



Vibrational temperature of the adlayer in the ‘hot-atom’ reaction mechanism



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ARTICLE INFO

Article history:

Received 27 April 2012
Received in revised form 28 September 2012
Available online 31 October 2012

Keywords:

Kinetics of atom recombination
Models of non-equilibrium phenomena
Energy distribution functions
Vibrational temperature of adatoms

ABSTRACT

The hot-atom reaction mechanism brings about reaction rates several orders of magnitude higher than those expected in the case of adatoms which have thermalized with the surface. This paper addresses the issue of a possible thermodynamic characterization of the adlayer under reactive conditions and at the steady state. In turn, this implies having to determine the temperature of the adatoms. This is done by means of a nonequilibrium statistical thermodynamic approach, by exploiting a suitable definition of the entropy. The interplay between reaction rate, vibrational temperature of the adatoms and adsorbed quantities is highlighted. This paper shows that the vibrational temperature depends on reaction rate, logarithmically and exhibits a non-linear scaling on physical quantities linked to the energetics of the reaction, namely the adsorption energy and the binding energy of the molecule. The present modeling is also discussed in connection with response equations of nonequilibrium thermodynamics.

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1. Introduction

During recent decades the study of atom recombination at catalytic surfaces has been a vital issue from both experimental and theoretical perspectives [1–11] and references therein. Experimental findings on reaction cross-sections which are intermediate between those belonging to the Langmuir–Hinshelwood (LH) and the Eley–Rideal (ER) mechanisms, open up the possibility of a different mechanism governed by the so-called ‘hot’ adatoms [12–15]. The adjective ‘hot’ refers to an adspecies which, although trapped in the adsorption potential well, has not thermalized with the surface. These adspecies are expected to be highly reactive on the surface and, for this reason, their role is thought to be fundamental for the kinetics of the process.

For reactions proceeding under steady state conditions, determination of the reaction rate requires the knowledge of how adatoms are distributed in energy, or more precisely, their occupation number in the vibrational level of the adsorption potential well. In the case of the ‘hot-atom’ reaction mechanism, these occupation numbers are expected to be greater than those of a Boltzmann distribution at the temperature of the surface; in this respect the energy distribution function (d.f.) of the adatoms is hyperthermal.

Modeling the energy d.f. of adatoms, in chemisorption and catalysis, has been the subject of several works in the literature [16–20]. In these approaches two processes have to be taken into account in computing the d.f., namely the accommodation of the adatom at the adsorption site and the formation of the diatom. The former is linked to the energy dissipation of the atom, trapped in the adsorption potential well during adsorption, into the solid. The latter implies binary collisions among reacting species. An approach suitable for computing the vibrational d.f. is based on kinetic equations where energy dissipation and atom recombination are described as first and second order reactions, respectively. Also, continuum approaches based on the use of the Fokker–Planck equation have been employed in the literature [16,18]. In particular, in

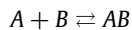
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these models gas atoms enter the adsorption potential well in the upper bound level of the vibrational ladder, and descend the ladder owing to the energy transfer to the solid surface and/or to the adlayer. It is the interplay between adsorption, recombination rates and energy disposal to the solid, which affects the vibrational d.f. of the adatoms. At the steady state these models lead to analytical solutions for the d.f. which, in turn, have been employed for interpreting experimental data in order to gain information on both the reaction rate and the process of energy disposal [21].

Hitherto these approaches, being 'kinetic' in nature, have been aimed at characterizing the system (substrate–adlayer) through kinetic quantities, such as the reaction rate and the rate coefficients for energy transfer. The purpose of the present paper is to attempt a thermodynamic characterization of the adlayer, under nonequilibrium reaction conditions, at the steady state. This is achieved through the computation of the entropy of the adsorbate together with a suitable definition of the temperature of the adlayer. To this end it is necessary to know the d.f., for instance computed using the kinetic approach as quoted above. These quantities are further employed to estimate parameters typical of the nonequilibrium thermodynamic equations, in order to bridge the gap between the previously employed kinetic approach and that based on the response equations of the nonequilibrium thermodynamics.

2. The model

In this contribution we consider the surface reaction



where A, B denote the adatoms and AB the gas molecule. The reaction rate is given by

$$\frac{dn_{AB}}{dt} = r = R_d - R_r, \quad (1)$$

that is the difference between direct and reverse reaction rates. In the following we deal with a mobile adlayer model according to which adatoms are trapped in a 1D potential well (along the normal to the surface) and move freely on the surface plane. By considering the reaction taking place between A and B species in the vibrational ladder of the adsorption potential well, these rates are

$$R_d = \sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} n_{i_\alpha}^{(A)} n_{j_\lambda}^{(B)}, \quad (2a)$$

$$R_r = \sum_{k, i_\alpha j_\lambda} w_{k, i_\alpha j_\lambda} n_k^{(AB)} \quad (2b)$$

where $n_{i_\alpha}^{(A)}$, $n_{j_\lambda}^{(B)}$ and $n_k^{(AB)}$ are the amount of species (as specified by the superscript), $w_{i_\alpha j_\lambda, k}$ the state to state transition probability for the open reaction channel $A_{i_\alpha} + B_{j_\lambda} \rightleftharpoons AB_k$ between an A adatom in vibrational level i and translational state α , and a B adatom in its vibrational level j , and translational state λ , to produce a molecule in state k . In Eq. (2) the sum is performed over vibrational and translational states. The index of the vibrational state of the adatoms takes the values $i = 1, 2, \dots, \nu^*$ where ν^* denotes the last vibrational level. For each reaction channel energy conservation holds, namely $E_k^{(AB)} = E_{i_\alpha}^{(A)} + E_{j_\lambda}^{(B)}$. The probability $p_{i_\alpha}^{(A)}$, to find the adatom A in the state i_α , is given by $p_{i_\alpha}^{(A)} = \frac{n_{i_\alpha}^{(A)}}{n_A}$ with $n_A = \sum_{i_\alpha} n_{i_\alpha}^{(A)}$ the total number of species. Similar expressions hold for both $p_{j_\lambda}^{(B)}$ and $p_k^{(AB)}$. The reaction rate Eq. (1) becomes

$$r = k_d n_A n_B - k_r n_{AB} \quad (3)$$

where

$$k_d = \sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} p_{i_\alpha}^{(A)} p_{j_\lambda}^{(B)} \quad (4a)$$

$$k_r = \sum_{k, i_\alpha j_\lambda} w_{k, i_\alpha j_\lambda} p_k^{(AB)} \quad (4b)$$

are the rate coefficients [22]. In Eq. (4) the sums are performed over the states of the open reaction channels. Specifically, in these expressions the sums run over the initial and final states and $p_{i_\alpha}^{(X)} \equiv p(E_{i_\alpha}^{(X)})$ is the energy distribution function of the vibrational ladder ($X = A, B$). The ratio between these two constants reads $\frac{k_d}{k_r} = \frac{\sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} p_{i_\alpha}^{(A)} p_{j_\lambda}^{(B)}}{\sum_{k, i_\alpha j_\lambda} w_{k, i_\alpha j_\lambda} p_k^{(AB)}}$ where for each reaction channel the transition probabilities of direct and reverse processes are equal (microscopic reversibility), i.e. $w_{i_\alpha j_\lambda, k} \equiv w_{k, i_\alpha j_\lambda}$.

Let us first consider the case of a reaction in which the reagents (adatoms) and the product (AB molecules) are in thermal equilibrium at the substrate temperature, T_s . Moreover, as far as the adspecies are concerned, we are dealing with a mobile adlayer model where the probability function is $p_{i_\alpha}^{(X)} = \frac{e^{-\beta_s E_{i_\alpha}^{(X)}}}{q_{s, X}}$ with $q_{s, X} = \sum_{i_\alpha} e^{-\beta_s E_{i_\alpha}^{(X)}}$ the single particle partition function

($X = A, B$) and $\beta_s = 1/k_B T_s$, k_B being the Boltzmann constant. By inserting this expression in the relation above, and exploiting the equality of the transition probabilities, we get

$$\frac{k_d}{k_r} = \frac{q_{s,AB}}{q_{s,A}q_{s,B}} = e^{-\beta_s(\mu_{AB}^0 - \mu_A^0 - \mu_B^0)}, \quad (5)$$

where $\mu_X^0 = -k_B T_s \ln q_{s,X}$ is the standard chemical potential and $\mu_X = \mu_X^0 + k_B T_s \ln n_X$ the chemical potential. This expression of the chemical potential is attained by considering independent and indistinguishable particles. Eq. (5) is the detailed balance, i.e. the ratio between the rate constants is equal to the equilibrium constant of the reaction. It is worth noting, in passing, that writing the equilibrium constant of the reaction as $\frac{k_d}{k_r} = \frac{P_{AB}}{\theta_A \theta_B}$ (with P being the gas pressure and $\theta_{A(B)}$ the surface coverage at equilibrium) would require the following definition of the standard chemical potentials: $\tilde{\mu}_{A(B)}^0 = \mu_{A(B)}^0 + k_B T_s \ln M$ and $\tilde{\mu}_{AB}^0 = \mu_{AB}^0 + k_B T_s \ln \beta_s V$ where M is the number of adsorption sites and V the volume of the reactor. Using the chemical potential the reaction rate can be rewritten as

$$\begin{aligned} r &= \left(\sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} e^{-\beta_s(E_{i_\alpha}^{(A)} + E_{j_\lambda}^{(B)})} \right) e^{\beta_s(\mu_A + \mu_B)} - \left(\sum_{i_\alpha j_\lambda, k} w_{k, i_\alpha j_\lambda} e^{-\beta_s E_k^{(AB)}} \right) e^{\beta_s \mu_{AB}} \\ &= \left(\sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} e^{-\beta_s(E_{i_\alpha}^{(A)} + E_{j_\lambda}^{(B)})} \right) e^{\beta_s(\mu_A + \mu_B)} (1 - e^{\beta_s A_r}) = R_d (1 - e^{\beta_s A_r}), \end{aligned} \quad (6)$$

where $A_r = \mu_{AB} - \mu_A - \mu_B$ is the affinity of the reaction. In the case of a small departure from equilibrium Eq. (6) leads to the 'kinetic law of mass action' [23,24] which implies $r \propto -A_r$. It goes without saying that when the direct reaction prevails (for instance, when the products are continually removed), $A_r \rightarrow -\infty$ in Eq. (6) and $r = R_d > 0$. Furthermore, if equilibrium is established between adsorbed species and the same component in the gas phase, then the chemical potentials entering Eq. (6) are equal to those of the atoms in the gas phase.

Let us go on to discuss the nonequilibrium case where adspecies have not thermalized with the surface in the course of the recombination reaction at the steady state. Under these circumstances differences arise in relation to the situation previously studied, due to both the rate constant and the determination of the adsorbed quantities (surface coverage). The rate constant depends on the probability function p_{i_α} , which is no longer given by the Boltzmann distribution; in turn, as discussed in more detail below, it is expected to depend upon the reaction rate. As regards the surface coverage, while in the equilibrium case this can be linked to thermodynamic quantities (such as the chemical potential), under nonequilibrium conditions it is determined by the reaction kinetics. For a non-Boltzmannian energy distribution function of the vibrational ladder it is not straightforward to define the adlayer temperature, although the mean energy and the entropy of the adlayer can both be defined. In fact, the entropy of the adlayer can be estimated by exploiting the definition proposed in Ref. [25,26]; this definition also holds in the nonequilibrium case

$$s_X = -k_B \left[\sum_{i_\alpha} p_{i_\alpha}^{(X)} \ln p_{i_\alpha}^{(X)} + \ln n_X \right], \quad (7)$$

s_X being the partial molar entropy ($X = A, B$). In order to write the reaction rate through an expression similar to Eq. (6) (as usually employed in nonequilibrium thermodynamics) one defines the quantity $\mu'_X = \bar{E}_X - T_s s_X = \sum_{i_\alpha} E_{i_\alpha}^{(X)} p_{i_\alpha}^{(X)} + k_B T_s \sum_{i_\alpha} p_{i_\alpha}^{(X)} \ln p_{i_\alpha}^{(X)} + k_B T_s \ln n_X$, which resembles the thermodynamic expression of the chemical potential. (Please notice that in this definition the term $-a \frac{\partial(\bar{E} - T_s s)}{\partial a}$, where $a = A/n$ is the area per particle, has been omitted. This is in view of the following presentation where only vibrational states are taken into account, with vibrational frequency independent of a .) In the equation above $\bar{E}_X = \sum_{i_\alpha} p_{i_\alpha} E_{i_\alpha}^{(X)}$ is the mean energy of the adatom. However, one has to bear in mind that in the present context μ' is merely a mathematical definition suitable for expressing the rate in the form of Eq. (6). Nevertheless, since it is possible to define a vibrational temperature of the adlayer (see below), the μ' quantity could be also estimated at this temperature. By means of the μ' expression and neglecting the rate of the reverse reaction, Eq. (1) becomes

$$r = \sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} p_{i_\alpha}^{(A)} p_{j_\lambda}^{(B)} n_A n_B = \left(\frac{e^{-\beta_s(\bar{E}_A + \bar{E}_B)} \sum_{i_\alpha j_\lambda, k} w_{i_\alpha j_\lambda, k} p_{i_\alpha}^{(A)} p_{j_\lambda}^{(B)}}{e^{\sum_{j_\lambda} p_{j_\lambda}^{(B)} \ln p_{j_\lambda}^{(B)}} e^{\sum_{i_\alpha} p_{i_\alpha}^{(A)} \ln p_{i_\alpha}^{(A)}}} \right) e^{\beta_s(\mu'_A + \mu'_B)}, \quad (8)$$

to be compared with Eq. (6) (for $A_r \rightarrow -\infty$). In the case of a thermalized adlayer the temperature of the system is T_s and, since $p_{i_\alpha}^{(X)} = \frac{e^{-\beta_s E_{i_\alpha}^{(X)}}}{q_{s,X}}$ in this case, Eq. (8) actually reduces to Eq. (6) ($q_{s,X} = q_X(T_s)$).¹

¹ In the present modeling the surface is considered as a thermal reservoir whose temperature is independent of the reactive process.

The temperature of the adlayer can be defined by employing the concept of ‘generalized heat’ [25,26] through the relationship

$$d\bar{E} = T ds \equiv -k_B T \sum_{i_\alpha} dp_{i_\alpha} \ln p_{i_\alpha}, \quad (9)$$

where the number of adatoms and the area of the surface are taken as constants and $d\bar{E} = \sum_{i_\alpha} E_{i_\alpha} dp_{i_\alpha}$. In Eq. (9) and in the equations that follow, the index of adspecies is omitted since we are considering a one component system. Eq. (9) is to be considered as the definition of temperature in terms of d.f. and the energy spectrum of the single particle. For instance, in the case of an equilibrium adlayer $p_{i_\alpha} = (\sum_{i_\alpha} e^{-\beta_s E_{i_\alpha}})^{-1} e^{-\beta_s E_{i_\alpha}}$ and Eq. (9) gives $T = T_s$. To give a more concrete example, let us consider the case of a vibrational ladder where the levels are overpopulated with respect to the Boltzmann distribution computed at the temperature of the surface, T_s . To simplify the discussion, from now on the vibrational states are assumed to be non-degenerate, i.e. the α index is dropped in the sums.

In order to arrive at a more manageable expression for T , the d.f. is rewritten here in terms of the ‘overpopulation factor’, $f_i = \frac{n_i}{(\frac{n_i}{n_0})_B} = \frac{n_i}{n_0} e^{\beta_s E_i}$, namely the ratio between the relative population of the actual system and the relative population of the Boltzmann distribution computed at the same n_0 value. The energy of the ground level is set equal to zero ($E_0 = 0$). Accordingly, $p_i = \frac{n_i}{n} = \frac{n_0}{n} e^{-\beta_s E_i} f_i$ and Eq. (9) gives rise to $\sum_i dp_i E_i = -k_B T \sum_i dp_i [\ln f_i - \beta_s E_i]$, namely

$$\frac{1}{T_s} - \frac{1}{T} = \frac{k_B \sum_i \ln f_i dp_i}{\sum_i E_i dp_i}, \quad (10a)$$

where $p_0 = \frac{n_0}{n}$ and the condition $\sum_i dp_i = 0$ has been used. Clearly, the case $f_i = \text{constant}$ reduces to the Boltzmann distribution function, for $f_0 = 1$ always holds true. Furthermore, $dp_i = e^{-\beta_s E_i} f_i dp_0 + p_0 e^{-\beta_s E_i} df_i$. One can now conjecture that the variation of the overpopulation is a one parameter function of the form $df_i = \frac{\partial f_i}{\partial \xi} d\xi$. Under these circumstances and using the constraint above one evaluates $g_i = \frac{dp_i}{dp_0}$ as

$$g_i = \begin{cases} e^{-\beta_s E_i} f_i - \frac{e^{-\beta_s E_i} \frac{\partial f_i}{\partial \xi}}{p_0 \sum_{i=1}^{v^*} e^{-\beta_s E_i} \frac{\partial f_i}{\partial \xi}} & \text{for } i \neq 0 \\ g_0 = 1 \end{cases} \quad (10b)$$

with v^* being the vibrational quantum number of the upper bound level, $p_0^{-1} = \sum_{i=0}^{v^*} e^{-\beta_s E_i} f_i$ and $\sum_{i=0}^{v^*} g_i = 0$.² From Eq. (10a) the following relation is obtained for the vibrational temperature of the adlayer

$$\frac{1}{T_s} - \frac{1}{T} = k_B \frac{\sum_{i=1}^{v^*} g_i \ln f_i}{\sum_{i=1}^{v^*} g_i E_i}. \quad (11)$$

Two cases are worthy of note. In the first the overpopulation factor is independent of quantum number according to the expression $f_i = 1 + (1 - \delta_{i,0})\xi$ where $\delta_{i,0}$ is the Kronecker delta, and ξ is a positive constant. For a harmonic vibrational ladder $E_v = vE_{01}$, E_{01} being the energy spacing of the ladder, and Eq. (11) eventually becomes (see also Appendix A),

$$\frac{1}{T_s} - \frac{1}{T} = \frac{k_B}{E_{01}} (1 - \gamma) \ln(1 + \xi) \quad (12)$$

where $\gamma = e^{-\beta_s E_{01}}$ and the case $\beta_s E_{01} > 1$ is considered. It is apparent from Eq. (12) that in this case the temperature scales logarithmically with the nonequilibrium parameter, ξ .

The second example concerns the d.f. previously derived in Refs. [17,27] in the case of prevailing vibrational quantum exchange between adatoms. The d.f. reads,

$$p_v = \frac{n_0}{n} e^{-\beta_s E_v} e^{v\xi}, \quad (13)$$

² As obtained from the constraint $\sum_{i=0}^{v^*} p_i = 1$.

where $f_v = e^{v\xi}$ is the overpopulation factor and ξ is a positive constant. For the harmonic vibrational ladder, Eqs. (11) and (13) give

$$\frac{1}{T} = \frac{1}{T_s} - \frac{\xi k_B}{E_{01}}. \quad (14)$$

Alternatively, Eq. (14) defines the nonequilibrium parameter in terms of T : $\xi = (1 - \frac{T_s}{T}) \beta_s E_{01}$. The details of the derivation of Eq. (14) are reported in Appendix A. It is worth noticing that, differently to the case above, the ratio T_s/T scales linearly with ξ .

Eq. (11) can be rewritten in the alternative form

$$\frac{T}{T_s} = \frac{\beta_s \sum_i g_i E_i}{\sum_i g_i (\beta_s E_i - \ln f_i)}, \quad (15)$$

which holds true provided that $f_i < e^{\beta_s E_i}$. In fact, for the d.f. Eq. (13) this constraint implies $\xi < \beta_s E_{01}$ in agreement with the above result.

3. Application to adatom recombination at the steady state

3.1. Vibrational temperature of the adlayer

The aim of this section is to compute the vibrational temperature and the entropy of the adatoms in the case of diatom formation, A_2 , at the steady state. The model takes into account several reaction channels where adatoms, in vibrational levels n (A_n) and m (A_m), react to produce a molecule. As far as the energy transfer is concerned, only energy exchange between the adatom and the solid lattice is taken into account. A reaction channel is open for $E_m + E_n \geq E^\#$ where $E^\#$ is the activation energy and E_n the vibrational energy of the adatom (Fig. 1). Owing to the greater occupation number of the ground level, contributions of reaction channels involving only this level are considered in the computation. For a harmonic ladder the d.f. is given by [20],

$$f_{\kappa+j} = \frac{(1+\rho)^j}{\gamma^j} \left[\eta + \frac{\rho + (1-\gamma)z^j}{(1+\rho-\gamma)} \right] \quad 1 \leq j \leq v^* - \kappa \quad (16a)$$

$$f_j = 1 + \frac{\gamma^\kappa}{\gamma^j} \eta \quad 0 < j \leq \kappa \quad (16b)$$

where $\rho = w\theta_0/k$, $z = \gamma(1+\rho)^{-1}$, with w being the rate constant for diatom formation, k the rate constant for the loss of a vibrational quantum to the solid, and θ_0 the occupation number (in monolayer units) of the ground level. Furthermore, $\eta = \frac{\rho(1+\rho)^{v^*-\kappa}}{2-(1+\rho)^{v^*-\kappa+1}}$ where $E_\kappa = E^\#$ and E_{v^*} is the energy of the upper bound vibrational level. It is worth noticing that ρ is an important quantity of the model, for it determines the displacement of the d.f. from the Boltzmann one. The reaction rate, Φ , is given by $\Phi = \Phi_B \frac{\eta}{\rho}$ and in the limit $\rho \rightarrow (2^{1/(v^*-\kappa+1)} - 1)$ it becomes several orders of magnitude higher than the value computed for the Boltzmann d.f. at the surface temperature, namely $\Phi_B = 2w\theta_0^2 \gamma^\kappa$. Also, $\lim_{\rho \rightarrow 0} \Phi = \Phi_B$. It needs to be stressed, however, that the condition $\Phi \cong \Phi_B$ does not necessarily imply that the adlayer has thermalized with the surface. In fact, according to Eq. (16) the Boltzmann d.f. is recovered only in the case of a *non-reactive* adlayer, for in this case the overpopulation factors – of the whole ladder – are negligible when compared to unity. For high exoergic adsorption and/or low surface temperature this condition is fulfilled, in general, for $w \rightarrow 0$, i.e. for $\Phi_B \rightarrow 0$.

To reduce the complexity of the computation in the following we consider the functional form taken by Eq. (16) for ρ much lower than unity. Under these circumstances the d.f. becomes

$$f_i = 1 + \frac{\xi}{\gamma^i} \quad \kappa < i \leq v^* \quad (17a)$$

$$f_i = 1 + \frac{\xi}{2\gamma^i} \quad 0 < i \leq \kappa, \quad (17b)$$

where the parameter ξ is proportional to the ratio between reaction rate and rate coefficient for energy disposal to the solid: $\xi = \frac{\Phi}{k\theta_0}$. In fact, the d.f. Eq. (17) is typical of a reactive adlayer at steady state. This d.f. also holds for reaction channels involving adatoms in the same vibrational level although, in this instance, a multiplicative factor enters the definition of ξ [15]. Accordingly, in what follows the general form of the vibrational distribution, Eq. (17), will be employed. In Fig. 2 the typical trend of the overpopulation factor given by Eq. (17) is reported for $\gamma = 0.05$, and $\xi = 10^{-14}$ and $\xi = 10^{-16}$, values which are representative of real systems. In the same figure the overpopulation factor given by Eq. (13), in the case of a harmonic ladder, is also displayed for comparison. Notably, Eq. (13), as derived by Treanor et al. in Ref. [27], applies

with $c(\kappa, \nu^*) = [2\nu^*(\nu^* + 1) - \kappa(\kappa + 1)]$. Since $\frac{1}{2}D_{A_2} + E_a \cong \nu^*E_{01}$, with D_{A_2} being the dissociation energy of the molecule, the term $c(\kappa, \nu^*)$ in Eq. (18) can be rewritten as $c(\nu^*, D) = -2\nu^{*2} + 4\nu^*D - D(D - 1)$ where $D = \frac{D_{A_2}}{E_{01}}$ and $\frac{1}{2}D < \nu^* < D$ is assumed. The activation energy of the reaction therefore reads $E^\# = 2E_a = (2\nu^* - D)E_{01}$ where E_a is the adsorption energy (Fig. 1).

The contribution of the last level to the vibrational temperature of the adlayer is attained by retaining in Eq. (18) only the term at $i = \nu^*$ according to

$$\left(\frac{T_s}{T}\right)_{\nu^*} = 1 - \frac{4}{\beta_s E_{01} c(\nu^*, D)} \ln\left(1 + \frac{\xi}{\gamma^{\nu^*}}\right). \quad (19a)$$

For an ample class of exoergic reactions the constraint $\gamma^{\nu^*} \ll \xi < 1$ is fulfilled, and (19a) becomes

$$\left(\frac{T_s}{T}\right)_{\nu^*} \cong \left(1 - \frac{4\nu^*}{c(\nu^*, D)}\right) + \frac{4}{\beta_s E_{01}} \frac{1}{c(\nu^*, D)} |\ln \xi|. \quad (19b)$$

Eq. (19b) allows us to determine the upper bound of the contribution of the level ν^* to the vibrational temperature according to $1 \leq \left(\frac{T_s}{T}\right)_{\nu^*} < \left(1 - \frac{4\nu^*}{c(\nu^*, D)}\right)^{-1}$ which is a function of both adsorption energy of the adatom and binding energy of the molecule. Eqs. (19a) and (19b) are important for they make it possible to characterize the non-equilibrium state of the system. In fact, the displacement from equilibrium of the vibrational levels – i.e. the overpopulation – is expected to be greater at $i = \nu^*$. In addition, the population of the last level is shown to be important for reaction kinetics under nonequilibrium condition [28]. The behavior of Eq. (19a), as a function of the activation energy, is reported in Fig. 3(a) for several values of D_{A_2} and at given values of ξ and $\beta_s E_{01}$. In particular, for H recombination on metals $D \approx 36$ (at $E_{01} \cong 0.12$ eV) and ξ is of the order of magnitude of $\xi \cong 10^{-14}$. The non-linear trend of $(T_s/T)_{\nu^*}$ on adsorption energy (in Fig. 3(a)) is mainly due to the $c(\nu^*, D)$ function which depends on the energetics of the process. In panel (b) $(T_s/T)_{\nu^*}$ is plotted as a function of the parameter $\xi = \frac{\phi}{k\theta_0}$ for several values of D , activation energy and $\beta_s E_{01}$. For H recombination on metals the interval of the experimental values of $\xi = \frac{\phi}{k\theta_0}$ is also marked by the arrows in Fig. 3(b). For a given system $(T_s/T)_{\nu^*}$ increases with reaction rate. In turn, shifting from one system to another, (i.e. changing the ν^*, D couple) the temperature exhibits the complex behavior brought about by the non-linear term $c(\nu^*, D)$. With reference to Fig. 3(b), at the lowest binding energy ($D = 10$) the adlayer has thermalized (at $\beta E_{01} = 6$) provided $\xi < 10^{-17}$, while at $\beta E_{01} = 8$ its vibrational temperature can be higher than that of a system which is more exoergic, depending on ξ . In general, in the case of a highly exoergic reaction and/or sufficiently low substrate temperature, for realistic values of ξ the adlayer has not thermalized with the surface. The minimum values $(T_s/T)_{\nu^*, \min}$, as defined by Eq. (19b), are displayed in Fig. 3(c). These values are characteristic of each ‘reaction–catalyst’ system, for they depend solely on the energetics. Values of $(T_s/T)_{\nu^*, \min}$ in Fig. 3(c) span the ample range 0.6–0.9; as a general trend the higher D the higher this figure.

To include in the computation of T_s/T the contribution of all levels, the sum over the logarithms of the overpopulation factors has to be carried out. This can be accomplished, analytically, by retaining in the sum only the leading terms for which $\frac{\xi}{\gamma^i} \gg 1$. This condition is usually well satisfied for energies greater than the activation energy, i.e. for $E_i > E_\kappa$. According to the derivation reported in Appendix B, Eq. (18) becomes

$$\frac{T_s}{T} = \frac{\kappa(\kappa + 1)}{c} + \frac{4(\nu^* - \kappa)}{c\beta_s E_{01}} |\ln \xi|, \quad (20)$$

to be compared with Eq. (19b). Computations of the vibrational temperature according to Eq. (20) are reported in Fig. 4 as a function of ξ and for several values of D , and ν^* . This figure shows that the contribution of levels at $i > \kappa$ is important in determining the vibrational temperature; the contribution of the whole ladder is, on average, twice that of the last level. On the one hand, for a given system and at a given ξ the vibrational temperature of the adlayer decreases with substrate temperature, in other words the adlayer is more ‘hot’ the lower T_s . On the other hand, the vibrational temperature increases with D : i.e. the hotter the system, the higher the energy released by the reaction.

Above we have defined the quantity $\Phi_B = 2w\theta_0^2 \gamma^\kappa$ as the ‘hypothetical’ recombination rate for a Boltzmann d.f., at the temperature of the surface, and at the actual value of $\rho = \frac{w\theta_0}{k}$. The behavior of $(T_s/T)_{\nu^*}$ for $\Phi = \Phi_B$ is displayed in Fig. 5a as a function of $E^\#$ for two values of D . The same figure also reports the $(T_s/T)_{\nu^*}$ ratio for parameter values typical of H recombination on metals ($D \approx 36$ and $\xi \approx 10^{-14}$) where adsorption energies are in the interval 0.3–0.6 eV and $E^\#/E_{01}$ ranges between 5 and 12 [21]. One notices that for $\xi = 2 \times 10^{-14}$ the recombination rates are several orders of magnitude higher than Φ_B , although this entails a vibrational temperature increase, on average, of a factor of two (Fig. 4). This is due to the strong non-linear dependence of reaction rate on adatom vibrational temperature. This aspect is further discussed in Section 3.3.

The entropy of the adlayer is computed through Eq. (7) by means of the d.f. Eq. (17). Performing the sums of the arithmetic series and retaining the leading term of the logarithmic contributions, one ends up with (see also Appendix C)

$$s = s_0 - k_B \ln n + \frac{1}{4} k_B p_0 \xi \beta_s E_{01} c(\nu^*, D) \frac{T_s}{T}, \quad (21a)$$

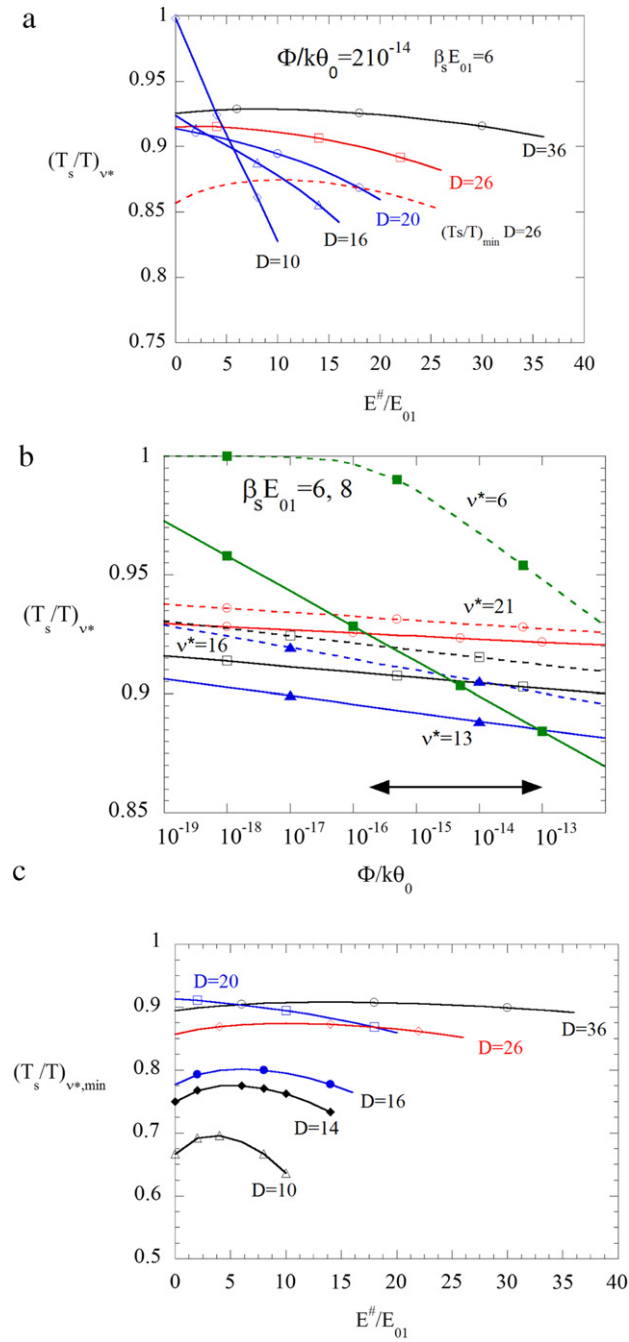


Fig. 3. In panel (a) the contribution of the upper bound level to the vibrational temperature is reported as a function of the activation energy $E^\#$, for several values of the diatom binding energy ($D = D_{A_2}/E_{01}$) in the range 10–36. The computations refer to $\Phi/k\theta_0 = 2 \times 10^{-14}$ and $\beta_s E_{01} = 6$. In the figure the behavior of the minimum value of $(T_s/T)_{v^*}$ is also displayed for $D = 26$ (dashed line). Panel (b) shows the $(T_s/T)_{v^*}$ ratio as a function of the parameter $\xi = \Phi/k\theta_0$ for several values of D , at $\beta_s E_{01} = 6$ (dashed lines) and $\beta_s E_{01} = 8$ (solid lines). In particular, $D = 36$, $v^* = 21$ (open circles); $D = 26$, $v^* = 16$ (open squares); $D = 20$, $v^* = 13$ (solid triangles) and $D = 10$, $v^* = 6$ (solid squares). Panel (c): minimum values of $(T_s/T)_{v^*}$ as a function of activation energy for several values of D in the range 10–36. Since $E^\# = (2v^* - D)E_{01}$ the activation energy is in the range $0 < \frac{E^\#}{E_{01}} < D$.

where $s_0 = -k_B \ln p_0 + k_B p_0 \beta_s E_{01} \frac{\gamma}{(1-\gamma)^2}$. For $\xi = 0$ (i.e. $\Phi = 0$), $T = T_s$, $p_0 = q_\zeta^{-1}$, Eq. (21a) gives the usual expression of the entropy. Moreover, for $\beta_s E_{01}$ values much higher than unity $p_0 \cong 1 - \gamma$. The excess entropy (with respect to that of the thermalized adlayer) reads

$$s^{ex} = s_0^{ex} - k_B \ln(n/n_{eq}), \quad (21b)$$

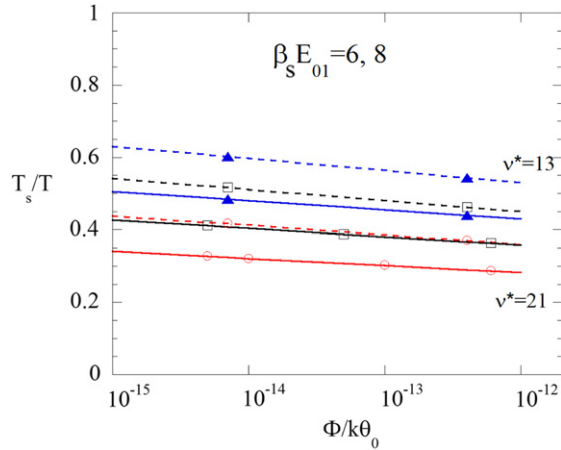


Fig. 4. Vibrational temperature of the adlayer as a function of $\xi = \Phi/k\theta_0$ computed through Eq. (20). Dashed and solid lines refer to $\beta_s E_{01} = 6$ and $\beta_s E_{01} = 8$, respectively. Parameter values are: $D = 36$, $\nu^* = 21$ (open circles); $D = 26$, $\nu^* = 16$ (open squares) and $D = 20$, $\nu^* = 13$ (solid triangles).

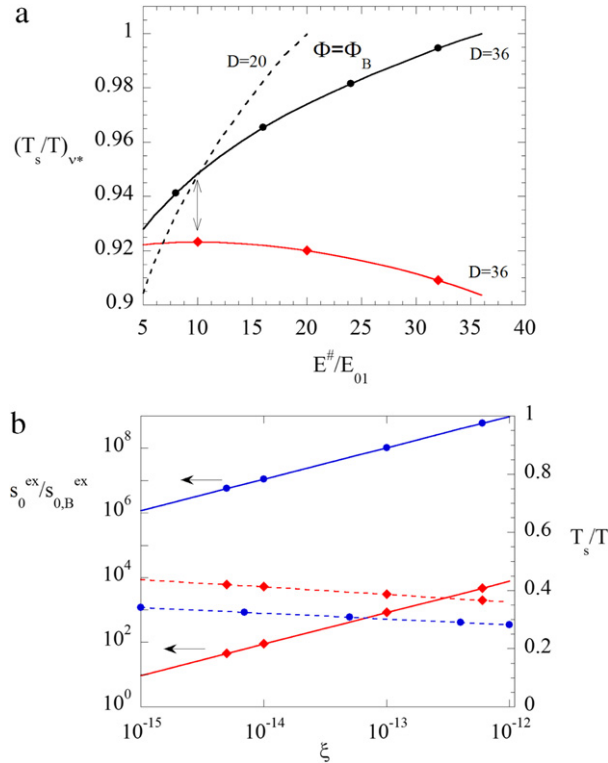


Fig. 5. Panel (a). The temperature ratio $(T_s/T)_{\nu^*}$ is displayed as a function of activation energy for the ‘Boltzmann recombination rate, Φ_B , at $w\theta_0/k = 0.1$, for $D = 36$ (solid circles, full line) and $D = 20$ (dashed line) at $\beta_s E_{01} = 8$. The computation for $\xi = \Phi/k\theta_0 = 2 \times 10^{-14}$ and $D = 36$ is also shown (solid diamonds). The arrow indicates the typical value of the activation energy for H recombination on metals. Specifically, $E_a \approx 0.6$ eV, $E_{01} \cong 0.12$ eV and $D_{H_2} \cong 4.5$ eV. Panel (b). The normalized excess entropy of the adlayer, $s_0^{\text{ex}}/s_{0,B}^{\text{ex}}$ is shown as a function of recombination rate for $D = 36$, $\nu^* = 21$ at $\beta_s E_{01} = 6$ (solid diamonds, full line) and $\beta_s E_{01} = 8$ (solid circles, full line). $s_{0,B}^{\text{ex}}$ is the excess entropy at $\Phi = \Phi_B$ ($w\theta_0/k = 0.1$). The computation is performed for $\xi = \Phi/k\theta_0 = 2 \times 10^{-14}$ and $n = n_{eq}$. The behavior of the T_s/T ratio is also displayed as dashed lines for $D = 36$, $\beta_s E_{01} = 6$ (solid diamonds) and $\beta_s E_{01} = 8$ (solid circles).

where $s_0^{\text{ex}} = \frac{1}{4} k_B p_0 \xi \beta_s E_{01} C(\nu^*, D) \frac{T_s}{T}$ and n_{eq} the adsorbed quantity at equilibrium. The ratio between the excess entropy of the adlayer, s_0^{ex} , and that of the same system at $\Phi = \Phi_B$, $s_{0,B}^{\text{ex}}$, is displayed in Fig. 5b as a function of ξ . Vibrational temperatures of the adlayer are also reported. The plot shows that the excess entropy scales almost linearly on ξ , i.e. on the recombination rate.

3.2. Equilibrium condition and linear response equation

This section is devoted to the equilibrium condition of the adlayer that is actually achieved, as discussed in the previous section, at $\Phi = 0$ ($T = T_s$). So far we have dealt with the adlayer, alone. In order to study the system at equilibrium, however, the species in the gas phase also have to be considered. In fact, at the steady state the reaction rate (expressed as the number of adatoms that recombine per unit of time) is linked to the process of adsorption–desorption through the expression

$$2r \equiv \Phi = F(1 - \theta) - \nu_0 p_{v^*} \theta, \quad (22)$$

where $F = \frac{P}{N\sqrt{2\pi mk_B T_s}}$ is the flux of incoming gas atoms at the surface, P the gas pressure, N the surface density of adsorption sites, m the mass of the adatom, ν_0 the rate constant for desorption and θ the total surface coverage. By exploiting the definition of gas and adatom chemical potentials, $\mu_g = \mu_g^0 + k_B T_s \ln P/P^0$ and $\mu' = \mu'^0 + k_B T_s \ln \theta$, respectively, Eq. (22) can be rewritten as $\Phi = \alpha(1 - \theta)e^{\beta_s(\mu_g - \mu_g^0)} - \nu_0 p_{v^*} e^{\beta_s(\mu' - \mu'^0)}$ with $\alpha = \frac{P_0}{N\sqrt{2\pi mk_B T_s}}$. Alternatively, exploiting the equilibrium condition, $\Phi = 0$, $\theta = \theta_{eq}$, Eq. (22) becomes

$$\begin{aligned} \Phi &= \frac{(1 - \theta)}{(1 - \theta_{eq})} \nu_0 p_{v^*,eq} e^{\beta_s(\mu'_{eq} - \mu'^0)} - \nu_0 p_{v^*} e^{\beta_s(\mu' - \mu'^0)} \\ &= \frac{(1 - \theta)}{(1 - \theta_{eq})} \nu_0 p_{v^*,eq} e^{\beta_s(\mu'_{eq} - \mu'^0)} \left[1 - \frac{(1 - \theta_{eq})}{(1 - \theta)} \frac{p_0}{p_{0,eq}} f_{v^*} e^{\beta_s(\mu' - \mu'_{eq} - (\mu'^0 - \mu'^0_{eq}))} \right]. \end{aligned} \quad (23)$$

In the limiting case of a very small departure from equilibrium, $\theta \cong \theta_{eq}$ and the thermodynamic equation of motion is

$$\Phi \approx -\frac{\nu_0 \gamma^{v^*} \theta_{eq}}{k_B T_s} (\mu' - \mu'_{eq}), \quad (24)$$

with the linear response coefficient $L = \frac{\nu_0 \theta_{eq}}{k_B T_s} e^{-\beta_s(\frac{1}{2} D_{A_2} + E_a)}$. In Eq. (23) the difference $\mu'^0 - \mu'^0_{eq} = (\bar{E} - \bar{E}_{eq} - T_s s_0^{ex})$ has been neglected in the exponential function. In fact, in the expression $\bar{E} - \bar{E}_{eq} \approx (f_1 - 1)\gamma E_{01}$, $\gamma < 1$ and $f_1 - 1 \ll 1$ hold, while the excess entropy is of the order of magnitude of ξ that is in the range 10^{-15} – 10^{-12} . However, the validity of the linear approximation is linked to the value of the coverage at steady state and, in turn, to the energetics of the reaction as discussed in the next section. Moreover, as maintained in Ref. [24], catalytic processes usually take place under far from equilibrium conditions where the linear response theory does not apply.

3.3. Surface coverage and reaction rates

On the basis of the present approach, under nonequilibrium conditions the fractional surface coverage is a function of recombination rate. Also, the relationship between these two quantities is, in general, non-linear. Specifically, both Φ (i.e. ξ) and θ can be determined by solving the system of Eqs. (8) and (22), where the equilibrium condition implies $w = 0$. For the d.f. Eq. (17) with activation energy $E^\# = E_k$, the system can be solved analytically by employing reasonable approximations. Using Eq. (17) in Eq. (8) the reaction rate is computed as

$$\Phi = w' p_0^2 \theta^2 \left[\left(\gamma^\kappa + \frac{\xi}{2} \right) + \sum_{j=1}^{v^* - \kappa} (\gamma^{j+\kappa} + \xi) \right] \cong w' p_0^2 \theta^2 [\gamma^\kappa + c' \xi] \quad \text{where } c' = \frac{1}{2} [2(D - v^*) + 1],$$

$w' = 2w$ and $p_0 = (\sum_n \gamma^n f_n)^{-1} \cong 1 - \gamma(\gamma \gg \xi)$. Consequently, since by definition $\Phi = k\xi\theta$ one gets

$$\theta \cong \frac{k}{w'} \left(\frac{\xi}{e^{-\beta_s E^\#} + c' \xi} \right), \quad (25)$$

where $p_0 \cong 1$ was employed. By means of Eqs. (22) and (25) the following equation is obtained for ξ eventually

$$\bar{k} \xi'^2 + \left(\lambda - \frac{w'}{k} c' \right) \xi' - \frac{w'}{k} = 0, \quad (26a)$$

where $\xi' = \xi e^{\beta_s E^\#}$, $\bar{k} = \frac{1}{F} [k + \nu_0] e^{-\beta_s E^\#}$, $\lambda = \frac{1}{\theta_{eq}} = 1 + \frac{\nu_0 e^{-\beta_s E_{v^*}}}{F}$, and $p_0 \cong 1$ was again assumed. The solution for ξ' reads,

$$\xi' = \frac{1}{2\bar{k}} \left(- \left(\lambda - \frac{w'}{k} c' \right) + \left| \lambda - \frac{w'}{k} c' \right| \sqrt{1 + \frac{4 \frac{w'}{k} \bar{k}}{\left(\lambda - \frac{w'}{k} c' \right)^2}} \right). \quad (26b)$$

One notices that in the limit $\frac{w'}{k} \rightarrow 0$, $\xi' \approx \frac{w'}{k} \frac{1}{\lambda}$ and Eq. (25) gives $\theta \cong \frac{1}{\lambda} = \theta_{eq}$. For $(\lambda - \frac{w'}{k}c') \rightarrow 0$ $\xi' \approx \left(\frac{w'}{kk}\right)^{1/2}$ and the surface coverage (Eq. (25)) becomes $\frac{1}{\theta} = \frac{1}{\theta_{eq}} + \left(\frac{\bar{k}}{\theta_{eq}c'}\right)^{1/2}$. On the other hand, in the case of high desorption energy of the adatoms ($\beta_s E_{v^*} \gg 1$), high reaction rates are attained for $\frac{w'}{k}c' > \lambda \cong 1$ and $\bar{k} < 1$. In fact, under these circumstances $\xi' \approx \frac{1}{k} \left(\frac{w'c'}{k} - 1\right)$ where $c' > 1$ and $\lambda \cong 1$ is used. In addition $\frac{1}{\theta} = \frac{w'}{k} \left[\frac{\bar{k}}{\left(\frac{c'w'}{k} - 1\right)} + c' \right] \approx \frac{w'c'}{k}$ that is greater than $\frac{1}{\theta_{eq}} = \lambda \cong 1$. Consequently, the ratio $\frac{\Phi}{\Phi_B}$, being $\Phi_B = w'\theta^2 e^{-\beta_s E^\#}$ the reaction rate for the Boltzmann d.f., reads

$$\frac{\Phi}{\Phi_B} = \frac{c'}{\bar{k}} \left(\frac{c'w'}{k} - 1 \right) \approx \frac{F}{(k + \nu_0)} e^{\beta_s E^\#} \quad (27)$$

that can be several orders of magnitude higher than one. Interestingly, the value of this ratio is dictated by the relative magnitude of the rate constant for energy disposal (desorption) and the activation energy containing term. In the case of highly exoergic reactions the conditions that validate Eq. (27) are usually satisfied. For $k \approx 10^{13} \text{ s}^{-1}$ the constraint $\bar{k} < 1$ is verified for $\beta_s E^\# > 29$. In particular, in the case of H recombination on metals $F \approx 0.1 \text{ s}^{-1}$, k and ν_0 are of the order of 10^{13} s^{-1} and for $E_{01} \approx 0.12 \text{ eV}$ and $E_a \approx 0.3 \text{ eV}$ one gets $c' = \frac{1}{2} \left[\frac{D_{H_2} - 2E_a}{E_{01}} + 1 \right] \approx 16$ [21]. At $T = 150 \text{ K}$ one obtains $\bar{k} \approx 10^{-6}$ and $\frac{1}{\theta} \cong \frac{c'w'}{k}$ is therefore a very good approximation.

It is instructive to estimate the vibrational temperature of the adlayer for the kinetic model discussed so far. Use of Eq. (20) gives

$$\frac{T_s}{T} = \frac{\kappa(\kappa + 1)}{c} + \frac{4(\nu^* - \kappa)}{c} \left[\kappa - \frac{1}{\beta_s E_{01}} \left(\ln \frac{w'}{k} + \ln \theta + \ln \frac{\Phi}{\Phi_B} \right) \right], \quad (28)$$

where the logarithmic dependence of T_s/T on reaction rate and surface coverage has been made explicit. In terms of rate coefficients the temperature becomes $\frac{T_s}{T} = \frac{\kappa(\kappa+1)}{c} - \frac{4(\nu^*-\kappa)}{c\beta_s E_{01}} \ln \left[\left(\frac{c'w'}{k} - 1 \right) \frac{F}{k+\nu_0} \right]$ where the argument of the logarithmic term is expected to be lower than one. For instance, for hydrogen recombination at $\theta \approx 0.25$, using the quantities above one gets $\frac{T_s}{T} \cong 0.3$ and $\Phi/\Phi_B \cong 10^7$; in other words, a factor of three variation of the temperature of the adlayer entails a reaction rate enhancement of several orders of magnitude.

4. Conclusions

A thermodynamic approach has been developed for determining the vibrational temperature of the adlayer during diatom formation under steady state conditions. The model exploits the definition of generalized heat, together with the definition of nonequilibrium entropy, and requires the knowledge of the energy distribution function of the adatoms. These d.f. have been computed by means of kinetic rate equations. It is shown that, provided the reaction rate is different from zero, the temperature of the adlayer is higher than the temperature of the substrate to an extent that depends, logarithmically, on both the coverage and the reaction rate normalized to the reaction rate of a fully thermalized adlayer. Typical figures for H recombination on metals indicate that a vibrational temperature increase of a factor of three brings about a reaction rate enhancement of several orders of magnitude. On the other hand, the adlayer temperature exhibits a complex non-linear dependence on adsorption energy and binding energy of the molecule.

The present approach is discussed in connection with the linear equations of the nonequilibrium thermodynamics. The response coefficient has been determined; in particular it has been shown to be proportional to the rate constant for desorption.

The definition of the adlayer temperature here proposed is shown to be consistent with the results previously attained in the literature in the case of prevailing VV quantum exchange.

Appendix A

In this appendix we report the computations of Eq. (11) for the two d.f. discussed in Section 2. The evaluation of Eq. (11) requires the determination of the sum $\sum_{i=1}^{v^*} E_i g_i$, that is,

$$\begin{aligned} \sum_{i=1}^{v^*} (iE_{01}) g_i &= E_{01} \left[(1 + \xi) \sum_{i=1}^{v^*} i e^{-\beta_s E_{01} i} - \frac{\sum_{i=1}^{v^*} i e^{-\beta_s E_{01} i}}{p_0 \sum_{i=1}^{v^*} e^{-\beta_s E_{01} i}} \right] \\ &\cong E_{01} \left[(1 + \xi) \frac{\gamma}{(1 - \gamma)^2} - \frac{1}{p_0(1 - \gamma)} \right] \end{aligned} \quad (A.1)$$

with $\gamma = e^{-\beta_s E_{01}}$. Since $\sum_{i=0}^{\nu^*} p_i = 1$ one gets $\frac{1}{p_0} = 1 + (1 + \xi) \frac{\gamma}{1-\gamma}$ which can be used in Eq. (A.1) to eliminate p_0 . Moreover, $\sum_{i=1}^{\nu^*} g_i \ln f_i = \sum_{i=0}^{\nu^*} g_i \ln(1+\xi) - g_0 \ln(1+\xi) = -\ln(1+\xi)$, where the condition $\sum_i g_i = 0$ has been exploited. Accordingly,

$$\frac{1}{T_s} - \frac{1}{T} = k_B \frac{\ln(1 + \xi)}{E_{01}(1 - \gamma)^{-1}}, \tag{A.2}$$

namely, Eq. (12).

For the d.f. $f_\nu = e^{\nu\xi}$, one obtains

$$\begin{aligned} \sum_{i=1}^{\nu^*} g_i E_i &= \left(\sum_{i=1}^{\nu^*} e^{-\beta_s E_i} f_i E_i - \frac{\sum_{i=1}^{\nu^*} e^{-\beta_s E_i} E_i \frac{\partial f_i}{\partial \xi}}{p_0 \sum_{i=1}^{\nu^*} e^{-\beta_s E_i} \frac{\partial f_i}{\partial \xi}} \right) = E_{01} \left(\sum_{i=1}^{\nu^*} i e^{-(\beta_s E_{01} - \xi)i} - \frac{\sum_{i=1}^{\nu^*} i^2 e^{-(\beta_s E_{01} - \xi)i}}{p_0 \sum_{i=1}^{\nu^*} i e^{-(\beta_s E_{01} - \xi)i}} \right) \\ \sum_{i=1}^{\nu^*} g_i \ln f_i &= \left(\sum_{i=1}^{\nu^*} e^{-\beta_s E_i} f_i \ln f_i - \frac{\sum_{i=1}^{\nu^*} e^{-\beta_s E_i} \frac{\partial f_i}{\partial \xi} \ln f_i}{p_0 \sum_{i=1}^{\nu^*} e^{-\beta_s E_i} \frac{\partial f_i}{\partial \xi}} \right) = \xi \left(\sum_{i=1}^{\nu^*} i e^{-(\beta_s E_{01} - \xi)i} - \frac{\sum_{i=1}^{\nu^*} i^2 e^{-(\beta_s E_{01} - \xi)i}}{p_0 \sum_{i=1}^{\nu^*} i e^{-(\beta_s E_{01} - \xi)i}} \right) \end{aligned}$$

that is

$$\sum_i g_i \ln f_i = \frac{\xi}{E_{01}} \sum_i g_i E_i, \tag{A.3}$$

from which Eq. (14) is derived.

Appendix B

For the d.f. Eq. (17) the g_i terms are given by ($0 < i \leq \kappa$)

$$g_i = \gamma^i + \frac{\xi}{2} - \frac{\frac{1}{2}}{p_0 \left(\sum_{n=1}^{\kappa} \frac{1}{2} + \sum_{j=1}^{\nu^* - \kappa} 1 \right)} = \gamma^i + \frac{\xi}{2} - \frac{1}{p_0(\kappa + 2(\nu^* - \kappa))} = \gamma^i f_i - \frac{1}{p_0 D} \tag{B.4}$$

where $D = (2\nu^* - \kappa)$. Similarly, for $\kappa < i \leq \nu^*$

$$g_i = \gamma^i + \xi - \frac{1}{p_0 \left(\sum_{n=1}^{\kappa} \frac{1}{2} + \sum_{j=1}^{\nu^* - \kappa} 1 \right)} = \gamma^i f_i - \frac{2}{p_0 D}. \tag{B.5}$$

It follows:

$$\begin{aligned} \sum_i g_i \ln f_i &= \sum_{i=1}^{\kappa} \left(\gamma^i f_i - \frac{1}{p_0 D} \right) \ln f_i + \sum_{i=\kappa+1}^{\nu^*} \left(\gamma^i f_i - \frac{2}{p_0 D} \right) \ln f_i \\ &= \sum_{i=1}^{\nu^*} \gamma^i f_i \ln f_i - \frac{1}{p_0 D} \left(\sum_{i=1}^{\kappa} \ln f_i + 2 \sum_{i=\kappa+1}^{\nu^*} \ln f_i \right), \end{aligned} \tag{B.6}$$

and

$$\begin{aligned} \sum_{i=1}^{\nu^*} g_i E_i &= -\beta_s^{-1} \sum_{i=1}^{\nu^*} g_i \ln \gamma^i = -\beta_s^{-1} \sum_{i=1}^{\nu^*} \gamma^i f_i \ln \gamma^i - \frac{1}{p_0 D} E_{01} \left(\sum_{n=1}^{\kappa} n + 2 \sum_{n=\kappa+1}^{\nu^*} n \right) \\ &= -\beta_s^{-1} \sum_{i=1}^{\nu^*} \gamma^i f_i \ln \gamma^i - \frac{1}{p_0 D} E_{01} \left[\nu^*(\nu^* + 1) - \frac{1}{2} \kappa(\kappa + 1) \right] \\ &= -\beta_s^{-1} \sum_{i=1}^{\nu^*} \gamma^i f_i \ln \gamma^i - \frac{c}{2p_0 D} E_{01} \end{aligned} \tag{B.7}$$

with $c = 2v^*(v^* + 1) - \kappa(\kappa + 1)$. Using Eq. (11) one eventually gets

$$\frac{T_s}{T} = 1 + \frac{\sum_{i=1}^{v^*} \gamma^i f_i \ln f_i - \frac{1}{p_0 D} \left(\sum_{i=1}^{\kappa} \ln f_i + 2 \sum_{i=\kappa+1}^{v^*} \ln f_i \right)}{\sum_i \gamma^i f_i \ln \gamma^i + \frac{c \beta_s E_{01}}{2 p_0 D}} \cong 1 - \frac{2}{c \beta_s E_{01}} \left(\sum_{i=1}^{\kappa} \ln f_i + 2 \sum_{i=\kappa+1}^{v^*} \ln f_i \right) \quad (\text{B.8})$$

where terms of the order of $\gamma^i \ln f_i$ have been neglected. In addition, the leading terms in the bracket are those involving vibrational levels with $i > \kappa$ where the approximation $f_i \approx \frac{\xi}{\gamma^i} \gg 1$ is expected to hold for realistic values of ξ . Eq. (B.8) becomes

$$\begin{aligned} \frac{T_s}{T} &\cong 1 - \frac{4}{c \beta_s E_{01}} \sum_{i=\kappa+1}^{v^*} (-\ln \gamma^i + \ln \xi) = 1 - \frac{c - \kappa(\kappa + 1)}{c} - \frac{4(v^* - \kappa)}{c \beta_s E_{01}} \ln \xi \\ &= \frac{\kappa(\kappa + 1)}{c} + \frac{4(v^* - \kappa)}{c \beta_s E_{01}} |\ln \xi|, \end{aligned} \quad (\text{B.9})$$

where $\xi \ll 1$.

Appendix C

In this appendix the term $s' = -k_B \sum_i p_i \ln p_i$, which enters Eq. (7), is computed. By using the p_i expression in terms of f_i one obtains

$$\begin{aligned} -\frac{s'}{k_B} &= \sum_i p_0 f_i \gamma^i [\ln(p_0 \gamma^i) + \ln f_i] = \sum_{i=1}^{\kappa} p_0 \left(\gamma^i + \frac{\xi}{2} \right) \ln(p_0 \gamma^i) + \sum_{i=\kappa+1}^{v^*} p_0 (\gamma^i + \xi) \ln(p_0 \gamma^i) \\ &\quad + \sum_{i=1}^{\kappa} p_0 \left(\gamma^i + \frac{\xi}{2} \right) \ln f_i + \sum_{i=\kappa+1}^{v^*} p_0 (\gamma^i + \xi) \ln f_i \end{aligned} \quad (\text{C.10})$$

that is

$$-\frac{s'}{k_B} = -\frac{s_0}{k_B} + \sum_{i=1}^{\kappa} p_0 \frac{\xi}{2} \ln(p_0 \gamma^i) + \sum_{i=\kappa+1}^{v^*} p_0 \xi \ln(p_0 \gamma^i) + \sum_{i=1}^{\kappa} p_0 \left(\gamma^i + \frac{\xi}{2} \right) \ln f_i + \sum_{i=\kappa+1}^{v^*} p_0 (\gamma^i + \xi) \ln f_i. \quad (\text{C.11})$$

The first two sums give the term $-\frac{1}{4} p_0 \xi \beta_s E_{01} c + \frac{1}{2} \xi (2v^* - \kappa) p_0 \ln p_0$. Moreover, using Eq. (B.8) the contribution $p_0 \xi \left(\sum_{i=1}^{\kappa} \frac{1}{2} \ln f_i + \sum_{i=\kappa+1}^{v^*} \ln f_i \right)$ can be rewritten in terms of T_s/T as follows

$$\frac{p_0 \xi}{2} \left(\sum_{i=1}^{\kappa} \ln f_i + 2 \sum_{i=\kappa+1}^{v^*} \ln f_i \right) = \frac{p_0 \xi}{2} \frac{\beta_s E_{01} c}{2} \left(1 - \frac{T_s}{T} \right). \quad (\text{C.12})$$

Inserting these expressions in Eq. (C.11) and neglecting terms of the order of $\ln p_0$ and $\gamma^i \ln f_i$ (Appendix B) the entropy is eventually computed as

$$s' \cong s_0 + \frac{1}{4} k_B p_0 \xi \beta_s E_{01} c \frac{T_s}{T}. \quad (\text{C.13})$$

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