

## Combined Theoretical and Experimental Study of Bisphenol A Photolysis

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Bisphenol A (BPA) is a chemical of the phenol class. The structural formula of BPA is shown in Fig. 1. The photolysis of BPA under the action of UV irradiation was studied. However, the mechanism of photodegradation is not fully understood. The photolysis of the neutral molecular form of BPA has been described in a joint experimental and theoretical. Quantum-chemical methods using the theory of intramolecular photophysical processes have been used to interpret the spectral-luminescent properties of BPA in hexane and toluene, to establish the orbital nature of photodissociative states and the mechanism of C<sub>5</sub>–C<sub>8</sub> and C<sub>8</sub>–C<sub>11</sub> bonds splitting. The effect of excitation energy on the efficiency of photoreactions has been found.

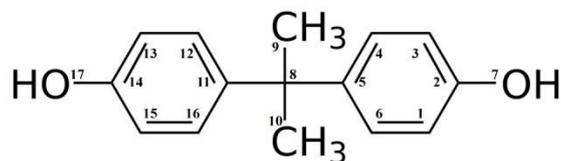


Figure 1: structure and atom numbering of BPA

The absorption and fluorescence spectra of BPA in hexane and toluene were recorded. The maximum of the long-wavelength absorption band of BPA in hexane is 274 nm ( $36496\text{ cm}^{-1}$ ), in toluene – 282 nm ( $35461\text{ cm}^{-1}$ ). These bands look broad to be from a single electronic transition. The theoretical studies were carried out using a software package based on the semi-empirical method INDO/s. It follows from the calculations that the long-wavelength band of the absorption spectrum is formed by three  $\pi\pi^*$ -type electronic transitions that are close in energy and intensity. During absorption, energy transfer occurs in the x and y planes with oscillator strengths of transitions of no more than 0.1. The breaking of C<sub>5</sub>–C<sub>8</sub> and C<sub>8</sub>–C<sub>11</sub> bonds was calculated. When excited, the energy is localized on the bond to be broken due to the high value of the transition rate constant from the potential state curve  $S_1(\pi\pi^*)$  to the photodissociative potential curve. The constants of nonradiative processes are calculated: the internal conversion at the  $S_2(\pi\pi^*) \rightarrow S_1(\pi\pi^*)$  transition and the singlet-triplet conversion of  $S_1(\pi\pi^*) \rightarrow T_9(\pi\sigma^*)$ . The break of the C<sub>8</sub>–C<sub>11</sub> bond in the BPA molecule occurs with an increase in the bond length from 1.501 Å to 1.801 Å. The nonradiative transition between two states of the same multiplicity with an increase in coupling by  $\Delta R = 0.3\text{ Å}$  is a fast process  $S_2(\pi\pi^*) \rightarrow S_1(\pi\pi^*)$  with a rate constant of  $10^{13}\text{ s}^{-1}$ . Additionally, singlet-triplet crossing  $S_1 \rightarrow T_9$  region has been found. However, the rate constant was not great and was  $10^8\text{ s}^{-1}$ . It has been shown that, when excited to the region of the long-wavelength absorption band, BPA photolysis occurs through the break of the C<sub>8</sub>–C<sub>11</sub> bond mainly by the mechanism of predissociation and is most effective in the singlet state of the  $\pi\sigma^*$  type.

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