

Accurate Ab Initio Thermal Rate Constants for Reaction of O(P) with H and Isotopic Analogs

Thanh Lam Nguyen, and John F. Stanton

J. Phys. Chem. A, **Just Accepted Manuscript** • Publication Date (Web): 10 Jun 2014

Downloaded from <http://pubs.acs.org> on June 20, 2014

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



ACS Publications
High quality. High impact.

The Journal of Physical Chemistry A is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036
Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works
produced by employees of any Commonwealth realm Crown government in the course
of their duties.

Accurate Ab Initio Thermal Rate Constants for Reaction of O(³P) with H₂ and Isotopic Analogs

Thanh Lam Nguyen and John F. Stanton*

Department of Chemistry, The University of Texas at Austin, Texas 78712-0165, USA

*Corresponding author: jfstanton@mail.utexas.edu

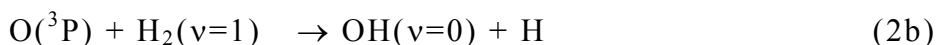
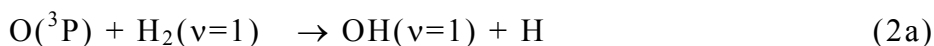
Abstract:

Semi-classical transition state theory, in combination with high accuracy quantum chemistry, was used to compute thermal rate constants from first principles for the O(³P) + H₂ reaction and its isotopic counterparts. In the temperature regime of 298-3500K (which spans eight orders of magnitude for rate constants), our theoretical results are in excellent agreement (within 5 to 15%) with all available experimental data from 298 to 2500K, but somewhat too low (from 15 to 35%) at higher temperatures. A number of possible reasons that might cause the degradation at high temperatures are discussed. Vibrational state-selected rate constants and their correlations with normal thermal rate constant are derived and given in supporting information.

Keywords: HEAT, SCTST, VPT2, VSSRC, Hydrogen-Fuel, 2DME

Introduction

The reaction of a ground-state oxygen atom with a hydrogen molecule to produce a hydroxyl radical and hydrogen atom is an important chain-propagation step in H_2 combustion and that of hydrogen-containing fuels.¹⁻⁵



In term of atmospheric chemistry, the high classical barrier for the reaction of about 13.0 kcal/mol,⁶⁻¹¹ and the small concentration of ground-state oxygen atoms in air renders it unlikely to be an important reaction in the troposphere. However, numerous recent studies¹²⁻¹⁴ have shown that reactions of triplet oxygen atoms with vibrationally excited hydrogen molecules ($\nu_{\text{HH}}=1$, see reactions (2a) & (2b)) might play some roles in the upper mesosphere. Given that molecules in this reaction system are quite small, very accurate theoretical and experimental methods can be applied. Therefore, this reaction is an interesting benchmark system for comparing theory and experiment.^{15-30,31-51} The title reaction has been both extensively reviewed^{2,3,5,7,9,10,19,22} and studied.¹⁻⁵¹ Experimentally,¹⁵⁻³⁰ thermal reaction rate constants have been measured by numerous techniques for a wide range of temperature from 298 K to 3500 K.¹⁵⁻³⁰

Reaction dynamics studied by crossed molecular beams are also available.^{38,47,48} On the theoretical side,^{6-14,31-47,49-51} global potential energy surfaces with an accuracy of better than 0.5 kcal/mol have recently become available.⁶⁻¹⁴ Calculations of thermal rate constants,^{7,33-36} quasi-classical trajectory (QCT) and quantum dynamics calculations^{11,37-47,49-51} have been reported using these surfaces. In general, the theoretical results are consistent with what has been observed experimentally.

In this work, we calculate thermal rate constants for the title reactions using semi-classical transition state theory (SCTST),⁵²⁻⁵⁵ which naturally includes multi-dimensional quantum mechanical tunneling and fully coupled anharmonic vibrations. SCTST has recently been implemented and used in a number of studies.⁵⁴⁻⁵⁷ As in the previous work, the input data for SCTST were obtained using the high accuracy extrapolated ab initio thermochemistry (HEAT) protocol.⁵⁸⁻⁶⁰ Our recent work for various reaction systems has shown that a combination of SCTST and HEAT can provide thermal reaction rate constants with an accuracy comparable to that from experiments.^{55,61-65} As will be shown below, this behavior is also true for the title reactions. In addition, thermal rate constants for reactions of triplet oxygen atoms with vibrationally excited hydrogen molecules ($v_{HH}=1$ & 2) are computed and compared to the experimental work of Light.⁶⁶

Theoretical Methodology

Quantum Chemical Calculations

Energies of various species in the reaction of ground-state oxygen atom with molecular hydrogen were calculated using HEAT-345(Q) and HEAT-456(Q) protocols,⁵⁸⁻⁶⁰ which have been described in detail in previous papers.⁵⁸⁻⁶⁰ In this work, we have slightly modified two terms in the original HEAT protocol as detailed below:

- i) Zero-point vibrational energies (ZPE) were calculated using the CCSD(T) method (in the frozen-core approximation) in combination with the “*NASA Ames*” atomic natural orbital (ANO) basis set of Taylor and Almlöf.⁶⁷⁻⁶⁹ Harmonic force fields were calculated using the ANO2 basis set,⁶⁹ while the ANO1 basis set⁶⁹ was used to obtain anharmonic force fields. Second-order vibrational perturbation theory (VPT2)⁷⁰ was then used to compute anharmonic constants and the anharmonic ZPE.
- ii) Experimental spin-orbit (SO) corrections were used for the ground-state oxygen atom ($\text{SO}_\text{O} = 78 \text{ cm}^{-1}$) and hydroxyl radical ($\text{SO}_\text{OH} = 69.6 \text{ cm}^{-1}$).⁷¹ A spin-orbit correction for the transition structure (TS) is neglected, however, as our calculations show that the predicted kinetics are very insensitive to the magnitude of the SO correction at the TS (see Table S1 in supporting information). Hence, the barrier we compute corresponds to the average of two components of the transition state. It should be

mentioned that the earlier work of Wagner et al⁷² included a treatment of the Renner-Teller effect at this linear electronically degenerate TS and indicated that the magnitude of the effect is significant at room temperature.⁷² However, our SCTST rates without the Renner-Teller effect at around room temperature agree well with experiments (see Figure 2A) as well as with full quantum dynamics rates of Balakrishnan⁴³ who used two GLDP surfaces (³A'' and ³A'), which are coupling. However, the Renner-Teller effect is negligible at high temperatures typical of combustion. Therefore, neglect of the Renner-Teller effect in our model does not appear to affect our SCTST rates significantly. To include an appropriate treatment of the Renner-Teller effect (where Born-Oppenheimer approximation breaks down) on this linear electronically degenerate TS in our SCTST model, one must include an additional term of vibronic coupling into Hamiltonian and solve this Schrodinger equation for two surfaces (³A'' and ³A') in order to obtain geometries, rovibrational parameters, anharmonic constants, and energy barriers. Such work is possible in our group, which works on both kinetics and vibronic coupling, but is currently not available and in progress.

The CFOUR quantum chemistry program⁷³ was used for CCSD(T) and CCSDT calculations, while CCSDT(Q) calculations used the MRCC code,⁷⁴ as interfaced with the CFOUR.

Chemical Kinetics Calculations

Thermal reaction rate constants of the title reaction as displayed in Figure 1 can be expressed as:

$$k(T) = \frac{1}{h} \times \frac{Q_{trans}^{\ddagger} \times Q_{elec}^{\ddagger}}{Q_O \times Q_{H_2}} \times \sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} G_{rv}^{\ddagger}(E, J) \exp(-E/k_B T) dE \quad (3)$$

Where h is Planck's constant, k_B is the Boltzmann constant; Q_{trans}^{\ddagger} and Q_{elec}^{\ddagger} are the translational and electronic partition functions of the TS, respectively. Q_{elec}^{\ddagger} is equal to $3 \times 2 = 6$, in which 3 represents the triplet electronic state degeneracy and 2 is for the twofold degeneracy (neglecting SO effects) of Π symmetry of TS. Q_{H_2} and Q_O are the complete partition functions for molecular hydrogen and triplet oxygen atom, respectively. The Morse vibrational potential energy levels are used for molecular hydrogen in order to compute its vibrational partition function. Effects of coupling between the vibration and rotations in H_2 molecule were also investigated and found to be small (<5% at 4000 K, see Table S2 in the supporting information). Note that there are three low-lying spin-orbit electronic states of triplet atomic oxygen: 0 cm^{-1} for 3P_2 with

an electronic degeneracy ($g=5$), 158.5 cm^{-1} for $^3\text{P}_1$ with $g=3$ and 226.5 cm^{-1} for $^3\text{P}_0$ with $g=1$.⁷¹ Therefore, the electronic partition function for triplet oxygen atom is calculated as Eq. (4):

$$Q_{elec}^o(T) = 5 + 3\exp\left(-\frac{158.5}{k_B T}\right) + 1\exp\left(-\frac{226.5}{k_B T}\right) \quad (4)$$

Where k_B is approximately equal to $0.695 \text{ cm}^{-1}/\text{K}$.

$G_{rv}^\ddagger(E, J)$ is the ro-vibrational cumulative reaction probability at each set of values of the internal energy E and total angular momentum J . Assuming that rotations and vibrations can exchange energy freely, $G_{rv}^\ddagger(E, J)$ can be computed by convolution of rotations and vibrations using Eq. (5):

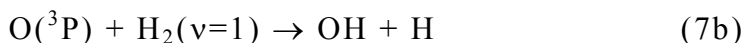
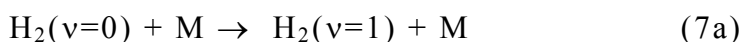
$$G_{rv}^\ddagger(E, J) = \int_0^E G_v^\ddagger(E - E_{rot}) \rho_r^\ddagger(E_{rot}) dE_{rot} \quad (5)$$

$G_v^\ddagger(E_v)$ is the vibrational cumulative reaction probability for TS, which is calculated by direct summation and evaluated with SCTST using an energy bin of 1 cm^{-1} and a ceiling energy of $7 \times 10^4 \text{ cm}^{-1}$. The latter is chosen to ensure that all $k(T)$ calculated as a function of temperature (from 200 K to 4000 K) are converged. Rotational energy levels of the linear TS are from Eq. (6), in which B is a two-dimensional rotor constant. The maximum angular momentum quantum number (J) is chosen to be 300.

$$E_{rot}^{\#}(J) = BJ(J + 1) \quad (6)$$

In this work, thermal reaction rate constants were computed with Eq. (3) by simple two-dimensional sums of internal energy and angular momentum with a step size of 1 cm^{-1} for ΔE and 1 for ΔJ , respectively.

Rate constants $k(T)$ calculated with Eq. (3) are in quite good agreement with experimental data (within 5% to 15%), for a wide range of temperature with $T \leq 2500 \text{ K}$ (see below). Above 2500 K, the theoretical $k(T)$ values using Eq. (3) underestimate the experimental measurements. The magnitude at this underestimation is found to be about 35% at 3500 K. Earlier, Zellner¹ and then Sutherland et al¹⁹ speculated that at high temperatures, a large fraction of the reactive flux occurs via reactions (7a) and (7b), so total reaction rate constants are predicted to be influenced by the contributions from reaction (7b) of triplet oxygen atoms with vibrationally excited hydrogen molecules.



The effect of vibrational rate enhancement, first experimentally detected by Light,⁶⁶ was found to be of the order of 10^3 at room temperature. This finding was later confirmed by theoretical calculations reported by Garrett and Truhlar^{34,35} as well as by other authors.^{37,39-43} Since there are no

experimental measurements of vibrational state-selected reaction rate constants at higher temperatures, possible contributions of vibrationally excited H_2 fractions to total thermal rate constants under combustion conditions are unknown. It is easy to compute Boltzmann thermal population fractions of vibrationally excited H_2 molecules and these are indeed used in our SCTST calculations, but non-statistical fractions that would result from a departure from thermal equilibrium are unknown. In this work, formulas of vibrational state-selected reaction rate constants within the SCTST framework are derived and then calculated. In addition, their relationship with the “*normal*” thermal rate constant is given in the supporting information.

Results and Discussions

HEAT Results

Table 1 displays energy contributions of various terms to total HEAT energies. As can be seen, Hartree-Fock energies are (typically) far from adequate; the CCSD(T) corrections, as always, play the most important role. The second most important correction is the ZPE, with contributions of -0.94 and -2.28 kcal/mol, respectively, for the reaction enthalpy and the barrier height. Although other corrections are much smaller (< 0.2 kcal/mol), these contributions are crucial fine-tunings needed to bring theory into agreement with experiment. HEAT calculations predict the title reaction is endothermic by 1.45 kcal/mol, which agrees well with the

ATcT value of 1.54 ± 0.01 kcal/mol,⁷⁵⁻⁷⁷ off by only *ca.* 0.1 kcal/mol. HEAT also provides a vibrationally adiabatic energy barrier of 11.2 kcal/mol, with an estimated maximum error bar of *ca.* 0.3 kcal/mol.

A comparison of geometries of TS and classical barrier heights obtained with various levels of theory is shown in Table 2. Agreement of HEAT values with values in the literature is found to be quite good, within ± 0.4 kcal/mol for the energy barrier and 0.01 Å for bond lengths. HEAT classical barrier heights are predicted to be 13.1 ± 0.2 kcal/mol (without spin-orbit corrections and DBOC) and 13.5 ± 0.2 kcal/mol (with both DBOC and spin-orbit (SO) corrections included). Note that the energy barriers reported in previous literature did not account for DBOC and SO corrections, which were obtained as +0.17 and +0.22 kcal/mol, respectively (see Table 1). Therefore, a small difference of *ca.* 0.4 kcal/mol between our barrier height and recent calculations by other levels of theory⁶⁻¹¹ are mainly due to these small corrections. To the best of our knowledge, the present work documents the highest level of theory yet applied to this system.

It should be mentioned that we were able to locate two pre-reactive stationary points of triplet oxygen atoms with H₂, designated as PRC1 and PRC2. PRC1 has *C*_{2v} symmetry while PRC2 is linear. PRC2 was characterized by harmonic vibrational analysis to be a first-order saddle point connecting two identical PRC1. Without ZPE and DBOC, PRC1 and PRC2 are 81 and 16 cm⁻¹ below the energy level of the initial reactants

(O+H₂), which are in excellent agreement with values of 74 and 18 cm⁻¹ obtained by Atahan et al⁴⁹ for the same two complexes. However, after including ZPE and DBOC, both PRC1 and PRC2 become higher in energy than the asymptotic energy of the initial reactants. So, they do not appear to exist as minima on the vibrationally adiabatic PES and will not be considered further.

Vibrationally adiabatic energy barriers for rare isotope reactions were calculated and are presented in Table 3. The main differences between the title reaction and its isotopic variants are due to two mass-dependent factors, namely the DBOC and ZPE. After including these, both barrier heights and reaction enthalpies of isotopic species change slightly (by less than 0.8 kcal/mol, see Table 3). Of these two factors, the ZPE is well known to play the most important role. Although contributions of DBOC are smaller (< 0.2 kcal/mol), including DBOC is required in order to obtain first-principles thermal rate constants with high accuracy; this is especially important at low temperatures characteristic of the atmosphere, and with light-molecule reaction systems. In addition, the DBOC becomes proportionately more important for light species, like H₂.

Thermal Reaction Rate Constants

O(³P) + H₂ → OH + H: For this reaction, experimental rate constants for a wide range of temperature, from room temperature up to about 3500 K, are available;^{5,15-30} they span eight orders of magnitude from *ca.* 10⁻¹⁷ to

ca. 10^{-10} cm³ molecule⁻¹ s⁻¹.⁵ For the purpose of a careful comparison of our calculated $k(T)$ values with experimental data, we divide temperature into three different regions, namely low to moderate T (298-1000K), moderate to high T (1000-2500K), and high to very high T (2500-4000K), and results are displayed in Figures 2A, 2B and 2C, respectively. For $T=298-1000$ K (see Figure 2A), our calculated $k(T)$ values are in line with most experimental data, except two sets of rate constants reported by Dubinsky & McKenney³⁰ and Marshall & Fontijn.²¹ The difference between the calculation and experiment is better than 10%, which is comparable to the typical uncertainty of a measurement. From 298 to 1500 K, there are basically two distinct trends of the data (see Figures 2A and 2B): the first is that of Dubinsky & McKenney³⁰ and Marshall & Fontijn,¹⁵ and the other is that seen in all remaining works. Our SCTST prediction supports for the latter experiments. In contrast, Baulch's recommendation⁵ appears to fit the Marshall et al. and Dubinsky et al. data. For $T=1000-2500$ K (see Figure 2B), the experimental data⁵ are scattered; generally speaking, agreement between theory and experiment is excellent, within 10-15%. For $T=2500-4000$ K (see Figure 2C), thermal rate constants underestimate experimental values moderately, by about 15 to 35%. The disagreement becomes worse with increasing temperature. The underestimation at very high temperatures may be due to the fact that there are a number of other possible factors that have not been included in our calculations. They may include (i) reactions of non-statistical

distributions of vibrationally excited H_2 molecules with oxygen atoms. As will be shown in the supporting information, by increasing the population fraction of vibrationally excited $\text{H}_2(v_{\text{HH}}=1)$ molecules, we are able to match the calculated $k(T)$ with experiment; (ii) the second factor may be due to limits of second-order vibrational perturbation theory (VPT2) in treating anharmonicity. One might suspect that VPT2 applied to this problem could be insufficient at very high temperatures, therefore higher order vibration perturbation theory if available might be desired (a similar systematic error seen at high temperatures is also obtained in our work on the $\text{HO} + \text{CO}$ reaction (see Ref. 65)); (iii) the third factor may arise from rovibrational parameters. This will be discussed in the next section in the context of sensitivity analysis; and finally, (iv) we did not incorporate coupling of vibrations and rotations in the TS. It is however expected that the latter is a small effect because it should be largely cancelled out by the corresponding terms for the H_2 reactant. Additionally, the effects of coupling of the vibration with rotations in H_2 molecule were found to be small (less than 4% at 3500 K).

It is of interest to compare our SCTST rates with prior quantum dynamics calculations using GLDP surface reported by Balakrishnan.⁴³ It should be mentioned that Balakrishnan assumed electronic partition function of triplet oxygen atom has nine-fold degeneracy;⁴³ except at extremely high temperatures (e.g. T approaches to infinity), which is clearly in error and needs to be corrected. Therefore, first of all Balakrishnan's quantum

dynamic rates are corrected by the appropriate values of electronic partition function for triplet oxygen atom given in Eq. (4) and then included into Figure 2A for a direct comparison. Figure 2A shows that our SCTST rates slightly underestimate quantum dynamic rates at T below 400 K, but are too high at T above 500 K. Overall, our SCTST rates agree well with Balakrishnan's results. A small difference (likely within 20%) between two sets of rates may be due to differences in potential energy surfaces and methodologies that are applied. In addition, we also compared our SCTST results with ICVT/LAG⁷ (see Table S10 on pages 13-14 in supporting information); an excellent agreement between two approaches is also observed.

O(³P) + D₂ → OD + D: To be convenient for comparison, we split temperature into two different regions for this isotopic variant. Figure 3A displays thermal reaction rate constants for temperatures from 298 to 1000K, while k(T) values with T ≥ 1000K are illustrated in Figure 3B. As can be seen, an excellent agreement (within 10%) between theory and experiment can be seen for the whole range of temperatures. Again, the calculated k(T) appears to systematically underestimate experiments at very high temperatures (T ≥ 2500 K).

O(³P) + HD/DH → OH/OD + D/H: Total thermal rate constants from these two reactions are computed and shown in Figure 4. Again, excellent

agreement is seen between theory and experiment (within 5%); although this comparison is limited to a small range of temperature (from 420 to 475 K), where the experimental data is available.

Kinetic Isotope Effects (KIE)

Kinetic isotope effects (KIE) are defined as ratios of thermal reaction rate constants for isotopically substituted systems under the same conditions (e.g. temperature and also pressure if reaction rate constants depend on pressure). For the title reaction, rate constants are pressure-independent, so pressure-dependence can be disregarded. KIEs are often used as a diagnostic in the study of reaction mechanisms and to understand the role of tunneling. Therefore, the KIE is frequently considered at low temperatures where tunneling plays a central role. In Figure 5, we compare our calculated KIEs with those derived from the experimental measurements done by Gordon and co-workers^{18,23,25} in a small range of temperature, 340-475K. Figure 5 shows that above 420K, our predicted KIE values are in excellent agreement (within the experimental error bar) with values derived from the experiment.^{18,23,25} However, we slightly underestimate the KIE(k_{O+H_2} / k_{O+D_2}) values at lower temperatures ($T < 350K$). This seems to be due to the fact that we marginally overestimated rate constants for O + D₂ reaction in this temperature range (see Figure 3A). Overall, the agreement between our KIE values with the experiment

is reasonably good, at roughly the best level one can expect from such a comparison.

Quantum Mechanical Tunneling Correction

The tunneling correction is defined as a ratio of the actual rate constant ($k(T)_e$) to classical mechanical rate constant ($k(T)_c$) at a particular temperature,⁷⁸ and is calculated using Eq. (12):

$$\Gamma(T) = \frac{\text{quantum mechanical rate}}{\text{classical mechanical rate}} = \frac{k(T)_e}{k(T)_c} \quad (12)$$

The current SCTST approximation to the exact rate constant, $k(T)_e$, can be obtained as discussed earlier while the classical mechanical rate constant, $k(T)_c$ can be calculated within the same framework with the following caveat. Note that “classical” here means just for the reaction coordinate. Specifically, after the value of θ is calculated (see Eq. 6 of Ref 55), which corresponds to the state-resolved transition probability according to the semiclassical relationship $P(\theta) = [1 + \exp(2\theta)]^{-1}$, the reaction probability is set to unity for $\theta < 0$ (available energy for reaction is below the barrier) and to zero for $\theta > 0$ (above the barrier). This preserves the coupled anharmonic treatment provided by SCTST, but also enforces proper classical behavior (no tunneling or reflection of flux that crosses above the barrier). Basing the summation $G_v^\ddagger(E)$ on this ansatz,

vibrational partition function of TS can then be computed using a sum of vibrational states, Eq. (13).

$$Q_{no-tun}^{\ddagger}(T) = \frac{1}{k_B T} \int_0^{\infty} G_v^{\ddagger}(E) dE \quad (13)$$

Quantum mechanical tunneling corrections for the title reaction and its isotopic analogs are calculated and displayed in Figure 6. Figure 6 shows that the tunneling corrections for O + H₂ are similar to that for O + HD, but of course much larger than for O + D₂. This behavior, of course, can be expected because the H-atom is lighter; as a result, it tunnels much more efficiently than does the D-atom. As can be seen in Figure 6, tunneling corrections decrease nearly exponentially with temperature. Considering O + H₂, the calculated tunneling enhancement is 516 at 200K, drops to *ca.* 14 at 300K, and becomes about 2.5 at 500K and only 1.2 at 1000K. So, tunneling is extremely important at low temperatures, but negligible at typical combustion temperatures. At room temperature, the tunneling correction of 14 for O + H₂ reaction means that more than 90% of the total reactive flux is achieved by tunneling.

Sensitivity Analysis

Calculated rate constants are exquisitely sensitive to the input data used, which include rotational constants, harmonic vibrational frequencies, imaginary (barrier) frequency, anharmonic constants, and an energy

1
2
3 barrier.^{61,62,65} Of these parameters, the energy barrier and barrier
4
5 frequency are most important,^{61,62,65} especially at the low temperatures in
6
7 the atmosphere. In addition to these factors, we also studied effects of
8
9 various basis sets on ro-vibrational parameters that will in turn affect the
10
11 calculated rate constants. We found that the effects of basis sets on rate
12
13 constants are generally fairly small for this reaction system (see Figure S1
14
15 in the supporting information). Because the HEAT protocol was used, the
16
17 calculated energy barrier in this work is unlikely to be wrong by more
18
19 than 0.3 kcal/mol. The effects of such an energy error are negligible at
20
21 very high temperatures ($T > 2500\text{K}$), but may be significant at very low
22
23 temperatures. At room temperature, a change of barrier height by 0.2
24
25 kcal/mol can result in an alteration of rate constant of about 40%.
26
27 However, our calculated rate constants agree well with available
28
29 experiments at around room temperature, and we therefore conclude that
30
31 our calculated barrier is quite accurate. In addition, there are no
32
33 experimental data below room temperature, because the reaction rate
34
35 under these temperature conditions is too slow to be measurable.
36
37
38
39
40
41
42
43
44

45 46 **Conclusions**

47
48 In this work, we have used high accuracy quantum chemistry to compute
49
50 ro-vibrational parameters and energies of the title reaction system,
51
52 followed by calculation of thermal rate constants using the SCTST/VPT2
53
54
55
56
57
58
59
60

approach. Some salient results of this study can be summarized as follows:

- (i) The reaction of $O(^3P) + H_2 = OH + H$ is predicted to be endothermic by 1.45 ± 0.10 kcal/mol, in excellent agreement with an ATcT value of 1.54 ± 0.01 kcal/mol.
- (ii) Classical barrier heights are predicted to be 13.1 ± 0.2 kcal/mol (without DBOC and SO corrections) and 13.5 ± 0.2 kcal/mol (including both DBOC and SO corrections). The former agrees well (within 0.1 kcal/mol) with all barriers reported recently in the literature, where the smaller SO and DBOC effects have heretofore been ignored.
- (iii) For $T \leq 2500K$, calculated thermal rate constants for the title reaction and its isotopic analogs are in quantitative agreement (within 5-15%) with all experimental data where they are available. For $T > 2500K$, the calculated $k(T)$ values systematically underestimate the experiment by about 15 to 35%. This underestimation may be due to the fact that non-statistical population fractions of vibrationally excited $H_2(v_{HH}=1&2)$ molecules exist, and/or because of shortcomings of the VPT2 model. Other possible sources of error include rovibrational parameters, and/or neglecting coupling of vibrations and rotations in TS.

(iv) Thermal reaction rate constants of ground state oxygen atoms with vibrationally excited hydrogen atoms are derived and computed (see the supporting information). We are able to match the calculated $k(T)$ values with experiment by increasing the thermal population fractions of vibrationally first-excited hydrogen atoms ($v_{HH}=1$) with respect to the Boltzmann distribution. However, this is not in any way to be interpreted as convincing evidence of non-statistical behavior; in our view, a breakdown of VPT2 at very high temperatures is the more likely source of error.

Supporting information

Optimized geometries, rovibrational parameters, anharmonic constants, thermal rate constants, and energies for various species in the reaction of $O(^3P)$ with H_2 and its isotopic counterparts are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgements

JFS and TLN are supported by the Robert A. Welch Foundation (Grant F-1283) and the Department of Energy, Office of Basic Energy Sciences (Contract Number DE-FG02-07ER15884). We would like to thank John R. Barker, University of Michigan for bringing this reaction to our attention and his advice. We would like to thank an anonymous reviewer for

pointing us to Refs. 30, 43 and 72 and other comments that led to improvement of this work.

Table 1: Calculated relative energies (kcal/mol) of various terms in HEAT-345(Q) protocol

Species	δ_{HF}	$\delta_{\text{CCSD(T)}}$	δ_{CCSDT}	$\delta_{\text{CCSDT(Q)}^{\text{a)}}$	δ_{REL}	δ_{ZPE}	$\delta_{\text{DBOC}}^{\text{b)}$	δ_{SO}	δ_{HEAT}
$\text{O}(^3\text{P}) + \text{H}_2$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$\text{OH}(^2\Pi) + \text{H}$	15.3913	-13.0763	0.0308	-0.1239	0.1255	-0.9420	0.0168	0.0241	1.4463 (1.3351) ^{c)}
TS ($\text{O}-\text{H}-\text{H}, ^2\Pi$)	32.1324	-18.7682	-0.1756	-0.1064	0.0405	-2.2853	0.1704	0.2228	11.2306 (11.1799) ^{c)}

- a) Calculated at CCSDT(Q)/cc-pVTZ level of theory
b) Obtained with CCSD/aug-cc-pVTZ level of theory
c) Obtained with HEAT-456(Q) protocol

Table 2: A comparison of classical barrier heights and geometrical parameters of collinear TS in the $\text{O}(^3\text{P}) + \text{H}_2 = \text{OH} + \text{H}$ reaction calculated using various levels of theory

Method	Authors	Year	V_o (kcal/mol)	O—H (Å)	H—H (Å)
MRCI+Q/ [5s5p3d2f]g/4s3p2d1f]	Walch ^{a)}	1987	12.4	1.225	0.893
J3 surface	Joseph-Truhlar-Garrett ^{b)}	1988	13.03	1.217	0.915
Ext-CAS+1+2+Q/CBS	Peterson-Dunning ^{c)}	1997	13.1	1.215	0.894
RMOS surface ICCI+Q/CBS(aT,aQ,a5)	Rogers et al ^{d)}	2000	13.26 ± 0.3	1.244	0.865
GLDP surface ICCI+Q/CBS(aT,aQ,a5)	Rogers et al ^{d)}	2000	13.04 ± 0.3	1.217	0.903
BMS1 surface	Brandao et al ^{e)}	2004	$13.08 \pm <0.3$	1.203	0.922
BMS2 surface	Brandao et al ^{e)}	2004	$13.04 \pm <0.3$	1.201	0.920
AP surface MRCI+Q/aug-cc-pV5Z	Zhai et al ^{f)}	2012	13.40	1.206	0.887
HEAT-345(Q)	This work	2013	$13.13 \pm 0.20^{\text{g)}$ $[13.35 \pm 0.20]^{\text{h)}$ $(13.52 \pm 0.20)^{\text{i)}$	1.210	0.894
HEAT-456(Q)	This work	2013	$13.07 \pm 0.20^{\text{g)}$ $[13.29 \pm 0.20]^{\text{h)}$ $(13.46 \pm 0.20)^{\text{i)}$	1.210	0.894
FC-CCSD(T)/ aug-cc-pVQZ	This work	2013		1.213	0.894
FC-CCSD(T)/ aug-cc-pV5Z	This work	2013		1.215	0.893
FC-CCSD(T)/cc-pV5Z	This work	2013		1.213	0.894
FC-CCSD(T)/cc-pV6Z	This work	2013		1.215	0.893

- a) Ref. 6
- b) Ref. 7
- c) Ref. 8
- d) Ref. 9
- e) Ref. 10
- f) Ref. 11
- g) The values exclude both DBOC and SO corrections.
- h) The values in brackets include SO corrections, but not DBOC.
- i) The values in parentheses include both DBOC and SO corrections.

Table 3: Classical barrier heights (V_o), vibrationally adiabatic barrier heights (V_a), DBOC and zero-point vibration energies (ZPE) for $O(^3P) + H_2$ and its various isotopes. All are in kcal/mol.

Reactions	V_o	DBOC	$V_o + \text{DBOC}$	ZPE	V_a
$O(^3P) + H_2$	0.0000	0.0000	0.0000	0.0000	0.000
$OH + H$	2.3714	0.0168	2.3882	-0.9420	1.446
TS (O—H—H)	13.3455	0.1704	13.5159	-2.2853	11.231
$O(^3P) + D_2$	0.0000	0.0000	0.0000	0.0000	0.000
$OD + D$	2.3714	-0.0199	2.3515	-0.5600	1.792
TS (O—D—D)	13.3455	0.0865	13.4320	-1.5847	11.847
$O(^3P) + HD$	0.0000	0.0000	0.0000	0.0000	0.000
$OH + D$	2.3714	0.0133	2.3847	-0.1148	2.270
TS (O—H—D)	13.3455	0.1583	13.5038	-2.2276	11.276
$O(^3P) + DH$	0.0000	0.0000	0.0000	0.0000	0.000
$OD + H$	2.3714	-0.0163	2.3551	-1.5440	0.811
TS (O—D—H)	13.3455	0.0986	13.4441	-1.7425	11.702

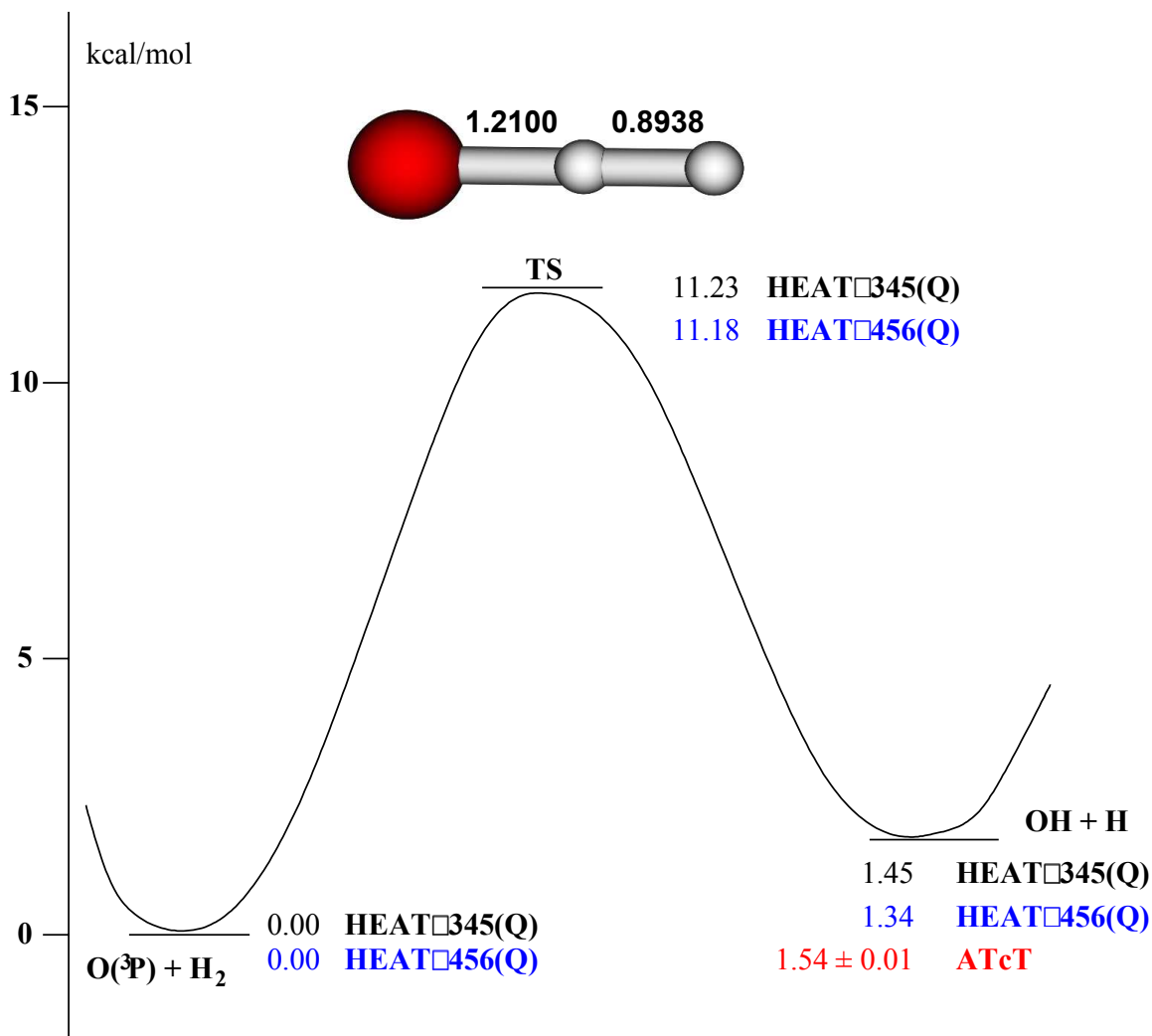


Figure 1: Schematic reaction energy profile of $\text{O}(^3\text{P})$ with H_2 was constructed using HEAT protocol.

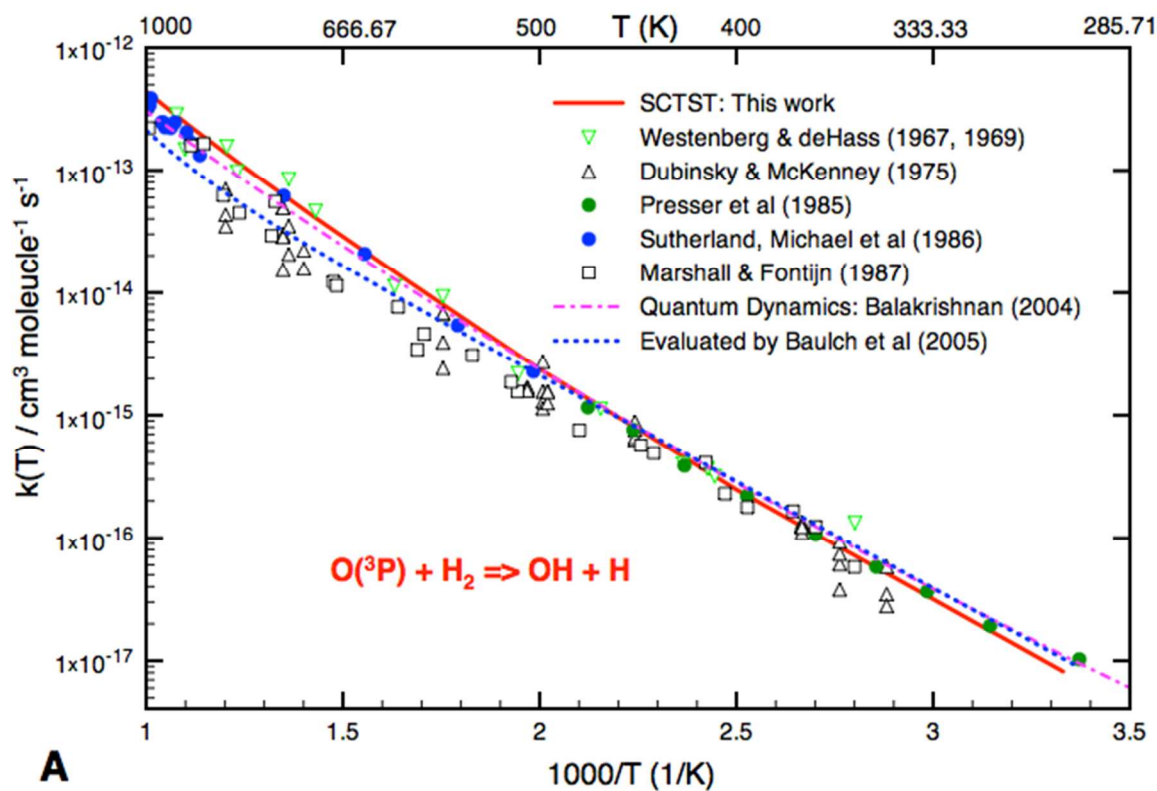


Figure 2A:

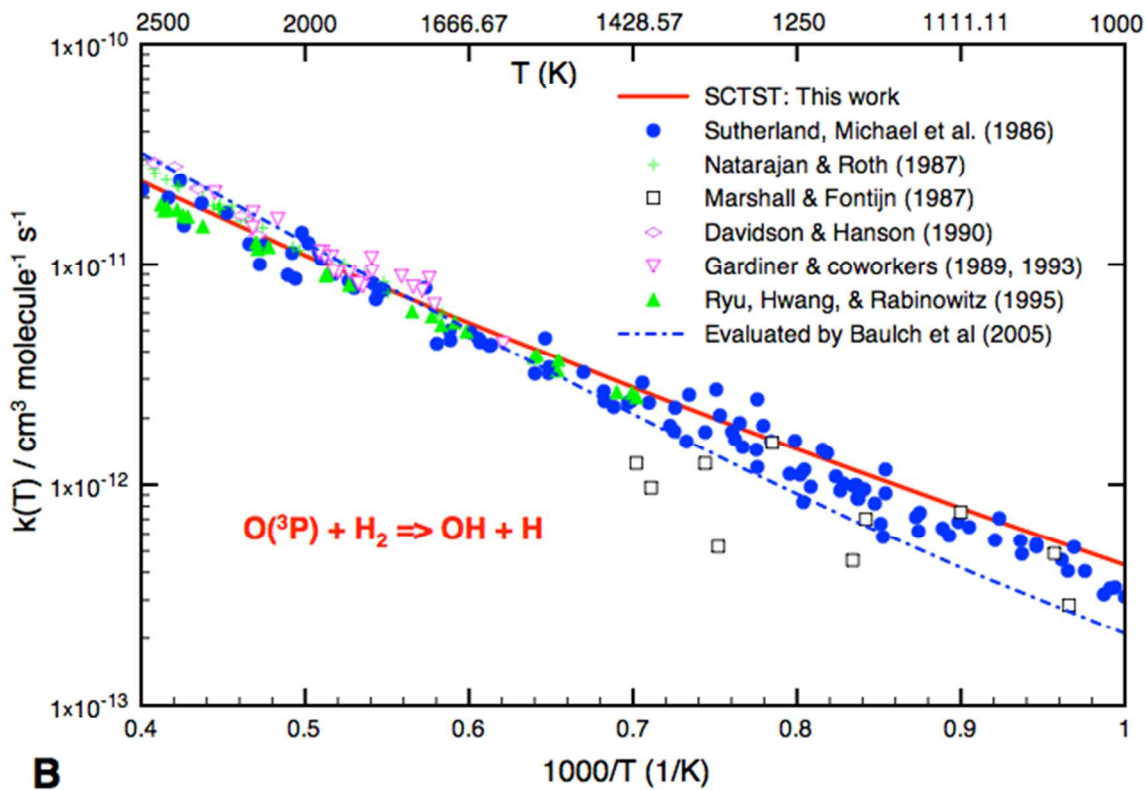


Figure 2B:

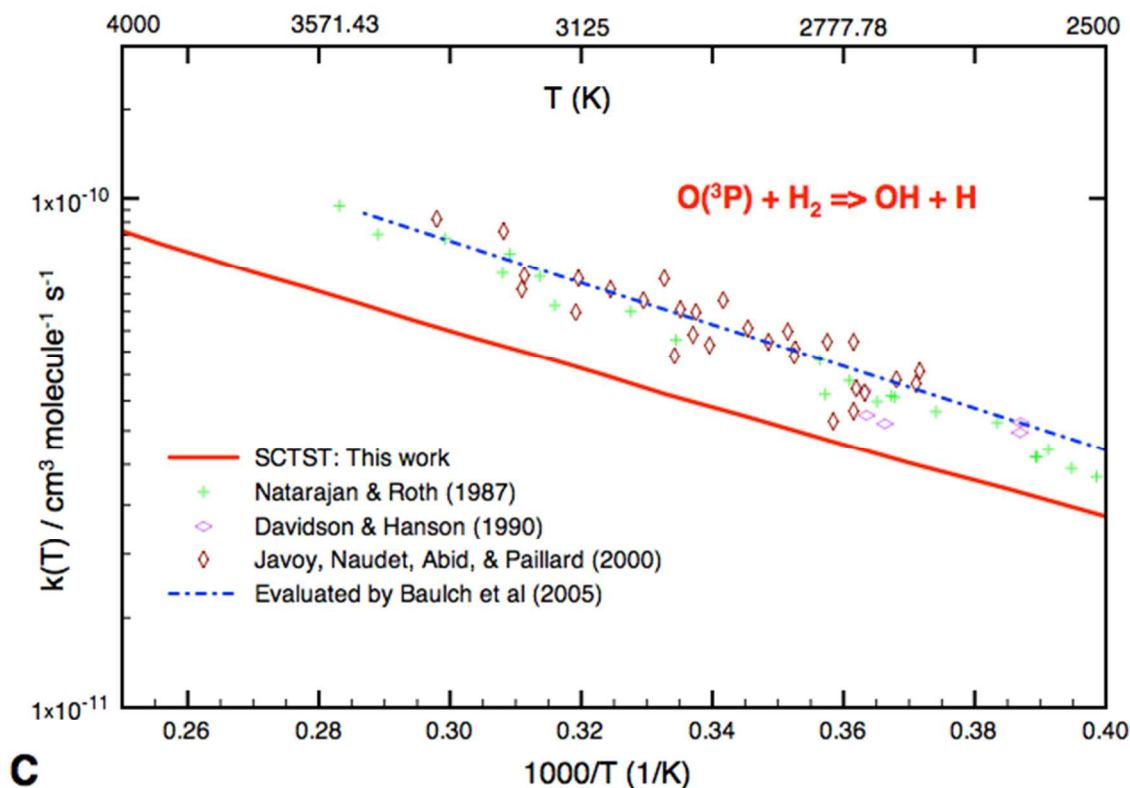


Figure 2: Thermal reaction rate constants for reactions of $O(^3P)$ with H_2 molecules were calculated for a wide range of temperature: 298-1000K (Fig. 2A), 1000-2500K (Fig. 2B), and 2500-4000K (Fig. 2C). Available experimental data are also included for comparison.

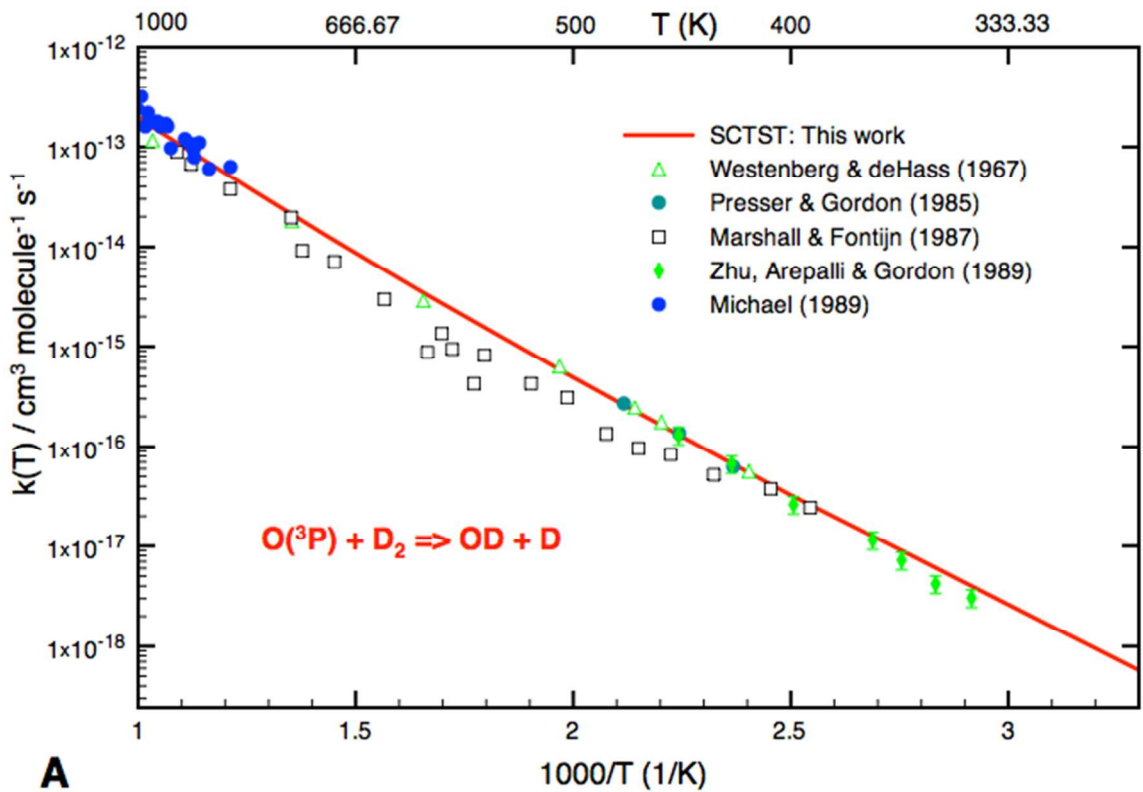


Fig. 3A:

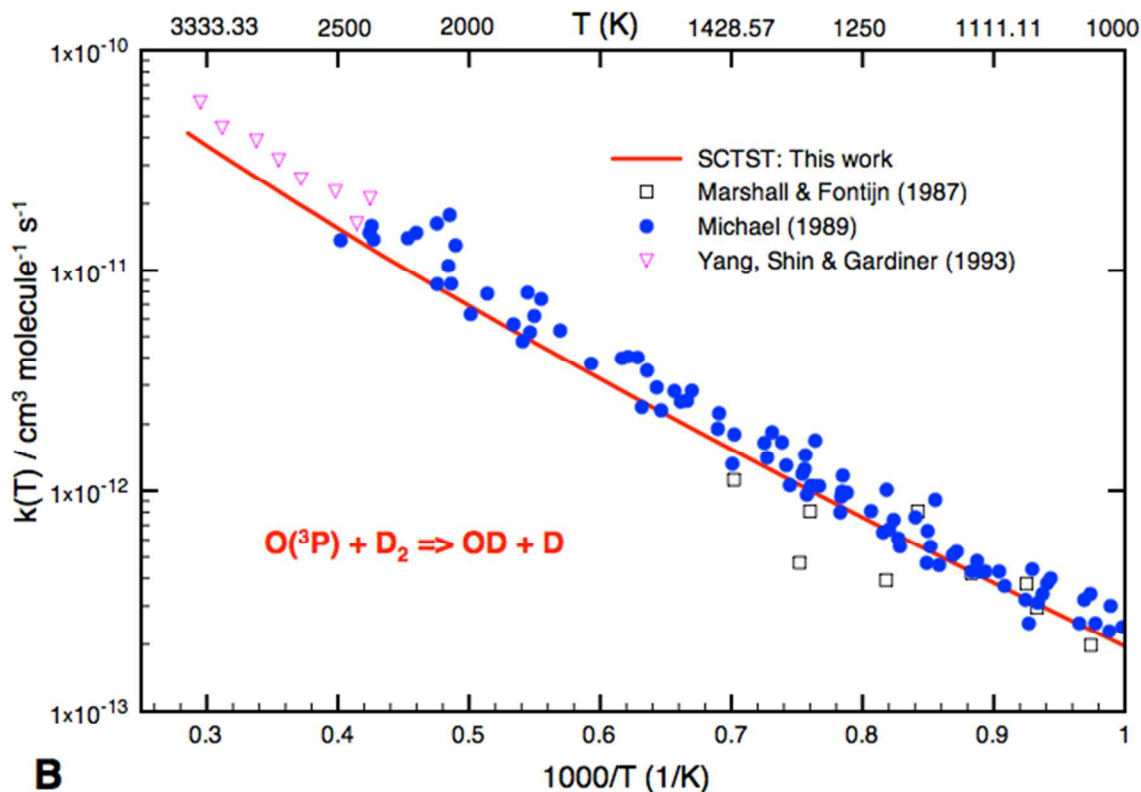


Figure 3: Thermal rate constants for reactions of $\text{O}(^3\text{P})$ with D_2 molecules were calculated for a wide range of temperature: 298-1000K (Fig. 3A) and 1000-3500K (Fig. 3B). Available experimental data are also included for comparison.

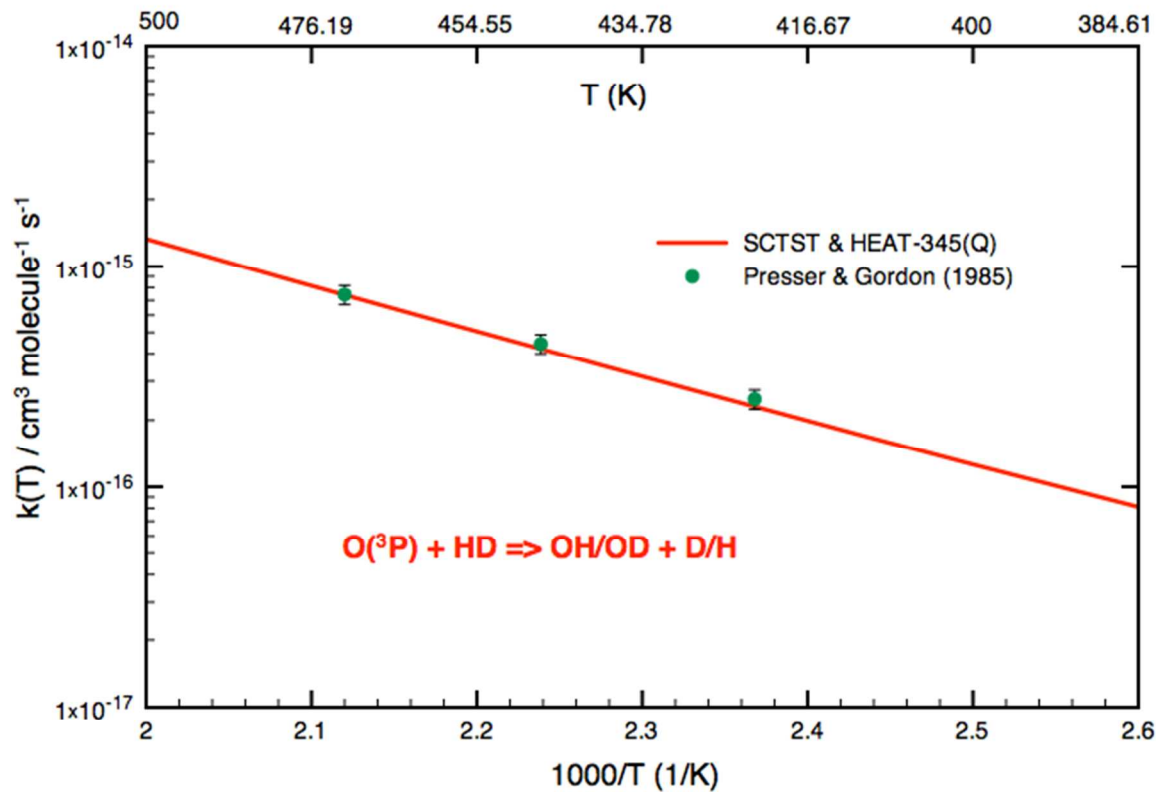


Figure 4: Thermal rate constants for $\text{O}(^3\text{P})$ with HD were calculated for a short range of temperature from 390 to 500K. Available experimental data were also included for comparison.

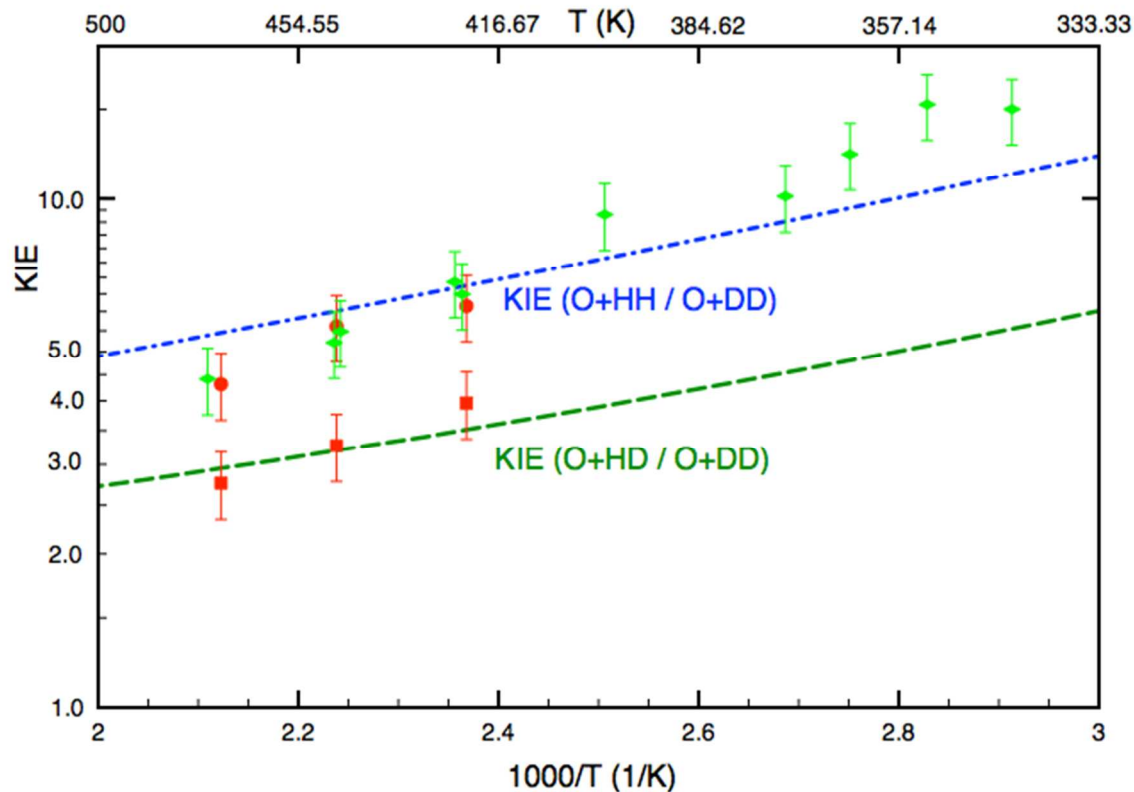


Figure 5: A comparison of theoretical with experimental kinetic isotope effects (KIE) in a short range of temperature, 333-500K. Dash and dot-dash lines are theoretical results calculated with SCTST approach. The symbols are experimental data from Gordon's group: the red symbols are taken from ref. 18 and the green symbols are from ref. 23.

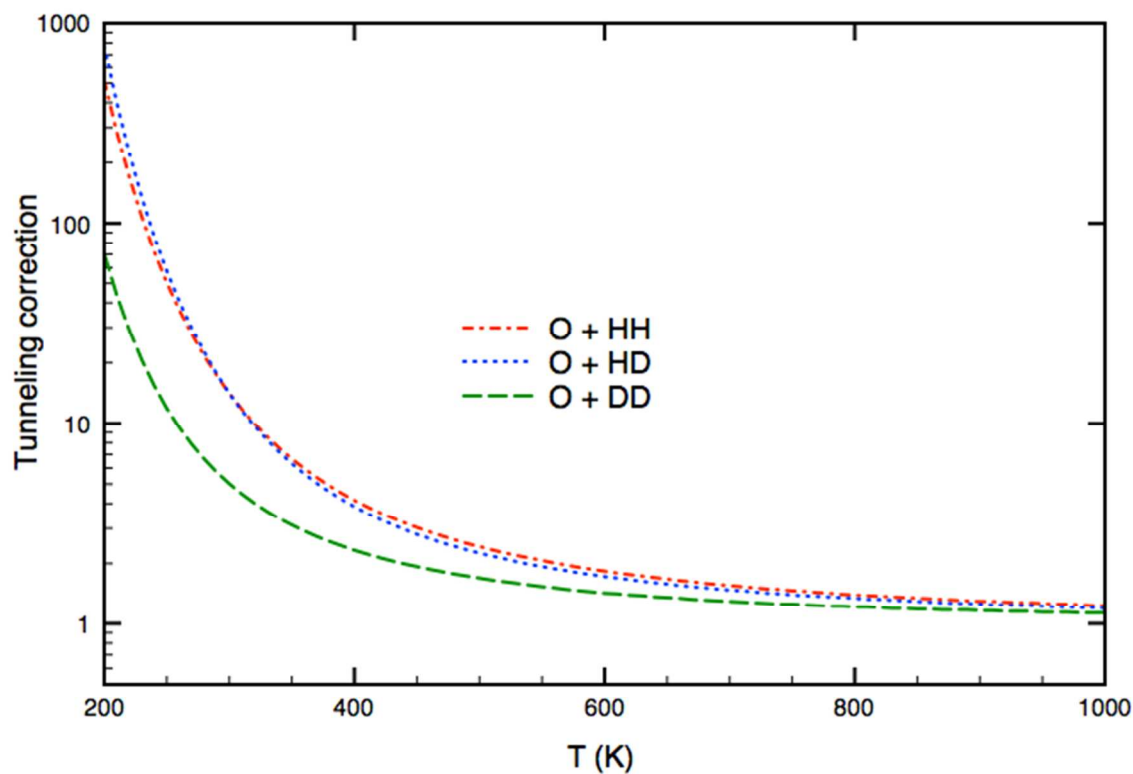


Figure 6: SCTST tunneling corrections for $\text{O}(^3\text{P}) + \text{H}_2$ and its isotopic analogs calculated as a function of temperature.

References

- (1) Zeller, R. in “*Combustion Chemistry*”, edited. by Gardiner Jr. W. C., Springer-Verlag New York Inc., **1985**.
- (2) Miller, J. A.; Pilling, M. J.; Troe, J. Unravelling Combustion Mechanisms through a Quantitative Understanding of Elementary Reactions. *Proc. Comb. Inst.* **2005**, *30*, 43-88.
- (3) Konnov, A. A. Remaining Uncertainties in the Kinetic mechanism of Hydrogen Combustion. *Combustion and Flame*, **2008**, *152*, 507-528.
- (4) Dautove, N. G.; Starik, A. M. Kinetics of Combustion of $\text{H}_2 + \text{O}_2$ Mixture with Participation of Vibrationally Excited Molecules. *Combustion, Explosion, and Shock Waves*, **1994**, *30*, 571-581.
- (5) Baulch D. L. et al. Evaluated Kinetic Data for Combustion Modeling: Supplement II. *J. Phys. Chem. Ref. Data* **2005**, *34*, 757-1397.
- (6) Walch, S. P. Extended Active Space CASSCF/MRSD CI Calculations of the Barrier height for the Reaction $\text{O} + \text{H}_2 = \text{OH} + \text{H}_2$. *J. Chem. Phys.* **1987**, *86*, 5670-5675.
- (7) Joseph, T; Truhlar, D. G.; Garrett, B. C. Improved Potential Energy Surfaces for the Reaction $\text{O}(^3\text{P}) + \text{H}_2 = \text{OH} + \text{H}$. *J. Chem. Phys.* **1988**, *88*, 6982-6990.
- (8) Peterson, K. A.; Dunning Jr., T. H. Benchmark Calculations with Correlated Molecular Wave Functions. 11. Energetics of the Elementary Reactions $\text{F} + \text{H}_2$, $\text{O} + \text{H}_2$ and $\text{H} + \text{HCl}$. *J. Phys. Chem. A*, **1997**, *101*, 6280-6292.
- (9) Rogers, S.; Wang, D.; Kuppermann, A.; Walch S. Chemically Accurate ab Initio Potential Energy Surfaces for the Lowest $^3\text{A}'$ and $^3\text{A}''$ Electronically Adiabatic States of $\text{O}(^3\text{P}) + \text{H}_2$. *J. Phys. Chem. A*, **2000**, *104*, 2308-2325.
- (10) Brandao, J.; Mogo, C.; Silva, B. C. Potential Energy Surface for $\text{H}_2\text{O}(^3\text{A}'')$ from Accurate an Initio Data with Inclusion of Long-Range Interactions. *J. Chem. Phys.* **2004**, *121*, 8861-8868.
- (11) Zhai, H.; Zhang, P.; Zhou, P. Quantum Wave Packet Calculation of the $\text{O}(^3\text{P}) + \text{H}_2$ Reaction on the New Potential Energy Surfaces for the Two Lowest States. *Comp. Theo. Chem.* **2012**, *986*, 25-29.
- (12) Reynard, L. M.; Donaldson, D. J. OH Production from the Reaction of Vibrationally Excited H_2 in the Mesosphere. *Geo. Res. Letters* **2001**, *28*, 2157-2160.
- (13) Balakrishnan, N. On the Role of Vibrationally Excited H_2 as a Source of OH in the Mesosphere. *Geo. Res. Letters* **2004**, *31*, L04106(1-4).
- (14) Sultanov, R. A.; Balakrishnan, N. Oxygen Chemistry in the Interstellar Medium: the Effects of Vibrational Excitation of H_2 in the $\text{O}(^3\text{P}) + \text{H}_2$ Reaction. *The Astrophysical Journal*. **2005**, *629*, 305-310.

- (15) Westenberg, A. A.; de Haas N. Atom-Molecule Kinetics at High Temperature Using ESR Detection. Technique and Results for $O + H_2$, $O + CH_4$, and $O + C_2H_6$. *J. Chem. Phys.* **1967**, *46*, 490-501.
- (16) Westenberg, A. A.; de Haas N. Atom-Molecule Kinetics Using ESR Detection. III. Results for $O + H_2 = OD + D$ and Theoretical Comparison with $O + H_2 = OH + H$. *J. Chem. Phys.* **1967**, *47*, 4241-4246.
- (17) Westenberg, A. A.; de Haas N. Reinvestigation of the Rate Coefficients for $O + H_2$ and $O + CH_4$. *J. Chem. Phys.* **1969**, *50*, 2512-2516.
- (18) Presser, N.; Gordon, R. J. The Kinetic Isotopic Effect in the Reaction of $O(^3P)$ with H_2 , D_2 , and HD . *J. Chem. Phys.* **1985**, *82*, 1291-1297.
- (19) Sutherland, J. W.; Michael, J. V.; Pirraglia, A. N.; Nesbitt, F. L.; Klemm, R. B. Rate Constant for the Reaction of $O(^3P)$ with H_2 by the Flash Photolysis-Shock Tube and Flash Photolysis-Resonance Fluorescence Techniques; $504K \leq T \leq 2495K$. *21st Sym. Int. Comb. Inst.* **1986**, 929-941.
- (20) Natarajan, K.; Roth, P. High-Temperature Rate Coefficient for the Reaction of $O(^3P)$ with H_2 Obtained by the Resonance-Absorption of O-Atoms and H-Atoms. *Combustion & Flame*, **1987**, *70*, 267-279.
- (21) Marshall, P.; Fontijn, A. HTP Kinetics Studies of the Reactions of $O(2^3P_1)$ Atoms with H_2 and D_2 over Wide Temperature Ranges. *J. Chem. Phys.* **1987**, *87*, 6988-6994.
- (22) Michael, J. V. Rate Constants for the Reaction $O + D_2 = OD + D$ by the Flash Photolysis-Shock Tube Technique over the Temperature Range 825-2487K: The H_2 to D_2 Isotope Effects. *J. Chem. Phys.* **1989**, *90*, 189-198.
- (23) Zhu, Y. F.; Arepalli, S.; Gordon, R. J. The Rate Constant for the Reaction $O(^3P) + D_2$ at Low Temperatures. *J. Chem. Phys.* **1989**, *90*, 183-188.
- (24) Shin, K. S.; Fujii, N.; Gardiner Jr., W. C. Rate-Constant for $O + H_2 = OH + H$ by Laser-Absorption Spectroscopy of OH in Shock-Heated H_2 - O_2 -Ar Mixtures. *Chem. Phys. Lett.* **1989**, *28*, 4358-4366.
- (25) Robie, D. C.; Arepalli, S.; Presser, N.; Kitsopoulos, T.; Gordon, R. J. The Intramolecular Kinetic Isotope Effect for the Reaction $O(^3P) + HD$. *J. Chem. Phys.* **1990**, *92*, 7382-7393.
- (26) Davidson, D. F.; Hanson, R. K. A Direct Comparison of Shock-Tube Photolysis and Pyrolysis Methods in the Determination of the Rate Coefficient for $O + H_2 = OH + H$. *Combustion & Flame* **1990**, *82*, 445-447.
- (27) Yang, H. X.; Shin, K. S.; Gardiner Jr., W. C. Rate Coefficients for $O + H_2 = OH + H$ and $O + D_2 = OD + D$ by Kinetic Laser Absorption Spectroscopy in Shock Waves. *Chem. Phys. Lett.* **1993**, *207*, 69-74.

- (28) Ryu, S. O.; Hwang, S. M.; Rabinowitz, M. J. Rate Coefficient of the $O + H_2 = OH + H$ Reaction Determined via Shock Tube-Laser Absorption Spectroscopy. *Chem. Phys. Lett.* **1995**, *242*, 279-284.
- (29) Javoy, S.; Naudet, V.; Abid, S.; Paillard, C. E. Rate Constant for the Reaction of O with H_2 at High Temperature by Resonance Absorption Measurements of O Atoms. *Int. J. Chem. Kinet.* **2000**, *32*, 686-695.
- (30) Dubinsky, R. N.; McKenney, D. J. "Determination of the Rate Constant of the $O + H_2 \rightarrow OH + H$ Reaction using Atomic Oxygen Resonance Fluorescence and the Air Afterglow Techniques". *Can. J. Chem.* **1975**, *53*, 3531-3541.
- (31) Schatz, G. C.; Wagner, A. F.; Walch, S. P.; Bowman, J. M. A Comparative Study of the Reaction Dynamics of Several Potential Energy Surfaces of $O(^3P) + H_2 = OH + H$. *J. Chem. Phys.* **1981**, *74*, 4984-4996.
- (32) Lee, K. T.; Bowman, J. M.; Wagner, A. F.; Schatz, G. C. A Comparative Study of the Reaction Dynamics of Several Potential Energy Surfaces of $O(^3P) + H_2 = OH + H$. II. Collinear Exact Quantum and Quasiclassical Reaction Probabilities. *J. Chem. Phys.* **1982**, *76*, 3563-3582.
- (33) Garrett, B. C.; Truhlar, D. G.; Bowman, J. M.; Wagner, A. F.; Robie, D.; Arepalli, S.; Presser, N.; Gordon, R. J. An Initio Prediction and Experimental Confirmation of Large Tunneling Contributions to Rate Constants and Kinetic Isotope Effects for Hydrogen Atom Transfer Reactions. *J. Am. Chem. Soc.* **1986**, *108*, 3515-3516.
- (34) Garrett, B. C.; Truhlar, D. G.; Bowman, J. M.; Wagner, A. F. Evaluation of Dynamical Approximations for Calculating the Effects of Vibrational Excitation on Reaction Rates. $O + H_2(n=0,1) \rightleftharpoons OH(n=0,1) + H$. *J. Phys. Chem.* **1986**, *90*, 4305-4311.
- (35) Garrett, B. C.; Truhlar, D. G. Thermal and State-Selected Rate Constant calculations for $O(^3P) + H_2 = OH + H$ and Isotopic Analogs. *Int. J. Quant. Chem.* **1986**, *29*, 1463-1482.
- (36) Haug, K.; Schwenke, D. W.; Truhlar, D. G.; Zhang, Y.; Zhang, J. Z. H.; Kouri, D. J. Accurate Quantum Mechanical Reaction Probabilities for the Reaction $O + H_2 = OH + H$. *J. Chem. Phys.* **1987**, *87*, 1892-1894.
- (37) Han, J.; Chen, X.; Weiner, B. R. Reaction Dynamics of $O(^3P) + H_2(v=1)$. *Chem. Phys. Lett.* **2000**, *332*, 243-250.
- (38) Garton, D. J.; Minton, T. K.; Maiti, B.; Troya, D.; Schatz, G. C. A Crossed Molecular beam Study of the $O(^3P) + H_2$ Reaction: Comparison of Excitation Function with Accurate Quantum Reactive Scattering Calculations. *J. Chem. Phys.* **2003**, *118*, 1585-1588.

- (39) Balakrishnan, N. Quantum Mechanical Investigation of the $O + H_2 = OH + H$ Reaction. *J. Chem. Phys.* **2003**, *119*, 195-199.
- (40) Maiti, B.; Schatz, G. C. Theoretical Studies of Intersystem Crossing Effects in the $O(^3P, ^1D) + H_2$ Reaction. *J. Chem. Phys.* **2003**, *119*, 12360-12371.
- (41) Braunstein, M.; Adler-Golden S.; Maiti, B.; Schatz, G. C. Quantum and Classical Studies of the $O(^3P) + H_2(v=0-3, j=0) = OH + H$ Reaction Using Benchmark Potential Surfaces. *J. Chem. Phys.* **2004**, *120*, 4316-4323.
- (42) Sultanov, R. A.; Balakrishnan, N. Isotope Branching and Tunneling in $O(^3P) + HD = OH + D$; $OD + H$ Reactions. *J. Chem. Phys.* **2004**, *121*, 11038-11044.
- (43) Balakrishnan, N. Quantum Calculations of the $O(^3P) + H_2 = OH + H$ Reaction. *J. Chem. Phys.* **2004**, *121*, 6346-6352.
- (44) Weck, P. F.; Balakrishnan, N. Reactivity Enhancement of Ultracold $O(^3P) + H_2$ Collisions by van der Waals Interactions. *J. Chem. Phys.* **2005**, *123*, 144308(1-7).
- (45) Garashchuk, S.; Rassolov, V. A.; Schatz, G. C. Semiclassical Nonadiabatic Dynamics Based on Quantum Trajectories for the $O(^3P, ^1D) + H_2$ System. *J. Chem. Phys.* **2006**, *124*, 244307(1-8).
- (46) Weck, P. F.; Balakrishnan, N.; Brandao, J.; Rosa, C.; Wang, W. Dynamics of the $O(^3P) + H_2$ Reaction at Low Temperatures: Comparison of Quasiclassical Trajectory with Quantum Scattering Calculations. *J. Chem. Phys.* **2006**, *124*, 074308(1-8).
- (47) Garton, D. J.; Brunsvold, A. L.; Minton, T. K.; Troya, D.; Maiti, B.; Schatz, G. C. Experimental and Theoretical Investigations of the Inelastic and Reactive Scattering Dynamics of $O(^3P) + D_2$. *J. Phys. Chem. A*, **2006**, *110*, 1327-1341.
- (48) Lahankar, S. A.; Zhang, J.; McKendrick, K. G.; Minton, T. K. Product-State-Resolved Dynamics of the Elementary Reaction of Atomic Oxygen with Molecular Hydrogen, $O(^3P) + D_2 = OD(X^2\Pi) + D$. *Natural Chemistry*, **2013**, *5*, 315-319.
- (49) Atahan, S.; Klos, J.; Zuchowski, P. S.; Alexander, M. H. An ab initio Investigation of the $O(^3P)-H_2$ van der Waals Well. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4420-4426.
- (50) Wang, W.; Rosa, C.; Brandao, J. Theoretical Studies on the $O(^3P) + H_2 = OH + H$. *Chem. Phys. Lett.* **2006**, *418*, 250-254.
- (51) Han, B.; Zheng, Y. Nonadiabatic Quantum Dynamics in $O(^3P) + H_2 = OH + H$: A Revised Study. *J. Comp. Chem.* **2011**, *32*, 3520-3525.
- (52) Miller, W. H., Semi-Classical Theory for Non-Separable Systems: Construction of "Good" Action-Angle Variables for Reaction Rate Constants, *Faraday Disc. Chem. Soc.* **1977**, *62*, 40-46.
- (53) Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D.; Willets, A. Ab Initio Calculation of Anharmonic Constants for a Transition-State, with Application to

Semiclassical Transition-State Tunneling Probabilities. *Chem. Phys. Letters* **1990**, *172*, 62-68.

(54) Nguyen, T. L.; Stanton, J. F.; Barker, J. R., A Practical Implementation of Semi-Classical Transition State Theory for Polyatomics, *Chem. Phys. Lett.* **2010**, *499*, 9-15.

(55) Nguyen, T. L.; Stanton, J. F.; Barker, J. R., Ab Initio Reaction Rate Constants Computed Using Semiclassical Transition-State Theory: $\text{HO} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ and Isotopologues. *J. Phys. Chem. A* **2011**, *115*, 5118-5126.

(56) Nguyen T. L.; Barker, J. R. Sums and Densities of Fully Coupled Anharmonic Vibrational States: A Comparison of Three Practical Methods. *J. Phys. Chem. A* **2010**, *114*, 3718-3730.

(57) Barker, J. R.; Ortiz, N. F.; Preses, J. M.; Lohr, L. L.; Maranzana, A.; Stimac, P. J.; Nguyen, T. L.; Kumar, T. J. D. Ann Arbor, Michigan, USA (<http://aoss.engin.umich.edu/multiwell/>), 2011.

(58) Tajti, A.; Szalay, P. G.; Csaszar, A. G.; Kallay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vazquez, J.; Stanton, J. F. HEAT: High Accuracy Extrapolated Ab Initio Thermochemistry. *J. Chem. Phys.* **2004**, *121*, 11599-11613.

(59) Bomble, Y. J.; Vazquez, J.; Kallay, M.; Michauk, C.; Szalay, P. G.; Csaszar, A. G.; Gauss, J.; Stanton, J. F. High-Accuracy Extrapolated Ab Initio Thermochemistry. II. Minor Improvements to the Protocol and a Vital Simplification. *J. Chem. Phys.* **2006**, *125*, 064108-8.

(60) Harding, M. E.; Vazquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. High-Accuracy Extrapolated Ab Initio Thermochemistry. III. Additional Improvements and Overview. *J. Chem. Phys.* **2008**, *128*, 114111-15.

(61) Nguyen T. L.; Stanton, J. F. Ab Initio Rate Calculations of $\text{HO} + \text{HO} = \text{O}(^3\text{P}) + \text{H}_2\text{O}$ Reaction and Isotopologues. *J. Phys. Chem. A* **2013**, *117*, 2678-2686.

(62) Nguyen T. L.; Li, J.; Dawes, R.; Stanton, J. F.; Guo, H. Accurate Determination of Barrier Height and Kinetics for the $\text{F} + \text{H}_2\text{O} = \text{HF} + \text{OH}$ Reaction. *J. Phys. Chem. A* **2013**, *117*, 8864-8872.

(63) Barker, J. R.; Nguyen, T. L.; Stanton, J. F. Kinetic Isotopic Effects for $\text{Cl} + \text{CH}_4 = \text{HCl} + \text{CH}_3$ Calculated Using ab Initio Semiclassical Transition-State Theory. *J. Phys. Chem. A* **2012**, *116*, 6408-6419.

(64) Weston, R. E.; Nguyen, T. L.; Stanton, J. F.; Barker, J. R. $\text{HO} + \text{CO}$ Reaction Rates and H/D Kinetic Isotope Effects: Master Equation Models with an Initio SCTST Rate Constants. *J. Phys. Chem. A*, **2013**, *117*, 821-835.

(65) Nguyen, T. L.; Xue, B. C.; Weston, R. E.; Barker, J. R.; Stanton, J. F. Reaction of HO with CO : Tunneling is Indeed Important. *J. Phys. Chem. Lett.* **2012**, *3*, 1549-1553.

- (66) Light, G. C. The Effects of Vibrational Excitation on the Reaction of $O(^3P)$ with H_2 and the Distribution of Vibrational Energy in the Product OH. *J. Chem. Phys.* **1978**, *68*, 2831-2843.
- (67) Almlof, J.; Taylor, P. R. General Construction of Gaussian-Basis Sets. 1. Atomic Natural Orbitals for 1st-Row and 2nd-Row Atoms. *J. Chem. Phys.* **1987**, *86*, 4070-4077.
- (68) Almlof, J.; Taylor, P. R. General Construction of Gaussian-Basis Sets. 2. Atomic Natural Orbitals and the Calculation of Atomic and Molecular-Properties. *J. Chem. Phys.* **1990**, *92*, 551-560.
- (69) McCaslin L. M.; Stanton J. F. "Calculation of Fundamental Frequencies for Small Polyatomic Molecules: A Comparison of Correlation-Consistent and Atomic Natural Orbital Basis Sets", *Mol. Phys.* **2013**, *111*, 1492-1496.
- (70) Mills, I. M. Vibration-Rotation Structure in Asymmetric- and Symmetric-Top Molecules. In *Molecular Spectroscopy: Modern Research*; Rao, K. N.; Mathews, C. W., Eds.; Academic Press: New York, **1972**; Vol. 1, p 115.
- (71) NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 16a, August **2012**, Editor: Russell D. Johnson III; <http://cccbdb.nist.gov/>
- (72) Wagner, A. F.; Bowman, J. M.; Harding, L. H. "Inclusion and Assessment of Renner-Teller Coupling in Transition State Theory for States: Application to $O(^3P) + H_2$ ", *J. Chem. Phys.* **1985**, *82*, 1866-1872.
- (73) Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G.; Auer, w. c. f. A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; et al. CFOUR, *Coupled-Cluster Techniques for Computational Chemistry*, **2009**.
- (74) Kállay, M. Mrcc, a Quantum Chemical Program Suite Written by M. Kállay, Z. Rolik, I. Ladjánszki, L. Szegedy, B. Ladóczki, J. Csontos, and B. Kornis. See Also M. Kállay and Z. Rolik, *J. Chem. Phys.* **135** 104111 (2011) as Well As: www.mrcc.hu.
- (75) Ruscic, B.; Pinzon, R. E.; Morton, M. L.; von Laszewski, G.; Bittner, S. J.; Nijssure, S. G.; Amin, K. A.; Minkoff, M.; Wagner, A. F., Introduction to Active Thermochemical Tables: Several "Key" Enthalpies of Formation Revisited, *J. Phys. Chem. A* **2004**, *108*, 9979-9997.
- (76) Ruscic, B.; Pinzon, R. E.; von Laszewski, G.; Kodeboyina, D.; Burcat, A.; Leahy, D.; Montoya, D.; Wagner, A. F., Active Thermochemical Tables: Thermochemistry for the 21st Century, *J. Phys. Conf. Ser.* **2005**, *16*, 561-570.
- (77) Ruscic, B. Updated Active Thermochemical Tables (ATcT) Values Based on ver. 1.110 of the Thermochemical Network (2012); available at ATcT.anl.gov

(78) Bell, R. P. *The Tunnel Effect in Chemistry*, Chapman & Hall, London & New York, **1980**.

(79) Truhlar, D. G.; Isaacson, A. D. Statistical-Diabatic Model for State-Selected Reaction Rates. Theory and Application of Vibrational-Mode Correlation Analysis to $\text{OH}(\text{n}_{\text{OH}}) + \text{H}_2(\text{n}_{\text{HH}}) = \text{H}_2\text{O} + \text{H}$. *J. Chem. Phys.* **1982**, 77, 3516-3522.

Table of Contents (TOC) Image:

