Ortho/para conversion of H_3^+ in collisions with H_2 and H

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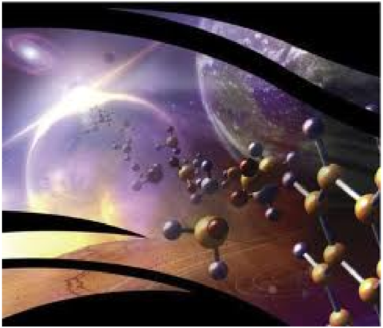


Outline

1. Introduction
2. H_n^+ PES's
3. H_2+H_3^+ exchange reaction
4. Reactions with barriers
   - H+H_3^+ exchange reaction
   - COM's with OH
5. Conclusions

Hydrogen in Universe

- Hydrogen is $\approx 90\,\%$ of the mass of Universe

- The most abundant ion is H_3^+:

  - Participate in the formation cycle of many molecules at low T

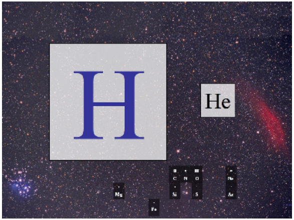
  - Absence of many reaction rate constants

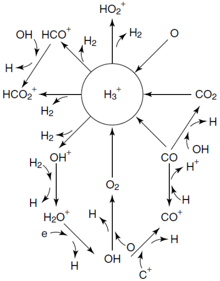
  $$H_3^+ + HD \rightarrow H_2D^+ + H_2$$

  Deuterated species $>$ D quantity

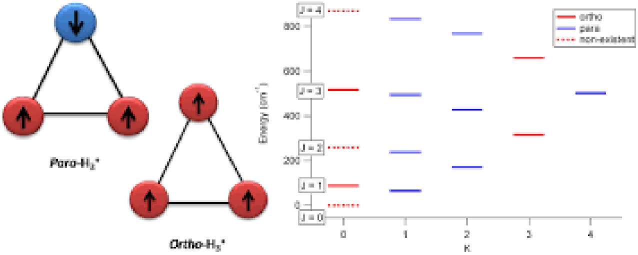
  - Formation: $H_2 + H_2^+ \rightarrow H_3^+ + H$

- Quantum behaviour and low temperatures





Ortho/para H_3^+



- Differences between ortho/para energies at low T
- Nuclear spin is non-separable for three particles
  But Full symmetry as: $\Gamma^{Spin} \times \Gamma^{Rovib}$
  For H_3^+ this is possible using hyperspherical coor.
  Bound states: Aguado et al. ('00)
  Collisions: Honvault et al. ('06,...)

For larger systems ?

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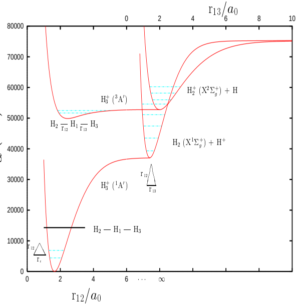
H_n^+: Potential energy surfaces

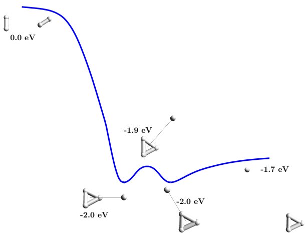
$$H^+ + H_2 \rightarrow H_2 + H^+$$



3 Dimensions

Aguado, et al.('00)

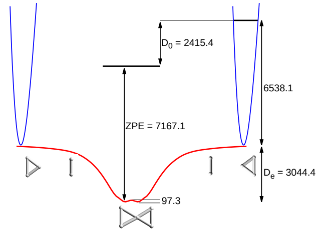
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$



6 Dimensions

Sanz-Sanz, et al.('13)

$$H_3^+ + H_2 \rightarrow H_2 + H_3^+$$



9 Dimensions

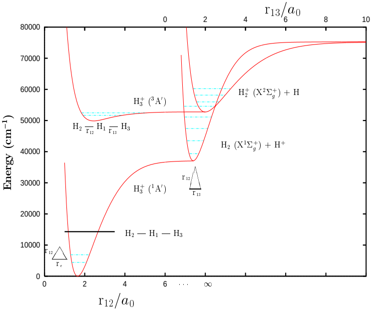
Aguado, et al.('10)

- Proton exchange reaction: multistate problem
- Long interaction to describe low temperature

Fitting procedure for H_n^+

Need of Multiple Surface to describe charge transfer

- H_3^+: $V = H_{DIM} + V_{3B}$ Aguado *et al* ('00)
  - Long range behavior: Charge-quadrupole & induced dipole in diagonal of DIM matrix Velilla *et al* ('08)
  - Coupled diabatic PES's: 3-body terms in DIM matrix Varandas & co. ('07)



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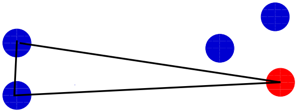
  - - Long range behavior: Charge-quadrupole & induced dipole in diagonal of DIM matrix Velilla *et al* ('08)
  - - Coupled diabatic PES's: 3-body terms in DIM matrix Varandas & co. ('07)
- H_4^+ & H_5^+: $V = H_{TRIM} + V_{NB}$ Aguado et al.('10), Sanz et al.('13)

$$\hat{H}_{TRIM}(i) = \sum_{n>i,o>n} \hat{H}^+_{ino}(n-i,o-i) - 2\sum_{p>i} \hat{H}^+_{ip}(p-i)$$



- High accuracy in fitting
- Long range interaction
- Symmetric under permutation
- Accurate triatomic fragments
- Non-adiabatic couplings

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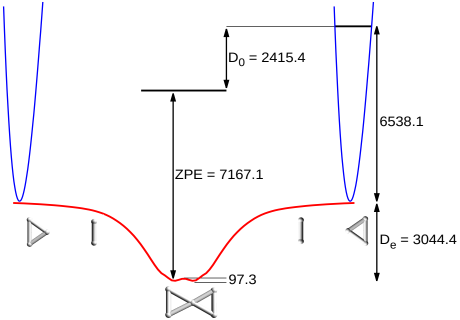
$H_3^+ + H_2 \rightarrow H_2 + H_3^+$ exchange reaction

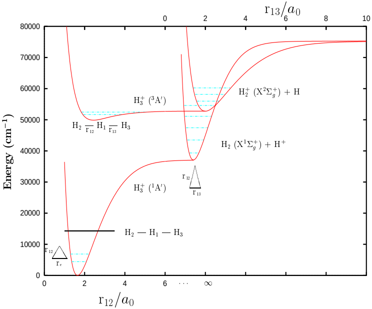
- Production of H_2D^+
- Ortho/para conversion of H_3^+
- Large Zero Point energy

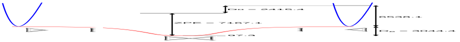


$$
\begin{aligned}
(HHH)^+ + HH &\rightarrow (HHH)^+ + HH && \text{inelastic} \\
&\rightarrow HH + (HHH)^+ && \text{hop}: \quad 3\,\text{channels} \\
&\rightarrow HH + (HHH)^+ && \text{exchange}: \quad 6\,\text{channels}
\end{aligned}
$$

Each pathway obeys strict nuclear spin selection rules Cordonnier et al. ('00)
This allows to "infer" the hop/exchange ratio: $\alpha = k^H/k^E$ Crabtree et al. ('11)

$H_3^+ + H_2 \rightarrow H_2 + H_3^+$ exchange reaction





$$\begin{array}{lll} (HHH)^+ + HH & \rightarrow & (HHH)^+ + HH \\ & \rightarrow & HH + (HHH)^+ \\ & \rightarrow & HH + (HHH)^+ \end{array}$$

inelastic

hop : 3 channels

exchange : 6 channels

Each pathway obeys strict nuclear spin selection rules Cordonnier et al. ('00)

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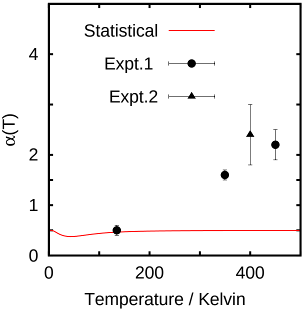
hop/exchange ratio, α, and statistical behaviour



α inferred from observed p-H_3^+ fraction vs. p-H_2 enrichment

Expt. 1: Crabtree et al. JCP ('11)
Expt. 2: Cordonnier et al. JCP ('00)

H_5^+ complex lives enough
to allow full scrambling

Statistical limits:

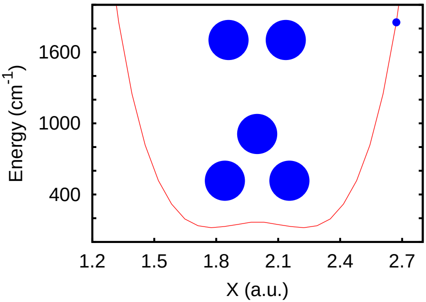
Parker& Light('07), Hugo *et al.*('09)

- no scrambling $S_M = \{1/4, 3/4, 0\}$ $\alpha = \infty$
- full scrambling $S_M = \{1/10, 3/10, 6/10\}$ $\alpha =$0.5

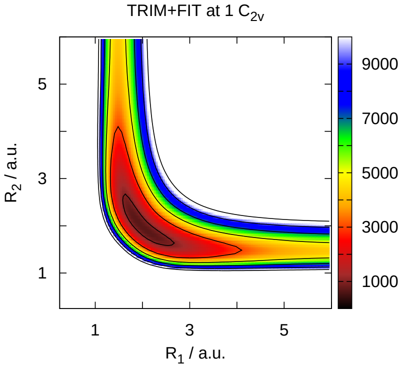
Need of dynamics to describe transition

Proton hop: direct mechanism

Double well for proton hop:
barrier < 100 cm^{-1}



Stabilization of the complex

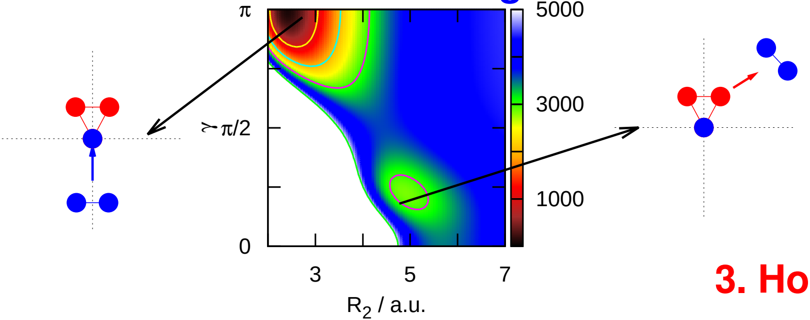


Exchange: indirect mechanism

1. Hop

Three steps mechanism:

2. Scrambling



3. Hop

Rotation of H_2 subunit with Scrambling barrier < 1500 cm^{-1}

≈ 1500 cm^{-1} below H_2 + H_3^+ asymptotic energy

Beyond Pure Statistical Models

- Need of dynamics to describe α transition

  - Many degree of freedom (10D)
  - Low energy and long-lived resonances
  - All atoms are equivalent: NO reduced dimension models
  - Quantum and many semiclassical methods difficult

- Introduce dynamical Bias through determination of S_M using Quassi-classical trajectories

Gómez-Carrasco et . al. JCP **137**, ('12), 094303

H_2+ H_3^+: Statistical model of Park & Light, JCP ('07)

For total angular momentum, J, and nuclear spin, I, the reaction probability

$$P^{JI\Omega}_{sr,M's'r'}(E) = \frac{g_{Is}\,\gamma^{M'}_{sIs'}\,W^{J\Omega}_{sr\nu\Omega_t}(E)\,W^{J\Omega}_{s'r'\nu'\Omega'_t}(E)}{\sum''\gamma^{M''}_{sIs''}\,W^{J\Omega}_{s''r''\nu''\Omega''_t}(E)}$$

1. Nuclear spin statistical weight matrix, g
2. Capture probability, $W^{J\Omega}_{sr\nu\Omega_t}$: Using full PES
3. Spin branching ratio matrices, $\gamma^{M'}_{sIs'}$
4. Scrambling matrix, $S_M = \{1/10, 3/10, 6/10\}$

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4. Scrambling matrix, S_M from dynamical calculations

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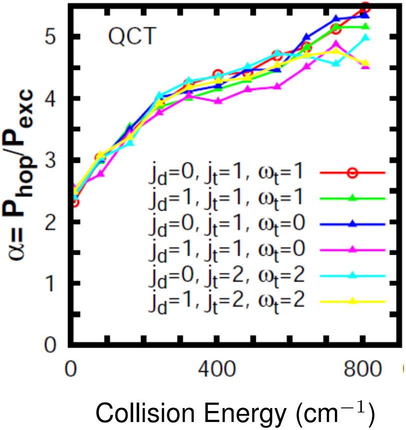
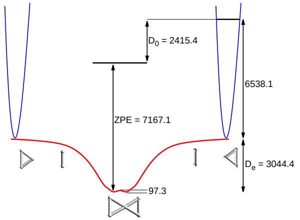
QCT Dynamically biased S_M and ZPE

$S_M(E)$ = QCT prob.



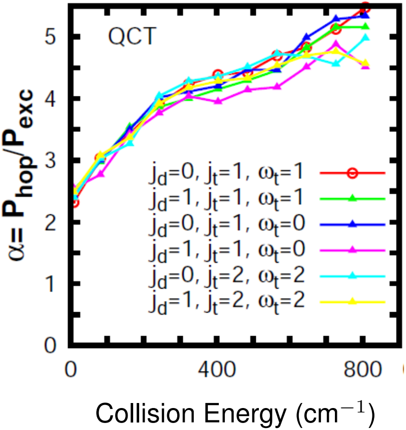


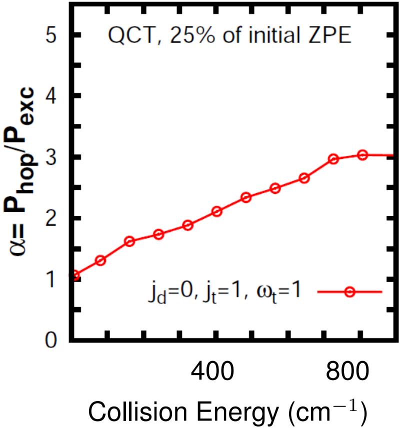
- α too high!!
- ZPE favors direct hop mechanism

QCT Dynamically biased S_M and ZPE

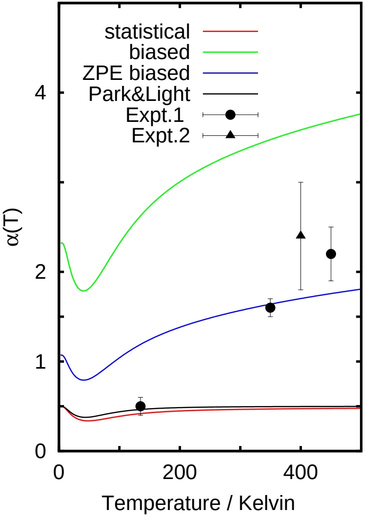
$S_M(E)$ = QCT prob. ZPE$_{H_2}$ + ZPE$_{H_3^+}$ = 6538 $\approx$ ZPE$_{H_5^+}$ =7167 cm^{-1}

ZPE reduction: Manikandan & Hase ('12)





Comparison with Experiments



Expt. 1: Crabtree, *et al.*, J. Chem. Phys.,**134**,('11)
Expt. 2: Cordonnier, *et al.*, J. Chem. Phys.,**113**,('00)
Simul. Gómez-Carrasco *et al* J. Chem. Phys.,('12)

- ZPE plays a fundamental role
- ZPE-biased "works" at T $>$ 300 K
- Statistical behaviour at T$<$ 200 K
- Need of quantum treatments
- Direct experimental information in infrared predissociation spectra

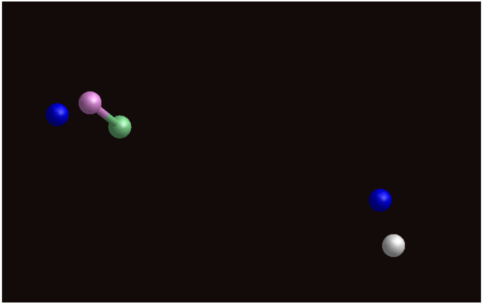
Experiments by Cheng et al. JPCI ('10)

Ring Polymer Molecular Dynamics: Ceriotti, *et al.* JCP ('10)

To include Zero Point Energy

The ussual approach is
for reactions with barriers

with Yuri Suleimanov



Here implemented in two steps:

1) Equilibration:

2) Direct dynamics of polymers:

Problems:
- Thermalized results:
  no state-to-state resolution
- At low temperatures (100K)
  very long trajectories

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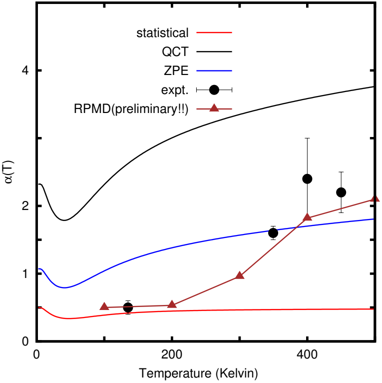

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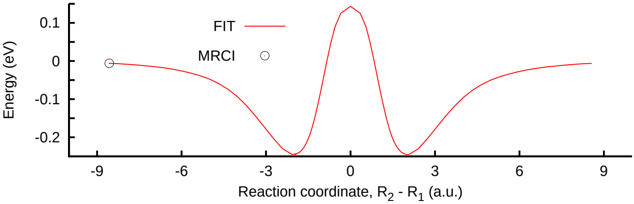
$H + H_3^+ \to H_3^+ + H$ exchange: MEP and PES

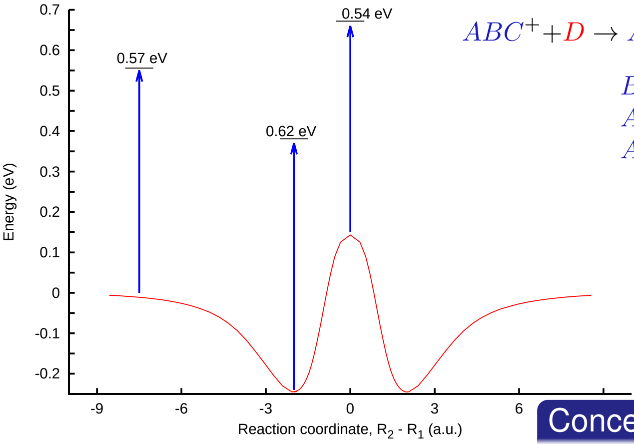
$ABC^+ + D \to ABC^+ + D \to$ inelastic

$$\left.\begin{array}{l} BCD^+ + A \\ ACD^+ + B \\ ABD^+ + C \end{array}\right\} \text{exchange}$$



Planar TS and well

$H + H_3^+ \rightarrow H_3^+ + H$ exchange: MEP and PES



$ABC^+ + D \rightarrow ABC^+ + D \rightarrow$ inelastic

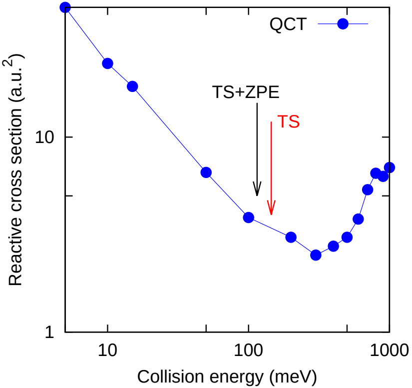
$$\left.\begin{array}{l} BCD^+ + A \\ ACD^+ + B \\ ABD^+ + C \end{array}\right\} \text{exchange}$$

Planar TS and well

Concerted mechanism

1. formation of complex
2. exchange

$H + H_3^+ \rightarrow H_3^+ + H$ exchange: cross section



• σ increases with decreasing E below the TS.

in agreement with Moyano, Pearson Collins ('04) for $E >>$

• Reactive trajectories are correlated to long time propagations associated to the formation of a H_4^+ complex

• need of experimental or quantum results to confirm

• Similar to reactions of COM's with OH

Chemisty at Cold Interstellar Clouds

- Experiments on "Accelerated chemistry at low temperatures" for CH_3OH + OH
  Shannon *et al.* Nature Chem. ('13)
  Gómez Martín *et al.* J. Phys. Chem.A ('14)

  Antiñolo *et al.* ApJ ('16)
- Use of TST including tunneling

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Antiñolo *et al.* ApJ ('16)

- Use of TST including tunneling
- CH_3OH + OH Imaginary frequency at TST unrealistic

Siebrand *et al.* PCCP ('16)

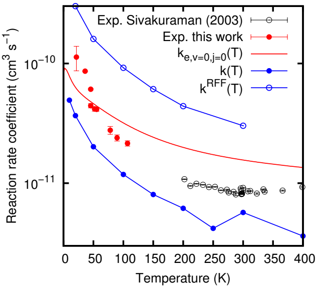
Reactivity due to dimer formation

- New experiments on H_2CO+OH

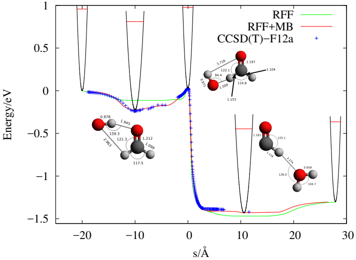
for $20 < T < 100$ K

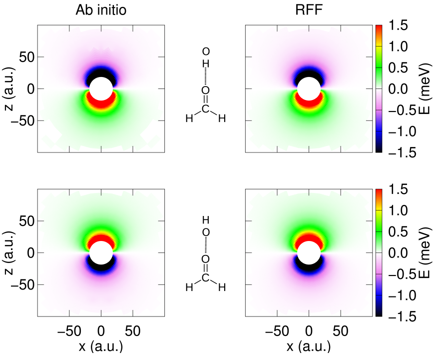
Ocaña *et al.* (in prep.)

barrier of 0.02 eV



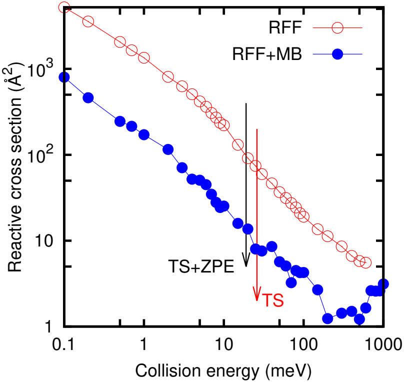
PES: IRC and long range check





Reactive cross sections: QCT treatment

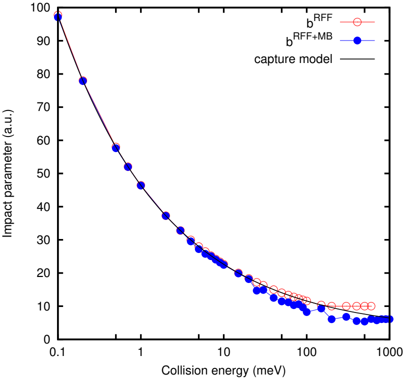
OH (j=0) +H_2CO (J=0) → HCO + H_2O



- $\sigma(E) = \pi \quad b_{max}^2 \quad P_r(E)$
- $\sigma(E)$ increases below TS!!

Impact parameter

OH (j=0) +H_2CO (J=0) → HCO + H_2O



- Long range interaction

  $$V(R\rightarrow\infty) = A/R^3$$

  The two dipoles re-orient at very long distances

- Assuming a capture model

  $$b_{max} = \sqrt{3}\;(A/2E)^{1/3}$$

Levine & Bernstein in “Molecular Reaction Dynamics”

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Conclusions ?

- H_2+ H_3^+ collisions: α ratio presents a transition from statistical behaviour at T$<$ 200K and a more direct mechanism at T$>$ 300 K.
  Need of Quantum methods to study this transition & to understand the statistical behaviour at low temperatures, due to long-lived resonances
- Ring Polymer Molecular Dynamics is a promising method

  Still challenging for low T
- H+ H_3^+ exchange reaction cross section, with a barrier (of 0.15 eV)
  H_2CO+OH rate, also with a barrier (of 0.02 eV),
  studied with classical methods increase at low temperature

  Capture at low energies, non TST valid for dynamics far from IRC
- Experimental evidence in the case of reactions of COM's with OH

  Need of Quantum methods for large systems and low energies

Acknowlegments

Collaborators

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