

# Hot chemistry with frozen molecules

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# Why study ultracold reactions

- **Explore long-range forces on reactivity**
- **Quantum control of reactions with E and B fields**
- **Explore Quantum effects and tunneling in chemical reactions**
- **Quantum collective effects on reactivity**
- **Highly selective in initial and (in some cases) final states**
- **Investigate resonant and quasi-resonant energy transfer**
- **Applications to astrochemistry**

## Key steps in first-principles calculation of rate constants for molecular processes

- Electronic structure calculations of the interaction potential for the collision system
  - GAUSSIAN, MOLPRO, GAMESS, NWCHEM, etc.
- Fitting the interaction potential to suitable functional form for dynamics calculations
- Collision dynamics calculations for various chosen initial conditions (vibrational, rotational levels of the molecules) and energies to evaluate cross sections
  - Classical trajectory method
  - Semiclassical methods
  - Quantum scattering methods
- Calculate rate coefficients from the corresponding cross sections

# Quantum mechanical approaches – Time-dependent vs time-independent

## Time-dependent wave packet method

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

For time-independent Hamiltonians,

$$\Psi(t + \Delta t) = \exp(-iH\Delta t / \hbar) \Psi(t)$$

$\Psi(t = 0) \Rightarrow$  wave function corresponding to reactants in a given initial state.

Efficient numerical methods available to solve the time-evolution.

Scales as  $N \log(N)$  where  $N$  is the number of grid points. Initial value problem.

Matrix elements of  $\hat{H}$  are not explicitly constructed.

Less accurate at low energies

## Time-independent coupled-channel method

$$\hat{H} \psi = E \psi$$

For an atom-diatom non-reactive system

$$\psi(\vec{R}, \vec{r}) = \frac{1}{R} \sum_n C_n(R) \phi_n(\vec{R}, \vec{r}),$$

$$n \equiv (v, j, l; JM)$$

$$\phi_n(\vec{R}, \vec{r}) = \frac{1}{R} \chi_{vj}(r) \times$$

$$\sum_{m_j, m_l} (j, l, J | m_j, m_l, M) Y_{m_j}^j(\hat{r}) Y_{m_l}^l(\hat{R})$$

Explicit construction of Hamiltonian Matrix is required. Computational effort scales as  $N^3$  where  $N$  is the number of coupled channels. Each energy point requires a separate calculation.

More accurate at low energies

# Non-reactive diatom-diatom scattering

- Jacobi vectors  $\{\vec{R}, \vec{r}_a, \vec{r}_b\}$

- Expansion of the total wave function :

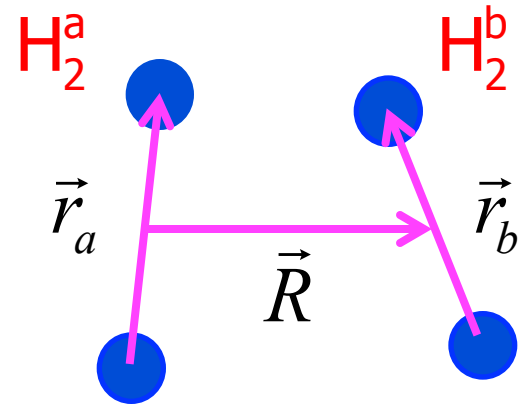
$$\Psi^E = \sum_{JM} C_{JM} \psi^{JME} \quad (\hat{H}, \hat{J}, \hat{J}_Z)$$

$$\psi^{JME} = \frac{1}{R} \sum_{v_a v_b j_a j_b j_{ab} l} \Phi_{v_a v_b j_a j_b j_{ab} l}^{JME} F_{v_a v_b j_a j_b j_{ab} l}^{JME}(R)$$

$$\Phi_{v_a v_b j_a j_b j_{ab} l}^{JME} = \chi_{v_a j_a}(r_a) \chi_{v_b j_b}(r_b) \langle \hat{r}_a \hat{r}_b \hat{R} | j_a j_b j_{ab} l J M \rangle$$

- Schrödinger equation :  $\hat{H} \psi^{JME} = E \psi^{JME}$

- System of close coupling equations, propagation of the log-derivative matrix, matrices K, S, T, cross sections



# Computational bottlenecks

- Optimization of basis set ( $v_{1\max}, v_{2\max}, j_{1\max}, j_{2\max}, J$ )
- Basis set determines the number of coupled equations to be solved (typically ranges from several hundred to several thousand). Large basis set is required for large  $J$ .
- Range of radial integration,  $R_{\min}$  to  $R_{\max}$  (larger  $R_{\max}$  is needed for low energy calculations)
- For each initial ( $v_1 j_1 v_2 j_2$ ) combinations, cross sections are computed for several hundred energies to accurately describe resonance structures
- Computing (and optionally storing) the matrix elements of the interaction potential (for a given  $J$  it is independent of the collision energy) is a bottleneck in the calculations (storage requirements can exceed 100 Gb for high  $J$  values)

# Basis set size

$$N = \sum_{v_1=0}^{v_{1\max}} \sum_{v_2=0}^{v_{2\max}} \sum_{j_1=0}^{j_{1\max}} (2j_1 + 1) \sum_{j_2=0}^{j_{2\max}} (2j_2 + 1)$$

$$= (v_{1\max} + 1)(v_{2\max} + 1)(j_{1\max} + 1)^2(j_{2\max} + 1)^2$$

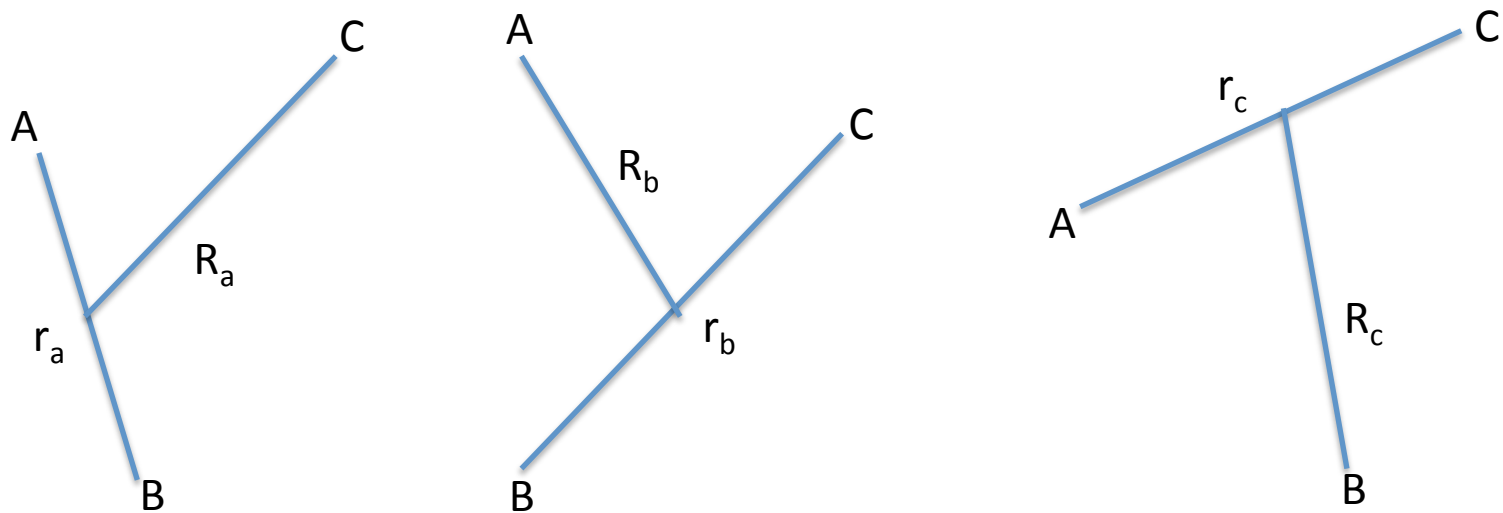
For  $v_{1\max} = 1$ ,  $v_{2\max} = 1$ ,  $j_{1\max} = 10$ ,  $j_{2\max} = 10$ ,

$N = 58564$  and computational expense scales as  $N^3$

In practical calculations, number of channels are reduced ( $\sim$  factor of 2) by parity considerations, symmetrization of identical particle wave functions ( $\sim$  factor of 2) and energy cut - off to omit high energy states in the basis set

## Reactive scattering

- ✧ Due to atom-exchange, coordinates appropriate for reactants are not suitable for products
- ✧ A coordinate transformation is required if Jacobi coordinates are used
- ✧ Hyperspherical coordinates avoid the need for coordinate transformation
- ✧ All three product arrangements (A+BC, AB+C, AC+B) in an ABC system are even handedly described by hyperspherical coordinates
- ✧ Reactive problem can essentially be solved as an inelastic problem in a single set of coordinates

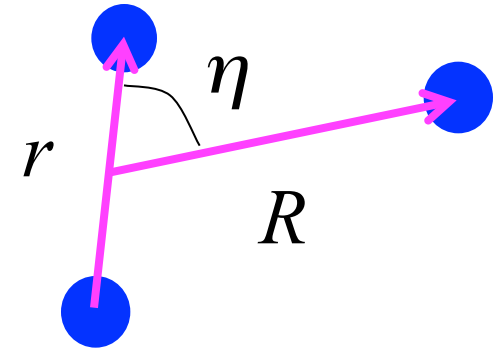


Hyperradius  $\rho = (r^2 + R^2)^{1/2}$  (independent of arrangement channel)



# Hyperspherical coordinates

- Code **ABC** (Skouteris, Castillo, Manolopoulos)
- Time-independent quantum formalism
- Hyperspherical coordinates  $\rho$ ,  $\theta$ ,  $\phi$  from the Jacobi coordinates



- For a fixed  $\rho$ , the hyperangular Hamiltonian in  $\theta$ ,  $\phi$  is diagonalized and leads to adiabatic energies and adiabatic hyperangular functions
- Expansion of the total wave function :

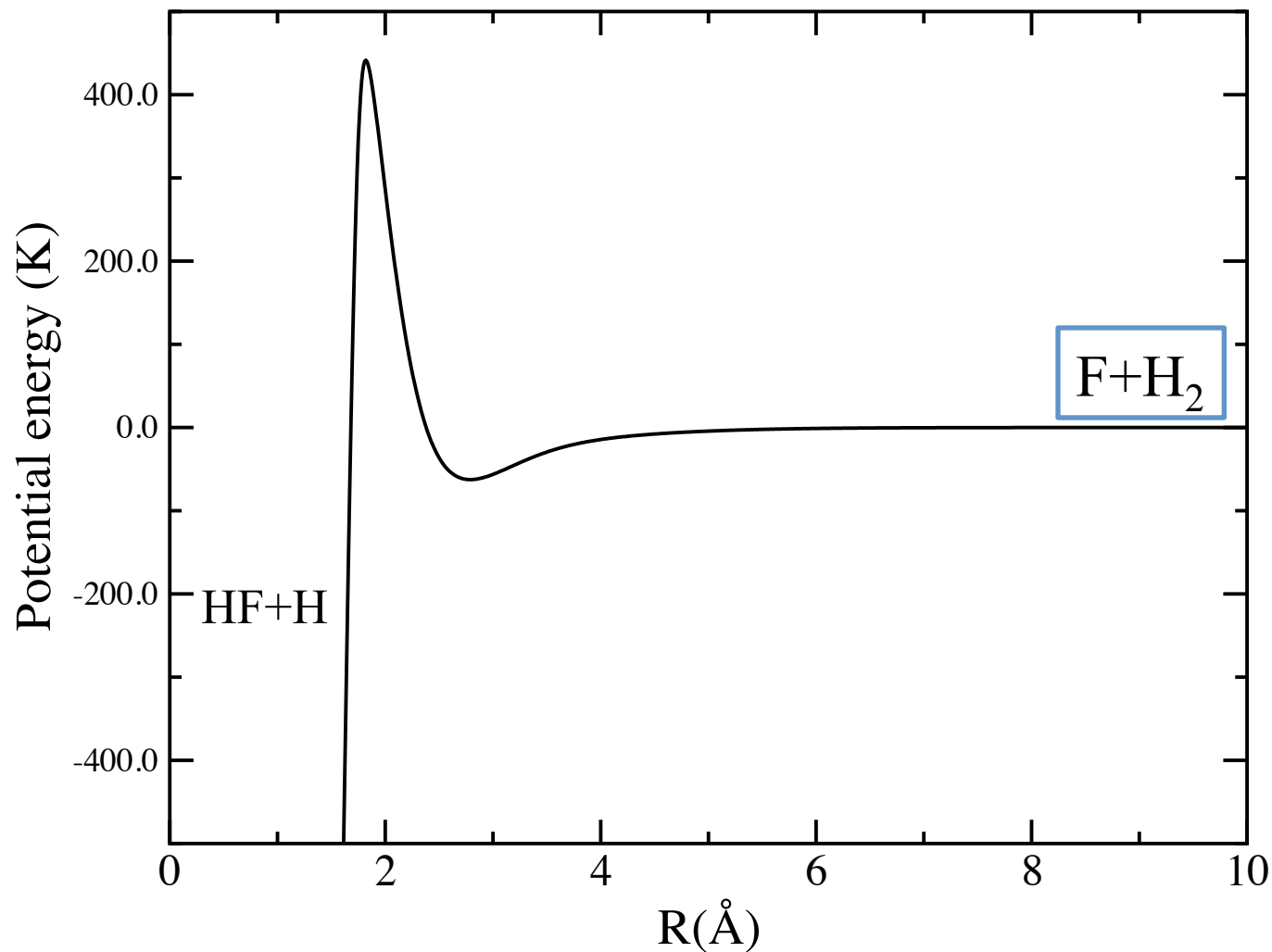
$$\Psi^E = \sum_{JM} C_{JM} \psi^{JME} \quad \psi^{JME} = \frac{1}{\rho^{5/2}} \sum_{vj\Omega} \Phi_{vj\Omega}^{JME}(\rho; \hat{\rho}) F_{vj\Omega}^{JME}(\rho)$$

- Schrödinger equation :  $\hat{H}\psi^{JME} = E\psi^{JME}$

- System of close coupling equations, propagation of the log-derivative matrix, K,S,T, matrices & cross sections.

# Barrier Reaction

Adiabatic potential for the  $F+H_2$  reaction



# F+H<sub>2</sub> Reaction

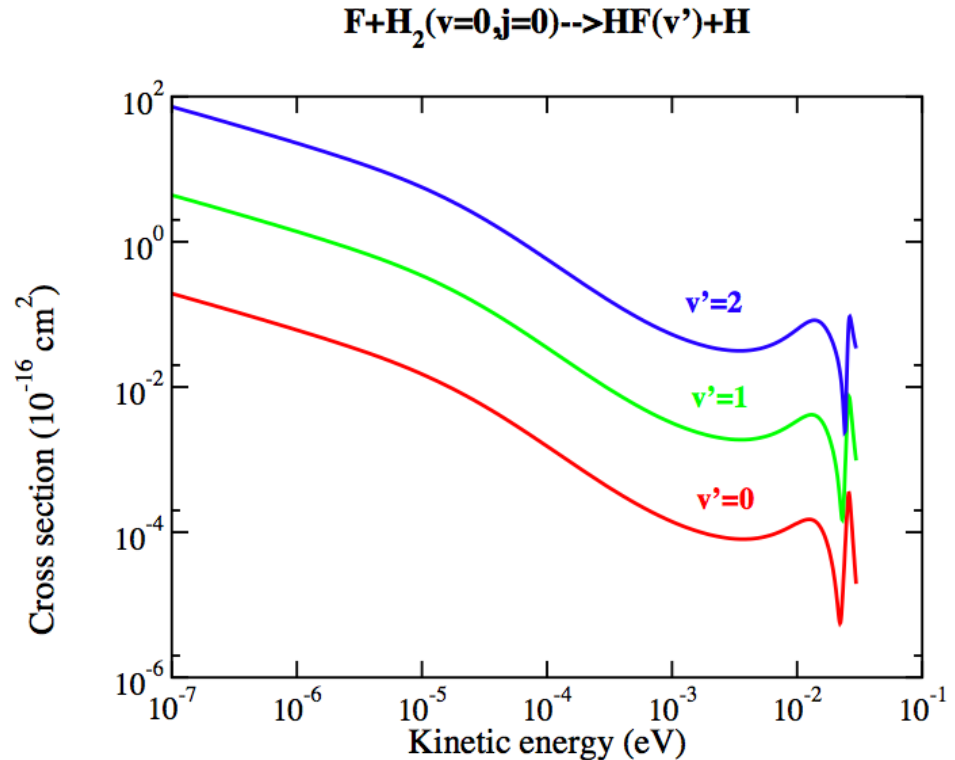
The F+H<sub>2</sub> reaction is exoergic by about 1.4 eV. The reaction has an energy barrier of about 400 K.

Zero Temperature Limiting value of The rate coefficient

$$\sim 1.25 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

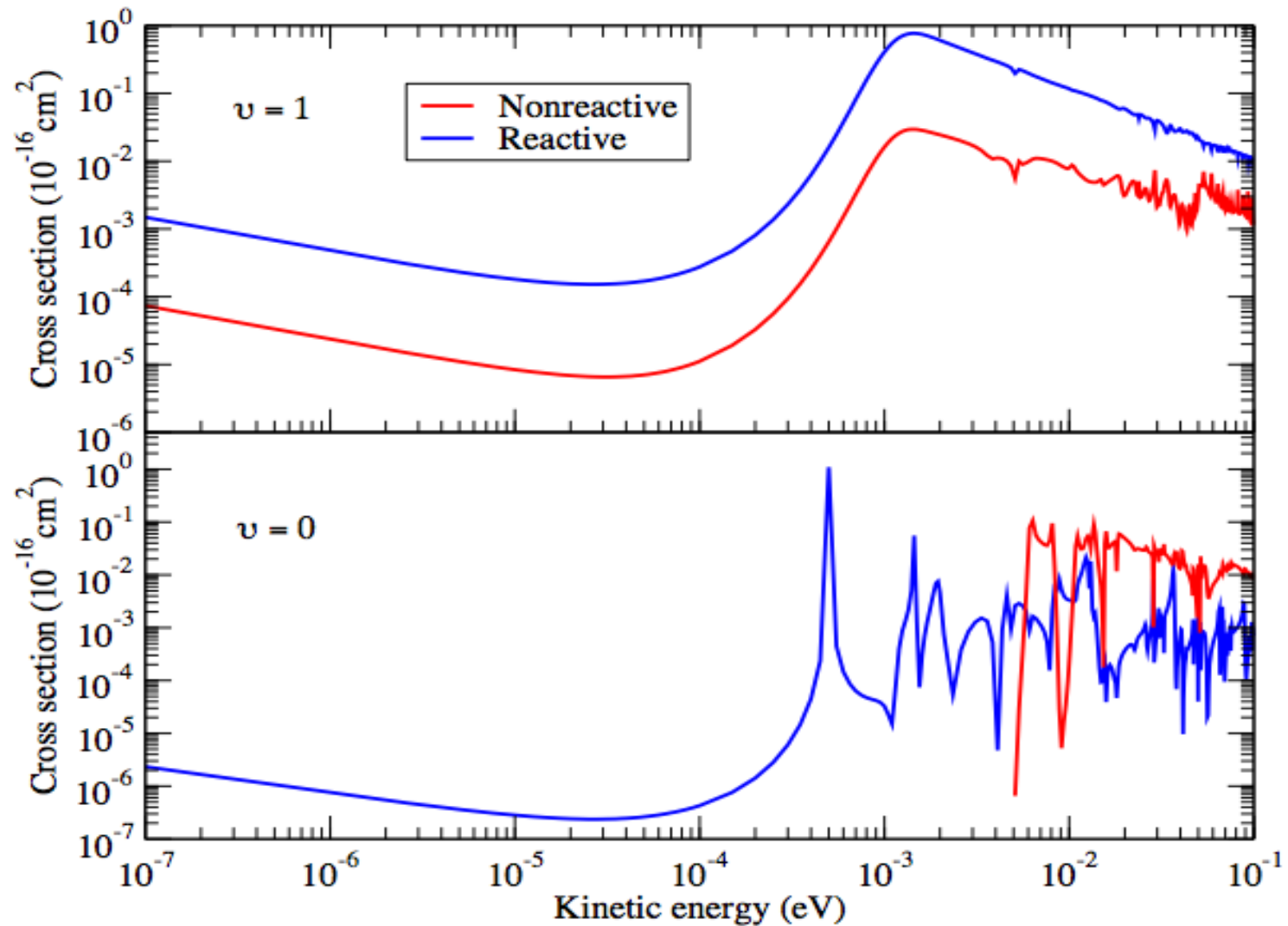
The F+H<sub>2</sub> reaction is thought to play a crucial role in fluorine chemistry in interstellar medium. HF is the main reservoir of F atoms in interstellar gases.

Balakrishnan and Dalgarno, Chem. Phys. Lett. (2001)



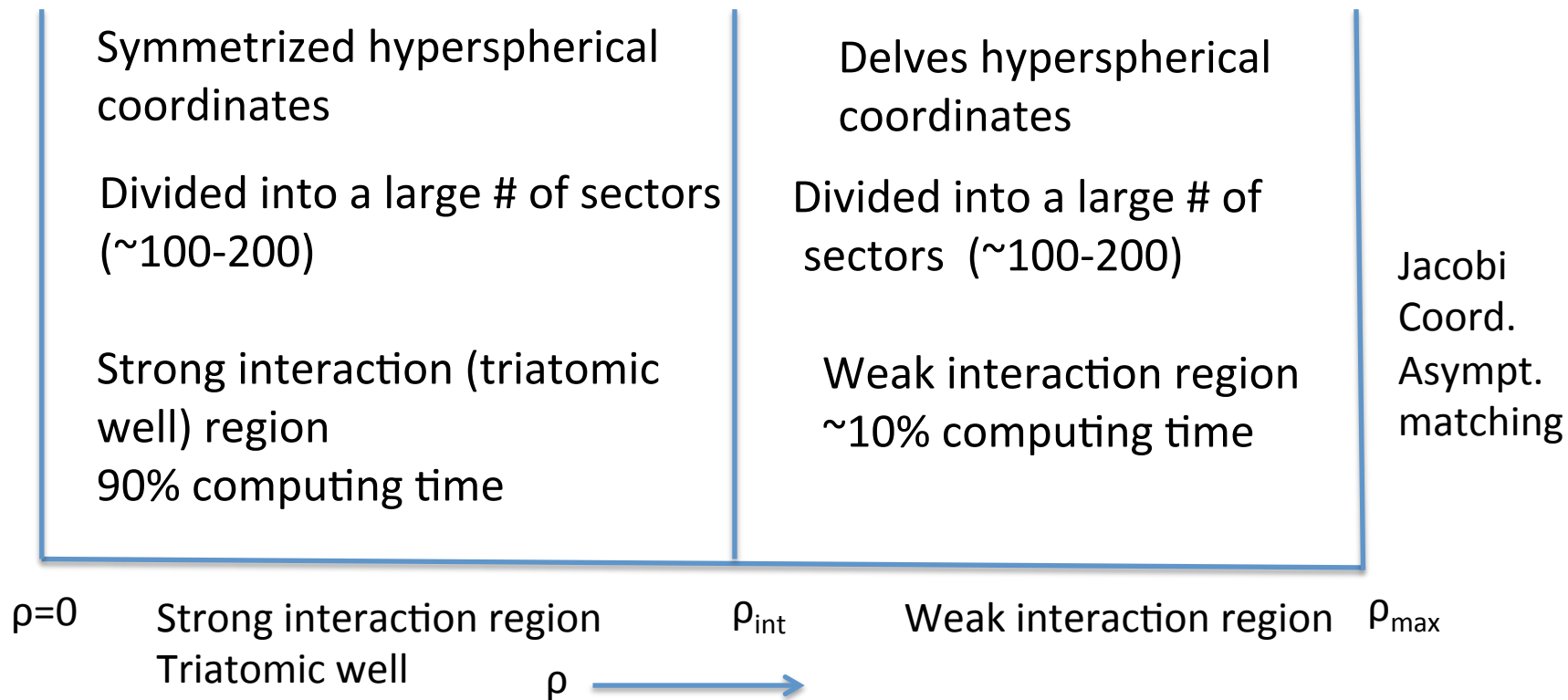
# Li+HF( $v=0,1$ ) $\rightarrow$ LiF+H reaction

At low energies, the reaction occurs tunneling of the F atom

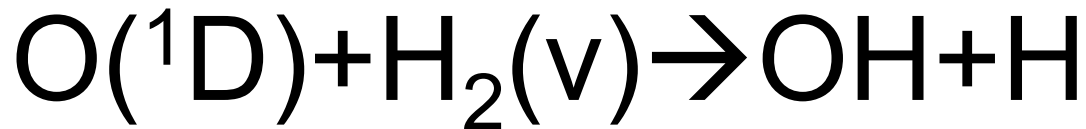


Weck and Balakrishnan, JCP (2005)

# Reactions with deep potential wells

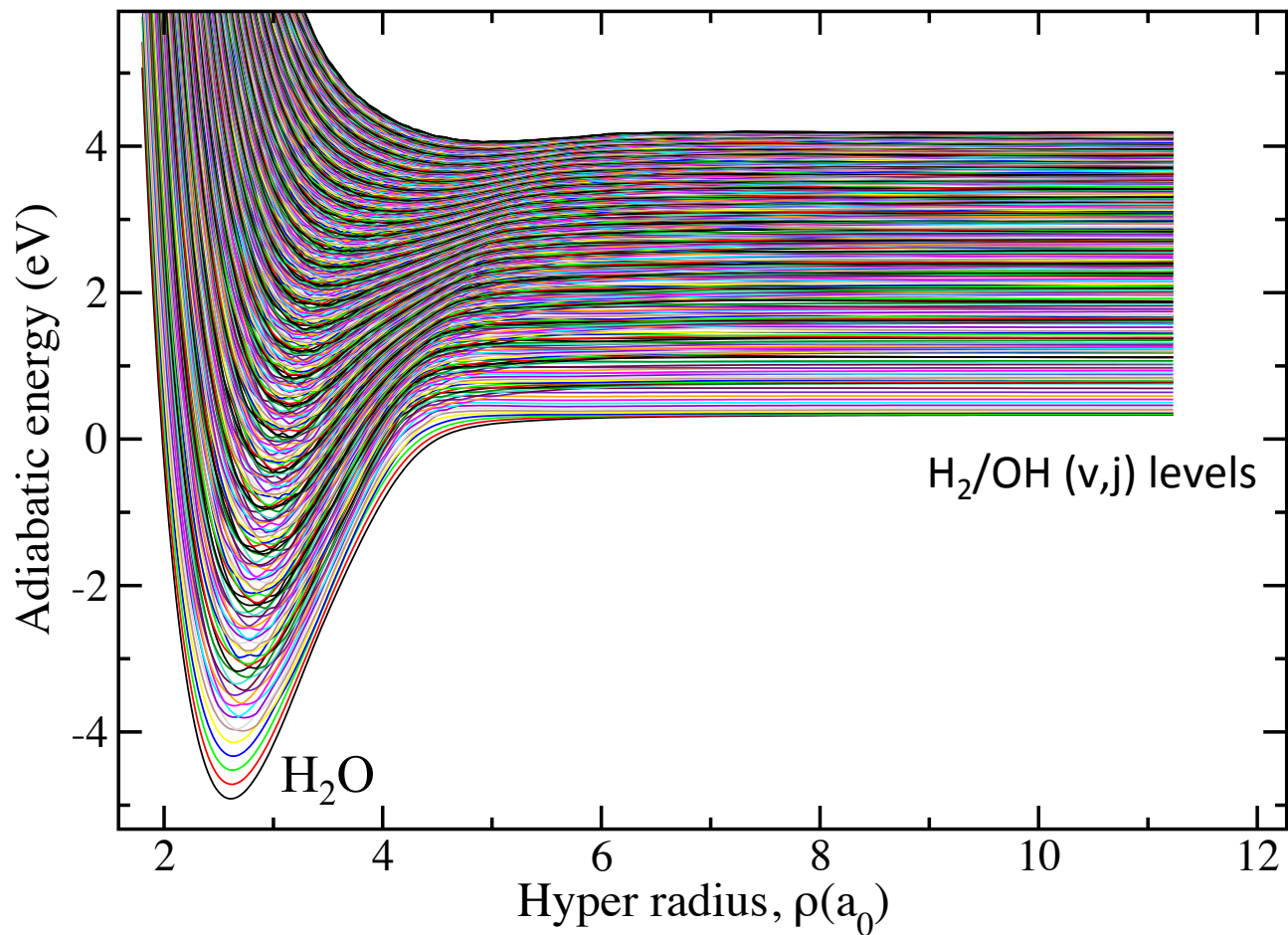


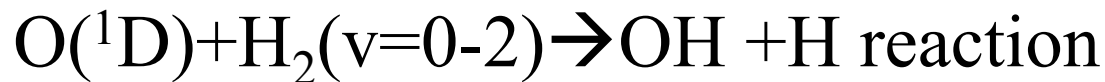
Pack and Parker, JCP **87**,3888 (1987)



- A benchmark barrierless reaction for insertion mechanism
- Deep potential well corresponding to the formation of  $\text{H}_2\text{O}$  ground state
- Explore the effect of vibrational excitation of  $\text{H}_2$  on the reaction dynamics
- An interesting candidate for ultracold barrierless reaction involving  $\text{H}_2$

# Adiabatic energy levels of O(<sup>1</sup>D)+H<sub>2</sub>

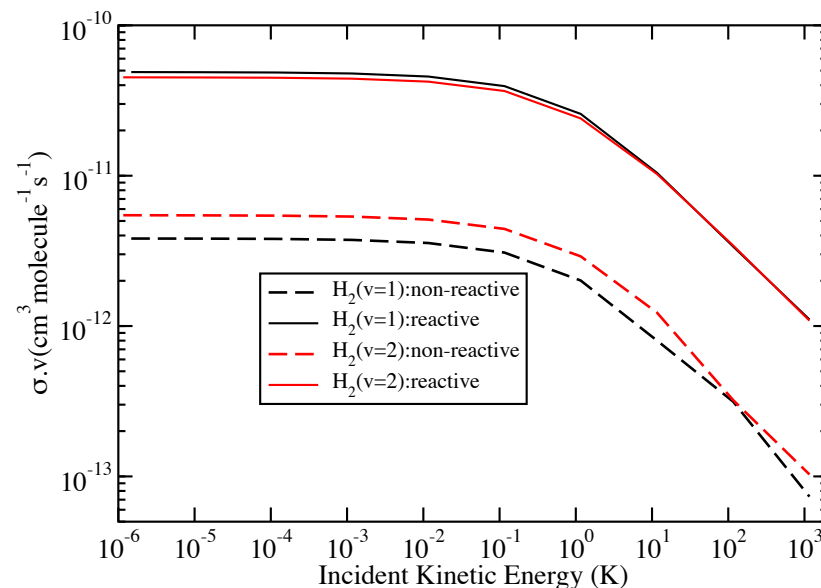
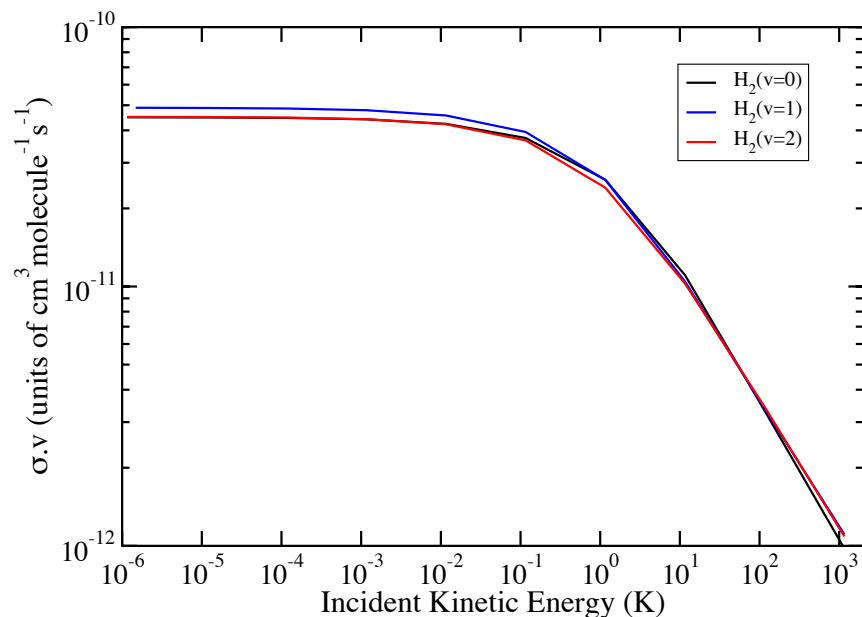




$$k(T\rightarrow 0) \sim 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ for } v=0-2$$

$$k(300 \text{ K}) \sim 1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

(Experiment)



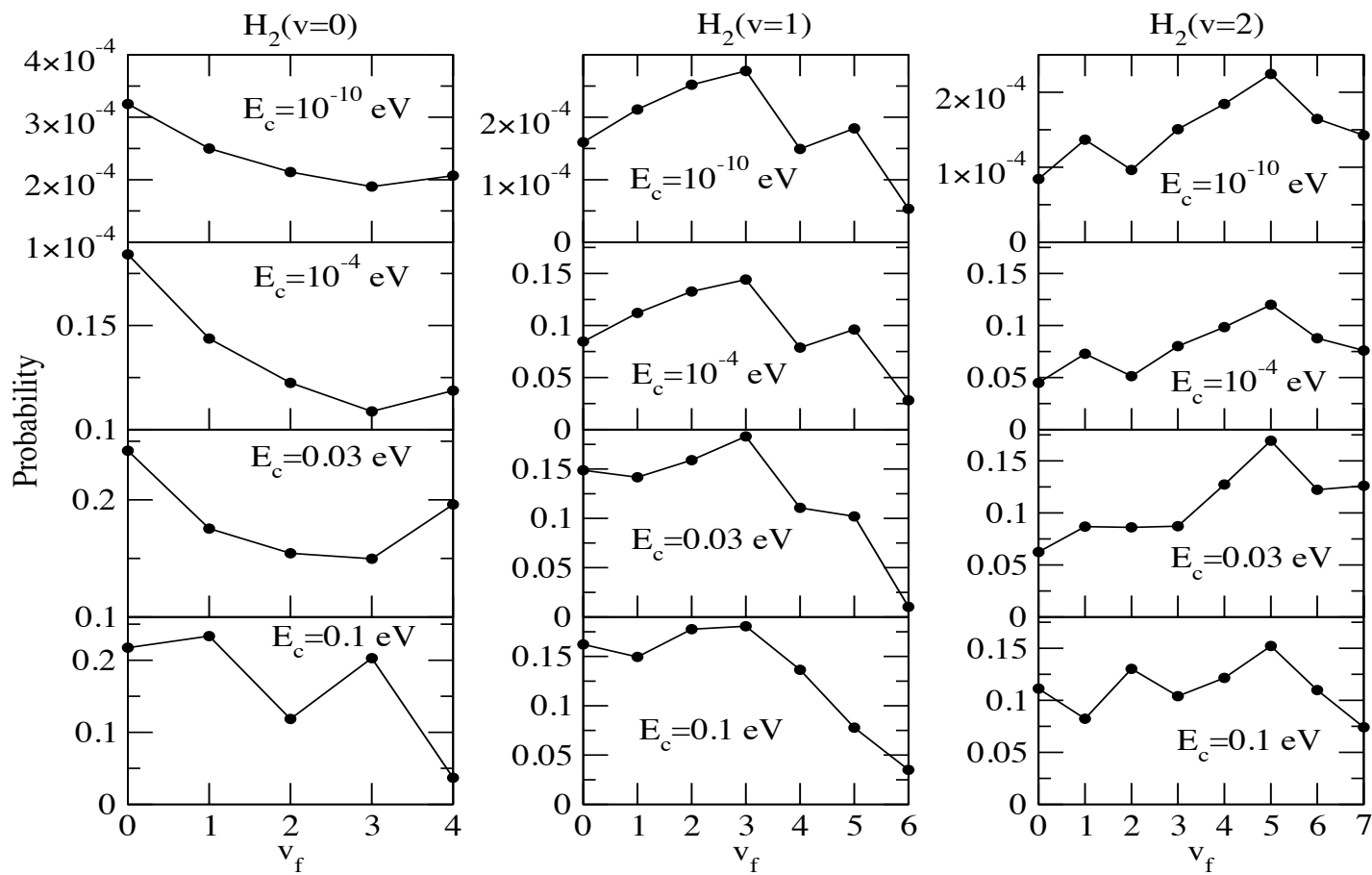
For  $v=1$  and 2, Chemical reaction dominates over vibrational quenching

Rate coefficients almost independent of  $H_2$  vibrational level for  $v=0-2$

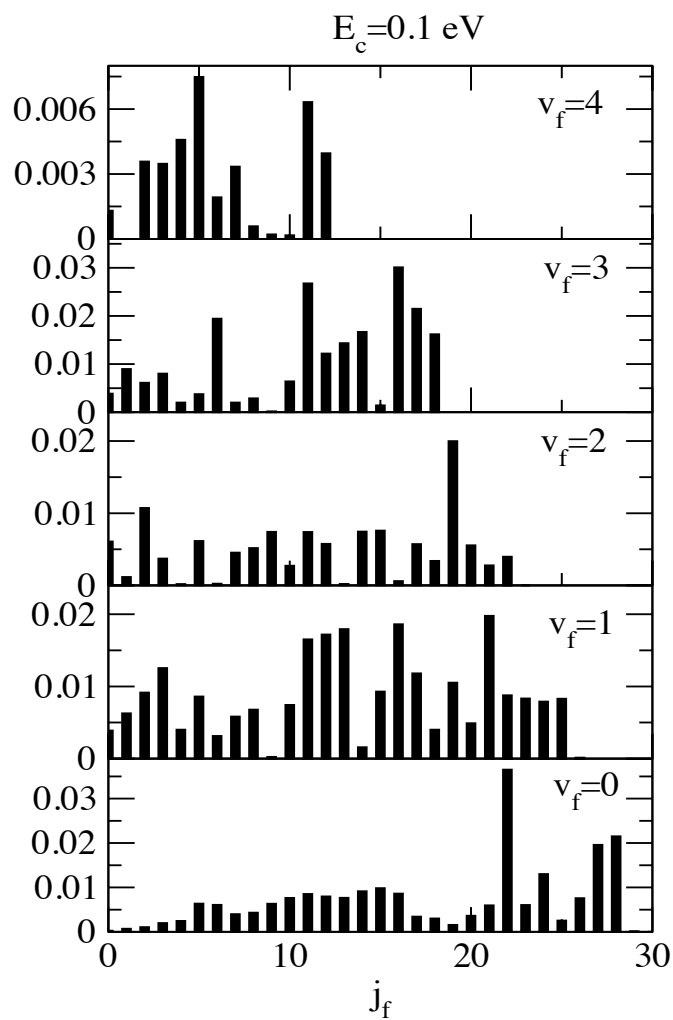
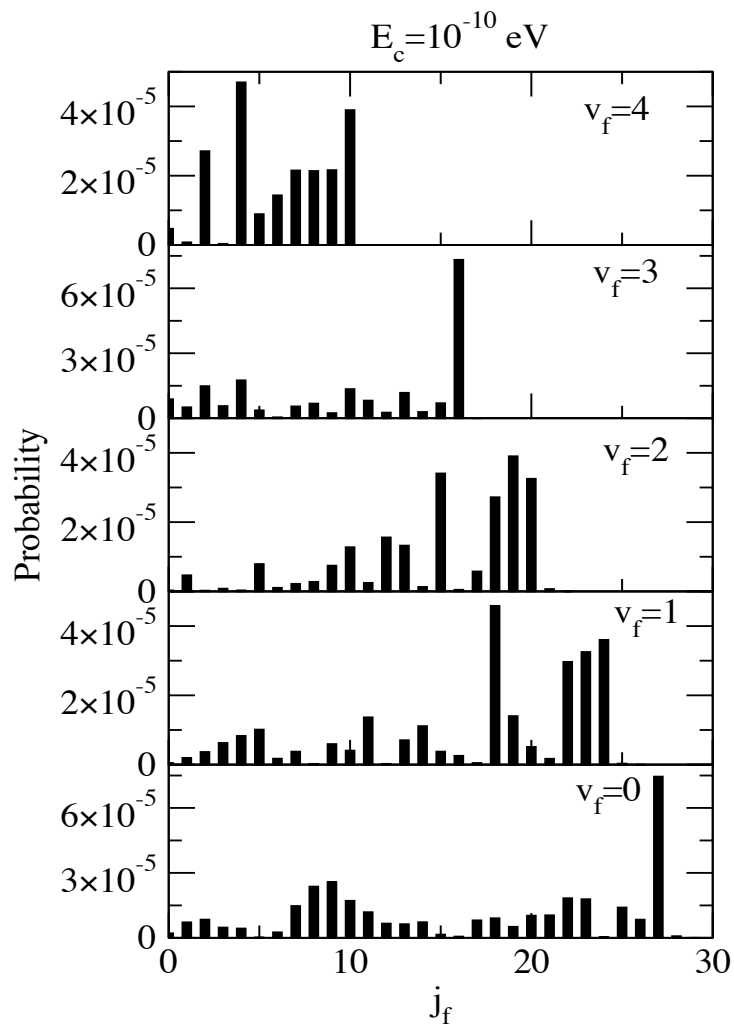
G. P. Pradhan, N. Balakrishnan and B. K. Kendrick (unpublished)



# OH vibrational populations in $O(^1D)+H_2(v)$ reactions



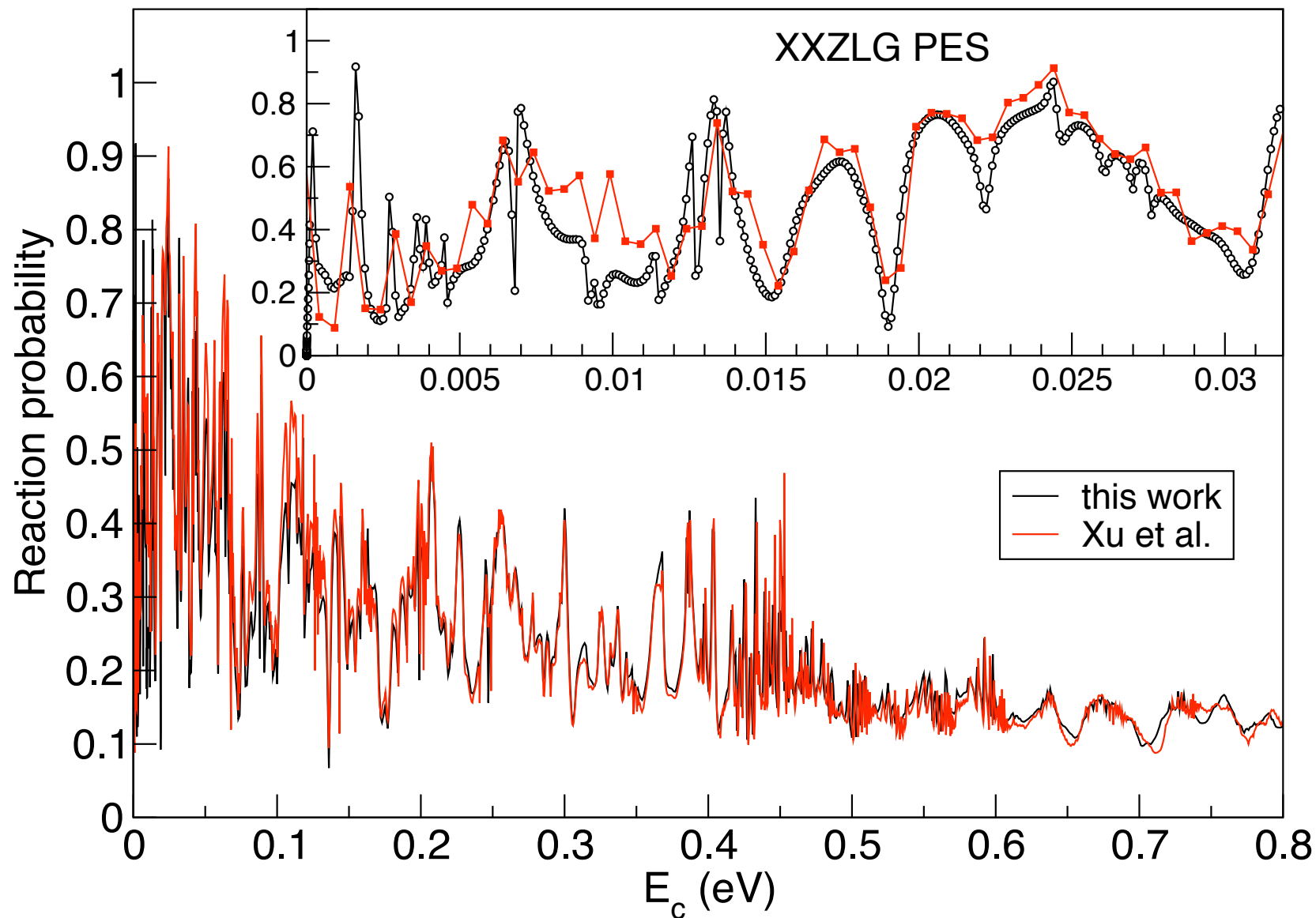
# OH rotational populations in $O(^1D)+H_2(v=1)$ reaction



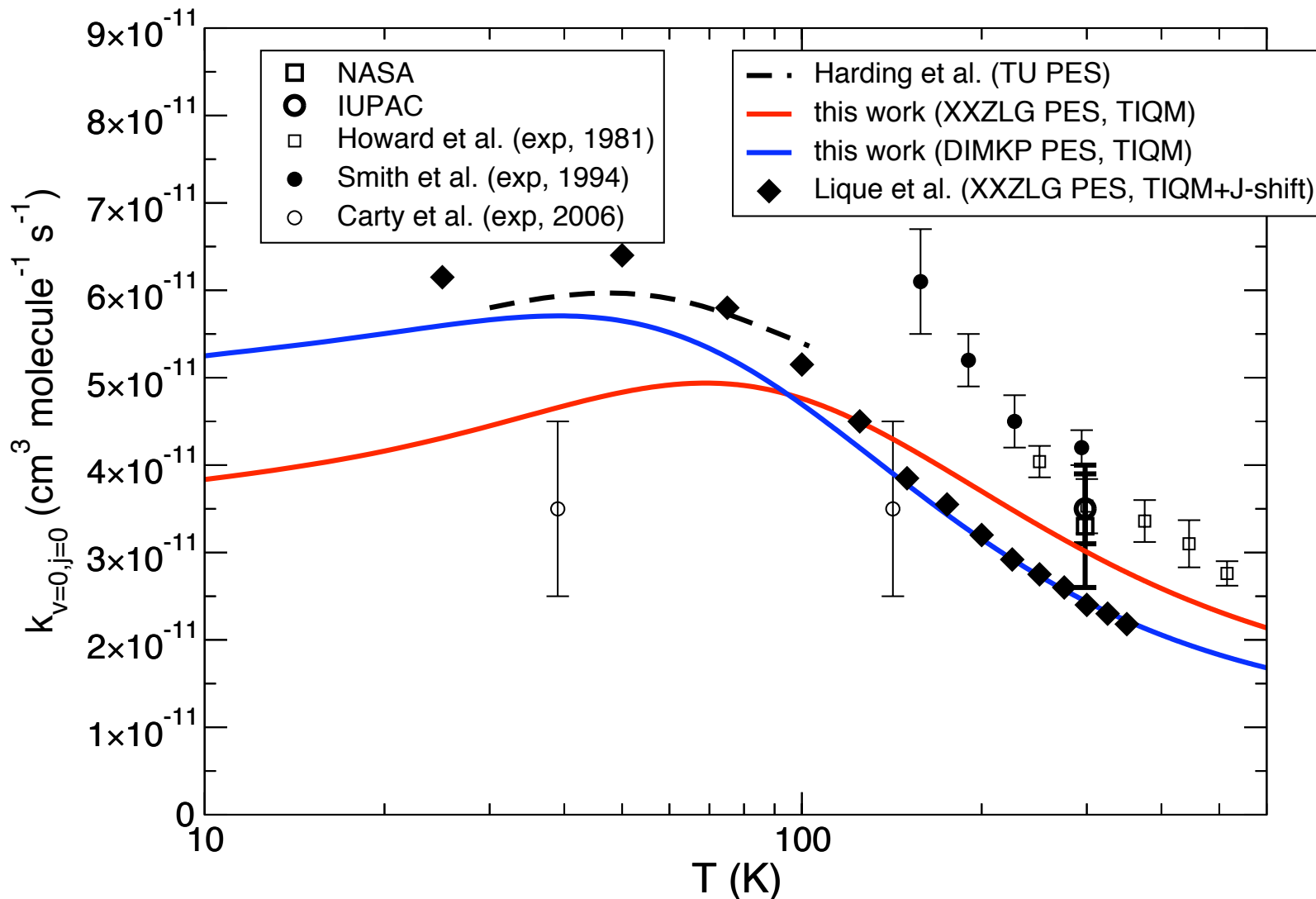
# OH + O $\rightarrow$ H+O<sub>2</sub> Reaction

- Computationally challenging due to two heavy O atoms
- Deep potential well corresponding to the HO<sub>2</sub> species
- Long-range dipole-quadrupole interaction in the entrance channel
- Key reaction in mesospheric OH chemistry and oxygen chemistry in the interstellar medium
- H+O<sub>3</sub>  $\rightarrow$  OH(v)+O<sub>2</sub> populates vibrational levels as high as v=10
- Rate coefficients for OH(v)+O reaction are poorly known at temperatures below 100 K.

# Sensitivity to energy resolution

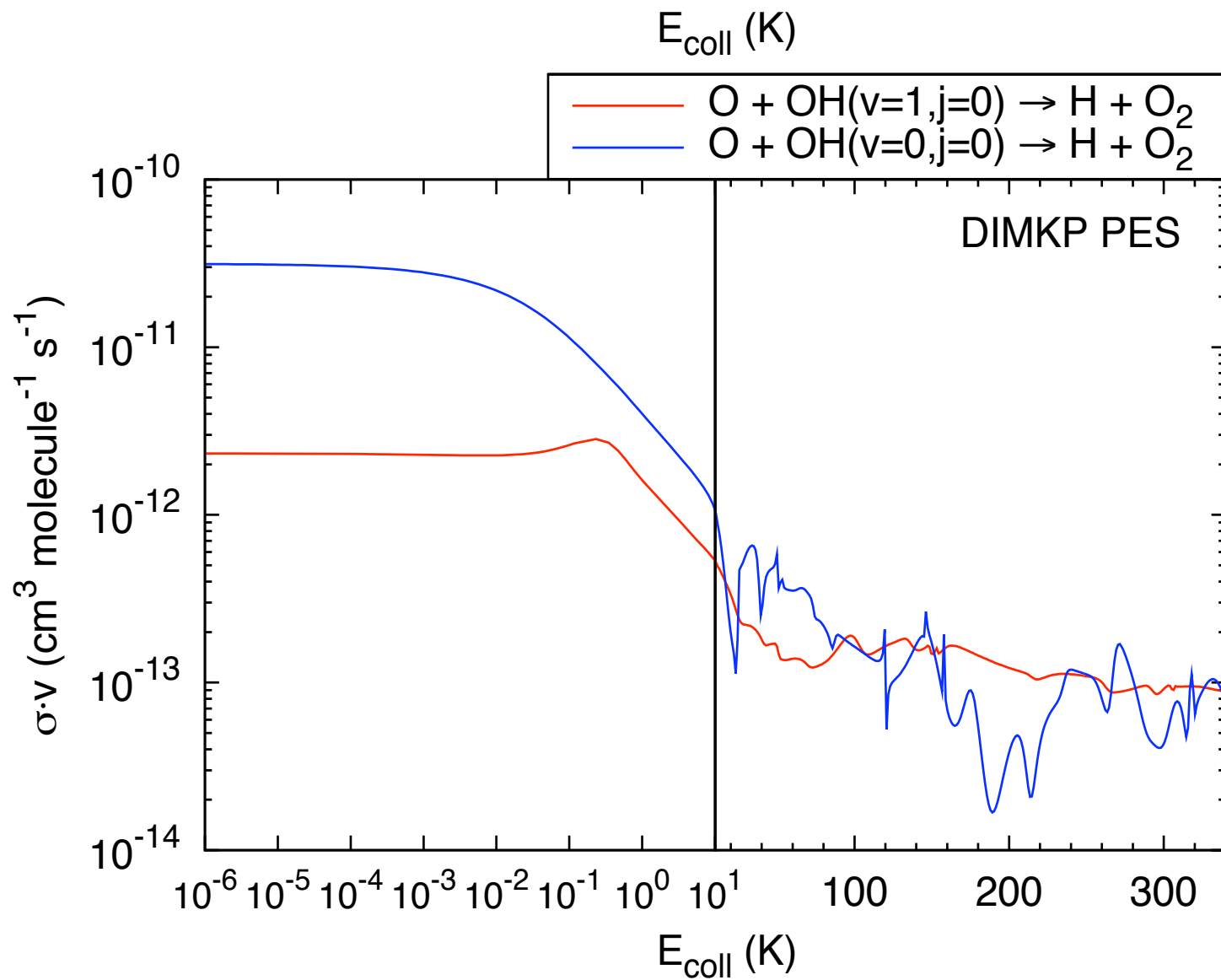


# Rate constants for the O+OH(v=0) reaction



Quemener, Balakrishnan, and Kendrick, JCP (2008)

# Reactivity of vibrationally excited OH(v=1)



# Sensitivity to small changes in interaction potential (DIMKP PES)

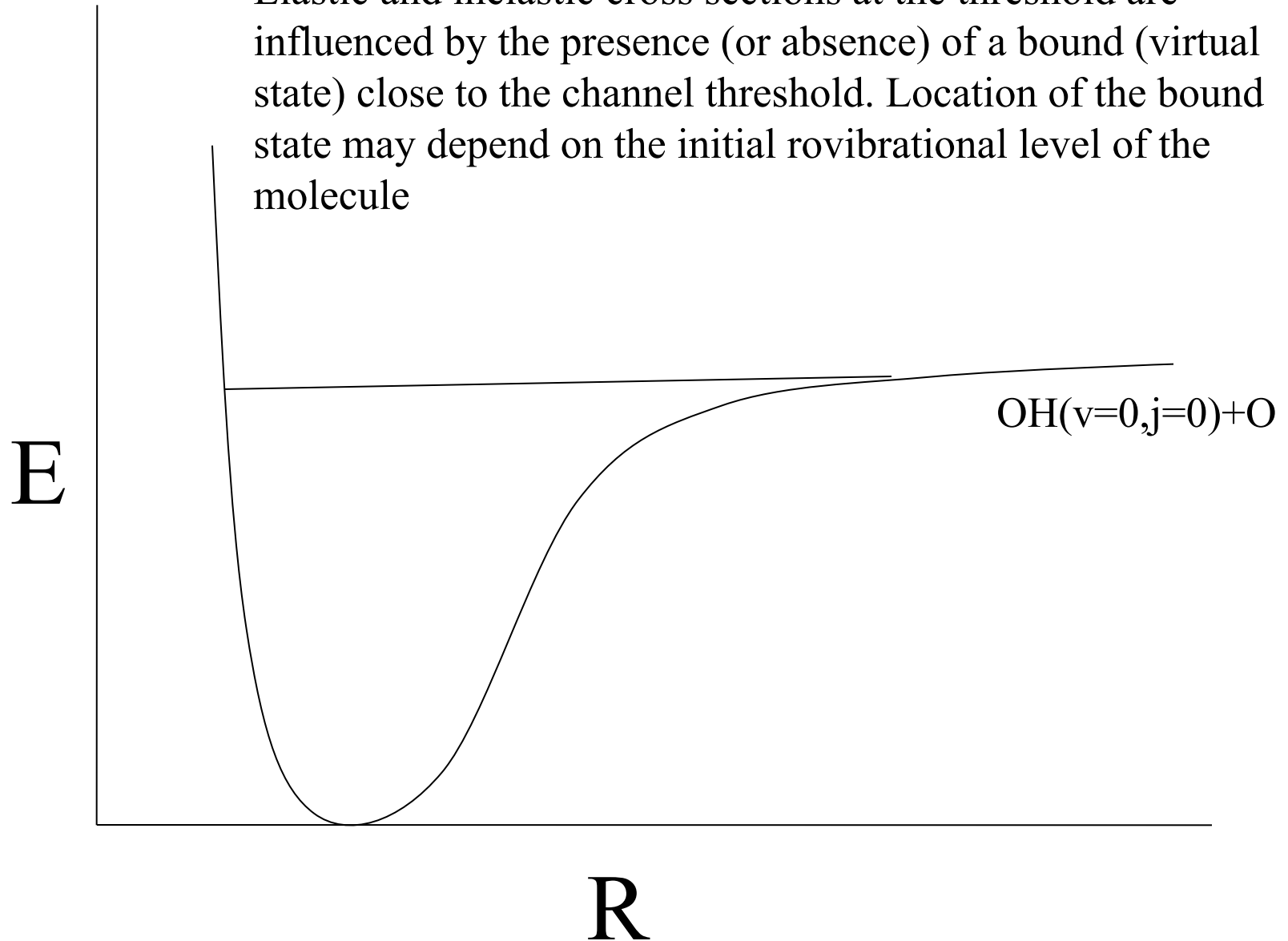
$$V = \alpha V$$

$$k(T=0) = v_{\text{rel}} \cdot \sigma = \text{constant}$$

$\alpha$	$v_{\text{rel}} \sigma_{\text{reactive}}$ ( $v=0$ ) $\text{cm}^3 \text{s}^{-1}$	$v_{\text{rel}} \sigma_{\text{reactive}}$ ( $v=1$ ) $\text{cm}^3 \text{s}^{-1}$	$v_{\text{rel}} \sigma_{\text{inelastic}}$ ( $v=1$ ) $\text{cm}^3 \text{s}^{-1}$
0.99	1.5E-12	1.4E-12	2.0E-12
1.00	3.2E-11	2.3E-12	3.5E-12
1.01	7.0E-12	4.9E-12	4.4E-12

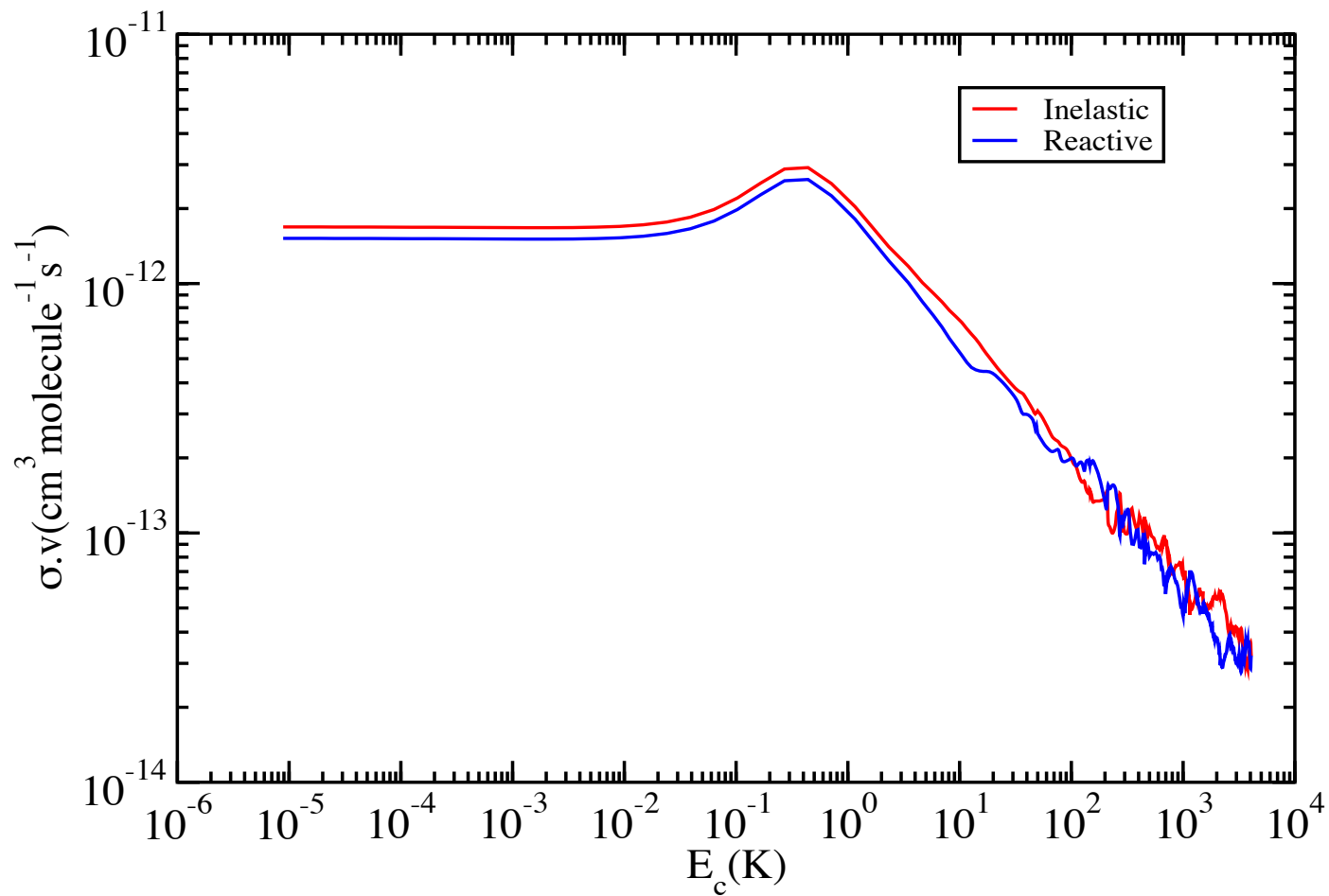
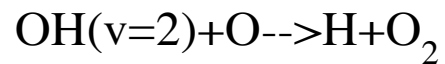
Juanes-Marcos et al. PCCP (2011)

Elastic and inelastic cross sections at the threshold are influenced by the presence (or absence) of a bound (virtual state) close to the channel threshold. Location of the bound state may depend on the initial rovibrational level of the molecule

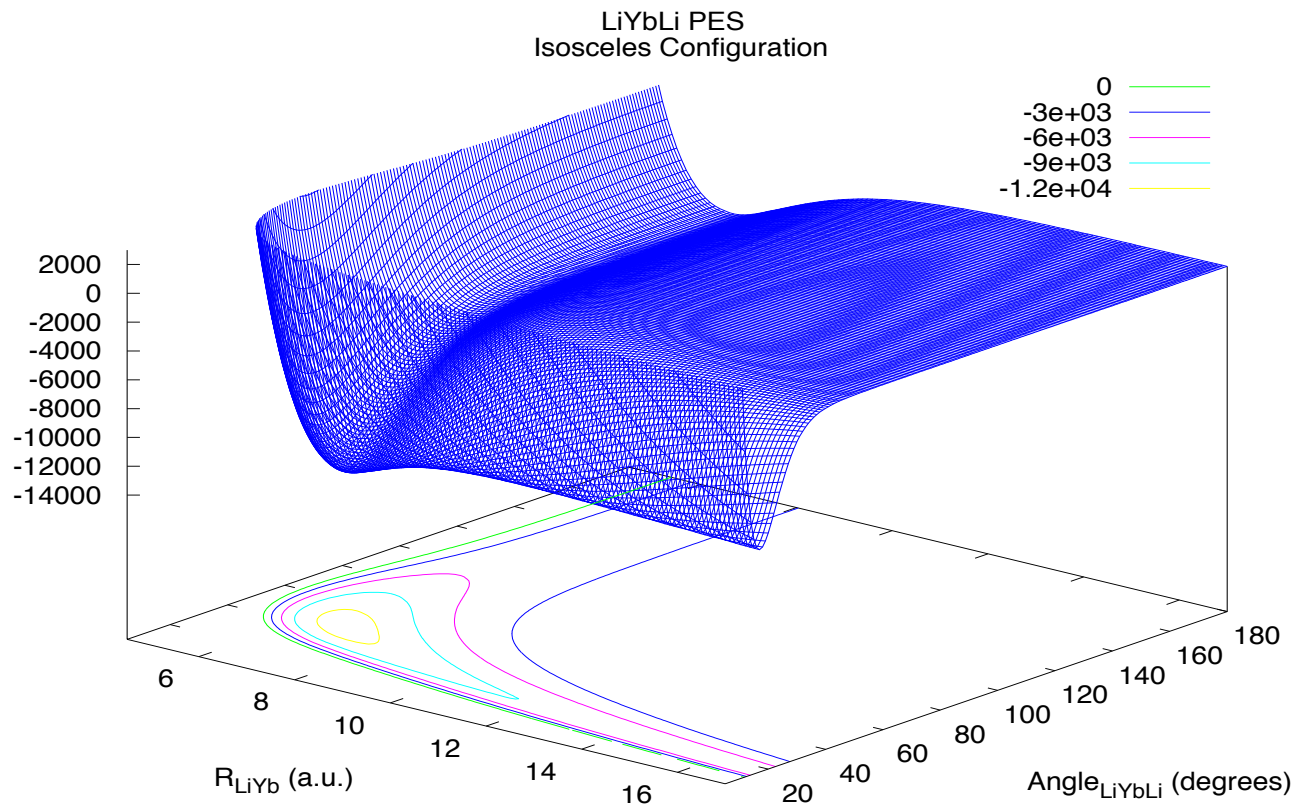




# OH( $v=2$ )+O collisions ( $J=0$ )



# Li<sub>2</sub>Yb system (collaboration with S. Kotochigova)

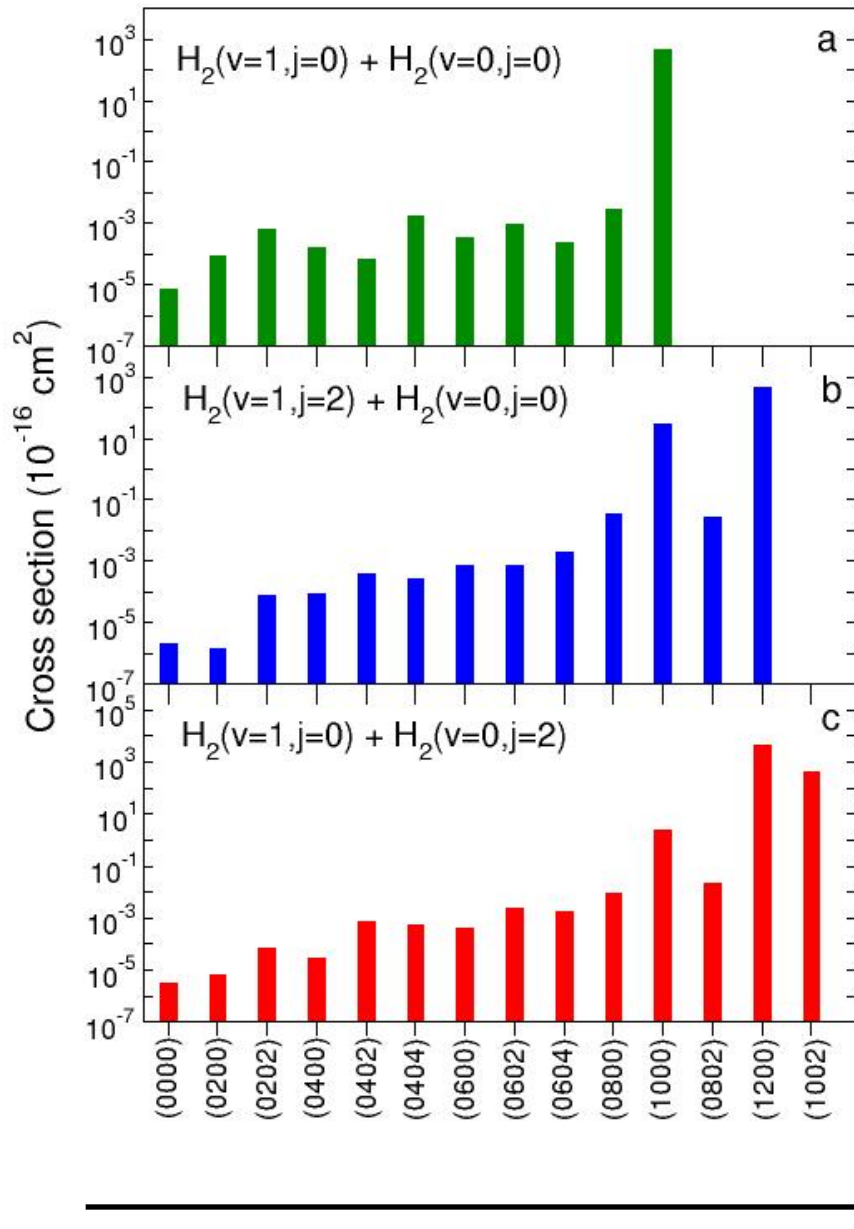


# Ultracold Molecule-molecule collisions

- Molecule-molecule collisions important at high densities of trapped molecules
- Effect of vibrational and rotational excitations
- Energy & angular momentum gaps
- Quasi-resonant rotation-rotation (QRRR) and vibration-vibration (QRVV) transitions

# Quasi-resonant energy transfer

$$E_{\text{coll}} = 10^{-6} \text{ K}$$



2 conditions :

- propensity to conserve the internal energy of the 2 molecules

$$\epsilon_a^i + \epsilon_b^i \approx \epsilon_a^f + \epsilon_b^f$$

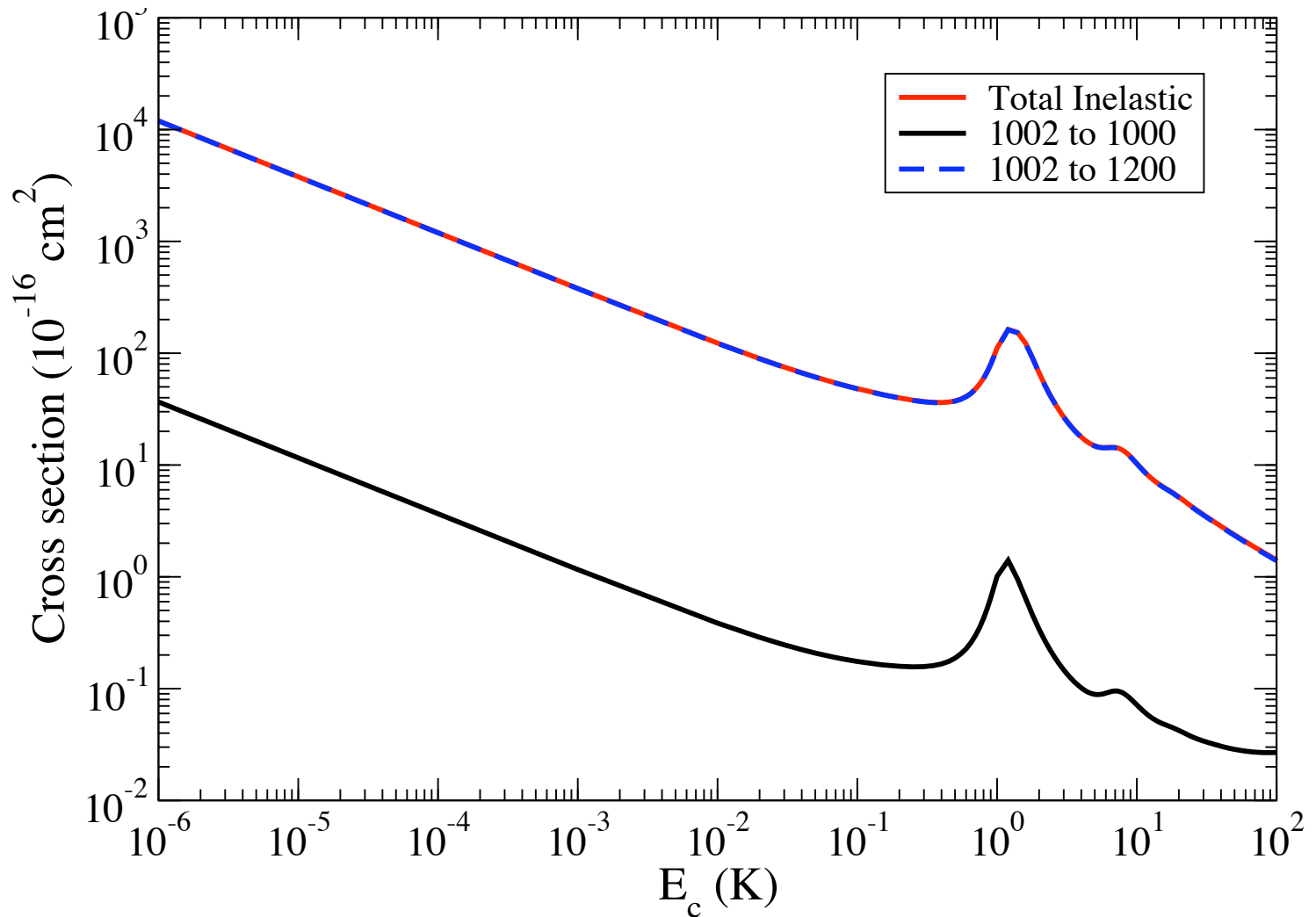
$$\Delta \epsilon \approx 0$$

- propensity to conserve the total rotational angular momentum

$$\mathbf{j}_{ab}^i = \mathbf{j}_{ab}^f$$

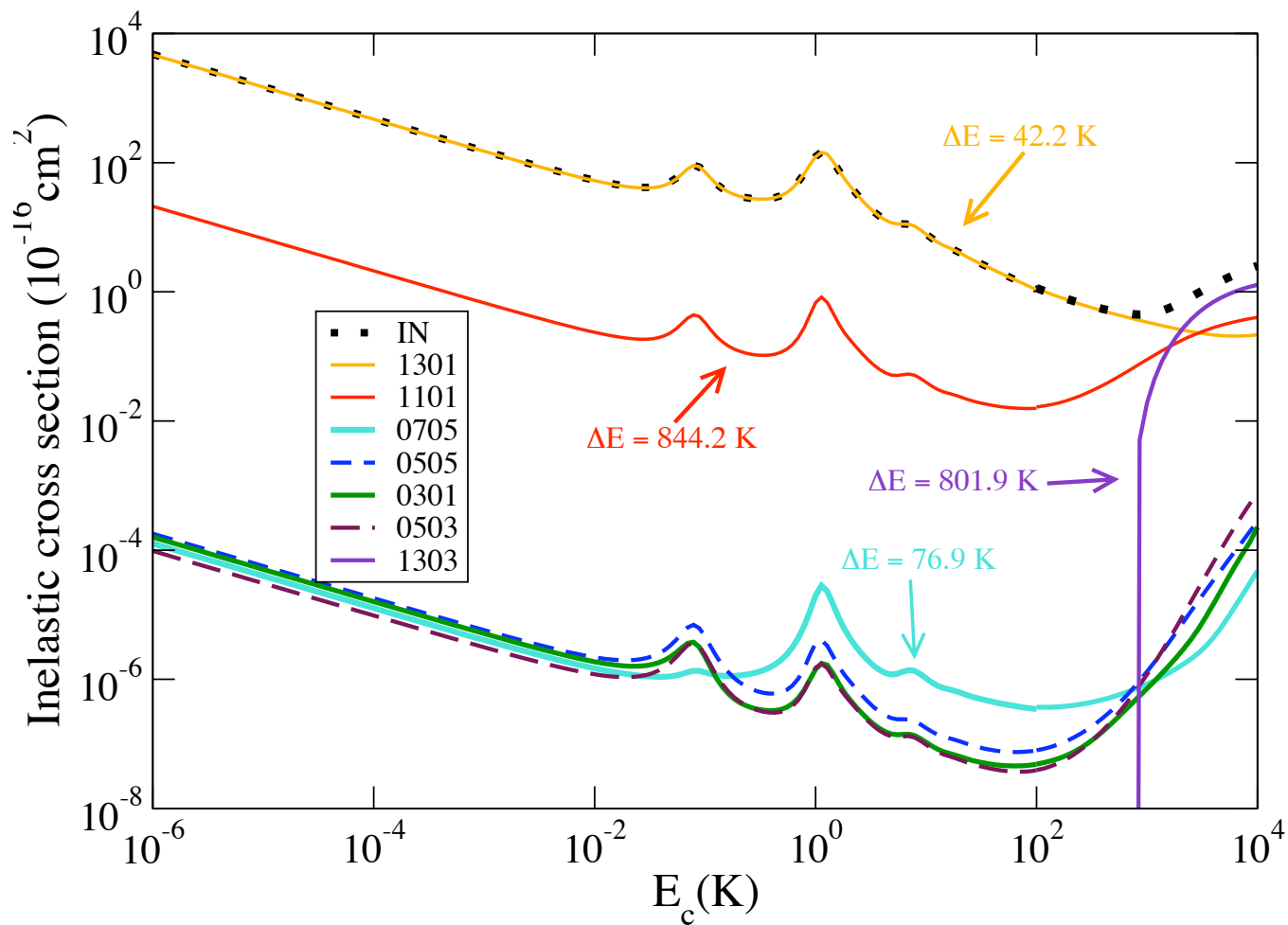
$$\Delta \mathbf{j}_{ab} = 0$$

# QRRR transitions dominate the total inelastic cross sections

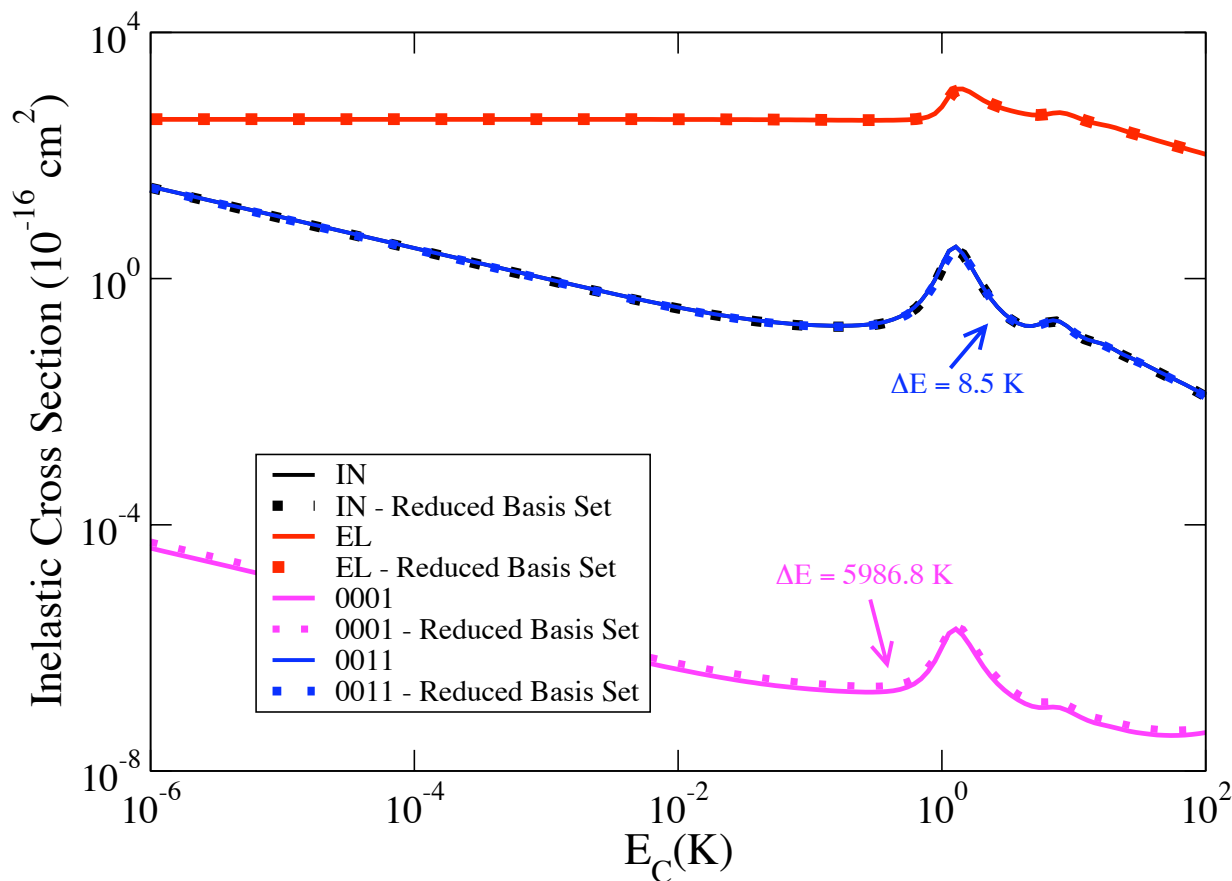
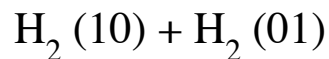


# Ortho-ortho case

$\text{H}_2(11) + \text{H}_2(03)$



# Reduced basis set calculations: Ortho-para case



Dotted curves – results with reduced basis set that only includes quasi-resonant channels

Solid curves – results with a full basis set that only includes all channels needed for converged results