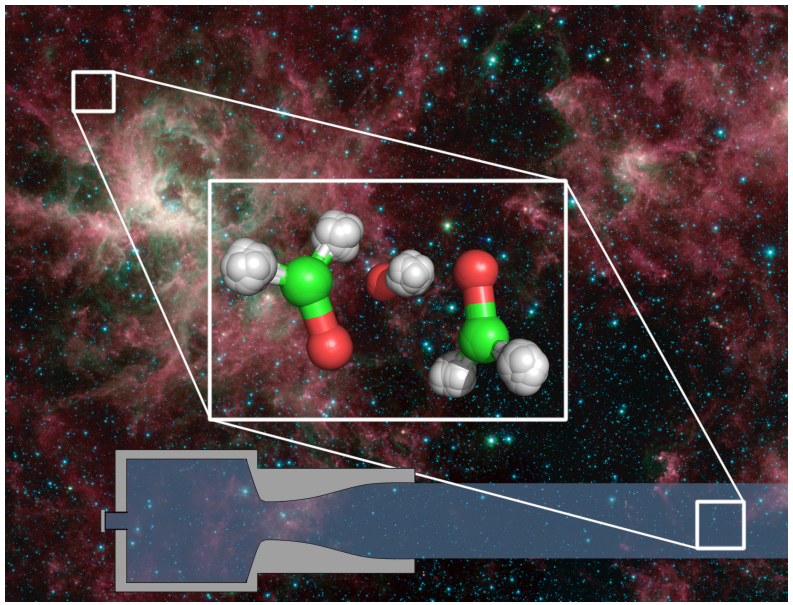
Complex forming reactions at the low temperatures of interstellar medium: from statistical to dynamical methods

Octavio Roncero

Inst. Física Fundamental, CSIC

Madrid (Spain)

octavio.roncero@csic.es



©P. del-Mazo-Sevillano et al.

Acknowledgements

Theory-Team

Alexandre Zanchet IFF-CSIC, Spain

Alfredo Aguado Univ. Autónoma Madrid, Spain

Pablo del Mazo Univ. Autónoma Madrid, Spain

Daniel Félix-González Univ. Autónoma Madrid, Spain

Susana Gómez-Carrasco Univ. Salamanca, Spain

Astro-team

J. Cernicharo IFF-CSIC, Spain

Javier Goicoechea IFF-CSIC, Spain

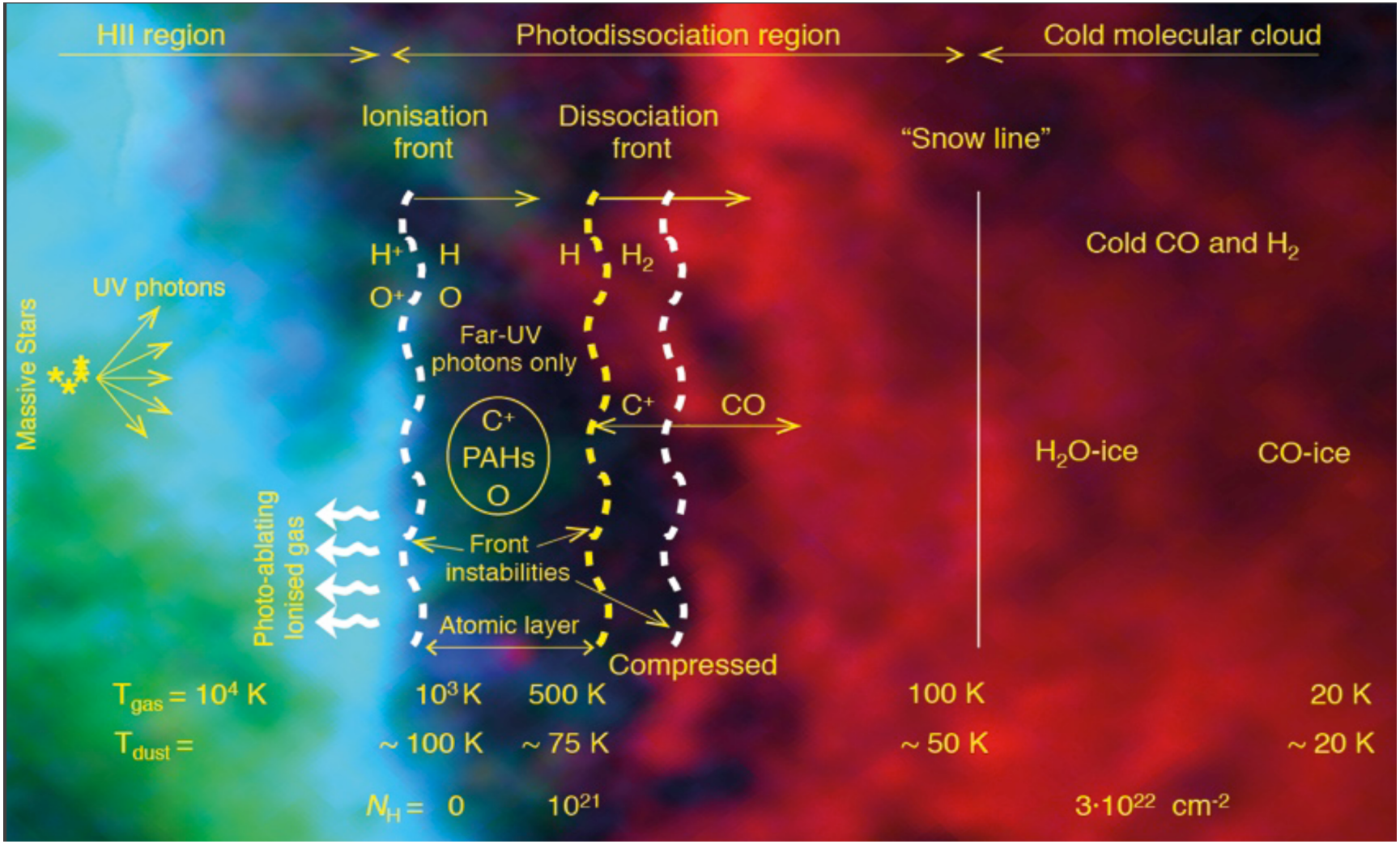
M. Agúndez, IFF-CSIC, Spain

Experimental-team

E. Jiménez, A.J. Ocaña, B. Ballesteros, M. Antiñolo, J. Albadalejo Univ. Castilla La Mancha, Spain

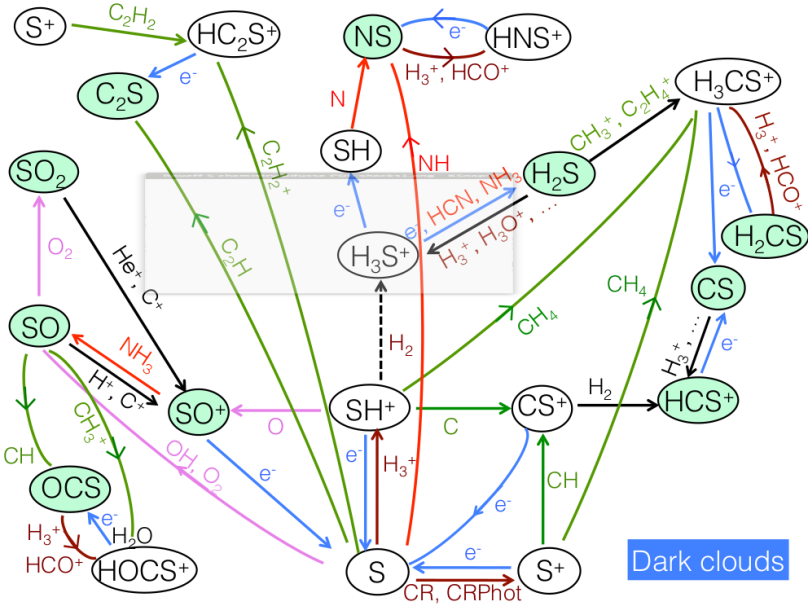
André Canosa Univ. de Rennes 1, France

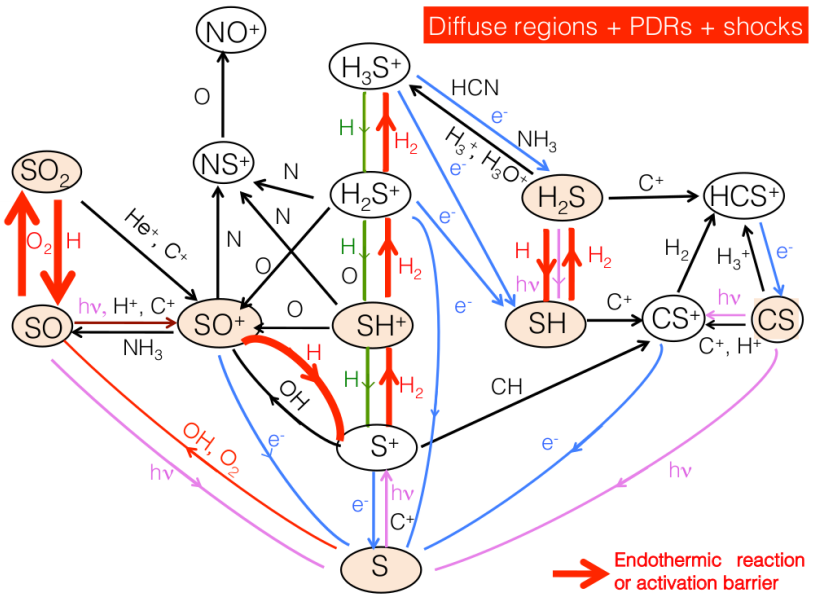
From PDR's to molecular clouds: chemical evolution



Courtesy J.R. Goicoechea

Chemical Networks:
Eg. Sulfure Chemistry (by Evelyn Roueff)





Objective: calculation of reaction rates under wide conditions

- To model molecular abundances → physical conditions
  Gas phase abundances → what is in condensed phases?
- To understand formation of new observed molecules

Outline: Reaction rates at low T (10 K)

- Statistical: formation of NH^+
  $N^+(^3P_J) + H_2 \rightarrow NH^+(X^2\Pi, a^4\Sigma^-, X^3\Sigma^-) + H$
  Gómez-Carrasco + ('22)
- Dynamics: reactions of COM's
  $H_2CO/CH_3OH + OH$
  del Mazo-Sevillano + ('21)
- Role of dimers at low temperature
  $(H_2CO)_2 + OH$
  del Mazo-Sevillano + ('23)

Nitrogen hydrides

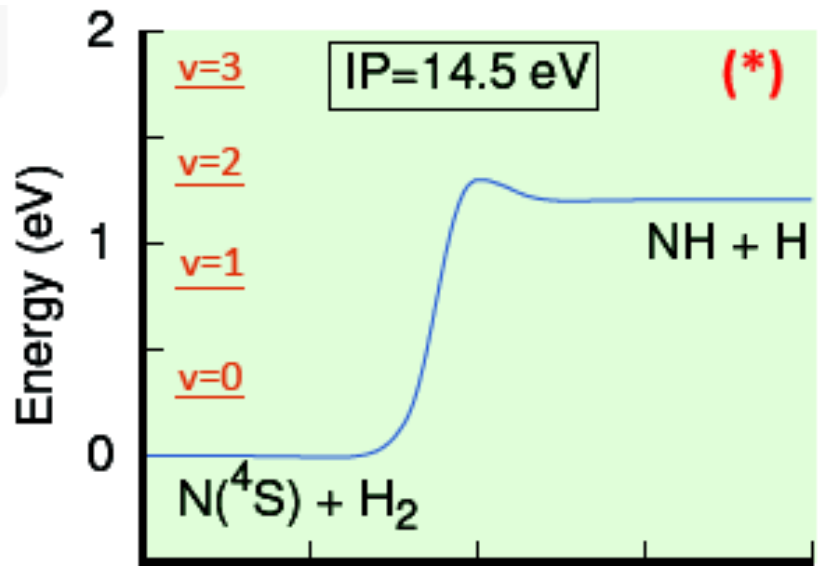
Chemical network for nitrogen hydrides:

$$N^+ \xrightarrow{H_2} NH^+ \xrightarrow{H_2} NH_2^+ \xrightarrow{H_2} NH_3^+ \xrightarrow{H_2} \begin{array}{c} H_4N^+ \\ \downarrow e \\ NH_2, NH_3 \end{array}$$

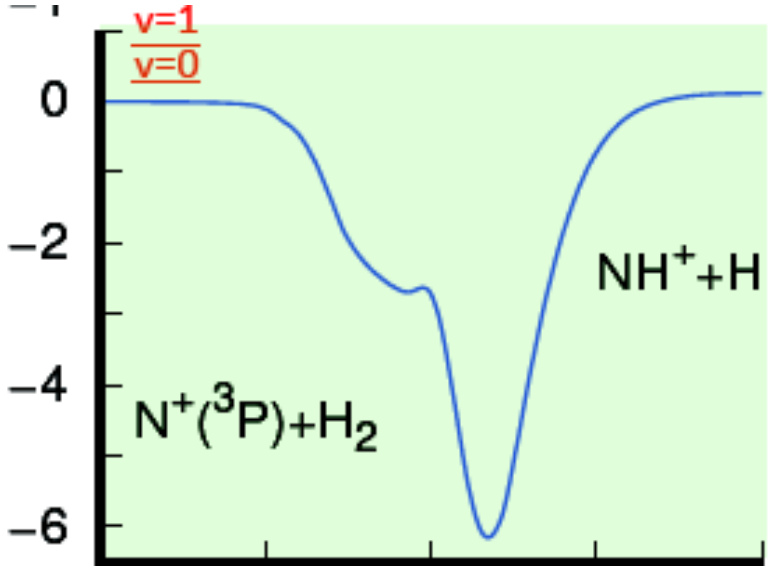
NH_2, NH_3 detection in Sgr B2 by van Dishoeck + ('93)
N has a large ionization potential
Le Gal + ('16); Pearson + (16): ...
BUT **NH^+** not detected yet: neutral route is an alternative?

$$N \xrightarrow{H_2} NH \xrightarrow{H_2} NH_2 \xrightarrow{H_2} NH_3$$

NH and NH^+ nitrogen hydrides

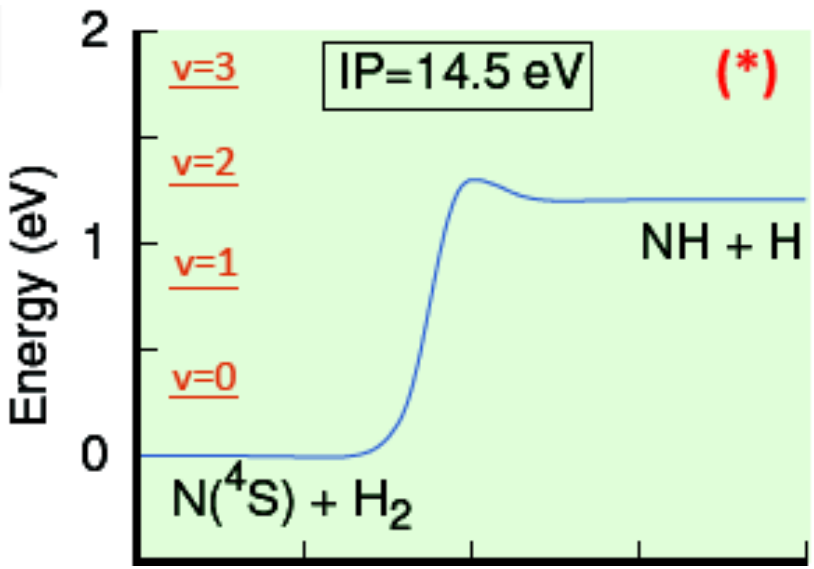


Large endoergicity
Low reactivity

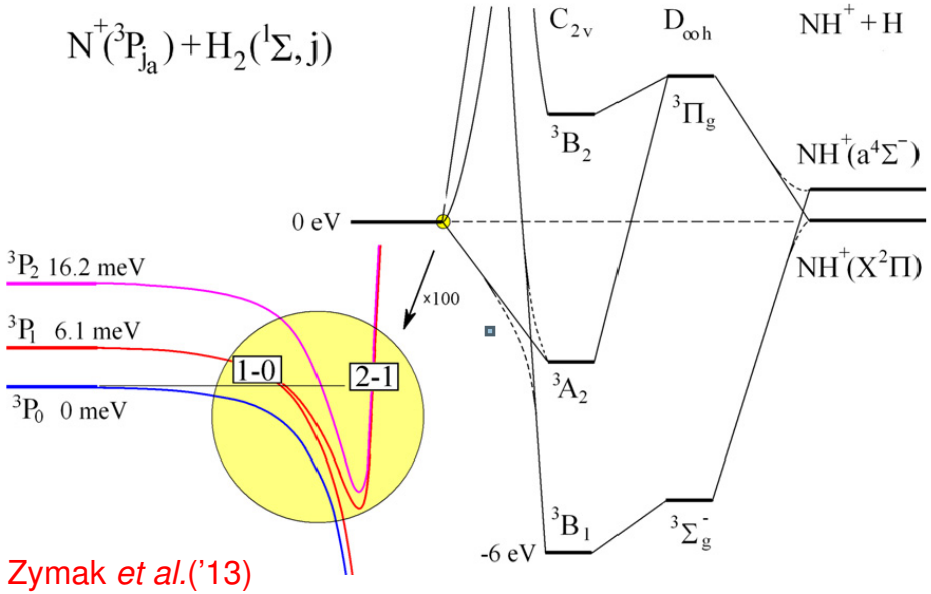


large ionization potential
low abundance

NH and NH^+ nitrogen hydrides



Large endoergicity
Low reactivity



Zymak *et al.*('13)

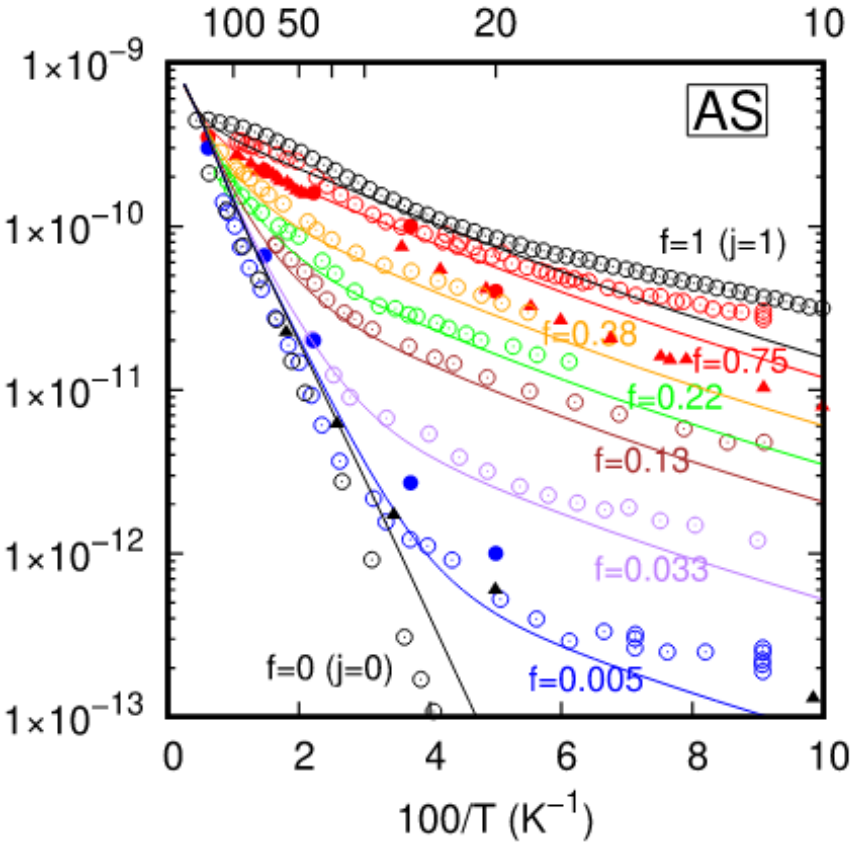
large ionization potential
low abundance
Spin-orbit reactivity: only the lowest 3?

NH^+ formation rate constants

- $N^+(^3P_{J_A})$ + H_2
  a) Diabatization $N^+(^3P)$ states
  b) spin-orbit only for N^+
- NH^+ + H: with SO
  $NH^+(X^2\Pi, a^4\Sigma^-, X^3\Sigma^-)$ + $H(^2S)$
- Quantum statistical method

  Rackham, Huarte-Larrañaga, Manolopoulos (2001)
- Adiabatic statistical method

  Quack and Troe (1974)
- Gómez-Carrasco + ('22)



Exp: Zymak *et al.*('13), open circles

Exp: Marquette *et al.*('88), full circles

Exp: Fanghänel, PhD Univ. Köln (2018), full triangles

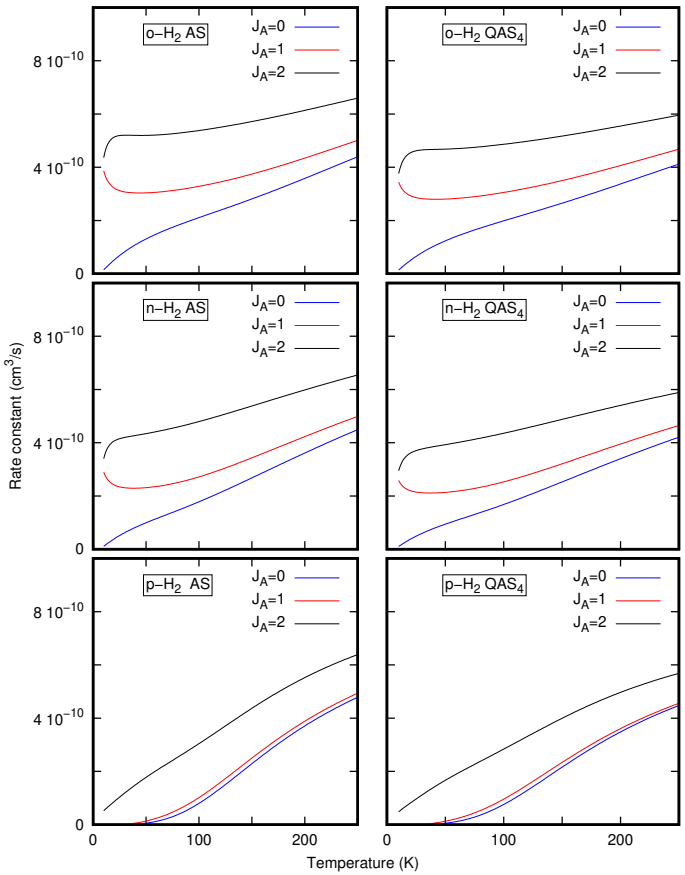
Quantum-Adiabatic statistical, Gómez-Carrasco+('22), full lines

NH^+ formation rate constants

- $N^+(^3P_{J_A})$ + H_2
  a) Diabatization $N^+(^3P)$ states
  b) spin-orbit only for N^+
- NH^+ + H: with SO
  $NH^+(X^2\Pi, a^4\Sigma^-, X^3\Sigma^-)$ + $H(^2S)$
- Quantum statistical method

  Rackham, Huarte-Larrañaga, Manolopoulos (2001)
- Adiabatic statistical method

  Quack and Troe (1974)
- Gómez-Carrasco + ('22)



YES, excited N($^3P_2$) react!

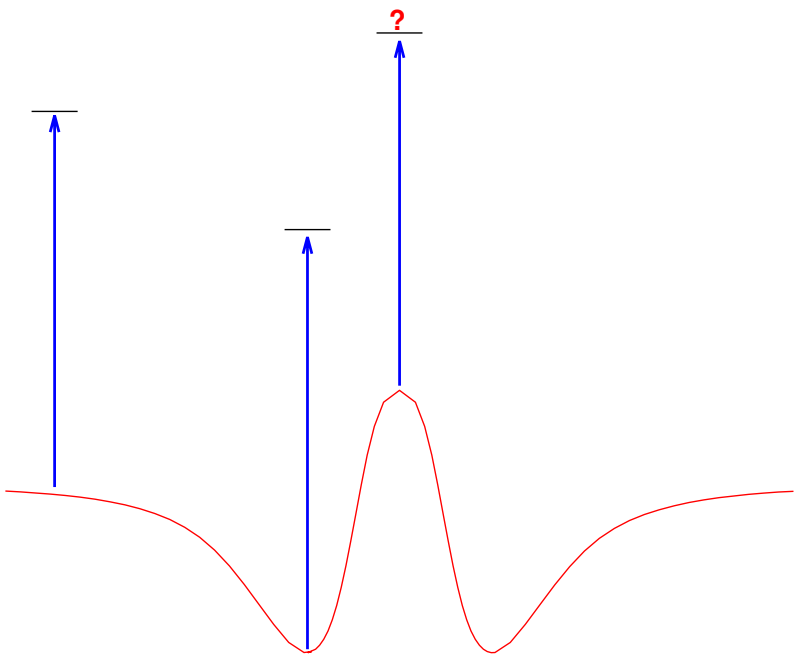
Should be considered in experiments

Complex-forming reactions: wells and barriers

General case of reactions of organic molecules (OM)

Quantum effects are very important at low temperatures

- Zero point energies

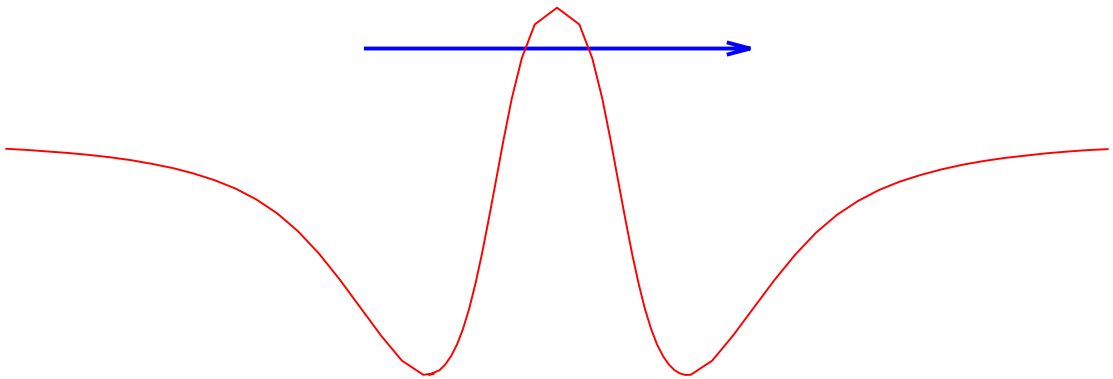


Complex-forming reactions: wells and barriers

General case of reactions of organic molecules (OM)

Quantum effects are very important at low temperatures

- Zero point energies
- Tunneling

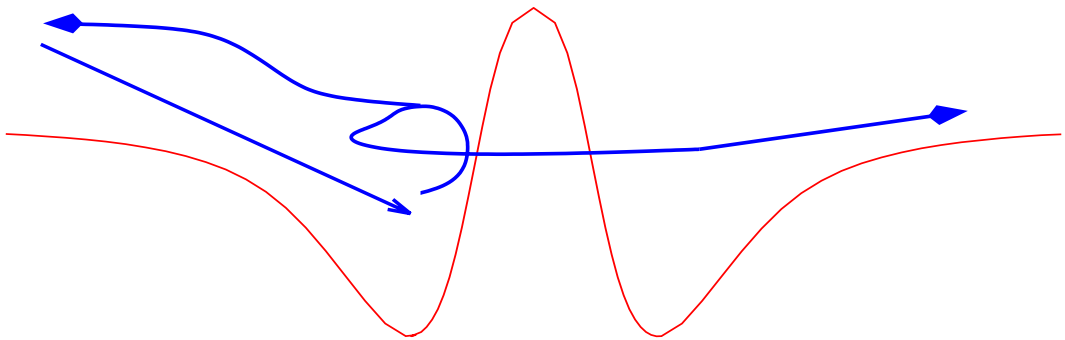


Complex-forming reactions: wells and barriers

General case of reactions of organic molecules (OM)

Quantum effects are very important at low temperatures

- Zero point energies
- Tunneling
- Collision complex



Complex Organic Molecules: COMs

- COMs first detected in hot cores

  - formed in ices
  - thermaldesorbed to gas phase

- In 2012 detected in cold cores (10K)

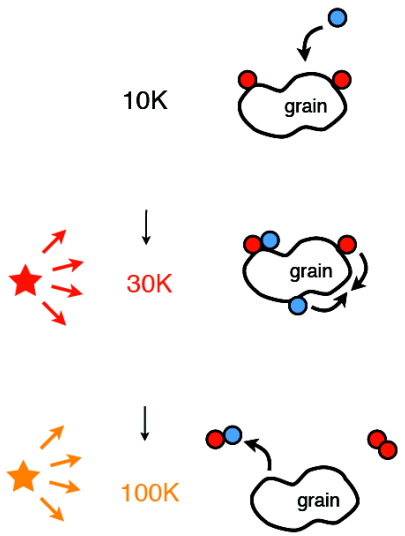
  Backman et al '12 Cernicharo et al '12

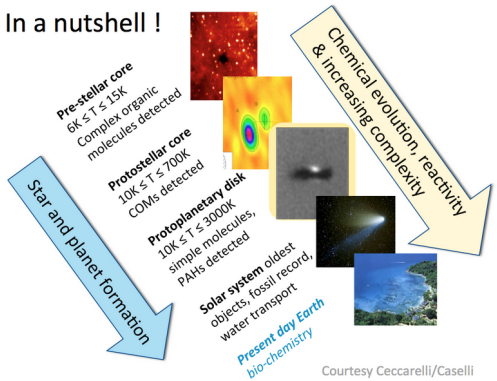
  - How do they desorb ?
    - Chemidesorption
    - Cosmic rays and UV photons

  - Any gas phase formation route ?

- Since then COMs are detected in many objects

(e.g. Garrod & Herbst 2006)



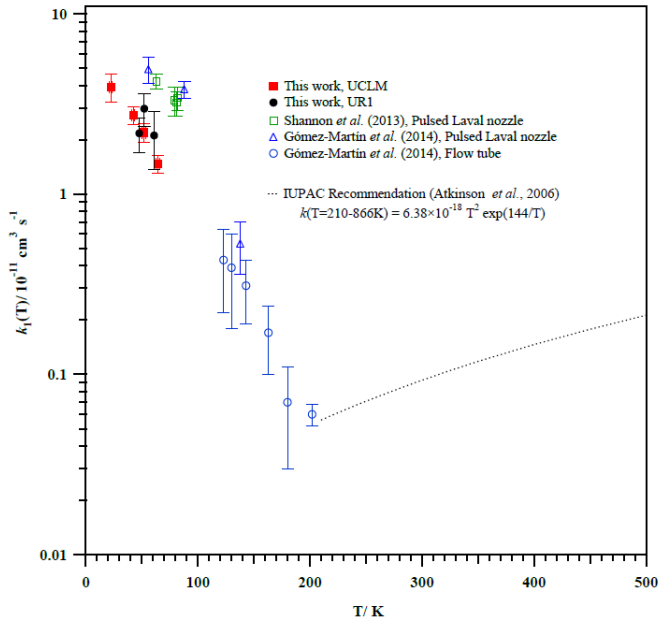


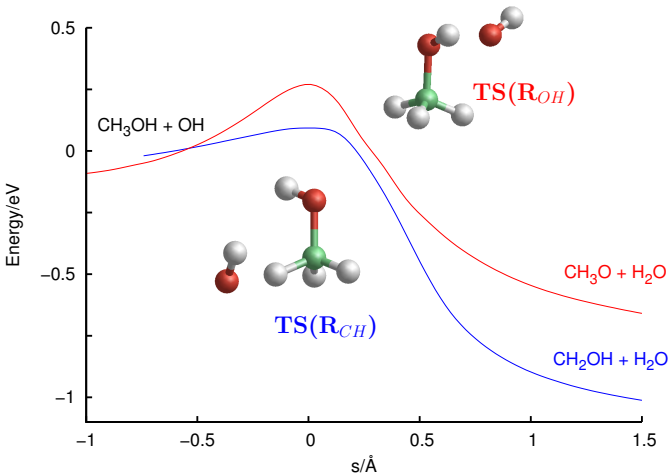
Accelerated gas chemistry at low temperature

- Experiments for CH_3OH + OH
  Shannon *et al.* Nature Chem. ('13)
  Gómez Martín *et al.* J. Phys. Chem.A ('14)

  Antiñolo *et al.* ApJ ('16)

- Reaction barriers of 0.3-0.09 eV
  tunneling with TST theory





Accelerated gas chemistry at low temperature

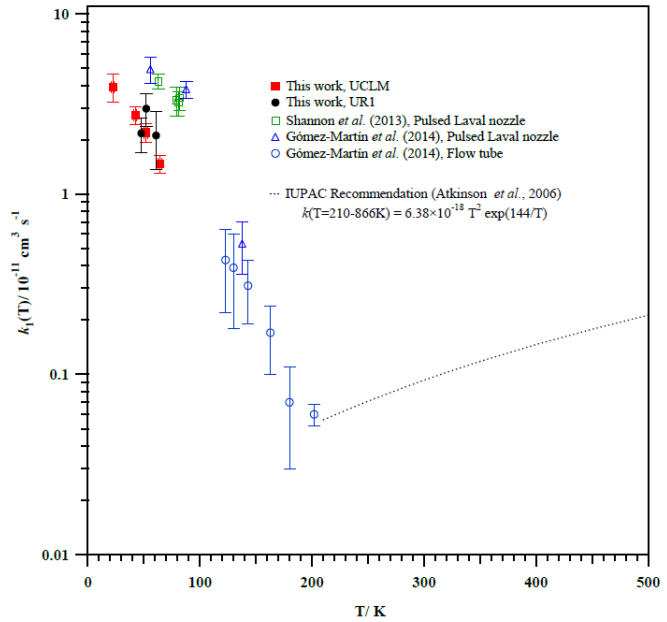
- Experiments for CH_3OH + OH
  Shannon *et al.* Nature Chem. ('13)
  Gómez Martín *et al.* J. Phys. Chem.A ('14)

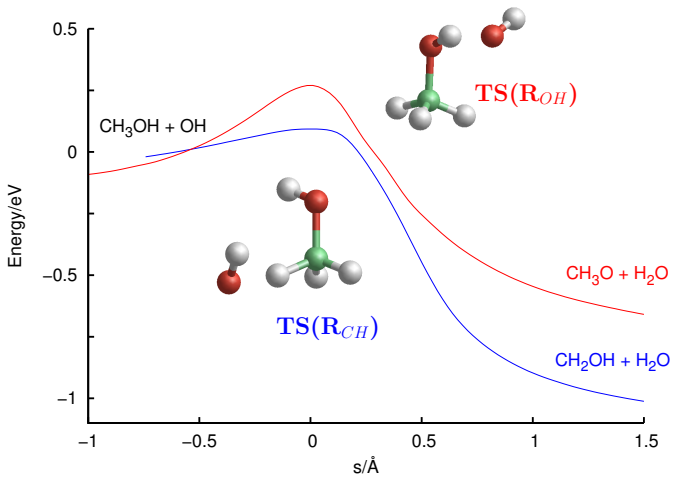
  Antiñolo *et al.* ApJ ('16)
- Reaction barriers of 0.3-0.09 eV
  tunneling with TST theory
- CH_3OH + OH Imaginary frequency at TST unrealistic

  Siebrand *et al.* PCCP ('16)

  Reactivity due to dimers
- Dimer concentration too low at experimental conditions

  Shannon *et al.* PCCP ('18)
- Other systems (H_2CO +OH) show the same exp. behavior





CH_3OH + OH reaction: TST + pressure effects?

Gao *et al.*, JACS ('18)

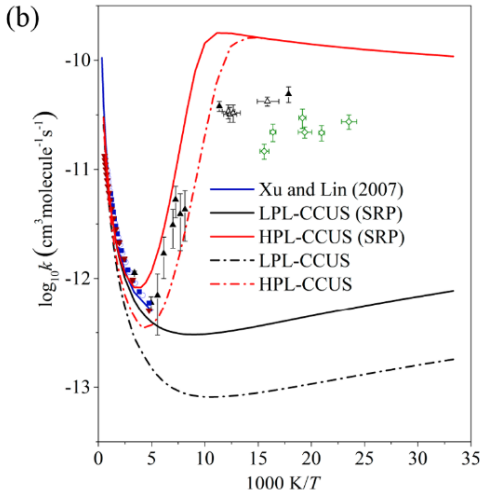


Figure 7. Present theoretical results compared to one set of calculations from the literature and to experimental data; all results are total rate constants (sum of rate constants for R1 and R2). Previous theoretical results are from Xu and Lin.[8] Experimental data are from (▲) Gómez Martin et al. (2014);[13] (△) Shannon et al. (2013);[11] (○) Atkinson et al. (1997);[71] (blue ■) Dillon et al. (2005);[7] (green ◇) Antiñolo et al. (2016);[14] (purple ▼) Srinivasan et al. (2007).[72] The present theoretical results are shown as dash–dot lines when obtained using the standard scaling factor for frequencies and as solid lines when obtained using SRP scaling factors and are as follows:

Ocaña *et al*, PCCP ('19)

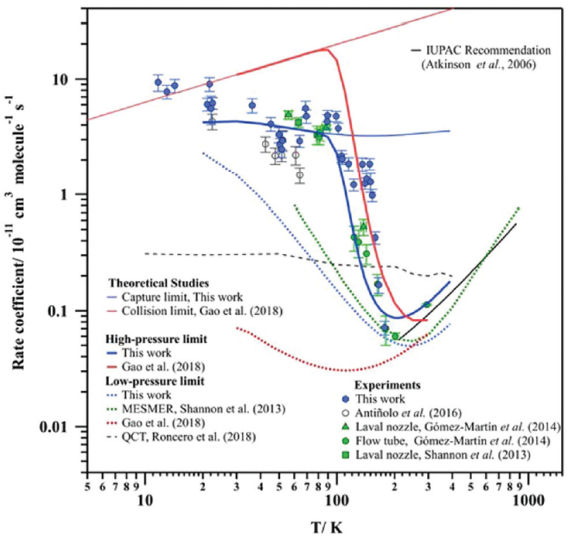


Fig. 7 Experimental and theoretical rate coefficients for the reaction of OH with CH_3OH as a function of temperature between 11.7 K and 500 K.

Nguyen *et al.*, JCP ('19)

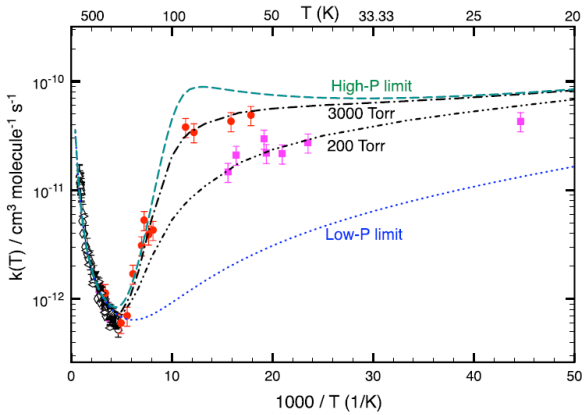


FIG. 4. Bimolecular rate constants calculated for an extensive temperature range of 20-2500 K and as a function of pressure using the 2DME/SCTST/VPT2+ approach. Symbols are experimental data: filled red circles from Refs. 2 and 3 with $P_{exptl.} < 2$ Torr; filled pink squares from Ref. 17 with $P_{exptl.} < 0.4$ Torr.

Pressure effects through fitting parameters

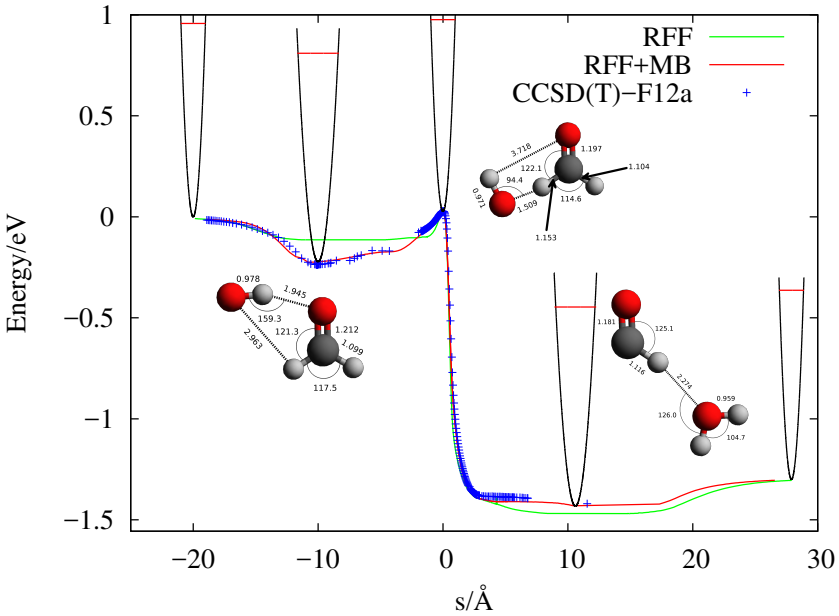
Need of dynamical studies beyond TST

Need of "zero-pressure" rate constants

Full dimension PES for OH + H_2CO/CH_3OH reactions

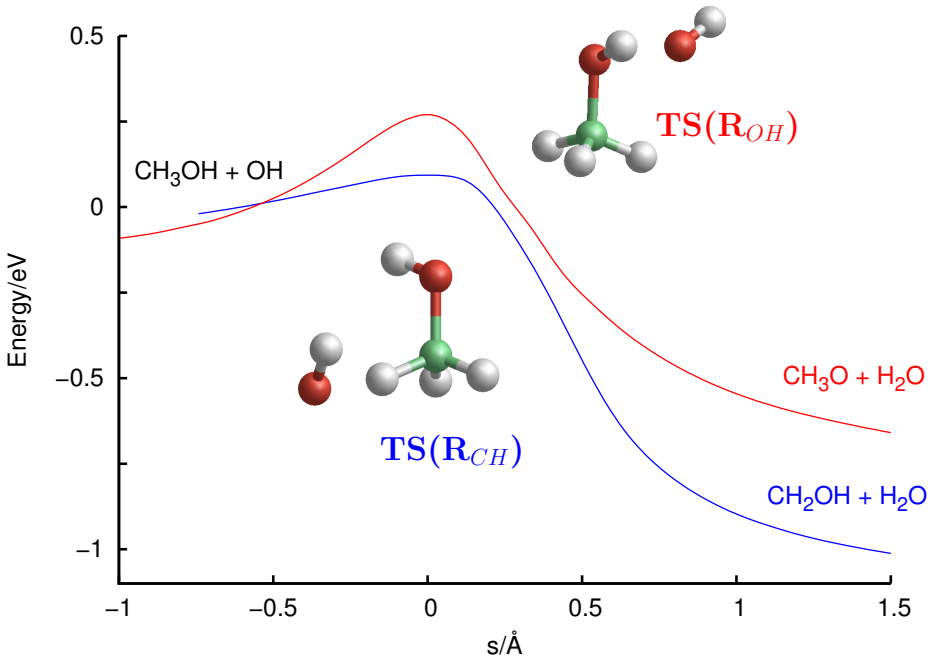
A. Zanchet *et al.* PCCP (2018)

P. del Mazo-Sevillano *et al.* JCP (2021)



barrier of 0.02 eV (≈ 232 K)

Roncero *et al.* PCCP ('18)



barrier of 0.289 eV (≈ 3353 K)

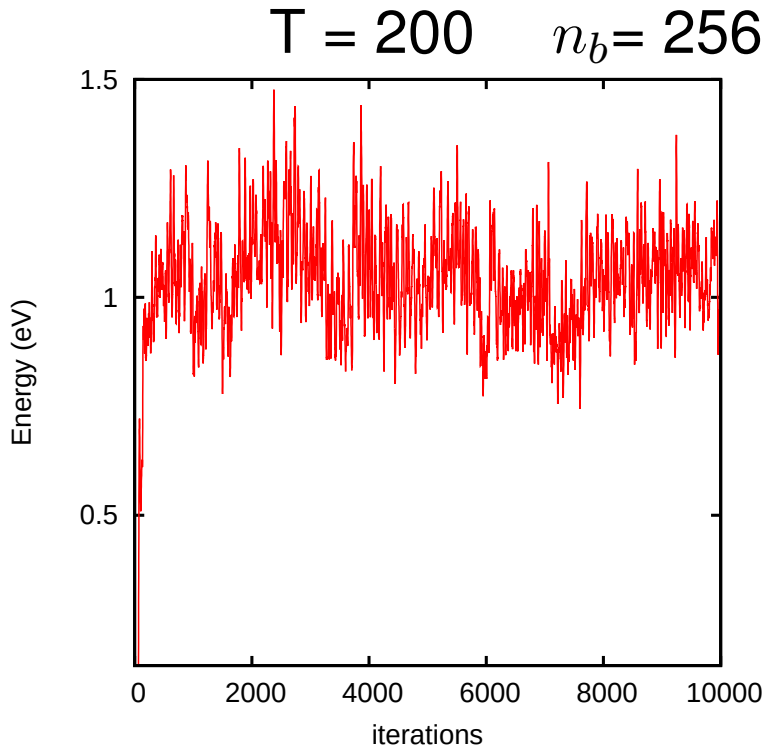
barrier of 0.089 eV (≈ 1033 K)

H_2CO and CH_3OH are among the most abundant molecules in the ISM

Ring Polymer Molecular Dynamics Craig & Manolopoulos, JCP ('05)

Two steps

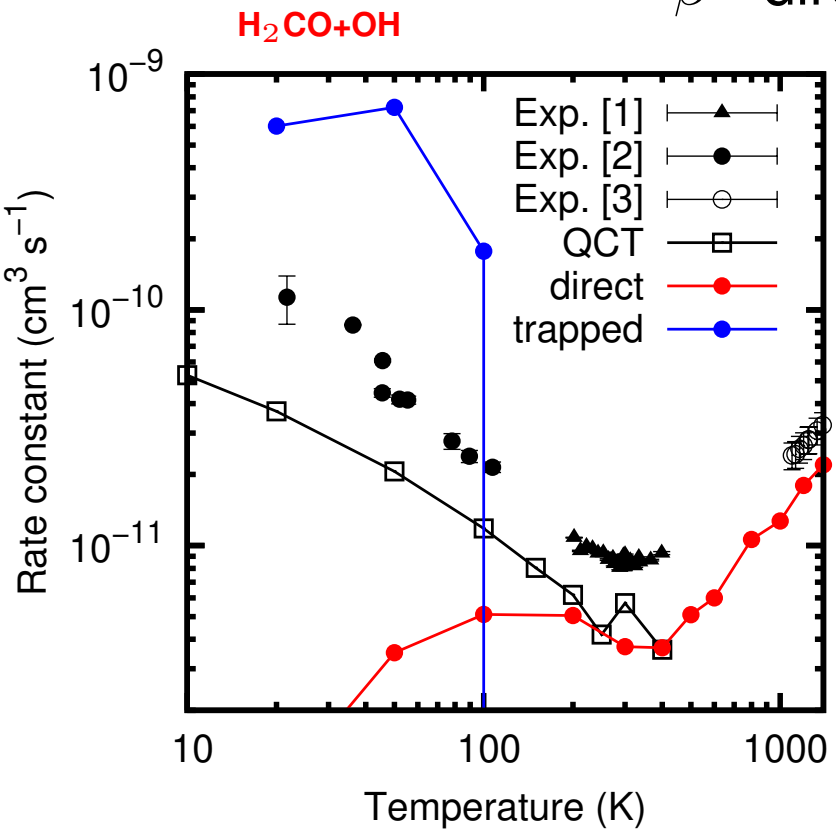
1. **Thermalization**
   Path Integral Molecular dynamics:
   - thermostat (Andersen)
   - constraints
   n_b(T=20 K)= 1920
2. **Real dynamics**
   Switch off thermostat and constraints
   Δt= 0.1 fs

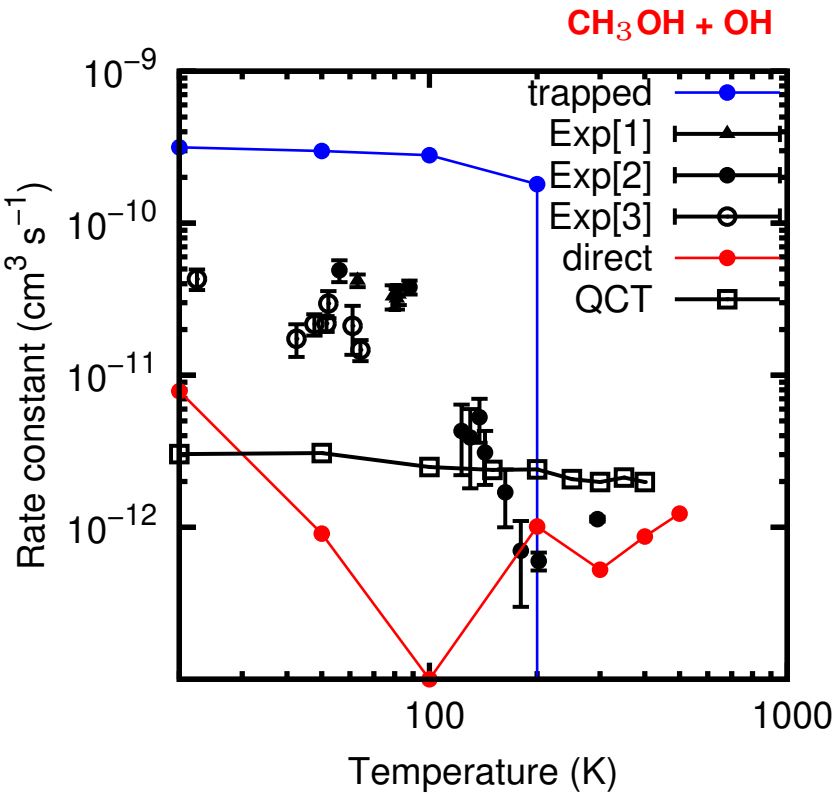


RPMD dynamics: direct vs trapping mechanisms

$$k_\beta(T) = p_e(T)\sqrt{\frac{8k_BT}{\pi\mu}}\,\pi(b_{max}^{\beta})^2\,P_\beta(T)$$

β= direct or trapping





Total reaction rate

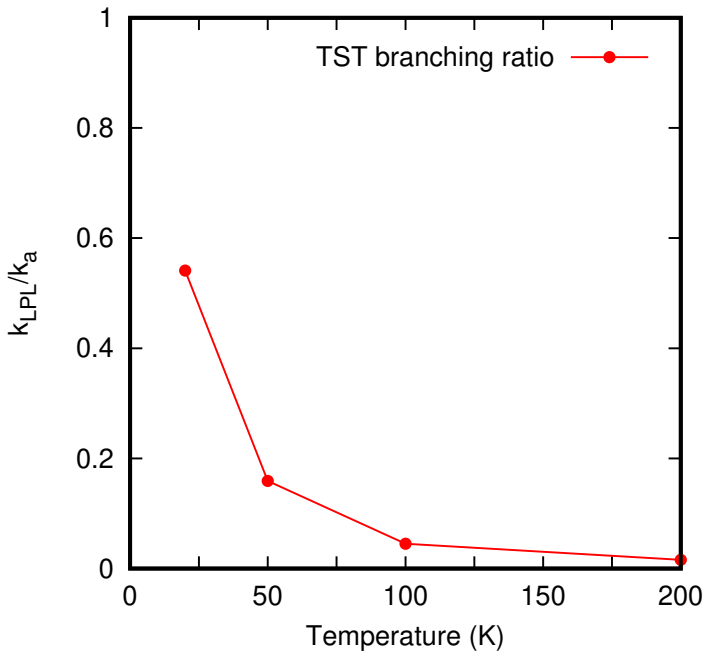
$$k(T) = k_{direc}(T) + k_{trap}(T) \times \frac{k_{tunel}(T)}{k_{tunel} + k_{redis}}$$

Trapped trajectories cannot be finished:

Ratio $k_{tunel}(T)/(k_{tunel} + k_{redis})$ obtained as

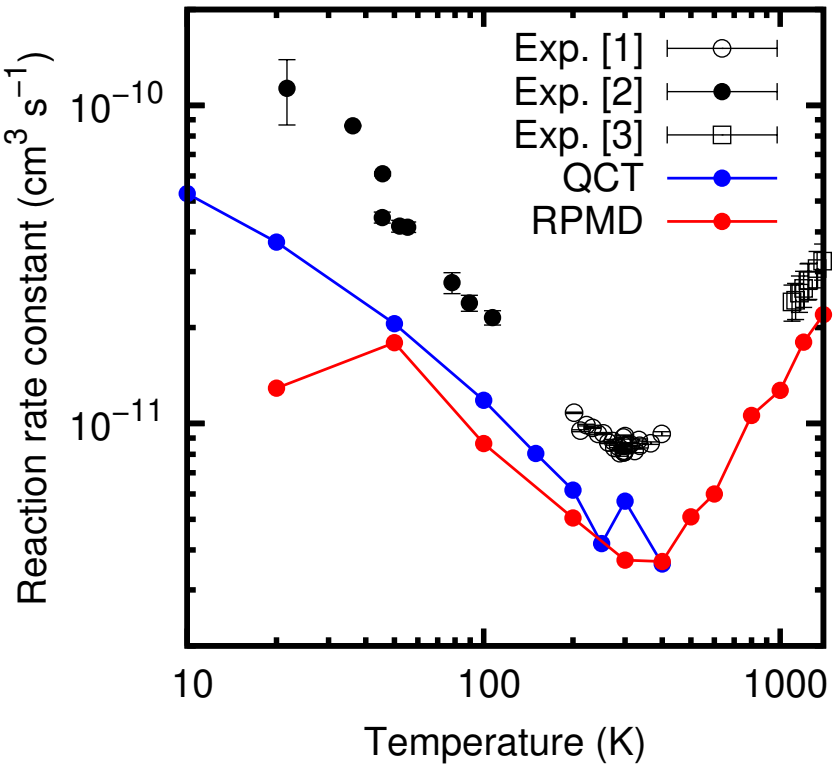
- H_2CO + OH:
  from QCT results
- CH_3OH + OH:
  from TST-RRKM results
  by Ocaña *et al*, PCCP ('19) as

$$\frac{k_{tunel}(T)}{k_{tunel}+k_{redis}} = \frac{k_{LPL}^{TST}(T)}{k_a^{TST}(T)}$$

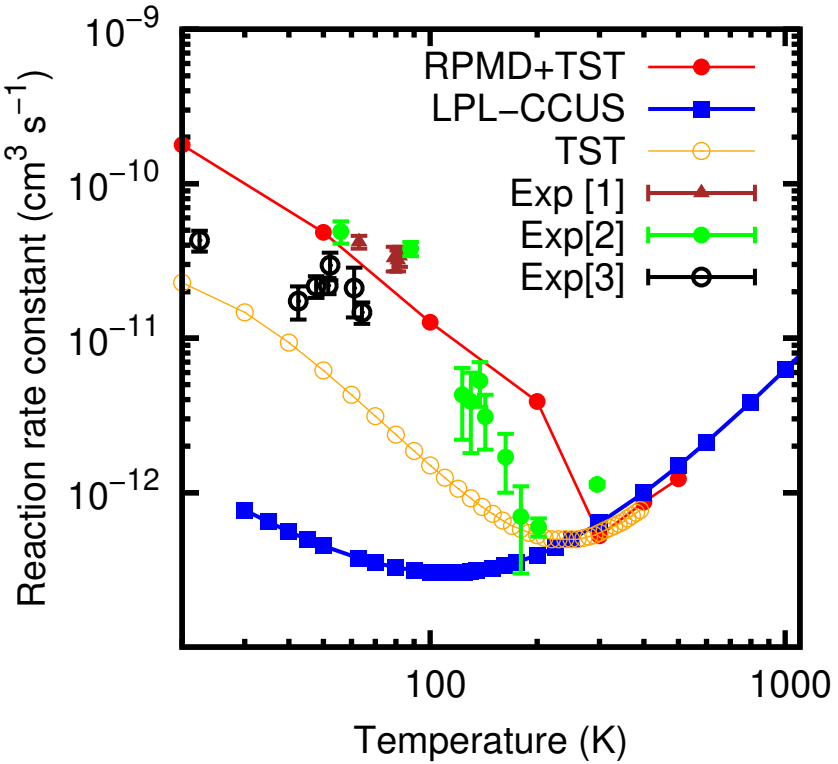


Total reaction rates: theory vs experiment

del Mazo-Sevillano *et al.* JPCl ('19)



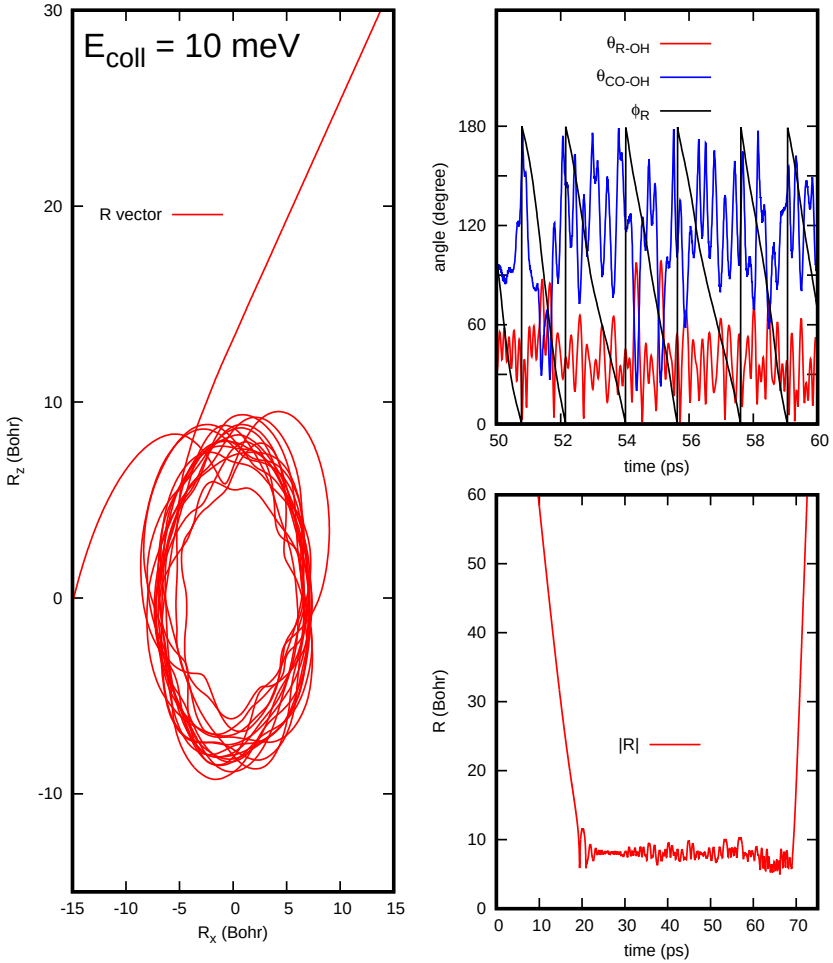
Exp. 1: Sivakumaran *et al*, PCCP ('03)
Exp. 2 & QCT: Ocaña *et al*, ApJ ('17)
Exp. 3 : Wang *et al.*, Proc. Combust. Inst. ('15)



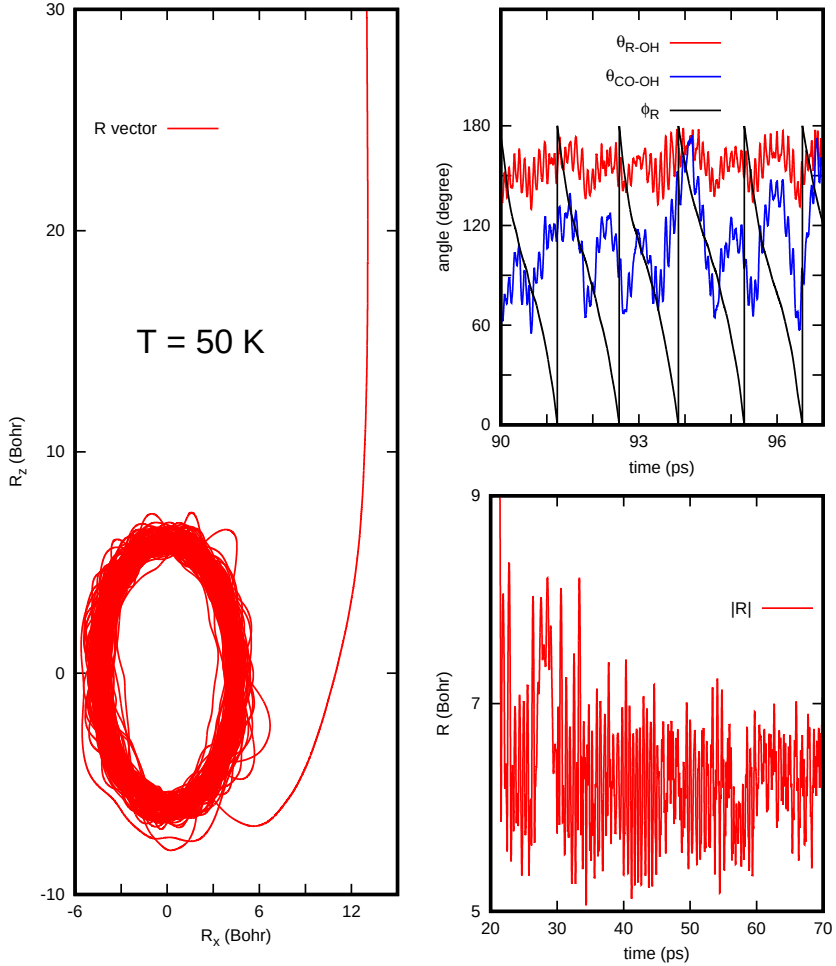
Exp. 1: Shannon *et al*,Nat. Chem ('13)
Exp. 2: Gómez-Martín *et al*, JPCA ('14)
Exp. 3: Antiñolo *et al.*, ApJ ('16)
Exp. 3 & TST: Ocaña it et al., PCCP ('19)
LPL-CCUS: Gao *et al.* JACS ('18)

QCT vs. RPMD Trapping: quantum roaming ?

QCT at 0.1 meV



RPMD at 50 K



Quantum description:

lower density of reactant states → longer lifetimes

Zero-pressure vs high pressure

- RPMD+RRKM zero-pressure rate constant similar to experiments
  Is the problem solved?
  Are the RPMD "resonances" real?
  RPMD complex lifetimes, are they quantitative?
- Are they attributted to specific systems?
  Improve PES accuracy
- Are they "artificial resonances"?
  Use thermostated RPMD to check (Rossi et al. '14)

Zero-pressure vs high pressure

- RPMD+RRKM zero-pressure rate constant similar to experiments
  Is the problem solved?
  Are the RPMD "resonances" real?
  RPMD complex lifetimes, are they quantitative?

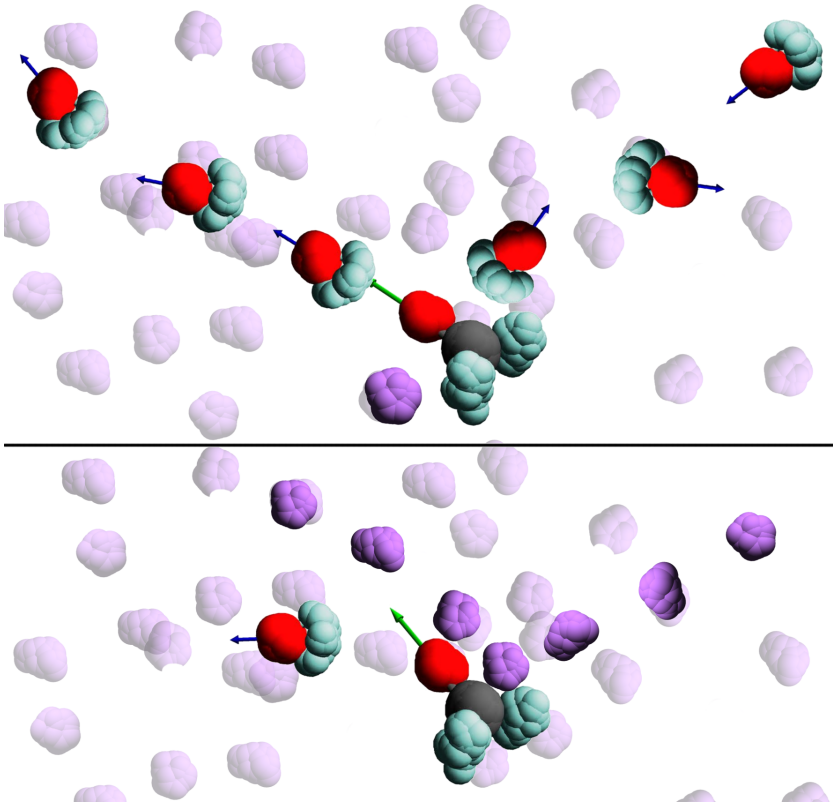
- Are they attributted to specific systems?
  Improve PES accuracy
  NEW PES and other systems done. del Mazo-Sevillano +('21)

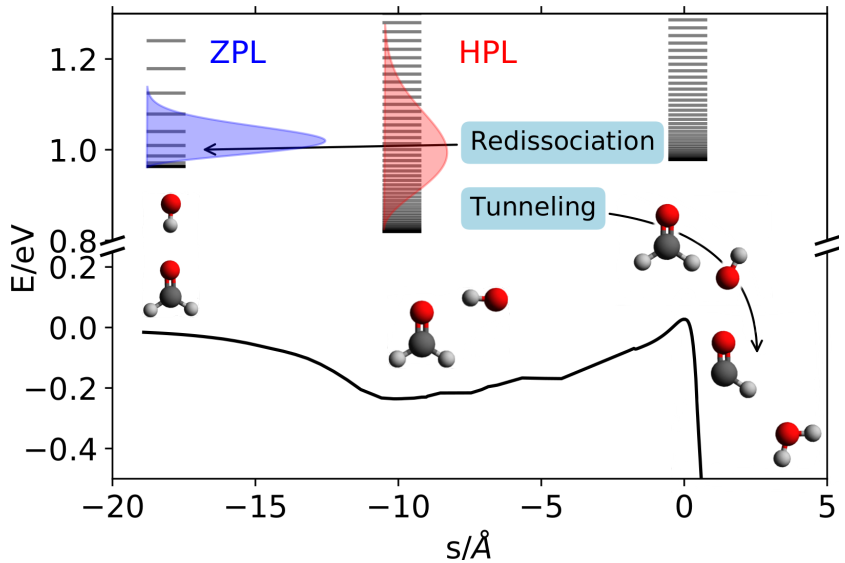
- Are they "artificial resonances"?
  Use thermostated RPMD to check (Rossi et al. '14)
  t-RPMD is similar to RPMD del Mazo-Sevillano +('23)

- If complex lifetimes are so long ...
  What is the role of complexes in the reaction dynamics?

Dimers: "microscopic" pressure effects

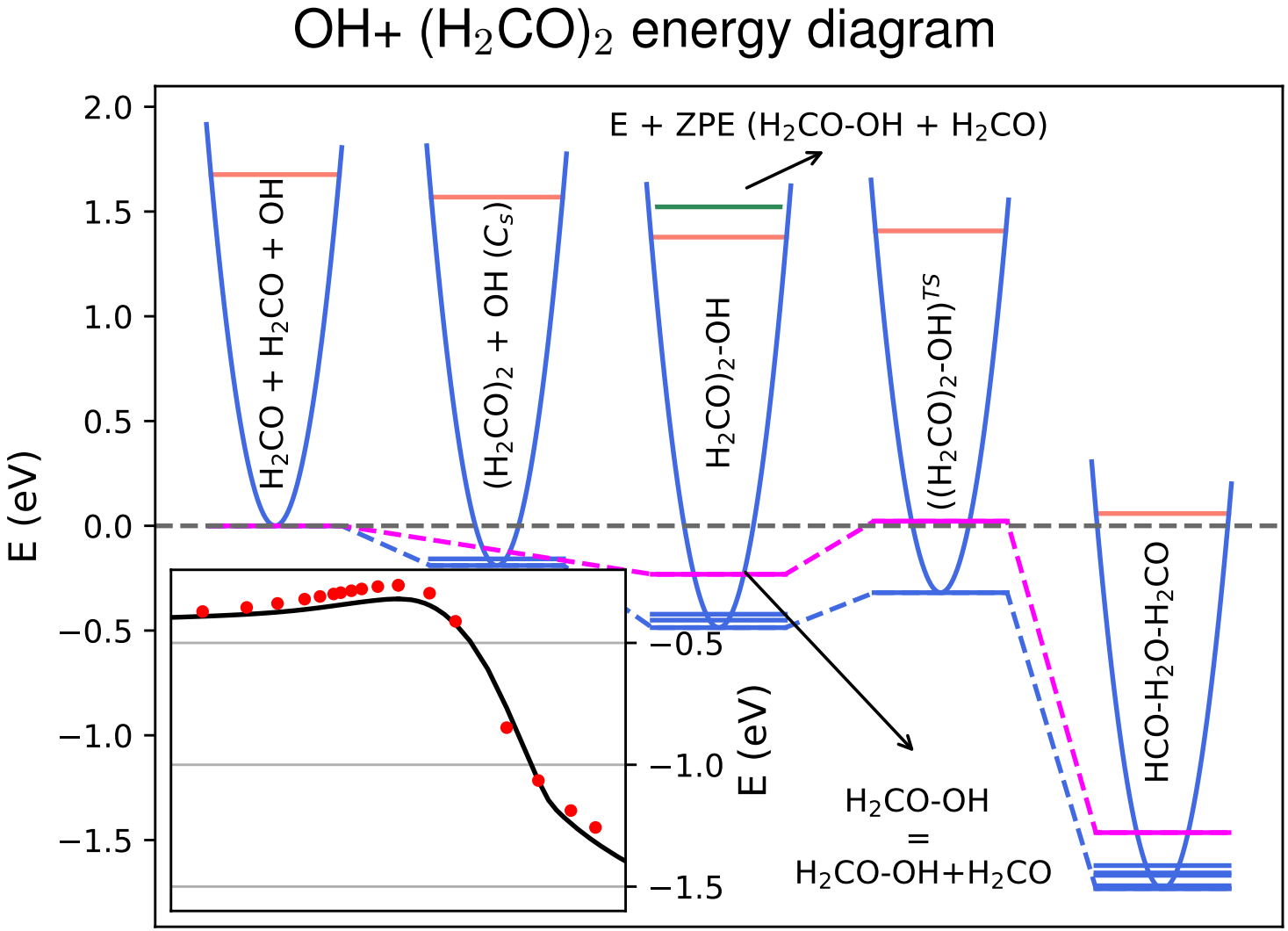
TST includes pressure effects by broadening the energy distribution





- Neglecting three-body collisions
- Collisions with buffer gas ?
- Which complexes are formed ?
- What is the reactivity of dimers?

OH + $(H_2CO)_2$ reactivity: RFF+ 6-body NN PES



Comparison with *ab initio* CCSD(T)-F12a for lower TS

Dimers and trimers: RFF+ 2 6NB PES CHECK

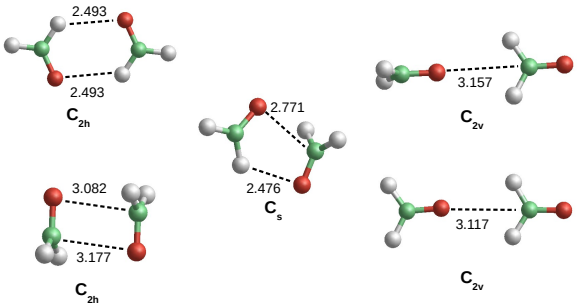
$D_0(T)$ using PIMC for dimers and trimers

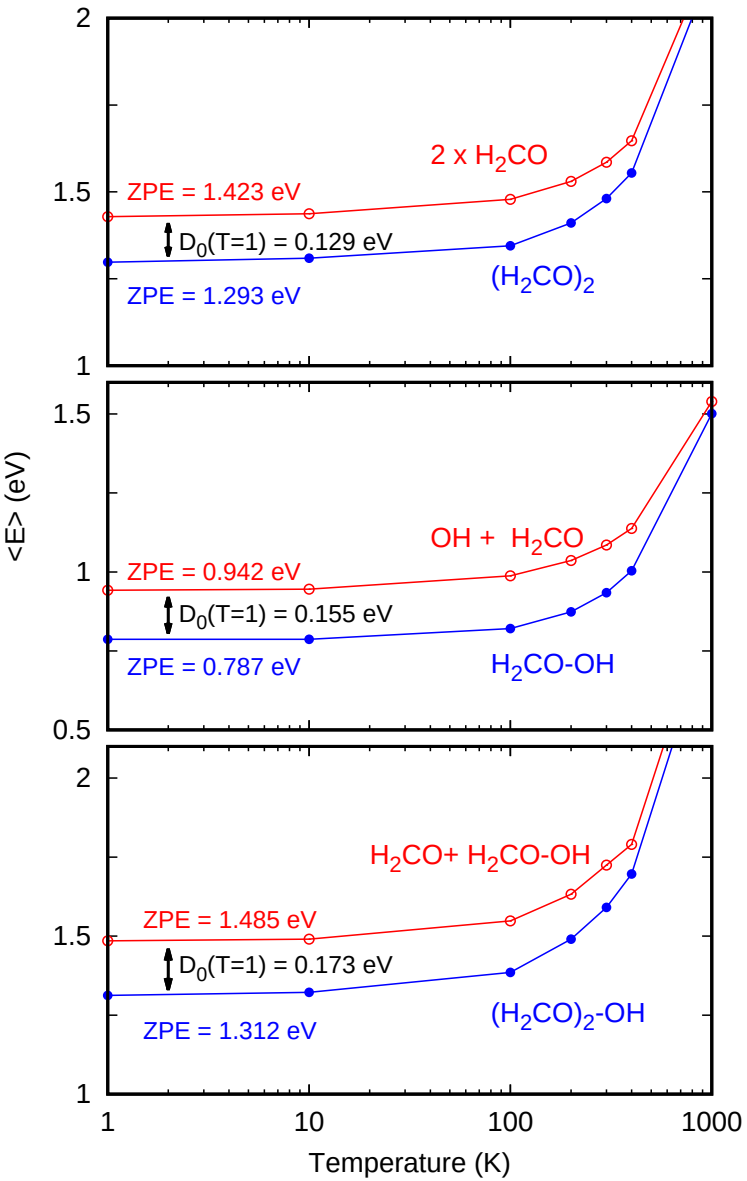
Pressure broadening measurements

D_0^{exp}(T=300 K) = 0.097 $\pm$ 0.015 eV

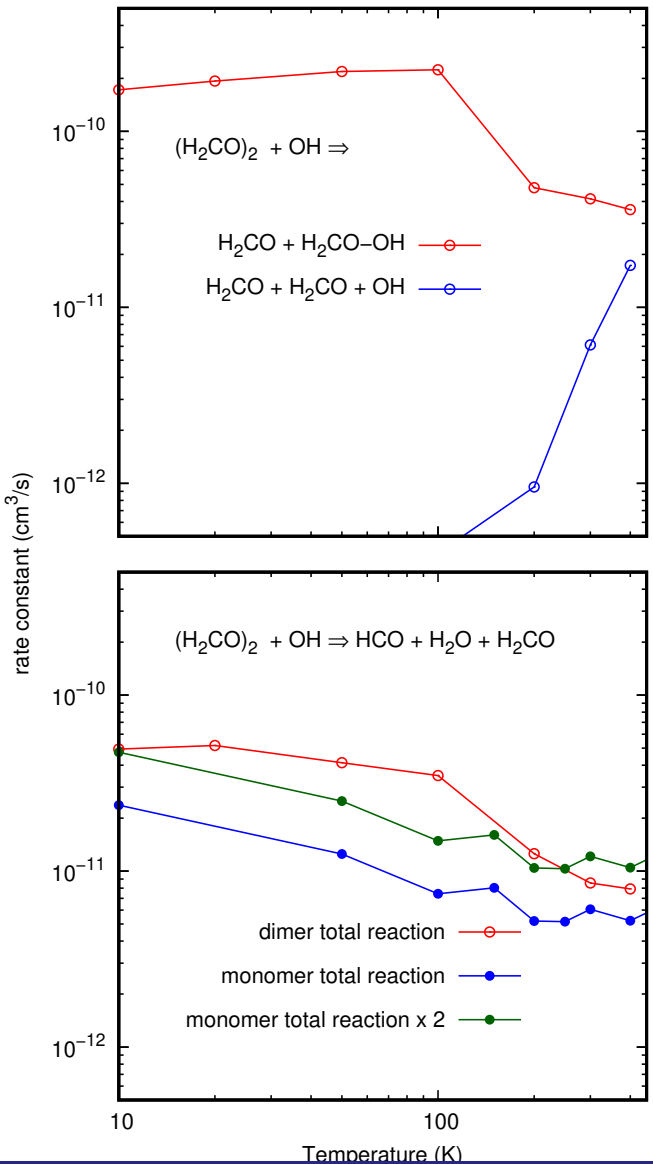
Barry *et al.* PCCP (2003)

D_0^{PIMD}(T=300 K) = 0.105 eV





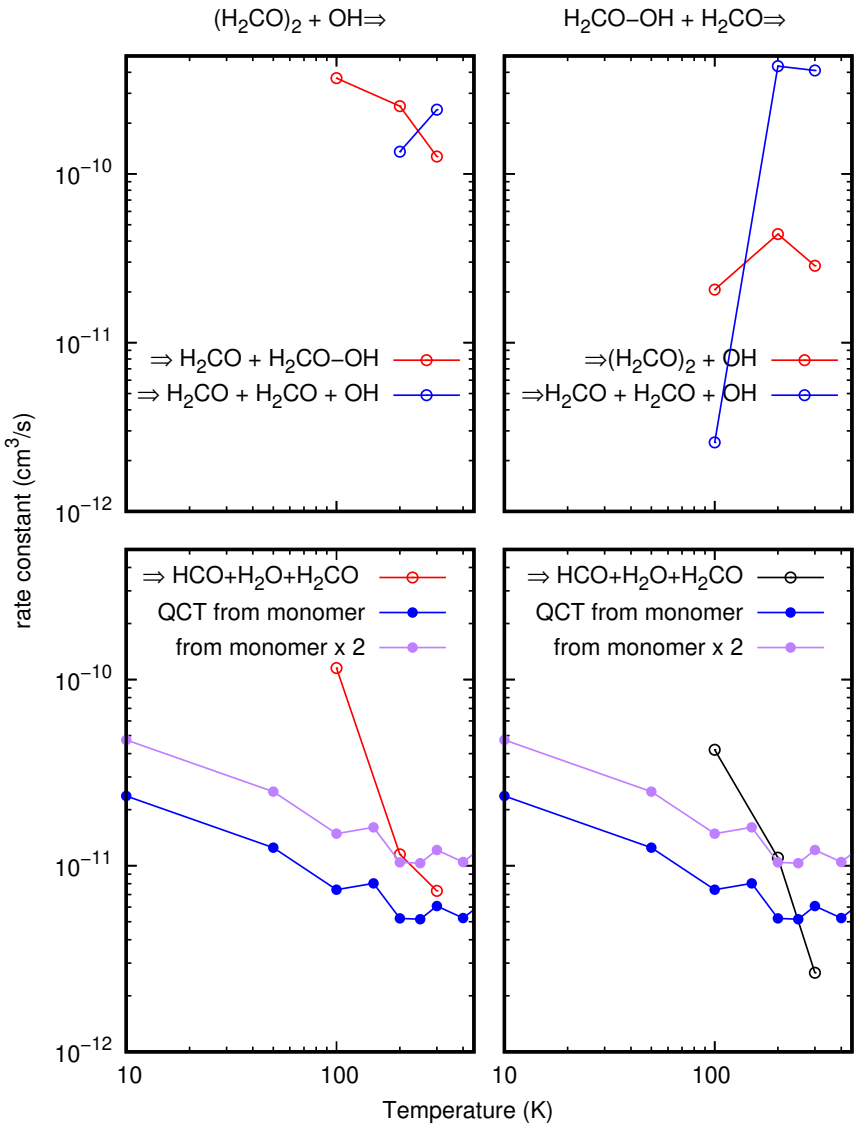
OH + $(H_2CO)_2$ reactivity: QCT dynamics



- QCT calculations
- Initial conditions: “Adiabatic Switching”
- $(H_2CO)_2$ long time stability
- H_2CO-OH short time stability: not possible
- ZPE corrected inelastic processes

del Mazo-Sevillano *et al.*(2023)

OH + $(H_2CO)_2$ reactivity: RPMD dynamics



- RPMD calculations
- Trapping problem T$<$ 100 K
- At T=100 K

  $K_{dimer}(T) \approx 10 \times K_{monomer}(T)$

  At other temperatures

  $K_{dimer}(T) \approx K_{monomer}(T)$

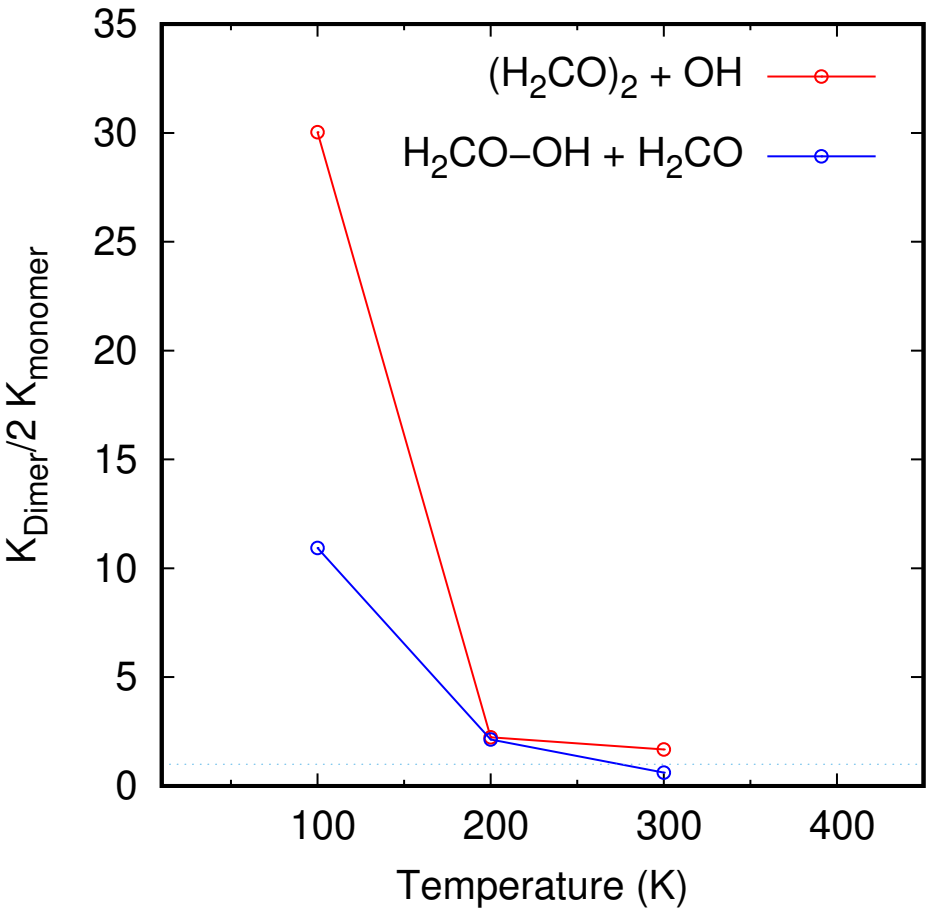
  Need of new methods to analyse T$<$ 100 K !

del Mazo-Sevillano *et al.*(2023)

Tunneling vs. direct dynamcis of dimers

Direct dynamics (no trapping)

$K_{Dimer}/2K_{Monomer}$



T = 100 K $\rightarrow$ $K_{dimer} >> K_{monomer}$

BUT trapping fraction is dominant

In "dimer hypothesis" by Siebrand, *et al.*, PCCP(2016)

$$(CH_3OH)_2 + OH \rightarrow CH_3OH \cdots OH + CH_3OH$$

$$E_{CH_3OH\cdots OH} < E_{reactants}$$

$$\tau_{tunnel} >> \text{experiment} \quad \text{time?}$$

Take home message

- Quantum and adiabatic statistical methods good for insertion reactions at low T: J_A=2 contributes to the reaction for $N^+(^3P_{J_A})$+H_2 with coupled spin-orbit electronic states.
- RPMD includes quantum effects and is adapted to study complex forming reactions for T$>$ 100-200 K
- Below 100 K, RPMD shows trapping & is NOT directly applicable

  - Need of alternative methods: Instanton, Centroid MD, ?
- Combining RPMD and RRKM, rates for monomers are close to experiments
- Direct reaction rates for dimers $>$ monomers at 100 K

  - Reason of the rise of the experimental rate below 100 K?

  - Need of determination of pressure/dimers experimental contribution