Resonant IR Photon Induced Dissociation in Organic Molecules with Chain-like Substructures

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A nonstatistical model for the resonant IR photon induced dissociation of organic molecules by IR photons is suggested. The model is based on the excimol theory for molecules which contain chains of identical diatomic dipole groups. IR photon radiation can induce resonantly collective vibrational excitations (excimols) in these molecular substructures. The accumulation of several excimols in the molecular chain causes a local heating of the molecule and its fragmentation on a time scale of several hundreds of femtoseconds. An analytical expression for the fragmentation probability is derived and analysed.

Key words: Photon induced Dissociation.

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Introduction

Photon induced dissociation (PID) of molecules due to action of low intensity IR radiation is the subject of several experimental investigations [1–12]. The interest in this field arose, as information of molecular dissociation by IR photons is important not only for the development of quantum chemistry of organic molecules and for the theory of laser beam interactions with large molecules, but also for practical applications. It was shown experimentally that the PID of molecules consisting of chain-like substructures can be induced resonantly by IR radiation with frequencies which do not coincide with the vibrational frequencies of the diatomic valence groups contained in these molecules [4, 5]. Also, it was shown that IR photon induced dissociation (IR-PID) leads with high probability to fragments consisting of small atomic groups. These groups are mainly the end groups of the chain-like substructures inside the irradiated molecules [6–12]. The abundance of different fragments depends on the photon fluence, on the number of diatomic groups in the chains and on the corresponding dissociation energies [6–12].

In the present work a model for the dissociation of organic molecules with chain-like substructures by IR-PID is suggested. The model is based on the excimol theory for excitation and fragmentation of organic molecules, which was worked out previously [13]. In the frame of the excimol theory the collection of internal molecular energy occurs in chain-like molecular substructures consisting of identical diatomic groups with significant dipole momenta. In these chains many collective vibrational states (excimols) with frequency ω_{ex} are induced by a resonant external periodic field, e.g. IR photons. The excimol energy $E_{\mathrm{ex}} = \hbar\,\omega_{\mathrm{ex}}$ is less than the energy $E_{01} = \hbar\,\omega_{01}$ of the first vibrational state of an isolated diatomic quantum oscillator. This energy difference is caused by the energy E_{tr} required for energy transitions within the chain from one diatomic oscillator to another. These tansitions are due to resonance dipole–dipole interactions between identical molecular dipoles and the transition energy E_{tr} which strongly depends on the dipole moment of the diatomic groups and on the three-dimensional structure of the chain [14, 15]. The excimol lifetime τ_{ex} is larger than the lifetime τ_{01} of the excitation of an isolated diatomic oscillator in the first vibrational state, because the resonance interaction of the diatomic dipoles within the chain decreases the probability of vibrational relaxation in each dipole. For example, the excimol lifetime τ_{ex} in a $(CH_2)_n$ chain is two orders of magnitude higher than the lifetime τ_{01} of the excitation of an isolated CH-group.

Resonant excimol excitation can be induced by periodic electromagnetic fields including IR-fields, if the frequency of the field is equal to the excimol frequency. Several excimols can be excited independently in a chain. They are not accumulated in a single diatomic group because of the unharmonic energy spectra of the diatomic oscillators. The accumulation of excimols in the chain increases the internal energy of the molecule. Thus the internal energy is concentrated in a specific chain-like substructure and causes a “local heating” of the molecule. The accumulated excimol energy can be transferred by dipole-dipole interaction to a trap-bond, which is also a dipole. One part of the trap-bond dipole belongs to the skeleton of the chain of dipoles, the other part is a side or end group of the chain. The dissociation of a trap-bond occurs with the highest probability if the accumulated energy $E(K) = KE_{ex}$ coincides with the trap-bond dissociation energy E_d (K is the number of excimoles accumulated in the chain) [16].

In this work an analytical expression of the probability of excimol excitation by IR photons and its dependence on laser fluence is derived. The main parts of the presented theoretical model were proven by analysing some experimental results presented in [4–10].

Excimol Excitation

As discussed in the introduction, an excimol can be excited in chain-like substructures of organic molecules by IR photons if the frequency ω of the radiation coincides with that of an excimol ω_{ex}. The energy E_{ex} of one excimol can be calculated in the approximation presented in [15]. It corresponds to the lowest collective vibrational energy state of a chain substructure and can be expressed by

$$E_{ex} = E_{01} - E_{tr}\,. \tag{1}$$

Here E_{01} is the energy of the first vibrational state of one dipole group, and

$$E_{ex} = \sum_{j} E_{ij} \tag{2}$$

corresponds to the maximal “red shift” of the excimol frequency and is the sum of matrix elements E_{ij} of the dipole-dipole interaction potential V_{ij} of any diatomic group (i) in the first vibrational state with each neighboured group (j) in the ground state. The value V_{ij} can be considered as an energy needed for the transmission of vibrational excitation along the skeleton of the chain of diatomic dipoles. The energy E_{ij} can be calculated in the frame of stationary perturbation theory. The perturbation potential V_{ij} of the dipole–dipole interaction of two neighboured identical diatomic groups (i) and (j) is given by the equation

$$V_{ij} = \frac{1}{R_{ij}^3}\left[\boldsymbol{d}_i\,\boldsymbol{d}_j - \frac{3(\boldsymbol{d}_i\,\boldsymbol{R}_{ij})(\boldsymbol{d}_j\,\boldsymbol{R}_{ij})}{R_{ij}^2}\right]. \tag{3}$$

In (3) R_{ij} is the projection of the distance between the centres of mass of the diatomic groups (i) and (j) on the direction of the chain backbone, which is defined by the unit vector $\boldsymbol{n}_{ex}$, and thus $\boldsymbol{R}_{ij} = R_{ij}\,\boldsymbol{n}_{ex}$. Since the diatomic groups in the molecular chain are considered as electric dipole oscillators, the dipole moments $\boldsymbol{d}_i$ and $\boldsymbol{d}_j$ of the groups (i) and (j) can be presented by the equation

$$\boldsymbol{d}_k = \frac{e D_0}{r_0}\, r\,\boldsymbol{n}_k\,; \quad k = i, j\,. \tag{4}$$

In (4) the term eD_0 is the amount of the dipole moment of any diatomic group in the chain, r is the variable, r_0 the average length of the dipole groups, and $\boldsymbol{n}_k$ is the unit vector in the direction of the dipole moment.

The interaction energy E_{ij} can be calculated [14, 15] using the first approximation of the perturbation theory by the expression

$$E_{ij} = \frac{(e D_0)^2}{r_0^2}\, M_{01}^2\, \Theta_{ij}\, \frac{1}{R_{ij}^3}\,. \tag{5}$$

The term M_{01} is given by the matrix element $\langle \varphi_0(r)\,|\,r\,|\,\varphi_1(r)\rangle$, where $\varphi_0(r)$ and $\varphi_1(r)$ are the oscillator wave functions of the ground and first excited states, respectively, for any two neighboured groups (i and j). Θ_{ij} is defined by the expression

$$\begin{aligned}\Theta_{ij} = {} & \cos\theta_i^x \cos\theta_j^x + \cos\theta_i^y \cos\theta_j^y \\ & + \cos\theta_i^z \cos\theta_j^z\,,\end{aligned} \tag{6}$$

where θ_i^x, θ_i^y, θ_i^z and θ_j^x, θ_j^y, θ_j^z are the angles between the vectors $\boldsymbol{n}_i$ and $\boldsymbol{n}_j$ and the coordinate axes $0X$, $0Y$, and $0Z$, respectively, in a coordinate system in which the axis $0Z$ coincides with the vector $\boldsymbol{n}_{ex}$. Equation (5) implicates that even for chains which differ only in the parameter R_{ij} or Θ_{ij}, one has to expect different values for the excimol energy. This leads to different IR resonance frequencies for excimol excitation in hydrocarbon chains of different structures.

For example, in a normal hydrocarbone chain (alkane) each carbon atom is a part of two CH-groups which are located in a plane perpendicular to $\boldsymbol{n}_{ex}$. Taking into account the stereometric structure formula of alkane chains $(CH_2)_n$ one can proof that four neighboured dipoles (j) contribute to the value of the dipole interaction potential V_{ij} of any CH-dipole (i). Thus excimol transmission along the backbone direction of an alkane chain is ruled by the interaction of an excited dipole with the four dipole groups next to it. The energy E_{ij} calculated in a case of an alkane chain has the value E_{ij} = 0.068 eV. With (2) and E_{01} = 0.34 eV the excimol energy E_{ex} is given by E_{ex} = 0.074 eV. The corresponding excimol frequency $\omega_{ex} = 1.2 \cdot 10^{14}\ s^{-1}$ agrees with that obtained experimentally [16].

It is estimated that the excimol energy for the different hydrocarbon chains is in the range of (0.07 – 0.14) eV. If the wave number of the IR is in the range of (600 – 1200) cm^{-1}, than this radiation can excite excimols. These wave numbers can be achieved by a CO_2-laser.

When molecules are in a weak IR field, the excimol excitation probability $\tilde{P}_{ex}$ per unit time can be calculated using the time-depending perturbation theory [17]:

$$\tilde{P}_{ex} = \frac{4\pi^2}{3} \frac{e^2}{\hbar c} \left(\frac{D_0}{r_0} \right)^2 M_{01}^2 J\,, \tag{7}$$

where D_0/r_0 is a nondimensional parameter of the diatomic group of the corresponding chain. Equation (7) contains $J = 2\,\Phi/E_{ex}$, where Φ is the laser fluence.

Accumulation of Excimols

As shown previously [16], several excimols can be excited independently in molecular chain-like substructures. They are not accumulated in one diatomic group because of the unharmonic energy spectra of diatomic oscillators. The lifetime τ_{ex} of an excimol is much longer than the time $\tau_{tr} = 2\pi\hbar/E_{ij}$ of the energy transfer from one group to the next within the chain. Thus each of the diatomic groups can be excited N times during τ_{ex} with $N = \tau_{ex}/\tau_{tr}$. If the chain consists of M_{ch} diatomic groups, the effective number M of diatomic groups which can accumulate an independent excimol is given by $M = N M_{ch}$.

Using the asymptotic binomial representation, the probability P_M^K to excite K excimols ($K < M$) is given by

$$P_M^K = (2\pi M P_{ex}(1-P_{ex}))^{-1/2} \cdot \exp\left(-\frac{(K - M P_{ex})^2}{2 M P_{ex}(1-P_{ex})} \right). \tag{8}$$

P_{ex} is the probability of excimol excitation in an IR field during the lifetime τ_{ex} of the excimol, i.e. $P_{ex} = \tilde{P}_{ex}\,\tau_{ex}$. The probability P_{ex} is a function of the IR fluence and depends on the properties of the diatomic dipoles in the chain. Equation (8) implicates that P_M^K strongly depends on τ_{ex}, since M and P_{ex} are functions of τ_{ex}. In addition, P_M^K as a function of K has a maximum for $K = M P_{ex}$. The position of the maximum of P_M^K as a function of the IR fluence Φ_{max} for any fixed K and M depends on the strength of the dipole momentum of the diatomic groups and on the excimol lifetime. Thus the IR induced accumulation of a definite internal energy in a molecular chain-like substructure is a resonant process, which occurs with noticeable probability within a limited interval of IR intensity. The position of this interval depends on τ_{ex}.

As an example, Fig. 1 shows the results of calculations in which $P_M^K(\Phi)$ was computed versus τ_{ex} and Φ using the parameters $M = 120$, $K = 3$, and $D_0/r_0 = 1$. Figure 1 shows clearly the high sensitivity of $P_M^K(\Phi)$ to the parameter τ_{ex} and to the fluence Φ.

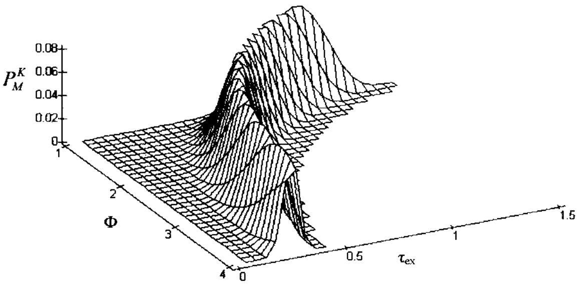

Fig. 1. The calculated probability P_M^K versus Φ measured in 10^{10} erg/(cm^2 · s) and τ_{ex} measured in 10^{-10} s for fixed $K = 60$, $M = 100$.

From (8) follows that by fixed M the maximum position of P_M^K versus Φ depends on K (the number of accumulated excimols). To demonstrate this, we present in Fig. 2 calculated functions P_M^K versus K and Φ by fixed M, τ_{ex} and D_0/r_0. The probability P_M^K is sensitive to the parameter M (corresponding to the number of degrees of freedom of the chain). In Fig. 3 the calculated probability P_M^K is presented versus M and Φ by fixed K, τ_{ex} and D_0/r_0.

As was discussed before, the function P_M^K depends also on the parameter D_0/r_0. This is demonstrated in Fig. 4, where the calculated probability P_M^K is presented versus D_0/r_0 and Φ with fixed M, K and τ_{ex}.

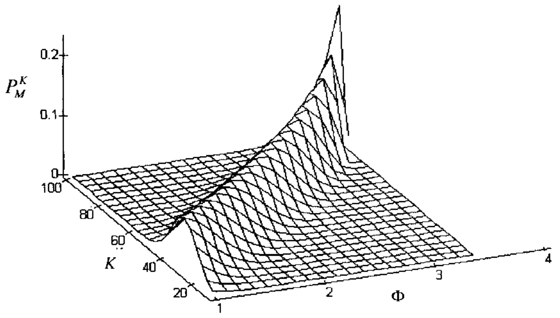

Fig. 2. The calculated probability P_M^K versus K and Φ measured in 10^{10} erg/(cm^2 · s) and $\tau_{ex} = 0.5 \cdot 10^{-10}$ s for fixed $M = 100$.

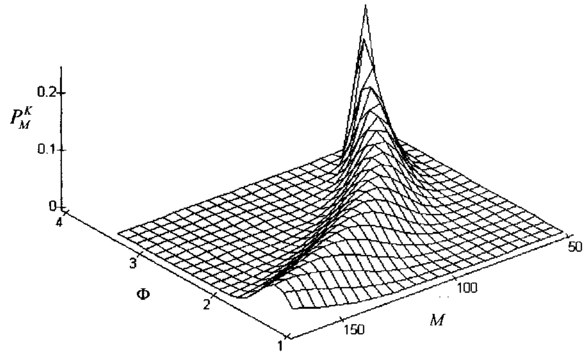

Fig. 3. The calculated probability P_M^K versus M and Φ measured in 10^{10} erg/(cm^2 · s) for fixed $K = 60$, $\tau = 0.5 \cdot 10^{-10}$ s.

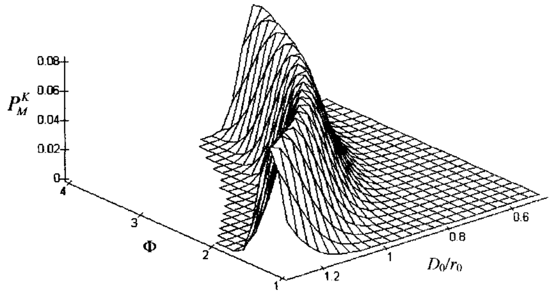

Fig. 4. The calculated probability P_M^K versus Φ measured in 10^{10} erg/(cm^2 · s) and parameter D_0/r_0 for fixed $M = 100$, $K = 60$, $\tau = 0.5 \cdot 10^{-10}$ s.

Trap-bond Dissociation

The energy $E(K) = K \cdot E_{ex}$ of K excimols accumulated in a chain-like substructure can be transmitted to a trap-bond dipole due to dipole-dipole interaction. The trap-bond can dissociate if $E(K)$ reaches the level of its dissociation energy E_d. The probability P_f of molecular fragmentation is the product of three different probability functions:

$$P_f = P_M^K \, P_{tr} \, P_d \, . \tag{9}$$

In (9) P_{tr} is the probability of the transmission of the accumulated excimol energy $E(K)$ from the chain to the trap-bond, and P_d is the probability of trap-bond dissociation. The function $P_d\,(E(K))$ has a sharp maximum at $E(K) \approx E_d$ [16].

The probability P_{tr} can be considered as the transition probability from the first vibrational state to the ground state of the diatomic group (i) in the chain, which is nearest to the trap-bond. The transitions are possible by the electric field of the trap-bond dipole. This field abruptly shifts the position of hydrogen atoms without changing the Hamiltonian of the diatomic dipoles, which is assumed to be an oscillator system. Thus, the probability function P_{tr} is given by

$$P_{tr} = \left[\int\limits_{-\infty}^{+\infty} \varphi_1(r)\, \varphi_0(r+a)\, \mathrm{d}r \right]^2 . \tag{10}$$

The parameter a in (10) is the value of the shift, which can be calculated in the frame of the presented model by

$$a = \frac{(\boldsymbol{F}\,\boldsymbol{d}_i)}{\mathrm{m}\,\omega_{01}^2} \, , \tag{11}$$

where $\boldsymbol{F}$ is the vector of the electric field and m is the mass of the diatomic group (i).

Main Conclusions of the Model

1. The IR radiation frequency which induces resonant molecular fragmentation, is defined by the excimol frequency of the chain-like molecular substructure, i.e. by the dipole properties and locations of the diatomic constituents of the chain.
2. Molecular fragmentation occurs due to dissociation of particular molecular bonds (trap-bonds), which are not part of the excited chain, but connected to a chain skeleton atom.
3. The probability of molecular fragmentation depends on the IR-radiation fluence and on the dipole properties of the diatomic groups in the chains.
4. Trap-bond dissociation occurs, if energy of the excimols sums up to the dissociation energy of a trap-bond. The accumulation probability for a given number of excimols in a chain with a fixed number of dipoles depends resonantly on the radiation intensity. The length of the chain (the number of dipoles) de-

fines the value of the radiation intensity needed to dissociate a particular trap-bond.

5. The fragmentation time is defined by the time needed for the energy transfer from the chain to the trap-bond. As this energy transfer process is based on dipole-dipole interactions, this time is essentially less than the energy transmission time calculated by statistical models.

Discussion

In the frame of the presented model we can explain from one point of view a set of phenomena experimentally observed in the fragmentation of organic molecules by external IR radiation.

The “red shift” of laser frequency was always noticed in experiments on multiquanta fragmentation of molecules containing chain of diatomic dipoles. Namely, the laser frequency which is needed for this process occurs to be lower than the eigenfrequency of one dipole in the chain. This experimentally observed effect can be explained by the accumulation of the excimols in the chain. The frequency of these excimols is less than the eigenfrequency of the chain’s dipoles and depends on the three dimensional chain structure and on electronic properties of the chain dipoles.

To demonstrate the above presented theoretical consequences we consider the experimental results given in [4], where the fragmentation of protonated diglyme molecules was observed when applying CO_2 laser fields with wave numbers in the range of (1099–924) cm^{-1}. The protonated diglyme molecule has a linear structure:

$$\begin{aligned} &CH_3 - OH^+ \overset{1}{-} CH_2 - CH_2 - O \\ &\qquad \overset{2}{-} CH_2 - CH_2 - O \overset{3}{-} CH_3 \,. \qquad (12) \end{aligned}$$

Such a molecule consists of two chain substructures ($CH_2{-}CH_2$) bound by oxygen atoms and two end groups ($CH_3{-}OH^+$ and $CH_3{-}O$).

The oxygen atoms in the diglyme molecule do not violate the coplanar system of the skeleton carbon atoms. The orientation of CH dipoles in this molecular chain is similar to the orientation of the CH dipoles in the alkane chains. Due to the negligible dipole momentum of CO compared to the CH one, the chain substructure in this molecule consists of 12 CH diatomic dipole groups in which the excimols are accumulated and can be presented in the simplified form $CH_2{-}C_2H_4{-}C_2H_4{-}CH_2$ for the purpose of our energy calculations. Nevertheless, the presence of oxygen atoms periodically increases the distance between carbon skeleton atoms in the chain-like substructures and therefore diminishes the transmission energy E_{tr} for the vibrational excitation along the chain compared to the one in alkane chains. Our calculations show that in diglyme molecules excimols with an energy $E_{\mathrm{ex}} = 0.112$ eV and a corresponding frequency $\omega_{\mathrm{ex}} = 1.8 \cdot 10^{14}\ \mathrm{s}^{-1}$ (wave number 945 cm^{-1}) can be excited. This frequency differs substantially from the frequency ($1.2 \cdot 10^{14}\ \mathrm{s}^{-1}$) of excimols in alkane chains.

It was established experimentally [4] that the fragmentation probability of protonated diglyme molecules depends resonantly on the laser radiation frequencies and that the measured resonant wave number is equal to 944 cm^{-1}. This measured value agrees well with the above predicted frequency. It proves the conclusion of the presented model, since the resonance frequency coincides with the calculated excimol frequency but not with the eigenfrequency of a CH-bond or other bonds in the diglyme molecule.

In the frame of the presented model we also can explain and predict a specific type of molecular fragments produced by IR-PID. In the considered fragmentation process, bonds which connect end and side groups to the skeleton atoms dissociate with highest probability. This means on the other hand that the dissociation probability of internal bonds linking skeleton atoms is very low. This important effect is mentioned in experimental studies on photo fragmentation of diglyme molecules [4] and *n*-alkenes [6], using laser radiation.

Due to our model the diglyme fragmentation in a laser field can occur by dissociation of the C–O-bonds 1 and 3 in (12) with yields corresponding to the dissociation probabilities of the end groups CH_3OH and CH_3. After the bond 1 has been cleaved, the bond 2 can dissociate releasing secondary end group C_2H_4O (Table 1).

It was observed in the experiment [4] that the protonated diglyme molecules fragment in the CO_2-laser field due to cleavage of C–O bonds but not C–C skeleton bonds, which agrees with the second conclusion of the presented model.

In case a molecule has several different trap-bonds with different dissociation energies, it is possible to predict the pathways of its fragmentation (simultaneous as well as sequential), because the fragmentation depends on the accumulation probability of an appropriate number of excimols needed for the dissociation of a specific trap-bond. As an example, we calculated the accumulation probabilities for different numbers of excimols in protonated diglyme molecules as functions of the laser

Table 1. IR-induced sequential fragmentation of a diglyme molecule as shown in (12) for three trap-bond locations.

Trap-bond in (12)	Dissociation energy E_d	Number K of excimols	Fragmentation at C–O bond with	Fragment mass
1	0.35 eV	3	end group CH_3OH	32 u
3	0.45 eV	4	end group CH_3	15 u
2	0.70 eV	6	secondary end group C_2H_4O	44 u

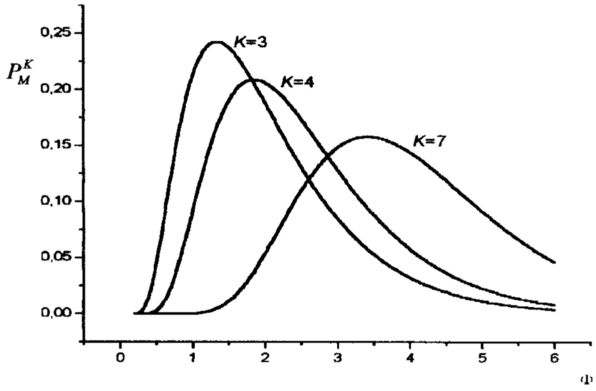

Fig. 5. The calculated probability P_M^K versus Φ measured in 10^9 erg/(cm^2 s) for fixed $M = 120$ but different K.

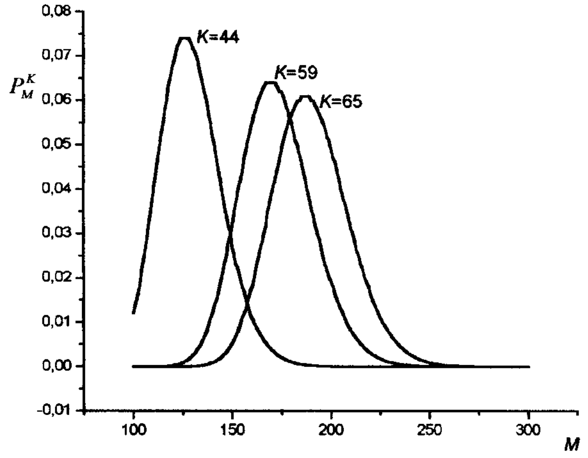

Fig. 6. The calculated excimol accumulation probability P_M^K versus the effective number of chained dipoles M for fixed IR fluence $\Phi = 1.5 \cdot 10^{12}$ erg/(cm$^2 \cdot$ s) and different numbers K of accumulated excimols.

fluence J and compared the results at a fixed fluence $\Phi = 1.4 \cdot 10^9$ erg/cm^2 used in the experiment [4].

The diglyme molecule has 3 trap-bonds with different dissociation energies (Table 1). For each trap-bond dissociation a definite number of excimols must be accumulated in the molecule. To calculate the probability P_M^K we defined the effective number of diatomic groups (dipoles) taking part in the excimol accumulation with $M = M_{ch} N$ and $N = \tau_{ex}/\tau_{tr}$.

The lifetime of the excimol in a diglyme molecule is $\tau_{ex} \approx 1.5 \cdot 10^{-12}$ s, and the time of energy transfer from one group to the next within the chain is $\tau_{tr} \approx 1.5 \cdot 10^{-13}$ s. Thus, each of the diatomic groups can be excited 10 times ($N = \tau_{ex}/\tau_{tr} = 10$). Therefore one has to consider an effective number of about 120 CH-bonds ($M = M_{ch} \cdot N = 120$) which are able to contribute to excimol production in this chain.

For the protonated diglyme molecule the sequential fragmentation of the two trap-bonds 1 and 3 may occur after accumulation of 7 excimols ($K = 7$) in the chain consisting of 120 effective dipoles ($M = 120$). The release of CH_3OH fragment by cleavage of bond 1 requires 3 excimols, the cleavage of release of bond 3 requires 4 excimols (Table 1).

Our calculations show that P_{120}^7 is lower than P_{120}^3 and P_{120}^4 for the same value of Φ; see Figure 5. Thus we expect a sequential fragmentation in this case, which agrees with the experimental results [4]. The calculated probability P_{120}^3 is higher than P_{120}^4, thus the fragment with the highest yield is generated by dissociation of bond 1.

After a first fragmentation step, e.g. by cleavage of bond 1, the chain of diatomic dipoles C–H, in which excimoles are accumulated, gets shorter, resulting in $M = 100$. The next step in the interpretation of the fragmentation is to compare the probabilities P_{100}^{10} (for the simultaneous fragmentation of bond 2 and 3) with P_{100}^6 and P_{100}^4. Our calculation yields the relation $P_{100}^6 > P_{100}^4 \gg P_{100}^{10}$. Thus we can conclude that a sequential process is most likely to occur: first bond 2, then bond 3 is cleaved.

This conclusion agrees with the experimental result that the third fragment CH_3 is not a significant IR-induced fragmentation product [4].

An important support for the presented model follows from the analysis of photo fragmentation experiments with *n*-alkenes, which always contain normal hydrocarbon chains as substructures [6]. According to our model, excimols can be excited and accumulated in these chains, finally leading to cleavage of the *n*-alkene end groups.

Dissociation of *n*-alkenes was experimentally observed [6]. Ths dissociation probability of skeleton C–C bonds in their hydrocarbon chains was negligibly small compared to the dissociation probability of the end groups. It was noted in [6] that the relative abundance of end group fragments depends on the number of carbon atoms in the *n*-alkene molecules.

Let us consider the relative abundance of the two opposite end groups C_3H_5 and C_3H_7 in *n*-alkenes. The fragmentation probability of these groups is defined by the function P_M^K, because the excimol energy transmission probabilities P_{tr} have similar values due to the similar values of their dipole moments. The dissociation energies of the bonds connecting the end groups to the hydrocarbon chain are $E_\text{d} \approx 3.1$ eV for C_3H_5 and $E_\text{d} \approx 4.4$ eV for C_3H_7 in the considered *n*-alkene molecule [6].

Since the excimol energy for the normal hydrocarbone chain is 0.07 eV [16], it is necessary to accumulate $K = 44$ and $K = 65$ excimols for the dissociation of the end groups C_3H_5 and C_3H_7, respectively.

Our calculations of excimol accumulation probabilities P_M^K for $K = 44$, $K = 59$ and $K = 65$ versus the hydrocarbon chain length (M) are presented in the Figure 6. We took for these calculations the laser radiation from [6] and defined $D_0/r_0 = 1$ for the CH-groups of alkane chains. The curves plotted in Fig. 6 demonstrate that the fragmentation probabilities follow a resonance behaviour. The maximum yield of the fragment C_3H_5 ($K = 44$) corresponds to *n*-alkenes with $n = 7-10$, equivalent to $M = 100-160$, and for the fragment C_3H_7 ($K = 65$) the maximum yield is obtained for $n = 10-13$, equivalent to $M = 160-220$. These results, derived from the excimol theory, with the experimental data [6].

Thus, the presented analysis shows that the excimol model permits to explain the known experimental degrees of freedom effect [11–12], i.e. the fragmentation depends on the number of identical bonds in the polyatomic molecules.

Conclusion

In this article he application of the excimol theory to photon induced dissociation (PID) of organic molecules containing chain-like substructures was analysed. It was shown that an IR-field can induce collective vibrational excitations /excimols) in such substructures, if they consist of identical diatomic dipole groups and if the frequency of the IR-radiation coincides with the frequency of the excimol. The accumulation of several excimols in the dipole chains leads to a fast local heating of the molecule. The accumulated excimol energy is transmitted to a trap-bond which differs from the bonds of the dipole chain and which is directly bound to the backbone of the chain. Trap-bond dissociation occurs, if the accumulated excimol energy exceeds the dissociation energy of this bond. The analytical expression of the molecular fragmentation probability, given in the present paper, shows that the production probability of a specific fragment type depends on the frequency and the radiation fluence. The fragmentation probability maximum on the frequency scale depends on the three-dimensional structure of the molecular chain and on the interaction of the diatomic dipoles. The position of the fragmentation probability maximum also depends on the dissociation energies, on the effective number of dipoles in the chain, and on the excimol life time. Thus IR-photon induced dissociation (IR-PID) of molecules with chain-like substructures can be controlled by the choice of the photon (radiation) frequency and fluence

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