

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/228462971>

Reactivity enhanced by under-barrier tunneling and resonances: The $F + H_2 \rightarrow HF + H$ reaction

ARTICLE in CHEMICAL PHYSICS LETTERS · APRIL 2003

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(03)00311-7

CITATIONS

36

READS

14

8 AUTHORS, INCLUDING:



Vincenzo Aquilanti

Università degli Studi di Perugia

315 PUBLICATIONS 6,454 CITATIONS

SEE PROFILE



Simonetta Cavalli

Italian National Research Council

119 PUBLICATIONS 2,890 CITATIONS

SEE PROFILE



Dario De Fazio

Italian National Research Council

57 PUBLICATIONS 1,014 CITATIONS

SEE PROFILE



Xavier Giménez

University of Barcelona

77 PUBLICATIONS 977 CITATIONS

SEE PROFILE

Reactivity enhanced by under-barrier tunneling and resonances: the $F + H_2 \rightarrow HF + H$ reaction

Vincenzo Aquilanti ^{a,*}, Simonetta Cavalli ^{a,1}, Dario De Fazio ^{a,2},
Alessandro Volpi ^{a,3}, Antonio Aguilar ^b, Xavier Giménez ^b, Josep Maria Lucas ^b

^a Dipartimento di Chimica dell'Università, Perugia 06123, Italy

^b Departament de Química Física, Universitat de Barcelona, Barcelona 08028, Spain

Received 28 January 2003; in final form 20 February 2003

Abstract

Accurate quantum mechanical rate constants (all contributing partial waves, fine energy grid Boltzmann averaging) for the title reaction are obtained by the *hyperquantization algorithm*, covering the range from above room temperature down to the cold regime (few K). The good agreement with available experiments down to ~ 200 K, obtained by blending ab initio description of the transition state and molecular beam scattering experimental characterization of the entrance channel, establishes the reliability of the approach to describe deviations from Arrhenius behavior at those low temperatures where quantum mechanics can induce specific selectivity in chemical reactivity

© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Rate constants have a central importance in chemical kinetics. Both experimental and theoretical investigations have focused on their study in an effort to provide insight into the detailed mechanism of chemical reactions, and ultimately for testing theoretical models of reaction rates. An ample phenomenology is available for a large

number of systems in a broad range of temperatures, a commonly established finding being that reaction rates have an Arrhenius-like behavior (exponential fall-off with inverse temperature) interpreted as manifestation of the fact that typically reactivity proceeds overcoming a natural energy barrier – the ‘activation energy’. Statistical theories satisfactorily reproduce these features, but when this picture breaks down (cold and ultracold conditions), a full quantum mechanical approach is needed. However, the exact computation of rates is a very hard task, involving proper sums over states in the entrance channel and velocity averaging over Boltzmann distribution of integral state-to-state cross-sections. The latter quantities in turn involve a sum (overall participating partial waves) of quantum mechanical reactive probabil-

* Corresponding author. Fax: +39-075-585-5606.

E-mail address: aquila@dyn.unipg.it (V. Aquilanti).

¹ Also: INFN – Unità di Perugia, 06123 Perugia, Italy.

² On leave from: IMIP, CNR – Sezione di Bari, 70100 Bari, Italy.

³ Present address: Central Chemistry Laboratory, University of Oxford, Oxford OX1 3QH, UK.

ities, to be obtained by accurately solving the scattering Schrödinger equation.

Here, we have investigated the reaction



which is a prototype of exothermic exchange reactions with a barrier, using three potential energy surfaces (PES) of progressive quality, denoted I, II, and III in the following (Fig. 1). This reaction has been over the years the object of an impressive amount of theoretical and experimental work, that has been summarized elsewhere [1]. This was the first reaction (beyond the hydrogen atom–molecule exchange) for which a full quantum dynamical approach was demonstrated [2]. Further key-references will be given below. In a recent paper by us [3], we have presented our latest integral and differential cross-section results on a set of different PESs including I and II, pointing out the role of long-range and spin–orbit interactions on the reaction dynamics, and still finding unsatisfactory

the description of the entrance channel and of the barrier height. In Section 2, we give an account of our approach to the dynamics and to the construction of the potential energy surfaces. The main results are presented and discussed in Section 3. The Letter ends with a short summary (Section 4).

2. Approach

In this Letter, we report calculations of reaction rate constants exploiting the accuracy and efficiency of the *hyperquantization algorithm*, our method for the solution of the reactive scattering Schrödinger equation. This method, widely described elsewhere [4–6], is based on properties of the Hahn orthogonal polynomials, which are defined on a lattice of points and are the discrete analogs of hyperspherical harmonics [7]. Our accurate quantum calculations include all the possible contributing values of the total angular momentum and cover a range – from room temperature down to 10 K – never investigated before, providing a link between the high temperature regime, where the reactivity is above the barrier, and the low one, where the mechanism of the reaction is basically a tunnel effect through the barrier.

On the experimental side, a series of works dating back to the 80s [8–11], will serve as a stringent test for our results. Although available data for comparison cover the range down to only ~200 K, this work provides a reliable extension toward the comprehension of reactivity features down to cold and possibly ultracold (sub-Kelvin) conditions, which have come under focus very recently [12,13].

Present-day dynamical calculations have reached such a level of reliability that it is possible to establish a direct link between the potential energy surface and the dynamical observables of a chemical reaction. The PES designated as I (based on Stark and Werner ab initio data [14]) has now the status of the benchmark theoretical PES for the $\text{F} + \text{H}_2$ system. In the context of a study of the effect of non-adiabatic coupling to electronically excited PESs [15], the important conclusion was reached that the reaction was essentially electronically adiabatic. The surface I was also used and the proposed modifications were minor. In spite of this, it is

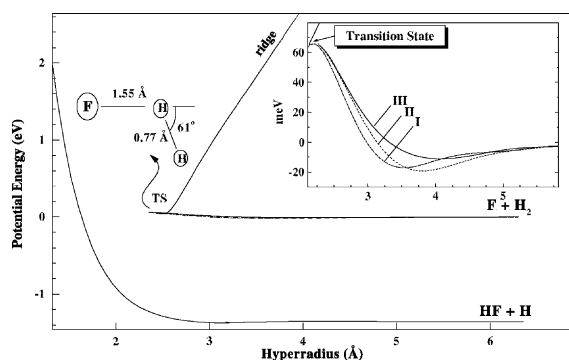


Fig. 1. Energy profiles, as measured from the entrance channel, as a function of the hyperradius (a mass-weighted root-mean square average of the interatomic distances), the natural reaction coordinate and a measure of the system total inertia [27]. Evolutions are given of the entrance and exit channel valley-bottom profiles and of the ridge line from the triatomic interaction region to the large hyperradius asymptotic limit, where the two reaction channels are well separated. In the inset, the comparison in the entrance channel among the three employed surfaces I, II, and III is magnified: they only differ in the entrance valley characteristics and have a common barrier height of 66.7 meV to the transition state (TS), whose geometry is illustrated. All three surfaces employed in the present work as well as further information and results are made available at the web site http://bong.chm.unipg.it/research_topics/PES.html/.

generally accepted that the PES I is not able to provide a satisfactory theory-experiment agreement for all the dynamical properties of the reaction, as it will be further shown in this Letter. The impasse situation (see [3]) can be stated by saying that the PES I appears accurate regarding transition state properties, but inadequate for the description of features of the $F + H_2$ reactant's channel. This was not remedied by modifications proposed in [16,17] by modeling the role of the spin-orbit interaction. Indeed, unexpectedly a more thoughtfully reliable description of the entrance channel features spoiled the ability of PES I of reproducing the currently accepted experimental values of exothermicity and barrier height. This was emphasized by further attempts at refinements (such as our SW-LR-SO widely described in [3]), where inclusion of the spin-orbit interaction as a correction in the entrance channel, ended up underestimating the reaction exothermicity and overestimating the barrier height by roughly one-third of the atomic fine-structure splitting Δ (equal to 50.1 meV).

These studies had the merit of indicating us the direction to be taken in this work. After calculations of rates on the benchmark surface I, we have reconsidered the PES II (which was denoted SW-LR in [3]), which describes properly the long-range interaction in the entrance-channel according to our molecular-beam inelastic scattering experiments [18,19] (see [3] for the merging procedure to the same transition state and exit channel ranges as in PES I). Then we have introduced the spin-orbit interaction but, as an improvement on the surface denoted SW-LR-SO in [3], we have shifted up the entrance channel by $1/3\Delta$. This moves the $F + H_2$ asymptote leaving it unaltered with respect to the original position of surface I. This surface III therefore exhibits the correct exothermicity, permitting us also to transparently 'isolate' the effects due to long-range and spin-orbit corrections on the dynamical properties of the system.

3. Results

We have studied collision energies from about 0.1 up to 300 meV above the H_2 ($v = 0, j = 0$) asymptote. The number of total J values to be re-

tained in the calculations is determined by numerical convergence on the integral cross-sections at the various collision energies, and has been set to the overconvergent value of 30 for the highest investigated energies. Convergence has been achieved as well on the numbers of projections K of the total angular momentum along the minimum inertia axis. We have found that K values up to 3 must be included in the calculations.

Integral and differential cross-sections have been calculated for both *para*-hydrogen and *ortho*-hydrogen. The normal hydrogen for comparison with experiments is then taken as a mixture of the two with statistical weights.

Integral cross-sections are reported in Fig. 2 as a function of the collision energy. Note a marked effect of resonances at low energy, especially for the lowest rotational entrance channel, $j = 0$. Also one can see that cross-sections grow up near the origin due to Wigner threshold laws (this effect has been studied at ultralow energy [12,13]). By comparing the maxima of the Maxwell-Boltzmann distributions for the two sample temperatures with the reaction barrier height, one can infer that the reactivity is essentially under-threshold, the most important contribution coming from collision energies lower than the height of the reaction barrier. This is the region that is dominated by the presence of reactive resonances, which have deserved close scrutiny to be described elsewhere (see also [20], and references therein). This region is more extensively accessible to $j = 0$ than for higher entrance channels (for $j = 1$, see panel (b) in Fig. 2). We find that, comparing the considered PESs, the position in energy of resonances remains unaltered, while a different intensity is observed. This is consistent with the modifications we have introduced, which involve only the entrance channel of the reaction, while the quasi-bound states responsible for the resonances lie either in the transition state region or in the exit channel [21,22]. So positions remain unchanged, while intensities depend on the barrier width, which becomes larger going from I to II to III (see Fig. 1). It is thus made clear why reactivity below the threshold is lower for II than for I, and is even lower for III. Remarkably this trend is inverted for high collision energies: in this case, the larger reactivity found on

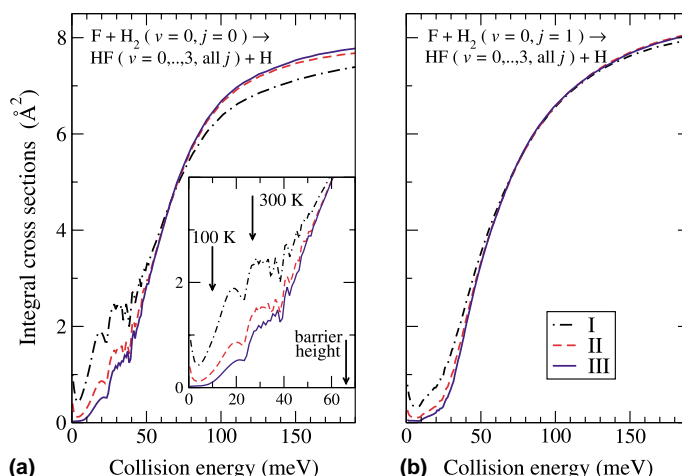


Fig. 2. Integral cross-sections as a function of the collision energy resolved for the initial rotational state of the H_2 molecule. Panel (a) and panel (b) refer to initial $j = 0$ and $j = 1$, respectively. The barrier height and the positions of the maximum of the Maxwell–Boltzmann distribution for $T = 100$ and 300 K are also shown, in order to make visible that reactivity proceeds mostly via under-barrier tunneling. A rich resonance pattern (prominent for the $j = 0$ case) is crucial in enhancing the reaction rate and extremely sensitive to the details of the interaction.

the modified PESs can be attributed to the different features of the entrance channel van der Waals well. Well minima for II and III PESs lie at larger intermolecular distances, both being characterized by a more marked orientational anisotropy [3,19]. Since all the surfaces have the same bent transition state, PESs II and III are more effective in inducing the rotations which bring the randomly oriented reactants on the bent configuration, more favorable for the approach to the transition state (for similar effects on the product branching ratio of the $\text{Cl} + \text{HD}$ reaction, see [23]).

In Fig. 3 we have plotted rate constants in the entire range of temperatures considered in this Letter. Again, results for PES I, II, and III can be directly compared. The observed behavior is non-Arrhenius, demonstrating the deviations to be expected when, as in this case, the temperature goes down to regimes where non-classical under-barrier reactivity emerges. We note that our low-temperature limit-value for the rate constant on the I surface ($8.71 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 10$ K) is roughly two thirds of a recent nearly zero-energy value (≤ 0.2 K) for the reaction of *para*- H_2 [12], a value only attributable to a rise as the temperature goes down to the ultra-cold limit.

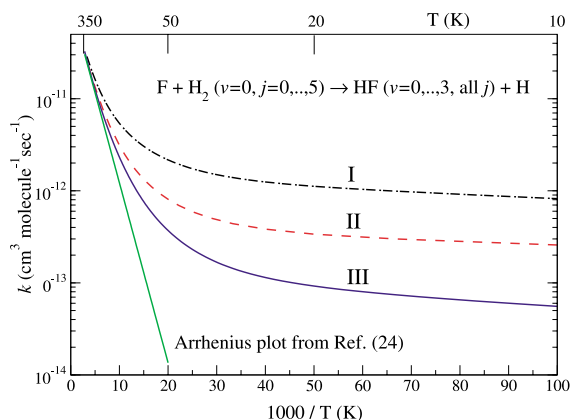


Fig. 3. Logarithm of the calculated rate constants versus the inverse of the temperature for the $\text{F} + \text{H}_2$ reaction in the range 10 – 350 K on the three PESs I, II, and III. The best experimental Arrhenius plot as proposed in [24] is also reported and extrapolated down to 50 K in order to emphasize the low-temperature deviation from the Arrhenius behavior.

In Fig. 4, we show a blow-up of the previous plot in a reduced range of temperatures, for purposes of comparison with the available experimental works. The most meaningful comparison is with results of [11], with which we have the largest overlap as for the investigated temperature range

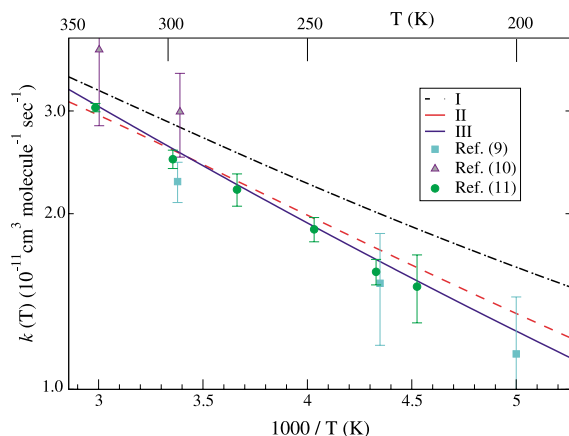


Fig. 4. Detailed view of present results on the three employed PESs compared with previous experimental results in the range of temperatures where the latter are available.

(moreover, they are considered together with those of [9] the most accurate and reliable kinetics data [24]). The satisfactory agreement for the III PES assesses its reliability. We note that in a previous quantum-mechanical rate calculation [17] on the original Stark–Werner [14] surface (denoted here as I) and on a refined version including the spin–orbit correction in the entrance channel, only some of the contributing partial waves were included, fitting the missing ones to a linear functionality. We tested this to be unsatisfactory in the present temperature range, and likewise inapplicable are methods of other recent studies, which employed a truncating negative imaginary potential within the coupled-state approximation [25], or used a time-dependent flux–flux autocorrelation function approach [26].

4. Conclusion

Conclusions of this work can be summarized as follows. For the first time, quantum mechanical exact rate constants (i.e., including all contributing partial waves) have been calculated for a key-system in reaction dynamics, obtaining agreement with available kinetics experiments and assessing the reliability of our improvements on the potential energy surface. Simulations run for low collision energies permit extrapolation to low and

possibly ultralow temperatures, whose importance is increasingly gaining attention in chemistry for perspectives of selective control of reactivity.

Acknowledgements

We are grateful to Andrea Simoni for discussions. The work is supported by Italian MIUR and ASI. International collaboration is made possible by EU through a Large Scale Facilities project, an RTN-Network and a COST action.

References

- [1] D.E. Manolopoulos, J. Chem. Soc., Faraday Trans. 93 (1997) 673.
- [2] J.M. Launay, M. Le Dourneuf, Chem. Phys. Lett. 169 (1990) 476.
- [3] V. Aquilanti, S. Cavalli, D. De Fazio, A. Volpi, A. Aguilar, X. Gimenez, J.M. Lucas, Phys. Chem. Chem. Phys. 4 (2002) 401.
- [4] V. Aquilanti, S. Cavalli, D. De Fazio, J. Chem. Phys. 109 (1998) 3792.
- [5] V. Aquilanti, S. Cavalli, D. De Fazio, A. Volpi, A. Aguilar, X. Gimenez, J.M. Lucas, J. Chem. Phys. 109 (1998) 3805.
- [6] V. Aquilanti, S. Cavalli, D. De Fazio, A. Volpi, Adv. Quantum Chem. 39 (2001) 103.
- [7] V. Aquilanti, S. Cavalli, D. De Fazio, J. Phys. Chem. 99 (1995) 15694.
- [8] D.S. Perry, J.C. Polanyi, Chem. Phys. 12 (1976) 419.
- [9] E. Wurzberg, P.L. Houston, J. Chem. Phys. 72 (1980) 4811.
- [10] R.F. Heidner, J.F. Bott, C.E. Gardner, J.E. Melzer, J. Chem. Phys. 72 (1980) 4815.
- [11] P.S. Stevens, W.H. Brune, J.G. Anderson, J. Phys. Chem. 93 (1989) 4068.
- [12] N. Balakrishnan, A. Dalgarno, Chem. Phys. Lett. 31 (2001) 652.
- [13] E. Bodo, F.A. Gianturco, A. Dalgarno, J. Chem. Phys. 116 (2002) 9222.
- [14] K. Stark, H.-J. Werner, J. Chem. Phys. 104 (1996) 6515.
- [15] M.H. Alexander, D.E. Manolopoulos, H.-J. Werner, J. Chem. Phys. 113 (2000) 11084.
- [16] J.F. Castillo, B. Hartke, H.-J. Werner, F.J. Aoiz, L. Bañares, B. Martínez-Haya, J. Chem. Phys. 109 (1998) 7224.
- [17] F.J. Aoiz, L. Bañares, J.F. Castillo, J. Chem. Phys. 111 (1999) 4013.
- [18] V. Aquilanti, R. Candori, D. Cappelletti, E. Luzzatti, F. Pirani, Chem. Phys. 145 (1990) 293.
- [19] V. Aquilanti, S. Cavalli, D. Cappelletti, F. Pirani, A. Volpi, J. Phys. Chem. A 105 (2001) 2401.
- [20] R.T. Skodje, D. Skouteris, D.E. Manolopoulos, S.H. Lee, F. Dong, K. Liu, Phys. Rev. Lett. 85 (2000) 1206.

- [21] J.F. Castillo, D.E. Manolopoulos, K. Stark, H.-J. Werner, *J. Chem. Phys.* 104 (1996) 6531.
- [22] S.D. Chao, R.T. Skodje, *J. Chem. Phys.* 96 (2000) 4134.
- [23] D. Skouteris, D.E. Manolopoulos, W.S. Bian, H.-J. Werner, *Science* 286 (1999) 1713.
- [24] A. Persky, H. Kornweitz, *Int. J. Chem. Kin.* 29 (1997) 67.
- [25] E. Rosenman, S. Hochman-Kowal, A. Persky, M. Baer, *Chem. Phys. Lett.* 257 (1996) 421.
- [26] H. Wang, W.H. Thompson, W.H. Miller, *J. Phys. Chem. A* 102 (1998) 9372.
- [27] V. Aquilanti, S. Cavalli, D. De Fazio, A. Volpi, A. Aguilar, X. Gimenez, J.M. Lucas, *Phys. Chem. Chem. Phys.* 1 (1999) 1091.