

# Quantum-chemical research into the photolysis of heptane molecule

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The quantum-chemical study of the possibility of photobreak of C–C and C–H bonds in heptane is carried out. It is shown that the electronic excitation to the  $S_1$  state results in the strongest decrease of the two central C–C bonds and C–H bonds connected with them. Photodissociative states are found. The potential curves of excited states are obtained. It is established that the photobreak of the C–C and C–H bonds is possible through direct dissociation in a singlet electronic excited state.

It is known that a solvent has a marked effect on the spectral-luminescent properties of multiatomic molecules, as well as on the ways and efficiency of phototransformations in the molecular structures.<sup>1–3</sup> Thus, for example, Köhler and Getoff,<sup>4</sup> studying the dependence of the quantum yield of fluorescence of the phenol solution on the excitation energy, showed that the decrease of the quantum yield with the increasing excitation energy is caused by photobreak of the O–H bond, whose efficiency is different in different solvents. It was shown that the quantum yield of the reaction is higher in hydrocarbon solvents than in solvents capable of forming hydrogen bonds with phenol. The allowance for the solvent effect is important, in particular, in developing new laser active media based on solutions of organic compounds, because the solvent, along with active molecules, takes part in photophysical and photochemical processes arising in the medium under the exposure to pumping radiation.<sup>2</sup> Therefore, it becomes clear why we are interested in studying the possibility of phototransformations of the solvent itself.

The aim of this paper was to study the possibility of photobreak of C–C and C–H bonds in the heptane molecule based on the earlier proposed<sup>2</sup> quantum-chemical approach. According to this approach, the first stage includes quantum-chemical calculations, determination of the nature of electronic excited states and the degree of localization of the electronic excitation energy at some molecular bonds, and revealing of the bonds, whose strength decreases in the corresponding electronic states, i.e., whose break is potentially possible. Populations of the bonds  $P_{AB}$  between the atoms  $A$  and  $B$  are taken as characteristics responsible for the bond strength. The decrease of  $P_{AB}$  at the corresponding electronic transition points to weakening of the  $A$ – $B$  bond. At the next stage, spectra of the excited states are calculated while varying the lengths of these bonds, what allows us to determine the character of the potential curves of the molecule in the corresponding excited states and to find the molecule's photodissociative states.

In this work, for quantum-chemical calculations of the electronic structure and wavefunctions, we used the semiempiric Partial Neglect of Differential Overlap (PNDO) method with a special spectroscopic parameterization.<sup>5</sup> With the use of the wavefunctions obtained by the PNDO method, we have calculated the matrix elements of the spin-orbital interaction operator, rate constants of intramolecular nonradiative processes, and populations of chemical bonds (by Malliken<sup>6</sup>). The rate constants of intersystem crossing  $k_{ISC}$  and internal conversion  $k_{IC}$  were calculated according to Ref. 2.

The experimental results have shown that the band in the electronic spectrum of heptane absorption peaks at  $\sim 58000$   $\text{cm}^{-1}$ , and the peak of the fluorescence band is at  $\sim 48000$   $\text{cm}^{-1}$ , the quantum yield of fluorescence of the heptane solution varies from  $0.6 \cdot 10^{-3}$  to  $1.6 \cdot 10^{-3}$  depending on the excitation energy.<sup>7</sup>

It should be recognized that the direct use of parameterization<sup>5</sup> in quantum-chemical calculations gives the energy of the  $S_0 \rightarrow S_1$  transition much smaller than that observed experimentally.<sup>7</sup> In this connection, the values of the parameters for carbon atoms were fitted for more adequate description of the absorption spectra.

For calculating spectral properties of the heptane molecule and studying the mechanism of photobreak of the bonds, we have selected the model geometry of heptane. All interatomic C–C distances were taken the same and equal to 1.53 Å, and the lengths of the C–H bonds were taken equal to 1.11 Å.

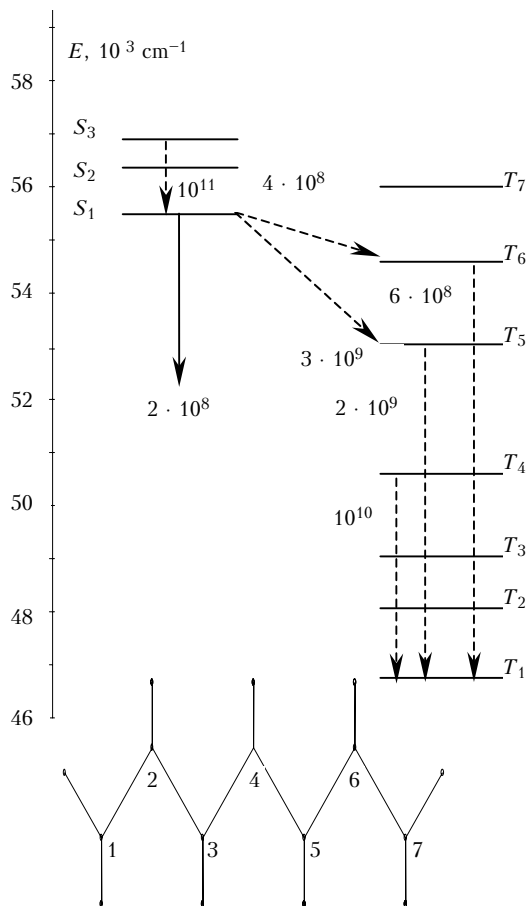
The first absorption band is formed by the  $S_0 \rightarrow S_1$  transition, as the most probable transition (the oscillator strength  $f = 0.11$ ). This transition is mostly formed by the electron configuration, whose orbitals are localized at the central fragment of the molecule (C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> atoms). In the ground state, the central fragment has the positive charge, whereas the lateral fragments (C<sub>1</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>7</sub> atoms) have negative charges. The transition from the ground state to the first singlet excited state is accompanied by transfer of the electron density from atoms C and H of the lateral fragments to the central one. However, as this occurs,

the population of the C–C and C–H bonds of the central fragment decreases (see Table).

**Table. Populations of C–C and C–H bonds in the heptane molecule**

Bond	State	
	$S_0$	$S_1$
C <sub>1</sub> –C <sub>2</sub>	0.624	0.298
C <sub>2</sub> –C <sub>3</sub>	0.645	–0.044
C <sub>3</sub> –C <sub>4</sub>	0.643	–0.185
C <sub>1</sub> –H <sub>1</sub>	0.809	0.713
C <sub>1</sub> –H <sub>2</sub>	0.812	0.762
C <sub>1</sub> –H <sub>3</sub>	0.812	0.762
C <sub>2</sub> –H <sub>4,5</sub>	0.840	0.670
C <sub>3</sub> –H <sub>6,7</sub>	0.839	0.596
C <sub>4</sub> –H <sub>8,9</sub>	0.838	0.573

Figure 1 depicts the scheme of electronic excited states of the heptane molecule along with the rate constants of the most efficient photophysical processes (values nearby arrows).



**Fig. 1.** Scheme of electronic excited states and photophysical processes ( $s^{-1}$ ) in the heptane molecule: radiative decay (solid line) and internal and intersystem crossing (dashed lines).

All electronic excited states are states of the  $\sigma\sigma$  type. Once the molecule absorbs radiation quantum and

transits into the  $S_1$  state, the energy is deactivated mostly through singlet-triplet conversion and radiative decay (internal conversion  $S_1 \rightarrow S_0$  is low). Note that the intersystem crossing  $S_1 \rightarrow T_5$  and  $S_1 \rightarrow T_6$  prevails among various ways of deactivation. The state  $T_5$  is formed largely by the electronic configuration characterized by the electronic transition from the molecular orbital localized at the central fragment of the molecule to the orbital localized largely on the lateral fragments, i.e., the initial and final states in the transition  $S_1 \rightarrow T_5$  are localized at different fragments of the molecule. For this reason, the conversion  $S_1 \rightarrow T_5$  is somewhat higher than  $S_1 \rightarrow T_6$ . The calculated quantum yield of the fluorescence is equal to 0.06.

The calculation of populations of the C–C and C–H bonds of the molecule shows that the strength of the central C<sub>3</sub>–C<sub>4</sub> and C<sub>4</sub>–C<sub>5</sub> bonds decreases most strongly at excitation to the  $S_1$  state. The C<sub>4</sub>–H<sub>8</sub> and C<sub>4</sub>–H<sub>9</sub> bonds connected with the central carbon atom also weaken at excitation, but not so strongly as the central C–C bonds (see Table).

To find the form of the potential curves in the electronic excited states, the quantum-chemical calculations were performed for the energy of the  $S_1$  state with variation of the length of the central C–C and C–H bonds weakening at excitation. The potential curves of the ground state were modeled by Morse potential,<sup>8</sup> and the curves of the electronic excited states were obtained through summation of the potential energy of the ground state and the energy of the electronic transition at every point of the abscissa. In calculating Morse potential, the following experimental data were used: for the C–C bond: break energy of the bond  $D_{C-C} = 352 \text{ kJ} \cdot \text{mol}^{-1}$  (Ref. 9), frequency of the bond oscillations  $\nu = 1100 \text{ cm}^{-1}$  (Ref. 10), and equilibrium length of the bond  $R_{C-C} = 1.53 \text{ \AA}$ ; for the C–H bond: break energy of the bond  $D_{C-H} = 401 \text{ kJ} \cdot \text{mol}^{-1}$  (Ref. 9), frequency of the bond oscillations  $\nu = 2900 \text{ cm}^{-1}$  (Ref. 10), and equilibrium length of the bond  $R_{C-H} = 1.11 \text{ \AA}$ .

The shape of the potential curves of the ground and the first excited singlet states at the varying C–C and C–H bond lengths (Fig. 2) indicates that the potential curves of the  $S_1$  state in both of these cases are repulsion curves. To break the C–C bond, it is necessary to overcome the energy barrier equal to  $\sim 10000 \text{ cm}^{-1}$ , whereas for the C–H bond this energy barrier is weakly pronounced.

Thus, the obtained results indicate that the break of the C–H bonds related with the central C<sub>4</sub> atom through direct dissociation is the most probable in the heptane molecule. Photobreak of the C<sub>3</sub>–C<sub>4</sub> and C<sub>4</sub>–C<sub>5</sub> bonds is unlikely, because the energy barrier is high enough. We can assume that in the actual situation the radiative decay competes with the break of the C–H bonds, and this competition leads to a decrease in the quantum yield of fluorescence as compared to that we have calculated.

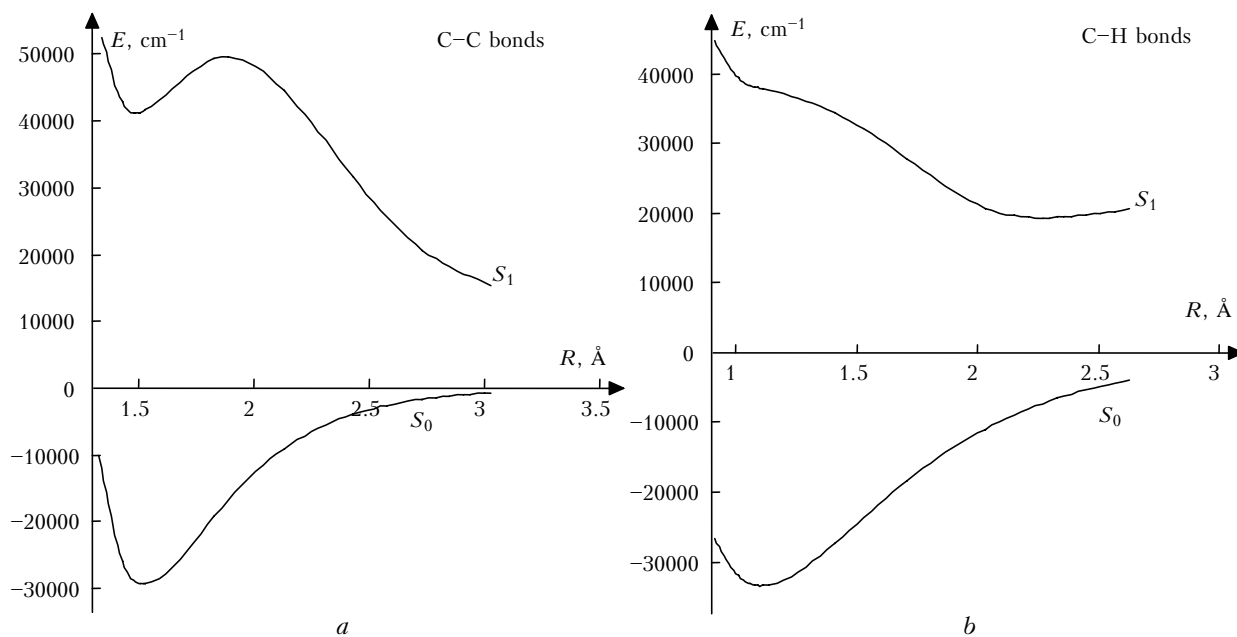


Fig. 2. Potential curves of electronic excited states of heptane: C<sub>3</sub>-C<sub>4</sub> and C<sub>4</sub>-C<sub>5</sub> bonds (a) and C<sub>4</sub>-H<sub>8</sub> and C<sub>4</sub>-H<sub>9</sub> bonds (b).

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