Role of Vibrational Excitation of the Adlayer in ‘Precursor-Mediated’ Sticking Probabilities of CO on Metal Surfaces: A Kinetic Model

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(Received November 18, 2011; accepted in revised form 15 March 2012)
(Published online April 23, 2012)

Precursor-Mediated Adsorption / Adsorption Kinetics / Non Equilibrium / CO Sticking Probability on Metals

The available experimental and theoretical evidence for vibrational excitation of the adlayer in CO chemisorption on metal surfaces raises the question on the validity of the generally accepted model of ‘precursor-mediated’ adsorption in the presence of adsorption–stimulated desorption (asd) as triggered by the hyperthermal conditions of the adlayer. The analysis shows that a ‘precursor-mediated’ kinetics still describes the total rate of adsorption, but that sticking probability measurements carried out in the presence of asd might actually measure the net adsorption rate, that is a lower sticking probability. Literature data, on the decrease of the sticking probability at increasing energies of the impinging CO molecular beams, have tentatively been interpreted by assuming an enhancement of the desorption rate caused by the energy transfer from the beam. The analysis is supported by a theoretical kinetic model of ‘precursor-mediated’ adsorption which takes into account, explicitly, the vibrational excitation of the adspecies.

1. Introduction

It is a well established fact that the kinetics of chemisorption of CO on metal surfaces doesn’t follow a ‘hit and stick’ model, rather it should be described by phenomenological equations of the form of Eqs. (1a) or (1b) below. Equation (1a) reads

\[
\dot{\theta} = \dot{\theta}(0)(1 - \theta^m) \quad \text{with} \quad m \geq 1,
\]

where \( \theta \) is the ratio between adsorbed particles and surface metal atoms, \( \dot{\theta} = \frac{d\theta}{dt} \) the rate of adsorption, \( \dot{\theta}(0) \) the initial rate at the bare surface, \( \dot{\theta} = \frac{\theta}{\theta_{eq,sat}} \) with \( \theta_{eq,sat} \) the surface coverage at equilibrium or at saturation, respectively, i.e. at \( \dot{\theta} = 0 \). For Eq. (1b) one

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writes
\[ \dot{\theta} = \dot{\theta}(0) \left( 1 + \frac{n\theta'}{1 - \theta'} \right)^{-1} \quad \text{with} \quad n \leq 1. \]  

For \( m = 1 \) or \( n = 1 \) these equations both yield \( \dot{\theta} = \dot{\theta}(0)(1 - \theta'). \)

Whenever Eqs. (1a) and/or (1b) holds true, one presumes, in general, that the observed chemisorption kinetics is 'precursor-mediated', as defined in early contributions [1–4]. A precursor is envisaged as a weakly bound transient state into which a particle is trapped before it converts to the final chemisorption state. In particular, Eq. (1b) has widely been applied for fitting sticking probabilities \( S(\theta) = \dot{\theta}/F \), \( F \) being the flux of CO molecules impinging on the surface, on single crystal surfaces such as, for example, Pt(100), Pt(110), Pt(111) and Pd(100) [5], Pd(110) [6], Ru(0001) [7,8], Rh(111) [9], Ni(111), Ni(110) [10], Ni(100) [10,11].

In a recent contribution [12] attention has been drawn on the experimental adsorption–desorption kinetics of various CO-metal systems (polycrystalline Pd [13], Ni [14], Rh [15] and single crystals of Ni(100) [16], Ru(0001) [17] and Ir(111) [18]), where the rates of CO desorption measured in the presence of the adsorbing gas are approximately proportional to the gas pressure and could be orders of magnitude higher than those obtained under vacuum conditions at the same temperature, except at adsorption equilibrium [12,18]. Although this phenomenon of adsorption stimulated desorption (asd) was considered rather puzzling [19], it has recently been shown [12] that this effect could be interpreted in the framework of the non-equilibrium model proposed in Ref. [20]. This model predicts the existence of hyperthermal vibrational distribution functions of the adspecies in the presence of exoergic surface processes, \( i.e. \) an over-population of the vibrational levels with respect to the Boltzmann distribution function. Interestingly, the analysis of experimental adsorption rates shows that both Eqs. (1a) and (1b) provide satisfactory fits to the experimental \( \dot{\theta}(\theta) \) curves.

On account of this observation one wonders whether the validity of these equations should be ascribed to the existence of precursors, as generally assumed, or to non-equilibrium conditions of the adlayer prevailing in the adsorption. The aim of the present contribution is to address this question and to examine the consequences of this emerging point of view.

A brief discussion on ‘precursor-mediated’ adsorption, vibrational excitation of the adlayer and on the observed sticking probabilities of high energy CO molecular beams [8,11] will be presented in Sects. 2, 3 and 4, respectively. In Sect. 5 a kinetic model is presented that takes into account both the formation of the precursor and the possibility of a non-equilibrium state of the adspecies. This model provides the guidelines for the interpretation of sticking probabilities in the presence of adsorption–stimulated desorption (asd) as well as of their reported decrease at increasing energies of the molecular beam. The kinetic model is applied to interpret experimental data available from the literature.

2. Precursor-mediated adsorption

If one recognizes the possibility of physical adsorption, a molecule which on impinging from the gas does not make a successful encounter with an empty site is no longer
Fig. 1. Direct, $S_{\text{dir}}$, and “precursor-mediated”, $S_{\text{prec}}$, sticking probabilities of CO on Pt(111) at $T = 450$ K (full line and blue-dotted line) and at $T = 100$ K (long-dashed lines), as calculated in [22], plotted as a function of fractional surface coverage $\theta$. Red dashed lines (solid line at $m = 2.5$) are fits by means of Eq. (1a) with $m$ values also reported in the figure. Solid symbols are the normalized experimental data for Pt(111) at $T = 310$ K from [24].

immediately eliminated, it may still be chemisorbed at any time during its life time in the physically adsorbed layer [1]. Particles in the precursor state are mobile across the surface and one classifies precursors into *intrinsic* when the particle is trapped at an *empty* lattice site and *extrinsic* when trapped above an *occupied* site. A kinetic lattice gas model has recently been employed [21] for computing the dependence of $S$ on surface coverage and temperature in the presence of precursors and lateral interactions and applied to CO adsorption on Pt(111) [22] and Ru(0001) [23].

Figure 1, reproduced from [23], shows the theoretical behavior of $S_{\text{dir}}$ (top-sites + bridge-sites) on Pt(111) in the case of direct sticking and in the presence of lateral repulsion, which implies site exclusion during adsorption. In addition, the computation of the sticking coefficient, $S_{\text{prec}}$, has also been performed in [23] in the case of negligible desorption rate from the chemisorbed state. In particular, $S_{\text{dir}}$ and $S_{\text{prec}}$ are related through the equation [22]

$$S_{\text{prec}}/S_0 = \frac{S_{\text{dir}}/S_0}{S_{\text{dir}}/S_0 + r/w}, \quad (2)$$

where $S_0$ is the sticking probability at the bare surface, $r$ the rate constant for desorption from the precursor state, $w$ the rate constant for conversion from the precursor to the chemisorbed state and $\frac{r}{w} \propto \exp(-\beta (E_p - E^*_p))$. In this equation $E_p$ is the binding energy of the precursor, $E^*_p$ the energy barrier for the transition from precursor to chemisorbed state and $\beta = (k_B T)^{-1}$, $k_B$ and $T$ being Boltzmann constant and surface temperature, respectively. The solid circles in Fig. 1 refer to the experimental sticking probabilities of CO on Pt(111), normalized to $S_0$, as determined in [24] at $T = 310$ K.
Fig. 2. Rates of adsorption and desorption (in MLs$^{-1}$) as a function of coverage, for polycrystalline Pd at $T = 380$ K (panel a), $T = 466$ K (panel b) and at a gas pressure of $2 \times 10^{-6}$ Pa. In the figures $\dot{\theta}$ is the adsorption rate, while $\Phi$, $\Phi_B$ and $\Phi_{asd}$ are the total, the Boltzmann and the adsorption–stimulated desorption rates, respectively. The total flux of adsorbing molecules, $J = \dot{\theta} + \Phi$, is also shown. In panel c) data at $T = 380$ K and CO pressures between 2 and $13 \times 10^{-6}$ Pa are reported (indicated in the figure in $10^{-6}$ Pa units). The equilibrium values $\theta_{eq}$ and $\Phi_{eq} = \Phi_{Beq}$ have also been indicated. Data are from [12,13].
3. Vibrational non-equilibrium in the adlayer

Let us now examine Fig. 2a,b: these figures show the experimental adsorption rates $\hat{\theta}$ determined at $T = 380$ K and 466 K on polycrystalline Pd [12,13] and the corresponding desorption rates, $\Phi$, as measured in the presence of the adsorbing CO gas ($p_{\text{CO}} = 2 \times 10^{-6}$ Pa) by means of the isotope-jump method of Refs. [13–18].

Also shown are the desorption rates $\Phi_{\text{ads}}$, as derived from the expression $\Phi_{\text{ads}} = \nu_0 \delta \exp(-\beta E_{\text{d}}(\theta))$ for $\nu_0 = 5 \times 10^{13}$ /s$^{-1}$ using the desorption energy $E_{\text{d}}(\theta)$ of Ref. [12], and the total flux of adsorbing CO molecules $J = \hat{\theta} + \Phi$. The experimental $\hat{\theta}$ vs. $\theta$ curves can be fitted by means of Eqs. (1a) or (1b). It is apparent from this figure that desorption rates ($\Phi$) measured in the presence of the adsorbing gas are higher than the corresponding $\Phi_{\text{ads}}$, up to equilibrium. Figure 2c shows the desorption rates at $T = 380$ K measured in the presence of CO at increasing pressures from $2 \times 10^{-6}$ to $13 \times 10^{-6}$ Pa. The red curves are the quantities $\Phi_{\text{ads}} = \Phi - \Phi_{\text{ads}}$ that are the rate of ‘adsorption-stimulated desorption’ (asd) defined in [12]. $\Phi_{\text{ads}}$ is also shown in Fig. 2a–c (thick dashed black line) and is obviously independent of gas pressure. Figure 3a,b shows, on logarithmic scale, the ratio $\Phi/\Phi_{\text{ads}} = \phi$ between the desorption rates $\Phi$ observed at different temperatures (Fig. 3a) and at different pressures (Fig. 3b), and the corresponding rates $\Phi_{\text{ads}}$ calculated as described above.

Let us consider, for the sake of simplicity, a harmonic vibrational ladder of the metal–CO bond with spacing $E_{01}$ and the upper bound level at energy $E^* = E_{\text{d}} = \nu^* E_{01}$, $\nu = \nu^*$ being the vibrational quantum number. By denoting with $\theta^*$ the population of this upper bound level the desorption rate reads $\Phi = \nu_0 \theta^*$. For a Boltzmannian vibrational distribution function one writes $\theta^*_B = \theta_0 \exp(-\beta E_{01})$, with $\theta_0$ the population of level $\nu = 0$ and $\theta_0 \simeq \theta$. The Boltzmann desorption rate is then $\Phi_B = \nu_0 \theta^*_B$. Experimental values of $\Phi/\Phi_B = \phi > 1$, as in Fig. 3a,b, therefore imply $\theta^* > \theta^*_B$, i.e. an over population of level $\nu^*$ with respect to the Boltzmann value. When $\theta \to \theta_0$, $\phi \to 1$.

It was shown in Ref. [12] that the rationale to these findings could be provided by the theoretical model presented in [20] (and references therein). According to this model a chemisorbing gas species enters the adsorption potential well at a high thermally activated state conditions. For a harmonic potential well, the following distribution function is obtained

$$
\theta_v = \theta_0 e^{-\beta v E_{01}} + \theta \alpha_v \left(1 + \sum_{\nu = 1}^{\nu = n} \frac{\alpha_{\nu-1}}{\alpha_{\nu}} e^{-\beta \nu E_{01}}\right),
$$

(3a)
where $E_v = vE_{01}$ gives the energy of level $v$, $\dot{\theta}$ is the adsorption rate, $\alpha_v = (k_v + P_v)^{-1}$ with $k_v$ and $P_v$ the rate coefficients for the transfer of a vibrational quantum to the lattice and to the adlayer, respectively, that is for the transition $A_v \rightarrow A_{v-1}$, as discussed above. Equation (3a) shows that, provided the adsorption rate is different from zero, the distribution is hyperthermal to an extent that depends upon the ratio between adsorption rate and rate constant for energy disposal, $\dot{\theta}/(k_v + P_v)$. By considering energy dissipation to the solid, only, and retaining the leading term in the brackets, Eq. (3a) becomes

$$\frac{\theta_v}{\theta} = e^{-\beta v E_{01}} + \frac{\dot{\theta}}{k \theta} ,$$

where $k$ is taken independent of $v$. The first term in the right member of Eq. (3b) is the relative population of level $v$ given by the Boltzmann distribution function and the second gives the excess relative population of this level. Displacement from the equilibrium distribution is expected for sufficiently large fluxes of adsorption $\dot{\theta}$ and/or for sufficiently small values of $k$, i.e. when energy disposal is inefficient. Therefore, the
Precursor-Mediated Sticking Probabilities of CO on Metals

Fig. 4. Experimental sticking probabilities $S_{\text{exper}}$ at beam energies $e$ increasing from 0.09 to 2.07 eV (reported in the figures in eV units), as measured in [8] for Ru(0001) at $T = 390$ K a) and at $T = 100$ K b).

model deals with a mobile adlayer of oscillators populating the vibrational ladder in the adsorption potential well where occupation probabilities are higher than those of a Boltzmann distribution, i.e. what might be called a vibrationally hot adlayer under quasi steady state conditions.

It is worth stressing that in the model above (Eq. 3a) the non equilibrium state is brought about by the energy release during the exoergic adsorption. The kinetic energy of the incoming gas species does not play any role in that context.

Since $\Phi = \nu_0 \theta^*$, using Eq. (3b), with $\nu = \nu^*$, one receives

$$
\Phi - \Phi_B = \Phi_{\text{asd}} = \frac{\nu_0 \dot{\theta}}{k}.
$$

(4)

The rate coefficient $k(\theta)$ can be estimated through Eq. (4) by using the experimental rates $\dot{\theta}$ and $\Phi_{\text{asd}}$. It was shown in Ref. [12] that, for all the systems examined, $\log k = \log k(0) - b \theta$ with $b$ an increasing function of temperature (in the range 2–5) and $\log k(0)$ of the order of 14–15.

4. Sticking probabilities of high energy molecular beams

Sticking probabilities of CO on both Ru(0001) [8] and Ni(100) [11] have been measured by employing molecular beams of kinetic energies in the range 0.09–2.07 eV.
Figure 4a,b illustrate the results at $T = 390$ K and 100 K for Ru(0001). Sticking probabilities for Ni(100) at $T = 300$ K and 100 K show similar behavior.

The interpretation suggested by the observed dependence of $S(\theta)$ on molecular beam energy were based on the assumption of a precursor-mediated adsorption and ascribed to a reduced probability of the high-energy molecules to accommodate into the weakly bound precursor state, i.e. to the fact that faster molecules have a greater probability of being reflected than trapped [8,11].

We propose a different approach that implies an increase of the desorption rate at increasing kinetic energies of the beam that will obviously correspond to a decrease of the adsorption rate. The increase of the desorption rate is attributed, as discussed in Sect. 5.4, to the creation of a vibrationally excited adlayer that is maintained in a quasi-steady state by energy transfer from the high energy beam to the adlayer.

5. Discussion

5.1 Adsorption-desorption kinetics

In this section we shall develop a kinetic model for adsorption that takes into account both the formation of a precursor and the possibility of a non-equilibrium state of the adspecies in the chemisorption well. The chemisorption kinetics is modelled by dealing with two adsorption wells, one of which, being quite shallow, allows for the formation of the precursor [25]. In addition, the kinetic approach exploits the quasi steady state approximation. In particular, by denoting with $A^*$ the precursor and with $r$ and $k_c$ the rate constants for precursor desorption and for the conversion of precursor to the chemisorbed state, respectively, the surface coverage of $A^*$ reads

$$\theta_{A^*} = \frac{S^*F}{r + k_c}, \quad (5)$$

where $S^*F$ is the rate of adsorption of the gas species in the precursor state, $F$ being the flux of gas species incoming on the surface and $S^*$ the sticking coefficient. We also assume that the precursor enters the final adsorption well at the upper bound level of the vibrational ladder and moves down rapidly to the ground level, i.e. the final chemisorbed state, owing to the dissipation of the vibrational energy into the substrate [20]. By dealing, for simplicity, with two vibrational levels the rate equation for the population of the upper bound level is

$$\dot{\theta}^* = -(v_0 + k)\theta^* + k_c\theta_{A^*} + k'\theta_B, \quad (6)$$

where $v_0$ is the rate constant for desorption from the upper bound level, $k$ is the rate coefficient for energy transfer from the adspecies to the solid lattice and $k'$ the rate coefficient for the reverse process i.e. for energy transfer from the solid lattice to the adspecies. Using the detailed balancing to eliminate $k'$, at steady state Eq. (6) gives

$$\theta^* = \frac{k_c\theta_{A^*} + k\theta_B^*}{(v_0 + k)}, \quad (7)$$
where $\theta_0^* = \theta_0 e^{-\beta E^*} \approx \theta e^{-\beta E^*}$ is the population of the upper bound level for a Boltzmann vibrational distribution function, $k'/k = e^{-\beta E^*}$ and $k'\theta_0 = k\theta_0^*$. In the equation above $\theta_0$ is the population of the ground level and $\theta \approx \theta_0$ the total surface coverage. The rate of adsorption in the chemisorbed state can then be written as $\dot{\theta} = k\theta^* - k'\theta_0$ or

$$\dot{\theta} = k(\theta^* - \theta_0^*) \tag{8}$$

and $\dot{\theta}$ is eventually computed using Eqs. (5)–(8) as

$$\dot{\theta} = \frac{S^*F}{(1 + r/k_c)(1 + v_0/k)} - \frac{\nu_0\theta_0^*}{(1 + v_0/k)} \tag{9}$$

One easily verifies that Eq. (8) is consistent with the basic equation of the model Eq. (3b). Equation (8) identifies the adsorption rate, $\dot{\theta}$, with the net rate of dissipation of the adsorption energy to the solid, i.e. with the net rate of the process

$$\text{CO}_2(\nu^*) \xrightarrow{k_0^0} \text{CO}_2(0)$$

where an adspecies $\text{CO}_2(\nu^*)$ in the upper vibrational level $\nu^*$ is converted to the stable species in the ground vibrational level. This is the main assumption of the model. The desorption rate from the chemisorption well is $\Phi = \nu_0\theta^*$ and can be estimated by computing the population of the upper bound level through Eqs. (5) and (7). It is possible to show that the following equation holds true (see the appendix),

$$\dot{\theta} + \Phi = \frac{S^*F}{(1 + r/k_c)} \tag{10}$$

The total rate of desorption from the chemisorption well splits as $\Phi = \Phi_0 + \Phi_{\text{asd}}$, where $\Phi_0 = \nu_0\theta_0^*$ and $\Phi_{\text{asd}} = \nu_0\frac{\alpha}{k}$ are the ‘thermal’ and ‘adsorption–stimulated’ desorption rates, respectively.

The rate coefficient for the conversion of the precursor to the chemisorbed state depends on surface coverage according to $k_c(\theta, T) = k_c(\theta, T)(1 - \theta)$. In this expression the term $(1 - \theta)$ is the probability that an empty site is available to the adspecies in the precursor state and $k_c(\theta, T)$ gives account of the lateral interaction among molecules (coverage dependent). By exploiting the approximation [22] $S_{\text{dir}}(0, T)k_c(\theta, T)(1 - \theta) \approx w(T)S^*(\theta, T)$ and $S^* = S_{\text{dir}}(0, T) \equiv S_0$, Eq. (10) leads to

$$\dot{\theta} + \Phi = F \frac{S^*}{S_{\text{dir}}(\theta)/S_0 + r/w},$$

or

$$\frac{\dot{\theta} + \Phi}{FS_0} = \frac{S_{\text{dir}}(\theta)/S_0}{S_{\text{dir}}(\theta)/S_0 + r/w} \equiv \frac{S^*}{S_0^*},$$

that is the sticking coefficient $S^*/S_0$ given in Ref. [22] and reported in Eq. (2) of Sect. 2. Equation (11) can be rewritten in the form

$$\dot{\theta} + \Phi = SF,$$ \hspace{1cm} (12)

that is the mass balance of the chemisorption process. On the other hand the overall mass balance reads

$$\dot{\theta} + \Phi + r\theta_A = \frac{S^*F}{(1 + r/k_c)} + r\theta_A = S^*F,$$

or

$$S + \frac{r\theta_A}{F} = S^*,$$ \hspace{1cm} (13)

where $r\theta_A$ is the desorption rate of the precursor with $\theta_A$ given by Eq. (5).
Fig. 5. Sticking coefficient of Pt(111) at \( T = 450 \text{ K} \) a) and \( T = 330 \text{ K} \) b). The figures show the total adsorption rates \( J = FS^{\text{prec}} \) as given by the theoretical \( S^{\text{prec}} \) of [22] and \( F/\text{ML s}^{-1} = 1 \); the thermal desorption rates \( \Phi_B \) as calculated from experimental desorption energies [26]; total desorption rates in the presence of \( \text{asd} \) \( \Phi = \Phi_B + \Phi_{\text{asd}} \) as given by Eq. (14) (red dashed thick lines); net adsorption rates \( \dot{\theta}_B \) expected for a thermalized adlayer (thin blue lines); net adsorption rates \( \dot{\theta}_{\text{asd}} \) expected in the presence of \( \text{asd} \) (thick full red lines). Also shown are the total adsorption rates expected in the absence of precursor, \( FS^{\text{dir}} \), derived from the theoretical \( S^{\text{dir}} \) of [22] (thin dashed lines).

When desorption from the chemisorption potential well is active theoretical models of the sticking coefficient \( S \) should therefore match the experimental quantity \( J/F = (\dot{\theta} + \Phi)/F \). Alternatively, Eq. (12) could be regarded as an operative definition of the sticking probability \( S \) in the general case, which must include desorption from the chemisorbed state.

This point is made clearer in Fig. 5. This figure shows: the total adsorption rate \( J = FS^{\text{prec}}(\theta) \) at \( T = 450 \text{ K} \) (Fig. 5a) and \( T = 330 \text{ K} \) (Fig. 5b), as calculated for Pt(111) in [22], with \( F = 1 \text{ ML s}^{-1} \); the Boltzmann desorption rate \( \Phi_B \) at \( T = 450 \text{ K} \) and \( 330 \text{ K} \), as calculated from the desorption rate measurements of [26]; the net adsorption rate, \( \dot{\theta}_B = FS^{\text{prec}} - \Phi_B \), of a thermalized adlayer.

In the presence of \( \text{asd} \) there will be a total desorption rate \( \Phi \) and a corresponding net adsorption rate \( \dot{\theta}_{\text{asd}} = FS^{\text{prec}} - \Phi < \dot{\theta}_B \). The total rates of desorption (\( \Phi \)) displayed in Fig. 5a,b (thick dashed red straight lines) are given through the expression

\[
\Phi = \frac{\theta}{\theta_{\text{eq}}} \Phi_B(\text{eq}) ,
\]

(14)
Precursor-Mediated Sticking Probabilities of CO on Metals

263

where \( \theta_{\text{eq}}(T, p) \) is the surface coverage at equilibrium, \( \Phi_B(\text{eq})(p, T) = \nu_0 \theta_{\text{eq}} \exp(-\beta E_d(\theta_{\text{eq}})) \) the corresponding desorption rate, with \( E_d(\theta_{\text{eq}}) \) the desorption energy at \( \theta = \theta_{\text{eq}} \) and \( E_d(\theta) \) a decreasing function of \( \theta \) [5]. The validity of Eq. (14) is suggested by the data of Fig. 2, which are representative of all the systems studied in [12–17].

5.2 The measure of the sticking probabilities

Most of the experimental determination of sticking probabilities are based on the method originally proposed by King and Wells [27] and on successive improvements [11,21,28] (and references therein). The method is based on the mass balance of CO in a UHV chamber where the gas is injected as a molecular beam and the pressure in the chamber detected by a Quadrupole Mass Spectrometer (QMS). The base pressure in the absence of the adsorbing surface generates a current, \( I_0 \), in the QMS while the presence of the adsorber will reduce the pressure in the chamber, hence the current \( I(t) \), as a function of time. Therefore, the experimental sticking probability at time \( t \) is given by

\[
S_{\text{exper}}(t) = \frac{I_0 - I(t)}{I_0}.
\]  

(15)

In order to derive \( S_{\text{exper}}(\theta) \) from \( S_{\text{exper}}(t) \) proper calibration of the system is obviously required. The QMS measurements of the gas flux in the absence and in the presence of the sample are, respectively, \( I_0 \propto F \) and \( I(t) \propto \Phi + (1 - S^*) F + r \dot{\theta} A^* \equiv \Phi + (1 - S) F \) as follows form Eq. (13). Therefore, \( \frac{I_0 - I(t)}{I_0} = \frac{S_{\text{exper}}}{F} = \frac{\dot{\theta}}{F} \) which defines \( S_{\text{exper}} \). The following expression then holds

\[
S = S_{\text{exper}} + (\Phi_B + \Phi_{\text{asd}})/F,
\]  

(16)

i.e. a different form of Eq. (12), with \( S \) again the ‘true’ or theoretical sticking probability and

\[
S_{\text{exper}}(\theta) = \frac{\dot{\theta}(\theta)}{F},
\]  

(17)

which defines \( S_{\text{exper}} \).

If the molecular beam is chopped at the frequency \( \omega_0 \) and the current \( I \) in the QMS detected by a lock-in amplifier then, for a sufficiently high ratio \( \omega_0/k_d \) (\( k_d \) is the rate constant of the thermal desorption process), the signal contains only contributions from molecules that did not chemisorb, i.e. the contribution to the QMS signal from continuously desorbing molecules is suppressed by the lock-in amplifier [11,21,28]. In other words, in the presence of thermal desorption (\( \Phi \equiv \Phi_B \), \( I_{\text{cont}} < I_{\text{cont}} \) hence \( S_{\text{exper}} > S_{\text{cont}} \). (Eq. 15) and \( S_{\text{exper}} = J/F = S \). In fact, in this case contributions at the frequencies of the thermal rate of desorption are not present in the Fourier spectra. Accordingly, only the term \( (1 - S^*) F + r \dot{\theta} A^* \) is measured [11].

The situation is however different in the presence of \( \text{asd} \) owing to the close coupling between \( \Phi \) and \( \dot{\theta} \) as shown by Fig. 2. In turn, these results can be explained through Eq. (4). Under these circumstances the contribution of \( \Phi \) to the QMS signal is chopped at the same frequency \( \omega_0 \) and can’t therefore be suppressed by the lock-in amplifier. Consequently, Eq. (17) is expected to hold in this case as well.
Fig. 6. Expected signals, \( I(t) \) in arbitrary units, as calculated from the curves of Fig. 5a for \( F/\text{ML s}^{-1} = 1 \): curve 1 from \( J = S^{\text{prec}} \), curve 2 from \( \dot{\theta}_{\text{ads}} \), curve 3 from \( \dot{\theta}_{\text{B}} \). \( I_0 \) is the QMS signal in the absence of the adsorber.

Fig. 7. Ru(0001)-sticking probabilities \( S^{\text{exper}} \) as determined in [17] from experimental \( \dot{\theta} \), (open circles) and in [8] from the direct determination according to the method of Sect. 5.2 (solid diamonds). “True” sticking probabilities \( S \) as determined in [17] from the observed total adsorption rate \( J/F \) (full circles) and in [23] from theoretical calculations (dashed red line). Thin lines are guides for the eyes.

These results are illustrated in Fig. 6 where three \( I(t) \) curves, leading to different \( S^{\text{exper}}(\theta) \), have been shown. In particular, these \( I(t) \) curves are derived from the \( FS^{\text{prec}} \), \( \dot{\theta}_{\text{B}} \) and \( \dot{\theta}_{\text{ads}} \) curves of Fig. 5a (with \( F = 1 \text{ ML s}^{-1} \)) which yield three different \( S^{\text{exper}}(t) \) (Eq. 15).

5.3 Analysis of experimental data

The data presented in Fig. 7 for Ru(0001) show normalised sticking probabilities derived as follows: \( S^{\text{exper}} \) [17] from the experimental \( \dot{\theta} \) of Ref. [17] at \( T = 394 \text{ K} \), as elaborated in [12]; \( S \) [17] from the experimental \( J/F = (\dot{\theta} + \Phi)/F \) of Ref. [17] at \( T = 394 \text{ K} \); \( S^{\text{exper}} \) [8] from the sticking probability measurements carried out in Ref. [8] at \( T = 390 \text{ K} \) according to the method described above and theoretical values of \( S \)
Fig. 8. “True” sticking probabilities $S$ as determined at two temperatures from the observed total adsorption rates $J/F$ on polycrystalline (p.c.) Pd at $2 \times 10^{-6}$ Pa [13], Rh at $7.3 \times 10^{-6}$ Pa [15] and Ni at $1.3 \times 10^{-6}$ Pa [14].

from Ref. [23] ($S[23]$). Adsorption-stimulated desorption is thus apparently important at $T = 394$ K and is still present at $T = 334$ K [12,17] so that the sticking probability measurements of Ref. [8] at $T = 390$ K should include the asd contribution and, in
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fact, $S_{\text{exp}}$ [17] and $S_{\text{exp}}$ [8] compare favourably. The ‘true’ sticking probability $S$ [17], derived from the experimental $J$ at $T = 394$ K, can then be compared with the theoretical predictions of Ref. [23] for precursor-mediated adsorption at $T = 400$ K. The data of Fig. 7 lead to the conclusion that precursor-mediated adsorption should govern the kinetics also in the presence of adsorption—stimulated desorption.

This conclusion is supported by the data of Fig. 8. In this figure one displays the sticking probabilities $S$ determined for polycrystalline Pd, Rh, and Ni as derived from the experimental $J$ of Refs. [12–15], with $S = J / F(T, p) = \dot{\theta}_{\text{exp}} + \Phi_{\text{exp}}$ and $F(T, p) = 3.26 \times 10^4 \sqrt{T} \ Pa$.

The experimental $S(\theta)$ curves of Fig. 8 can all be fitted by either Eqs. (1a) or (1b), with $\dot{\theta} = \dot{\theta}_{\text{s}}$. It is therefore apparent that also in the presence of non negligible desorption rates, $\Phi = \Phi_{\text{as}} + \Phi_{\text{B}}$, i.e. in the presence of a temperature dependent vibrational excitation of the adlayer, the experimental sticking probabilities $S$ determined for polycrystalline Pd, Rh and Ni correspond to a precursor-mediated adsorption kinetics. A comparison between Figs. 5a and 5b shows that it will only be below about $T = 300$ K that $\dot{\theta}_{\text{as}} \approx F S_{\text{prec}}$ and $S_{\text{exp}} \approx S = S_{\text{prec}}$. This is also true for CO chemisorption on most Pt group metal surfaces and on Ni.

5.4 Sticking probabilities of high energy molecular beams

In Sect. 4 we hypothesized that the observed decrease of the sticking probability at increasing kinetic energy of the molecular beam (Fig. 4), is linked to the increase of the desorption rate of a vibrationally excited adlayer that is maintained in a quasi-steady state by continuous energy transfer from the high energy beam. This suggestion is based on the following observations:

- According to [12,20] and to the previous discussion, vibrational excitation of the adlayer at steady-state, in the course of chemisorption, is highly probable in these systems.
- Impinging of Xe, with energies between 1 eV and 8 eV, at $T = 100$ K on Pt(111) pre-covered with molecular O$_2$ and CO, induces both the desorption of molecular oxygen and the formation of CO$_2$, well below the surface temperature where any thermal reaction occurs [29]. CO$_2$ formation was detected at beam energies above 4 eV only, and the initial oxidation probabilities per incident Xe atom increased with beam energies ranging between $5 \times 10^{-5}$ and $7 \times 10^{-4}$. The final step of the oxidation reaction could be written as $\text{O}_2^* + \text{CO}^* \rightarrow \text{CO}_2$ gas, i.e. a Langmuir–Hinshelwood mechanism involving a vibrationally hot O-adspecies (O*) and a vibrationally hot CO-adspecies (CO$_2^*$). Steady-state populations of these vibrationally hot adspecies are rapidly generated upon impingement of Xe and depend on the beam energy. Vibrational excitation of the adlayer in CO oxidation on Pt group metals has recently been postulated for the high-rate regime of this reaction [30] and for interpreting the non-equilibrium vibrational distributions of product CO$_2$ gas [31].
- The contribution to the QMA current $I(t)$ (Sect. 5.2) of the extra flux of desorbing molecules caused by energy transfer from the beam can’t be suppressed by the ‘chopped beam + lock-in’ system because this extra flux is chopped at the same frequency of the molecular beam, as discussed in Sect. 5.2 for asd.
In order to develop an appropriate kinetic model we employ a computation pathway similar to that of Sect. 5.1 and include, in the rate equations, an extra term which takes into account the effect of the beam on the vibrational state of the adlayer. In particular, Eqs. (7) and (8) take the form

\[
\dot{\theta}^* = \frac{1}{(k + \nu_0)}(k_e \theta_{A^*} + k \theta_B^* + F \theta k_e), \quad (18a)
\]

\[
\dot{\theta} = k(\theta^* - \theta_B^*) - F \theta k_e, \quad (18b)
\]

where \( F k_e \) is the rate coefficient for vibrational excitation of the adspecies from the beam and \( \theta_{A^*} \) is given by Eq. (5). The meaning of Eq. (18b) is that the net rate of energy dissipation is reduced as a consequence of the increased rate of the reverse process (\( \text{CO}_s(0) \rightarrow \text{CO}_s(\nu^*) \)) caused by the molecular beam. By using Eq. (18a), Eq. (18b) becomes,

\[
\dot{\theta} = \frac{S^* F}{(1 + r/k_e)}(1 + \nu_0/k) - \frac{\Phi_B}{(1 + \nu_0/k)} - \frac{F \theta k_e}{(1 + \nu_0/k)} \cdot \quad (19)
\]

The population \( \theta^* \) is also given through Eq. (18b) as

\[
\theta^* = \frac{\dot{\theta}}{k} + \frac{\theta_B^*}{k} + \frac{F \theta k_e}{k}. \quad (20)
\]

Moreover, since \( \Phi = \nu_0 \theta^* \), from Eqs. (19) and (20) one eventually attains: \( \dot{\theta} + \Phi = \frac{S^* F}{1 + r/k_e} \equiv SF \), i.e. again Eqs. (10) and (12) where the desorption rate, \( \Phi \), is now given through Eq. (20) according to

\[
\Phi = \Phi_B + \Phi_{\text{asd}} + \Phi_e, \quad (21)
\]

with

\[
\Phi_e = \nu_0 \frac{F \theta k_e}{k} \quad \text{(22a)}
\]

the extra desorption rate caused by the beam of kinetic energy \( e \). Equation (22a) can be rewritten as

\[
\frac{\Phi_e}{F} = \left( \frac{\nu_0}{k_e} \right) \theta = \tilde{k}_e \theta, \quad (22b)
\]

where \( \tilde{k}_e = \frac{\nu_0}{k} k_e \) with \( k \) and \( k_e \) both functions of \( \theta \) and \( T \). \( \frac{\Phi_e}{F} \) can be derived from the experimental \( S_e^{\text{exper}} \) of Fig. 4 as follows: According to Eqs. (17) and (21) one writes \( S_e^{\text{exper}} = \dot{\theta}/F \) and the relation holds,

\[
S_e^{\text{exper}} + (\Phi_B + \Phi_{\text{asd}} + \Phi_e)/F = S_e. \quad (23)
\]

\( S_{0.09}^{\text{exper}} \) is also taken as the ‘base line’ since the beam of 0.09 eV can be considered thermal, to a first approximation, and therefore one expects \( \Phi_{0.09} \approx 0 \). At \( T \leq 300 \text{ K} \) (see Sect. 5.3) \( (\Phi_B + \Phi_{\text{asd}}) \approx 0 \) and \( S_{0.09}^{\text{exper}} \approx S_{0.09} \). On the other hand, at \( T > 300 \text{ K} \)
[Ru(0001) at 390 K in Fig. 4a], \(\Phi_e + \Phi_{\text{ads}} > 0\), \(S_{\text{0.09}}^{\text{exper}} + (\Phi_e + \Phi_{\text{ads}})/F = S_{\text{0.09}}\). Therefore, at a given temperature Eq. (23) gives

\[
\frac{\Phi_e}{F} = (S_{\text{0.09}}^{\text{exper}} - S_e^{\text{exper}}) + (S_e - S_{\text{0.09}}).
\] (24)

The interpretation of the data of Fig. 4 suggested in Refs. [8,11] is based on the assumption \(S_e^{\text{exper}} = S_{\text{0.09}}, S_{\text{0.09}}^{\text{exper}} = S_{\text{0.09}}\) (which implies \(\Phi_e = 0\)) for reasons specified in Sect. 4.

In the following we analyze the consequences of the different assumption \(S_e \approx S_{\text{0.09}}, \) i.e. ‘true’ sticking probabilities independent of beam energy, at least as a heuristic first approximation. From Eq. (24) then follows

\[
\frac{\Phi_e}{F} = (S_{\text{0.09}}^{\text{exper}} - S_e^{\text{exper}}).
\] (25)

The normalized desorption rates \(\Phi_e/F\) derived from the experimental curves of Fig. 4 for Ru(0001) [8] and for Ni(100) [11] are displayed in Figs. 9a,b and 9c,d, respectively. Figure 9e, derived from Fig. 4 of [11], shows the dependence of the normalized initial desorption rate \(\Phi_e(0)/F\) on the incidence angle \(\varphi\) of molecular beams at various energies.

These normalized desorption rates provide the yield of the excitation process (the flux of desorbing molecules, \(\Phi_e\) divided by the flux of impinging molecules \(F\)). \(\Phi_e/F\) increases with molecular beam energy and is almost independent of temperature below about 0.5 \(\theta_{\text{sat}}\) for both Ru(0001) and Ni(100). Above 0.5 \(\theta_{\text{sat}}\) the desorption yield becomes strongly temperature dependent in both systems and reaches its maximum at \(T = 100\) K: 0.55 for Ru(0001) and 0.7 for Ni(100).

From the experimental \(\Phi_e/F\) and Eq. (22b) one obtains \(\tilde{k}_e\), with \(S = S(T) = S_{\text{0.09}}^{\text{exper}}(T)\) for \(T \leq 300\) K and \(S(T) = J/F\) from [17] for Ru(0001) at \(T = 394\) K. Plots of \(\tilde{k}_e\) vs. \(\theta\) at different temperatures and at fixed beam energy are shown in Fig. 10a for Ru(0001) and in Fig. 10b for Ni(100). The determination of the rate coefficient for vibrational excitation of the adspecies, \(k_e\), from the experimental \(\tilde{k}_e\) requires the knowledge of \(k\), the rate coefficient for energy transfer from the adatom to the solid lattice. This data is only available for Ru(0001) at \(T = 394\) K [12,17] and Fig. 10c shows \(\tilde{k}_e\) and \(k_e\) vs. \(\theta\) at different values of the beam energy. The employed values are \(v_0 = 5 \times 10^{13}\) [12,30] and \(\log k = \log k(0) - b\theta\) at \(\theta > 0.05\), with \(\log k(0) = 14.81\) and \(b = 3.37\) [12,17]. For all the systems studied in [12] \(b\) increases with temperature and one therefore expects, let us say at \(T < 300\) K, \(k_e \propto \tilde{k}_e\), approximately. Also included in Fig. 10c is a plot of the direct sticking probability, \(S^{\text{dir}}(\theta)\), at \(T = 400\) K, as estimated from theoretical calculations [23].

In order to comment the results of Figs. 9 and 10 some preliminary information are needed:

- For the CO-Ru(0001) system the surface coverage of 0.33 ML is a critical value. Around this value there is a sharp decrease of the heat of adsorption of CO from 170 to 120 kJmol\(^{-1}\), the repulsive energy of the adlayer being highest and this implies a decrease of \(S^{\text{spec}}\) (Fig. 6). For \(\theta > 0.33\) the surface structures are complex but characterized by finite values of \(S\), which will drop to zero around saturation \((\theta_{\text{sat}} \approx 0.5)\) [7,23].
The CO-Ni(100) system is characterized by the presence of surface species of low adsorption energies, labeled as $\alpha_1$, $\alpha_2$, $\beta_1$ [32], which prevail at low temperature.

The rate constant $k_e$ is certainly an involved quantity since the energy transfer to the adlayer not only involves the energy transfer from Translational to Vibrational de-
Fig. 10. The quantity \( \tilde{k}_e \) (Eq. 24) is plotted as a function of \( \theta \) at various temperatures as derived for Ru(0001) in a) and for Ni(100) in b). c) refers to Ru(0001) at \( T = 390 \) K and shows \( \tilde{k}_e \) and \( k_e \) at beam energies of 2.07, 0.98 and 0.38 eV (from the top) plotted vs. \( \theta \) (left log-scale). Also shown in this figure is a theoretical \( S_{\text{dir}} \) (red dashed line, right log-scale) estimated at \( T = 400 \) K from data of [23].

degrees of freedom, but also Vibration–Vibration exchange, which can be quite efficient in increasing the population of the vibrational ladder [12,20]. There are, however, some general behaviors that are characteristic of a desorption process generated by energy transfer from a molecular beam, namely:
• larger desorption rates at increasing translational energy of the beam, as follows from general principles [33].
• Larger desorption rates at decreasing adsorption energy as follows from the reduction of energy spacing between vibrational levels, which increases the probability of Translational-Vibrational energy transfer [33].
• Smaller desorption rates at increasing repulsive energy among adspecies.
• Desorption rates that depend on the incidence angle of the beam because of angle dependent trajectories in the process of thermalization (partial or total) of the beam molecules in the adlayer.

Figures 9 and 10 show that the above mentioned features are indeed all present:

• the expected dependence of $\Phi_e$ and $k_e$ on the beam energy (Figs. 9 and 10c);
• the concurrent decrease of $\tilde{k}_e$, $k_e$ and $S_{\text{dir}}$ (Fig. 10c) indicates an increase of the lateral repulsion among adspecies [21–23].
• At beam energies higher than $k_B T$, $\Phi_e/F$ and $\tilde{k}_e$ are practically independent of temperature for $\theta < 0.5 \theta_{\text{sat}}$. The temperature dependence observed at higher surface coverage (Figs. 9 and 10a,b) should be ascribed to the increasing coverage of surface species of lower adsorption energy both in Ru(0001) and Ni(100), which more than compensates for the increased repulsion, almost up to saturation.
• The dependence of $\Phi_e(0)/F$ with the incidence angle $\varphi$ (Fig. 9e) suggests an angular dependence of the scattering probability, which increases by increasing the component of the molecule momentum parallel to the surface.

6. Conclusions and prospects

The present data analysis leads to conclusions that are consistent with the assumption of a beam-stimulated desorption. This certainly makes the assumption plausible but can not, however, be taken as a proof of the proposed mechanism. In fact, one should expect that vibrational excitation of the adlayer by energy transfer from the molecular beam and the decrease of $S_e$ at increasing beam energy $e$, suggested in [8, 11], should both contribute, with different weights, to the behavior of $S_{\text{exper}}$. In fact, a greater probability for the molecules of high kinetic energy to be scattered would result in a lower sticking probability, i.e. exactly the same effect predicted in the presence of stimulated desorption. On theoretical grounds the relative importance of these two mechanisms is very difficult to ascertain, seen the complexity of the energy transfer processes. In our opinion a definitive answer might come, however, from new experiments coupling isotope jump techniques to sticking probability measurements: the simultaneous determination of adsorption and desorption rates, at variable beam energies and intensities, should actually provide the solution of the problem. These experiments should be worthwhile because a positive answer to the suggested mechanism would imply that heterogeneous reactions of CO on metal surfaces could be triggered, by means of molecular beams of CO, well below the surface temperature where any thermal reaction occurs. Desorption yields of Fig. 9 are $10^2$–$10^3$ times larger than the reaction yields obtained in [29] by means of energetic Xe beams and suggest that the transfer of the CO beam energy to the reacting adlayer could be quite efficient.
Appendix

The validity of Eq. (10) can be checked by inserting Eq. (7) in the desorption rate $\Phi = \nu_0 \theta^*$ according to

$$\Phi = \nu_0 \theta^* = \nu_0 \left( \frac{k_c \theta^*_A + k \theta^*_B}{\nu_0 + k} \right) = \nu_0 \left( \frac{S^* F}{1 + r/k_c} + k \theta^*_B \right).$$

(A.1)

From Eq. (8) one gets $\dot{\theta} = k \left( \frac{\nu_0}{\nu_0} - \theta^*_B \right)$ that is $k \theta^*_B = k \frac{\nu_0}{\nu_0} - \dot{\theta}$. Using this expression Eq. (A.1) can be recast as

$$\Phi = \frac{\nu_0}{\nu_0 + k} \left( \frac{S^* F}{1 + r/k_c} - \dot{\theta} + k \frac{\Phi}{\nu_0} \right)$$

(A.2)

that is $\dot{\theta} + \Phi = \frac{S^* F}{1 + r/k_c}$, namely Eq. (10).

References