Vibration Energy Accumulation and Redistribution in Organic Molecules Irradiated by Infrared Photons

Hartmut Jungclas, Anna M. Popova, Viacheslav V. Komarov, Lothar Schmidt, and Alexander Zulauf

Fachbereich Chemie, Philipps-Universität, D-35032 Marburg, Germany

Reprint requests to Prof. Dr. H. J.; E-mail: jungclas@staff.uni-marburg.de

Z. Naturforsch. **62a,** 324 – 330 (2007); received February 5, 2007

A theoretical approach to the dissociation and low-energy electronic excitation of polyatomic organic molecules with donor and acceptor substructures is suggested. The donor hydrocarbon molecular substructures can serve as antennas for low-energy infrared (IR)-photon absorption, which coherently induce collective vibrational excitations (excimols). Due to dipole-dipole interactions, the accumulated energy can transit to the molecular acceptors: dipole-type trap-bonds or molecular parts with π-electron orbits. The analytical expressions for the probability functions of molecular fragmentation and electronic excitation induced by IR-multiphoton absorption are derived. The vibrational energy accumulation and redistribution in the molecules of diphenylalkanes irradiated by infrared photons are considered from the presented point of view. – PACS numbers: 30.00 – 34.10 – 36.40

Key words: Organic Molecules; Energy Accumulation.

1. Introduction

The infrared (IR)-multiphoton-induced excitation and the following transformations of a single organic molecule have been extensively studied in the last few decades [1 – 7], since these processes are able to give valuable information about the intermolecular energy redistribution and molecular transformation. In a few series of experiments it has been shown that the probability and the duration of the photon-induced processes in molecules irradiated by mid-IR-photons significantly depend on the radiation fluence and frequency as well as on the topological and spectral properties of the considered molecules [8 – 21].

This explains the necessity to develop a suitable theoretical approach to the mentioned nonstatistical femtosecond processes in organic molecules consisting of a few substructures with different topological and spectral properties.

In this paper we present a theoretical model for the multiphoton-induced vibration energy accumulation and transformation in large organic molecules consisting of donor-acceptor-type substructures. We consider molecules in which the donor is a hydrocarbon chain $(CH_2)_n$ serving as an antenna for mid-IR-photons. The intramolecular vibrational energy accumulated in the donor can be transferred through a dipole-dipole valve to the acceptor parts of the same molecule, causing various molecular transformations.

2. Alkanes as Antennas for Mid-IR Radiation and Molecular Energy Donors

As it was shown by us earlier [22 – 23], hydrocarbon chains in single organic molecules can serve as antennas for external IR-photons. A band of collective low-energy vibrational states can arise in $(CH_2)_n$, due to the relatively high dipole moment of the CH-bonds and the small distance between them of about 1.5 Å in the chain. The state in the band with the lowest energy $E_{ex} = 0.07$ eV and the lifetime $\tau_{ex} = 5 \cdot 10^{-11}$ s is called excimol [24]. An excimol can travel from one CH-dipole to the neighbour dipole along the antenna due to the resonant dipole-dipole interaction between the CH-valence bonds in the time interval $\tau_{tr} = 10^{-14}$ s without energy loss and phase change. As a result, N excimols can be excited in one antenna dipole, where $N = \tau_{ex}/\tau_{tr}$. Thus, the excitation process of M effective dipoles takes place, if $M = N \cdot M_r$, and M_r is the real number of CH-dipoles in the antenna.

In the excimol model [25], due to the large unharmonicity of the CH-dipoles, which we consider as oscillators, the excimols can not concentrate in one CH-bond, and there is no interaction between the excimols

0932–0784 / 07 / 0500–0324 $ 06.00

in the antenna. Then we can define a probability of independent excitation of K excimols in M effective dipoles in an antenna by the relation

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

where P_{01} is the probability of resonant excitation of one excimol in a CH-dipole during τ_{ex}. The probability of one excimol excitation per time unit, calculated in the dipole approximation, has the form

$$\tilde{P}_{01} = \frac{4\pi^2}{3\hbar c}\left(\frac{eD_0}{r_0}\right)^2 M_1^2 J, \tag{2}$$

where eD_0 is a parameter of the CH-dipole of the corresponding chain.

Equation (2) contains $J = 2F/\Delta E$, where F is the radiation flux. M_1 is a matrix element of the dipole transition, ΔE is the energy width of the radiation flux with the frequency ω_{ex}. r_0 and r are equilibrium and variable CH-dipole lengths.

The energy $E(K)$ of K excimols accumulated in the antenna can transfer radiationless to the acceptor due to dipole-dipole interaction. The number of excimols accumulated in the antenna depends linearly on the intensity of external IR-radiation with the frequency ω_{ex}. This statement follows from the properties of the function P_M^K, which reaches its maximum by the condition

$$K = M \cdot P_{01}. \tag{3}$$

The number of excimols K, as it follows from (3), depends linearly on P_{01}, and P_{01} in turn depends linearly on the value F. Therefore K depends linearly on F, i. e. the accumulated excimol energy $E(K) = K \cdot E_{\text{ex}}$ depends linearly on the radiation flux F. This result explains the experimental data of the work [26], where it was observed, that the number of absorbed photons in organic molecules with hydrocarbon chains depends linearly on the radiation flux.

Thus for the excitation of a definite number K of excimols in the antenna with fixed M, a certain value of radiation flux is required, and this value is smaller than the value of the flux, which is needed for the excitation of one dipole with $P_{01} = 1$.

The relation (1) shows that the probability P_M^K for a fixed energy $E(K) = K \cdot E_{\text{ex}}$ corresponding to a number K of accumulated excimols in the antenna with M_{r} oscillators is depending resonantly on the radiation flux F. Then, the accumulation of a certain amount of excimol energy in an oscillator chain with $M_{\text{r}} \gg 1$ is a double resonance process, since its probability depends resonantly on the field frequency and radiation flux.

3. Molecular Substructures as Acceptors of Excimol Energy

The acceptors in a single polyatomic organic molecule can be either valence bonds of dipole-type, the so-called trap-bonds, or electronic trap-bonds, which define low-energy π-π^* excitation of some molecular parts with π-electron orbits. If the electronic trap-bonds or acceptors of composite molecules are not directly joined together but separated by the donor substructure, then it is allowed to assume that the absorption spectrum of each acceptor is not influenced by the presence of another one.

Let us consider the donor-acceptor interaction in the mentioned molecule, which is a dipole-dipole interaction. The vibration energy transfer is defined by the interaction potential W_{B} between K identical antenna dipoles and one acceptor dipole. The function W_{B} has the form

$$W_{\text{B}} = \sum_{i=1}^{K} w_{i\text{B}} \quad \text{with}$$
$$w_{i\text{B}} = \frac{e^2 D_0 D_{\text{B}}}{r_0 R_0} \Phi_{i\text{B}}(\vartheta_i, \vartheta_{i\text{B}}) \frac{r_i R_{\text{B}}}{L_{i\text{B}}^3}. \tag{4}$$

Here $L_{i\text{B}}$ is the distance between the origin of the dipole moment $\boldsymbol{D}_i = eD_0\boldsymbol{r}_i/r_0$ of any CH-bond in the chain and the origin of the trap-bond's dipole moment $\boldsymbol{D}_{\text{B}} = eD_{\text{B}}\boldsymbol{R}_{\text{B}}/R_0$.

The function $\Phi_{i\text{B}}(\vartheta_i, \vartheta_{\text{B}}) = \cos\vartheta_i^x \cos\vartheta_{\text{B}}^x + \cos\vartheta_i^y \cos\vartheta_{\text{B}}^y - 2\cos\vartheta_i^z \cos\vartheta_{\text{B}}^z$ in (4) takes into account the position of the trap-bond's dipole moment relative to the position of any CH-dipole moment in the antenna. The angles ϑ_i and ϑ_{B} define the direction of $\boldsymbol{r}_i$ and $\boldsymbol{R}_{\text{B}}$ in a coordinate system, where axis OZ coincides with the vector $\boldsymbol{L}_{i\text{B}}$.

The value of the potential $w_{i\text{B}}$ strongly depends on the distance $L_{i\text{B}}$ and the angle function $\Phi_{i\text{B}}(\vartheta_i, \vartheta_{\text{B}})$. The potential $w_{i\text{B}}$ reaches its maximum when $L_{i\text{B}}$ has its smallest value. This minimum of $L_{i\text{B}}$ is the distance $L_{1\text{B}} = L$ between the trap-bond dipole $\boldsymbol{D}_{\text{B}}$ and the nearest dipole $\boldsymbol{D}_1$ in the antenna.

A necessary condition for a bond to act as a trap-bond is that the excimol transition time along the antenna to dipole $\boldsymbol{D}_1$ is much shorter than the excimol transition time from dipole $\boldsymbol{D}_1$ to the trap-bond. This makes it possible to assume that the excimols accumulated in an antenna can transit practically simultaneously and coherently from the antenna dipole $\boldsymbol{D}_1$ to the trap-bond. Thus, we can conclude that the energy $E(K)$ of K accumulated excimols transits coherently from the antenna to the trap-bond as one photon with the energy $E(K)$.

In our model the number of trap-bonds, which are dissociated in a molecule by an IR-radiation pulse, is limited by the number of excimols which can be accumulated in the molecular antenna substructures during irradiation time, because the maximum of the accumulated excimol energy can not be less than the sum of dissociation energies of these trap-bonds. The maximum amount of energy, which can be transmitted to a trap-bond, is the sum of excimol energy quanta $E(K) = K_{\max} \cdot E_{\mathrm{ex}}$ with $K_{\max} = M$ accumulated in the adjacent antenna.

Since the potential W_{B} defines the probability for the transition of vibrational energy from the antenna to the acceptor, we can consider it as an energy valve driven by the potential parameters. For example, as it follows from (4), according to the property of the function $\Phi_{1\mathrm{B}}$, if the dipole $\boldsymbol{D}_1$ is perpendicular to the dipole momentum of some trap-bond, then the excimol energy is not able to transit to this bond.

4. Molecular Fragmentation by Multiphoton Absorption

In agreement with the excimol theory suggested by us earlier [22], the excimol energy accumulated in the antenna happens to be high enough to excite a trap-bond up to its dissociation. When $E(K)$ exceeds the dissociation energy $E_{\mathrm{d}}(B)$ of a trap-bond B, it can be cleaved.

The dissociation probability per time unit P_{f} for a certain trap-bond can be calculated on the basis of the perturbation theory [25] with the result

$$P_{\mathrm{f}} = P_M^K P_{01} P, \quad \text{where}$$
$$P = \frac{2\sqrt{\pi}}{\hbar E_{\mathrm{q}}} K^2 \left(\frac{2e^2 D_0 D_{\mathrm{B}}}{r_0 R_0} M_1 \Phi_{1\mathrm{B}}(\vartheta_1, \vartheta_{\mathrm{B}}) \right)^2 \cdot \frac{q^3 \alpha_{\mathrm{B}}^5 \exp(-q^2 \alpha_{\mathrm{B}}^2)}{L^6}. \tag{5}$$

We propose that the energy of all K excited dipoles is transmitted via dipole $i = 1$ to the trap-bond. The value L in (5) is a distance between the antenna's dipole $\boldsymbol{D}_1$ and the dipole $\boldsymbol{D}_{\mathrm{B}}$. In the model, the trap-bond B is defined and handled as a vibrational quantum oscillator with the ground state energy $\varepsilon_{\mathrm{B}}^0 = \hbar\omega_{\mathrm{B}}^0/2$, corresponding to the oscillator wave function $\varphi_{\mathrm{B}}^0(R_{\mathrm{B}})$ with $\alpha_{\mathrm{B}} = (\hbar/2\mu_{\mathrm{B}}\omega_{\mathrm{B}}^0)^{1/2}$ and reduced mass μ_{B}. 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 molecular fragments.

The analytical expression (5) for the probability of trap-bond dissociation allows to analyze its dependence on the variables and molecular parameters.

5. Molecular Electronic Excitation by Multiphoton Absorption

Let us consider the excimol energy transition to the electronic trap-bond induced by the energy potential (4). The probability function P_{el} per time unit of π-electron excitation of acceptor B induced by the transition of excimol energy $E(K)$ from the hydrocarbon antenna can be calculated by perturbation theory with the result

$$P_{\mathrm{el}} = \frac{2\pi}{\hbar} \frac{P_M^K P_{01}}{E(K)} K^2 \left(\frac{2e^2 D_0 D_{\mathrm{el}}}{r_0 R_0} M_1 M_{\mathrm{el}} \right)^2 \cdot \Phi_{1,\mathrm{el}}\,(\vartheta_1, \vartheta_{\mathrm{el}})^2 \frac{1}{R_1^6}, \tag{6}$$

where R_1 is the distance between the antenna dipole $\boldsymbol{D}_1$ and the dipole $\boldsymbol{D}_{\mathrm{B}}$, M_{el} is a matrix element of the π-π^* transition in the considered acceptor. Equation (6) is valid if $E(K) = \varepsilon_{\mathrm{el}}^* - \varepsilon_{\mathrm{el}}^0$, i. e. the excimol energy is equal to the electronic excitation energy of the acceptor. Therefore, molecular electronic excitation induced by mid-IR-multiple photon absorption occurs, when a proper number K of the accumulated excimols appears during the IR-radiation pulse period. The function P_{el} depends resonantly on the frequency of the external mid-IR-photons. As in the case of the molecular fragmentation, the probability function P_{el} of molecular electronic excitation has a maximum value when the relation $K = M \cdot P_{01}$ is fulfilled. This last relation determines a connection between the electronic excitation energy and the value of the radiation flux for the

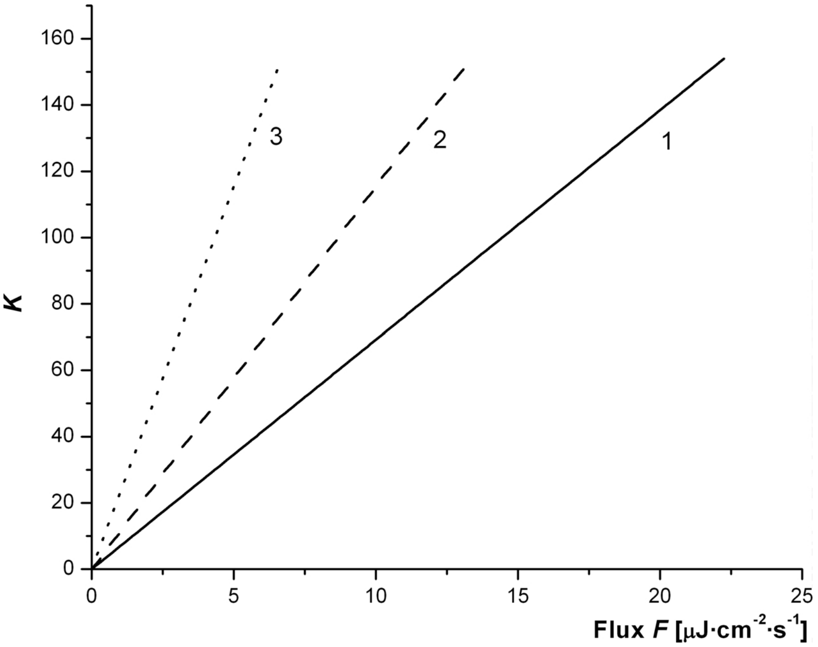

Fig. 1. The calculated excimol number K versus flux F for diphenylalkanes. The curves 1, 2, 3 correspond to molecular hydrocarbon antennas with the dipole numbers $M_r = 6$; 10; 20.

maximum of P_{el}. We note, that the probability function P_{el} has the same properties as the function P_f presented above.

Analysis of the analytical expressions for P_f and P_{el} as functions of K shows, that these functions have resonant behaviour, when $K \cdot E_{ex} = E_d$ and $K \cdot E_{ex} = \varepsilon_{el}^* - \varepsilon_{el}^0$, correspondingly. Another important property of these probabilities is, that since the excimol accumulation depends resonantly on the IR-flux, the considered processes are essentially resonant processes versus the IR-flux, and consequently have a threshold behaviour.

6. Model Calculations for Diphenylalkanes

The model outlined above of the processes initiated in polyatomic organic molecules by action of mid-IR-photons was applied to diphenylalkane molecules [C_6H_5-$(CH_2)_n$-C_6H_5, for $n > 2$]. The donor substructures $(CH_2)_n$ in these molecules are antennas for photons with an energy equal to the excimol energy $E_{ex} = 0.07$ eV. The vibration energy of K excimols accumulated within $\tau_{ex} = 5 \cdot 10^{-11}$ s in the antenna can transit radiationless to the acceptor consisting of two valence bonds C-C, which connect the alkyl group with the phenyl groups acting as electronic trap-bonds. Resonant absorption of photons from an IR-radiation pulse with a frequency equal to the excimol frequency and with an intensity less than 10^6 J/cm^2 s leads to accumulation of the vibration energy $E(K)$ by excitation of K excimols in the antenna with $M_r \approx 20$ CH-dipoles. The number of excited excimols during the excimol lifetime depends on the radiation intensity F, and on the real dipole number M_r in the antenna.

We calculated the number of excimols K excited in the hydrocarbon antenna versus the radiation intensity for $M_r = 6$; 10; 20. The result of the calculation is presented in Figure 1. One can see, that excitation of a fixed number of excimols occurs by an intensity value reciprocal to the number of real dipoles in the antenna.

As is known, the energy of 3.5 eV ($K = 50$ excimols) is needed to dissociate a C-C bond [27]. The energy of 4.42 eV ($K = 64$ excimols) is needed for the electronic π-π^* transition in the phenyl group [28]. Then, a variety of processes can be induced in diphenylalkane molecules by IR-radiation with the resonance frequency $\omega = \omega_{ex}$, when the radiation intensity is increased or when the number of accumulated excimols in the antenna increases ($K = 50$; 64; 100; 114; 128): one C-C trap-bond dissociation; electronic excitation of one phenyl group; two simultaneous C-C bond dissociations; simultaneously one C-C bond dissociation and electronic excitation of one phenyl group; and finally electronic excitation of two phenyl groups. By using (5) and (6), we calculated the dissociation and electronic excitation probabilities of the diphenyl

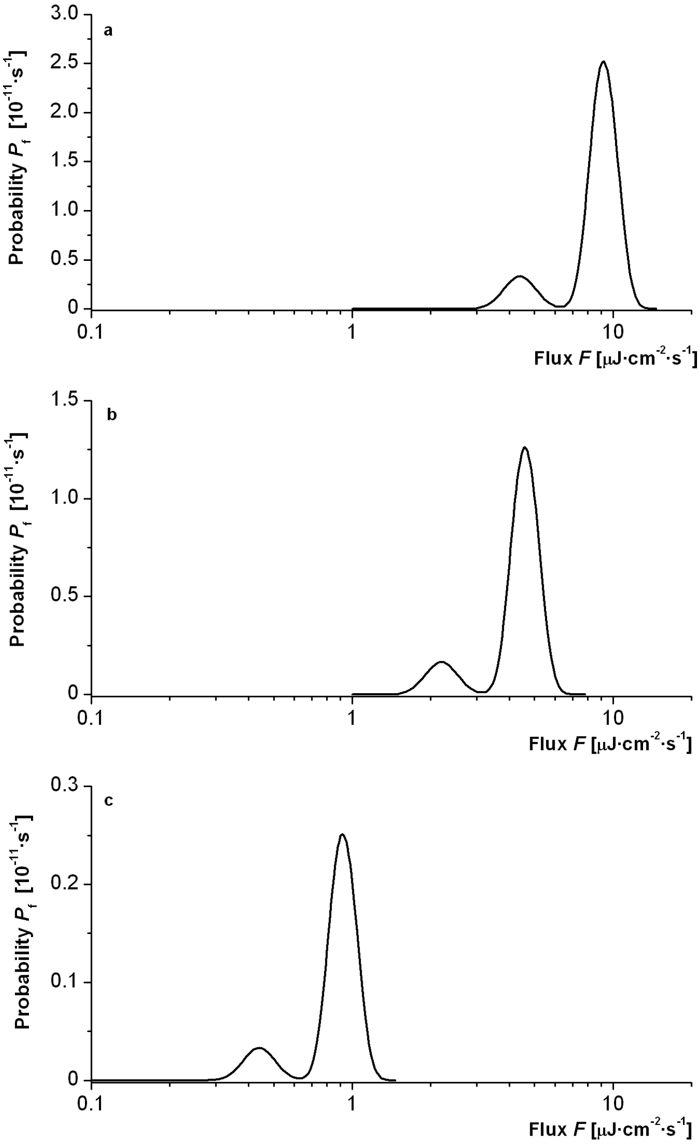

Fig. 2. The dissociation probability function P_f versus flux F for diphenylalkanes, calculated by (5) with the parameters: $K = 50$; $D_0/r_0 = 0.7$; $D_B/R_0 = 0.7$; $L = 0.5$ Å; $\Phi_{1B} = 0.9$; $M_l = 2\cdot 10^{-9}$ cm. The plots (a), (b), (c) correspond to molecular hydrocarbon antennas with the dipole numbers 10, 20, 100.

molecule versus the intensity of the radiation flux, taking into account the processes mentioned above. The results of the calculations for $M_r = 10$; 20; and 100 are presented in the Figs. 2 and 3.

As one can see from the figures, the considered processes are super fast and occur in different intensity intervals with respect to the number of dipoles in the molecular antenna.

7. Conclusions

The theoretical approach presented in this article to IR-multiphoton absorption by organic molecules with donor-acceptor substructures led to the development of a nonstatistical model for the vibration energy accumulation and redistribution in the considered molecules. By using the excimol theory, analytical expressions were obtained for the probability functions of molecular fragmentation and electronic excitation activated by collected excimol energy. The following consequences of this model were established.

The probability functions P_f and P_{el} of both considered processes depend resonantly on the frequency ω_R of the external IR-radiation. The value ω_R must be

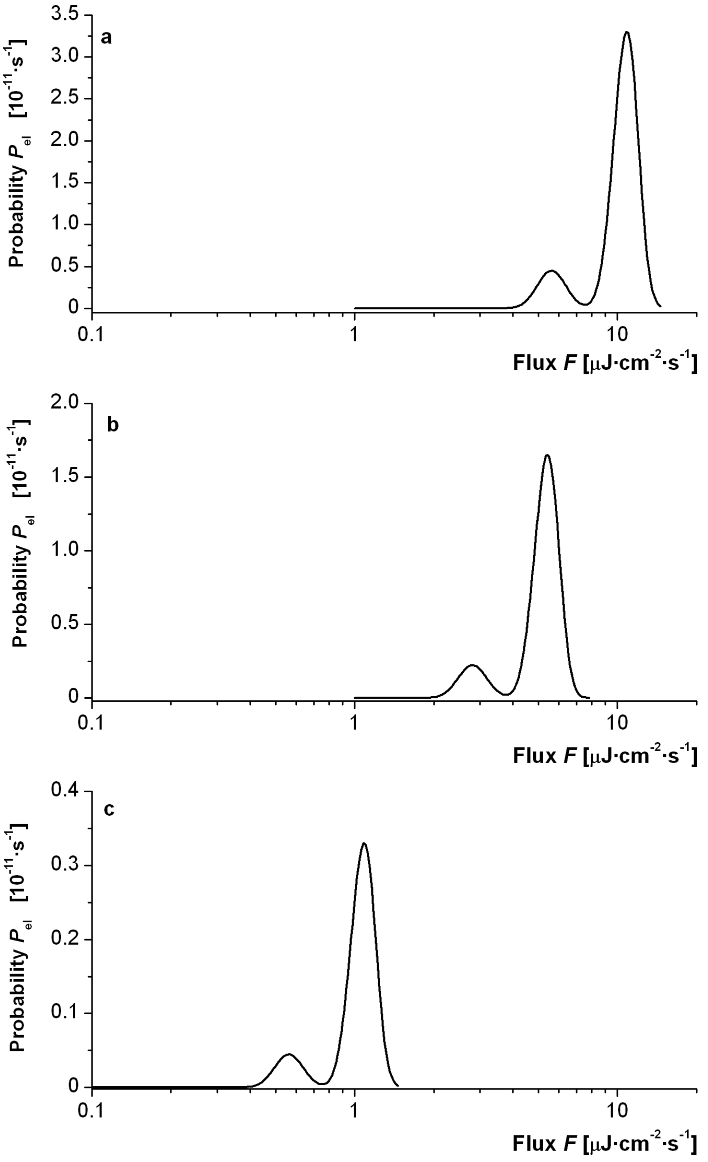

Fig. 3. The electronic excitation probability function P_{el} versus flux F for diphenylalkanes, calculated by (6) with the parameters: $K = 64$; $D_0/r_0 = 0.7$; $D_{el}/r_0 = 1$; $R_1 = 2.72$; $M_{el}^2 = 8 \cdot 10^{-17}$ cm^2. The plots (a), (b), (c) correspond to molecular hydrocarbon antennas with the dipole numbers 10, 20, 100.

equal to the excimol frequency in the molecular hydrocarbon antenna.

In addition, the probability functions P_f and P_{el} depend resonantly on the energy $E(K)$ of the excimols accumulated in an antenna. The energy $E(K)$ must be equal either to the value of the trap-bond's dissociation energy in the case of molecular fragmentation, or to the value of the energy E_{el} in the case of electronic excitation (π-π^*). Since the probability to accumulate the energy $E(K)$ in the antenna depends resonantly on the IR-flux, the probabilities P_f and P_{el} also depend resonantly on the IR-flux like the functions P_M^K and P_{01}. Moreover, trap-bonds of a particular molecule with different dissociation energies break at different radiation fluencies. It also can be concluded that the probability of a specific low-energy π-π^* transition in an unsaturated hydrocarbon substructure has a maximum at a certain radiation flux.

The analytical expressions for the fragmentation and π-electron excitation probabilities of organic molecules induced by multiple IR-photons demonstrate the strong dependence of these processes on the number M_r of dipoles in antennas, because the probability to accumulate K excimols in the antenna reaches the maximum when the relation $K = M_r \cdot P_{01}$ is fulfilled. Therefore, the radiation flux, which is needed for the excitation of K excimols in the antenna with maximum probability is reciprocal to the number M_r. Thus, organic molecules with antennas containing a big number of identical dipoles can be fragmented or electronically excited by a much lower IR-radiation flux than molecules with short antennas only.

The probability functions P_f and P_{el} are very sensitive to the molecular structure parameters and the functions $\Phi(\vartheta_l \vartheta_B)$ and $\Phi(\vartheta_l \vartheta_{el})$, correspondingly. These parameters define angles between the direction of the dipole moment of the biatomic groups in the antenna and the direction of the dipole moment $\boldsymbol{D}_B$ of a trap-bond or the dipole moment $\boldsymbol{D}_{el}$ related to the π-electron. If the moments $\boldsymbol{D}_B$ or $\boldsymbol{D}_{el}$ are perpendicular to the moment $\boldsymbol{D}_0$ and to the vectors $\boldsymbol{L}_B$ or $\boldsymbol{L}_{el}$, correspondingly, then the considered processes are forbidden, i. e. there exists a dipole valve between molecular antenna and the rest of the molecule. The energy transmission from the antenna to the rest of molecule in this case strongly depends on the orientation of the antenna dipoles relative to the orientation of the trap-bond dipole.

The probability functions P_f and P_{el} depend on L_B^{-6} and L_{el}^{-6}, correspondingly. This strong dependence shows, that molecular fragmentation or π-electron excitation occurs in the trap-bond which is closest to the antenna.

The resonance dependence of the fragmentation on the field frequency and intensity opens the possibility to control the molecular fragmentation and the luminescence processes experimentally to a certain extent by the parameters of the external radiation.

[1] P. A. Schulz, A. S. Sudbø, D. I. Krajnovich, H. S. Kwok, Y. R. Shen, and Y. T. Lee, Annu. Rev. Phys. Chem. **30**, 379 (1979).

[2] M. Quack, Annu. Rev. Phys. Chem. **41**, 839 (1990).

[3] F. F. Crim, Annu. Rev. Phys. Chem. **44**, 397 (1993).

[4] D. J. Nesbitt, Annu. Rev. Phys. Chem. **45**, 367 (1994).

[5] B. J. Schwartz, Annu. Rev. Phys. Chem. **54**, 141 (2003).

[6] Y.-P. Lee, Annu. Rev. Phys. Chem. **54**, 215 (2003).

[7] D. J. Nesbitt and R. W. Field, J. Phys. Chem. **100**, 12735 (1996).

[8] K. L. Kompa, H. Lamprecht, H. Schröder, A. A. Puretzky, and V. V. Tyakht, J. Chem. Phys. **84**, 2020 (1986).

[9] M. H. Yu, M. R. Levy, and C. Wittig, J. Chem. Phys. **72**, 3789 (1980).

[10] C. N. Plum and P. L. Houston, Chem. Phys. **45**, 159 (1980).

[11] E. Stone, K. J. Gillig, B. Ruotolo, K. Fuhrer, M. Gonin, A. Schultz, and D. H. Russell, Anal. Chem. **73**, 2233 (2001).

[12] L. Windhorn, J. S. Yeston, T. Witte, W. Fuß, M. Motzkus, D. Proch, K.-L. Kompa, and C. B. Moore, J. Chem. Phys. **119**, 641 (2003).

[13] T. Witte, T. Hornung, L. Windhorn, D. Proch, R. de Vivie-Riedle, M. Motzkus, and K. L. Kompa, J. Chem. Phys. **118**, 2021 (2003).

[14] J. C. Stephenson and D. S. King, J. Chem. Phys. **69**, 1485 (1978).

[15] T. A. Watson, M. Mangir, C. Wittig, and M. R. Levy, J. Phys. Chem. **85**, 754 (1981).

[16] P. A. Schulz, A. S. Sudbø, E. R. Grant, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **72**, 4985 (1980).

[17] J. L. Stephenson, Jr., M. M. Booth, J. A. Shalosky, J. R. Eyler, and R. A. Yost, J. Am. Soc. Mass Spectrom. **5**, 886 (1994).

[18] J. D. Williams, R. G. Cooks, J. E. P. Syka, P. H. Hemberger, and N. S. Nogar, J. Am. Soc. Mass Spectrom. **4**, 792 (1993).

[19] S. E. Van Bramer, P. L. Ross, and M. V. Johnston, J. Am. Soc. Mass Spectrom. **4**, 65 (1993).

[20] P. F. Bente, F. W. McLafferty, D. J. McAdoo, and C. Lifshitz, J. Phys. Chem. **79**, 713 (1975).

[21] P. J. McKeown and M. V. Johnston, J. Am. Soc. Mass Spectrom. **2**, 103 (1991).

[22] L. Schmidt, A. M. Popova, V. V. Komarov, and H. Jungclas, Z. Naturforsch. **51a**, 1144 (1996).

[23] H. Jungclas, A. Wieghaus, L. Schmidt, A. M. Popova, and V. V. Komarov, J. Am. Soc. Mass Spectrom. **10**, 471 (1999).

[24] V. V. Komarov, L. Schmidt, H.-W. Fritsch, and H. Jungclas, Computational Mater. Sci. **2**, 427 (1994).

[25] H. Jungclas, L. Schmidt, V. V. Komarov, A. M. Popova, and I. O. Stureiko, Z. Naturforsch. **57a**, 270 (2002).

[26] N. Presser, J. R. Barker, and R. J. Gordon, J. Chem. Phys. **78**, 2163 (1983).

[27] A. A. Radzig and B. M. Smirnov, Reference Data on Atoms, Molecules and Ions, Springer Verlag, Berlin 1985.

[28] F. Hirayama, J. Chem. Phys. **42**, 3163 (1965).