Proc. Estonian Acad. Sci. Phys. Math., 1995, 44, 4, 481–483
https://doi.org/10.3176/phys.math.1995.4.08

CHEMICAL REACTION IN A STRONG COHERENT LIGHT FIELD

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Presented by V. Hizhnyakov

Received 6 October 1995, accepted 1 November 1995

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ХИМИЧЕСКАЯ РЕАКЦИЯ В СИЛЬНОМ КОГЕРЕНТНОМ СВЕТОВОМ ПОЛЕ. Олев СИЛЬД

Key words: chemical reaction, activation energy, coherent laser field.

A system of atoms participating in a chemical reaction (reagents system) can be considered as a molecule. The dynamics of the nuclear motion in the reagents system is determined by its potential energy surface (PES). The PES is computable as the quantum-mechanical electronic average of the Hamiltonian of the reagents system H:

$$U(\vec{R}) = \langle \psi(\vec{r}, \vec{R}) \,|\, H \,|\, \psi(\vec{r}, \vec{R}) \rangle, \tag{1}$$

where $\vec{r}$ and $\vec{R}$ are the sets of the position vectors of electrons and nuclei, respectively, $\psi(\vec{r}, \vec{R})$ is the full wave function of the reagents system. Whereas the chemical reaction means the nuclear motion from a certain nuclear configuration of the reagents system to another one, the PES has been termed the cornerstone of the theory of chemical reaction [1].

In a chemical reaction, the initial and final nuclear configurations correspond to certain minima of the PES. The energetically most favourable trajectory in the $\vec{R}$ space between the two minima is called the reaction path. The energy maximum of the reaction path occurs in a saddle point of the PES. The nuclear configuration of the saddle point is called the transition structure or the activated complex. The energy difference between the activated complex and the initial configuration makes the activation energy E_A. In accordance with the Arrhenius law, it determines the reaction rate as a function of temperature T [1]:

$$k = k_0 \exp(-E_A/RT), \tag{2}$$

where R is the universal gas constant.

The simplest way to increase the rate k is to raise the temperature T. Another possibility is to decrease the E_A by suitably changing the PES. By the way, usually a catalyst does it.

An essential change of the PES of a molecular system is achieved through the interaction with the strong light field. The field transfers a great part of the systems into an excited quantum state which results in an altered PES and, possibly, in a decreased E_A.

The coherent laser field transfers the system into a superposition state [2], which also results in an altered PES. This short note considers one possible mechanism of the decrease of E_A for the reagents system interacting with the strong coherent laser field.

Let us have a simple chemical reaction:

$$AB+C \Rightarrow A+BC. \tag{3}$$

The exact quantum-mechanical (*ab initio*) calculation of the PES and E_A for reaction (3) is a labour-consuming computer problem. Here, the next quite approximate model estimation will be done. In accordance with [3], the activation energy of reaction (3) is mainly determined by the exchange energy

$$E^{\text{ex}}_{AB} = e^2 \int d\vec{r}_a \int d\vec{r}_b r_{ab}^{-1} \psi_a^*(\vec{r}_a)\psi_b(\vec{r}_a)\psi_a(\vec{r}_b)\psi_b^*(\vec{r}_b), \tag{4}$$

where e is the elementary charge, $r_{ab}=|\vec{r}_a-\vec{r}_b|$, $\vec{r}_a$ and $\vec{r}_b$ are the position vectors of electrons in atoms A and B, respectively; ψ_a and ψ_b are the electronic wave functions of atoms A and B, respectively. The one-electron atoms A, B, C are supposed.

Assume the laser field being in resonance with the electronic transition g (ground) $\Rightarrow e$ (excited) in atom A. Let the wave function of the state e be denoted as ψ^e_a. In the strong coherent laser field the dynamic hybridization of the states g and e takes place [4]. As a result the wave function ψ_a has to be replaced by the next superposition of the dressed wave functions ψ_a and ψ^e_a:

$$\psi(\vec{r}_a, t) = \sum_{N=0}^{\infty} K_N (1/\sqrt{2}) (|\psi_a(\vec{r}_a)\rangle |N\rangle + \\ + |\psi^e_a(\vec{r}_a)\rangle |N-1\rangle) \exp[-it(N\hbar\Omega + E_N)/\hbar]. \tag{5}$$

Here $K_N = \exp(-\overline{N}/2)(\overline{N})^{N/2}/\sqrt{N!}$, $|N\rangle$ is the eigenstate of the laser field with N photons, $\overline{N}$ is the mean number of photons, Ω is the laser frequency, and E_N is the electron energy eigenvalue in the laser field with N photons.

Along the reaction path, the real energy gap between the PESs of the ground and excited states varies. It means the absence of the exact resonance of the light field with the electronic transition $g \Rightarrow e$ (i. e. detuning), at least in the majority of the points of the reaction path. Nevertheless, the hybridization of the states g and e is achievable if the interaction with the light field exceeds the detuning. To guarantee the hybridization in all points of the reaction path, the field strengths 10^7 and 10^8 V/cm (in the case of the transition dipole 1 D) are necessary for the detunings 0.1 and 1.0 eV, respectively.

Now, in formula (4), let the eigenfunction ψ_a be replaced by wave function (5):

$$E^{\text{ex}}_{AB}(\text{laser}) = e^2 \int d\vec{r}_a \int d\vec{r}_b r_{ab}^{-1} \psi^*(\vec{r}_a, t)\psi_b(\vec{r}_a)\psi(\vec{r}_b, t)\psi^*(\vec{r}_b). \tag{6}$$

Suppose the axially symmetric interaction between atoms A and B. According to the selection rule of dipole transitions the states g and e are of different parity. Due to the parity properties, some parts of integral (4) can be cancelled at certain reagents configuration. For example, if the laser field is polarized perpendicularly in regard to the axis $A—B$, then ψ_a and ψ^e_a are of different parity with respect to vertical plane.

At such a configuration of reagents

$$\int d\vec{r}_a r_{ab}^{-1} \psi_a^{e*}(\vec{r}_a) \psi_b(\vec{r}_a) = 0,$$

$$\int d\vec{r}_b r_{ab}^{-1} \psi_b^{*}(\vec{r}_b) \psi_a^{e}(\vec{r}_b) = 0,$$

which results in (supposing unchanged one-electron wave functions ψ_a and ψ_b in the laser field)

$$E_{AB}^{\mathrm{ex}}(\mathrm{laser}) = E_{AB}^{\mathrm{ex}}/2. \qquad (7)$$

The reduction of the exchange energy by 50% in the laser field and the corresponding decrease of E_A increases the reaction rate (2). So the strong coherent laser field acts like a catalyst of the chemical reaction.

The effect of a strong coherent laser field on a chemical reaction via excited rovibronic states has been considered basing on the quantum-states concept [5]. This short note considers the effect basing on the PES concept, i.e. via a potential barrier of the height E_A.

REFERENCES

1. Salem, L. Electron in Chemical Reactions: First Principles. John Wiley and Sons, New York, 1982.
2. Allen, L., Eberly, J. H. Optical Resonance and Two-Level Atoms. John Wiley and Sons, New York, 1975.
3. Веселов М. Г. Элементарная квантовая теория атомов и молекул. ГИТТЛ, Москва, 1995.
4. Sild, O. Optics Commun., 1993, 102, 36—42.
5. Shapiro, M., Brumer, P. Int. Rev. Phys. Chem., 1994, 13, 187—229.