SAND2007-5207C

Computational study of the reactions OH + O ↔ HO_2 ↔ H + O_2 and H + OH ↔ H_2O

Stig R. Sellevåg,[1] Yuri Georgievskii,[2] and James A. Miller[2]

(1) SINTEF Energy Research, NO-7465 Trondheim, Norway, (2) Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551-0969, USA

Summary

Potential energy surfaces involved in the reactions OH + O ↔ HO_2 ↔ H + O_2 and H + OH ↔ H_2O have been characterized at the CASPT2/aug-cc-pVTZ level of theory. High-pressure limiting rate coefficients for the reactions H + O_2 → HO_2 and H + OH → H_2O have been calculated using variable reaction coordinate transition state theory. Over the temperature range 300-3000 K the following expressions were obtained: $k_\infty(\mathrm{H+O_2}) = (25T^{-0.367} + 0.075T^{0.702}) \times 10^{-11}$ and $k_\infty(\mathrm{H+OH}) = 4.17\times10^{-11} T^{0.234}\exp(57.5/T)$ cm^3 molecule^{-1} s^{-1}. The pressure dependence of the reaction H + O_2 + M was investigated using a 2D Master equation. For Ar and N_2 as bath gases, the following low-pressure limiting rate coefficients were obtained over the temperature range 300-2000 K: $k_{0,\mathrm{Ar}} = 7.1\times10^{-29}T^{-1.37}\exp(-119/T)$ and $k_{0,\mathrm{N2}} = 1.6\times10^{-27}T^{-1.7}\exp(-258/T)$ cm^6 molecule^{-2} s^{-1}. The possible contribution from the $^2A'$ electronic state to the reaction OH + O → H + O_2 has also been considered. The high value of the minimum of the seam of crossing between the $^2A'$ and $^4A''$ states suggests that the contribution is small.

Motivation

Today it is evident that the use of fossil fuels has significantly increased the atmospheric concentration of CO_2 and contributed to an unequivocal warming of the climate system. Use of H_2 manufactured from natural gas to create "decarbonized fuels" has the potential to significantly reduce CO_2 emissions from the power production industry. Utilization of H_2 as gas turbine fuel necessitates accurate description of the combustion process at elevated pressures. However, even apparently small differences between the available chemical mechanisms for H_2 combustion can have a significant effect on predicted flame properties. To help improve the chemical insight into the combustion of H_2, we have initiated a quantum chemistry study of the reactions OH + O ↔ HO_2 ↔ H + O_2 and H + OH ↔ H_2O at conditions relevant for gas turbines.

Results

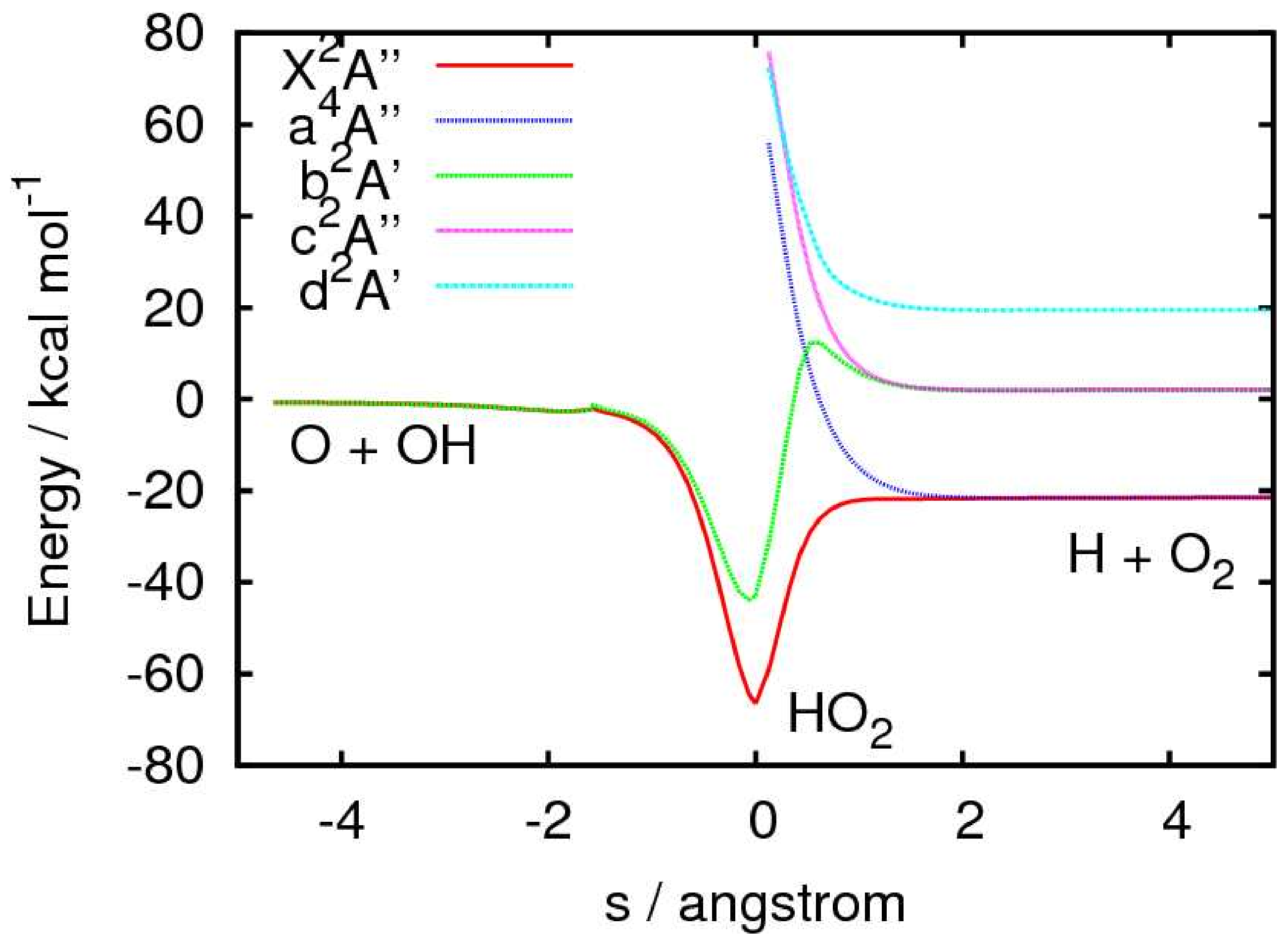

Figure 1. Vertical excitation energies along the ground-state minimum energy path for the reaction O + OH ↔ HO_2 ↔ H + O_2 as calculated at the CASPT2/aug-cc-pVTZ level of theory.

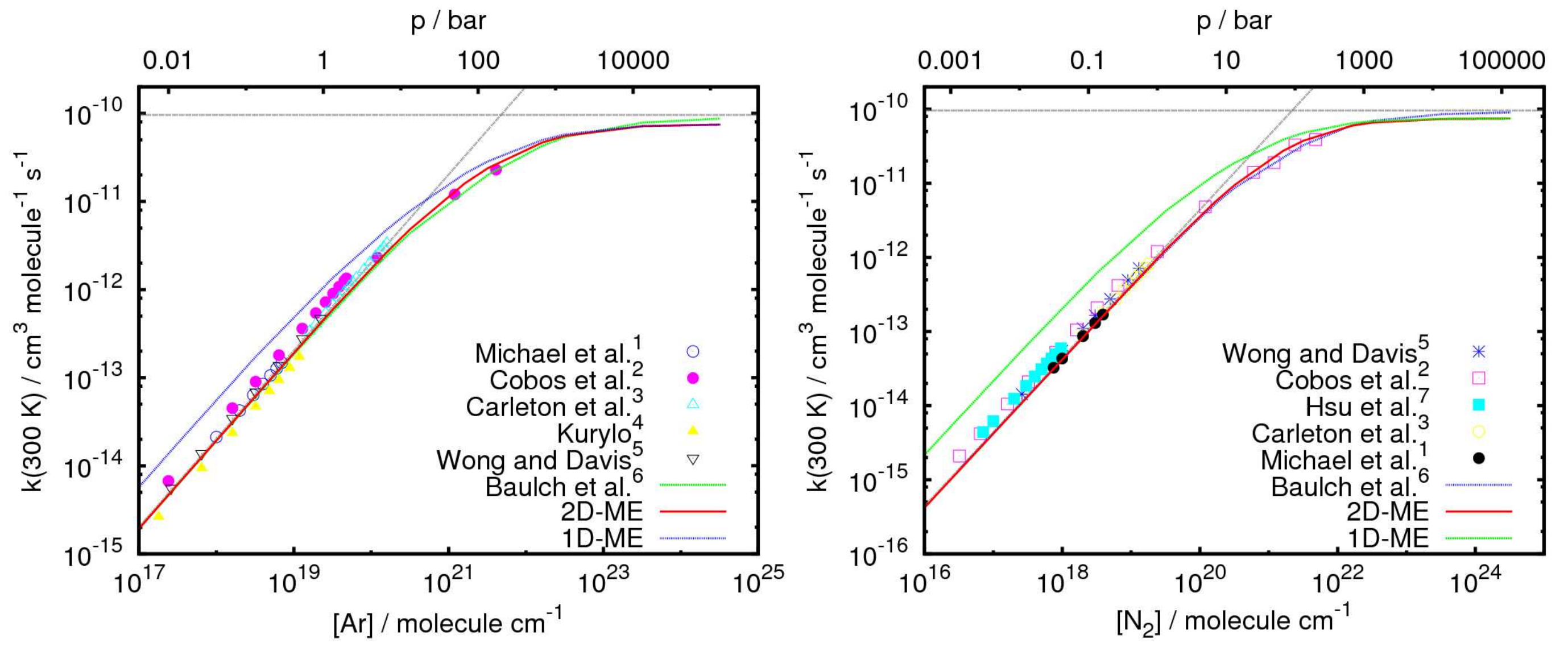

Figure 2. Falloff curves for the reaction H + O_2 + M → HO_2 + M with Ar (*left*) and N_2 (*right*) as bath gas at 300 K as calculated using 1D and 2D Master equations. The plotted low-pressure and high-pressure limiting rate coefficients are the values preferred by the IUPAC panel.[6] $\langle \Delta E_{\mathrm{down}} \rangle = 45(T/298\ \mathrm{K})^{0.95}$ cm^{-1} for Ar as bath gas, and $\langle \Delta E_{\mathrm{down}} \rangle = 100(T/298\ \mathrm{K})^{0.65}$ cm^{-1} for N_2 as bath gas.

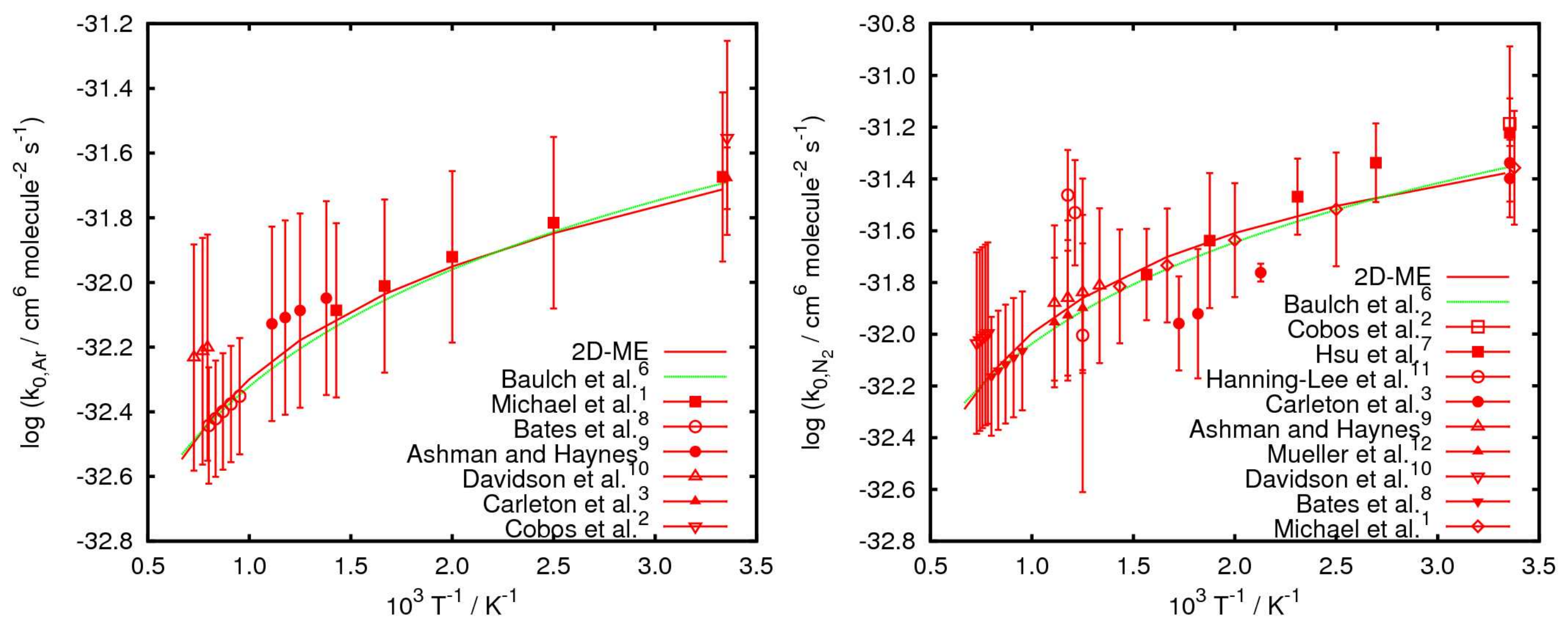

Figure 3. Low-pressure limiting rate coefficient as a function of temperature for the reaction H + O_2 + M → HO_2 + M with Ar (*left*) and N_2 (*right*) as bath gas as calculated using a 2D Master equation.

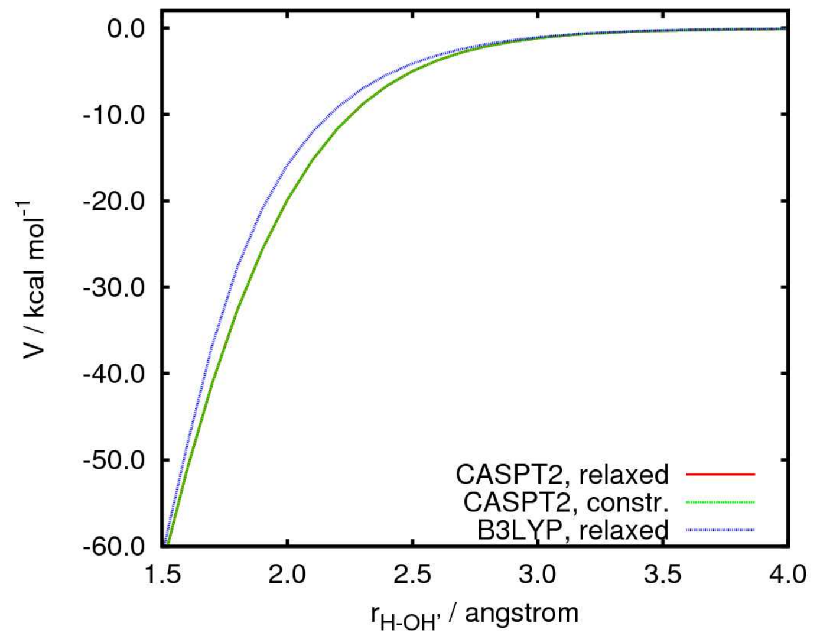

Figure 4. Minimum energy path for the reaction H + OH → H_2O as a function of the H-OH′ bond length as calculated using the CASPT2 and B3LYP models employing the aug-cc-pVTZ basis set with relaxed and constrained HO-H′ bond length.

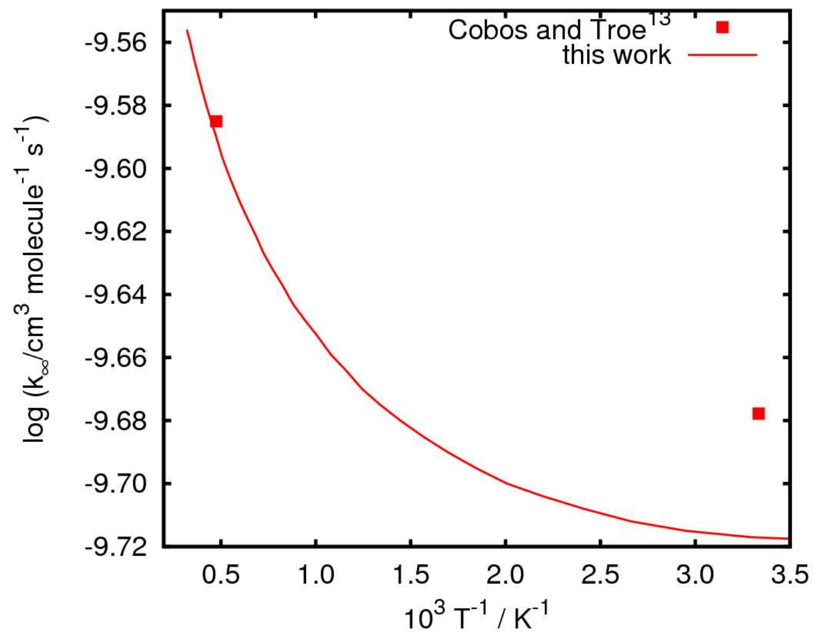

Figure 5. High-pressure limiting rate coefficient as a function of temperature for the reaction H + OH → H_2O as calculated using variable reaction coordinate transition state theory.

Methods

Potential energy hypersurfaces of the studied reaction systems were investigated using the CASPT2 method. The active space used to describe the H + O_2 reaction system consisted of 7 electrons in 5 orbitals, while the active space used for the H + OH system consisted of 4 electrons in 3 orbitals. For the H + OH reaction system, spin-orbit matrix elements were computed using the Breit-Pauli Hamiltonian. The CASPT2 calculations were carried out using the MOLPRO 2006 package. Additional calculations were carried out with the B3LYP model using Gaussian 98. Dunning's correlation-consistent aug-cc-pVTZ basis set was employed in all calculations except in the calculation of the spin-orbit matrix elements where the Pople-style 6-311++G(3df,p) basis set was used.

High-pressure limiting rate coefficients were calculated using variable reaction coordinate transition state theory with multifaceted dividing surfaces (VRC-TST).[14] Within VRC-TST, dividing surfaces are defined in terms of a fixed distance between pivot points on each fragment, and both the location and the separation between the pivot points are varied to determine the minimum reactive flux through a dividing surface. The pivot points were located on each nuclei for both the H + O_2 and the H + OH reaction systems. The reactive flux through a dividing surface was determined using a crude Monte Carlo sampling method where the electronic structure of points on the dividing surface was calculated on the fly.

The pressure dependence of the reaction H + O_2 + M → HO_2 + M was investigated using a two-dimensional Master equation (2D-ME). The 2D-ME was solved using the methods of Miller et al.[15] The energy transfer function for deactivating collisions was modeled using a "single exponential down" expression, and the collision rate was taken as the Lennard-Jones collision rate.

Acknowledgement

This work was supported by the Norwegian Research Council under Contract No. 173826/I30. The Norwegian High Performance Computing Consortium is acknowledged for grants of computing time. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94-AL85000. The authors are grateful to Dr. S. J. Klippenstein and Dr. L. B. Harding for discussions.

References

1. Michael, J. V.; Su, M. C.; Sutherland, J. W.; Carroll, J. J; Wagner, A. F. *J. Phys. Chem. A* **2002**, *106*, 5297.
2. Cobos, C. J.; Hippler, H.; Troe, J. *J. Phys. Chem.* **1985**, *89*, 342.
3. Carleton, K. L.; Kessler, W. J.; Marinelli, W. J. *J. Phys. Chem.* **1993**, *97*, 6412.
4. Kurylo, M. J. *J. Phys. Chem.* **1972**, *76*, 3518.
5. Wong, W.; Davis, D. D. *Int. J. Chem. Kinet.* **1974**, *6*, 401.
6. Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, T.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **2005**, *34*, 757.
7. Hsu, K. J.; Anderson, S. M.; Durant, J. L.; Kaufman, F. *J. Phys. Chem.* **1989**, *93*, 1018.
8. Bates, R. W.; Golden, D. M.; Hanson, R. K.; Bowman, C. T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2337.
9. Ashman, P. J.; Haynes, B. S. *Proc. Combust. Inst.* **1998**, *27*, 185.
10. Davidson, D. F.; Petersen, E. L.; Roehrig, M.; Hanson, R. K.; Bowman, C. T. *Proc. Combust. Inst.* **1996**, *26*, 481.
11. Hanning-Lee, M. A.; Pilling, M. J.; Warr, J. F. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2907.
12. Mueller, M. A.; Yetter, R. A.; Dryer, F. L. *Proc. Combust. Inst.* **1998**, *27*, 177.
13. Cobos, C. J.; Troe, J. *J. Chem. Phys.* **1985**, *83*, 1010.
14. (*a*) Georgievskii, Y.; Klippenstein, S. J. *J. Chem. Phys.* **2003**, *118*, 5442. (*b*) Georgievskii, Y.; Klippenstein, S. J. *J. Phys. Chem. A* **2003**, *107*, 9776.
15. (*a*) Miller, J. A.; Klippenstein, S. J.; Raffy, C. *J. Phys. Chem. A* **2002**, *106*, 4904. (*b*) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2004**, *108*, 8296. (*c*) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2006**, *110*, 10528.

Contact information: stig.r.sellevag@sintef.no (S.R.S.), ygeorgi@sandia.gov (Y.G.), jamille@sandia@gov (J.A.M.)