Dissociation of Slow Polyatomic Molecules by Grazing Scattering at Surfaces

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We consider polyatomic molecules containing peripheral chains of valence groups, which slide along crystallic surfaces at grazing incidence. The periodically located Coulomb centres of the crystallic surfaces interact with the moving valence group dipoles like a time-dependent oscillation potential. This interaction can lead to multiple resonant vibrational excitations of the peripheral valence group dipoles. Accumulation of such collective excitations in the valence group chains (excimols) eventually can lead to the cleavage of particular bonds (trap bonds) inside the molecule. A model for this complex process is presented including a parameterised formula for the dissociation probability of polyatomic molecules scattered by a surface at grazing incidence. The model is supported by the experimental observation of dissociation energy thresholds.

Key words: Surface induced dissociation, Polyatomic molecules.

Introduction

Quantum processes of polyatomic molecules caused by interactions with surfaces are an important part of fundamental solid state and molecular physics. The current interest in such processes is indicated by a growing number of publications [1–20]. Most papers on the problem are devoted to the elastic and inealastic interactions of two-, three- and four-atomic molecules with surfaces at different incidence angles and initial velocities $v \leq v_B$, where $v_B \approx 10^8$ cm/s = 1 m/µs is the atomic unit of velocity or Bohr velocity. Analysis of experimental results presented in these papers permits to conclude that the probability P_{01} for excitation of the first vibrational level of diatomic molecules with a normal-to-surface velocity component $v_\perp < 10^5$ cm/s is very small ($P_{01} \sim 10^{-2} - 10^{-3}$) [15, 16]. P_{01} is getting noticeable, however, if the velocity component $v_\parallel$ parallel to the surface reaches the Bohr velocity v_B [8, 9]. This was shown for grazing incidence of biatomic molecules using the model to energy exchange between the molecules and surface phonons or electrons.

The literature related to molecule-surface collisions for molecules consisting of more than four atoms is rather limited and well reviewed in [18].

There is experimental evidence for deposition of a considerable amount of internal energy by molecular collisions with surfaces [18]. This accumulation of energy depends on the initial molecular velocity and on the internal molecular structure. New dissociation channels for polyatomic molecules sliding along surfaces can be opened with an increasing $v_\parallel$ [17–21].

To our knowledge, no consistent theoretical description has been published on the whole complex of processes connected with the grazing incidence of polyatomic molecules on surfaces with velocities $v_T < v_\parallel \leq v_B$, where v_T is a thermal velocity. Nevertheless, there are some phenomenological models describing the dissociation of polyatomic molecules induced by collisions with surfaces. For instance, the thermo-kinetic model is based on the assumption that the normal component of the kinetic energy can be transformed into internal vibrational energy [17]. In another model [10] a mechanism for the transformation of translational energy into rotational energy is suggested for rigid atomic clusters sliding in a surface potential field.

In this paper we present theoretical and experimental investigations of excitation and dissociation processes involved in the grazing scattering of polyatomic, organic molecules at crystallic and metallic surfaces. We limit our considerations to molecular velocities within the interval $v_T < v_\parallel \leq v_B$. In particu-

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lar, we focus on activation energy thresholds for dissociation.

Polyatomic molecules incident upon a smooth surface at grazing angles less then one degree do not penetrate into the surface but are subjected to a predominantly specular scattering by the first layer of surface atoms. This fact permits us to exclude from our considerations a number of complex phenomena associated with molecular penetration into a surface. When $v_{\|} \ll v_B$, a large excitation probability for polyatomic molecules can be observed, eventually leading to dissociation due to their interaction with the surface potential.

Small values of incidence angles $\Phi \leq 1^\circ$ and incidence velocities of $v_{\perp} < 10^4$ cm/s, $v_{\|} < v_B$ make negligible such phenomena like molecular thermal deformation and energy exchange between molecules and surface electrons or phonons. We believe that under these circumstances the excitation and dissociation of polyatomic molecules can occur as a result of their interaction with the surface potential field, which decreases along the surface normal and, more importantly, has a periodical structure due to the regularity of the surface lattice.

We consider polyatomic organic molecules consisting of regularly chained identical valence groups (for instance $C=0$, $N=O$, $C-H$) with relative distances larger than the mean free path of electrons in the surface electron gas. Thus the polyatomic molecule is characterised by a set of chains or rings of valence groups. The following two main interaction mechanisms can be analysed on the base of the above mentioned assumptions about surfaces and polyatomic molecules:

(i) vibrational excitation of separate valence bonds in the polyatomic molecule by the averaged surface potential field;

(ii) resonant vibrational excitation of separate valence bonds by periodic surface potential fields [22]. The basic resonance condition is $\omega^{01} = \omega^1 - \omega^0 = 2\pi v_{\|}/d$, with eigenfrequency ω^0 for the ground state and ω^1 for the first vibrational excited state of a valence bond and d is the lattice constant of the periodic potential. This resonance excitation of a valence bond in a molecule sliding along the periodic surface field is similar to the well known resonance perturbation of gas-atoms channelling inside a crystal [23, 24] or to coherent atomic interactions with light [25].

The probabilities for these two mechanisms depend on the kinetic energy of the molecule, the geometry of the experiment and the structures of molecules and surfaces. In general, the excitation probability for the averaged field acting on the grazing molecule is estimated to be small compared to the resonance excitation probability.

Our approach to polyatomic dissociation is based on our excimol theory [26]. We consider trigger excitations of one or more bonds in valence group chains or rings. The spectral analysis of energy operators for quantum systems (molecules and surfaces) allows to treat excited states in valence groups as quasi-stationary excited states (excimols). The excitation energies of these quasi-stationary states have complex values permitting to take into account relaxation processes and the inharmonic character of bond vibrations.

It was shown that the excimol life time is several orders of magnitude longer than the life time of trigger excitations [27]. The energy of one excimol is not sufficient to destroy any internal bond, but excimols can accumulate in certain bonds inside the polyatomic molecule, which do not belong to the chain and can serve as trap bonds. If n excimols arise in the polyatomic molecule, a total energy $E(n)$ can concentrate in the trap. Dissociation of this trap bond can occur, if $E(n) \geq E_D$, with E_D being the trap bond's dissociation energy.

Theory

Valence groups of a polyatomic molecule experience the interaction with $N_1 \cdot N_2$ surface ions located on the square $L_1 \cdot L_2$. We assume that a molecular valence bond is a quantum oscillator with the dipole momentum

$$\boldsymbol{D} = D_0 \cdot \boldsymbol{S} \cdot \frac{r}{r_0}, \qquad \boldsymbol{S} = \{S_x, S_y, S_z\}, \tag{1}$$

where D_0 is a value of dipole momentum, $\boldsymbol{S}$ a unit vector along the oscillator's axis from the negative charge to the positive one, r_0 an equilibrium distance between the atoms of the valence group and r its variable length.

For a given part of surface with $N_1 \cdot N_2$ centres on the square $L_1 \cdot L_2$ the potential of dipole interaction with all centres denoted by $n_i \in \{1, 2, \ldots, N_i\}$, $i = 1, 2$ can be represented in the form

$$\tilde{V}(\boldsymbol{R}, \boldsymbol{D}) = \boldsymbol{D} \cdot \operatorname{grad} V(\boldsymbol{R}). \tag{2}$$

The surface potential $V(\boldsymbol{R})$ is taken as

$$V(\boldsymbol{R}) = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_1} V(|\boldsymbol{R}_{n_1 n_2}|)\,,$$

$$\boldsymbol{R}_{n_1 n_2} = \boldsymbol{R} + \boldsymbol{Q}_{n_1 n_2}\,, \qquad \boldsymbol{R} = \{R_x, R_y, R_z\}\,, \tag{3}$$

where $\boldsymbol{R}$ is the radius-vector of a dipole c.m., corresponding to surface ion (00), and $\boldsymbol{Q}_{n_1 n_2}$ is the vector directed from ion (00) to surface ion $(n_1 n_2)$. If we denote the lattice vectors as $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$, then we have

$$\boldsymbol{Q}_{n_1 n_2} = n_1 \boldsymbol{b}_1 + n_2 \boldsymbol{b}_2\,, \tag{4}$$

We approximate the potential of surface ion $(n_1 n_2)$ by Moliere's representation of the Thomas-Fermi potential, e.g. [28]:

$$V_{n_1 n_2}(R_{n_1 n_2}) = \frac{Z e}{R_{n_1 n_2}} \chi(R_{n_1 n_2}, a_{\mathrm{TF}}) \quad \text{with}$$

$$\chi = \sum_{i=1}^{3} \alpha_i \exp(-\beta_i R_{n_1 n_2}/a_{\mathrm{TF}})\,, \tag{5}$$

where Z is the atomic number of the surface ion,

$$\{\alpha\} = \{0.1; 0.55; 0.35\},$$
$$\{\beta\} = \{6.0; 1.2; 0.3\},$$
$$a_{\mathrm{TF}} = 0.8853\, Z^{-1/3}\, a_0\,,$$

and a_0 is Bohr's radius.

We introduce a coordinate system (xOy), which coincides with the surface plane. The axis (Oz) is a surface normal. The coordinate origin coincides with the position of the ion (00). If the dipole is moving along the surface with the velocity $\boldsymbol{v} = \{v_x, v_y, 0\}$, the c.m. coordinate is a time-dependent function:

$$\boldsymbol{R}(t) = \{R_x + v_x t, R_y + v_y t, R_z\}\,. \tag{6}$$

Thus, the surface potential is also a function of time

$$V(\boldsymbol{R}(t)) = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_1} V_{n_1 n_2}(|\boldsymbol{R}(t) + \boldsymbol{O}_{n_1 n_2}|)\,. \tag{7}$$

To factorize the time dependent function in expression (2), let us expand the potential over the surface vectors $\boldsymbol{G}_{mn} := 2\pi(n\boldsymbol{a}_1 + m\boldsymbol{a}_2)$, where $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are reciprocal vectors of $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$:

$$V(\boldsymbol{R}, t) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} V_{mn}(R_z, t) \exp\{i \boldsymbol{G}_{mn} \cdot \boldsymbol{R}_{xy}\}\,,$$

$$\boldsymbol{R}_{xy} = \{R_x, R_y\} \tag{8}$$

with

$$V_{mn}(R_z, t) = \frac{\exp\{i \boldsymbol{G}_{mn} \cdot \boldsymbol{v} t\}}{b_1 b_2} \int_0^{b_1} \mathrm{d}R_x \int_0^{b_2} \mathrm{d}R_y \cdot \exp\{-i \boldsymbol{G}_{mn} \cdot \boldsymbol{R}_{xy}\} \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_1} V(|\boldsymbol{R}_{n_1 n_2}|)\,.$$

Then we obtain

$$\tilde{V}(\boldsymbol{R}, t, \boldsymbol{D}) = \sum_{mn} \tilde{K}_{mn}(\boldsymbol{R}_{xy}, R_z, t, \boldsymbol{D})\,, \tag{9}$$

$$\tilde{K}_{mn} = \boldsymbol{D} \cdot \nabla (V_{mn}(R_z) \exp\{i \boldsymbol{G}_{mn} \cdot \boldsymbol{R}_{xy}\}) \exp\{i \boldsymbol{G}_{mn} \cdot \boldsymbol{v} t\}\,,$$

$$\tilde{K}_{mn} = K_{mn} \exp\{i \boldsymbol{G}_{mn} \cdot \boldsymbol{v} t\}\,,$$

$$K_{mn} = \frac{D_0 r}{r_0} \left(S_z \frac{\partial}{\partial z} V_{mn}(R_z) + i V_{mn}(R_z) \{m S_x/b_1 + n S_y/b_2\} \right) \exp\{i \boldsymbol{G}_{mn} \cdot \boldsymbol{R}_{xy}\}\,. \tag{10}$$

From (10) one can see that the valence group feels a time- and velocity-independent component $\tilde{K}_{00}$ of the potential and time- and velocity-dependent periodical potential components $\tilde{K}_{mn} (m \neq 0$ or $n \neq 0)$ with frequencies $\omega_{mn} = (\boldsymbol{G}_{mn} \cdot \boldsymbol{v})$, where $\boldsymbol{v}$ is the parallel component of the molecule velocity.

Let us first estimate the vibrational excitation probability for the valence bond induced by the interaction with potential K_{00}. The interaction potential has the form

$$K_{00} = \frac{D_0 r}{r_0} S_z \frac{\partial}{\partial z} V_{00}(R_z)\,, \tag{11}$$

where $V_{00}(R_z)$ is the average surface potential, which has the form

$$V_{00}(R_z) = \frac{2\pi Z e a_{\mathrm{TF}}}{b_1 b_2} \sum_{i=1}^{3} \frac{\alpha_i}{\beta_i} \exp(-\beta_i R_z/a_{\mathrm{TF}})\,. \tag{12}$$

Valence groups are assumed to orientate by the surface field like diatomic molecules during adsorption [29]. The dipole vector of the valence bond is orientated parallel to the Oz axis at a c.m. distance $R_z \geq 3 a_0$ from the surface. For a distance $a_0 < R_z < 3 a_0$ the valence bond is orientated parallel to the surface.

The valence bond vibrational excitation by interaction with the component K_{00} of the surface potential can be considered in the frame of the first order time-dependent perturbation theory. By this the different braking forces for the different valence group atoms are taken into account. The contribution of this mechanism to the excitation probability of the first vibrational state by our estimation is about 7–10% and does not depend on the molecular velocity in the considered energy range.

Let us now consider the resonant vibrational excitation of a valence bond and the subsequent molecular dissociation caused by $\tilde{K}_{mn}$, with $m \neq 0$ or $n \neq 0$, part of the interaction potential between surface and valence groups. The molecular valence groups are assumed as quantum oscillators, and the vibrational transition inside is possible only from the ground to the first excited state. Resonant excitation is expected, when the valence group eigenfrequency ω^{01} of the first vibrational state coincides with one of the field frequencies ω_{mn}. The relation $\omega^r_{mn} = \omega^{01}$ defines the value of the molecular resonance velocity v^r_{mn} by the equations

$$\omega^{01} = (\boldsymbol{G}_{mn} \cdot \boldsymbol{v}^r_{mn}) = (\boldsymbol{G}_{mn} \cdot \boldsymbol{v}_0)\, v^r_{mn}\,,$$

$$v^r_{mn} = \frac{\omega^{01}}{(\boldsymbol{G}_{mn} \cdot \boldsymbol{v}_0)} = \frac{2\pi\,\varepsilon^{01}\,2.4 \cdot 10^6}{(\boldsymbol{G}_{mn} \cdot \boldsymbol{v}_0)}\ \text{cm/s}\,, \quad (13)$$

where $\boldsymbol{v}_0$ is the dimensionless unit vector in the direction of $\boldsymbol{v}^r_{mn}$ and ε^{01} is the energy of the first vibrational state expressed in eV. The value of G_{mn} is

$$|\,G_{mn}| = 2\pi\,\{(m/b_1)^2 + (n/b_2)^2\}^{1/2}\,. \quad (14)$$

where b_1 and b_2 are the surface lattice constants expressed in [Å] and $m, n \in N$. The lowest ω^r_{01} we define as the fundamental resonance frequency, and the corresponding molecular grazing velocity v^r_{01} as the fundamental resonance velocity, which has the form

$$v^r_{01} = \max_{i=1,2} \left\{ \frac{\varepsilon^{01}\,2.4 \cdot 10^6\, b_i}{(\boldsymbol{e}_i \cdot \boldsymbol{v}_0)} \right\} \text{cm/s}\,, \quad (15)$$

where $\boldsymbol{e}_i$ is a unit vector in direction $\boldsymbol{b}_i$, $i = 1, 2$.

From this it is clear that for the valence group with eigenfrequency ω^{01} the resonance process can occur only for velocities in the half interval $I(\omega^{01}) = (0, v^r_{01}]$. Resonance velocities in this interval have discrete values. The maximum resonance velocity is v^r_{01}. Other resonance velocities can be expressed as

$$v^r_{mn} = v^r_{01}\,\frac{(\boldsymbol{G}_{01} \cdot \boldsymbol{v}_0)}{(\boldsymbol{G}_{mn} \cdot \boldsymbol{v}_0)}\,. \quad (16)$$

The amplitudes of the periodical surface field components are defined by V_{mn}. From this it is clear that for $m, n \gg 1$ the spectrum of frequencies ω^r_{mn} can be considered to be continuous. The corresponding velocities v^r_{mn} for $m, n \gg 1$ are smaller than the value of the fundamental velocity v^r_{01}, which is well separated from the other resonance velocities.

If one is interested in the excitation probability due to the fundamental field harmonic, it is possible to use the well known two-level approximation of nonstationary perturbation theory. To calculate the total action of the periodic surface field on molecules one has to use the first order time-dependent perturbation theory:

$$P_{01}(R_z) = \sum_{m,n} P^{mn}_{01}(R_z) = \sum_{m,n} \frac{(K^{01}_{mn}(R_z))^2 \cdot \sin^2\left\{(\omega_{mn} - \omega^{01}) \cdot \frac{t}{2}\right\}}{(\omega_{mn} - \omega^{01})^2}\,. \quad (17)$$

Now we infer the probability of vibrational molecular excitation as a function of velocity v in the interval, which corresponds to the "nearly continuous" spectrum of ω^r_{mn}. To do this one has to sum the transition probabilities defined in the first order time-dependent perturbation theory over all values m and n. Starting from the periodic field frequency $\omega_{mn} = 2\pi(v_x m/b_1 + v_y n/b_2)$, we can make the transition from summation to integration over continuous variables using the relations $\omega_m = 2\pi v_x m/b_1$ and $\omega_n = 2\pi v_y n/b_2$.
Then we get the considered probability per time unit

$$P_{01}(R_z, \boldsymbol{v}) = \frac{b_1 b_2}{v_x v_y} \int_0^\infty \mathrm{d}\omega_n \int_0^\infty \mathrm{d}\omega_m (K^{01}(\omega_n, \omega_m, R_z))^2 \cdot \frac{\sin^2((\omega_n + \omega_m - \omega^{01}) \cdot t/2)}{(\omega_n + \omega_m - \omega^{01})^2 \cdot t}\,, \quad (18)$$

where K^{01} is a matrix element calculated in the approximation of a constant trajectory:

$$K^{01}(\omega_n, \omega_m, R_z) = \frac{1}{\hbar^2} \left\langle \Phi_1(r) \left| \frac{D_0}{r_0}\, r \left\{ S_z \frac{\partial}{\partial z} V(\omega_n, \omega_m, R_z) + [S_x \omega_n/v_x + S_y \omega_m/v_y]\, V(\omega_n, \omega_m, R_z) \right\} \right| \Phi_0(r) \right\rangle. \quad (19)$$

Here Φ_0, Φ_1 are the oscillator functions for the states 0 and 1 respectively.

Now we integrate (18) over frequency ω_m. Taking into account that the time-factor in (18) has a pole at $\hat{\omega}_m = \omega^{01} - \omega_n$, we extract the factor $[K^{01}(\omega_n, \omega_m, R_z)]^2$ from the integrand by $\omega_m = \hat{\omega}_m$ and average over R_z:

$$P_{01} = \frac{2\pi\, b_1 b_2}{(R^{(2)}_z - R^{(1)}_z)(\omega^{01}\hbar)^2\, v_x v_y} \cdot \int_{R^{(1)}_z}^{R^{(2)}_z} \mathrm{d}R_z \int_0^\infty \mathrm{d}\omega_n \{K^{01}(\omega_n, \hat{\omega}_m, R_z)\}^2\,, \quad (20)$$

where $R^{(1)}_z$ and $R^{(2)}_z$ delimit a distance interval for adsorbed atoms at a given surface. This formula is analogue to the well known Fermi's second golden rule.

We consider polyatomic organic molecules, which contain chains of valence groups of the type C=O, N=O, C−H and so on. The characteristic frequencies of these valence groups are between 1000−3000 cm^{-1} and the corresponding energies of first vibrational states are between 0.15−0.38 eV. By sliding movement of these molecules along crystallic surfaces resonant excitation of the first vibrational states can be expected at velocities $v_{\|} < 3 \cdot 10^6$ cm/s. At these velocities the braking excitation probabilities of the first vibrational states in the considered valence groups do not exceed 10%. The resonant vibrational excitation is the main mechanism for valence group trigger excitations with a life time of $10^{-12} - 10^{-13}$ s. Each trigger excitation of one valence bond leads to the appearance of an excimol with an energy E_{exc} and a life time of $10^{-10} - 10^{-11}$ s [26, 27]. The excimol is a vibrational excitation, which is transferred from one valence group to the next one within a valence group chain induced by the interaction between parallel oriented valence group dipoles.

Each valence bond trigger excitation in the chain can produce an excimol. The interexcimol interaction is as small as the interexciton interaction in solids. The possibility of the independent existence of many excimols in a chain is an explanation for the energy accumulation $E(n)$ inside a molecule, which contains a chain of n valence bonds. The average accumulated energy can be defined as

$$\bar{E}(n) = \bar{n}_{\mathrm{exc}} E_{\mathrm{exc}} \quad \text{with} \quad \bar{n}_{\mathrm{exc}} = n\, P_{01}(\boldsymbol{v}) . \tag{21}$$

If a chain of identical valence groups with eigenfrequency ω_1^{01} and dipole momentum $\boldsymbol{D}_1$ is connected with another valence group with $\omega_2^{01} > \omega_1^{01}$ and $\boldsymbol{D}_1 \neq \boldsymbol{D}_2$, $\cos\gamma \neq 1$ (γ is the angle between $\boldsymbol{D}_1$ and $\boldsymbol{D}_2$), then the latter valence bond can be a trap for the excimols arising in the chain. It means that the probability $P(t)$ for excimols to be collected inside the trap is much higher than the probability for excimols to be collected inside a valence group of the chain. Using the two-level time-dependent quantum theory, by which one can take into account a diagonal disorder $\omega_1^{01} \neq \omega_2^{01}$ in valence group chains, it is possible to obtain the excimol transition probability to the trap similar to the case of an exciton trap [30]:

$$P(t) = 1 - \frac{B^2}{\Delta^2 + B^2} \cdot \sin^2 t \sqrt{\Delta^2 + B^2} , \tag{22}$$

where $\Delta^2 = 1/4\,|\omega_2^{01} - \omega_1^{01}|^2$, and B^2 is a matrix element depending on $\gamma, \boldsymbol{D}_1, \boldsymbol{D}_2$, and the distance between the c.m. of the two valence groups. It follows that for $\Delta \gg B$ a total energy of n excimols $E(n)$ can concentrate in the trap and dissociation of this trap bond can occur if $E(n) \geq W$, with W being the trap bond's dissociation energy.

Let us define the excimol accumulation energy E_{thres} which satisfies the relation $E_{\mathrm{thres}} = W$. From this relation and (21) one can define the threshold velocity v_{thres} of the grazing molecule for which the dissociation channel is opened. Then the dissociation probability of the trap bond $P_{\mathrm{d}}(v)$ as a function of velocity has a threshold behaviour:

$$\begin{aligned} &P_{\mathrm{d}}(v) \approx 0 \quad \text{for} \quad v < v_{\mathrm{thres}} \quad \text{and} \\ &P_{\mathrm{d}}(v) \approx [P_{01}(v) - P_{01}(v_{\mathrm{thres}})] \quad \text{for} \quad v \geq v_{\mathrm{thres}} . \end{aligned} \tag{23}$$

From numerical analysis of (20) it follows that the probability $P_{01}(v)$ depends on the velocity in the following way. It increases for $v \ll \omega^{01} a_{\mathrm{TF}}$, decreases for $v \gg \omega^{01} a_{\mathrm{TF}}$ and has a plateau behaviour around $v \approx \omega^{01} a_{\mathrm{TF}}$. This permits the conclusion that the function $P_{\mathrm{d}}(v)$ increases with increasing v in the interval $[v_{\mathrm{thres}}, \omega^{01} a_{\mathrm{TF}}]$. The steepness of the increase and the threshold velocity v_{thres} depend on the parameters of the molecule-surface system, in particular on ω^{01} and a_{TF}.

We now consider a molecule containing k different trap bonds with the dissociation energies W_i, $i \in (1, \ldots, k)$ and

$$\begin{aligned} &W_1 > W_2 > \ldots > W_k , \quad \text{leading to} \\ &E_{\mathrm{thres}}^{(1)} > E_{\mathrm{thres}}^{(2)} > \ldots > E_{\mathrm{thres}}^{(k)} . \end{aligned} \tag{24}$$

To dissociate one of the trap bonds it is necessary to accumulate the excimol energy $E(n) \geq E_{\mathrm{thres}}^{(i)}$. According to (21) the energy accumulation is depending on the number n of valence bonds, which are part of the chain closest to the surface, on the excimol energy E_{exc} and on velocity v. As the excitation probability $P_{01}(v)$ is increasing in the threshold velocity range $v_{\mathrm{thres}}^{(i)} < \omega^{01} a_{\mathrm{TF}}$, the threshold excitation probabilities for the different trap bonds are satisfying the inequality

$$\begin{aligned} &P_{01}(v_{\mathrm{thres}}^{(1)}) > P_{01}(v_{\mathrm{thres}}^{(2)}) > \ldots > P_{01}(v_{\mathrm{thres}}^{(k)}) , \\ &\text{with} \quad v_{\mathrm{thres}}^{(1)} > v_{\mathrm{thres}}^{(2)} > \ldots > v_{\mathrm{thres}}^{(k)} . \end{aligned} \tag{25}$$

Thus, for a given molecule we have different threshold velocities for the dissociation of trap bonds with different dissociation energies.

The above presented theoretical model of surface induced dissociation (SID) for grazing incidence takes into account the internal chain like structure of the polyatomic molecule and thus is essentially different from the well known RRKM theory, see e.g. [31]. RRKM is based on thermo-dynamic statistics, does not take into account the influence of the molecular structure on the dissociation process and applies to an energy range 100 times higher than typical energies considered here.

Experiment

To test our grazing incidence SID theory, we investigated experimentally the dissociation of the organic complex ion $M_1^+ = [Bu_{14}Ac_7 - \beta - CD + Cs_2I]^+$ into the channel $M_1^+ \rightarrow M'_1 + Bu^+$ and the complex ion $M_2^+ = [Pe_{14}Ac_7 - \beta - CD + Cs_2I]^+$ into the channel $M_2^+ \rightarrow M'_2 + Cs^+$ by their grazing collision with an aluminium oxide surface. The molecular kinetic energy $E_{\|}$ parallel to the surface was varied in the range: 100 to 1000 eV. The fourteen peripheral hydrocarbon valence group chains (butyl or pentyl) of the molecular ions served as the accumulators for excimol energy. The bonds, which connect the butyl groups with M'_1 and the Cs with M'_2, were regarded as the trap bonds for the accumulated excimols.

The aim of our experiments was to measure the expected kinetic energy thresholds for the dissociation of the above characterised complex ions by using a modified ^{252}Cf-plasma desorption mass spectrometer (PDMS). A beam of the primary ions M_1^+ or M_2^+ was deflected towards a tilted converter (Figure 1). Depending on the polarity of the applied converter potential U_{con}, the primary ions were postaccelerated or decelerated in the homogeneous electrostatic field of the converter. After impacts of primary ions at the flat converter surface the secondary electrons or the secondary ions were accelerated and detected after having passed a short drift path to the micro channel plate detector (MCP). For a defined decelerating converter potential $U_{con} = U_{crit}$ the fully accelerated, intact primary ions collide with the converter surface at grazing incidence and low kinetics energies ($E_{impact} = E_{\|} = E_{acc} - E_{con}$). By variation of the acceleration voltage U_{acc} and the converter potential U_{con} accordingly, the setup allows to study the dissociation efficiency depending on the grazing velocity or energy. Details of the experimental setup have been described earlier [19].

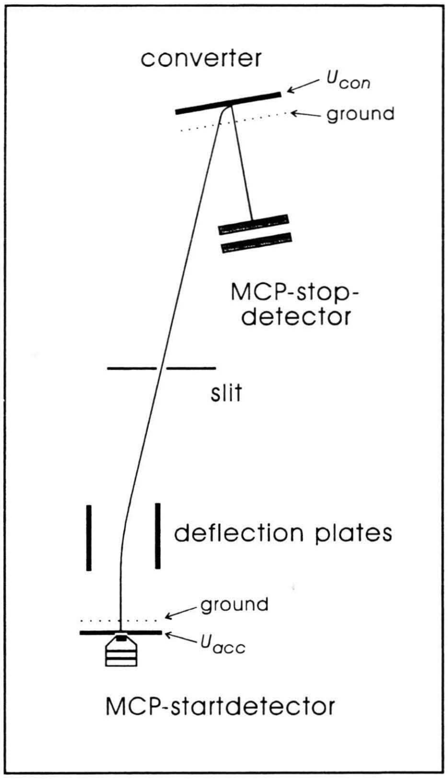

Fig. 1. Scheme of the modified plasma desorption mass spectrometer with deflection plates for accelerated ions, converter foil acting as scattering surface and micro channel plate detectors (MCP) for start and stop signals used in time-of-flight mass spectrometry.

As expected, threshold impact energies are observed, which have to be exceeded to produce secondary fragment ions. These activation energies are in the order of a few hundred eV depending on the types of primary and secondary ions. The generation of the low mass fragments (Bu^+, Pe^+) of the molecular ions $[Bu_{14}Ac_7 - \beta - CD + Cs_2I]^+$ and $[Pe_{14}Ac_7 - \beta - CD + Cs_2I]^+$ obviously needs higher impact energies than necessary for Cs^+-secondary ions, and Cs^+ is easier released by $[M + Cs]^+$ than by $[M + Cs_2I]^+$-primary ions.

The measured fragment ion intensities, which are proportional to the dissociation probabilities $P_d(E)$ of the corresponding dissociation channels, are presented in Figure 2.

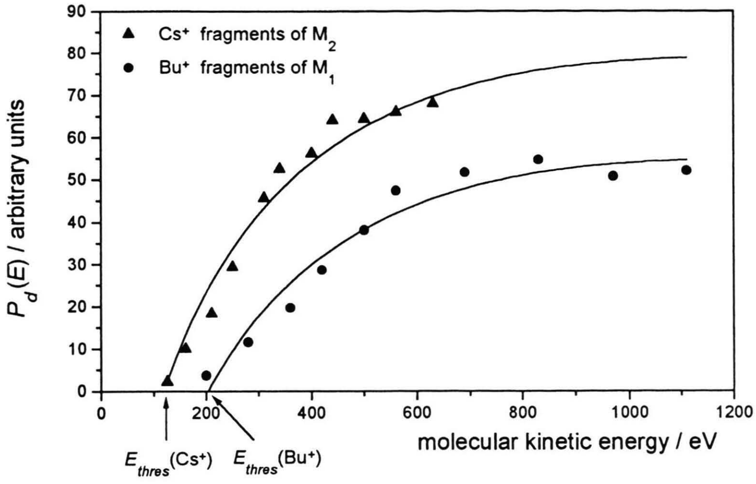

Fig. 2. Experimental dissociation probabilities $P_d(E)$ for molecule M_1 in the channel $M_1^+ \rightarrow M_1' + Bu^+$ (dots) and molecule M_2 in the channel $M_2^+ \rightarrow M_2' + Cs^+$ (triangles) as functions of the grazing kinetic energy. The curves represent the fitted functions (26) with $\omega^{01} = 2\pi \cdot 0.9 \cdot 10^{14}\ s^{-1}$ corresponding to the C−H valence bond and $a_{TF} = 0.4\, a_0$ as an average value for aluminium and oxygen.

Discussion

The experimental data have been analysed by using (23) for the trap bond dissociation probability. This formula can be presented in a parameterised form:

$$P_d(v) = F \cdot \tilde{P}_{01}(\omega^{01}, v, a_{TF}) - C\,, \tag{26}$$

where $\tilde{P}_{01}$ is the integral part in (20), averaged over the dipole momenta directions $\boldsymbol{S}$ and velocity $\boldsymbol{v}$ (see Appendix). Obviously it depends on the molecular velocity or energy, the characteristic frequency ω^{01} for the valence bond in the chain and the Thomas-Fermi radius a_{TF} of the surface ions. The parameters ω^{01} and a_{TF} are known for each system consisting of a given molecule and surface. Consequently, the probability P_d as a function of the molecular kinetic energy depends on two parameters F and C. The parameter F is the same for any dissociated trap bond in a given molecule, but it depends on the surface potential and the valence bond chain, in which the excimols are collected. The constant C is defined by the dissociation threshold probability and depends on the necessary number of collected excimols and trap-bond properties.

In the present case, the surface consisted of aluminium and oxygen ions and the chains consisted of C−H valence groups. The corresponding parameters were $\omega^{01} = 2\pi \cdot 0.9 \cdot 10^{41}\ s^{-1}$ and $a_{TF} = 0.4\, a_0$ as an average value for aluminium and oxygen. The dissociation probabilities for the channels $M_1^+ \rightarrow M_1' + Bu^+$ and $M_2^+ \rightarrow M_2' + Cs^+$ are presented in Fig. 2, calculated by (26) with parameters F and C chosen by the best fit to the experimental data. We calculated the function $\tilde{P}_{01}$ by expanding the integrand in a series. The fitted F-values occurred to be the same for the different trap bonds in the given molecule and C is proportional to the dissociation energies of the trap bonds. The different dissociation energy thresholds for molecule M_1 in the channel $M_1^+ \rightarrow M_1' + Bu^+$ and molecule M_2 in the channel $M_2^+ \rightarrow M_2' + Cs^+$ are reflected by the different fit values of the constant C.

The sensitivity of our model for variations of the parameter ω^{01} was tested by calculation of $\tilde{P}_{01}$ for the dissociation channel $M_1^+ \rightarrow M_1' + Bu^+$ using (26) with $\omega^{01} = 2\pi \cdot 0.5 \cdot 10^{14}\ s^{-1}$ and $\omega^{01} = 2\pi \cdot 0.6 \cdot 10^{14}\ s^{-1}$ corresponding to C=O and N=O valence bonds, respectively. From the curves displayed in Fig. 3 one can see that the model clearly can distinguish different compositions of the valence bond chains. Also the influence of the surface parameter a_{TF}, determined by the nuclear charge of the surface ions, was checked by calculation of $\tilde{P}_{01}$ for a gold surface ($a_{TF} = 0.2\, a_0$) and for a carbon surface ($a_{TF} = 0.5\, a_0$). The curves calculated by (26) with parameter C equal to zero also demonstrate the high sensitivity of the model for the chemical composition of the crystallic surface (Figure 4).

The analysis shows that the suggested model is well describing the experimental data and can be used for the investigation of surface and molecular properties by grazing collision experiments.

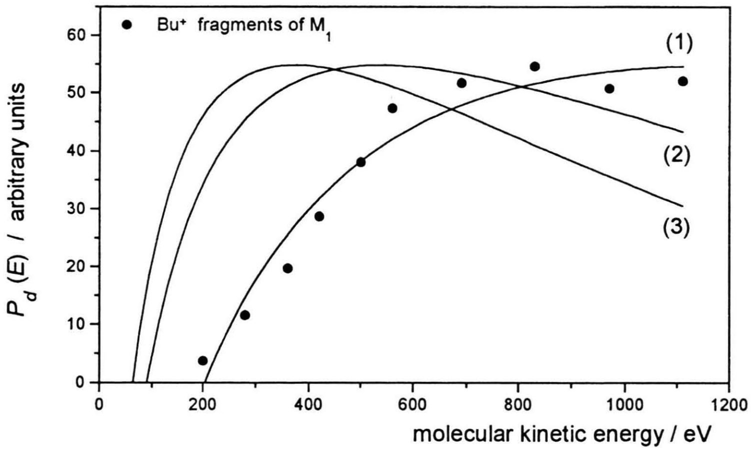

Fig. 3. Dissociation probability $P_d(E)$ for molecule M_1 in the channel $M_1^+ \rightarrow M_1' + Bu^+$ as a function of the molecular kinetic energy:

(1) experimental data and fitted function (26) with $\omega^{01} = 2\pi \cdot 0.9 \cdot 10^{14}\,s^{-1}$ (C–H);
(2) same function with $\omega^{01} = 2\pi \cdot 0.6 \cdot 10^{14}\,s^{-1}$ (N=O);
(3) same function with $\omega^{01} = 2\pi \cdot 0.5 \cdot 10^{14}\,s^{-1}$ (C=O).

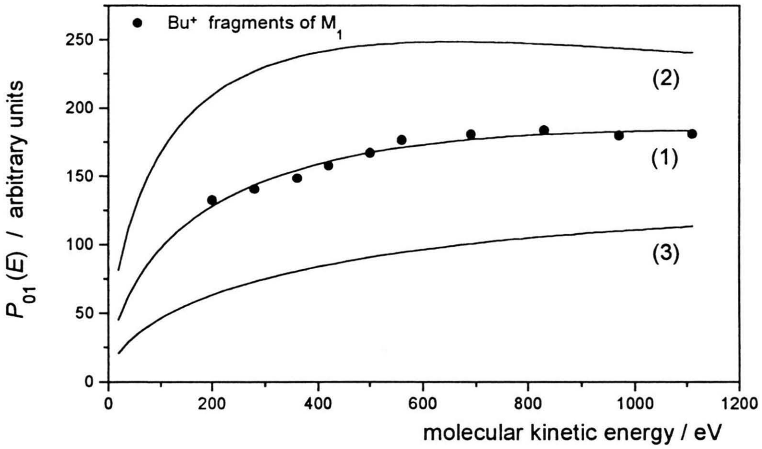

Fig. 4. Excitation probability $P_{01}(E)$ for valence bond C–H in molecule M_1 as a function of the molecular kinetic energy:

(1) experimental data for dissociation channel $M_1^+ \rightarrow M_1' + Bu^+$ and fitted function (26) with $a_{TF} = 0.4\,a_0$ and constant C equal to zero;
(2) same function with $a_{TF} = 0.2\,a_0$ (gold);
(3) same function with $a_{TF} = 0.5\,a_0$ (carbon).

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Appendix

In order to calculate the dissociation probability $P_d(v)$ for polyatomic molecules as a function of the kinetic energy E or the velocity v, (23) is rewritten in the form

$$P_d(\boldsymbol{v}) = A \cdot (P_{01}(\boldsymbol{v}) - P_{01}(\boldsymbol{v}_{\text{thres}})) \quad \text{for} \quad v \geq v_{\text{thres}} \,. \tag{23a}$$

Here A does not depend on v. The excitation probability $P_{01}(\boldsymbol{v})$ given in (18) was integrated over R_z. After averaging P_{01} as specified in (19) over the unit-vector $\boldsymbol{S}$ of the dipole momentum and over the velocity $\boldsymbol{v}$ of molecules grazing along the surface, the excitation probability will have the form $P_{01}(v) = B \cdot \tilde{P}_{01}(v)$, where

$$\tilde{P}_{01}(v) = \left(\frac{\omega^{01}\sqrt{2}}{v}\right)^2 \cdot \int_0^{+\infty} \mathrm{d}\omega_n (\tilde{K}_n^{01}(\omega_n, \hat{\omega}_m, R_z^0))^2 \,,$$

$$\tilde{K}^{01} = M(r) \cdot \frac{D_0}{r_0} \cdot \left\{ \frac{1}{\sqrt{3}} \frac{\partial}{\partial z} V_{mn}(\omega_n, \hat{\omega}_m, R_z^0) - i \frac{\sqrt{2}}{\sqrt{3}} \frac{\omega^{01}}{v} V_{mn}(\omega_n, \hat{\omega}_m, R_z^0) \right\},$$

$$M(r) = \langle \Phi_1(r) | r | \Phi_0(r) \rangle \,.$$

Here $R_z^0 \in (R_z^{(1)}, R_z^{(2)})$ and B does not depend on v:

$$B = \frac{2\pi b_1 b_2}{(\omega^{01}\hbar)^2}.$$

Using the expression of $\tilde{P}_{01}$ as given above, we obtain $P_\mathrm{d}(v)$ in the following form:

$$P_\mathrm{d}(v) = F \cdot \tilde{P}_{01}(v) - C,$$

where $F = A \cdot B$ and $C = A \cdot B \cdot \tilde{P}_{01}(v_\mathrm{thres})$. The dissociation probabilities of polyatomic molecules presented in Figs. 2 and 3 have been calculated numerically using (26).

[1] J. A. Barker and D. J. Auerbach, Surf. Sci. Rep. **4,** 1 (1985).
[2] M. G. Tenner and E. W. Knipers, J. Chem. Phys. **94,** 5197 (1991).
[3] C. T. Rettner, J. Chem. Phys. **99,** 5481 (1993).
[4] D. M. Newns, Surf. Sci. **171,** 600 (1986).
[5] W. Brenig, Z. Phys. B. **36,** 81 (1979), Z. Phys. B. **36,** 245 (1980).
[6] P. M. Holmblad, J. Wambach, and J. Chorkendorff, J. Chem. Phys. **102,** 8255 (1995).
[7] R. Zimmy, Z. L. Miškovic, N. N. Nedeljkovic, and Lj. D. Nedeljkovic, Surf. Sci. **255,** 135 (1991).
[8] A. A. Lucas, Phys. Rev. **10,** 4990 (1979).
[9] W. Heiland, V. Beltat, and E. Taglauer, Phys. Rev. B **19,** 1677 (1979).
[10] I. S. Bitensky, Surf. Sci. Lett. **297,** L104 (1993).
[11] Th. Lill, H.-G. Busmann, B. Reif, and I. V. Hertel, Appl. Phys. A **55,** 461 (1992).
[12] K. J. Snowdon, D. J. O'Connor, and R. J. MacDonald, Radiat. Eff. Def. Solids **109,** 33 (1992).
[13] A. Närmann, K. Schmidt, W. Heiland, R. Monreal, F. Flores, and P. M. Echenique, Nucl. Instrum. Methods B **48,** 387 (1990).
[14] A. Närmann, H. Franke, K. Schmidt, A. Arnau, and W. Heiland, Nucl. Instrum. Methods B **69,** 158 (1992).
[15] B. D. Kay, T. D. Raymond, and M. E. Coltrin, P. Rev. Lett. **59,** 2792 (1987).
[16] S. T. Rettner, J. Kimman, F. Fabre, D. J. Auerbach, and H. Moravitz, Surf. Sci. **192,** 107 (1987).
[17] H. Vach, M. Benslimane, M. Chatelet, A. De Martino, and F. Pradere, J. Chem. Phys. **103,** 1972 (1995).
[18] R. G. Cooks, T. Ast, and M. D. A. Mabud, Int. J. of Mass Spec. Ion Process. **100,** 209 (1990).
[19] L. Schmidt, H.-W. Fritsch, and H. Jungclas, Rap. Comm. Mass Spectrom. **7,** 507 (1993).
[20] L. Jones, A. R. Dongre, and A. Somogy, J. Amer. Chem. Soc. **116,** 8368 (1994).
[21] K. L. Schey, D. A. Durkin, and K. R. Thornburg, J. Amer. Soc. Mass Spectrom. **6,** 257 (1995).
[22] V. V. Komarov, A. M. Popova, L. Schmidt, and H. Jungclas: preprint FB14 UMR 96-01, Philipps-Universität Marburg, June 1996.
[23] C. D. Moak, S. Datz, O. H. Crawford, H. F. Krause, P. F. Dittner, J. Gomez del Campo, J. A. Biggerstaff, P. D. Miller, P. Hvelplund, and H. Knudsen, Phys. Rev. A **19,** 977 (1979).
[24] V. V. Okorokov, Yad. Fis. **2,** 1009 (1995), Sov. J. Nucl. Phys. **2,** 719 (1966).
[25] F. J. Dyson and H. Überall, Phys. Rev. **99,** 604 (1995).
[26] H.-W. Fritsch, H. Jungclas, V. V. Komarov, and L. Schmidt, J. Phys. II France **4,** 567 (1994).
[27] V. V. Komarov, L. Schmidt, H.-W. Fritsch, and H. Jungclas, Computational Materials Science **2,** 427 (1994).
[28] R. Pfandzelter and F. Stölzle, Nucl. Inst. Meth. Phys. Res. B **72,** 163 (1992).
[29] J. Dai and J. Z. Zhang, J. Chem. Phys. **102,** 6280 (1995).
[30] R. Silbey, Ann. Rev. Phys. Chem. **27,** 203 (1976).
[31] D. L. Bunker and F. M. Wang, J. Amer. Chem. Soc. **99,** 7457 (1977).