Chapter 3  Interaction with Surfaces

Introduction

The interaction of charged particles with matter is determined, for the most part, by the atomic character of matter. Therefore, particle impact quantities such as penetration depths scale very nearly with the atomic (molecular) density of the material. This is true even for metals, for which the electrons in the solid state show cooperative (plasma) effects absent in gases and insulating solids. Notable exceptions are crystalline solids in which channeling (small angle internal reflections) of incident charged particles along open crystal axes or planes result in increased penetration depths. In fact, except for low-energy incident charged particles (< 100 eV/amu), target molecular species (e.g., CO₂) can be thought of as a sum of their constituents (i.e., 1C + 2O), referred to as Bragg’s rule. In the subsequent discussions we will ignore any special properties so that all materials are treated as gases of a given density when discussing incident particle penetration and energy deposition. The material properties are introduced latter when describing the fate of the energy deposited.

The slowing down of a fast particle in a target is described here by collisions with randomly located atoms. The possible behavior of the incident and target particles can be described using a Monte Carlo procedure to simulate the random nature of the stopping process (Robinson 1981). However, as one is generally interested in the average behavior of large numbers of incident and target particles, transport equations (e.g., Boltzmann’s equation) can be used to describe the energy and spatial distributions of the incident and target particles (Sigmund 1981). In such equations the randomly located target atoms are treated as a medium parameterized by the number density of the material. These equations are often treated in two regimes. At high energies when electronic excitation and ionization events dominate the energy loss, the deflections of the incident particles are small and the stopping can be thought of as continuous. That is, even though the stopping power is an atomic quantity [see Eq. (2.11)], written in the form (dE/dx) it suggests a continuous slowing-down process, very much like a drag force [see Eqs. (2.12 and 2.14)]. However, for both low incident ion energies, for which nuclear elastic collisions dominate and very high velocities, at which nuclear reactions occur, the deflections need to be incorporated.

In this chapter the physics and chemistry of the irradiation effects are described. The penetration (or, in solids, implantation) depths and distributions
are discussed first. This is followed by a description of the motions of the target particles produced by collisions with the incident particle. The target particles set in motion are generally referred to as secondaries or recoils. However, it is often useful to distinguish between particles struck by the incident particle, the primary recoils, and those subsequently set in motion, the secondary recoils. Effects produced by the incident and recoil particles involve the breaking of bonds, and therefore, the possibility of forming new species and producing changes in the state of a solid. In a solid, recoil particles near the surface may attain an appropriate energy and direction of motion to escape from the surface as ground-state neutrals, excited neutrals, or ions. This results in the erosion of the surface, a process referred to as sputtering. Sputtering of neutrals has historically been a means of producing a vapor from solids having low vapor pressures, and the detection of the ejected ions has been a means of material analysis referred to as SIMS (Secondary Ion Mass Spectroscopy) (Benninghoven et al. 1982). Here, of course, we are interested in how such processes modify materials exposed to plasmas in space and add new species to the plasma.

In most of the following we will be discussing a solid with a surface. This surface, however, marks only the point of origin of the cascade of events produced by the incident particle. For particle bombardment of atmospheres (planetary, satellite, or cometary) the "surface" is roughly that column density of gas equal to a monolayer in the condensed phase (~ 10^{15} molecules/cm^2) called the exosphere (Chamberlain and Hunten 1987). Therefore, many of the ideas developed apply to plasma ion interactions with gravitationally bound gases.

Particle Penetration and Implantation

Using the stopping powers in the previous chapter, the distance traveled in a target material (Fig. 3.1) by an incident particle can be calculated in the continuous slowing-down approximation. In this approximation the particles all

![Fig. 3.1. Penetration of a particle into a surface. The path length traveled in the material before stopping is R, the range; the penetration along the incident direction is the projected range, R_p](image)
travel the same average distance, called the mean range, \( \bar{R} \), where

\[
\bar{R}(E_A) = \frac{E_A}{\int_0^{E_A} \frac{dE}{|dE/dx|}}
\]

(3.1)

if the target material has a constant density. For an atmosphere of variable density this is replaced by a mean column density \( \bar{N} \) traversed, using \( |dE/dx| = n_b S(E) \) in Eq. (2.11),

\[
\frac{\bar{N}(E_A)}{S(E)} = \frac{E_A}{\int_0^{E_A} dE/S(E)}
\]

(3.2)

where \( S(E) \) is the stopping cross section. Such distances are given in Fig. 3.2 for a number of particles penetrating \( H_2O \). The range is often given in g/cm² for fast particles as the mass density of a material is roughly proportional to the electron density. In this form the range is similar in all materials.

\( \bar{R} \) (or \( \bar{N} \)) given in Eq. (3.1) is the total distance traveled by the incident particle and not the penetration depth, as the particles may be deflected significantly at

![Fig. 3.2. Range of fast electrons or ions in \( H_2O \) given as mass stopping in g/cm² (J. Cooper, pers. comm.). For ice divide by 1 g/cm² to get range in cm. In these units the range is similar in all materials for fast particles \( v > \nu_e \) because the electron density in the target is roughly proportional to the mass density]
lower energies. In the electronic stopping regime (see Fig. 2.4), and for heavy ions incident on a low-mass atomic target, deflections can be safely ignored so that the mean range is also the mean penetration depth. Whenever deflections are important or the energy losses in a collision are not small compared to the initial energy, then Monte Carlo calculations or transport equations (Ziegler et al. 1985) are required to obtain the penetration depth as well as other properties associated with the stopping of the incident particles. Although the transport equations are simple conceptually, they can be difficult to solve. However, solutions for many of the quantities of interest have been accumulated, and references to a number of reviews are given in the bibliography.

The mean projected range measured parallel to the incident velocity is written as \( \bar{R}_p \) for the constant density case, or as a column density, \( N_p \). It can be obtained as a solution to

\[
\bar{R}_p(E_A) = \left[ n_B \sigma \right]^{-1} + \int \frac{d\sigma}{\sigma} \bar{R}_p(E_A - \Delta E) \cos \theta(\Delta E)
\]

(3.3)

(see also Appendix 3A). In Eq. (3.3) \( \bar{R}_p \) is seen to be equal to the mean-free-path for the first collision, \( [n_B \sigma]^{-1} \) [see Eq. (2.2)], plus the distance traveled following that collision. In the first collision the particle has a probability \( (d\sigma/\sigma) \) of losing energy \( \Delta E \) and moving at an angle \( \theta(\Delta E) \) to the initial direction, where \( d\sigma \) is the differential cross section [e.g., \( d\sigma = (d\sigma/d\Omega) d\Omega \) in Eq. (2.4) and following]. Therefore, the integral is an average over all possible distances traveled after the first collision. On taking the small \( \Delta E \) limit, with \( \cos \theta \approx 1 \) (i.e., no deflections), the projected range, \( \bar{R}_p \), becomes equal to the continuous slowing down calculation of the range, \( \bar{R} \), in Eq. (3.1). In Fig. 3.3a and b we also show results for the penetration depth, \( \bar{R}_p \), obtained by solving Eq. (3.3). When the incident particle momentum is large then \( \bar{R} \approx \bar{R}_p \), but for incident electrons \( \bar{R} \) and \( \bar{R}_p \) begin to differ even at high velocities. Estimates of the column of mass penetrated, based on the discussion following Eq. (2.42), are \( (\rho_B \bar{R}_p) \approx (E_A/30 \text{ MeV})^{1.78} \) (g/cm\(^2\)) for protons (0.2 MeV < \( E_A < 400 \text{ MeV} \)) and \( (\rho_B \bar{R}_p) \approx 4.6 \times 10^{-6} \) (\( E_A/1 \text{ keV} \)) for keV electrons (Banks and Kockarts 1973). Paretzke (1987) uses \( \bar{R}_p \approx 40(\bar{R}_A/1 \text{ keV})(1 + 0.5(E_A/\text{keV})) \) nm for \( \rho_B = 1 \text{ g/cm}^3 \) for electrons for \( E_A < 20 \text{ keV} \).

As energy is deposited all along the particle's path, \( \bar{R}/\bar{R}_p \) gives a rough estimate of the increase in the energy density deposited in the material due to deflections. A secondary ion or electron can have a relatively large ratio of \( \bar{R}/\bar{R}_p \) for stopping in the material. This implies that it rattles around a lot before coming to a stop, but does not travel very far from where it was produced. For a slow

\[\text{Fig. 3.3. a Mean projected ranges for incident ions H}^+ \text{ (dash-dot), O}^+ \text{ (dashed) and S}^+ \text{ (solid) in H}_2\text{O, given as a mean column density, N}_p \text{, right hand axis depth in ice. b Mean projected range for H}^+ \text{ (solid lines), O}^+ \text{ (long dashes), S}^+ \text{ (short dashes) in N}_2 \text{ and SiO}_2 \text{ given in } \mu\text{g/cm}^2 \text{ (}\rho_B \bar{R}_p = M_B N_p \text{)}}]
secondary particle stopping in a diffuse medium made up of particles of the same mass, $\bar{R}_p \sim 3.2(n_B\bar{\sigma}_d)^{-1}$ is obtained from Eq. (3.3) using a power law cross section section with $n \rightarrow \infty$ and $\bar{\sigma}_d$ is the average diffusion cross section in Chapter 2 (R.E. Johnson 1982). That is, a low energy particle of mass equal to the target atom mass penetrates of the order of the three mean-free paths. (In a solid, $(\bar{\sigma}_d)^{1/2}$ for low energy atoms may exceed the target atom spacing further limiting the penetration.)

Because of the statistical nature of atomic collision processes, the incident particles do not, of course, all stop at $\bar{R}_p$ (Biersack 1987). The distribution of the implanted particles, $F_i(p, z)$, for particles of type $i$ and initial momentum $\vec{p}$ is also obtained from transport equations (Appendix 3A). For fast ions, the implantation distribution is roughly a narrow gaussian centered on $\bar{R}_p$. The width is referred to as the range straggling (Winterbon 1986) and is a tabulated quantity (Winterbon 1975; Ziegler et al. 1985). For low-energy particles the straggling becomes comparable to the penetration depth and backscattering occurs. As most of the backscattering occurs in the first few monolayers of the target, the reflection coefficient can be estimated without solving the full transport equation (Vukanic and Sigmund 1976). Experimental values of this coefficient (fraction of energy or particles reflected) for a few materials and incident ions are given in Fig. 3.4 for laboratory surfaces. In the low energy regime power law and scaled "universal" potentials are often used to describe elastic collisions (Winterbon et al. 1970) and the solutions for the range distribution can be scaled using characteristic lengths and energies in Appendix 2B.

![Fig. 3.4. Backscattering coefficients $H^+$ incident perpendicular to solid carbon) given as fraction of energy reflected or number reflected (or probability of reflection) (lines-theory; data indicated). (Ito et al. 1985)
Secondary Particles and the Partitioning of Energy

On traversing a region of the target material, an incident ion loses energy by electronic ionizations and excitations as well as by nuclear collisions. In losing this energy the incident ions produce a variety of secondary particles. An ionization event can result in the production of an energetic electron, and a nuclear collision may involve sufficient energy transfer to set in motion an energetic target atom. These secondary particles, if produced near the surface, can escape from the material. Otherwise they lose their energy in the solid, much like the incident particle, producing additional secondary electrons and atoms. This cascade of events initiated by an incident ion can also be treated via transport equations. However, when keeping track of a number of particle types, Monte-Carlo calculations are often more reasonable. In Fig. 3.5, the “tracks” of ionizations and excitations produced by protons and electrons in condensed H₂O are shown. Although a 1 keV electron, for example, has a speed, hence ionization efficiency, comparable to a 2 MeV proton, the distributions of excitation energy deposited by protons and electrons in Fig. 3.5 are very different because the electron is easily deflected, primarily by the target electrons, whereas the proton is not. In order to determine the effects on the solid of these events, we first consider the partitioning of the energy deposited.

Ignoring nuclear reactions, it is customary to divide the electronic energy loss by an ion or electron into the mean energy lost to ionization (\(\bar{E}_i\)), excitation (\(\bar{E}_{ex}\)), and that going to subexcitation electrons (\(\bar{E}_e\)). Whereas the first two quantities are clear, the latter is not. Those fast secondary electrons (often called delta rays) produced by the ion lose energy rapidly to electronic excitations contributing to \(\bar{E}_i\) and \(\bar{E}_{ex}\). The mean energy of the secondary electrons produced in H₂O or N₂ by a fast ion or electron is of the order of 50–60 eV. By additional ionization and excitations, these electrons “cool” to energies below the threshold of the lowest electronic excited state of the atoms and molecules in the target. The electrons will then “cool” by vibrational or rotational excitation of molecules and by elastic momentum transfer collisions with atoms. (In a solid, rotational excitations and elastic collisions are replaced by optical and acoustical phonon production.) Therefore, \(\bar{E}_e\) is the energy carried by the electrons that goes directly into the atomic and molecular motions (Platzman 1967; Andersen 1984).

For a nonrelativistic incident particle, the energy loss is partitioned

\[
E_A = N_i \bar{E}_i + N_{ex} \bar{E}_{ex} + N_i \bar{E}_e + \nu(E_A),
\]

\[
= \eta(E_A) + \nu(E_A)
\]

(3.4)

where \(N_i\) and \(N_{ex}\) are the mean number of ionizations and excitations produced during the stopping of particles with initial energy \(E_A\). \(\nu(E_A)\) accounts for the elastic nuclear energy loss by the incident particle, and \(\eta(E_A)\) is the total electronic energy. In Fig. 3.6 values of \(\nu\) vs. ion energy are given.

The average energy expended by the incident ion that goes into ionization (electron-hole pair) is \(W_e = \eta(E_A)/N_i\) which is approximately \(E_A/N_i\) for a fast
Ionizations in Proton Tracks in H₂O

MeV

0.1

0.5

1.0

5.0

100 Å

Simulated Electron Tracks in Water

(• Ionis., • Exc.)

50 eV

100 eV

200 eV

500 eV

1 keV

2 keV

Fig. 3.5. a Monte Carlo calculation of ionizations produced by protons of varying energies in condensed H₂O. b Ionizations and excitations produced by electrons. Although electron and proton ionizations cross sections are similar at the same velocities (Chap. 2), the large momentum differences result in different track structures. (Turner 1986; Paretski 1987)

ion or electron. A quite useful and remarkable result is that the quantity Wₑ is similar in size for most types of ionizing radiation (charged particles, X-rays, γ-rays) absorbed in a given material as long as the incident energy is large compared to the ionization energy and the average nuclear elastic energy loss, \( \nu(E_A) \), is negligible for the charged particles (Bischel et al. 1979). Measured values for ions are given in Table 3.1. Dividing Wₑ by the ionization energy, I (or in condensed matter, by the band gap, \( E_g \)), and subtracting one indicates that fraction of the energy, beyond the minimum required, which is expended in
Fig. 3.6. Fraction of energy deposited collisionally, \( \nu(E_A)/E_A \), for protons (solid line), oxygen ions (long dashes), and sulfur ions (short dashes) on SiO\(_2\) and H\(_2\)O. (Data supplied by K.B. Winterbon)

Table 3.1. Ionization potentials and \( W \) values

<table>
<thead>
<tr>
<th>Gas</th>
<th>I</th>
<th>( W_e )</th>
<th>( W_e/I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.6</td>
<td>44</td>
<td>1.8</td>
</tr>
<tr>
<td>Ar</td>
<td>15.8</td>
<td>27</td>
<td>1.7</td>
</tr>
<tr>
<td>H(_2)</td>
<td>15.4</td>
<td>36</td>
<td>2.3</td>
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<tr>
<td>N(_2)</td>
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<td>37</td>
<td>2.4</td>
</tr>
<tr>
<td>O(_2)</td>
<td>12.1</td>
<td>31</td>
<td>2.6</td>
</tr>
<tr>
<td>CO</td>
<td>14.0</td>
<td>34</td>
<td>2.4</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>13.8</td>
<td>34</td>
<td>2.5</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>12.6</td>
<td>30</td>
<td>2.4</td>
</tr>
<tr>
<td>(Condensed)</td>
<td>11.</td>
<td>20</td>
<td>2.2</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>10.2</td>
<td>26</td>
<td>2.5</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>12.6</td>
<td>31</td>
<td>2.5</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>11.5</td>
<td>25</td>
<td>2.1</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>10.5</td>
<td>26</td>
<td>2.5</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>11.4</td>
<td>26</td>
<td>2.3</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>12.3</td>
<td>32</td>
<td>2.6</td>
</tr>
</tbody>
</table>

* Averages: values for proton, He\(^{2+}\) and \( \beta \) particles differ <10\% with \( \beta \) particles having smaller values: applies to \( v > v_o \). (Bischel et al. 1979). Liquids and solids have lower values (\( \sim 70-90\% \)) of I (electron-hole formation energy) and \( W \) values, but the ratios are about the same.
producing an ionization (or electron-hole pairs). In atomic gases, \( W_e \) is seen in Table 3.1 to vary from \( \sim 1.7 \) to \( \sim 1.8 \) times \( I \), whereas in molecular gases and condensed materials it varies from \( \sim 2.3 \) to \( \sim 2.5 \). The larger values arise because secondary electrons lose energy more efficiently to vibrational and phonon excitations than they do to elastic collisions with gas-phase atoms.

Using the ionization cross sections given earlier, along with the stopping powers, the amount of energy deposited per primary ionization by an incident fast charged particle is \( S_e/\sigma_i \). This quantity is about twice \( W_e (v > v_0) \) indicating that, on the average, two ionizations result per ionization produced by the incident particle. That is, each secondary electron created by the incident ion produces, on the average, one additional ionization. Remarkably, this is also true for low band gap (2–5 eV) solids. Dividing Eq. (3.4) by \( E_A \), the fraction of the incident ion's energy which is lost to each process is obtained. For a variety of target materials these fractions are similar and nearly independent of velocity when \( v(E_A) \) is small. At lower ion energies this is not the case since energetic secondary electrons are not produced and the charge-exchange cycle is a source of electronic energy loss and ionization (Chap. 2). The fractions of energy expended by ionization, excitation, and subexcitation processes are given in Table 3.2 for fast ions and electrons incident on an atomic and a molecular material.

For low energy, heavy ions nuclear elastic energy loss eventually dominates the stopping (see Fig. 2.4). In a solid one often wants to know the number of displaced atoms produced by the incident ion after the cascades have dissipated. In crystalline materials such displacements are referred to as defects. Because the removal of an atom from a site by a nuclear collision has similarities with the removal of an electron from an atom by electronic energy transfer, a quantity \( W_\sigma \) is used by analogy with \( W_e \). \( W_\sigma \) is the average nuclear elastic energy expended per atom displaced by an ion stopping in a solid. That is, \( W_\sigma \) is equal to \( v(E_A) \) in Eq. (3.4) divided by the average number of displaced atoms produced by an incident ion. If the minimum energy required for a displacement is \( E_D \), then one finds, in parallel with the ionization process, that \( W_\sigma \approx 2.5 \) \( E_D \) (Sigmund 1981). \( E_D \) is a quantity which is much larger than the sublimation energy, \( U \), of the solid because energy is required for the lattice to accommodate the displaced atom in addition to that energy required to remove the atom from its original site (\( E_D \approx 5U \)). For an atom ejected from the surface (i.e., sputtering) then \( E_D \) approaches \( U \). Such expressions (\( W_e \) and \( W_\sigma \)) allow one to quickly

<table>
<thead>
<tr>
<th>Target</th>
<th>( f_i )</th>
<th>( f_{ex} )</th>
<th>( f_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.7</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Quantities are from Eq. (3.4) \( f_i = N_i E_i/E_A \), \( f_{ex} E_{ex}/E_A, N_i E_i/E_A \). Results are for \( v > v_0 \).
Spatial Distribution of Deposited Energy

For a particle of energy $E_A$ incident on a material at an angle $\theta_A$ to the normal, the average energy of the particles at a depth $z$, $E(z)$, can be estimated using the continuous slowing down approximation in Eq. (3.2). Writing

$$\bar{N}(z) = \cos \theta_A \int_{E(z)}^{E_A} dE/S(E),$$

(3.6)

where $\bar{N}(z)$ is the mean column density of material penetrated, $E(z)$ is obtained for a given $\bar{N}(z)$. [For a constant density target, $\bar{N}(z) = n_d z$.] Knowing $E(z)$, then the average energy deposited at any depth $z$ is given by $\frac{dE}{dx} = \sum n_i S_i(E(z))$, where $n_i$ is the number density of atoms of type $i$. In Fig. 3.7a energy deposition profiles are shown for fast ions incident on an organic material. For such ions it is seen that the region of highest deposited energy density is at the end of the particle’s path. Prior to this, the ion loses energy gradually and the peak in the energy deposition
Fig. 3.7. a Rate of electronic energy deposition, $(dE/dx)_e$, by ions in an organic material for normal incidence. Data indicated. Thickness and energy loss given in mass stopping; multiply rate and divide thickness by mass density for other units (Brustad 1961). b Nuclear elastic component (damage) of energy deposition, $F_D$ (dashed lines, left hand axis), electronic component $F_e$ (solid lines, right hand axis) for 80 keV and for 400 keV He$^+$ in C. Scaling the depth by $R_p$ and the energy deposition by $\langle \nu / R_p \rangle$ or $\langle \eta / R_p \rangle$, such profiles are similar below maximum in electronic stopping (Winterbon 1975)
profile corresponds to the maximum in \((dE/dx)_e\) in Fig. 2.4. If the incident ion or electron is deflected significantly, transport equations (Appendix 3A) have to be solved for the electronic energy, \(F_e(E_A, \cos \theta_A, z)\), or nuclear elastic energy, \(F_D(E_A, \cos \theta_A, z)\) deposited at depth \(z\) by an incident electron or ion with initial energy \(E_A\) and direction of motion to the surface normal, \(\cos \theta_A\). The subscript \(D\) is traditionally used, as the incident particle produces displacement damage (previous section) according to the amount of nuclear energy deposited. Hence, the cascade contribution is often referred to as the damage distribution. A profile for the nuclear and electronic energy deposited per unit path length is shown in Fig 3.7b. Such a distribution corresponds to the end of an ion path in Fig. 3.7a.

The energy loss distributions in Fig. 3.7 also give the average energy of transmitted particles if the thickness of the target is less than \(R_p\). Such estimates are of interest for MeV cosmic-ray ions penetrating an atmosphere, an interstellar molecular cloud, or an ice grain, and for a plasma ion penetrating Io's exosphere. Because stopping is a statistical process, the emerging particles do not all have the same energy. In traversing a very thin layer, \(\Delta x\), in which the likelihood of more than one collision by an incident particle is small, the mean-squared width in the measured energy loss to the target, \(\Delta E\), is written

\[
(\Delta E - \bar{\Delta E})^2 \equiv \bar{\Delta E}^2 = n_b \Delta x \cdot S^{(2)},
\]

where \(S^{(2)}\) is called the energy straggling cross section [see Eq. (2.33b)], a tabulated quantity, and \(\Delta E\) is the mean energy loss.

The radial extent of electronic energy loss about the path of an incident ion is determined by the maximum impact parameter which can lead to an energy transfer and by the radial distribution of secondary particles. Therefore, the "track" produced in a solid by fast incident ions has two regions each containing about half of the deposited energy. (Brandt and Ritchie 1974; Fano 1964). The radius of the inner track ("infra-track"), determined by the Bohr adiabatic cut-off for excitations, goes roughly as \(r \approx v/\omega\) for fast ions (Chap. 2 and Appendix 2). When \(v\) becomes small, then \(r\) is of the order of the atomic size, (i.e., only close collisions produce excitations). The radius of the outer track ("ultra-track") is determined by the mean distance traveled by the fast secondary electrons ("delta rays"). As the most energetic secondary electrons are created in close collisions between the incident particle and an electron, the radial distribution of energy deposited at large radii can be estimated from the BEA (Chap. 2). It is found that it falls off as approximately \(1/r^2\) for \(r > v/\omega\), as indicated by the measurements in Fig. 3.8, where \(r\) is the radial distance from the path of the ion. As the velocity decreases the track width decreases so that, below the maximum in the stopping power (see Fig. 2.4), the energy density in the track is larger for the same \((dE/dx)\).

In the elastic collision regime (low \(E_A\)) the transport equations are solved for the deposited energy (damage) distribution (Winterbon 1975). In Fig. 3.9 results for the projected range and damage distributions are shown. These were obtained for a power law interaction, \(n = 2\), which is appropriate over the region of the nuclear stopping maximum. The results for \(M_A = M_B\) in Fig. (3.9) are useful for
Fig. 3.8. Energy deposition per unit volume in an organic solid (\( \sim 1 \text{ g/cm}^2 \)) vs. radial distance from fast ion track; line is fit \((r^{-2})\). Data taken for low density gas of equivalent composition and scaled to the solid state. (Varma and Baum 1980)

describing cascades initiated by a secondary atom. It is seen that the mean penetration depth of the stopped particle occurs at a larger depth than that at which the largest number of particles are stopped, and is more than twice that depth at which most of the energy is deposited. Therefore, most of the energy of low energy secondaries is deposited close to the point of production of the secondary, and it is not unreasonable to treat these low energy cascades as isotropic. The physical size of the volume directly affected, of course, depends on the density of the medium. Near the surface of an ice grain this region is of the order of 10 nm, while near the exobase of an atmosphere it is of order of a few scale heights, often hundreds of kilometers.

Extensive tables and graphical data have been accumulated for the quantities discussed above and are listed in the references and bibliography. Because \((dE/dx)\) changes only slowly with the \(Z_\text{eff}\) of the target particles, the results given in the previous figures can be applied to similar target molecules or mixtures of
Fig. 3.9. Damage, $F_d(z)$, and projected range, $F(z)$, distributions for low energy ions. a Solid lines ratios of the mean penetration depth along the incident direction $\langle z \rangle$ to the mean range, $R$; long-dashed line the mean width of the distribution at this depth $\langle \Delta z^2 \rangle$ divided by $\langle z \rangle^2$ and short-dashed line the mean squared width perpendicular to the incident direction $(1/2) \langle r^2 \rangle$ divided by $\langle z \rangle^2$. Shown for different target to incident particle mass ratios. b Penetration (range) and energy deposition (damage) contours for $M_A = M_B$. Contours correspond to 10% of the maximum. Depths are scaled to the mean range, $R$. $\langle z \rangle$ is the mean depth for the particular distribution ($R_p$ for range distribution). (Winterbon et al. 1970)

molecules. For example, $CO_2$ is similar to 1.5 CO molecules and CO is like $N_2$. $O_2$ is also similar to $N_2$ or two $H_2O$ etc. Silicates and organics can be thought of as characteristic of more refractory solids, etc.

Up to this point we have not considered the fate of the energy deposited. Clearly most of the energy eventually degrades to heat, but during the degradation process permanent changes, beyond the displacements described here, can take place. These alterations and their consequences are examined in the following sections.

**Chemical Alterations in the Gas Phase**

Atmospheres are composed of atoms or molecules which have closed-shell electronic systems and, hence, do not react easily. A principal effect of ionizing radiations, such as UV photons, is the breaking of this closed-shell structure, which is then followed by a series of chemical reactions. These can produce compositional changes in the gas (e.g., $CO_2 \rightarrow O_2^+$, CO in the Martian
atmosphere: Stewart 1972). Studies of the effect of photons or electrons absorbed in molecular gases have a long history (Dalgarno 1988), and many of the results are applicable to incident ions. We present here only a few useful results and refer the readers to texts on atmospheres in the Bibliography.

A typical potential energy diagram for a molecule is shown in Fig. 3.10. This is seen to consist of both bound state curves having minima and repulsive curves (monotonically decreasing with increasing separation, R) as discussed in Chap. 2 (see. Fig. 2.8 and accompanying discussion). Because the times for producing electronic transitions ($\sim 10^{-16}$ s) are short compared to the vibrational period of the nuclei ($\sim 10^{-12}$ to $10^{-13}$ s), the nuclei remain very nearly stationary during a change in electronic state (the Frank-Condon principle). For example, on excitation of the ground state, X, to the state labeled $\gamma$ in Fig. 3.10, the molecule goes from one bound state configuration to another. On the other hand, for the transition from the X state to the state labeled $\alpha$, the electronic structure changes from a bound state in which the nuclei are shielded to one in which the nuclei are not fully shielded and is therefore repulsive. Such an excitation will be followed by dissociation of the molecule with the nuclei obtaining kinetic energy.

The excited bound state of a molecule will decay by emission of a photon (luminescence) unless it is 'crossed' by a repulsive potential (see Chap. 2) in which case a nonradiative dissociation of the molecule will occur [process (3) in Fig. 3.10]. For a large molecule a third possibility exists. The electronic energy can be distributed among many internal (vibrational) modes and eventually be dissipated by ejection of low energy species or by IR photons. Because the nonradiative transitions are fast ($\sim 10^{-12}$ to $10^{-13}$ s) compared to photon emission ($\sim 10^{-9}$ s), the former is the preferred mode of decay. However, in a gas a sufficient number of photons may be produced to modify the composition at some distance from the ion path, as is the case for cosmic rays penetrating molecular clouds in the interstellar medium (Sternberg et al. 1988).

On ionization of $\text{H}_2$, the $\text{H}_2^+$ molecule faces a similar set of possibilities. Therefore, on absorbing electronic energy the $\text{H}_2$ gas will rapidly relax to a gas containing $\text{H}_2^+$, $\text{H}^+$, $\text{H}$, and $\text{H}_2$ all of which may be in excited states. As the excited

---

**Fig. 3.10.** Hypothetical molecular potential energy curves indicating excitation processes (*vertical arrows*) leading to dissociation: 1 collision induced; 2 dissociation following electronic excitation; 3 electronic excitation to a bound state followed by tunneling to a dissociative state (predissociation)
and ionized species are open-shell structures, they are also highly reactive. A number of possible reactions are

\begin{align*}
H_2^+ + H_2 &\rightarrow H_3^+ + H \\
H^+ + H_2 + M &\rightarrow H_3^+ + M \\
H + H + M &\rightarrow H_2 + M \\
H^+ + H + M &\rightarrow H_2^+ + M \\
H_2^+ + e &\rightarrow H + H^* \\
H_3^+ + e &\rightarrow H_2 + H^* \\
H^+ + e &\rightarrow H^* + hv
\end{align*}

(3.7)

With the exception of process g, the net effect of these reactions is a continual reduction in the level of excitation of the gas with a concomitant production of kinetic energy. The rates for these reactions depend on the densities of the reacting species and the details of the potentials. The atomic recombination process (g) requires emission of a photon and is generally slow compared to processes (e) or (f). Therefore, in relatively dense gases any H^+ produced will tend to go through processes such as (b) or (c) in order to form a molecular ion, which will then recombine rapidly with “cool” electrons [e.g., processes (e) and (f)] (Bates 1979). In a very low density gas [e.g., diffuse interstellar cloud] processes such as (g) become important.

If the exciting radiation is turned off, these reactions will continue until the gas consists of neutral molecules in low-lying excited states or in the ground state. The excited atoms and molecules unable to react further will eventually emit radiation or lose their excitation energy collisionally (AB* + M → AB + M). Therefore, the total energy deposited by the ionizing radiation eventually appears as photons or kinetic energy of motion of the molecules.

In a gas of water molecules, more complex reactions can occur. For example, following ionization the reactions below are possible

\begin{align*}
H_2O^+ + H_2O &\rightarrow H_3O^+ + OH \\
OH^+ + H_2O &\rightarrow OH + H_2O^+ \\
H^+ + H_2O + M &\rightarrow H_3O^+ + M \\
H_2O^+ + e &\rightarrow OH + H \\
H_2O^+ + e &\rightarrow H_2O + H \\
OH + H + M &\rightarrow H_2O + M \\
OH + OH + M &\rightarrow H_2O_2 + M \\
&\quad\quad\quad\quad\rightarrow H_2O + O + M \\
H + H + M &\rightarrow H_2 + M \\
H_2O_2 + H_2 &\rightarrow 2H_2O
\end{align*}

(3.8a)

It is seen from these reactions that, although there are many intermediate
products, the water molecule fragments tend to recompose H$_2$O. In the above, any one of the products on the right-hand side may be in excited states, and such channels as

\[
\begin{align*}
H_2O^* & \rightarrow H_2 + O \\
& \rightarrow H + OH
\end{align*}
\]

(3.8b)

can occur by direct excitation or following electron recombination. In addition O$_2$ can be formed from the products in Eq. (3.8a),

\[
\begin{align*}
O + OH & \rightarrow O_2 + H \\
H_2O_2 + OH & \rightarrow H_2O + O_2H \\
O + O_2H & \rightarrow OH + O_2 \\
H_2O_2 + H & \rightarrow H_2O + OH \\
O_2H + OH & \rightarrow O_2 + H_2O
\end{align*}
\]

(3.9)

At very high densities of excitation, or when the H$_2$ is “lost” (e.g., by gravitational separation in an H$_2$O atmosphere), then the reactions in Eq. (3.9) become favored (Yung and McElroy 1977). If O$_2$ is formed, it is relatively stable, and the gas remains partially decomposed into O$_2$ molecules and H$_2$ molecules. That is, unlike the example of an H$_2$ gas, which on “cooling” eventually reforms the H$_2$ molecule, it is possible in gases such as H$_2$O for ionizing radiation to produce stable alterations. In most carbon-containing gases and gas mixtures this is also likely. For example, in CO$_2$, both CO and O$_2$ are produced, and in methane, H$_2$ and C$_2$H$_6$ are produced. In such gases polymerization can also occur for very high doses of radiation as seen in Table 3.3 (Capone et al. 1983; Delitsky and Thompson 1987; Piscitelli et al. 1988) producing precipitates (Calcagno et al. 1983b; Khare et al. 1984; Sack et al. 1988).

**Solid State Radiolysis**

Processes similar to those described above occur in a condensed gas solid which, to first order, can be thought of as an extremely high density gas. However, most of the chemical activity takes place close to the track of the particle or in the spurs associated with fast secondary electrons because the chemical species are not very mobile at the very low temperatures in deep space. In the high excitation density regions of the track fragment densities can be high so that reactions occur efficiently. Before considering this, we note that at very low temperatures radicals can be stored for long periods of time. That is, the reaction process remains incomplete. On raising the temperature, the “stored” radicals can be made mobile and the reactions proceed. For example, following the production by extensive photoabsorption of a very high density of radicals in ices at low temperatures, rapid warming can cause the irradiated material to “explode” (d’Hendecourt et al. 1986). This warming may be induced in grains in molecular clouds by heavy cosmic-ray nuclei (Leger et al. 1985) or grain-grain collisions (d’Hendecourt et al. ...)
Therefore, the molecular species originally condensed on the grain may be released into the gas phase chemically altered.

Quantities, similar to the W values discussed earlier, are often used to describe the number of new species produced in liquids and solids by radiation. For example, \( G_i \) = number of species of type \( i \) produced per 100 eV of ionizing radiation energy deposited in a solid (Magee and Chatterjee 1987) which is, roughly, the inverse of W. In the early days of solid state radiolysis the changes induced in an ice by ionizing radiations were studied by subliming the solid after irradiation and collecting the new molecular species produced (Hart and Platzman 1961). This simulates certain problems in astrophysics. For example, as an ice grain or a comet approaches a sun, the irradiated, condensed material can release new species on warming. Results for a few species and a polymer are given in Table 3.3. All such values depend on the temperature of the solid during irradiation.

A similar set of experiments has been performed for implantation of energetic ions in various low-temperature frozen gases. For example, low doses of C atoms in H\(_2\)O at 77 K result in the production of CO molecules, as does carbon from the solar wind implanted into the lunar rock (Rocard and Bibring 1982). Energetic ions may be implanted from an external source or from nuclear reactions induced in the solid (Wolf and Rössler 1987; Matsuura 1984). Energetic protons on H\(_2\)O initiate a reaction \([^{16}\text{O}(p, xpn)\ ^{11}\text{C} \text{ or } ^{16}\text{O}(p, x)^{13}\text{N}]\) which results in small quantities of CO and NO in the ice (Rössler et al. 1984).

### Table 3.3. Radiolysis yields

<table>
<thead>
<tr>
<th>Material(^a)</th>
<th>Product</th>
<th>( G(\text{no.}/100\text{eV}) )</th>
<th>Radiation(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O (gas)</td>
<td>H(_2)</td>
<td>0.03</td>
<td>( \alpha, \beta )</td>
</tr>
<tr>
<td>H(_2) + 1/2 O(_2) (gas)</td>
<td>H(_2)O</td>
<td>9</td>
<td>( \alpha, \beta )</td>
</tr>
<tr>
<td>H(_2)O (liq.)(^c)</td>
<td>H(_2)</td>
<td>1–0.5</td>
<td>(1–10(^3) \text{keV})e</td>
</tr>
<tr>
<td>H(_2)O (77 K)</td>
<td>H(_2)</td>
<td>0.7</td>
<td>( \alpha )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>( \beta )</td>
</tr>
<tr>
<td>O(_3) (gas)</td>
<td>O(_3)</td>
<td>9</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>CO(_2) (gas)</td>
<td>CO</td>
<td>0.03</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>CO(_2) (liquid)</td>
<td>CO</td>
<td>4</td>
<td>( \gamma, ff )</td>
</tr>
<tr>
<td>CO(_2) (77 K)</td>
<td>CO</td>
<td>9</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>CO (gas)</td>
<td>[CO(_2), C(_3)O(_n)]</td>
<td>6</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>CH(_4) (77 K)(^d)</td>
<td>C(_2)H(_6)</td>
<td>0.6</td>
<td>( \gamma )</td>
</tr>
<tr>
<td>CH(_4) (gas)</td>
<td>C(_2)H(_6)</td>
<td>2</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Cross link</td>
<td>2</td>
<td>( \gamma )</td>
</tr>
<tr>
<td></td>
<td>H(_2)</td>
<td>4</td>
<td>( \gamma )</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Cross link</td>
<td>0.05</td>
<td>( \gamma )</td>
</tr>
<tr>
<td></td>
<td>H(_2)</td>
<td>0.02</td>
<td>( \gamma )</td>
</tr>
</tbody>
</table>

\(^a\)Room temperature unless specified. Results taken from Hart and Platzman (1961). Note at 164°C, \( G(H_2) \), from H\(_2\)O becomes 1.6 (Matsuura 1984).

\(^b\)\( \alpha, \beta, \gamma \) are usual radiations, ff (fission fragment).

\(^c\)Magee and Chatterjee (1987).

\(^d\)Horigome et al. (1978). CH\(_4\) in liquid N\(_2\).
METHANE DECOMPOSITION

$1.5 \text{ MeV He}^+$

$\text{CH}_4 \rightarrow \text{CH}_n$

$\phi \left(10^{15} \frac{\text{He ions}}{\text{cm}^2}\right)$

Fig. 3.11. The H to C ratio in solid methane (~10 K) as a function of fluence of 1.5 MeV He$^+$ ions. (Lanzerotti et al. 1985)

T = 88 K

WAVELENGTH (MICRONS)

Fig. 3.12. a Infrared absorption spectrum of an SO$_3$ ice (~18 µm thick) at 88 K before and after irradiation with 1 MeV protons. Bands due to SO$_3$ and Poly (SO$_3$) are indicated. Curve A, B and C simulate equivalent doses of 0.1, 1 and 10 years of irradiation on Io. (Moore 1984). b Infrared absorption spectrum of an H$_2$O + NH$_3$ + CH$_4$ (~1:3:2) ice mixture at 20 K before and after irradiation by 1 MeV protons to ~$2 \times 10^{14}$ ions/cm$^2$. Synthesized species noted and CH$_4$ is noticeably decreased. (Moore and Donn 1982, 1983)
With the development of accurate spectroscopic and electron spin resonance techniques, measurements of species in the solid have also been made. Radical species, such as H and OH, have been identified in irradiated ice at very low temperatures (140 K). As the temperature is increased, the disappearance of these species has also been followed (Hart and Platzman 1961). In ice, as in the gas phase, it is found that water molecules tend to reconstitute from the dissociated species. On the other hand, if the density of excitation is high, as in the vicinity of an ion or secondary electron (delta-ray) track, water has been found to decompose into H₂ and O₂. In the solid the H₂ aggregates in the defects (bubbles) formed in the ice by irradiation, and at a vacuum surface H₂ is lost readily even at quite low temperatures. The loss of H₂ and formation of O₂ is similar to processes occurring in an H₂O atmosphere.

In all condensed gases containing carbon, carbon-carbon bonds form from dissociated fragments, and in addition CO is a relatively stable product if oxygen is available (Venkatesan et al. 1987). On irradiation of methane in a vacuum, H₂ is formed in the defects and at the surface, as in water ice, and eventually exits the material (Lanzerotti et al. 1987b). This leaves behind a polymeric material which is depleted in hydrogen, as shown in Fig. 3.11. On extensive irradiation or warming, a residue remains which will be discussed later. Such residues are also formed on extensive irradiation of sulfur containing condensed gases such as H₂S, CS₂ (Boring et al. 1985) and SO₂ (Moore 1984; Melcher et al. 1982). In ammonia ice, H₂ and N₂ are formed (Haring et al. 1983, 1984b), in CO₂ ice, CO and O₂ are formed as stable species (Brown et al. 1984), as in the gas phase, and in CO ice, CO₂ and O₂ are formed (Chrisey et al. 1986a, 1989; Haring et al. 1983, 1984a), although very inefficiently, as well as carbon suboxide (Chrisey et al. 1989). Even in condensed S₈ polymeric sulfur is produced, along with fragments (e.g., S₂) (Torrisi et al. 1988; Chrisey et al. 1986b).

Because molecules dissociate, producing energetic fragments, “hot” atom reactions can play an important role in the solid phase (Rössler et al. 1984). An example of this is the formation of formaldehyde in irradiation of a H₂O, CO₂ mixture (Pirronello et al. 1982; Haring et al. 1984a). Pirronello 1985 uses a G ~ 0.004. By using isotopically labeled species, Pirronello et al. (1982) found that D₂O¹⁶ + C¹³O₂¹⁸ produced D₂C¹³O¹⁶, where the carbon formed the new species by hot atom insertion into D₂O¹⁶. Such reactions can be important in the solid phase because of the proximity of the species (Matsuura 1986). Continued irradiation can then lead to a polymeric form of formaldehyde.

Because the irradiated layers are altered chemically, their spectra can change dramatically. In some cases, films which are relatively inactive in the IR before irradiation can exhibit distinct IR features. Irradiated SO₂, of interest at Io, showed SO₃ in the spectra (Fig. 3.12a) and irradiation of a hypothetical cometary ice mixture (60% H₂O, 10% NH₃, 20% CO, 10% CH₄) by MeV protons exhibited a number of synthesized species (Fig. 3.12b). The spectrum of irradiated ice exhibits a slight amorphous to crystalline changes due to local agitation of the lattice as well as the changes in the band structure seen in Fig. 3.13. Irradiated
organics have strong C-H absorptions near 3.5 \( \mu \text{m} \) at low doses (Fig. 3.14) and eventually become black (Calcagno et al. 1986; Khare et al. 1989) on long-term bombardment.

We now turn our attention to the removal of material from the surface of the solid. For radiations with small absorption cross sections (e.g., \( \gamma \)-rays, cosmic-ray particles, visible photons, etc.) surface processes are not important. However, for radiations which have large cross sections (e.g., UV photons and ions and electrons at velocities \(< 10 \, v_o\)), the surface will play a role in determining the material alterations.

**Sputtering of a Solid**

*Nuclear Elastic Collisions*

Plasma ions incident on a surface can eject atoms and molecules into the gas phase. This can occur by an increase in the surface temperature enhancing sublimation. The ejection rate for this process depends non-linearly on the ion flux, so that at low fluxes considered in Chapter 1 it can be ignored for a solid target. Of more interest to the fate of surfaces in space is sputtering. For this process the ejection rate is determined by the energy deposited by each ion separately, so that the flux of sputtered surface material is proportional to the
incident ion flux. That is, the number of target particles ejected per incident ion, called the yield, \( Y \), is independent of the incident ion flux.

An incident ion collides with atoms near the surface, initiating cascades of collisions between target particles as shown in Fig. 3.15. For an ion incident normal to the surface, the struck atoms are directed inward. After a number of collisions, however, a recoil can be produced near the surface which has momentum directed outward and, therefore, may exit from the solid. These multiple collision events are called sputtering when the energy of the recoils is greater than the background thermal energy. Sputtering due to cascades of collisions is described below. Superimposed on this are prompt, "single collision" ejection processes in which the primary recoil (struck by the incident ion) is

---

**Fig. 3.14.** a Infrared spectra of residues extracted from irradiated (1 MeV H\(^+\)) ice mixtures. (Moore and Donn 1982, 1983): Ia, \( \text{H}_2\text{O} + \text{NH}_3 + \text{CH}_4(1:3:2) \times 10^{14} \text{ MeV/cm}^2 \); VI a, \( \text{H}_2\text{O} + \text{NH}_3 + \text{C}_2\text{H}_6(9:5:4) \times 10^{14} \text{ MeV/cm}^2 \). Shows band structure near 3.5 \( \mu \text{m} \) band. b Infrared spectra of various residues for comparison of 3.5 \( \mu \text{m} \) band. Top an irradiated polymer. (Foti et al. 1984)
Fig. 3.14b
itself ejected (Kelly 1987). This process is generally a small contribution, but becomes important at grazing incidence, near threshold, and for thin targets. Finally, at latter times, quasithermal processes occur during energy dispersal.

**Cascade Sputtering**

When the density of primary recoil atoms set in motion by an incident ion is small, these recoils deposit their energy and interact with other atoms in the target independently. If these independent cascades occur close to the surface, target particles can be displaced from the solid, i.e., sputtering of the surface occurs. The average number of sputtered particles is determined by contributions from all of those primary recoils produced close to the surface (see Fig. 3.15). The yield is then determined as a ratio between two lengths

\[ Y \approx \sum \Delta z_s(T_i)/\lambda_e(T_i). \]  

(3.10a)

Here \( \Delta z_s \) is a ‘sputter depth’ for a cascade produced by a primary recoil of energy \( T_i \), and \( \lambda_e^{-1} \) is average number of such recoils produced per unit path length by the incident ion. The ratio is evaluated in Appendix 3B. Here we note that an estimate is easily obtained using quantities already discussed. The average \( \lambda_e^{-1} \) is proportional to \( (dE/dx)_n/\cos \theta_A \) divided by a mean energy transfer, \( T \), where \( \theta_A \) is the angle of incidence. As low energy recoils can have
a mean projected range, $\bar{R}_p \approx 3.2(n_0\bar{\sigma}_d)^{-1}$ then $\bar{d}_z$ is proportional to $(n_0\bar{\sigma}_d)^{-1}$ times the number of 'displacements' near the surface, which is proportional to $\tilde{T}/U$ (see discussion following Eq. (3.5)). Writing $(dE/dx)_n = n_0S_n$ (Chap. 2), the yield has the form

$$Y \approx C \frac{S_n}{U\bar{\sigma}_d} (\cos \theta_A)^{-1}.$$  \hspace{1cm} (3.10b)

This is seen to be independent of the number density of the target, as both lengths depended on the material density. (Thompson 1968; Sigmund 1981). Hence, this form for the yield applies whether we consider the sputtering of a solid surface, in which the binding, $U$, is produced by the atomic or molecular forces, or of an atmosphere in which gravitational binding limits escape (Haff et al. 1981a). The proportionality constant, $C$, in Eq. (3.10b) is obtained in the following from the point of view outlined by P. Sigmund (1969, 1981).

A determination of the flux of energized particles across the surface requires the solution of the transport equation for the flow of moving atoms in a material. However, the number of recoil atoms set in motion by an incident particle is directly proportional to the nuclear elastic energy deposited so that the sputter yield has the very general form

$$Y(E_A, \cos \theta_A) \approx F_D(E_A, \cos \theta_A, 0)\Lambda.$$  \hspace{1cm} (3.11)

Here $F_D(E_A, \cos \theta_A, 0)$ is the net elastic collision energy deposited per unit path length at the surface (Fig. 3.7b) by an incident ion of energy $E_A$ and direction of motion to the surface normal indicated by $\cos \theta_A$. $\Lambda$ is a sputter efficiency which is estimated as follows. Using Eq. (3.5), the number of recoils set in motion is proportional to the collisional energy deposited. Therefore, the number of recoils per unit depth set in motion in the surface region with energy between $\varepsilon'$ and $\varepsilon' + d\varepsilon'$ is

$$\beta_n F_D(E_A, \cos \theta_A, 0)/\varepsilon'^2.$$  \hspace{1cm} (3.12)

In order for one of these recoils to escape from the material, it must have the appropriate energy and direction of motion to be able to overcome the binding, and it must make no further collisions while exiting. The latter criterion means that the particle no longer participates in the cascade of collisions initiated by the incident ion. For a recoil of energy $\varepsilon'$ and direction of motion $\cos \theta'$ to the surface normal, we write the probability of escape as $P_e(\varepsilon', \cos \theta')$ and the mean path length for escape as $\lambda_d(\varepsilon')\cos \theta'$. Here $\lambda_d(\varepsilon')$ is the mean free path for an energy transfer collision by a recoil particle.

The number of particles ejected is obtained by multiplying the number of recoils per unit depth set in motion in Eq. (3.12) by the escape depth and the probability of escape. Assuming the recoils move isotopically in the solid, a very rough assumption (see Fig. 3.9b), and using $\beta_n = 6/\pi^2$ for the low energy recoils, the contribution to sputter yield from energies $\varepsilon'$ to $\varepsilon' + d\varepsilon'$ and angular
region $d\Omega$ is

\[
6 \frac{F_D(E_A, \cos \theta_A, 0)}{e^2} \int \frac{d\Omega'}{4\pi} P_{es}(e', \cos \theta') \lambda_d(e') \cos \theta'. \tag{3.13a}
\]

The factor $d\Omega/4\pi$ accounts for the assumed isotropic distribution of recoils. The total yield is obtained by integrating over energy and angle, and $\lambda_d$ is replaced by an averaged value $\overline{\lambda}_d$. In determining $P_{es}$, the forces at the surface of a solid are often represented by a planar barrier of energy $U$ if the atomic binding is large and the yields small, as for refractory solids (Thompson 1968). Therefore,

\[
P_{es}(e', \cos \theta') = \begin{cases} 1, & e' \cos^2 \theta' \geq U, \cos \theta' \geq 0, \\ 0, & \text{otherwise}. \end{cases} \tag{3.13b}
\]

On integration of Eq. (3.13a) subject to the conditions in Eq. (3.13b), the sputter factor in Eq. (3.11) is

\[
\Lambda_p = \frac{3}{4\pi^2} \frac{\lambda_d}{U}. \tag{3.13c}
\]

Where the $p$ implies planar binding condition. In obtaining this expression the upper limit on the energy of the recoils, $e' = \gamma E_A$ (Chap. 2), was assumed to be much larger than $U$.

If the surface is very rough on an atomic scale (Sigmund 1969), if the yields are large as for condensed gases (O’Shaughnessy et al. 1988b), or if sputtering is from an atmosphere (McGrath and Johnson 1987), then “spherical” binding conditions are more appropriate. That is,

\[
P_{es}(e', \cos \theta') = \begin{cases} 1, & e' \geq U, \cos \theta' \geq 0 \\ 0, & \text{otherwise} \end{cases} \tag{3.14a}
\]

giving

\[
\Lambda_s = 2\Lambda_p. \tag{3.14b}
\]

For macroscopically rough surfaces (e.g., a regolith of a moon) the sticking of a sputtered species on a nearby surface and the variety of incident angles will be considered in Chapter 4.

For the sputter ejection of many layers of a solid $U$ is roughly equivalent to the sublimation energy. The mean free path for an energy transfer collision can be estimated $\lambda_d \approx e'(de'/dx)^{-1}$, where $(de'/dx)$ is the stopping power of the recoils of energy $e'$. As the ejection is dominated by low-energy particles the average can be written using Eq. (2.14) as $\overline{\lambda}_d \sim (n_b \overline{\sigma}_d/2)^{-1}$, where $\overline{\sigma}_d$ is an average diffusion cross section. As the quantity $F_D$ in Eq. (3.13a) is also proportional to the number density $n_b$, Sigmund writes $F_D \approx x(dE/dx)_n = x n_b S_n$, where $S_n$ is the nuclear elastic stopping power of the incident ion and $x$ is a parameter which has to be determined. The yield now has the “standard” form for planar
binding which is

\[ Y \approx \frac{3}{2\pi^2} \frac{\alpha S_n}{\bar{\sigma}_d U} \approx 0.042 \alpha S_n/(U \text{Å}^2), \] (3.15)

in which Sigmund used \( \bar{\sigma}_d \sim 3.6 \text{ Å}^2 \) for metals, which is of the order gas phase cross sections in the eV range for atoms (Yee and Dalgarno 1987). This result is like that in Eq. (3.10b), but more recent work suggests a smaller \( \bar{\sigma}_d \) (larger \( \bar{\sigma}_d \)), of the order of a monolayer of material when considering solids (Kelly 1987; Cui et al. 1988).

The factor \( \alpha \) in Eq. (3.15) accounts for the fraction of \( S_n \) participating in the cascade of collisions near the surface as indicated in Fig. 3.15. Therefore \( \alpha \) accounts for: the dependence of \( F_D \) on angle of incidence; the fact that the cascades do not fully develop at the surface and are not located at the point of production of the primary recoil, the deflection of the incident atom in the surface region, and that fraction of the energy of the secondaries lost to inelastic processes [\( \eta \) in Eq. (3.4)] (Sigmund 1981).

Anderson and Bay (1981) have summarized the extensive data for incident keV ion sputtering of metals and semi-conductors which have relatively large binding energies \( \sim 2–6 \text{ eV} \). In Fig. 3.16 are shown data for various ions sputtering carbon (graphite) at normal incidence. Such data can be organized using the expression in Eq. (3.15), in which case \( \alpha \) is determined by fitting the data. In Fig. 3.17 empirical values for \( \alpha \) for keV ions at normal incidence are given for use with Eq. (3.15) with the assumed \( \bar{\sigma}_d \) above. Quite remarkably, at normal incidence, \( \alpha \) is primarily a function of the mass ratio. As the assumptions in the above model are very rough, the empirical values of \( \alpha \) in Fig. 3.17 can be used with Eq. (3.15) to estimate yields (to within a factor of two) when data is not available.

For the important molecular condensed gases (\( \text{H}_2\text{O}, \text{CO}, \text{SO}_2, \text{S}_8 \), etc) and for certain other interesting molecular compounds (e.g., \( \text{Na}_2\text{S} \)) (Chrisey et al. 1986a, b, 1988) Eq. (3.11) can also be used to estimate the total yield at low temperatures to within a factor of two. The yield in molecules removed per ion incident is obtained by using the material cohesive energy (molecular sublimation energy), \( \alpha \) from Fig. 3.17, and dividing the expression in Eq. (3.11) by the number of atoms per molecule. This is equivalent to using the atomic \( \bar{\sigma}_d \) as a size for each atom (roughly equivalent to replacing \( \bar{\sigma}_d \approx n_b^{-2/3} \) the molecular size). For tightly bound molecular materials (e.g., \( \text{SiO}_2 \), Fig. 3.16b) with low yields, the above procedure also gives roughly correct yield values when surface charging is controlled (Betz and Wehner 1983).

We have concentrated above on what is commonly referred to as back sputtering: particles leaving a surface with motion opposite to the incident ion. For thin samples (e.g., the Io corona, ice grains) sputtering is also produced on transmission. The expression in Eq. (3.11) still applies, but \( F_D \) is the energy deposited per unit path length at the exiting surface (i.e., \( \alpha \approx 1 \) if the ion has
Fig. 3.16 a Sputtering yield of carbon (C atoms removed per ion incident) for incident ion energy $E_x$ for a variety of incident ions. Dashed lines are cascade model calculation. Symbols indicate incident ion (different data set shaded differently. Andersen and Bay 1981). b Same for SiO$_2$ target (total material removed given as equivalent SiO$_2$ molecules per ion incident). (Betz and Wehner 1983)
Fig. 3.16b

Fig. 3.17. Experimental values of $\alpha$ of Eq. (3.15) at normal incidence versus the ratio of target mass, $M_b$, to incident mass $M_A$. Line is a model fit at low mass ratio. (Andersen and Bay 1981)
not lost much energy). In this case the “single collision” ejecta, not included in Eq. (3.15), play a larger role (Chap. 4).

The dependence of \( x \), hence the yield, on the angle of incidence is shown in Fig. 3.18 for back sputtering, indicating that for most ion/target combinations \( Y \) varies as a higher power of \( \cos \theta_A^{-1} \) at small angles (Oliva-Florio et al. 1987), going through a maximum and decreasing again at large values of \( \theta_A \). This dependence (\( \sim \cos \theta_A^{-1.6} \)) is due to the forward directedness of the cascade of collisions in the surface region (see Fig. 3.15; Sigmund 1969). The maximum (at \( \sim 80^\circ \)) is associated with total reflection from the surface and surface roughness. Of course, the planetary regoliths and interplanetary grains have very “rough” surfaces (Chap. 4).

**High (dE/dx) Sputtering**

The above discussion applies when the density of atoms set in motion is low, as when light ions are incident. For high \((dE/dx)\), the cascades in Fig. 3.15 can overlap and an energized cylindrical region is produced about the ion’s track. The region so “heated” is often referred to as a “thermal” or “diffusive” spike (Vineyard 1976). The diffusion equations for dissipation of the energy in the spike are considered in Appendix 3C. Ejection occurs, per incident particle, due to the local energy density, \( \varepsilon \), and its gradient produces a volume force (Johnson et al. 1989b). The yield of atoms or small molecules subliming from the cylindrical spike produced by a single ion is written

\[
Y_s = \int_0^\infty dt \int_0^\infty \pi dr^2 \Phi \left[ \varepsilon(r, t) / n_B U \right],
\]  

(3.16)
where \( \Phi \) is the flux of atoms or molecules from a surface due to the surface energy density, \( \varepsilon_s \), which depends on the radial distance from the track of the ion, \( r \), and the time, \( t \), after the passage of the ion. Using the escape criterion [e.g., Eq. (3.13b) or (3.14a)] this yield is

\[
Y_s \approx c_s \left[ l_s (dE/dx)_n / U \right]^2 g(x_0), \quad x_0 = n_B U / \varepsilon_s(0,0)
\]

(Evatt and Johnson 1980; Sigmund and Claussen 1981). In this expression the constant \( c_s \) and the function \( g(x_0) \) depend on the local energy spectrum (Appendix 3C) and the escape criterion, and \( l_s \) is the average thickness of a monolayer of material: \( l_s \approx n_B^{-1/3} \). Because the yield in Eq. (3.17) depends on the material density via \( (dE/dx)_n \), spike effects are important only in a condensed medium.

The function \( g(x_0) \) in Eq. (3.17) depends on the initial energy density at the track center, \( \varepsilon(0,0) \). For a hot narrow spike the yield is quadratic in the stopping power as \( g(x_0) \) approaches unity for \( U \ll \varepsilon(0,0) \). This implies that \( (dE/dx)_n \gg U n_B \pi r_0^2 \), where \( r_0 \) is the initial mean radius of the deposited energy distribution.

At large \( (dE/dx)_n \) a volume of material may be ejected due to the rapid material expansion (pressure pulse) about the ion track (the gradient of \( \varepsilon \)), leaving a small crater (Carter 1983). This means large whole molecules can be ejected into space from the solid state (Sundqvist 1989). In this region the yield eventually becomes proportional to \( (dE/dx)_n^2 \) for fast ions (Johnson et al. 1989b). Because random motion is detrimental to organic molecules, this mechanism will dominate for large molecule ejection. Calculating a net yield over a broad range of \( (dE/dx)_n \), it is common to sum the various contributions. For metals sputtered by fission fragments with high \( (dE/dx)_n \), a nonlinear dependence on \( (dE/dx)_n \) is indeed measured (Andersen and Bay 1981). Because of the dependence on \( U \), nonlinear yields are also found for weakly bonded materials, such as the condensed gas solids, even for light incident ions. However, because such materials are not good conductors, the electronic contribution to the energy deposition is also important, as discussed shortly.

**Threshold Yield**

The behavior of the sputter yield at low ion bombardment energy is much less certain. This region is of considerable interest for erosion of grains by shocks in the interstellar medium (Kimura 1962; Draine et al. 1983). Below some incident ion energy (see Appendix 2A and 2B), the diffusion cross section becomes a constant, and the nuclear stopping cross section \( S_n = \sigma_d (\gamma E_A / 2) \) [Eq. (2.14)] is linear in \( E_A \). Therefore, the expressions in Eqs. (3.10b) and (3.15) also become roughly linear in \( E_A \) (Sigmund 1981). At very low energies, a threshold for ejecting a surface atom occurs when the maximum energy transfer is of the order of the surface binding energy. This can be approximated by replacing \( \gamma E_A \) by \( (\gamma E_A - U) \) in
the expression for yield. As the mean projected range, $\bar{R}_p(E_A)$, of the incident particle also becomes comparable to the mean sputter depth $\Delta z_s$ in Eq. (3.10a), the incident ion can be thought of as creating a hot spot (Appendix 3C) about $\bar{R}_p(E_A)$.

Anderson and Bay (1981) have summarized the data for the threshold regime. In Fig. 3.19 are given the threshold energies, $E_t$, vs. $M_B/M_A$. These approach $U/\gamma$ at large $M_B/M_A$, as discussed above, but approach $U[8(4/\gamma)^{1/3}]$ at small $M_B/M_A$. Writing $\epsilon' = E_A/E_t$, with $E_t$ from Fig. 3.19, the semi-empirical expression for the yield applicable for $\epsilon' < 10$ is

$$Y(\epsilon') \approx Q(M_A, M_B, U)\hat{f}_t(\epsilon')$$ \hspace{1cm} (3.18a)

with

$$\hat{f}_t(\epsilon') \approx 0.0085(\epsilon')^{1/4}(1 - \epsilon'^{-1})^{7/2}.$$ \hspace{1cm} (3.18b)

This exhibits a slower dependence on $E_A$ than suggested above, and $Q \approx 0.75 M_B^{-5/3}$ gives yields within a factor of 2 for most measured ion-target combinations, with $M_B$ in amu.

**Energy Spectra**

The sputtering regimes discussed above (separate cascades and cylindrical spike) exhibit rather different velocity spectra also. The number of particles

![Graph](image-url)

*Fig. 3.19. Threshold energy $E_t$(eV) divided by the sublimation energy, U, vs. target particle mass divided by incident ion mass. Data indicated. Lines are models. (Andersen and Bay 1981)*
ejected with energy between \( E \) and \( E + dE \) and angle to the surface normal \( \theta \) is written

\[
Y(E, \cos \theta) = Y(E, \cos \theta). \tag{3.19}
\]

Using the description of moving recoils in Eq. (3.5) along with the exit criteria, \( P_{es} \) in Eq. (3.13b) and Eq. (3.14a), the energy distributions for the independent cascades (low energy density) with planar or spherical binding are

\[
f_0^p(E, \cos \theta) \approx \frac{4UE}{(E + U)^3} \cos \theta \tag{3.20a}
\]

\[
f_1^p(E, \cos \theta) \approx \frac{2U}{(E + U)^2} \cos \theta \tag{3.20b}
\]

normalized over the integration range \((0 \leq \cos \theta \leq 1; 0 \leq E < \infty)\). These expressions exhibit the characteristic \(1/E^2\) dependence at high energies (Thompson 1968) based on the recoil energy distribution in Eq. (3.5) and observed in many experiments (Andersen and Bay 1981). Depending on the angle of incidence a “single collision” component adds to this at large \( E \) and this component exhibits preferential ejection angles (Betz and Wehner 1981).

For the case of a high density of cascades, the calculated energy distribution for the spike with cylindrical geometry and spherical binding (Appendix 3C)

\[
f_s^p(E, \cos \theta) = \frac{4U^2}{(E + U)^3} g(x_0, E) \cos \theta, x_0 = n_B U \varepsilon_s(0, 0) \tag{3.20c}
\]

gives a lower average energy. For a narrow spike for which \( g(0, E) \to 1 \) as \( x_0 \to 0 \), the sputtered-particle energy dependence goes as \(1/E^3\) at large \( E \). For a spike with a significant initial width, \( r_0 \), the dependence on \( E \) at large \( E \) is much more rapid, decaying roughly exponentially with \( E \). At very high \((dE/dx)_n\), rapid ejection also occurs due to an impulsive expansion about the track again modifying the energy spectra of the ejecta. This regime has been less severely tested by experiment. Because of the rough additivity of the linear and spike contributions to the yield [Eq. (3.17)], the forms above are often used to fit experimental data with an effective \( U \) as a parameter (Reimann et al. 1984; Boring et al. 1984a, b; Haring et al. 1984c).

**Sputtering of Multicomponent Materials**

For a material consisting of different atomic species (e.g., metal alloy or molecular solid) the sputtering process is more complicated (Betz and Wehner 1983). For a porous mineral regolith, Hapke (1986) shows that the adsorption of the ejected atoms on neighboring grains controls the net loss rate. That is, sputtering of each species in their absorbed state and not their state in the mineral is important.
In the spike regime for a laboratory solid the individual constituents will evaporate independently according to their separate sublimation rates (Roth 1983). For a given average spike temperature, \( T \),

\[
Y'_1/Y'_2 \approx (c_1/c_2)(M_2/M_1)^{1/2} \exp \left[ (U_2 - U_1)/kT \right].
\]  

(3.21)

Here \( Y'_1 \) and \( Y'_2 \) are the actual yields of the two species occurring with concentrations \( c_1 \) and \( c_2 \) [i.e., \( c_i = n_i/(n_1 + n_2) \) where \( n_i \) is a number density]. It is seen that the more weakly bound and lightest species sputter more efficiently. (The binding energies are concentration-dependent, but using the separate \( U \) is generally sufficient.)

For a low cascade density, a number of detailed models have been published in order to describe the sputtering of mixtures (Sigmund 1981; Betz and Wehner 1983). When the masses are nearly equal, then the earlier expressions apply,

\[
Y'_1/Y'_2 \approx \frac{c_1 Y_1}{c_2 Y_2} \approx \frac{c_1 U_2}{c_2 U_1}
\]  

(3.22a)

and

\[
Y'_1 \approx \frac{c_1}{U_1} [c_1 U_1 Y_1 + c_2 U_2 Y_2],
\]  

(3.22b)

where the quantities \( U_i Y_i \) are the yield times sublimation energy for the pure substance. For the nonequal mass case there is a weak dependence on mass,

\[
Y'_1/Y'_2 = \frac{c_1}{c_2} \left( \frac{M_2}{M_1} \right)^{2/n} \left( \frac{U_2}{U_1} \right)^{1-(2/n)}
\]  

(3.22c)

where \( n \) is the power law dependence for the low energy recoil collisions. As stated earlier, the low energy collisions are reasonably well approximated by \( n \to \infty \), in which case Eq. (3.22c) is equivalent to Eq. (3.22a). However, small isotopic fractionation effects have been seen for elemental substances (\( U_1 = U_2 \)) (Watson and Haff 1979). In minerals, isotopic fractionation of the heavy elements (Mg, Si, Ca, etc.) is such that the lighter isotope is lost preferentially in agreement with Eq. (3.22c), but for the lighter constituents (e.g., O) the heavier isotope is lost preferentially, at the few percent level in both cases (Haff et al. 1981b).

Because the relative yields of the separate constituents may differ, their concentration in the surface region will eventually become different from that in the bulk. After long-term irradiation, the surface concentrations will become such that the species eject stoichiometrically according to their bulk concentrations. That is, as the material is modified down to the full depth of penetration of the ions, removal of a small amount of surface allows ions to penetrate into and modify an equivalent amount of fresh material. Therefore, one is, in effect, always removing fresh material, and the ratio of the yields approaches (see Eq. (4.11b))

\[
Y'_1/Y'_2 \to (c_1/c_2) \text{ bulk.}
\]  

(3.22d)

After large fluences, the bulk concentrations can be used along with an effective
(empirical) binding energy ($\sim U_1 \sim U_2 \sim U_{\text{eff}}$) to estimate the yield. Care must be taken in using such expressions as extensively bombarded surfaces are often chemically altered in the penetrated region (Betz and Wehner 1983; Roth 1983). Therefore $\text{SiO}_2$ does not sputter as Si and O atoms, but rather as Si, O, SiO, $\text{O}_2$, and $\text{SiO}_2$, with the most volatile component ($\text{O}_2$) being lost preferentially.

In general, ion bombardment displaces atoms and, hence, would tend to convert crystalline materials into amorphous materials down to the penetration depth of the ion. However, the residual energy deposited by the ion agitates the atoms and molecules in the solid. This results in ion beam enhanced diffusion in which the more volatile species reach the vacuum interface (Arnold and Mazzolli 1987), and are ejected as discussed earlier (e.g., Na from silicates). It is also possible that in an amorphous material the residual heat can be sustained long enough to form crystalline regions if the thermal diffusivity of the material is low. Therefore, materials with high thermal diffusivity will generally become amorphous under bombardment, while those with low thermal diffusivity can form crystallites. Evidence for the latter in ice was found (Benit et al. 1987). In addition, in molecular materials such as SiO or $\text{SiO}_2$, the preferential loss of O (as $\text{O}_2$) can result in the formation of Si crystallites within the solid after long-term irradiation (Walters et al. 1988).

**Mixing, Adhesion, and Desorption**

When gases condense on a surface, at submonolayer to few monolayer coverage, an incident ion may cause mixing with the surface or desorption of the absorbed molecules, depending on how these molecules are struck by the ion. For example, "knock-on" collisions of the ion and an atom of the absorbed gas can drive the atom into the substrate, a process used to intentionally modify surfaces. The surface can also be modified simply by bombarding it with those ions (atoms) which one would like to implant. The incident particles penetrate and stop in the material, as discussed earlier, changing the character of the surface (Roth 1983), a process used in the electronics industry and used to reduce surface corrosion. A region of the order of the penetration depth of the ion will become a new mix of the original components and the bombarding particles. If, in addition, the electronic structure is disrupted, then reactions can be induced. If the new species produced are volatile, they may be lost rapidly (chemi-sputtering).

These process occur also when an ion or an electron traverses the interface between two materials (metals, semi-conductors, or insulators). What is found experimentally is that the adhesion between two materials in physical contact generally is increased by ion and electron bombardment (Werner et al. 1983). This occurs when the adhesion forces are weak (van der Waals) contact forces, and binding is enhanced by mixing and the formation of covalent bonds between atoms on the two surfaces (Ingemarsson et al. 1989). Such enhanced adhesion may be important, for example, in the formation of Brownlee particles from
cometary grains (see Fig. 4.6) for which the icy mantles are lost (Johnson 1985b; Johnson and Lanzerroniti 1986).

An incident slow ion can also eject absorbed surface gases. This desorption can be described in the same manner as the sputtering process if account is taken of the mass differences of the surface atoms and absorbed species. A rough estimate of the cross section for desorption can be obtained from the sputtering yield expressions just discussed. For submonolayer coverage

$$\sigma_{de} \sim Y \sigma_d \sim \frac{3}{2\pi^2} \frac{\alpha S_n}{U},$$

(3.23)

Where $U$ is the binding energy of the species absorbed on the substrate and $\sigma_d$ is assumed to describe the collision between substrate and adsorbed atoms. In this expression $(\alpha S_n)$ is calculated for the energy deposition in the substrate and the yield is given by $(\sigma_{de} N)$, where $N$ is the coverage of the surface expressed as a column density. As $N$ increases, both $U$ and $(\alpha S_n)$ gradually become characteristic of a solid made up of the adsorbed species. For thicknesses greater than the sputter depth, the substrate does not play a role and the standard sputtering expressions apply.

**Electronically Induced Desorption**

Ionizing radiations (photons, electrons, and ions) have been shown to eject molecules condensed on a substrate (Tolk et al. 1983; Brenig and Menzel 1985; Stuhlen and Knotek 1988). For submonolayer to few monolayer thicknesses, the condensed gas is said to be desorbed by the radiation a process of interest in interstellar clouds (Greenberg 1973). For thick condensed-gas layers the ejection process is referred to as electronic sputtering, discussed in the next section.

The electronic energy deposited in a solid by an ion, electron, or photon is dissipated via the processes described earlier. Most of the energy is eventually converted to heat and is finally radiated in the IR or thermally conducted to a cooler region. Higher energy photons (luminescence) may also be emitted because of electronic and vibrational transitions in a molecular solid. In addition, ejection of atoms or molecules can result from the changed electronic binding produced by the excitations. This occurs when the electrons are excited to repulsive states or to states which relax to a repulsive state as in Fig. 3.10. In such a process the electronic energy deposited in the solid is converted to atomic motion (Menzel and Gomer 1964; Redhead 1964). If the repulsive state is excited in the surface layer or between a surface atom (molecule) and its substrate, then desorption can occur. Depending on the nature of the electronic states excited, the repulsive ejection can lead to the desorption of either an ion or a neutral. In general, neutrals are the dominant ejected species, although most experimental work has been on the ejection of the easier to detect ionic species. The dominance of neutral species occurs because the ions are more strongly attracted to the
surface (e.g., polarization or image charges) and ions exiting the surface can be neutralized by electron capture. In general, the average repulsive energies transferred to the neutrals are small. For example, for H₂ O on TiO₂ (Avouris et al. 1986), OH is observed with ~0.25 eV, whereas ions are typically ejected with energies >1 eV.

A number of general statements can be made about the importance of the substrate in the desorption process. Electronic energy deposited in the metallic substrate is quickly dissipated, and in many instances the metallic substrate acts as a sink for energy initially deposited in the adsorbed layer, decreasing the efficiency of the desorption process. On the other hand, for an insulating substrate, electronic excitation produced near the surface may result in a repulsive relaxation which can enhance the ejection of adsorbed species. Therefore electronically stimulated desorption occurs much more efficiently on an insulating than on a metallic substrate. Further, the different substrates can result in different ratios of ions to neutrals ejected. Metallic surfaces, for example, can donate electrons, neutralizing exiting ions. Such processes are very sensitive to the nature of the surface and the adsorbed species (Maidy 1986).

The desorption rate is expressed in terms of a cross section, as in the previous section. For submonolayer coverage, the yield per incident ion, electron or photon is \( N\sigma_{De} \). Roughly, \( \sigma_{De} \approx \sigma_{ex} P_D \) where \( \sigma_{ex} \) is the cross section for excitation to the repulsive (desorbing) state and \( P_D \) is the probability of desorption. This can be much less than one because of energy dissipation to the substrate. For example, whereas valence excitation cross sections for ~100 eV electrons are \( \sim 10^{-16} \) cm², cross sections for ion desorption for such electrons are \( \gtrsim 10^{-20} \) cm² and for neutral desorption \( \gtrsim 10^{-18} \) cm² (Maidy 1986). \( \sigma_{De} \) for neutrals can approach the electronic excitation cross section. For CO molecules adsorbed on a metallic surface by van der Waals forces (physisorbed), the desorption cross section is close to the cross section for electronic excitation of a free CO molecule to an internal repulsive state (Leung et al. 1977), of the order of \( 10^{-16} \) cm² for electrons with energies of the order 50 eV. For low energy ions charge exchange may also excite a surface repulsive state (Baragiola 1984).

An oxygen (hydrogen) atom attached chemically to a metallic surface (chemisorbed) requires the excitation of the metal-oxygen (metal-hydrogen) bond to a repulsive state. When either of these species is adsorbed on an insulating surface, \( \sigma_{De} \) will be larger. Photon-stimulated desorption cross sections are estimated in the same way and are, therefore, much smaller than those for electrons and ions, because UV cross sections for excitation to a repulsive state are smaller. For desorption of ionic species, \( \sigma_{De} \sim \sigma_{ex} P_D (1 - P_N) \), where \( P_N \) is the neutralization probability. Here \( \sigma_{ex} \) is the excitation to a repulsive curve that separates to an ionic state (Brenig and Menzel 1985). Not only is \( P_N \) close to one for many surfaces, but the excitation cross section \( \sigma_{ex} \) is smaller than the cross sections for valence electron excitations leading to neutral desorption. Therefore, ion desorption cross sections are smaller, requiring more energetic excitations (e.g., shake-up excitations or inner shell excitations). For example, for neutral
CO on a metal substrate the metallic-CO bond can be excited at about 5 eV, leading to desorption (Feulner et al. 1981), whereas states leading to ion desorption are typically $\sim 15$ eV (Avouris and Walkup 1989).

**Sputtering of a Solid: Electronic Stimulation**

Electronic states excited in the solid by photons, electrons or ions can result in the energetic repulsion of neighboring atoms, as exemplified by desorption from and defect formation in insulators (Brown 1987). These are the surface and bulk ramifications of the same processes. When the thickness of the layer of adsorbed gases, N, increases beyond some depth, the "substrate" becomes unimportant and the ejection process is called electronic sputtering. This occurs, for instance, following the production of a track of electron-hole pairs produced by a fast ion see Fig. 3.20.

**Linear Yields**

If a repulsive state is produced at the surface of a molecular solid, atoms are generally ejected. If this state occurs below but close to the surface of a molecular

---

Fig. 3.20. a Ionization pairs formed along path of the incident ion. b Mini-cascades initiated by repulsive recombination of electrons with a molecular ion
solid, the energized atoms produced can transfer their energy collisionally to other target molecules, creating a mini-cascade of collisions, as indicated in Fig. 3.20b, which can cause molecules to be sputtered from a weakly bound solid. These low energy cascades can be incorporated into our earlier description of sputtering. That is, the yield is written as in Eq. (3.11),

$$Y \approx F_e(E_A, \cos \theta_A, 0) \Lambda_e,$$

(3.24a)

where $F_e$ is the electronic energy deposited in the surface regime (e.g., Fig 3.7b) and $\Lambda_e$ the efficiency factor for electronic sputtering. The yield can also be conveniently described in terms of the individual energizing processes (Johnson and Brown 1982),

$$Y = \sum_i \Delta z_e(\Delta E_i)/\lambda_i$$

(3.24b)

as in Eq. (3.10a). Here $\lambda_i^{-1}$ is the mean-free path for excitation of an electronic process which will lead to a repulsive energy $\Delta E_i$ and $\Delta z_e(\Delta E_i)$ is the average sputter depth (Appendix 3B) for this $\Delta E_i$. As typical outer-shell repulsive energies (Chap. 2) of the order of one to a few eV, are comparable to or larger than the cohesive energies of the condensed gas solids, Table 3.4, electronic sputtering occurs from such solids. In semi-conductors and room temperature insulators, which have much larger cohesive energies, multiple excitations or inner shell excitations are required (Brenig and Menzel 1985).

Computer simulations of the cascade of collisions following a few eV repulsive energy input in a condensed-gas solid (Cui et al. 1988, 1989) indicate the ejection occurs from the surface layer and

$$\Delta z_e(\Delta E) \approx 0.15 l_s \frac{\Delta E - U}{U}$$

(3.25a)

with the average layer spacing $l_s \sim n^{-1/3}$. If the $\Delta E_i$ in Eq. (3.24b) are all roughly the same for the principal electronic excitations produced, then

$$Y \approx 0.15 \left( \frac{\Delta E - U}{U} \right) l_s/\lambda_e.$$  

(3.25b)

Here $\lambda_e^{-1}$ is the mean free path for producing an excitation near the surface. For incident electrons and fast ions, ionization is the dominant electronic excitation process (Table 3.2), so that $\lambda_e^{-1} \approx F_e/W_e$, [roughly $W_e^{-1}(dE/dx)_e \cos \theta_A^{-1}$]. Therefore the efficiency factor in Eq. (3.24a) is

$$\Lambda_e \approx 0.15 f_e l_s/U,$$

(3.26)

where $f_e (\approx \Delta E/W_e)$ is the fraction of the electronic energy deposited that goes into repulsive decay (nuclear motion) (Brown and Johnson 1986; Schou 1987). Results for the sputtering of $N_2$ and $O_2$ by fast protons and helium ions in Fig. 3.21a are close to linear at low $(dE/dx)_e$. The size of $f_e$ is $\sim 0.1$ for $N_2$ and
Table 3.4. Electronic sputtering yield parameters

<table>
<thead>
<tr>
<th>Condensed gas</th>
<th>( n_B ) ((10^{22} \text{ mol/cm}^2))</th>
<th>U  ((\text{eV}))</th>
<th>( C_{ef}^2 )</th>
<th>T (^c)</th>
<th>New species ( ^d ) ejected</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CO</td>
<td>2.2</td>
<td>0.088</td>
<td>( 5 \times 10^{-4} )</td>
<td>7–20 K</td>
<td>( \text{O}_2, \text{CO}_2 ) (residue ( \sim 5% ))</td>
</tr>
<tr>
<td>(2) ( \text{O}_2 )</td>
<td>2.4</td>
<td>0.095</td>
<td>( 2 \times 10^{-4} )</td>
<td>8–20 K</td>
<td>( \text{H}_2(\text{D}_2), \text{O}_2 )</td>
</tr>
<tr>
<td>(3) ( \text{N}_2 )</td>
<td>2.2</td>
<td>0.075</td>
<td>( 0.4 \times 10^{-4} )</td>
<td>20 K</td>
<td>( \text{H}_2, \text{N}_2 )</td>
</tr>
<tr>
<td>(4) ( \text{H}_2\text{O(} \text{D}_2\text{O}) )</td>
<td>3.3</td>
<td>0.52</td>
<td>( 8 \times 10^{-4} )</td>
<td>7–77 K</td>
<td>( \text{H}_2(\text{D}_2), \text{O}_2 )</td>
</tr>
<tr>
<td>(5) ( \text{NH}_3 )</td>
<td>2.9</td>
<td>0.31</td>
<td>( 3 \times 10^{-3} )</td>
<td>7–10 K</td>
<td>( \text{H}_2(\text{D}_2), \text{O}_2 )</td>
</tr>
<tr>
<td>(6) ( \text{CH}_4(\text{CD}_4) )</td>
<td>2.7</td>
<td>0.18</td>
<td>( 7 \times 10^{-4} )</td>
<td>7–10 K</td>
<td>( \text{H}_2(\text{D}_2), \text{O}_2 )</td>
</tr>
<tr>
<td>(7) ( \text{SO}_2 )</td>
<td>1.3</td>
<td>0.38</td>
<td>( 5 \times 10^{-4} )</td>
<td>10–70 K</td>
<td>( \text{O}_2, \text{SO}_3 ) (residue ( 10% ), sulfur suboxide)</td>
</tr>
<tr>
<td>(8) ( \text{CO}_2 )</td>
<td>2.3</td>
<td>0.27</td>
<td>( 1 \times 10^{-3} )</td>
<td>7 K</td>
<td>( \text{CO}, \text{O}_2 ) (residue ( \sim 5% ))</td>
</tr>
<tr>
<td>(9) ( \text{CS}_2 )</td>
<td>1.0</td>
<td>0.32</td>
<td>( - )</td>
<td>77 K</td>
<td>( \text{S}_2, \text{S} ) (residue ( \sim 90% ))</td>
</tr>
<tr>
<td>(10) ( \text{S}_8 )</td>
<td>0.45</td>
<td>1.2</td>
<td>( 9 \times 10^{-5} )</td>
<td>150 K</td>
<td>( \text{S}_2, \text{S} ) (polymeric sulfur residue)</td>
</tr>
</tbody>
</table>

\( ^a \)Yield is given in equivalent molecules removed per ion (see also Johnson et al. 1984a).
\( ^b \)Electronic sputtering yields in the quadratic regime [see Eq. (3.27)]. \( Y \approx C_{ef}^2 [I_0(dE/dx)_o/U]^2, I_0 \approx n_B^{-1/3} \). Linear yields have been observed for \( \text{O}_2 \) and \( \text{N}_2 \). Used gas-phase \( dE/dx \).
\( ^c \)Approximation temperature below which results apply, as each species exhibits temperature-dependent regimes.
\( ^d \)The amount of new species and residue produced is strongly temperature- and \( (dE/dx)_o \)-dependent; e.g., for \( \text{S}_8 \) and \( \text{CH}_4 \) protons produce \( \sim 90\% \) residue and little sputtering, but MeV \( \text{He}^+ \) residues are much smaller \( \sim 20\% \). The residue fractions are estimated for energetic protons. Further, with increasing irradiation time the C to H decreases (Fig. 3.11)


\( \textbf{Fig. 3.21.} \) a Sputtering yield vs. \((dE/dx)_o \) of \( \text{N}_2, \text{O}_2, \) and \( \text{CO} \) at 10 K in molecules removed per ion incident by incident \( \text{He}^+ \), (\( \text{He}^+ \)) in an equilibrated charge state (\( \text{He}^++ \)) (Chap. 2) (approximately \( \text{He}^{++} \) at these energies). Yield linear in \((dE/dx)_o \) for \( \text{N}_2 \) and \( \text{O}_2 \) becoming quadratic at high \((dE/dx)_o \). CO shows quadratic dependence down to lowest \((dE/dx)_o \). (Gibbs et al. 1988). b Sputtering yield vs. \((dE/dx)_o \), scaled by \( \text{U} \), the cohesive energy and \( I_0 \), the thickness of a monolayer, for condensed gas solids at 10 K (Table 3.4) and leucine at room temperature, whole leucine molecules ejected. (Hedin et al. 1987) (from Johnson 1990)
\( \sim 0.2 \) for \( \text{O}_2 \) which is consistent with incident electron results (Ellegaard et al. 1986, Pedrys et al. 1989). Since condensed gases at the few monolayer level are generally very nonuniform, the yields are enhanced, as "islands" of material can be ejected by a single ion or electron.

---

**Fig. 3.22.** a Sputtering yield (equivalent molecules removed) vs. \( (dE/dx)_e \) for ions incident on \( \text{H}_2\text{O} \) at low temperatures (\(< 100 \text{ K}\)). Symbols are data sets; line drawn through data proportional to \( (dE/dx)_e^2 \). (Brown et al. 1982b). b Yield as in a for incident \( \text{H}^+ \) (right hand axis) and \( \text{O}^+ \)-like species (left hand axis) vs. ion energy in eV/amu. Symbols for data from various groups; solid lines drawn through data; dashed lines extrapolations based on formulas in text. (Johnson et al. 1988a; data of Christiansen et al. (1986) added (corrected for incident angle))
Sputtering of a Solid: Electronic Stimulation

The expression in Eq. (3.25b) applies also to yields for photon-stimulated sputtering (Harrison and Schoen 1967; Cheng and Johnson 1988; Stuhlen and Knotek 1988). In this case, \( \lambda_e^{-1} \) is the target number density times the photoabsorption cross section to the lowest repulsive or to an excited state which lies above it and \( f_e \sim \Delta E/\hbar \nu \) in Eq. (3.26). The excitation cross sections in the UV are of the order of \( 10^{-17} \) to \( 10^{-18} \) cm\(^2\). Therefore, using \( \Delta E \sim 2\text{eV} \), the photo-sputtering yield is of the order of \( 10^{-2} \) to \( 10^{-3} \).

**Nonlinear Yields**

The yields for small molecules at the higher \( (\text{dE/dx})_e \) shown in Fig. 3.21a and 3.21b go roughly as \( (\text{dE/dx})_e^2 \) if the penetration depth is 'large' due to the overlap of the energized regions at high excitation densities. Therefore the form in Eq. (3.17) has been useful for extrapolating experimental results.

\[
Y_e \approx C_e \left[ f_e \cdot (\text{dE/dx})_e / U \right]^2,
\]  

(3.27)

where \( f_e \) is the fraction of the deposited electronic energy contributing to sputtering (Rook et al. 1985; Gibbs et al. 1988). In Table 3.4 we summarize much of the data available for the electronic sputtering of condensed gases. At higher \( (\text{dE/dx})_e \) a steeper, nearly cubic, dependence on \( (\text{dE/dx})_e \) occurs due to the impluse volume expansion of the material around the track (Johnson et al. 1989b, 1990).

Shown in Fig. 3.22a is the sputtering yield of \( \text{H}_2\text{O} \) at low temperatures, which is, roughly, quadratic in \( (\text{dE/dx})_e \), down to very low \( (\text{dE/dx})_e \). Following
ionization, the electron recombination processes in Eq. (3.8a) produce an energetic H or H\textsubscript{2} (e.g., H\textsubscript{3}O\textsuperscript{+} + e → H\textsubscript{2}O + H, H\textsubscript{2}O\textsuperscript{+} + e → OH + H or O + H\textsubscript{2}). An (∼ 1 eV) H or H\textsubscript{2} produced at the surface will escape, but it is very inefficient at ejecting additional H\textsubscript{2}O molecules which are bounded by ∼0.52 eV. Therefore, more than one excitation is required for sputtering H\textsubscript{2}O at low S\textsubscript{e}. At very high S\textsubscript{e}, a somewhat steeper dependence on S\textsubscript{e} is seen (Cooper and Tombrello 1984; Benit et al. 1987). Large molecules, which are also damaged by the energy deposited (e.g., organic molecules), respond primarily to the impulsive, roughly (dE/dx)\textsubscript{e}\textsuperscript{3}, volume ejection caused by the pressure pulse (Hedin et al. 1987; Fenyo et al. 1989; Cui and Johnson 1989). The leucine data in Fig. 3.21b, which are the yields of whole leucine molecules ejected, exhibit this.

In Fig. 3.22b the results for sputtering of water ice over a broad range of ion energies are presented for incident protons and oxygen-like ions. What is clearly seen is the dependence of S\textsubscript{e} on S\textsubscript{e} at low energies and on S\textsubscript{e} at high energies. In Fig. 3.23 is shown the dependence of the yield on the angle of incidence, θ\textsubscript{A}, for CO at 10 K (Brown et al. 1984). These results are well approximated by

\[
Y(θ\textsubscript{A}) \approx Y(0) \cos θ\textsubscript{A}^{-1.6}.
\]

(3.28)

Similar results have been found for the other condensed gases in the quadratic sputtering regime (Gibbs et al. 1988; Johnson 1989a), and appear to confirm the spike character of the ejection.

Of interest on planetary satellites are the ejection energies of the sputtered molecules. Sample energy distributions are shown in Fig. 3.24. These energies are much lower, on the average, than those predicted in Eq. (3.20a) if U is the
sublimation energy. Such differences are also seen for sputtering of condensed gases when the nuclear stopping dominates the energy loss (e.g., 50 keV Ar\(^+\) in Fig. 3.24). The measured energy distributions appear to be more closely described by the spherical binding condition Eq. (3.20b). Because of deficiencies in the models at small E an empirical “effective” U is often used in Eq. (3.20a) to fit the data (Reimann et al. 1984; Haring 1984c).

For incident electrons, nonlinear yields are also expected when the excitation densities are comparable to those for the ions. Because of the deflection of incident electrons, however, \( F_e \) is not very close to \( (dE/dx)_e \) (Schou, 1987). Because UV photons typically produce single excitations, materials which do not exhibit a linear sputtering regime at a given temperature will not be sputtered efficiently by UV photons. Energetic photons, however, can produce inner shell excitations or multiple excitations. It is also possible for radicals or other new species to be stored in the solid and be acted upon by subsequent photons, as will be discussed, or ejected on warming (d’Hendecourt et al. 1986), therefore the water ice yields for MeV protons at T > 110 K may be linear (Brown et al. 1980b).

**Track Production**

An early ramification of highly ionizing particles penetrating insulators was the use of tracks to identify particles (Fleischer et al. 1975). These tracks are damage paths in a solid and are often directly observable in an electron microscope, but were initially studied using chemical etching. It is assumed that the incident ion
produces a large number of defects and displacement per unit path length in the solid. If this damage density is sufficiently high, the track can be chemically etched to enhance its visibility. In nuclear physics, the track characteristics are associated with a particle type and energy. Because the cosmic rays and solar energetic particle spectra contain highly ionizing particles, tracks can be seen in materials collected from space (Bradley et al. 1984; Taylor 1982). In addition, energetic protons and alpha particles, which do not produce tracks efficiently, can induce nuclear fragmentation, thereby producing track forming particles in the solid. In Fig. 3.25 are indicated the energy and particle types for which tracks appear in typical insulators.

The process of track formation is thought to occur when the level of primary ionization close to the ion’s path is so high that all the molecules in the track core are ionized. This would lead to an explosive outward repulsion of the nuclei of the solid (a pressure pulse), an extreme case for the repulsive decay described earlier. That multiple excitations are required can be inferred from the fact that the materials of interest in Fig. 3.25 are room temperature insulators with sublimation energies $\sim 5\text{eV}$ and even larger bulk displacement energies, $E_D$. Therefore, in a low-temperature condensed gas the effect of a highly ionizing particle can be dramatic. Because the secondary electrons produce ionization at some distance from the ion’s path, the primary ionization rate ($\sim n_0 \sigma_I$) most closely correlates with the onset of track formation in Fig. 3.25. This quantity has a dependence similar to $(dE/dx)_e$ at large velocities.

**Chemical Effects in Sputtering**

The yields described above are measured at low temperatures, where they have been found to be independent of the initial temperature of the condensed gas solid. These yields become temperature-dependent when the temperature is
increased, as seen in Fig. 3.26. In all cases shown, the loss of molecules due to sublimation during the measurements is subtracted from the total loss of material in order to obtain a sputtering yield, (i.e., molecules ejected per incident ion). At higher temperatures, sublimation will eventually dominate sputtering and ion bombardment can enhance the ejection rate (Lanzerotti and Brown 1983).

The temperature dependence observed in Fig. 3.26 is a result of the onset of solid-state chemical reactions between species produced by the incident radiation (Brown et al. 1984). Such reactions were discussed earlier, and the mass spectra measurements of the ejected species confirm that chemical processes occur (deVries et al. 1984a). In Fig. 3.27 are shown the signals for the ejection of masses 20 (\( \text{D}_2\text{O} \)), 32 (\( \text{O}_2 \)) and 4 (\( \text{D}_2 \)) from an initially pure \( \text{D}_2\text{O} \) ice. These are plotted vs irradiation time for 1.5 MeV \( \text{Ne}^+ \) ions incident on the solid (\( \sim 10\,\text{K} \)). The irradiation time is expressed as a fluence, the number of ions incident per unit area, so that the results are independent of beam intensity at low beam intensities.

The \( \text{D}_2\text{O} \) signal in Fig. 3.27 rises "immediately" from zero to a constant value showing no fluence dependence. The radicals produced can react to form species

![Graph](image_url)

**Fig. 3.26.** Yield (molecules per ion incident) vs. sample temperature for incident 1.5 MeV \( \text{He}^+ \) Lines drawn through data. (Brown et al. 1984)
which are more weakly bonded to the solid and are ejected by subsequent ions, as indicated by the fluence dependence of the O\textsubscript{2} and D\textsubscript{2} yields. Whereas the O\textsubscript{2} yield rises from zero linearly, the D\textsubscript{2} yield rises promptly, indicating formation and ejection occur in a single event. It then also exhibits a slow steady rise due to solid-state chemical process. In all these measurements, when the beam is turned off, the signal rapidly decays to zero. When it is turned back on again, the signal immediately returns to that value which it had prior to being turned off. This indicates that the changes produced in the ice by the ions at the observed temperature are permanent over time periods of the order of minutes to hours. We also note that O\textsubscript{2} is readily formed in the solid, so that permanent decomposition of the ice is taking place.

In Fig. 3.28 the temperature dependence of the D\textsubscript{2} and O\textsubscript{2} yields are given at a fluence of $\sim 10^{15}$ ions/cm\textsuperscript{2}. (Such plots, of course, are fluence-dependent.) This clearly indicates that the observed temperature dependence in Fig. 3.26 is due to formation of new species. Using the measured activation energies, $\Delta E_a$, the yield

Fig. 3.27. Energetic ions incident on D\textsubscript{2}O ice. Relative yields (given as a signal in a quadrupole mass spectrometer) vs. irradiation time, given as a fluence of ions. (a) Mass 20 (D\textsubscript{2}O), (b) Mass 4 (D\textsubscript{2}), (c) Mass 32 (O\textsubscript{2}), (d) ion current on to target vs. time. Ion current interrupted for minutes at fluences indicated. Signals all returned indicating material is permanently altered. (Reimann et al. 1984)
Fig. 3.28. Yields (molecules removed per ion incident) vs. D_2O ice temperature. For each data point a fluence \( \sim 10^{13} \text{ ions/cm}^2 \) was used (see Fig. 3.27). Yields are reported in quadruplicate mass spectrometer normalized to absolute yield measurements. (Brown et al. 1982b)

can roughly be written

\[
Y(T) \approx Y(0) + c_1 [I_s (dE/dx)_e/U]^n \exp(-\Delta E_a/kT)
\]

(3.29)

where \( Y(0) \) is the low temperature yield [e.g., Eq. (3.27)] and \( c_1 \) and \( n \) are constants. It is found that \( \Delta E_a \approx 0.05 \) to 0.07 eV for \( \text{O}_2 \) ejection from \( \text{H}_2\text{O} \) with \( n \approx 1 \) (Brown et al. 1980b; Reimann et al. 1984).

For water ice, the end-state species are more easily ejected than the original molecules. That is, \( \text{D}_2 \) is attached to ice with an energy of the order of 0.02 eV and \( \text{O}_2 \) is attached with energies of the order of 0.10 eV, whereas \( \text{H}_2\text{O} \) requires 0.52 eV for removal. In the sputtering process, radicals (e.g., OD) produced by an incident ion and stored in the ice at low temperature are also ejected (Haring et al. 1983; Bar Nun et al. 1985). Even though radicals are produced more efficiently than \( \text{O}_2 \) [see Eqs. (3.8) and (3.9)], they form a much smaller fraction of the yield because of the higher attachment energies to the lattice, consistent with the dependence on \( U \) in Eq. (3.27). This selectivity in the ejection process due to surface bonding enhances the likelihood of formation and ejection of species having saturated bonds and low attachment energies (e.g., \( \text{O}_2 \) and \( \text{D}_2 \)). Therefore, ions, which have even higher removal energies than radicals, exhibit very low yields (\( \sim 10^{-3} \) to \( 10^{-4} \) ion/neutral).
In Fig. 3.29 are shown for 1 keV energy ions incident on ice, the yields of the various masses of neutrals which are ionized and then detected. At these energies, collisional interactions are the dominant dissociation and ejection processes. However, after the dissociation occurs, the subsequent reactions are very nearly independent of the dissociation mechanism. We therefore find chemical alterations similar to those in the electronic sputtering of H$_2$O, but because of the more efficient ejection of material, a larger fraction of radicals is observed (Haring et al. 1983, 1984a,b; Bar-Nun et al. 1985), after correcting for fragmentation due to ionization.

The mass 20 signal in Fig. 3.28 is seen to be independent of temperature up to temperatures close to the point where sublimation becomes important, and is the dominant species ejected at the lower temperatures. At these temperatures electron spin resonance measurements on an irradiated ice clearly indicate the presence of radicals in the solid as discussed (Hart and Platzman 1961). Further, warming the sample makes these radicals mobile and reactive so that the signal disappears ~150 K. In this regard the O$_2$ signal in Fig. 3.27 exhibits two separate regions of increasing signal. One of them is predominant at low temperatures and one at high temperatures. The slopes of these transients vs. the inverse of the temperature are displayed in Fig. 3.30. The activation energies

\[
\text{Ar}^+ \rightarrow \text{H}_2\text{O} + \text{C}^{16}\text{O}
\]

\[
\text{Ar}^+ \rightarrow \text{H}_2\text{O} + \text{C}^{18}\text{O}
\]

\[
\text{Ar}^+ \rightarrow \text{H}_2\text{O} + \text{C}^{16}\text{O}
\]

\[
\text{Ar}^+ \rightarrow \text{D}_2\text{O} + \text{C}^{16}\text{O}
\]

Fig. 3.29. Signals in quadruple mass spectrometer for keV ions on a low temperature mixture of condensed gases, H$_2$O + CO. Isotopes of O are used to identify reaction pathways. Note C$^{18}$O forms in H$_2$$^{18}$O + C$^{16}$O, indicating bonds breaking and reforming. (Haring et al. 1983)
Fig. 3.30. Slope of the $O_2$ yield vs. fluence (Fig. 3.27) plotted vs. $10^3 K/T(K)$ where $T$ is the $D_2O$ ice temperature. Two regions are indicated. In the first $O_2$ form in single ion tracks; in the second tracks overlap to form $O_2$. Processes have similar activation energies (indicated). (Reimann et al. 1984)

indicated by these plots are similar for the two processes, but the onsets in fluence and temperature are quite different. The increase at low temperature is due to $O_2$ forming in the track without significant diffusion. (The $O_2$ so formed is then ejected by a subsequent ion.) As the track radii are of the order of 1 nm, the observed saturation of this component at a fluence of about $10^{14}$ ions/cm$^2$ is understandable. The second rise is predominantly due to the formation of $O_2$ from dissociated species produced by two separate incident particles. Its onset influence occurs when the tracks begin to overlap.
In the second process above, the dissociated species would tend to favor recombination to form ice [e.g., see reactions in Eqs. (3.8)]. However, at all temperatures the D$_2$ signal in Fig. 3.27 saturates at high fluence and then declines. Further, the size of the signal depends on the thickness of the sample. As the incident ion passes through the sample and stops in the substrate, the thickness dependence implies that D$_2$ comes from all depths. Hence, D is being preferentially depleted from the film via the diffusion of D$_2$ to the surface and subsequent loss. Strazzulla et al. (1988) recently related the loss of D$_2$ (H$_2$) to film damage as indicated by increased light scattering (Brown et al. 1978; Johnson et al. 1985). The preferential depletion of D (H) assures the formation of O$_2$ rather than the reconstitution of the D$_2$O (H$_2$O) molecules. This is confirmed by the fact that the rate of decrease in the D$_2$ signal in Fig. 3.27 is close to the rate of increase of O$_2$ at the higher temperatures. O$_2$ once formed also diffuses to the surface, where it is ejected (Reimann et al. 1984; Benit et al. 1988). For ions which stop in a thick ice layer, an equilibrium level of O$_2$ and D$_2$ ejection is obtained (Bar-Nun et al. 1985; Chrisey et al. 1986a).

Even more dramatic changes in the sputtering rates occur when ices containing either carbon or sulfur are bombarded. The yields for CO ejected by keV ions (Chrisey et al. 1986a; Haring et al. 1984a), electrons (Schou et al. 1985), and MeV ions (Chrisey et al. 1989) are strongly fluence-dependent. In addition, the mass spectra indicate that O atoms are lost (via CO$_2$, O$_2$, O) more rapidly than the carbon atoms: ~10% surplus in the rate of loss of O (as O$_2$ and CO$_2$) over that of C. At very high fluences the residual carbon (or carbon suboxide (Chrisey et al. 1989)) is observable as a dark residue with a low sputtering yield. Carbon suboxide is also apparently produced with UV irradiation (Anicich et al. 1989). Similar observations have been made for CH$_4$, other organics, and CO$_2$. Sulfurous residues have been formed after extensive irradiation of CS$_2$, SO$_2$, and H$_2$S (Boring et al. 1985) and SO$_3$ and, probably sulfur suboxide, formed from SO$_2$ (Moore 1984; Boring et al. 1983, 1984a). A few percent of the initial carbon remains behind as a residue when CO is bombarded. This amount is typical of most of the condensed gases except for CS$_2$ and organics such as CH$_4$. For these systems, very little sputtering occurs for incident light ions and the condensed gas is rapidly polymerized and then transformed into a refractory, sputter-resistant solid (Calcagnio et al. 1983b).

The process of polymerization and residue formation can be understood quite simply even if the details cannot be described very accurately. As molecules such

Fig. 3.31. a Ejected D$_2$ from CD$_4$ at 10 K by incident H$^+$ (see Fig. 3.11). A small yield occurs at low fluences and then a threshold is reached beyond which the yield is large until the film is depleted in D. Indicates a change in the material structure (flux-independent) at low temperatures (Brown et al. 1987). b The threshold fluence, given in H$^+$ per cm$^2$ bombarding the CD$_4$ film vs. electronic stopping power, $S_e$. This is the fluence (independent of flux) at which the low temperature film changes structures as in a. Fluence depends nonlinearly on the electronic stopping cross section $S_e$ at the higher $S_e$ but becomes linear at low $S_e$ corresponding to a dose of 53 eV/mol. (Courtesy of L.J. Lanzerotti)
as CH$_4$ are dissociated, carbon atoms are able to form C—C bonds, and H$_2$ is formed as in the case of water ice (i.e., H$_2$ and O—O bonds). A very simple example is 2CH$_4$ → C$_2$H$_4$ + 2H$_2$ or C$_2$H$_6$ + H$_2$. For incident light ions, the larger molecules, C$_2$H$_4$ or C$_2$H$_6$, sputter much less efficiently than CH$_4$ but the H$_2$ is lost easily. Therefore the region penetrated by the radiation is driven to a new mixture of H$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, and radicals in our simplified picture.

In solid methane two additional effects occur. First, H$_2$ and H are not very mobile in CH$_4$. Therefore, the H$_2$ ejected comes primarily from the surface layer until sufficient alteration of the ice occurs (Fig. 3.31a), after which loss of H$_2$ occurs from all depths penetrated by the ion. Second, whereas O$_2$ (or H$_2$O$_2$, O$_3$) saturate the ability of O to bond, in a carbon (or sulfur) containing material polymers can form. Therefore, as hydrogen is continuously lost, first a polymeric material and, eventually, a predominantly carbon material is formed, as suggested in Fig. 3.11. This carbonized material becomes, locally, graphite or diamond-like. Therefore, the presence of a vacuum-solid interface insures an irreversible change in the material. This reverses the gas-phase equilibrium process which led originally to the formation of CH$_4$ and “permanently” separates the C and H. At low (dE/dx)$_e$ and low fluences, $\langle \Phi t \rangle$ ions per unit area, the statistical nature of the interactions [see Eq. (2.2)] is such that the fraction of the carbon converted into sputter-resistant (refractory) material can be written (Calcagno et al. 1985a) as $[1 - \exp(-\sigma_x^{\Phi}(\Phi t))]$. In this expression the “cross-linking” cross section, $\sigma_x$, is roughly, $\sigma_x \approx (S_e/W_x)$ with $W_x \approx 130$ eV. For large fluences $W_x$, gradually increases. Rather than express the alterations as a cross section times a fluence, it has become customary in radiation effects to use doses ($D_M$, in eV/molecule) times the G-values (see Table 3.3; alterations per 100 eV deposited). Therefore the fraction converted is $[1 - \exp(-D_M G)]$ where $D_M = S_e$

$\langle \Phi t \rangle$ and $G = W_x^{-1}$ which is $G \approx 0.6/100$eV for linking of carbon at low doses. This is a G value typically found for 2(CH$_4$) $\rightarrow$ (C$_2$H$_6$) + H$_2$ for incident $\gamma$-rays (Horigome et al. 1978; Johnson 1989d).

Condensed-gas films irradiated at low temperatures deteriorate in quality (Johnson et al. 1985) because of the formation of defects (interior surfaces) which allow H$_2$ to be formed efficiently (Strazzulla et al. 1988). On a stable surface the defects eventually create a path to the full penetration depth of the ions. The refractory film produced by continued sputtering or on warming, although locally dense, is riddled with large voids, forming fairy-castle-like materials (Foti et al. 1984). This means that to the full depth of penetration of the ion, any newly created volatiles have access to the vacuum. It is of more than passing interest, therefore, that polymeric materials may have been identified at Halley (Huebner 1987) and that cometary dust (debris) is an underdense, fluffy material at the submicron level (Kissel et al. 1986). However, the relevance of these organics to space is still controversial (Chyba and Sagan 1988; Wdowiak et al. 1989; Strazzulla and Johnson 1989).

Since all ionizing radiations cause such changes, it is important to make quantitative distinctions between the radiation types. By examining the (dE/dx)$_e$ dependence of the sputtering processes, Brown, Lanzerotti and coworkers have
shown that there are distinct linear and nonlinear regimes. Effects occurring in the linear regime are similar for all ionizing irradiations depending only on the energy absorption cross section as discussed. For the higher \( \langle \text{d}E/\text{d}x \rangle_\text{e} \), nonlinear regimes this is not the case.

Since the threshold dose for the onset of \( \text{H}_2 \) loss given in eV deposited per molecule in Fig. 3.31b becomes constant at low \( \langle \text{d}E/\text{d}x \rangle_\text{e} \) the process is linear. Therefore, very energetic photons and GeV cosmic rays can also produce the modifications in \( \text{CH}_4 \) described above (Johnson 1989d). The size of this dose is \( \sim 60 \text{eV/mol} \), a value close to the average energy lost per primary event produced by the incident ion. The temperature dependent contribution of the sputtering yields by protons also appears to be linear at some fluence, Eq. (3.29) (Brown et al. 1980b).

The alteration of materials also depends on its ability to store radicals over those periods of time of interest in astrophysics. Whereas in the low flux, ion beam experiments at low temperature and high vacuum the diffusion and recombination of radicals was found to be slow on the time scale of the experiments (typically hours), loss of precursor radicals may still occur for the very low fluxes over the long storage times expected in astrophysical applications. Quantitative use of these data, therefore, requires care. Further, data obtained from discharge or very high fluxes of particles or photons cannot be used because heating of the solid is likely to have occurred, enhancing the reactivity. Finally, as the species most readily lost is hydrogen, back reactions of stored radical with available hydrogen (low energy adsorbed \( \text{H}_2 \) or high energy implanted \( \text{H} \)) can inhibit material alteration particularly when photons are the stimulating flux.

Appendix to Chapter 3

A Transport Equations and the Recoil Energy Distribution

In describing the statistics of the energy loss by fast ions or electrons in solids, Monte Carlo calculations are made in which the probabilities are determined by the cross sections in Chapter 2. Alternatively, transport equations, described in the text, are solved. The average collision probability is \( \text{d}\sigma/\sigma \), where \( \text{d}\sigma \) is that part of the total cross section, \( \sigma \), associated with a given range of deflections and energy transfers. Because the classical value of \( \sigma \) is infinite for long-range forces, Eq. (3.3) is often rewritten as

\[
1 = n_0 \int \text{d}\sigma [ \bar{R}_\text{p}(E_A) - \cos \theta \bar{R}_\text{p}(E_A - \Delta E) ],
\]

where \( \theta \) is the deflection associated with energy transfer \( \Delta E \). In this form, when \( \Delta E \to 0 \) (i.e., \( \text{d}\sigma \) becomes large) then substituting \( \bar{R}_\text{p}(E_A - \Delta E) \approx \bar{R}_\text{p}(E_a) + (\text{d}\bar{R}/\text{d}E_A)\Delta E \) and \( \cos \theta \approx 1 \), gives, \( \bar{R}_\text{p} \to \bar{R} \) the continuous slowing-down result in Eq. (3.1). Analytic solutions to Eq. (3A.1) are obtained using cross sections for the power-law potentials in Chapter 2; i.e., \( \bar{R}_\text{p}(E_A) \propto E_A^{-2/n} \) (Sigmund 1981; R.E. Johnson 1982).
The distribution of particles of type i and initial momentum \( \vec{p} \) “stopped” between \( z \) and \( z + dz \) is given by a Boltzman equation in which all the collisions of the moving particles are with target particles which are stationery,

\[
- \cos \theta_A \frac{\partial}{\partial z} F_i(\vec{p}, z) = n_T \int d\sigma \left[ F_i(\vec{p}, z) - \vec{p} \cdot \vec{p}' F_i(\vec{p}', z) \right],
\]

where \( d\sigma = d\sigma(\vec{p}, \vec{p}') \) and \( \cos \theta_A \) is the direction of \( \vec{p} \) relative to the z axis. In this form the contribution to particles stopping between \( z \) and \( z + dz \) is described by the differences between those that change their momentum in this layer from \( \vec{p} \) to \( \vec{p}' \) and those that do not. Therefore, the distribution functions for all particles having momenta less than \( p \) must be obtained in order to find \( F_i(\vec{p}, z) \). The average penetration depth obtained from \( F_i(\vec{p}, z) \) is equal to \( R_p \) as determined from Eq. (3A.1). An equation similar to Eq. (3A.2a) can be constructed to describe the distribution in the energy deposited in the material.

Numerical solutions to Eq. (3A.2a) for the penetration (implantation) distribution are required. However, if the average energy loss in a collision is small compared to the CM energy and the deflections are small (\( \vec{p} \cdot \vec{p}' \approx 1 \), for electronic energy loss \( Q \)), then, using the energy-loss cross section (i.e., \( d\sigma = (d\sigma/dQ)dQ \)), Eq. (3A.2a) can be rewritten in the form

\[
- \cos \theta_A \frac{\partial}{\partial z} F_i(\vec{p}, z) = n_T \int d\sigma \frac{dQ}{dE} \frac{\partial F_i}{\partial E}(\vec{p}, z)
\]

\[
= \left( \frac{dE}{dx} \right) \frac{\partial F_i}{\partial E}(\vec{p}, z).
\]

This is the continuous slowing-down result as \( z \) and \( E \) (or \( p \)) are related by \( (dE/dx) \) so that \( F_i(\vec{p}, z) = \delta(z - R \cos \theta_A) \). That is, all the particles stop at the same depth, \( R \cos \theta_A \). This form for \( F_i \) describes the stopping of fast ions in the electronic energy loss regime and very heavy slow ions stopping in a material consisting of much lighter atoms. At the other extreme, if an incident particle loses most of its forward momentum in a single collision (i.e., \( \vec{p} \cdot \vec{p}' \approx 0 \)), the contribution from scattered particles, \( F_i(\vec{p}', z) \) in Eq. (3A.2a), can be ignored and

\[
- \cos \theta_A \frac{\partial}{\partial z} F_i(\vec{p}, z) = n_T \sigma F_i(\vec{p}, z).
\]

Letting \( \lambda = (n_T \sigma)^{-1} \), the mean free path the first collision, then \( F_i(\vec{p}, z) = F_i(\vec{p}, 0) \exp(-z/\lambda \cos \theta_A) \). This is the penetration distribution in Eq. (2.2). Such a result for \( F_i \) is appropriate for neutron and photon penetration, and is not a bad estimate for low energy electrons or slow light ions in a material of heavy atoms replacing \( \sigma \) by \( \sigma_\delta \), the diffusion cross section of Chapter 2.

In Eq. (3A.2a) we gave the energy distribution of target atoms set in motion by a primary target recoil of energy \( E_A \) stopping in a gas composed of atoms of the same mass, which is the basis for many of the results obtained on multiple collision phenomena in Chapters 3 and 4. Calling \( G(E_A, E)dE \) the number of
recoils produced with energy between E and E + dE by a particle of energy \( E_A \) and the same mass, then
\[
G(E_A, E) = (d\sigma/dE)/\sigma + \int \left[ \frac{(d\sigma/dT)/\sigma}{G(E_A - T, E) + G(T, E)} \right] dT. \tag{3A.3}
\]
Here \((d\sigma/dT)/\sigma\) is the probability that in the first collision the particle \( E_A \) loses energy \( T \). Therefore, the first term is the probability of producing a recoil in the appropriate energy range, and the next term is a sum of the subsequent recoils produced by the two colliding species, integrated over all possible energy transfers. This is solved subject to the boundary condition that \( G(T, E) = 0 \) for \( T \leq E \). For the simple hard sphere collision (Chapter 2) \((d\sigma/dT)/\sigma = (\gamma E_A)^{-1}\) with \( \gamma = 1 \) for equal mass, the result is \( G(E_A, E) = E_A/E^2 \) as can be verified by substitution in Eq. (3A.3). For realistic classical cross sections, \( \sigma \to \infty \), so Eq. (3A.3) is written in the form of Eq. (3A.1). Sigmund (1969) has shown that, for the power law potentials in Chapter 2, \((d\sigma/dT) = (C_{\alpha}/E_A^n)/T^{1+n}\), the lead term is \( G(E_A, E) \approx \beta_n(E_A/E^2) \) with \( \beta_n = 6/\pi^2 \).

B Cascade Sputtering

In Eq. (3.10a) and Eq. (3.24b) are expressions for sputtering in a solid in which an amount of kinetic energy, \( \Delta E_i \), is imparted to the atoms or molecules either directly via nuclear elastic collision or indirectly, via repulsive electronic relaxation (electronic sputtering). Defining the yield from an event at depth \( z \) in the solid as \( Y(\Delta E_i, z) \), then
\[
\Delta z_s(\Delta E_i) = \int_0^z d\tilde{z} \, Y(\Delta E_i, \tilde{z}). \tag{3B.1}
\]
Therefore, the average yield when such events occur randomly with depth (but with a very small probability of overlapping) is
\[
Y(\Delta E_i) = \frac{\Delta z_s(\Delta E_i)}{\lambda_i}, \tag{3B.2}
\]
where \( \lambda_i \) is the average spacing of the excitations (Johnson and Brown 1982). \( Y(\Delta E_i, z) \), hence \( \Delta z_s \), is calculated using the escape probabilities defined for Eq. (3.13a) and the recoil spectrum above. That is, a recoil atom of energy \( \epsilon' \) generated near \( z \) can escape if it produces no additional recoils while exiting the solid. If the recoils are produced isotopically
\[
\Delta z_s \approx \int_0^\infty dz \int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} G(\Delta E_i, \epsilon') \cos \theta d\phi d\cos \theta d\epsilon'. \tag{3B.3}
\]
Here \( G \) is the number of recoils produced by an event of energy \( \Delta E_i \) [Eqs. (3.5) and (3A.3)] and \( \Theta(x) \) is a step function, indicating that the depth of origin of an escaping recoil is less than the mean-free path for a collision. Finally, \( P_{\epsilon, i} \) is
the planar or spherical binding condition [e.g., either Eq. (3.13b) or (3.14a)]. For $\Delta E_i \gg U$, this integrates to

$$\overline{\Delta z_s(\Delta E_i)} \approx \left( \frac{\beta_n v(\Delta E_i) \overline{r_d}}{2U} \right) \left\{ \begin{array}{ll} \frac{1}{2}, & \text{planar} \\ \frac{1}{3}, & \text{spherical} \end{array} \right. \quad (3B.4)$$

Sigmund (1969) uses a factor of two reduction in $G$ because of the presence of a surface. This gives the result in Eq. (3.15) and the sputtered energy distribution in Eq. (3.20a) is obtained by not carrying out the integral over $\varepsilon'$.

### C Spike Sputtering

If the energy density deposited by the incident ion is high, then, following the initial cascade of collisions, energy is dispersed by diffusion. Calling the kinetic energy density at time $t$ and position $\overline{r}, \varepsilon(\overline{r}, t)$, then

$$\nabla(\kappa(\varepsilon) \nabla \varepsilon) - \varepsilon/\tau = \partial \varepsilon/\partial t \quad (3C.1)$$

describes this process. Here $\kappa(\varepsilon)$ is the diffusivity, which in the gas phase is determined by the elastic collision cross sections in Chapter 2 and $\tau$ is a dissipation time. Analytic solutions are useful for $\varepsilon$ in an infinite material assuming either spherical or cylindrical symmetry and $\kappa(\varepsilon) = \kappa_0$ (Vineyard 1976; Johnson and Evatt 1980; Sigmund and Claussen 1981; Johnson 1989a).

For a solid, the surface is approximated in two ways. If the escape rate of molecules is large, the effect of the surface on $\varepsilon$ is ignored; if it is very small, the surface is treated as an energy reflector. Using the value of $\varepsilon$ at the surface, $\varepsilon_s$, the flux of material, $\Phi$, is obtained assuming a form for the energy distribution about $\varepsilon_s$. If the molecules are in local thermodynamic equilibrium, then the sublimation flux can be obtained from the vapor pressure, $P(T_s)$, at the surface:

$$\varepsilon_s \approx (3/2)n_k kT_s \quad \text{and} \quad \Phi(T_s) \approx P(T_s) \exp(-U/kT_s)/(2\pi M_b kT_s)^{1/2}.$$ For a randomly deposited spherical or point energy input of size $\Delta E_i$ with $\tau \to \infty$, $\Delta z_s$ of Eq. (3B.2) is

$$\overline{\Delta z_s(\Delta E_i)} = \frac{1}{2} \int d^3r \int_0^\infty dt \Phi(T_s(\overline{r}, t)) \propto \Delta E_i^{5/3}. \quad (3C.2)$$

For a narrow cylindrically symmetric energy deposition (closely spaced $\Delta E_i$) about the path of an ion

$$Y = \int d^2r \int_0^\infty dt \Phi(T_s) \propto (\Delta E_i/\lambda_i)^2 \propto (dE/dx)^2 \quad (3C.3)$$
as $\varepsilon_s$ (hence $T_s$) depends on the number of excitations per unit path length $\lambda_i^{-1}$. The latter result has been used in the text to discuss the measured yields Eq. (3.16). The incident angle dependence, Eq. (3.28), has been confirmed for condensed-gas solids (Johnson 1989a). The energy distribution of ejecta can be obtained letting $Y \to Y(E)$ and $\Phi(T_s) \to \Phi(T_s) \cdot \left[E^{1/2} \exp(-E/kT_s)/\pi^{1/2}(kT_s)^{3/2}\right]$.
in Eq. (3C.3). If the initial radius of the energy deposition is small, then, using planar binding, \( Y(E) \propto E/(E + U)^{4} \) for the cylindrical case, and for the nonoverlapping point sources \( Y \propto E/(E + U)^{10/3} \). The latter is not very different from the cascade result \( E/(E + U)^{3} \). The spike yields have been heavily discussed in the sputtering literature (Sigmund 1981; Kelly 1987) but not extensively verified. However, they provide a useful way of thinking about the low-energy contribution to the ejecta. Leger et al. (1985) use a spike model to discuss interstellar grain erosion. At very high \( (dE/dx) \) the gradient in \( \varepsilon \) gives a momentum to a volume at the surface. For normal incidence this ejects a hemi-spherical volume with radius proportional to \( (dE/dx) \) (Fenyő et al. 1989; Johnson et al. 1989b; Cui and Johnson 1989).