Local Heating and Dissociation of Organic Molecules by IR Fields

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A nonstatistical model for internal transition of collective vibrational energy to specific bonds in organic molecules is presented. The model is developed for molecules which contain a chain of identical biatomic dipoles, e.g. C–H groups. Resonant IR fields can induce collective vibrational excitations (excimols) in the dipole chain. The accumulated vibrational energy can be transmitted to particular bonds, which are not part of the chain but close enough for dipole-dipole interactions. Specific properties of such bonds enable a pile up of harvested excimol energy there, thus making dissociation of these bonds a likely exit channel. An analytical expression for the calculation of dissociation probabilities was derived and analysed. It is shown that the dissociation probability strongly depends on the position and orientation of the bond relative to the position and orientation of the dipoles in the chain. The consequences of the presented model were experimentally checked by comparing the fragmentation of the isomers Leucine and Isoleucine. — PACS: 30.00 - 34.10 - 36.40

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1. Introduction

The fragmentation of organic molecules in grazing incidence surface induced dissociation (GI-SID) has been studied in a number of experiments [1 – 3]. According to our theoretical concept this fragmentation is caused by interaction of the projectile ions with the Coulomb field of surface atoms. While moving parallel to the target surface at atomic distances with a velocity v less than the Bohr velocity ($v < 5 \cdot 10^8$ cm/s) biatomic dipoles of the projectile molecule experience field frequencies in the IR range, and thereby have the chance to get into a vibrational excited state.

Experimental results indicate a pronounced dependence of fragmentation probabilities on the structure of the projectile molecules. It seems that the chain consisting of identical closely coupled biatomic dipoles (e.g. a hydrocarbon chain) in the projectile molecules strongly enhances the fragment ion rates [3].

It was also noticed that most of the dissociated bonds in the GI-SID are not chain dipoles, but connect the detected fragments to chain skeleton atoms [2]. Intensities of the peaks in the GI-SID mass-spectra of organic molecules seem to depend on the number and dipole moment of the chained dipoles and additionally on the dissociation energies of the fragmented bonds [1, 2].

The same properties of organic molecule dissociation were observed in experiments with IR-laser radiation [4 – 6]. For the analysis of these effects we suggested to apply the excimol induced dissociation model, which is based on the excitation of collective low energy vibrational states in dipole chains by IR fields. These collective vibrational states we call excimols, because they exist only in the molecular substructure consisting of chained identical biatomic groups.

We suggest the model for superfast fragmentation of organic molecules in an external IR field considering organic molecules containing substructures of biatomic identical periodically located valence groups. Each of these groups has a dipole moment, and the distance between the groups is about 1 Å. This model takes into account the following specific molecular properties.

a) The considered molecular substructures have a length which is shorter than the wave length of IR radiation. This leads to a coherency of vibrational quanta absorption during the irradiation time which is less or equal of the excimol's lifetime.

b) The resonant dipole-dipole interaction between the valence groups of the substructures leads to the superfast (10^{-13} s) transmission of excimols inside the substructure. The anharmonicity of the oscillators (valence groups) does not allow the collection of more than one excimol in each valence group.

c) Transition of a suitable amount of accumulated excimol energy into a specific bond outside the substructure eventually causes dissociation of this bond (trap bond) [3], which occurs during a time period less than the excimol lifetime ($\tau_{\mathrm{ex}} \sim 10^{-11}$ s). The characteristic properties of a trap bond are its dipole moment and its suitable orientation and distance to the closest dipole in the substructure. Excimols accumulated in substructures pass to the trap bond in a time much longer than the transmission time of the excimols inside the substructure. Thus we assume that all K excimols excited in the substructure are transmitted into the trap bond due to dipole-dipole interaction between the trap bond's dipole and the nearest dipole in the substructure.

In our model we consider specific molecular substructures consisting of a finite number of dipoles, which are two-levels oscillators. Thus substructures are located in vacuum and activated by low energy IR radiation producing several excimols. There is no energy exchange between a dissociating molecule and its surrounding matter. The substructures deexcitation occurs by radiationless transition from the substructures to the trap bond.

In the frame of this model a probability function P_{01} of excimol excitation was derived, which is applicable not only for IR laser radiation induced fragmentation [7], but also in GI-SID processes [1, 3, 8], where excitation is thought to be caused by equivalent fields and mechanisms.

It was shown that in the case of GI-SID the probability function P_{01} and the probability function P_M^K for excitation of K excimols in a dipole chain consisting of M dipoles resonantly depend on the grazing velocity [3]. Here we present a model yielding the probability function P_{f} for trap bond fragmentation per time unit induced by IR fields.

2. Theory

2.1. Main Assumptions and Definitions

The theoretical approach presented here is an analysis of the process of low energy vibrational excitation followed by dissociation of polyatomic molecules which contain a substructure of M_r regularly chained identical biatomic dipoles. Electronic excitation is not considered in this approach. Each dipole $i, i \subset \{1, K, M_r\}$, has a dipole moment

$$\boldsymbol{D}_i = eD_0 \boldsymbol{r}_i / r_0, \tag{1}$$

where eD_0 is the value of the dipole moment, and r_0 and r_i are the equilibrium and the variable bond length. It was proposed that these dipoles can be considered as a chain of linear quantum oscillators with distance (a) between two neighbouring oscillators i and $j, i \neq j \subset \{1, K, M_r\}$. Any oscillator i has only two vibrational states with the ground state energy ε_0 and the excited state energy ε_1. The corresponding oscillator eigenfunctions $\phi_0(r_i, t)$ and $\phi_1(r_i, t)$ at the time t are denoted by

$$\varphi_0(r_i, t) = \exp\Big(-i\frac{\varepsilon_0}{h}t\Big)\frac{1}{\sqrt{\alpha_0\sqrt{\pi}}}\exp\Big(-\frac{r_i^2}{2\alpha_0^2}\Big),$$

$$\varphi_1(r_i, t) = \exp\Big(-i\frac{\varepsilon_1}{h}t\Big)\frac{1}{\sqrt{\alpha_0\sqrt{\pi}}}\frac{\sqrt{2}}{\alpha_0}\exp\Big(-\frac{r_i^2}{2\alpha_0^2}\Big)$$

$$\text{with } \alpha_0 = \sqrt{\frac{\eta}{\mu\,\omega_{01}}}, \tag{2}$$

where $\hbar\omega_{01} = \varepsilon_{01} = \varepsilon_1 - \varepsilon_0$, and μ is the oscillator's reduced mass. As is known, the bonds in organic molecules in the first vibrational excited state are not stable.

In organic molecules the bond's deexcitation of vibrational states occurs mainly radiationless by resonant vibrational energy transition to the neighbour bonds. Thus the probability of this process is rather high and the lifetime is short.

Thus it is proposed that the first vibrational excited state of each oscillator in the dipole chain has a lifetime $\tau_{01} \sim 10^{-12}$–10^{-11} s. There is a dipole-dipole interaction V_{ij} between the oscillators (i) and (j). The potential V_{ij} is defined by the equation

$$V_{ij} = \{eD_0/r_0\}^2 r_i r_j \varPhi_{ij}(\varTheta_i, \varTheta_j) R_{ij}^{-3}, \tag{3}$$

where the angle function $\varPhi_{ij}(\varTheta_i, \varTheta_j)$ is given by

$$\begin{aligned}\varPhi_{ij}(\varTheta_i, \varTheta_j) = {} & \cos\varTheta_i^x \cos\varTheta_j^x + \cos\varTheta_i^y \cos\varTheta_j^y \\ & - 2\cos\varTheta_i^z \cos\varTheta_j^z.\end{aligned} \tag{4}$$

The angles $\varTheta_i^{x,y,z}$ and $\varTheta_j^{x,y,z}$ define the directions of the vectors $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ in the coordinate system where the axis OZ coincides with the vector $\boldsymbol{R}_{ij}$ directed from the dipole i to the dipole j. The value $R_{ij} = a$ is the module of $\boldsymbol{R}_{ij}$.

2.2. Excimol Concept

The energy of the first vibrational state of one oscillator in the system of M_r interacting oscillators transforms into M_r collective vibrational states [2] in the energy interval $[E^{(-)}, E^{(+)}]$ with $E^{(-)} = \varepsilon_1 - E_{\mathrm{tr}}$, $E^{(+)} = \varepsilon_1 + E_{\mathrm{tr}}$ and $E_{\mathrm{tr}} = \sum_{j=1}^{m} \langle \varphi_1(r_i)\varphi_0(r_j)|V_{ij}|\varphi_0(r_i)\varphi_1(r_j)\rangle$.

The value of transmission energy E_{tr} is resulting from perturbation theory. The value m corresponds to the number of neighbour oscillators (j), which are in the ground state and located at the distance (a) from the oscillator (i).

The value E_{tr} defines the time $\tau_{\mathrm{tr}} = 2\pi\hbar/E_{\mathrm{tr}}$, which can be considered as the time needed for transmission of the excitation along the dipole chain. The low energy edge $E^{(-)}$ of the band of vibrational states defines the special type of vibrational quanta with the energy $E_{\mathrm{ex}} = \varepsilon_{01} - E_{\mathrm{tr}} = \hbar\omega_{\mathrm{ex}}$, which we named excimol. This type of excitation can be produced coherently in the dipole chain by alternating Coulomb fields with phase zero, if the field wave length is larger than the linear size of the dipole chain [8]. Additionally, the field frequency ω must be equal or very close to ω_{ex}. This resonance condition $\omega = \omega_{\mathrm{ex}}$ provides the highest excimol excitation probability [2].

We note that the range of IR-irradiation frequencies covers the values of vibrational eigenfrequencies of biatomic organic molecular bonds.

As shown in [8] the excimol's lifetime τ_{ex} is less then τ_{01}. For example, the calculated τ_{ex} for the molecular chain $(\mathrm{CH}_2)_n$, $n \gg 2$ is $\tau_{\mathrm{ex}} \sim 10^{-10}$ s and $\tau_{\mathrm{ex}} \gg \tau_{\mathrm{tr}} \sim 10^{-14}$ s [2]. The lifetime of any other state of the band of collective states is even smaller than τ_{ex} [8].

The transition of excimols along the chain occurs without energy loss. After energy transition, the phase of the excited state wave function remains equal to zero.

As it was shown in [2], the probability P_{01} of one excimol excitation by an IR field with $\omega = \omega_{\mathrm{ex}}$ is a function of its fluence $J(\omega_{\mathrm{ex}})$ and can be calculated in the frame of perturbation theory. The vibrational energy states of the dipoles in the chain are not equidistant. Thus we consider two levels of dipoles only. Two or more excimols can not be accumulated in a single dipole oscillator. Several excimols can be excited independently by radiation during the time $\tau_{\mathrm{R}} \leq \tau_{\mathrm{ex}}$ and accumulated in the dipole chain.

The resonant dipole-dipole interaction between the valence groups of the substructures leads to the superfast (10^{-13} s) transmission of excimols inside the substructure. The anharmonicity of the oscillators (valence group) prevents excimols collection in one valence group.

Excimol accumulation leads to local heating of the molecule. The accumulation of internal energy occurs only in biatomic periodic molecular substructures (not in the entire molecule), which leads to local molecular heating.

If the inequality $\tau_{\mathrm{R}} > \tau_{\mathrm{tr}}$ is fulfilled, each dipole in the substructure can be excited N times during the radiation time τ_{R}, since the lifetime of its vibrational excitation can not exceed $\tau_{\mathrm{tr}}(\tau_{\mathrm{R}} \gg \tau_{\mathrm{tr}})$. This leads to an effective number $M = NM_{\mathrm{r}}$ of chained dipoles which take part in the excimol acquisition. Since we do not assume any interactions between excimols, the probability P_M^K for accumulation of K excimols in the chain with M dipoles can be calculated in the frame of the probability theory using the Bernoulli relation

$$P_M^K = \frac{1}{\sqrt{2\pi M P_{01}(1-P_{01})}} \exp\left\{-\frac{(K - MP_{01})^2}{2MP_{01}(1-P_{01})}\right\}. \tag{5}$$

As follows from (5) the probability P_M^K as a function of the field fluence $J(\omega_{\mathrm{ex}})$ reaches its maximum when the relation

$$K = MP_{01} \tag{6}$$

is fulfilled. This relation shows that the probability P_M^K for a fixed energy $E(K) = KE_{\mathrm{ex}}$ corresponding to a number K of accumulated excimols in the chain with M_{r} oscillators is depending resonantly on the radiation fluence $J(\omega_{\mathrm{ex}})$.

This shows that accumulation of a certain amount of excimol energy in an oscillator chain with $M_r \gg 1$ is a double resonance process, since its probability depends resonantly on the field frequency and radiation fluence.

2.3. Trap-bond Concept

The excimol energy accumulated in a dipole oscillator chain during an IR irradiation period τ_{R} persists on average for a period τ_{ex}.

A peripheral substructure of the molecule, adjacent to the chain, can serve as an energy trap, provided that it is coupled to the rest of the molecule by a valence bond (B), which has a dipole moment $\boldsymbol{D}_\mathrm{B}$ defined as

$$\boldsymbol{D}_\mathrm{B} = eD_\mathrm{B}\boldsymbol{R}_\mathrm{B}/R_0, \tag{7}$$

where eD_B is the value of the dipole moment, and R_0 and $\boldsymbol{R}_\mathrm{B}$ are the equilibrium and variable dipole length. $\boldsymbol{D}_\mathrm{B}$ results from the vector sums of all individual dipole moments within each of the two parts linked by the bond B. The calculation of $\boldsymbol{D}_\mathrm{B}$ can be performed in a conventional way, e. g. as presented in [9].

In the model, B is presented as a vibrational quantum oscillator with the ground state energy $\varepsilon_\mathrm{B}^0 = h\omega_\mathrm{B}^0/2$, corresponding wave function $\varphi_\mathrm{B}^0(R_\mathrm{B})$ with $\alpha_\mathrm{B} = (h/2\mu_\mathrm{B}\omega_\mathrm{B})^{1/2}$, and reduced mass μ_B. Excimol energy can be transferred from the dipole chain to this oscillator due to interactions between each dipole $\boldsymbol{D}_i$ of the chain and dipole $\boldsymbol{D}_\mathrm{B}$, where the vibrational energy can pile up under certain conditions. If this process occurs, $\boldsymbol{D}_\mathrm{B}$ acts as excimol energy trap and the bond B can be called a trap bond. The potential function (W) of the dipole-dipole interaction is defined as

$$W = \sum_{i=1}^{K} w_{i\mathrm{B}} \text{ with } w_{i\mathrm{B}} = \frac{e^2 D_0 D_\mathrm{B}}{r_0 R_0} \Phi_{i\mathrm{B}}(\theta_i, \theta_\mathrm{B}) \frac{r_i R_\mathrm{B}}{L_{i\mathrm{B}}^3}. \tag{8}$$

Here $L_{i\mathrm{B}}$ is the distance between the origin of the vector $\boldsymbol{D}_i$ in the chain and the origin of the vector $\boldsymbol{D}_\mathrm{B}$ [9]. The function $\Phi(\theta_i, \theta_\mathrm{B})$ in (8) has the form

$$\Phi(\theta_i, \theta_\mathrm{B}) = \cos\theta_i^x \cos_\mathrm{B}^x + \cos\theta_i^y \cos_\mathrm{B}^y - 2\cos\theta_i^z \cos_\mathrm{B}^z .$$

The angles θ_i and θ_B define the direction of $\boldsymbol{r}_i$ and $\boldsymbol{R}_\mathrm{B}$ in a coordinate system where the axis OZ coincides with the vector $\boldsymbol{L}_{i\mathrm{B}}$.

The value of the potential $W_{i\mathrm{B}}$ strongly depends on the distance $L_{i\mathrm{B}}$ and the angle function $\Phi(\theta_i, \theta_\mathrm{B})$. As a function of $L_{i\mathrm{B}}$ the potential $W_{i\mathrm{B}}$ reaches its maximum when $L_{i\mathrm{B}}$ has its minimum value. The minimum of $L_{i\mathrm{B}}$ is the distance $L_{1\mathrm{B}} = l$ between the origins of D_1 and D_B.

A necessary condition for a bond to act as a trap bond is that its dipole moment is significantly weaker than the moment of a chain dipole. This leads to the following consequences for the trap bond dipole as quantum oscillator:

a) The probability to receive an excimol is much higher than the probability to emit an excimol back to a chain dipole.

b) The lifetime of a trap bond excitation exceeds the excimol acquisition and transmission time.

2.4. Fragmentation Probability Function

The energy, which is transmitted due to the interaction W is $E(K) = KE_\mathrm{ex}$. When $E(K)$ exceeds the dissociation energy E_d(B) of the trap bond B, it can be cleaved. In our model a number of dissociated bonds is determined by a number of excimols excited in the substructures or by the accumulated excimol's energy during the radiation time.

If dissociation of the oscillator bond B occurs, the fragments (the products of this dissociation) move apart with a relative kinetic energy $E_q = \hbar^2 q^2/2\mu_\mathrm{B}$ with $q = p/\hbar$, where p is the value of the relative momentum of the two fragments. For this we define the wave function $\varphi_\mathrm{d}(R_\mathrm{B}, q)$ of the oscillator B in the continuous spectrum as solution of the one dimensional Schrödinger equation for the free fragments

$$\varphi_\mathrm{B}(R_\mathrm{B}, q) = \sqrt{2/\pi}\sin(qR_\mathrm{B0}).$$

The potential W is the perturbation leading to the transition of the system consisting of a dipole chain and a trap bond B from the initial state with the energy $E_\mathrm{ini} = KE_\mathrm{ex} + K\varepsilon_0 + \varepsilon_\mathrm{B}^0$ to the final state with the energy $E_\mathrm{f} = K\varepsilon_0 + E_\mathrm{d}(\mathrm{B}) + E_q$.

Here the initial state is characterized by the K excited excimols in the dipole chain and the trap bond in the ground state. In the final state, the K priory excited dipoles are back in the ground state, and the trap bond is in the dissociated state. Since the potential W does not depend on time, the transition of the system from one state to the other does not change its total energy content.

The partial probability per time unit P_f for a trap bond dissociation event can be calculated on the basis of perturbation theory. In first approximation the function P_f has the form

$$p_\mathrm{f} = \frac{2\pi}{ht} \left| \int_0^t \langle \psi_\mathrm{ini} | W | \psi_\mathrm{fin} \rangle \mathrm{d}t \right|^2 \mathrm{d}q. \tag{9}$$

Here ψ_ini is the wave function of the state with the energy E_ini. To construct this function it is necessary to take into account that the wave function $\psi_{i,\mathrm{ex}}$ of the excited dipole (i), which produces the excimol, has the form

$$\psi_{i,\mathrm{ex}}(r_i, t) = \sqrt{P_M^K} \left[\sqrt{P_{01}}\varphi_1(r_i) \exp\left(-i\frac{\varepsilon_0 + E_\mathrm{ex}}{h}t\right) + \sqrt{1 - P_{01}}\varphi_0(r_i) \exp\left(-i\frac{\varepsilon_0}{h}t\right)\right].$$

From this the function ψ_{ini} can be presented in the form

$$\psi_{\text{ini}} = \left(\prod_{i=1}^{K} \psi_{i,\text{ex}}(r_i,t)\right) \varphi_{\text{B}}^{0}(R_{\text{B}}) \exp\left(-i\frac{\varepsilon_{\text{B}}^{0}}{h}t\right).$$

The function ψ_{fin} is the wave function of the final state

$$\psi_{\text{ini}} = \left[\prod_{i=1}^{K} \varphi_0(r_i)\exp(i\varepsilon_0 t/h)\right] \varphi_{\text{B}}(R_{\text{B}},q) \cdot \exp\left(-i\frac{E_{\text{d}}+E_q}{h}t\right).$$

The calculation of the matrix element in (9) leads to the following result:

$$P_{\text{f}} = \frac{2\pi}{h} P_M^K P_{01} \left(\frac{e^2 D_0 D_{\text{B}}}{r_0 R_0} M_1 M_2 \sum_{i=1}^{K} \frac{\Psi(\theta_i,\theta_{\text{B}})}{L_{i\text{B}}}\right)^2 \cdot \delta(KE_{\text{ex}} - E_{\text{d}} - E_q)\mathrm{d}q. \tag{10}$$

Here

$$M_1 = \langle\varphi_0(r)|\varphi_1(r)\rangle = \sqrt{\frac{h}{2\mu\omega_{01}}},$$

$$M_2 = \langle\varphi_0(R_{\text{B}})|R_{\text{B}}|\varphi_{\text{B}}(R_{\text{B}},q)\rangle = \left[\pi^{-1/2} q^2 \alpha_{\text{B}}^5 \exp\{-q^2\alpha_{\text{B}}^2\}\right]^{1/2}.$$

In this calculation all terms with $(P_{01})^{\xi}$, $\xi \geq 2$ were omitted, since $P_{01} < 1$. The integration of the expression (9) over q leads to the result

$$P_{\text{f}} = \frac{2\sqrt{\pi}}{hE_q} P_M^K P_0 1 \left(\frac{2e^2 D_0 D_{\text{B}}}{r_0 R_0} M_1\right)^2 q^3 \alpha_{\text{B}}^5 \cdot \exp\{-q^2\alpha_{\text{B}}^2\} \left[\sum_{i=1}^{K} \frac{1}{L_{i\text{B}}^3} \Phi(\theta_i,\theta_{\text{B}})\right]^2. \tag{11}$$

To simplify the expression (11) for P_{f} we can take advantage of the particular properties of the system. Since all dipoles in the chain are assumed to be identically oriented, any function $\Phi(\theta_i,\theta_{\text{B}})$ can be approximated by the function $\Phi(\theta_1,\theta_{\text{B}})$.

The period τ_{f} needed for the excimol energy transition from the chain to the trap bond is longer than the excimol transmission time τ_{tr}, which is characterizing the excitation energy propagation inside the chain.

We propose that the energy of all K excited dipoles is transmitted via dipole $i = 1$ to the trap bond. The partial dissociation probability per time unit P_{f} for the organic molecule, which is exposed to an IR field, can then be presented in the following form

$$P_{\text{f}} = \frac{2\sqrt{\pi}}{hE_q} P_M^K P_0 1 K^2 \left(\frac{2e^2 D_0 D_{\text{B}}}{r_0 R_0} M_1 \Phi(\theta_i,\theta_{\text{B}})\right)^2 \cdot \frac{q^3 \alpha_{\text{B}}^5 \exp(-q^2\alpha_{\text{B}}^2)}{l^6}. \tag{12}$$

As a consequence, the dissociation happens within the period $1/P_{\text{f}} \leq \tau_{\text{ex}}$. This result proofs that in the presented model molecular dissociation induced by IR fields is a nonstatistical process.

Function P_{f} of (12) reveals the strong dependence of the fragmentation probability on the trap bond related structure parameters l and $\Phi(\theta_i,\theta_{\text{B}})$. This consequence of the model gives us the opportunity to check it experimentally by analysing the fragmentation of organic isomers in GI-SID. If their fragmentation patterns turn out to be different, we should be able to attribute this phenomenon to different structural trap bond parameters.

3. Experimental Evidence

Equation (12) points out that the fragmentation probability is extremely influenced by the distance l between the dipole chain and the trap bond dipole. The GI-SID method can be used to check this fragmentation dependence. Isomers of organic molecules are suitable candidates for such studies, as l is varying slightly because of the structural differences, while the fragment masses should be equal.

We investigated the GI-SID mass spectra of the dipeptides LR and IR. The amino acids Leucine (L) and Isoleucine (I) contain short hydrocarbon chains with different structures and two adjacent bonds α and β, which are suitable to serve as trap bonds:

(LR) $\mathrm{CH_3{-}CHCH_3{-}CH_2}\overset{\alpha}{\text{—}}\mathrm{CHNH_3}\overset{\beta}{\text{—}}\mathrm{CONH{-}R}$

and Isoleucine–Arginine (IR)

(IR) $\mathrm{CH_3{-}CH_2{-}CHCH_3}\overset{\alpha}{\text{—}}\mathrm{CHNH_3}\overset{\beta}{\text{—}}\mathrm{CONH{-}R}$.

In both cases dissociation of the trap bond α should yield a fragment with $m/z = 57$, namely $\mathrm{CH_3{-}CHCH_3{-}CH_2}$ for LR and $\mathrm{CH_3{-}CH_2{-}CHCH_3}$ for IR.

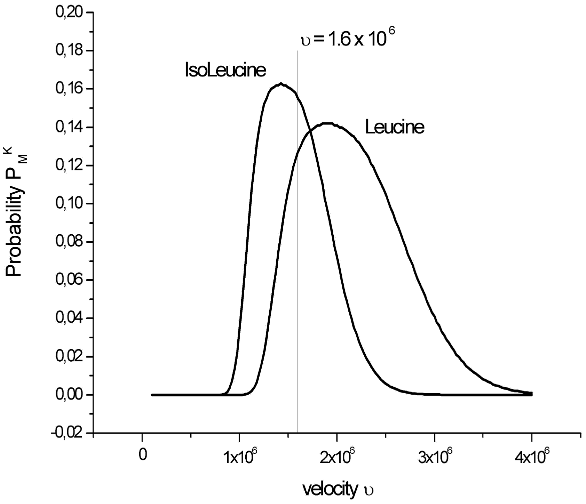

Fig. 1. The calculated probability function $P_M^K(v)$ of excimols accumulation in the hydrocarbon chains with M effective dipoles for Leucine ($K = 17$, $M = 30$) and Isoleucine ($K = 22$, $M = 30$).

The dissociation of α and β bonds in LR and IR yield a fragment NH_3CH^+ with $m/z = 30$.

Due to the known geometrical structure of these end-groups the distances are estimated: $l = 2.4$ Å for LR and $l = 1.85$ Å for IR. According to (12) the intensity of the peak $m/z = 57$ in the GI-SID spectrum of LR is expected to be about 5 times lower than the corresponding peak intensity in the fragment mass spectrum of IR.

The experimental technique we used for GI-SID was based on time of flight mass spectrometry combined with MALDI [10]. The peptide ions were moving along a mineral oil surface with grazing velocity $v = 1.6 \cdot 10^6$ cm/s at distance $R_0 \cong 1$ Å within a period $t_{gr} \cong 10^{-12}$ s. During this time the molecules are in the IR field of surface atoms [1–3].

The different structures of the hydrocarbon chains lead to the excimol energies $E_{ex}(I) = 0.11$ eV for Isoleucine and $E_{ex}(L) = 0.15$ eV for Leucine. Since the energy needed to dissociate the trap bond α is $E_d = 2.4 \pm 0.2$ eV [11], it is necessary to accumulate $K = 22$ excimols in the hydrocarbon chain of Isoleucine and $K = 17$ excimols in the hydrocarbon chain of Leucine.

Dissociation of trap bond α induced by accumulation of a sufficient number of excimols in the dipole chains of L and I is likely to occur for the given grazing velocity. To prove this, the function P_M^K was calculated for $M = M_r \cdot t_{gr}/\tau_{tr}$ and $M_r = 6$. The surface parameters were taken from [2]. The results of these calculations are presented in Fig. 1, where the Isoleucine and Leucine curves correspond to accumulation of $K = 22$ (I) and $K = 17$ (L) excimols.

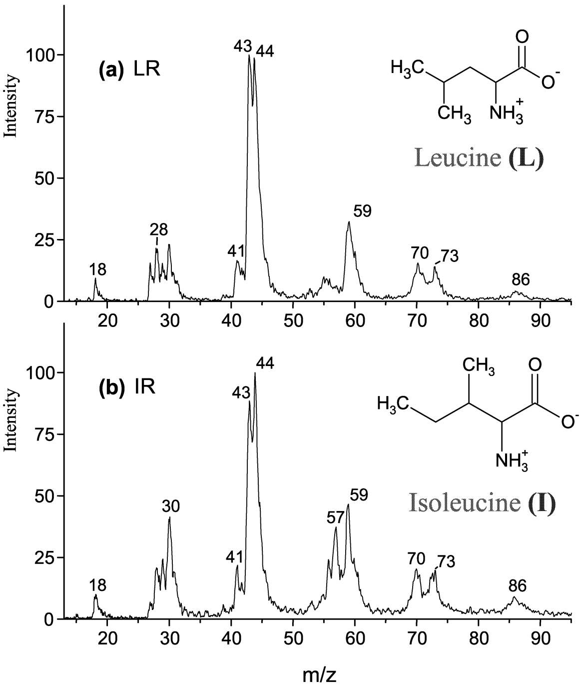

Fig. 2. The experimental GI-SID fragments mass-spectra of isomeric dipeptides LR (a) and IR (b) for grazing velocity $v = 1.6 \cdot 10^6$ cm/s. The two isomeric structures of L and I are included.

As one can see, the grazing velocity used in the GI-SID experiments is in a range, where the probability to generate a sufficient number of excimols for dissociation is nearly the same for I and L. Thus, in the GI-SID fragment ion spectra of the dipeptides LR and IR (Fig. 2) the peak intensity at $m/z = 57$ only reflects the influence of the distance parameter l on the transfer probability of the excimol energy to the trap bond. The spectra [10] for the dipeptides LR and IR are presented in Figure 2. The spectrum for LR displays no significant peak at $m/z = 57$. In the case of Isoleucine, however, one of the most prominent peaks appears at this m/z ratio.

This experimental result agrees well with the presented theoretical prediction about the strong dependence of the fragment production probability on the parameter l.

In conformity with the vanishing peak intensity at $m/z = 57$ a strong decrease of the intensity at

$m/z = 30$ is observed in the fragment ion spectrum of LR (Fig. 2). This fragment corresponds to the ion NH_3CH^+ and can be produced by dissociation of both trap bonds α and β.

Our estimation shows that for the considered grazing velocity the dissociation probability of simultaneous dissociation of α and β bonds is sufficiently high.

4. Conclusion

Intense electromagnetic fields in the IR frequency range are able to dissociate specific bonds in organic molecules. The preconditions for IR-field induced excitation and dissociation are investigated and described in the presented model.

A basic process in our theoretical concept is the accumulation of vibrational energy in chained substructures. Dissociation occurs, if the excitation energy moves on to a neighboured trap bond and if it piles up there to a sufficient level.

Interpretation of our experimental results supports the following view of the characteristics of those particular bonds, which are able to act as attractors (temporary traps) for collective vibrational energy in organic molecules:

(a) A trap bond is a valence bond inside a molecule connecting a substructure, which contains a chain of identical biatomic dipoles, with the rest of the molecule. Both parts form a vibrational quantum oscillator and a dipole with a moment, which is considerably weaker than the moment of a chain dipole. The trap bond dipole is located adjacent to the dipole chain, which is able to accumulate excimol energy quanta during resonant IR-irradiation. The acquired excimol energy is transferred to the trap bond by dipole-dipole interactions, finally leading to dissociation of the bond.

(b) The dissociation probability of a trap bond correlates inversely with the distance l between the trap bond's dipole and that dipole in the chain, which is closest to the trap bond.

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