

QUANTUM CHEMICAL STUDY OF MECHANISM OF THE PHOTODISSOCIATION REACTION IN POLYATOMIC MOLECULES

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The study of the photodissociation reaction of disulfide molecules based on the quantum chemistry methods is presented. A reaction mechanism is proposed as a result of analysis of photophysical processes and the dependences of quantum yield of photodissociation are explained on the exciting light frequency and on the electronic structure of the species under study.

The question on the mechanism of photochemical dissociation of polyatomic molecules is of primary importance in the current molecular photochemistry. Recently, we have developed an approach which allows one to find the electron excited states from which photodissociation can occur on the basis of quantum chemical calculations.¹ The proposed approach was tested on molecules whose photodissociation was well studied experimentally, i.e., diphenyldisulfide, bis-(π -aminophenyl) disulfide, π -aminothioliol, and phenol.^{2–5}

Let us remind the basic features of the proposed approach. At the initial stage the scheme of electron excited states, matrix elements of the spin–orbital coupling (SOC) operator and the rate constants of internal conversion are calculated that enables one to draw conclusions regarding the physical processes in a molecule and formation of its spectral and luminescent properties. Investigation of the origin of the electron excited states and the degree of localization of the excitation on some bonds together with the calculation of the bond populations in the ground and electron excited states allows one to reveal those of them which are essentially weakened at the electron excitation. Such states of the molecules under study turned out to be the states of $\pi\sigma$ type, where the σ -orbital is mostly localized on the bond to be broken.

At the next stage the potential curves of the electron excited states are constructed based on the quantum chemical calculations with variation of the length of the bond to be broken and using the Morse potential for the ground state.⁶ The potential curves of electron excited states of a diphenyldisulfide molecule are shown in Fig. 1, where the lengths of bonds with populations sharply reducing at excitation are taken as the reaction coordinate. It follows from Fig. 1 that only the potential curves of singlet and triplet $\pi\sigma_{ss}$ states are the repulsion curves while all other potential curves have their minima.

The proposed approach allows one not only to relate the photochemical processes to the origin of the electron excited states but also to describe in detail the primary mechanisms of the photodissociation reactions.

Let us consider the photodissociation mechanism in disulfides in more detail. It was found experimentally for these compounds^{3–5} that the photoexcitation is followed by the break of the S–S bond (the structures of molecules under study are presented in Figs. 2 *a* and *b*) and by the formation of phenyl–thiol radicals S–RX (where X = H, NH₂) whose formation is detected in the absorption spectra.

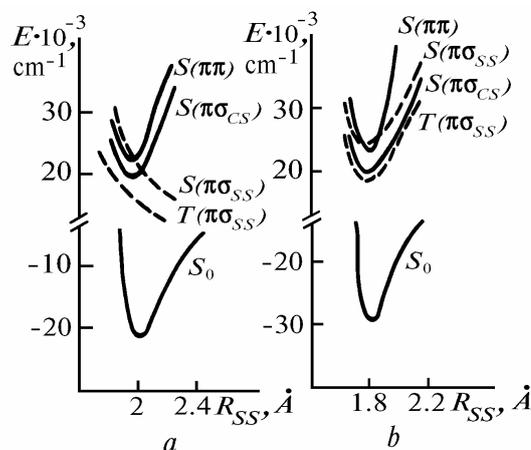


FIG. 1. Potential curves of the electron excited states of a diphenyldisulfide molecule: *a*) the length of S–S bond is changed and *b*) the length of the C–S bond is changed.

The energy schemes of electron excited states of disulfides and the values of matrix elements of the SOC operator calculated using the PIDO/s method^{8–10} are shown in Fig. 2.

To calculate the constant of the internal conversion process we have employed a formula which enables us to take into account explicitly the orbital origin of wave functions of interacting electron states, keeping the dependence of the rate constant of the internal conversion on the energy gap (E_{pq})

$$K_{pq} = G_{pq} N_{X-H} \cdot K_{pq}(E_{pq}), \quad (1)$$

where $K_{pq}(E_{pq})$ is the value of the rate constant evaluated according to the Plotnikov–Dolgikh formula,⁷ N_{X-H} is the number of the X–H bonds and X is the heavy atom.

$$G_{pq} = \sum_{\alpha}^{N_{X-H}} |\Omega_{pq}^{\alpha}|^2, \quad (2)$$

where the sum over α denotes the summing over oscillators corresponding to the X–H bonds in the molecule. Within the framework of the MO–LCAO method,

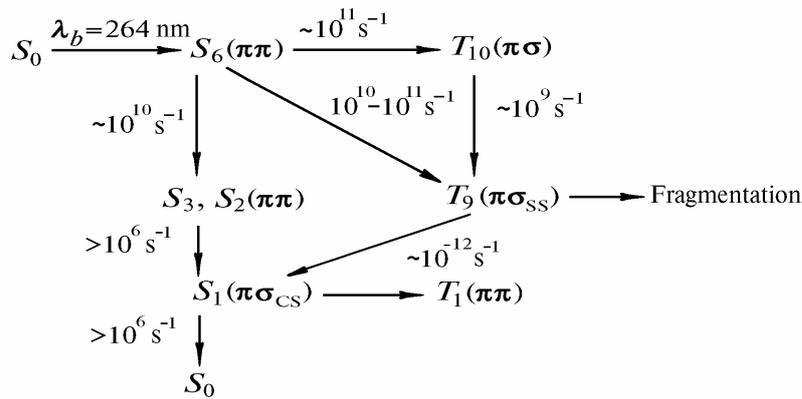


FIG. 3. Scheme of photodissociation mechanism of disulfide molecules.

The above results allow one to understand qualitatively and to explain noticeable difference in quantum yields of photodissociation of the diphenyldisulfide molecule ($\eta = 0.18$) and of its aminosubstituted molecule ($\eta = 0.57$) in the case of excitation in the short-wave region of the absorption band.

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