DESORPTION INDUCED BY ELECTRONIC TRANSITIONS: APPLICATION TO IONIC COMPOUNDS

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1. INTRODUCTION

The ejection of atoms and molecules from the surface of solids subject to the bombardment of energetic particles is a well known phenomenon that is employed routinely in laboratories and industrial plants for cleaning a surface, determining surface composition or ejecting material from a solid for deposition on adjacent targets. This emission, called sputtering, is the result of a direct momentum transfer from the incident particles to the atoms of the solid.

Also low intensity beams of photons and electrons produce the emission of constituent atoms or surface adsorbates (photon- or electron- stimulated desorption, respectively). However, in this case the energy of the incident particles is substantially lower than that necessary to create the elastic knock-on process. Thus, the desorption is triggered by electronic transitions induced by the incident photons or electrons.

Several mechanisms have been proposed for desorption. One model proposed for the desorption of adsorbed species derives from the dissociation theory of gas–phase molecules: desorption is the result of an electronic transition from the bonding ground state to an anti bonding excited state of a surface atom or molecule with final energy above the dissociation limit.¹, ² Another model has been proposed for several transition metal oxides.³ For these materials the electron–stimulated desorption yield of positive ions (O⁺, OH⁺) has a threshold at the highest-lying atomic core levels. The interatomic Auger decay of the excited ion core state removes two valence electrons from the anion, which is transformed into a neutral atom or even in a positive ion. If this ion is on the surface, it will experience a repulsive force from the neighbouring cations and then it will be desorbed.

The desorption of constituent particles from alkali halides does not fall in either scheme. The electronic transition occurring in the bulk material is followed by several relaxation processes that may involve atomic displacements and defect formation. The three step model that is generally adopted for desorption is sketched in Fig. 1:
1. **Electronic transition.** An incident particle, either a photon or an electron, excites an atom inside the crystal.

2. **Defect formation and transport.** Either the excited state migrates directly near the crystal surface, or it decays first into lattice defects, which migrate to the surface.

3. **Desorption.** When the excited state reaches the surface, an atom can be emitted.

In spite of the large amount of photon- and electron-stimulated desorption experiments performed on alkali halides, the entire set of processes sketched in Fig. 1 is not yet completely understood. The main experimental findings reported in the literature are:

i) The emission of both alkali and halogen neutral atoms in the ground state is indeed the most efficient process, being some orders of magnitude larger than the emission of excited atoms. The desorption of excited alkali atoms as well as of alkali ions have been observed too.

ii) The desorption yield is temperature dependent. At room temperature it is very small and it increases fast with the sample temperature.

iii) At room temperature the sample surface becomes rich of alkali metal. This layer evaporates above the boiling point of the alkali metal and the crystal surface becomes stoichiometric.

iv) The desorption yield of both atomic species is a function of the energy of the incoming particles. It shows a threshold at the onset of the absorption coefficient of the alkali halide sample. Further thresholds and structures occur at the energies of multiple excitations and at the energies of core level thresholds.

v) The velocity distribution of the desorbed neutral atoms follows the Maxwell–Boltzmann distribution of a gas of free particles with the sample temperature. In several, but not all, alkali halides the desorption of the halogen neutral atoms shows an additional non–thermal component, that becomes dominant at room temperature.

vi) Alkali and halogen atoms with thermal energy are emitted isotropically with a cosine distribution around the normal to the sample surface, whereas the non–thermal halogen component is emitted along the (100) direction.

vii) Time dependent measurements show a delay in the desorption process, with at least three different time constants: a very fast one in the nanosecond region, a fast component, of the order of $10^{-3}$ s, and a slow component of the order of several seconds.

In this review we shall focus our attention to the desorption of neutral atoms from alkali halides following a historical approach. At the end we shall discuss the state of the art of the understanding of desorption induced by electronic transitions in these