A NEW MODEL FOR COSMIC-RAY ION EROSION OF VOLATILES FROM GRAINS IN THE INTERSTELLAR MEDIUM

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ABSTRACT

Erosion of small grains or grain mantles is important in a number of astrophysical environments. Since energy deposition events produced by energetic ions can create a "hot" region in a grain, simple thermal spike models have been applied to estimate the sputtering efficiency. Here the results of molecular dynamics (MD) simulations are used to describe sputtering from the "heat spike" formed by a heavy cosmic-ray (CR) ion. These results are compared to extrapolations of laboratory sputtering data for frozen volatiles and to earlier models for CR ion-induced desorption. The CO and H$_2$O desorption rates for thick mantles or for whole volatile grains are given and are found to disagree with results obtained using heat spike models. Further, the rates are an order of magnitude smaller and an order of magnitude larger, respectively, than the rates typically used for desorption of CO and H$_2$O from a thin mantle on a 0.1 $\mu$m silicate core in a molecular cloud. The model given here can now be used for calculating energetic ion-induced desorption from grains in a variety of astrophysical environments and of other compositions and sizes.

Subject headings: astrochemistry — cosmic rays — dust, extinction — molecular processes

1. INTRODUCTION

In dense clouds in the interstellar medium (ISM), grains acquire a mantle of condensed molecules (Charnley et al. 2001; Greenberg & Shen 2000). These mantles are in turn eroded (sputtered) by the local plasma, photons, grain-grain collisions, or cosmic-ray ions. That is, a loss process competes with mantle growth by accretion; otherwise molecular clouds would be devoid of gases (Charnley et al. 2001). Similarly, in certain cold regions of young stellar objects (YSOs), more gas-phase CO is seen than expected, suggesting a stimulated desorption process is occurring (Hasegawa & Herbst 1993). Heavy cosmic-ray (CR) ions are thought to be the best candidate for mantle desorption in molecular clouds (Willacy & Williams 1993; Bergin et al. 1995; Shematovich, Shustov, & Wiebe 1997; Nguyen et al. 2002), whereas X-rays have been suggested as a likely desorption agent in YSOs (Glassgold, Feigelson, & Montmerle 1999).

Models for erosion of grain mantles typically assume the energy deposited forms a "hot spot" at the surface from which condensed species evaporate (Watson & Salpeter 1972; Leger et al. 1985). Such models are referred to as thermal spike models and have been extensively applied in describing desorption (sputtering) processes (Sigmund & Claussen 1981; Johnson & Brown 1982; Johnson & Schou 1993). Recently, spike models have been tested both experimentally and by modern computational simulations of the transport of energy in a solid (Bringa & Johnson 2000). We use these results to show that the models typically used for mantle erosion are incorrect. However, because of cancellation of errors, the predictions are often reasonable. Here we give a model for mantle erosion by "spot" heating. We then use that model and extrapolations of laboratory data for fast ions to give new estimates of the desorption yields for describing CR ion erosion of volatiles. Results are given for CO and H$_2$O and are applicable to thick mantles on a grain and to grains consisting of frozen volatiles.

2. CR ION DESORPTION

There have been a number of studies of the desorption produced by CR ions penetrating a cold region of space (Watson & Salpeter 1972; Leger et al. 1985; Hasegawa & Herbst 1993; Kalinichenko et al. 1996). The light ions (H$^+$, He$^{++}$) cause little direct desorption but produce photons in gas-phase collisions. These photons can in turn produce desorption (Westley et al. 1995). However, a heavy CR ion penetrating a grain can directly cause ejection of significant amounts of material from the surface of a grain. That is, although such impacts are rare (every $\sim 10^{13}$ s), the net effect can be considerable. This process has been described analytically using simplified spatial distributions of deposited energy along with analytic thermal spike models of desorption by Leger et al. (1985, hereafter LJO85) and Hasegawa & Herbst (1993, hereafter HH93).

After a heavy ion penetrates a grain, the sputtering yield, $Y$, defined as the number of molecules ejected per impact, is determined by the following sequence of events. The times given are very rough and depend on the material and the incident ion parameters:

1. $10^{-17} - 10^{-15}$ s. Excitations and ionizations are produced over a region with a radius of the order of 100 Å, creating a shower of electrons that produce further ionizations (Paretzke et al. 1995).

2. $10^{-13} - 10^{-11}$ s. When the excitations relax or the ionization sites neutralize, hot atoms (up to a few eV) are produced (Johnson et al. 1991b; Johnson & Schou 1993). At the surface, these can cause prompt desorption (sputtering), $Y_{\text{prompt}}$. 

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At low ionization densities, the statistics of the energy release events determine the average yield. At high ionization densities, a “heat spike” is rapidly formed, producing a melt and a pressure pulse (Bringa et al. 1999a, 1999b) that carries away a significant fraction of the deposited energy.

3. $10^{-11} - 10^{-9}$ s. Following the cooling of the energetic recoils, thermal diffusion and evaporation determine the yield, $Y_{\text{th-early}}$. This is often referred to as “thermal spike sputtering” and was used to describe spot heating in LJO85.

4. $10^{-9} - 10^{-5}$ s. Finally, the temperature in a small grain becomes roughly uniform and decreases gradually through evaporative cooling. For a small grain, this can give a large contribution to the yield, $Y_{\text{th-late}}$, referred to as whole-grain heating in HH93 and LJO85.

The total sputtering yield is then

$$Y = Y_{\text{prompt}} + Y_{\text{th-early}} + Y_{\text{th-late}}. \quad (1)$$

2.1. Spot Heating

In their spot heating model, LJO85 assume a CR ion penetrating a grain of radius $a$ releases on average an energy $\Delta E$, forming a cylindrical heat spike of radius, $r_{\text{cyl}}$. To accurately simulate the sputtering produced from a cylindrical heat spike, we have carried out molecular dynamics (MD) (Bringa et al. 1999b, 1999a; Bringa & Johnson 2000) and hydrodynamic (Jakas & Brino 2000; Jakas, Bringa, & Johnson 2002) simulations of the energy transport and desorption in low-temperature condensed gas solids. Because of sample size limitations, the MD simulations describe times $\lesssim 0.5 \times 10^{-9}$ s and, therefore, determine the first two contributions in equation (1), $Y_{\text{MD}} = Y_{\text{prompt}} + Y_{\text{th-early}}$. If the grain survives, then its average temperature, $T_f$, at the end of the simulation can be determined. Typically $k_B T_f \ll U$, where $U$ is the cohesive energy per molecule of the grain. The value of $T_f$ can then be used as input to a thermal evaporation model to determine $Y_{\text{th-late}}$.

The details of the simulations are described elsewhere (Bringa & Johnson 2002, 2000). Because MD simulations are computationally intensive, we use scaling to extend the results to a variety of materials (Bringa et al. 1999b). That is, the $Y_{\text{MD}}$ yields scale with $U$ and the mean molecular separation, $l = n^{-1/3}$, where $n$ is the molecular number density. Since energy deposition events are actually statistically distributed along the CR ion’s path, the spot heating model in LJO85 is intended to represent an average impact. Earlier, we determined the effect of such statistics on the erosion of small refractory grains in a shocked gas (Jurac et al. 1998) and on the erosion of ice grains in a hot (keV–MeV) plasma (Jurac et al. 2001). We return to this later when we describe the experimental results. Below we give expressions for $Y_{\text{MD}}$ as a function of excitation density, track radius, and grain size for an ion at normal incidence piercing the grain center. As in LJO85, we use an average energy release per unit path length in the grain, $(dE/dx)_{\text{eff}} = \Delta E/2a$.

Figure 1 shows schematically the regimes for sputtering by a cylindrical heat spike with width $r_{\text{cyl}} \leq a/3$. The $x$-axis is the grain radius, $a$, and the $y$-axis is the energy deposited in the cylindrically excited region per unit path length, $(dE/dx)_{\text{eff}}$. These are scaled by the cohesive energy, $U$, and the mean molecular separation, $l$. In region I, $\Delta E$ is sufficient to completely destroy the grain. The minimum energy necessary to melt the whole grain, which gives the boundary of region I, is $f \Delta E \geq N_C T_m$, where $T_m$ is the melting temperature, $N_C$ is the number of molecules in the grain $n 4\pi a^2/3$, and $(1 - f)$ is the fraction of the energy that leaves via prompt ejecta. For the frozen gases in the MD simulations, $k_B T_m \approx 0.1 U$, and we find that $f \approx \exp \left[-4(\Delta E/N_C U) + 0.2\right]$ for $\Delta E/N_C \gtrsim 0.05U$ and $f \approx 1$ otherwise. In regions II and III, the grain is large enough or the energy deposition low enough that disruption does not occur. Writing the ratio of the excitation density in the cylindrical spike to the cohesive energy density of the material, $\xi = [(dE/dx)_{\text{eff}}/\pi r_{\text{cyl}}^2] / (n U)$, then region II applies to small energy densities ($\xi < 1$). The boundary between regions II and III, $\xi = 1$, is given by the horizontal line in Figure 1, and its position depends on the value of $r_{\text{cyl}}/l$. In region II, the yield can be calculated from analytic thermal spike models (Sigmund & Clausen 1981; Johnson & Schou 1993):

$$Y_{\text{MD}} \approx Y_{\text{th-early}} \approx \zeta A n^{1/4} r_{\text{cyl}}^2 \exp(-1.5/\xi),$$

$$\xi \ll 1; \quad A = 0.124 \text{ Å}^2. \quad (2)$$

In region III, ($\xi \gtrsim 1$), the yield from the MD simulations for a molecular solid (Bringa & Johnson 2000) can be approximated by

$$Y_{\text{MD}} \approx 0.1 (r_{\text{cyl}}/U) (dE/dx)_{\text{eff}}. \quad (3)$$

In these equations, $\zeta = 1$ at normal incidence for large grains. The variable $\zeta$ increases with incidence angle and with decreasing grain size (Jurac et al. 1998).

Although LJO85 used an expression like that in equation (3), the similarity is fortuitous. If the heat transport in the grain is determined only by thermal diffusion, as they assume, then it is well established that the yield is quadratic in $(dE/dx)_{\text{eff}}$ at large $\xi$ as in equation (2) (Johnson et al. 1991b; Jakas 2000) and not linear as they assume. However, transport is not diffusive at the energy densities typically deposited by a CR iron ion. Transport is determined by a pressure pulse and a melt, giving the approximate expression for $Y_{\text{MD}}$ in equation (3).

In region IV, the finite size of the grain is also important. In this region, the yields calculated using equations (2) or (3) can be used to obtain lower bounds to the actual yield. Simulations for a grain of radius, $a \approx 0.013$ µm (Bringa &
Johnson 2002) indicate that the grain size effect is small for \( \xi \ll 1 \). However, \( \zeta \) (in eq.[3]) is about 5 for \( \xi > 1 \), eventually leading to complete destruction (region I, Fig. 1). The boundary between regions III and IV is determined by the grain curvature. For energy release events producing recoils of \( \sim 1 \) eV in a thick CO mantle, the escape depth (Bringa 1999) is roughly \( 10^4 \) Å, therefore, for the \( r_{\text{cyl}} \) used in LJO85, finite size effects on \( Y_{\text{MD}} \) are unimportant for \( a \sim 0.02 \) μm. The yield \( Y_{\text{th-late}} \) determined by whole-grain heating, depends, by definition, on the grain size as discussed below.

2.2. Whole Grain Heating

At the end of the MD simulations for a semi-infinite sample, the surface temperature is low, and the deposited energy is distributed over distances of nearly 1 μm. In such samples, the evaporation is complete. This is not the case for a small grain. Because radiative cooling is slow, the temperature at the end of the MD simulations, \( T_f \), can be used to estimate the whole-grain heating contribution to the yield as discussed. The yield in HH93 can be written (see Appendix) as

\[
Y_{\text{th-late}} \approx N_s t_{pb} k_{\text{evap}}(T_f),
\]

where \( k_{\text{evap}}(T_f) \) is the probability per unit time of a molecule evaporating at temperature \( T_f \), \( N_s \) is the number of surface molecules on the grain, and \( t_{pb} \) is an average desorption time. Based on the MD simulations (Bringa & Johnson 2002), \( T_f \) can roughly be determined from the fraction of the deposited energy remaining in the grain, \( f \Delta E \approx N_s C T_f \). For a size appropriate to a grain in a molecular cloud, \( \sim 0.1 \) μm, “heated” by a heavy CR ion, \( Y_{\text{th-late}} \) can be significant for a volatile species like CO but not for H2O. Below we first use MD simulations to calculate the yield for the hot spot and whole-grain heating by a CR ion. We then compare these results to those obtained by extrapolating measured yields.

2.3. Total Yield

CR ions deposit their energy primarily in ionization events as discussed. Therefore, at low excitation density, the prompt component is determined by the statistical distribution of such events near the surface. Approximating this by spot heating, as in LJO85, is only valid at high excitation densities and requires knowledge of both \( r_{\text{cyl}} \) and \( (dE/dx)_{\text{eff}} \) in equation (3). The average energy deposited per unit path length deposited in a solid by a fast ion, \( dE/dx \), can be obtained from freeware programs like SRIM 2000 (Ziegler 2000).\(^2\) However, the fraction of that energy that goes into prompt molecular motion in the solid, \( (dE/dx)_{\text{eff}} \), is not well known. Estimates range from \( \sim 10\% \) to 50% (Johnson & Brown 1982; Johnson & Schou 1993; Szenes 1995), with a fraction contributing to luminescence and the remaining heat spatially distributed by the cooling electrons. In addition, \( r_{\text{cyl}} \) varies with incident velocity (Bringa & Johnson 2000). For a CR iron ion penetrating a grain, LJO85 assumed unit efficiency and a fixed effective radius \( \sim 50 \) Å in their “spot” heating model. They suggest that \( \sim 40\% \) of the energy is lost by fast secondary electrons exiting from a 0.1 μm grain. They also use a correction factor of \( \sim 2 \) to account for nonnormal incidence, so that \( (dE/dx)_{\text{eff}} \approx 1.2(dE/dx) \). In a previous publication, we found that sputtering at the entrance and exit points and grazing incidence increased the average yield by a factor somewhat larger than that estimated in LJO85 (\( \geq 2.6 \); Jurac et al. 2001). Although the very energetic secondary electrons produced by the incident CR ions can remove energy from the grain (Leger et al. 1985), the yield is determined primarily by near-surface events. Therefore, the correction for that loss is probably smaller than the 40% suggested in LJO85. Increases in the yield of about a factor of 2 are more likely; therefore, in equation (3), we write \( (dE/dx)_{\text{eff}} \approx 2(dE/dx) \). We have used \( \zeta \) in equations (2) and (3).

The MD results for the sputtering of H2O and CO grains, using the initial radius assumed in LJO85, are used to give the total yield in equation (1). These are shown in Figure 2.\(^3\) The range of deposited \( dE/dx \) applicable to the CR iron impact extends over regions II and III in Figure 1 for 0.1 μm grains and the track parameters in LJO85. For fixed initial track radius, the yield for spot heating exhibits a steep “threshold,” the onset of which can be described using equation (2) (region II). The steep increase in the yield is seen to saturate at higher \( dE/dx \) through melting and energy removal by the pressure pulse and surface ejection. At these \( dE/dx \), the whole-grain heating increase occurs at higher \( dE/dx \) than that displayed in Figure 2.

Also shown in Figure 2 are the results from LJO85 and HH93 converted to a yield per CR impact. To describe

\[^2\] Available at http://www.srim.org/.

\[^3\] See http://www.people.virginia.edu/~rej/yieldfit.html.
whole-grain heating, HH93 noted that only the lowest energy CR iron impacts deposit enough energy to obtain significant desorption by whole-grain heating. They estimated that ~5% of the impacts resulted in \( T_e \approx 70 \) K in a 0.1 \( \mu m \) silicate or water ice grain, giving the value of \( dE/dx \) in Figure 2. They also assume that the CO mantle erosion is determined by the thermal properties of the grain core, which is taken be a silicate. Their result is larger than the yields obtained from our MD simulations. We describe a whole CO grain or a very thick mantle in which the thermal properties of CO rather than those of the silicate core determine the temperature. For H2O, they used a value of \( U \) that is about a factor of 3 too small. Using the correct \( U \) in their model, the yield would be many orders of magnitude lower than that in Figure 2 because of the exponential nature of the desorption rate (see Appendix).

In LJO85 an expression, \( Y \approx R_c \zeta (dE/dx)_{\text{eff}}/U \), was assumed to describe the sputtering yield, where \( R_c \) is an effective spike radius during ejection. They estimated \( R_c \) to be 150 and 6 A for CO and H2O, respectively, resulting in the solid lines in Figure 2. For CO, their yield is an order of magnitude too large over the range of relevant \( dE/dx \). MD simulations show that \( R_c \) should roughly be \( \sim r_{\text{cyl}}^{1/2} \) (Bringa et al. 2002). For H2O, their yield does not exhibit the steep decrease at low \( dE/dx \), but over the relevant \( dE/dx \), it fortuitously overlaps the yields obtained from equation (1).

### 2.4. Measured Yields

Measured yields are needed to calibrate the models, because of the significant uncertainties in determining the distribution of energy release following the passage of a fast ion through a solid. Measurements for the sputtering of low-temperature condensed gas solids by fast ions are not available in the velocity range of interest; therefore we use extrapolations based on models for sputtering (Johnson 1998; see also footnote 3).

The extrapolations used are rough lower bounds to the yield for three reasons. First, CR ions make deep excitations more efficiently than the MeV ions for which data are available. Such excitations occurring at the surface can directly lead to significant desorption. Second, surface species adsorbed at low temperature and not annealed can be easily ejected. Third, the late thermal yield component does not contribute to the experimental yields, since measurements are made on large samples and not on small isolated grains (see Fig. 1). Ignoring these enhancements, the extrapolated yields are given in Figure 2 as a function of \( dE/dx \) for normal incidence. Measurements have shown that such yields apply to mantles with thickness greater than a few monolayers (Johnson et al. 1991b; Johnson & Schou 1993).

From the extrapolated measurements, the concept of a cylindrical thermal spike (spot heating) fails at the lowest \( dE/dx \) for the water ice data. That is, by averaging the energy deposition over the cylindrical region, even the best MD simulations of a spike cannot reproduce the dependence of the measured yields on the energy deposition. This happens because energetic energy deposition events occurring near the surface directly produce sputtering in a low cohesive energy solid, even when the \textit{average} energy deposition density is small. Therefore, the statistics of the excitation events are critical at low \( dE/dx \) (Johnson et al. 1991b; Johnson & Schou 1993; Bringa & Johnson 2000). For H2O, the low-excitation density region has significant overlap with the range of CR ion energies, so a spot heating model is only appropriate at high-excitation densities if the dependence of \( r_{\text{cyl}} \) on ion velocity is included (Bringa & Johnson 2000). Fortuitously, there is again rough agreement between the LIJO85 yield and the yield based on the measurements. This is not the case for the much more volatile CO grains. The yields given by LIJO85 are more than an order of magnitude too large at the relevant \( dE/dx \). However, the model parameters from LIJO85 used in the MD simulations give rough agreement with experiment for a range of \( (dE/dx)_{\text{eff}} \). This suggests that sputtering can be reasonably described by MD simulations of a cylindrical heat spike over a range of \( (dE/dx)_{\text{eff}} \).

### 2.5. Erosion Rates

To determine desorption rates, we have integrated our extrapolated yields over the CR ion energy spectrum, \( \phi(\varepsilon) \), with the functional form suggested by LIJO85 where \( \varepsilon \) is the energy per nucleon. The units of \( \phi(\varepsilon) \) are CR (cm² ster s GeV/nucleon)⁻¹. (Note that the vertical axes in Figs. 4 and 5 of LIJO85 should be in (GeV/nucleon)⁻¹ and not GeV⁻¹.)

The time between impacts for a grain with radius \( a \) is

\[
t = \left[ 4\pi^2 a^2 \int_{\varepsilon_{\text{min}}}^{\varepsilon_{\text{max}}} \phi(\varepsilon) d\varepsilon \right]^{-1}.
\]

(5)

As in HH93, we calculated a desorption rate per molecule (see Appendix):

\[
k_{\text{erd}} = 4\pi^2 a^2 \frac{\int_{\varepsilon_{\text{min}}}^{\varepsilon_{\text{max}}} Y(\varepsilon) \phi(\varepsilon) d\varepsilon}{N_e}.
\]

(6)

where \( N_e \) is the total number of molecules on the surface layer. LIJO85 use \( \varepsilon_{\text{min}} = 0.02 \) GeV per nucleon (~1 GeV for Fe), because of the interstellar cloud modulation and \( \varepsilon_{\text{max}} = \infty \). HH93 used the same \( \varepsilon_{\text{min}} \) but assumed that, for \( \varepsilon > 0.07 \) (~4 GeV for Fe), desorption is not significant. This corresponds roughly to 5% of the impacts. We used \( \varepsilon_{\text{max}} = 2 \) (~100 GeV for Fe), since, beyond 100 GeV, relativistic effects may be important. Using \( \varepsilon_{\text{max}} = 10 \) changed \( k_{\text{erd}} \) by less than 1%. On the other hand, using \( \varepsilon_{\text{max}} = 0.07 \), as in HH93, decreased \( k_{\text{erd}} \) by 25%–80%. Impact times and desorption rates are given in Table 1 for a grain with radius \( a = 0.1 \) \( \mu m \). Note that the maximum in the electronic stopping power of Fe is located at roughly 0.065 GeV for both H2O and CO, i.e., \( \sim \)0.0011 GeV per nucleon.

These impact times imply that, in a cloud with a lifetime of 10⁷ yr, a grain experiences an energy deposition event, on average, from about 1 to 20 times, depending on the cutoff \( \varepsilon_{\text{max}} \) used. The rates in Table 1 obtained using the MD model and the experimental data are similar, since the principal contribution is from high \( dE/dx \) or low velocities. The rates for producing gas-phase molecules are an order of magnitude lower than those in HH93 for CO and more than an order of

### TABLE 1

<table>
<thead>
<tr>
<th>Method</th>
<th>( t_s ) (s/Fe)</th>
<th>( k_{\text{erd}} ) (H2O) (s⁻¹)</th>
<th>( k_{\text{erd}} ) (CO) (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD (eq. [1], ( \varepsilon_{\text{max}} = 2 ))</td>
<td>( 1.8 \times 10^{12} )</td>
<td>( 6.8 \times 10^{-17} )</td>
<td>( 9.8 \times 10^{-16} )</td>
</tr>
<tr>
<td>Exp.</td>
<td>( \varepsilon_{\text{max}} = 2 )</td>
<td>( 1.8 \times 10^{12} )</td>
<td>( 4.4 \times 10^{-17} )</td>
</tr>
<tr>
<td>HH93 (( \varepsilon_{\text{max}} = 0.07 ))</td>
<td>( 3.2 \times 10^{13} )</td>
<td>( 1.4 \times 10^{-18} )</td>
<td>( 9.8 \times 10^{-15} )</td>
</tr>
</tbody>
</table>

a Desorption rates using the extrapolations to the experimental values.
magnitude higher for H$_2$O. In our calculations, the whole-grain heating component, $Y_{\text{th-late}}$, is small for both H$_2$O and CO, so that whole-grain heating does not contribute for a thick volatile mantle or a volatile grain. It is important to remember that the desorption rates in HH93 are estimated for CO mantles on a silicate core and not for a volatile grain. In the former, the energy deposition in the core and the thermal properties of the core are used to determine the heat capacity and thermal desorption rate. The yield for NH$_3$, for which there are only a few measurements, can be roughly estimated by scaling to the H$_2$O yield inversely with the square of $U$ (Johnson et al. 1991b; Johnson & Schou 1993; Bringa & Johnson 2000). Expressions have also been given for mixed ices (Johnson 1990).

3. SUMMARY

In this paper, we present results from MD simulations of the sputtering of frozen volatiles. These are applied to sputtering of volatile grains and thick mantles on grains in molecular clouds from so-called spot heating by a heavy CR ion. We have also used extrapolations of laboratory measurements to estimate the sputtering efficiencies. We show that, at low excitation densities ($\xi \ll 1$ in eq. [2]), spike models cannot be used to represent the sputtering data. In this region, experiments show that the probability of energetic energy release events occurring near the grain surface determines the yield. When the energy density in the track is high, $\xi \gtrsim 1$, the sputtering of a grain consists of two contributions. The first can be described using the results from the MD simulations in equation (3). The second contribution can be described as a late thermal evaporation process determined by the average grain temperature (whole-grain heating). The MD simulations indicate that the prompt ejecta can carry off a significant fraction of the deposited energy. Whereas the late, whole-grain yield expression scales as $\exp(-U)$, laboratory data indicate that the prompt yield scales as $U^{-m}$ with $m \approx 2$ (Johnson et al. 1991b; Johnson 1990; Bringa & Johnson 2000; Johnson & Schou 1993). Therefore, the prompt yield can be significant, even for ices with relatively high binding energy like water ice or ammonia. Because of the statistics of the energy deposition events, heavy CR ion impacts can even cause the ejection of large organic molecules, as pointed out earlier (Johnson et al. 1991a; Fenyő & Johnson 1992).

The yields based on the experimental extrapolations are lower than the LJO85 estimates for both H$_2$O and CO grains, except at the highest excitation densities considered here. The new estimates of the sputtering yield for H$_2$O and CO surfaces are averaged over the CR iron flux in a molecular cloud. The desorption rates in Table 1 are determined primarily by the low energy ions for which the $dE/dx$ and the yields are largest and, therefore, they will be significantly affected by the assumed modulation of the CR ion flux. At the edge of the molecular cloud where CR with energies below 1 GeV may penetrate, desorption will be enhanced.

For the CR iron penetration flux used in both HH93 and LJO85, the extrapolated experimental yield gives desorption rates per surface molecule, $k_{\text{evap}}$ in the notation of HH93, $\sim 4.3 \times 10^{-16}$ s$^{-1}$ for CO and $\sim 4.4 \times 10^{-17}$ s$^{-1}$ for H$_2$O. The MD calculation based on equation (1) and the track parameters in the LJO85 model are slightly larger ($\sim 9.8 \times 10^{-16}$ s$^{-1}$ for CO and $\sim 6.8 \times 10^{-17}$ s$^{-1}$ for H$_2$O). The H$_2$O rate is seen to be about a factor of 50 larger than the estimate in HH93, but the fraction of H$_2$O in the gas phase is still small. This may not be the case for NH$_3$. On the other hand, the estimate in HH93 for a CO mantle on a silicate core is an order of magnitude larger than the desorption rate estimated here for a thick CO mantle or a whole CO grain. Since whole-grain heating depends critically on grain size, the rates in HH93 are sensitive to the size of the silicate core. For the 0.1 $\mu$m model grain, the whole-grain heating contribution was found to be small for both the CO and H$_2$O grains considered here. The models described here can now be applied to grains having other compositions and sizes.

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APPENDIX

CALCULATION OF HH93 YIELDS

In HH93 the contribution from whole-grain heating is determined by an evaporation rate from which an effective yield can be evaluated, as indicated in equation (4). They define a desorption probability per unit time for molecule $i$ at a temperature $T_D$ (eq. [14] in HH93)

$$k_{\text{evap}}(T_D) = \nu_0(i) \exp[-U/(k_B T_D)].$$

When applied at the end of the MD simulations, then $T_D \rightarrow T_f$. The desorption frequency, $\nu_0$, was estimated in HH93 using a harmonic approximation,

$$\nu_0 \approx \nu_{\text{HF}} = \sqrt{2n_s U/(\pi^2 m)},$$

with $n_s$ the surface density of species $i$ and $m$ the mass of a molecule. For a nonporous, amorphous material, $n_s$ is related to the bulk density by $n_s \approx n^{2/3}$. The desorption rate per surface molecule in HH93, $k_{\text{evap}}$, is then

$$k_{\text{evap}} \approx k_{evap}(T_D) T_f^{-1} \approx 3.16 \times 10^{-19} k_{\text{evap}}(70 \text{ K}).$$
In this estimate, $t_D$ is the effective desorption time and $t_{-1}^{-1}$ the rate of impact of the dominant eroding ions, 0.02–0.07 GeV per nucleon in HH93 (see eq. [5]). The rate of impact $t_{-1}^{-1}$ is about $\frac{1}{20}$ of the total number of CR iron impacts on an average grain of radius $a \approx 0.1 \mu m$: $\tau \approx 3.16 \times 10^{13}$ s. For such ions depositing their energy in the grain core, which is presumed to be a silicate, HH93 estimated that the whole-grain temperature during the evaporation process is on average $T_D = 70$ K and the half-time for the evaporation process is $t_D \approx 10^{-5}$ s, independent of the desorbed species. For faster iron ions, $T_D$ is lower and evaporation is inefficient. $T_D$ is based on the assumption that the energy is deposited in the silicate core using a specific heat from LJO85 and is sensitive to grain size. For a $0.1 \mu m$ grain, the value of $T_D$ is consistent with an average total energy deposited $\Delta E \approx 0.4$ MeV per CR, giving a stopping power

$$\frac{(dE/dx)_{eff}}{2a} \approx 20 \text{ GeV cm}^{-1}. $$

HH93 desorption rates are converted to a whole-grain yield (eq. [4]) for comparison to the yields in Figure 2. For $\frac{1}{20}$ of the impacts with a characteristic $(dE/dx)_{eff} \approx 20$ GeV cm$^{-1}$,

$$Y_{\text{th-late}} \approx N_e k_{\text{evap}}(70 \text{ K}) t_D,$$

where $N_e$ is the number of molecules on the surface of a spherical grain of radius $a$ (assuming a full monolayer), $N_e \approx 4\pi a^2 n_s$. At other CR iron energies, $Y_{\text{th-late}} \approx 0$ in HH93, which will also be the case for larger grains.

Table 2 contains the parameters used by HH93, corrected parameters from Johnson & Schou (1993) where appropriate, and the resulting whole-grain heating yields. The yields labeled HH93 are those associated with the values of $k_{\text{evap}}$ used in HH93. These yields are plotted in Figure 2. Different growth conditions for “ice” will result in different densities and binding energies. Density changes will only result in relatively small changes in the final value of the yield. There are reported values for $U$ in water ice in the range 0.44–0.55 eV (Sack & Baragiola 1993). For any of these values, the yield using the HH93 model is essentially zero.

**REFERENCES**

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Johnson, R. E., & Schou, J. 1993, Matematisk-fysiske Meddelelser, 43, 403
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**TABLE 2**

<table>
<thead>
<tr>
<th>$U$ (eV)</th>
<th>$U/k_B$ (K)</th>
<th>$n$ ($\AA^{-3}$)</th>
<th>$k_{\text{evap}}$ (s$^{-1}$)</th>
<th>$k_{\text{cond}}$ (s$^{-1}$)</th>
<th>$Y_{\text{HH93}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-HH93</td>
<td>0.104</td>
<td>1210.0</td>
<td>0.050</td>
<td>$3.1 \times 10^4$</td>
<td>$9.8 \times 10^{-15}$</td>
</tr>
<tr>
<td>CO</td>
<td>0.088</td>
<td>1021.2</td>
<td>0.020</td>
<td>$3.1 \times 10^5$</td>
<td>$9.8 \times 10^{-14}$</td>
</tr>
<tr>
<td>H$_2$O-HH93</td>
<td>0.160</td>
<td>1860.0</td>
<td>0.050</td>
<td>4.4</td>
<td>$1.4 \times 10^{-18}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.50</td>
<td>5802.2</td>
<td>0.030</td>
<td>$2.3 \times 10^{-24}$</td>
<td>$7.3 \times 10^{-43}$</td>
</tr>
</tbody>
</table>