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Angle-resolved thermal desorption of atoms from solid surfaces: one-phonon mechanism*

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A model for one-phonon thermal desorption is presented in which the structure of the substrate phonons, expressed as a projection on a surface atom of the phonon density of states, appears as a separate factor in the angle- and energy-resolved desorption rate. Desorption from both localized, and delocalized initial *adatom* states is considered. Under certain circumstances one can obtain the cosine-distribution of the equilibrium theory, but in general, the desorption flux from delocalized states deviates from the cosine law by being peaked away from the surface normal, whereas for localized initial states, the flux is concentrated more in the normal direction.

Key words: Desorption — Phonons — Thermal

1. Introduction

Quantum chemistry at solid surfaces has developed into a major scientific activity in the 31 years since Jaroslav Koutecký's pioneering paper [1] appeared in 1956, when there were probably no more than five theoreticians active in the field. As in chemistry generally, our ability to deal theoretically with dynamical processes at surfaces lags behind that for structural problems. In particular, *process dynamics* at solid surfaces presents some severe difficulties, and even some fundamental questions [2]. Nevertheless, the theory of phonon-driven adsorption and desorption of atoms has a far longer history than structural quantum chemistry at solid surfaces; it goes back more than 50 years [3] to a series of papers by Lennard-Jones, Devonshire, and Strachan (LJDS) in which however, essentially only a one-dimensional theory was constructed. A fully three-dimensional theory of desorption *from localized states* was constructed by Bendow and Ying [4], and computations were made for an *adatom*-phonon interaction derived from a gas-solid interaction potential which was a pairwise sum of Morse potentials,

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

using a bulk Debye model for the substrate phonons. The final-state continuum wavefunctions describing the desorbed atom were approximated by WKB wavefunctions for a flat potential, whereas the initial localized states were described by Gaussian wavefunctions. There are therefore inconsistencies, and unknown errors here. Evenso, Bendow and Ying made important contributions, and presented some details of the angle- and energy-resolved desorption flux computed for the one-phonon process.

Recent developments [5-11], among which the work of Kreuzer and Gortel, and their coworkers is prominent, include (a) exact evaluation of the matrix elements of the *adatom*-phonon coupling, (b) use of a master equation with one- or even multi-phonon cascading in the bound states, (c) more realistic treatment of the substrate phonons by drawing on Ezawa's [12] work on the phonons of a semi-infinite continuous solid. In addition, there have been papers, Ref. [13] for example, on the general theory of rate processes in condensed media which, although not designed for thermal desorption, could be adapted to this problem. With one exception [5, 14], the angle-resolved desorption spectrum could have been addressed in these papers, but in fact it was only mentioned once [6].

The present paper is concerned in a particular way with the angle-resolved desorption flux. In general, the angular distribution will depend in a complicated way on the phonon structure of the substrate, and the gas atom states in the static gas-solid potential. However, for correlating or interpreting experimental data, it could be useful to have a theoretical model where the rôle of the substrate phonons is differentiated from other factors. I describe such a model here. To achieve the required differentiation, the most important move is to simplify the atom-phonon coupling; the substrate phonons themselves can be described as accurately as one wishes. For the simplified model so obtained, I examine the one-phonon angle-resolved desorption flux for physisorbed atoms at zero surface coverage in the Golden Rule approximation. I do not think that it is possible to improve on the atom-phonon coupling used here without losing the phonon structure of the substrate as a distinct factor determining the angular dependence.

To avoid possible misunderstanding, I emphasize that I do not present a new theory of thermal desorption. What I do is to show how a not unreasonable simplification of the atom-phonon coupling directs attention to the rôle of the substrate phonons in determining the angular dependence of the one-phonon mechanism, and moreover, enables this angular dependence to be calculated rather easily for some limiting cases. I do not consider multi-phonon processes; for a light atom on a heavy substrate, provided single phonons with energy greater than the desorption energy exist, the one-phonon process dominates the desorption rate. Since Debye energies rarely exceed 50 meV, the above energy requirement means essentially that only physisorption systems are covered.

2. Desorption from delocalized states

The essential features of this first model are:

a) The static gas-solid interaction potential describes a flat surface with a hard wall repulsion.

b) The movement of a surface atom of the substrate due to lattice vibrations causes a small area of the hard wall round the surface atom to move with it.

c) The initial state of the system is drawn from the canonical ensemble at temperature T.

d) Umklapp processes are neglected.

In addition, and simply to obtain explicit results in some limiting cases, matrix elements of the inelastic potential causing desorption will be calculated here with WKB wavefunctions.

The Hamiltonian is

$$\mathscr{H} = \mathscr{K}_{\mathrm{A}} + \mathscr{K}_{\mathrm{L}} + V(\boldsymbol{x}, \boldsymbol{U}_L), \tag{1}$$

where $\mathscr{K}_{\mathrm{A}}$ and $\mathscr{K}_{\mathrm{L}}$ are the kinetic energy operators for the gas atom A, and the substrate lattice L. $\boldsymbol{x} = (\boldsymbol{X}, z)$ is the gas atom's position ($\boldsymbol{X}$ lies in the surface, and z is perpendicular to it), $\boldsymbol{U}_L$ is a many-dimensional vector specifying the displacements $\boldsymbol{u}_l$ of all the lattice atoms from their equilibrium positions; $V(\boldsymbol{x}, \boldsymbol{U}_L)$ is the potential energy of the system.

We separate the gas-solid potential $V(\boldsymbol{x}, \boldsymbol{0})$ for the rigid lattice, and introduce the Hamiltonian $\mathscr{H}_{\mathrm{rigid}}$ for the gas atom on this static potential,

$$\mathscr{H}_{\mathrm{rigid}} = \mathscr{K}_{\mathrm{A}} + V(\boldsymbol{x}, \boldsymbol{0}) \tag{2}$$

and then write Eq. (1) in the form

$$\mathscr{H} = \mathscr{H}_{\mathrm{rigid}} + \mathscr{H}_{\mathrm{ph}} + V_{\mathrm{A-ph}}, \tag{3}$$

where $\mathscr{H}_{\mathrm{ph}}$ is the Hamiltonian for the phonons of the (semi-infinite) substrate, and $V_{\mathrm{A-ph}}(\boldsymbol{x}, \boldsymbol{U}_{\mathrm{L}})$ describes the gas atom-phonon coupling. If we expand $V_{\mathrm{A-ph}}$ in a Taylor series in $\boldsymbol{U}_{\mathrm{L}}$, and retain only the linear term

$$V_{\mathrm{A-ph}} = \sum_l \boldsymbol{u}_l \cdot \boldsymbol{\nabla}_l V(\boldsymbol{x}, \boldsymbol{0}) \tag{4}$$

we obtain the *linear coupling model* with a 50-year history [3].

The normal modes of a semi-infinite solid with one atom per unit cell have surface wavevector $\boldsymbol{Q}$, perpendicular wavevector q_z (which will be complex for surface modes if any exist), and mode index $\sigma = 1, 3$. If we apply periodic boundary conditions over N meshes of the surface net, then for N_z layers of the crystal, the displacement of a lattice atom at $\boldsymbol{l} = (\boldsymbol{L}, l_z)$ in a normal mode is

$$\boldsymbol{u}_{l\sigma}(\boldsymbol{q}) = (NN_zM)^{-1/2}\, \boldsymbol{e}_\sigma(l_z, \boldsymbol{q}) \exp(i\boldsymbol{Q} \cdot \boldsymbol{L}),$$

where M is the mass of a lattice atom, $\boldsymbol{q} = (\boldsymbol{Q}, q_z)$, and $\boldsymbol{e}_\sigma$ is the unit polarization vector which is an eigenvector of the dynamical matrix. In a semi-infinite solid, $\boldsymbol{e}_\sigma$ depends on l_z in general, and on $\boldsymbol{q}$, not just on q_z.

An arbitrary vibration is a linear superposition of normal modes with amplitudes $B_\sigma(\boldsymbol{q})$, which go over to phonon operators in quantum theory;

$$B_\sigma(\boldsymbol{q}) = (\hbar/2\Omega_{q\sigma})^{1/2}[\mathscr{b}_\sigma(\boldsymbol{q}) + \mathscr{b}_\sigma^+(\boldsymbol{q})],$$

where $\Omega_{q\sigma}$ is the normal mode frequency, and $\mathscr{b}_\sigma^+(\boldsymbol{q})$ and $\mathscr{b}_\sigma(\boldsymbol{q})$ are the usual phonon creation and destruction operators. Thus Eq. (4) becomes

$$V_{\mathrm{A-ph}} = \sum_{q\sigma} g_{q\sigma}(\boldsymbol{x})[b_\sigma(\boldsymbol{q}) + b_\sigma^+(\boldsymbol{q})] \tag{5}$$

$$g_{q\sigma} = (\hbar/2NN_zM\Omega_{q\sigma})^{1/2} \sum_{l} \boldsymbol{e}_\sigma(l_z, \boldsymbol{q}) \cdot \boldsymbol{\nabla}_l V(\boldsymbol{x}, \boldsymbol{0}) \exp(i\boldsymbol{Q} \cdot \boldsymbol{L}). \tag{6}$$

If only the movement of atoms in the surface layer $l_z = 0$ changes the potential $V(\boldsymbol{x}, \boldsymbol{U}_L)$, and if further, parallel forces on the gas atom vanish (see below), Eq. (6) reduces to

$$g_{q\sigma} = (\hbar/2NN_zM\Omega_{q\sigma})^{1/2}\ e_{z\sigma}(l_z, \boldsymbol{q}) \sum_{\boldsymbol{L}} (\partial V(\boldsymbol{x}, \boldsymbol{0})/\partial z_{\boldsymbol{L}}) \exp(i\boldsymbol{Q} \cdot \boldsymbol{L}), \tag{7}$$

where $e_{z\sigma}$ is the z-component of $\boldsymbol{e}_\sigma$, and $z_{\boldsymbol{L}}$ is the z-displacement of the surface lattice atom at $(\boldsymbol{L}, 0)$.

The Golden Rule transition rate from an initial state $|I\rangle$ to a final state $|F\rangle$, both eigenstates of $\mathscr{H}_{\mathrm{rigid}} + \mathscr{H}_{\mathrm{ph}}$, is

$$R(F \leftarrow I) = (2\pi/\hbar)|\langle F| V_{\mathrm{A-ph}}|\mathrm{I}\rangle|^2 \delta(E_F - E_I). \tag{8}$$

$|I\rangle$ and $|F\rangle$ are product states $|\boldsymbol{i}\rangle\ |n_i\rangle$ and $|\boldsymbol{f}\rangle\ |n_f\rangle$ where $|\boldsymbol{i}\rangle$ and $|\boldsymbol{f}\rangle$ are gas atom states on $V(\boldsymbol{x}, \boldsymbol{0})$, and $|n_i\rangle$ and $|n_f\rangle$ specify the phonon states of the substrate.

Taking account of the translational symmetries of the initial and final state gas atom wavefunctions as specified by their parallel wavevectors $\boldsymbol{K}_i$ and $\boldsymbol{K}_f$, the matrix element in Eq. (8) has the form

$$\langle F| V_{\mathrm{A-ph}}|I\rangle = \sum_{q\sigma} c_{q\sigma}\langle \boldsymbol{f}|\partial V/\partial z|\boldsymbol{i}\rangle\ N^2 \tilde{\delta}_{\boldsymbol{K}_i+\boldsymbol{Q},\boldsymbol{K}_f}\ \delta_{n_f+1_{q\sigma},n_i}, \tag{9}$$

where

$$c_{q\sigma} = (\hbar/2NN_zM\Omega_{q\sigma})^{1/2} e_{z\sigma}(0, \boldsymbol{q}). \tag{10}$$

Here $\partial V/\partial z$ is the derivative of $V(\boldsymbol{x}, \boldsymbol{U}_L)$ with respect to the z-displacement of an arbitrary surface atom evaluated at $\boldsymbol{U}_L = \boldsymbol{0}$, and the tilde on the first Kronecker δ means that $\boldsymbol{K}_i + \boldsymbol{Q} = \boldsymbol{K}_f$ to within a reciprocal vector of the surface net. The second Kronecker δ comes of course from the linear coupling to the phonons as specified in Eq. (5).

The initial state being drawn from the canonical ensemble at temperature T, the desorption rate to $|F\rangle$ requires Eq. (8) to be summed on the initial states $|I\rangle$ with the usual Boltzmann weight factors. Furthermore, we sum on the phonon component of $|F\rangle$ which is not measured in thermal desorption, to get R_f, the rate to the gas atom final state $|\boldsymbol{f}\rangle$ irrespective of the final phonon state of the substrate. We find

$$\begin{aligned} R_f = (2\pi N^4/\hbar q_{\mathrm{A}}) \sum_{i} \sum_{q\sigma} \exp[-(\hbar\Omega_{q\sigma} + \varepsilon_i)/kT]|c_{q\sigma}|^2|\langle \boldsymbol{f}|\partial V/\partial z|\boldsymbol{i}\rangle|^2 \\ \times \delta(\varepsilon_f + V_0 - \varepsilon_i - \hbar\Omega_{q\sigma})\tilde{\delta}_{\boldsymbol{K}_i+\boldsymbol{Q},\boldsymbol{K}_f}. \end{aligned} \tag{11}$$

Here $q_{\mathrm{A}}(T)$ is the *adatom* partition function, ε_f is the energy of the gas atom state $|\boldsymbol{f}\rangle$ measured from the vacuum level, V_0 is the depth of the lowest bound state of $\mathscr{H}_{\text{rigid}}$ below the vacuum level, and ε_i is the energy of a bound state referred to the lowest bound state as zero. For a flat static potential where $V(\boldsymbol{x}, \boldsymbol{0}) = V(z, \boldsymbol{0})$, the wavefunctions and energies are

$$\begin{aligned} \langle \boldsymbol{x} | \boldsymbol{i} \rangle &= A^{-1/2} \exp(i\boldsymbol{K}_i \cdot \boldsymbol{X}) i(z), \qquad \varepsilon_{\boldsymbol{i}} = \varepsilon_i + \hbar^2 K_i^2/2m \\ \langle \boldsymbol{x} | \boldsymbol{f} \rangle &= A^{-1/2} \exp(i\boldsymbol{K}_f \cdot \boldsymbol{X}) f(z), \qquad \varepsilon_{\boldsymbol{f}} = \varepsilon_f + \hbar^2 K_f^2/2m, \end{aligned} \tag{12}$$

where A is the normalization area for the "parallel wavefunctions", and m is the mass of the gas atom. Since $\boldsymbol{i} = (\boldsymbol{K}_i, i)$, we can perform the sum on $\boldsymbol{K}_i$ in Eq. (11) to get

$$\begin{aligned} R_f = (2\pi N^4/\hbar q_{\text{A}}) \sum_i \sum_{q\sigma} & \exp[-(\hbar\Omega_{q\sigma} + \varepsilon_i + \hbar^2 |\boldsymbol{K}_f - \boldsymbol{Q}|^2/2m)/kT] \\ & \times |c_{q\sigma}|^2 |\langle f, \boldsymbol{K}_f | \partial V/\partial z | \boldsymbol{K}_f - \boldsymbol{Q}, i \rangle|^2 \delta(\varepsilon_f + \hbar^2 K_f^2/2m \\ & + V_0 - \varepsilon_i - \hbar^2 |\boldsymbol{K}_f - \boldsymbol{Q}|^2/2m - \hbar\Omega_{q\sigma}) + \text{umklapp terms}. \end{aligned} \tag{13}$$

Umklapp terms have $\boldsymbol{K}_i + \boldsymbol{Q} = \boldsymbol{K}_f + \boldsymbol{G}$ where $\boldsymbol{G}$ is a non-null vector in the reciprocal lattice of the surface net. Such terms will not be retained henceforth.

Next I suppose that each vibrating surface atom simply causes an area S of the hard repulsive wall round it to move with it. Then

$$\langle f, \boldsymbol{K}_f | \partial V/\partial z | \boldsymbol{K}_i, i \rangle = A^{-1} \langle f | \partial V/\partial z | i \rangle s(\boldsymbol{Q}) \tag{14}$$

$$\begin{aligned} s(\boldsymbol{Q}) = s(\boldsymbol{K}_i - \boldsymbol{K}_f) &= \int_S d\boldsymbol{X} \exp(i\boldsymbol{Q} \cdot \boldsymbol{X}) \\ &= s(Q) \text{ for a circular area } S. \end{aligned} \tag{15}$$

Furthermore, because for a hard wall at $z = 0$

$$\begin{aligned} \partial V/\partial z &= \operatorname*{Lim}_{V \to \infty} V\delta(z), \quad && X \text{ in } S \\ &= 0, && \text{otherwise} \end{aligned}$$

we have that

$$\langle f | \partial V/\partial z | i \rangle = \lim_{V \to \infty} V\phi_f * (0)\phi_i(0) = 2(a_i b)^{-1/2} [\varepsilon_i^2 \varepsilon_f (\varepsilon_f + V_0)]^{1/4} \tag{16}$$

the last form by using WKB wavefunctions for the one-dimensional states $|i\rangle$ and $|f\rangle$. Also in Eq. (16), b is the quantization length for the unbound gas atom state $|f\rangle$, and a_i is the length of the classical trajectory for the initial state $|i\rangle$. Consequently

$$\begin{aligned} R_f = (2\pi N^4/\hbar q_{\text{A}}) \sum_i \sum_{q\sigma} & \exp[-(\hbar\Omega_{q\sigma} + \varepsilon_i + \hbar^2 |K_f - Q|^2/2m)/kT] \\ & \times |c_{q\sigma} s(Q)/A|^2 (4/a_i b) [\varepsilon_i^2 \varepsilon_f (\varepsilon_f + V_0)]^{1/2} \delta(\varepsilon_f + \hbar^2 K_f^2/2m \\ & + V_0 - \varepsilon_i - \hbar^2 |K_f - Q|^2/2m - \hbar\Omega_{q\sigma}). \end{aligned} \tag{17}$$

The angle- and energy-resolved desorption flux $d^2\dot{N}/d\omega\, d\varepsilon_f$ (the flux into unit solid angle $d\omega$ at angle θ_f to the surface normal with energy between ε_f and $\varepsilon_f + d\varepsilon_f$) is

$$d^2\dot{N}/d\omega\, d\varepsilon_f = [\mathscr{V}m/(2\pi\hbar)^3\sqrt{2m\varepsilon_f}\, R_f \tag{18}$$

and the desorption rate $d\dot{N}/d\omega$ into unit solid angle at angle θ_f to the surface normal (there is no dependence on the azimuth for the present model) is

$$d\dot{N}/d\omega = [\mathscr{V}m/(2\pi\hbar)^3] \int_0^\infty d\varepsilon_f \sqrt{2m\varepsilon_f}\, R_f. \tag{19}$$

Using Eq. (17) for R_f, the angular dependences in Eqs. (18) and (19) are evidently determined in a complicated way by the detailed structure of the phonon modes of the substrate, and in general we can only proceed by making a computation for a particular system. This is the usual situation in quantum chemistry. However, I have not yet finished writing the programs, so here I will make a simplifying assumption which enables us to get to grips with some of the chemical physics of the phenomenon. It is the presence of Q along with $\Omega_{q\sigma}$ in the δ-function in Eq. (17) which is the barrier to progress without a large-scale computation. One way to proceed is to retain only the term with $\boldsymbol{Q} = \boldsymbol{0}$ in Eq. (17)[1]. But it is well-known that reducing the number of terms on the right in Eq. (17) in this way makes R_f vanishingly small compared with experimental desorption rates. It has therefore become common to retain the sum on all $\boldsymbol{q}$ on the right in Eq. (17) although setting $\boldsymbol{Q} = \boldsymbol{0}$ in the summand. I shall follow this practice here, but to put it on a proper footing, I note that it is a valid procedure if $K_f \gg Q$. Now the maximum value of Q is roughly π/d where d is the size of the surface mesh. For[2] $d = 10$ A.U., $Q_{\max} = 0.3$ A.U. Since $\hbar K_f = \sqrt{2\varepsilon_f m}\ \sin\theta_f$, we cannot have $K_f \gg Q$ for desorption exactly normal to the surface, but for $\theta_f > 5$ degrees for example, we need $\varepsilon_f m \gg 4.5$. For argon ($m = 8 \times 10^4$) this means $\varepsilon_f \gg 1.4$ meV, which is not an impossible requirement.

Setting $\boldsymbol{Q} = \boldsymbol{0}$ in Eq. (17), and defining

$$\hbar\Omega_{fi} = \varepsilon_f + V_0 - \varepsilon_i \tag{20}$$

we see the term

$$\hbar^{-1} \sum_\sigma \sum_{\boldsymbol{q}} |c_{q\sigma}|^2 \exp(-\hbar\Omega_{q\sigma}/kT)\,\delta(\Omega_{fi} - \Omega_{q\sigma}),$$

which is easily reduced to

$$(2NN_zM\Omega_{fi})^{-1} \exp(-\hbar\Omega_{fi}/kT)\,\rho_z(\Omega_{fi}),$$

where

$$\rho_z(\Omega) = \sum_\sigma \sum_{\boldsymbol{q}} |e_{z\sigma}(0, \boldsymbol{q})|^2 \delta(\Omega - \Omega_{q\sigma}) \tag{21}$$

is a projection on a surface atom of the phonon density of states. Now Eq. (17) becomes

$$\begin{aligned} R_f = {} & (\pi N/\hbar N_z M q_{\mathrm{A}})(NS/A)^2 \exp[-(\varepsilon_f + V_0)/kT] \\ & \times \sum_i (4/a_i b)[\varepsilon_i^2 \varepsilon_f(\varepsilon_f + V_0)]^{1/2} [\rho_z(\Omega_{fi})/\Omega_{fi}]. \end{aligned} \tag{22}$$

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[1] By further making S equal to the area of the surface mesh, this gives the "vibrating hard wall" model. I shall not consider this model here

[2] Atomic units are used. 1 A.U. of length = 0.0529 nm

Consequently, for atoms desorbed with high components of velocity perpendicular to the surface ($\varepsilon_f \gg V_0$, $\varepsilon_f = \varepsilon_f \cos^2\theta_f$), the angular dependence is determined by ρ_z;

$$R_f \propto \rho_z(\varepsilon_f \cos^2\theta_f/\hbar) \tag{23}$$

This simple prediction should be tested; ρ_z can be computed from the definition (21) for ball and spring models. In the meantime, interesting results are obtained if we assume that desorption is driven by surface phonons with

$$\begin{aligned}\rho_z(\Omega) &\propto \Omega \quad (0<\Omega<\Omega_{\max})\\ &= 0 \quad \text{otherwise.}\end{aligned} \tag{24}$$

Then, using Eq. (22), the angular dependence of the desorption flux from a single state $|i\rangle$ is given by

$$\begin{aligned}d\dot{N}/d\omega \propto \int_0^{Y_m} dY\sqrt{Y}\,[&Y\cos^2\theta_f(Y\cos^2\theta_f\\ &+V_0/\hbar\Omega_{\max})]^{1/2}\exp(-\hbar\Omega_{\max}Y/kT).\end{aligned} \tag{25}$$

Here

$$\begin{aligned}Y &= \varepsilon_f/\hbar\Omega_{\max}\\ Y_m &= (\hbar\Omega_{\max} - V_0 + \varepsilon_i)/V_0\cos^2\theta_f = c/\cos^2\theta_f.\end{aligned} \tag{26}$$

If we put $Y/Y_m = z$ so that $Y\cos^2\theta_f = cz$, then

$$\begin{aligned}d\dot{N}/d\omega &\propto Y_m^{3/2}\int_0^1 dz[cz^2(cz+V_0/\hbar\Omega_{\max})]^{1/2}\exp(-az)\\ a &= c\hbar\Omega_{\max}/kT\cos^2\theta_f.\end{aligned} \tag{27}$$

If a is large, small values of z contribute most to the integral, and in this case the upper integration limit can be pushed to infinity. Then if c, and $V_0/\hbar\Omega_{\max}$ are of order of magnitude unity, the integrand in Eq. (27) can be taken as $c^{1/2}z$ $\exp(-az)$. In this case

$$d\dot{N}/d\omega \propto (Y_m^3 c)^{1/2}\int_0^\infty dz\,z\exp(-az) = (Y_m^3 c/a^4)^{1/2} \propto \cos\theta_f \tag{28}$$

and remarkably, we have obtained the equilibrium-theory result [15] for a highly non-equilibrium situation (a single adatom desorbing into a vacuum). I note that $c \sim 1$, and $V_0/\hbar\Omega_{\max} \sim 1$ are expected for physisorption ($\hbar\Omega_{\max} \sim 30$ meV, $V_0 \sim$ 10 meV for example), so to have $a \gg 1$ requires from Eq. (27) that $\hbar\Omega_{\max} \gg kT$, i.e., low-temperature desorption. Thus the conditions for obtaining the equilibrium-theory result are rather special (recall too that the condition $K_f \gg Q$ required for Eq. (22) cannot be met if the expectation energy of the desorbed atom is too low), and in general Eq. (27) does not give the $\cos\theta_f$ angular dependence, but a distribution with maximum flux away from the surface normal [16].

3. Desorption from localized states

This case was treated in some detail by Bendow and Ying [4], Gortel et al. [6], and Goldys et al. [10]. I will adapt the model of Sect. 2 to the new situation in the simplest way. It is to be expected on general physical grounds that the parallel momentum distribution in the initial state will be a factor in determining the angular dependence of the desorption flux, and therefore that desorption with $\boldsymbol{K}_f = \mathbf{0}$, i.e., desorption normal to the surface, will now be favoured.

Let the initial state be localized on the surface atom at $\boldsymbol{L} = \mathbf{0}$, then in place of Eq. (9) I will use

$$\langle F|V_{\mathrm{A-ph}}|I\rangle = \sum_{q\sigma} c_{q\sigma}\langle f|\partial V/\partial z_0|\boldsymbol{i}\rangle \delta n_f + 1_{q\sigma}, n_i, \tag{29}$$

where z_0 is the z-displacement of the lattice atom at $\boldsymbol{L} = \mathbf{0}$. This assumes again that lattice vibrations do not exert parallel forces on the gas atom, although this cannot be true now that the static potential $V(\boldsymbol{x}, \mathbf{0})$ has deep wells to localize the *adatom*. In place of Eq. (11) we now have

$$\begin{aligned} R_f = {} & (2\pi/\hbar q_{\mathrm{A}}) \sum_i \sum_{q\sigma} \exp\left[-(\hbar\Omega_{q\sigma} + \varepsilon_i)/kT\right] |c_{q\sigma}|^2 \\ & \times |\langle f|\partial V/\partial z_0|\boldsymbol{i}\rangle|^2 \delta(\varepsilon_f + V_0 - \varepsilon_i - \hbar\Omega_{q\sigma}). \end{aligned} \tag{30}$$

I assume an initial state

$$\langle \boldsymbol{x}|\boldsymbol{i}\rangle = \phi(\boldsymbol{X}) i(z), \tag{31}$$

where $\phi(\boldsymbol{X})$ is for example, a 2-dimensional Gaussian. The final state should also be an eigenstate of the static potential, orthogonal to the initial state. But to make progress I follow Bendow and Ying [4] and use the "flat potential" form of Eq. (12) again. Thus only $i(z)$ and $f(z)$ are eigenfunctions of the same potential, but as these are the functions in the matrix element in Eq. (29), it is clear that not too much is being sacrificed by making this approximation [4]. The matrix element in Eq. (29) is now

$$\langle \boldsymbol{f}|\partial V/\partial z_0|\boldsymbol{i}\rangle = A^{-1/2}\langle f|\partial V/\partial z_0|i\rangle s(\boldsymbol{K}_f), \tag{32}$$

where

$$s(\boldsymbol{K}_f) = \int_S d\boldsymbol{X} \exp(-i\boldsymbol{K}_f \cdot \boldsymbol{X})\phi(\boldsymbol{X}) \tag{33}$$

and Eq. (30) becomes

$$\begin{aligned} R_f = {} & (\pi|s(\boldsymbol{K}_f)|^2/NN_zMAq_{\mathrm{A}}) \exp\left[-(\varepsilon_f + V_0)/kT\right] \\ & \times \sum_i |\langle f|\partial V/\partial z_0|i\rangle|^2 [\rho_z(\Omega_{fi})/\Omega_{fi}]. \end{aligned} \tag{34}$$

In general the factor $|s(\boldsymbol{K}_f)|^2$ contributes to the angular dependence of the desorption flux, but if S is small so that $SK_f^2 \ll 1$ for all important $\boldsymbol{K}_f$, then $s(\boldsymbol{K}_f) \sim s(\mathbf{0})$, and does not contribute to the angular dependence. In this case the angle- and energy-dependence of R_f is the same as in Eq. (22) for a delocalized initial state (after using WKB wavefunctions for $i(z)$ and $f(z)$ of course). Once again therefore we can obtain the equilibrium-theory result if Eq. (24) holds. On the other hand, if $\phi(\boldsymbol{X})$ is well localized, the factor $|s(\boldsymbol{K}_f)|^2$, which now approaches the parallel momentum distribution in $\phi(\boldsymbol{X})$, is not constant. To explore this case further, assume that S is a circular area, and that $\phi(\boldsymbol{X})$ is the Gaussian $(2\alpha/\pi)^{1/2}\exp(-\alpha X^2)$. Then for large α

$$s(\boldsymbol{K}_f)=s(K_f)=(2\pi/\alpha)^{1/2}\exp(-K_f^2/4\alpha)$$

and the effect of $|s(K_f)|^2$ is to redefine a in Eq. (27) as

$$a=(c\hbar\Omega_{\max}/kT\cos^2\theta_f)[1+(mkT/\hbar^2\alpha)\sin^2\theta_f].$$

Thus, the angular dependence for large a is changed from $\cos\theta_f$ to

$$d\dot{N}/d\omega\propto\cos\theta_f/[1+(mkT/\hbar^2\alpha)\sin^2\theta_f]^2.$$

As anticipated, the $\cos\theta_f$ distribution is modified by concentrating the flux more along the surface normal $\theta_f=0$.

A calculation for $mkT/\hbar^2\alpha=2$ shows a result for $d\dot{N}/d\omega$ qualitatively similar to Ying and Bendow's calculations for Ne on Xe-covered graphite with $d\dot{N}/d\omega$ sharply peaked in the normal direction following approximately $\cos^6\theta_f$. Similarly for R_f itself

$$R_f\propto\{Y\cos^2\theta_f[Y\cos\theta_f+(V_0/\hbar\Omega_{\max})]\}^{1/2}$$
$$\times\exp\{-Y[1+(mkT/\hbar^2\alpha)\sin^2\theta_f]\}$$

there is qualitative agreement with Ying and Bendow [4]; there is a peak in R_f which moves to lower energy, and sharpens with increasing θ_f. It is possible therefore, that the simple model presented here, which is very easy to use, could be useful for correlating and interpreting experimental data. In the meantime, it could be evaluated further by applying it to the theoretical model treated in detail by Goldys et al. [10] (semi-infinite continuum phonons driving desorption from the single bound state of a localized separable potential) for which all formulae for the exact Golden Rule angular dependence are published.

4. Concluding remarks

The simple microscopic model of the gas atom-phonon coupling used here enables angle-resolved desorption spectra to be calculated rather easily for some limiting cases, but more importantly, it directs attention to the details of the substrate phonons which contribute to the angular dependence of the one-phonon mechanism, and moreover, allows these details to be calculated independently as realistically as one wishes. This contrasts with previous work where the phonon structure of the substrate is simplified in favour of a more accurate calculation of the desorption rate due to these simplified phonons. For the model used here, there is in R_f, a complete separation into a phonon factor [the projected density of states $\rho_z(\Omega)$], and factors determined by the motion of the gas atom in the static atom-solid potential, and such a separation is a useful feature if a theory is to be used to correlate or interpret experimental data. I intend to investigate this aspect of the model further, not necessarily with WKB wavefunctions which have been used here simply to get explicit angular dependences for some limiting cases. With a more accurate model of the gas atom-phonon coupling where for example $\boldsymbol{e}_\sigma(0, \boldsymbol{q}) \cdot \nabla_0 V(\boldsymbol{x}, \boldsymbol{0})$ replaces $e_z\sigma(0, \boldsymbol{q})\partial V/\partial z_0$ in the matrix element, and parallel and perpendicular motions of the gas atom are not independent, the details of the substrate phonons, and those of the gas atom states in the static gas-solid potential become interwoven. In these circumstances, the calculation of the angular dependence of the desorption flux is a much larger computational task than for the model used here, and one would want to be sure that the gas-solid potential, and its gradient with respect to the displacement of a lattice atom, could be computed reliably for the chosen gas/solid system before embarking on it. Consequently, it is important to know more about the content of the simple models presented here, and to this end, I have begun to compute $\rho_z(\Omega)$ for (111)Ni and (111)Pt.

Finally, it should be emphasized that the theory presented here refers to the angle-resolved flux of structureless *adparticles* desorbing at low surface coverage by the one-phonon mechanism in the Golden Rule approximation. Relaxing any of these four restrictions leads to significant complications.

Acknowledgement. A referee cites "Physisorption Kinetics", by H. J. Kreuzer and Z. W. Gortel, Springer-Verlag Berlin Heidelberg (1986) for a review of thermal desorption. At the time of writing I have not seen a copy of this book.

References and notes

1. Koutecký J (1956) Z Elektrochem 60:835; Koutecký J (1958) Trans Faraday Soc 54:1038
2. For example, in the gettering of a gas in a closed vessel, how is the sticking coefficient defined if the initial quantum state decays faster than the classical collision number?
3. Lennard-Jones JE, Strachan C (1935) Proc Roy Soc London A150:442; Lennard-Jones JE, Devonshire AF (1936) Proc Roy Soc London A156:6; Lennard-Jones JE, Devonshire AF (1936) Proc Roy Soc London A156:29
4. Bendow B, Ying S-C (1973) Phys Rev B7:622; Ying S-C, Bendow B (1973) Phys Rev B7:637
5. Garrison BJ, Diestler DJ, Adelman SA (1977) J Chem Phys 67:4317
6. Gortel ZW, Kreuzer HJ, Spaner D (1980) J Chem Phys 72:234
7. Gortel ZW, Kreuzer HJ, Teshima R (1980) Phys Rev B22:512; Gortel ZW, Kreuzer HJ, Teshima R (1980) Phys Rev B22:5655
8. Gortel ZW, Kreuzer HJ, Teshima R, Turski LA (1981) Phys Rev B24:4456
9. Kreuzer HJ, Teshima R (1981) Phys Rev B24:4470
10. Goldys E, Gortel ZW, Kreuzer HJ (1982) Surf Sci 116:33
11. Efrima S, Jedrzejek C, Freed KF, Hood E, Metiu H (1983) J Chem Phys 79:2436
12. Ezawa H, (1971) Ann Phys NY 67:438
13. Fain B (1980) Physica 101A:67
14. In [5] it is assumed that the static atom-solid potential is a truncated harmonic oscillator potential, and that the atom desorbs if it reaches the top level of this potential. The rate constant is the reciprocal of this first mean passage time, but there being no consideration of how the atom passes into the unbound continuum, this model cannot give information on the angle-resolved spectrum.
15. Knudsen M (1915) Ann Physik 48:1113
16. Grimley TB (1985) Proc Indian Nat Sci Acad 51A:98