$

Gomez-Carrasco *et al.*, ApJ 794:33 ('14)

$$K(v,j,v',j')(T) = \left[\frac{8}{\pi\mu\,(k_B T)^3}\right]^{1/2}$$

$$\times \int_0^\infty E\,\sigma_{vj\to v'j'}(E) e^{-E/k_B T}\,dE$$



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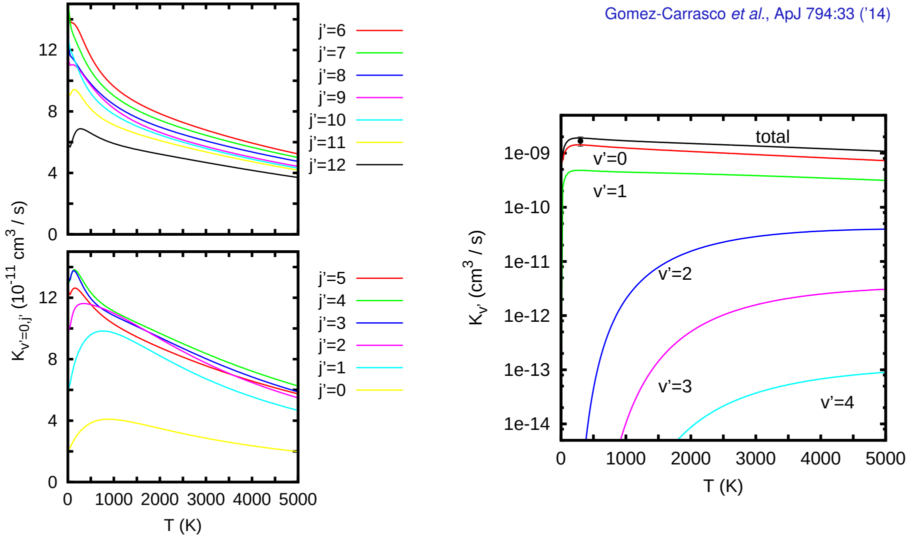
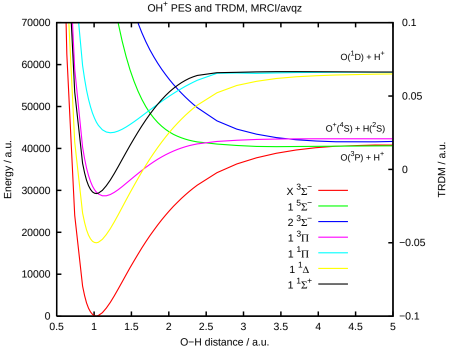
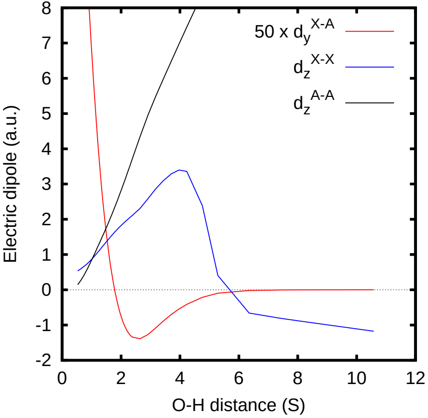


$OH^+(X^3\Sigma^-, A^3\Pi)$ radiative rates



- $OH^+(X^3\Sigma^-)$: Hund's case b
- $OH^+(A^3\Pi)$: Hund's case a
- Reasonable agreement with experiment
  Merer *et al.* ('75)

$OH^+(X^3\Sigma^-, A^3\Pi)$ radiative rates



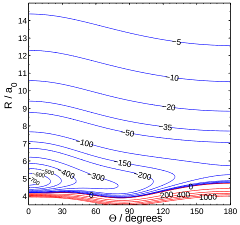
Radiative Lifetimes of A: τ_b

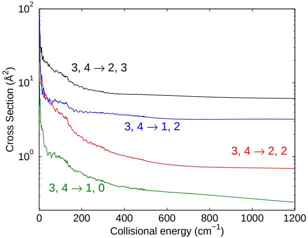
v	τ_v (ns)	τ_v^a (ns)	τ_v^b (ns)
0	2524	2410	2400±300
1	2665	2560	
2	2820	2930	
3	3004		
4	3233		
5	3534		
6	3960		
7	4637		
8	5961		
9	9559		
10	16118		

[a] Merchan *et al.* ('91) [b] Möhlman *et al.* ('78)

$OH^+(X^3\Sigma^-)$ collisional rates with He

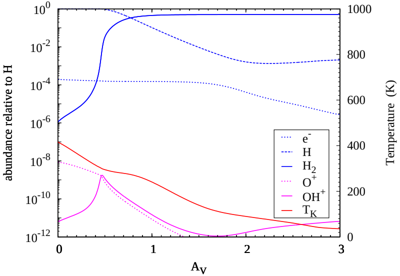
- New PES for He+ $OH^+(X^3\Sigma^-)$
  F. Lique and J. Kloss
- TI-CC calculations of inelastic rates
  F. Lique and J. Kloss
- H + OH^+ and H_2 + OH^+ rates were scaled

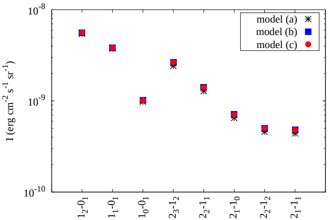




$OH^+(X^3\Sigma^-)$ in dense and hot PDR

Meudon PDR chemical model under 3 conditions: B. Godard
(a) only non-reactive collisions
(b) chemical pumping, products according to Boltzmann distribution at 2000K
(c) chemical pumping using WP state to state rates





χ =10^4 and n = 10^4 cm^3

Gomez-Carrasco *et al.*, ApJ 794:33 ('14)

- N $<$ 3 driven by OH^++H collisions
- Chemical pumping for N> 3 (?)

Outline

$OH^+(X^3\Sigma^-)$ + H inelastic collisions

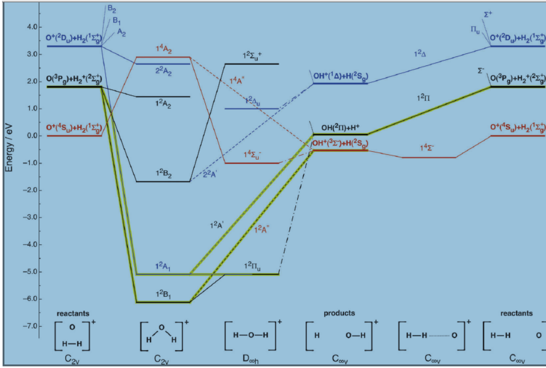
- Need of accurate description:
  - Beyond mass scaling
  - Validity of rigid rotor
- Exchange reaction:

$$H + OH^+(v,j) \rightarrow HO^+(v',j') + H$$

- 2 Open shell systems:

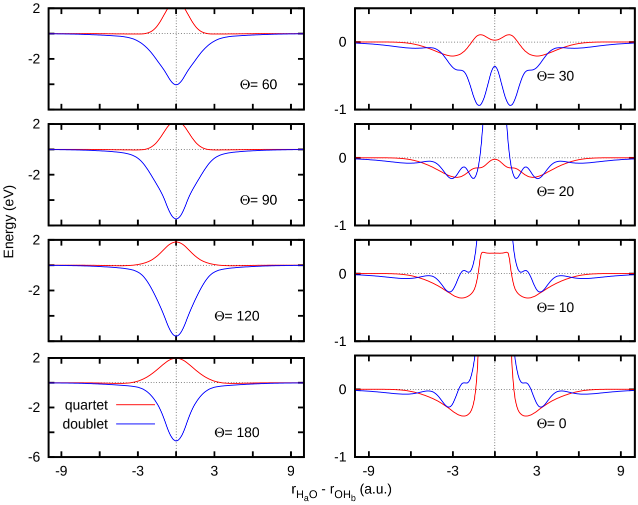
  $OH^+(^3\Sigma^+) + H(^2S)$

  doublet and quadruplet states

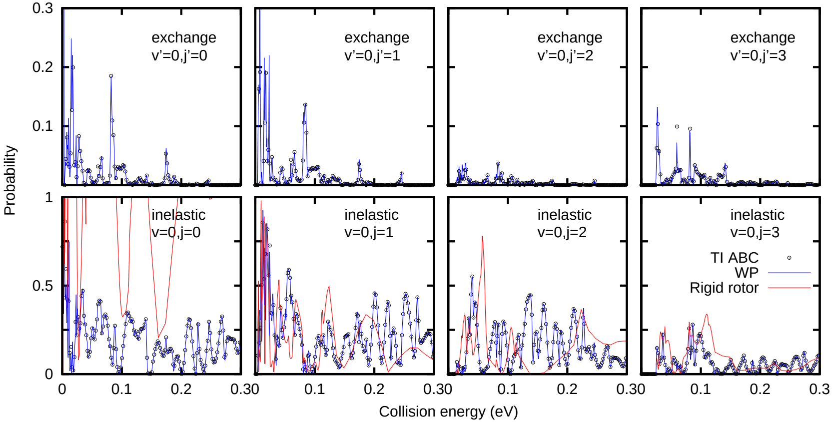


Paniagua *et al.*, PCCP,(2014),**16**, 23594

MEP's for exchange: two mechanisms



Quadruplet: H + $OH^+(v = 0, j = 0, J = 0)$



- Good agreement WP vs. TI-ABC
- Rigid rotor of the same order

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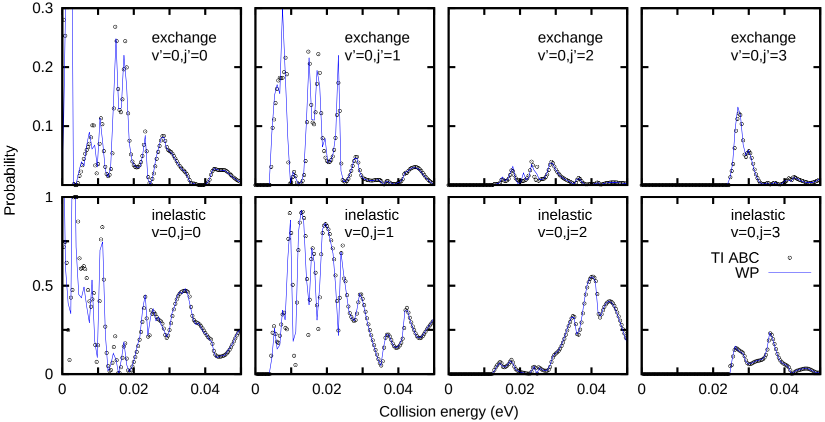
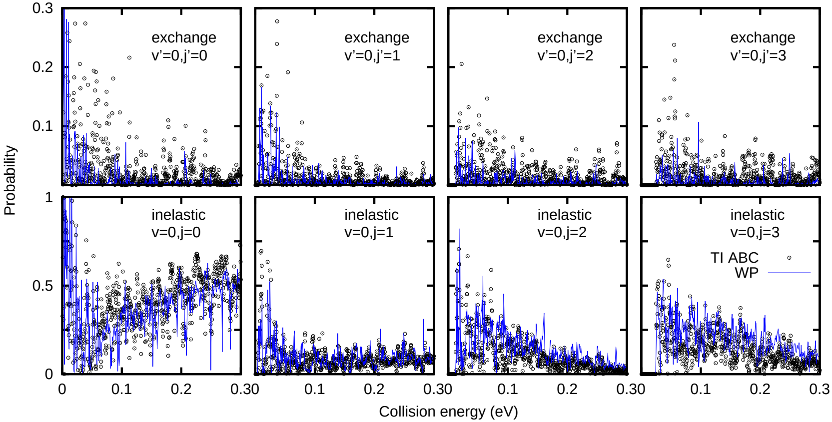


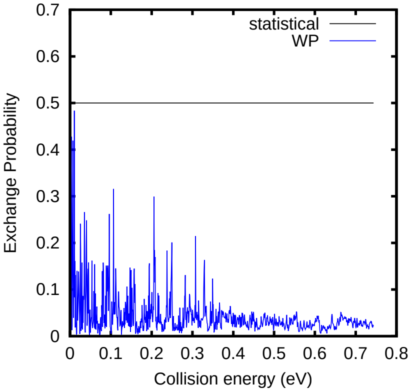
- Good agreement WP vs. TI-ABC, even at rather low energies!!
- Rigid rotor of the same order

Doublet: H + $OH^+(v=0, j=0, J=0)$



- **Many resonances**
- **Comparison difficult using different coordinates**
- **Even ABC has problems when** $D_{H-OH^+} \leq D_{OH^+}$

Is the exchange statistical in the doublet state?



Non statistical
energy transfer inefficient

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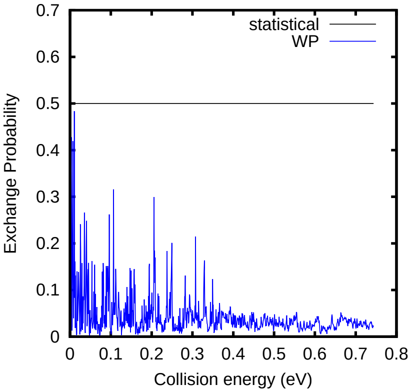
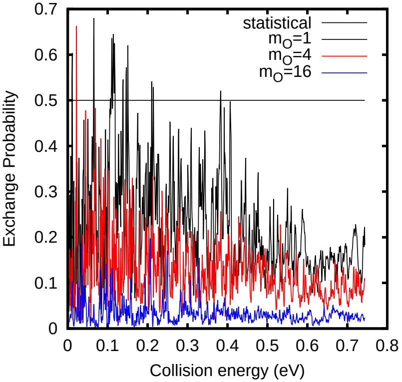




Non statistical
energy transfer inefficient

Energy redistribution increases
- **as energy decreases**
- **and mass difference reduces**

Cross sections: inelastic and exchange for quadruplet

$$\text{H} + \text{OH}^+ \ (v=0, j_i=0,1) \rightarrow \text{HO}^+ \ (v=0, j_f=0) + \text{H}$$

For quadruplet:

$8\ 10^4$ iterations

J=0,5,10,15,20,25,30,40,..., 110

Ω_{max}= 15

$j_i = 0, 1$

For doublet:

$2.5\ 10^5$ iterations and denser grids

Calculations still in progress

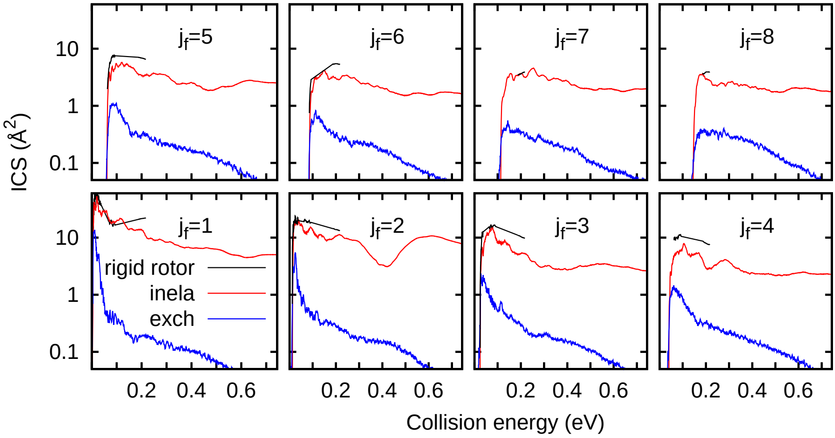
Ω_{max}= 19

$j_i = 0$

Cross sections: inelastic and exchange for quadruplet

$$\text{H+ OH}^+ \ (v=0, j_i=0,1) \rightarrow \text{HO}^+ \ (v=0, j_f=0) + \text{H}$$

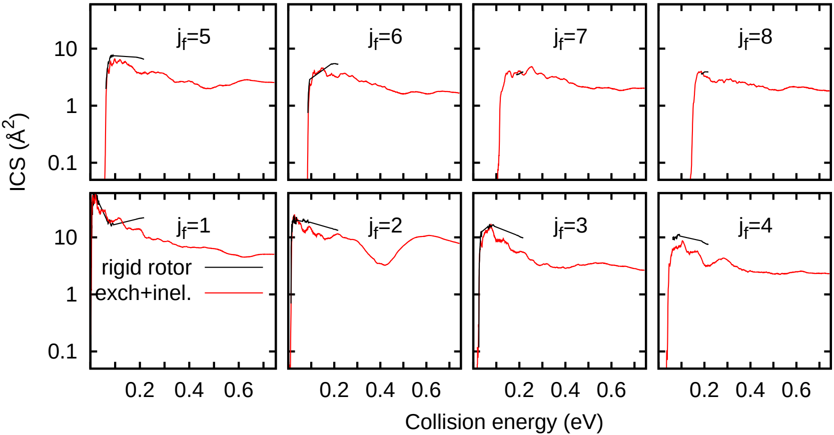
$j_i = 0$



Cross sections: inelastic and exchange for quadruplet

$$\text{H+ OH}^+ \ (v=0, j_i=0,1) \rightarrow \text{HO}^+ \ (v=0, j_f=0) + \text{H}$$

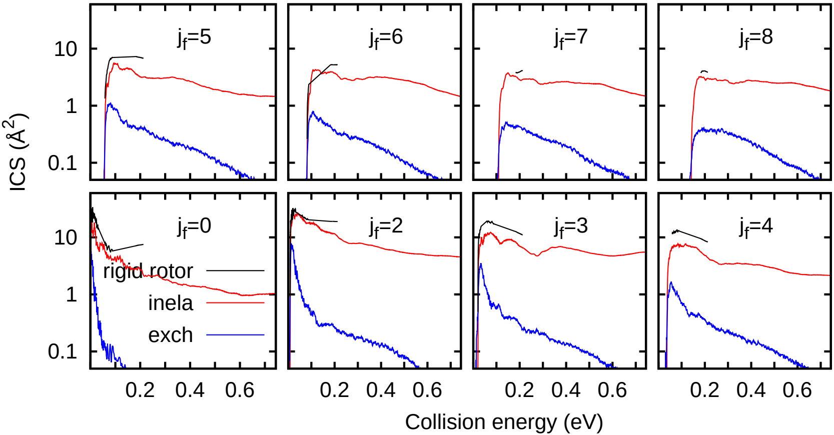
$j_i = 0$



Cross sections: inelastic and exchange for quadruplet

$$\text{H} + \text{OH}^+\ (v=0, j_i=0,1) \rightarrow \text{HO}^+\ (v=0, j_f=0) + \text{H}$$

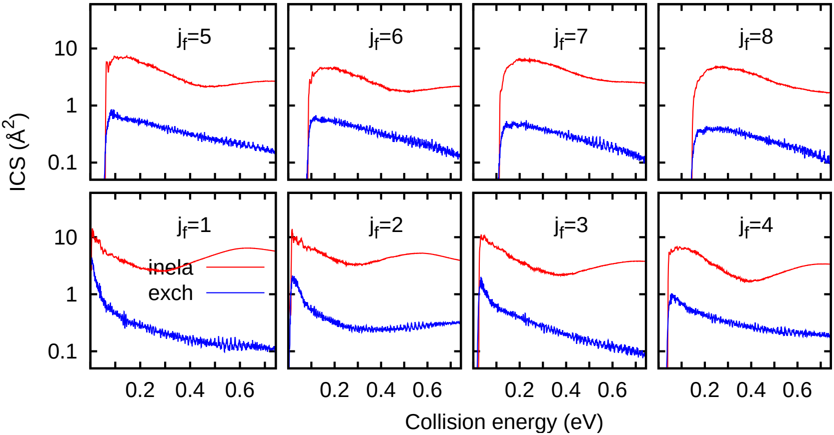
$j_i = 1$



Cross sections: inelastic and exchange for doublet

$$\text{H+ OH}^+ \ (v=0, j_i=0,1) \rightarrow \text{HO}^+ \ (v=0, j_f=0) + \text{H}$$

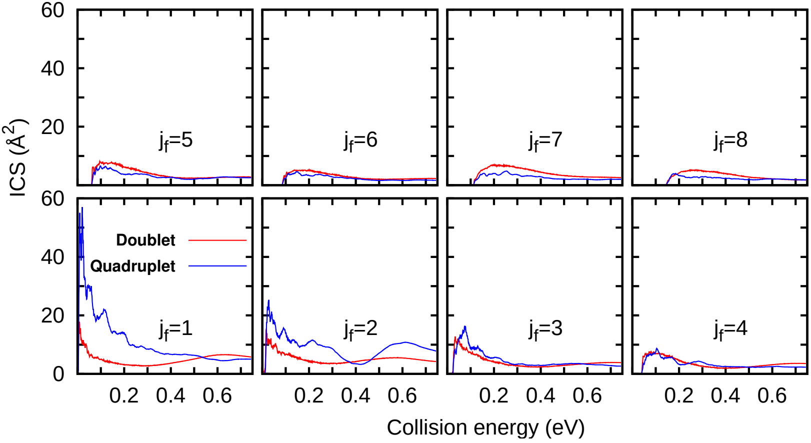
$j_i = 0$: Preliminary



Cross sections: inelastic and exchange for doublet

$$\text{H+ OH}^+ \ (v=0, j_i=0,1) \rightarrow \text{HO}^+ \ (v=0, j_f=0) + \text{H}$$

$j_i = 0$: Doublet vs. quadruplet



Outline

Conclusions and perspectives

- Chemical pumping improves the description of the flux of relatively high rotational excitations of hydrides
- For low rotational excitations, inelastic scattering with H and H_2 becomes dominant
- Collisions with H(^2S) imply several electronic states for open shell hydrides like $OH^+(^3\Sigma^-)$
- Exchange reactions have a considerably lower cross section than inelastic collisions
- In the quadruplet case, with a relatively shallow well, the agreement between rigid rotor and exact (including inelastic+exhance) is very good.
  This has to be checked for the doublet state with a deep insertion well.
- A proper electronic partition function need to be included in open shell systems
- Also the recoupling with the electronic spin should be done to provide results comparable with the observations