Theoretical investigations of rate coefficients of the H + H_2O_2 two-channel reaction on a full-dimensional potential energy surface

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Introduction

Due to its critical role in fundamental combustion chemistry and hydrocarbon/fuel combustion, the H_2/O_2 combustion system has been investigated over a rather large temperature range. In this work, we investigate the rate coefficients for the following two reactions, which play a eminent role in the H_2/O_2 combustion, using the ring polymer molecular dynamics (RPMD), quasi-classical trajectory (QCT), and canonical variational transition state theory (CVT) with the small curvature tunneling (SCT) correction at 200 K ≤ T ≤ 1000 K.

$$H + H_2O_2 \rightarrow HO_2 + H_2 \quad (R1)$$
$$H + H_2O_2 \rightarrow H_2O + OH \quad (R2)$$

Potential Energy Surface

ab initio: UCCSD(T)/aug-cc-pVTZ
data: ~110000 energy points
fitting : fundamental invariant-neural network (FI-NN)

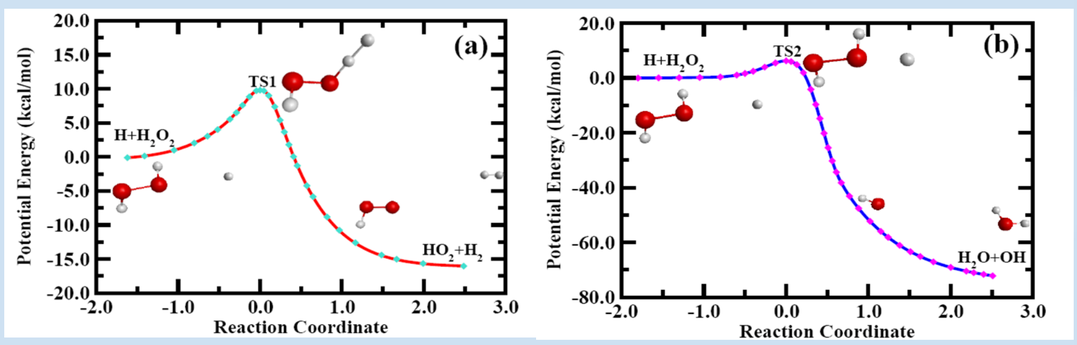

Fig1. The minimum energy paths for reaction R1 (a) and R2 (b) (solid lines) and those calculated from UCCSD(T)-F12b/aVTZ theory (symbols).

Methods

1. ring-polymer molecular dynamics (RPMD)

$$k_{RPMD}(T) = 4\pi R_\infty^2 \left(\frac{k_B T}{2\pi\mu}\right)^{\frac{1}{2}} \bullet \exp\left(-\frac{\Delta W^{(n)}(T)}{k_B T}\right) \bullet \kappa(t \rightarrow \infty, T, \xi^{\ddagger})$$

2. quasi-classical trajectory (QCT)

$$k_{QCT}(T) = \pi b_{max}^2 \sqrt{\frac{8k_B T}{\pi\mu}} \frac{N_r}{N_{total}}$$

3. canonical variational transition state theory (CVT) with small curvature tunneling (SCT) correction

Results

RPMD results for reaction R1

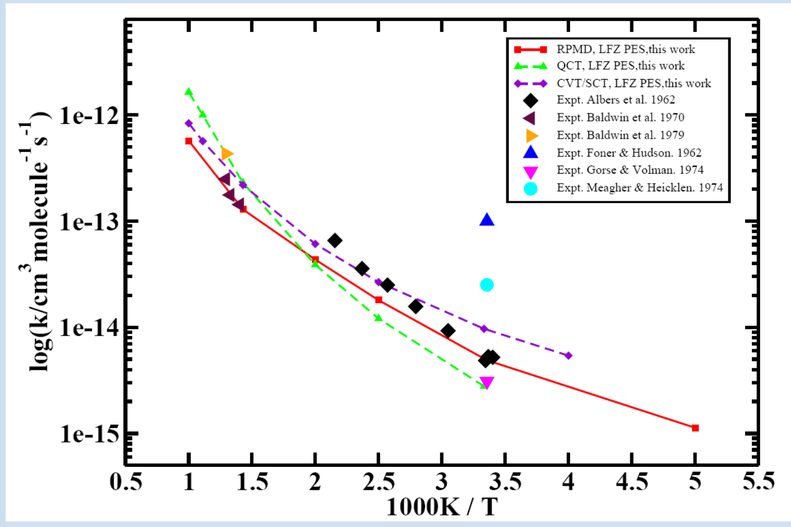

Fig4. Comparison of rate coefficients for R1 obtained from RPMD, QCT and CVT/SCT methods, together with experimental data.

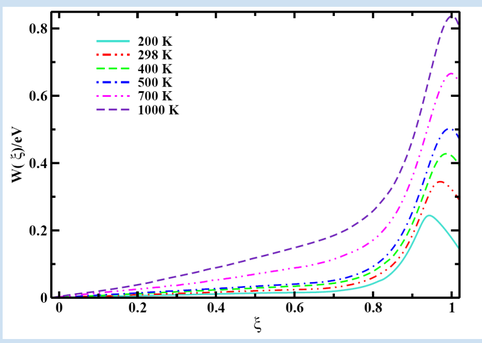

Fig2. Temperature dependence of the free-energy curves for reaction R1.

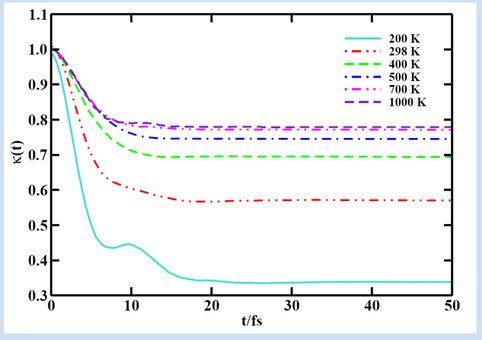

Fig3. Time dependence of the transmission coefficients for reaction R1.

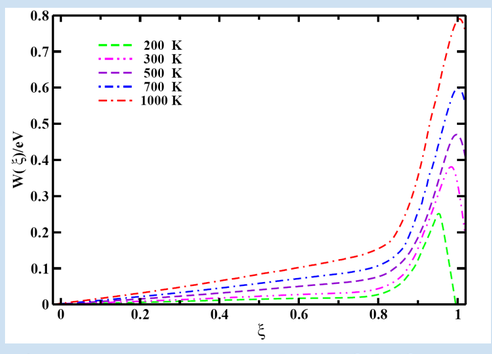

Fig5. Temperature dependence of the free-energy curves for reaction R2.

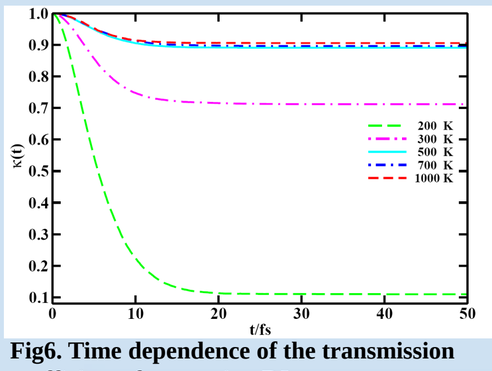

Fig6. Time dependence of the transmission coefficients for reaction R2.

RPMD results for reaction R2

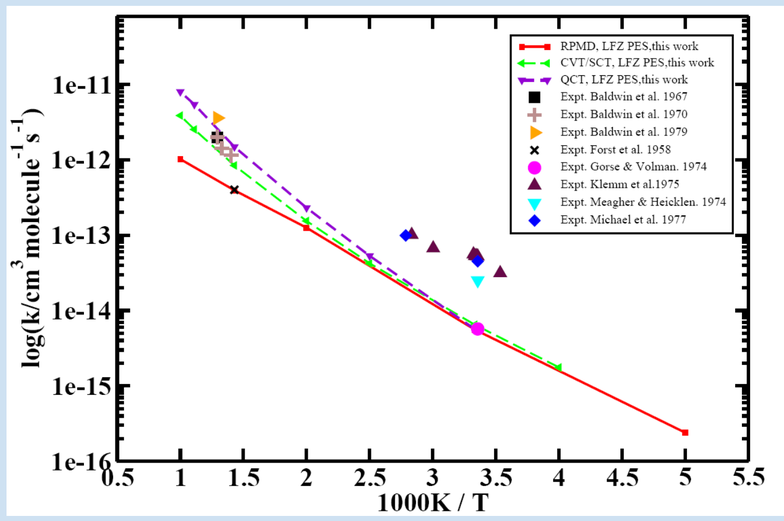

Fig7. Comparison of rate coefficients for R2 obtained from RPMD, QCT and CVT/SCT methods, together with experimental data.

Conclusions

In this work, we calculated the rate coefficients of the H + H_2O_2 reaction, covering both H_2 +HO_2 and OH + H_2O product channels, which are calculated using RPMD, QCT and CVT/SCT at 200 K ≤ T ≤ 1000 K. Considering that the previous experimental values vary widely, especially at low temperatures, the present RPMD rate coefficients show excellent agreement with most of the experimental values. In addition, the current QCT and CVT/SCT calculations also predict good results at some temperatures. These results demonstrate the good applications of the current dynamics to polyatomic chemical reactions and the accuracy of the full-dimensional FI-NN PES.

Reference

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[3] X. Lu, Q. Meng, B. Fu, X. Wang, and D. H. Zhang, *J. Chem. Phys.* **149**, 174303 (2018).