Energy Exchange During Grazing Collision of Two Chain Molecules

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Z. Naturforsch. **65a,** 568 – 572 (2010); received August 14, 2009 / revised November 30, 2009

A theoretical model is presented, which describes the collision of two polyatomic organic molecules grazing each other at relative velocities below Bohr velocity. If the interacting molecules contain chains of diatomic dipoles, each of these chains can acquire and accumulate IR energy quanta by transition into collective excited vibrational states (excimols) during the contact period ($\sim 10^{-12}$ s). The excimol energy transport from one of the chains to close trap-bonds (energy acceptors) of the molecule as well as the energy exchange processes between the two molecules can lead to their fragmentation or electronic excitation. The probability functions of all mentioned processes were derived and presented in analytical form.

Key words: Organic Molecules; Grazing Collision; Energy Exchange; Vibrational Excitation.

1. Introduction

Recently, the research interest in the interaction of polyatomic organic molecules particularly with other molecules bound to surfaces has increased [1 – 5]. In these papers processes are considered predominantly, in which the molecules hit the surfaces at angles close to the normal. It was established in another set of experiments [6 – 8] that hyperthermal polyatomic molecules can be vibrationally excited, when they slide at atomic distances along a set of periodically located screened atomic charges in the upper surface layers. It was noticed that the probability of these processes increases, when the grazing velocities reach some specific values, i. e., there is a resonance effect occurring on the femtosecond time scale. An important precondition and determinant for the resonance effect is the existence of specific chained substructures of a definite length in the grazing molecules. These molecular substructures consist of periodically located identical biatomic valence bonds, for example, hydrocarbon substructures $(CH_2)_n$, and each bond has a dipole momentum. A chain of dipoles can serve as an IR antenna, thus we call such a substructure just antenna.

In this paper we investigate simultaneous excitations of two hyperthermal organic molecules due to mutual grazing collisions at atomic distances. This process can be considered as a local heating of both molecules leading to different transformations and even to their fragmentation.

The following results of our previous investigations are used in the presented model.

The first model applied here describes the resonant excitation of collective vibrational states (excimols) in molecular IR antennas by external radiation. It has been worked out based on experimental observations [6, 9, 10]. According to this model excimols are coherently excited during the grazing process. The excimol is the lowest collective vibrational excitation state of the antenna dipoles, and its energy is lower than the energy of the lowest vibrational excitation state of one isolated dipole in the electronic ground state. The lifetime of the excimol is much longer than the lifetime of the lowest vibrational excitation state of one isolated dipole.

Secondly, we took into account the possibility to accumulate excimol energy during the radiation period, if this period is shorter than the excimol lifetime [6, 7]. This is possible because the transfer time of the vibrational excitation from one dipole to another one is shorter than the excimol lifetime. Thus each antenna dipole can produce more than one excimol within the radiation period.

Finally, we applied a model of excimol excitation in molecular antennas, which are grazing along a two-dimensional lattice of identical screened charges with hyper thermal velocities, but lower than Bohr velocity υ_B. During the grazing process the antenna dipoles are closer than 2.5 Å to a chain of the screened charges [6, 11, 12].

In the interaction model developed here two polyatomic organic molecules are mutually grazing each other, while simultaneous excitation of excimols in the antennas of both molecules can occur. In this process, the antennas serve as excimol energy accumulators and at the same time as a source of a periodical Coulomb field generated by the moving row of screened charges in it.

2. Model for the Interaction of Mutually Grazing Molecules

The main goal of the presented work is to analyze the processes of simultaneous energy accumulation of molecular antennas and energy exchange during low velocity grazing collisions of organic molecules. We will discuss here a model for the case, when each of the two organic molecules has an antenna substructure. Both molecules are interacting while grazing along each other with a hyper thermal velocity ($10^5 - 10^6$ cm/s), i. e. lower than the Bohr velocity ($\upsilon_B = 10^8$ cm/s). We assume that the distance between chained substructures in the grazing molecules is not more than 2.5 Å.

2.1. Energy Accumulation in the System of Two Slow Mutually Grazing Molecules

Here we calculate probabilities for energy accumulation and its transition into molecular trap-bonds, which are dipole-type diatomic bonds different from antenna bonds. In accordance with the excimol theory [6, 11], we must define some antenna parameters of both molecules participating in the grazing collision. In the following, parameters and variables relating to one of the mutually grazing molecules are denoted with index number 1 for the first and index number 2 for the second molecule.

In order to calculate the excimol energy ${}_i\varepsilon_{ex}$ (for $i = 1$ or 2) in the antenna of the ith molecule, we have to define the number ${}_iN$ of the identical biatomic valence dipoles in the antenna of each molecule i and the value of the dipole momentum ${}_i(D_0/r_0)$ of one of these antenna dipoles, the distance ${}_il$ to the neighboured antenna dipoles, and the angular function ${}_i\Phi$, which defines the location of a dipole in the antenna's chain. The calculation of ${}_i\varepsilon_{ex}$ was given in details in [6, 10].

The antennas in each of the interacting molecules i can serve simultaneously as the energy collector and as a lattice of screened atomic charges ${}_iZ$ at distance ${}_ia$ during the grazing collision. To calculate the probability of an excimol excitation with energy ${}_i\varepsilon_{ex} = \hbar\,{}_i\omega_{ex}$ in antenna i, we have to define a periodical Coulomb field with resonance frequency ${}_i\omega_{ex}$ experienced by molecule i when grazing along the atomic lattice of screened charges in the antenna of the collision partner. The periodicity and intensity of this field depends on the relative grazing velocity υ_{gr}, the value of the screened charges in the atomic lattice, and the effective atom radii in the lattice [12].

Excimol excitation probabilities ${}_1P_{01}$ and ${}_2P_{01}$ for fixed grazing time in the first and the second molecule, respectively, can be calculated analogous to the formulas given in our previous work [6, 11]:

$$
{}_1P_{01} = \frac{4\pi^2}{3\hbar}\left[{}_1M_{01}\cdot{}_1\left(\frac{D_0}{r_0}\right)e\right]^2 \frac{{}_2Z^2}{{}_2a^3\cdot b\upsilon_{gr}\cdot{}_1\Theta}
\cdot\left[\frac{{}_1\varepsilon_{ex}}{\hbar\cdot\upsilon_{gr}\cdot{}_1\Theta}-1\right]^2\exp(2R\cdot{}_1\Theta) \qquad (1)
$$

$$
\text{with}\quad {}_1\Theta = \left(\frac{{}_1\omega_{ex}^2}{\upsilon_{gr}^2}-\frac{1}{{}_2a_{eff}^2}\right)^{1/2},
$$

$$
{}_2P_{01} = \frac{4\pi^2}{3\hbar}\left[{}_2M_{01}\cdot{}_2\left(\frac{D_0}{r_0}\right)e\right]^2 \frac{{}_1Z^2}{{}_1a^3\cdot b\upsilon_{gr}\cdot{}_2\Theta}
\cdot\left[\frac{{}_2\varepsilon_{ex}}{\hbar\cdot\upsilon_{gr}\cdot{}_2\Theta}-1\right]^2\exp(2R\cdot{}_2\Theta) \qquad (2)
$$

$$
\text{with}\quad {}_2\Theta = \left(\frac{{}_2\omega_{ex}^2}{\upsilon_{gr}^2}-\frac{1}{{}_1a_{eff}^2}\right)^{1/2}.
$$

Here, ${}_iM_{01}$ are the matrix elements for the dipole transition from the ground state to the first vibrational state in the antenna of molecule i. The definition and the calculation method used for parameters b and R are taken from [6]. The analysis of expressions (1) and (2) shows, that the dimensionless probabilities ${}_1P_{01}$ and ${}_2P_{01}$ for the fixed grazing time as a function of the grazing velocity υ_{gr} have maxima.

The energies $E({}_1K)$ and $E({}_2K)$ of ${}_1K$ and ${}_2K$ excimols collected in the antennas of the molecules 1 and 2 during the grazing time, which is equal to or shorter than the excimol's lifetime, can be calculated by the following expressions:

$$
E({}_iK) = {}_i\varepsilon_{ex}\cdot{}_iK \quad \text{with} \quad {}_iK = {}_iN\cdot{}_iP_{01}\cdot\tau_{gr}/{}_i\tau_{tr}
$$

for $i = 1$ or 2,

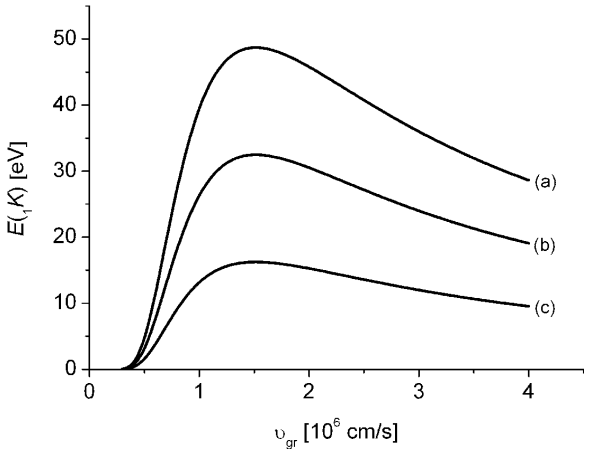

Fig.1. Calculated excimol energy $E(_1K)$ accumulated in molecule 1 during its grazing collision with molecule 2 at relative velocity υ_{gr}. Molecule 1 contains an antenna $C_{30}H_{60}$ (a) or $C_{20}H_{40}$ (b) or $C_{10}H_{20}$ (c), while molecule 2 contains in all 3 cases an antenna $C_{30}H_{60}$.

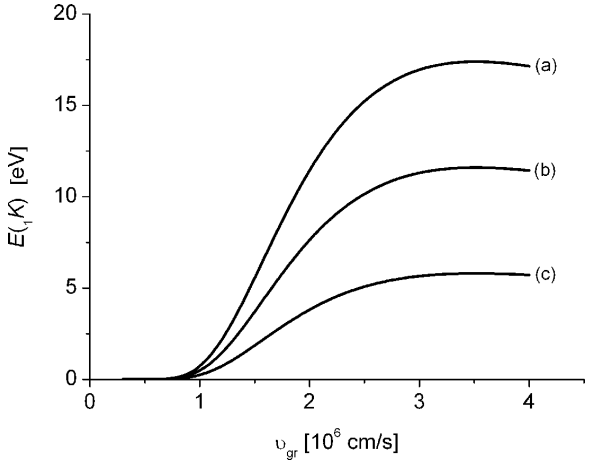

Fig. 2. Calculated excimol energy $E(_1K)$ accumulated in molecule 1 during its grazing collision with molecule 2 at relative velocity υ_{gr}. Molecule 1 contains an antenna $C_{30}H_{60}$ (a) or $C_{20}H_{40}$ (b) or $C_{10}H_{20}$ (c) as in Figure 1, but here molecule 2 contains an antenna $C_{15}F_{30}$.

where ${}_i\tau_{tr} = h/{}_iE_{tr}$ is the time needed for the excitation transition from one antenna dipole to another and ${}_iE_{tr}$ is the dipole-dipole interaction energy in the antenna of molecule i [6].

Since probabilities ${}_1P_{01}$ and ${}_2P_{01}$ are functions of the grazing velocity υ_{gr} and depend on the grazing time τ_{gr}, the energies $E(_1K)$ and $E(_2K)$ collected in both antennas are also functions of υ_{gr} and the parameter τ_{gr}. Moreover, these energies are resonance functions of the velocity υ_{gr} and depend linearly on the number of dipoles in the antennas. They also depend on the antenna structures and Coulomb properties of the antenna dipoles.

If the antenna dipoles of both mutually grazing molecules are identical, and the number of antenna dipoles in both molecules are equal, then the energy accumulated in the antennas of these molecules are the same.

As an example, we analysed the dependence of the energy accumulation on the number of antenna dipoles in the mutually grazing molecules. We consider the molecule 1 containing antenna C_nH_{2n} for different numbers n, when molecule 2 has antennas consisting of C_nH_{2n} or C_nF_{2n} chains with a fixed number n. The excimol energy accumulated in molecule 1 was calculated versus grazing velocity υ_{gr} by fixed grazing time τ_{gr} and definite structure parameters and Coulomb properties of the molecular antennas.

First, we investigate energy accumulation in antennas $C_{30}H_{60}$, $C_{20}H_{40}$, and $C_{10}H_{20}$ in molecule 1, when the molecule 2 has the antenna $C_{30}H_{60}$. We also consider the energy accumulation in molecule 1, which has antennas $C_{30}H_{60}$ or $C_{20}H_{40}$ or $C_{10}H_{20}$, while molecule 2 has the antenna $C_{15}F_{30}$. The calculation results of the energy functions $E(_1K)$ versus velocities for both cases are presented in the Figures 1 and 2. The calculation parameters were taken from [6]. As expected the accumulated excimol energy in the antenna of molecule 1 depends linearly on the number of dipoles in its antenna and has a maximum value at the same grazing velocity for each case of the length of the antenna. Moreover, since the absolute value of $E(_1K)$ for a fixed grazing velocity depends on the structures and charge distribution in the antenna of molecule 2, the calculated functions $E(_1K)$ in Figures 1 and 2 have different values for the equal grazing velocities and the equal number of dipoles in the antenna of molecule 1. Curve (a) in Figure 1 also represents the energy function $E(_2K)$. In this case the dipoles in the antennas of both molecules are identical and the energy accumulation in the antenna of molecule 2 does not depend on the number of dipoles in the antenna of molecule 1 when ${}_1N \geq 4$ [6].

2.2. Energy Transfer in the System of Two Mutually Grazing Molecules

There are two possibilities of excimol energy transition from molecular antennas to trap-bonds located inside a system of two mutually grazing molecules.

Firstly, the excimol energy accumulated in the antenna of molecule i, ($i = 1, 2$), transits by dipole-dipole interactions between antenna and trap-bond dipoles or π-electrons in the same molecule. This transition can lead to the dissociation of the considered trap-bond or its electronic excitation, if the accumulated excimol energy is sufficient for these processes. These processes were investigated in detail in our works [9, 11, 12], where we considered the processes of slow organic molecules grazing along two-dimensional lattices. Secondly, the excimol energy accumulated in the antenna of molecule 1 can transit to a trap-bond of molecule 2 and vice versa, if the grazing distance between both molecules is about 2–3 Å, and the dipoles of the antenna in molecule 1 are oriented properly (nearly perpendicular) to the trap-bond dipole of molecule 2 and vice versa. Thus, energy exchange between the mutually grazing molecules is possible.

By using the model, which was developed for the calculation of the probability of energy transition from the antenna to the trap-bond inside of a single molecule [9, 11], we calculated the probability ${}_{1,2}P_{\mathrm{f}}$ of the energy transition from the antenna of the first molecule to trap-bond B of the second molecule and dissociation of this trap-bond:

$$ {}_{1,2}P_{\mathrm{f}} = P({}_1M,{}_1K)\cdot {}_1P_{01}\cdot {}_2P, \tag{3} $$

$$ P({}_1M,{}_1K) = [2\pi\cdot {}_1M\cdot {}_1P_{01}(1-{}_1P_{01})]^{-1/2} \cdot \exp\left\{-\frac{({}_1K-{}_1M\cdot {}_1P_{01})}{2{}_1M\cdot {}_1P_{01}\,(1-{}_1P_{01})}\right\}. \tag{4} $$

$P({}_1M,{}_1K)$ is the probability to accumulate ${}_1K$ excimols in an antenna of molecule 1, which has ${}_1M$ effective dipoles, i. e. dipoles participating in excimol excitation.

${}_2P$ is the dissociation probability of trap-bond B in molecule 2 induced by the excimol energy transition from the antenna of molecule 1 to B. The analytical expression for ${}_2P$ was calculated by using the model formulated in [11].

$$ {}_2P = \frac{\sqrt{2\pi}}{\hbar E_{\mathrm{q}}}\cdot\left[{}_1K\cdot 2e^2\cdot {}_1\left(\frac{D_0}{r_0}\right)\,{}_2\left(\frac{D_{\mathrm{B}}}{r_{\mathrm{B}}}\right){}_1M_{01}\cdot {}_1\Phi_{\mathrm{B}}\right]^2 \cdot L^{-6}q^3\cdot\alpha_{\mathrm{B}}^5\exp\left(-q^2\cdot\alpha_{\mathrm{B}}^2\right), \tag{5} $$

where E_{q} and q are the energy and the momentum of the fragment of molecule 2, $\alpha_{\mathrm{B}} = \hbar(2\mu_{\mathrm{B}}\omega_{\mathrm{B}})^{1/2}$ is a bond parameter of trap-bond B, μ_{B} is the reduced mass of trap-bond B, ω_{B} is the vibrational eigenfrequency of trap-bond B, L is the distance between the antenna dipole of molecule 1, which is closest to trap-bond B in molecule 2, and this trap-bond B. The value of the dipole momentum of trap-bond B is ${}_2(D_{\mathrm{B}}/r_{\mathrm{B}})$.

The mutual orientation of the above mentioned dipoles participating in the energy exchange between molecules 1 and 2 is given by the angular function ${}_1\Phi_{\mathrm{B}}$. The general analytical expression for this angular function was obtained earlier in [11] and has the form

$$ {}_i\Phi_j = \cos\theta_i{}^{\mathrm{x}}\cos\theta_j{}^{\mathrm{x}} + \cos\theta_i{}^{\mathrm{y}}\cos\theta_j{}^{\mathrm{y}} - 2\cos\theta_i{}^{\mathrm{z}}\cos\theta_j{}^{\mathrm{z}}. \tag{6} $$

The angles $\theta_i{}^{\mathrm{x,y,z}}$ and $\theta_j{}^{\mathrm{x,y,z}}$ define the directions of the vectors $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ in the coordinate system, where axis OZ coincides with the vector $\boldsymbol{R}_{ij}$ directed from dipole i to dipole j.

The probability function ${}_{2,1}P_{\mathrm{f}}$ for the energy transition from molecule 2 (antenna) to molecule 1 (trap-bond) with its following dissociation can be obtained simply by exchanging the indexes 1 and 2 in (3).

The probability ${}_{1,2}P_{\mathrm{el}}$ of electronic excitation of molecule 2 induced by excimol energy transition from the antenna of molecule 1 during a grazing collision of the two molecules containing antennas can be calculated by a method, which we used in a very similar way for the case of an intra-molecular excimol transition from the antenna to an electronic energy trap-bond [12].

Then, the probability ${}_{1,2}P_{\mathrm{el}}$ of this process can be given in the form

$$ {}_{1,2}P_{\mathrm{el}} = \frac{2\pi\cdot P({}_1M,{}_1K)\cdot {}_1P_{01}}{\hbar\cdot E({}_1K)} \cdot\left[2\cdot {}_1K\cdot e^2\cdot {}_1\left(\frac{D_0}{r_0}\right)\cdot {}_2\left(\frac{D_{\mathrm{el}}}{r_{\mathrm{el}}}\right)\cdot {}_1M_{01}\cdot {}_2M_{\mathrm{el}}\right]^2 \cdot\frac{{}_1\Phi_{\mathrm{el}}(\vartheta,\vartheta_{\mathrm{el}})}{R^6}, \tag{7} $$

where ${}_2(D_{\mathrm{el}}/r_{\mathrm{el}})$ is the value of the dipole momentum of the π-electron in the second molecule, which is responsible for the electronic excitation due to the transition of the excimol energy $E({}_1K)$ from molecule 1 to the electronic trap-bond of molecule 2, R is the distance between the above mentioned π-electron dipole of molecule 2 and the antenna dipole of molecule 1 closest to it. M_{el} is the matrix element of the π-π^* transition in molecule 2, the angular function ${}_1\Phi_{\mathrm{el}}$ defines the direction of dipoles in the antenna of molecule

1 relative to the direction of the π-electron dipole in molecule 2 [12]. Electronic excitation of molecule 1 is also possible due to the excimol energy transition from the antenna of molecule 2 and the probability ${}_{2,1}P_{\mathrm{el}}$ of this process can be calculated by the same formula (7) with replaced indexes 1 and 2. The relaxation of the electronic excitation state of the molecule can lead to the emission of a photon with an energy much higher than the energy of one excimol. Thus, we can consider the system of two mutually grazing molecules as an energy amplifier. The obtained analytical expressions (5), (6), and (7) permit to calculate probabilities of photon emission with definite energies higher than the excimol energy.

3. Conclusions

The above suggested model of internal vibrational energy accumulation and transition in mutually grazing organic molecules allows one to draw conclusions about the dissociation probabilities for these molecules. The fragment spectrum resulting from such dissociations is the sum of the dissociation spectra of both molecules participating in the grazing event, and depends on Coulomb field and structure properties of the molecular antennas. The energy values accumulated in the antenna structures of the grazing molecules depend on the dipole numbers in these antennas. If the dipole number in one molecule is not sufficient to accumulate enough energy, dissociation is nevertheless possible due to an energy exchange with the other molecule in the grazing process. The excimols can transit from the antenna of one molecule to the trap-bond of another molecule and vice versa. Dissociations of both mutually grazing molecules are even possible, if one of the molecules hasn't any antenna substructure at all, provided it has a π-electron system serving as a dipole-type electronic energy trap. In this situation, the excimol transition from the molecule with antenna to the molecule without antenna can lead to a high electronic excitation, finally also leading to molecular fragmentation. The suggested model is essential not statistical. The derived analytical expressions for the probabilities of molecular fragmentation and electronic excitation clearly demonstrate their dependence on parameters of the considered molecules and the grazing velocity, and permit to predict the probabilities of energy processes in the considered systems of two mutually grazing molecules.

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