

INVESTIGATION OF THE MECHANISM OF PRIMARY PHOTOCHEMICAL REACTIONS IN ORGANIC MOLECULES BY THE QUANTUM CHEMISTRY METHODS

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Principles of investigating the mechanism of photobreaking of chemical bonds in complicated linear-chain or ring molecules are formulated by the quantum chemistry methods. These methods are then used to investigate photolysis of disulfides, chloronaphthalene, diphenyloxazole, thrinitrotoluene, and coumarine. Mechanisms of primary reactions are established. Electron excited states are determined in which the breaking of a chemical bond occurs as well as the possibility of occupation of these states.

In the experimental investigation of photochemical reaction mechanisms a researcher, with rare exception, deals with a photolysis product which is, as a rule, the result of multistage conversion of a molecule not only under exposure to light, but also with participation of molecules of a solvent or a solution matrix. To interpret strictly the photolysis products, the mechanism of primary conversion of the examined molecule should be known, which is relatively complex matter to establish in spite of application of the technology having high temporal resolution.

Under these conditions, the quantum chemistry methods have assumed the importance. Their application in combination with the modern theory of nonradiating transitions allows the mechanisms of primary photoconversions to be elucidated successfully, the nature of photoactive states to be established, and the dependence of the photoconversion efficiency of various types on the initial molecular structure, the parameters of the medium surrounding the molecule, and the energy of an exciting photon to be identified. Maier et al.¹ suggested an approach to the investigation of photoreaction of breaking of a chemical bond in molecules of organic compounds based on the results of quantum-mechanical calculations. Its essence is as follows.

From general consideration, it is clear that the chemical bond breaks with the participation of the σ electrons, that is, the electrons that are predominantly in the states $\pi\sigma^*$, $\sigma\pi^*$, $\sigma\sigma^*$, and so on. The probability of breaking of a specific bond should be determined largely by a degree of localization of the electron excitation energy on this bond as well as by the decrease of its strength under excitation. An important factor is the possibility of population of the photodissociating state excited directly or through intramolecular relaxation of the energy of electron excitation. This factor can be examined on the basis of the quantum-chemical approach to the estimation of the rate constants of the intramolecular nonradiative

transitions calculated by the procedure described in Refs. 2–5.

At the first stage, the nature of the electron excited states and the degree of energy localization on individual molecular bonds are examined in combination with the calculation of population of individual bonds in various electron excited states. The bond population introduced by Malliken⁶ was used as a parameter that characterizes the bond strength. Rate constants of photophysical processes are then estimated based on the wave functions of the electron excited states of molecules, from which the conclusions about the character of running of these processes in the molecule, its spectral-luminescent characteristics, and possibility of population of photodissociating states can be drawn.

At the next stage, potential curves of the electron excited states are constructed based on quantum-chemical calculations for variable length of the breaking bond using the Morse⁷ potential for the ground state calculated for the equilibrium bond lengths, oscillation frequencies, and energies of breaking of the bond borrowed from Refs. 8–11. The possibility of breaking of the examined bond in a certain electron excited state could be inferred by the shape of the potential curve.

In the calculations discussed below we used the semi-empirical quantum-chemical CPDP method with parametrization.¹²

To check this method, we took advantage of the results of experimental investigations into monomolecular photoreactions for which the primary stages of photochemical reactions had been established and studied in detail. Disulfide molecules and chloronaphthalene^{13–16} have been the subjects of our investigations. Borisevich et al.¹³ and Mel'nichuk¹⁴ established experimentally that a single-photon excitation of disulfide molecules leads to breaking of the S-S bond in the excited state and to the formation of phenylthiolic radicals (Fig. 1, scheme *a*).

Quantum-chemical investigation into the mechanism of photodissociation of the diphenylsulfide molecule allows the following conclusions to be drawn.¹ Photodissociation of the diphenylsulfide molecule occurs by the predissociative mechanism in the triplet state $T(\pi\sigma_{SS}^*)$. Small quantum yield of the photoreaction ($\varphi = 0.18$) can be explained by the competition of the chemical reaction of breaking of the S-S bond itself with nonradiative processes occurring through channels $T_5(\pi\sigma_{SS}^*) \sim > T_4(\pi\sigma_{SS}^*)$ and $T_5(\pi\sigma_{SS}^*) \sim > S_1(\pi\sigma_{SS}^*)$ ($H_{SO}^2 \approx 1300 \text{ cm}^{-2}$) with rate constants of $\sim 10^{13} \text{ s}^{-1}$. The rate constant of the chemical reaction estimated from the experimental data was $\sim 10^{12} \text{ s}^{-1}$. The dependence of the quantum yield of photoreaction on the energy of excitation for the bis(*n*-aminophenyl)disulfide molecule was also explained. The results of calculation showed that insertion of amino-groups led to the decrease of the energy of the state $T(\pi\sigma_{SS}^*)$ and changing of its position with respect to the state $S(\pi\pi^*)$ linked with the state $T(\pi\sigma_{SS}^*)$ by the pronounced spin-orbital interaction (Fig. 2). This means that the population of the state $T(\pi\sigma_{SS}^*)$ through the channel $S_6(\pi\pi^*) \sim > T(\pi\sigma_{SS}^*)$ for the bis(*n*-aminophenyl) disulfide molecule excited to different absorption bands will be different. These results allow us to analyze qualitatively the reason for the

difference in quantum yields of the reactions of photodissociation of diphenyldisulfide ($\varphi = 0.18$) and its aminosubstituted form ($\varphi = 0.57$) excited with the same energies.

Photodissociation of substituted forms of the naphthalene molecules comprising the halogen atoms was investigated experimentally using the technology with high temporal resolution. It was established that during excitation of I-chloromethylnaphthalene ($\lambda_{\text{exc}} = 313, 299, \text{ and } 266 \text{ nm}$) the C-Cl bond breaks and the methylnaphthalene radical is produced by the scheme shown in Fig. 1b. The reaction runs efficiently when the excitation occurs in two spectral regions: the quantum yields are $\varphi \sim 0.72$ at $\lambda_{\text{exc}} = 313 \text{ nm}$ and $\varphi \sim 0.61$ at $\lambda_{\text{exc}} = 266 \text{ nm}$. However, experimental investigations did not allow us to establish unambiguously the photoreaction mechanism and the nature of the photodissociating state. The breaking of the C-Cl bond was not observed ($\varphi \approx 0$) when I-chloronaphthalene was excited to the 266–313 nm region.

Let us analyze this photoreaction using the approach developed by us in Ref. 1. An analysis of the bond occupation showed that with excitation to singlet and triplet $\pi\pi^*$ states, the strength of all chemical bonds changed only insignificantly, whereas with excitation to the $\pi\sigma_{C-Cl}^*$ states of substituted forms, the strengths of the C-Cl bond and of the C-C bonds adjacent to it sharply decrease (Table I).

TABLE I. Populations of bonds of chlorosubstituted forms of naphthalene in the ground and excited states.

State	C-C		C-Cl		C-C		C-Cl	
	I-chloromethylnaphthalene				I-chloronaphthalene			
	1-2	1-10	1-11	11-12	1-2	1-10	1-11	11-12
S_0	1.025	0.976	0.817	0.429	1.043	1.006	1.019	0.458
$S_1(\pi\pi^*)$	0.963	0.965	0.838	0.435	0.978	0.999	0.916	0.468
$S_2(\pi\pi^*)$	0.906	0.954	0.846	0.436	—	—	—	—
$S(\pi\sigma_{C-Cl}^*)$	0.199	-0.442	-0.286	0.123	0.328	-0.873	0.511	-0.342
$T(\pi\sigma_{C-Cl}^*)$	0.200	-0.395	-0.273	0.130	0.979	0.997	0.915	-0.333
$T_1(\pi\pi^*)$	0.914	0.958	0.842	0.441	-0.313	0.851	0.500	0.475

Thus, the electron excited $\pi\sigma^*$ states are observed for the chlorosubstituted forms of the naphthalene molecules. The C-Cl bond takes part in the formation of these states. During excitation, the strength of this bond decreases.

The increments of the lengths of the bonds that weaken with optical excitation are taken as the reaction coordinates. An analysis of the behavior of the potential curves showed that curves with the minimum, corresponding to the stable state of molecules, are typical of the excited $\pi\pi^*$ states. This

fact substantiates the above conclusion about the low probability of breaking of the bond in the $\pi\pi^*$ states. The forms of the potential curves of the excited states of I-chloronaphthalene demonstrate the resistance of the molecule to the abstraction of chlorine in the $\pi\sigma_{C-Cl}^*$ states, in spite of a certain decrease of the bond strengths in these states. For the I-chloromethylnaphthalene molecule the potential curves of the states $\pi\sigma_{C-Cl}^*$ in the reaction coordinate of the length of the C-Cl bond have the forms of the repulsive curves (Fig. 3).

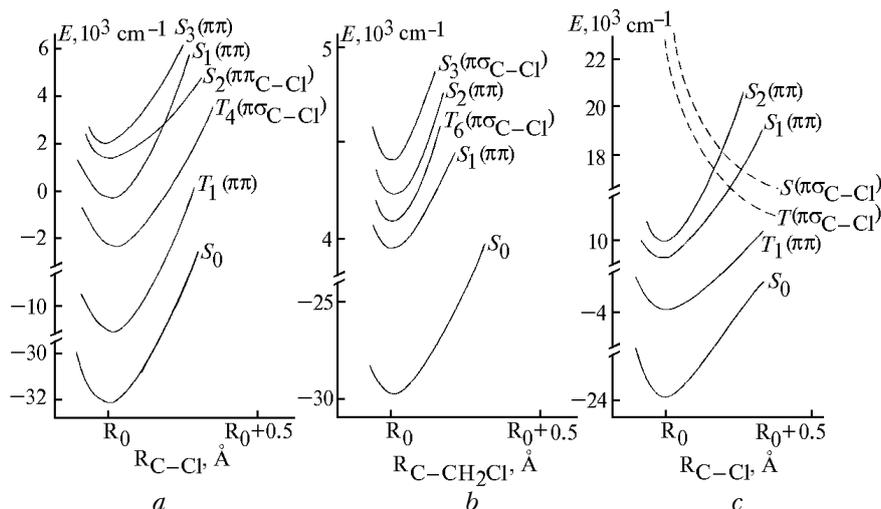
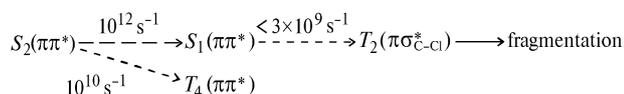


FIG. 3. Potential curves of electron excited states of chlorosubstituted forms of naphthalene in different reaction coordinates: a) I-chloronaphthalene, b and c) I-chloromethylnaphthalene.

Thus, three factors: lesser energy of dissociation of the bond C–Cl in comparison with I-chloronaphthalene, decreased strength of the bond with excitation, and repulsive character of the potential curves of the molecule allowed us to state that the abstraction of the chlorine atom from the I-chloromethylnaphthalene molecule can occur not only in singlet, but also in triplet $\pi\sigma_{\text{C-Cl}}^*$ states. The final choice of photodissociating state can be made after consideration of the dynamics of photophysical processes in the examined molecules. In the experimental study of photo-abstraction of the chlorine atom from I-chloromethylnaphthalene, the reaction was initiated by the photons with energies $\nu_{\text{exc}} = 31950 - 37950 \text{ cm}^{-1}$.

In the calculated scheme, the dissociating state $S(\sigma_{\text{C-Cl}}^*)$ has the energy in excess of $40,000 \text{ cm}^{-1}$ and hence cannot be populated optically for excitation energies used in the experiment. The photodissociating triplet stable $T_2(\pi\sigma_{\text{C-Cl}}^*)$ is populated according to the scheme



Thus, the breaking of the bond C–Cl in I-chloromethylnaphthalene occurs by the predissociation mechanism in the triplet state $\pi\sigma_{\text{C-Cl}}^*$. With excitation to the state S_1 ($\lambda_{\text{exc}} = 313 \text{ nm}$), the photodissociating state is populated through intercombination conversion $S_1(\pi\pi^*) \sim T_4(\pi\sigma_{\text{C-Cl}}^*)$. The excitation to the state S_2 ($\lambda_{\text{exc}} = 266 \text{ nm}$) does not introduce any significant change, because the predominant channel of deactivation of the state S_2 is the internal conversion $S_2 \rightarrow S_1$. At the same time, such excitation will be accompanied with a partial loss of the excited molecules through the channel

$S_2(\pi\pi^*) \sim T_4(\pi\pi^*)$. This is experimentally confirmed by the decrease of the quantum yield of fluorescence from 0.013 to 0.001. It should be noted that the suggested approach allowed the photodissociating mechanism and multiplicity of the photodissociating state to be established and reasons for the absence of the analogous photoreaction in I-chloromethylnaphthalene to be understood.

Later this approach was used for theoretical analysis of the possibility of breaking of a single bond¹⁸ and for interpretation of the experiments on investigation of the photoreaction mechanism.¹⁹

Thus, Bazyl' et al.¹⁸ investigated the possibility of photo-abstraction of the oxygen atom from the nitro-group in the trinitrobenzene (TNT) molecule. Quantum-mechanical calculations of the spectrum, bond populations, and rate constants of photophysical processes in the TNT molecule suggested that the states S_1 and S_2 ($\lambda_{\text{exc}} = 348-349 \text{ nm}$) are stable from the viewpoint of the abstraction of the oxygen atom from the NO_2 group being in the paraposition in relation to the CH_3 group of the TNT molecule. When the state S_3 ($\lambda_{\text{exc}} = 346 \text{ nm}$) is excited, the photo-abstraction of the oxygen atom is dominant, because the rate constant of this reaction significantly exceeds the rates of other deactivation processes (see Fig. 4).

The excitation of the states S_4 , S_5 , and S_6 ($\lambda_{\text{exc}} = 280 \text{ nm}$) introduces no principal changes in this scheme. Excitation of the molecule to the most intense absorption band ($\lambda_{\text{exc}} = 277 \text{ nm}$) causes its deactivation through two channels. The first and the main channel populates the states S_4 , S_5 , and S_6 through the internal conversion and then the processes described above take place. The second channel populates the states T_{14} and T_{15} through intercombination conversion. In the process of deactivation of the states T_{14} and T_{15} , the photodissociative state S_7 is populated, for which the abstraction of the oxygen atom is the only channel of dissociation.

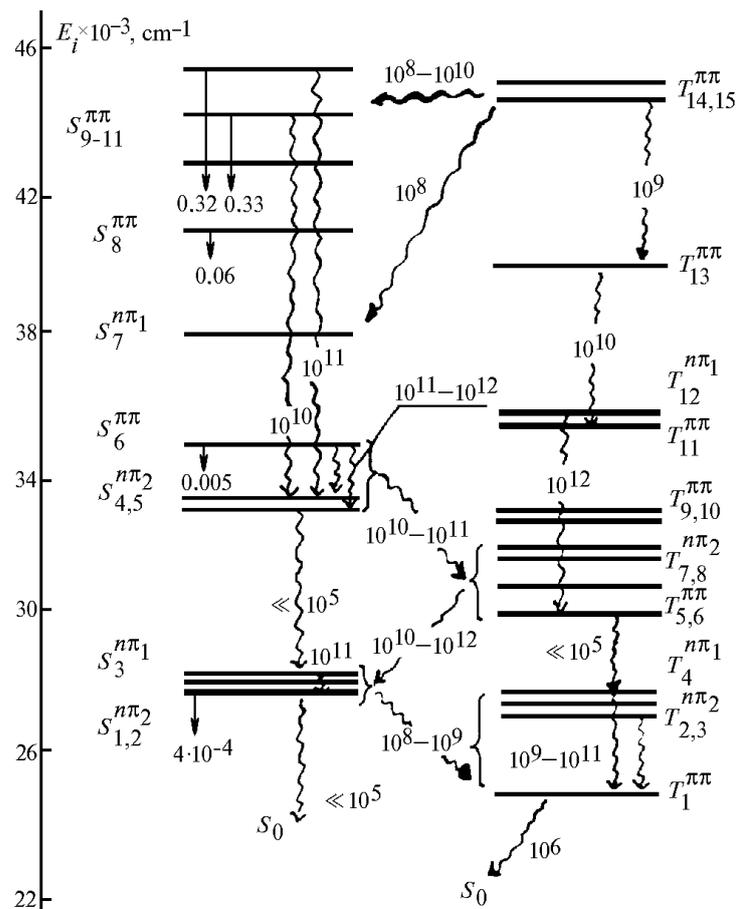


FIG. 4. Scheme of the electron excited states and rate constants (in s^{-1}) of the most important nonradiative processes in the TNT molecule.

The reaction of opening of five-membered ring in the 2,5-diphenyloxazole (PPO) molecule was considered in Ref. 19 together with the impact of substitution and protonation on this reaction. It was established experimentally that when the PPO molecule is excited to the intense long-wavelength absorption band in a hydrogen-containing medium (polystyrene matrix or ethanol solution), the oxazole ring opens with the formation of new NH, CO, and CH bonds by the scheme shown in Fig. 1 c. The interaction with a hydrogen-containing medium was modeled through protonation of the oxazole ring of the molecule to the nitrogen atom. The part of the structure taking part in the reaction and the probability of protonation were determined by the MESP method.²⁰

The results of quantum-chemical calculations and the approach to an analysis of the reaction of photobreaking of the chemical bond based on these results showed that opening of the oxazole ring through the breaking of the bond O_1-C_2 can occur in the proton-containing medium not only in the singlet, but also in the triplet states $\pi\sigma_{CO}^*$, whose molecular orbital σ^* is predominantly localized on this bond. With excitation to this state, the decrease of the strength of the bond O_1-C_2 is most

pronounced and the potential curve is repulsive in character. Photolysis with opening of the oxazole ring through the bond O_1-C_2 occurs by the predissociation mechanism in the state $T(\pi\sigma_{CO}^*)$, because the population of the photodissociating triplet significantly increases in the course of reaction (k_{ST} increases from $\sim 10^8 s^{-1}$ for the equilibrium conformation to $\sim 10^{10} s^{-1}$ for the stretched conformation). The efficiency of the reaction of opening of the oxazole ring depends on the degree of intramolecular interaction with the medium: a proton-donor medium (protonation to the N atom of the oxazole ring) considerably increases the probability of photoreaction of the breaking of the bond O_1-C_2 . A substituent introduced into the five-phenyl fragment may either intensify this interaction (a donor substituent), that is, increase the efficiency of photoconversion, or weaken it (an acceptor substituent) resulting in the decrease of the photoreaction efficiency (Table II).

Investigation of the mechanism of primary photoreaction of the coumarine molecule, which provides the basis for the production of molecules forming active media of lasers that generate in the blue-green spectral region, is important for the production of photostable active media. Experimental investigations of photolysis of the

molecule of nonsubstituted coumarine²¹ established the products formed through α - and β -breaking of the bond C–O of the quinoline ring (Fig. 1, scheme *d*). However, the conclusions of Ponomarev et al.²¹ about the nature and multiplicity of the photoactive state are doubtful.

TABLE II. Populations of the bonds C–O (P_{AB}) and the minimum MESP (U) of the nitrogen atom of the oxazole ring for different electron states of the PPO molecule and its substituted and protonated forms.

Molecule	State	P_{AB} , e		$U(N_{ox})$, kJ/mol
		O ₁ –C ₂	C ₅ –O ₁	
I	S_0	0.707	0.704	–187
	$S_1(\pi\pi)$	0.685	0.660	–160
	$S(\pi\sigma_{CO})$	0.296	0.200	–325
II	S_0	0.709	0.703	–122
	$S_1(\pi\pi)$	0.697	0.679	–92
	$S(\pi\sigma_{CO})$	0.441	0.367	–338
III	S_0	0.704	0.702	–216
	$S_1(\pi\pi)$	0.683	0.663	–229
	$S(\pi\sigma_{CO})$	0.371	0.190	–454
IV	S_0	0.703	0.731	–
	$S_1(\pi\pi)$	0.670	0.659	–
	$S(\pi\sigma_{CO})$	–0.033	0.471	–
V	S_0	0.707	0.732	–
	$S_1(\pi\pi)$	0.678	0.677	–
	$S(\pi\sigma_{CO})$	0.395	0.626	–
VI	S_0	0.700	0.797	–
	$S_1(\pi\pi)$	0.698	0.720	–
	$S(\pi\sigma_{CO})$	0.292	0.435	–

Note. Here, I denotes PPO, II denotes R = SO₂F, and III denotes R = N(CH₃)₂. Protonated forms: IV denotes PPO, V denotes R = SO₂F, and VI denotes R = N(CH₃)₂.

The calculation of population of the bonds of the coumarine molecule demonstrate the most significant decrease of the strength of the bond O₁–C₂ (α -bond) with electron excitation in the singlet and triplet states $\pi\sigma_{1-2}^*$ localized on this bond. The bond O₁–C₉ (β -bond) also weakens with excitation; however, it remains stronger than the bond O₁–C₂ (Table III).

TABLE III. Population of the C–O bonds in the coumarine molecule for different electron excited states.

State	1–2(α)	1–9(β)
S_0	0.663	0.637
$S(\pi\pi^*)$	0.635	0.634
$S(n\pi^*)$	0.637	0.631
$S(\pi\sigma^*)$	0.221	0.385
$T_1(\pi\pi^*)$	0.645	0.632
$T(\pi\sigma^*)$	0.207	0.386

Study of the behavior of potential curves attendant to variations of the lengths of the weakest

bonds C–O demonstrates that for the $\pi\sigma_{CO}^*$ states, the potential curves are repulsive in character. It follows from the calculations that the potential curves with the minima correspond to the states $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$, that is, the molecule remains stable in these excited states. For this reason, the conclusion drawn in Ref. 21 that the bond O₁–C₂ of the state S_1 of the coumarine molecule breaks is erroneous because, as follows from the above discussion, the state S_1 of the coumarine represents the $n\pi^*$ state for which the bonding curve is typical. Let us examine the possibility of population of photodissociating states for excitation energies used in Ref. 20. Because the singlet and triplet photodissociating $\pi\sigma_{CO}^*$ states in the equilibrium conformation of the molecule lie much higher than the energy of the exciting photon, we arrive at a conclusion that the direct photodissociation is impossible under these conditions. It is likely that the predissociation mechanism is realized under these conditions.

Considering the values of the energy of dissociation of the bond C–O ($D_{CO} \cong 30,000 \text{ cm}^{-1}$) and the excitation energy ($\nu_{exc} \cong 31,950 \text{ cm}^{-1}$), we will take into account only the electron excited states whose energies are no less than the dissociation energy and are equal or less than the excitation energy. For the examined scheme of calculation, only the states S_1 and S_2 meet these requirements. From the results of calculation, it follows that the main channel of deactivation of the state $S_2(\pi\pi^*)$ is singlet-triplet conversion and photobreaking of the β -bond in the state $S(\pi\sigma_{1-9})$ (see Fig. 5).

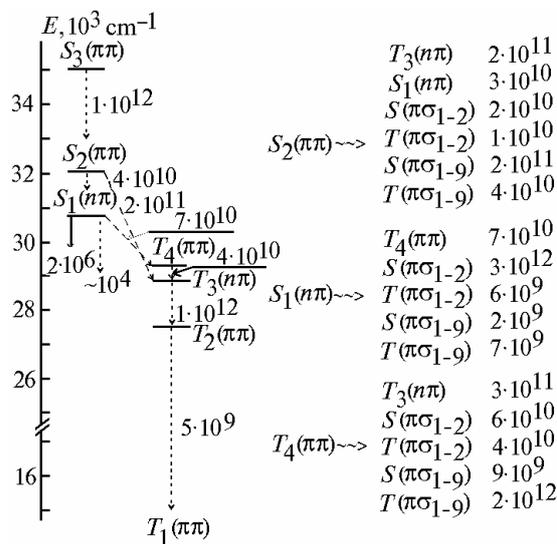


FIG. 5. Electron excited states and scheme of the energy deactivation for α - and β -breaking of the lactone ring of the coumarine molecule.

Because the energy of the state T_3 is less than the energy of dissociation of the bond C–O, the excited molecules deactivated through this channel

undergo no photolysis. A number of molecules excited to the state S_2 will be brought into the state S_1 through the channel of internal conversion $S_2 \sim > S_1$ and then will go almost completely to the photodissociative curve of the state $S(\pi\sigma_{1-2}^*)$ (see Fig. 5). Thus, both types of the photoreaction (α - and β -breaking) can run in the coumarine molecule for the excitation energy used in the experiment described in Ref. 21. It is hard to tell which type of the reaction has higher probability. However, considering that the α -bond weakens much greater than the β -bond with excitation (see Table III), it may be concluded that the α -breaking is more probable. It is evident from the obtained results that for nonsubstituted coumarine photoconversion occurs in singlet photodissociating states and that singlet rather than triplet electron excited states play the main role in population of photodissociating states.

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