

Seminar at Dalian Institute of Chem.
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**Quantum dynamics scattering study of AB+CDE reactions: A
seven-dimensional treatment for the $\text{H}_2+\text{C}_2\text{H}$ reaction**

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Quantum dynamics scattering study of AB+CDE reactions: a seven dimensional treatment for the H₂+C₂H reaction

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Abstract

A time-dependent wave-packet approach is presented for the quantum dynamics study of the AB+CDE reaction system for zero total angular momentum. A seven-degree-of-freedom calculation is employed to study the chemical reaction of H₂+C₂H → H + C₂H₂ by treating C₂H as a linear molecule. Initial state selected reaction probabilities are presented for various initial ro-vibrational states. This study shows that vibrational excitation of H₂ enhances the reaction probability, whereas the excitation of C₂H has only a small effect on the reactivity. An integral cross section is also reported for the initial ground states of H₂ and C₂H. The theoretical and experimental results agree with each other very well when the calculated seven dimensional results are adjusted to account for the lower transition state barrier heights found in recent *ab initio* calculations.

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INTRODUCTION

- Developments of quantum dynamics scattering calculations
 - First quantum dynamics calculation on H+H₂ system^a
 - First 3D quantum dynamics calculation on H+H₂ in 1976^b
 - First 6D quantum dynamics calculation on H₂+OH in 1994^c
- During the past two decades, quantum scattering theories well developed for 3 and 4 atom systems
- Now dynamics calculations compete with experiment in their accuracy
 - H+D₂^d and F+H₂^e give the same results as experiments
 - Some properties of H+H₂O, D₂O^f

^a F.Z. London, *Elektrochem.* **35**, 532 (1929); H. Eyring, and M.Z. Polani, *Phys. Chem.* (Munich), **B12**, 279 (1931).

^b G.C. Schatz and A. Kuppermann, *J. Chem. Phys.* **65**, 4642 (1976).

^c D.H. Zhang and J.Z.H. Zhang, *J. Chem. Phys.* **101**, 1146 (1994); D. Neuhauser, *J. Chem. Phys.* **100**, 9272 (1994).

^d M.P. de Miranda, D.C. Clary, J.F. Castillo and D.E. Manolopoulos, *J. Chem. Phys.* **108**, 3142 (1998).

^e D.E. Manolopoulos, *J. Chem. Soc., Faraday Trans.* **93**, 673 (1997).

^f D.H. Zhang, M.A. Collins and S.-Y. Lee, *Science* **290**, 961 (2000).

INTRODUCTION

- More than 4 atom systems – quantum dynamics computations still a formidable task.
 - almost all the calculations are reduced dimensional
 - a full dimensional quantum dynamics study for the H+CH₄^g
 - no full dimensional quantum dynamics been done on 5 atom systems
- Why study H₂+C₂H?
 - C₂H is one of the most abundant interstellar polyatomic molecules detected^h
 - found in Titan and Jupiter's atmospheresⁱ
 - dominant chain carrier to form acetylene
 - hydrocarbon reactions provide disequilibrium species
 - only 4D calculations available for this reaction ^{j,k}
 - PES of Wang and Bowman^j

^g F. Huarte-Larrañaga and U. Manthe, *J. Chem. Phys.* **113**, 5115 (2000); *J. Chem. Phys.* **116**, 2863 (2002).

^h K.D. Tucker, M.L. Kuther and P. Thaddeus, *Astrophys. J.* **L115**, 193 (1974).

ⁱ D.F. Strobel, *Planet. Space Sci.* **30**, 839 (1982); G.R. Gladstone, M. Allen and Y.L. Yung, **119**, 1 (1996).

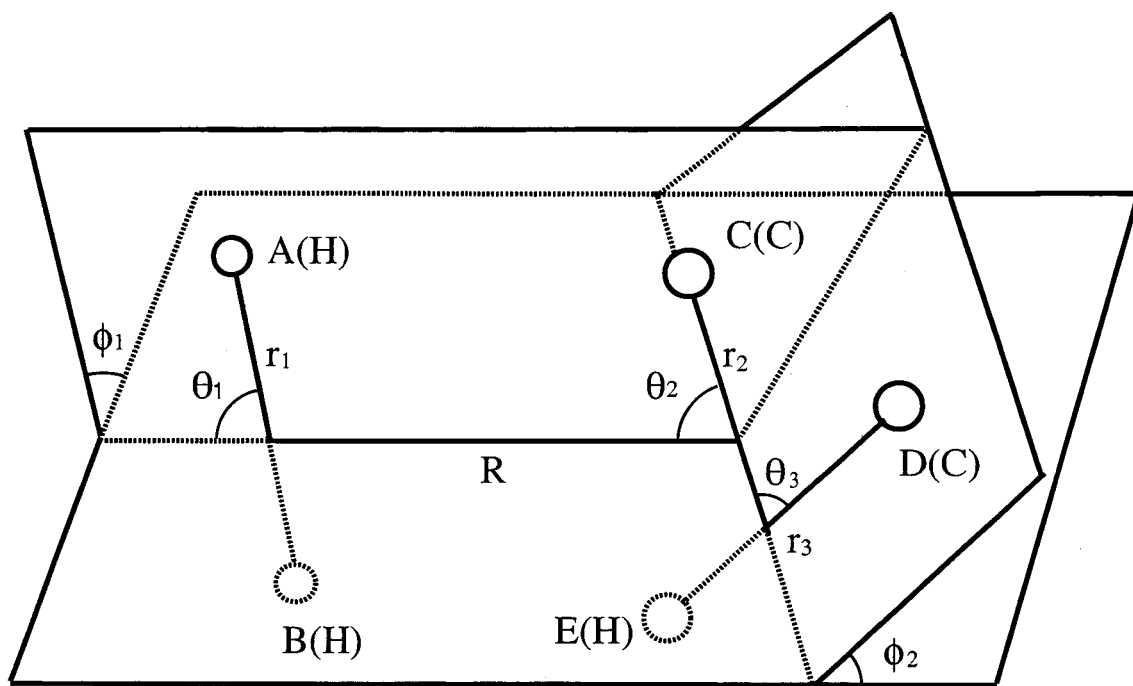
^j D. Wang and J.W. Bowman, *J. Chem. Phys.* **101**, 8646 (1994).

^kH. Szichman, M. Gilibert, M. González, X. Giménez, and A. Navarro, *J. Chem. Phys.* **113**, 176 (2000); *ibid*, *J. Chem. Phys.* **114**, 9882 (2001).

THEORETICAL METHODS

4

- Jacobi coordinates for the reaction AB+CDE



- Full-dimensional Hamiltonian

$$\begin{aligned}
 H = & -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{(\mathbf{J} - \mathbf{j}_{123})^2}{2\mu R^2} + h_{r_1}(r_1) + h_{r_2}(r_2) + h_{r_3}(r_3) + \frac{\mathbf{j}_1^2}{2\mu_1 r_1^2} \\
 & + \frac{\mathbf{j}_2^2}{2\mu_2 r_2^2} + \frac{\mathbf{j}_3^2}{2\mu_3 r_3^2} + V(R, r_1, r_2, r_3, \theta_1, \theta_2, \theta_3, \phi_1, \phi_2).
 \end{aligned} \tag{1}$$

THEORETICAL METHODS

- 1D vibrational reference Hamiltonians

$$h_{r_i}(r_i) = -\frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V_{1D}(r_i), i = 1, 2, 3 \quad (2)$$

- Total angular momentum function of $\mathbf{j}_{23} = \mathbf{j}_2 + \mathbf{j}_3$ in BF frame

$$Y_{j_2 j_3}^{j_{23} \Omega_{23}}(\hat{r}_2, \hat{r}_3) = \sum_m D_{\Omega_{23} m}^{j_{23}}(\chi, \theta_2, \phi_2) \sqrt{\frac{2j_2 + 1}{4\pi}} \langle j_3 m j_2 0 | j_{23} m \rangle Y_{j_3 m}(\theta_3) \quad (3)$$

- Overall internal angular momentum rotational function of the AB+CDE system, $\mathbf{j}_{123} = \mathbf{j}_1 + \mathbf{j}_{23}$

$$Y_{j_1 j_{23}}^{j_{123} K}(\hat{r}_1, \hat{r}_2, \hat{r}_3) = \sum_{\Omega_{23}} \langle j_1 K - \Omega_{23} j_{23} \Omega_{23} | j_{123} K \rangle Y_{j_1 K - \Omega_{23}}(\theta_1, \phi_1) \times Y_{j_2 j_3}^{j_{23} \Omega_{23}}(\hat{r}_2, \hat{r}_3) \quad (4)$$

- TD wavefunction expanded in terms of the BF rovibrational eigenfunctions

$$\Psi_{\nu j K}^{JM\epsilon} = \sum_{n\nu_1\nu_2\nu_3 j_1 j_2 j_3 K} F_{n\nu_1\nu_2\nu_3 j_1 j_2 j_3 K, \nu j K}^{JM\epsilon}(t) \mu_n^\nu(R) \phi_{\nu_1}(r_1) \phi_{\nu_2}(r_2) \phi_{\nu_3}(r_3) \times Y_{j_1 j_2 j_3}^{JM\epsilon}(R, \hat{r}_1, \hat{r}_2, \hat{r}_3) \quad (5)$$

THEORETICAL METHODS

- Relationship between the SF rotational basis function $y_{j_1 j_2 j_3 j_{123} L}^{JM}(\hat{R}', \hat{r}'_1, \hat{r}'_2, \hat{r}'_3)$ and BF rotational function $Y_{j_1 j_2 j_3 j_{123} K}^{JM}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3)$

$$\begin{aligned}
 Y_{j_1 j_2 j_3 j_{123} K}^{JM}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3) &= \sum_L \sqrt{\frac{2L+1}{2J+1}} \langle j_{123} K L 0 | J K \rangle \\
 &\times y_{j_1 j_2 j_3 j_{123} L}^{JM}(\hat{R}', \hat{r}'_1, \hat{r}'_2, \hat{r}'_3)
 \end{aligned} \tag{6}$$

- The SF rotational function $y_{j_1 j_2 j_3 j_{123} L}^{JM}(\hat{R}', \hat{r}'_1, \hat{r}'_2, \hat{r}'_3)$

$$\begin{aligned}
 y_{j_1 j_2 j_3 j_{123} L}^{JM}(\hat{R}', \hat{r}'_1, \hat{r}'_2, \hat{r}'_3) &= \sum_{m_j m_1 m_2} \langle j_{123} m_j L M - m_j | J M \rangle \\
 &\times \langle j_1 m_1 j_{23} m_j - m_1 | j_{123} m_j \rangle \\
 &\times \langle j_2 m_2 j_3 m_3 | j_{23} m_j - m_1 \rangle \\
 &\times y_{j_3}(\hat{r}'_3) y_{j_2}(\hat{r}'_2) y_{j_1}(\hat{r}'_1) y_L(\hat{R}')
 \end{aligned} \tag{7}$$

THEORETICAL METHODS

- Parity operator $\hat{\epsilon}$ on the BF rotational basis function gives

$$\begin{aligned}
 \hat{\epsilon} Y_{j_1 j_2 j_3 j_{123} K}^{JM}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3) &= \hat{\epsilon} \sum_L \sqrt{\frac{2L+1}{2J+1}} \langle j_{123} K L 0 | J K \rangle \\
 &\times y_{j_1 j_2 j_3 j_{123} L}^{JM}(\hat{R}', \hat{r}'_1, \hat{r}'_2, \hat{r}'_3) \\
 &= \sum_L (-1)^{j_{123}+L+J} \langle j_{123} - K L 0 | J - K \rangle \\
 &\times (-1)^{j_1+j_2+j_3+L} y_{j_1 j_2 j_3 j_{123} L}^{JM}(\hat{R}', \hat{r}'_1, \hat{r}'_2, \hat{r}'_3) \\
 &= (-1)^{j_1+j_2+j_3+j_{123}+J} Y_{j_1 j_2 j_3 j_{123} - K}^{JM}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3)
 \end{aligned} \tag{8}$$

- Parity adapted BF total angular momentum eigenfunction

$$Y_{j_1 j_2 j_3 j_{123} K}^{JM\epsilon}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3)$$

$$\begin{aligned}
 Y_{j_1 j_2 j_3 j_{123} K}^{JM\epsilon}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3) &= \sqrt{\frac{1}{2(1+\delta_{K0})}} [Y_{j_1 j_2 j_3 j_{123} K}^{JM}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3) \\
 &+ \epsilon (-1)^{(j_1+j_2+j_3+j_{123}+J)} Y_{j_1 j_2 j_3 j_{123} - K}^{JM}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3)]
 \end{aligned} \tag{9}$$

SEVEN-DIMENSIONAL TREATMENT

- 7D Hamiltonian

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{(\mathbf{J} - \mathbf{j}_{12})^2}{2\mu R^2} + h_{r_1}(r_1) + h_{r_2}(r_2) + h_{r_3}(r_3) + \frac{\mathbf{j}_1^2}{2\mu_1 r_1^2} + \frac{\mathbf{j}_2^2}{2\mu_2 r_2^2} + V_{7D}(R, r_1, r_2, r_3, \theta_1, \theta_2, \phi_1) \quad (10)$$

- $Y_{j_1 j_2 j_3 j_{12} j_{23} j_{123} K}^{JM\epsilon}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3)$ becomes two angular momentum coupling case

$$Y_{j_1 j_2 j_3 j_{12} j_{23} j_{123} K}^{JM\epsilon}(\theta_1, \theta_2, \phi_1) = \sqrt{\frac{1}{2(1 + \delta_{K0})}} [Y_{j_1 j_2 j_3 j_{12} j_{23} j_{123} K}^{JM}(\theta_1, \theta_2, \phi_1) + \epsilon(-1)^{(j_1 + j_2 + j_{12} + J)} Y_{j_1 j_2 j_3 j_{12} j_{23} j_{123} - K}^{JM}(\theta_1, \theta_2, \phi_1)] \quad (11)$$

- 7D initial wave-packet

$$\Psi_{n_0 \nu_0 j_0 K_0}(t = 0) = \Phi_{k_0}(R) \phi_{\nu_1 j_1}(r_1) \phi_{\nu_2 j_2}(r_2, r_3) Y_{j_1 j_2 j_3 j_{12} j_{23} j_{123} K_0}^{JM\epsilon} \quad (12)$$

- $\phi_{\nu_2 j_2}(r_2, r_3)$ is the eigenfunction of the two dimensional vibrational Hamiltonian

$$H = h_{r_2}(r_2) + h_{r_3}(r_3) + V_{2D}(R = \infty, r_1, r_2, r_3, \theta_1, \theta_2, \theta_3 = 0, \phi_1, \phi_2) \quad (13)$$

SEVEN-DIMENSIONAL TREATMENT

- Split-operator method to propagate the wave packet

$$\psi^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t + \Delta) = e^{-iH_0\Delta/2} e^{-iU\Delta} e^{-iH_0\Delta/2} \psi^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) \quad (14)$$

- Reference Hamiltonian H_0 defined as

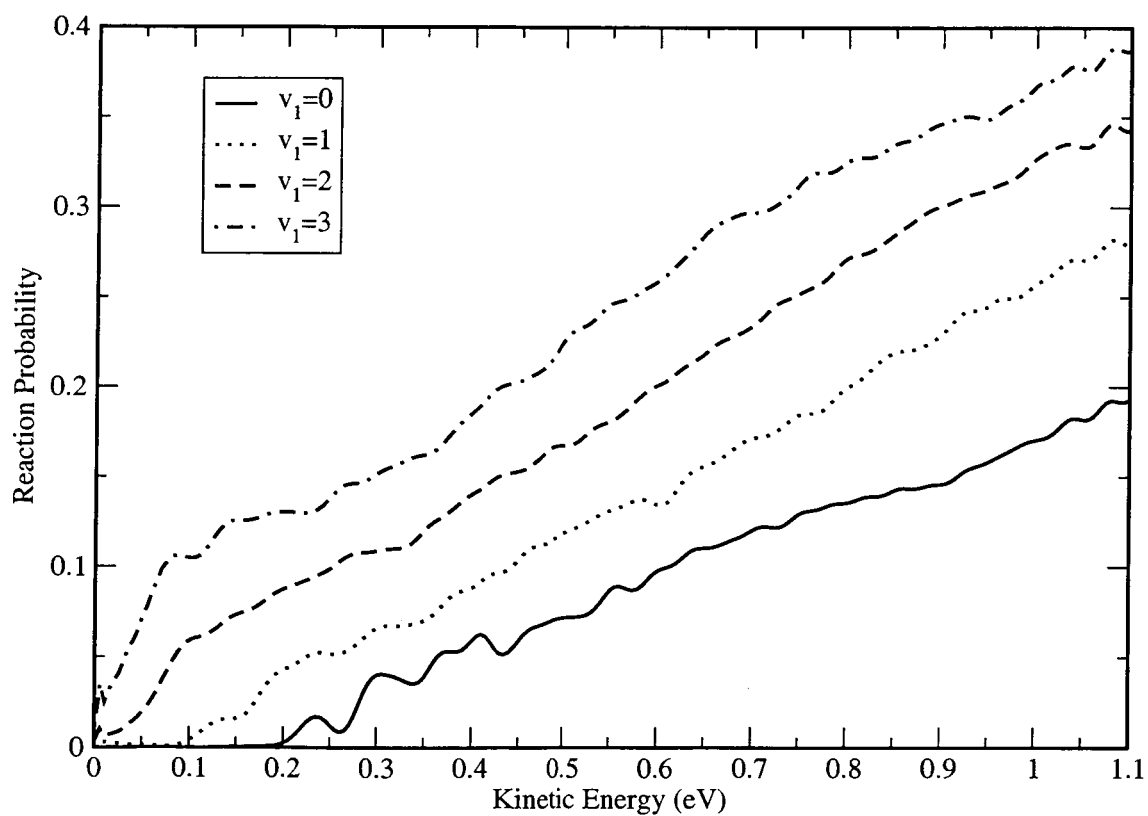
$$H_0 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + h_{r_1}(r_1) + h_{r_2}(r_2) + h_{r_3}(r_3) \quad (15)$$

- Effective potential operator

$$U = \frac{(\mathbf{J} - \mathbf{j}_{12})^2}{2\mu R^2} + \frac{\mathbf{j}_1^2}{2\mu_1 r_1^2} + \frac{\mathbf{j}_2^2}{2\mu_2 r_2^2} + V_{7D}(R, r_1, r_2, r_3, \theta_1, \theta_2, \phi_1) \quad (16)$$

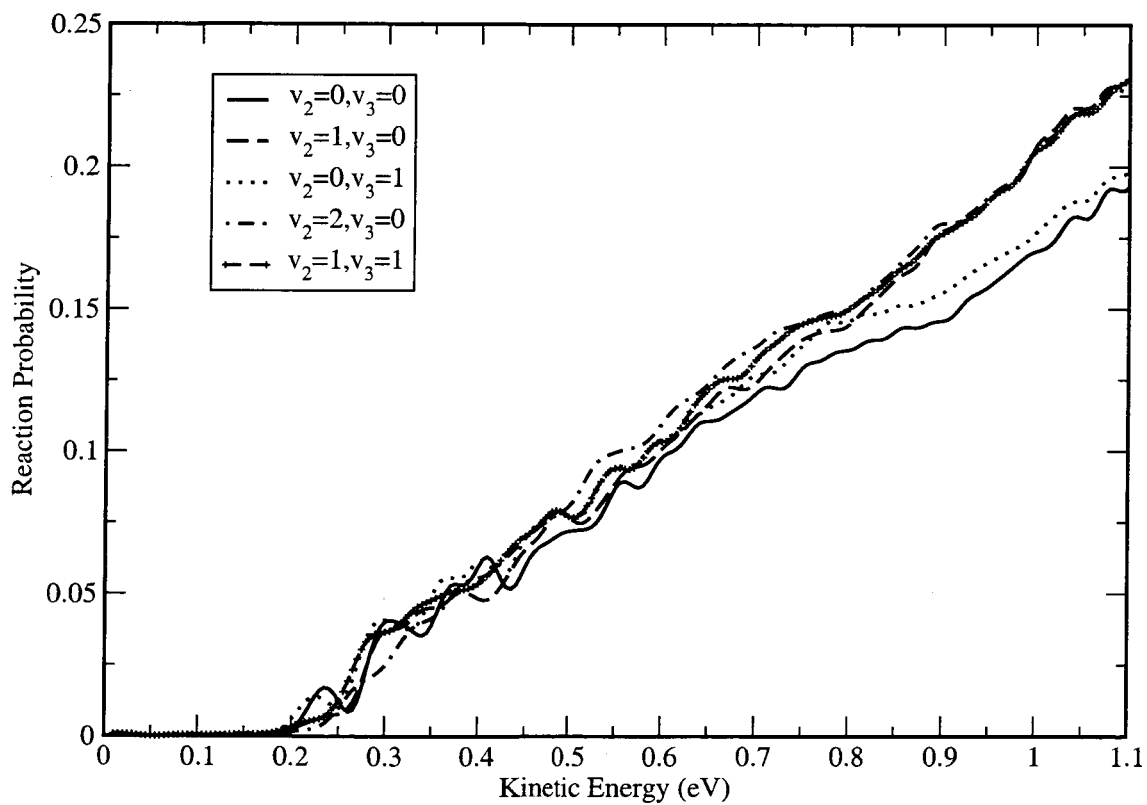
RESULTS AND DISCUSSION

- Initial state reaction probabilities for $\text{H}_2(\nu_1, j_1=0) + \text{C}_2\text{H}(\nu_2=\nu_3=0, j_2=0) \rightarrow \text{H} + \text{C}_2\text{H}_2$ as a function of kinetic energy for $J=0$



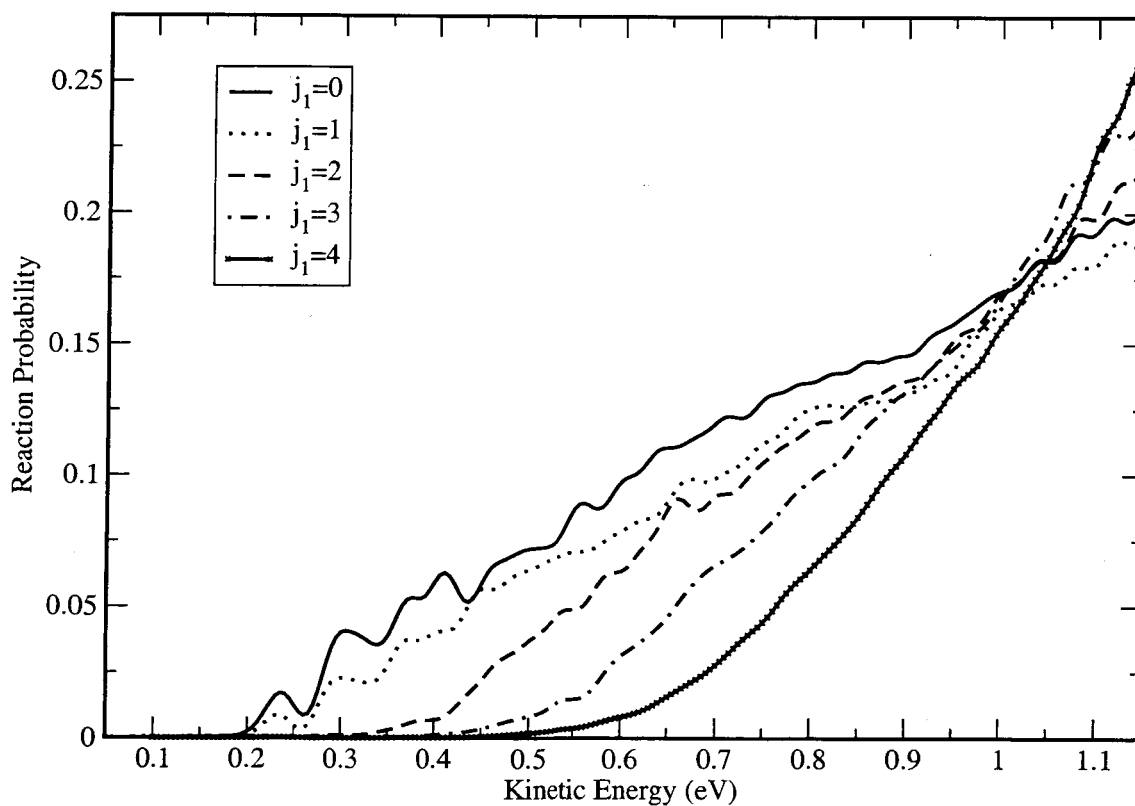
RESULTS AND DISCUSSION

- Initial state reaction probabilities for $\text{H}_2(\nu_1=0, j_1=0) + \text{C}_2\text{H}(\nu_2, \nu_3, j_2=0) \rightarrow \text{H} + \text{C}_2\text{H}_2$ as a function of kinetic energy for $J=0$



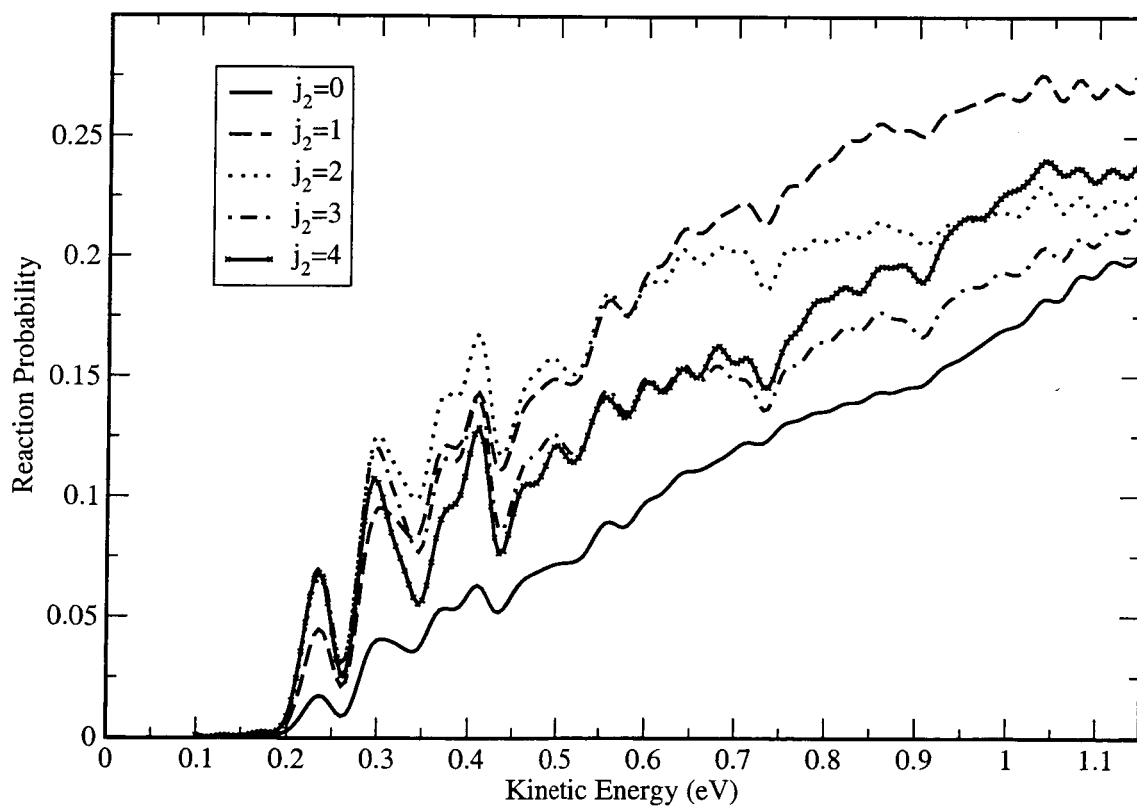
RESULTS AND DISCUSSION

- Initial state reaction probabilities for $\text{H}_2(\nu_1=0, j_1) + \text{C}_2\text{H}(\nu_2=\nu_3=0, j_2=0) \rightarrow \text{H} + \text{C}_2\text{H}_2$ as a function of kinetic energy for $J=0$



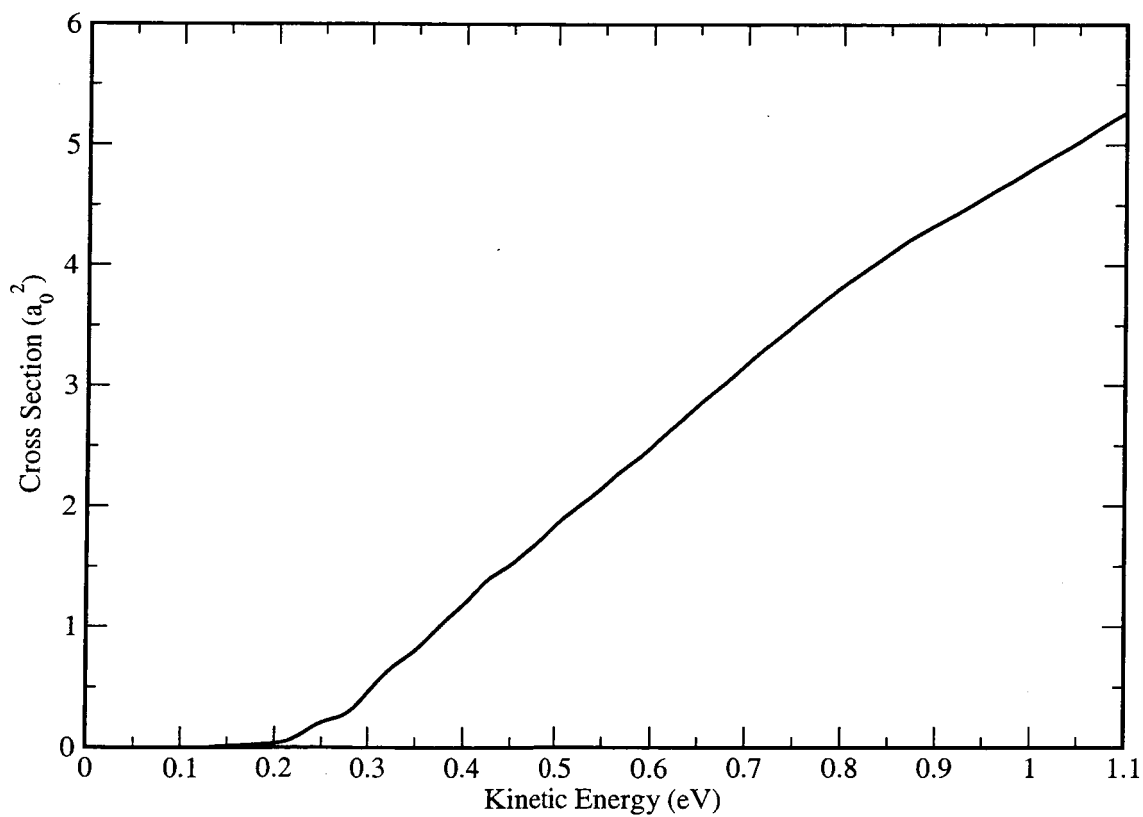
RESULTS AND DISCUSSION

- Initial state reaction probabilities for $\text{H}_2(\nu_1=0, j_1=0) + \text{C}_2\text{H}(\nu_2=\nu_3=0, j_2) \rightarrow \text{H} + \text{C}_2\text{H}_2$ as a function of kinetic energy for $J=0$



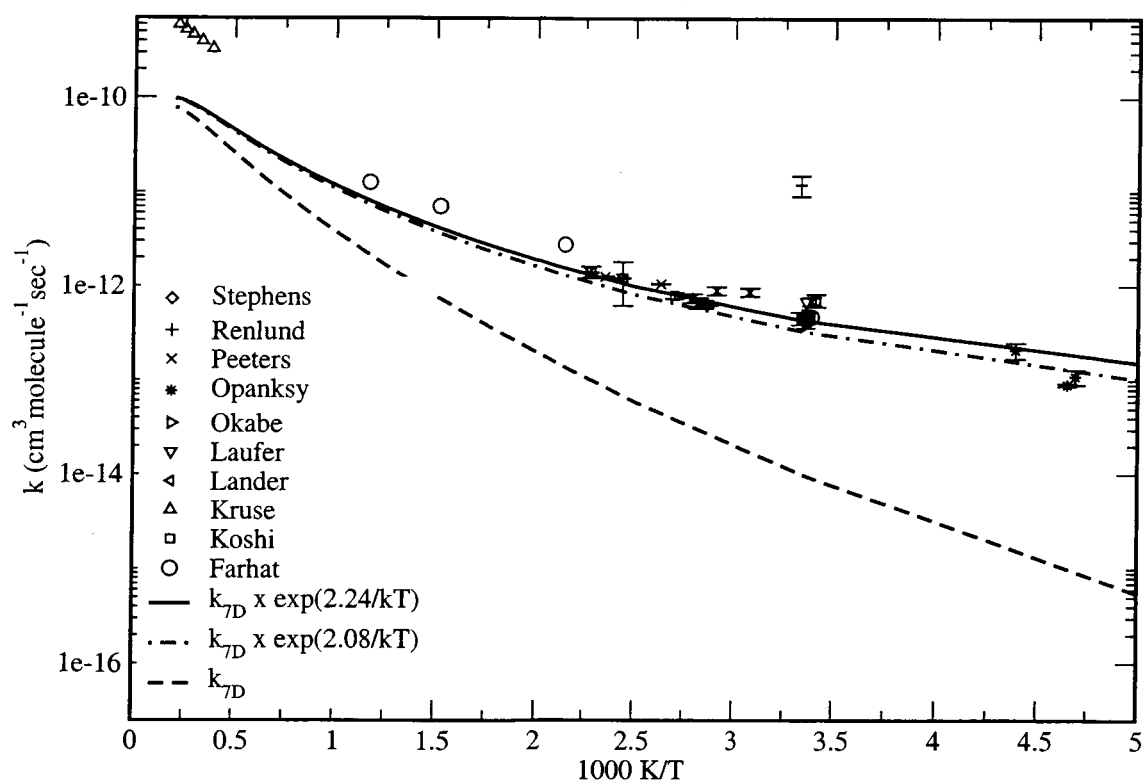
RESULTS AND DISCUSSION

- Integral cross section for the collision of ground state $\text{H}_2(\nu_1=0, j_1=0)$ with $\text{C}_2\text{H}(\nu_2=\nu_3=0, j_2=0)$ as a function of kinetic energy



RESULTS AND DISCUSSION

- Comparison between present 7D results k_{7D} , rescaled 7D results $k_{7D} \times e^{2.08/kT}$ and $k_{7D} \times e^{2.24/kT}$ using barrier height differences between Wang and Bowman's PES and *ab initio* results^l, and various experimental results



^l X. Zhang Y. Ding, Z. Li, X. Huang and C. Sun, *J. Phys. Chem.* **104**, 8375 (2000); Y. Kurosaki and T. Takayanagi, *J. Chem. Phys.* **113**, 4060 (2000).

CONCLUSIONS and FUTRUE WORK

- Conclusions

- vibrational excitation of H₂ molecule enhances the reaction probabilities; while the vibrational excitation of C₂H doesn't change the reactivity much
- ground rotational state of H₂ gives the largest probability; $j_2 = 1$ initial rotational state of C₂H gives the largest probability
- Both the 7D quantum calculation results and the *ab initio* studies indicate the current barrier height of Wang and Bowman's PES is too large

- Future work

- Extend the current 7D calculation to full-9D calculation
- Extend the AB+CDE calculation to A+BCDE calculation