Ion Formation from Alkali Iodide Solids by Swift Dust Particle Impact *

W. Knabe + and F. R. Krueger
Max-Planck-Institut für Kernphysik, Heidelberg, West Germany

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Swift Fe-dust particles (0.2—20 μm ∅; 1—50 km/s) are utilized to generate transiently ions from alkali iodide coated metal foils, analyzed by time-of-flight mass spectrometry. By means of a thermodynamic treatment it is shown that simple heating by the impact cannot be hold responsible for the ion formation. However, this process is very much related to the non-adiabatic ion formation by pulsed laser irradiation. The damage caused by the impact particle resulting in cratering and thermal effects, which are long-term processes, is not related to the instantaneous ion formation.

1. Introduction

It is well known that rapid dissipation of energy into a surface area of dielectrics may cause transient ion formation of high ionization efficiency. Due to the prompt ion ejection from the surface time-of-flight (TOF) mass spectrometry is the most useful tool for analysis of the ion mass and energy distributions. This ion formation has been investigated by means of laser pulse induced dissipation (LID) as done with the LAMMA®-instrument with alkali halides and reported in a recent paper [1], but also with thermally labile organic compounds [2, 3], because molecular information can be obtained with these dissipation techniques, too. Similar dissipation techniques are fast ion or atom impact like SIMS or FAB-MS (fast atom bombardment mass spectrometry) in the low energy elastic energy loss regime and fission fragment- (FFID) or fast heavy ion (HIID) induced desorption in the high energy inelastic energy loss regime.

Common to all these techniques is the fact that no Debye-shielded plasma is created, as single ions are not capable of ejecting too many ions at a time, and laser pulses are not either, if focal spots are small ($\ll 10\,\mu$m) and the flux density is well below 10^{10} W/cm^2 with pulse lengths of about tens of nanoseconds.

When impacting dust particles on a solid surface with high relative velocity, one is interested in the ion formation mechanisms with these events, as are expected on a fly-by mission to comet Halley in 1986 by the GIOTTO spacecraft [4]. One major question is whether particles of 0.1 to 100 μm diameter of a relative velocity of 70 km/s will form a shielded plasma by impacting on a metal foil, which would — at least in part — spoil the TOF mass spectra. These spectra will be taken and broadcasted to earth in order to analyze the constituents of the impacting comet particles. Investigating this problem dust particles of about 0.2 to 20 μm diameter have been accelerated to 1 to 60 km/s by the Heidelberg van-de-Graaf dust accelerator facility [5, 6]. One is now able to say that no Debye-plasma phenomena are expected with particles up to 70 km/s and about one μm diameter or less. However, with larger particles and/or higher velocities such phenomena may well occur.

On the contrary, very interesting ion formation phenomena are observed in our experimentally accessible regime, namely, cluster and molecular ion formation from the target (and, possibly, projectile) surface being ejected promptly correlated with the particle impact with low energy (some eV) and ion density thus making TOF-MS possible. These phenomena, being closely related to the other rapid dissipation — ion formation phenomena below the plasma formation regime, are the subject of this paper.

2. Experimental Conditions

Fe-dust particles of about $d = 0.2$ to 20 μm diameter (mass m) are charged up (charge q) at a 20 kV electrode and accelerated to a velocity $v = 1$ to

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Reprint requests to Dr. Franz R. Krueger, MPI für Kernphysik, Abt. Kosmophysik, Saupfercheckweg, D-6900 Heidelberg.

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60 km/s by an $U_0 = 2$ MV van-de-Graaf accelerator. As the kinetic energy E is given by

$$E = \tfrac{1}{2}\, m\, v^2 = q\, U_0$$

lower masses (diameters) refer mainly to higher velocities and vice versa. However, as the charge is limited by the capacity of the particle relative to the environment, which is an almost linear (or somewhat steeper, due to surface charge density effects) function of d, smaller particles carry less kinetic energy than larger ones. This has to be taken into account e. g., when comparing absolute secondary ion yields. A scaling $q \sim d^x$ may be appropriate. $x = 5/4$ seemed to be a practical value for our electrode configuration:

Kinetic energy

$$E \sim d^{5/4} \sim m^{5/12} \sim v^{-10/7}\,,$$

Impact energy density

$$E/d^2 \sim d^{-3/4} \sim m^{-1/4} \sim v^{6/7}\,.$$

Thus a mass-velocity proportionality of

$$v \sim m^{-7/24} \sim d^{-7/8}$$

can be approximately assumed. Thus the upper and lower limits of the accessible range are given nearly by the values in Table 1.

It is interesting to note that the secondary ion yields and the crater volume are subject to different empirical scaling laws, respectively. The crater volumes are almost proportional to the impact energy $E = \tfrac{1}{2}\, m\, v^2$. The secondary ion yields may be scaled according to $Q \sim m^\alpha \cdot v^\beta$, with $\alpha = 0.66$ to 1 and $\beta = 2.7$ to 4, depending on the ion types involved.

The velocity range is chosen and the exact velocity measured by means of a time-of-flight particle selection unit (PSU). A selected particle is bent to the target by a perpendicular electric field switched on by a PSU-produced trigger pulse (see Figure 1).

The target is prepared by electrospraying [7] a solution of the alkali iodides (or organic samples) in methanol on to a silver foil. Usually some 10 μg/cm² (~ 0.1 μm) thin layers of the dissolved material have been produced. All swift particles are able to pass through this layers into the silver bulk. The smaller (faster) particles are expected to evaporate completely due to the compression shock, the larger (slower) ones, however, are not. With particles of only 1 km/s even no melting of particle or target material is expected, but only a sticking of the particle on the target surface. This has been confirmed with electron microscope observations [6].

	Limit I	Limit II
d	0.15 μm	15 μm
m	$1 \cdot 10^{-14}$ g	$1 \cdot 10^{-8}$ g
v	55 km/s	1 km/s
E	15 nJ	5 μJ
$E/2\,d^2$	35 J/cm²	1.1 J/cm²

Table 1. Limits of the accessible swift particle regime.

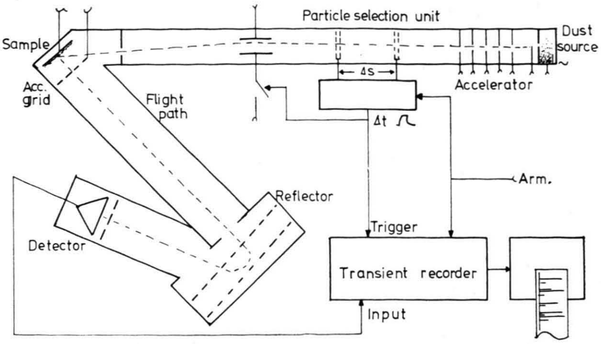

Fig. 1. Schematic view of the experimental set-up.

The impact angle is about 45°. The target is mounted on a resistive heating arrangement allowing temperatures to be applied up to 500 °C.

The instantaneously produced ions are accelerated by a 1 kV voltage between target and grid, and are mass-analyzed by a time-of-flight mass spectrometer with reflector. The time-dependent ion current at the detector is measured after logarithmic amplification (3.5 decades) by a Biomation transient recorder. As the total flight time is proportional to the square root of the specific mass m_r/z (z: charge state of the ion), a mass spectrum can be deduced from the time-of-flight spectrum. One mass number can be resolved at $m_r/z = 150$ amu. There are several classes of secondary ions, which apparently observe different scaling laws, especially in v of the primary particle. One has to distinguish:

- Metal ions
  - from the particle, e. g. Fe^+, Fe_2^+;
  - from the target, e. g. Ag^+, Ag_2^+, Ag_3^+, . . .
- Ions from preformed ionic species, like Na^+, K^+, $Na_{n+1}J_n^+$ (n: cluster orders) originating from salts (main interest of this paper).
- Ions from neutral organic substances, mainly protonated or alkali cationized, or even-electron fragment species.
- Metal-Atom/molecule cluster ions, like $FeAg^+$, $NaJAg^+$ (Organics + Ag)$^+$.

In three sets of experiments CsJ, a mixture of alkali iodides, and tetrabutylammonium iodide have been investigated. In all cases the mass spectra have been measured as a function of the particle impact velocity: The relative ion intensities are taken with about 100 impact events of different velocity. In the alkali iodide cases the target was also heated up to about 500 °C and some tens of events were recorded the same way. After cooling down to room temperature this procedure has been repeated.

The residual gas pressure was about 10^{-7} mbar, except for the heating experiments with some 10^{-6} mbar.

Only positively charged ions have been measured so far.

3. Results

With a CsJ layer on silver, only Cs^+, Cs_2J^+, Ag^+, Ag_2^+, and $CsJAg^+$ have been observed besides some impurity ions like Na^+ and K^+. To earn a better understanding of the thermodynamic properties of ion emission a $10^3 : 10^2 : 10 : 1$ molar mixture of Na/K/Rb/Cs-Iodide has been investigated due to the fact known from other dissipation processes [1] that the heavier alkali ion formation probability is enhanced relative to the lighter ones with extremely non-equimolar mixtures (not observed with equimolar mixtures!).

A typical mass spectrum is shown in Figure 2. All the lines are easily interpreted belonging to the types Alk^+, Ag_n^+ $(n = 1, 2, 3)$, Alk_2J^+ (type A), $AlkJAg^+$ (type B), and $Alk_3J_2^+$ (type C). Note that all atomic Alk^+ ion yields are in the same intensity range; the same is true for the first order $(n = 1)$ cluster ions A, however, at an intensity approximately one order of magnitude lower, and for the second order $(n = 2)$ cluster ions C, despite of their huge concentration ratios in the specimen.

This ionic distribution has been measured with many impact events at different velocities in the accessible mass/velocity range. A result is given in Figure 3. Moreover, one is able to say that the relative ion yield distributions *within* each class (Alk, A, B, C) are totally independent of v (experimental error factor: 2). However, the sum of all cluster ions (A, B, C) decreases slightly relative to the sum of all atomic ions (Alk) with increasing velocity. On heating the sample up to 500 °C all cluster ions disappear in the mass spectra: their yields dropped at least below 1/20 of their former value. No better information was available so far, as thermionic background reduced the dynamic range. Also the Rb^+ and Cs^+ signals disappeared. Cooling down to room temperature again resulted in a recovering of the Rb^+ and the Na_2J^+, $NaKJ^+$ and K_2J^+ cluster ions. Possibly, the CsJ and, in part, the RbJ vanished from the surface during the heating process due to the high vapor pressure at this temperature, although no optical change has been observed with the sample. This observation implies that at least no gross evaporation took place. Consequently one is able to say that the Na and K-iodide cluster ion formation has proved to be strongly

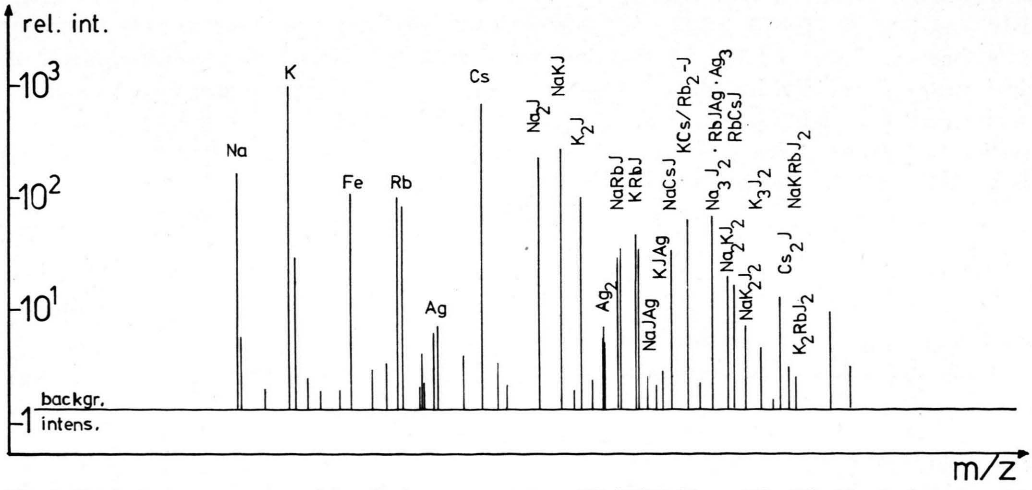

Fig. 2. Typical mass spectrum of the alkali iodide mixture (Na/K/Rb/Cs $= 10^3 : 10^2 : 10 : 1$) electrosprayed 10 μg/cm² on a silver foil bombarded by a $v = 3$ km/sec Fe-dust particle.

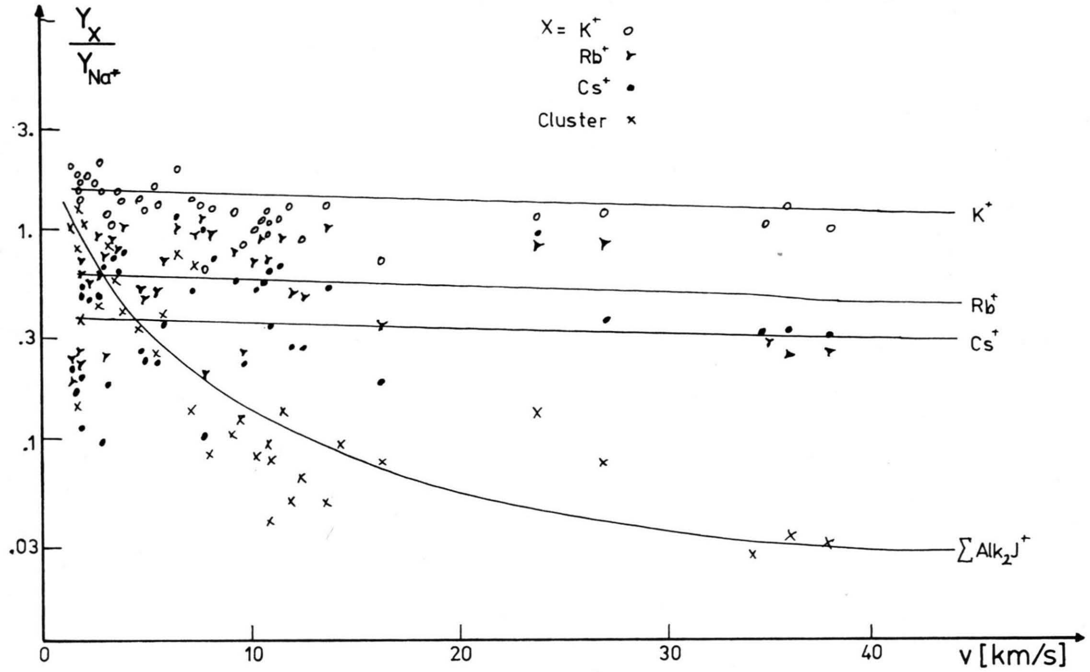

Fig. 3. Relative yields of atomic and cluster ions normalized to the Na$^+$-yield as a function of the particle velocity impacting the surface.

sample temperature dependent. This is the same behaviour as observed with laser pulse irradiation [8].

Instead of alkali iodides tetrabutylammonium iodide (AmmJ) has been investigated, too. Due to its thermal lability, no heating experiments have been performed. Nearly the same mass spectra as obtained with related methods have been observed [2], dominated by the parent ion Amm$^+$. Typical fragment ions have been observed, too. Their *relative* yields are nearly constant for $v = 1 \div 12$ km/s. Above $v = 15$ km/s (measured up to 35 km/s) the *absolute* ion yield dropped rapidly by almost a factor of ten accompanied by a slight increase of the fragment ion *relative* to the parent ion yield. This behaviour is discussed in greater detail elsewhere [9].

4. Discussion

We will discuss the quasiequilibrium mechanisms often hold responsible for related ion formation processes from surfaces in Chapter 4.1. – 2. As the experimental data are shown to be in sharp contrast to these models, the data will be interpreted in terms of a fast non-equilibrium surface-gas phase transition in Chapter 4.3.

4.1. The LTE-plasma Model

It is often assumed that the ion formation by rapid dissipation is maintained in a local thermal equilibrium (LTE) described by a Saha-equation for electronic ionization. Neutral molecules of alkali iodides, electrons, and ions would form this equilibrium:

$$\mathrm{Alk}_n\mathrm{J}_n \longleftrightarrow \mathrm{Alk}_n\mathrm{J}_n^{+\cdot} + e^- .$$

However, these ion types have never been observed, neither with particle impact nor with ion, atom, or laser beam pulses. The time needed to form such an equilibrium is, by the way, far to large with these low energy densities to allow TOF-MS with narrow lines. On the other hand, one could think of the formation of a pure ion LTE-plasma with the following reactions (as the plasma is not Debye-shielded, one may also easily calculate that a formation of an equilibrium would take too much time to allow sharp TOF-lines):

$$\mathrm{Alk}_{n+1}\mathrm{J}_n^+ \longleftrightarrow \mathrm{Alk}_n\mathrm{J}_n + \mathrm{Alk}^+ , \tag{a}$$

$$\mathrm{Alk}_n\mathrm{J}_n \longleftrightarrow \mathrm{Alk}_{n-1}\mathrm{J}_n^- + \mathrm{Alk}^+ , \tag{b}$$

and

$$\mathrm{Alk}_n\mathrm{J}_{n+1}^- \longleftrightarrow \mathrm{Alk}_n\mathrm{J}_n + \mathrm{J}^- , \tag{c}$$

$$\mathrm{Alk}_n\mathrm{J}_n \longleftrightarrow \mathrm{Alk}_n\mathrm{J}_{n-1}^+ + \mathrm{J}^- . \tag{d}$$

The enthalpies of formation $\Delta H_{a,c}$ for reactions (a) and (c) are in the order of 40 to 100 kJ/mole; the differences $\delta_{Na-Cs}\,\Delta H_{a,c}$ between Alk = Na and Alk = Cs are in the order of 10 kJ/mole. For the reactions (b) and (d) $\Delta H_{b,d}$ is some hundred kJ/mole, the differences about tens of kJ/mole (estimated from [10]). The entropy increases to the right hand side by about $\Delta S = 20$ J/K · mole.

With

$$\frac{Y_{Cs}}{Y_{Na}} = \frac{c_{Cs}}{c_{Na}} \exp\left\{-\frac{\delta\Delta H}{RT} + \frac{\delta\Delta S}{R}\right\}$$

(Y: ionic yield, c: concentration of the related species in the plasma):

$$T \approx \frac{\delta\Delta H}{R}\, 1/\ln\left(\frac{Y_{Na}}{Y_{Cs}}\,\frac{c_{Cs}}{c_{Na}}\right),$$

this yielding about $T \lesssim 300$ K for (a) and (c) and $T \approx 1000$ K for (b) and (d). This is totally unacceptable, as with these low temperatures no ions would be formed at all. By combination of (a)...(d) all reactions would end on the left hand sides of (b) and (d), i. e. in neutral states.

On the other hand, the relatively high number of atomic species compared with the clusters would point to a rather high temperature and/or very low pressure of the plasma in order to make the reactions (which are endothermic) exergonic to the right hand side. This, however, is again in sharp contrast to the Na/K/Rb/Cs ratios. So the possibility of a LTE-plasma is ruled out.

4.2. *The Thermal Evaporation Model*

A second model assumes that the ions are formed directly from the solid surface by a quasiequilibrium solid-gas phase transition, i. e. evaporation. As the enthalpies of formation for the observed ions are known [1, 10], the detected ion yields Y normalized to their relative abundance c in the solid state and a statistical factor $1/n$ are plotted vs. their formation enthalpies by evaporation in Figure 4. Thus one is able to determine an "evaporation temperature" of about $T = 2000$ K, when using only the information due to Alk^+. Similar temperatures are obtained by using only the information of class A or C ions. However, comparing the total amounts of each class of ions the model breaks down, as the cluster ions are extremely overrepresented: The ion/cluster ratios would lead to temperatures of about $T = 8000$ K.

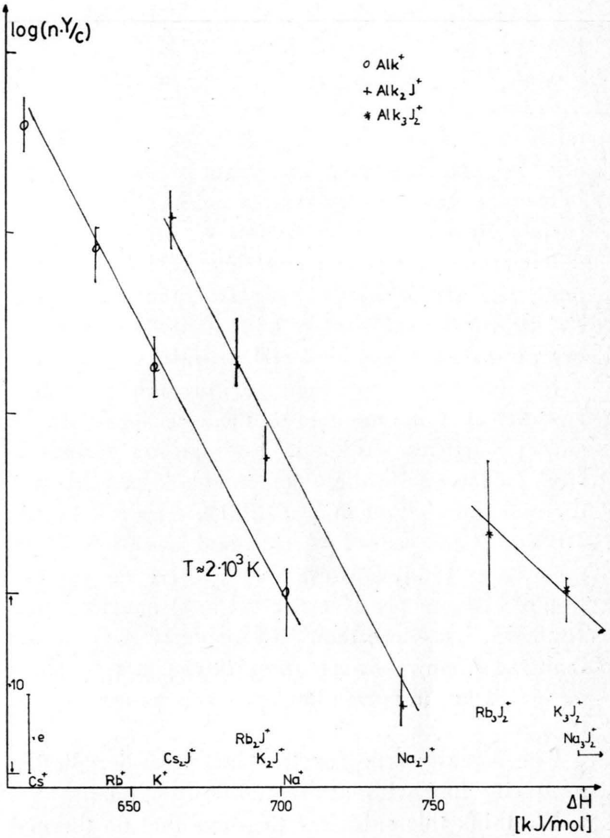

Fig. 4. Van't Hoff plot of the normalized ion yields vs. formation enthalpy for thermal evaporation. Each class of ions (atoms, first order clusters, second order clusters) may fit to a "temperature" of about $2 \cdot 10^3$ K. However comparing ions of different types from the same substance, one would get a "temperature" about 10^4 K, whereas the impact energy is not sufficient even to melt the target! (Limit II of Table 1.) Uniform behaviour *within* the same chemical class of ions, but different behaviour of the ion formation yields of several chemical classes is common to all dissipation techniques and can be explained in terms of fast non-equilibrium phase transition theory [12].

The observation that static heating of the sample decreases the cluster yields dramatically cannot be explained in both models. In the evaporation model heating paradoxically means *decreasing* the ion/cluster ratio-related "temperature".

In both models we are not able to understand the constancy of the "temperatures" over the entire particle velocity range (only the ion/cluster ratio-related "temperature" decreases (!) slightly with increasing v), where the energy density varies between 1 and 30 J/cm^2. An impact depth of about 2 µm in both cases would result in a 5 to 150 kJ/

cm^3 initial energy density. This would result in an temperature increase of about 10^3 K for the low v case. This fits well with the observation that with such large slower particles the hitted foil is even not melted on its surface. The particle sticks on the foil after impact. However, one cannot produce 10^6 ions in tens of nanoseconds from such a small cool surface by thermal evaporation, as one may easily derive from Hertz-kinetic equation: With $T = 2000$ K one gets $(\mathrm{d}^2 n/\mathrm{d}t)\,\mathrm{d}f = 1$ ion/100 nsec · µm^2; with $T = 1000$ K several orders of magnitude less. However, one observes at least 10^3 ions/100 nsec · µm^2.

Similar arguments hold for the ion formation from tetrabutylammonium iodide, especially with the slower particles. Although thermal ion formation from surfaces with these compounds is possible, the thermal ion current at $T = 1200$ K does not exceed 10^{10} ions/mm^2 · sec ~ 1 µA/cm^2, and is much lower in most cases [11]. However, we observe the production of 10^6 ions per 100 nsec (or less) and 10^{-2} mm^2 (or less), i. e. more than 10^{15} ions/mm^2 sec or more than 0.1 A/cm^2, however only during a very short period. The ion formation by a rate process seems thus very unlikely.

The same is true for transient laser irradiation producing ions without thermal destruction.

We think this sufficient to prove that no thermal evaporation process may be responsible for these phenomena either.

4.3. The Non-equilibrium Phase Transition Model

Due to the great similarities with other fast dissipation techniques, it may be justified to assume similar ion formation processes. The main features of ion formation common to all methods, such as dust particle impact, high energy and low energy ion impact, and pulsed laser irradiation are:

- relative secondary ion yields hardly dependent on the method
- relative secondary ion yields only slightly dependent on the primary impact parameters of each method (specific energy loss $\mathrm{d}E/\mathrm{d}x$ (Z, v) with ions; laser wave length, energy flux, if $\ll 10^{10}$ W/cm^2; dust particle mass and velocity)
- secondary ion TOF-line widths not broadened, i. e. low energy distribution $\sim$eV; prompt emission – almost no thermal tails
- large dependence of secondary ion properties on surface parameters, as preparation technique, chemical composition and pollution, and sample temperature
- heavily enlarged ion emission *rates* (orders of magnitude higher than expected from thermokinetic data)
- cluster ion formation decreases when approaching the melting point, i. e. lack of near neighbour correlations (measured with dust and lasers).

Thus one is able to say that the ionization by fast dissipation exhibits the in-situ ionic distributions at the solid surface, independent of the detailed kind of the primary excitation. This behaviour cannot be explained by thermal processes, but only by a sudden perturbation of the polar binding sites at the surface, not bothering homeopolar binding.

Prompt emission of heteropolar bound species is expected, if a perturbation of higher main frequencies compared to the vibration frequencies acts at the surface with field amplitudes exceeding the binding field strength.

Dust particles faster than $v = 300$ m/sec, i. e. 3 Å/psec $(\omega = (v/a) > 3 \cdot 10^{12}\,\mathrm{sec}^{-1}$; $a =$ oscillation amplitude of the atoms < 1 Å) are capable to produce appropriate collision spikes. As low frequent nonpolar binding sites are not affected, molecular ion formation is possible to a large extent. The details of this model are treated elsewhere [12].

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