Theoretical Reaction Kinetics Astride the Transition between Moderate and Deep Tunneling Regimes: The F + HD Case

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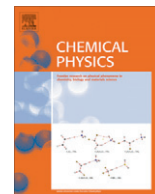**80** PUBLICATIONS **1,107** CITATIONS

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Exact activation energies and phenomenological description of quantum tunneling for model potential energy surfaces. The F + H$_2$ reaction at low temperature

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ABSTRACT

Activation energies E_a calculated as the negative of the logarithmic derivatives of rate constants with respect to the inverse of absolute temperature T, are presented for three potential energy surfaces previously introduced for the reaction F + H$_2$ → HF + H in the temperature range 10 < T < 350 K. Exact benchmark rate constants from quantum mechanical calculations on each surface have been reported [V. Aquilanti, S. Cavalli, D. De Fazio, A. Volpi, A. Aguilar, J.M. Lucas, Chem. Phys. 308 (2005) 237] and shown to deviate from Arrhenius behavior. The corresponding pronounced deviation from constancy of activation energy E_a represents a prototypical example of the role of quantum mechanical tunneling in propitiating a "sub Arrhenius" behavior. Four formulas are tested in order to provide a phenomenological description of the tunnel effect on reactivity, each introducing only one additional parameter with respect to the Arrhenius law. They correspond to: (i) the so-called *Modified Arrhenius Equation*, involving a linear dependence of E_a versus T; (ii) the *Curved Arrhenius Plot* description, implying a linear dependence of E_a versus inverse T; (iii) the *deformed Arrhenius law* recently proposed and the corresponding inverse E_a – inverse T linear relationship recently derived from the *deformed exponential distribution* appearing in non – extensive statistical thermodynamics; (iv) a *generalization of Mott's law* for electron and proton conduction in condensed matter, leading to an exponential relationship between E_a and T. Numerical investigation allows a discussion of merits of each formula from a temperature of 350 K down to 50 K. In all three cases, the deformed Arrhenius law provides a better description of the quantum mechanical trend.

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1. Introduction

The concept of activation energy was introduced for chemical reactions by Arrhenius in 1889 and found application in a variety of contexts when rates of processes are studied as a function of temperature. The name comes from the associated microscopic view that often a reaction, in order to proceed, encounters an energetic barrier to be overcome by kinetic energy. The identification between an empirical quantity and a microscopic feature of the potential energy surface has to be taken as an admirably fruitful intuition, to be scrutinized closely in each particular case. A well documented historical account of Arrhenius law has been given by Stiller [1].

Starting from early statistical mechanics work by Tolman [2] (see [3]), the concept of activation energy has been provided as

independent of the barrier height on a potential energy surface, and associated only to the experimentally measured or theoretically calculated temperature dependence of rate constants. We adopt this viewpoint here, as stressed in the current IUPAC definition [4], although we are well aware that ultimately the satisfactory description of the dependence of rate processes will require interpreting the phenomenological behavior at the microscopic level, linking it to topological properties of the potential energy surfaces through deep conceptual insight as provided by the celebrated transition state theory or its variants.

In this paper, we present exact activation energies computed from rate constants [5,6], available in an ample temperature range on three potential energy surfaces which model the reaction of a fluorine atom with a hydrogen molecule. For this reaction, which has a barrier of relatively low height, reactivity at sub thermal energies shows pronounced deviation from linearity because of the progressively large role played by quantum mechanical tunneling, as the temperature decreases, giving rise to a deviation from the linear log k versus 1/T relationship, the venerable Arrhenius

plot. This reaction provides therefore an example of "sub Arrhenius behavior", or concavity of the Arrhenius plot [7–9]). It is also among the most studied elementary reactions, both experimentally and theoretically; experimentally determined rate constants have been recently compared with our accurate quantum mechanical calculations [6], and this provides an opportunity to obtain activation energies on a wide temperature range.

Since the search for simple extensions of Arrhenius law to cases of deviation of Arrhenius plots from linearity has led to propose various phenomenological formulas, we had analyzed four of them and tested them against their ability to account for the deviation from constancy of the activation energy for the three cases available from our work.

This paper continues in Section 2 with definitions of activation energy and of the four formulas that we have considered. Section 3 provides information on the potential energy surfaces and on the available rate constant data. Section 4 reports results on the activation energies and provides tests of the formulas essentially in graphical form. A summary and concluding remarks are in the final Section 5. Tables with numerical data will be given as Electronic Supplementary Material.

2. Definitions and phenomenological formulas

2.1. Activation energy, E_a

The current (IUPAC) definition of the activation energy is as follows [4] (here reproduced, with slight changes in notation):

"The activation energy, also known as the energy of activation, is an operationally defined quantity expressing the dependence of a *rate constant* or *rate coefficient* k on the temperature, according to the relationship:

$$E_a = -R \frac{d \ln k}{d(1/T)}. \tag{1}$$

This equation is derived from the Arrhenius equation:

$$k(T) = A e^{-\frac{E_a}{RT}}, \tag{2}$$

in which A is termed the pre-exponential factor. The Arrhenius equation, with A and E_a, practically constant, applies to many *composite reactions* as well as to *elementary reactions*, and the activation energy can then be called the overall activation energy. The *rate constants* used to obtain the activation energy may be experimental or calculated ones. For an *elementary reaction* the activation energy can be shown to be the average energy of molecules actually undergoing reaction minus the average energy of reactant molecules".

Useful properties of the definition (1) of activation energy in terms of the logarithmic derivative of $k(T)$ is that E_a is independent of the units that we use for $k(T)$. This is important because often k is given either in relative units or in units that depend e.g. on the measurements of partial pressure or on the "molecularity" of the reactions, on "pseudo-unimolecularity" assumptions, etc.

The units of the activation energy depend only on those used for the gas constant R. In order to have J/mole for units, R is 8.314472 J(mol K)$^{-1}$, and T in Kelvin.

It is interesting to depart slightly from the common viewpoint and to look at (1) as a differential equation for $k(T)$ when $E_a(T)$ is assumed a known function of T. It is a first order equation in the variable $1/RT$ and is easily integrated. Accordingly, in the four cases which are given below, the symbol A is still used for a temperature independent generalized pre-exponential factor, and it can be considered as arising from (1) as the integration constant carrying the units for $k(T)$.

2.2. Modified Arrhenius Equation (MAE)

Quoting again the IUPAC [4] definition for the Modified Arrhenius Equation, which has been in common use for a long time:

"This is an extension of the simple Arrhenius equation in which the pre-exponential factor is proportional to T^α where T is the temperature and α a constant:

$$k(T) = A T^\alpha e^{-\frac{E^*}{RT}}, \tag{3}$$

A is a temperature-independent constant. According to Eq. (1), the activation energy is a linear function of the temperature:

$$E_a^{MAE} = E^* + \alpha RT,$$

and parameterized by the constant energy scaly parameter E^* and temperature power factor α". In Ref. [4] Eq. (3) is written in a slightly different notation.

This modification has a long history [1], the idea behind being to keep the meaning for E^* still associated with a barrier height in a potential energy surface, describing any temperature dependence by a nonzero value for the exponent α. In a thermodynamic-like interpretation, α would measure a temperature dependence of an "activation entropy". Collision theory suggests $\alpha = 1/2$ and transition state theory in its simplest form $\alpha = 1$. In applications, it is used as an adjustable fitting parameter. See also [7].

2.3. Curved Arrhenius plot (CAP)

In Refs. [7,9], deviations from linearity in Arrhenius plots are accounted for by an additional quadratic term in $1/RT$ according to:

$$\ln k(T) = \ln A + \frac{B}{RT} + \frac{C}{(RT)^2}, \tag{4}$$

where the sign of C dictates whether the plot is "concave" or "convex" (see Ref. [9]): correspondingly, we say that the reaction abides by a sub- or super-Arrhenius dependence. Accordingly, the activation energy E_a, being connected to the slope of the Arrhenius plot (Eq. (1)) is no longer a constant but depends linearly on $1/T$:

$$E_a(T) = -\frac{d \ln k}{d(1/RT)} = -B - \frac{2C}{RT}, \tag{5}$$

Here the parameters are B, which has the units of energy, and the C coefficient, which is given by

$$C = -\frac{d^2 \ln k}{d(1/RT)^2}, \tag{6}$$

and is positive or negative for the sub- or super-Arrhenius cases, respectively. Units of C are (energy)^2.

The sub-Arrhenius case, where higher than expected rates are observed as temperature decreases, corresponds to a "concave" curve (this occurs typically in the present case of quantum mechanical tunneling or for the emergency of competing mechanisms). In cases of higher than expected rates as temperature increases, we have according to a materials science nomenclature [7], super-Arrhenius behavior and a "convex" Arrhenius plot. See Fig. 1 in Ref. [8].

2.4. Deformed Arrhenius law (DAE)

In a recent paper [8] we have introduced a generalization of the Arrhenius law based on the definition of a *deformed* exponential function as follows:

$$\exp_d(x) \equiv [1 + dx]^{\frac{1}{d}}. \tag{7}$$

In the limit of the deformation parameter $d \to 0$, the d-exponential function (Eq. (7)) coincides with the usual exponential function according to the well known limit due to Euler:
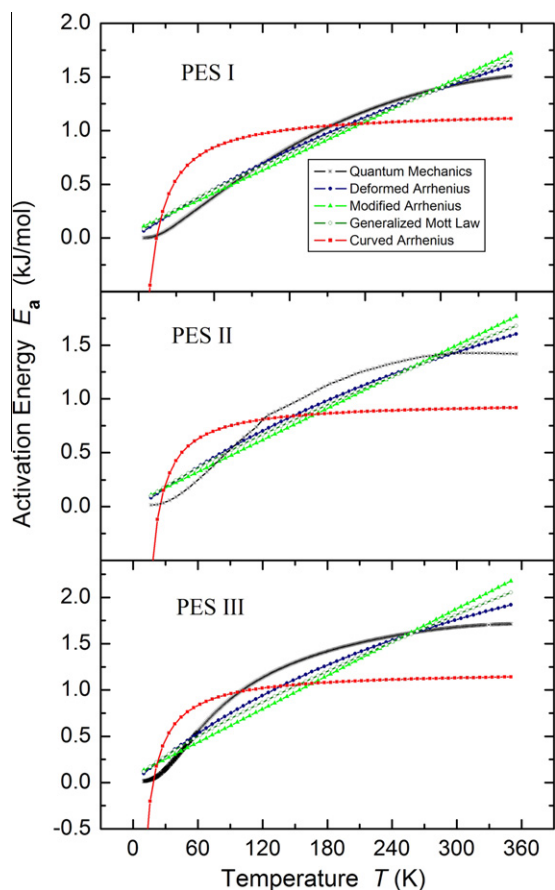
Fig. 1. In the three panels corresponding to the three potential energies surfaces employed in this work activation energies E_a are reported as a function of absolute temperature T, as calculated from the previously obtained benchmark quantum mechanical rate constants and from fits using the formulas of Section 2 with the parameters given in Table 1.

$$\exp(x) \equiv \lim_{n \to \infty} \left(1 + \frac{x}{n}\right)^n, \qquad (8)$$

where n is an integer. Eq. (7) is obtained by (8), identifying the deformation parameter d as a continuous generalization of $1/n$.

In the scientific literature there are a variety of deformed algebras with applications in different areas of science [10–12]. The present deformation of the exponential function occurs in the non-Boltzmann distribution of non-extensive Statistical Mechanics [10,13,14] and has been used in recent work on Eyring's transition state theory [15–17] and in other applications [18–23]. Our deformation parameter d corresponds to $1 - q$ of Refs. [10,13], and to $v - 1$ of Ref. [15]. Borges [10] provides basic mathematical background information. The value of d is, in principle, determined by the microscopic dynamics of the system, which is frequently unknown, so it generally cannot be predicted by first principles.

By means of the deformed exponential function (Eq. (7)) we have introduced a deformed Arrhenius law for the reaction rate $k(T)$ in the following way:

$$k(T) \equiv A \exp_d\left(-\frac{\varepsilon}{RT}\right) = A\left[1 - d\frac{\varepsilon}{RT}\right]^{\frac{1}{d}}. \qquad (9)$$

In the limit $d \to 0$ and $\varepsilon \to E_a$ (a constant) the usual Arrhenius reaction rate law is recovered. In applications, A, ε and d are three temperature independent phenomenological parameters.

Taking the logarithm of the reaction rate constant (Eq. (9)) we obtain the following expression for the Arrhenius plot:

$$\ln k(T) \equiv \ln A + \frac{1}{d} \ln\left(1 - d\frac{\varepsilon}{RT}\right). \qquad (10)$$

The logarithm of the reaction rate found in this way against reciprocal temperature shows a curvature, rather than the straight line behavior described by the Arrhenius law. In Ref. [8] (see Fig. 1), it is shown that the curvature of sub- and super-Arrhenius processes can be described by adjusting the value of the d parameter. The activation energy is now given by

$$\frac{1}{E_a} \equiv \frac{1}{\varepsilon} - \frac{d}{RT}, \qquad (11)$$

which provides a linear relationship between inverse activation energy and inverse temperature.

According to Eq. (10), we can use the logarithm of the reaction rate (Eq. (9)) to describe experimental data where curved (sub- or super-Arrhenius) plots are observed. It is important to point out that the success of this fitting procedure is, in part, due to the deformed exponential function's flexibility. Also, Eq. (10) uses only three parameters to fit the experimental data, while formulations based on Eyring's transition state theory [16,17] appear to need more parameters, like all treatments employing piecewise linear fits matched at an Arrhenius break temperature (see [7]).

2.5. Generalized Mott Law (GML)

As discussed at some length elsewhere [24] for a variety of conduction processes in materials science, a key quantity is the temperature dependence of the slope of logarithmic plots against inverse temperature. In analogy with the theory of rate processes, governed by Arrhenius type of formulas, such slopes can be associated to energetic gaps or to thresholds to be overcome in order for the process to evolve. An important formula given by Mott and used in the context of conduction processes can therefore be generalized and applied to the present discussion:

$$k(T) = A \exp-\left(\frac{T_o}{T}\right)^\gamma. \qquad (12)$$

Besides A, the parameters here are T_o, carrying the units of T, and γ, which in the famous case studies of the original Mott's formulation is ¼, and in recent applications is an empirical or theoretically justified parameter, sometimes related to the specific characteristics (e.g. "fractality") of the system. According to Eq. (1), we can define an activation energy as follows:

$$E_a = R\gamma \frac{T_o^\gamma}{T^{\gamma-1}}, \qquad (13)$$

which provides linearity between E_a and T on a log–log plot.

3. Potential energy surfaces and rate constants

In previous papers [5,6], we have presented quantum–mechanical cross sections and rate constants for the prototypical reaction $F(^2P_{3/2}) + H_2$ $(v = 0, j = 0,\ldots,5) \to HF$ $(v', j') + H$ for temperatures ranging from ~10 up to 350 K. Rate constants have been obtained by an essentially exact time-independent quantum mechanical calculation of cross-sections [25–27] on a very fine grid of collision energies, permitting accurate Boltzmann averaging including all the contributing partial waves. Quantum effects play a crucial role at the investigated temperatures, where the reactivity is essentially under-barrier and shows a non-Arrhenius behavior. The reaction was thus found to proceed efficiently by tunnel effect and to be enhanced by the presence of resonances.

As for the interaction potential, we have used three similar potential energy surfaces, PES-I, PES-II and PES-III. The PES-I is based on the benchmark *ab initio* potential energy surface by Stark and
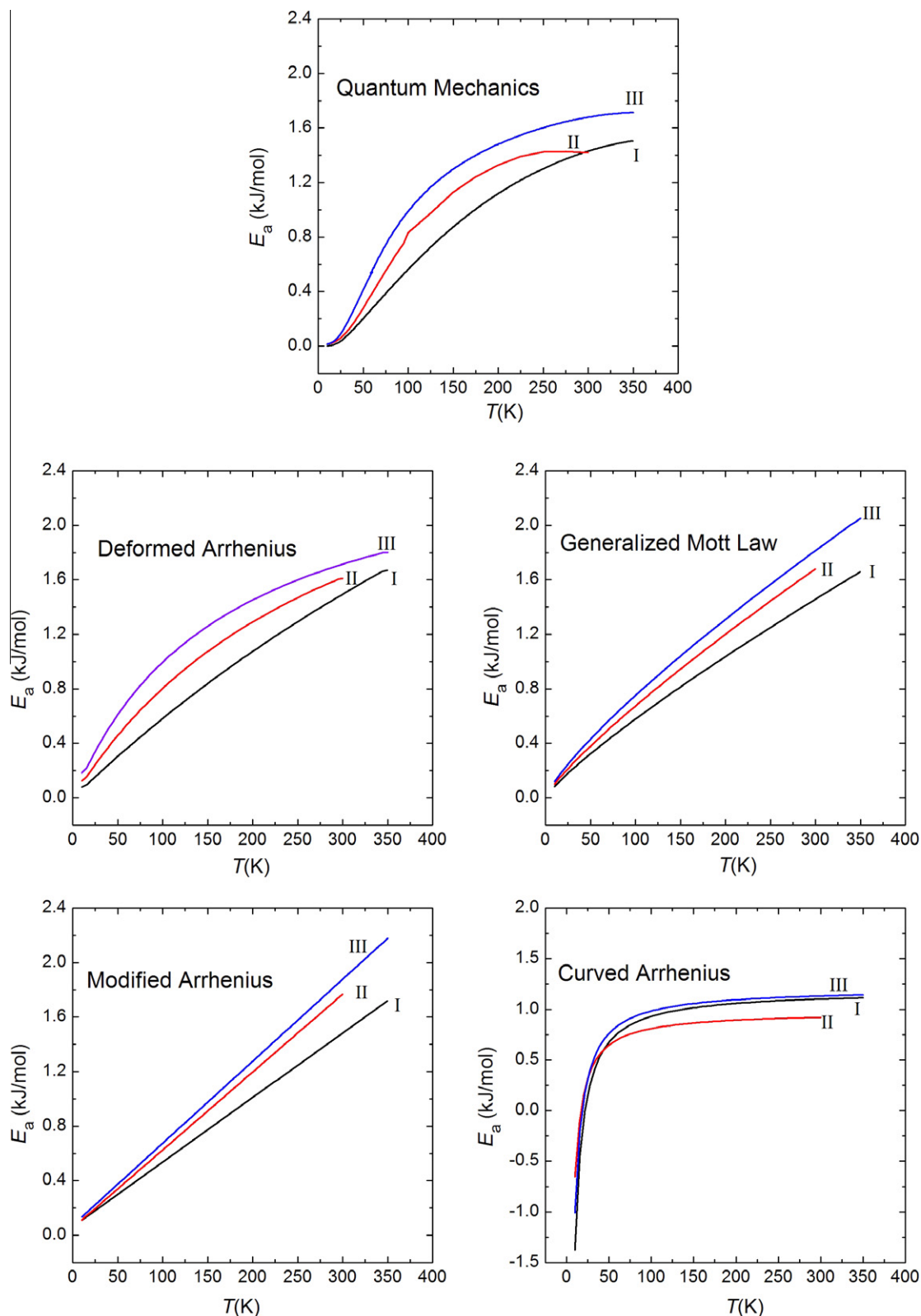
Fig. 2. Activation energies E_a as a function of absolute temperature T as previously obtained from benchmark quantum mechanical rate constants and from fits using the formulas of Section 2 with the parameters in Table 1. In each panel, results for the three potential energy surfaces employed in this work are compared.

Werner [28], the other ones are its modifications in the entrance channel according to molecular beam scattering experiments carried out in our laboratory [29]. This allowed us to provide a realistic description of the height and width of the reaction barrier, of

the long-range portion of the interaction (PES II) and to include the fluorine spin–orbit coupling contribution to the entrance channel energetic (PES III). Rate constants calculated with the variant PES III agree within uncertainties with experimental data in the

temperature range where they are available (i.e. down to ∼200 K) thus permitting the assessment of the reliability of calculated reactivity properties. Briefly discussed were also threshold behavior and some resonance features, particularly the previously overlooked ones associated to entrance channel characteristics [6]. These are important in the very cold (∼1 K) and ultra cold (≪ 1K) regimes.

The three potential energy surfaces have the same barrier height 66.7 meV = 6.43 kJ/mole. The profiles along the reaction path is shown in Fig. 1 of Ref. [6]. They differ in the barrier width, which increases for I to III. Accordingly, the importance of the tunnel effect decreases strongly from I to III, as documented in the Arrhenius plots of rate constants in Fig. 7 in Ref. [6]. The three surfaces employed in this and previous work are available at the website http://www.chm.unipg.it/chimgen/mb/theo2/ricerca/PES-FH2a/PES.html.

4. Activation energies. Quantum mechanical and model results

The rate constant data that were used for Fig. 7 in Ref. [6] are those employed here for calculating the activation energies E_a according to the definition, Eq. (1). Due to the fine grids of data available for surfaces I and III (*ca.* 350 and 800, respectively in the 10–350 K range) logarithmic derivatives were computed directly. For PES II, for which fewer data (*ca.* 30 in the 10–350 K range) are available, a Lagrange polynomial interpolation was used to compute logarithmic derivatives. All data are listed in the Supplementary Material. Calculated k, which are computationally converged to less than one percent in the room temperature range, drop by an order of magnitude down to 100 K and by two orders of magnitude below 50 K. The logarithmic derivative dependence of E_a from k attenuates uncertainties preserving quantitative accuracy down to 100 K, and reliability of the description of the trend down to at least 50 K, where rate constants are extremely small. Data are presented in graphical form in Figs. 1 and 2, together with best fits using the four formulas listed in the previous section. All four formulas can be cast as simple linear relationships, and this greatly facilitates the fitting procedure.

The corresponding parameters are given in Table 1, while those from the statistical analysis of the quality of the fits are given in Table 2. The latter are χ^2 and R^2. χ^2 is used in tests for goodness of fit of given distribution to a reference one, and in confidence interval estimation for a population standard deviation of a normal distribution from a sample standard deviation. R^2 is the coefficient of determination, used to obtain information about the goodness of fit of a model. In regression analysis, the R^2 coefficient of determination is a statistical measure of how well the regression line approximates the real data points. An R^2 of 1.0 indicates that the regression line perfectly fits the data.

A preliminary view of the results provides already several indications of the relative reliability of the four possible extensions of Arrhenius law. Except at the lower range of investigated temperatures (≲50 K), where all four visibly deviate, the CAP formula performs poorly, as already documented in other examples previously given [8], while the other three formulas appear reasonable. Note

that for those temperatures, as discussed in the previous paper [6], the quantum mechanical results are affected by resonances and contribution from long range forces, deteriorating numerically the stated accuracy (less than a few percent) of the calculations. Additionally in the low temperature range, effects such as those associated to threshold laws, isolated resonance features, limited number of contributed partial waves, etc., may invalidate the very same meaning of a canonical rate constant as a function of temperature.

In Figs. 1 and 2, the activation energies are reported as a function of temperature T. In the three panels of Fig. 1, the quantum mechanical behavior is given together with the corresponding trends provided by the fits by the four formulas. For all three PES the poor performance of the CAP formula is confirmed, as are the reliability of the other three formulas. A closer look allows us to confirm the analysis shown in Table 2 and to argue that the DAE, the GML and the MAE reasonably perform according to this sequence in terms of a decrease in quality.

The five panels of Fig. 2 exhibit the same data arranged in such a way to permit comparison of the quantum mechanical data and of the fits for the four formulas for the three surfaces. The above conclusions on their relative quality are confirmed. The prevalence of DAE is strengthened visually by its ability to better mimic the curvature of the E_a *versus* T behavior, present in the quantum mechanical data.

5. Summary and perspectives

In this paper we have exploited the availability of accurate quantum mechanical data on rate constants as a function of absolute temperature from 10 to 350 K, to compute activation energies for three model potential energy surfaces of a favorite reaction of chemical kinetics, $F + H_2 \rightarrow HF + H$.

The previous papers [5,6] presented comparisons with available experimental data in the temperature range, where the Arrhenius law is obeyed. Since the reaction has a low barrier (6.43 kJ/mole), at thermal or sub-thermal energies deviations from linearity of Arrhenius plots emerge. This paper presented activation energies, accurate down to ∼50 K. As stressed in [5,6] below this temperature canonical rate constants and activation energies progressively lose their reliability, both numerically and conceptually. In the search of a reasonable extension of Arrhenius law introducing only one additional parameter for the T dependence of activation energies, four formulas were tested. In particular the one proposed in [8], and designed DAE, was motivated mathematically from a modification suggested from deforming the Euler's defining limit for the exponential function, and physically from recent formulation of distribution law occurring in non-extensive statistical thermodynamics. The latter motivation is actually valid for the Super-Arrhenius, "convex" plot case. Its extension suggested in Ref. [8] to the Sub-Arrhenius, "concave" plot case is phenomenologically justified here as providing the formula which appears to give the best performance in the deep-tunneling situations.

Additional work is clearly needed in different directions. An interesting pattern of resonance features has been characterized,

Table 1
Parameters for fitting formulas.[a]

Potential energy surface	Deformed Arrhenius		Generalized Mott		Modified Arrhenius		Curved Arrhenius	
	E_o	d	T_o	γ	E^*	α	B	C
I	5091.79	−1.240	989067.01	0.1599	63.841	0.569	−1186.363	106510.405
II	4295.52	−0.975	1026781.09	0.1695	54.172	0.687	−972.922	67689.281
III	4183.48	−0.821	214458.64	0.1979	73.317	0.723	−1204.833	92063.918

[a] E_o
* E^* and B (J/mol), T_o (K), and C (J/mol)^2.

Table 2
Chi-square test and coefficient of determination.[a]

Formula	PES I		PES II		PES III	
	χ^2	R^2	χ^2	R^2	χ^2	R^2
Deformed Arrhenius	3894.0	0.983	13216.0	0.964	11741.0	0.950
Generalized Mott	6133.0	0.973	20998.0	0.940	16476.0	0.930
Modified Arrhenius	9032.0	0.960	19383.0	0.920	21610.0	0.920
Curved Arrhenius	102933.0	0.550	139448.0	0.610	124855.0	0.510

[a] See text.

see for example [30–33]. Relevant for modeling the temperature variation of activation energy is its possible association to stereo-dynamics [34].The similar system F + HD, giving HF and HD as products, is an obvious candidate for further study. Results of exact rate constants for both channels are becoming available [35–39], and should also provide a test for the ability of a phenomenologically description of the kinetic isotopic effect in the deep tunneling region. This region is difficult to study by current theoretical approaches.

The flux–flux correlation method for the direct generation of rate constants has been used by Moix and Huarte-Larranaga [40] for PES I and compared with [9], with satisfactory success above the tunnel region. The transition state theory and its variants, as well as quasi-classical trajectory methods, often introduce tunneling corrections according to recipes based on formulas initiated by Wigner [41] and Eckart [42]. They are implemented in most of current packages for rate constant calculations, to which one has to refer resort to in view of the difficulties of direct, exact quantum mechanical calculations. On account of the relevance of establishing a link between topological features of potential energy surfaces and usable phenomenological approaches such as those examined in this paper, it will be of interest to study the relationships between the parameters appearing in the formulae as discussed in this paper, and those of the Eckart or Wigner formulas and related treatments, which those topological features exploit.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemphys.2011.05.016.

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