Throwing Light on Reaction Dynamics:

H + HBr

The thermal reaction of hydrogen gas (**H_2**) and bromine gas (**Br_2**) to form hydrogen bromide vapor (**HBr**) is a classic reaction:

Energetics (**thermodynamics**) does **NOT** tell us how this reaction occurs or how rapidly equilibrium is established.

For answers to those questions, we need **kinetics** and **dynamics**.

Kinetic Studies of H_2 + Br_2

M. Bodenstein and S. Lind, *Z. physikal. Chem*. **57**, 168 (1906).

Rate of reaction:

Great surprise and mystery

Reaction Mechanism

Initiation:

Propagation:

Termination:

Kinetic Studies of H_2 + Br_2

M. Bodenstein and S. Lind, *Z. physikal. Chem*. **57**, 168 (1906).

Rate of reaction:

Reaction Mechanism

Christiansen, *Dansk. V. d. Math. Phys. Medd.* **1**, 14 (1919)

Herzfeld, *Ann. Phys*. **59**, 635 (1919)

M. Polanyi, *Z. El. Ch*. **26**, 10 (1920)

Reaction Mechanism

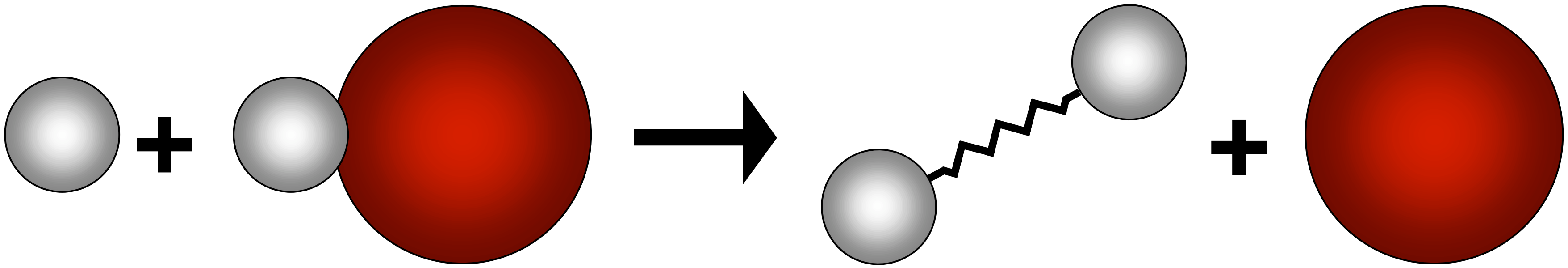
Initiation:

Propagation:

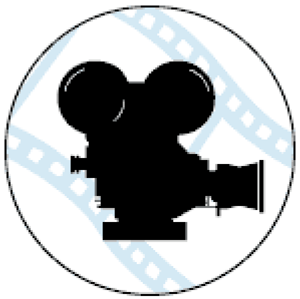
Inhibition:

Termination:

$H + HBr \rightarrow H_2 + Br$

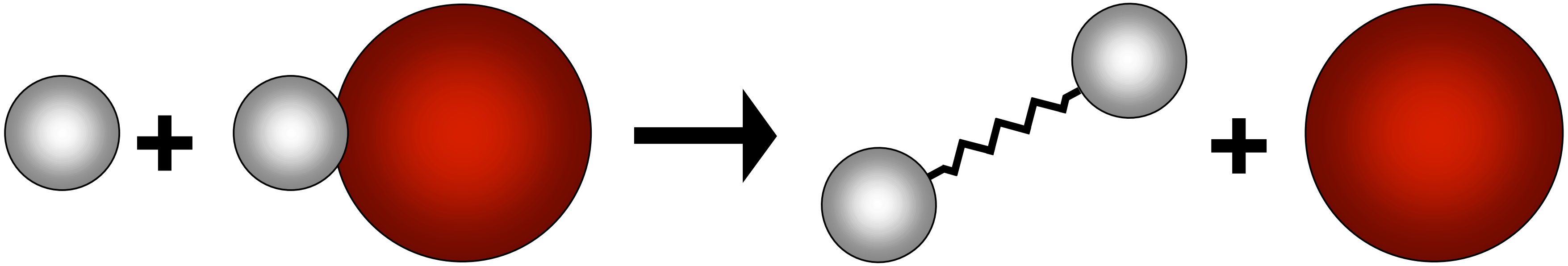


How does such a simple reaction occur?



Try to make a movie in your mind of how the reaction takes place.

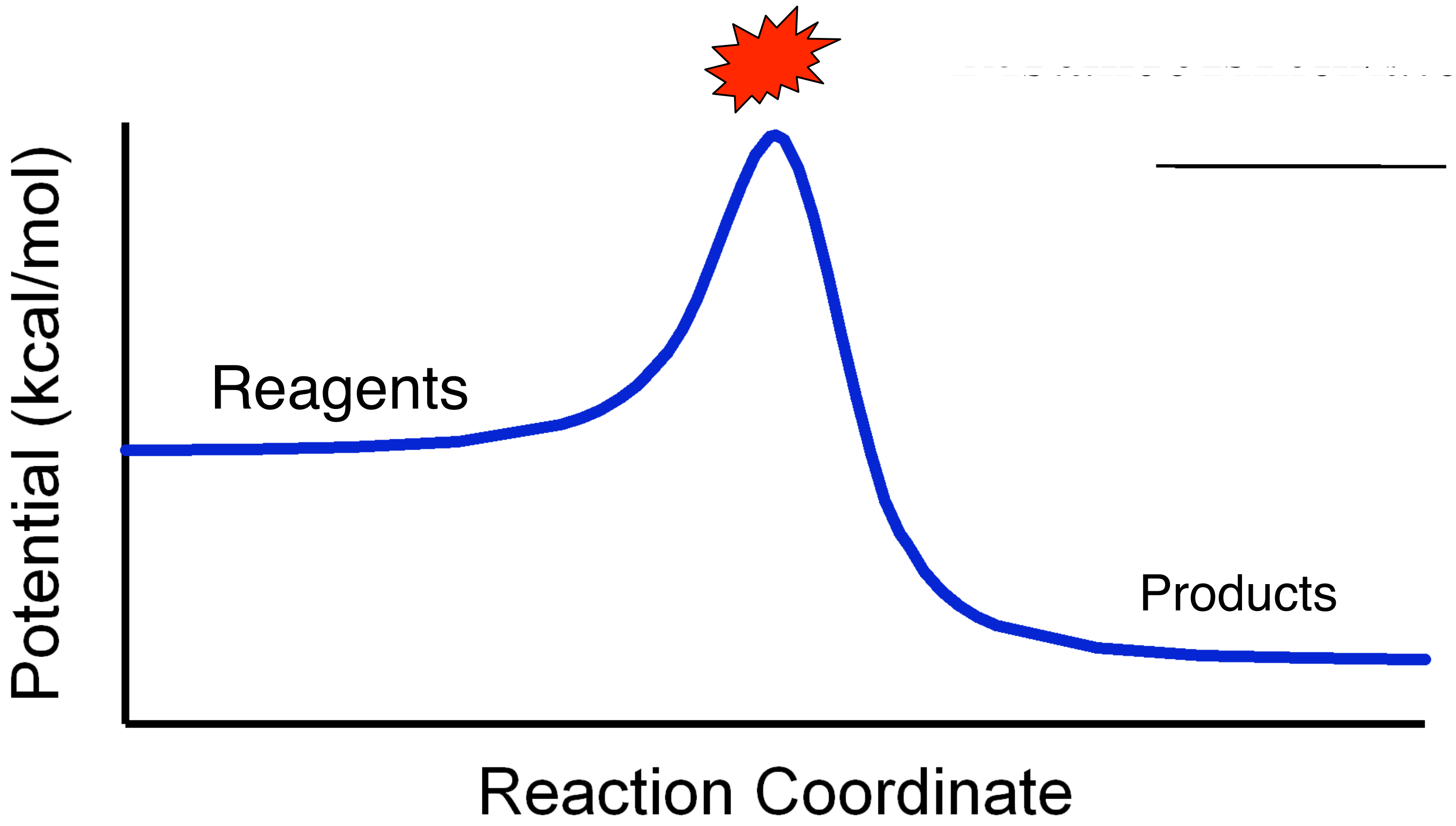
$H + HBr$ □ $H_2 + Br$



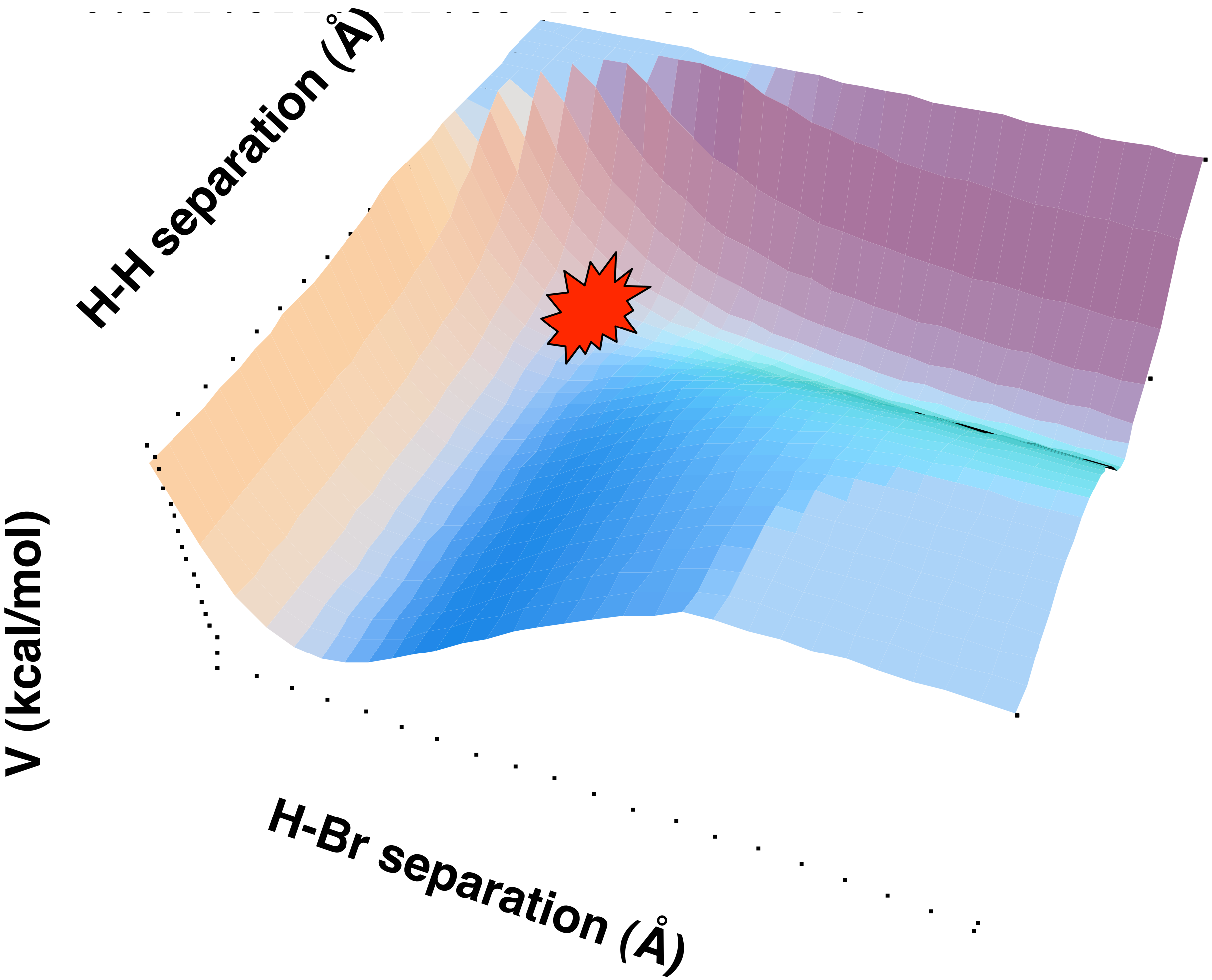
How much does the H_2 product vibrate and rotate?

Can a measurement of the rotation and vibration
tell us about the mechanism of a chemical reaction?

The Transition State



The Born-Oppenheimer Approximation



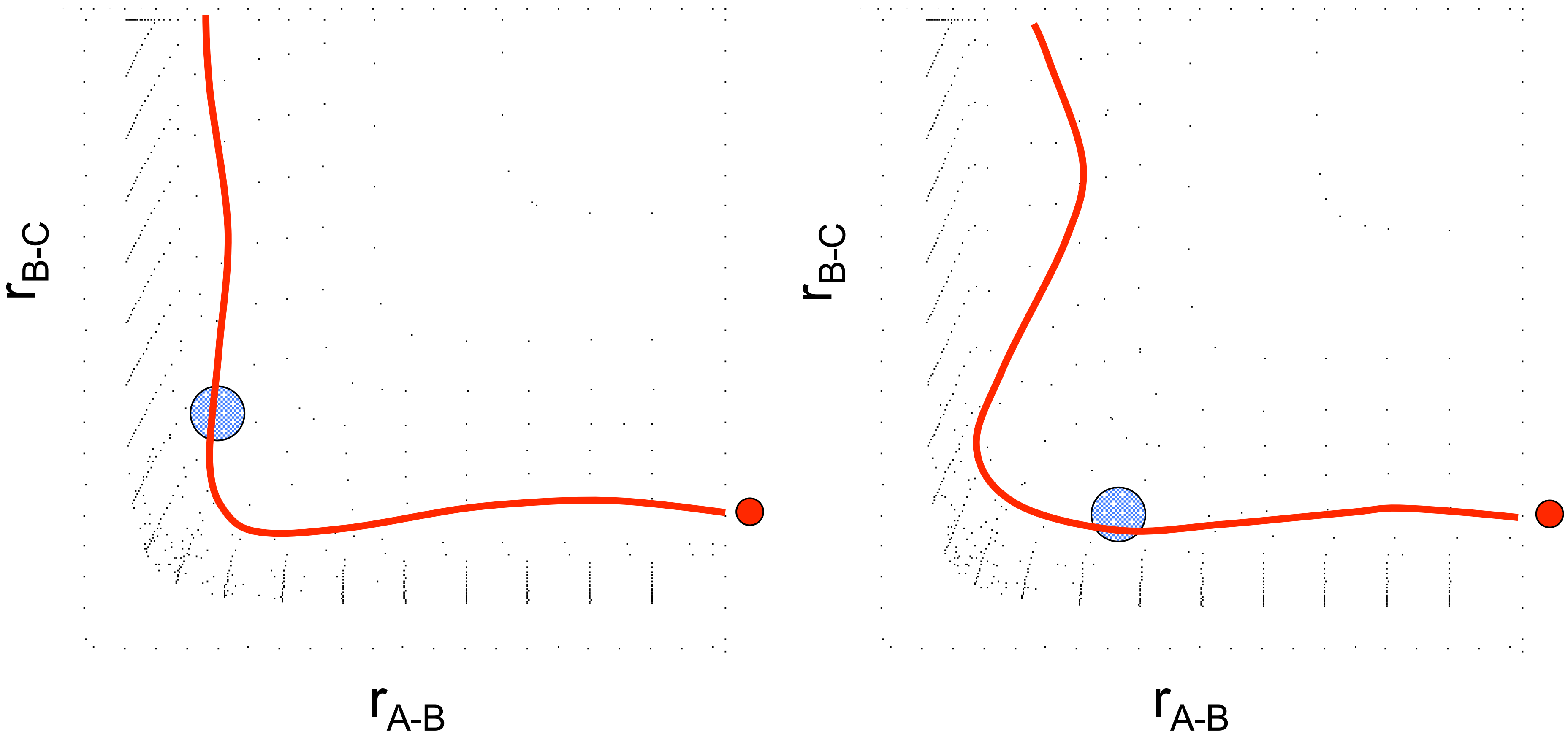
- •Separate wave equation; calculate the electronic energy as a function of nuclear geometry (PES).

- •Calculate motion along that PES (using classical or quantum mechanics).

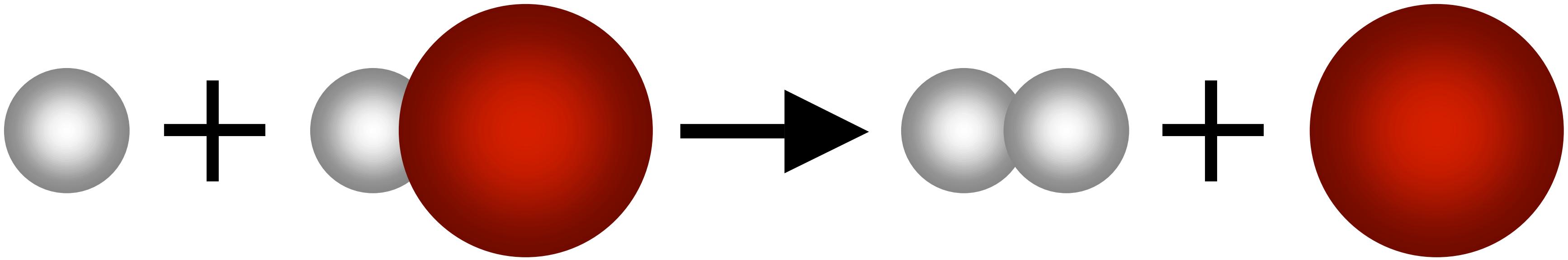
Asymptotic Approach

The product vibrational energy can be related to the location of the transition state.

A + BC _ AB + C

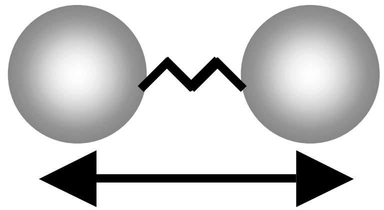


H + HBr □ H_2 + Br



- H_2 is described by two quantum numbers: *v′*, *j′*.
- Those quantum numbers describe the asymptotic state.
- We measure partial cross sections for forming individual quantum states: _(*v′*, *j′*).

***v'*:**

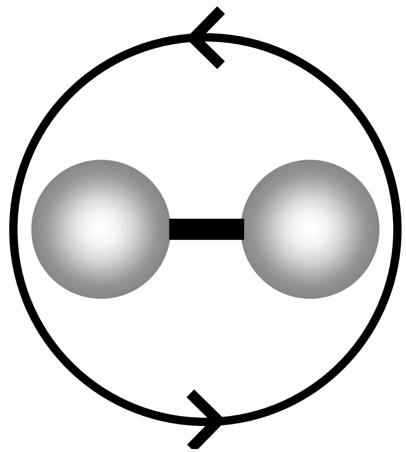


Classical Barrier Height: 1.7 kcal/mol

Reaction Exoergicity: 19.1 kcal/mol

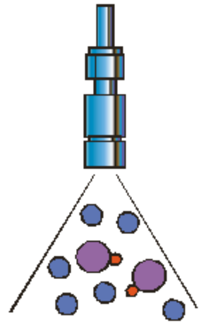
Total Reactive Cross Section: 1.2 Å^2

***j'* :**

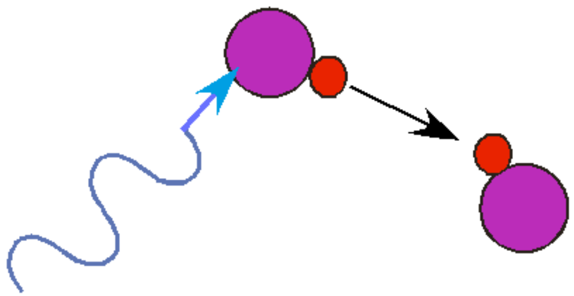


Experimental Protocol

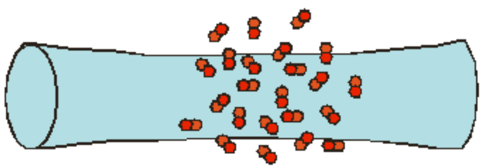
1) A gas jet expansion produces translationally and internally cold precursors.



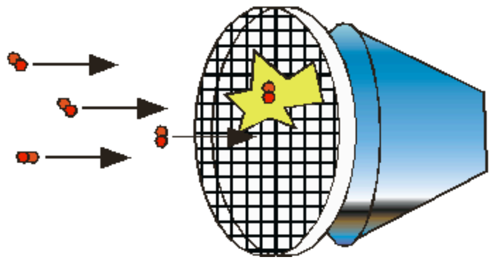
2) A tunable laser photolyzes HBr to produce fast H atoms with a well defined translational energy.



3) About 20 ns later, a focused, polarized laser ionizes $H_2(v', j')$ via (2+1) REMPI.

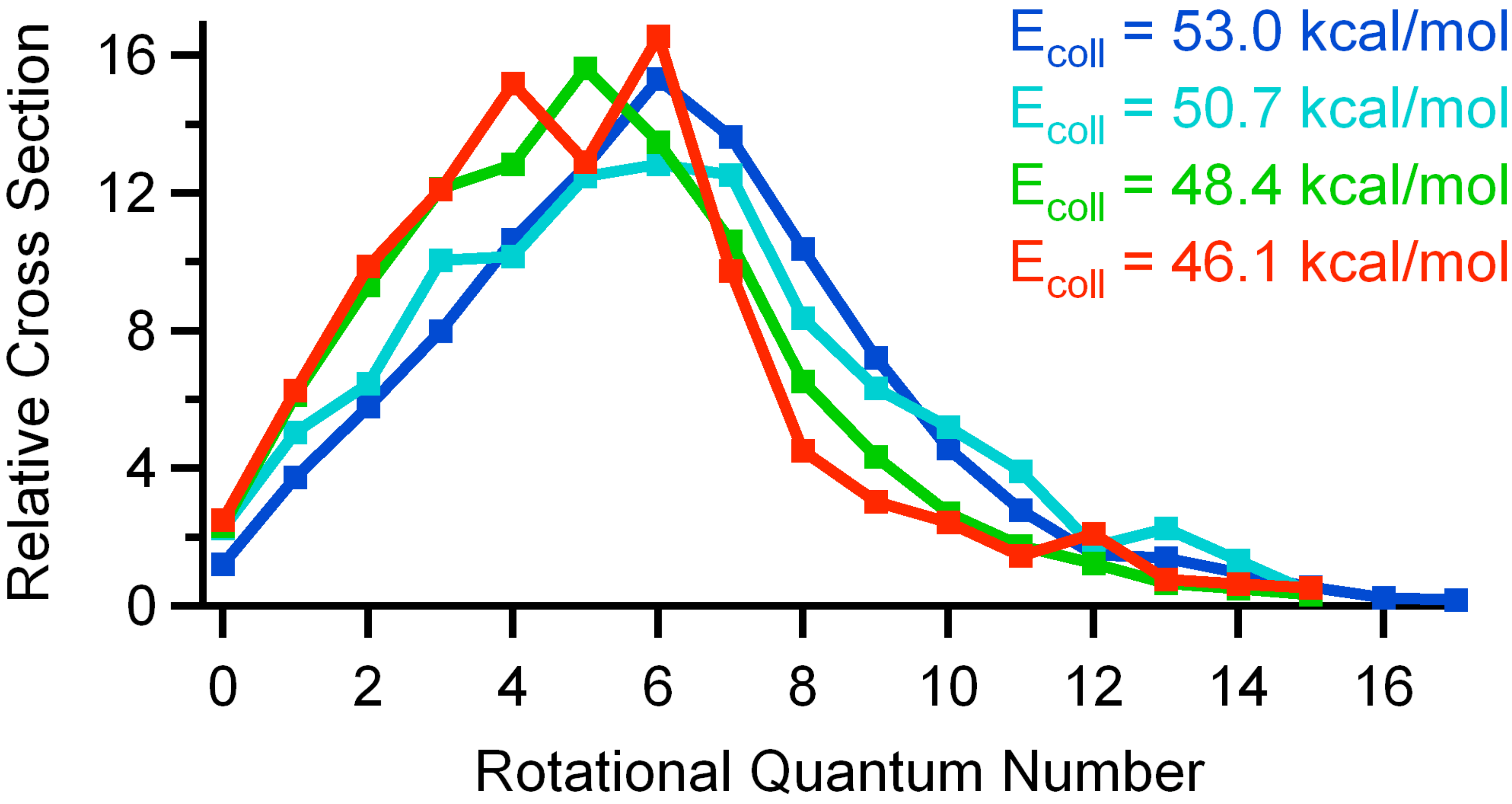


4) H_2^+ is propelled down the TOF by electric fields. A microchannel plate detector is used to count the ions.



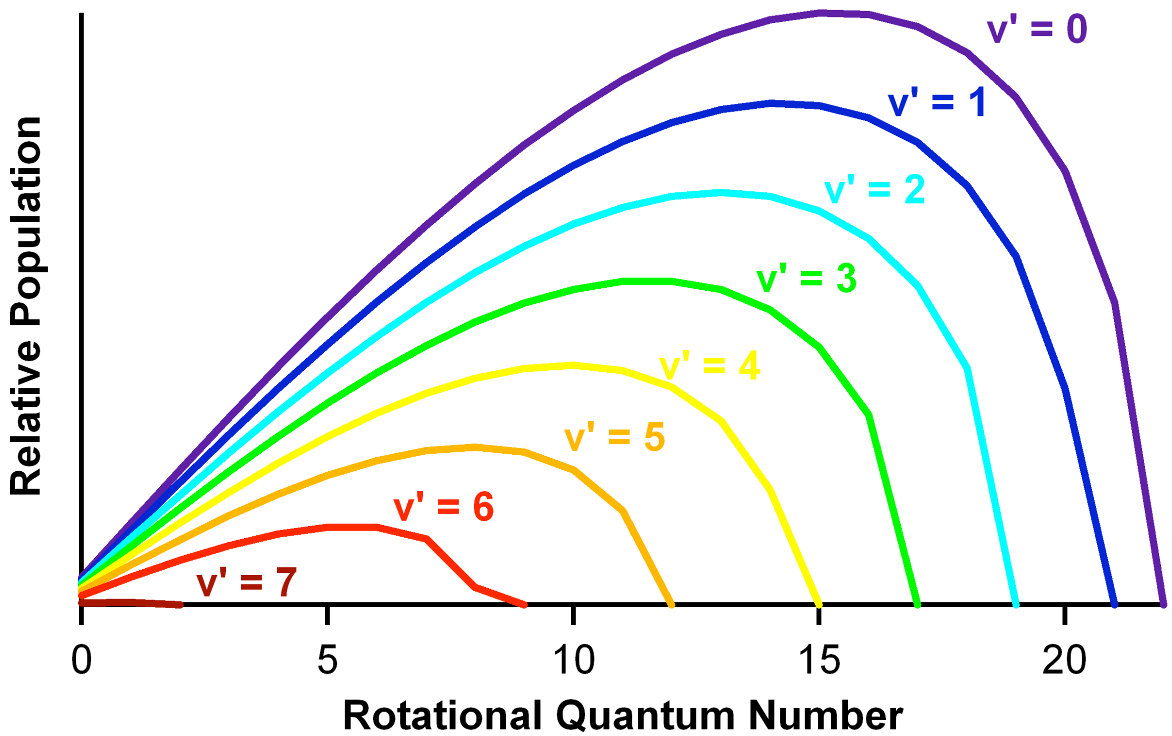
Experimental Results

H + HBr $H_2(v'=2, j') + Br$

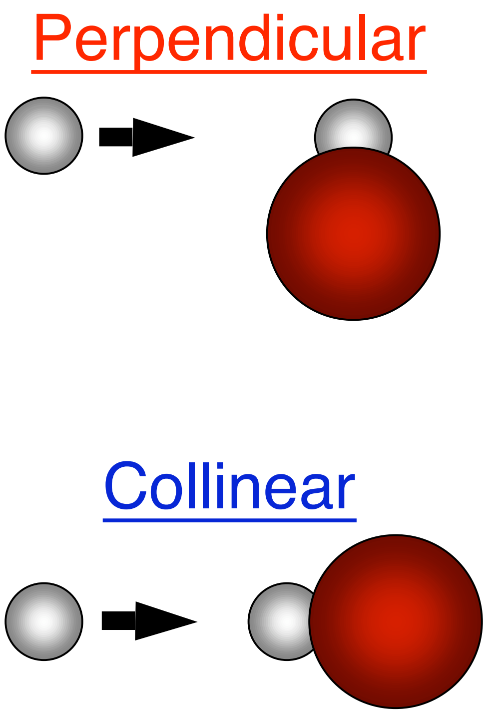


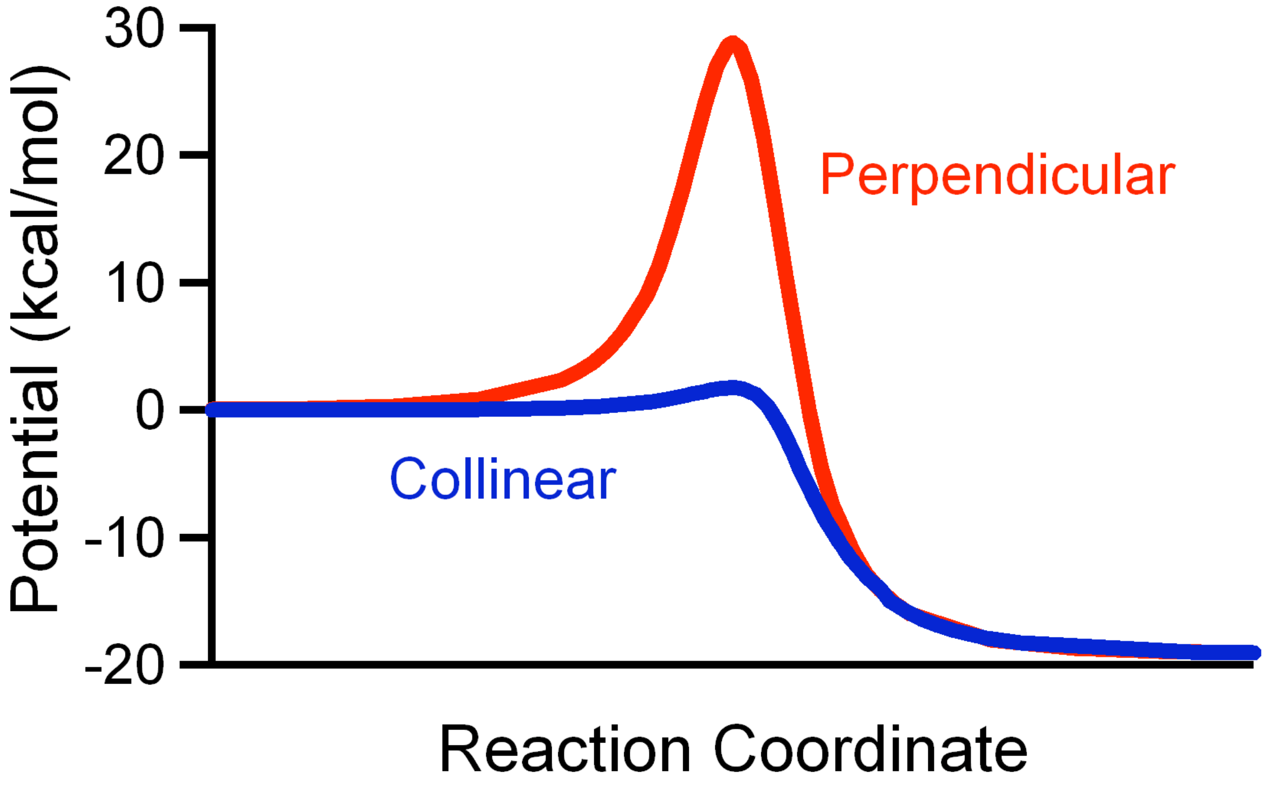
Possible State Distributions

Purely Statistical



Different Approach Geometries

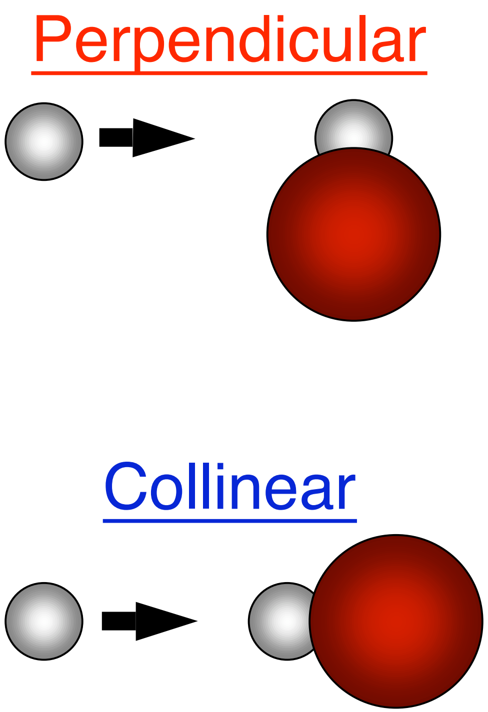


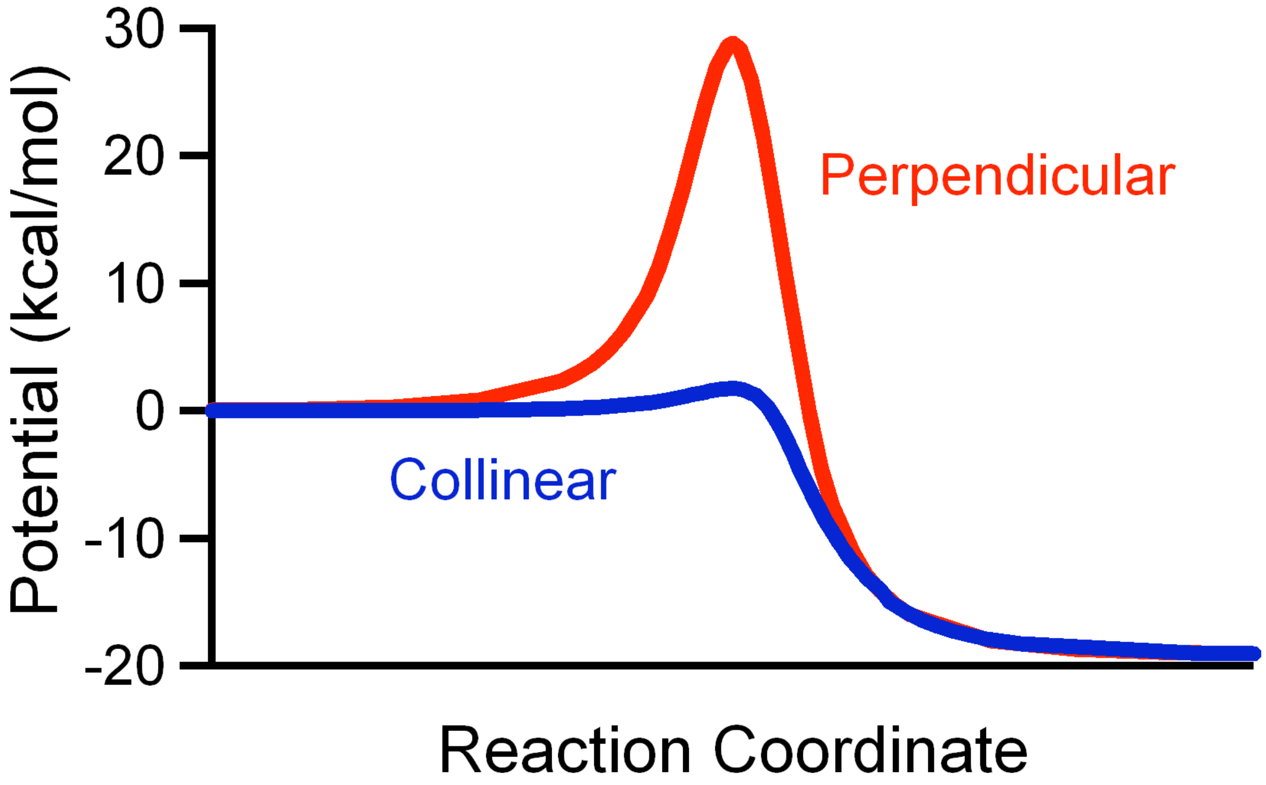


Kinematically Constrained State Distribution

Valentini and co-workers:

translational energy is needed to surmount the reaction barrier



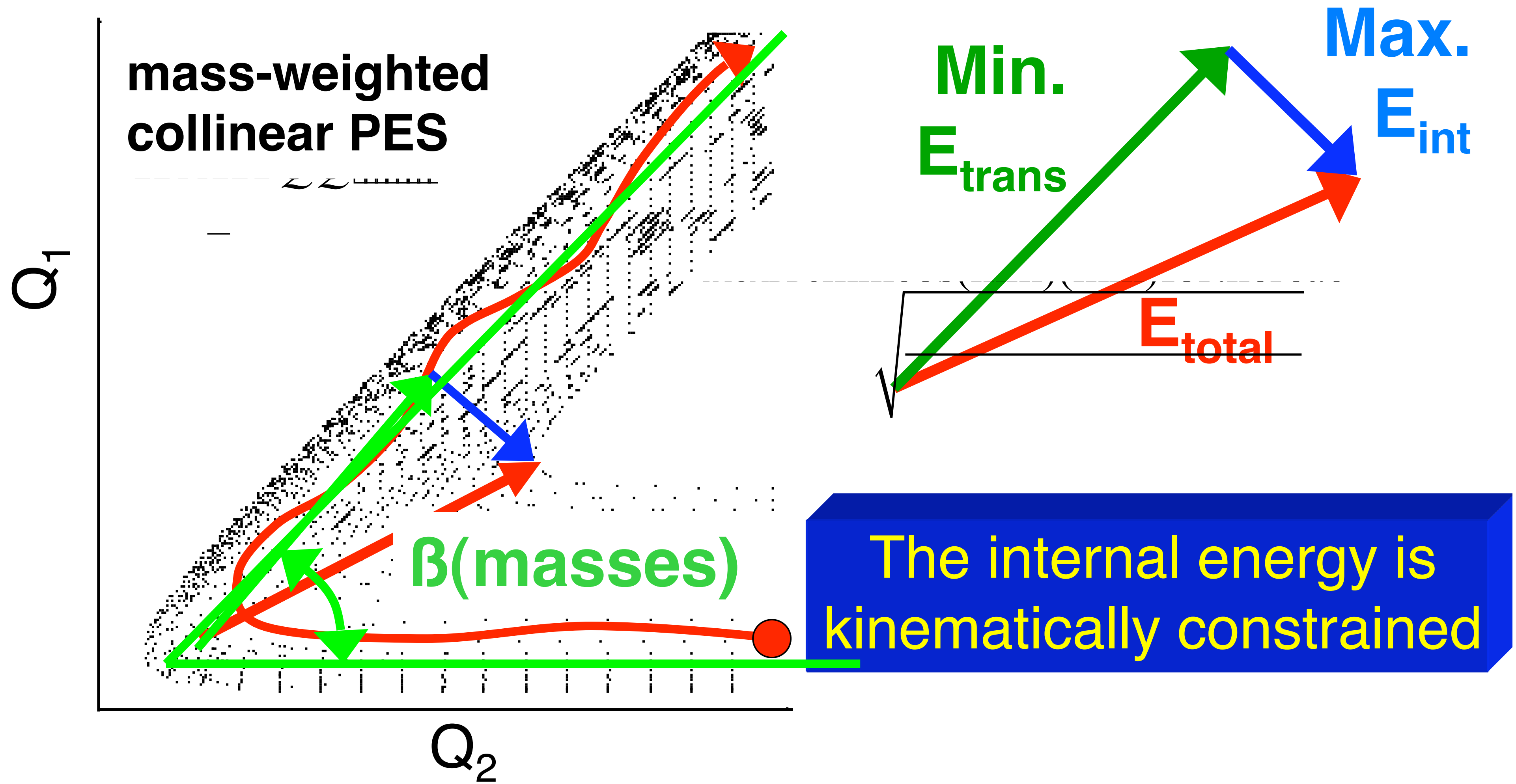


Video of PES

Video - Low >>

Video - High >>

Kinematically Constrained State Distribution



C. A. Picconatto, A. Srivastava, and J. J. Valentini, *J. Chem. Phys.* 114, 1663-1671 (2001).

The minimum translational energy of the products is

Reaction (E_{trans})	$j'_{max,meas}$	$j'_{max,model}$	$j'_{max\ (E avail)}$
H+HCl (37 kcal/mol)			
$H_2(v'=0)$	**11**	**11**	**15**
$H_2(v'=1)$	**7**	**7**	**13**

P. M. Aker, G. J. Germann, and J. J. Valentini, J. Chem. Phys. **90**, 4795 (1989).

Reaction (E_{trans})	$j'_{max,meas}$	$j'_{max,model}$	$j'_{max\ (Eavail)}$
H+HBr (37 kcal/mol)			
$H_2(v'=0)$	**13**	**15**	**19**
$H_2(v'=1)$	**11**	**12**	**17**
$H_2(v'=2)$	**5**	**8**	**15**

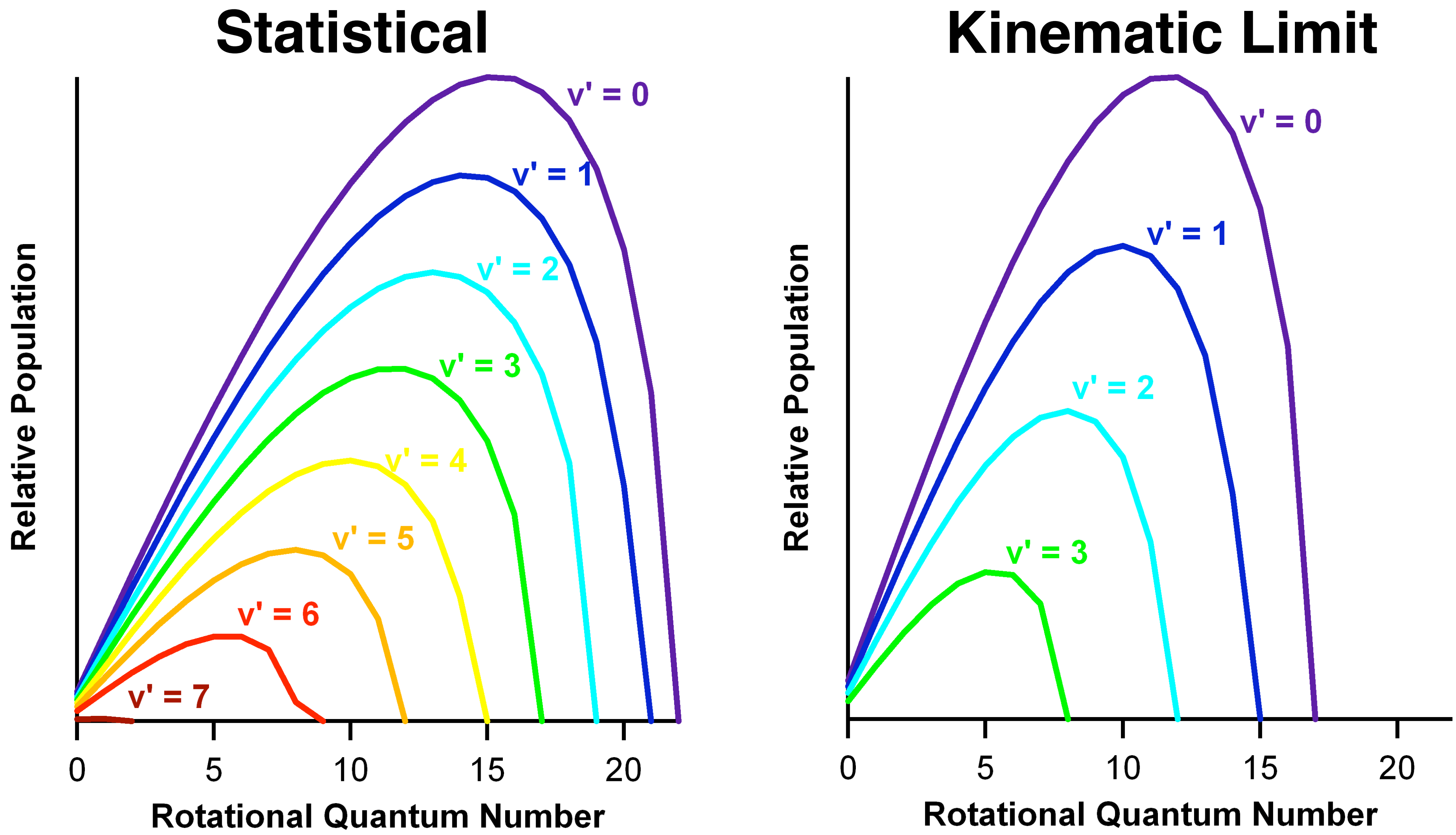
P. M. Aker, G. J. Germann, and J. J. Valentini, J. Chem. Phys. **90**, 4795 (1989).

Reaction (E_{trans})	$j'_{max,meas}$	$j'_{max,model}$	$j'_{max\ (E_{avail})}$
H+HI (37 kcal/mol)			
$H_2(v'=0)$	**17**	**19**	**23**
$H_2(v'=1)$	**17**	**17**	**21**
$H_2(v'=2)$	**15**	**15**	**19**
$H_2(v'=3)$	**11**	**11**	**17**
$H_2(v'=4)$	**5**	**7**	**14**

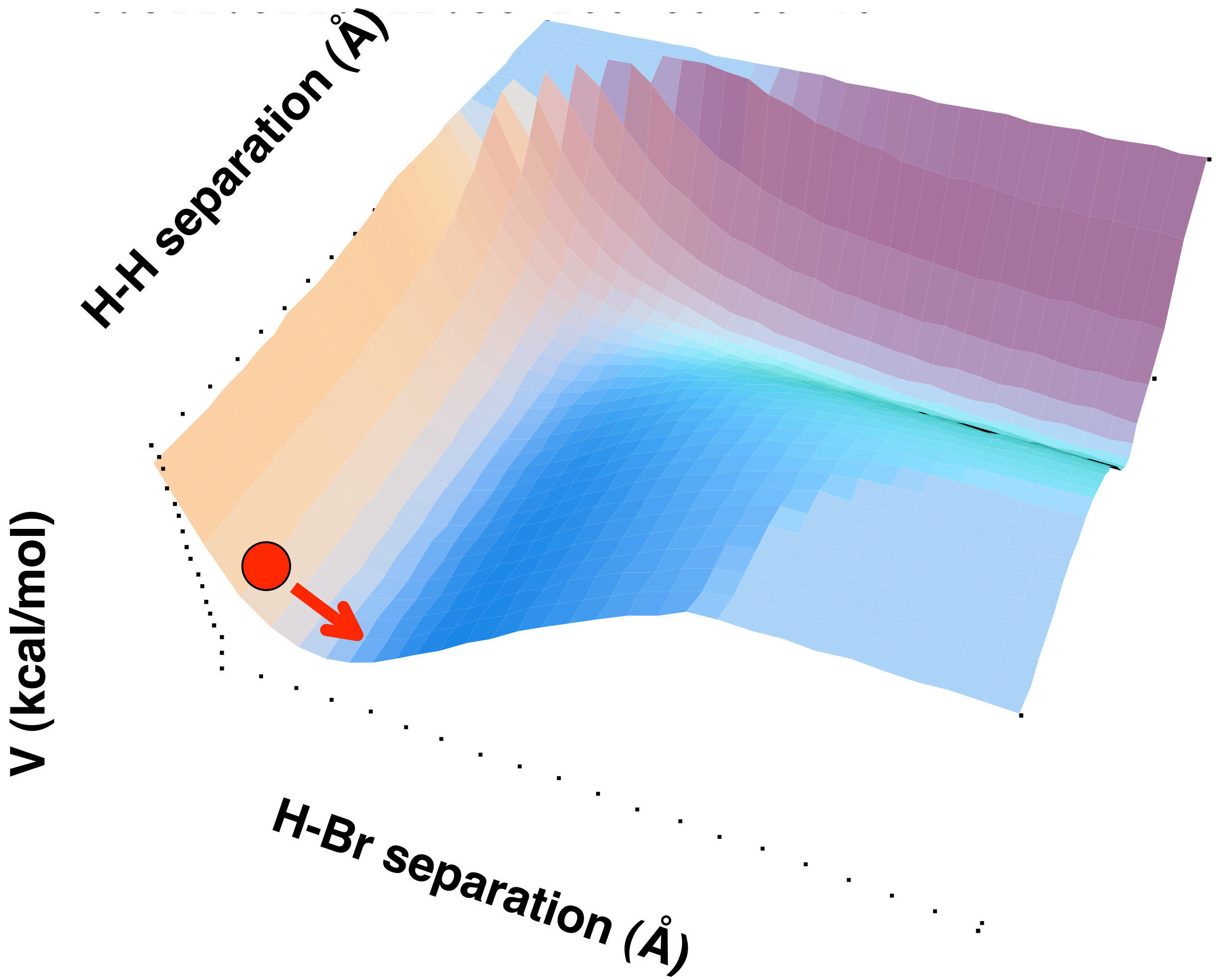
P. M. Aker, G. J. Germann, and J. J. Valentini, J. Chem. Phys. **96**, 2756 (1992).

$H + HBr \rightarrow H_2(v'=2, j') + Br$

E_{coll} = 53.0 kcal/mol



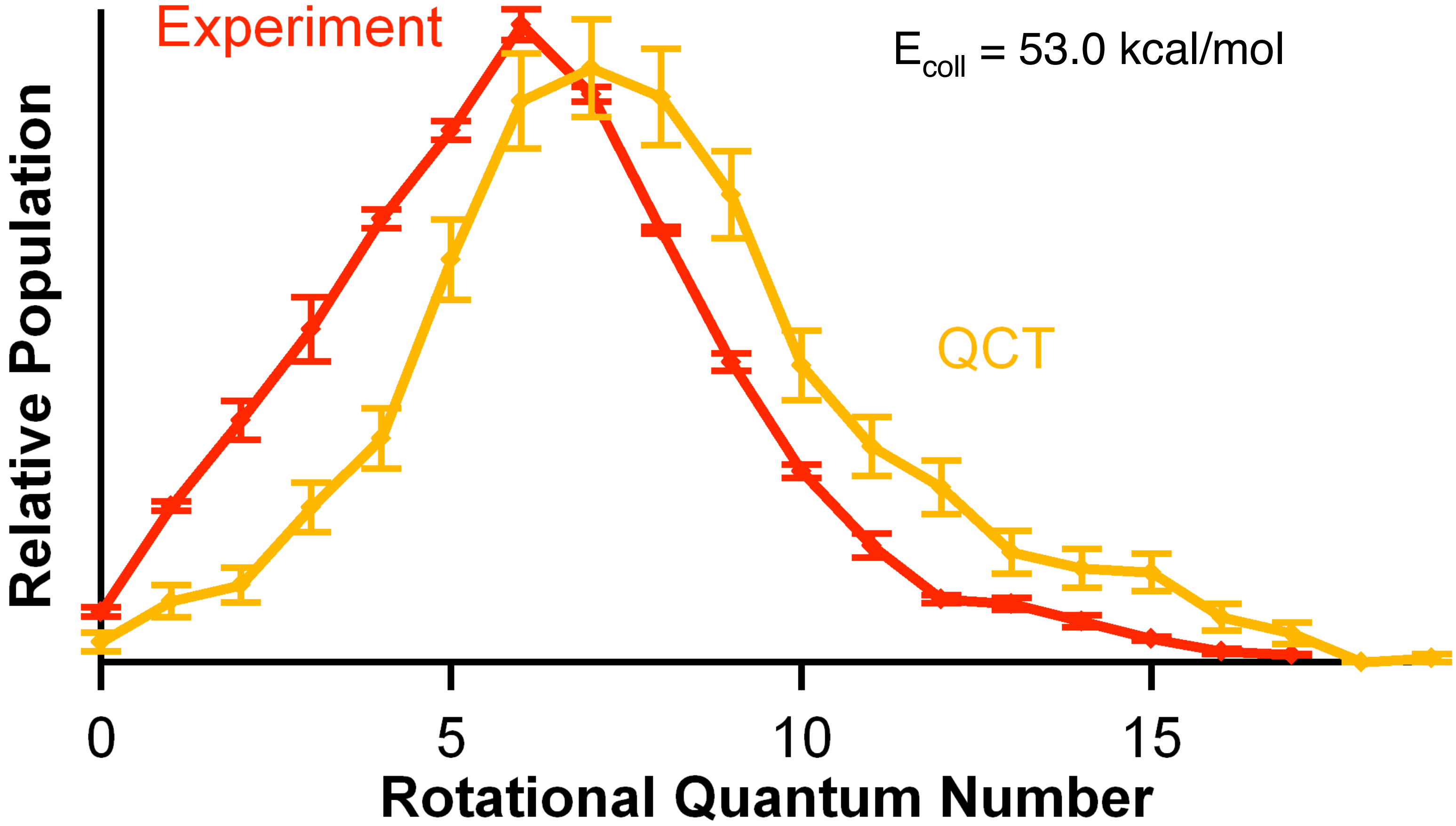
Quasiclassical Trajectory Method (QCT)



- Find potential quantum mechanically
- Take derivative to yield forces
- Solve Newton's equations of motion
- Find position of each atom at all times
- Bin into quantum states

Experimental and Theory

H + HBr → $H_2(v'=2, j')$ + Br



$H + HBr$ □ $H_2(v'=2, j') + Br$

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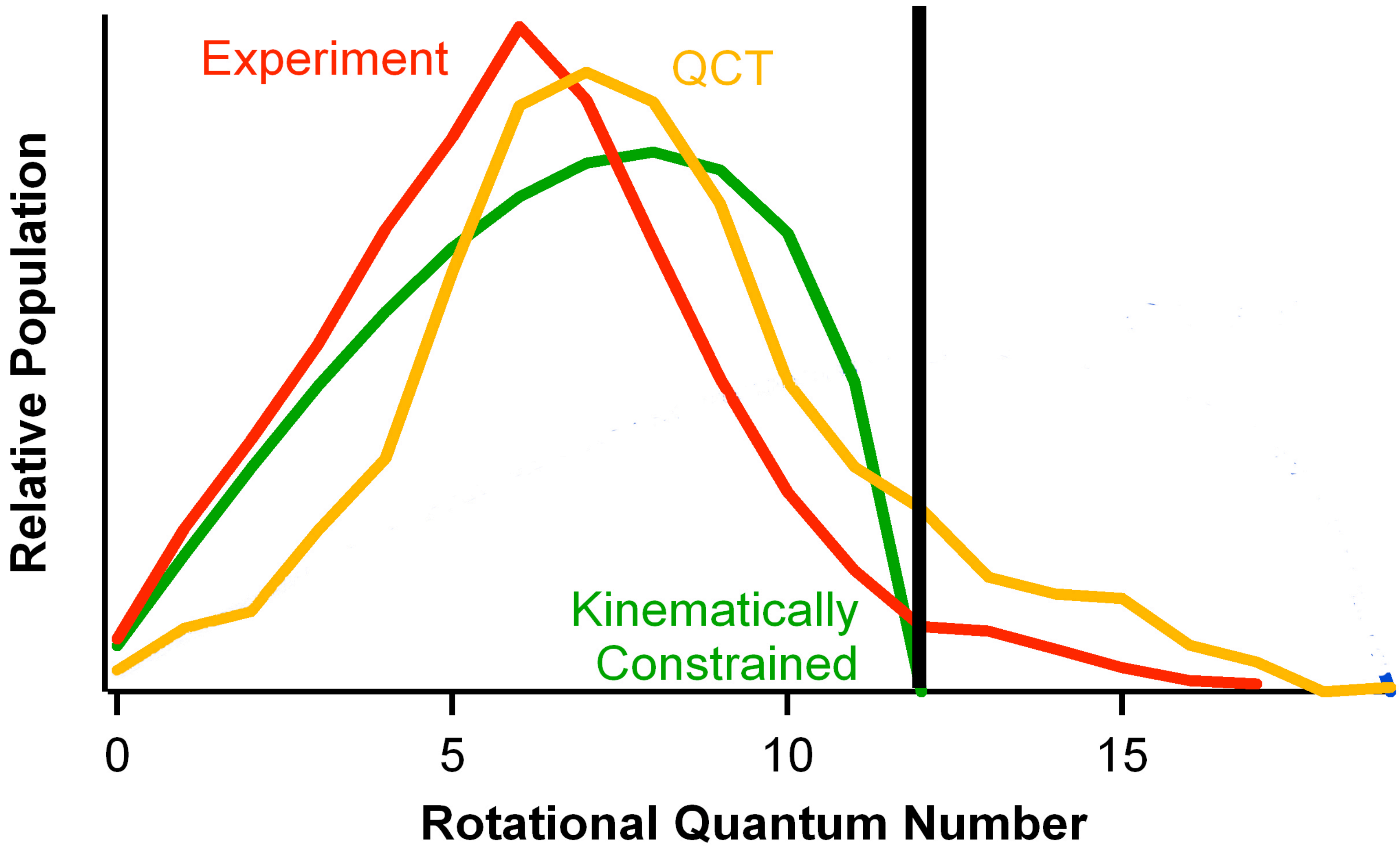
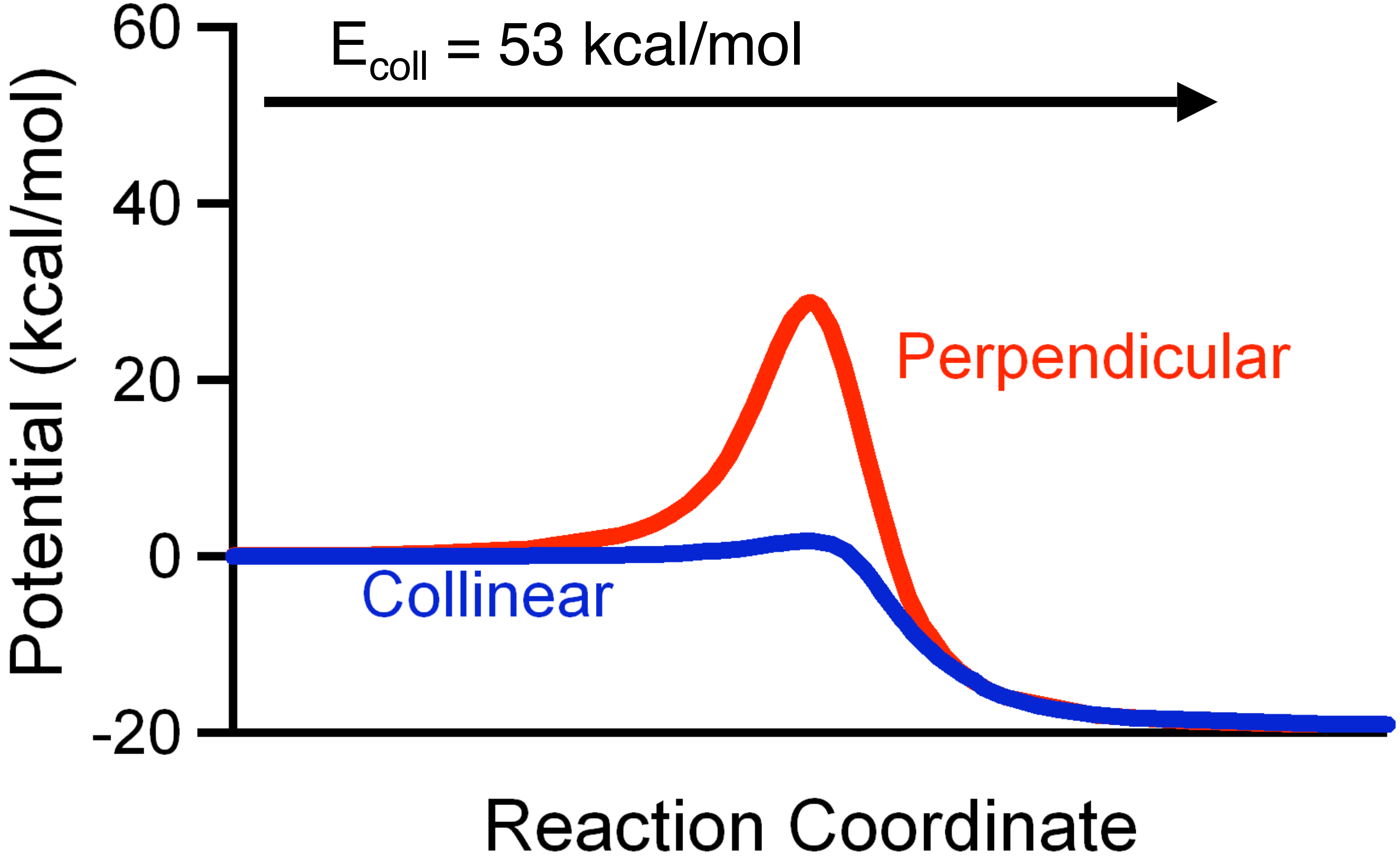
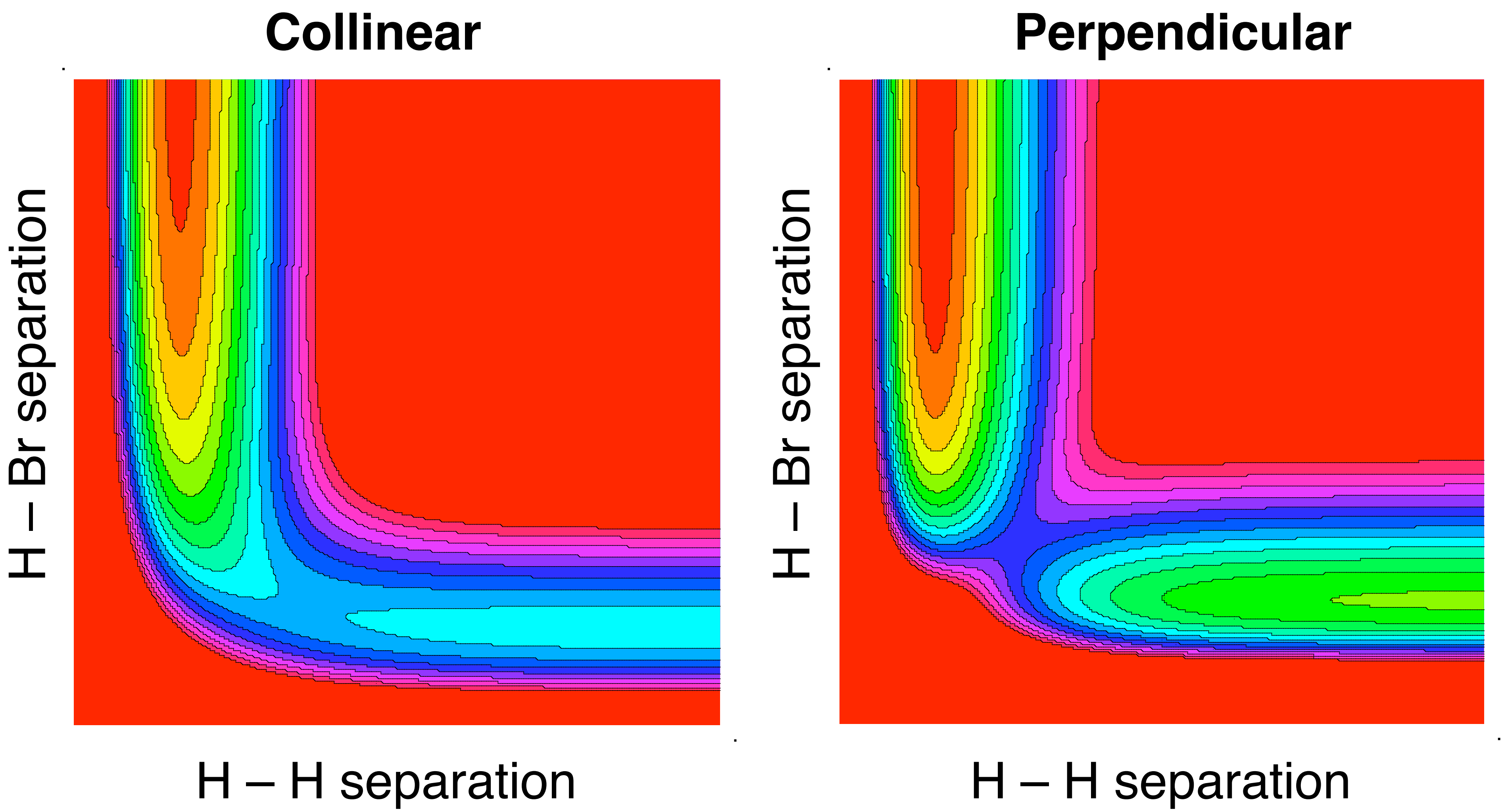


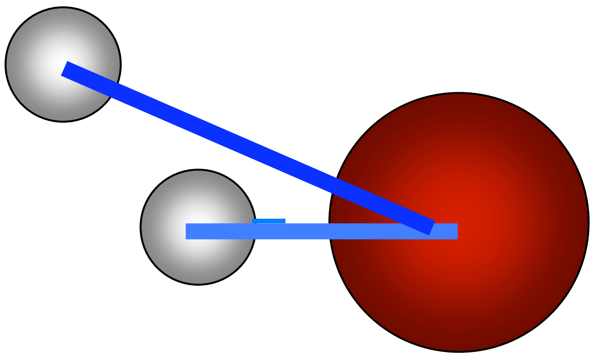
Kinematically Forbidden Quantum States



Kinematically Forbidden Quantum States

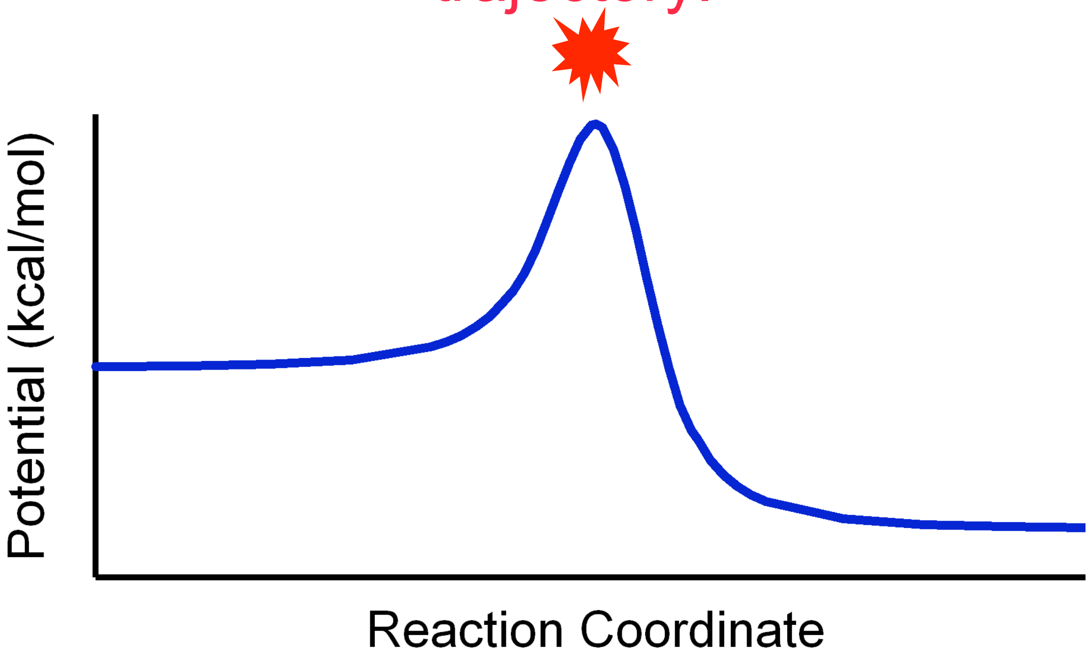


Transition State Geometry

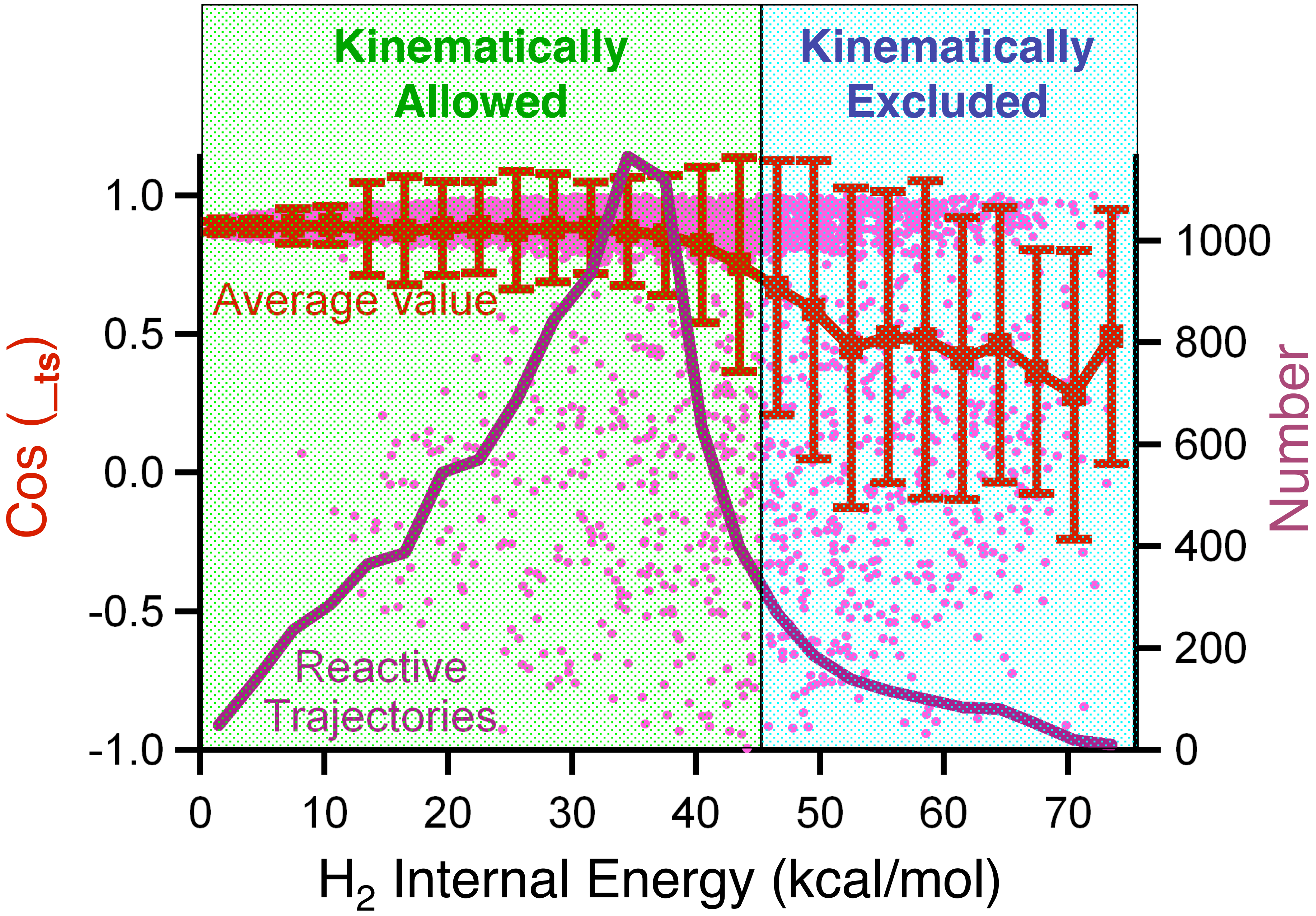


_ is the angle between the H–Br bond axis and line connecting the attacking H-atom with the HBr center of mass.

The transition state is the configuration for which potential energy reaches a maximum in a reactive trajectory.

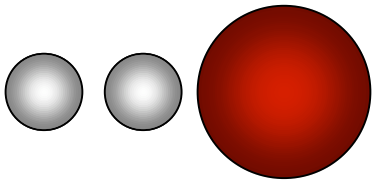


Quasiclassical Trajectory Calculations

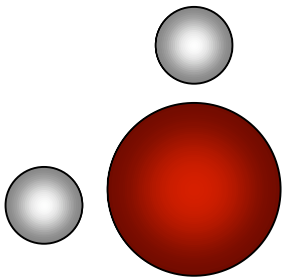


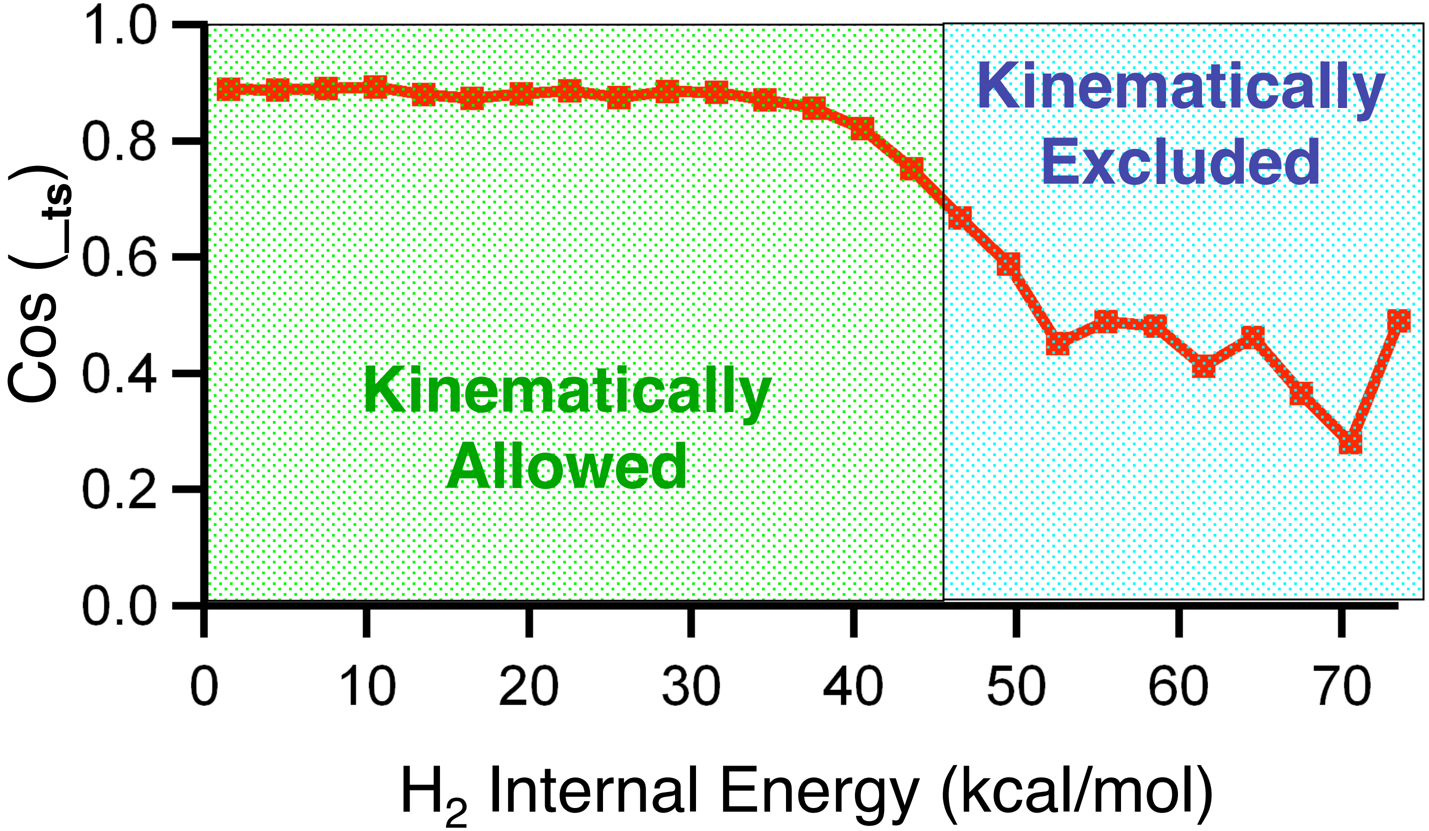
Spectroscopy of the Transition State

Collinear:

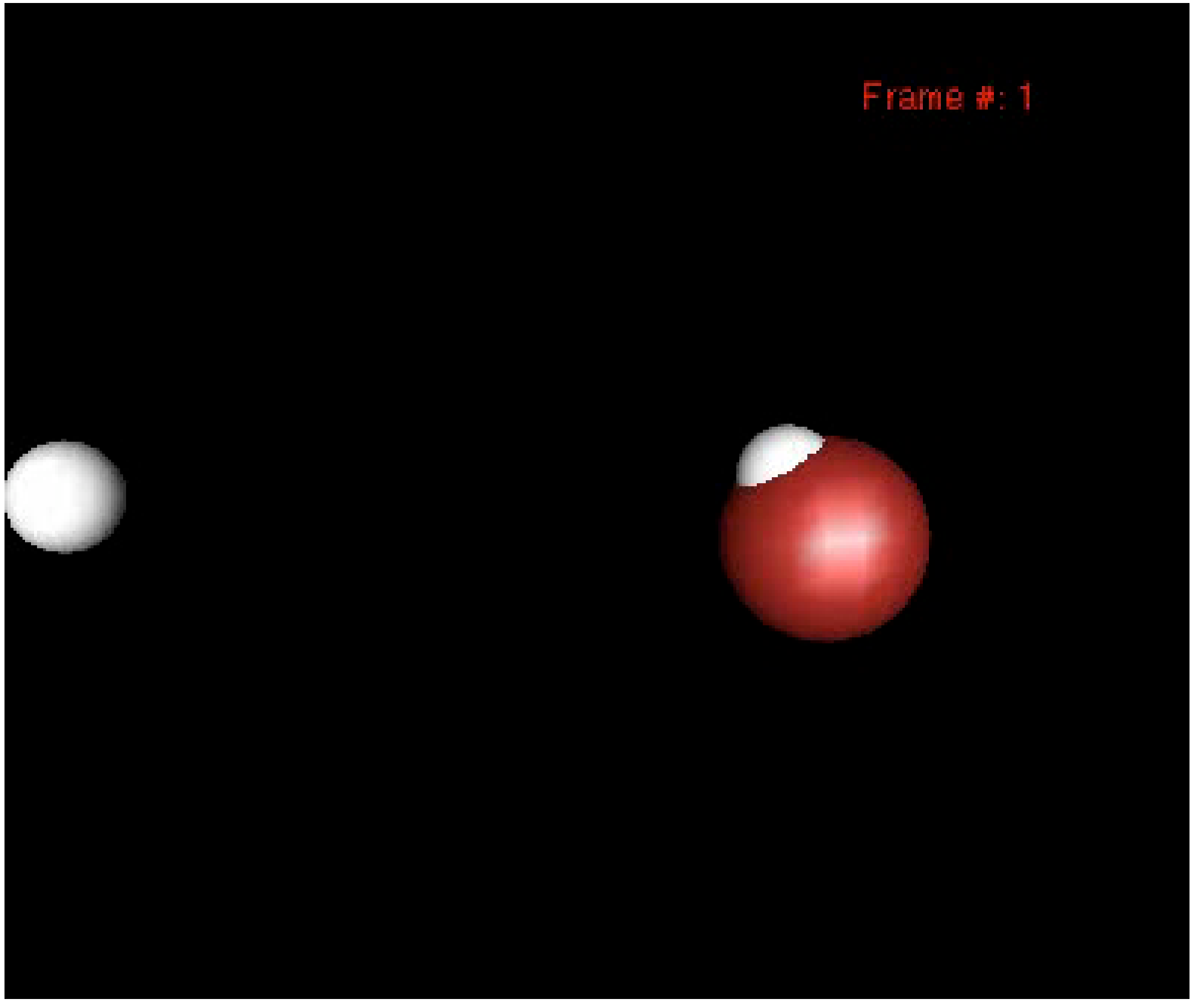


Perpendicular

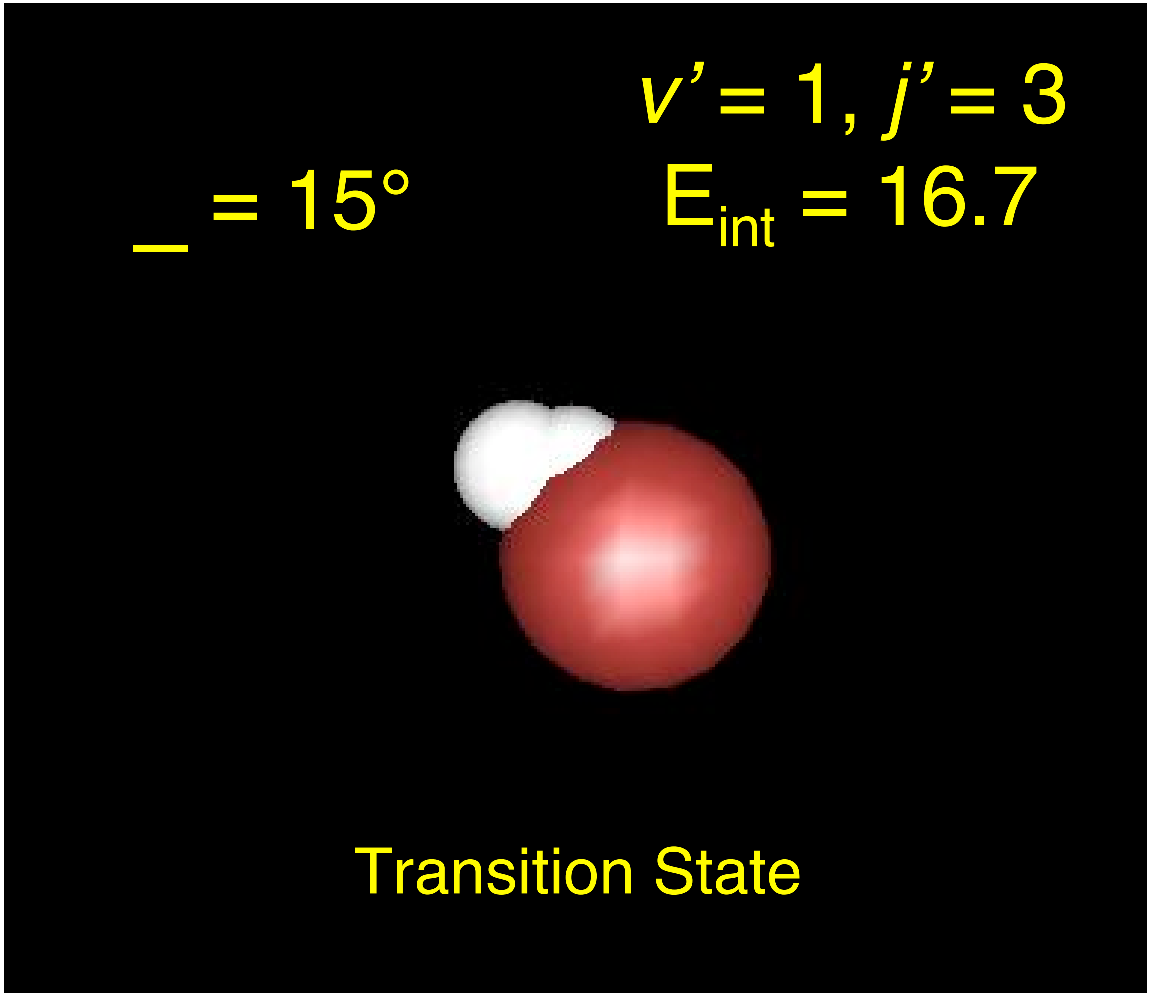




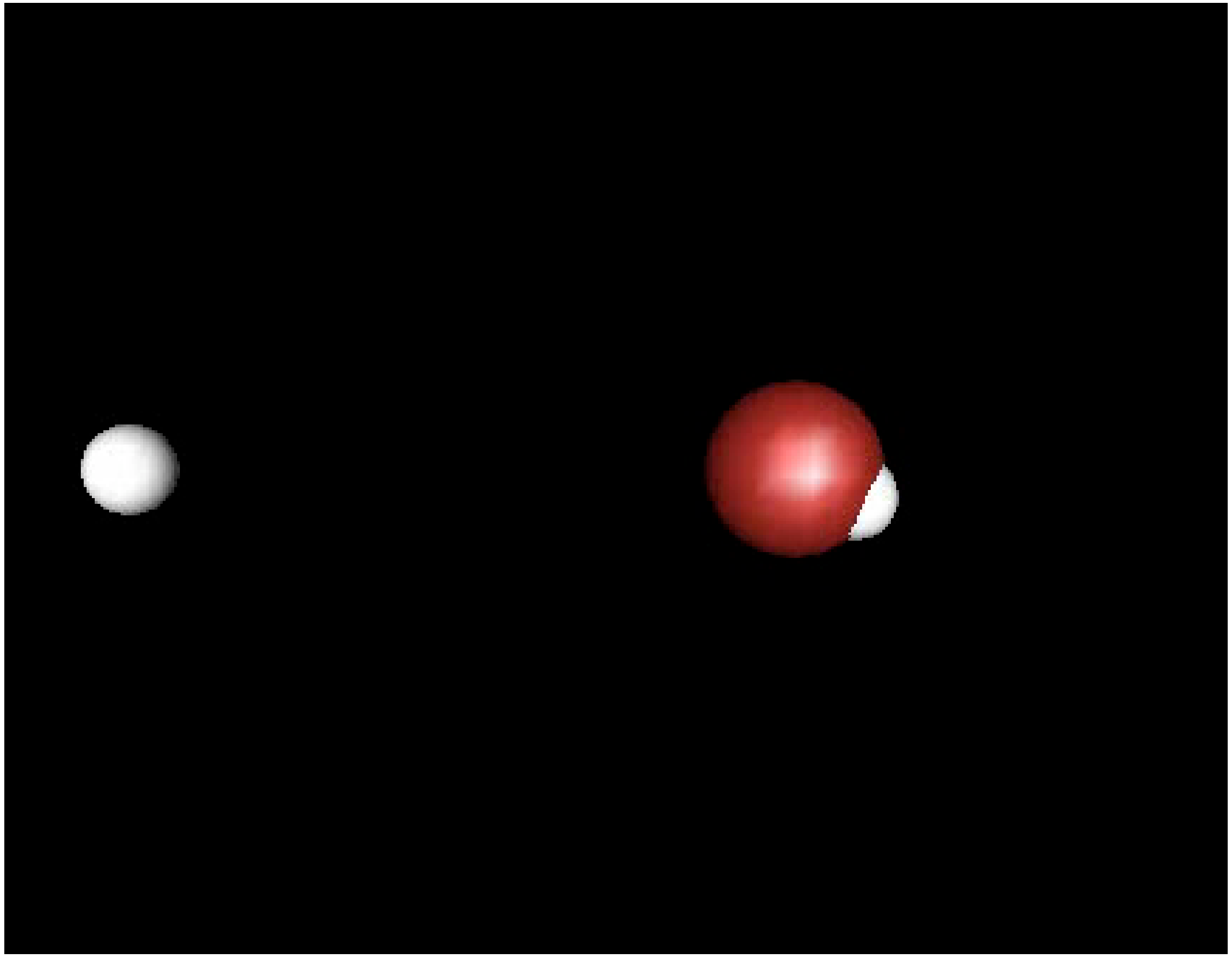
Mechanism for Forming Internally **Cold** H_2



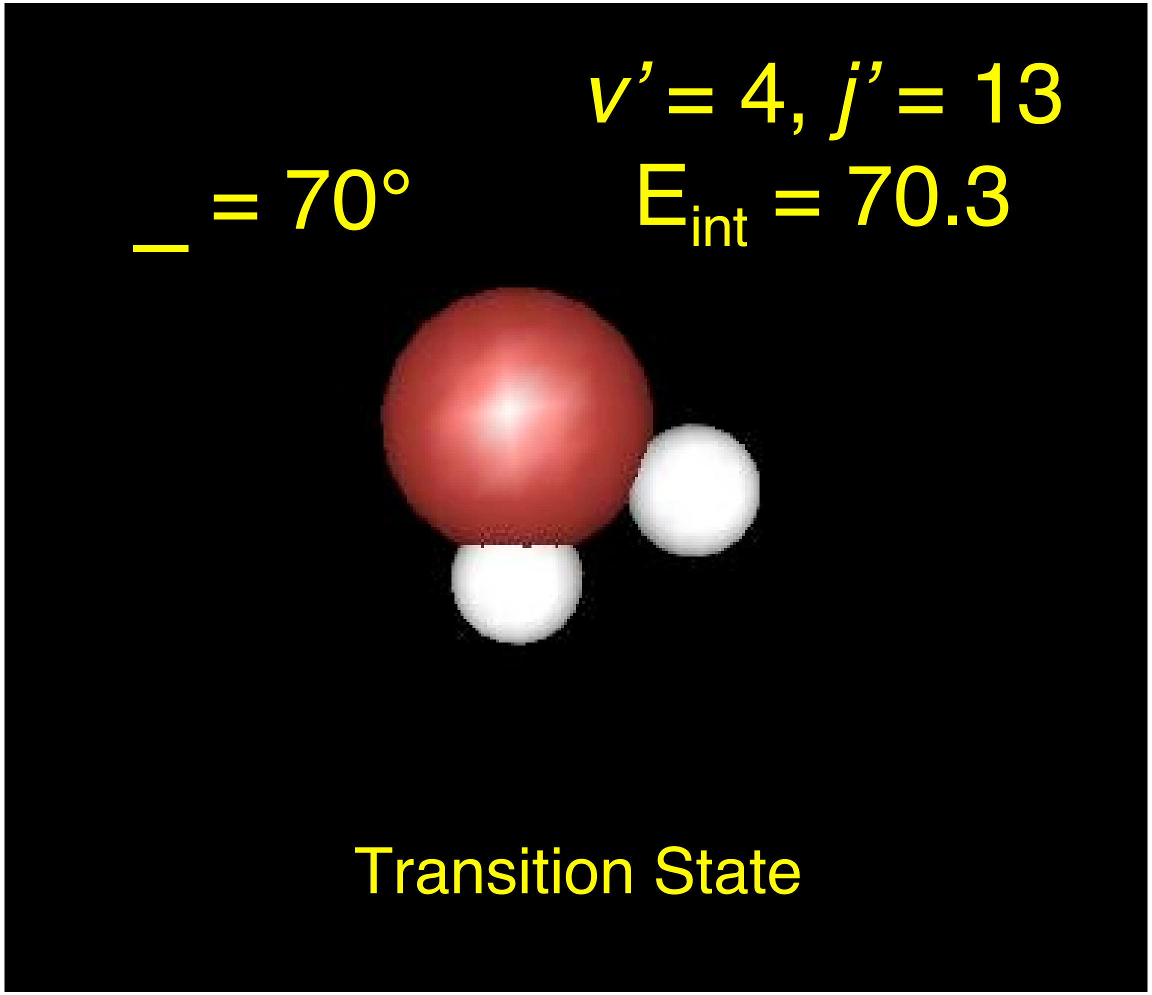
Mechanism for Forming Internally **Cold** H_2



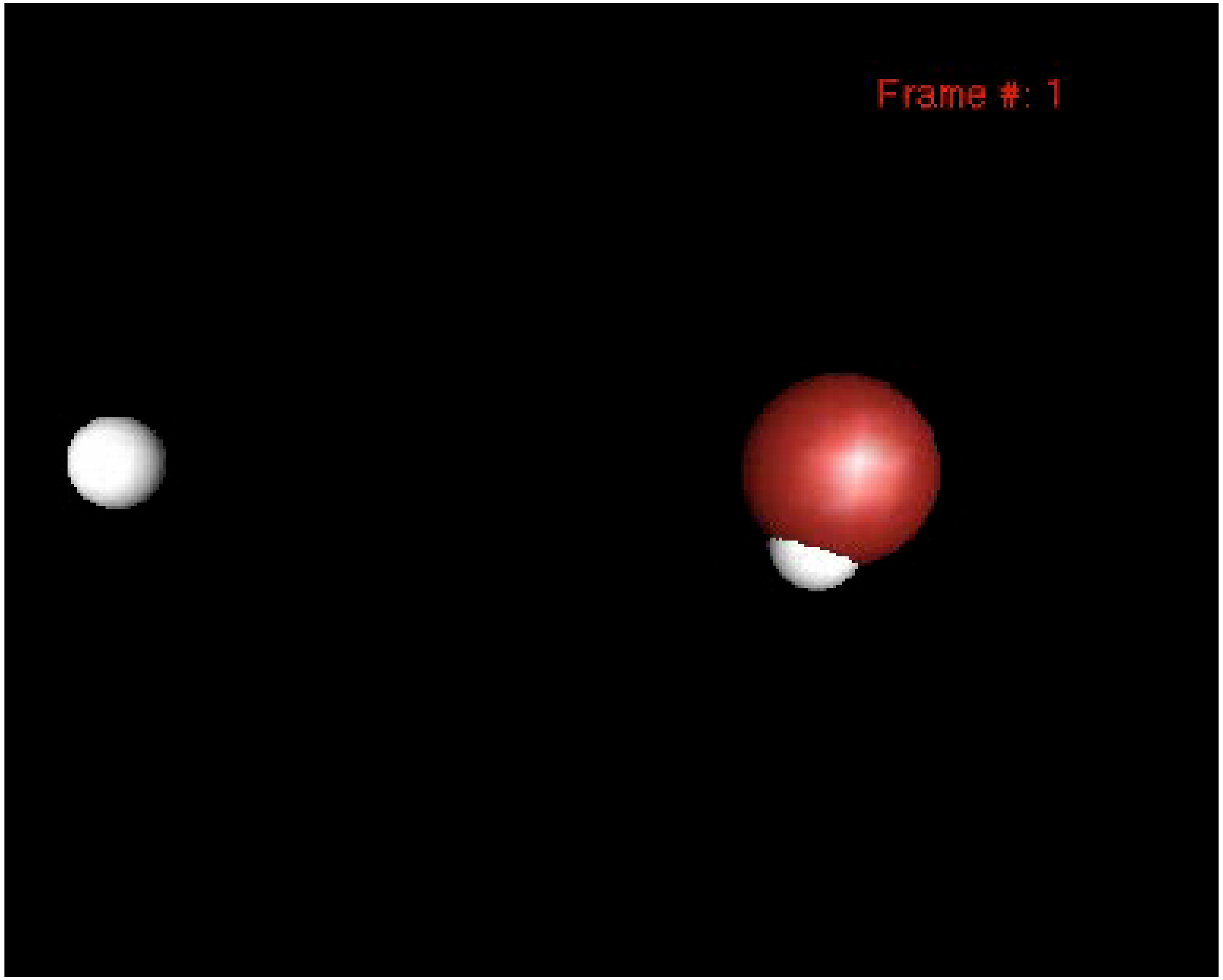
Mechanism for Forming Internally **Hot** H_2



Mechanism for Forming Internally **Hot** H_2



Direct Trajectory



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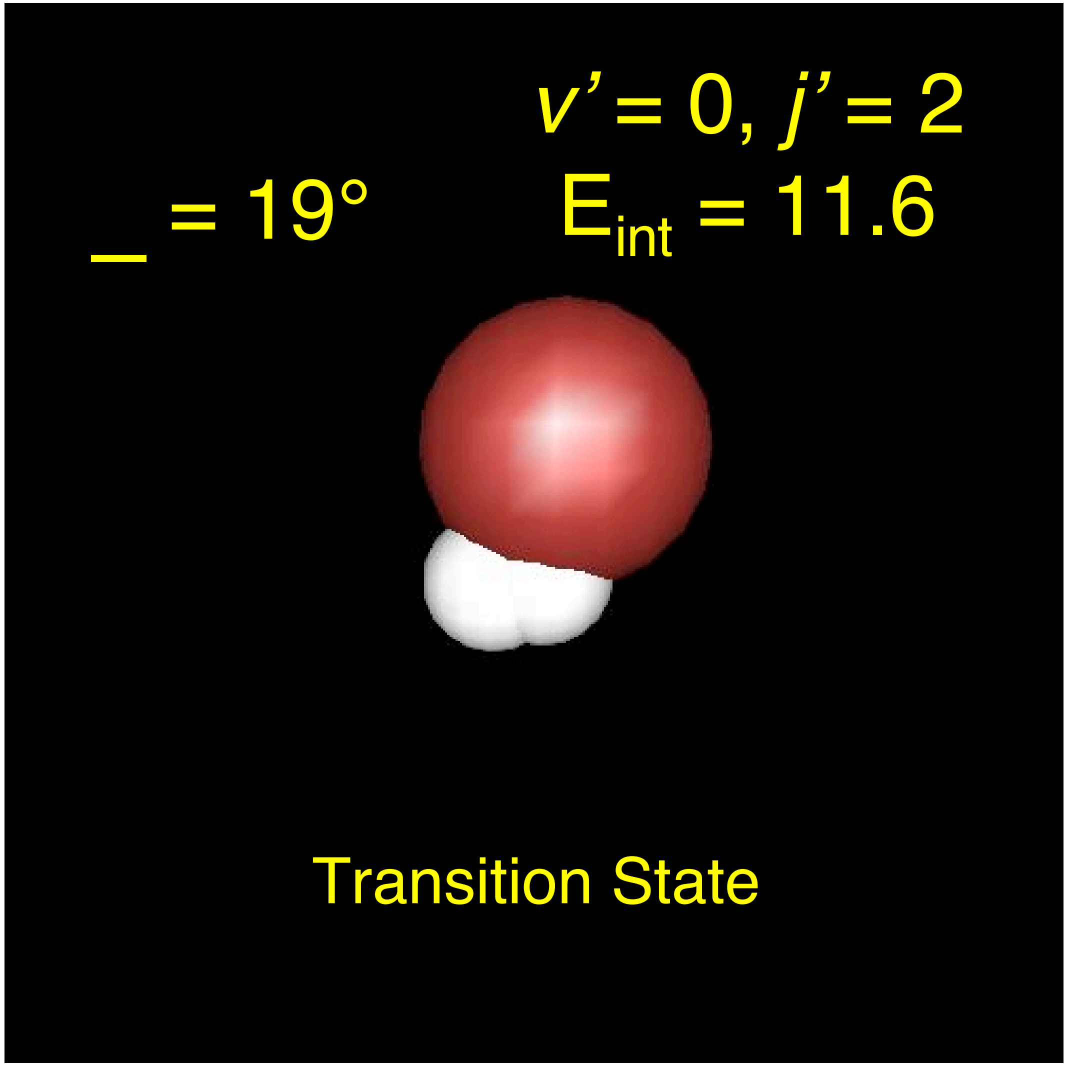
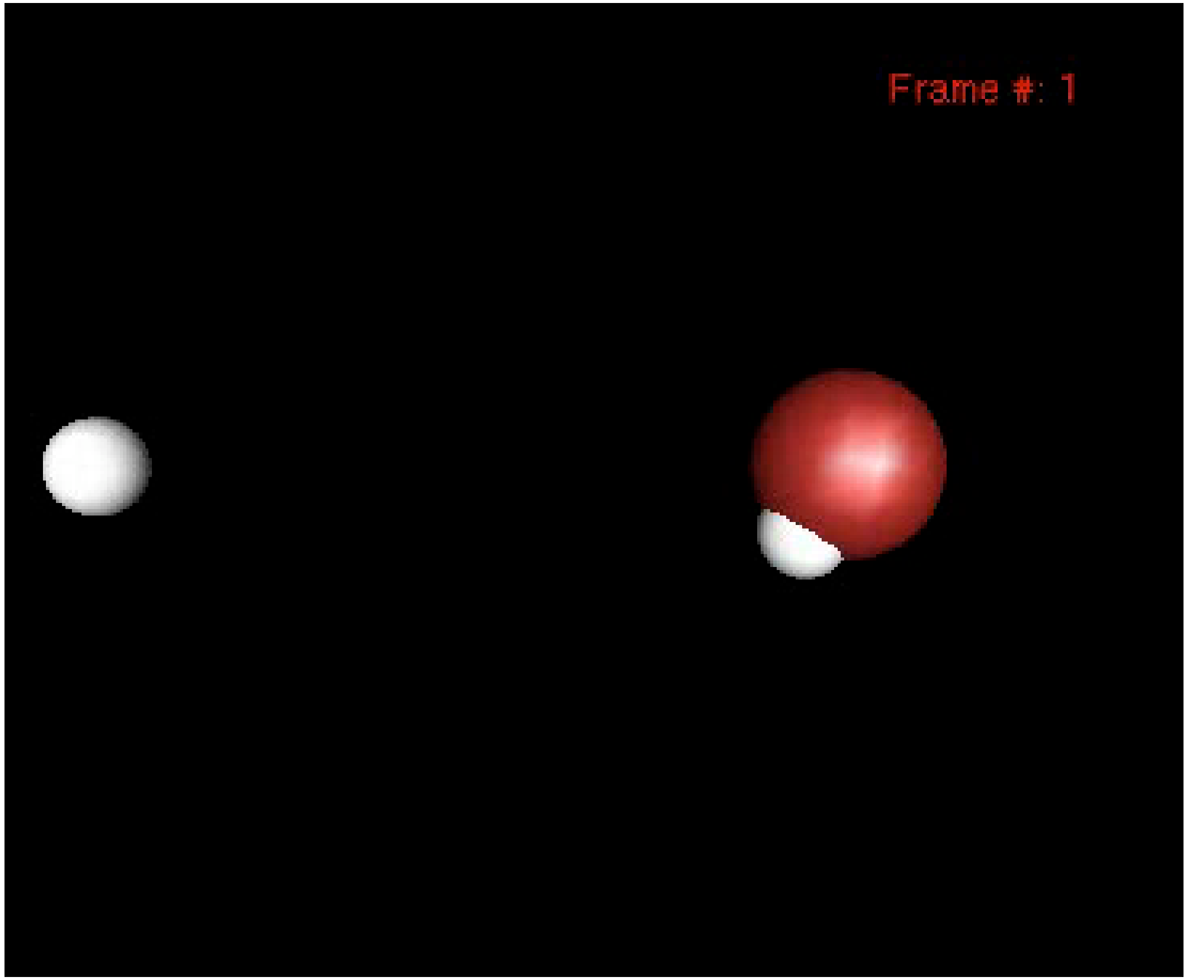
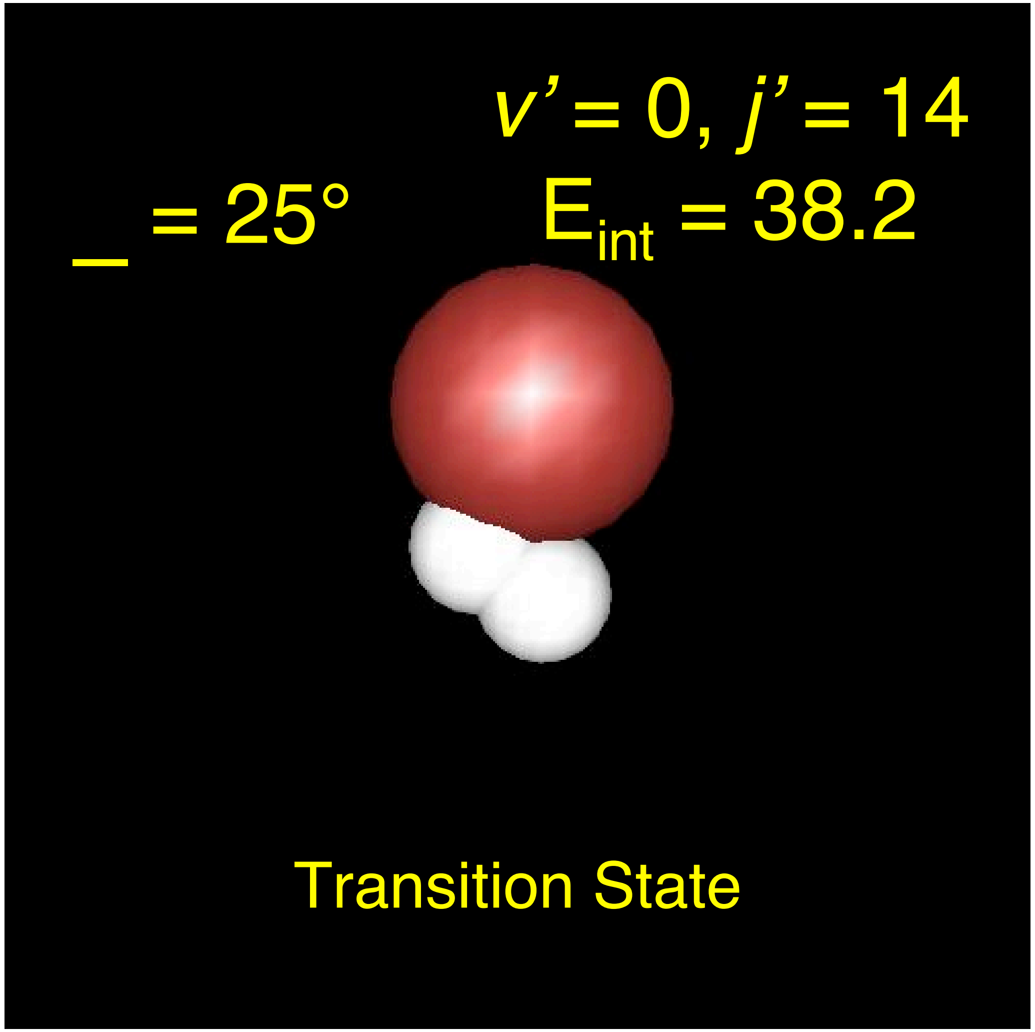


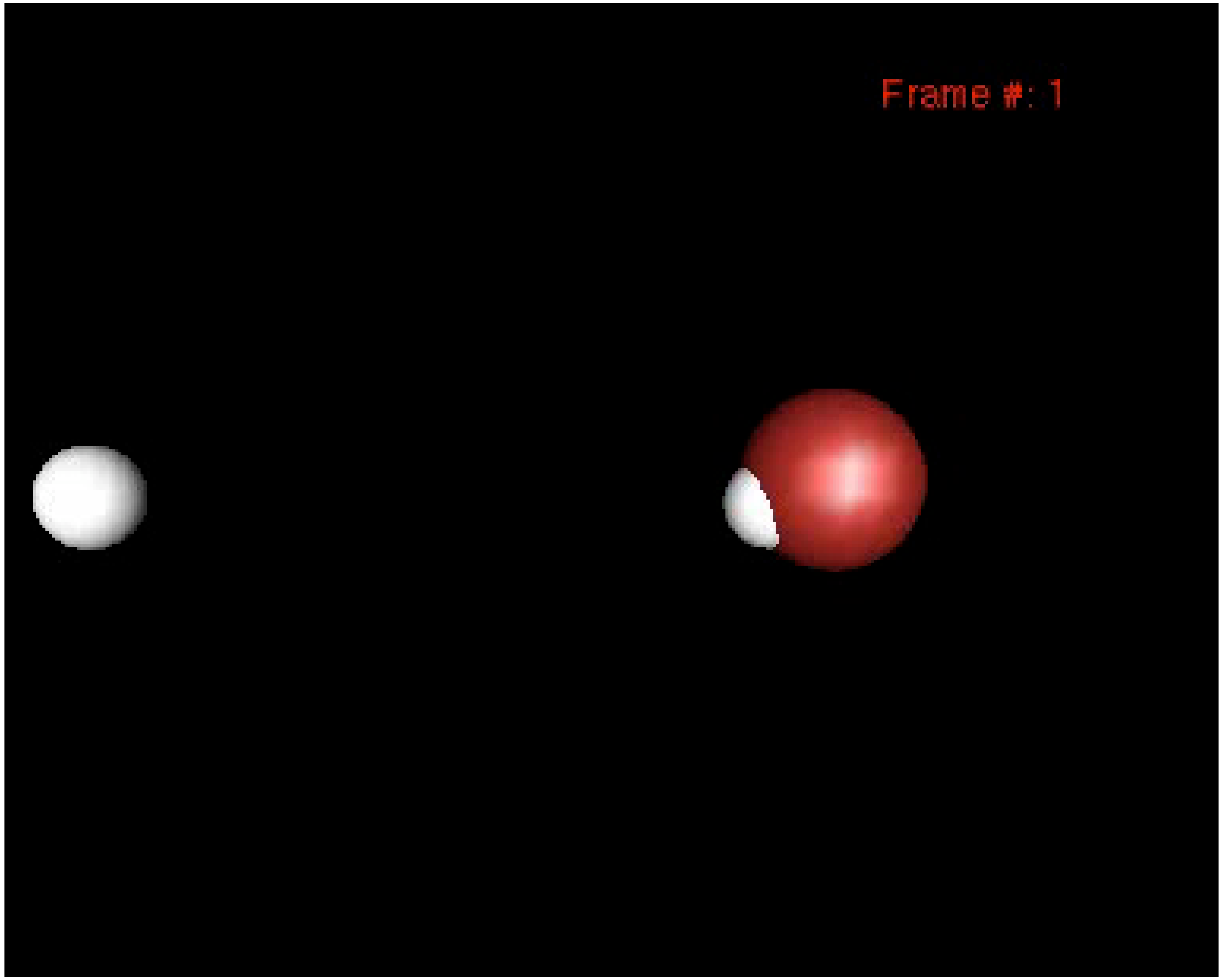
Direct Trajectory



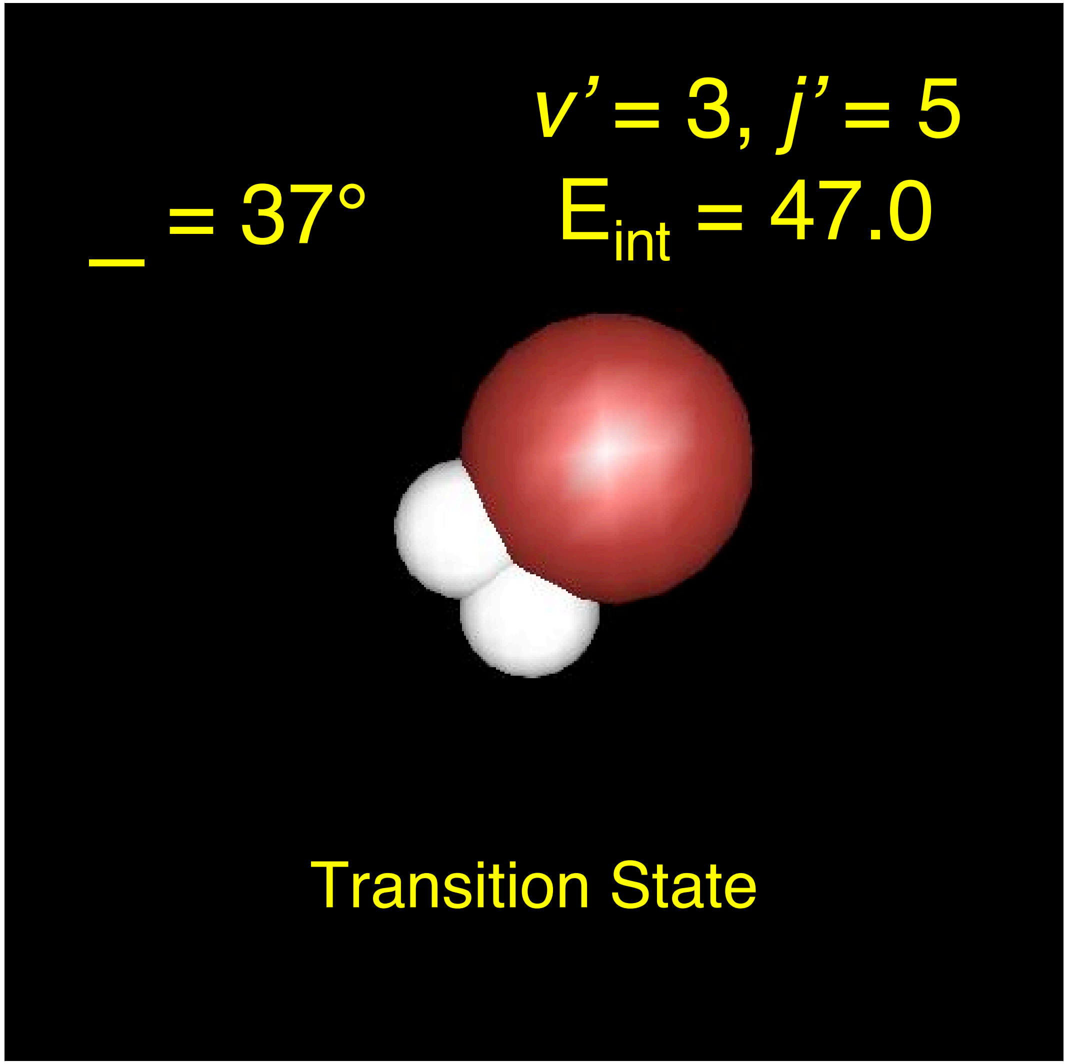
Direct Trajectory



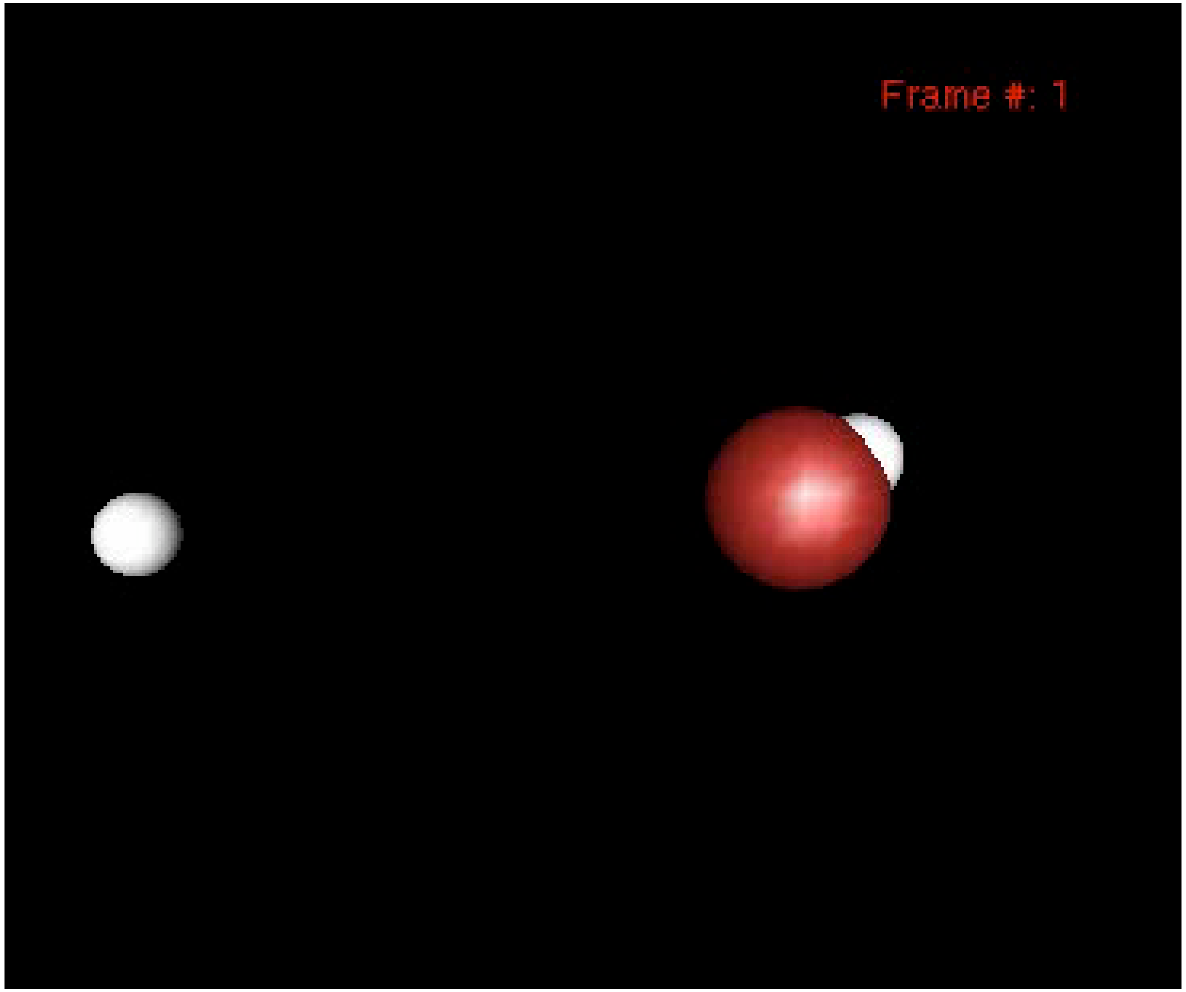
Direct Trajectory



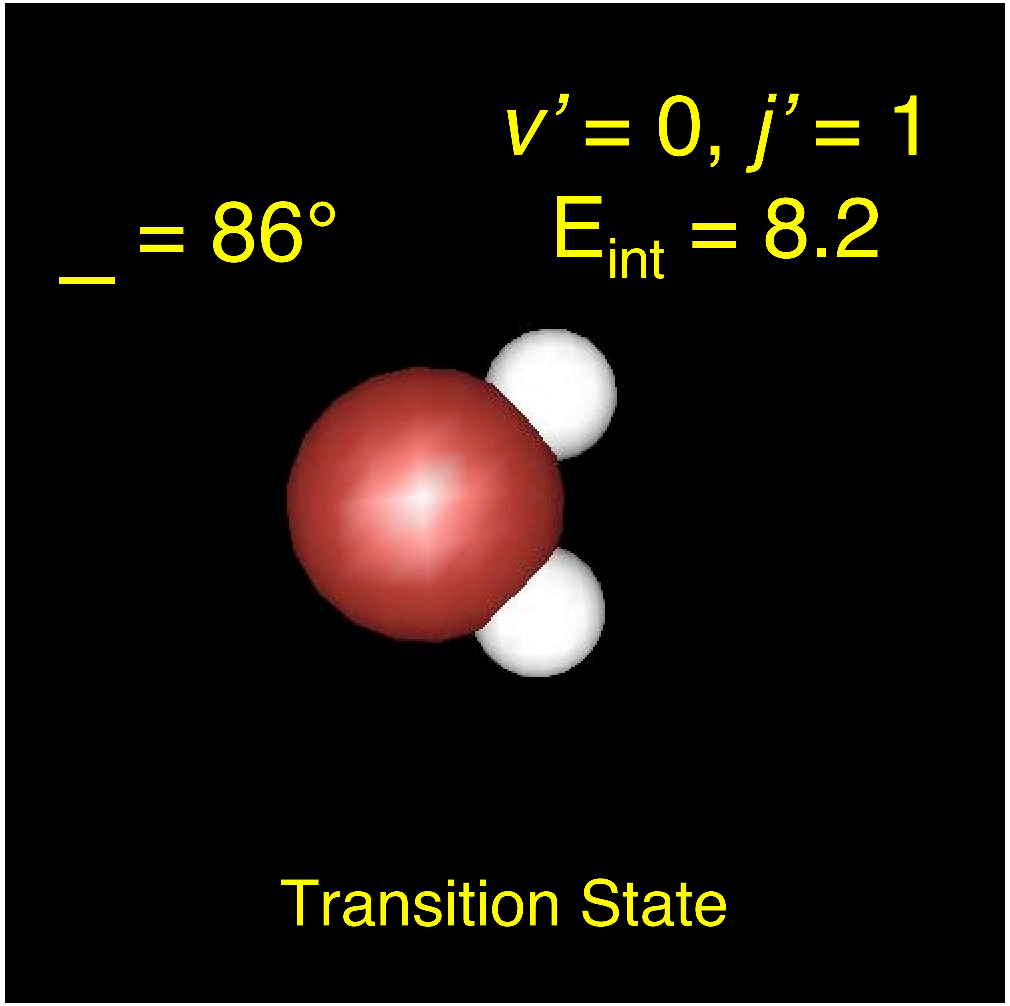
Direct Trajectory



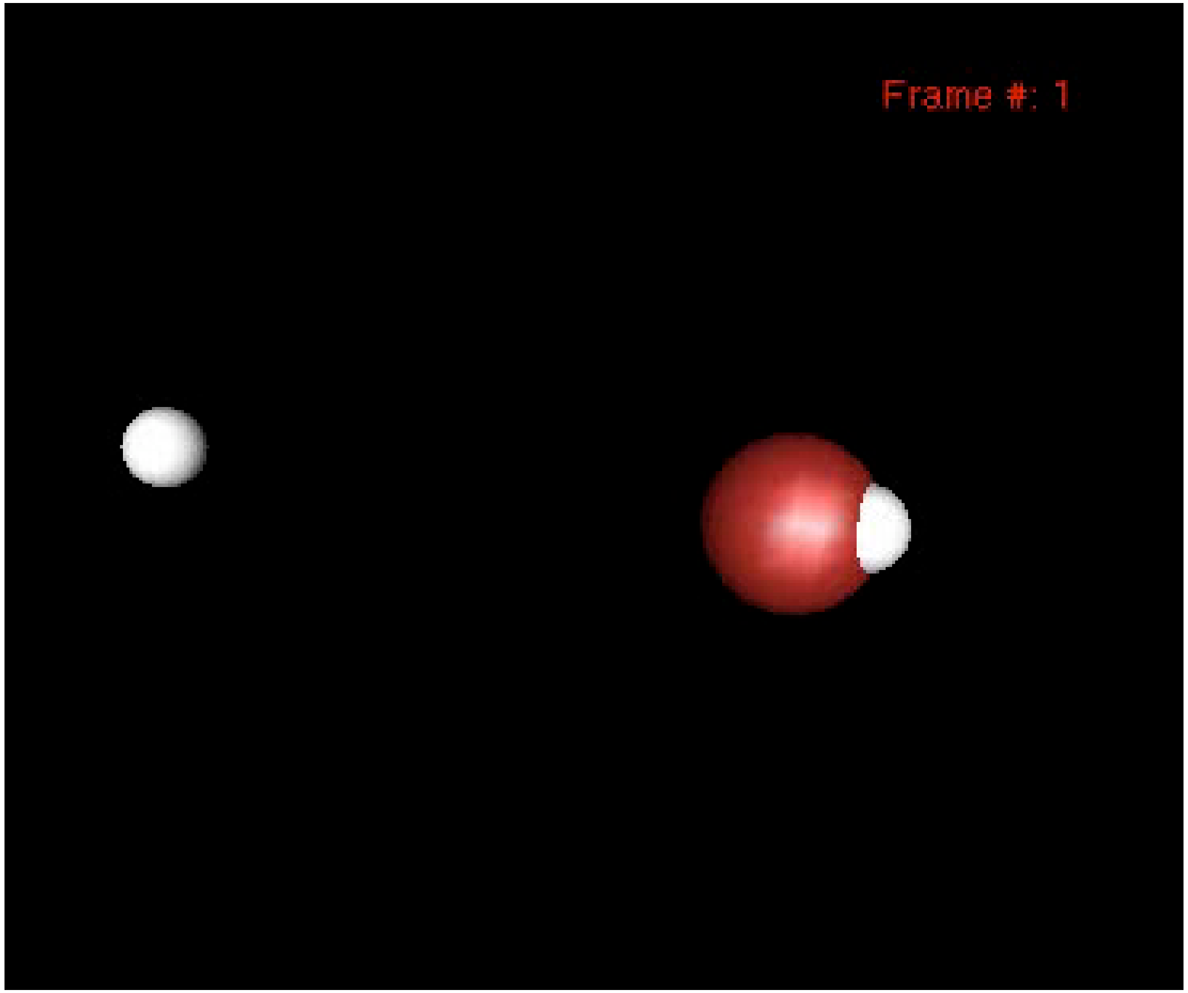
Medium-Lifetime Transition State



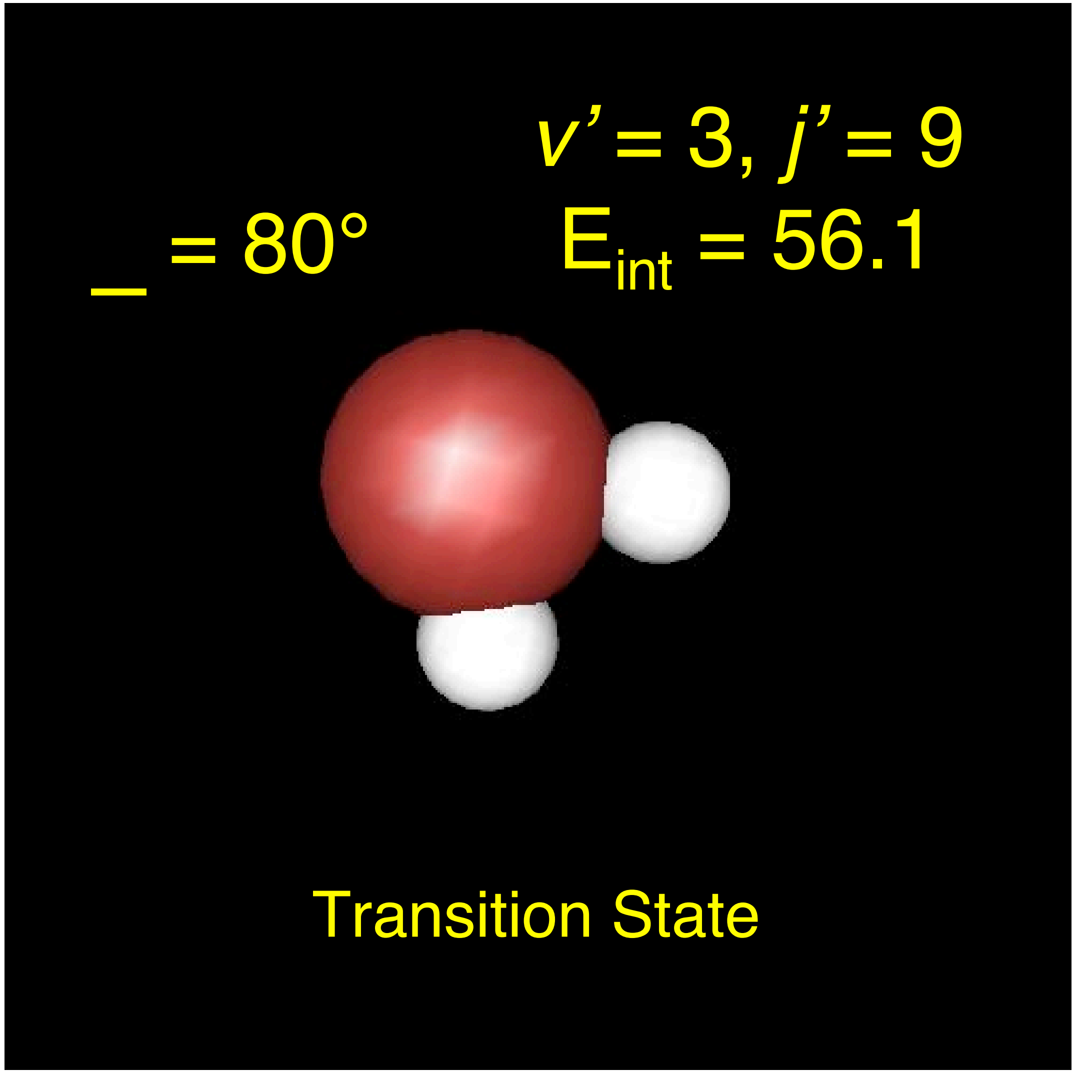
Medium-Lifetime Transition State



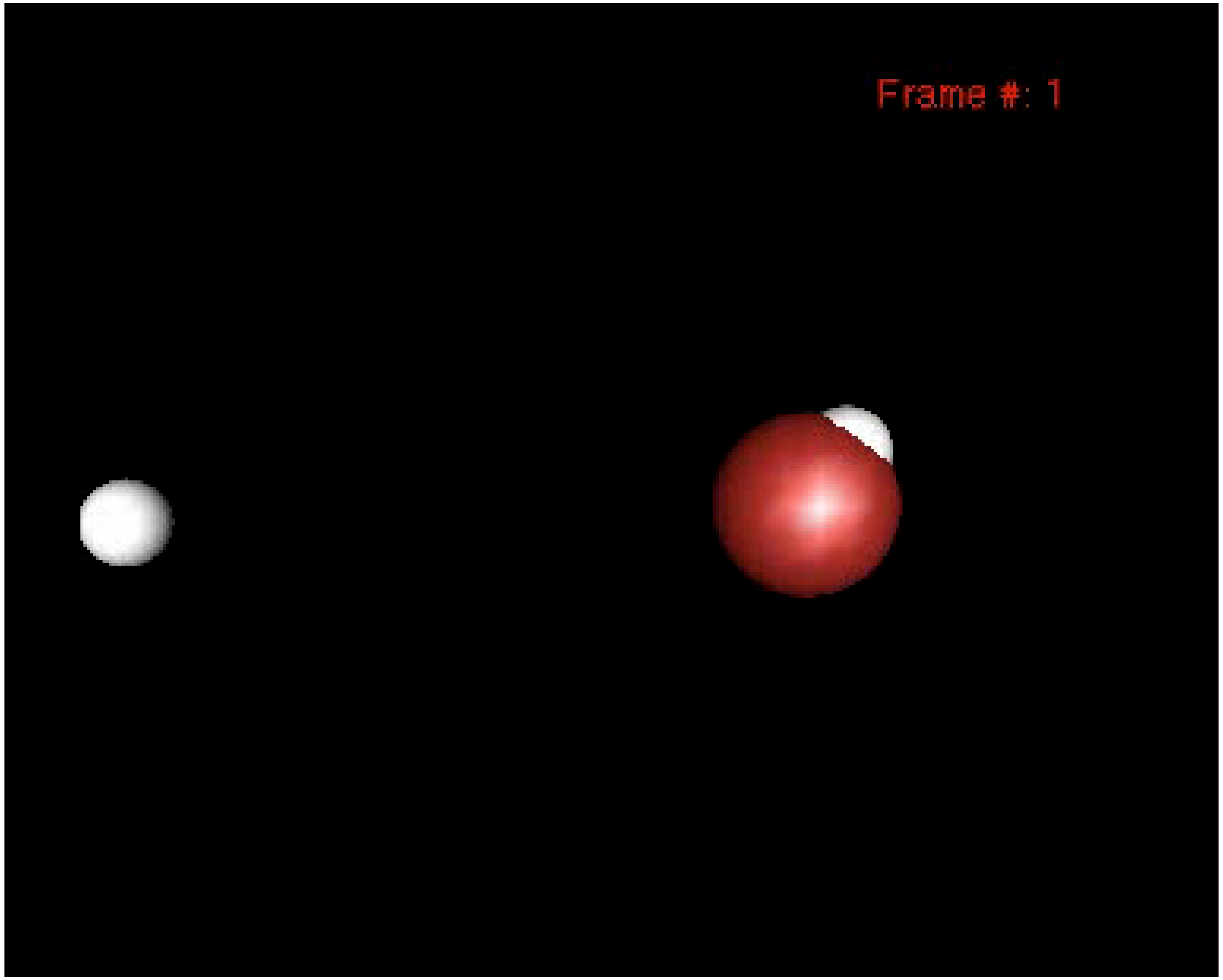
Medium-Lifetime Transition State



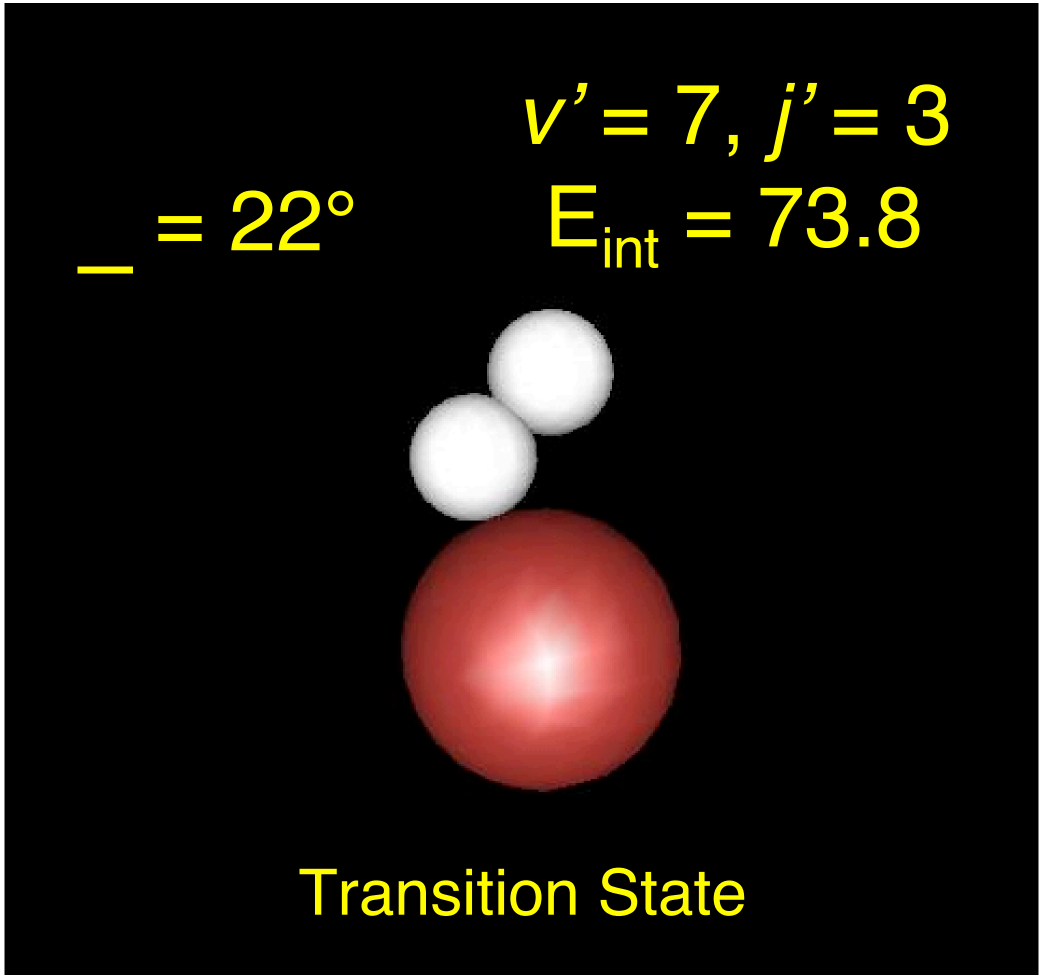
Medium-Lifetime Transition State



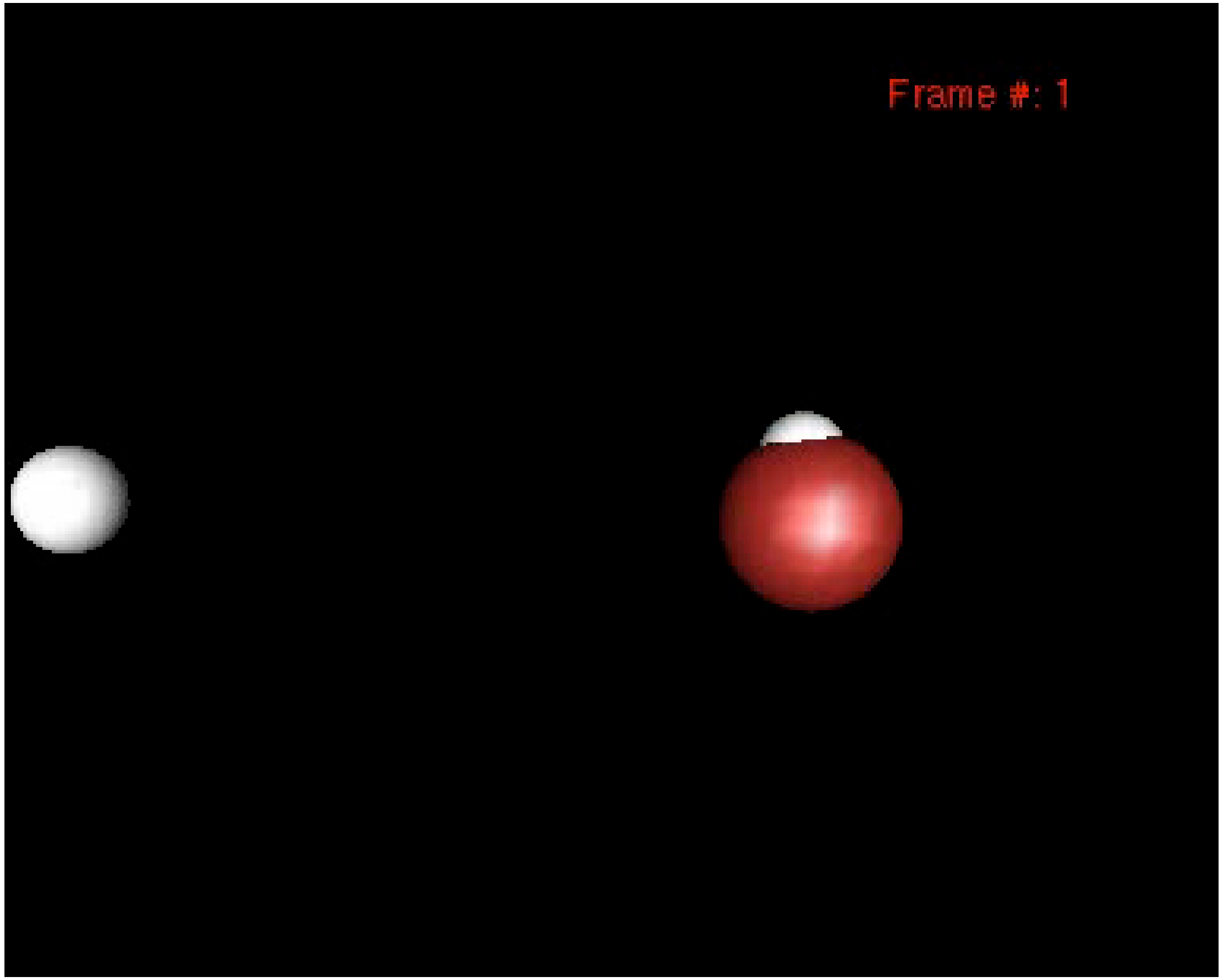
Long-Lifetime Transition State



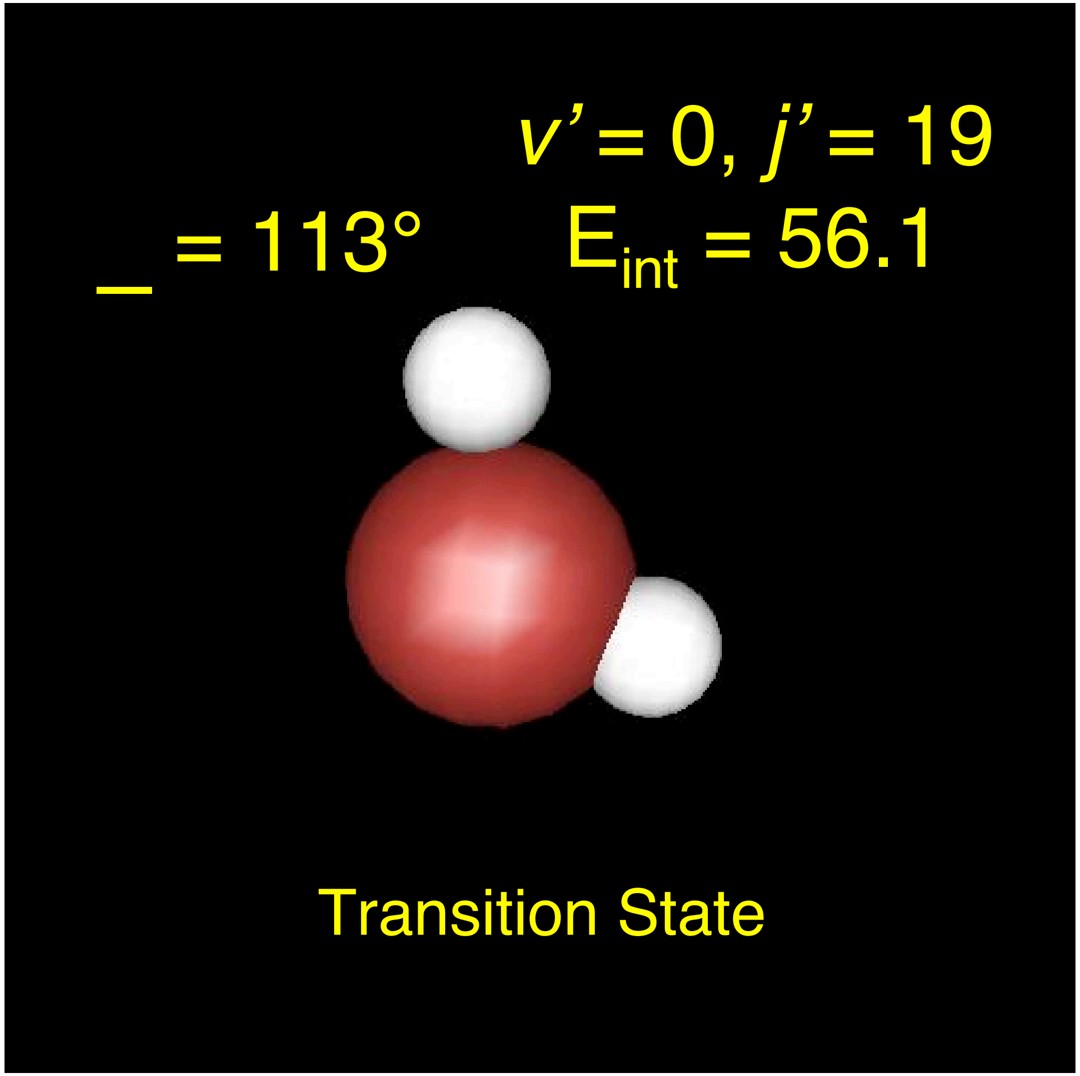
Long-Lifetime Transition State



Long-Lifetime Transition State

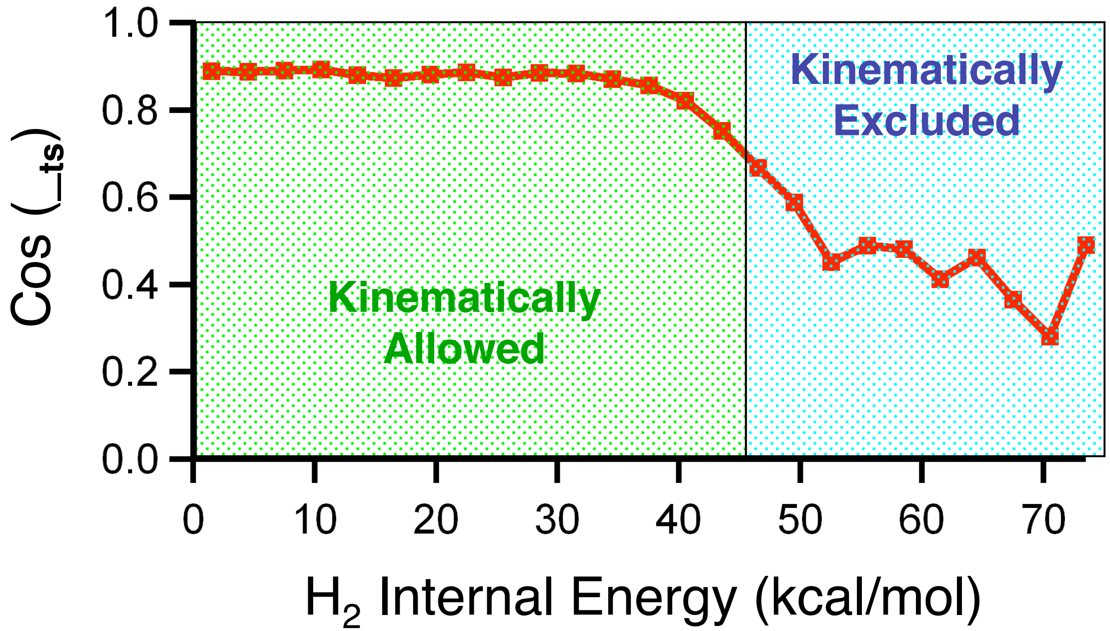


Long-Lifetime Transition State



What Did We Learn?

Using this principle, we have identified two simple pathways for the reaction H + HBr $H_2(v', j')$ + Br:



• Internally cold H_2 results from collinear transition states

• Internally hot H_2 results from bent transition states.

Overarching Conclusion

At sufficiently high energies some significant fraction of reactions do not proceed along or close to the minimum energy path.

Prediction

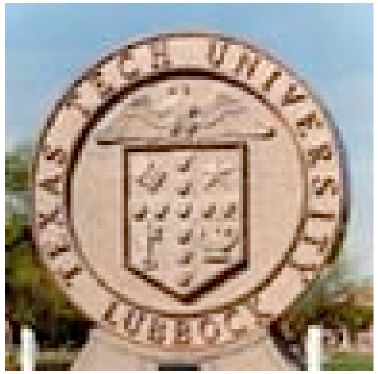
This behavior is general and more common than realized before.

Acknowledgments

Drew Pomerantz, Jon Camden,
Albert Chiou, Florian Ausfelder

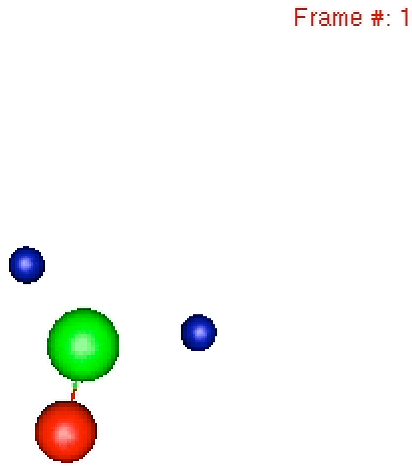
Navdeep Chawla

William Hase



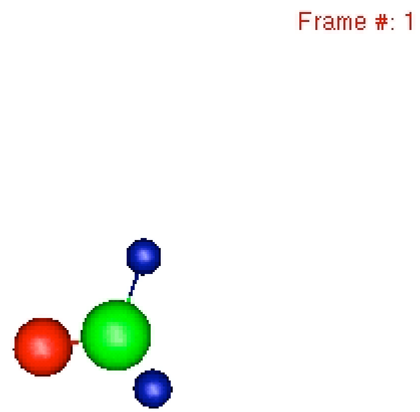
National Science Foundation

$H_2CO + h\nu \rightarrow H_2 + CO$: Production of Cold H_2



D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, Science **306**, 1158-1161 (2004).

$H_2CO + h\nu \rightarrow H_2 + CO$: Production of Hot H_2



D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, Science **306**, 1158-1161 (2004).

O + CH_3

Six possible sets of exothermic products:

CH_3 + O □	H + H_2CO	_*H*=-70 kcal/mol
	H_2 + HCO	_*H*=-84
	H + HCOH	_*H*=-13
	H_2 + COH	*H*=-44
	H + H_2 + CO	_*H*=-70
	CH + H_2O	_*H*=-10

Seakins and Leone (1992) reported the detection of CO (v) from this reaction using FTIR emission spectroscopy. They estimated the CO branching fraction to be 0.40 ± 0.10.

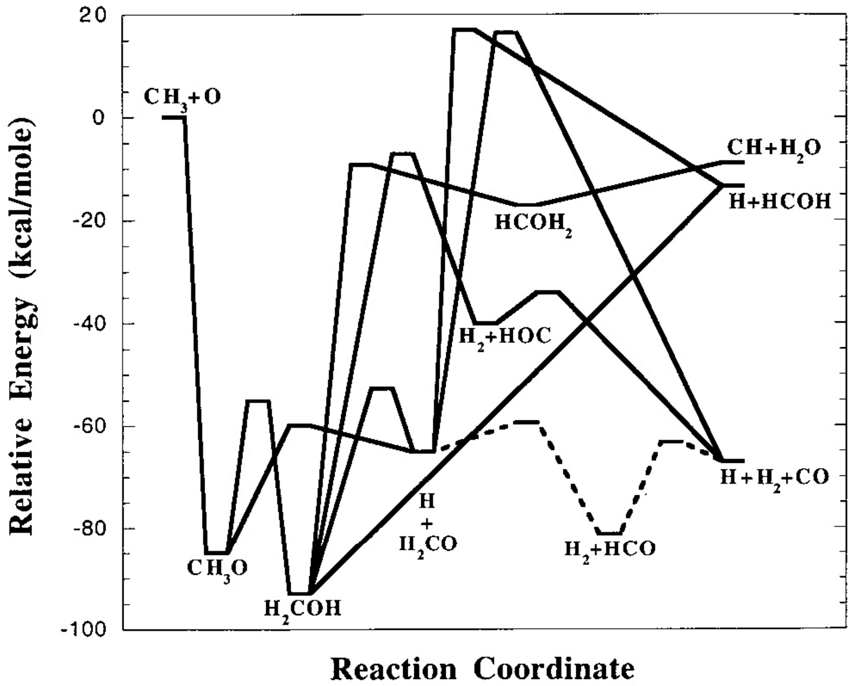
O + CH_3

Both experimental and theoretical studies confirm the existence of a CO producing channel in the reaction of CH_3 with O atoms [T. P. Marcy, R. R. Diaz, D. Heard, S. R. Leone, L. B. Harding, and S. J. Klippenstein, *J. Phys. Chem. A* **2001,** *105,* 8361-8369].

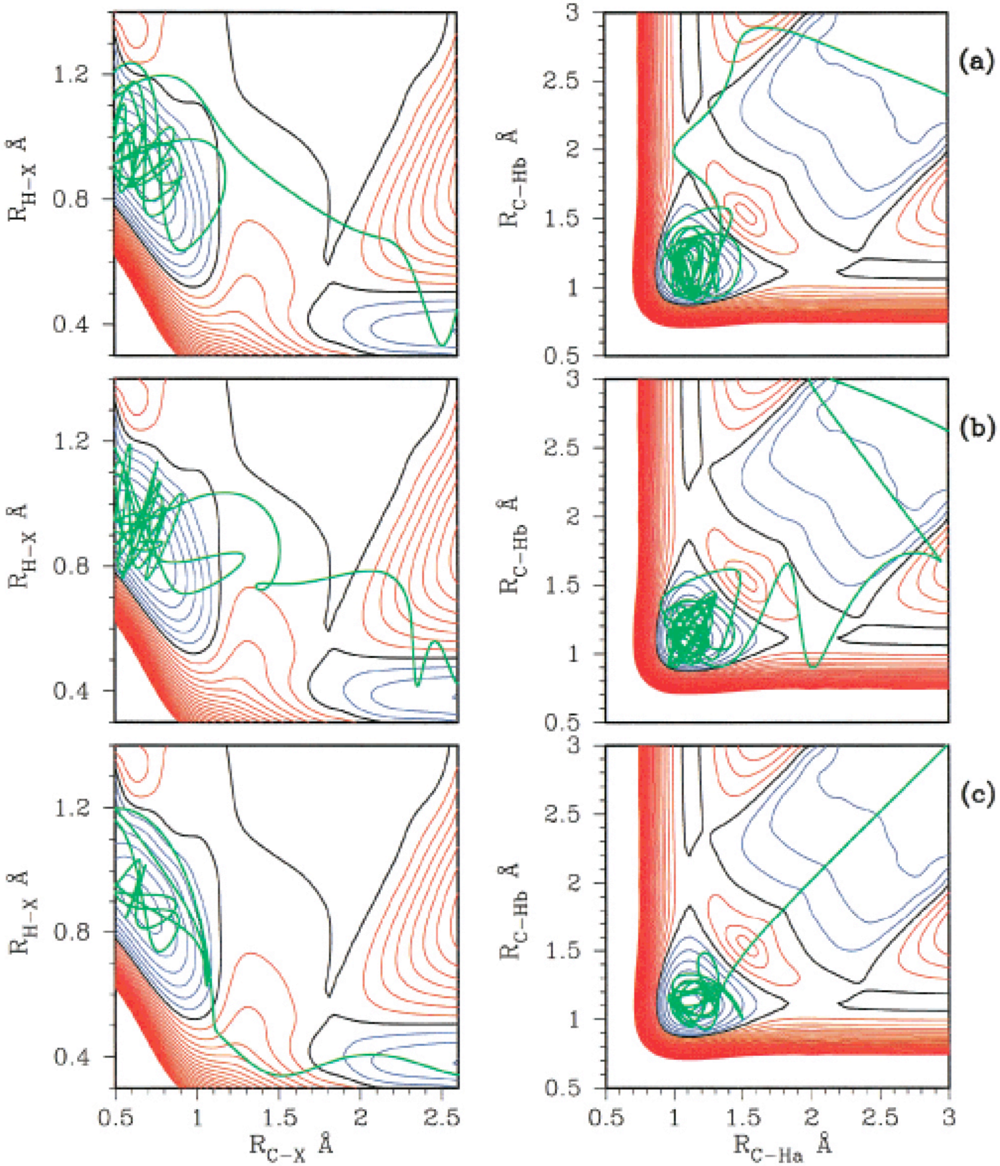
The mechanism involves the elimination of H_2 from an energy-rich CH_3O radical forming HCO, followed by the decomposition of HCO to form the observed CO (v) product. **The most unusual feature of this mechanism is that there appears to be no saddle point for the direct elimination of H_2 from CH_3O.**

O + CH_3

The methoxy radical is formed with 90 kcal/mol of excess energy, or 60 kcal/mol above its lowest barrier for decomposition (CH bond cleavage).



Schematic of the stationary point energies on the CH_3O potential surface. The results shown are from CCSD(T)/aug-cc-pvtz// CCSD(T)/cc-pvdz calculations (including zero point).



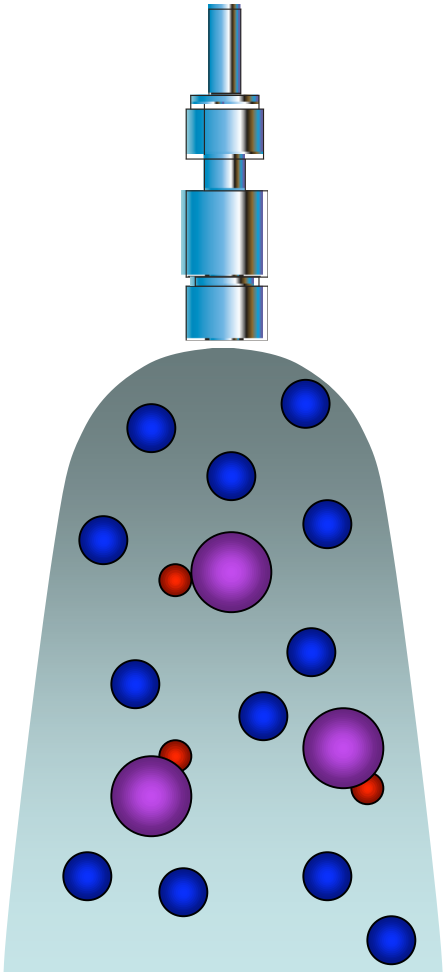
At these high energies, trajectories are found to stray far from the minimum-energy path, resulting in the production of unexpected products.

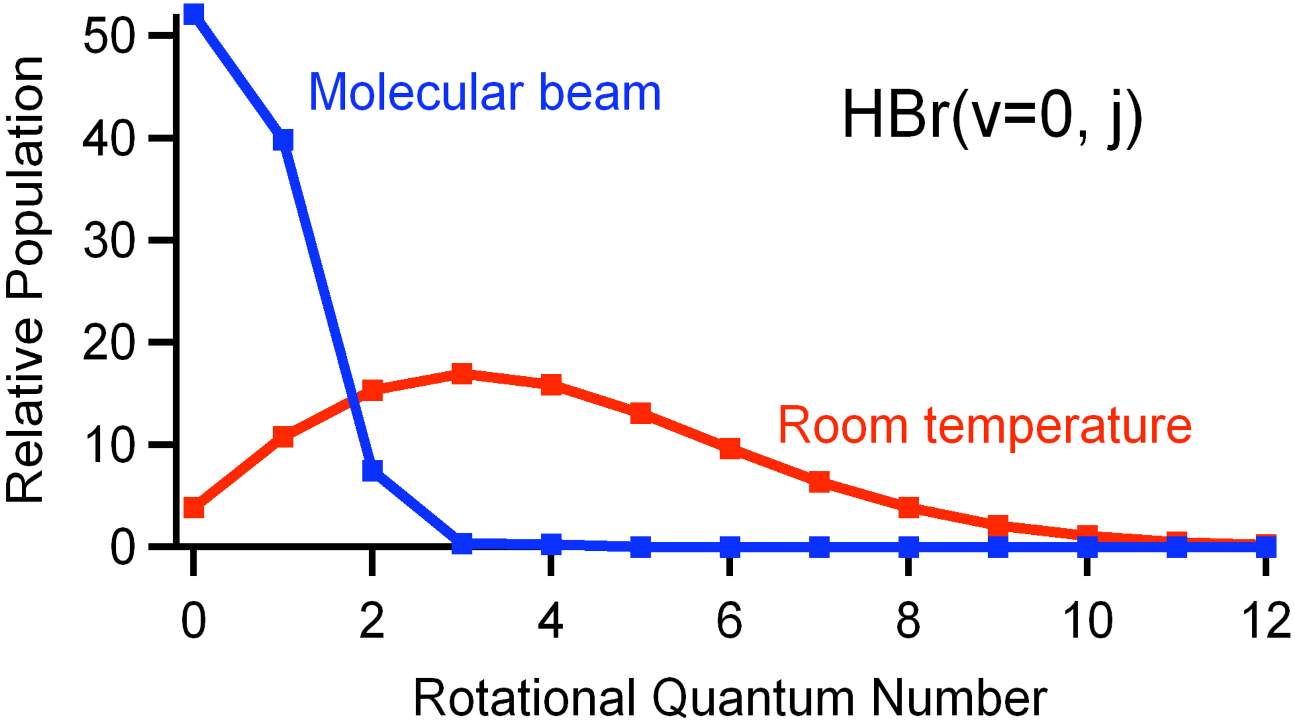
Two-dimensional projections of each of the three selected H_2-producing trajectories. The black contours correspond to the saddle point for the reaction $H + H_2CO$ □ $H_2 + HCO$. Blue contours are lower in energy and red contours are higher in energy.

Kinematic Limit Model

System	E_{coll} kcal/mol	v'	j'_{max} expt	j'_{max} model	j'_{max} energy
H + HCl	37	0	11	11	15
H + HCl	37	1	7	7	13
H + D_2	23	0	10	12	14
H + D_2	23	1	4	7	10
H + D_2O	60	0	16	17	21
H + D_2O	60	1	15	13	18
H + D_2O	60	2	11	9	14
Cl + CH_4	5	0	3	3	9

Jet Cooling

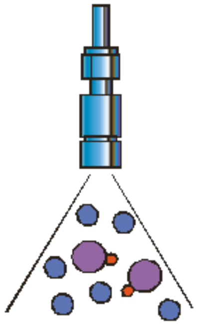




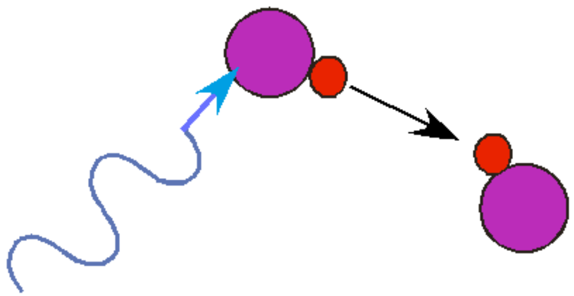
Molecular beam
HBr(v=0, j)
Room temperature
Relative Population
Rotational Quantum Number
0
10
20
30
40
50
0
2
4
6
8
10
12

Experimental Protocol

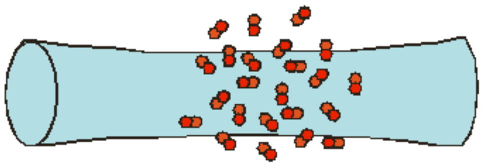
1) A gas jet expansion produces translationally and internally cold precursors.



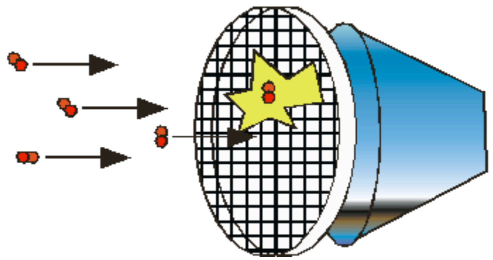
2) A tunable laser photolyzes HBr to produce fast H atoms with a well defined translational energy.



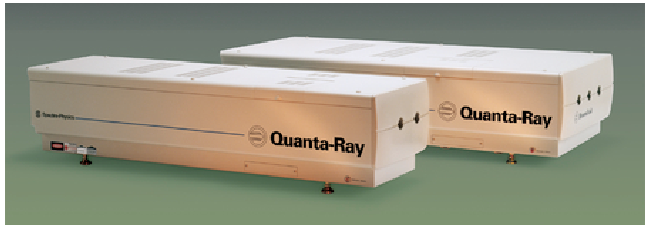
3) About 20 ns later, a focused, polarized laser ionizes $H_2(v', j')$ via (2+1) REMPI.



4) H_2^+ is propelled down the TOF by electric fields. A microchannel plate detector is used to count the ions.



Generating Laser Light



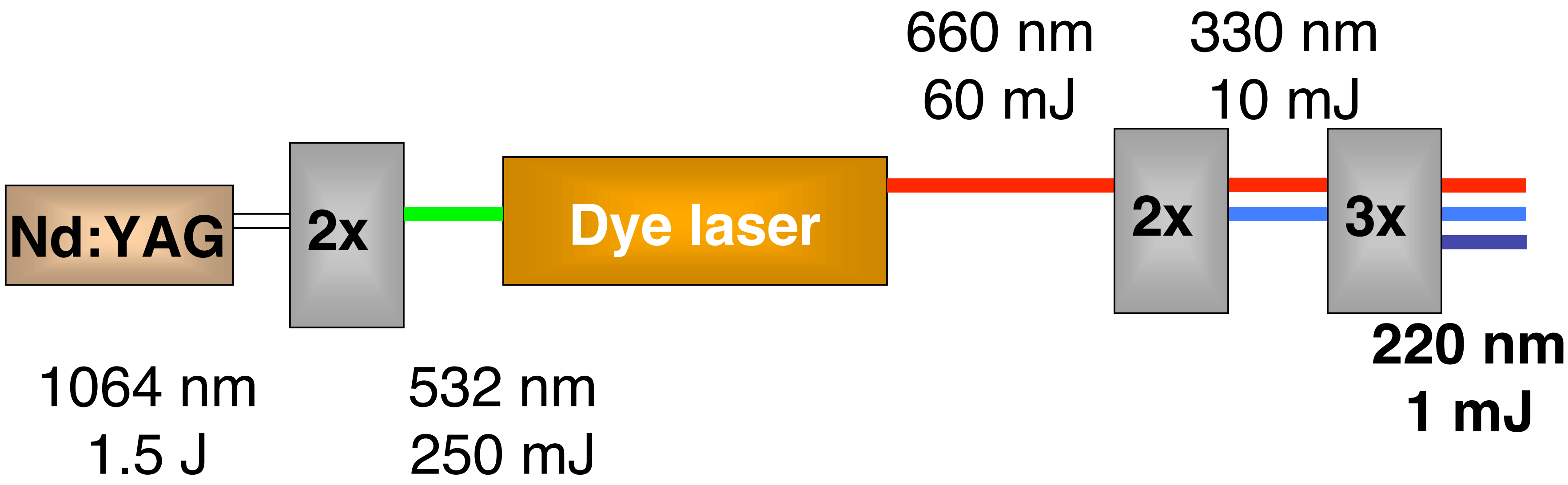
Nd:YAG laser: 1064 nm, 8 ns pulse, 0.001 - 1 cm^{-1} bandwidth, 1 J/pulse, 10 Hz rep rate.

Dye laser: pumped by Nd:YAG laser, tunable 450 – 800 nm, 0.1 cm^{-1} bandwidth, same temporal width as Nd:YAG, 25% efficiency.

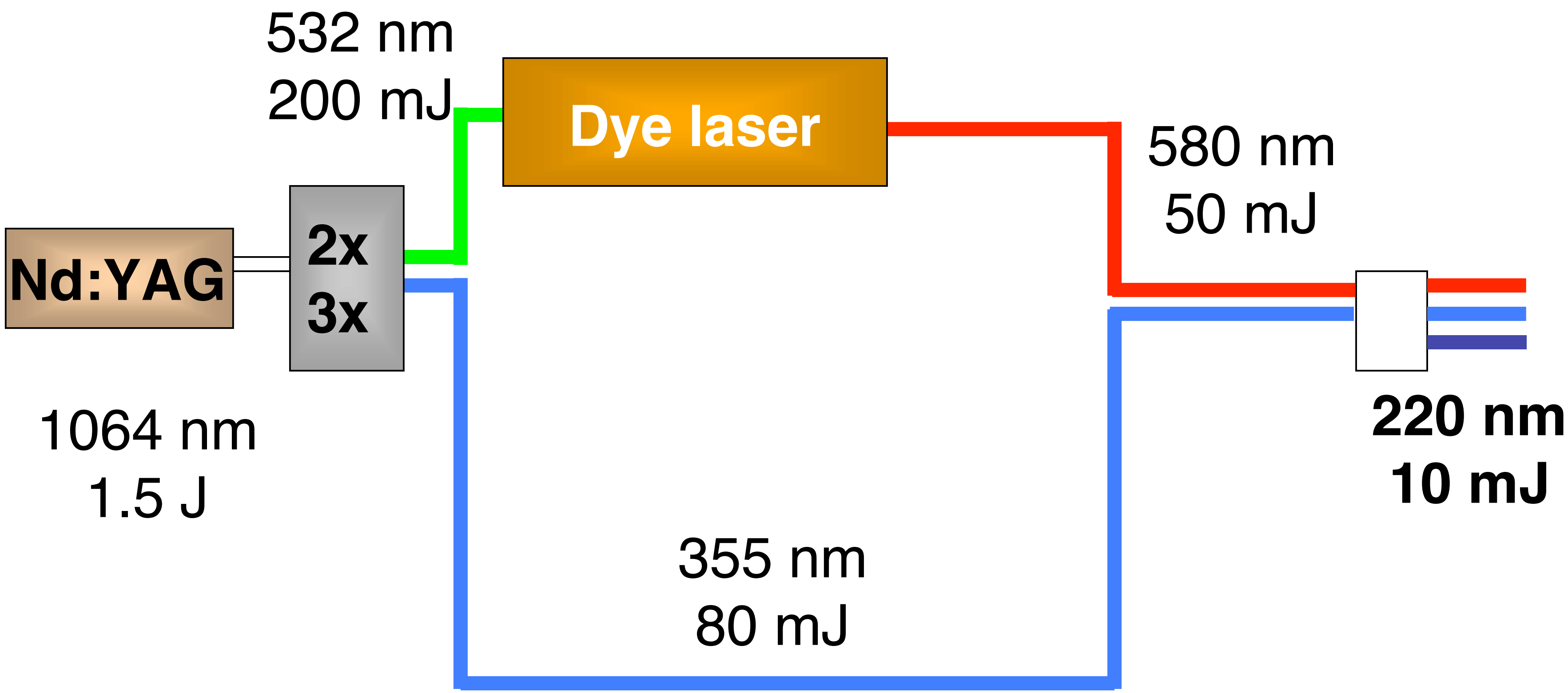
Non-linear optical crystals:

$\text{—}_3 = \text{—}_1 + \text{—}_2$, 10 – 50% efficiency.

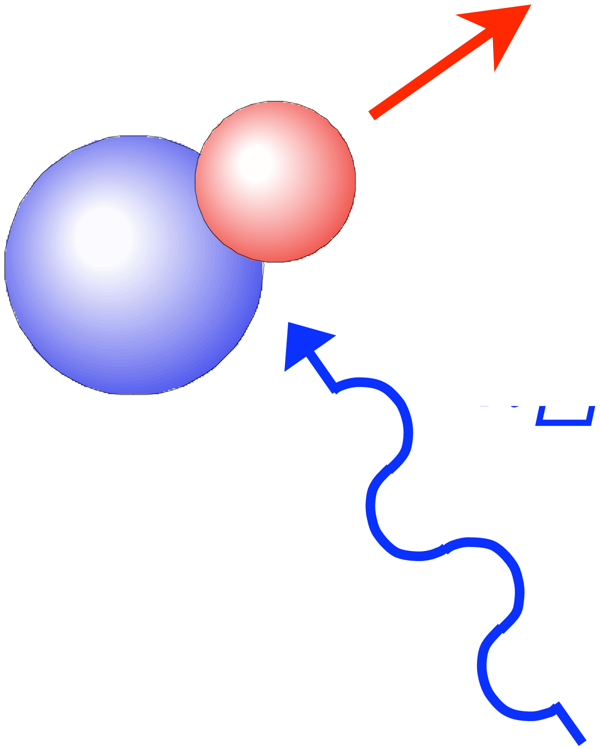
Generating Laser Light



Generating Laser Light



HBr Photolysis



Generate collisions energies
~ 50 kcal/mol

Experimental Protocol

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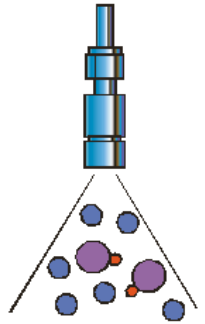

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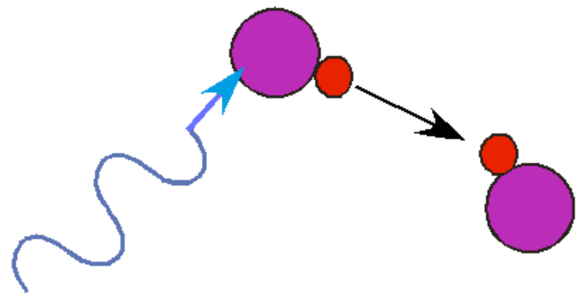

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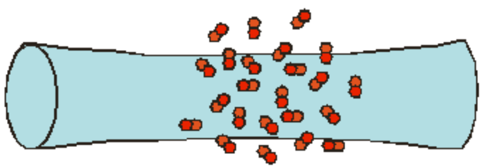

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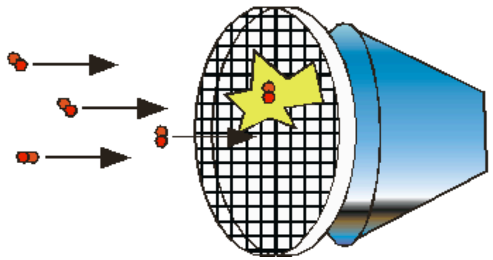
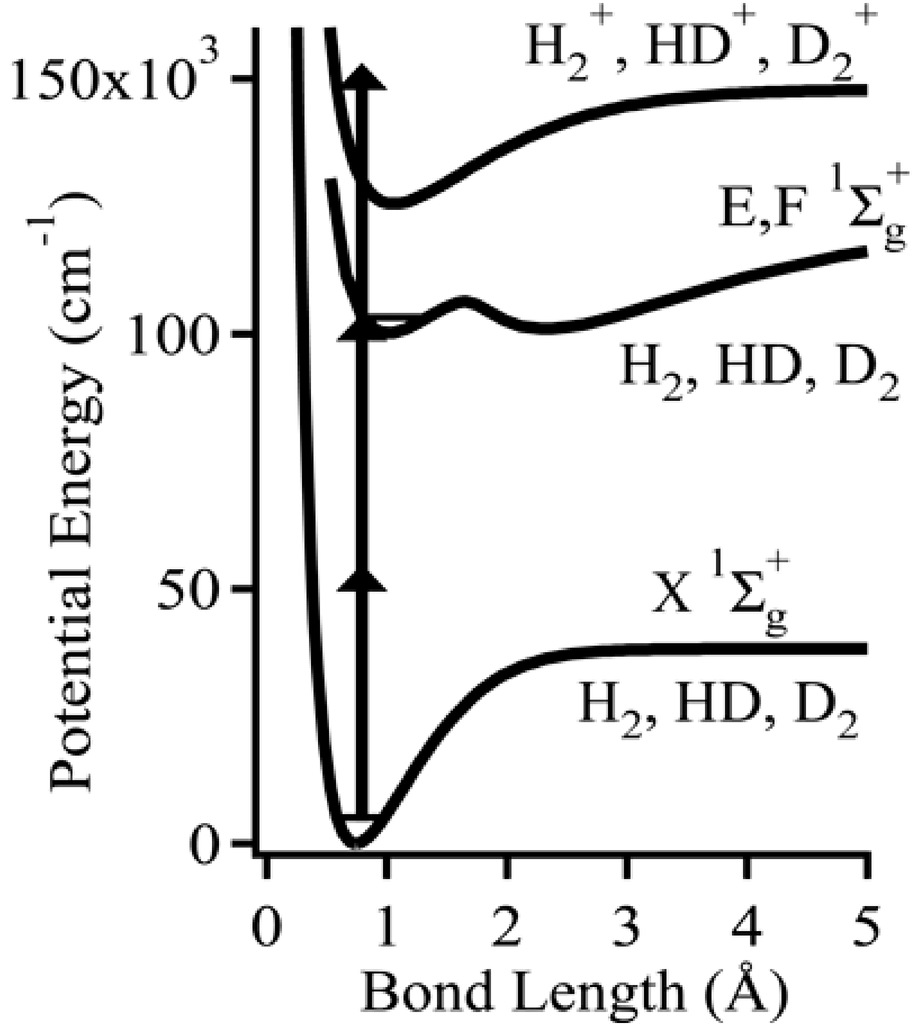


(2+1) Resonance-Enhanced Multiphoton Ionization

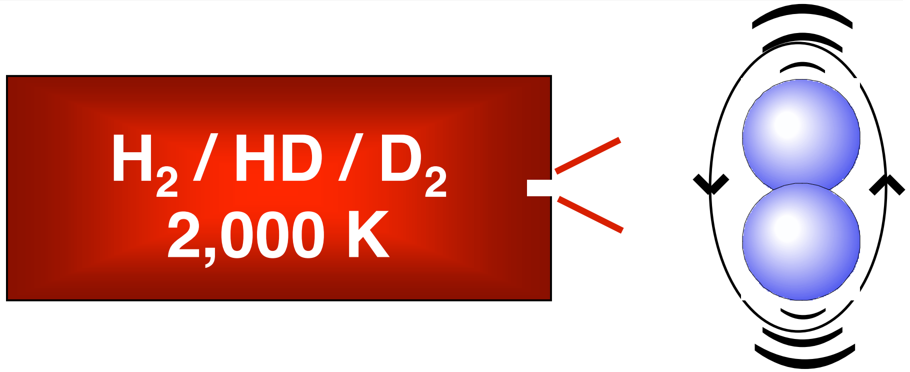


- Two-photon transition to a bound state.
- One-photon transition to the continuum.
- Transition line strengths may depend on quantum numbers.

These transitions require light in the 200-230 nm range: non-linear optical mixing

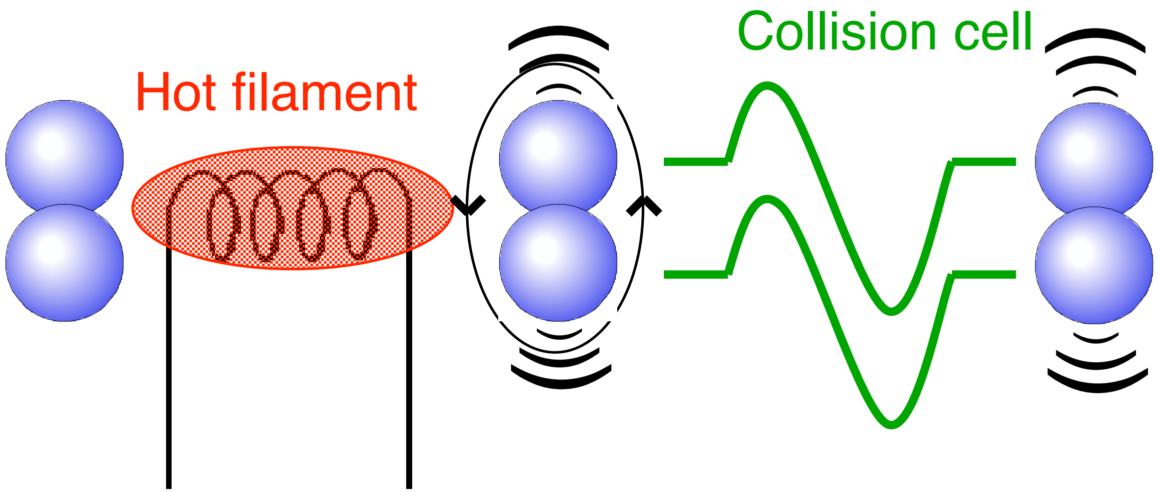
Measuring Line Strengths

- Source of excited $H_2/HD/D_2$
  1) Populate many states
  2) Known relative concentrations of each state



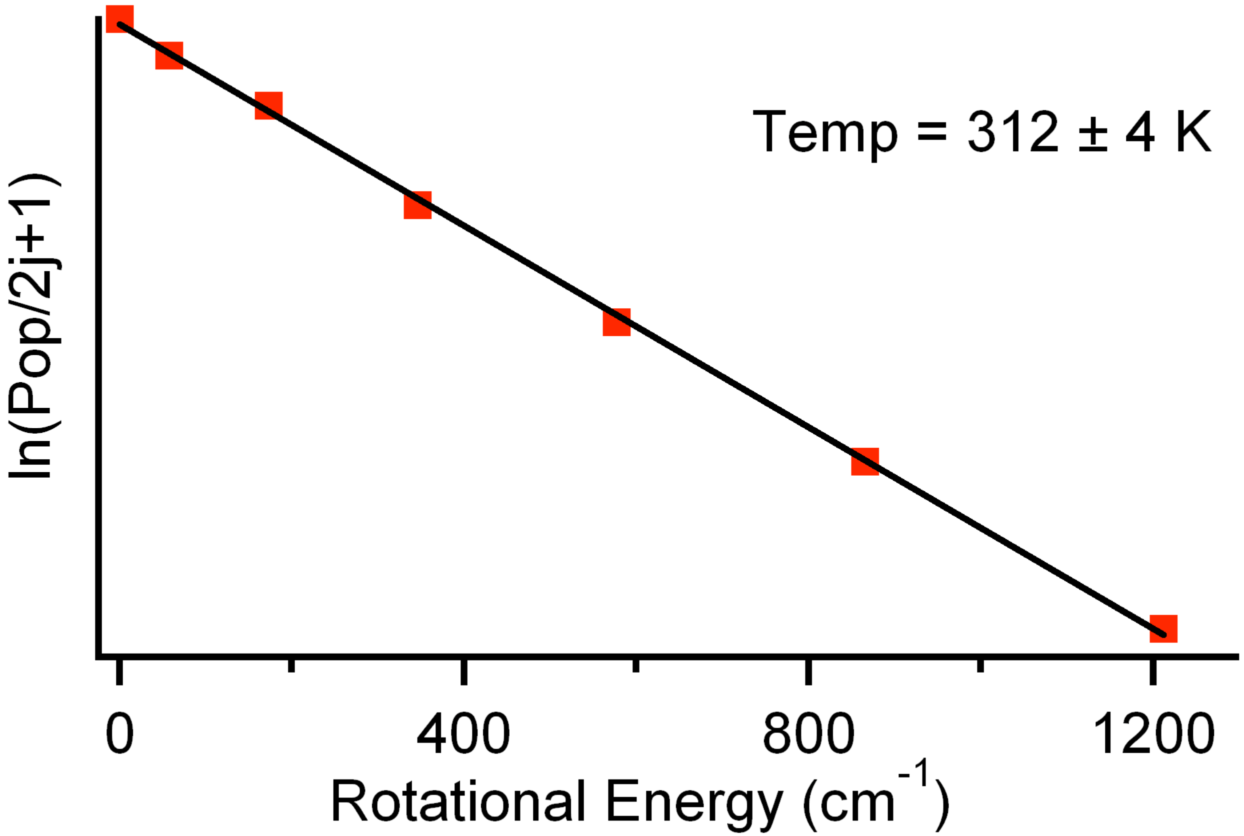
Rinnen et al., Israel Journal of Chemistry **29**, 369 (1989).

- Measure the relative concentrations in each quantum state.
- Any differences between known and measured concentrations result from differences in line strengths.



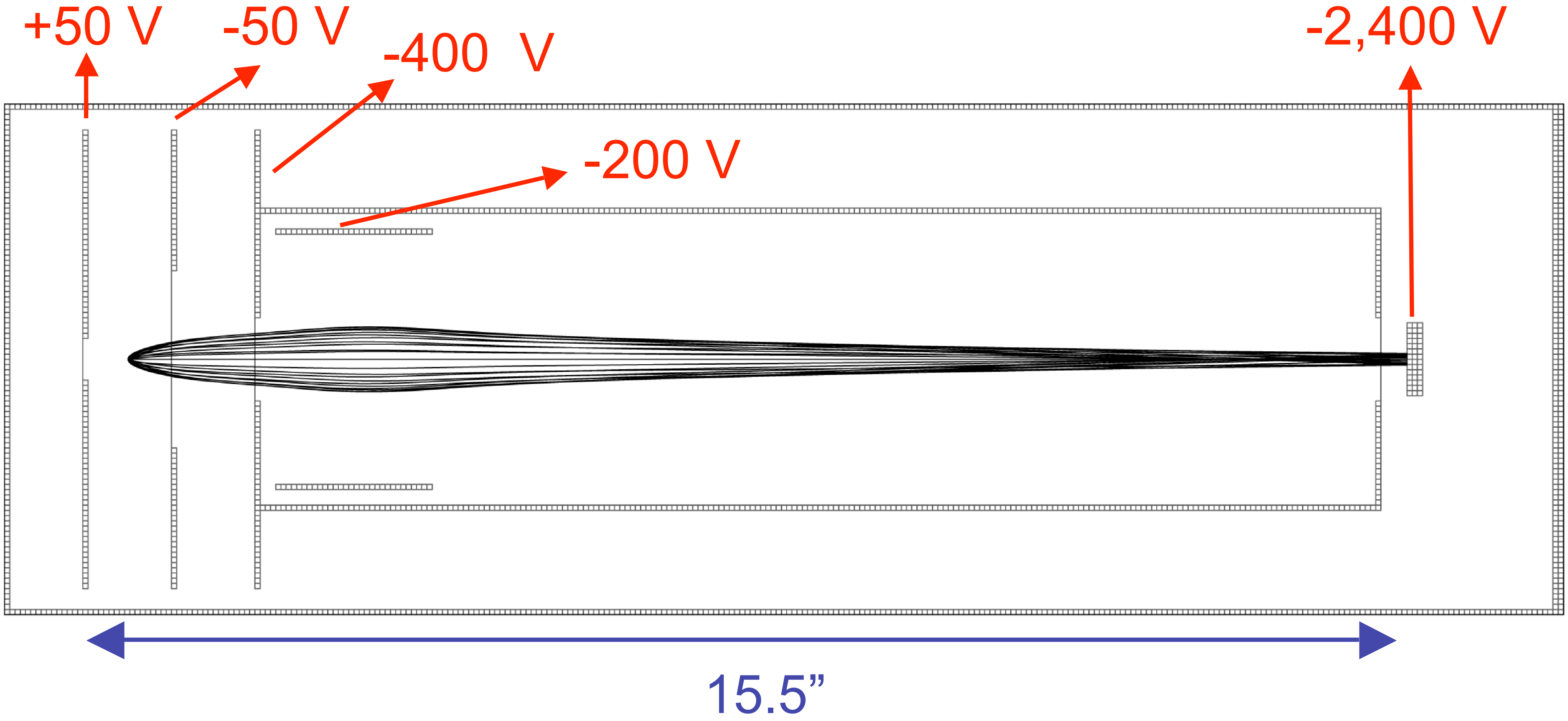
Pomerantz et al., Canadian Journal of Chemistry **82**, 723 (2004).

(2+1) REMPI Line Strengths



- Line strengths depend strongly on *v*, weakly on *j*.
- In agreement with calculations and earlier experiments
- In all, 142 quantum states calibrated.

Time-of-Flight Mass Spectrometry



Ortho/*Para* H_2

Pauli Principle: When the labels on two identical particles are exchanged, the wave function must change signs (fermions) or retain its sign (bosons).

Rotating a homonuclear diatomic molecule interchanges two identical particles, so symmetry must be considered.

J' = even: symmetric

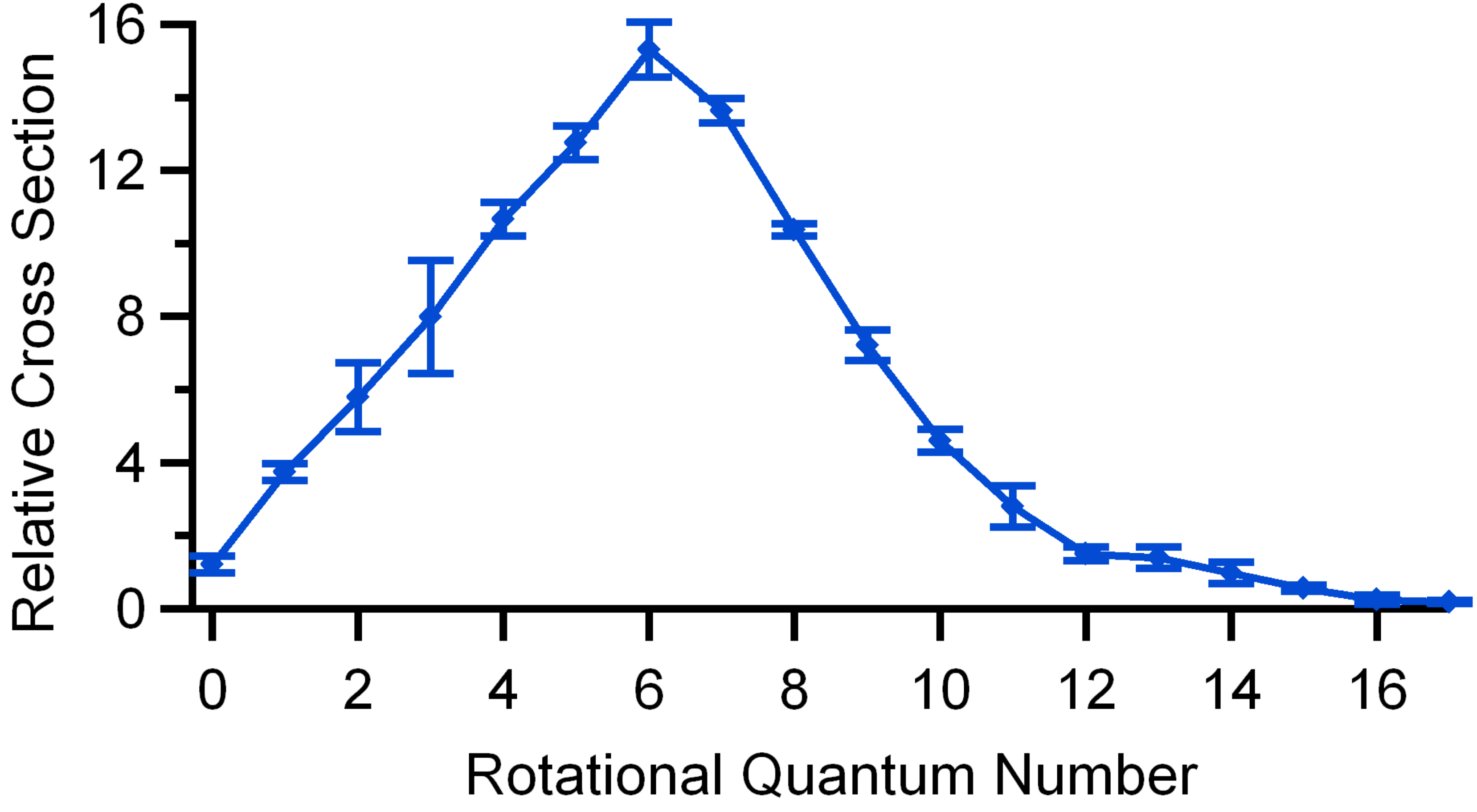
J' = odd: anti-symmetric

Symmetric state: triply degenerate

Anti-symmetric state: singly degenerate

Experimental Results
H + HBr $H_2(v'=2, j') + Br$

Collision Energy = 53.0 kcal/mol



Surprisal Analysis

R. D. Levine and R. B. Bernstein, Accounts of Chemical Research **7**, 393 (1974).

If conservation of energy is the only constraint, the partial cross sections for forming each state are equal to the degeneracy of that state.

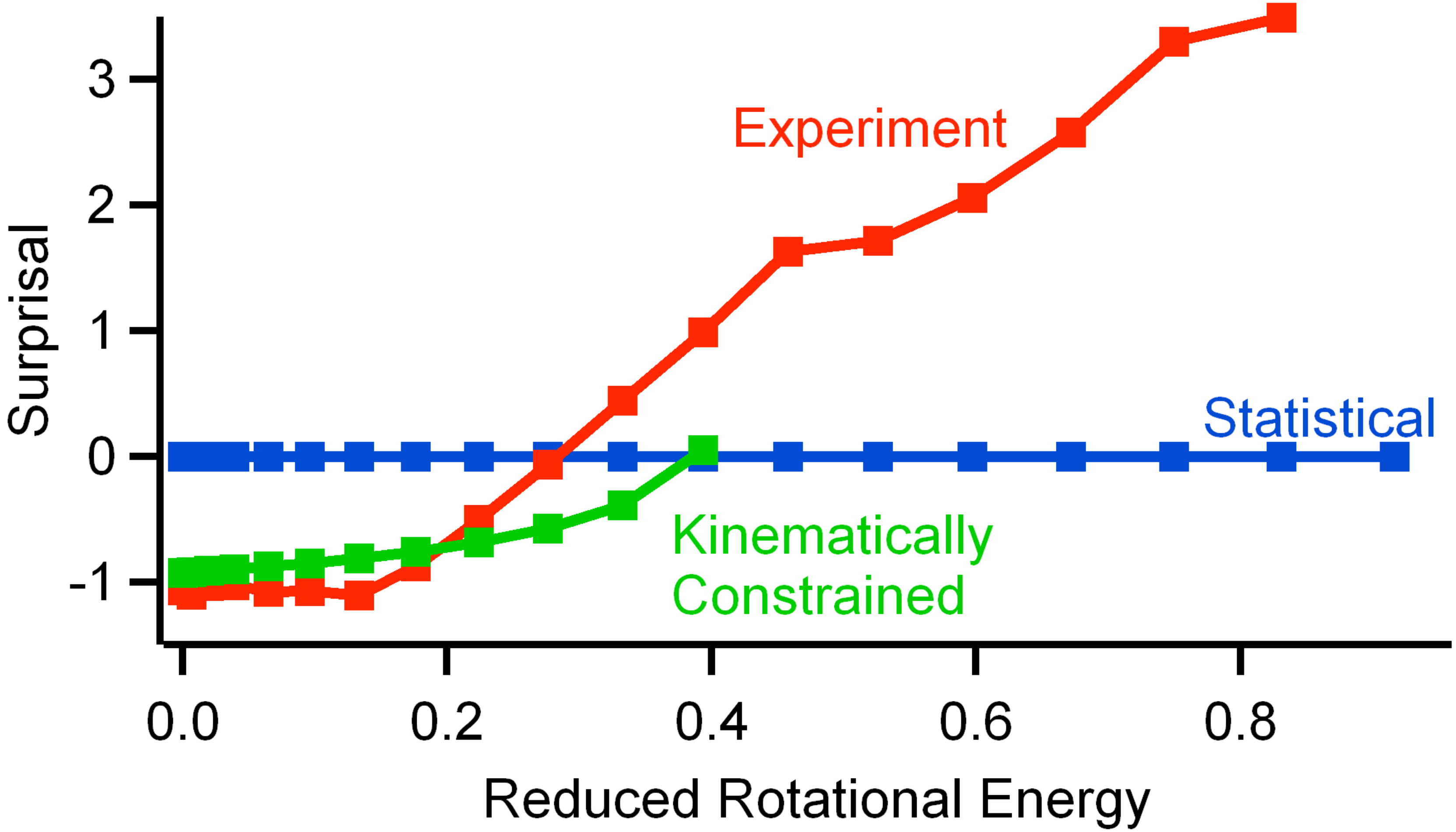
Use information theoretical techniques to compare the actual distribution to this “prior” distribution.

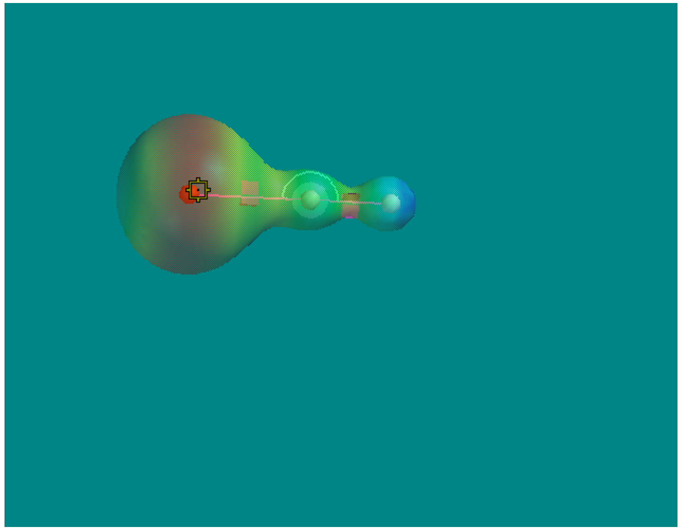
_>0: cold

_=0: statistical

_<0: hot

Surprisal Analysis





Br- H = 1.5 angstrom

H-H = 1.0 angstrom

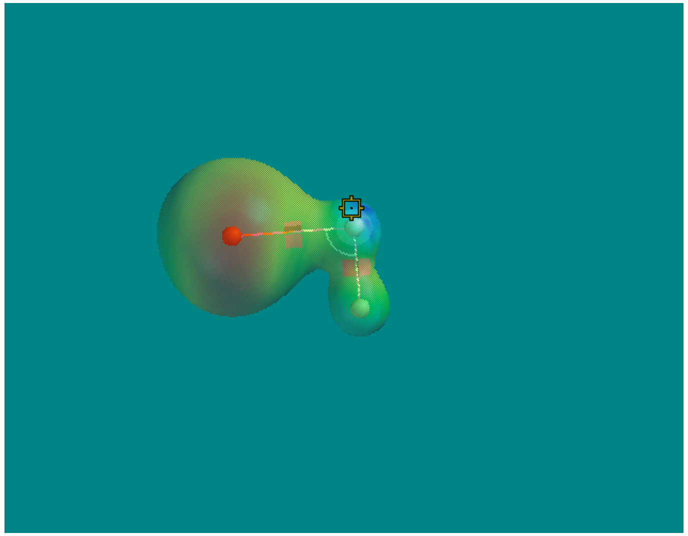
Br-H-H = 180 degrees

Density = $0.1e^{-}/au^{3}$

Red = +232 kcal/mol of positive electron charge

Blue = +497

Energy = -2574.98845 au



Br- H = 1.5 angstrom

H-H = 1.0 angstrom

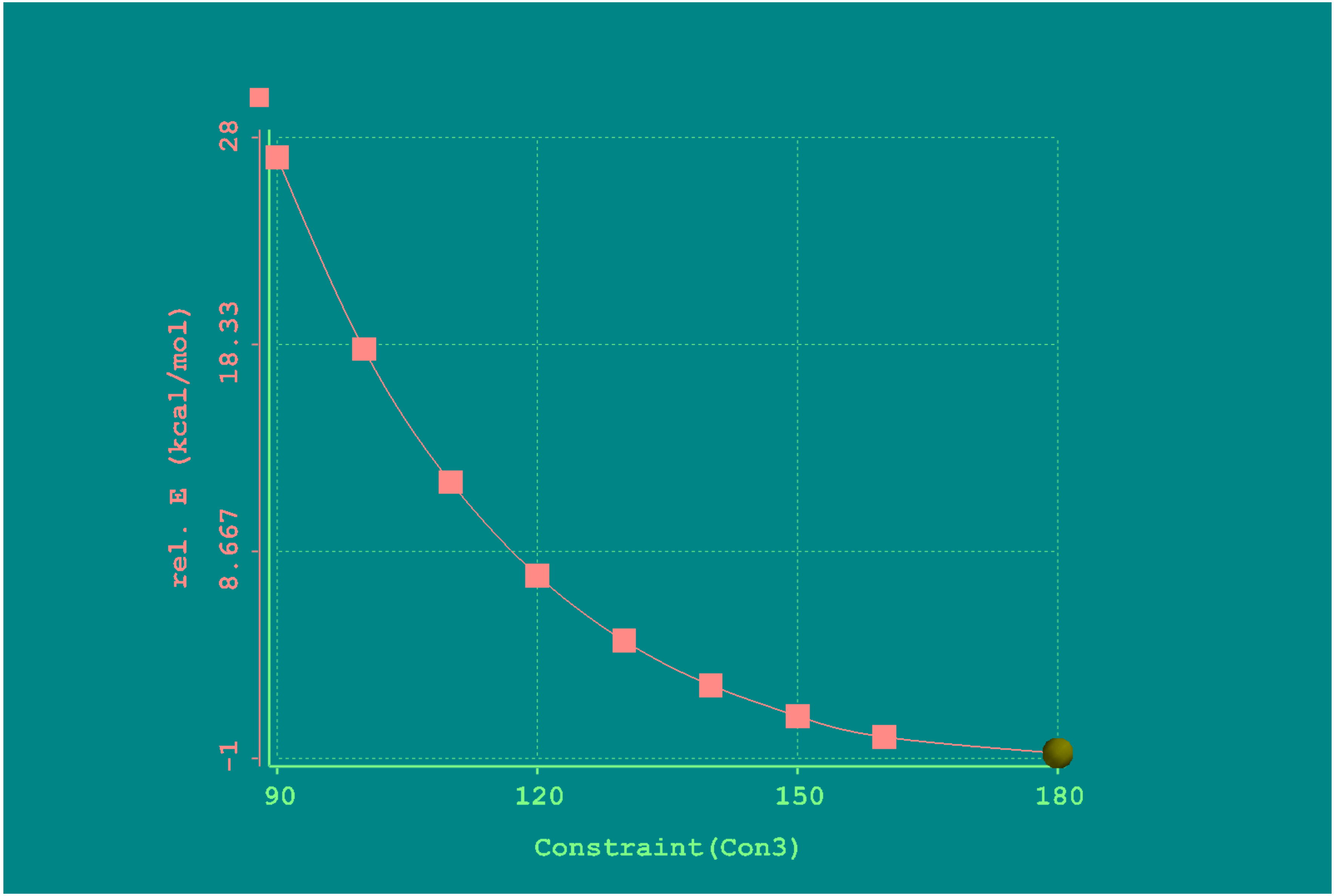
Br-H-H = 90 degrees

Density = $0.1e^{-}/au^{3}$

Red = +232 kcal/mol of positive electron charge

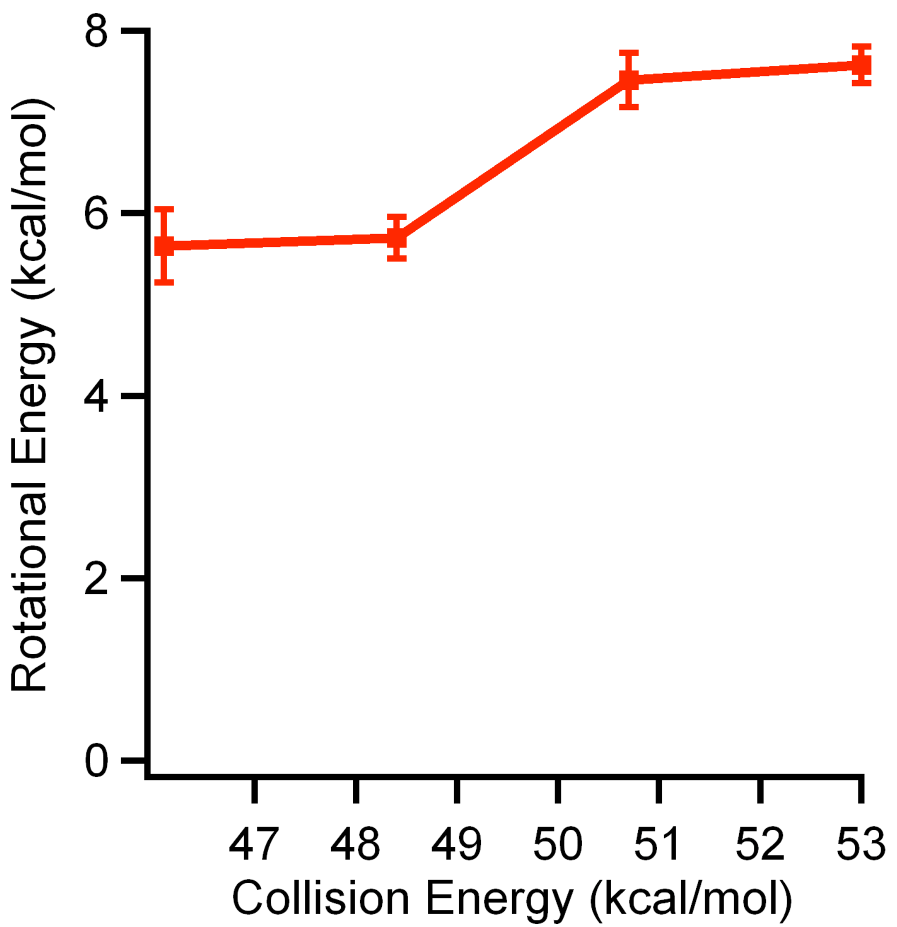
Blue = +497

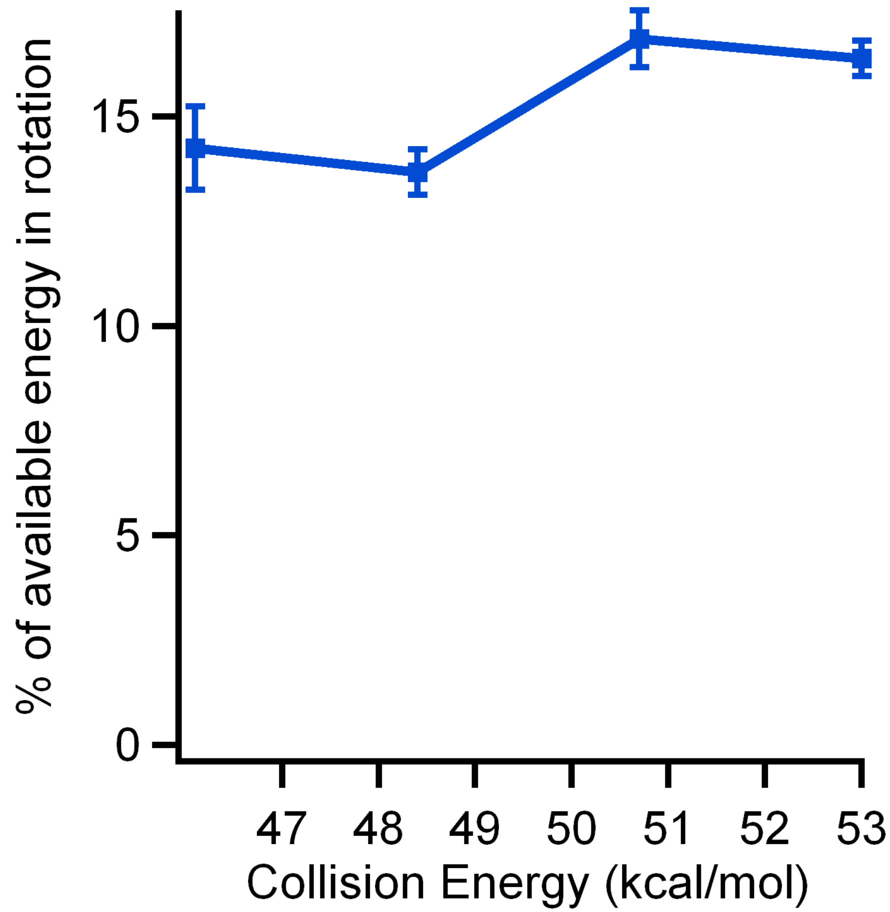
Energy = -2574.94415 au



28
18.33
8.667
-1
rel. E (kcal/mol)
90
120
150
180
Constraint(Con3)

Experimental Results
$H + HBr \rightarrow H_2(v'=2, j') + Br$






Is This The Movie
You First Imagined?
"That's all Folks!"

Mass-Weighted PES

Collinear reactive collision A + BC → AB + C

Two bond distances: $R_{AB}=R_A-R_B$ and $R_{BC}=R_B-R_C$

PROBLEM: The kinetic energy in the center of mass system is not a simple function of R_{AB} and R_{BC}.

Solution to Problem
Introduce New Coordinates

Interpretation

T represents the kinetic energy of a mass point (unit mass) whose position is specified by the the two cartesian coordinates Q_1 and Q_2.

If we regard the potential energy as a function of Q_1 and Q_2, the entrance and exit valleys will be an an angle _ to one another.