

## HOW MUCH QUANTITATIVE INFORMATION MAY BE EXPECTED FROM PROGRAMMED DESORPTION EXPERIMENTS?

J.M. SOLER and N. GARCÍA

*Departamento de Física Fundamental, Universidad Autónoma de Madrid, Canto Blanco, Madrid 34, Spain*

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We have integrated numerically the differential equation for temperature-programmed first order thermal desorption:  $d\theta/dt = -\theta\nu \exp(-E/kT)$ , where  $\theta$  is the coverage. By changing the dependence of  $\nu$  and  $E$  on  $\theta$  and  $T$  we can simulate diverse effects on the resulting spectra and predict which ones could be distinguished and which could not. The results show that considerably less quantitative information can be reliably obtained than it is generally supposed and that “refined” analysis may lead to unrealistic conclusions. We propose that good desorption experiments of light rare gases at low temperatures could be compared more reliably with existing one-phonon theories.

### 1. Introduction

Temperature-programmed desorption of aggregates from solid surfaces is a relatively “easy” way [1] to obtain information on the interaction forces and reaction mechanisms between the aggregate and the surface or between the aggregates themselves. Although this technique has been used to obtain quantitative information, we think that there is much confusion about the methods to interpret the resulting spectra in order to obtain valuable information. We will refer to the technique usually called temperature-programmed thermal desorption when used isolated, not in combination with other techniques. In what follows, although not expressly stated, the terms “desorption”, “desorption spectra” or “desorption peak” will refer to their usual meaning in this technique. We concentrate on first order desorption because even in this simplest case we intend to show that many of the methods of analysis currently being used are sometimes inadequate. It is usually assumed that first order thermal desorption may be described by a differential equation

$$d\theta/dt = -\theta\nu \exp(-E/kT), \quad (1)$$

where  $\theta$  is the coverage,  $t$  the time,  $T$  the temperature,  $k$  the Boltzmann constant and  $\nu$  and  $E$  are parameters characterizing the surface-aggregate

interaction. In principle  $E$  may depend on coverage and  $\nu$  may depend on both temperature and coverage but in the simplest approach they are assumed to be constant. The preexponential factor  $\nu$  may be expected to be of the order of magnitude of the frequency of vibration of the adsorbed molecule, that is  $\sim 10^{13} \text{ s}^{-1}$ . Then, the simplest thing to do [2] is to set  $\nu = 10^{13} \text{ s}^{-1}$  and find  $E$  to fit the position of the desorption peak. This can give an estimate of the energy of adsorption of the adsorbate on the surface. More refined methods [3,4] do not assume any value of  $\nu$ . Instead they use the width of the desorption peak as well as its position to obtain both  $\nu$  and  $E$ . We will show, however, that a very small variation of either  $\nu$  or  $E$  with coverage has a strong effect on the desorption peak.

The former methods do not consider that different desorption spectra may be obtained for different initial coverages  $\theta_0$ . If  $\nu$  and  $E$  are in fact constant or if they depend only on temperature, all these spectra are identical except for a factor proportional to  $\theta_0$ . However, both  $E$  and  $\nu$  may depend on  $\theta$ . The adsorption energy depends on coverage because the adsorbed molecules interact among themselves. It is known [5] that a repulsive interaction broadens the desorption peak and even splits it into two separated peaks. The preexponential factor depends on  $\theta$  as soon as desorption channels are affected by the neighbouring molecules. The neighbours affect the mobility of the adsorbed species and, more directly, the existence of a proposed "precursor state" prior to desorption [6]. In the inverse process of adsorption these channels result [7] in a non-linear dependence of the sticking coefficient with coverage. If  $E$  and  $\nu$  depend on coverage, a method has been devised by King [8] which gives in principle both dependencies. The problem remains, however, of how much resolution is necessary to apply this method.

We have proceeded in the opposite way: we have tried different functions  $\nu(\theta, T)$  and  $E(\theta)$ , looking at the resulting spectra. This gives us an insight into what can we expect to distinguish and on what effects may affect most our spectra. The equation we must solve is not simply (1) because it is the pressure what is measured in a typical thermal desorption experiment. Its derivative is given by

$$\frac{dP}{dt} = -\alpha \frac{d\theta}{dt} - \frac{P}{\tau}, \quad (2)$$

where  $\alpha$  is a constant which depends on the volume of the chamber, the area of the sample and the number of adsorption sites per unit surface.  $\tau$  is the characteristic pumping time which also depends on the volume of the chamber and the capacity of the pumps but which can be measured directly by observing the pressure decay of an amount of gas introduced in the chamber as it is pumped away. We now define a normalized pressure  $P^* = P/\alpha\tau$ . Then

$$\frac{dP^*}{dt} = \frac{1}{\tau} \left( -\frac{d\theta}{dt} - P^* \right), \quad (3)$$

which must be solved with the initial conditions  $P^* = 0$ , and  $\theta = \theta_0$  for  $t = 0$ . The derivative  $d\theta/dt$  is given by eq. (1), where  $T = T(t)$  is a known monotonic function. Observe that, for  $\tau \rightarrow 0$ ,  $dP^*/dt$  can only be finite if  $P^* = -d\theta/dt$ . Thus, for  $\tau$  small, the pressure gives a direct measure of  $d\theta/dt$ . This is the situation usually prevailing in experiment but we can also solve the more general eq. (3) when necessary. To solve (1) and (3) we have used a fourth order Runge-Kutta method.

## 2. Temperature and coverage dependence of $\nu$ and $E$

The first effect we have studied is the variation of the preexponential factor with temperature. We have tried the form  $\nu = 10^{13} \times (T/T_p)^n \text{ s}^{-1}$ , where  $T_p$  is the temperature at which the desorption peak appears and  $n$  is any real exponent. Theoretical studies [7,9,10] suggest that  $n$  may range between 0 and 2 depending on the mobility of the adsorbed molecule on the surface. We have chosen the form of  $\nu$  so that it always has the same value ( $10^{13} \text{ s}^{-1}$ ) at the peak because we want to study the effect of the *variation* of  $\nu$  with  $T$ . The result is shown in fig. 1 for an energy of  $E = 8.3 \text{ kcal/mol}$ . It may be seen that the variation of the width and shape of the desorption peak with this effect is practically negligible. We then conclude that, although the value of the

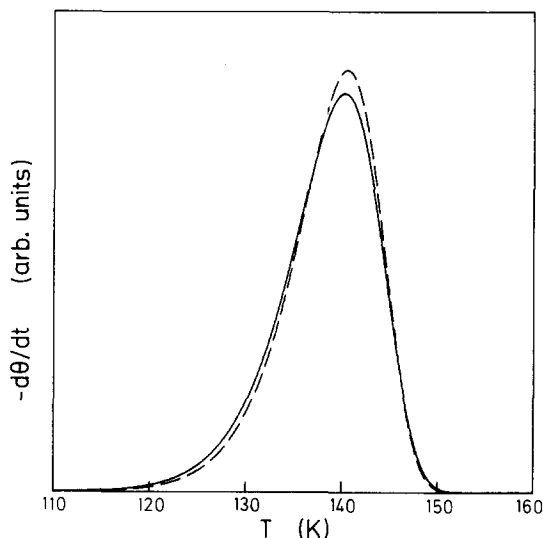


Fig. 1. Desorption peaks given by integration of eq. (1) with  $E = 8.30 \text{ kcal/mol}$  and  $\nu = 10^{13} \times (T/T_p)^n \text{ s}^{-1}$ .  $T_p = 140 \text{ K}$  and  $n = 0$  (solid line) or  $n = 2$  (dashed line). The heating rate  $\beta$  is  $5.5 \text{ K/s}$ .

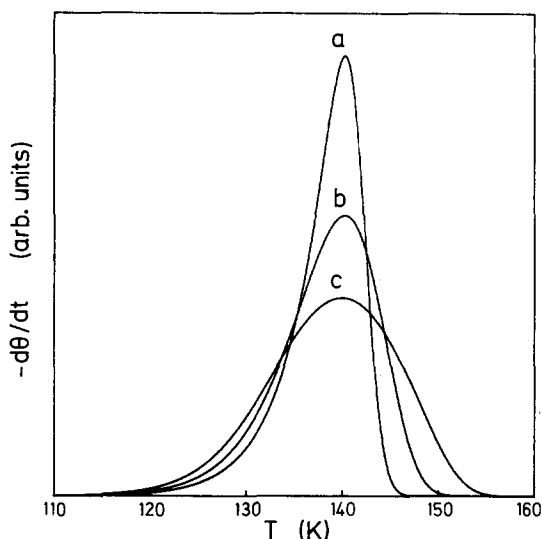


Fig. 2. Desorption peaks with  $\nu = 10^{13} \text{ s}^{-1}$  and  $E = E_0[1 + \epsilon(\theta - 0.75)]$  with  $E_0 = 8.30 \text{ kcal/mol}$ ,  $\theta_0 = 1$ ,  $\beta = 5.5 \text{ K/s}$ . (a)  $\epsilon = 0.05$ ; (b)  $\epsilon = 0$ ; (c)  $\epsilon = -0.05$ .

preexponential factor may depend itself on the mobility of the adsorbed molecules [7], the temperature dependence is not very important and we cannot expect to extract it from experimental spectra if these are not well resolved.

In contraposition to the case of the temperature dependence, we have found that the coverage dependence of  $\nu$  and  $E$  has an enormous effect on the width and shape of the desorption peak. Observe in fig. 2 the effect of only a  $\pm 5\%$  variation in  $E$  for  $\theta$  varying between 0 and 1. In this case the form of  $E(\theta)$  is given by  $E(\theta) = E_0[1 + \epsilon(\theta - 0.75)]$  with  $\epsilon = \pm 0.05$ ,  $E_0 = 8.3 \text{ kcal/mol}$  and  $\nu = 10^{13} \text{ s}^{-1}$ . As in fig. 1, this form of  $E(\theta)$  has been chosen so that the shape of the peak changes, but not its position. If we would try to fit the position and width of these peaks with a constant  $\nu$  and  $E$ , we would obtain  $\nu = 10^{22} \text{ s}^{-1}$  and  $E = 13.9 \text{ kcal/mol}$  for the narrower and  $\nu = 10^8 \text{ s}^{-1}$  and  $E = 5.2 \text{ kcal/mol}$  for the wider. On the other hand, if we would guess an incorrect value of  $\nu = 10^{15} \text{ s}^{-1}$  and find  $E$  to fit only the position of the peak, we would obtain in every case  $E = 9.8 \text{ kcal/mol}$ , which is good within 15%.

Now it is interesting to see what happens if, instead of letting  $E$  vary with coverage, we address this dependence to the preexponential factor. In this case we write  $\nu = 10^{13} \exp[-(E_0/kT_p)\epsilon(\theta - 0.75)] \text{ s}^{-1}$  and  $E = E_0 = \text{constant}$ . We can see in fig. 3 that the resulting peaks for  $\epsilon = -0.05$  are practically indistinguishable from those produced by a variation of  $E$  with  $\theta$ . Since this occurs for all initial coverages  $\theta_0$  we conclude that in practice it is not possible to

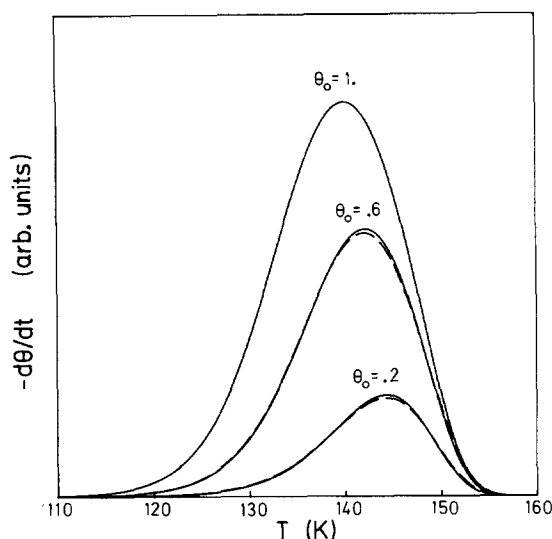


Fig. 3. Desorption peaks with: (i) solid lines,  $\nu = 10^{13} \text{ s}^{-1}$ ,  $E = E_0[1 - 0.05(\theta - 0.75)]$  and (ii) dashed lines,  $\nu = 10^{13} \exp[0.05E_0(\theta - 0.75)/kT_p] \text{ s}^{-1}$  and  $E = E_0$  with  $E_0 = 8.30 \text{ kcal/mol}$ ,  $T_p = 140 \text{ K}$ . For the initial coverage  $\theta_0 = 1.0$ , the dashed line is indistinguishable from the continuous one. The heating rate is  $\beta = 5.5 \text{ K/s}$ .

distinguish a dependence of  $\nu$  with  $\theta$  from a small variation of  $E$  with  $\theta$  in a standard thermal programmed desorption experiment. Of course, *this does not mean that the procedure proposed in ref. [8] by King is incorrect* but rather that the experimental resolution necessary to apply it is not practically attainable. It may be possible to distinguish better if additional techniques are used.

### 3. Non-self-consistent analysis

If one is going to use different flashes, starting at different initial coverages, to obtain the dependence  $E(\theta)$ , it is very important to use a self-consistent procedure. We will discuss the results obtained by Dresser, Madey and Yates (DMY) for the system Xe/W(111) [10] to show the problems at which one may arrive by using a non-self-consistent method. These authors used a constant  $\nu$  and  $E$  to fit each spectrum. The preexponential factor was always taken as  $\nu = 10^{15} \text{ s}^{-1}$  while  $E$  was chosen to optimize the fit for each spectrum, that is for each initial coverage  $\theta_0$ . Therefore, they generated a relation  $E(\theta_0)$  instead of  $E(\theta)$ . We have found that the experimental points they obtained may be well adjusted to the curve

$$E(\theta_0) = 9.26 + e^{-\theta_0/0.018} \text{ kcal/mol.} \quad (4)$$

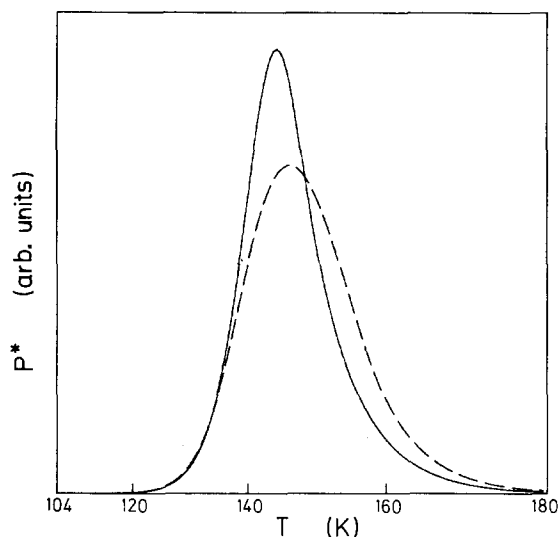


Fig. 4. Desorption peaks given by integrating eqs. (1) and (3) with  $\nu = 10^{15} \text{ s}^{-1}$  and  $E = \text{constant} = 9.61 \text{ kcal/mol}$  (solid line) or  $E = E(\theta)$  given by eq. (4) (dashed line). In both cases  $\tau = 1.3 \text{ s}$ ,  $T_0 = 104 \text{ K}$ ,  $\theta_0 = 0.021$  and the temperature-time relation is given by eq. (5).

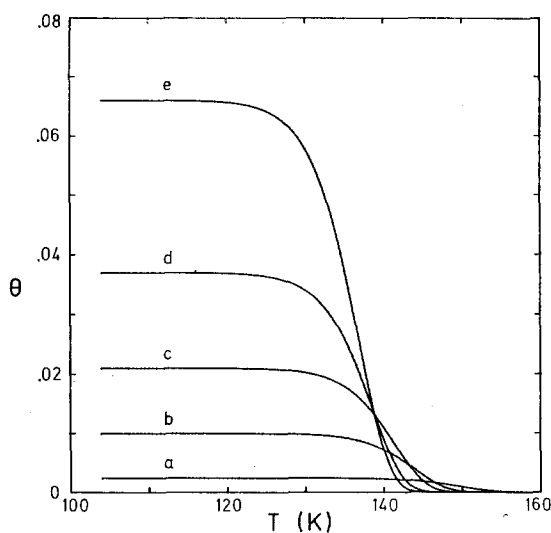


Fig. 5. Coverage as a function of temperature for different initial coverages  $\theta_0$  with  $\nu = 10^{15} \text{ s}^{-1}$  and  $E = \text{constant} = E(\theta_0)$  as given by DMY [10]: (a)  $\theta_0 = 0.0025$ ,  $E = 10.23 \text{ kcal/mol}$ ; (b)  $\theta_0 = 0.01$ ,  $E = 9.80 \text{ kcal/mol}$ ; (c)  $\theta_0 = 0.021$ ,  $E = 9.61 \text{ kcal/mol}$ ; (d)  $\theta_0 = 0.037$ ,  $E = 9.40 \text{ kcal/mol}$ ; (e)  $\theta_0 = 0.066$ ,  $E = 9.28 \text{ kcal/mol}$ . (The letters labeling the curves are not the same as in ref. [10].) Parameters for curve d were taken from a point in fig. 5 of DMY paper. In every case the time-temperature relation was given by eq. (5). Notice the crossing of the curves.

DMY considered these points as an approximation to the real relation  $E(\theta)$  which is what physically makes sense. But an obvious check is to integrate eq. (3) using the relation (4) as  $E(\theta)$  along the desorption instead of setting a constant  $E = E(\theta_0)$ . We have done this using the following temperature–time relation

$$t = -3.872 - 4.672 \times 10^{-2} T + 8.057 \times 10^{-4} T^2, \quad (5)$$

where  $t$  is the time in s and  $T$  the temperature in K. This equation fits well the experimental time–temperature relation of DMY. The characteristic pumping time was also set equal to 1.3 s and the initial temperature was taken at 104 K, as in the experiment. The result of this check is depicted in fig. 4 and it may be seen that it is not satisfactory. It is clear that if the theoretical peaks with  $E = E(\theta_0)$  fit the experimental spectra, those with  $E = E(\theta)$  cannot fit them. Therefore, relation (4) cannot describe the real dependence of  $E$  with  $\theta$ .

Even more serious is what happens with the constant-energy curves themselves. We have integrated eq. (1) with  $\nu = 10^{15} \text{ s}^{-1}$  and  $E = \text{constant}$  given by DMY for the different  $\theta_0$ . The resulting  $\theta(T)$  are shown in fig. 5. What is to be noticed most is that the curves cross. This means that, for the same  $T$  and  $\theta$ , different desorption rates are obtained depending on the initial coverage at which the flash was started. This is the more surprising since DMY have a good fit of the experimental curves. One may argue that the value of  $\tau$  washes out the high  $T$  end of the spectra. However the value  $d\theta/dt$  can be calculated if  $\tau$  is known. We have tried hard to obtain a good self-consistent fitting of the data by using a general function  $E(\theta)$ , but unfortunately we have not been able to reach it because the calculated  $d\theta/dt$  does not seem to be uniquely determined.

#### 4. Conclusions

We have found that:

- (1) The temperature dependence of the preexponential factor is not very important and we cannot generally expect to detect it because other much more important effects will hide it. One can then forget this dependence safely without affecting the fittings seriously.
- (2) The width of the desorption peak is not a good indication of the value of the preexponential factor  $\nu$  since a very slight dependence  $E(\theta)$  (of only a few percent) may thin or broaden the peak as much as changing  $\nu$  by many orders of magnitude. Since there are physical reasons to assign to  $\nu$  a value of  $\sim 10^{13} - 10^{15} \text{ s}^{-1}$ , it is preferable to accept an uncertainty of two orders of magnitude in  $\nu$  because this only introduce an error of  $\sim 15\%$  in  $E$ . On the other hand, trying to fit both  $\nu$  and  $E$  may lead to an unrealistic value of  $\nu$  and to much larger errors in  $E$ .

(3) It is not "feasible" to distinguish a coverage dependence of the preexponential factor from a coverage dependence of the adsorption energy  $E$  without additional techniques. Therefore, we favor to fix a constant value  $\nu = 10^{13} - 10^{15} \text{ s}^{-1}$  depending on the expected mobility of the adsorbed molecules. The only dependence which remains to be determined would be then  $E(\theta)$  which could be found through a simplified version of the method proposed by King [8].

(4) In order to obtain a consistent fit of  $E$  and  $\nu$  from a set of desorption spectra, a necessary condition is that the desorption rate  $d\theta/dt$  can be uniquely determined as a function of  $\theta$  and  $T$ . We have seen that this condition is not always fulfilled by experimental spectra and then a self-consistent analysis for obtaining  $E(\theta)$  is not possible.

(5) We propose that, in order to understand the desorption processes, it is necessary to make experiments with light rare gases at low temperature. In these conditions one-phonon processes are dominant and more reliable theories [11], related to atom scattering, are available, and then more first principle theoretical calculations are possible for comparing with precise experimental data. In this direction, a recent experiment has been performed [12] with a different technique, to which our analysis is not applicable.

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