Thermodynamics of Ion Formation by Fast Dissipation of Energy at Solid Surfaces *

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A fast dissipation of a certain amount of energy at a solid surface by a mechanism whatsoever may cause a non-equilibrium phase transition of the surface material forming nearly instantaneously a relatively large amount of gaseous molecular and atomic ions. This is known to be a phenomenon common to many techniques utilized to create ions especially from organic solids. The thermodymanics of these processes are deduced from first principles; physical properties (kinetic energy and angular distributions, excitation energy) and chemical properties (ion types, mass spectra and intensities) are derived. Like "temperature" as an intensive quantity plays a major role in equilibrium thermodynamics, "action" as an extensive quantity takes the counterpart in this very far-from-equilibrium behaviour.

1. Introduction

Several new techniques of transient formation of molecular ions from organic solids have been developed in the recent years. Equal preparation and thus equal chemical surface properties provided, they all produce very similar mass spectra, especially from polar and non-volatile compounds, although the techniques are very dissimilar. However, there is one item common to all of them: A certain amount of energy is dissipated to the lattice during a rather short time period. As a consequence ions are formed with rates many orders of magnitude larger than expected for ordinary thermal evaporation. However, the molecular ions are rather "cold", i.e. they decay only slowly in the gas phase, and large quasimolecular ions can be observed even from thermolabile compounds. It is already here worthwile to notice that the mass spectra and the energetic distributions of the produced ions are nearly independent of the detailed kind of primary excitation of the solid and of the quantitative amount of energy dissipated in the unit volume.

The techniques are in particular:

- Ion impact
  - – Impact of low energy ions or atoms (keV-range) in the elastic atomic collision regime: SIMS [1] (Secondary Ion Mass Spectrometry) and FAB-MS [2] (Fast Atom Bombardment-Mass Spectrometry)
  - – Impact of high energy ions (MeV-range) in the inelastic electronic energy loss regime: HIID [3] (Heavy Ion Induced Desorption), as special case FFID (^{252}Cf-Fission Fragment Induced Desorption – "Plasma Desorption") [4, 5].
- Laser pulse irradiation
  - – Infrared laser irradiation resulting in direct lattice excitation [6].
  - – Ultraviolet laser irradiation resulting primarily in an electronic excitation [5, 7, 9]. Also light in the non-absorbing visible regime works due to initiation of electronic absorption by multiphoton processes [9].
- Gross techniques
  - – Dust particle (micrometeorid equivalents) impact of μm diameter, some km/sec in velocity, or even lower [8].
  - – Fast electric discharge at wires in the Sub-GHz regime [10] (F.R.G.-patent No. 3303400).

Note with these three main groups of techniques that the first subgroup always deals with the direct lattice excitation, whereas the second one deals with an indirect lattice excitation mediated by the electrons. However, the ion formation phenomena are nethertheless very much comparable with only few exceptions. A general theoretical description may thus be worthwile. The gross techniques mentioned above have been found after their existence has been predicted from a preliminary model known as "sudden perturbation ion formation" [11, 12].

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In order to facilitate the description of the nonequilibrium thermodynamics used, analogous equilibrium thermodynamics will be remembered in due course.

2. General considerations

Let $P_\nu(m, t)$ be the probability of finding the surface system ν in a state m at a time t. The system ν may be represented by an atom or by a certain cluster of atoms with an energetic state m relative to its surrounding. m can be identified for an atom with the vibrational excitation number of the bound state or – for higher excitations – with the momentum in the continuum which has been coarse grained properly. For a cluster of atoms, m can be identified with the analoguous center-of-mass values. However, a cluster of atoms is defined only if at least no member atom finds itself in a continuum state.

Any excitation may alter the P_ν. The alteration per unit time is generally described by the master equation [13]:

$$\dot{P}_\nu(m, t) = \sum_{m'} w(m, m') \cdot P_\nu(m', t) - P_\nu(m, t) \cdot \sum_{m'} w(m', m) \tag{1}$$

if no cleavage of clusters ν is associated with the (m, m')-transitions. w as a conditional probability defines the transition probability (e.g. from m to m', provided that m is occupied), and is a function of the interactions V and the detailed kind of the initial and final states. Thus w may generally be described by a transition matrix element

$$w(m', m) = \left(\frac{2\pi}{\hbar}\right) |\langle m' | V | m \rangle|^2 \tag{2}$$

which to evaluate is for most cases an arduous task of quantum statistics. However, we are interested here only in two limiting cases: The first is the stationary detailed balance state, where $\dot{P} = 0$. In this case the structure of the solutions in independent of the detailed w. The second is the very sudden perturbation case, where (2) can be evaluated very simply.

Detailed balance would imply

$$w(n_j, n_{j+1}) P_\nu(n_{j+1}) = w(n_{j+1}, n_j) P_\nu(n_j) \tag{3}$$

for any states n_l on a chain between states n_0 and n_N. For $P_\nu(n_j) \neq 0$, (3) yields

$$\frac{P_\nu(n_{j+1})}{P_\nu(n_j)} = \frac{w(n_{j+1}, n_j)}{w(n_j, n_{j+1})}. \tag{4}$$

(For our cases it would be sufficient to consider only atoms for ν, as clusters would decay on the chain n_0 to n_N for high excitation densities.)

For the ratio of the probabilities of occupation of the final (n_N) to the initial state (n_0) one easily gets

$$\frac{P_\nu(n_N)}{P_\nu(n_0)} = \prod_{j=0}^{N-1} \frac{w(n_{j+1}, n_j)}{w(n_j, n_{j+1})}. \tag{5}$$

As a solution of this equation, putting

$$P(m) = \mathcal{N} \exp \Phi(m), \tag{6}$$

one gets

$$\Phi(n_N) - \Phi(n_0) = \sum_{j=0}^{N-1} \ln\{w(n_{j+1}, n_j)/w(n_j, n_{j+1})\}. \tag{7}$$

If we identify the n_l with a (for the moment: equidistant) ladder of excitations of energy distance ε of the species ν, we get the Boltzmann distribution function for the P_ν, especially

$$\frac{P_\nu(n_N)}{P_\nu(n_0)} = \exp\left(-\frac{N\varepsilon}{kT}\right) \tag{8}$$

or

$$\Phi(n_N) - \Phi(n_0) = \frac{N\varepsilon - \varepsilon_0}{kT}, \tag{9}$$

(ε_0: ground state energy)

and the partition function

$$Z = \sum_l \exp(\Phi(n_l)) = \sum_{l=0}^{\infty} \exp\left(-\frac{l\varepsilon}{kT}\right). \tag{10}$$

In this stationary equilibrium limit, one can easily derive from Z the relative number of species ν being excited over an energy limit $E_{\mathrm{act}} = r\varepsilon$. The rate of excitation over this limit (which must be equal to the rate of de-excitation under this limit) takes an Arrhenius form with (3) and (8):

$$P_\nu(r+1)\, w(r, r+1) = W(r+1, r) \exp\{-E_{\mathrm{act}}/kT\}. \tag{11}$$

The temperature T refers to the mean excitation energy $kT/2$ per degree of freedom.

From this point of view evaporation may be described as a quasiadiabatic rate process favoring species with lowest evaporation energy. The preexponential frequency factor in (11) plays a minor role, as w is considered to be a smooth function of the states and is related to the atomic oscillation frequencies. The evaporation of cluster species is in principle governed by the same behaviour. However, in practical cases they play a minor role: with high T most clusters may be dissociated, with low T they are hindered by its higher energy of formation compared with e.g. atomic ions. Desorption by fast dissipation, however, is phenomenologically inconsistant with these distributions as well as with the derived rates (kinetics) [8].

So, let us postulate the opposite case for the conditions of solutions of the master equation. It is assumed that transition takes place from a set of states m (e.g. Boltzmann distributed solid surface states at room temperature) into a set of free continuum (gaseous) states by a sudden and strong change of the binding potential. If this change is faster than the mean oscillation frequencies of the species v and the perturbation amplitude higher than the binding potential, the non-zero transition matrix element reduces simply to [11, 12]

$$w(m, n) = c_v \, |\langle n \mid m \rangle|^2 \tag{12}$$

(c constant) for each single state m, which is thus projected on to the basis (e.g. plane waves) of the free states. For atomic species v, n and m are the nuclear wave functions themselves, bound or free, respectively, but for molecular species they are their center-of-mass parts. The coupling factor c is mainly dependent on the charge density of the species v and will be considered further in the sequel (Chapter 4.3).

For this extreme far-from-equilibrium case the master equations reduce to

$$\dot{P}_v(m, t) = - P_v(m, t) \sum_n w(n, m) \left(+ \sum_n P_v(n, t)\, w(m, n)\right), \tag{13a}$$

$$\dot{P}_v(n, t) = + \sum_m P_v(m, t)\, w(n, m) \left(- P_v(n, t) \sum_m w(m, n)\right). \tag{13b}$$

As it has been shown already elsewhere [12] some recapture into bound states has to be considered, adding the terms in parenthesis, which will be omitted in the moment.

The relative number of species v released into the gas phase states n is thus a pure function of the solid state m distribution and does not depend on the detailed kind of interaction! This is a fair approximation to the experimental data from all techniques.

However, the absolute yield Y_v of the species produced is dependent on the *action* of the perturbation as follows:

$$Y_v = \iint_{F_v} \int_0^T \dot{P}_v(n, t)\, \mathrm{d}t \, \varrho(v)\, \mathrm{d}f. \tag{14}$$

Integration is taken over the surface area F_v where the perturbation exceeds the above amplitude limit and the time T it acts sufficiently. (Note that T depends explicitely on the surface coordinate, i.e. distance to the center of excitation.) With the surface density ϱ of the species v being constant the yield writes

$$Y_v = \varrho\, c \iint_F \int_0^T P_v(m, t)\, \mathrm{d}t\, \mathrm{d}f \, |\langle n \mid m \rangle|^2 \tag{15}$$

with the help of (13b).

If P_v does not decrease too steeply during this time interval T (no saturation) one may approximate (15) by

$$Y_v = \varrho\, F_v\, T\, c' \, |\langle n \mid m \rangle|^2 . \tag{16}$$

$\varrho\, F_v$ is the number N of species excitable over the binding energy E_v. Thus

$$A_{\max} = \varrho\, F_v\, E_v\, T = N E_v T \tag{17}$$

is the highest possible action $A_{\max}$, which may be denoted in Heisenberg-units h, whereas the second part of (16) is due to the efficiency of this action.

Namely, the action A on any excitable species is given by

$$A = - \hbar \int_0^T \frac{\dot{P}(m, t)}{P(m, t)}\, \mathrm{d}t = c' \hbar \int_0^T |\langle n \mid m \rangle|^2\, \mathrm{d}t . \tag{18}$$

With a transition probability proportional to the main frequency ω_i of the states m, which can be derived from fourier transform properties, if n are taken as sin- and cosin-functions, one gets with $f_i = T\, \omega_i \quad (f_i < 1)$

$$\begin{aligned} A &= c'' \hbar \int_0^T \omega\, \mathrm{d}t = c'' \hbar \int_{\omega_i}^{\omega_i/f_i} \frac{\mathrm{d}\omega}{\omega} \\ &= c'' \hbar \left(\ln(\omega_i/f_i) - \ln \omega_i\right) < E_0 T \approx f_i \hbar \end{aligned} \tag{19}$$

as $E_0 \approx \hbar\, \omega_i$ due to the well known virial theorem.

This action is related to the maximum specific entropy production $\Delta S/k$ (k: Boltzmann constant)

$$A > \hbar\, \Delta S/k . \tag{20}$$

This can be seen from the information flux I connected with the process via the maximum excitation probabilities $f_i = T_0 \omega_i$ of the mode i:

$$I = -k \sum_i f_i \ln f_i = -k \sum_i T_0 \omega_i \ln (T_0 \omega_i)\,. \quad (21)$$

On the other hand, the total action A from (19) is given by

$$A = h\,c'' \sum_i \frac{\omega_i}{\omega_{\min}} \ln \frac{\omega_i}{\omega_{\min}}\,; \quad \omega_{\min} = 1/T_0\,. \quad (22)$$

Thus the information production due to the released species (e.g. ions) is proportional to the effective action of the process, which is action of the perturbation (17) times effectivity (a chemical value as discussed in Chapter 4.2).

In this far-from-equilibrium situation the heat of formation is irrelevant for the ion formation probabilities: Instead, relevant parameters are the frequencies ω_i of the modes to be excited, dielectric coupling strengths c'', and the total action of the perturbation. Quantitative implications will now be deduced from the above relations.

3. Physical parameters of the desorbed ions

3.1. Kinetic energy distributions

Taking the sudden perturbation model seriously no real momentum transfer is to be considered; however, the sudden interaction can be taken like switching off the binding potential. Thus the momenta of the released particles are expected to reflect the distribution of momenta in the bound state. From (12) one could assume this distribution of momenta q as the fourier transform of the center-of-mass part $\psi(r)$ of the nuclear wave function of the preformed ion in the bound (surface) state. Thus the distribution would read

$$p(q) \sim \int_{-\infty}^{+\infty} \psi(r)\, e^{iqr}\, \mathrm{d}r \cong |\langle n \mid m \rangle|^2\,. \quad (23)$$

However, this distribution may well be altered by the recapture phenomenon as introduced in (13) in parentheses. Taking this into account line forms have been calculated in detail in former papers [12, 14].

As this procedure is difficult for molecular ions, another approach is elected. The well-known Virial theorem states for the mean kinetic energy $\overline{E_{\text{kin}}}$ of an object bound in a homogeneous potential of the order n with a potential energy E_{pot}

$$n\,E_{\text{kin}} - E_{\text{pot}} = \text{const}\left(= \frac{3}{2}\,\Pi\,\Omega_0\right). \quad (24)$$

(For surface states: Π surface tension, Ω_0 specific area of coverage.)

From this one can easily derive typical mean kinetic energies for molecular species of a few eV, independent of type and strength of interaction within the regime of validity of this "sudden" approximation. This has been verified experimentally for the HIID case [3] and seems to be credible also for the other techniques. The widths E_{kin} may thus be estimated to be a certain fraction (say: one third) of the binding energy.

With the direct lattice excitations, however, atomic and small molecular ions may well undergo also direct momentum transfer. This has been observed by Wien [15] as a line broadening of these species with *lower* kinetic energy of the primary ions approaching the sputtering regime. On the contrary, large molecular ions would be destroyed by direct momentum transfer. Consequently, the survived large molecular ions do not show such line broadening in the sputtering regime.

3.2. Secondary ion angular distribution

Secondary ions leaving the surface in oblique angles are more likely to be recaptured into a bound state than those leaving perpendicularly. Thus the angular distribution is expected to be peaked in forward directions, e.g. approximated by

$$\frac{\mathrm{d}N}{\mathrm{d}\Omega} \sim \cos^n \vartheta\,, \qquad n > 1\,. \quad (25)$$

A detailed calculation of this effect as given in [12] leads to an angular distribution

$$\frac{\mathrm{d}N}{\mathrm{d}\Omega} = \cos \vartheta \left(\exp\left(1 - \frac{1}{\cos \vartheta}\right)\right)^r \quad (26)$$

with $r > 0$ for $w(m, n) \neq 0$ in (13). As this recapture parameter r is also relevant for the kinetic energy distribution as discussed in Chapter 3.1, both distributions depend from each other. This has been shown to be valid for FFID by the investigations of Fürstenau and Knippelberg [16].

3.3. Yield dependence on the angle of primary high-energy-particle incidence

Let A_0 be the surface area on which the perturbation amplitude exceeds the minimum value sufficient for secondary ion formation, normal incidence of the primary ion/particle considered. For oblique incidence this area $A(\Theta)$ (Θ angle of incidence) would be increased due to

$$A^{\mathrm{ampl}}(\Theta) = A_0^{\mathrm{ampl}}/\cos\Theta\,. \tag{27}$$

However, in order to estimate the total yield of the secondary ions produced one has to consider the action (and not the energy) transferred.

Let l be the path of a primary ion within the solid target material. Then its action on a surface point P is given by its path integral (P′ entrance point on the surface)

$$A(\mathrm{P}) = \int_{\mathrm{P}'(l)}^{\infty} \varepsilon\,\varepsilon_0\,\mathrm{E}^2(l)\,\frac{\mathrm{d}l}{v(l)} \tag{28}$$

with E the polarization field strength at P according to the charge of the primary particle of velocity v, both functions of the path l. We have to ask for the quantity of surface points P where $A(\mathrm{P})$ exceeds a certain value. It is difficult to evaluate (28), as ε is frequency dependent and E and v are complicated functions. A calculation in the fourier space would thus be appropriate. But what one is able to say without further investigation is the fact that the area of minimum action varies with Θ as

$$A^{\mathrm{action}}(\Theta) = A_0^{\mathrm{action}}/\cos^n\Theta \tag{29}$$

because factorizing the action into an energy and a time part would leads to two contributions of factors $1/\cos\Theta$, this overestimating the angular dependence. At least one is able to say that the yield dependence $Y(\Theta)$ on the angle of incidence Θ is expected to be

$$Y(\Theta) = Y_0\cos^{-n}(\Theta)\,; \qquad (1 < n < 2) \tag{30}$$

which is an "over-crosine" behaviour.

This has been verified by recent experiments with HIID of Sundqvist et al. [17].

4. Chemical parameters of the desorbed ions

4.1. Classification of molecular oscillators

In Table 1 a frequency classification of the molecular oscillators relevant for the ion formation process is shown.

During the liberation process of a heavy molecule from a surface within about 10^{-11} sec the electronic system of the molecule plus its surrounding approaches a complete equilibrium at low energy. Thus the lowest electronic state is preferred. Radical ions, if formed, would recombine immediately in most cases, as an unpaired electronic state is usually more energetic than the Fermi level electrons. The electronic state of a doubly charged ion is even more energetic and full reneutralization is thus expected. However, this may not be true for some delocalized electronic π-structures, some unpolar compounds, and for inorganics with several oxidation states (esp. group VIb – VIIIb of the periodic table).

From this we may deduce a first rule of organic ion formation due to fast dissipation:

R1. Non-radical ion species are preferred in molecular ion formation.

A second rule is an almost trivial consequence:

R2. Preformed cations and anions (and charged order structures in the solid) can directly be formed as free gaseous ions [32].

As one can see further on in Table 1 proton hopping is a fast process [18] but comparable in frequency with some high-frequent molecular oscillations. Thus protons are able to occupy low energetic levels during ion formation. This statement is equivalent to saying that the Brønsted acidity and basicity relations in the condensed phase determine the ionic species actually formed according to rule 3:

R3. The non-radical cations $(\mathrm{m}+\mathrm{H})^+$ (m any stable neutral compound, e.g. parent molecule or part thereof, or neutral intermolecular order structure) and anions $(\mathrm{m}-\mathrm{H})^-$ are preferably formed, if m is a strong Brønsted base (for cations) or a strong Brønsted acid (for anions) in the condensed phase compared to competing acid-base reactions.

This has been found experimentally, too [19].

Due to the above frequency discrimination of proton transfer kinetics one may state the following isotopic rule:

R4. Ions formed with proton transfer during liberation from the surface will be subject to a $(\mathrm{m}\pm\mathrm{D})^\pm$ type ion hindrance in a deuteron environment compared to the $(\mathrm{m}\pm\mathrm{H})^\pm$ type ions in a proton environment.

This isotopic effect has been found quite early in the data of [20]. The Brønsted concept of basicity can be extended to metal cations Me^+ instead of protons. However, as these heavy particles are comparably slow, cationization, i.e. formation of

Table 1. Frequency order and coupling strengths of oscillator at the solid state surface.
Electronic perturbations are very fast and strongly coupled to molecular sites of permanent dipole structure. Thus bond cleavage at these polar sites during excitation is a very frequent process. On the other hand, ion formation itself is favored from such polar molecules. Unpolar sites of the molecule, however, are not excited due to lower frequency and low coupling with electronic perturbation. So, their fragmentation is a rare process; on the other hand, completely unpolar molecules are unlikely to be ionized, except for polarization by metal cations leading to some cationization.
Comparison of typical non-equilibrium and thermal equilibrium surface ion formation rates, theoretically and experimentally. Ion formation by fast dissipation is generally proved to be kinetically a far-from-equilibrium process.

	Typical $2\pi\nu=\omega$ [s^{-1}]	Type	Coupling properties
Electronic	$10^{16}-10^{17}$	plasmons, collective oscill.	coupling with optical phonons due to the dispersion relations, and with all localized polar structures
	$\sim 10^{16}$	free electron rearrangement	
	$\sim 10^{15}$	exciton resonances	
	$1\ldots 3\cdot 10^{14}$	alteration of charge distrib. by atomic collision cascades or shock waves	
Protonic	$8\cdot 10^{14}$	proton hopping, O–H, N–H stretching	excess production of free protons by high frequent electric interactions
	$5\cdot 10^{14}$	deuteron hopping	
Molecular vibrational		high frequent polar bonds	strongly excited frequent bond cleavage, high desorption yields with such groups
	$5\ldots 6\cdot 10^{14}$	alcohols, ethers	
	$5\cdot 10^{14}$	carboxylic acid (neutral)	
	$3\cdot 10^{14}$	carboxylic acid (as anion)	
	$3\cdot 10^{14}$	esters	
	$3\ldots 6\cdot 10^{14}$	amides	
	$7\cdot 10^{14}$	amines	
	$4\cdot 10^{14}$	thioalcoholes	
	$2\cdot 10^{14}-6\cdot 10^{13}$	high frequent unpolar bonds e.g. C–C, C=C, aromatics	weakly excited, some cleavage
	$10^{12}-10^{13}$	low frequent skeletal vibrations and relaxations	not excited

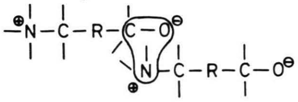
Rates r [$cm^{-2}\cdot s^{-1}$]	typical for
$\sim 10^{22}$	far-from-equilibrium "rates" (transiently) due to (13); theoretical value [8] (Pseudo-rates – no real rate process!)
	experimentally obtained limits (limited due to times resolution)
$> 10^{20}$	for FFID (^{252}Cf-fission fragments) [16]
$> 10^{18}$	for LAMMA 1000 [8], [28] UV-laser pulses
$> 10^{17}$	for dust particle induced desorption [29]
$< 10^{9}$	thermiionic ion formation, experimentally [31]
$\sim 10^{8}$	thermal rate due to (11), theoretically

$(M+Me)^+$ ions should be only possible as a preformation process prior to excitation, or as a relaxation of fast Me^+-particles in whole molecules M (parent type) [21]. Thus one expects the following rule due to heavier particle kinetics:

R5. Cationization $(M+Me)^+$, or $(2M+Me)^+$ is expected to occur only with M as parent molecules but not with neutral fragments m.

This does not exclude unimolecular decomposition of $(M+Me)^+$ particles to $(m+Me)^+$ in the vacuum as observed with magnetic spectrometers, but not with time-of-flight mass spectrometers, which are sensitive to the instantaneously formed ions.

We have to explain more precisely what is understood by an "intermolecular order structure". Let for instance two molecules of the same structure be represented by



At the surface they will be aligned due to the lowest energy constraint, i.e. sites of opposite charges will have a great chance to be neighbours. The circle indicates an intermolecular order structure of high polarity, namely the neutral $m_1 = HOCN$. As this is a relatively strong acid but a weak base in the condensed (high dielectricity) phase, one expects in such cases strong CNO^- lines but weak H_2CNO^+ lines, as always observed [22]. The same is true for several other lines which cannot be explained by unimolecular decomposition within nanoseconds as required for their appearence in time-of-flight mass spectra.

4.2. Absolute intensities of ion formation

The total yield Y produced in an interaction of maximal action $A_{\max}$ may be written as

$$Y \cong A_{\max} \cdot P_{\text{tot}} \tag{31}$$

according to (16) and (17), with a total interaction probability of the high-frequent perturbation with a main frequency $\Omega \gg \omega_n$ (ω_n oscillator frequencies (infrared) of the molecule). The probability P_{tot} can be described as the linear response of the system of the ω_n' due to the perturbation V, which is given by a set of amplitudes $a_n(\omega_n')$, which may be modeled by the light extinction coefficient of light frequency ω' as an electric interaction strength. Than P_{tot} is given due to linear response theory by

$$P_{\text{tot}} \sim \int_0^{\Omega} \left| \frac{a(\omega')\,\mathrm{d}\omega'}{\omega'^2 - \Omega^2} \right| . \tag{32}$$

The Kramers-Kronig relation, however, states a connection between the optical diffraction index $n(\omega)$ and the extinction coefficients $a(\omega')$:

$$n^2(\omega) - 1 \sim \int_0^{\infty} \left| \frac{a(\omega')\,\mathrm{d}\omega'}{\omega'^2 - \omega^2} \right| . \tag{33}$$

If we choose $\omega = \Omega_0$ well above all molecular oscillation frequencies in the infrared region, but also well below the electronic absorption bands in the ultraviolet region, we can approximately state

$$P_{\text{tot}} \sim n^2(\Omega_0) - 1 \tag{34}$$

with Ω_0 in the visible or near infrared region for most organic compounds.

R6. The absolute quantity of the ions formed by direct interaction (not by cationization or similar reactions) should be approximately proportional to the square of the diffraction index of the substance.

In Chapt. 4.3 we will discuss how the relative intensities in the mass spectra may be related to the detailed IR-spectra of the material.

With $\varepsilon = n^2$ the total ionization probability is directly related to the dielectricity of the substance, or the dipole density, as the molecular refraction is given by the Clausius-Mosotti formula:

$$R = \frac{n^2 - 1}{n^2 + 2}\,\frac{M}{\varrho} = \frac{4}{3} N_{\mathrm{L}} \left(\alpha + \frac{\mu^2}{3kT} \right) \tag{35}$$

with ϱ its density in weight, N_{L} Loschmidt's number, α the polarizability, and μ the permanent dipol moment of the molecule of weight M. Thus an empirically provable description as a high-frequency excitation of slow electric dipole oscillators is given.

If $\mu = 0$ the substance is named unpolar, however, the remaining polarizability α can be interpreted as a superposition of bond refractions giving still rise to a minor excitation, especially if halogens ($R_{\mathrm{Cl}} = 6$, $R_{\mathrm{J}} = 13.9$) are present in the molecule or with alkoholes, ethers, and ketones ($R_{-\mathrm{OH}} = 1.5$, $R_{-\mathrm{O}-} = 1.6$, $R_{-\mathrm{C=O}} = 2.2$; all refractions R in $\mathrm{cm}^3/\mathrm{mol}$). However, from these substances quasimolecular ion formation is very often only possible by cationization, which may be interpreted as a strong polarization by the metal cation. The polarization efficiency of halogen anions is much smaller, so anionization is expected to be a minor effect and has not yet been observed with these methods, but has been with field desorption [23]. (Do not confuse anionization of unpolar substances with halogenide salt formation of polar amines!)

Polar substances ($\mu \neq 0$) therefore exhibit much higher to yields. The most polar compounds are salts, which give rise to the highest absolute ion intensities known [5, 9].

4.3. Calculation of model mass spectra

From the above information one may try to calculate model mass spectra of organic compounds as expected instantaneously after desorption. As the formed ions contain a certain relaxation energy (typically some eV) further unimolecular decomposition in the gas phase may occur, which can be treated by the well-known quasiequilibrium theory [24, 25] (QET) being *not* under discussion here.

The high-frequency perturbation acts in a twofold manner: Liberation of complete molecular structures and excitation of bond oscillators, preferably those of higher frequency and polar structure, i.e. stronger coupling. The probability distribution $p(\beta)$ of bond β excitation determines the probability distribution $p(m)$ of fragment m formation. Fast hydrogen rearrangement at the fragment determines the real fragment ion formation according to rule R3. Bond cleavage is thus expected preferably near charged sites. These bonds β are treated as follows: $p(\beta)$ may be estimated proportional to an excitation amplitude, which depends on its dipolarity and may be approximated by an infrared absorption amplitude $a(\beta, \omega_i)$ of bond β and mode ω_i, and proportional to $(\Omega^2 - \omega_i^2)^{-1}$ ("resonance denominator"):

$$p(\beta) = c \sum_i \frac{a(\beta, \omega_i)}{(\Omega^2 - \omega_i^2)} . \tag{36}$$

The normalization constant c is set $p(\beta) = 0.5$ for high frequent and very polar bonds like the peptide bond. This normalization is purely empirical in the moment.

Now let us determine all fragment masses m_j which can be formed by one or more bond cleavages β. The probability $p(m_j)$ is then given by

$$p(m_j) = \prod_\beta p(\beta) = c \prod_\beta \left(\sum_i \frac{a(\beta, \omega_i)}{\Omega^2 - \omega_i^2} \right) . \tag{37}$$

The product is extended over all bond cleavages β necessary to form m. With the rules R1 – R3 we determine the exact mass and polarity $(m + n\,\mathrm{H})^{\pm}$ with $n = (-3, -2), -1, 0, +1, (+2, +3)$, respectively. Due to amphoteric behaviour of the fragments and more nucleophilic or electrophilic attack by the perturbation, both polarities may occur. But over all, positive fragment ions are preferred due to their lower ionic radii and thus higher polarization interaction. This is also found experimentally [4, 22]. –OH groups tend to an elimination of water.

The mass spectra of peptides, amino acids and several alkaloids can be modeled by this procedure fairly, but this is not treated further in this very context.

4.4. Relative intensities of cluster ions from chemical homologuous

If a thermal equilibrium at the surface would be responsible for ion formation, one would expect for the probability of formation $p(m)$ for any ion due to (8 – 10):

$$P_{\mathrm{equi}}(m) \sim \exp\left(-\frac{\Delta H(m)}{kT} + \frac{\Delta S(m)}{k} \right) = \sigma \exp\left(-\frac{H(m)}{kT} \right) \tag{38}$$

with $\Delta H(m)$ the enthalpy of formation of m and σ a statistical factor due to the entropy change

$$\Delta S = K \ln w_1 / w_0 = k \ln \sigma \tag{39}$$

with the ratio σ of statistical weights w of initial and final states. Types of ions and rates of their formation would be a function of the process temperature T being dependent on the energy density deposited. The rate of formation r is then given by

$$r \cong \omega_{\mathrm{osc}} \exp\{-A^*/kT\} \tag{40}$$

with A^* the activation energy ($A^* \gtrsim \Delta H$), and ω_{osc} the oscillation frequency of the initial state. All excitable degrees of freedom contain the average energy $E = kT/2$.

It has been shown that this equilibrium description is wrong for the phenomena treated here:

- ions of higher formation enthalpy are often more probable to be produced than those of lower one ("preference of polarity" [26]).
- van't Hoff plots do not exhibit a "temperature" (slope) change, when the specific energy loss of the primarily exciting particles is varied [3, 8].
- the observed rates of instantaneous ion formation exceed the rates of (40) by several orders of magnitude [8].

In our far-from-equilibrium sudden approximation the enthalpy of formation is no relevant quantity at all; the relative yields are determined by polarizability arguments (see above) independent from the irradiation energy flux, which is consistent with the observations), and the rates are determined from (13) with the transition probabilities from Table 1, which come out much higher than for the rates out of an equilibrium.

A sudden perturbation and ion liberation, however, results in an excitation of only few degrees of freedom as discussed in Chapter 4.3. All other degrees of freedom can be considered as still containing the average energy due to room temperature only.

A mean correlation number ν_0 can be defined, which is the mean number of "frozen" degrees of freedom during excitation per one excited. The probability distribution of correlation of ν atoms in the solid state at room temperature is given by

$$p(\nu)=\prod_{i=2}^{\nu}\exp\left(-\frac{kT_{\text{room}}}{2\Delta E}\right)=\exp\left(-\frac{\nu kT_{\text{room}}}{2\Delta E}\right) \tag{41}$$

with ΔE the valence energy of each bond due to Boltzmann's statistics. E.g. for alkali halides

$$n=2\nu-1 \tag{42}$$

i.e. a n-cluster [9] ($Cs_n J^+_{n-1}$ with $E=30$ kJ/mole) contains $2\nu-1$ atoms. Thus a linear plot of the logarithm of the statistically weighed ion formation yields vs. the number ν of atoms in each ion type can be drawn as follows

$$\ln(n\cdot Y_n)-\frac{kT_{\text{room}}}{2\Delta E}\cdot\nu \tag{43}$$

with Y_n the yield of a cluster of n-th order. The slope of this plot is proportional to the inverse of the number of "frozen" degrees of freedom per excited site during excitation, which is independent in this sudden approximation from the amplitude of perturbation as has been found in several experiments [3, 8]. However, increasing the sample (i.e. "room") temperature should lead to a decrease of the correlation ν_0, if a phase transition point of the solid is approached. This is also consistent with measurements performed with heated targets as reported elsewhere [27–29]. The quantitative behaviour of cluster ion formation by rapid energy transfer, which has not been understood in quasiequilibrium thermodynamics, has now got a consistent reinterpretation in non-equilibrium thermodynamics.

5. Conclusion

In a sudden approximation the ion formation does qualitatively depend only on sample parameters. Only the quantitative amount of ions being formed is a function of the primary perturbation action [erg · sec].

The fact that the mass spectra of various fast dissipation methods differ only little from each other and do not depend on the irradiation parameters in a wide range, can be explained easily from first principles of quantum statistics. On the other hand, it is worthwhile to notice that detailed information about the surface molecular structure can thus be gained as no new thermal equilibrium destroys it. So fast information transfer is quantitatively related to the Heisenberg uncertainty principle: From (2) one can see that if $h\rightarrow 0$ no information could be preserved in any interaction!

Namely, considering a system of oscillators in a frequency band near ω the information gain is directly connected to the entropy production rate $\dot{s}$ per degree of freedom:

$$\frac{\dot{s}}{k}\geqq\frac{\mathrm{d}\ln w}{\mathrm{d}t}\approx\frac{2\hbar\,\omega^2}{kT}. \tag{44}$$

As a philosophical consequence of critical empirism one may state that quantum mechanics as an indeterministic principle is a prerequisite of any knowledge systems exchange from each other [30, 33].

It has been reported [31] that a steady state irradiation of organic solids with IR laser beams may also cause quasimolecular ion formation from some thermolabile substances, whereas simple resistive heating does not. As this laser irradiation is absorbed in the uppermost layers (non-resonant irradiation does not work) one may think that excitation and desorption can be faster processes than thermal equilibration on the uppermost surface layers.

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