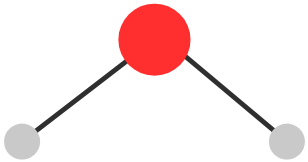
Collisional Excitation of Water

Theory and Experiment in Harmony



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hYdRiDeS

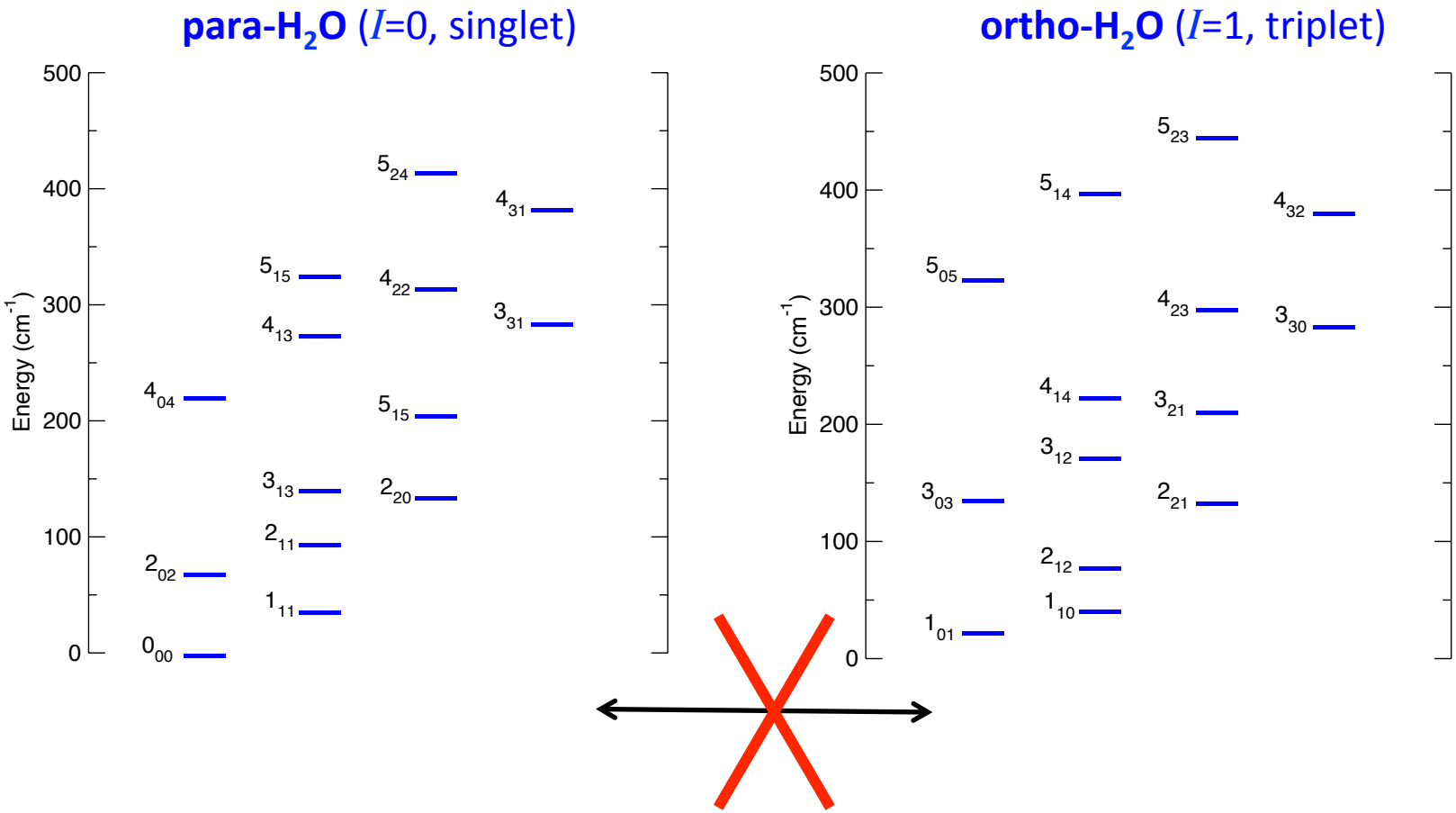
A collaborative work (2006-2016)

Outline

- Introduction
- Theory
- **Comparisons to Experiment**
- Isotopologues
- Future issues

INTRODUCTION

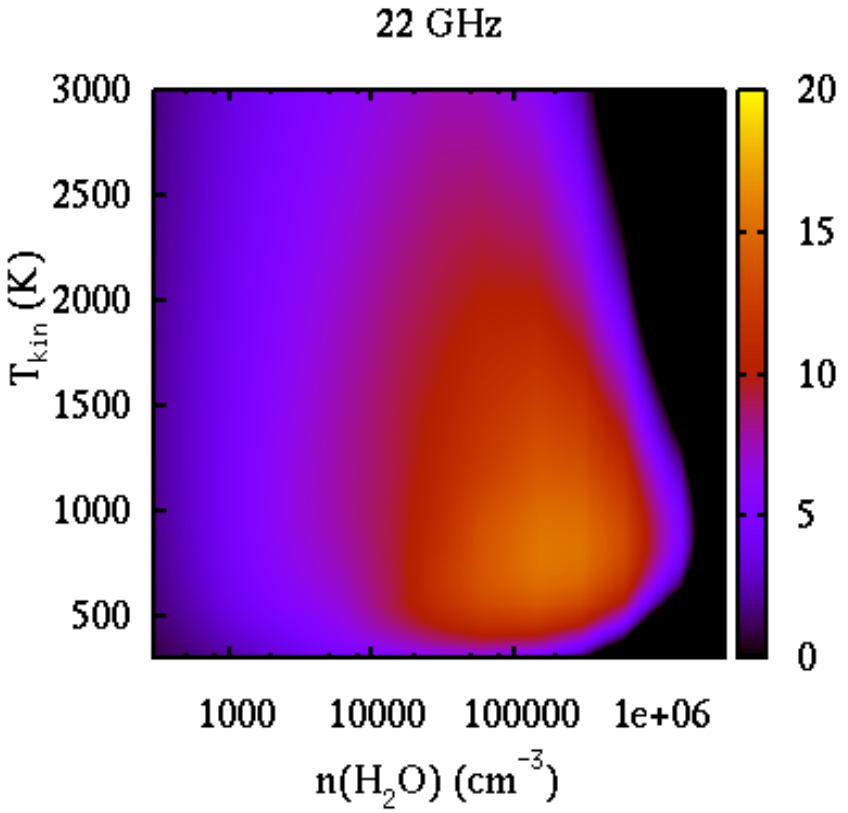
Basics



No interconversion by inelastic collisions

Non-LTE excitation

- In the ISM, collisions cannot maintain LTE
- Collisional rates are critical parameters



Gray et al. MNRAS (2016)

Water collisions in the ISM

- H_2O-He — everywhere (but second-order)
- H_2O-H — J-type shocks
- H_2O-e^- — diffuse ISM, shocks, PDRs
- H_2O-H_2 — dense ISM

Historical review (*before 2006*)

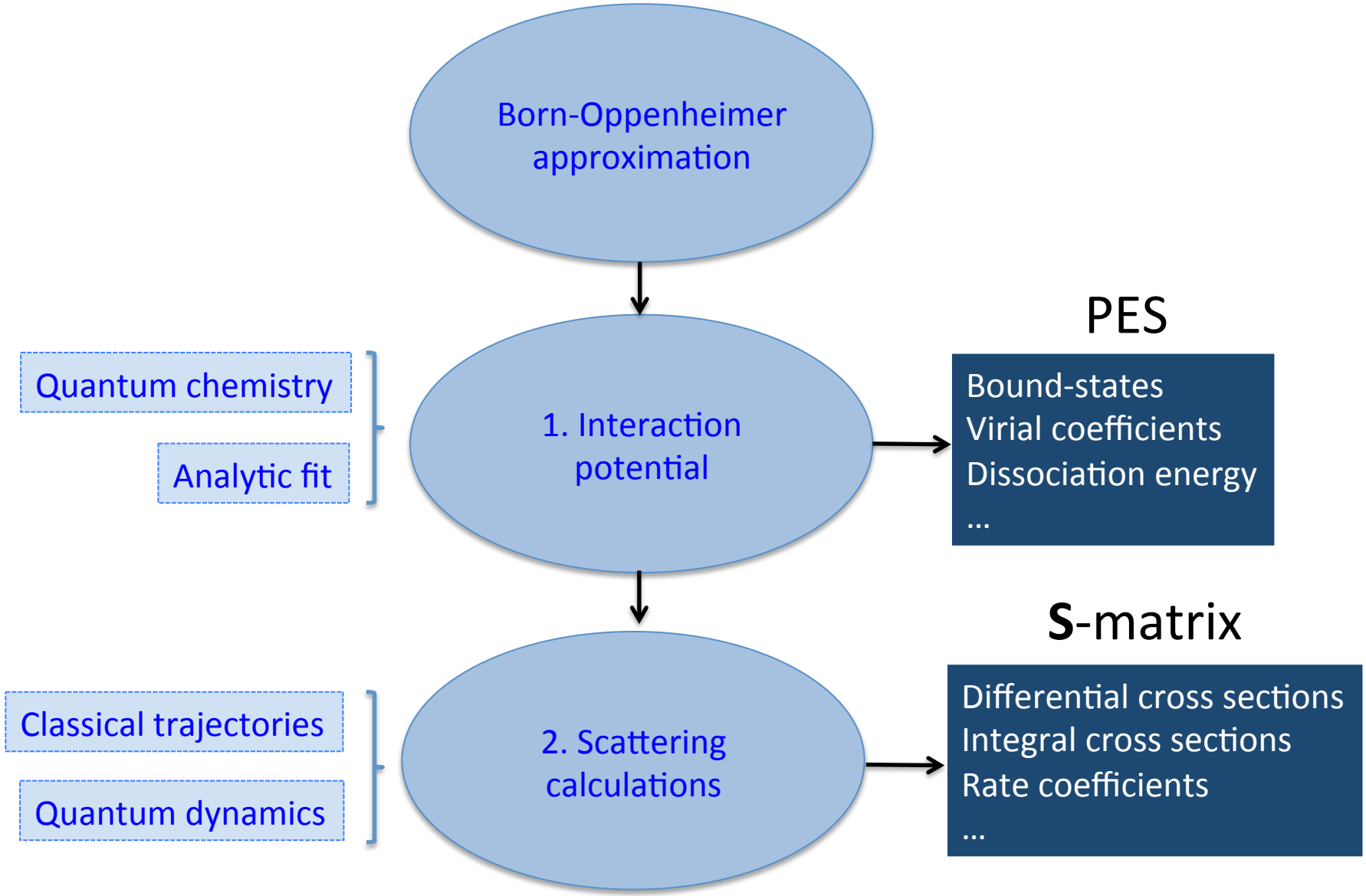
- H_2O-He
  - De Jong (1973)
  - Green (1980), Palma et al. (1988)
  - Maluendes et al. (1992)

- H_2O-H_2
  - Phillips et al. (1996)
  - Dubernet & Grosjean (2002)
  - Grosjean et al. (2003)

- H_2O-electron
  - Xie & Mumma (1992)

THEORY

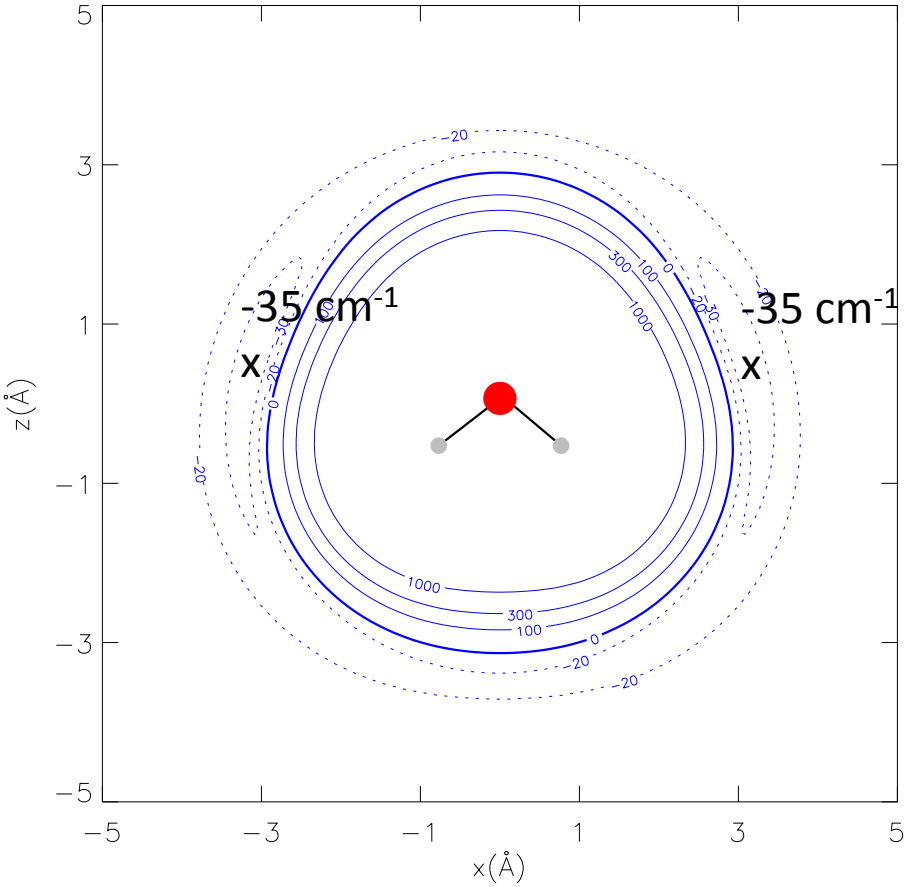
Theoretical ingredients



PES topology

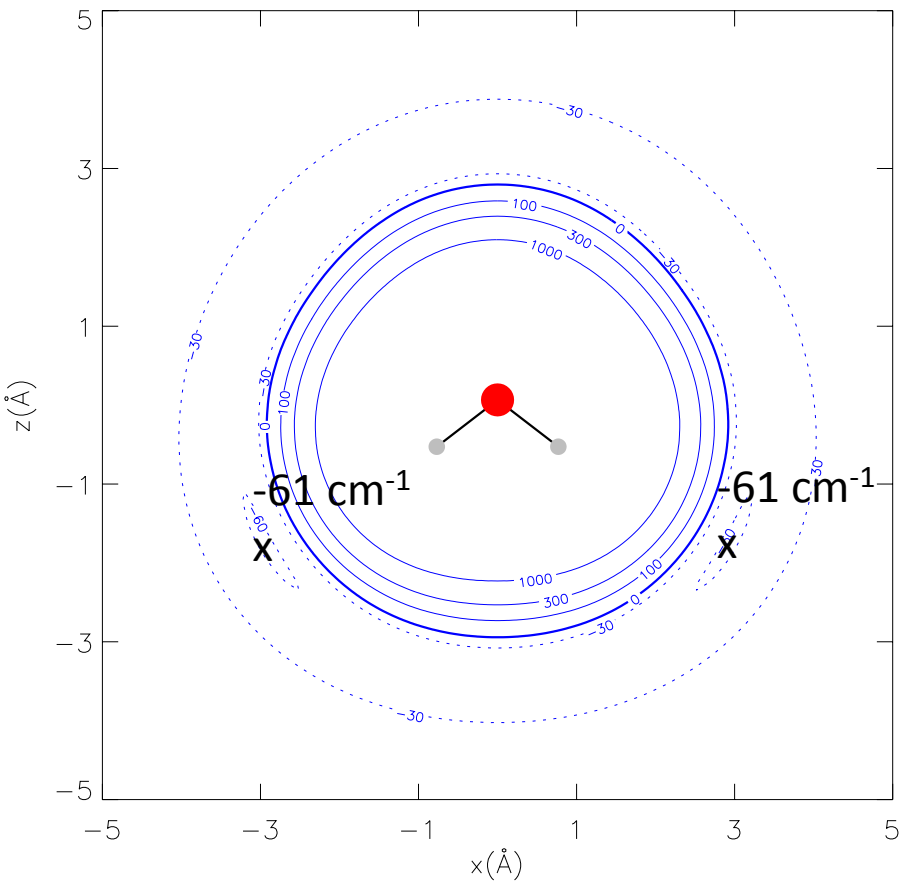
H_2O-He

(Hodges et al. 2002)



H_2O-H

(Dagdigian & Alexander 2013)



PES topology

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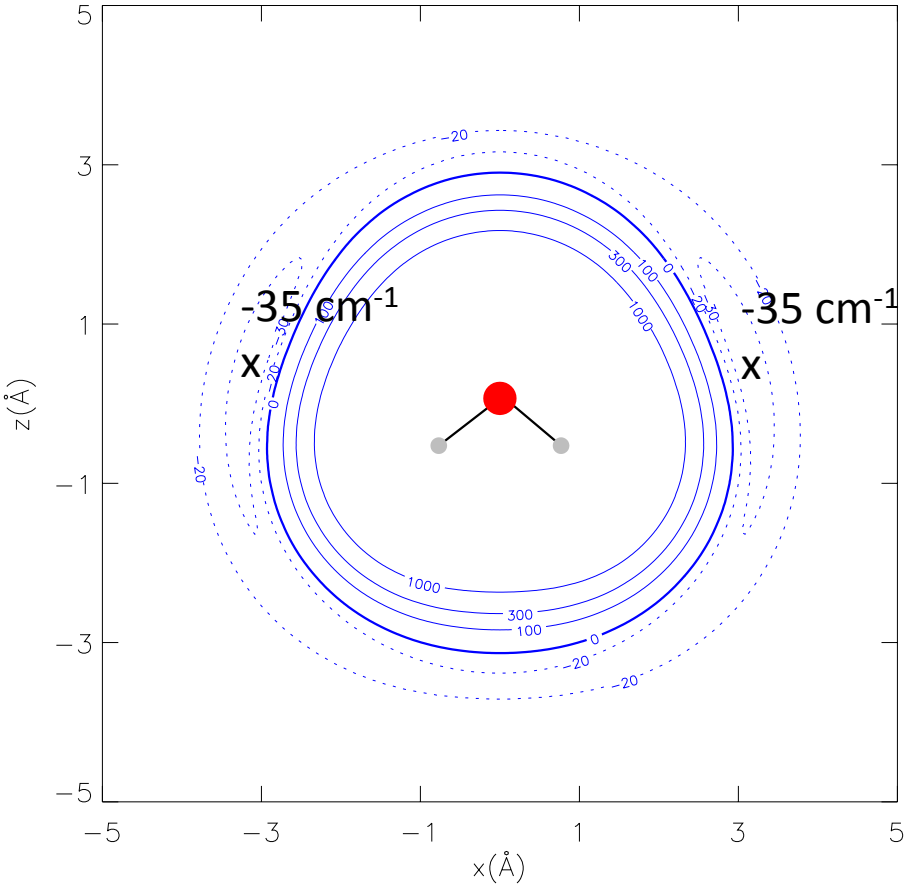
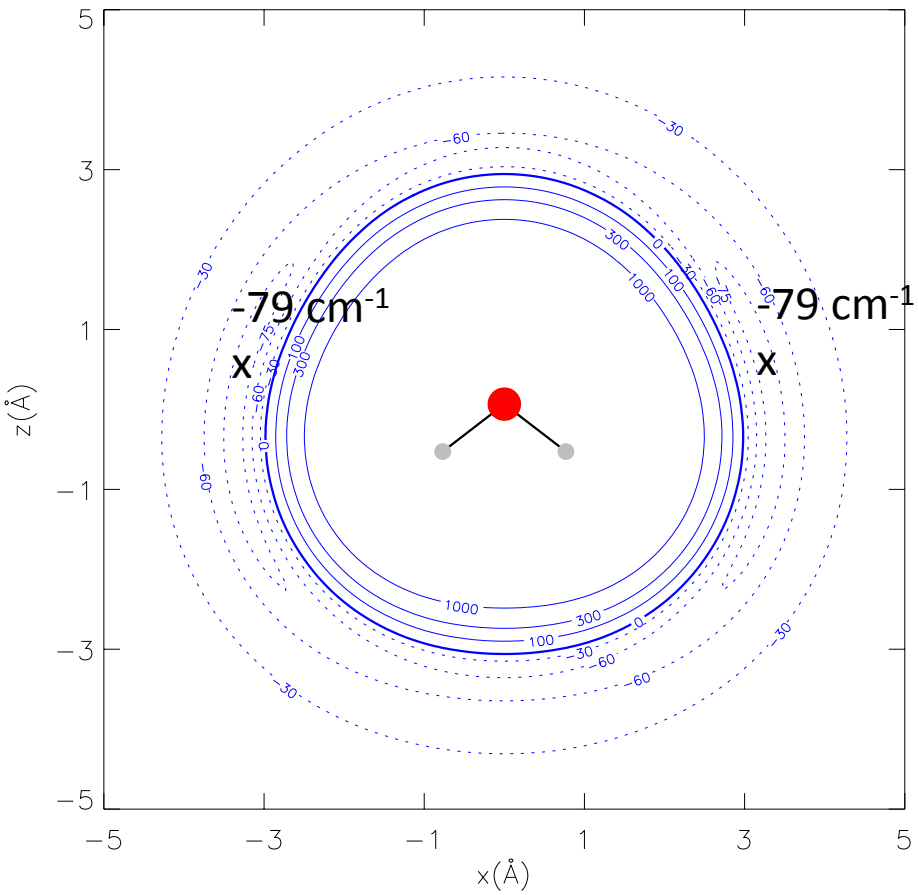


H_2O-pH_2

(Faure et al. 2005)



COMPARISONS TO EXPERIMENT

Testing the PES

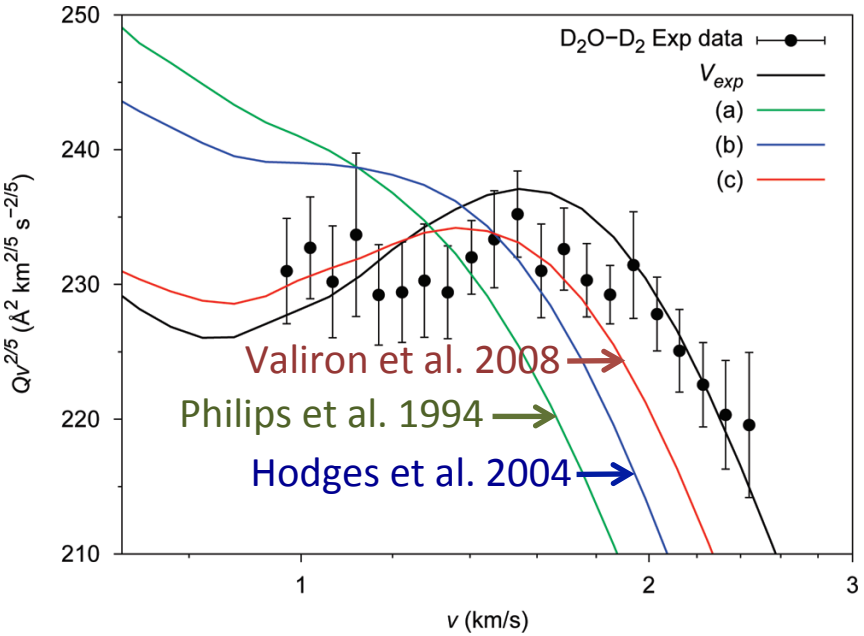
- Spectroscopic studies
  - Probe the shape of the potential well
- Collision experiments
  - Probe the short-range (repulsive) part
- Resonances (cold regime)
  - Probe the global shape, including long-range

A benchmark system: H_2O-H_2

Elastic cross sections

- Molecular-beam apparatus
- *Glory* quantum effect

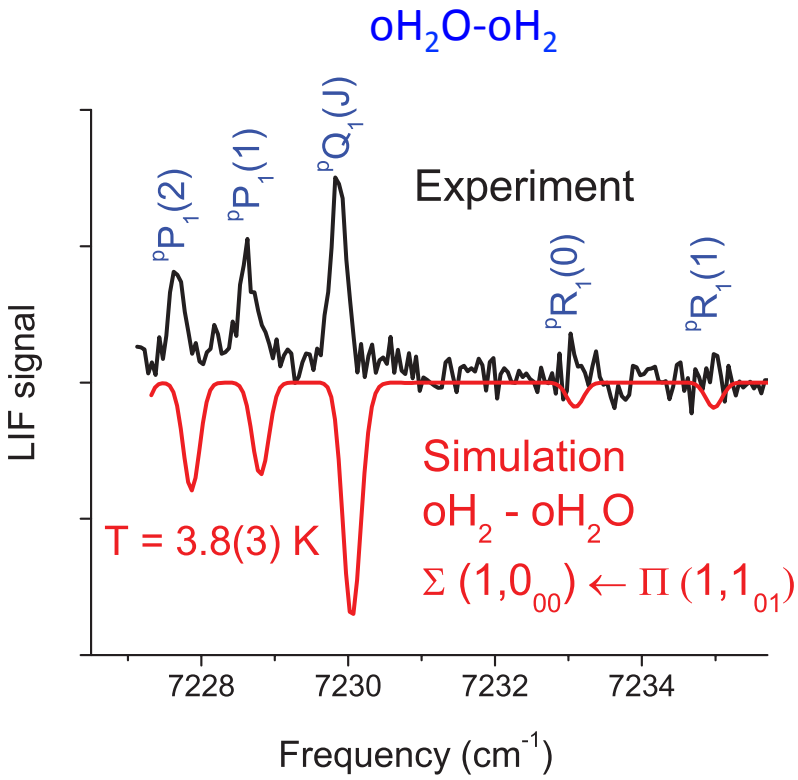
D_2O-D_2
E_{coll} = 150-900 cm^{-1}



Belpassi et al. JACS (2010)

Bound-states

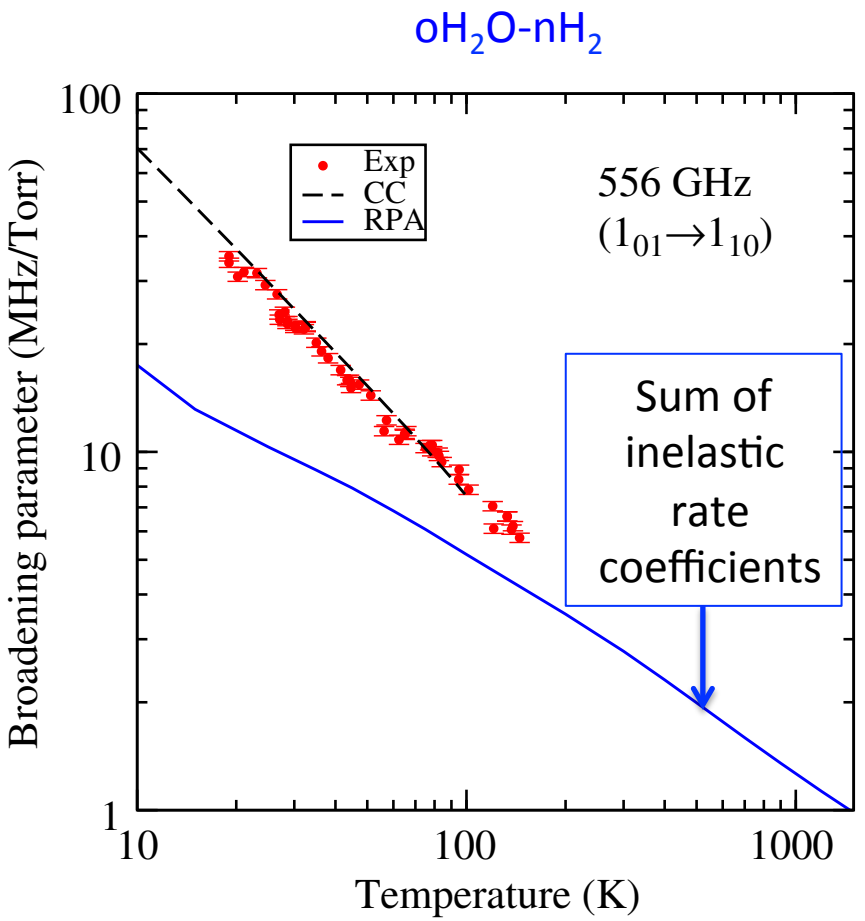
- High-resolution IR spectroscopy
- Rovibrational states supported by the PES



Ziemkiewicz et al. J Chem Phys (2012)
+ van der Avoird & Nesbitt J Chem Phys (2011)
+ Wang & Carrington J Chem Phys (2011)
+ van der Avoird et al. Chem Phys (2012)
+ Harada et al. Chem Phys Lett (2014)

Broadening cross sections

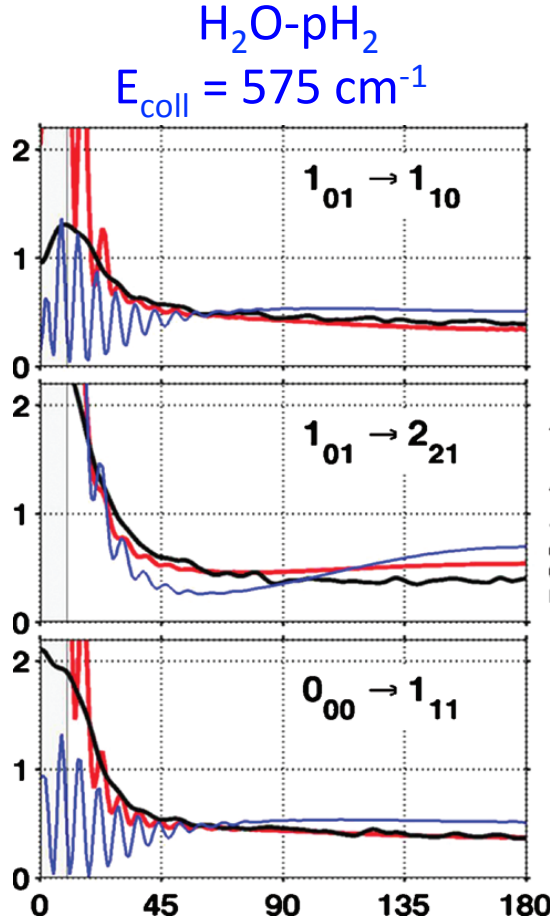
- Cryogenic gas apparatus
- *Absolute* metrics of the interaction



Faure et al. JQSRT (2013)
+ Drouin & Wiesenfeld Phys Rev A (2012)
+ Wiesenfeld & Faure Phys Rev A (2010)

Inelastic cross sections

- Crossed molecular beams + velocity map imaging
- Probe both attractive and repulsive parts of the PES

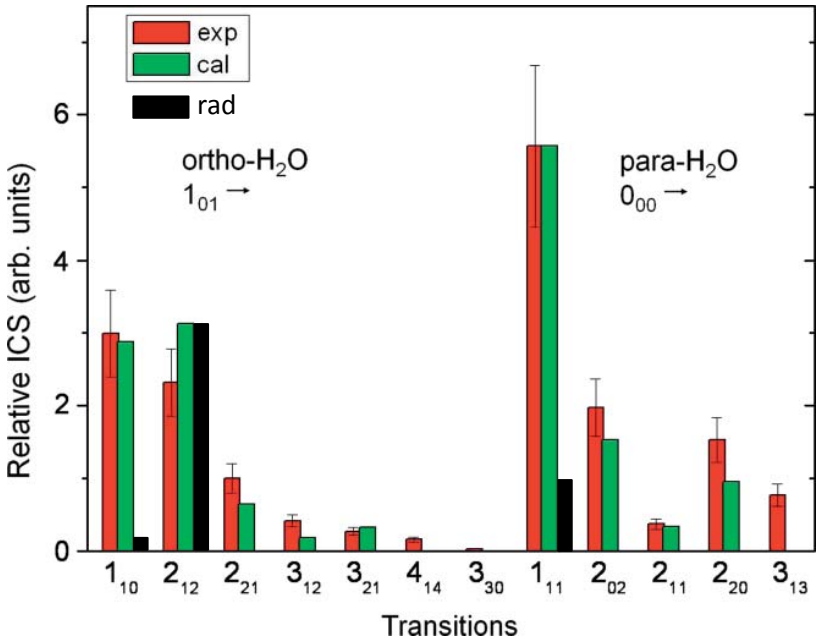


Yang et al. J Chem Phys (2010)

« Propensity » rules

- There is no selection rules in collisions
- But transitions with ΔJ =0, 1 are favored

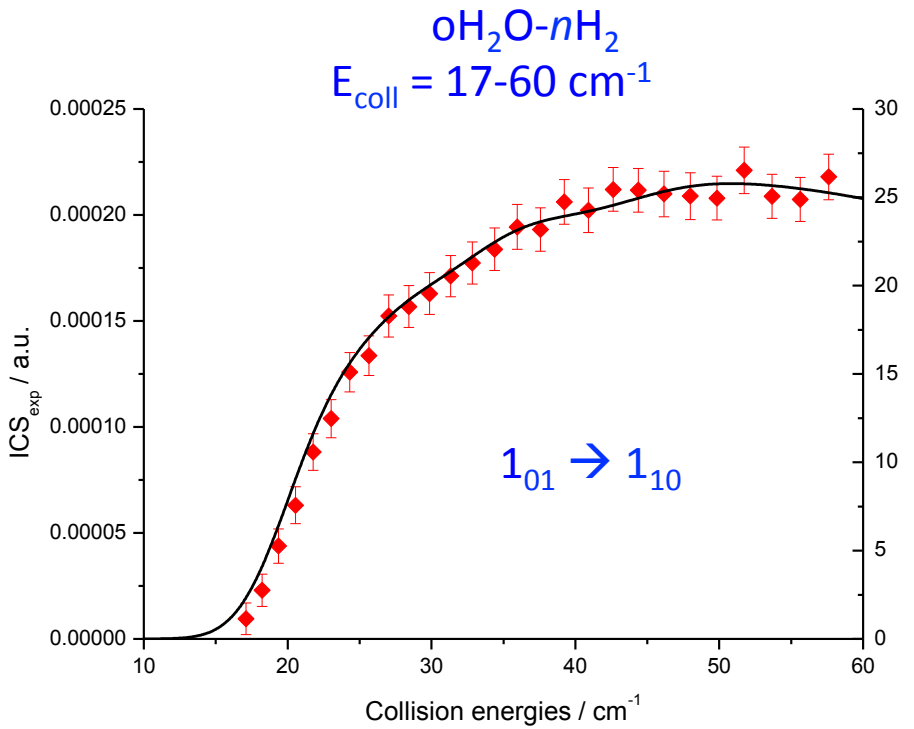
H_2O-pH_2
E_{coll} = 574 cm^{-1}



Yang et al. J Chem Phys (2011)

Inelastic cross sections

- Crossed molecular beams + variable crossing angle
- Near-threshold regime

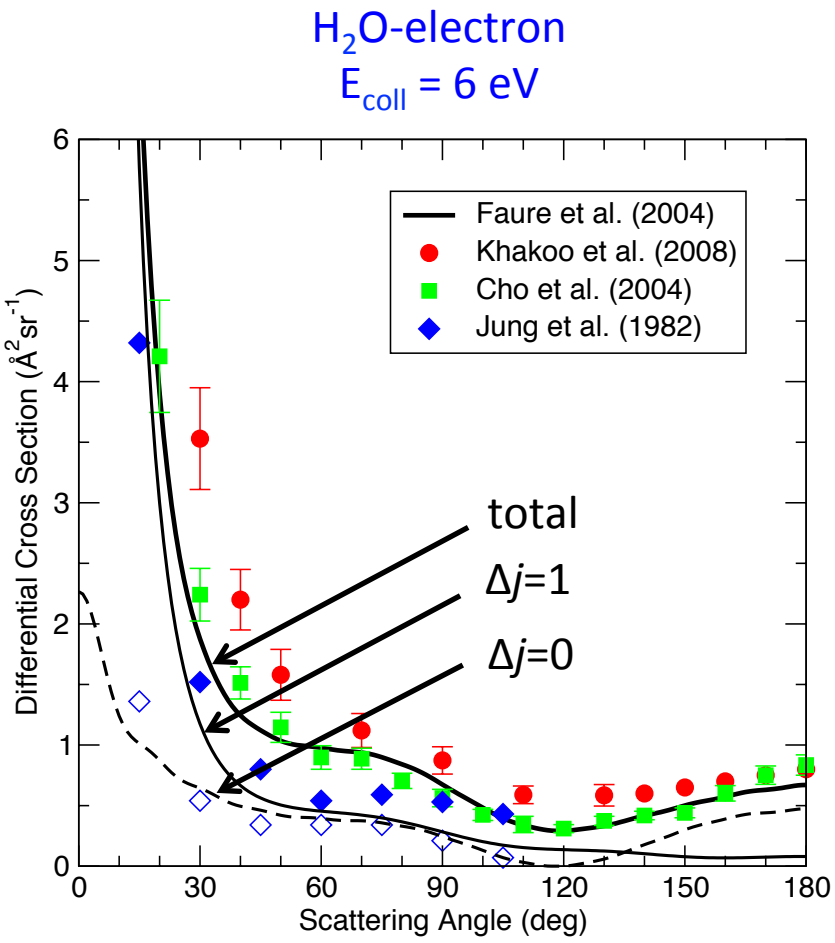


Bergeat et al., in preparation

H_2O-electron

Inelastic cross sections

- Electron-impact spectrometer
- Dipole-induced transitions favored

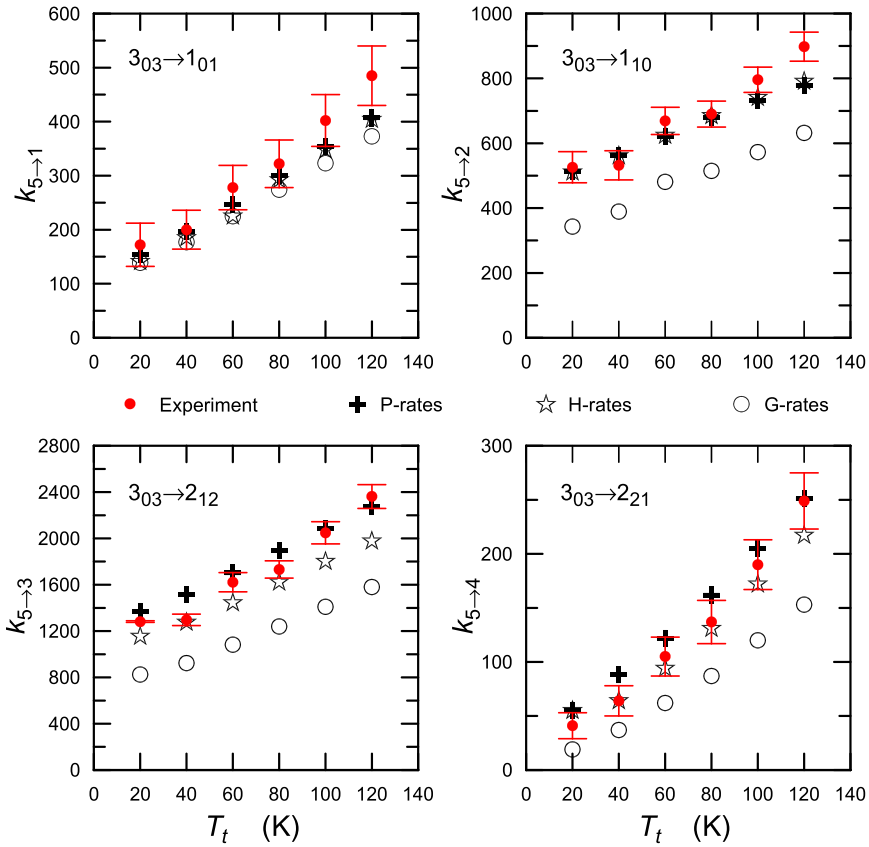


Zhang et al. Phys. Scr. (2009)

H_2O-He

Inelastic rate coefficients

- Raman spectroscopy in supersonic jets
- *Absolute* rate coefficients in cm^3s^{-1}



Tejeda et al. ApJS (2015)

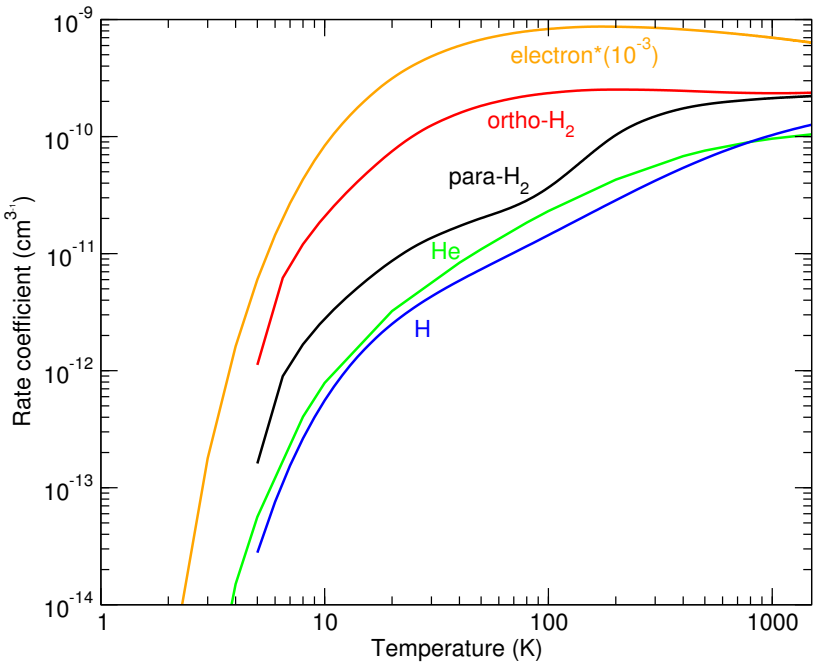
Summary of experiments

- Current PES are accurate to about 1% (≈ 1 cm^{-1})
- Inelastic cross sections have a 10-30% accuracy *rivaling or exceeding experiment*

Scaling relationship ?

- No simple scaling laws between H, He and pH_2
- Specific scattering calculations required

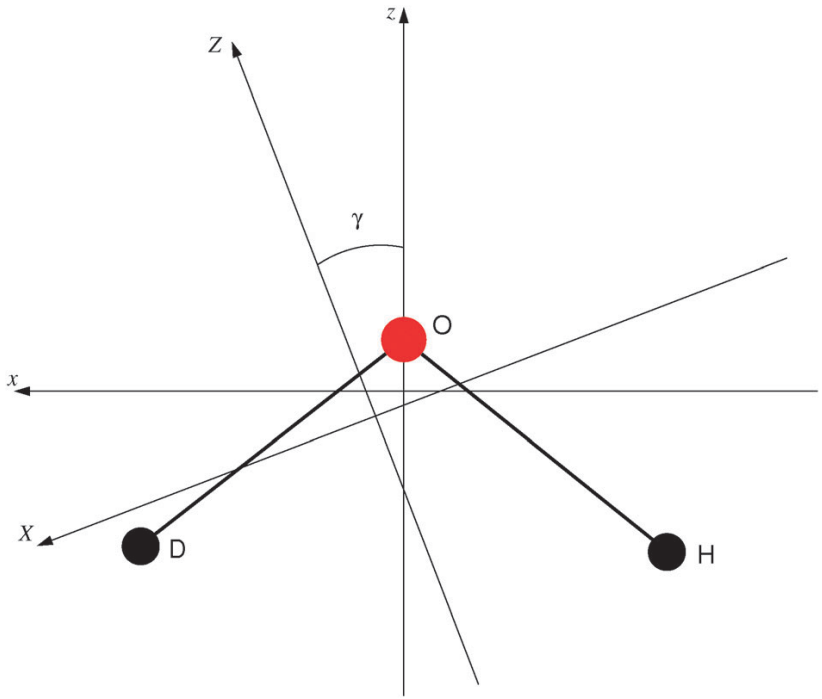
oH_2O $1_{01} \rightarrow 1_{10}$ @ 556 GHz



Daniel et al. MNRAS (2015)

Isotopologues

- Kinematic effects
  - Mass and velocities
- PES effects
  - Monomer geometries
  - Centre of mass
- Can be neglected in $H_2{}^{17}O$ and $H_2{}^{18}O$



Wiesenfeld et al. PCCP (2011)
Scribano et al. J Chem Phys (2010)

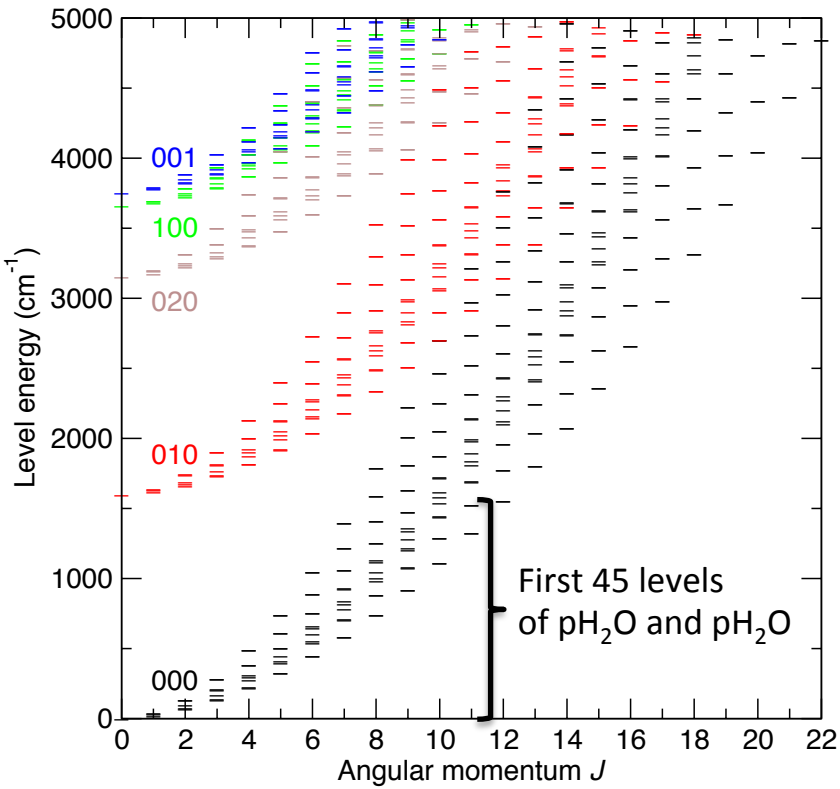
FUTURE ISSUES

Available data

- H_2O-He
  - Yang et al. ApJ (2013)
  - First 10 levels of oH_2O and pH_2O, T=1-3000 K
- H_2O-H
  - Daniel et al. MNRAS (2015)
  - First 45 levels of oH_2O and pH_2O, T=5-1500 K
- H_2O-H_2
  - Daniel et al. A&A (2011)
  - First 45 levels of oH_2O and pH_2O, T=5-1500 K
- HDO/D_2O-H_2
  - Faure et al. MNRAS (2012)
  - First 30 levels of HDO, first 12 levels of D_2O, T=5-300 K
- H_2O/HDO/D_2O-electron
  - Faure et al. MNRAS (2004)
  - First 28 levels of H_2O, HDO and D_2O, T=10-5000 K

Rovibrational excitation

- Current rovibrational data are based on extrapolations (Faure & Josselin 2008)
- Rigid-bender calculations in progress (Stoecklin et al.)



Lowest 824 rovibrational levels of H_2O

Related oxygen hydrides

- $OH + He$
  - Kalugina et al. Phys Chem Chem Phys (2015)
- $OH + H_2$
  - Schewe et al. J Chem Phys (2015)
- $OH^+ + He$
  - Gomes-Carrasco et al. ApJ (2014)
- $OH^+ + H$
  - Stoecklin et al. JPCA (2015)
  - Bulut et al. JPCA (2015)
- $H_2O^+ + H$
- $H_3O^+ + H_2$
- $H_2O + H_2O$ (for comets)
  - PES from Cencek et al. PCCP 2012

Conclusion

« Altogether, the collisional rate coefficients have now reached such high accuracy that they are no longer the limiting factor in the interpretation of the astronomical water data. This conclusion is a testimony to the decade long effort by molecular physicists and quantum chemists to determine them »

van Dishoeck, Herbst, Neufeld *Chem Rev (*2013)