$H + H_2$ Thermal Reaction: A Convergence of Theory and Experiment

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New experimental and theoretical rate constants for two isotopologs of the simplest chemical reaction, $H + H_2 \rightarrow H_2 + H$, are presented. The theoretical results are obtained using accurate quantum dynamics with a converged Born-Oppenheimer potential energy surface and include non-Born-Oppenheimer corrections. The new experiments are carried out using a shock tube and complement earlier investigations over a very large T range, 167 to 2112 K. Experiment and theory now agree perfectly, within experimental error, bringing this 75-year-old scientific problem to completion.

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The use of quantum mechanics for the theoretical prediction of thermal rate constants (k) for gas-phase chemical reactions has been a major goal of physical chemists for about 75 years [1,2]. This requires potential energy surfaces (PESs), which can be obtained by solving the electronic Schrödinger equation with fixed nuclei, and quantitative descriptions of the dynamics, which can be obtained in the Born-Oppenheimer (BO) approximation from the nuclear Schrödinger equation governed by that PES. The BO PES is independent of isotopic substitution. Early theoretical work involved semiempirical PESs and transition state theory [3,4]. By 1980, a PES [5–7] based on *ab initio* electronic structure calculations was used with variational transition state theory and multidimensional tunneling calculations to calculate k competitive in accuracy with experiment over a limited range of temperatures (T) [8–11]. This was followed shortly by an improved PES and various approximate calculations based on quantum scattering theory [12–15]; the agreement between experiment and these early calculations is good, though not perfect [16–18]. In recent years, investigations of the PES have continued unabated [19–24] eventually resulting in the CCI PES [23,24] that is globally accurate to within ~0.01 kcal/mol.

For accurate work, one should also include corrections to the BO approximation, due to the expectation value of nuclear kinetic energy operator in the electronic ground state [25,26]. This so-called adiabatic or Born-Oppenheimer diagonal correction has received less attention.

Accurate quantum dynamics calculations of k (by which we mean calculations that agree with converged quantum scattering results for a given PES within ~3%) have until very recently been restricted to the $D + H_2$ reaction, where results have been obtained for four PESs in the T range 167–1500 K [27,28]. At low T, k was very sensitive to the PES, and some results were as much as a factor of 2 higher than experiment.

There are four previous experimental investigations each for $D + H_2$ [29–32] and $H + D_2$ [30,33–35]. At high Ts, data for both reactions were obtained by the flash photolysis-shock tube (FPST) technique [32,35] in the T range ~700 to 2000 K. The results had a standard deviation (1σ) of ~25% due, in part, to corrections for secondary reaction complications, particularly at Ts above ~1400 K. These complications can be eliminated (though the range in T is substantially decreased) by using a thermal source for atoms under such low precursor conditions that secondary reactions are totally negligible. In recent studies [36,37], both deuterated and protonated isotopomers of ethyl iodide, C_2H_5I, have been used to prepare small concentrations of D and H atoms, respectively.

By using this hydrogen atom source, experimental ks for both reactions have been measured by the reflected shock tube technique [38,39] over the T range ~1150 to 2100 K. In these experiments, the thermodynamic state of the hot stagnant gas is calculated from the measured velocity of the incident shock wave and the preshock thermodynamic condition of the test gas, and corrections for nonidealities caused by boundary layer formation are applied [40,41]. Since the initial mole fractions of reactants are known, and the reflected shock wave density and T are determined from the shock strength, $[H_2]$ (or $[D_2]$) can be determined for each experiment. The D or H atoms formed from the thermal decompositions of ethyl iodide-d_5 or ethyl iodide were temporally monitored by atomic resonance absorption spectroscopy [42]. With excess H_2 or D_2 the concentration of atoms follows a pseudo-first-order rate law. Hydrogen atom product profiles were additionally measured in both cases, and k was also determined from pseudo-first-order buildup constants.

The results from both types of experiments are shown in Fig. 1 for the T range of ~1150–2100 K. The solid lines represent linear-least-squares fits which are listed in Table I with corresponding T ranges and 1σ deviations

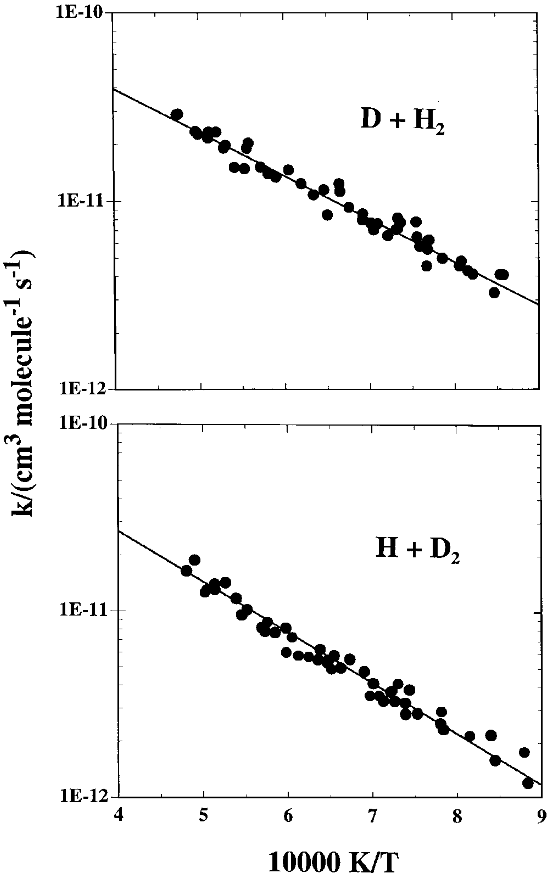

FIG. 1. Arrhenius plots of new shock tube data. Top: D + H_2; bottom: H + D_2. The solid lines in represent linear-least-squares fits to log(k) against T^{-1}, and the expressions thereby derived are given in Table I.

of the data from the lines. Earlier results [32,35] using the FPST technique are also listed in Table I. It is gratifying to note that the earlier shock tube data overlap the new results within the combined 1σ uncertainties of the two sets. The lower-T experimental results [29–31,33,34] are also listed in Table I; on experimental grounds suggested in the original references, we have eliminated the lowest-T point from each of three D + H_2 studies [29–31]. For each reaction, the data summarized by the expressions in Table I were used to evaluate k over the extended T range, ~200–2200 K. We have statistically weighted each study equally over its T range. The results of this procedure have then been least-squares fitted to a fifth-order polynomial expression of $\log k$ against T^{-1} resulting in the solid lines shown in Figs. 2 and 3. All of the data used in the evaluations are plotted in the figures. For D + H_2 and H + D_2, the individual data points (~ 200 points in both cases) show 1σ deviations of only 32% and 23%, respectively, from polynomial fits over the entire T ranges. Considering the variety of experimental methods and apparatuses (with attendant calibration issues), the fits are remarkably good over very large T ranges.

The theoretical calculations employed the outgoing wave variational principle [43–45] to calculate cumulative reaction probabilities (CRPs) for the CCI PES which were then integrated with Boltzmann weighting and divided by the reactant partition function to yield k. For the D + H_2 reaction, the CRPs were calculated for all significant total angular momentum, J, over the energy range 0.28–1.60 eV (relative to classical H + H_2) at an interval of 0.02 eV. For H + D_2, the CRPs were calculated for J = 7, 10, and 11 over the energy range 0.28–2.02 eV at an interval of 0.03 eV, and the sum over all J was calculated via a separable rotation approximation [27] with an effective transition state rotational constant that varies with T; this is typically accurate to within a few tenths of a percent, except at the lowest Ts where the errors may be as large as 1%–2% [27]. For both reactions only the even symmetry block of the CRP needed to be explicitly calculated since the contributions for the even and odd

TABLE I. Least-squares experimental rate constant expressions for D + H_2 and H + D_2.[a]

Ref.	A[b]	n	B K	T range K	σ[c] %
D + $H_2 \rightarrow$ HD + H					
29	4.08(−11)[d]	0	3628	274–468	±20
30	4.41(−11)	0	3560	252–745	±12
31	2.48(−25)	4.757	1870	167–346	±15
32	3.75(−10)	0	4984	655–1979	±28
New	3.17(−10)	0	5207	1166–2112	±11
H + $D_2 \rightarrow$ HD + D					
33	7.24(−12)	0	3671	368–468	±10[e]
34	2.12(−11)	0	4181	274–364	±11
30	4.28(−11)	0	4362	299–745	±19
35	3.95(−10)	0	5919	724–2160	±25
New	2.67(−10)	0	5945	1132–2082	±12

[a] Rate constants are $k = AT^n \exp(-B/T)$. [b] Units are cm^3 molecule^{-1} s^{-1}. [c] The 1σ standard deviation of the data from the fit, except where indicated otherwise. [d] Numbers in parentheses are powers of 10. [e] Estimated, considering systematic and random errors.

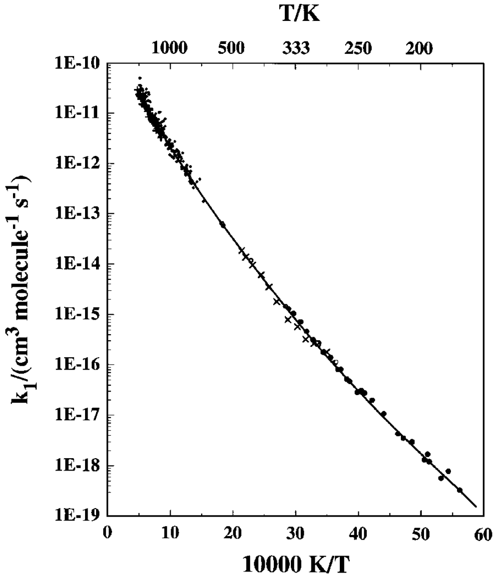

FIG. 2. Arrhenius plot of experimental data for the D + H_2 reaction. ×: Ref. [29], ○: Ref. [30], ●: Ref: [31], +: present work, and •: Ref. [32]. The solid line evaluation is a fifth-order least-squares polynomial fit to the data that is obtained by giving each set equal statistical weight.

blocks are essentially identical [27]. Contributions to k from CRPs at energies greater than those calculated were estimated via extrapolation; this increases the uncertainty in the calculations by an additional 1%–2% for the highest Ts. The reactant partition functions were obtained by eigenvalue summation, and the calculations included ortho-para weightings of 3 to 1 for D + H_2, and 2 to 1 for H + D_2. In other respects the calculations are similar to those performed previously [27].

TABLE II. Quantal rate constants calculated with the CCI PES and including non-Born-Oppenheimer corrections.[a]

T/K	k_{D+H_2}	k_{H+D_2}
170	2.16(−19)	⋯
180	4.57(−19)	⋯
200	1.86(−18)	2.51(−20)
250	3.40(−17)	1.19(−18)
300	2.96(−16)	1.86(−17)
350	1.51(−15)	1.43(−16)
400	5.38(−15)	6.85(−16)
450	1.48(−14)	2.38(−15)
500	3.38(−14)	6.54(−15)
600	1.21(−13)	3.10(−14)
800	6.46(−13)	2.37(−13)
1000	1.90(−12)	8.65(−13)
1200	4.12(−12)	2.16(−12)
1500	9.53(−12)	5.75(−12)
2000	2.45(−11)	1.64(−11)
2200	⋯	2.21(−11)

[a] All rate constants are in units, cm^3 molecule^{-1} s^{-1}.

Convergence and sensitivity studies indicate that the quantal k calculated using the CCI PES are within 3% of those for the *true* BO PES. The diagonal correction has little effect on the shape of the barrier, so its effect on k can be approximated with high accuracy by multiplying the BO quantal results by $\exp(-\Delta E_b/kT)$, where ΔE_b is the amount by which the barrier is raised for a given isotopolog. We calculated ΔE_b to an accuracy of about 1 cal/mol by multireference configuration interaction calculations employing extended reference spaces and large basis sets. The correction raises the barrier heights

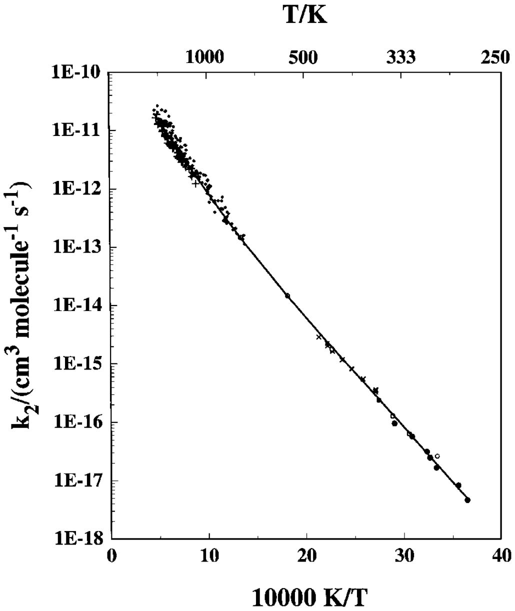

FIG. 3. Same as Fig. 2 for the H + D_2 reaction. ×: Ref. [33], ○: Ref. [30], ●: Ref. [34], +: present work, and •: Ref. [35].

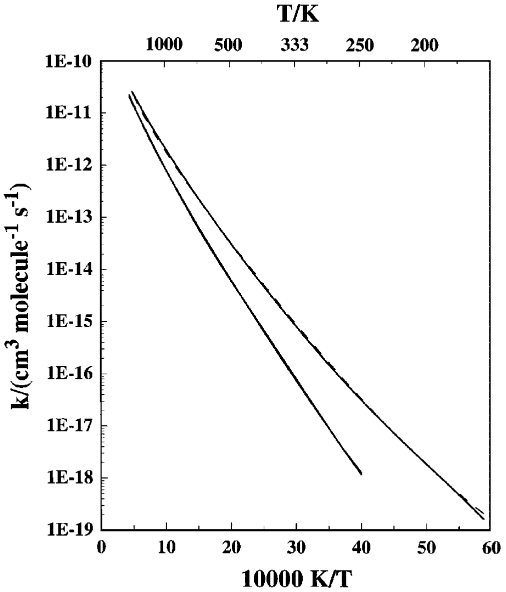

FIG. 4. Arrhenius plots of experimental evaluations (solid line) and theoretical calculations (Table II) (dashed line) for the D + H_2 (top) and H + D_2 (bottom) reactions.

by 139 cal/mol and 90 cal/mol for $D + H_2$ and $H + D_2$, respectively. For $D + H_2$, this correction reduces k at 167, 1000, and 2000 K by 34%, 7%, and 3%, respectively. The calculated non-BO quantal ks for both reactions are given in Table II.

Figure 4 compares the theoretical k to the evaluated experimental ones shown in Figs. 2 and 3. The new theoretical ks agree well with experiment, which is especially noteworthy in the low-T region where previous predictions [27,28] were not as accurate. Over the entire T range, the mean unsigned deviation of the experimental fit from theory is 10% for $D + H_2$ and 5% for $H + D_2$. Table I shows that no data set for either reaction has a smaller uncertainty than these values. Therefore theory and experiment agree within the new, smaller experimental error bars, and the theoretical ks of Table II should now be used to describe the rate behavior for these reactions. The list of solved problems in molecular quantum mechanics is very short, e.g., the electronic spectra of the hydrogen [46] and helium [47] atoms and the vibrational-rotational spectra of H_2 [48,49], H_2^+ [50,51], and H_3^+ [52,53]. Now the $H + H_2$ thermally averaged reaction rate constant can be added to the list.

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[1] F. London, Z. Elektrochem. Angew. Phys. Chem. **35**, 552 (1929).
[2] L. Farkas and E. Wigner, Trans. Faraday Soc. **32**, 708 (1936).
[3] D. G. Truhlar and R. E. Wyatt, Annu. Rev. Phys. Chem. **27**, 1 (1976).
[4] D. G. Truhlar and R. E. Wyatt, Adv. Chem. Phys. **36**, 141 (1977).
[5] B. Liu, J. Chem. Phys. **58**, 1925 (1973).
[6] P. Siegbahn and B. Liu, J. Chem. Phys. **68**, 2457 (1978).
[7] D. G. Truhlar and C. J. Horowitz, J. Chem. Phys. **68**, 2466 (1978).
[8] B. C. Garrett and D. G. Truhlar, Proc. Natl. Acad. Sci. U.S.A. **76**, 4755 (1979).
[9] B. C. Garrett and D. G. Truhlar, J. Chem. Phys. **72**, 3460 (1980).
[10] D. K. Bondi *et al.*, J. Chem. Phys. **76**, 4986 (1982).
[11] B. C. Garrett *et al.*, Int. J. Chem. Kinet. **18**, 1065 (1986).
[12] A. J. C. Varandas *et al.*, J. Chem. Phys. **86**, 6258 (1987).
[13] J. V. Michael *et al.*, Science **249**, 269 (1990).
[14] T. J. Park and J. C. Light, J. Chem. Phys. **94**, 2946 (1991).
[15] T. J. Park and J. C. Light, J. Chem. Phys. **96**, 8853 (1992).
[16] J. V. Michael and K. P. Lim, Annu. Rev. Phys. Chem. **44**, 429 (1993).
[17] J. V. Michael, in *Gas-Phase Chemical Reaction Systems: Experiments and Models 100 Years after Max Bodenstein*, edited by J. Wolfrum, H.-R. Volpp, R. Rannacher, and J. Warnatz (Springer-Verlag, Heidelberg, 1996), p. 177.
[18] S. S. Kumaran and J. V. Michael, J. Phys. Chem. **100**, 20172 (1996).
[19] A. I. Boothroyd *et al.*, J. Chem. Phys. **95**, 4343 (1991).
[20] A. I. Boothroyd *et al.*, J. Chem. Phys. **104**, 7139 (1996).
[21] H. Partridge, C. W. Bauschlicher, Jr., and J. R. Stallcop, J. Chem. Phys. **99**, 5951 (1993).
[22] D. L. Diedrich and J. B. Anderson, Science **258**, 786 (1992).
[23] S. L. Mielke, B. C. Garrett, and K. A. Peterson, J. Chem. Phys. **111**, 3806 (1999).
[24] S. L. Mielke, B. C. Garrett, and K. A. Peterson, J. Chem. Phys. **116**, 4142 (2002).
[25] C. J. Ballhausen and A. E. Hansen, Annu. Rev. Phys. Chem. **23**, 15 (1972).
[26] B. C. Garrett and D. G. Truhlar, J. Chem. Phys. **82**, 4543 (1985).
[27] S. L. Mielke *et al.*, J. Phys. Chem. **98**, 8000 (1994).
[28] L. Banares and M. J. D'Mello, Chem. Phys. Lett. **277**, 465 (1997).
[29] B. A. Ridley, W. R. Schulz, and D. J. Le Roy, J. Chem. Phys. **44**, 3344 (1966).
[30] A. A. Westenberg and N. De Haas, J. Chem. Phys. **47**, 1393 (1967).
[31] D. N. Mitchell and D. J. Le Roy, J. Chem. Phys. **58**, 3449 (1973).
[32] J. V. Michael and J. R. Fisher, J. Phys. Chem. **94**, 3318 (1990).
[33] W. R. Schulz and D. J. Le Roy, Can. J. Chem. **42**, 2480 (1965).
[34] I. S. Jayaweera and P. D. Pacey, J. Phys. Chem. **94**, 3614 (1990).
[35] J. V. Michael, J. Chem. Phys. **92**, 3394 (1990).
[36] M.-C. Su and J. V. Michael, Proc. Combust. Inst. **29**, 1219 (2002).
[37] M.-C. Su *et al.*, J. Phys. Chem. A **106**, 8261 (2002).
[38] J. V. Michael, Prog. Energy Combust. Sci. **18**, 327 (1992).
[39] J. V. Michael, in *Advances in Chemical Kinetics and Dynamics*, edited by J. R. Barker (JAI, Greenwich, CT, 1992), Vol. 1, p. 47.
[40] J. V. Michael and J. W. Sutherland, Int. J. Chem. Kinet. **18**, 409 (1986).
[41] J. V. Michael, J. Chem. Phys. **90**, 189 (1989).
[42] J. V. Michael and A. Lifshitz, in *Handbook of Shock Waves*, edited by G. Ben-Dor, O. Igra, T. Elperin, and A. Lifshitz (Academic Press, New York, 2001), Vol. 3, p. 77.
[43] Y. Sun, D. J. Kouri, and D. G. Truhlar, Nucl. Phys. **A508**, 41c (1990).
[44] Y. Sun *et al.*, Phys. Rev. A **41**, 4857 (1990).
[45] D. W. Schwenke, S. L. Mielke, and D. G. Truhlar, Theor. Chim. Acta **79**, 241 (1991).
[46] E. Schrödinger, Ann. Phys. (Paris) **79**, 361 (1926).
[47] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
[48] W. Kołos and L. Wolniewicz, J. Mol. Spectrosc. **54**, 303 (1975).
[49] L. Wolniewicz, J. Chem. Phys. **103**, 1792 (1995).
[50] R. E. Moss, Mol. Phys. **80**, 1541 (1993).
[51] J. Taylor *et al.*, Mol. Phys. **97**, 25 (1997).
[52] R. Jaquet *et al.*, J. Chem. Phys. **108**, 2837 (1998).
[53] J. Tennyson *et al.*, Spectrochim. Acta, Part A **58**, 663 (2002).