Effect of surface binding energy on molecule sputtering

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Abstract. The sputtering of molecules from a solid surface induced by energetic ion impact is studied. Specifically, a scenario is considered where diatomic molecules close to the target surface obtain a kick from a recoil atom in the ion-induced collision cascade. The change in their translational, rotational and vibrational energies due to the passage of the surface barrier is calculated. Two extreme cases are studied. (i) The molecular centre of mass is bound to the surface. The internal degrees of freedom are then not affected by the surface barrier. (ii) The surface binding acts separately on each atom of the molecule. Classical perturbation theory then shows that translational and rotational energy are changed in a complicated manner, depending on the molecular orientation and the emission angle. Vibrational excitation passes the surface barrier adiabatically.

1. Introduction

The impact of energetic ions on a solid or liquid surface can lead to the emission of particles—atoms, molecules and clusters—from its surface (i.e. *sputtering*). In this paper, the sputtering of diatomic molecules from the target surface is studied. In particular, a situation is considered where the molecules to be emitted are already pre-existent at the surface before emission; they are sputtered by obtaining a kick from a recoil atom in the course of the collision cascade induced in the target by the bombarding ion. Such a mechanism appears to be at work in the sputtering of molecular solids, or in general for molecules the dissociation energy of which is large compared to the intramolecular binding energy (de Vries 1987, Urbassek 1987, Hofer 1991).

In this paper, the last step of the emission process shall be studied. Consider a diatomic molecule which has received a kick from a recoil atom. Before it is actually emitted from the solid, it has to surpass the attractive binding forces of the surrounding material. For the case of an atom being sputtered, it is often sufficient to assume a planar surface binding potential (Thompson 1968, Sigmund 1981), which acts in such a way as to reduce the velocity component of the atom perpendicular to the surface. For the case of a molecule, the binding can be considerably more complicated.

Two extreme binding situations will be considered (figure 1). In one model, the surface binding potential acts only on the centre of mass of the molecule. Thus the translational energy of the molecular centre of mass will be diminished, and the emission angle will be refracted away from the surface normal. The internal degrees of freedom, on the other hand, will not be affected. Such an energy barrier may be
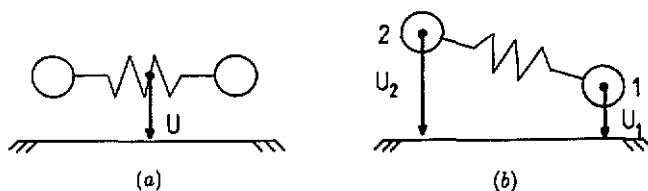
Figure 1. Two models of the action of a surface barrier on a molecule. (*a*) The surface binding energy acts on the molecular centre of mass. (*b*) The surface binding energy acts on each atom of the molecule individually.

realistic for weakly physisorbed molecules, such as H_2/Cu (Harris and Liebsch 1983), or for metallically bound clusters (Snowdon and Heiland 1984).

For other systems, such as chemisorbed molecules and clusters bound ionically or covalently to the surface, one may assume that each atom of the molecule is bound individually to the surface (figure 1(*b*)). In general, the binding situation of a molecule will be in between these two extremes. Obviously, the latter binding model will lead to the most drastic change of the internal degrees of freedom of the sputtered molecule. It appears worthwhile, therefore, to study this latter model in order to understand the change of translational, rotational and vibrational energy due to the surface barrier.

To this end, a classical perturbation treatment will be introduced in the following section, which is valid if the surface binding energy is small compared to the molecular dissociation energy. This calculation will show that vibration is only weakly affected by the surface barrier, whereas translation and rotation may change strongly. These two degrees of freedom may be understood quantitatively in a simple model, which assumes a *sudden* transit through the surface barrier. Finally, the change of the molecular energy distributions shall be considered.

2. Surface barrier

Consider a diatomic molecule situated at the surface of a solid (figure 2). Due to energetic ion impact, a collision cascade builds up in the solid. The molecule receives a kick by a recoil atom or molecule energized by the collision cascade, and thus is about to leave the surface. Let us denote the molecular centre-of-mass velocity by V and its angular momentum by j; its translational energy is $E_{tr} = MV^2/2$, its rotational energy is $E_{rot} = j^2/2\mu d^2$, and its vibrational energy is E_{vib}. Here, d is the equilibrium distance between the two atoms 1 and 2 of the molecule, m_1 and m_2 are their masses, $M = m_1 + m_2$ is the total molecular mass, and $\mu = m_1 m_2/M$ is its reduced mass.
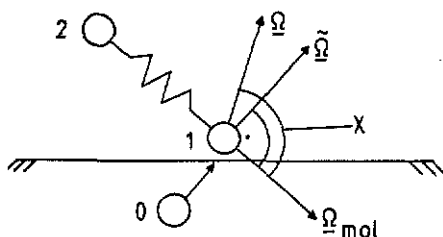
Figure 2. Geometry of a collision event leading to the emission of a molecule from the surface. Atom 1 of the molecule receives a momentum in direction Ω from a kick by the recoil atom 0. The molecular centre of mass starts moving in this direction, which forms an angle χ with the molecular axis Ω_{mol}. $\tilde{\Omega}$ denotes the initial direction of the rotational motion.

After the collision, the molecule is under the influence of a *planar* surface barrier. We consider two extreme cases:

(i) The surface barrier acts on the molecular centre of mass (figure 1(a)):

$$U = U(Z) \tag{1}$$

where Z denotes the distance of the molecular centre of mass from the surface plane. Evidently, this potential cannot affect the internal degrees of freedom of the molecule. By E'_{tr}, we denote the translational energy of the molecule after passage through the surface barrier, and by $\Delta E_{tr} = E'_{tr} - E_{tr}$ we denote its change (and analogously for all other quantities). For this surface barrier, therefore, one has

$$\Delta E_{rot} = \Delta E_{vib} = 0 \qquad \Delta E_{tr} = -U \tag{2}$$

where $U = U(Z = \infty) - U(Z = 0)$ denotes the height of the surface barrier. The direction cosine of the molecular velocity with respect to the outward surface normal, $\eta = V_z/V$, changes during emission. The direction cosine η' after passage through the surface barrier is calculated from the requirement that the component of the centre-of-mass velocity of the molecule parallel to the surface is unchanged,

$$E_{tr}(1 - \eta^2) = E'_{tr}(1 - \eta'^2) \tag{3}$$

and hence

$$\eta' = \sqrt{\frac{\Delta E_{tr} + E_{tr}\eta^2}{E_{tr} + \Delta E_{tr}}}. \tag{4}$$

Equations (2) and (4) give us complete information about the motion and state of the molecule after emission in terms of its state before passage through the surface barrier. For the case of monatomics, this surface barrier is equivalent to the well known planar surface barrier used in sputtering theory (Thompson 1968, Sigmund 1981).

(ii) The surface barrier acts on each atom of the molecule independently (figure 1(b)), i.e.

$$U = U(z_1, z_2) = U_1(z_1) + U_2(z_2) \tag{5}$$

where the z axis lies in the direction of the outward surface normal, e_z. The surface barrier may then affect the internal degrees of freedom of the molecule, as well as its centre-of-mass motion. An analysis of the action of this surface barrier on molecule emission can hardly be done without further assumptions. The next two sections will be devoted to such an analysis.

3. Classical perturbation theory

Let us now perform a classical perturbation analysis of the action of the surface barrier on the molecule. A surface barrier which acts on each atom of the molecule individually (5) will be assumed. The forces $F_i(z_i) = F_i(z_i)e_z = -dU_i(z_i)/dz_i e_z$

act on the molecule; they are directed in the $-z$ direction. The change of the centre-of-mass momentum is given by the time integral of the forces

$$M\Delta V = \int_0^\infty \mathrm{d}t\,(F_1(z_1) + F_2(z_2)). \tag{6}$$

The molecular angular momentum changes due to the time integral of the torques

$$\Delta j = \mu \int_0^\infty \mathrm{d}t\,(\mathbf{r} \times F_1(z_1) - \mathbf{r} \times F_2(z_2)) \tag{7}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. In a first-order perturbation analysis, the unperturbed positions $z_i = z_i(t)$ of the molecular atoms have to be inserted in the calculation of the forces, i.e. without including the effect of the surface barrier.

One hence obtains, to first order,

$$\Delta E_{\mathrm{tr}} = V_z M\Delta V_z = V_z \int_0^\infty \mathrm{d}t\,(F_1(z_1) + F_2(z_2)) \qquad \Delta E_{\mathrm{rot}} = \frac{1}{\mu d^2}j \cdot \Delta j. \tag{8}$$

Denoting the height of the surface barrier by $U_i = U_i(z_i \to \infty) - U_i(z_i = 0)$ and the equilibrium positions of the molecular atoms by $z_i = 0$, the total change of the molecular energy amounts to

$$\Delta E_{\mathrm{tr}} + \Delta E_{\mathrm{rot}} + \Delta E_{\mathrm{vib}} = -U_1 - U_2. \tag{9}$$

Thus the vibrational energy changes by

$$\Delta E_{\mathrm{vib}} = -U_1 - U_2 - \Delta E_{\mathrm{tr}} - \Delta E_{\mathrm{rot}}. \tag{10}$$

Perturbation theory is meaningful if the molecule travels only for a short period of time through the range of the surface potential, since then the insertion of the unperturbed trajectories $z_i(t)$ into (6) and (7) does not lead to errors. Furthermore, the change of V (i.e. $|\Delta V|$) must be small compared to V_z; thus at glancing emission, where $\eta = V_z/V \cong 0$, perturbation theory fails. Obviously, as soon as the internal degrees of freedom are excited so strongly as to lead to molecular dissociation, perturbation theory must also fail.

In the following, the results shall be specified for the case of Morse potentials

$$U_i(z_i) = U_i(1 - \mathrm{e}^{-z_i/\lambda_i})^2. \tag{11}$$

The influence of the surface barrier on molecular rotation and vibration will be studied separately. The intramolecular binding shall be modelled as a harmonic oscillator of frequency ω; coupling of rotation and vibration will be neglected. The collision starting the molecule from the surface shall be modelled as a simple spectator collision, in which only one atom of the molecule receives momentum (cf figure 2).

3.1. Vibration

Let us first consider the case where the molecular axis Ω_{mol} (i.e. the unit vector in the direction of $r = r_1 - r_2$) is perpendicular to the surface. If we denote the direction cosine of vectors with respect to the outward surface normal by the symbol η, then $\eta_{mol} = -1$. Atom 1 obtains a kick in the direction of the molecular axis, $\eta = 1$, and velocity v. One then has the unperturbed trajectories

$$z_1 = Vt + (m_2/M)(v/\omega)\sin \omega t \qquad z_2 = Vt - (m_1/M)(v/\omega)\sin \omega t \qquad (12)$$

where

$$V = (m_1/M)v$$
$$E_{tr} = (M/2)V^2 = \tfrac{1}{2}(m_1^2/M)v^2 \qquad E_{vib} = (\mu/2)v^2 = (m_2/m_1)E_{tr}. \qquad (13)$$

Inserting (12) in (6)–(8), one obtains

$$\Delta E_{tr} = -U_1 I_1 - U_2 I_2 \qquad \Delta E_{vib} = -U_1(1 - I_1) - U_2(1 - I_2)$$
$$\Delta E_{rot} = 0 \qquad (14)$$

with

$$I_1 = 2\gamma_1 \int_0^\infty d\tau \left\{ e^{-\gamma_1[\tau + (m_2/m_1)\sin \tau]} - e^{-2\gamma_1[\tau + (m_2/m_1)\sin \tau]} \right\}$$
$$I_2 = 2\gamma_2 \int_0^\infty d\tau \left\{ e^{-\gamma_2[\tau - \sin \tau]} - e^{-2\gamma_2[\tau - \sin \tau]} \right\}. \qquad (15)$$

These functions, and hence ΔE_{tr} and ΔE_{rot}, are independent of E_{tr} and E_{rot}.

The adiabaticity parameter for vibrational excitation is

$$\gamma_i = \frac{1/\omega}{\lambda_i/V} = \frac{V}{\omega\lambda_i}. \qquad (16)$$

It denotes the ratio of the vibrational period $1/\omega$ to the time it takes to pass the surface potential λ_i/V.
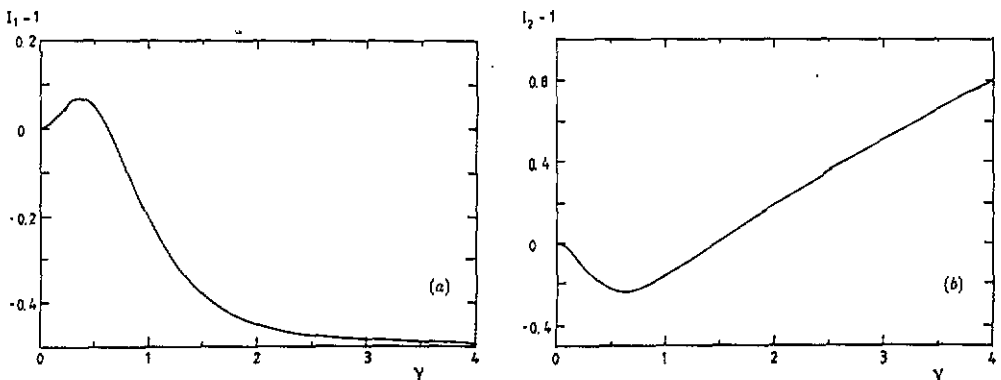

Figure 3. Functions $I_1(\gamma) - 1$ (a) and $I_2(\gamma) - 1$ (b) (15) for a homonuclear molecule. These functions indicate the fraction of the surface binding energy affecting vibration (14) and rotation (20).

In figure 3, the functions $I_{1,2}(\gamma) - 1$ are plotted versus γ. These functions determine the fraction of the surface binding energy U_i which enters the vibrational energy. The non-monotonous behaviour is due to the superposition of two exponential functions in (15); for an exponential potential, $I_{1,2}(\gamma)$ is monotonous. For small $\gamma \lesssim 1$, vibration passes the surface barrier adiabatically; the surface potential then only affects the centre-of-mass motion. For large values of γ, i.e. small potential ranges λ_i, U_1 decelerates vibration, while U_2 excites it further. While $I_1(\gamma)$ quickly reaches its limiting value of $\frac{1}{2}$, $I_2(\gamma)$ diverges for $\gamma \to \infty$. This happens since atom 2 initially has zero velocity and hence reacts sensitively to a decrease of the potential range λ. For a realistic collision model in which atom 2 also obtains a momentum, this divergence does not occur.

As an example, for a CO molecule adsorbed perpendicularly on a Ni surface, we have $d = 1.1$ Å, $\omega = 4 \times 10^{14}$ s^{-1} (Herzberg 1950) and $\lambda_1 = 0.4$ Å (Andersson 1979, Ishi *et al* 1985). Thus one has

$$\gamma \lesssim \tfrac{1}{2}. \tag{17}$$

This is the maximum value that the vibrational adiabaticity parameter can assume; it applies if the molecule is emitted with a velocity such that vibration is about to dissociate it. One may hence conclude that vibration will typically pass the surface barrier adiabatically.

3.2. Rotation

Let us now assume that the molecule lies on the surface with its molecular axis parallel to the surface, $\eta_{\text{mol}} = 0$. Atom 1 obtains a kick perpendicular to the molecular axis, $\eta = 1$, and with velocity v. Then we have

$$z_1 = Vt + (m_2/M)d\sin(vt/d) \qquad z_2 = Vt - (m_1/M)d\sin(vt/d) \tag{18}$$

where the centre-of-mass velocity is $V = m_1 v/M$. Thus it follows that

$$E_{\text{tr}} = \frac{M}{2}V^2 = \frac{1}{2}\frac{m_1^2}{M}v^2 \qquad E_{\text{rot}} = \frac{\mu}{2}v^2 = \frac{m_2}{m_1}E_{\text{tr}} \tag{19}$$

and one obtains

$$\Delta E_{\text{tr}} = -U_1 I_1 - U_2 I_2 \qquad \Delta E_{\text{rot}} = -U_1(1 - I_1) - U_2(1 - I_2)$$
$$\Delta E_{\text{vib}} = 0 \tag{20}$$

where the I_i denote the same functions (15) as in the case of vibrational excitation.

The adiabaticity parameter for rotational excitation

$$\gamma_i = \frac{d/v}{\lambda_i/V} = \frac{m_1}{M}\frac{d}{\lambda_i} \tag{21}$$

denotes the ratio of the period of rotation, d/v, to the time, λ_i/V, which the molecule needs to pass the surface barrier.

For $d = 1.0 - 1.1$ Å and $\lambda = 0.4$ Å, as above, one obtains $\gamma = 1.2 - 1.5$. It is hence concluded that I_1 attains its sudden value $I_1(\gamma \to \infty)$, while $I_2 - 1 \cong 0$. Thus, U_2 does not affect rotation in this case, while U_1 decelerates it.

4. A sudden passage approximation for rotational motion

Perturbation theory allows us to study the influence of the surface binding on the centre-of-mass motion and the internal degrees of freedom as a function of the adiabaticity parameter γ. As parameters, the mass ratio m_1/m_2, the molecular orientation Ω_{mol} and the emission direction η enter the analysis and complicate a detailed discussion. As was shown above, *rotational* excitation can be described by assuming a *sudden* passage through the surface barrier, i.e. $\gamma \to \infty$. In this case, the results become independent of the shape of the surface barrier and depend only on its height U_i. *Vibration*, on the other hand, passes the surface barrier adiabatically.

In the following, the sudden passage approximation will be introduced. It will fail if one of the atoms of the molecule initially receives no momentum in the direction of the surface normal. Let us assume atom 1 received a momentum in direction Ω and an energy $E = m_1 v_1^2/2$. Thus the molecule will start moving away from the surface, and its centre of mass obeys

$$R(t) = Vt = (m_1/M)v\Omega t. \tag{22}$$

The initial trajectories of the two molecular atoms are hence given by

$$r_1(t) = R(t) + (m_2/M)r(t) \qquad r_2(t) = R(t) - (m_1/M)r(t) \tag{23}$$

where $r(t = 0) = d\Omega_{mol}$ and $r = r_1 - r_2$. Since vibration is treated adiabatically, the fast oscillations in r due to vibration shall be neglected. In a sudden passage approximation, only those parts of the trajectories (23) which are linear in t will be considered. This is a reasonable approximation for small ranges λ of the surface binding.

Rotational motion starts in a direction $\tilde{\Omega}$

$$\tilde{\Omega} = [\Omega - \Omega_{mol}(\Omega \cdot \Omega_{mol})]/\sin\chi \qquad |\tilde{\Omega}| = 1 \tag{24}$$

which is perpendicular to the molecular axis (figure 2). Here, χ is the angle between Ω and Ω_{mol}. Since the magnitude of the imparted angular momentum is

$$j = \mu v d \sin\chi \tag{25}$$

one has (to first order in t)

$$r(t) = d\Omega_{mol} + v\sin\chi\,\tilde{\Omega}t. \tag{26}$$

The deviations from the initial positions then read

$$r_1(t) - r_1(0) = V\Omega t + (m_2/M)v\sin\chi\,\tilde{\Omega}t$$
$$r_2(t) - r_2(0) = V\Omega t - (m_1/M)v\sin\chi\,\tilde{\Omega}t. \tag{27}$$

For an arbitrary surface potential (5) scaling as

$$U_i(z_i) = U_i f_i(x) \qquad x = z_i/\lambda_i \qquad f_i(0) = 0 \qquad f_i(\infty) = 1 \tag{28}$$

one obtains, using (8), the result

$$\Delta E_{tr} = -U_1 I_1 - U_2 I_2 \qquad \Delta E_{rot} = -U_1(1 - I_1) - U_2(1 - I_2)$$
$$\Delta E_{vib} = 0 \tag{29}$$

which is of identical form to (20). The functions

$$I_i = -\frac{\eta V}{U_i} \int_0^\infty dt\, F_i(z_i(t)) \tag{30}$$

can be calculated easily. Scaling the forces F_i as

$$F_i(z_i) = -(U_i/\lambda_i) f'_i(x) \tag{31}$$

where the prime denotes the derivative with respect to the variable x, one obtains

$$I_1 = \eta V \int_0^\infty dt\, \frac{1}{\lambda_1} f'_1 \left(\frac{V \eta t + (m_2/M) v \tilde{\eta} t \sin \chi}{\lambda_1} \right) = \frac{\eta}{\eta + (m_2/m_1) \tilde{\eta} \sin \chi}$$
$$I_2 = \frac{\eta}{\eta - \tilde{\eta} \sin \chi} \tag{32}$$

The quantity

$$\tilde{\eta} = \frac{\eta - \eta_{mol} \cos \chi}{\sin \chi} \tag{33}$$

denotes the initial direction cosine of the rotational motion with respect to the surface normal.

If $\eta_{mol} = 0$, one has $\tilde{\eta} = \eta / \sin \chi$. For $m_1 = m_2$, the result of section 3 is thus recovered, $I_1 = \frac{1}{2}$, while I_2 diverges (figure 3).

Equations (29) and (32) are the central results of the present analysis of the action of the surface binding on the centre-of-mass motion and the excitation of the internal degrees of freedom of an emitted molecule. Summarizing, one obtains

$$\Delta E_{tr} = -U_1 \frac{\eta}{\eta + (m_2/m_1) \tilde{\eta} \sin \chi} - U_2 \frac{\eta}{\eta - \tilde{\eta} \sin \chi}$$
$$\Delta E_{rot} = -U_1 \frac{(m_2/m_1) \tilde{\eta} \sin \chi}{\eta + (m_2/m_1) \tilde{\eta} \sin \chi} + U_2 \frac{\tilde{\eta} \sin \chi}{\eta - \tilde{\eta} \sin \chi}$$
$$\Delta E_{vib} = 0. \tag{34}$$

ΔE_{tr} and ΔE_{rot} are independent of the energies E_{tr} and E_{rot}. This holds true generally in a first-order perturbation analysis, as long as vibration passes the surface barrier adiabatically (15),(20). The energy changes depend only on the height of the surface barrier, the direction of emission of the molecule, and its orientation. This is obviously a consequence of the assumption that the recoil atom undergoes a sudden, hard collision with the molecule. As a consequence, the angular momentum j and centre-of-mass momentum MV are proportional to each other (25). This assumption is justified in the case of rotational excitation for collision energies in the eV range, such as they are of interest here.

The surface binding energy of atom 1 is spent in de-exciting molecular rotation and centre-of-mass motion in a ratio $m_2 \bar{\eta} \sin \chi / m_1$ corresponding to the ratio of initial centre-of-mass velocity ηV to the initial rotational velocity $m_2 \bar{\eta} v \sin \chi / M$; in each case, the components perpendicular to the surface are taken. The analogous result holds for atom 2. This is a consequence of first-order perturbation theory: the energy changes are proportional to the initial velocities (8). If the rotational velocity is initially antiparallel to the centre-of-mass velocity, such as for atom 2, then the surface barrier *heats* rotational excitation further. If rotational and centre-of-mass motion cancel each other in z direction, perturbation theory breaks down for that particular atom.

5. Distribution functions

In (34) it was shown how the translational and rotational energy of an individual molecule are changed by the passage through the surface barrier. This allows us to calculate how a flux of molecules changes while passing through the surface. Let us denote by $j(E_{tr}, E_{rot}, E_{vib}, \eta)$ the molecular flux before passage through the surface barrier. After passage it is

$$j'(E'_{tr}, E'_{rot}, E'_{vib}, \eta') = j(E_{tr}, E_{rot}, E_{vib}, \eta) \left| \frac{\partial(E_{tr}, E_{rot}, E_{vib}, \eta)}{\partial(E'_{tr}, E'_{rot}, E'_{vib}, \eta')} \right|. \tag{35}$$

The direction cosine η' has been calculated above (4). The functional determinant in (35) can be simplified further: $E_{vib} = E'_{vib}$; E'_{tr} and η' do not depend on E_{rot}; and furthermore $\Delta E_{rot} = E'_{rot} - E_{rot}$ does not depend on E_{rot}. Hence one has:

$$\begin{aligned}
\frac{\partial(E'_{tr}, E'_{rot}, E'_{vib}, \eta')}{\partial(E_{tr}, E_{rot}, E_{vib}, \eta)} &= \frac{\partial(E'_{tr}, \eta')}{\partial(E_{tr}, \eta)} = \frac{\partial \eta'}{\partial \eta} - \frac{\partial \eta'}{\partial E_{tr}} \frac{\partial E'_{tr}}{\partial \eta} \\
&= \frac{\eta E_{tr}}{\eta' E'_{tr}} + \frac{1 - \eta^2}{2\eta'} \frac{1}{E'_{tr}} \frac{\partial \Delta E_{tr}}{\partial \eta}.
\end{aligned} \tag{36}$$

Let us consider first the case where the surface barrier acts on the molecular centre of mass (1). We then obtain the simple result

$$j'(E'_{tr}, E'_{rot}, E'_{vib}, \eta') = \frac{\eta'}{\eta} \frac{E'_{tr}}{E'_{tr} + U} j(E_{tr} = E'_{tr} + U, E_{rot}, E_{vib}, \eta). \tag{37}$$

Let us take an example. In the mechanism on which the present analysis is based—near-surface molecules getting a kick from a recoil atom or molecule in the course of an energetic-ion induced collision cascade—the flux j of molecules can be assumed to be cosine-distributed, and to obey a $1/E_{tr}^2$ distribution in kinetic energy (Sigmund 1981). Rotational and vibrational energy can be taken to depend on the kinetic energy received (Sigmund *et al* 1986, Urbassek 1987); $E_{rot} = E_{rot}(E_{tr})$, $E_{vib} = E_{vib}(E_{tr})$. Thus we assume the flux of the molecules before passage through the surface barrier to be of the form

$$j(E_{tr}, E_{rot}, E_{vib}, \eta) = C\eta \frac{1}{E_{tr}^2} F(E_{rot}(E_{tr}), E_{vib}(E_{tr})) \tag{38}$$

where C is a constant. It then follows that

$$j'(E'_{tr}, E'_{rot}, E'_{vib}, \eta') = C\eta' \frac{E'_{tr}}{(E'_{tr} + U)^3}$$
$$\times F(E'_{rot} = E_{rot}(E'_{tr} + U), E'_{vib} = E_{vib}(E'_{tr} + U)). \qquad (39)$$

As expected, the flux of emitted molecules is cosine-distributed and obeys a Thompson distribution in kinetic energy, in exact analogy to the case of monatomics (Thompson 1968, Sigmund 1981). The rotational and vibrational energies are unchanged, but, in the correlation of the internal energies with the measured translational energy, the decrease of the translational energy due to the surface barrier has to be taken into account.

For the case that the surface binding acts on both atoms of the molecule individually, expression (36) can in general not be simplified further, since ΔE_{tr} depends in a complicated manner on η (34).

For the special case such that $\eta' = \eta = 1$ (i.e. only those molecules that leave the surface perpendicularly are detected), it follows that

$$j'(E'_{tr}, E'_{rot}, E'_{vib}, \eta' = 1) = \frac{E'_{tr}}{E_{tr}} j(E_{tr}, E_{rot}, E_{vib}, \eta = 1). \qquad (40)$$

Let us consider the dependence of the translational energy, integrating over E_{rot} and E_{vib}. Assuming $j(E_{tr}, \eta = 1) = C E_{tr}^{-2}$, as above, one obtains:

$$j(E'_{tr}, \eta' = 1) = C \frac{E'_{tr}}{E_{tr}^3} = C \frac{E'_{tr}}{(E'_{tr} - \Delta E_{tr})^3}. \qquad (41)$$

For $\eta = 1$, one has $\tilde{\eta} = \sin \chi$ and $\cos \chi = \eta_{mol}$. The term $-\Delta E_{tr}$ can be considered to be an effective surface binding energy for translational motion. It depends in a complicated way on the molecular orientation η_{mol}. One has

$$j(E'_{tr}, \eta' = 1) = C \frac{E'_{tr}}{(E'_{tr} + U_{eff})^3} \qquad (42)$$

where

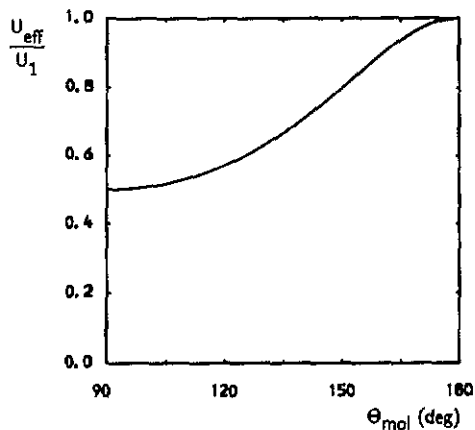$$U_{eff} = \frac{U_1}{1 + (m_2/m_1)(1 - \eta_{mol}^2)} + \frac{U_2}{\eta_{mol}^2}. \qquad (43)$$

Figure 4. Effective surface binding energy for the translational energy distribution of homonuclear molecules emitted in a direction perpendicular to the surface (43) for $U_2 = 0$. Θ_{mol} is the angle the molecular axis makes with the surface normal; $\Theta_{mol} = 180°$ for a molecule standing upright on the surface, and $\Theta_{mol} = 90°$ for a molecule lying horizontally on the surface.

Figure 4 displays this effective surface binding energy for homonuclear molecules, $m_1 = m_2$, for the case when the binding energy of atom 2 can be neglected ($U_2 = 0$). It shows that a surface binding energy which acts on each molecular atom individually leads to a Thompson distribution of the translational energy of the molecules emitted in the perpendicular direction. The effective surface binding energy then depends on the molecular orientation of the molecule on the surface before collision. It is obvious that in general U_2 cannot be neglected.

6. Summary

(i) The influence of the surface binding energy on the flux of molecules sputtered by ion impact has been studied. It is assumed that diatomic molecules close to the target surface obtain a kick from a recoil atom in the ion-induced collision cascade. Two simple models are studied: (a) the surface barrier acts only on the molecular centre of mass; (b) the surface binding acts on each atom of the molecule individually. In both cases a planar surface barrier is assumed which exerts forces only in the direction of the surface normal.

(ii) In the first model, the internal molecular degrees of freedom are not affected by the surface barrier. Only the translational motion is altered in a way analogous to the sputtering of monatomics.

(iii) The analysis of the second model is more complicated. By classical perturbation theory, the changes of the translational, rotational and vibrational energy on passage of the surface barrier have been calculated. Vibration typically passes the surface barrier adiabatically. Rotation, on the other hand, is strongly affected by the torques exerted by the surface barrier.

(iv) Assuming a *sudden* passage of the surface barrier, the dependence of the translational and rotational energy change on the initial orientation and emission angle of the molecule has been calculated.

(v) If the surface binding energy acts on each atom of the molecule individually, then the distribution function of a molecule after passage through the surface barrier depends in a complicated way on emission angle and orientation. A simple result can be obtained for perpendicular emission, in which case the translational energy follows a Thompson law similar to the case of atom sputtering. However, the effective surface binding energy entering into the translational energy distribution depends on the molecular orientation before emission.

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