Oxygen Chemistry in the Interstellar Medium

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Outline

- **Overview of molecular calculations of interest in Astrophysical Modeling**
- **Oxygen Chemistry in the interstellar medium**

  - The role of vibrational excitation of H_2 in $O(^3P)+H_2$ reaction
- **Summary and Conclusions**

Collisional Systems of Astrophysical interest

He-H_2

He-CO

H-CO

H+H_2 – work in progress

H_2+H_2 - work in progress

He-H_2 rovibrational calculations

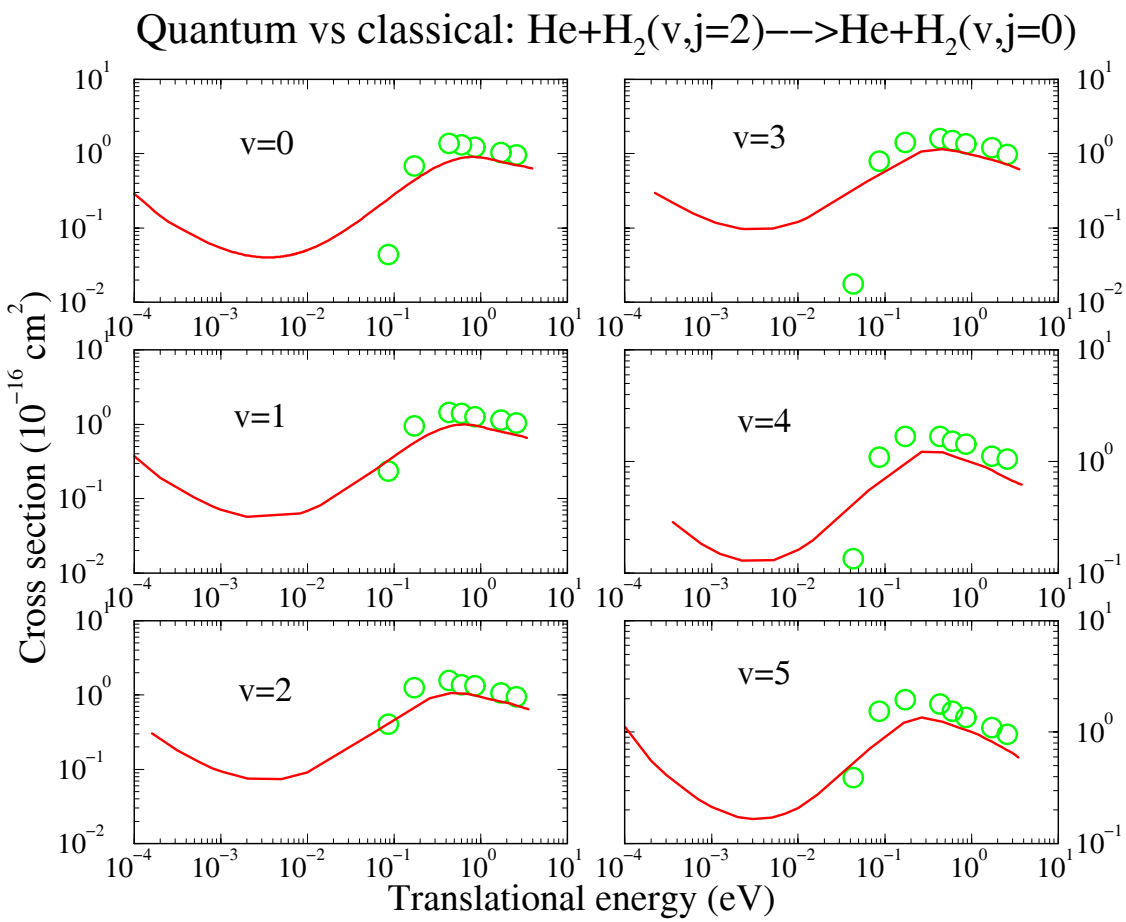
Rovibrational transition rate coefficients reported for v=0-6, j=0-11 of H_2

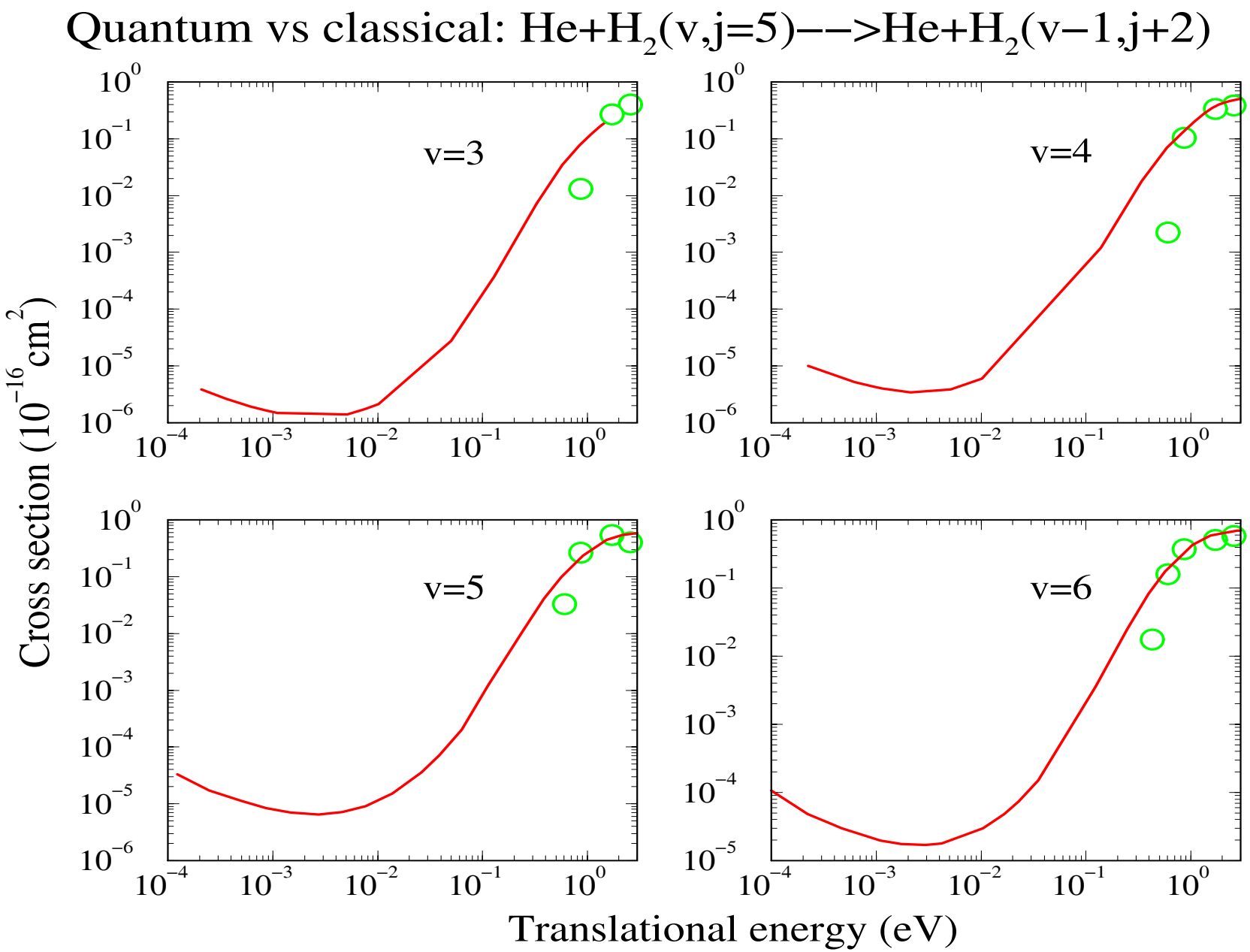
Balakrishnan, Forrey and Dalgarno, ApJ, 514, 520 (1999)

Balakrishnan et al., ApJ, 524, 1122 (1999)

Potential energy surface: Muchnick and Russek (J. Chem. Phys. 100, 4336 (1994)).

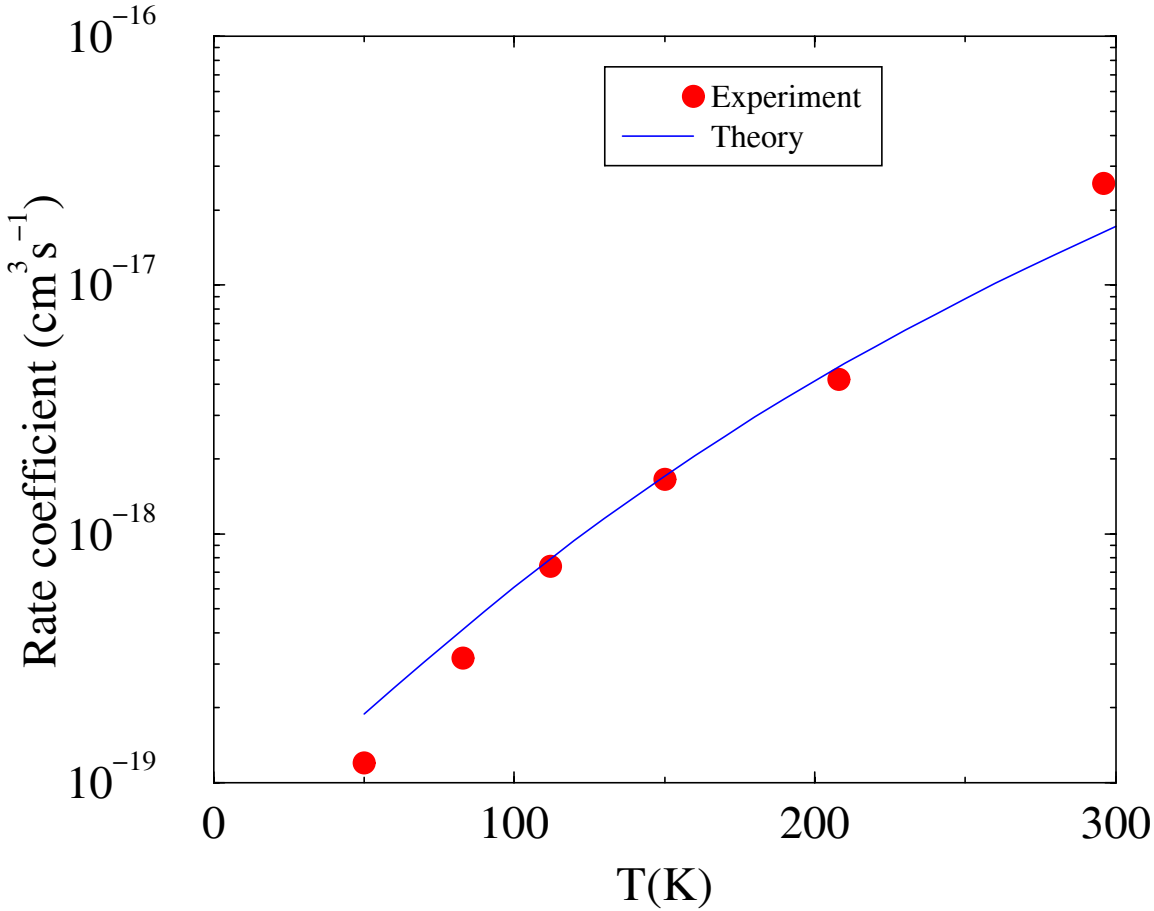
Quantum vs Classical Dynamics




Quantum vs classical: He+H2(v,j=5)-->He+H2(v-1,j+2)
v=3
v=4
v=5
v=6
Cross section (10^-16 cm^2)
Translational energy (eV)

He-H_2 vibrational relaxation collisions

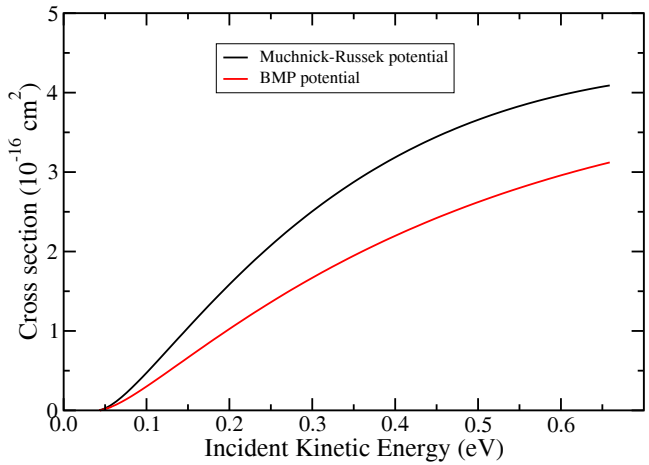
$He+H_2(v=1) \dashrightarrow He+H_2(v=0)$



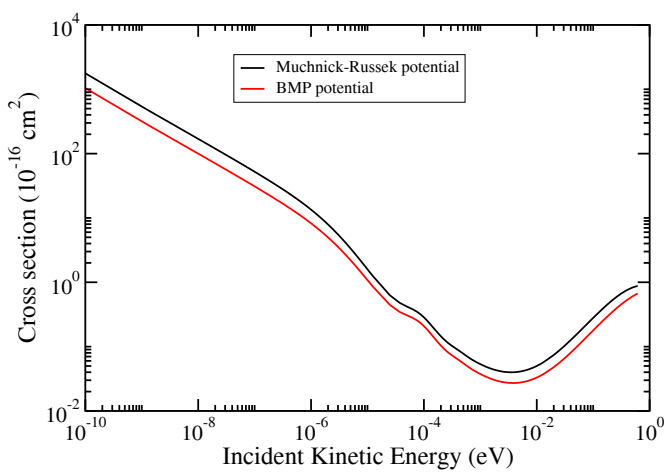
Experimental data from: Audibert et al. Chem. Phys. Lett. 37, 408 (1976)

He-H_2 rotational transitions: sensitivity of results to PES

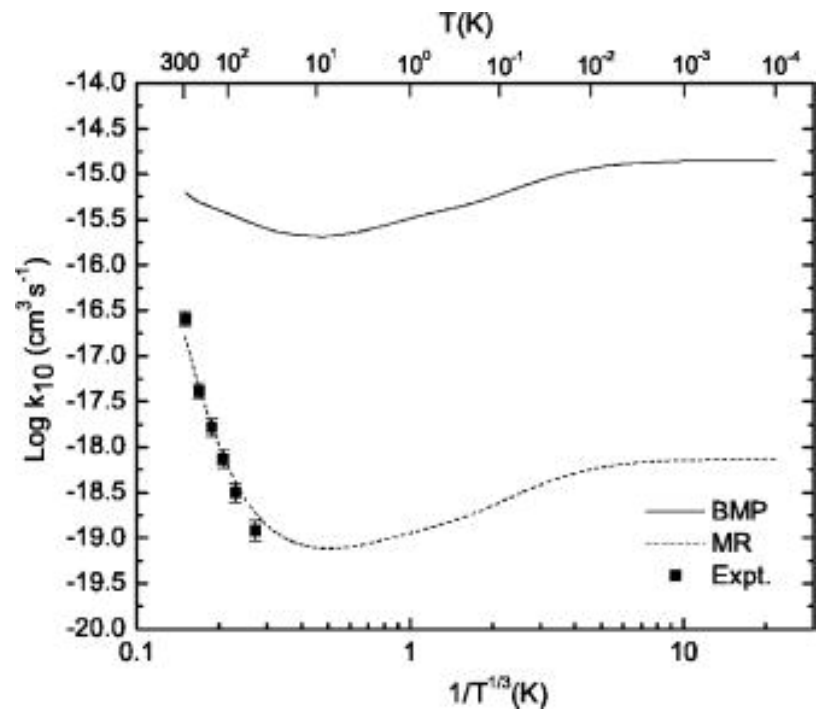
He+H_2(j=0)→He+H_2(j=2)



He+H_2(j=2)→He+H_2(j=0)

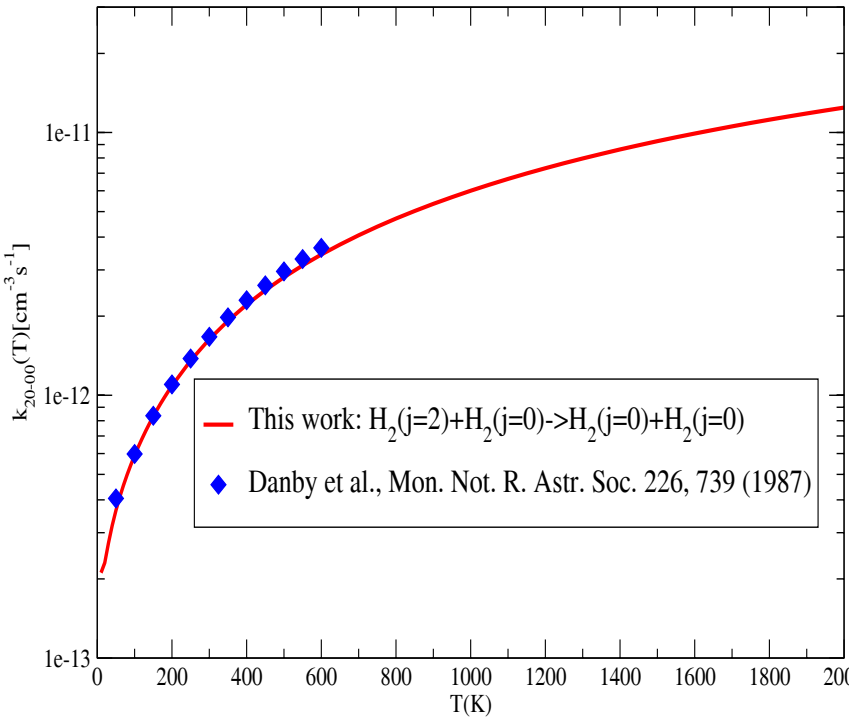


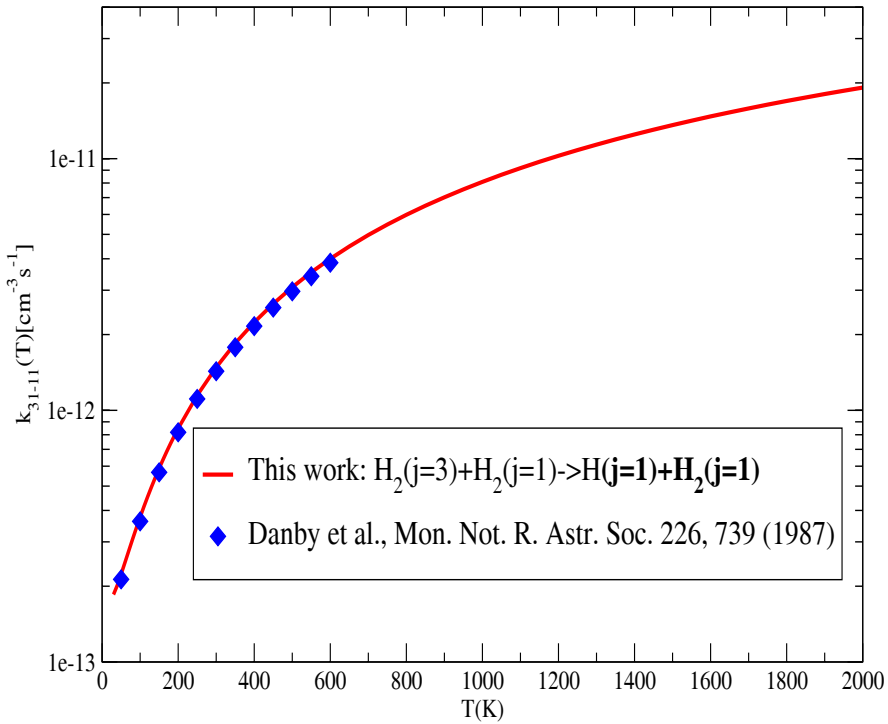
He+H_2(v=1)→He+H_2(v=0)
Teck et al., JCP 122, 024307 (2005)



Muchnick and Russek, J. Chem. Phys. 100, 4336 (1994)
Boothroyd, Martin & Peterson, J. Chem. Phys. 119, 3187 (2003)

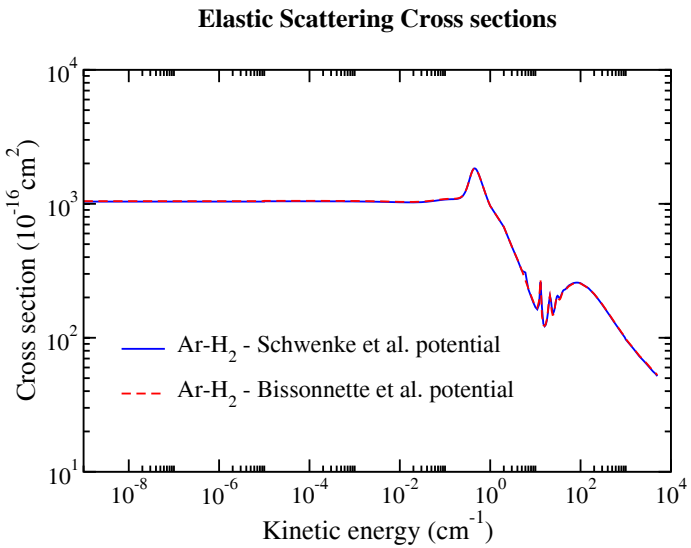
H_2-H_2 Rotational Transition Collisions

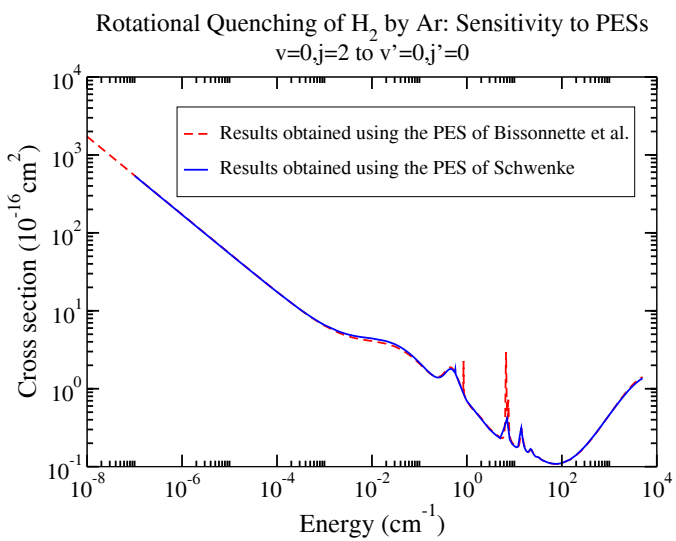


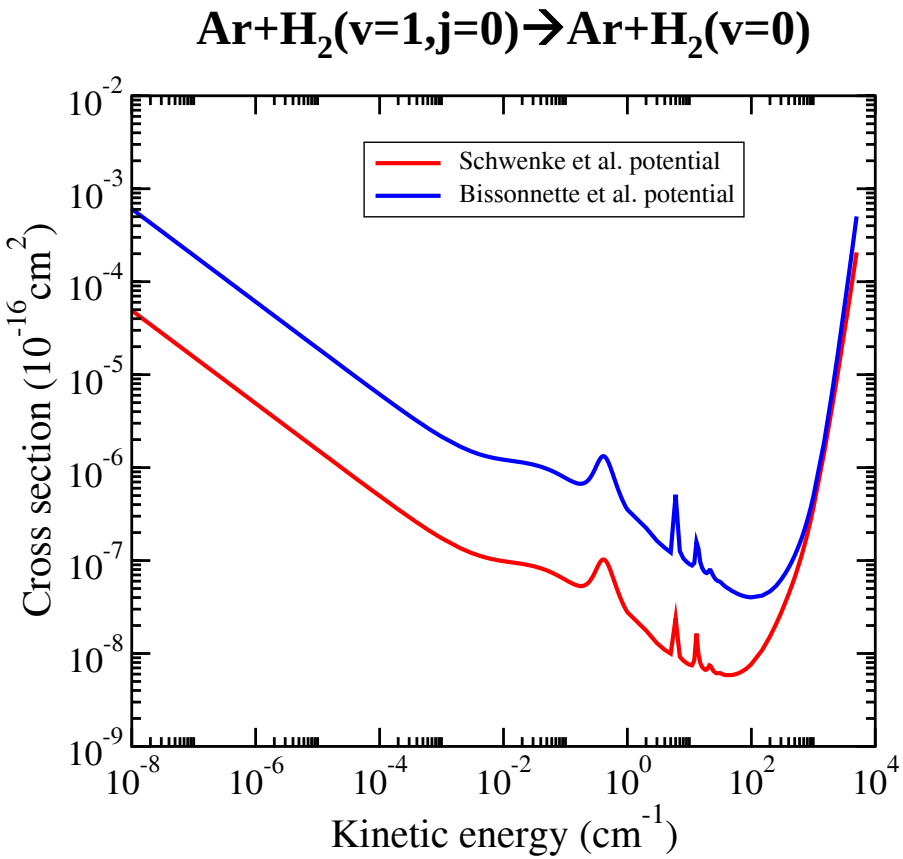


PES used in the present work: Diep and Johnson, J. Chem. Phys. 112, 4465 (2000)

Ar-H, rovibrationa





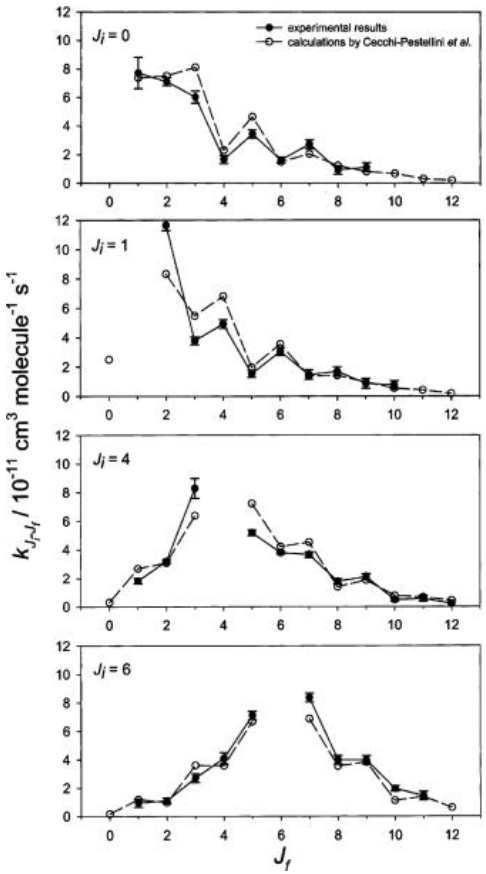


chwenke et al., J. Chem. Phys. 98, 4738 (1993)
issonnette et al., J. Chem. Phys. 105, 2639 (1996).

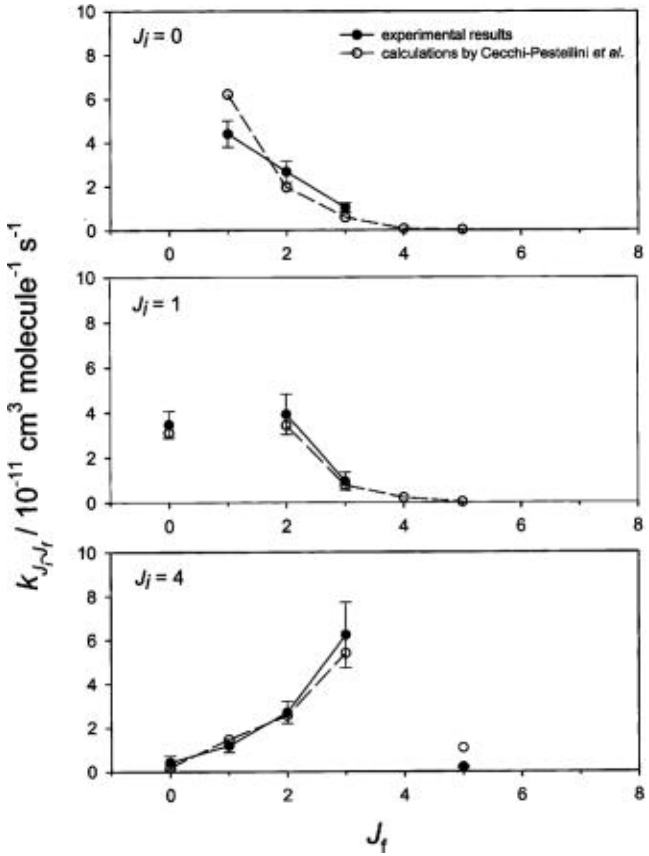
He-CO system

He+CO(v=2,j_i)→He+CO(v=2,j_f)

294 K

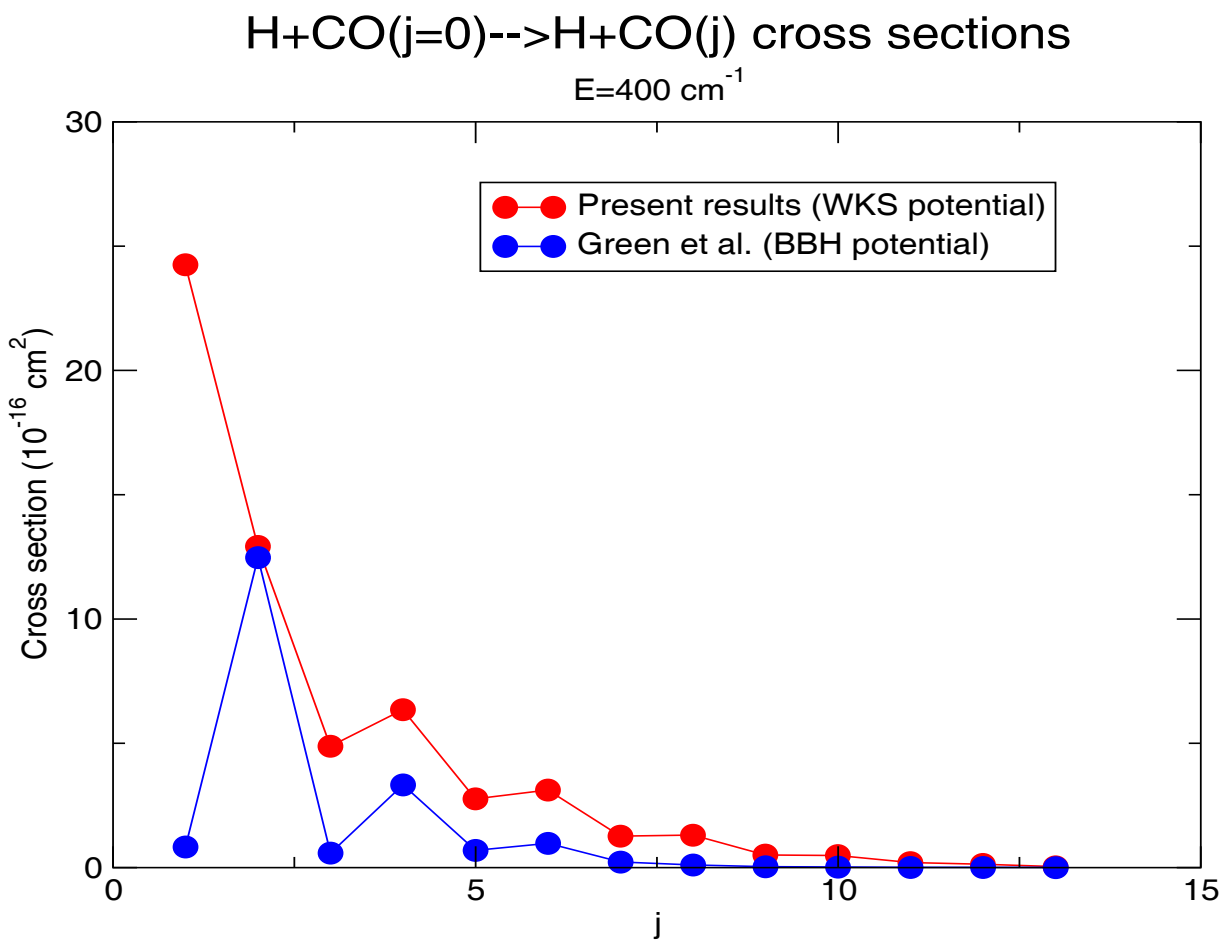


15 K



Calculations: Cecchi Pestellini, Bodo, Balakrishnan and Dalgarno, ApJ 571, 1015 (2002)
Experiment: Carty et al. J. Chem. Phys. 121, 4671 (2004).

H+CO collisions: Sensitivity of results to details of the interaction potential



Present work: Balakrishnan, Yan & Dalgarno, ApJ, 568, 443 (2002)
Green et al., J. Chem. Phys. 102, 8800 (1995).

Oxygen Chemistry in the interstellar medium

- In shock heated gases, oxygen chemistry begins with the reaction $O+H_2 \rightarrow OH+H$
- The reaction has a substantial energy barrier (~0.4 eV)
- Vibrational excitation of H_2 may have a significant effect on reactivity
- Accurate calculations of the rate coefficients for $O+H_2(v)$ for $v>0$ are not available

Dominant Oxygen-hydrogen reactions in shock heated gas

$$H + OH \rightarrow O + H_2$$

$$OH + H_2 \rightarrow H_2O + H$$

$$H + H_2O \rightarrow OH + H_2$$

$$OH + OH \rightarrow H_2O + O$$

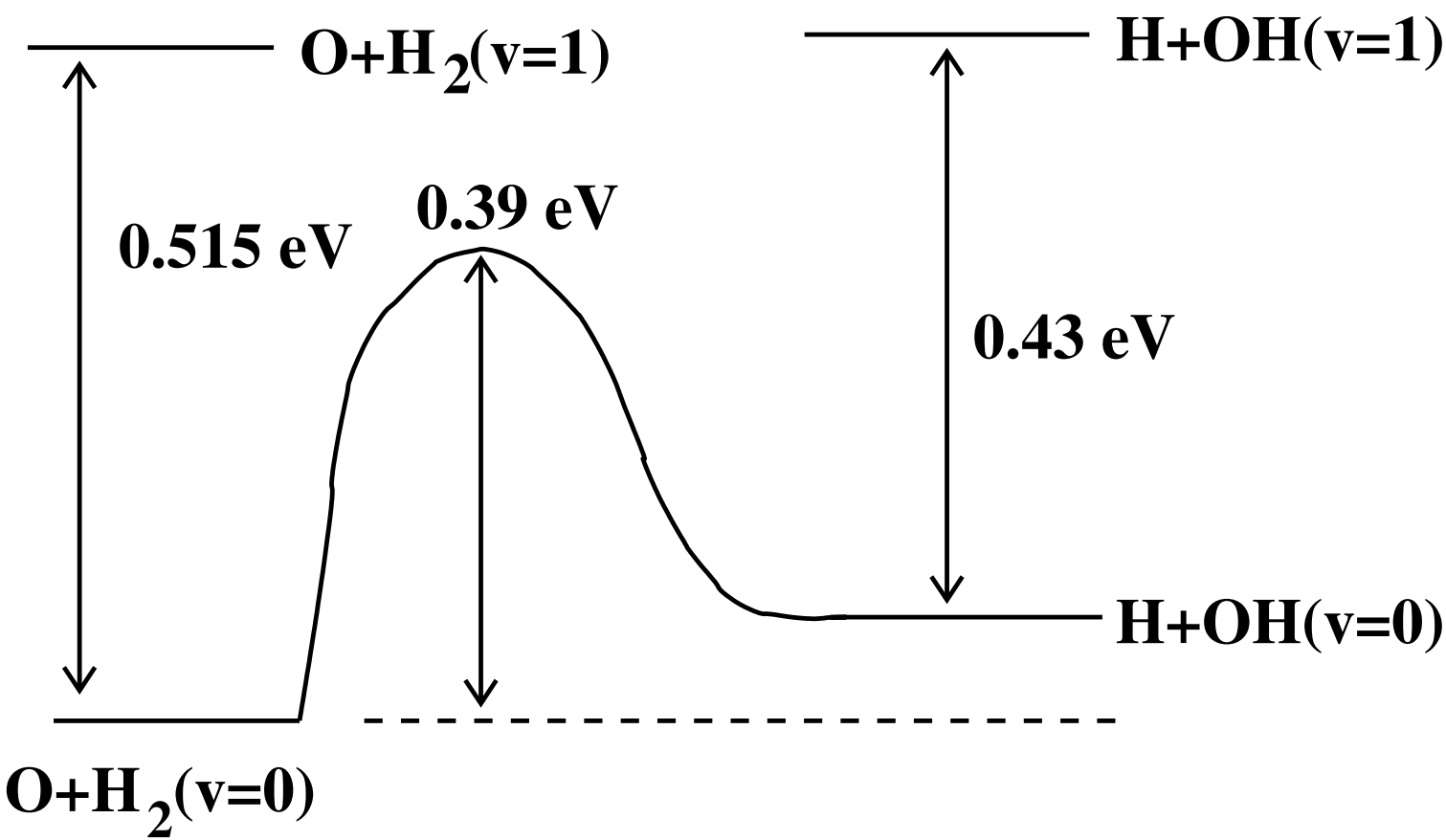
$$O + H_2O \rightarrow OH + OH$$

$$O + OH \rightarrow O_2 + H$$

$$H + O_2 \rightarrow OH + O$$

Ref: Wagner and Graf, ApJ 317, 423 (1987)
Graf and Dalgarno, ApJ 317, 432 (1987)

Energy level diagram of the $O+H_2$ (v=0,1) reaction



$O+H_2$ Calculations

- Chemically accurate potential energy surfaces available (Rogers et al. J. Phys. Chem. A 104, 2308 (2000)).
- Full Quantum calculations reported for the v=0 reaction (Balakrishnan, JCP 121, 6346 (2004)).
- J-shifting approximation works extremely well.

J-shifting approximation

$$\sigma_{vj}(E_{kin}) = \frac{\pi}{k_{vj}^2(2j+1)} \sum_J (2J+1) P_{vjJ}^{\neq}(E_{kin})$$

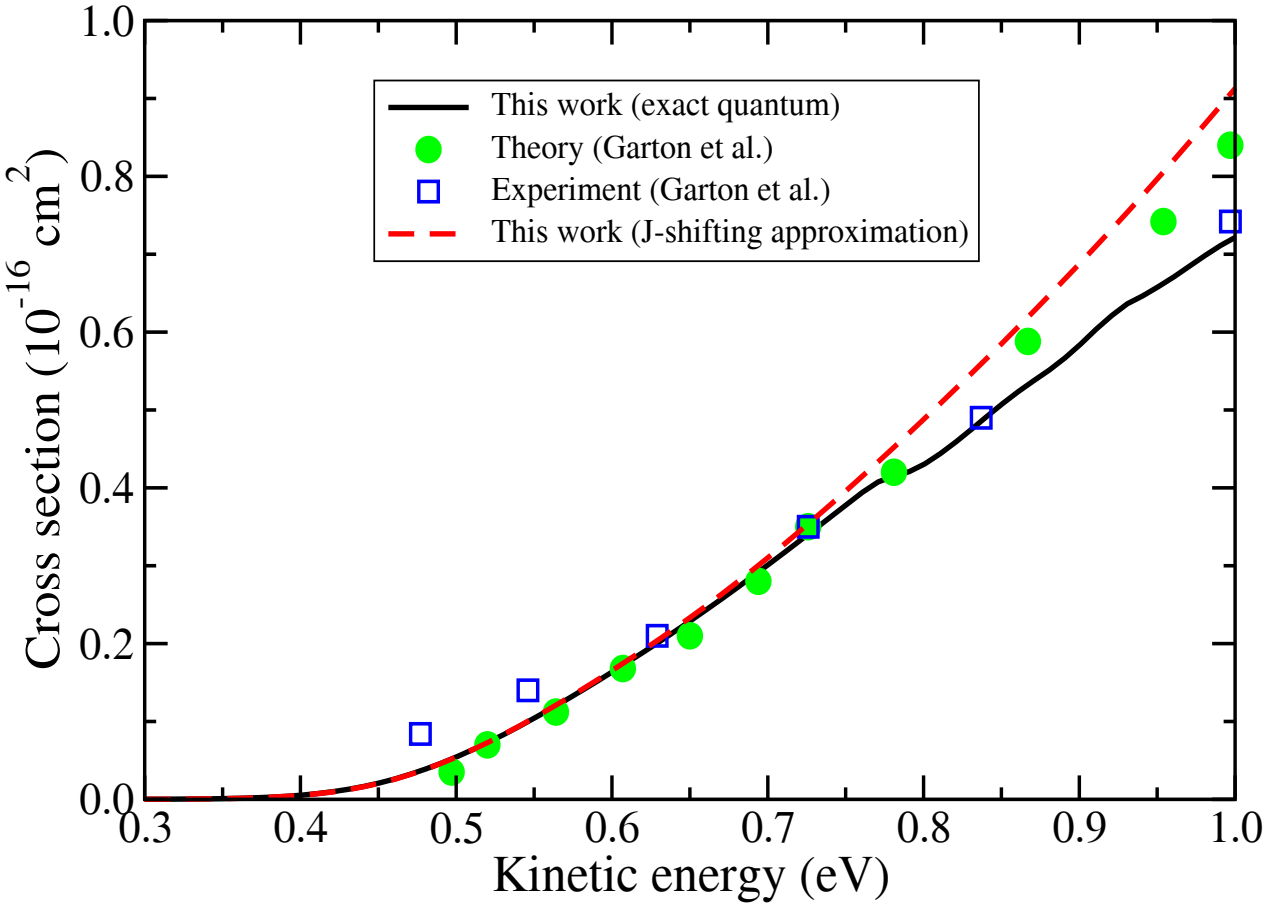
$$P_{vjJ}^{\neq}(E_{kin}) = P_{vjJ=0}^{\neq}(E_{kin} - E_J^{\neq})$$

$$E_J^{\neq} = B^{\neq} J(J+1)$$

For O+H_2 reaction, the transition state is linear

J-shifting approximation: J. M. Bowman, J. Phys. Chem. 95, 4412 (1991)

$O+H_2$ reaction cross sections:



Balakrishnan, J. Chem. Phys. 121, 6346 (2004)
Garton et al., J. Chem. Phys. 118, 1585 (2003)

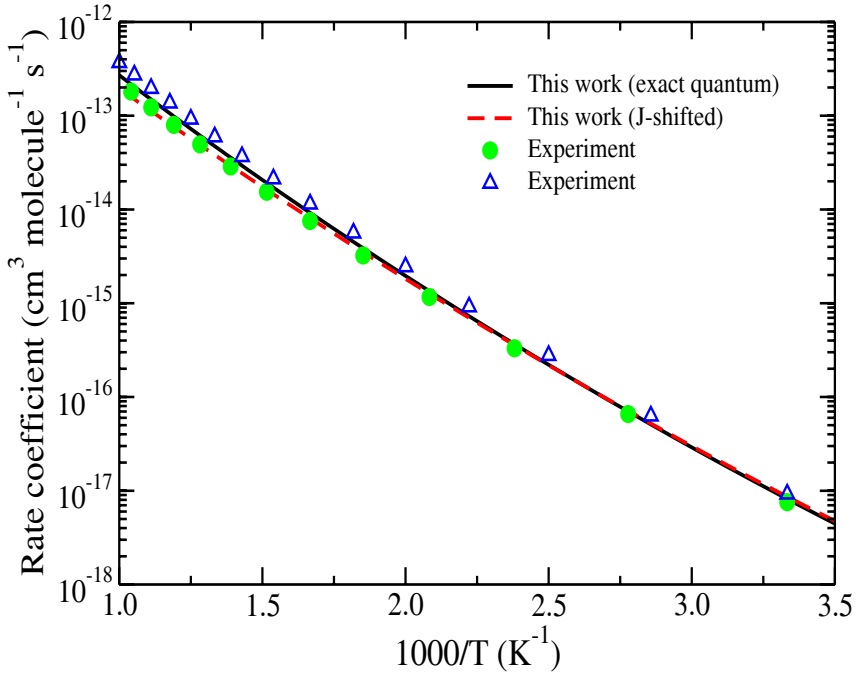
Thermal rate coefficients

$$k(T) = \frac{\int_{-\infty}^{+\infty} dE \exp(-E/k_B T) N(E)}{2\pi\hbar Q_R(T)}$$

$$N(E) = \sum_J (2J+1) N_J(E)$$

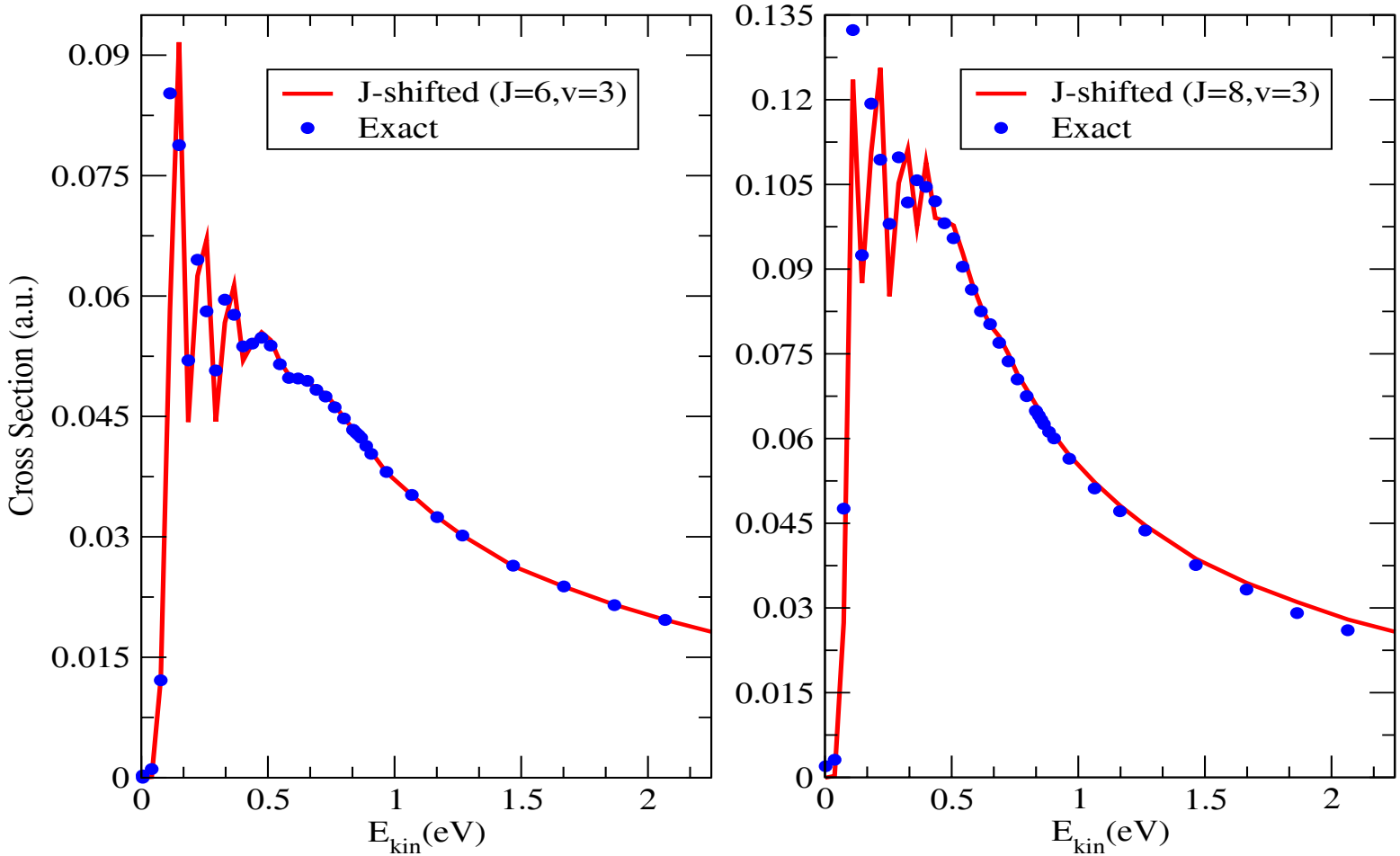
$$N_J(E) = \sum_{vjk,v'j'k'} \left| S^J_{v'j'k',vjk} \right|^2$$

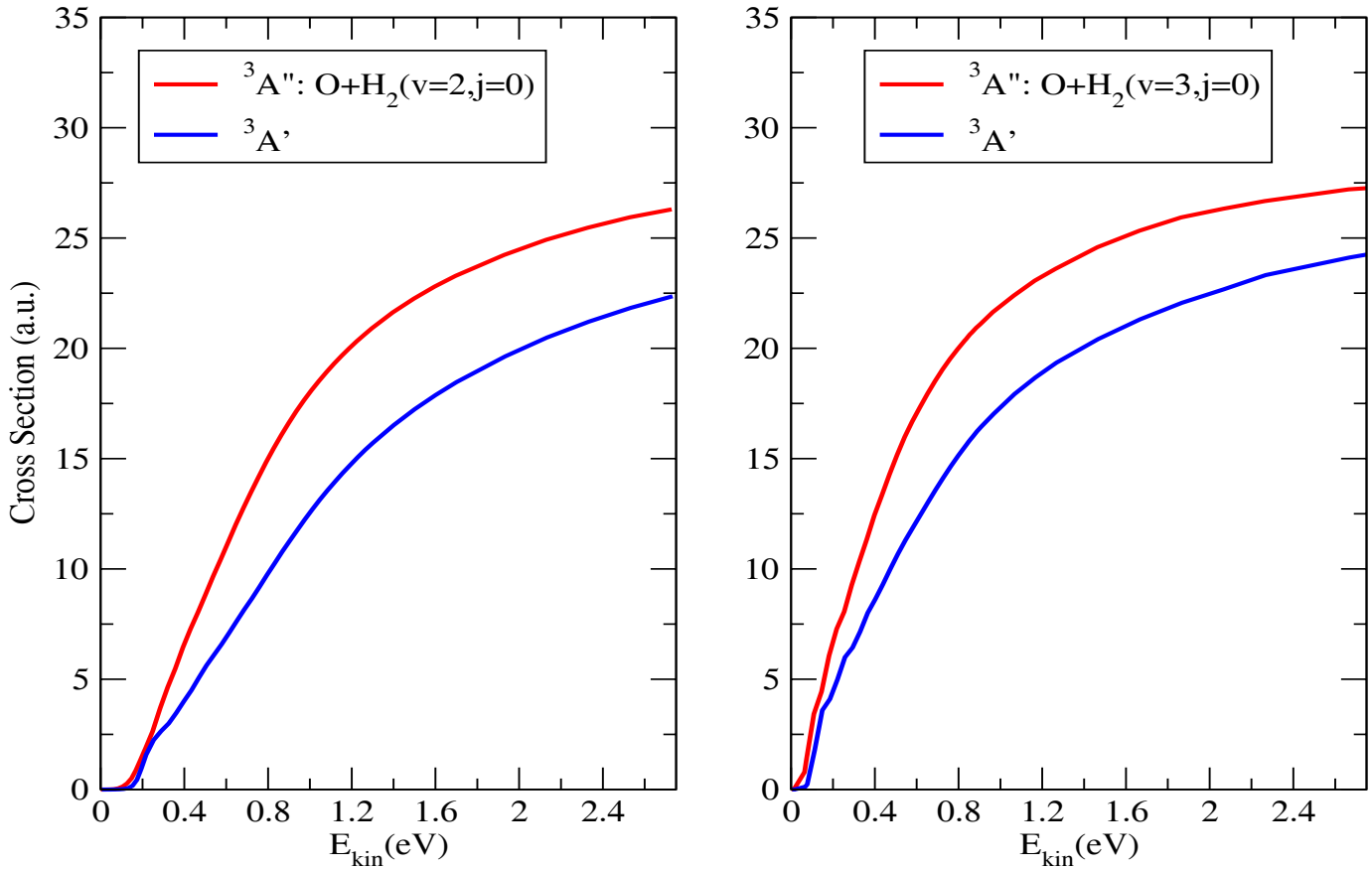
$$Q_R(T) = Q_{trans}(T) Q_{vib}(T) Q_{rot}(T)$$



Balakrishnan, J. Chem. Phys. 121, 6346 (2004)

O+H$_2$(v) Reaction – Test of the J-shifting

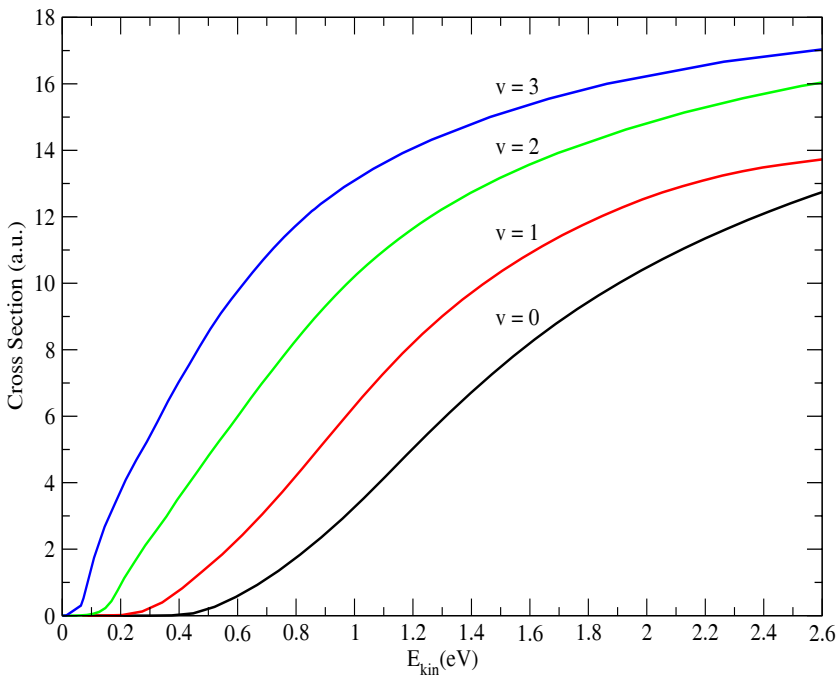




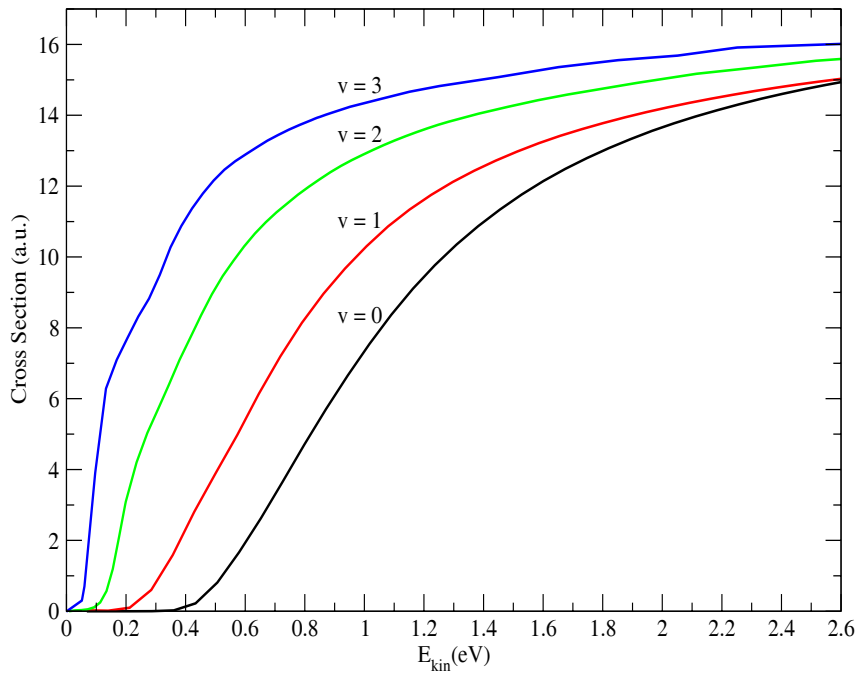
$$k(T) = \frac{1}{3}\left(k(^3A') + k(^3A'')\right)$$

$O+H_2$ reaction: the effect of vibrational excitation of H_2

$O+H_2(v,j=0)$



$O+H_2(v,j=1)$



R. A. Sultanov and N. Balakrishnan, ApJ (in press).

Rate coefficients for $O+H_2(v)$ reaction

T(K)	v=0	v=1	v=2	v=3
100	5.94E-25	3.38E-18	1.83E-15	5.36E-14
200	1.05E-20	2.00E-16	2.05E-14	6.10E-13
300	2.27E-18	2.64E-15	1.28E-13	2.14E-12
500	7.40E-16	6.15E-14	1.04E-12	7.57E-12
1000	1.50E-13	1.55E-12	8.54E-12	2.75E-11
2000	4.14E-12	1.42E-11	3.84E-11	7.65E-11
3000	1.64E-11	3.83E-11	7.76E-11	1.28E-10
4000	3.63E-11	6.92E-11	1.19E-10	1.77E-10

Comparisons between rate coefficients obtained assuming thermal and statistical equilibrium of ortho and para-H_2

Rate coefficients assuming thermal equilibrium between Ortho and para H_2

$$k_v^t(T) = \frac{\sum_{j=0,2,4,..} Q_j k_{vj}^{para}(T) + 3\sum_{j=1,3,5,..} k_{vj}^{ortho}(T)}{Q_{para} + 3Q_{ortho}}$$

$$Q_j = (2j+1)\exp(-E_j / k_B T)$$

$$Q_{para} = \sum_{j=0,2,4,..} Q_j$$

$$Q_{ortho} = \sum_{j=1,3,5,..} Q_j$$

Rate coefficients assuming statistical Equilibrium between ortho and para H_2

$$k_v^s(T) = \frac{1}{4}k_v^{para}(T) + \frac{3}{4}k_v^{ortho}(T)$$

T(K)	$k^t_{v=2}$	$k^s_{v=2}$
100	2.17E-15	4.87E-15
200	1.43E-14	1.40E-14
300	5.17E-13	3.49E-13
500	3.78E-12	2.67E-12
1000	2.36E-11	1.81E-11
2000	8.50E-11	6.48E-11
3000	1.51E-10	1.14E-10
4000	2.11E-10	1.61E-10

Conclusions

- Quantum Calculations have been carried out for a number of molecular systems of interest in astrophysical environments
- Determination of accurate molecular potentials is still a key issue
- Non-equilibrium chemistry may play an important role in astrophysical environments

Acknowledgements

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