HDO (and H_2O/D_2O) quenching rates

Theory & experiments

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A venture of IPAG and several institutes in France and worldwide

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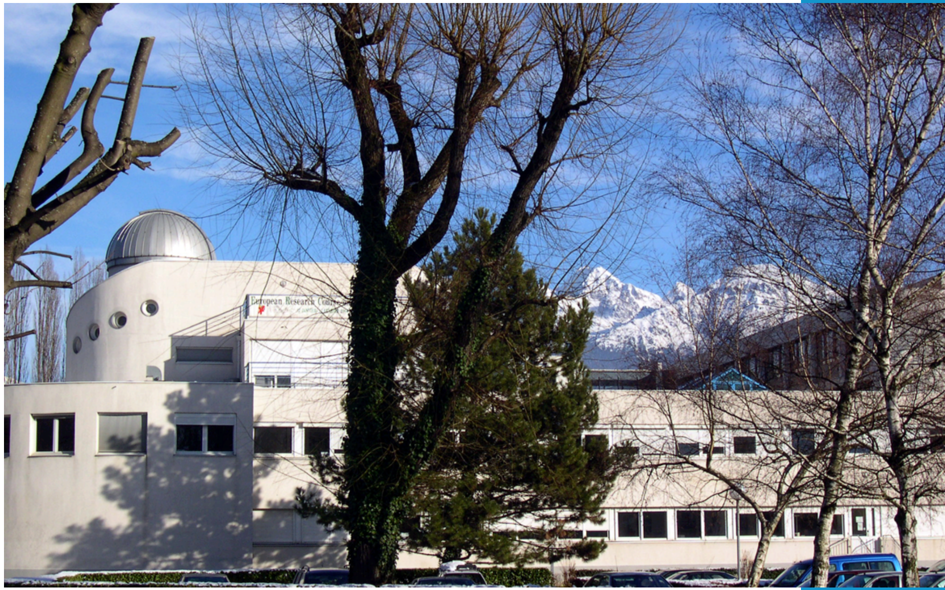


Meudon, Le Havre, Dijon, Lille,
Rennes, Bordeaux
Nijmegen (NL), JPL-Pasadena (US),
Durham (UK)

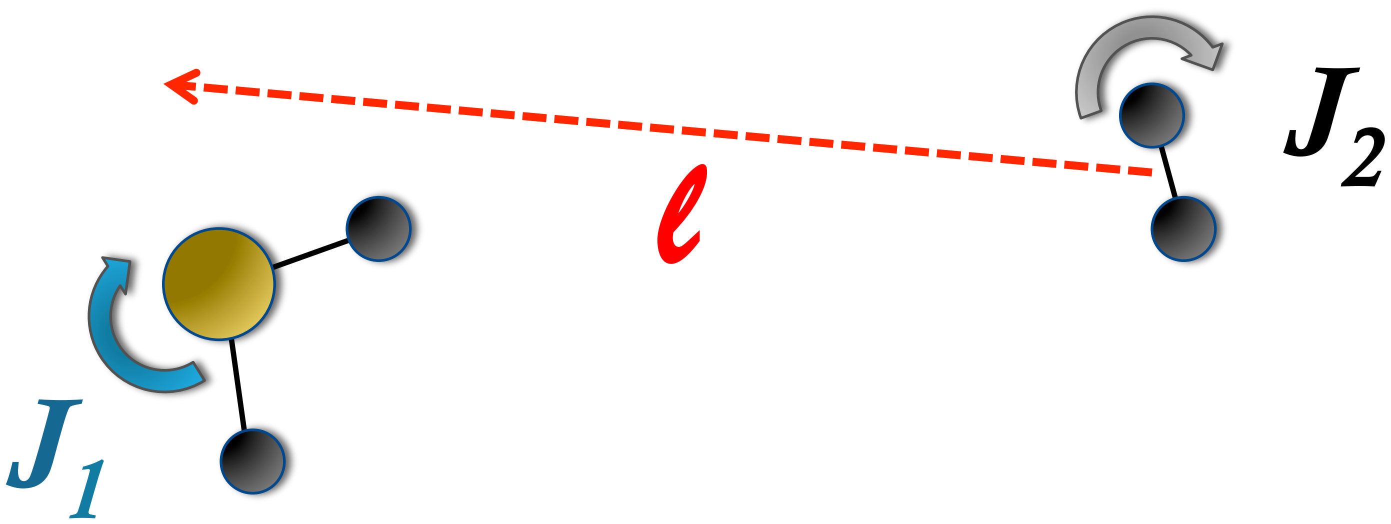
Also: ML Dubernet, F Daniel

€ :
EU FP6 'Molecular Universe',
CHESS KP HSO CNES,
ANR FORCOMS
COST ' The Chemical Cosmos', PCMI-INSU-CNRS, LABEX OSUG@2020, NWO

Collisional quenching/excitation :What is the physical process?

Rotational quenching (& fine structure, hyperfine, ro-vibrational quenching) :

Transfer between projectile and target of kinetic energy /angular momentum (external and/or internal) + transient polarization



Level populations

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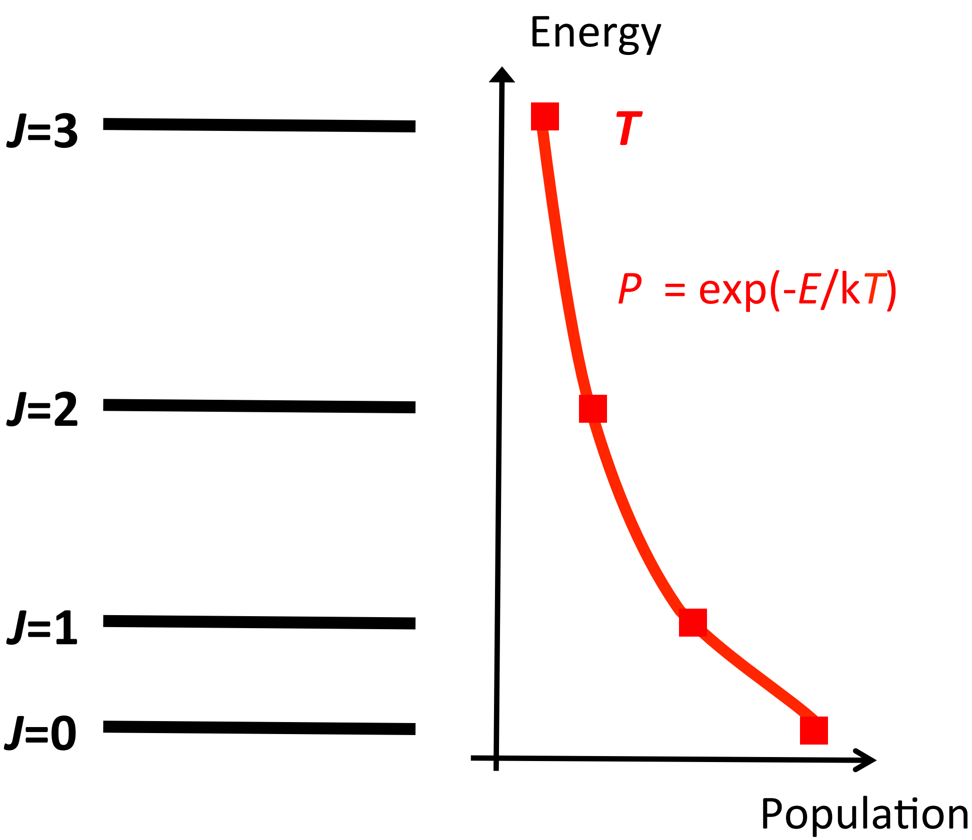
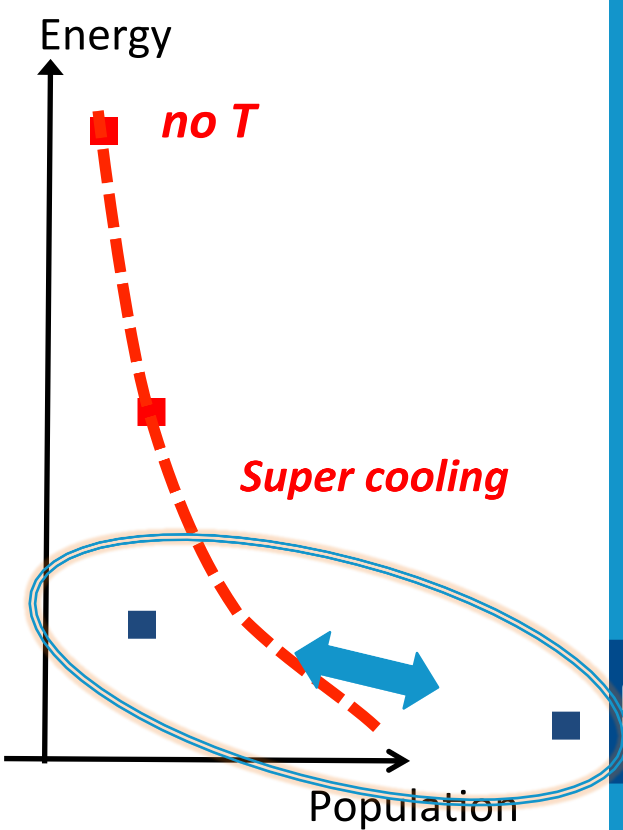
Levels and Temperature; Equilibrium with the photon gas or the buffer gas



Out of equilibrium : no *T*. Competition between photon interactions and collisions



Dividing point: critical density

Spontaneous emission (s^{-1})

$$n^*(H_2) = \frac{\sum_{j<i} A_{ij}}{\sum_{j<i} k_{ij}} \quad (cm^{-3})$$

Collision rates ($cm^3\ s^{-1}$)

Potential energy surface: ***Water–molecular hydrogen*** van der Waals interaction

- Full 9D PES,with
  - High precision 5D PES (rigid monomers), at CCSD(T)+ R12 corrections
  - Extrapolation for R > 15 A
  - Expansion around equilibrium points $(x-x_{eq})^n$, n=2,3

  - Average over *v*=0 ground state wave function : V(average), 5D
  - Average over v>0 wave functions : collision with excited H_2O (or H_2)
  - <v=1 | V | v=0> matrix elements : vibrational quenching

Valiron et al JCP, 2005 and 2009.

  - Monomer water : Kyro Hamiltonian, …

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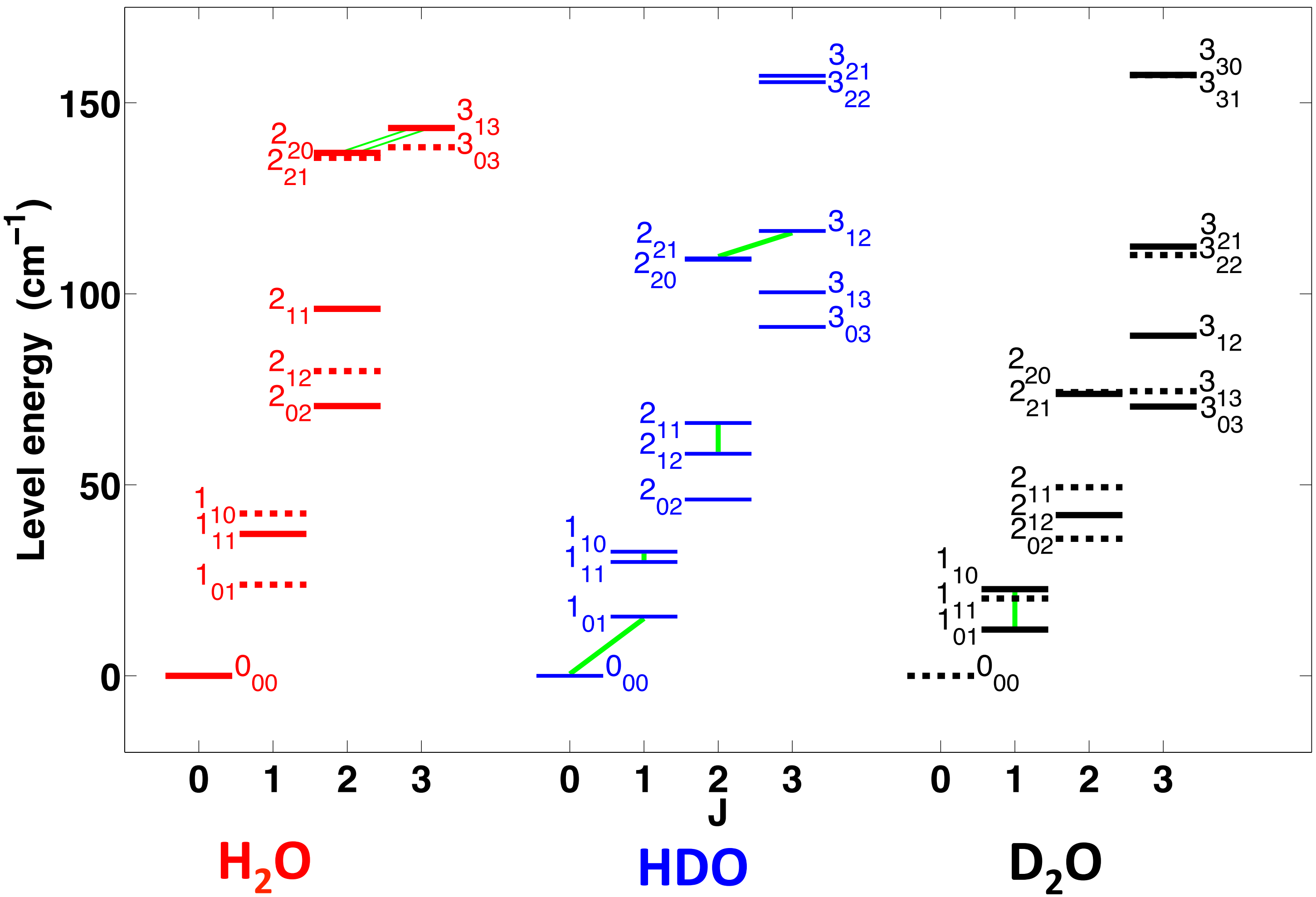
Rotational levels
H_2O, HDO, D_2O



Using the full PES

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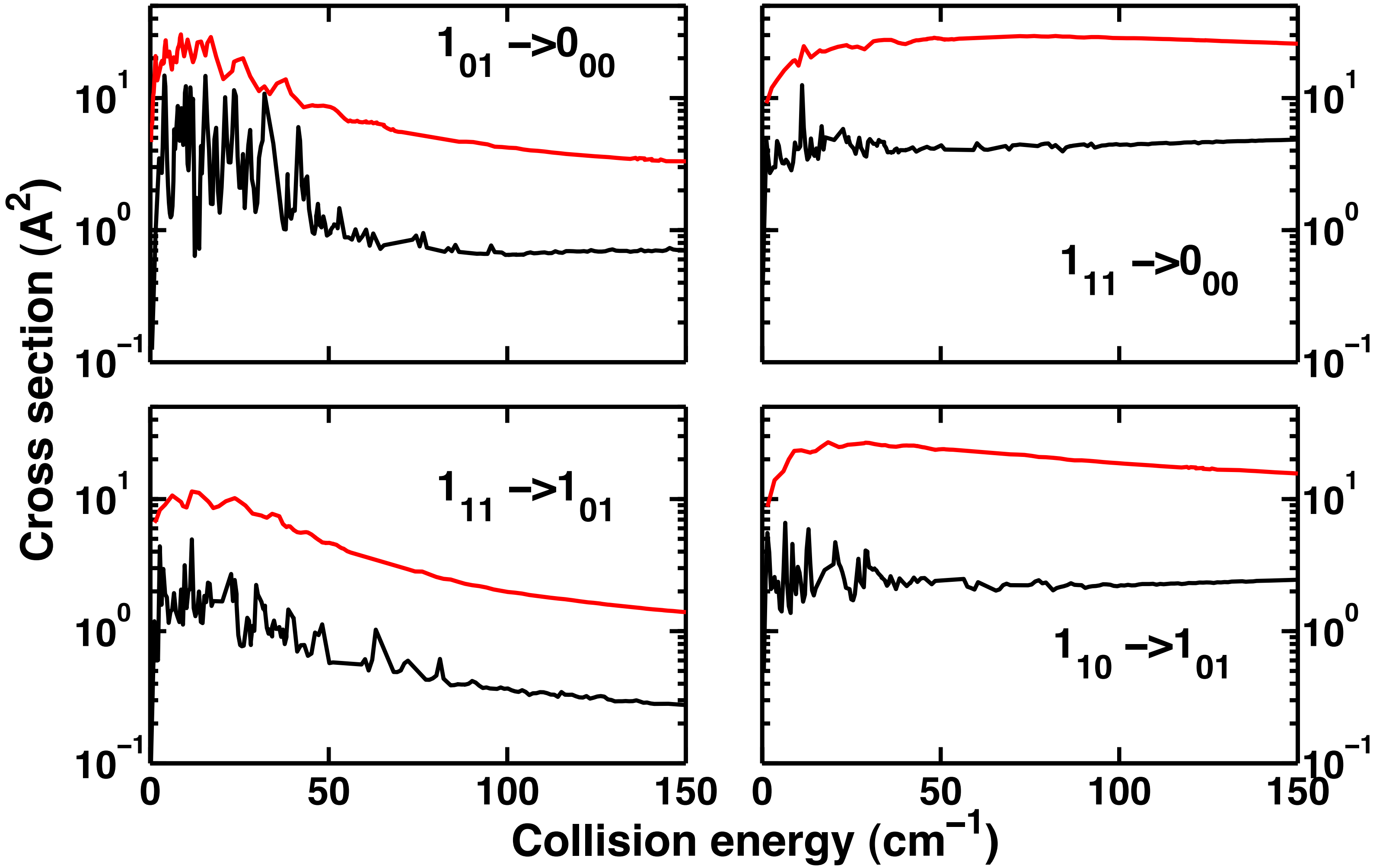
Property	Isotope	Calculation
Cross section, rotational excitation	$H_2O - H_2$	Quantum/ semi-classical
Rates	$H_2O - H_2$	Quantum
		Classical/statistical
Cross sections,rates	**$HDO - H_2$**	**Quantum**
	D_2O	Quantum
Differential Cross Section	$H_2O - H_2$	Quantum
	HDO-H_2; $D_2O - H_2$	Quantum
	$H_2O - D_2$	Quantum
Pressure Broadening	$H_2O - H_2$	Quantum
Vibrational excitation	$H_2O - H_2$	Classical, **quantum**

Cross sections, HDO-H_2

σ ($E_{collision}$)

Ortho H_2 j=1

Para H_2 j=0,2



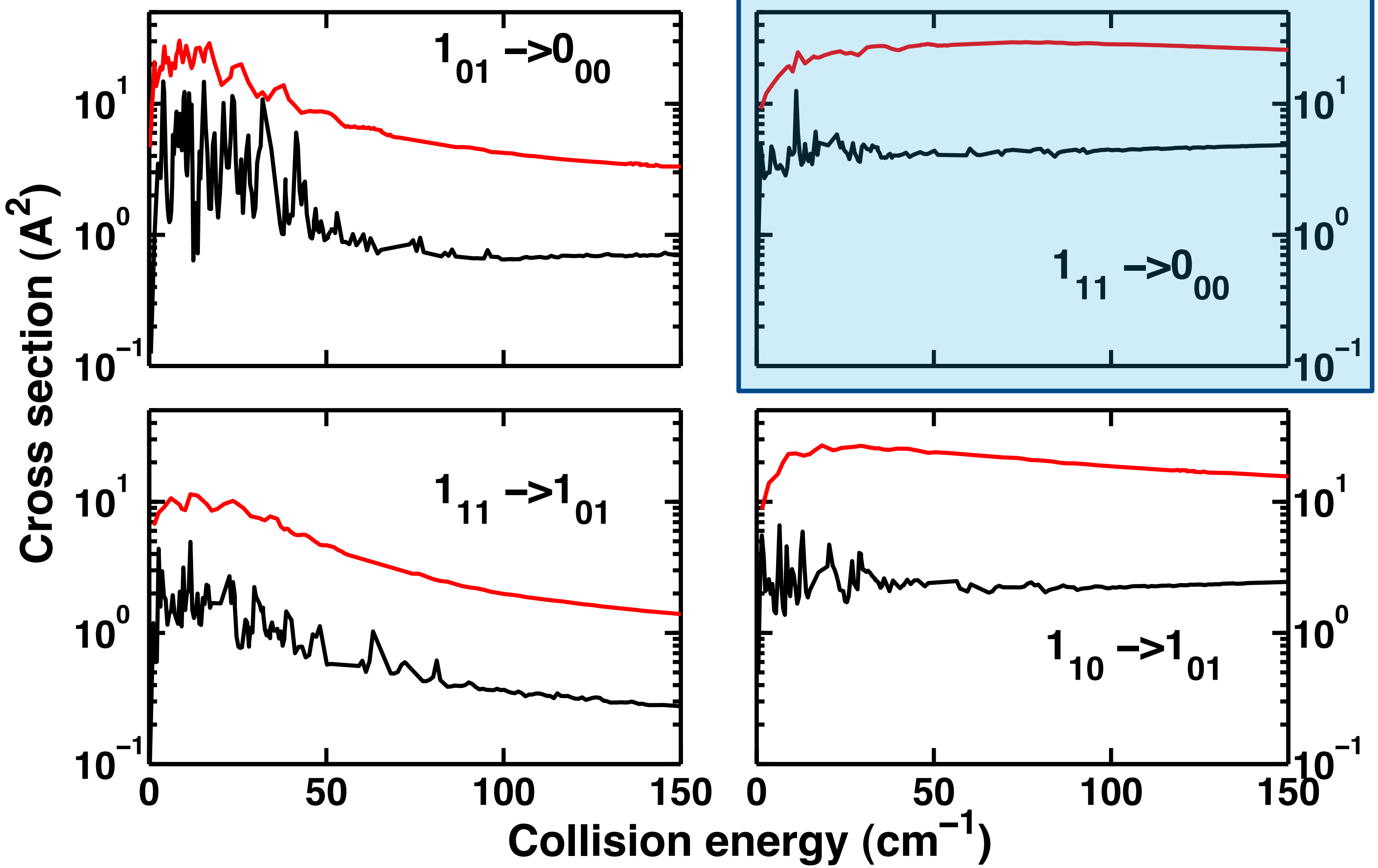
LW et al, PCCP, JCP, & MNRAS, 2011,2012

Cross sections, HDO-H_2

$\sigma\ (E_{collision})$

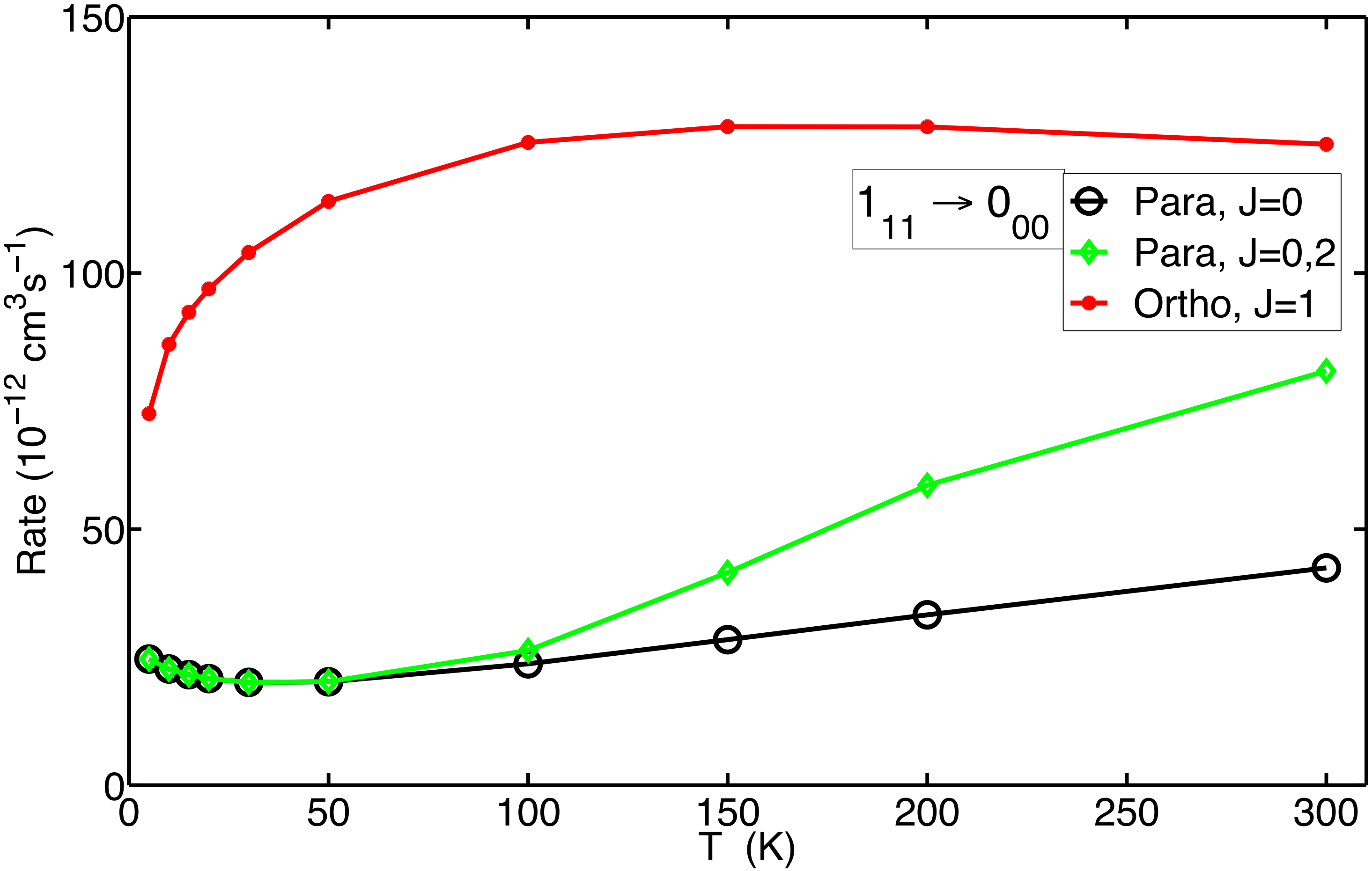
Ortho H_2 *j*=1

Para H_2 *j*=0,2



LW et al, PCCP, JCP, & MNRAS, 2011,2012

One example of rates



LW et al, PCCP, JCP, & MNRAS, 2011,2012

The file… as in LAMDA :

To be used in radiation transfer codes.

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- HDO rates; ortho H2, J=1

i	f	4	10	20	30	40	50	60	70	80	90	100
2	1	68.70	65.50	55.87	48.09	42.38	38.14	34.93	32.41	30.40	28.76	27.40
3	1	61.94	83.57	94.97	101.74	107.44	112.19	115.99	118.95	121.23	122.96	124.26
3	2	64.48	78.22	75.16	67.86	61.19	55.68	51.18	47.46	44.37	41.75	39.51
4	1	7.28	10.98	10.77	9.47	8.23	7.20	6.36	5.67	5.11	4.63	4.23
4	2	112.91	180.29	212.04	223.60	229.98	233.84	236.04	237.09	237.33	236.99	236.26
4	3	51.15	71.42	71.53	67.06	62.82	59.21	56.15	53.52	51.24	49.25	47.49
5	1	17.30	20.70	21.41	21.50	21.63	21.78	21.91	22.02	22.12	22.21	22.29
5	2	35.26	42.49	42.03	40.16	38.60	37.31	36.22	35.29	34.48	33.78	33.17
5	3	102.42	125.31	129.32	127.62	125.08	122.13	119.04	115.95	112.96	110.13	107.46
5	4	49.04	51.33	47.62	44.29	41.67	39.49	37.60	35.95	34.49	33.19	32.04
6	1	5.98	7.58	8.37	8.97	9.37	9.63	9.80	9.91	9.99	10.04	10.07
6	2	71.93	86.73	93.27	100.90	107.12	111.70	115.00	117.39	119.12	120.40	121.35
6	3	35.88	41.20	39.63	38.56	37.62	36.68	35.77	34.90	34.09	33.36	32.69
6	4	53.64	64.95	67.11	68.04	67.74	66.64	65.16	63.53	61.89	60.29	58.76
6	5	57.87	61.02	52.66	46.89	42.45	38.77	35.67	33.02	30.76	28.80	27.10
7	1	7.32	8.34	9.45	10.40	10.93	11.19	11.31	11.34	11.34	11.30	11.26
7	2	12.09	13.70	13.38	12.90	12.28	11.64	11.06	10.54	10.09	9.69	9.34
7	3	57.84	64.92	74.44	83.60	89.32	92.71	94.70	95.82	96.42	96.67	96.72
7	4	18.71	23.10	24.24	24.83	24.91	24.73	24.43	24.10	23.76	23.43	23.11
7	5	121.05	139.28	158.27	176.12	187.14	193.54	197.13	199.01	199.82	199.93	199.59
7	6	49.41	57.06	57.04	55.79	53.45	50.80	48.23	45.86	43.74	41.85	40.17
8	1	0.13	1.18	2.34	2.90	3.22	3.43	3.58	3.69	3.79	3.87	....

A Faure et al
MNRAS, 2012

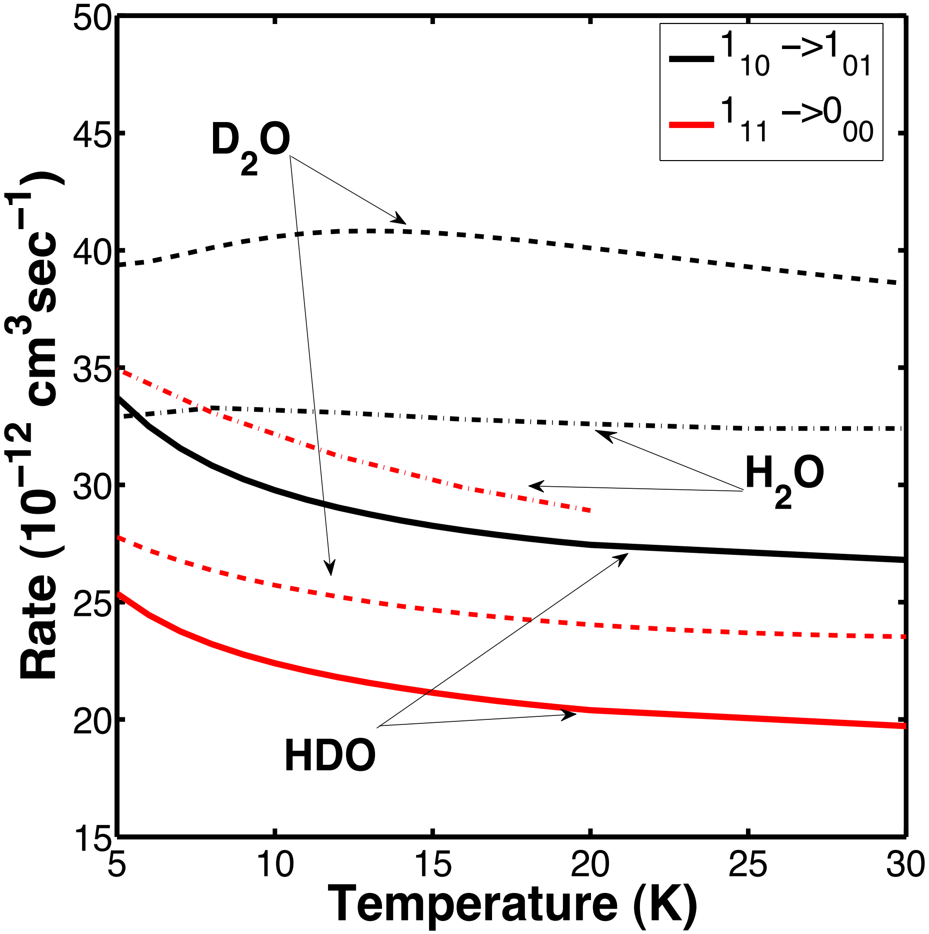
Rates

Compare ***red to red***, ***black to black..***

H_2O vs HDO

HDO –H2 rates similar to H_2O – H_2 rates, but not quite…

300K, o & p H_2
Effort 10-15 times as large as H_2O



LW et al, PCCP, JCP, & MNRAS, 2011,2012

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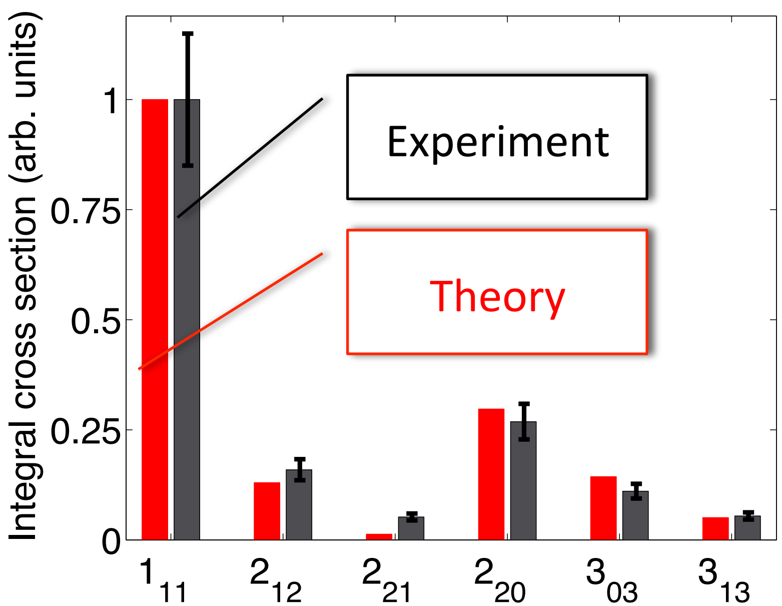
Using, testing the PES

Property	Test	Status	
		Experiment	Theory
Overall shape	Pressure broadening	✓	✓
	Virial coefficients	?	☐
Wells	Bound states spectroscopy	✓	✓
Repulsive wells	Inelastic DCS	✓	✓
Vibrational transitions	Total cross section	1	In progress

Experimental comparisons

- The same PES for each H_2O, HDO, and D_2O. Test for one is valid for the others, except for
  - Experimental procedures
  - Specific numerical difficulties

- Tests:
  - Differential Cross Section
  - Pressure broadening
  - Integral Cross Section
  - Comparison ICS HDO – ortho H_2



Sarma et al, JCP, 2013
Parker & LW, PCCP feature article, 2013, in prep.

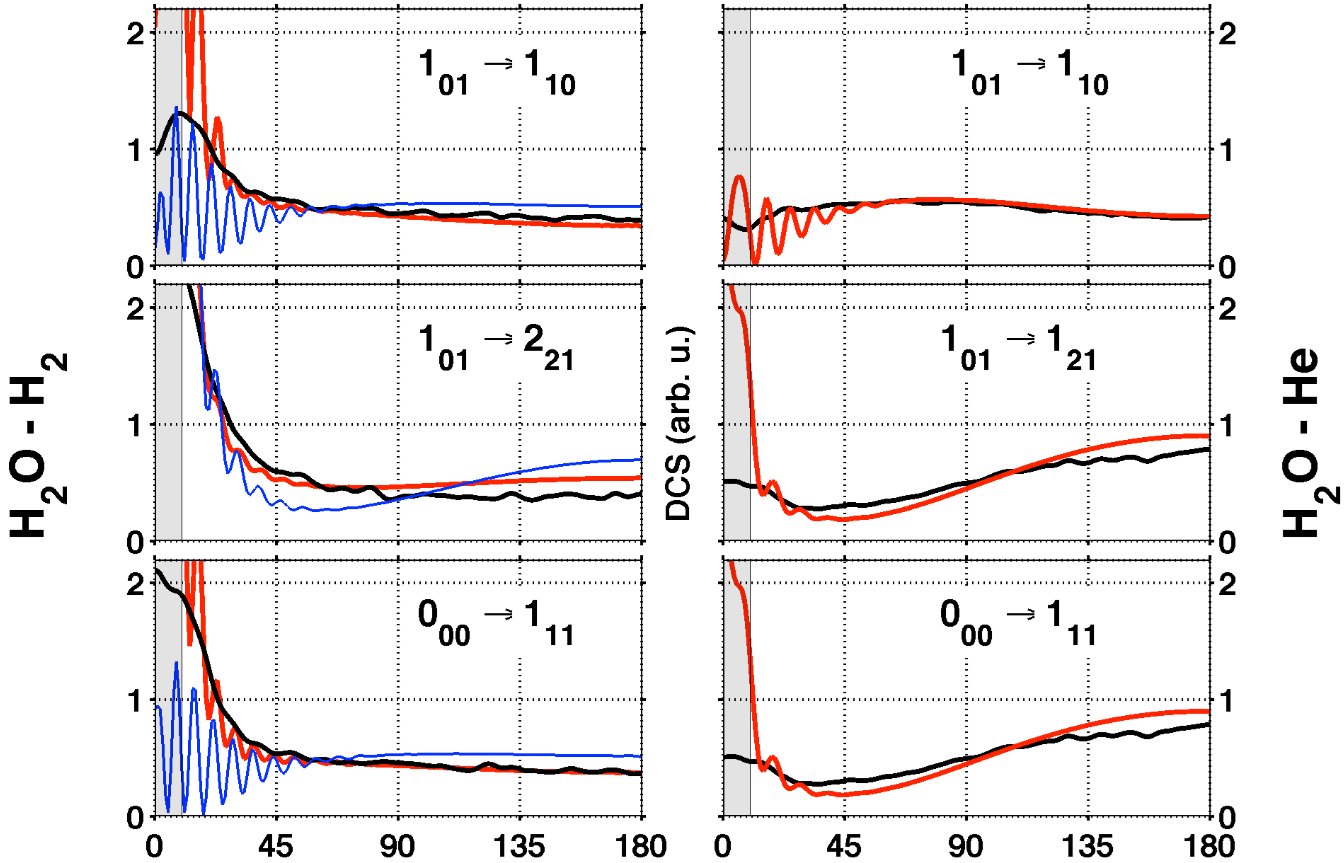
H_2O- H_2 DCS

Theory:

Experiment:

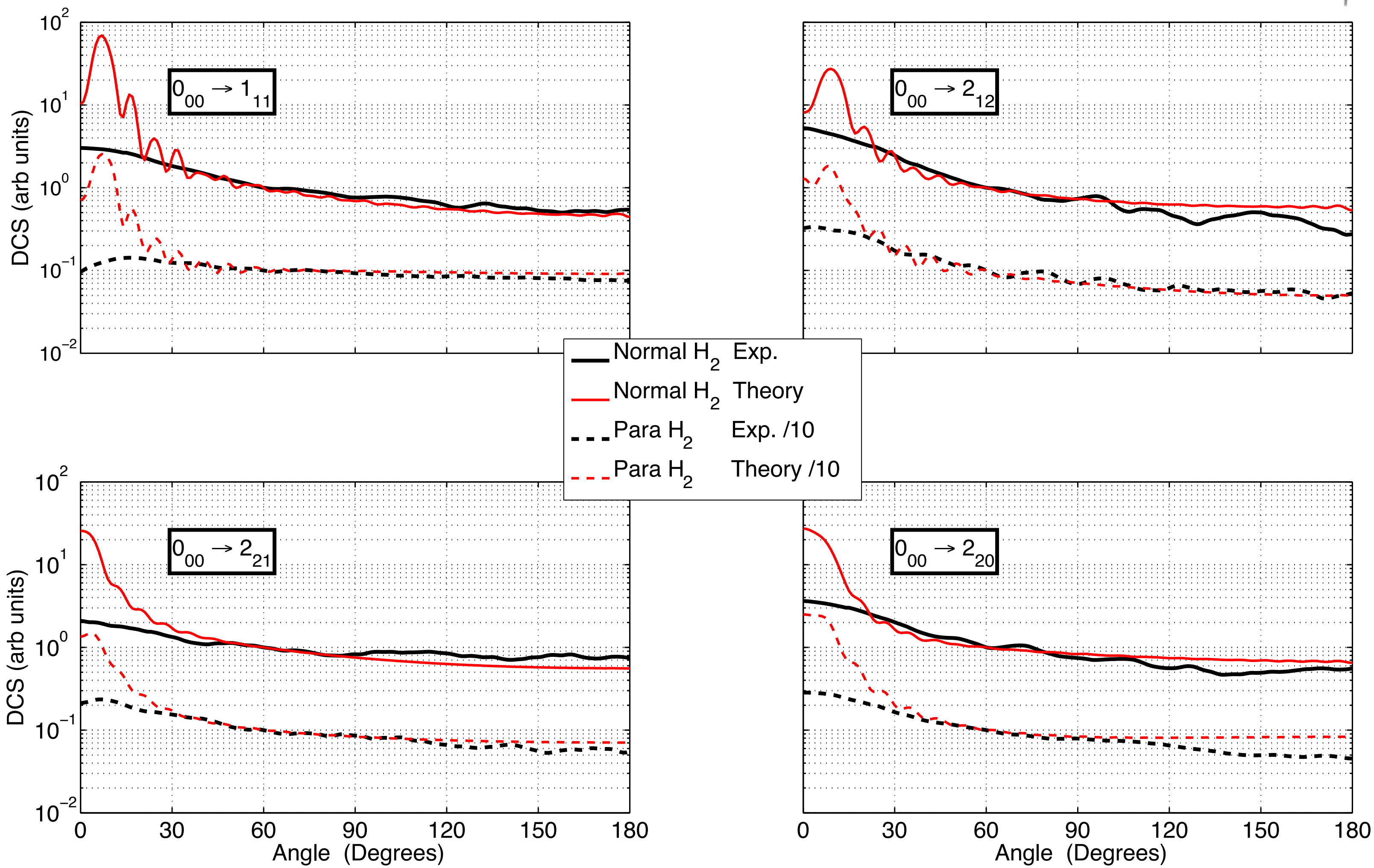
Normalized, no adjustable parameter (H_2 J=0,1,2, exp. abundances)

E collision : 574 cm-1



CH Yang et al; J Chem Phys, 2010, 2011

HDO- H_2 DCS



G. Sarma et al. JCP 2013

Pressure broadening

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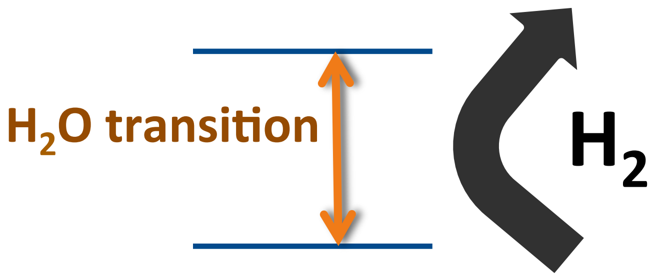
Theory



The collisions have two effects :

Virtual inelastic scattering
Dephasing of the transition

Result in a spectral line profile + spectral line shift

Approximation of isolated collisions + isolated spectallines.

Experimental set up, Drouin et al, JPL

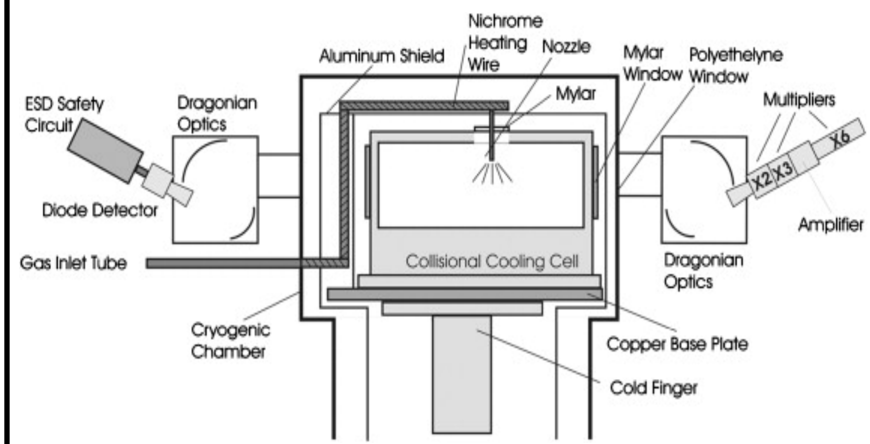
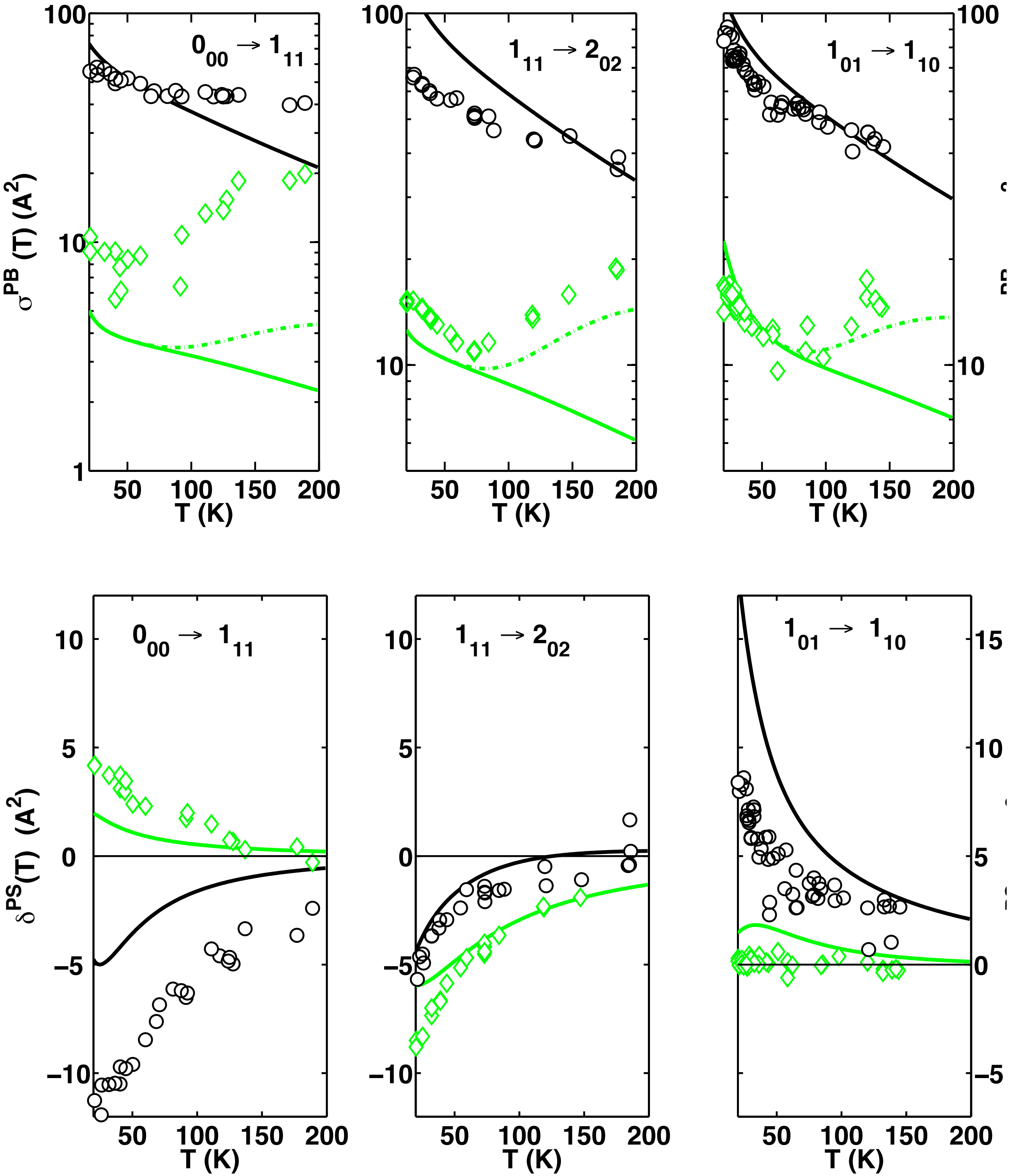


Fig. 1 Side-view of the collisional cooling experiment. The collisional cooling cell is housed inside the cryogen cell, cooled by a cold finger coupled to a helium cryo-refrigeration system and isolated from the warm cryogen cell walls via an Alu...

Michael J. Dick , Brian J. Drouin , Timothy J. Crawford , John C. Pearson



Pressure broadening and shift,
H_2O in H_2

B. Drouin (JPL), LW, Phys Rev A 2012.

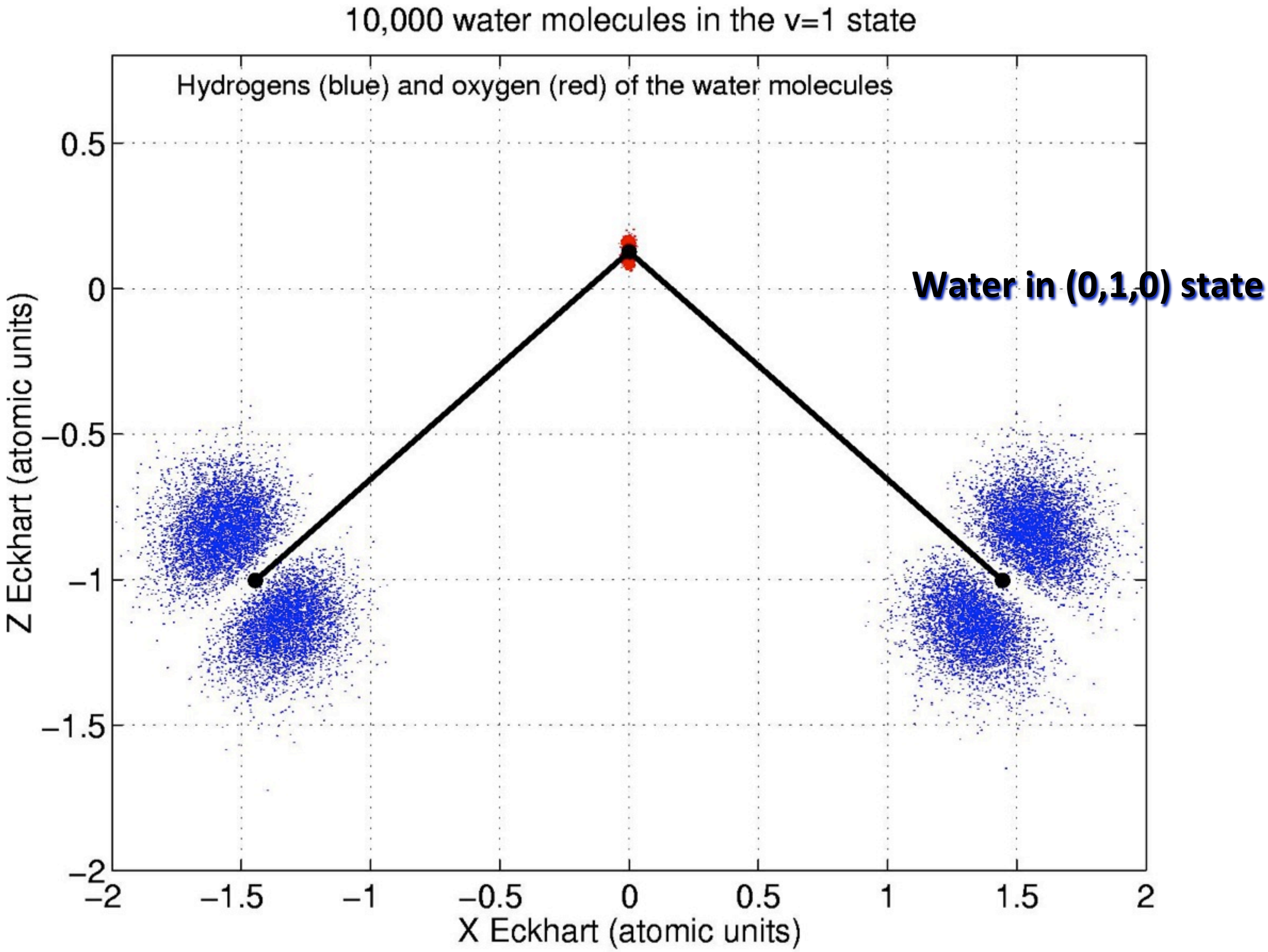
BLACK: Broadening with normal H2;

Green , broadening by para H2.

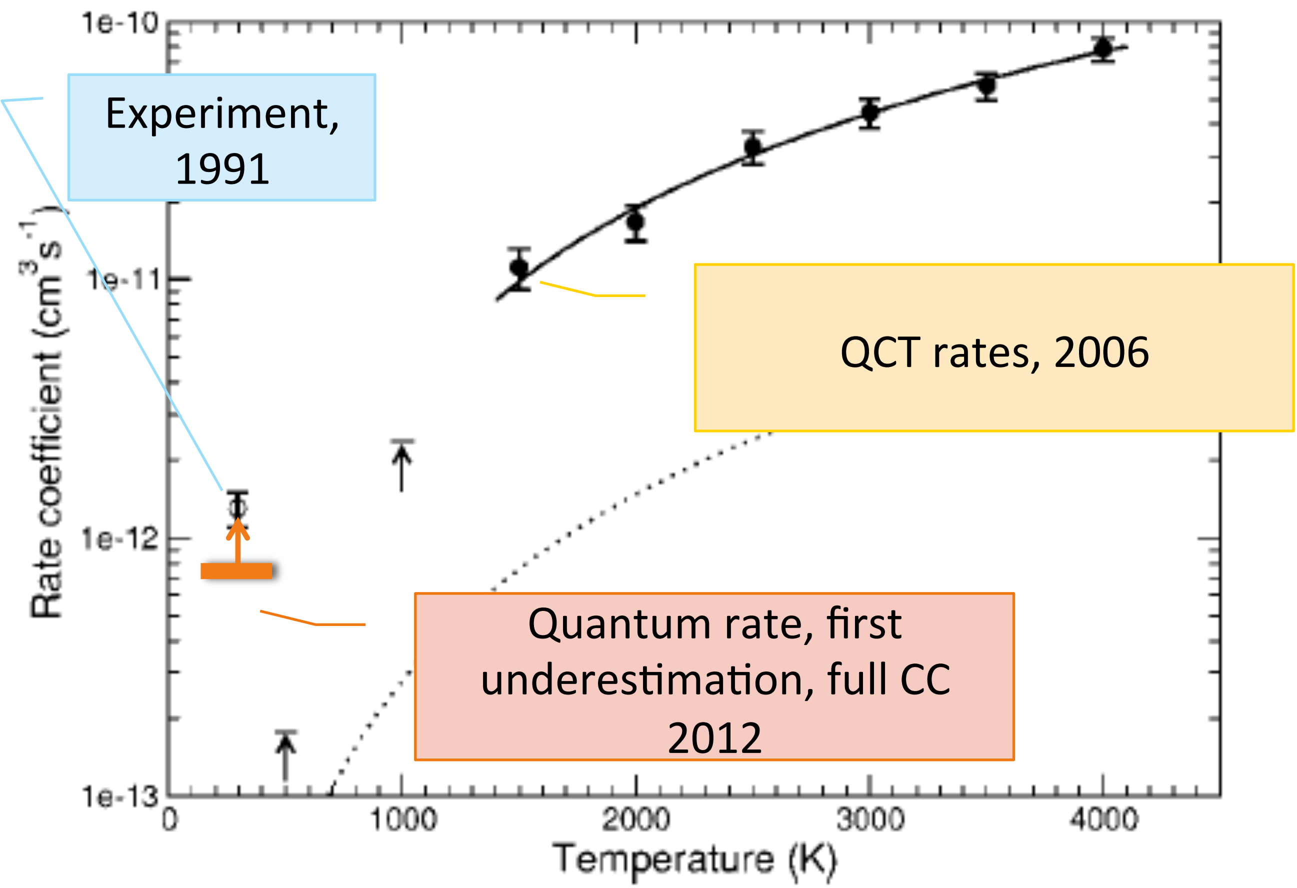
Lines : theory; symbols: experiments.

Vibrational quenching :

<v=1 | V | v=0> matrix elements



Vibrational quenching v=1 -> v=0 H_2O – o-H_2



LW, M Gonzalez, J Hutson, in preparation