Theoretical Studies of High Energy Oxygen Atom Chemistry

M. Braunstein, J. Duff, R. Shroll, L. Bernstein,
S. Adler-Golden, and R. Panfili

Spectral Sciences, Inc.

(www.spectral.com)

The 2004 Air Force Office of Scientific Research

Molecular Dynamics and Theoretical Chemistry Contractor's Meeting

24-26 May 2004 Newport, Newport, RI.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **13 APR 2004**	2. REPORT TYPE	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Theoretical Studies of High Energy Oxygen Atom Chemistry**	5a. CONTRACT NUMBER **F04611-03-C-0015**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **M. Braunstein; J. Duff; R. Shroll; L. Bernstein; S. Adler-Golden**	5d. PROJECT NUMBER **BMSB**
	5e. TASK NUMBER **R2FT**
	5f. WORK UNIT NUMBER **BMSBR2FT**
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Spectral Sciences Incorporated,4 Fourth Avenue,Burlington,MA,01803-3304**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

The original document contains color images.

14. ABSTRACT

Ab-initioModeling of the Following Reactions:¨CO + H2¡úOH + H¨CO + H2O ¡úO + H2O*, OH + OH*¨CO + HCl¡úO + HCl*, Cl+ OH***

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**45**	

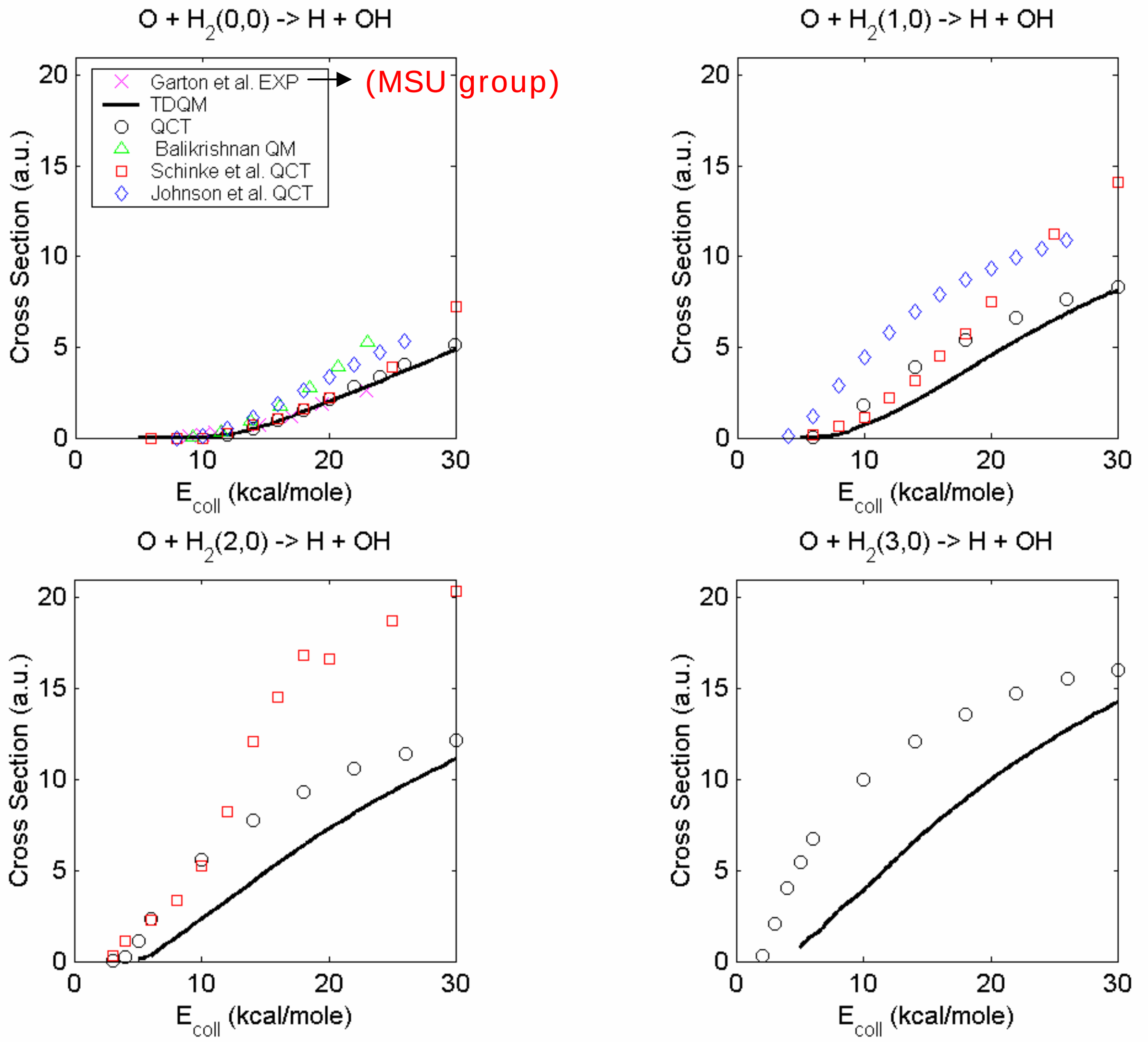
Acknowledgements

- Missile Defense Agency Phase II SBIR Award
  - Contract Number F04611-03-C-0015
- Department of Defense
  - Contract Number F19628-00-C-0006
- Air Force Research Laboratory, Edwards AFB, California
  - M. Venner, Technical Monitor
- Collaborators:
  - G. C. Schatz, B. Maiti, Northwestern University
  - B. Ramu Ramachandran, Louisiana Technical University
  - J. Bowman, T.Xie, Emory University
  - T. Minton, Montana State University

Outline

- Ab-initio Modeling of the Following Reactions:
  - $O + H_2 \rightarrow OH + H$
  - $O + H_2O \rightarrow O + H_2O^*, OH^{**} + OH^*$
  - $O + HCl \rightarrow O + HCl^*, Cl + OH^*$

Cross Sections vs. Energy $H_2(v)$



$O + H_2(0,0) \rightarrow H + OH$

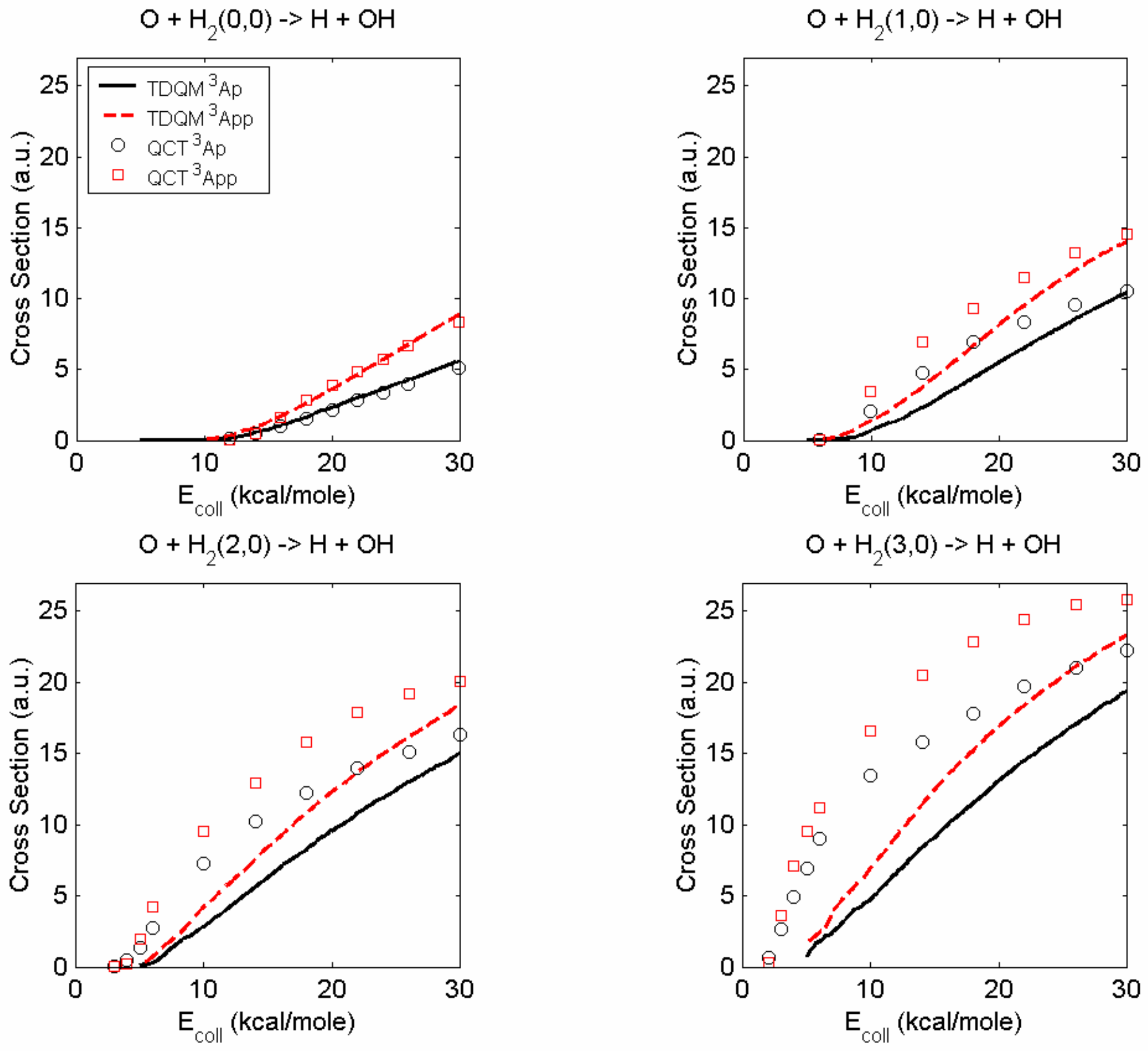
$O + H_2(1,0) \rightarrow H + OH$

$O + H_2(2,0) \rightarrow H + OH$

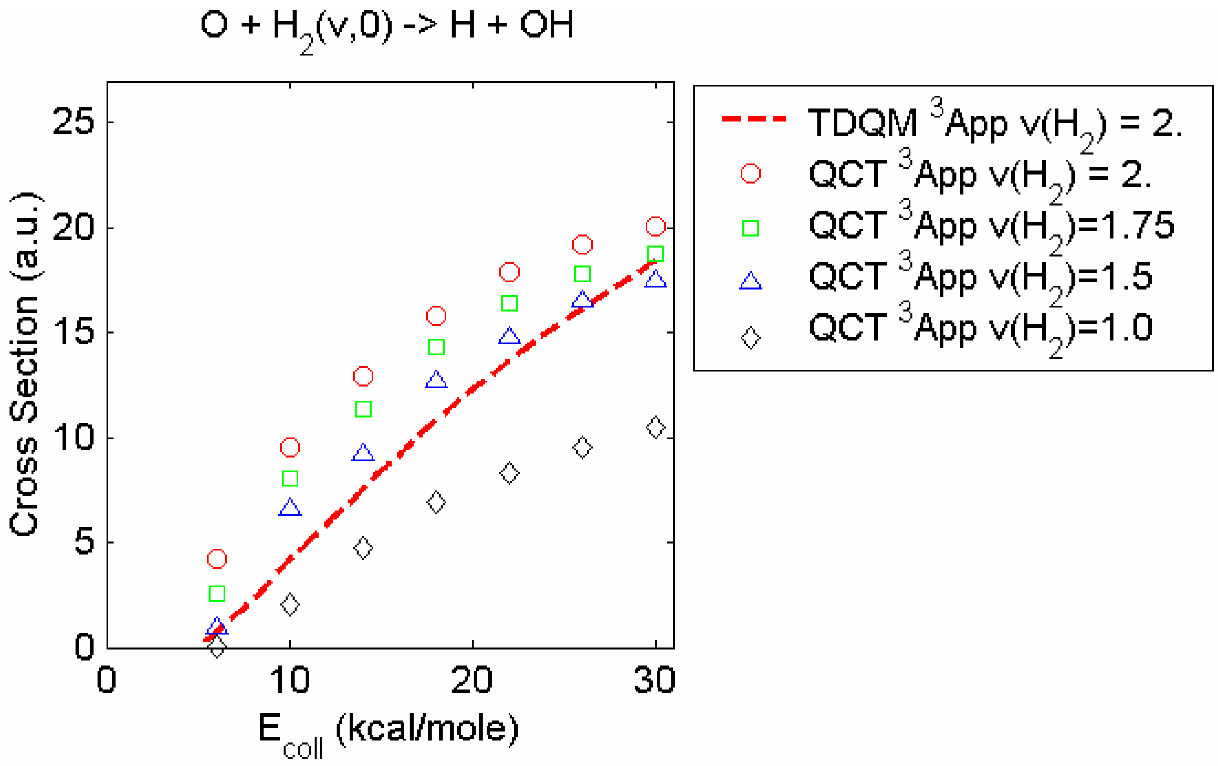
$O + H_2(3,0) \rightarrow H + OH$

(MSU group)

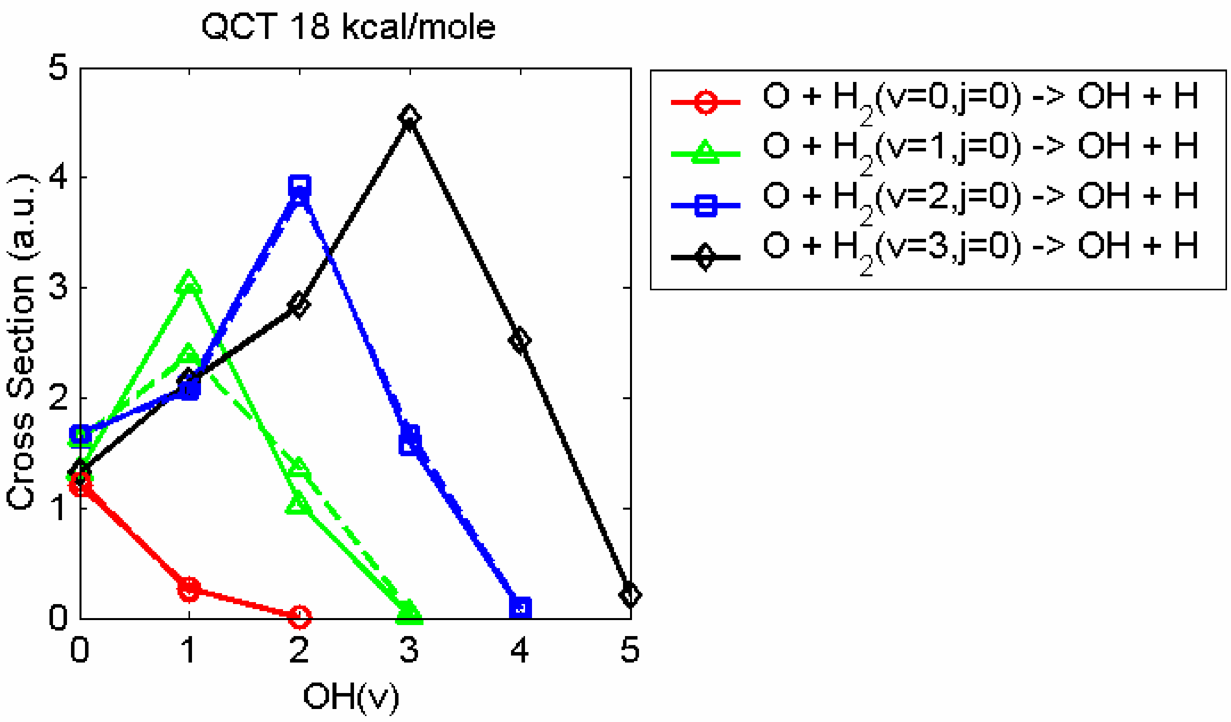
Comparisons with QM



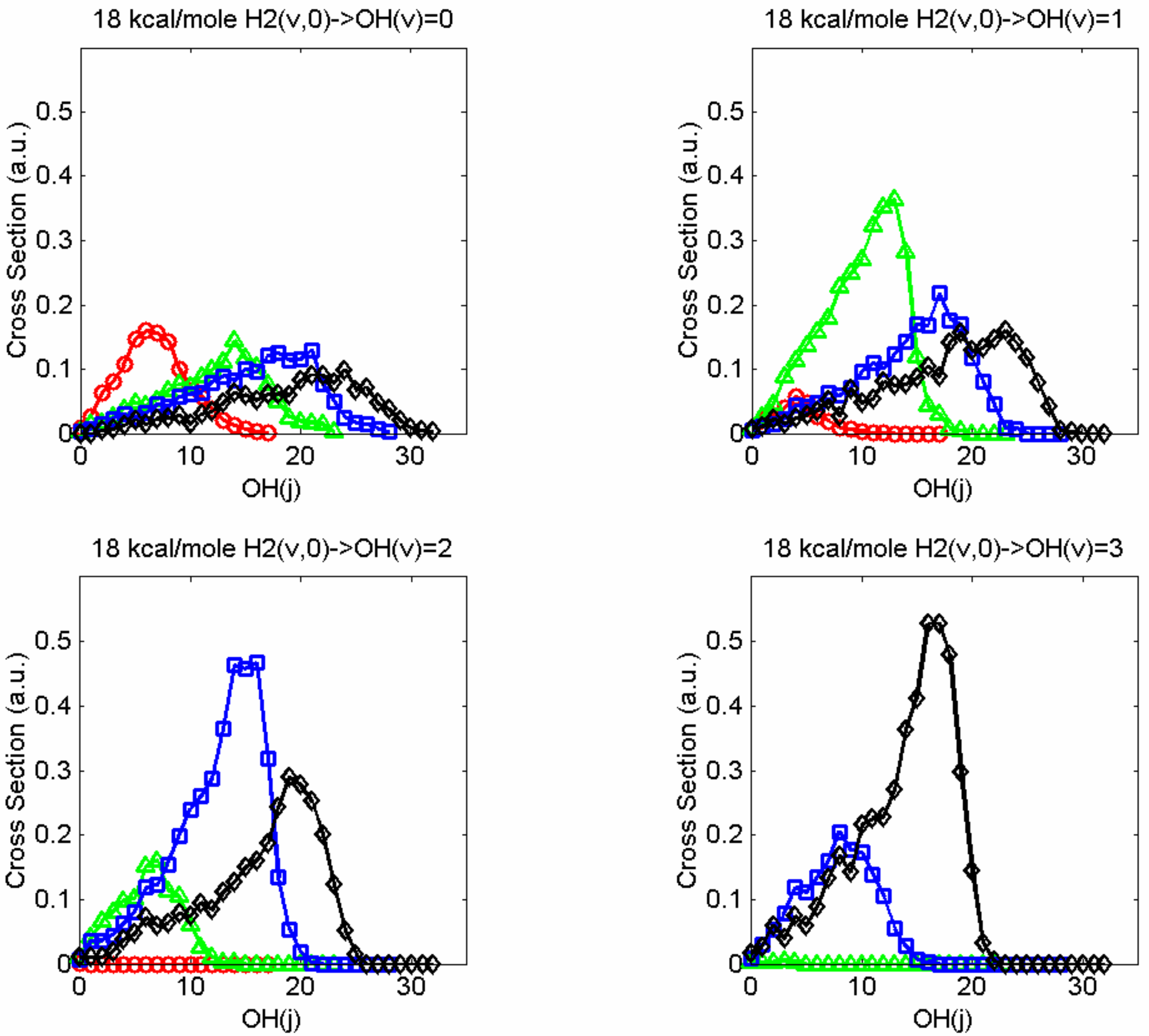
Adjusting QCT to Match QM



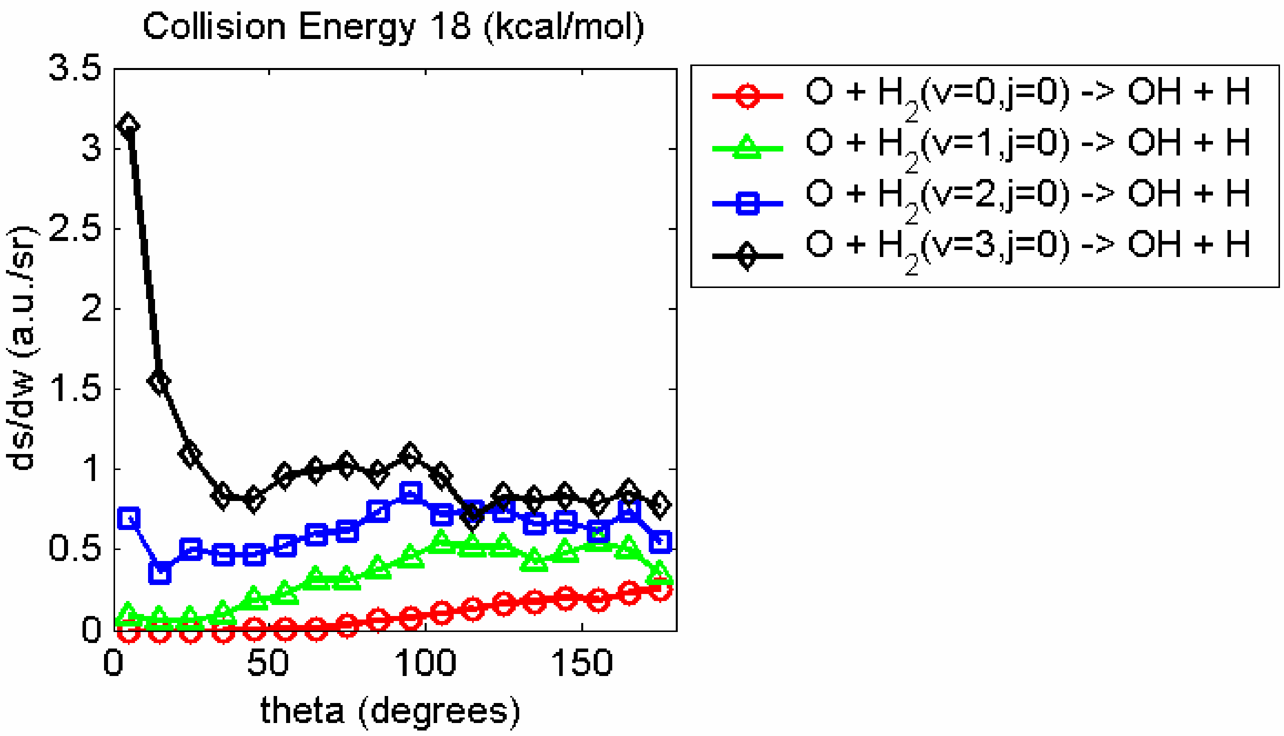
Vibrational Distributions



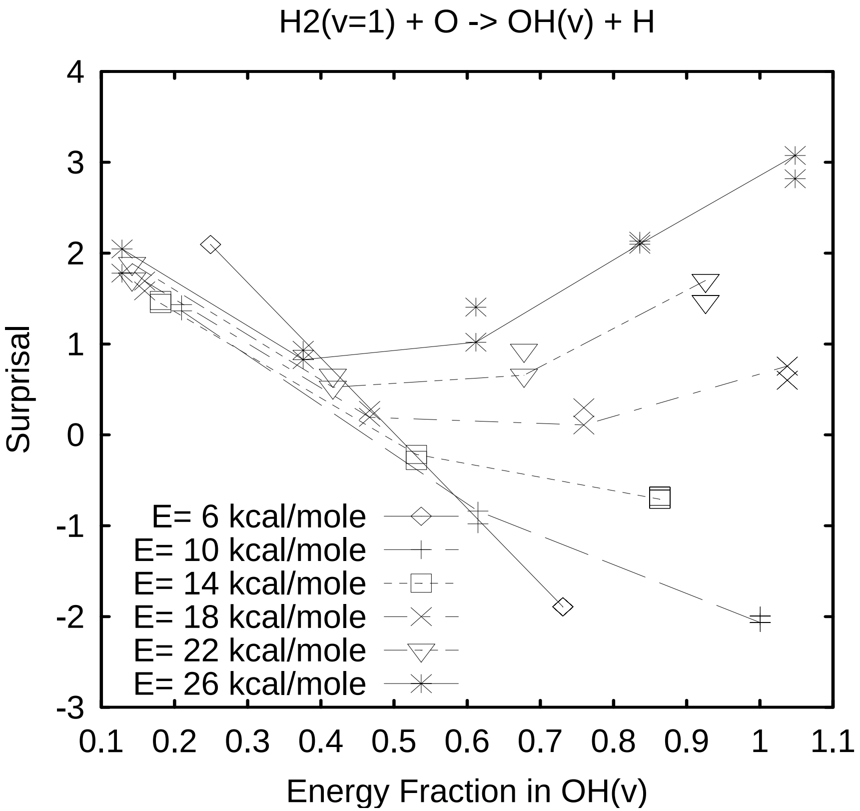
Rotational Distributions

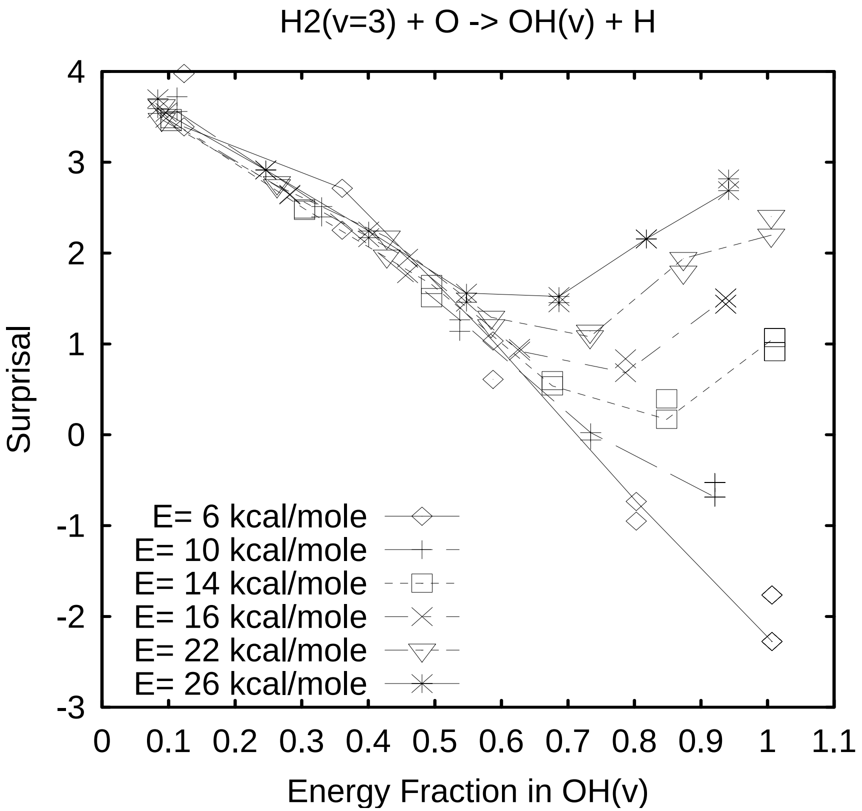


Angular Distributions

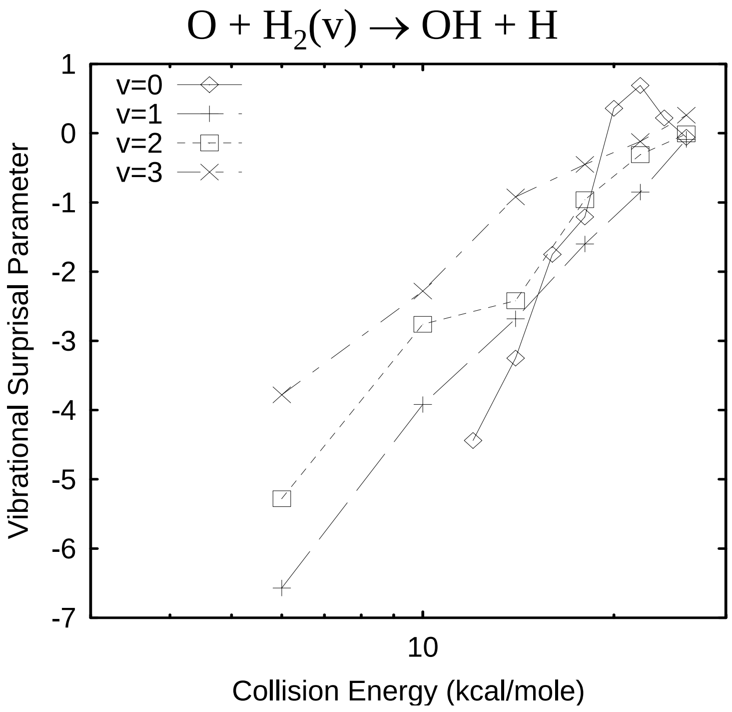


Surprisal Fits of Vibrational Distributions





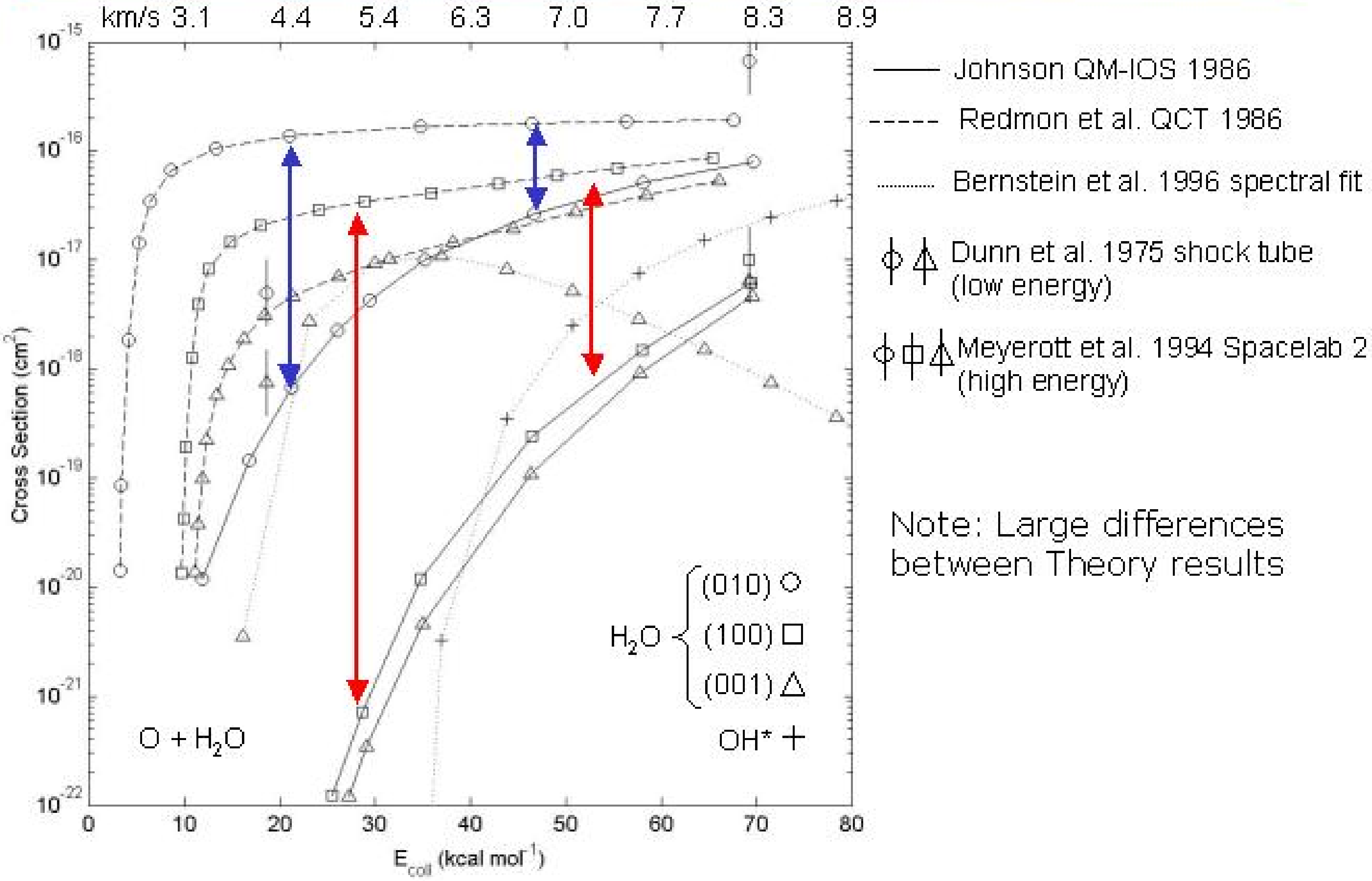
Vibrational Surprisal Parameter vs. Energy



Overview of the O + H_2O System

- Principal channels
  - $O + H_2O \rightarrow O + H_2O^*$
  - $O + H_2O \rightarrow OH^{**} + OH^*$
- Experimental Studies
  - Shuttle Observations (~8 km/s)
  - Shock Tube (~4.3 km/s)
  - Physical Sciences Inc. (CVF) measurements (~8 km/s)
  - Rate constants up to ~2500 K
  - Recent measurements
    - $(H_2O)O^- + \text{photon} \rightarrow OH^* + OH^{**}$ (transition state information)
    - $O + HOD(4v_{OH}) \rightarrow OH^* + OD^*$
- Theory
  - Old 'non-reactive' surface
    - Johnson (Quantum)
    - Redmon et al. (Classical)
  - Large disagreements
- Measurements are sparse and Theory not really helpful

Calculations and Measurements of the O + H_2O Cross Sections



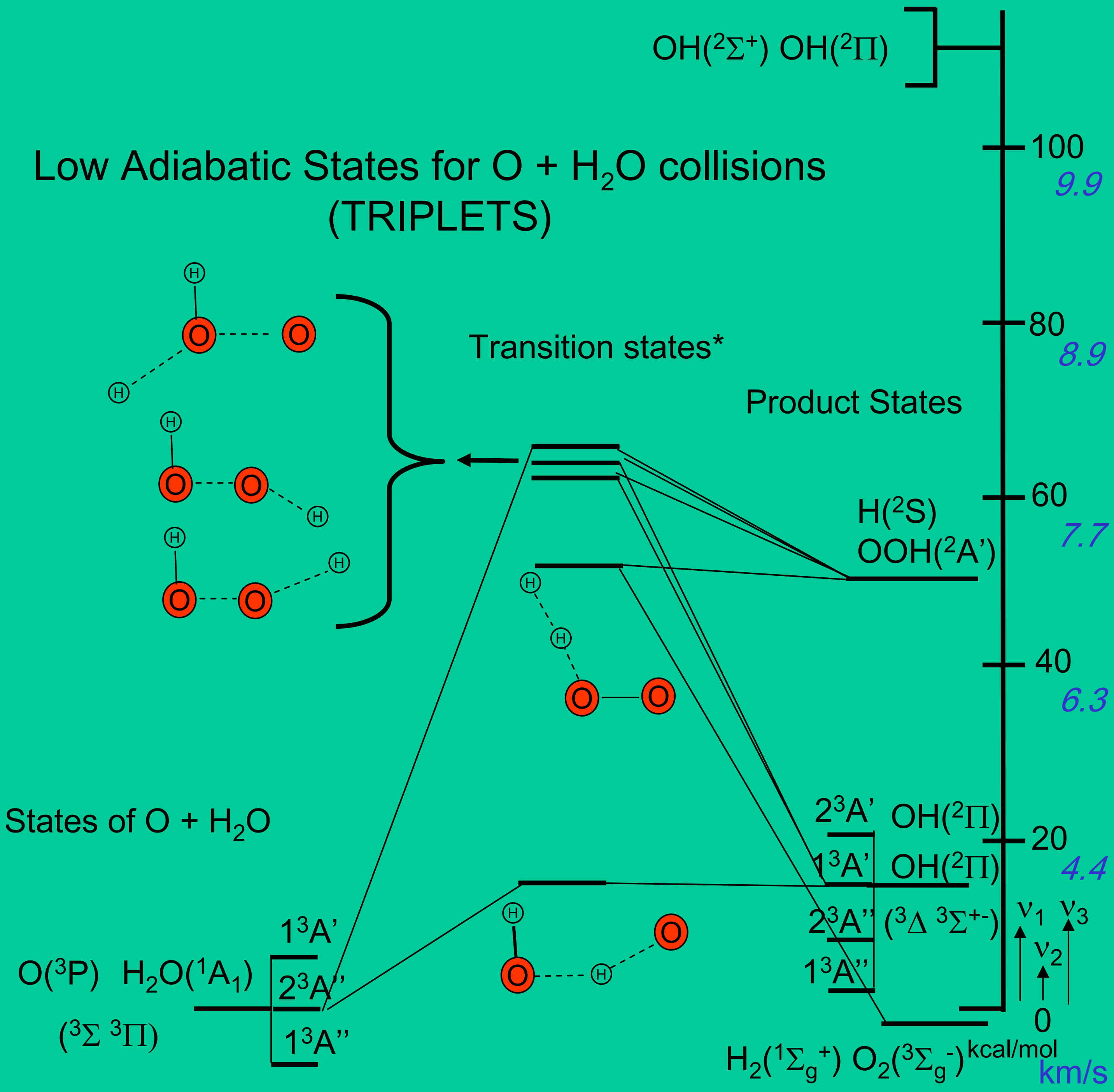
Note: Large differences between Theory results

O + H_2O Reaction Approach

- Short Term:
  - Perform direct dynamics calculations with VENUS
    - Quick picture of reaction chemistry (but less accurate)
    - AM1, PM3 level of theory (approximate)

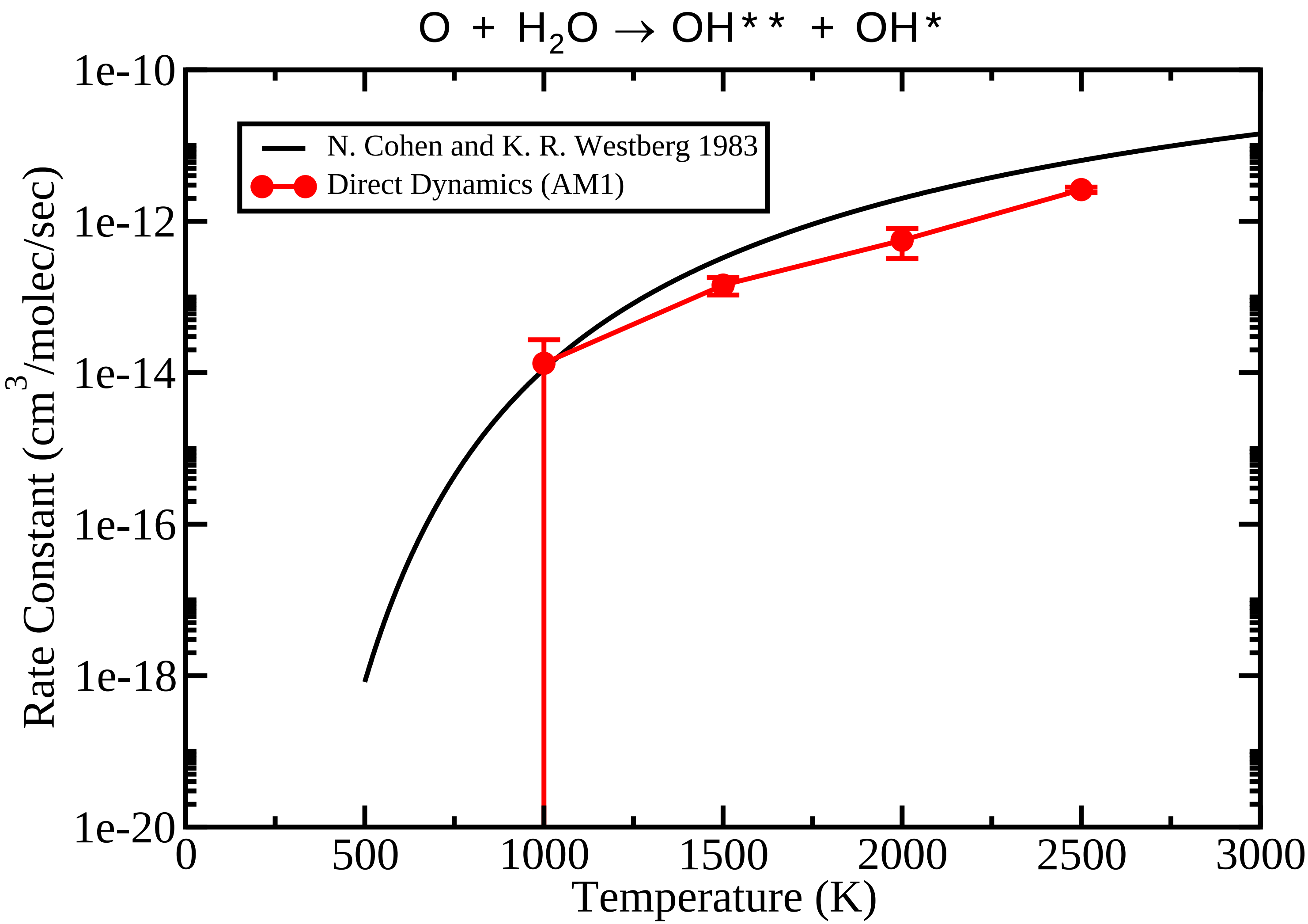
- Long Term:
  - Generate new O + H_2O surfaces and do reactive scattering calculations
    - Compute new high level *ab-initio* reactive surface
    - Fit surface
    - Run classical trajectory calculations with VENUS

Low Adiabatic States for O + H_2O collisions (TRIPLETS)



*Karkach and Osherov, JCP, 110 11918 (1999)

Reactive Rate Constant:



$O + H_2O \rightarrow OH^{**} + OH^{*}$

HOD* + O Direct Dynamics Results: Comparisons to Experiment

$$O + HOD(4v_{OH}) \rightarrow OH^* + OD^*$$

Pfeiffer *et al.* J. Chem. Phys. Vol. 113, 7982 (2000): Experiment

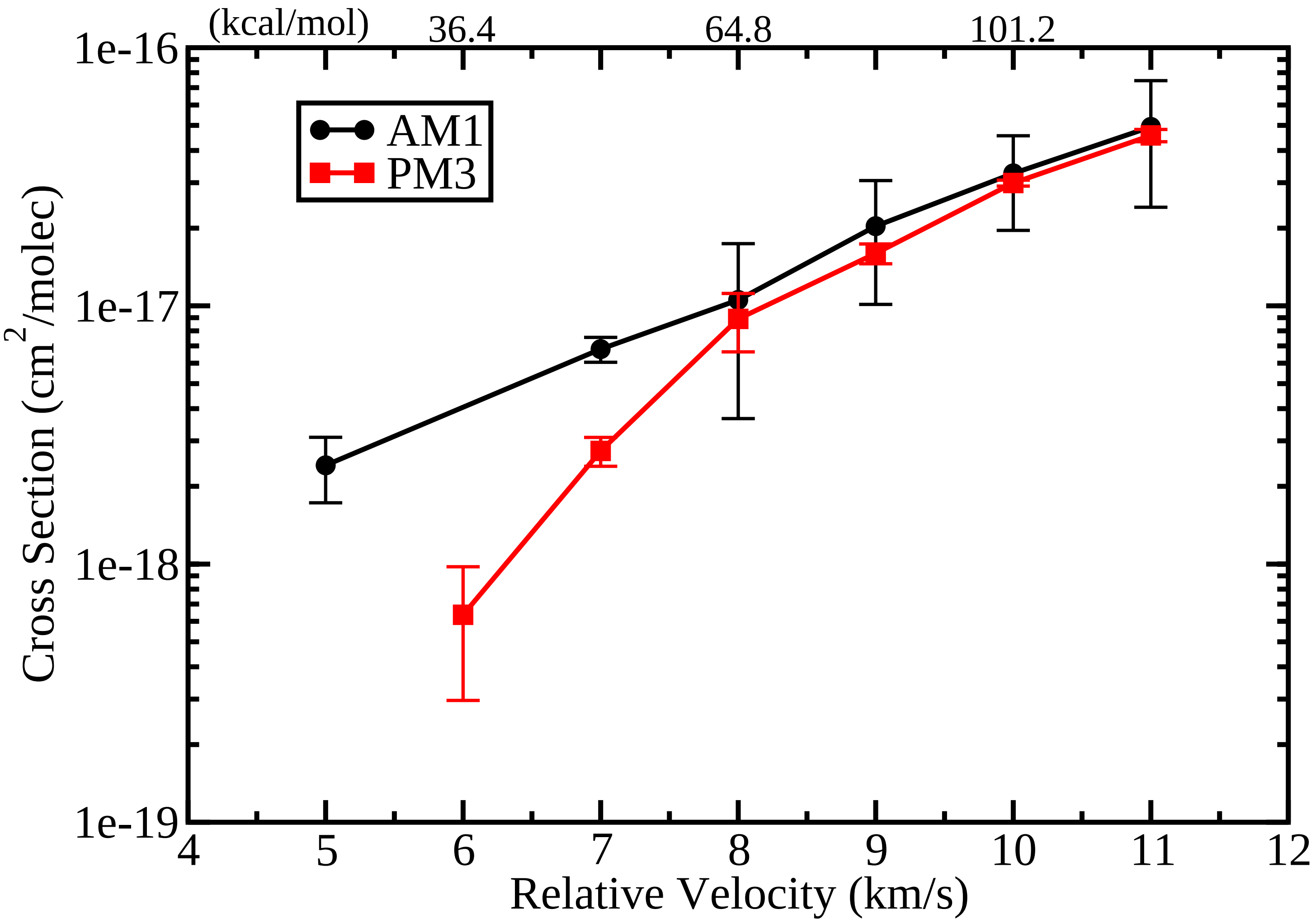
1) Excite OH bond in HOD with 4 quanta (about 20 kcal mol^{-1} over barrier)
2) Let excited HOD react with very low energy (590 cm^{-1}) O atom
3) LIF detection of product OH and OD

v	OH(v)-DD	OH(v)-Exp.	OD(v)-DD	OD(v)-Exp.
0	0.02		0.97	0.93 ±0.03
1	0.04		0.02	0.07 ±0.03
2	0.32	1.0±0.04	0.00	
3	0.62		0.00	

- Theory yields somewhat hotter distributions than measurements
- Relaxation certainly a factor in experimental set up

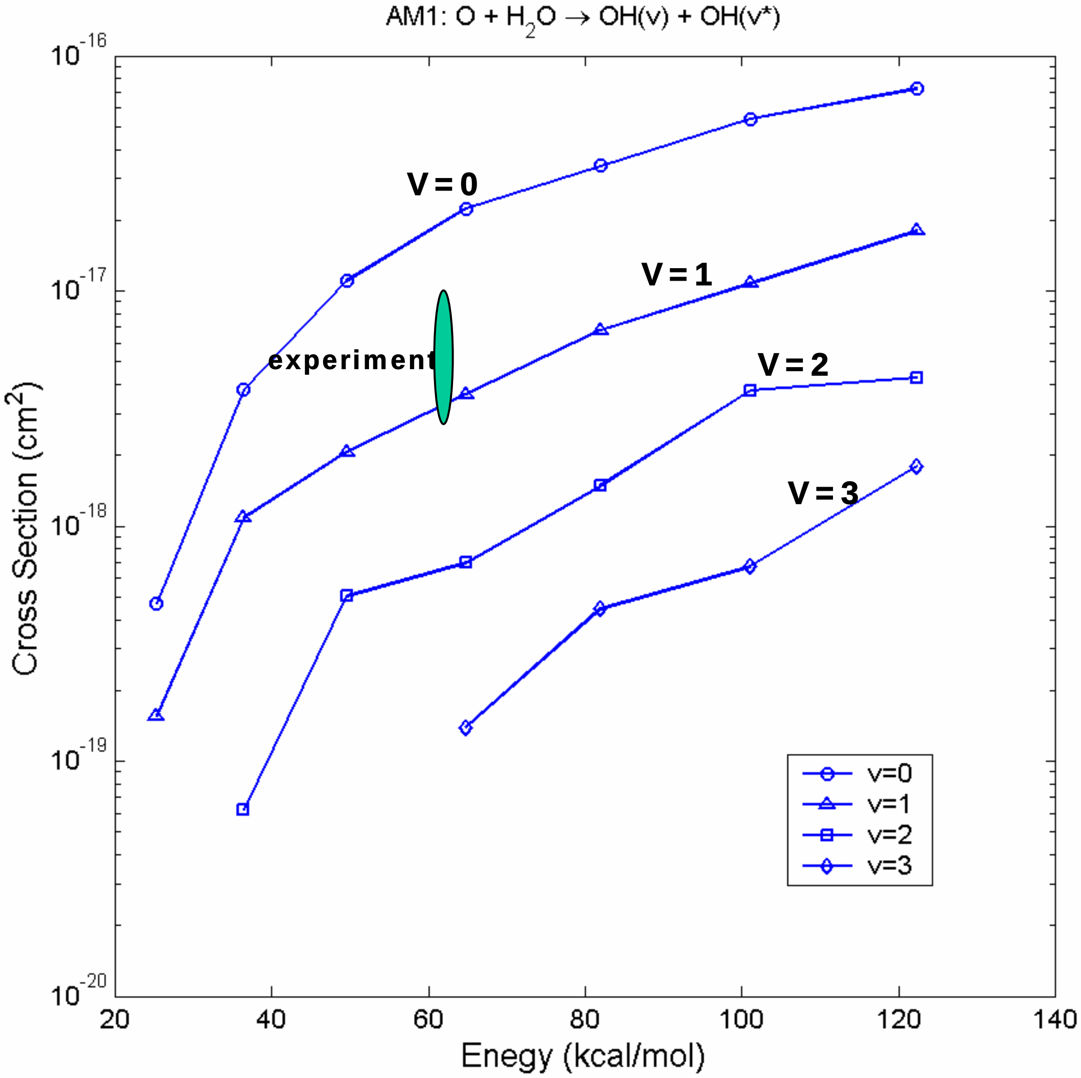
Consistency of Direct Dynamics Approaches

$O + H_2O(0,0,0) \rightarrow 2OH$



Direct Dynamics Predictions for OH* Production

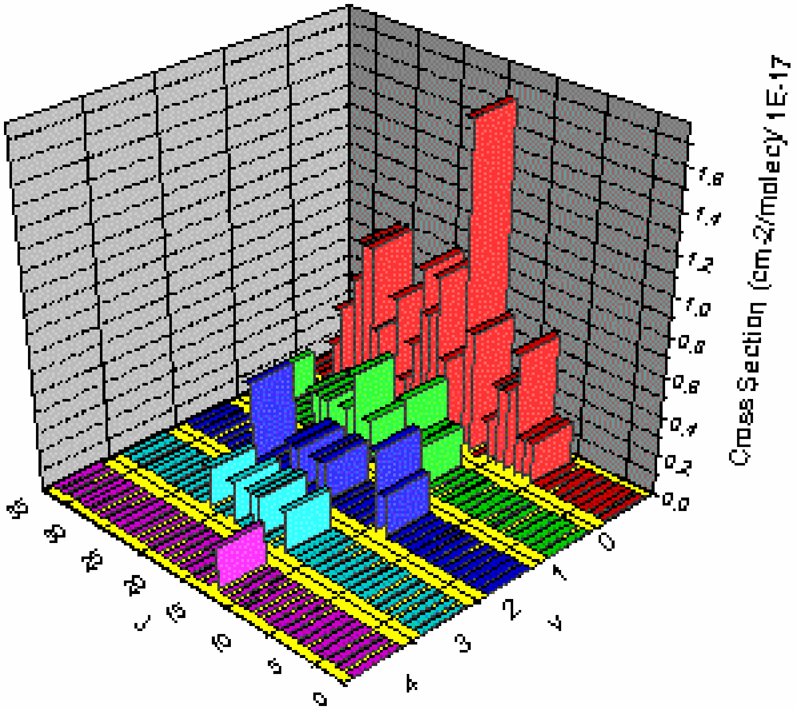
- Direct dynamics cross sections are comparable to experimental measurements at ~8 km/s
- Need further analyses, especially spectral comparisons with measurements



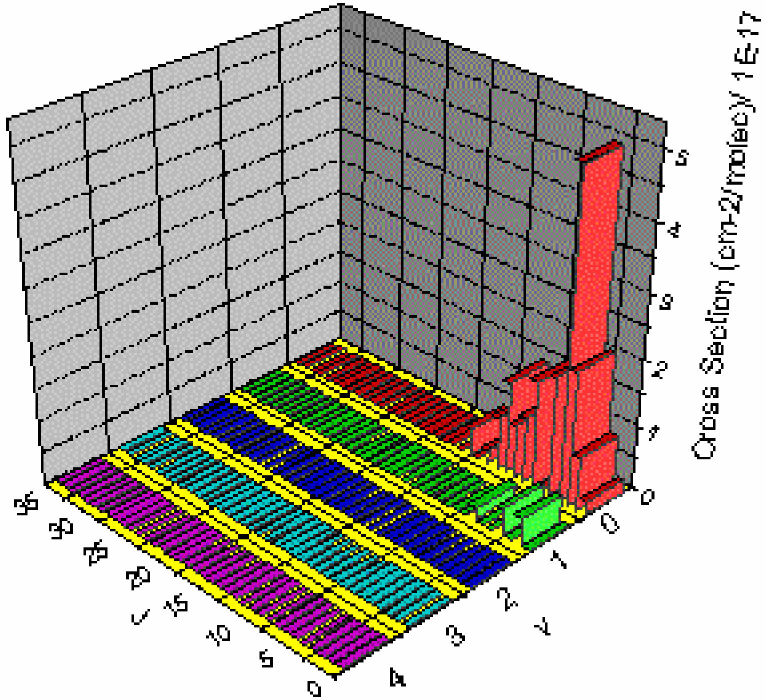
State Specific Reactive Cross Sections
$O + H_2O \rightarrow OH(v,J) + OH(v',J')$
10 km/s

Note that OH products are formed in ‘hot’ and ‘cold’ populations

OH(v,J)



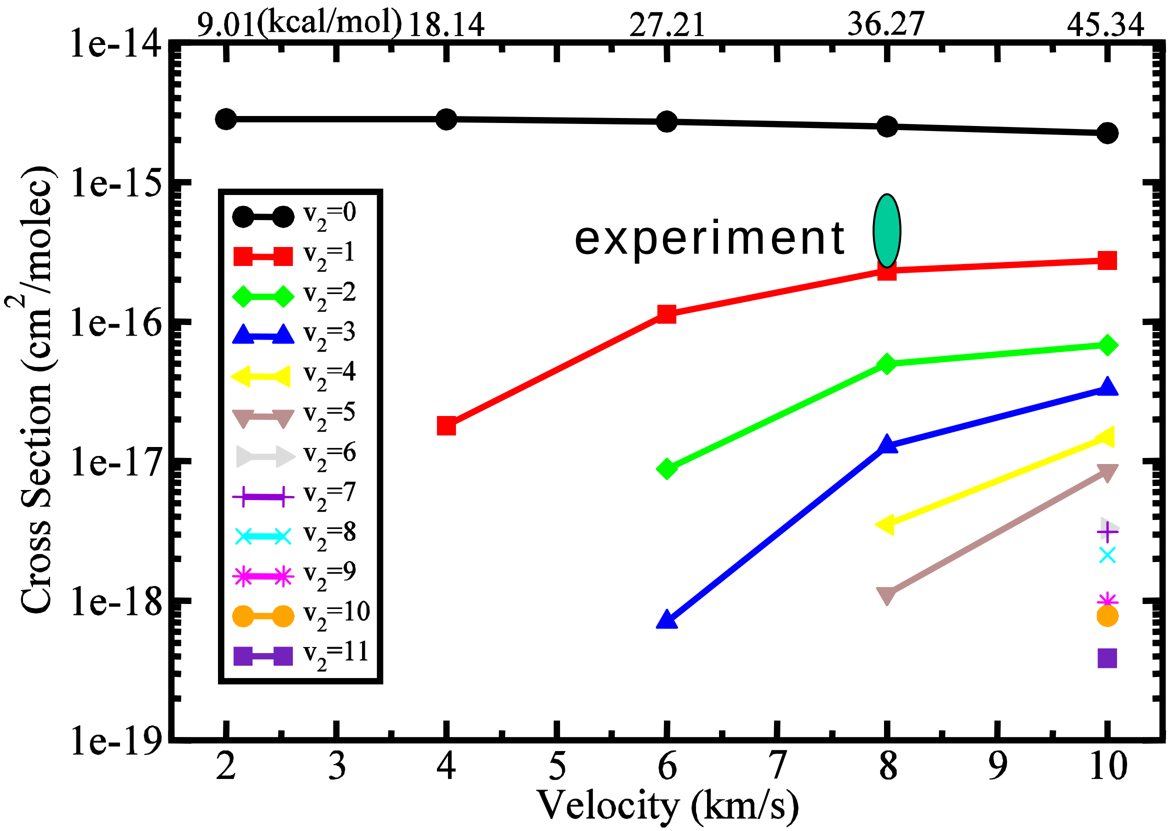
OH(v,J)



Direct Dynamics Results for
O + H_2O → O + H_2O^*

- With classical approach, it is not straightforward to determine product vibrational mode
  - Assume most vibrational energy goes into $H_2O(v_2)$
  - Preliminary results are comparable to experiment

$O + H_2O(0,0,0) \rightarrow O + H_2O(0,v_2,0)$



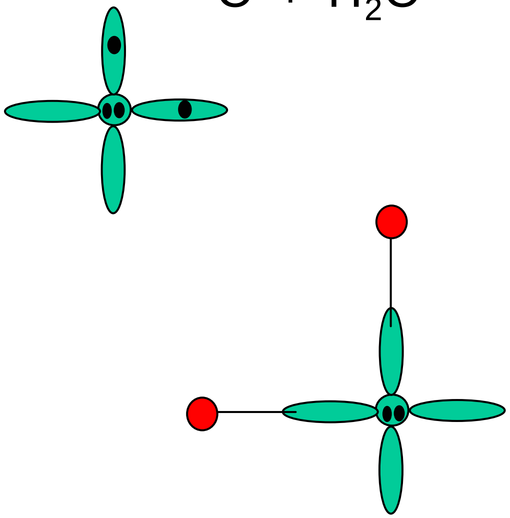
Status of Direct Dynamics Calculations

- Investigating possible H + OOH product channel (high energies)
- More calculations for better statistics
- Simulating spectra from final OH distributions
  - Two temperature fit
  - Compare to PSI CVF measurements (OH overtone)
  - Other spectral data
- Continue comparisons with HOD* + O measurements

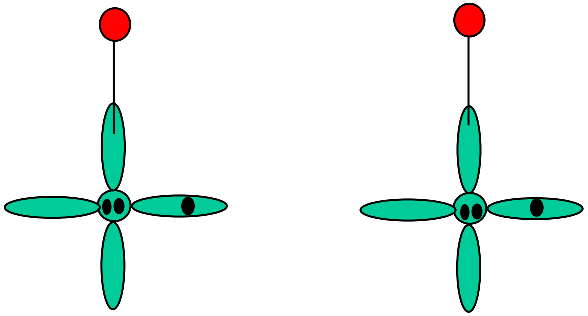
O + H_2O Potential Energy Surface: Electronic Structure Calculations

- Basis: TZV + 2d,1f on O + 2p on H; 90 total basis functions
- 10e8o CASSCF + MP2 (1s,2s frozen, 2 lone pair, 2 bonding, 2 alpha, 2 anti-bonding)
- No symmetry; 3 state average
- Calculated ΔH = 15.6 kcal mol^{-1}, exp. = 14.7 kcal mol^{-1}

O + H_2O

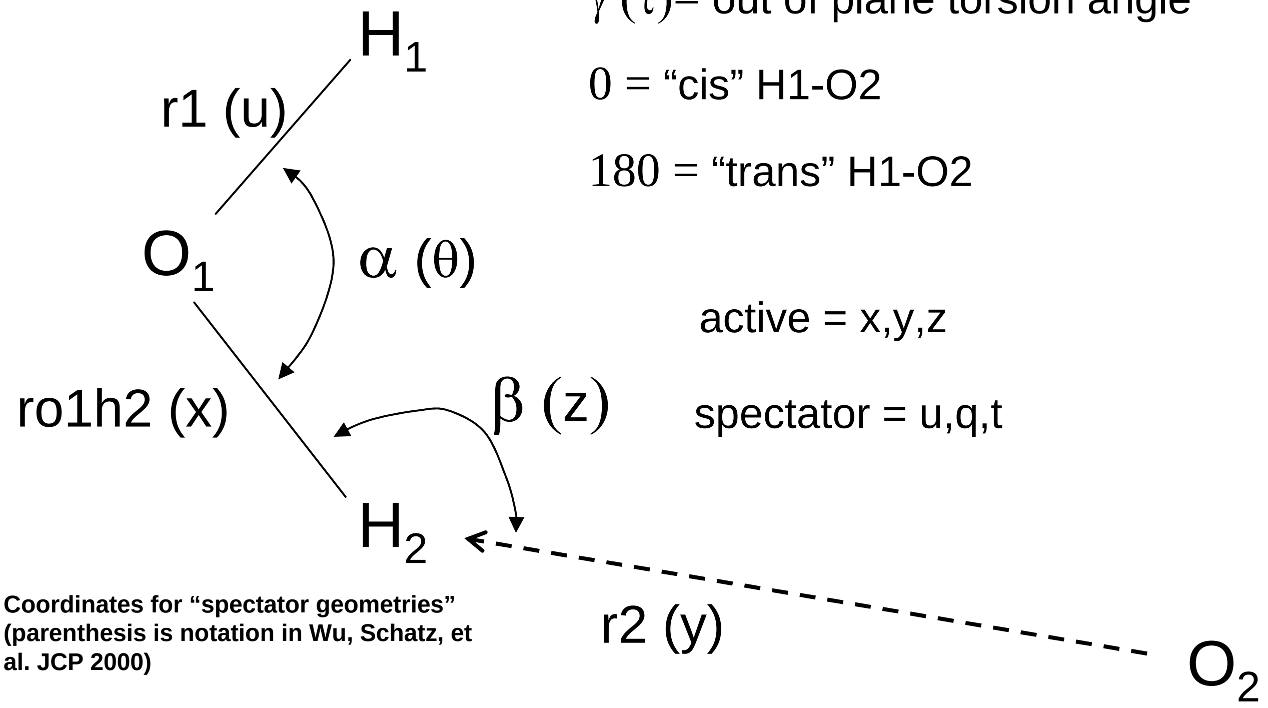


OH + OH



Internal Coordinates for Electronic Structure Calculations

- As reaction proceeds, x and y change
  - –For Reagents: x is small, y is large
  - –For Products: x is large, y is small
- Performed ~1.e5 fixed point calculations
- Surface fitting code nearly complete,
  - – Unit testing in progress



γ (τ)= out of plane torsion angle

0 = “cis” H1-O2

180 = “trans” H1-O2

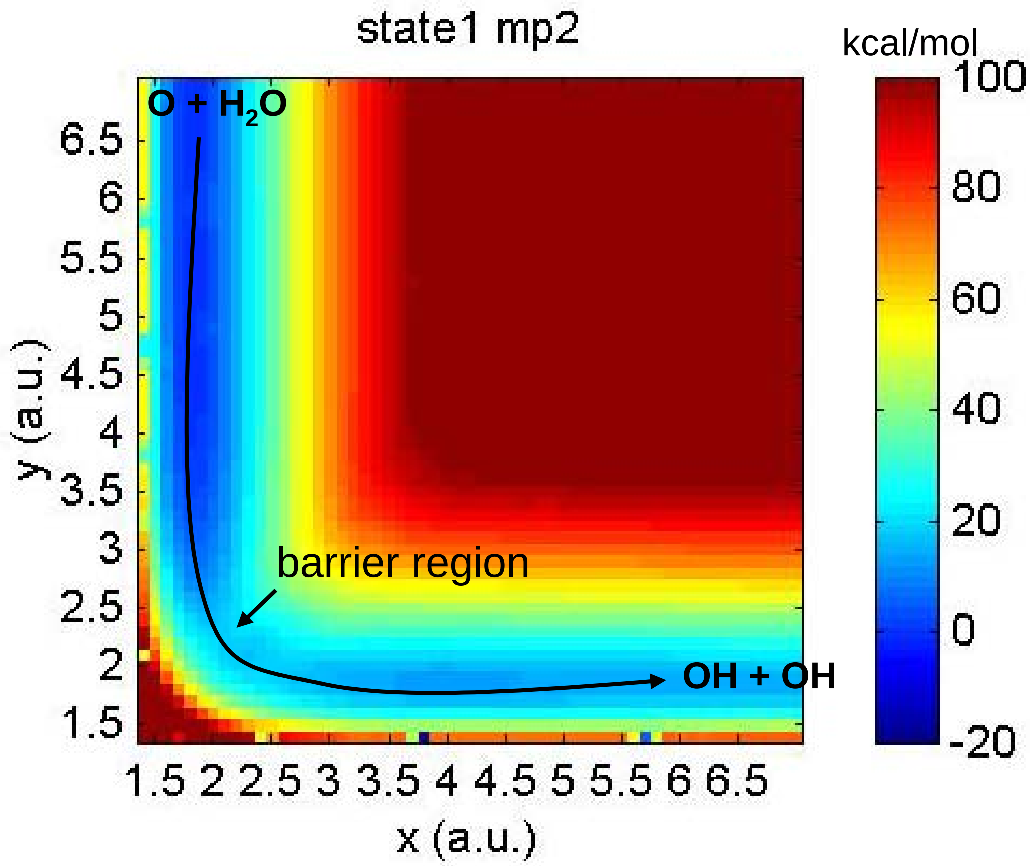
active = x,y,z

spectator = u,q,t

Coordinates for “spectator geometries” (parenthesis is notation in Wu, Schatz, et al. JCP 2000)

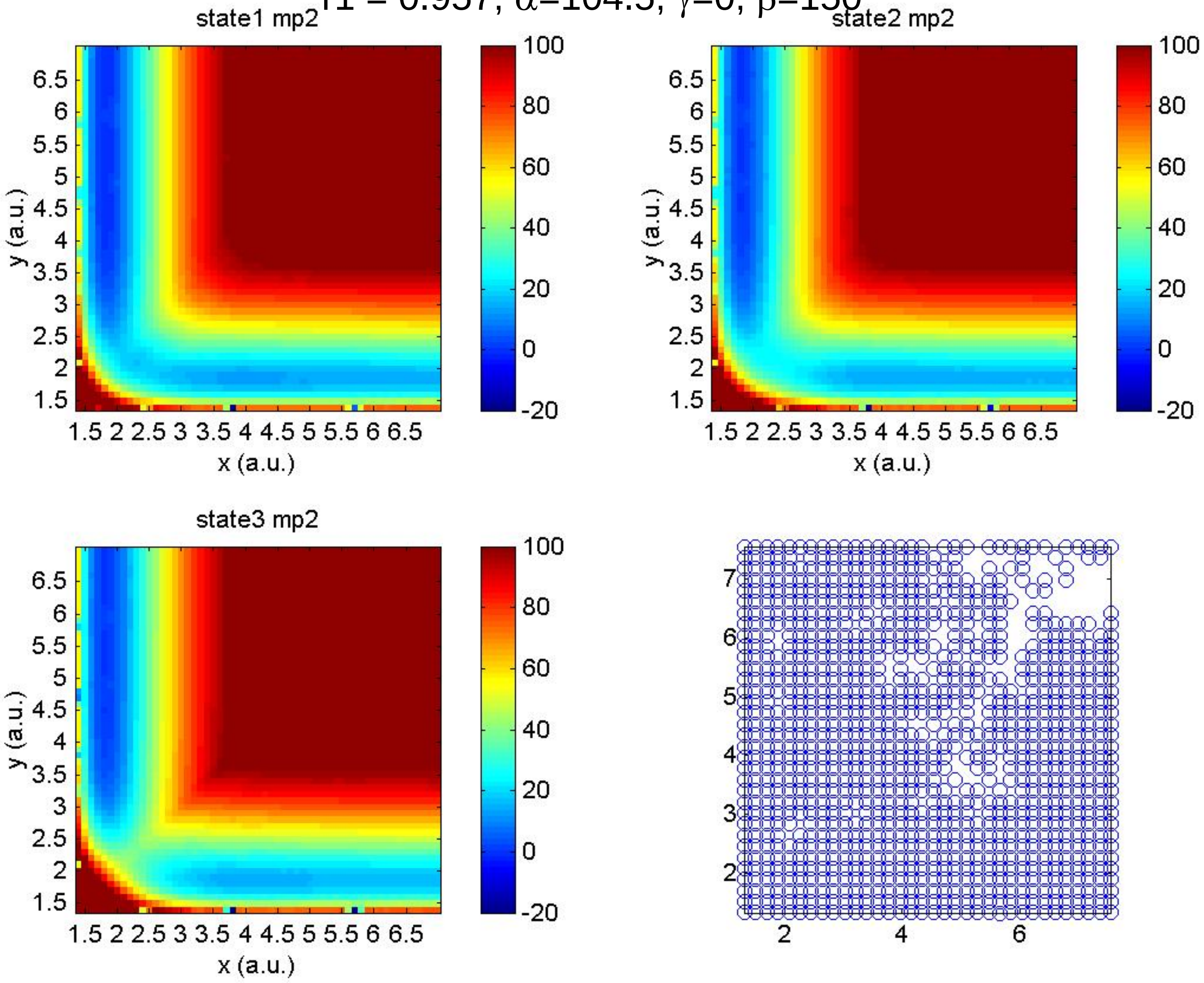
Electronic Structure Calculations: All Coordinates Fixed Except x and y

r1 = 0.957, α=104.5, γ=0, β=150



Intend to Follow Lowest Three Electronic States

r1 = 0.957, α=104.5, γ=0, β=150



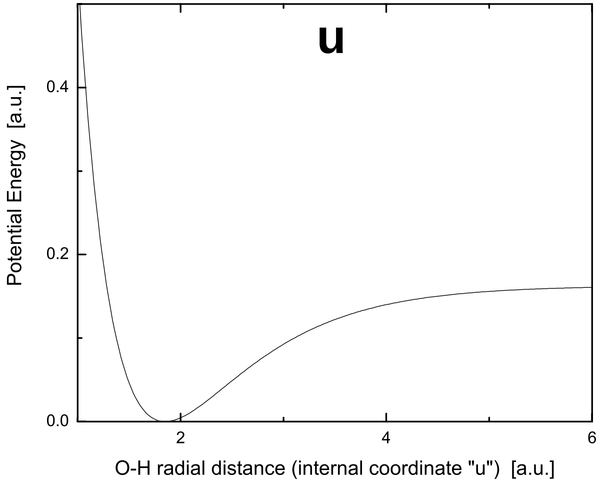
Surface Fitting Computation Procedure

- First, compute electronic energies for selected geometries
- Then, generate a potential-energy surface from data using a combination of pre-determined functional behavior and multidimensional spline interpolation
  - Multi-dimensional spline routines from Princeton Plasma Physics Lab
  - Water and OH potentials from Schwenke et al. [J. Chem. Phys., 1996]
  - Functional fits to least sensitive coordinates from Schatz et al. [J. Chem. Phys., 2000]
- Once complete, the potential corresponding to an arbitrary set of Cartesian coordinates can be computed within a classical dynamics simulation.

Spectator and Active Coordinates

The twelve Cartesian coordinates of our four-atom system can be uniquely described by a set of six “internal” coordinates. These six coordinates are separated into three “active” coordinates (x,y,z), which will be fit using multidimensional splines and three spectator “coordinates” (u, θ, τ), which will be fit using pre-determined functional forms.

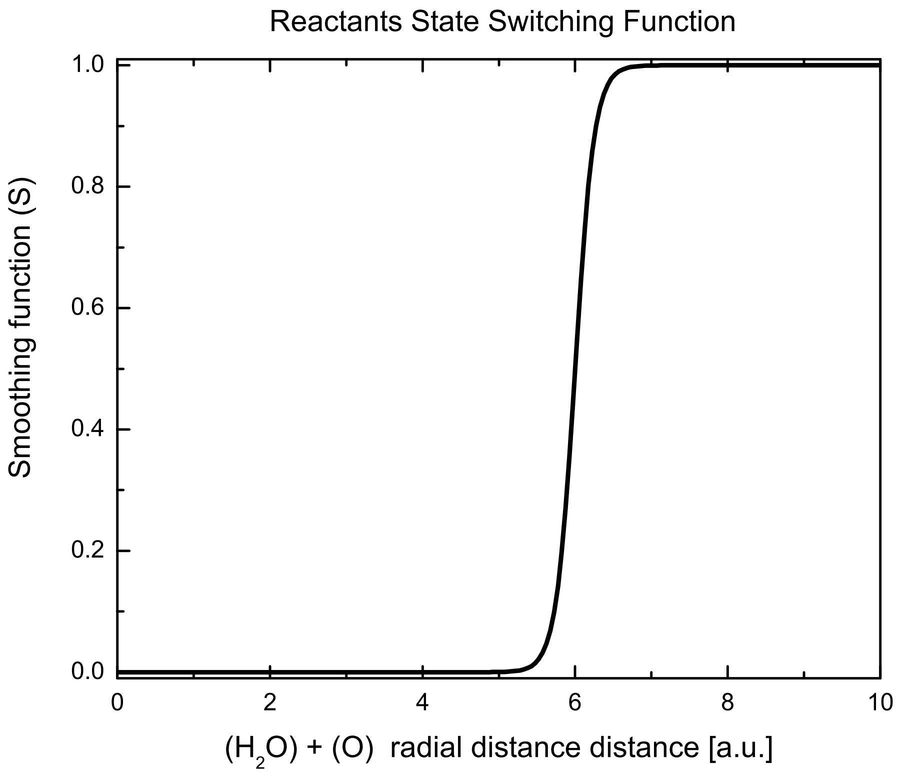
$$V_Q = V_{active}\left(x, y, z\right) + V_{spectator}\left(u, \theta, \tau; x, y, z\right)$$

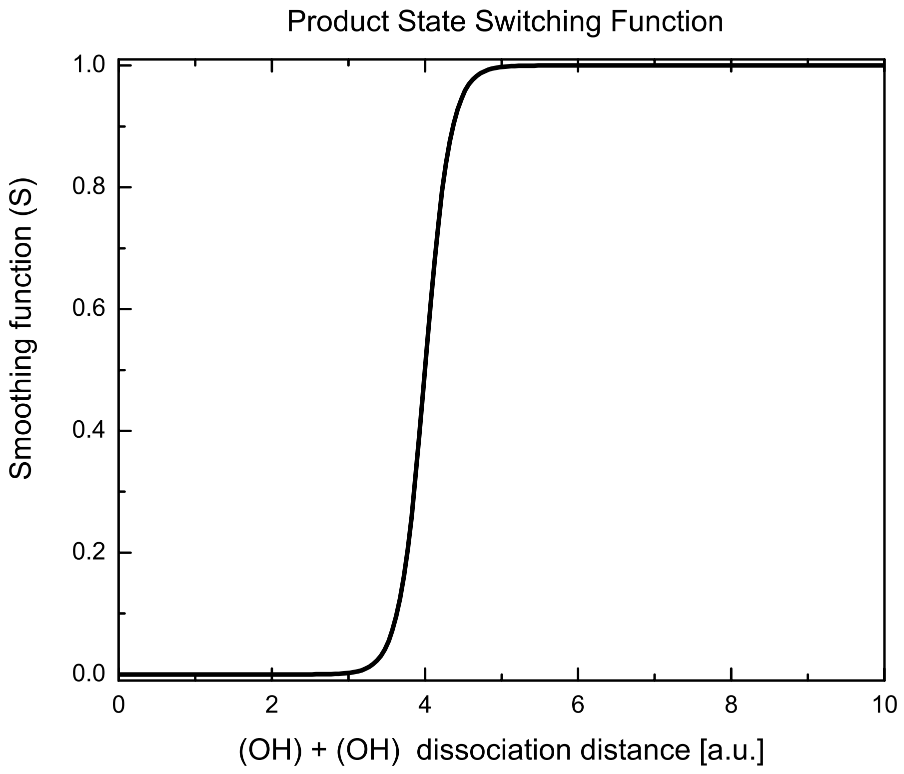


From Reactants to Products

The potential energy surface ("V") will transition smoothly from the initial reactants state ("R") to final products state ("P") using smoothing functions ("S"):

$$V = \left(1 - S_R - S_P\right)\cdot V_Q + S_R \cdot V_R + S_P \cdot V_P$$

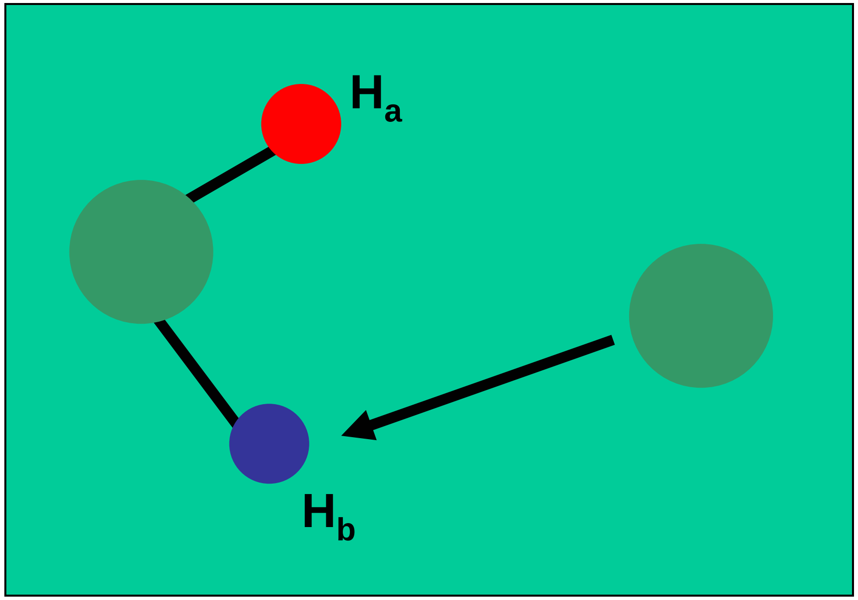


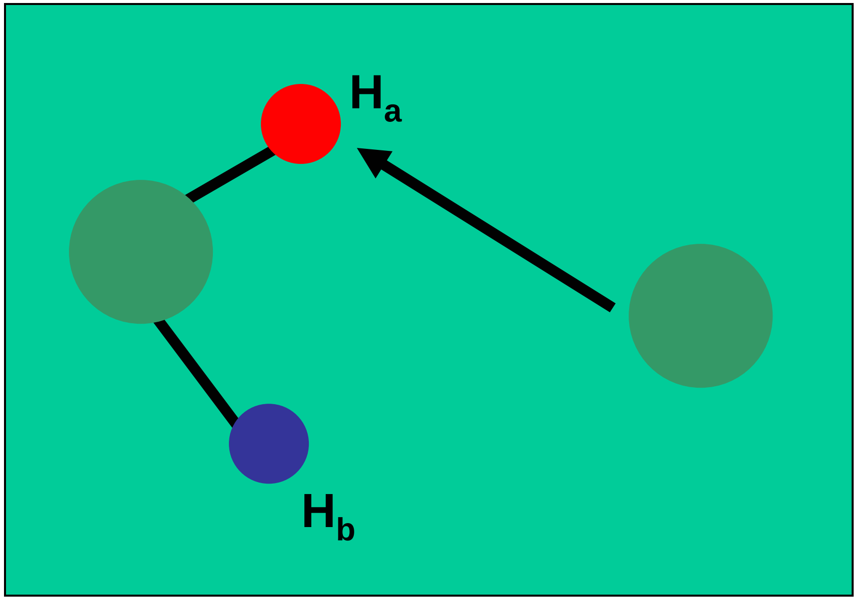


Potential Symmetrization

The incoming oxygen atom can bind to either hydrogen atom in the water molecule. To model two possible scenarios using a single set of Cartesian coordinates, a ‘symmeterization’ procedure is added in which the position of the two hydrogen atoms are transposed. Transitioning between the two orientations is provided by a smoothing function (S).

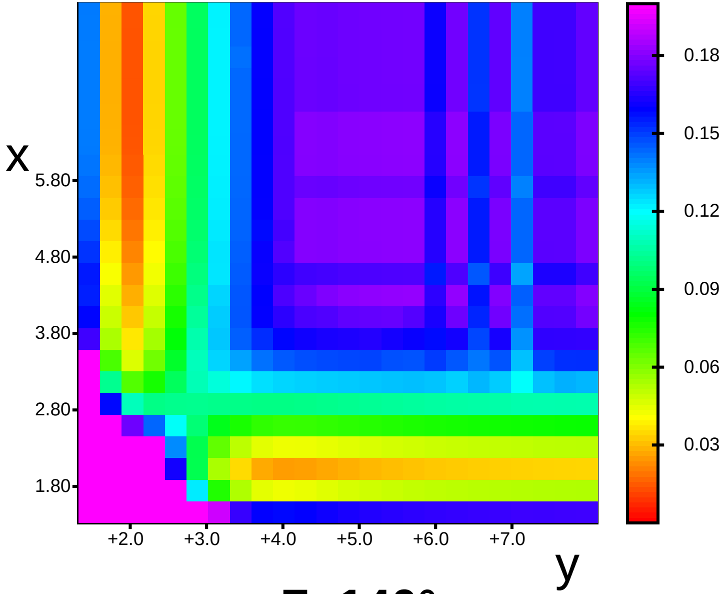
$$V_{Final} = (1 - S_s) \cdot V((H_a - O_a - H_b) + O_b) + S_s \cdot V((H_b - O_a - H_a) - O_b)$$



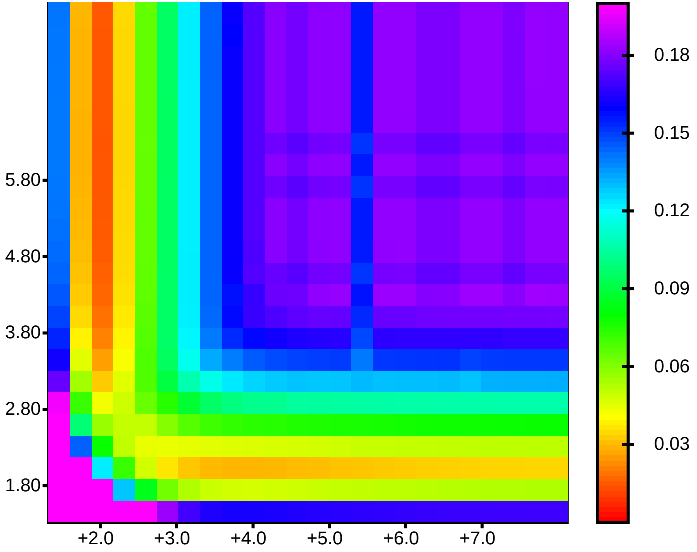


Interim Fitting Results – Spline fit with Interpolation

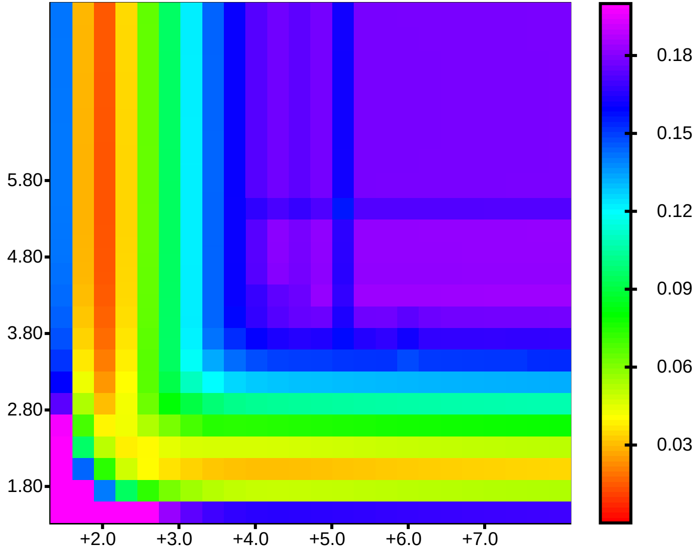
Z=80°



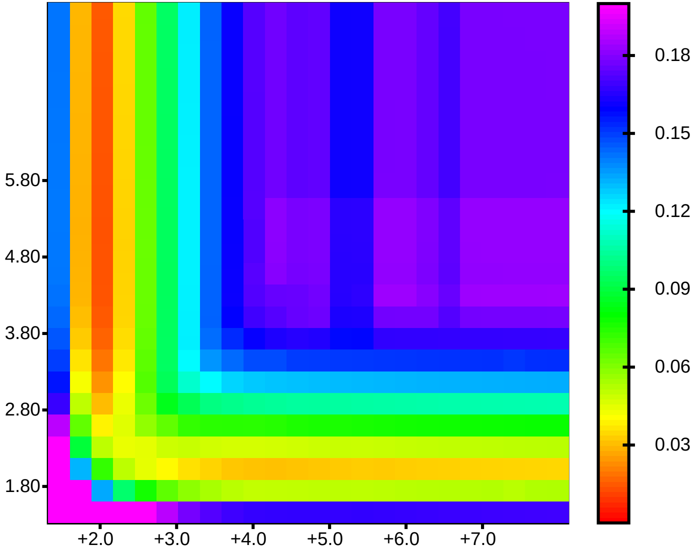
Z=110°



Z=140°



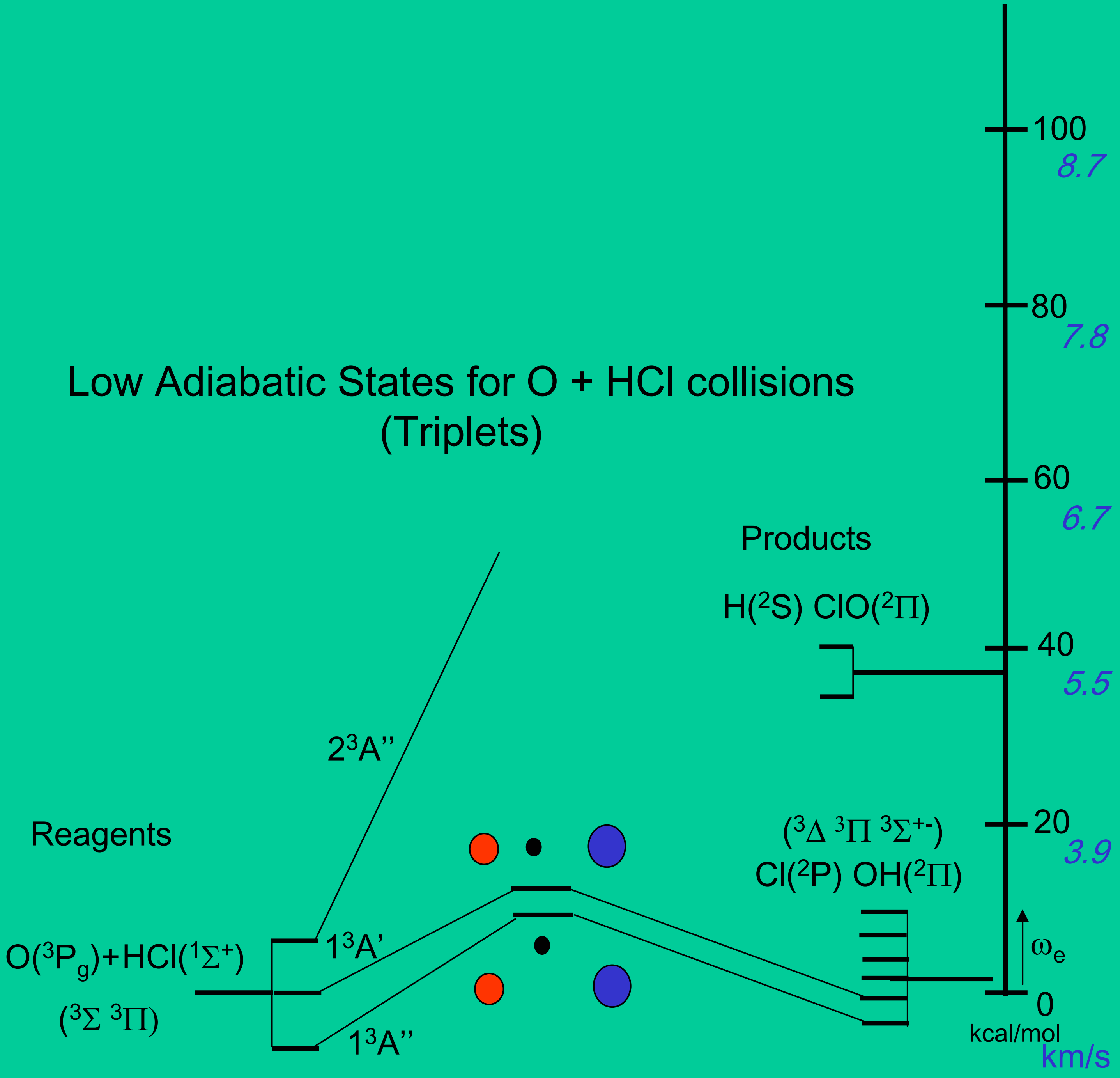
Z=170°



Overview of O + HCl System

- Many important studies, but very little information at high velocities
  - major channels O + HCl → O + HCl*, Cl + OH*
- Experimental Studies:
    - Numerous experimental studies of the rate constant up to ~2500 K
    - Final state resolved measurement of O + HCl*
- Theory
  - Large body of work over many years up to the present
    - Detailed, high level potential energy surfaces (PES)
    - Classical and Quantum studies (rate constant)
    - Very recent study (PES+dynamics):
      - » *Ramachandran (Louisiana Tech), Peterson, Bowman*
    - Note: H + OCl channel missing in all studies
- No clear picture of magnitude or relative importance of channels

Low Adiabatic States for O + HCl collisions (Triplets)

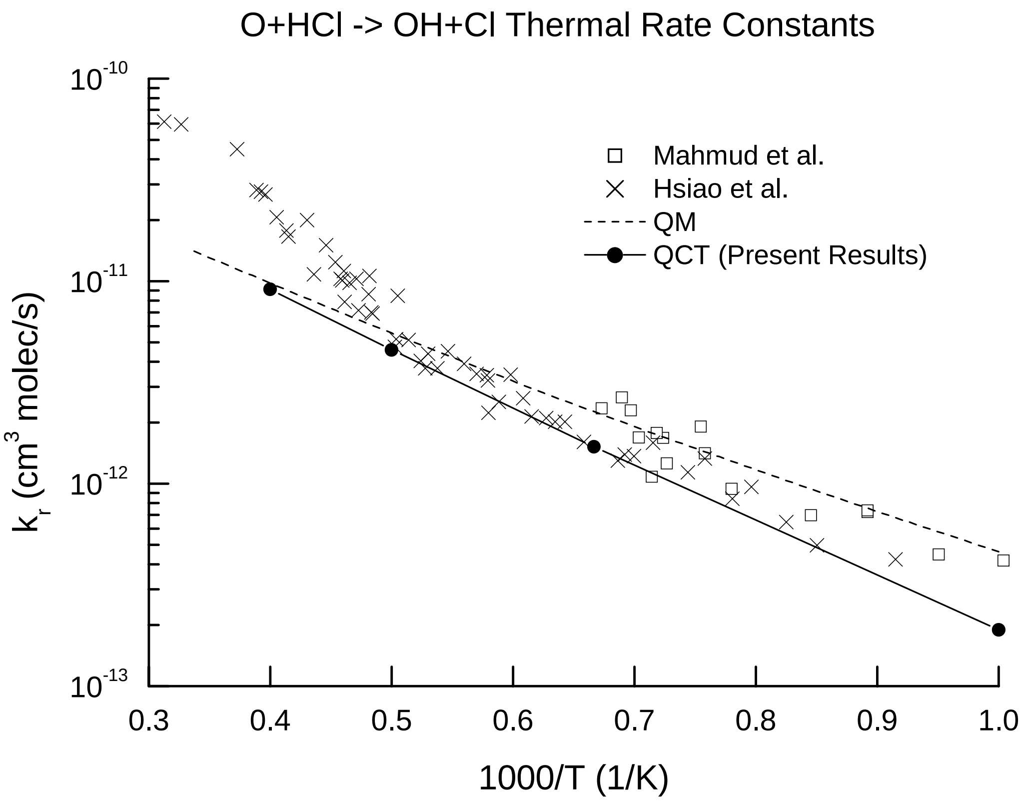


O + HCl Reaction Approach

- Perform classical dynamics calculations
  - Use latest surfaces provided by Professor B. “Ramu” Ramachandran (Louisiana Tech)
  - Generate temperature dependent rate constants to compare with available experimental data
  - Generate velocity dependent, state-specific cross sections
  - Analyze final state distributions

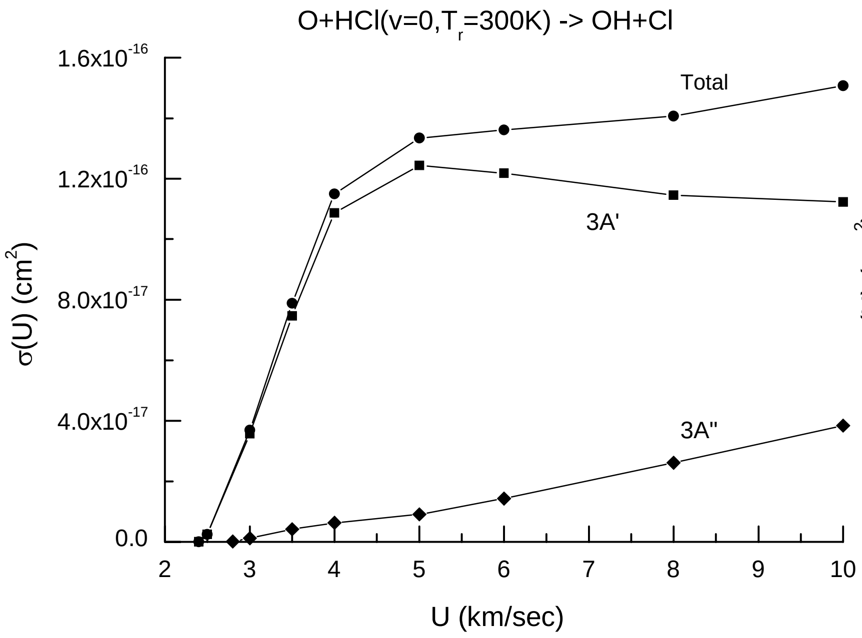
- Collaboration with Ramachandran/Bowman groups
  - Quantum/classical dynamics study

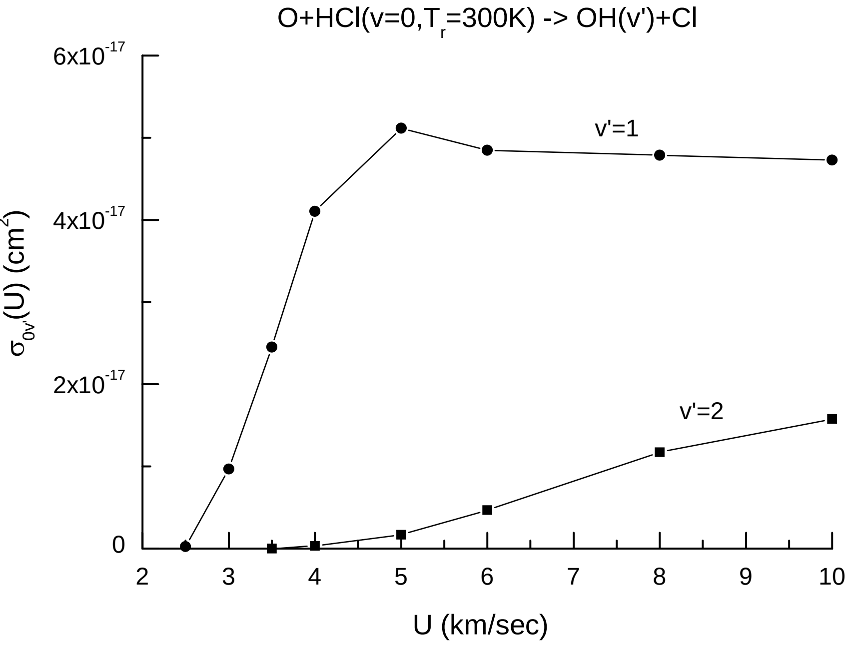
Thermal Rate Constant for O+HCl Reaction



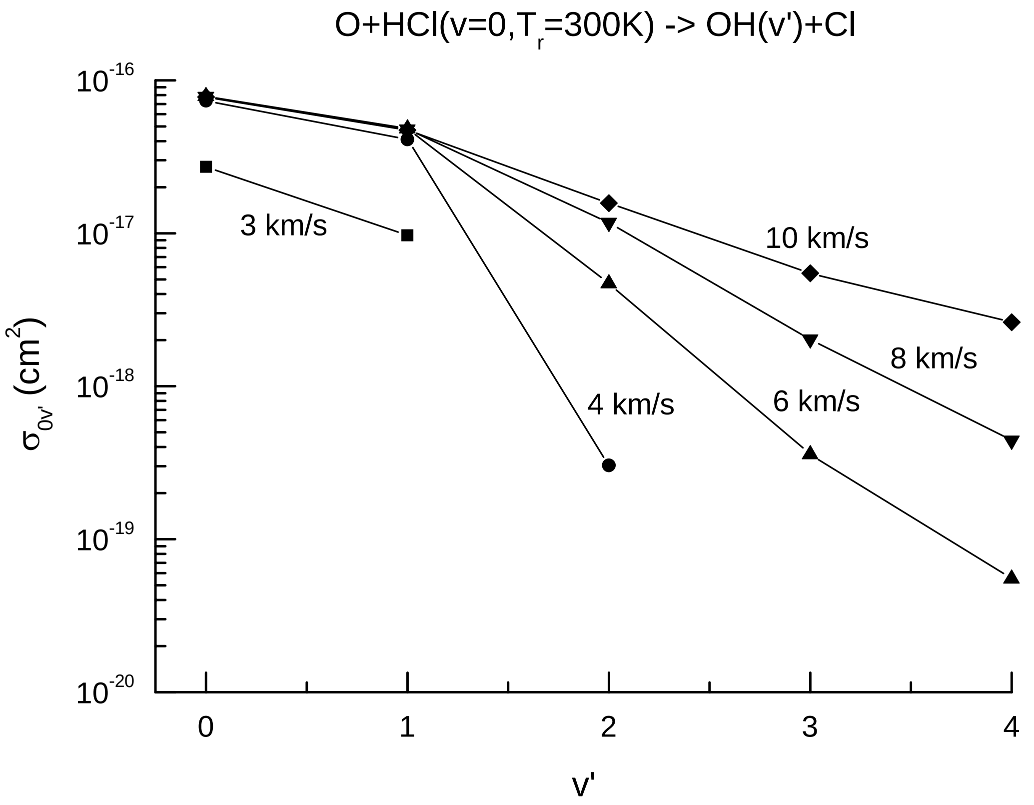
- Good agreement between present calculations (QCT) and experiment/QM results for T<2000K
  - -Possible quantum (tunneling) effects < 1500 K
- Disagreement between theory and experiment for T>2000K is not currently understood
  - – O(^{1}D) contamination
  - – OCl channel accessible

Velocity Dependence of O+HCl Reaction



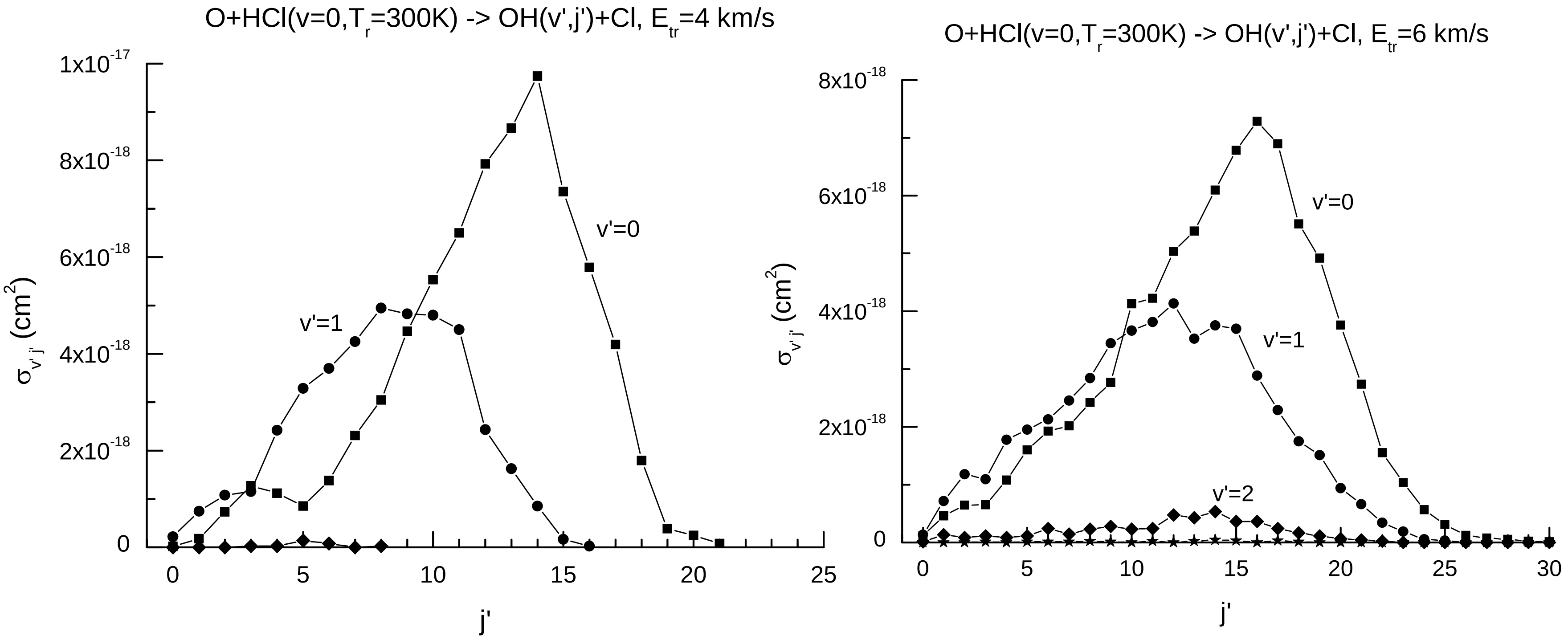


Velocity Dependence of OH Vibrational Distributions

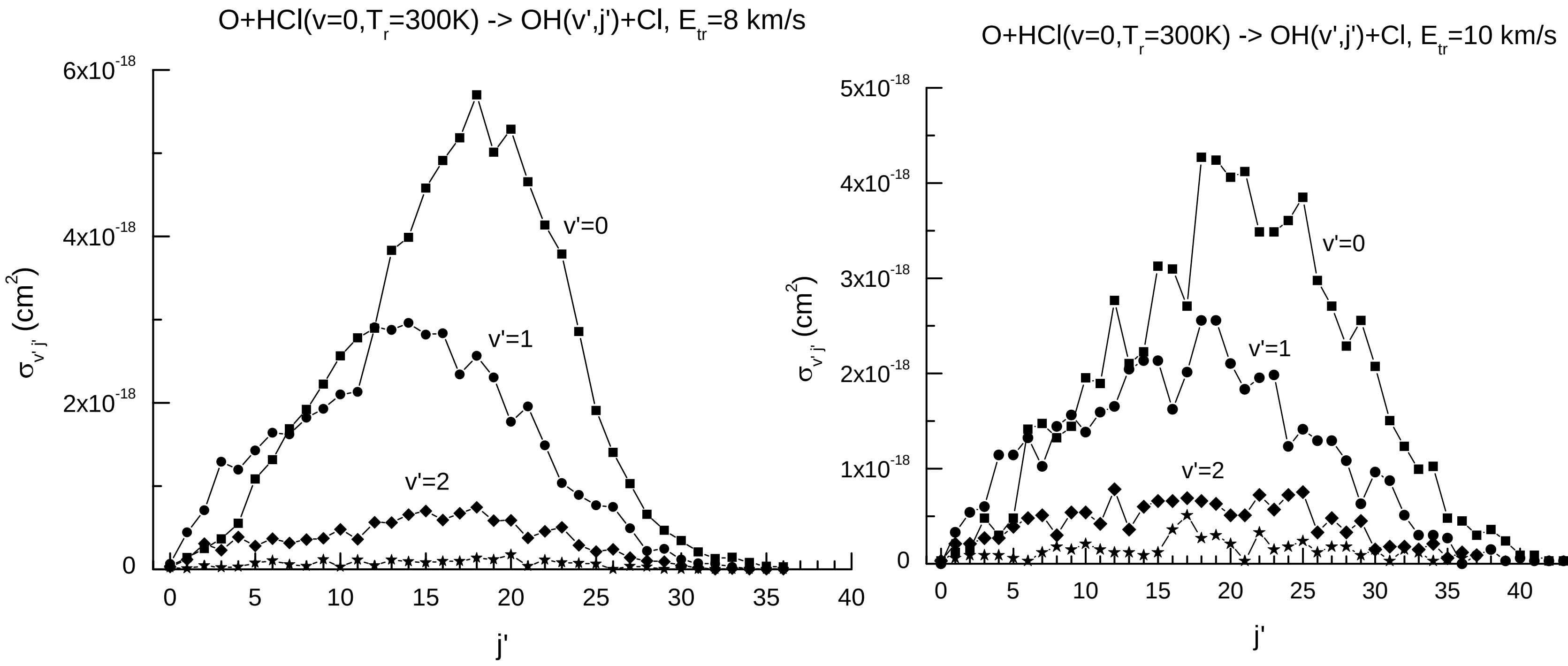


- Exponential falloff of vibrational distributions consistent with Polanyi studies of the effect of barrier location of vibrational energy in products
  - Late barriers (in product channel) result in mixed energy release into translation & rotation

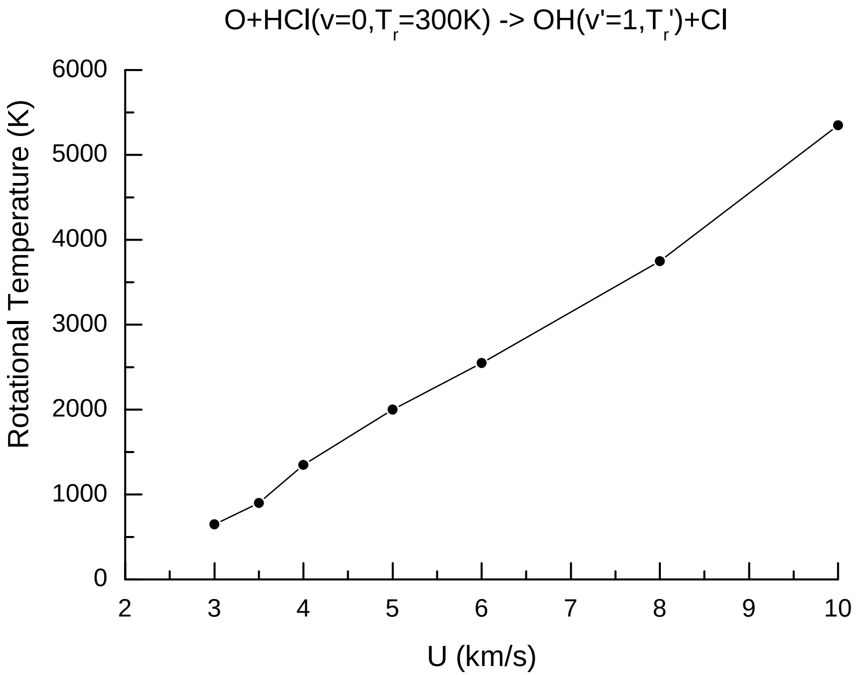
Velocity Dependence of OH Vibrational/Rotational Distributions

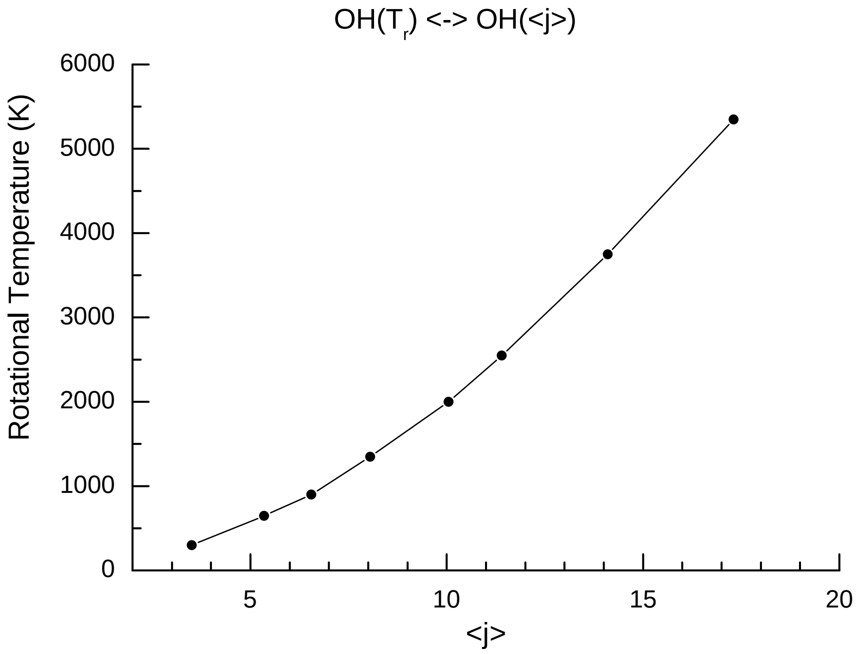


Velocity Dependence of OH Vibrational/Rotational Distributions



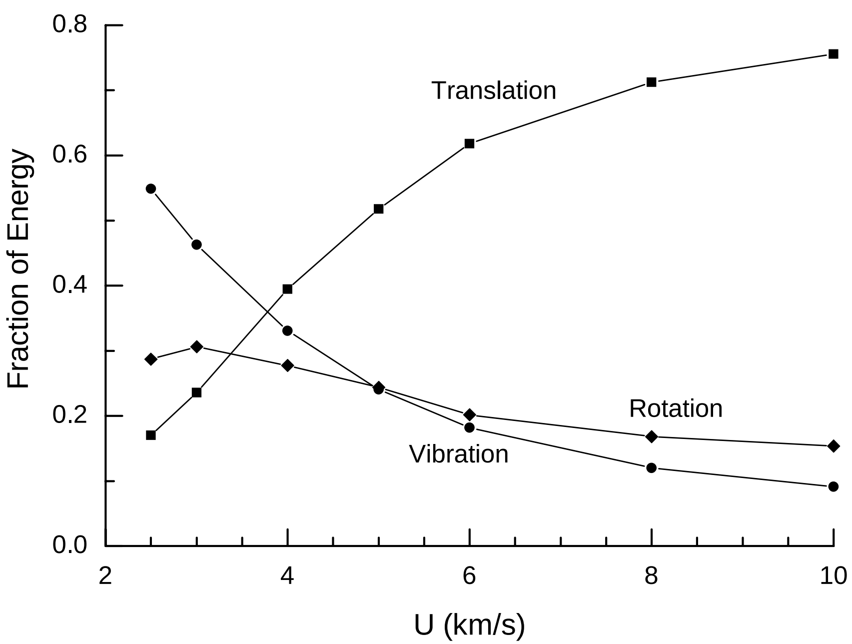
Estimate of OH(v'=1) Rotational Temperatures

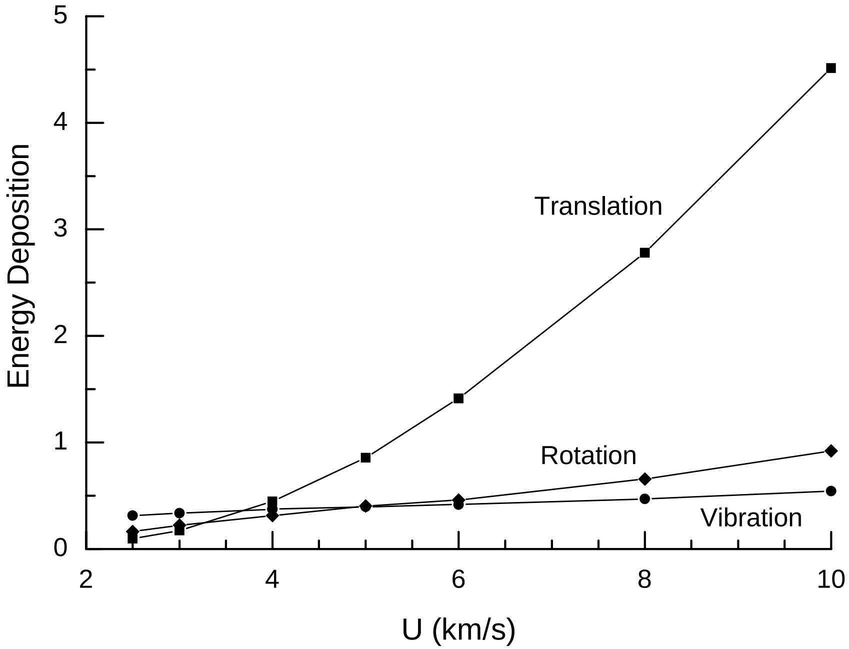

$O+HCl(v=0,T_r=300K) \rightarrow OH(v'=1,T_r')+Cl$


$OH(T_r) \leftrightarrow OH(<j>)$

Based on 1st moment of rotational distributions (assuming a Boltzmann distribution of OH(v'=1,j)), OH rotational temperatures approach 6000K

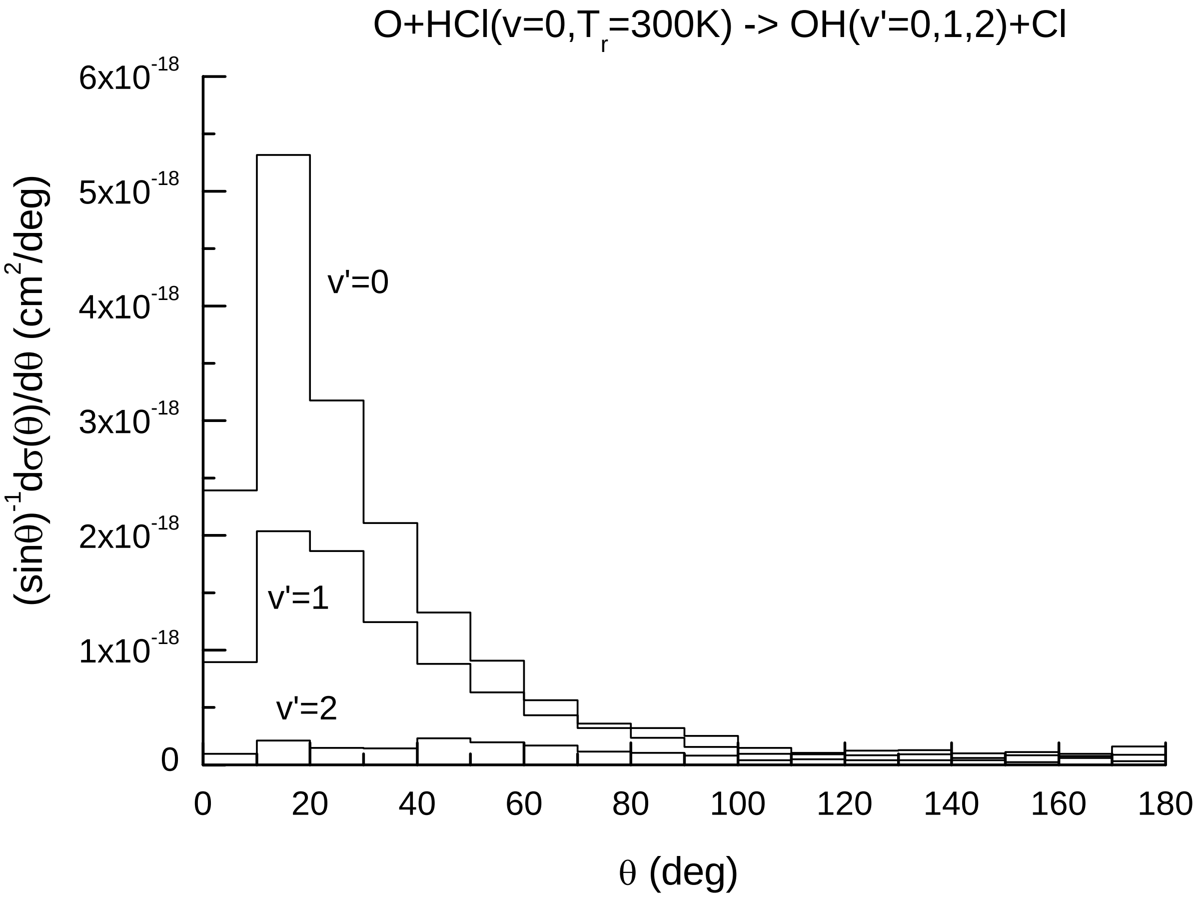
Energy Deposition in O+HCl Reaction


Fraction of Energy in Various Product Modes


Energy in Various OH+Cl Product Modes

- Reactant translational energy is preferentially channeled into product translational energy
- Rotational excitation is substantial for U> 4 km/s

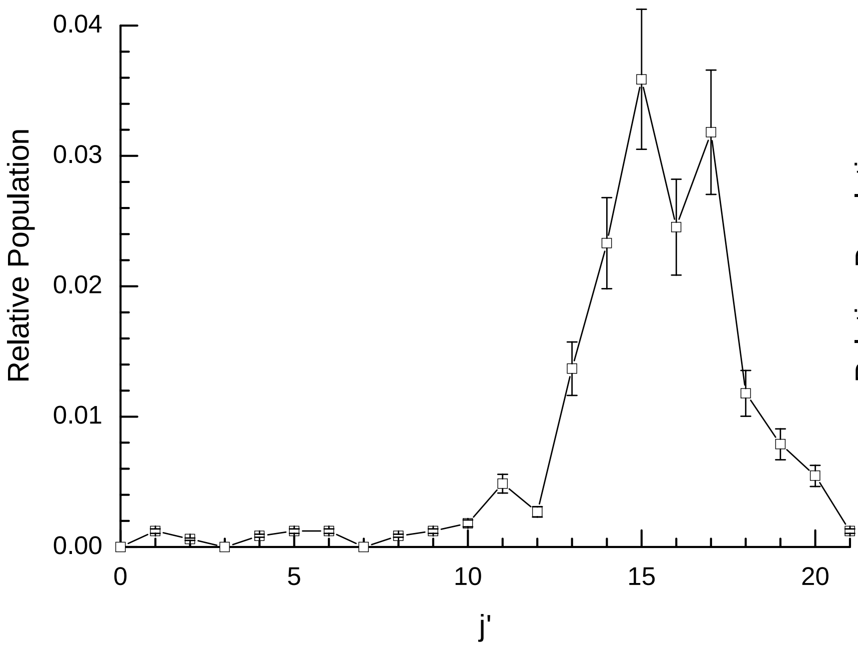
OH Differential Cross Section at 8 km/s



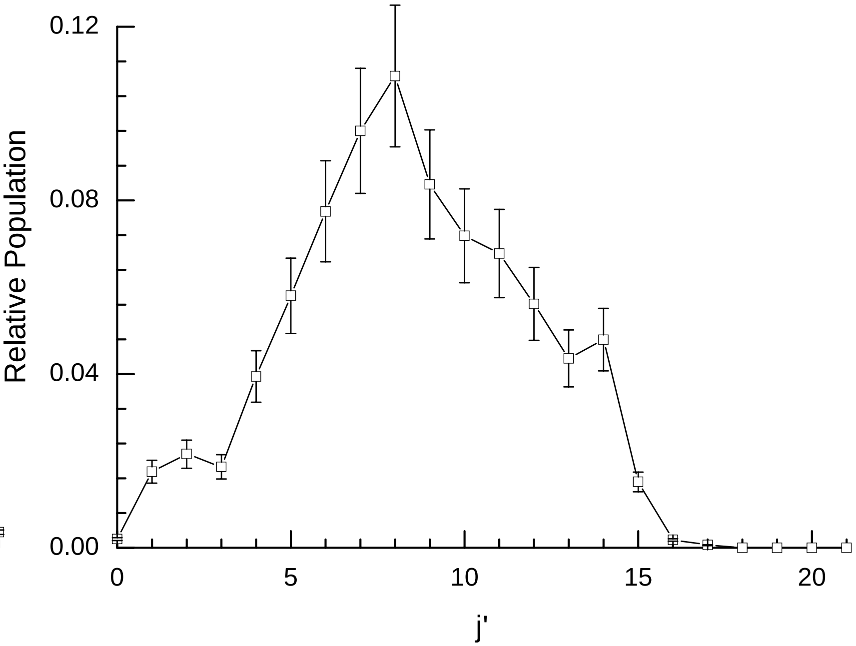
OH(v'=0,1;j') Rotational Distributions

(Averaged over Experimental E_{tr} Distribution)

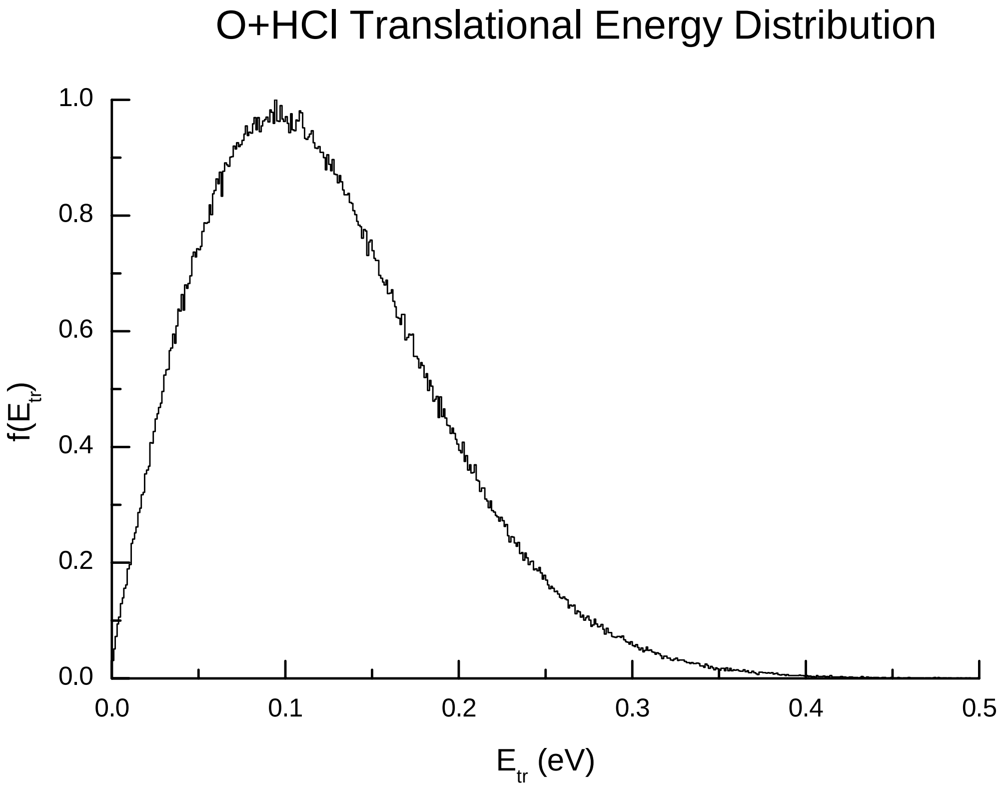
O+HCl(2,1) -> OH(v'=0,j')+Cl



O+HCl(2,1) -> OH(v'=1,j')+Cl



O+HCL Energy Distribution

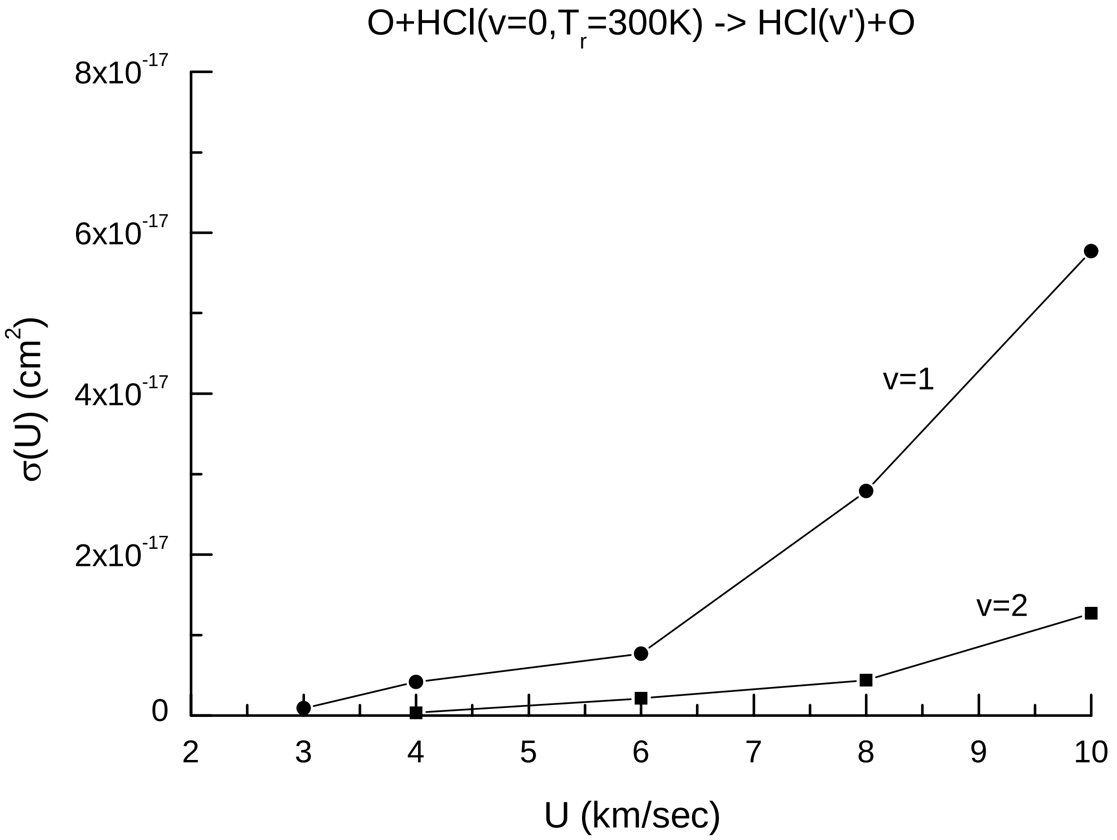


- Experimental velocity distribution of Hradil et al. is fit to sum of Gaussians

- Velocity distribution is first convolved with thermal motion of NO_2 precursor and then with thermal motion of HCl [van der Zande et al., 1991; Brouard et al., 1992]

- Figure shows resultant O+HCl relative energy distribution generated by trajectory code

HCl Vibrational Excitation



- Rotational excitation is estimated to be 5000K-8000K in the 6-10 km/s velocity range