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Role of internal molecular structures in grazing surface induced dissociation

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Abstract. Polyatomic molecules containing chains of identical valence groups are dissociated with high probabilities when sliding along crystallic surfaces. Recently, we developed a model of collective vibrational excitation and dissociation of such molecules. In the present article we use this model to elucidate the specific influence of chains formed by identical valence groups in polyatomic molecules on their dissociation probability. In addition, a new experiment is presented providing evidence of this influence.

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The problem of molecular dissociation by surface collisions is of growing interest and there are many articles related to this subject; see *e.g.* the review [1]. Most of the articles are devoted to processes involving small molecules (not more than 4 atoms) with velocities around Bohr's velocity ($\upsilon_\mathrm{B} \approx 10^8$ cm/s = 1 m/μs) and to steep angles of incidence. For the dissociation of polyatomic molecules the number of publications is limited, see *e.g.* review [2] and references [3,4].

Experimental results have proven the existence of processes, which are specific for slow ($\upsilon \le \upsilon_\mathrm{B}$) polyatomic molecules with regular periodic substructures of identical valence groups (*e.g.* chains of C–H, C=O, N=O *etc.*) [5]. It was concluded that polyatomic molecules of this type can accumulate internal energy by collecting a number of low energy excitations [6,7]. It was also noticed that the probability of grazing surface induced dissociation (grazing SID) is a function of molecular velocities, in particular characterised by a threshold behaviour [8]. To discuss the observed effects we suggested a theoretical model for energy accumulation in molecules with chain-like structures and for the grazing SID-process [8–10].

The presented article is devoted to experimental check of the main point of this model, *i.e.* the influence of chain like substructures inside polyatomic molecules on the grazing SID-process. In the proposed model the process is analysed in three steps. In the first step the excitation of collective vibrational states (excimols) [6] takes place in the chains of identical valence groups inside the polyatomic molecules sliding with velocity $\boldsymbol{v}$ along the surface consisting of periodically located (N_1N_2) ions. This excitation occurs due to the superposition of the surface ions' Coulomb potential. For the sliding molecules this perturbation can be presented as a sum of time-dependent periodic potentials [8]:

$$\tilde{V}(\mathbf{R},t) = \sum_{m,n} K_{mn}\ \exp\{i\omega_{mn}t\},\ \text{with}\ m,\ n = 1,\ 2,\ ..., \tag{1}$$

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

$$V_{mn}(R_z)=\frac{1}{b_1 b_2}\int_0^{b_1}\mathrm{d}R_x\int_0^{b_2}\mathrm{d}R_y V(\mathbf{R})\exp\{-i\mathbf{G}_{mn}\cdot\mathbf{R}_{xy}\},$$
$$\omega_{mn} = \mathbf{G}_{mn}\cdot\boldsymbol{v} = \omega_m + \omega_n.$$

with $\mathbf{R}_{xy} = \{R_x,\ R_y,\ 0\}$, $\mathbf{S} = \{S_x,\ S_y,\ S_z\}$ is a unit vector along the valence bond axis and $\mathbf{G}_{mn} = 2\pi(n\mathbf{a}_1 + m\mathbf{a}_2)$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are reciprocal vectors of lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$. $V(\mathbf{R})$ is the Coulomb potential of a surface ion, where $\mathbf{R} = \{R_x,\ R_y,\ R_z\}$ is the radius-vector of a dipole c.m., corresponding to surface ion (00) located in the coordinate origin. Resonant vibrational collective excitation in the valence group chain is likely to occur when its eigenfrequency ω^{01} fulfils the relation $\omega^{01} = \omega^\mathrm{r}_{mn} = \mathbf{G}_{mn}\cdot\boldsymbol{v}^\mathrm{r}_{mn}$. One has to use the first order time-dependent perturbation theory to calculate the

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probability P_{01} of the excimol production in the form [8]:

$$P_{01}=\frac{4\pi b_1 b_2 D_0^2}{3(\upsilon h r_0)^2}\int_0^{+\infty}\mathrm{d}\omega_n\langle\Phi_1(r)|r|\Phi_0(r)\rangle^2 \times\left\{\frac{\partial}{\partial z}V_{mn}(\omega_n,\,\hat{\omega}_m,\,R_z)\bigg|_{R_z^0}-\frac{i\sqrt{2}\omega^{01}}{\upsilon}V_{mn}(\omega_n,\,\hat{\omega}_m,\,R_z^0)\right\}^2 \tag{2}$$

where R_z^0 shows the possible position of the valence bond under the surface, Φ_0 and Φ_1 are the oscillator functions for the states 0 and 1, D_0 is a value of dipole momentum, r_0 is an equilibrium distance between the atoms and r is its variable length, $\upsilon=\frac{\omega^{01}}{2\pi}$, $\hat{\omega}_m=\omega^{01}-\omega_n$. Formula (2) is analogue to the well known Fermi's second golden rule.

The second step in our model for grazing SID-process is the accumulation of excitation energy in one valence group chain inside the molecule. The possibility of independent and simultaneous existence of n_{exc} excimols in a chain explains how an energy $E(n)$ can accumulate inside a molecule, which contains a chain of n valence groups. The accumulated energy can be defined as $E(n_{\mathrm{exc}})=N_{\mathrm{exc}}E_{\mathrm{exc}}$, where E_{exc} is the energy of one excimol.

The third step of our model is the transition of the accumulated energy to a trap bond [8]. A total energy $E(n_{\mathrm{exc}})$ of the accumulated excimols can concentrate in the trap and induce its dissociation if $E(n_{\mathrm{exc}})\geq E_{\mathrm{thres}}=W$, with W being the trap bond's dissociation energy. Since n_{exc} depends on P_{01} which is a function of velocity υ, $E(n_{\mathrm{exc}})$ is also a function of velocity. It means that one can define a threshold velocity $\upsilon_{\mathrm{thres}}$ of the grazing molecule for which the dissociation channel is opened.

The dissociation probability of the trap bond $P_{\mathrm{d}}(\upsilon)$ as a function of velocity has a threshold behaviour and can be found in a parameterised form on the basis of the general probability theory *i.e.* by the asymptotic form of Bernoulli formula [8]:

$$\begin{aligned} &P_{\mathrm{d}}(\upsilon)\approx 0 && \text{for } \upsilon<\upsilon_{\mathrm{thres}} \text{ and}\\ &P_{\mathrm{d}}(\upsilon)=FP_{01}(\upsilon)-C && \text{for } \upsilon\geq\upsilon_{\mathrm{thres}}\\ & && \text{and } C=F\,P_{01}(\upsilon_{\mathrm{thres}}). \end{aligned} \tag{3}$$

Actually $P_{\mathrm{d}}(\upsilon)$ describes the probability to excite a sufficient number of excimols in a chain of n valence groups to destroy a trap bond inside a molecule. The constant value of F depends on the surface-ion potential, lattice constant and the properties and numbers of valence groups in a chain. The constant C depends on the dissociation trap bond energy W and thus on the number of excimols needed to destroy a trap bond. The function $P_{01}(\upsilon)$ in the equation (3) is an integral term in the expression for the probability P_{01} in the equation (2). All constants in front of the integral term in equation (2) are included in parameter F. The function $P_{01}(\upsilon)$ is calculated by averaging the integral term in equation (2), which corresponds to the condition $\omega_n=0$, and by analytical calculation of the functions $V_{m0}(\hat{\omega}_m,\,R_z)$ and $\frac{\partial}{\partial z}V_{m0}(\hat{\omega}_m,\,R_z)$ in equation (2).

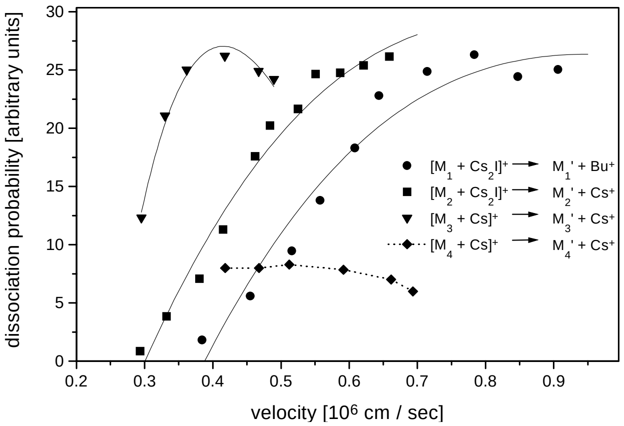

Fig. 1. Experimental dissociation probabilities plotted versus molecular velocities investigated at grazing SID for different probe ions at 10^{-6} mbar. The solid curves represent the dissociation probability $P_{\mathrm{d}}(\upsilon)$ calculated from equation (3). Molecules M_1, M_2 and M_3 include chains of identical valence groups C−H, not present in molecule M_4; the dashed curve is not calculated.

From the described sketch of our model it is clear how to check experimentally the main features of the model [8]. First, the dissociation can only occur, if the molecules contain one or more chains of periodically located identical valence groups, which can accumulate the vibrational excitation by small portions while grazing along surfaces. Thus, in our experiments described below we compare the grazing SID-process for two types of polyatomic molecules, with and without chains. Second, the dissociation probability functions of polyatomic molecules containing equal valence bond's chains should have an equal F-parameter, if the grazing conditions are the same, and an equal C-parameter, if the dissociation fragments are the same. Thus we use equation (3) to fit experimental data and analyse these two parameters.

We investigated experimentally the dissociation of β−cyclodextrine (β−CD) ions by detection of light ions after grazing collision with an aluminium oxide surface:

$$\begin{aligned} \mathrm{M}_1^+ =&[\mathrm{Bu}_{14}\mathrm{Ac}_7{-}\beta{-}\mathrm{CD}+\mathrm{Cs}_2\mathrm{I}]^+\\ &\text{into the channel}\quad \mathrm{M}_1^+\to\mathrm{M}_1{}'+\mathrm{Bu}^+,\\ \mathrm{M}_2^+ =&[\mathrm{Pe}_{14}\mathrm{Ac}_7{-}\beta{-}\mathrm{CD}+\mathrm{Cs}_2\mathrm{I}]^+\\ &\text{into the channel}\quad \mathrm{M}_2^+\to\mathrm{M}_2{}'+\mathrm{Cs}^+,\\ \mathrm{M}_4^+ =&[\beta{-}\mathrm{CD}\,+\,\mathrm{Cs}]^+\\ &\text{into the channel } \mathrm{M}_4^+\to\mathrm{M}_4{}'\,+\,\mathrm{Cs}^+ \end{aligned}$$

and with a fluorine surface:

$$\begin{aligned} \mathrm{M}_3^+ =&[\mathrm{Pe}_{14}\mathrm{Ac}_7{-}\beta{-}\mathrm{CD}+\mathrm{Cs}]^+\\ &\text{into the channel } \mathrm{M}_3^+\to\mathrm{M}_3{}'+\mathrm{Cs}^+. \end{aligned} \tag{4}$$

While the fourteen peripheral hydrocarbon valence group chains (butyl or pentyl) in the molecular ions M_1^+, M_2^+ and M_3^+ serve as accumulators for excimol energy, the ion M_4^+ with simple $\beta-$cyclodextrine has no identical regularly chained C−H valence groups. The bonds, which connect the butyl groups with $M_1{}'$ and the Cs with $M_2{}'$ and $M_3{}'$, are regarded as the trap bonds for the excimols.

In our experiments we used a modified ^{252}Cf−Plasma Desorption Mass Spectrometer (PDMS). A beam of the primary ions M_1^+ or M_2^+ was deflected towards a converter. 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 after passing a short drift path they were detected by a Micro Channel Plate detector (MCP).

For a defined decelerating converter potential $U_{\text{con}} = U_{\text{crit}}$ the fully accelerated, intact primary ions collide with the converter surface at grazing incidence and low kinetic energies ($E_{\text{impact}} = 1/2\, mv_\perp^2 = eU_{\text{acc}} - eU_{\text{con}}$). 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 [9].

The molecular kinetic energy $E_{\|}$ parallel to the aluminium oxide or fluorine surface was varied in the range 100 to 1000 eV.

The measured dissociation probabilities are presented in Figure 1. The solid curves are calculated by equation (3) in the following procedure: the value of parameters F_1 and C_1 were chosen to fit the experimental data for the channel $M_1^+ \rightarrow M_1{}' + \text{Bu}^+$. Then fixing the value $F_2 = F_1$ we fitted the data for the channel $M_2^+ \rightarrow M_2{}' + \text{Cs}^+$ and choosing C_2. Then fixing $C_3 = C_2$ we fitted the data for the channel $M_3^+ \rightarrow M_3{}' + \text{Cs}^+$ by choosing F_3. We performed this procedure as we obtained our experimental data in arbitrary units but in one scale.

Still this analysis shows that the suggested model is well describing the predicted velocity dependence and the threshold effect of the measured probability function P_{d} for these molecules with a regular periodic chain of C−H valence groups.

As it was proposed, the fitting parameter F in the equation (3) for equal grazing condition in the case of molecules M_1^+ and M_2^+ dissociation is the same. For the case of the molecule M_3^+ we found the parameter F to be different compared to molecules M_2^+ and M_1^+ because of different converter surfaces in the grazing experiment.

The fitting parameter C in equation (3) was found to be equal for equal dissociation fragments Cs^+ in case of molecules M_2^+ and M_3^+, and was found to be different for the molecule M_1^+, as it follows from our model, because the dissociation channel is different.

According to our model the grazing SID-probability must be strongly dependent on the presence of regular periodic chains of identical valence groups inside the polyatomic molecule. To proof the influence of molecular structures we repeated the experiment on $M_4^+ \rightarrow M_4{}' + \text{Cs}^+$ with $M_4{}' = \beta-$cyclodextrine, which has no regularly chained identical C−H valence groups. The measured dissociation probabilities for this case are presented in Figure 1 too. Obviously the dissociation probability for this case changed significantly compared to molecules with peripheral substructures, which consist of identical regularly chained valence groups and serve as antennas for resonance excitations. This result demonstrates the validity of the suggested grazing SID dissociation mechanism.

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