

# GROUND-STATE AND EXCITED ATOM EMISSION UNDER ION AND ELECTRON BOMBARDMENT OF NaCl AND CaF<sub>2</sub>\*

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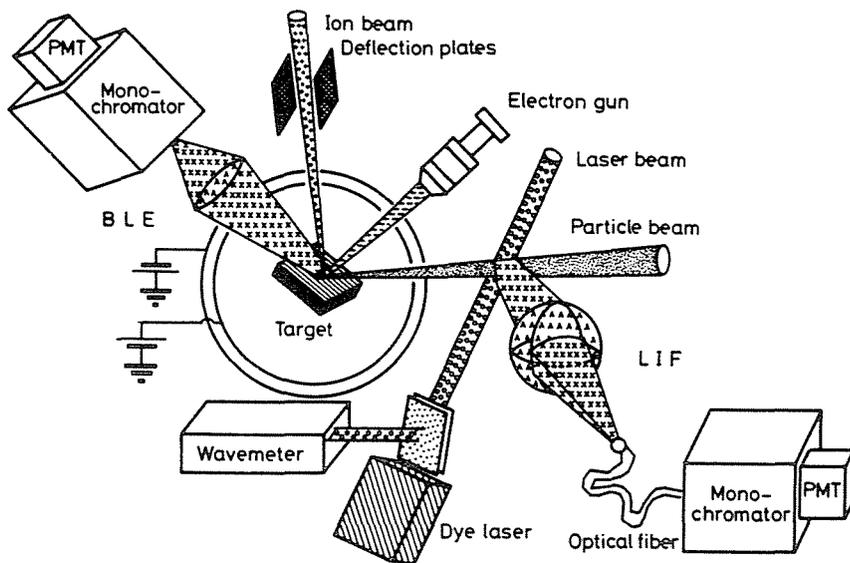
## Abstract

The particle emission process for ion bombardment and electron bombardment of NaCl and CaF<sub>2</sub> using high resolution optical spectroscopy and Laser Induced Fluorescence (LIF) has been compared. The energy distribution of ground-state as well as excited Na atoms from NaCl under electron bombardment was found to be thermal, while under ion bombardment the excited Na atoms were found to be energetic in the range of 2 eV. However for ground-state Na atoms even under heavy ion bombardment (Xe) the energy distribution was found, surprisingly, to be almost purely thermal. In the case of Ca from CaF<sub>2</sub> we observed under ion bombardment a non-thermal energy distribution for Ca ground-state atoms at low temperatures, but at higher temperatures (above 600 K) a thermal, ion beam induced component became dominant. Similar under electron bombardment only desorption of Ca ground state atoms at elevated temperatures was observed and the energy distribution was purely thermal. In addition no electron induced desorption of Ca\* was observed for all energies and all temperatures, while under ion bombardment non-thermal emission of Ca\* was found.

## Introduction

For alkali and alkali earth halides ion, electron as well as photon bombardment are efficient processes leading to continuous surface erosion Postawa et al., 1978; Haglund Jr. et al., 1987). While sputtering of metals under ion bombardment is well understood in terms of a collision cascade emission mechanism based on momentum transfer due to elastic collisions (Sigmund, 1969), for electron or photon bombardment no such processes can account for any particle emission due to the negligible momentum transfer. Electronic processes have been proposed to explain such electron or photon induced desorption processes (Townsend, 1982; Itoh, 1987). Selective emission of the halogen atoms and molecules is ascribed to the H-centre migration model leading to the formation of a metal overlayer on the surface. If the vapour pressure of the alkali/alkali earth metal layer at the target temperature is high enough this excess metal atoms will desorb thermally, thus leading to

\* Dedicated to Prof. J. Giber on the occasion of his 60th birthday.



*Fig. 1.* Laser Induced Fluorescence (LIF) and Bombardment Induced Light Emission (BLE) Spectrometer for the detection and velocity measurement of neutral ground-state and excited atoms. Ion bombardment is performed with mass analyzed ions (typ. current density:  $5 \mu\text{A}/\text{cm}^2$  at 15 keV). Simultaneous electron bombardment (typ. current density: 200 mA at 400 eV) can be performed. A small hole in a cylinder surrounding the target (not shown) defines a sputter beam direction. The intersection of the laser beam from a c.w. tunable dye laser with the particle beam occurs approximately 5 cm away from the target. BLE and Doppler broadening measurements of line profiles were performed with a 1 m grating monochromator (resolution 0.005 nm)

continuous particle emission. Otherwise the excess metal layer will eventually prevent any further halogen emission and the emission process will be only of a transient nature (Kelly, 1979). We have compared the particle emission processes for ion and electron bombardment of NaCl and CaF<sub>2</sub> to differentiate between a collision cascade induced contribution and one due to Desorption Induced by Electronic Transitions (DIET) under ion bombardment and in addition to compare DIET processes under ion and electron bombardment to obtain a better understanding of the desorption mechanisms involved.

Even though emission of ions, excited and ground state metal atoms has been observed there is evidence that the majority of the electronically desorbed particles are neutrals (Tolk *et al.*, 1984). Using high resolution optical spectroscopy (Betz, 1987) and Laser Induced Fluorescence Spectroscopy (LIF) (Husinsky *et al.*, 1987) we have studied the energy distributions of ground state as well as of excited Na and Ca atoms at different target temperatures. In addition the yield — temperature dependence for ground state as well as excited atoms was studied to gain insight if excited atoms are formed by an

intrinsic process at the surface or by post-excitation of emitted ground state atoms in the gas phase due to secondary electrons or the primary electron beam. The experimental set-up is shown in Fig. 1.

### The velocity distribution of ground-state Na and Ca atoms under ion and electron bombardment

LIF, employing the Doppler effect was used to measure the velocity distribution of emitted Na/Ca atoms from NaCl/CaF<sub>2</sub> single crystals under 15 keV Ar ion (current density 5 mA/cm<sup>2</sup>) or 400 eV electron (current density 200 mA/cm<sup>2</sup>) bombardment in the temperature range from 300 to 700 K. In the case of Na in essence the velocity distribution was found to be identical for electron and ion bombardment at all temperatures within the accuracy of our measurements (see Fig. 2) and in addition the distribution was purely thermal and could be always fitted with a Maxwell Boltzman distribution at target temperature. No cascade contribution was observed (which should exhibit a maximum at much higher energies around 0.5 eV, which is half the binding energy for Na (Husinsky et al., 1979)).

To check for the absence of any cascade contribution under ion bombardment of a clean NaCl target further experiments showed that if the

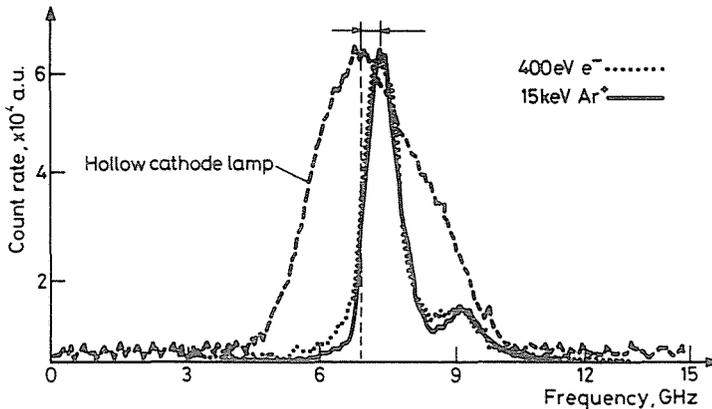


Fig. 2. LIF spectra over the velocity distribution of emitted ground-state Na atoms from a NaCl single crystal under ion or electron bombardment. The center of the curve labelled hollow cathode lamp corresponds to the zero point of the velocity spectrum. A frequency shift of the signal towards the right of this point indicates Na atoms with increasingly higher velocities. Deconvolution of the frequency shift spectrum into a velocity spectrum is complicated due to the hyperfine structure of the Na D<sub>2</sub> resonance line at 588.9 nm (second small peak). Therefore the frequency shift spectra are used to show that ion and electron bombardment yield identical distributions within the accuracy of measurements. The indicated shift of the maximum agrees with a thermal Maxwell—Boltzmann distribution at target temperature (300 K)

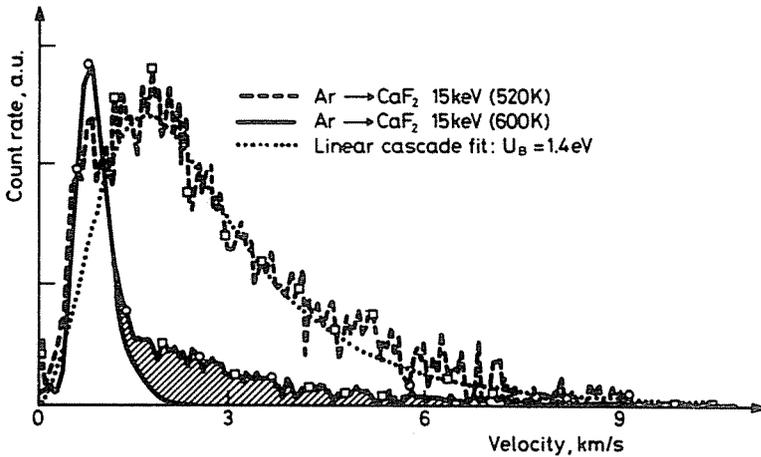


Fig. 3. Normalized velocity spectra of ground-state Ca atoms under 15 keV  $\text{Ar}^+$  bombardment from  $\text{CaF}_2$ . At 520 K the distribution is mainly collisional and can be fitted by the linear cascade theory assuming a surface binding energy of 1.4 eV. At 600 K the spectrum is already mainly thermal and the cascade contribution is only visible in the tail of the distribution (shaded area). The thermal part of the spectrum always corresponds to a Maxwell—Boltzmann distribution at target temperature

oxygen partial pressure in the vacuum chamber is increased up to  $10^{-6}$  mbar the sputtered thermal Na flux decreases by about a factor of 5 and in addition a nonthermal cascade contribution becomes now evident.

On the other hand in the case of ion bombardment of  $\text{CaF}_2$  at room temperature and up to 500 K the velocity distribution is purely collisional and a fit of the distribution using the Thompson formula (Sigmund, 1969) for metals gives a surface binding energy of 1.4 eV in perfect agreement with previous measurements we have performed for metallic Ca (Husinsky *et al.*, 1985). Starting with temperatures above 500 K, in addition a thermal component appears in the energy distribution and for temperatures above 650 K this becomes the dominant contribution to the sputtered flux (Fig. 3). The differences between the velocity distributions for Na and Ca under ion bombardment can be easily explained in terms of the much higher vapor pressure of Na. Thus we assume that for NaCl already at room temperature the thermal component is so dominant that the cascade contribution cannot be observed.

For both materials under ion bombardment the thermal component in the emitted flux is ion beam induced and not a pure thermal evaporation as was confirmed by chopping the ion beam. In addition for Ca emission from  $\text{CaF}_2$  we investigated the time dependence of the LIF signal in more detail. As can be seen from Fig. 4 at least three different contributions to the sputtered flux can be identified for temperatures above 500 K.

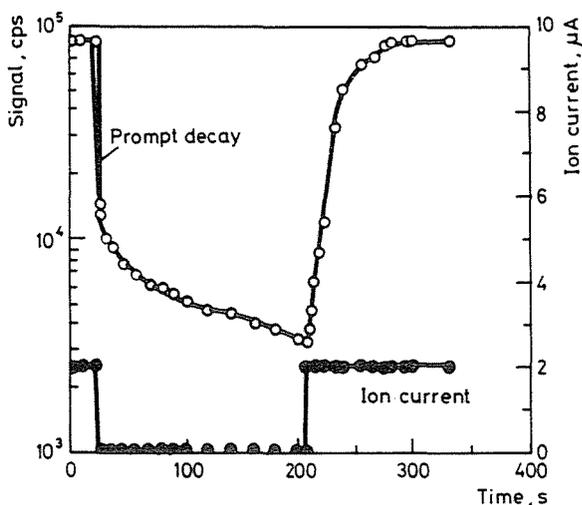


Fig. 4. Time dependence of the Ca ground-state signal from a  $\text{CaF}_2$  target at 600 K if ion bombardment is interrupted. The fully drawn part of the curve, labelled "prompt decay", corresponds to a signal decrease within less than 0.1 s

a) A *prompt decrease* of the signal by almost an order of magnitude was observed immediately after the ion beam was removed from the target. Due to the limited time resolution we only know that the decrease is faster than 0.1 s. As at 550 K the thermal contribution is dominant (more than 90%), we assume that these promptly emitted atoms consist in reality of two contributions: the *cascade* contribution at nonthermal energies which should not last longer than  $10^{-12}$ – $10^{-11}$  s (Kelly, 1984) after the ion bombardment is stopped and a *thermal* contribution due to  $V_k$  centers. These  $V_k$  centers cause emission of the halogen atoms and as a consequence evaporation from a Na enriched surface occurs. As the life time of these  $V_k$  centers is in the order of msec they will also contribute to the prompt decrease (Townsend, 1982).

b) a *slow thermal contribution* exhibiting a life time in the order of 30 sec, which we assume to be caused by long lived trapped exciton states diffusing to the surface and in turn causing Na emission similar to the  $V_k$  centers.

c) a weak purely *thermal evaporation* component, not caused by ion bombardment.

Under electron bombardment  $\text{CaF}_2$  showed no emission of Ca ground state atoms up to 500 K, the same temperature for which under ion bombardment a thermal contribution appeared. At temperatures above 500 K as outlined above pure thermal evaporation occurs and in addition under electron bombardment Ca desorption (signal size under our experimental conditions about 4 times the thermal evaporation at 550 K) occurred. After turning off the electron beam a delayed signal with a decay time constant in

the order of 3 min was observed in this case (target temperature 550 K) possibly indicating that under electron bombardment either other long lived defects are created or that the different decay time as compared to ion bombardment is caused by the greater penetration depth of the primary electrons. In all cases under electron bombardment the velocity distribution was thermal corresponding to a temperature equal to the target temperature.

### **Energy distribution of excited Na and Ca atoms under electron and ion bombardment**

To obtain information which process causes emission of excited Na and Ca atoms, we measured the energy distribution of excited Na (NaI 588.9 nm) and Ca (CaI 422.5 nm) atoms using high resolution optical spectroscopy studying the Doppler line profile broadening of the cited lines (Betz, 1987). For NaCl under ion as well as electron bombardment strong optical emission is observed and the analysis shows that under ion bombardment excited atoms are nonthermal, peaking at about 3 eV, while under electron bombardment a thermal distribution was found for the NaI atoms (Husinsky *et al.*, 1987). These results are in good agreement with measurements by WALKUP (Walkup *et al.*, 1986), who, using a similar technique, obtained the same results. The high energies of excited atoms under ion bombardment indicate that these atoms are part of the cascade contribution being excited when leaving the surface during the last collision.

In the case of CaI from  $\text{CaF}_2$  only under ion but not under electron bombardment emission of excited atoms was observed over the whole temperature range investigated. For ion bombardment the velocity distribution of CaI was identical to the emission from a pure Ca target, and a mean energy of 6 eV was derived from the analysis.

### **The dependence of yield of ground state and excited atoms on the target temperature**

To gain additional information if excited atoms under electron bombardment are caused by secondary effects (excitation by secondary or primary electrons) (Postawa *et al.*, 1987; Walkup *et al.*, 1986) or due to an intrinsic process (Haglund Jr. *et al.*, 1986), we studied the temperature dependence of the yields by LIF or light emission, respectively. Fig. 5 a, b give the results, which clearly show that under electron bombardment the excited yield is proportional to the ground state yield and both increase exponentially with temperature. Contrary, under ion bombardment only the ground state yield shows a significant dependence on temperature. The independence of the yield of

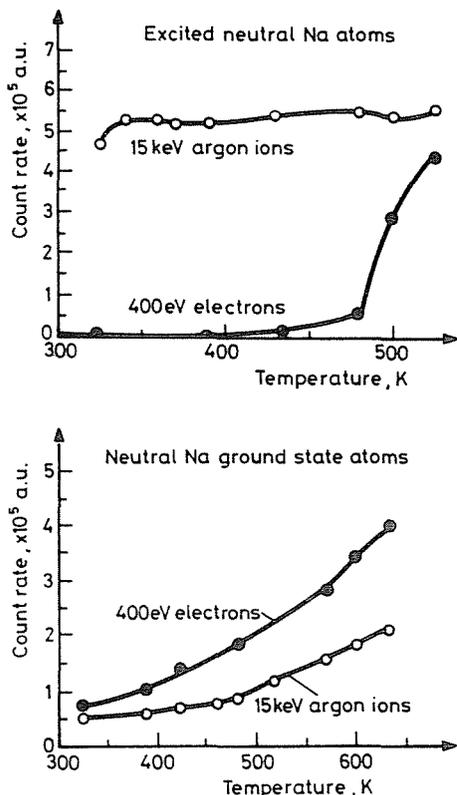


Fig. 5. Temperature dependence of the Na ground- and excited state (Na I, 588.9 nm) yield under 15 keV  $\text{Ar}^+$  or 400 eV electron bombardment of NaCl measured by LIF or BLE, respectively

excited atoms with temperature and their non thermal energies strongly suggest their origin from the collision cascade. The increase in the ground state yield follows from the observation that the majority of emitted Na atoms are thermal and caused by thermal evaporation following electronic desorption of the halogen. The results for electron bombardment together with the thermal energy distribution of the excited atoms are in favour or at least do not contradict a formation mechanisms due to gas phase collisions. However their absence of any excited  $\text{Ca}^*$  under electron bombardment of  $\text{CaF}_2$ , contradicts the assumption of gas phase collisions.

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