7.1 The Non-Linear Erosion Yield of Condensed Gas Solids Electronically Excited by Fast Light Ions

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1. Introduction

The erosion of rare gas and simple molecular gas solid films (i.e., H₂O [1-4], Xe [5], Ar [6], CO₂ [3], SO₂ [7,8], CO) by fast ions is a special case of desorption due to electronic excitation. It is special in several respects. First, the films studied are not monolayers as in most desorption work, but are typically \( \leq 1000 \) Å thick, essentially bulk material. Second, the surface binding energies of the condensed gas species are low (\( \leq 0.5 \) eV), characteristic of VdW bonded atoms and molecules or, in the case of water, hydrogen bonded molecules. Third, all of the films are insulators. Fourth, the use of MeV ions allows large changes in the density of electronic excitation along well-defined linear paths by choosing the nuclear charge and velocity of the incident ions. Fifth, the erosion or desorption yields are large, from 0.1 to 1000 molecules desorbed per incident ion even for H and He ions.

The focus of this paper is to draw attention to the strong non-linearity in the erosion (desorption) yield with electronic excitation density that has been observed in every condensed gas that has been studied to date. The recent availability of both electron and ion-induced erosion yields for solid CO films indicates that the non-linearity extends to ionization densities even lower than those encountered in many electron-stimulated desorption experiments. The paper also discusses possible erosion mechanisms.

2. Experimental Approach

In all cases the films that we have studied have been condensed from the gas phase on a cold beryllium substrate, usually at a temperature of about 10K [9]. The principal experiments have been carried out using Rutherford backscattering of MeV helium ions to provide a measurement of the average molecular thickness of the films, as grown and at various stages in the erosion process. In many cases backscattering also provides the average atomic composition of the films as they are eroded, for example, by giving independent measurements of the column density of C and O atoms in a CO films. Collimation of the eroding ion beam and current measurements at the target permit absolute determination of erosion (desorption) yields, i.e., the number of molecules or atoms lost per incident ion. Observation that the erosion yield is independent of current density over an order of magnitude in current density gives assurance that the phenomena we are studying occur on a per-particle basis and are not due, for example, to macroscopic heating effects [9].

We focus our attention on erosion produced by MeV He and H ions for which the overwhelmingly dominant energy loss process in the films is electronic
excitation and ionization. We have used \((dE/dx)_e\), the electronic stopping power or the energy loss per unit path length of the incident ion as a measure of the initiating effect, since the relative importance of individual excitation events is not yet understood. This regime is in contrast to the collisional stopping regime at keV energies in which the dominant energy loss of the incident ion is in collisions with the nuclei of the solid. It is the latter regime which leads to conventional sputtering [10].

3. Results and Discussion

The erosion yield \(Y\) for H\(_2\)O ice is shown in Fig. 1 as a function of \((dE/dx)_e\) [9]. The yield is highly non-linear in \((dE/dx)_e\); the plotted line in the figure has a slope of 2. The overall trend of the data indicates the process is roughly proportional to \((dE/dx)_e^2\). Deviations from the trend, particularly the high points for He ions at low \((dE/dx)_e\), arise from a combination of non-equilibrium charge state of the incident ions, velocity dependent track radius and collision cascade contributions [11]. A striking feature of Fig. 1 is the close to quadratic dependence on \((dE/dx)_e\) for hydrogen ions, for which these three effects are all small.

![Graph 1](image1)

**Fig. 1.** Erosion yield \(Y\) of H\(_2\)O ice at low temperature plotted as a function of \((dE/dx)_e\) for H and He ions. The He points plotted as open squares are from [2]

![Graph 2](image2)

**Fig. 2.** Erosion yield \(Y\) for solid CO at 10 K plotted as a function of \((dE/dx)_e\) for H and He ions and for 2 keV electrons. The electron data point is due to SCHOU [12]
Approximately the same non-linearity is found for Ar [6], CO₂ [3], SO₂ [7] and CO. Recent measurements in our laboratory for the case of solid CO are shown in Fig. 2. The data is much less extensive than for H₂O, but the same approximate (dE/dx)ₑ trend is evident. The absolute yields are much higher: for 1.5 MeV He ions, Y for CO is approximately 220 compared with about 7 for H₂O. This is the direction that would be expected from the difference in intermolecular binding for the two cases (0.55 eV/molecule for H₂O; 0.08 eV/molecule for CO). However, the ratio of yields depends more strongly than linearly on the inverse of the binding energy [11,6]. One important question is whether the yield becomes linear or remains non-linear at low (dE/dx)ₑ where the average separation betwen individual ionization events becomes large. This effect can be studied for ions by using higher energy MeV protons. Alternatively, it can be studied with keV electrons which have the same ionization probabilities as protons of the same velocity.

The erosion of frozen gases with keV electron bombardment is under investigation by SCHOU and his associates at Riso, Denmark [12]. Preliminary, as yet unpublished, work suggests that for solid hydrogen targets the erosion is linear in (dE/dx)ₑ. The group has also determined a value of Y = 0.6 for 2 keV electrons on CO. This value has been placed on Fig. 2 at the appropriate (dE/dx)ₑ for such electrons (equivalent to (dE/dx)ₑ for 3.7 MeV protons). Considering the small number of points and the very different measuring techniques, the agreement of the electron value with the ion results is good. Nevertheless, the electron point lies above the (dE/dx)ₑ line drawn through the ion data by more than the 10-20% uncertainty the experiments are believed to have. This suggests that a transition to a linear dependence may occur at (dE/dx)ₑ ≈ 4 eV/10¹⁵ molecules/cm². It is important to extend the (dE/dx)ₑ measurement range to lower values in order to follow this transition in detail if indeed it does occur.

4. The Question of Mechanism

A major issue in these results, as in the case of electron or photon stimulated desorption, is how electronic excitation is transferred to the atomic motion required for release or ejection of atoms or molecules. There are only two general means of generating nuclear motion from electronic excitation and ionization produced in the material. The first is 'free electron' heating of the molecules of the solid [13] and we do not consider it here. The second is due to repulsive forces between neighboring atoms and molecules. These forces must occur in response to the change in the local electronic state of the solid. In an insulating material such forces become important because the excitations remain localized. The differences in possible models (mechanisms) therefore reduce to a consideration of the spatial extent (along the track and radially) of the effect of these repulsive forces [11].

Two models, both of which can account for erosion yields that vary non-linearly with (dE/dx)ₑ have frequently been discussed in the ion erosion literature: thermal spike and coulomb explosion. In a thermal spike one envisions an extremely rapid (≈ 10⁻¹² sec) transfer of energy from the electronic system to random atomic motion (heat) in a narrow cylinder (20-40 Å radius) around the ion track. Where this cylinder meets the surface, a transient in sublimation takes place as the cylinder is very rapidly heated and then very rapidly cooled by radial heat conducton to the surrounding material. Such a transient will give a net sublimation yield which is non-linear in the thermal source strength [14]. Under appropriate conditions the non-linearity can be quadratic. The crucial step in this picture is not
really the transient sublimation, which may or may not be treated correctly as a local Maxwellian process subject to thermal diffusion, but rather the rapid transfer of energy from excitation and ionization in the electronic system. Both the transfer time and the fraction of the energy which is rapidly transferred are critical to the results [11]. For the thermal spike formulation to give a quadratic result the individual sites at which electronic-to-atomic energy transfer takes place must be close enough together temporally and spatially so that the ion track can be treated as a very hot cylinder. Individual hot spheres will give a sublimation yield that depends linearly on \((dE/dx)_e\). At a \((dE/dx)_e\) of 3 eV/10^6 molecules/cm^2 in CO the individual ionization events are spaced about 40 Å apart on the average along the electron path. Using Eq. 3a of ref [11], if rapid transformation of 3-4 eV of electronic excitation to atomic motion occurs at each of these ionization locations, the local "hot" spots will just overlap. This is the critical condition for which a transition between a linear and a quadratic dependence on \((dE/dx)_e\) would be expected to occur.

In the coulomb explosion picture, electrons are radially separated from positive ions in the ionization process along an ion track. If the resulting space charge persists, the ions can be set in motion, similar to the mechanism proposed for formation of etchable tracks in room temperature insulating solids [15]. At the surface, the fields and forces are such as to promote ejection from the solid and the process has a quadratic dependence on the charge density and hence also on \((dE/dx)_e\) [16,9]. Preserving the space charge long enough for this to happen seems very improbable [11, 12]. Extensions of the coulomb explosion model have been proposed in which the coulombic force along the track is incompletely screened by the excited electrons [11,18]. That is, even though the free electrons return rapidly to the vicinity of the track they may remain in an excited state long enough to allow the generation of nuclear motion by the repulsive ion cores. Even at low \((dE/dx)_e\) a coulomb repulsion model can retain a quadratic dependence. That is, the probability of one ion being formed close enough to the surface to be ejected and that of a second ion being formed close enough to the first to provide a force for ejection of the first are both linear in the electronic stopping power, giving a yield with a quadratic dependence [11].

A large scale collective coulomb explosion seems unlikely to explain the erosion process. At the low ionization densities of interest in this discussion, atomic scale coulomb explosions seem much more likely to provide a means for rapid transfer of electronic excitation to atomic motion. For rare gas solids, such a possibility has been treated by JOHNSON and INOKUTI [17]. If a transition from quadratic to linear erosion with electronic stopping power is confirmed at low stopping power, a picture of the collective aspects of erosion as being due to overlapping "hot" spots produced by atomic scale explosions will be relatively convincing. The quantitative aspects of the energy transfers will remain the main issue.

5. Summary

The erosion yields of condensed gas solids by fast light ions are non-linear and approximately quadratic in their dependence on the excitation density down to quite low densities for H2O, CO2, SO2, Ar and CO. Recent measurements of the erosion of CO with keV electrons confirm the conclusion of the MeV ion results that the important processes of excitation are electronic, not collisional. However, the electron results show a possible transition from a quadratic dependence toward a linear dependence at very low \((dE/dx)_e\).
At low excitation density the observation of a non-linear dependence of the erosion yield on excitation density demands one of two types of cooperative processes by which electronic energy is transferred to atomic motion: 1. Rapid electron-atom energy transfers initiated by individual excitation or ionization events are closely enough spaced for them to overlap in a hot cylinder. Such a model would be related to the MGR model of desorption [19]. 2. Two ionization events are produced close together by passage of a single particle. These two events might be on neighboring molecules giving rise to mutual repulsion related to the KE model of desorption [20]. Such events might also be related to a double ionization model proposed for laser stimulated desorption [21]. For the case of solid CO, the indications of the most recent results with electrons and ions suggest that process 1 is dominant. In the case of solid H₂O, this picture still poses some quantitative difficulties.

References

12. J. Schou, Private Communications.