Electronic Accommodation and Photocatalysis of Heterogeneous Reaction, Stimulated by Ionizing Radiation

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Abstract – Presented results point on significant contribution of electronic channel in energy accommodation of heterogeneous reaction on wide-band solids surface to the field of ionizing radiation. The rate constants of the electronic accommodation of energy of vibrationally excited molecules depending on electron traps depth have been specified. In addition, the long-range mechanism of electronic relaxation catalysis has been offered.

1. Introduction

In the investigation of nature of catalytic reactions the consideration of active centres of the surface plays the important role. Sensitivity of catalytic reactions for electronic processes in the chemical environment of active centres, caused by ionizing radiation, determines theoretical and practical importance of consider mechanisms. The most popular theory of electronic catalysis is the theory of F.F. Volkenstein [1]. According to this theory the elementary act of adsorption and catalysis is described from the point of view of change of charge of the adsorption centres at a capture of charge bearers of semiconductor. It was proposed in [2] to take into account the influence of energy-release at capture of bearers on surface states on the speed of photocatalytic processes. According to the work [3], dissipation of this energy may lead to the excitation and to the increase of molecules reactivity [4]. In exothermic reactions energy is released and vibrationally excited molecules are generated, which are relaxed subsequently. It has been shown in theoretical works [5], that the speed of relaxation on metals is determined by nonequilibrium electronic channel of energy accommodation. In the case of dielectrics and semiconductors the mechanism of electronic accommodation is considered to be unlikely because of small concentration of free electrons. However, a chemiluminescence of solids [6] point to the existence of the electronic channel of energy accommodation on semiconductors. The output of luminescence quanta on the act of atoms recombination is less than 10^{-2}. That is why the contribution of the electronic channel of accommodation into the speed of reaction on wide-band solids has been neglected.

In work [7] a new phenomenon has been discovered – the high-efficiency electronic heterogeneous accommodation (HEHA) of energy of the chemical reaction on the surface of the electronically excited wide-band solids. HEHA is, that the speed of the reaction increases several times at the excitation of the samples by UV light, which is the result of the relaxation of energy of vibrationally excited molecules on the surface along the electronic channel. Also, the speed of electron generation increases by several orders of magnitude owing to the energy of reaction. The problem in question is of great general value, because the processes of the dissipation of energy play an important role in heterogeneous processes (catalysis, epitaxy of semiconductors, plasma etching, etc.) and processes connected with the use of lasers.

The point of this work was the investigation of the relaxation processes of vibrational-excited molecules via electronic channel for wide-gap solids, which is exited by ionizing radiation.

2. Experimental

The main subject of investigation was the monocrystal ZnS which exhibits good luminescence at photo and chemical excitation (λ_{max}=525 nm), has a broad forbidden band (3,7 eV) and a system of electron traps. Powder-like crystalline phosphors ZnS,CdS-Ag (λ_{max}=528 nm) was also used. The experiments were carried out in vacuum setups, where the admission of atomic gas could be done either in the regime of molecular beams [8], or in the diffused regime [9]. The use of the Ramsey accumulation effect [10] allowed to elaborate [11] method of measuring the coefficient of recombination γ on the samples.

3. Results

At the switch-on of the atoms flux (H, O) on the samples under consideration the heterogeneous chemiluminescence (HCL) of the surface appeared. Preliminarily exposed to UV light samples were excited by the stream ($j=5\cdot10^{14}$ sm^{-2} s^{-1}) of atoms H (O). The stream was switched on for 1–2 seconds in the process of de-excitation by the sample of the accumulated light sum, and the intensities of the appearing HCL – $I^{e}_{HCL}(t_1)$ and the afterglow $I_A(t_i)$ were registered (Fig. 1). The intensity of HCL ZnS,CdS-Ag turned out to be proportional to I_A (Fig. 1, the insertion) and on the 5th second by the order of 10^3 exceeded the HCL intensity I_{HCL}, when all the traps had been already de-excited. The value $I_A(t_i)$ served as a measure of the surface concentration of electrons m^{e}_{s} at the moment t_i. The results of investigating the HCL, excited by the atoms O, were alike.

It was investigated the dependence of I_{HCL}, excited by the impulsive stream of atoms H, of the ZnS,CdS-Ag, on the fixed stream of UV light Φ. I^e_{HCL} was depended on Φ, and increased by 3 orders of magnitude at $\Phi=10^{12}$ quanta/sm^2 in comparison with I_{HCL} of the unexposed to light sample for ZnS,CdS-Ag and by 5 order of magnitude for ZnS monocrystal.

The sample ZnS,CdS-Ag has 2 types of traps: E_1=0,17 eV and E_2=0,4 eV. For evaluation of its effectiveness the experiment was carried out according to the following scheme (Fig. 2). The sample has been cooled to T=180 K and has been illuminated by the UV light, then the light has been switched off and in the traps thermal emptying process with E_1=0,17eV the I^e_{HCL} has been measured at a pulsed switching of H-atoms.

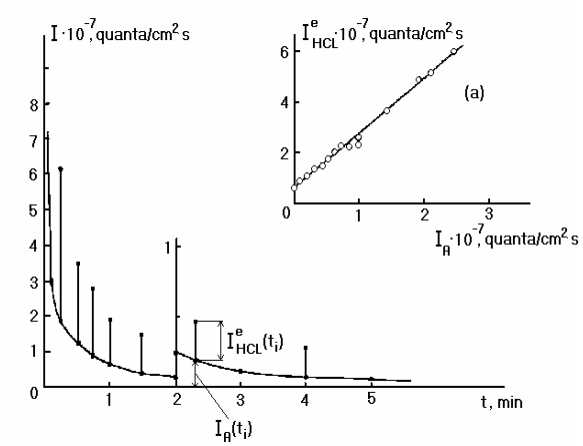

Fig. 1. Time dependence of the intensities of persistence (I_A) and HCL excited by the atomic H probe at moments t_i of ZnS,CdS-Ag sample. (a) Dependence of I^e_{HCL} on the afterglow intensity I_A. T = 295 K

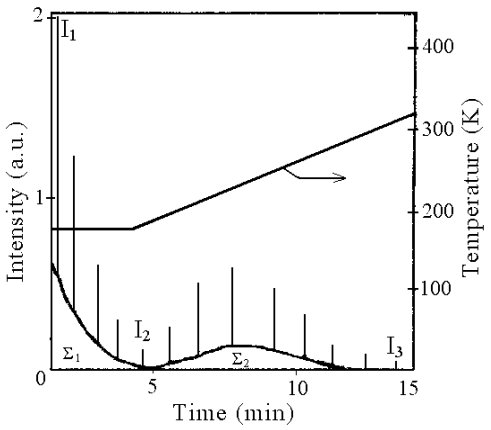

Fig. 2. Time dependence of the intensities of persistence, HCL excited by the atomic H probe at moments t_i and temperature of ZnS,CdS-Ag sample (explanations in text)

The intensity $I^e_{HCL} = I_1$, when traps were most filled, was related to the intensity I_2, when all traps with E_1 were de-excited, and to the I_3, when traps with E_1 and E_2 are de-excited, as 570:56:0,8 respectively. The relation of lightsums for these traps was 77:56. I.e. the electronic accommodation rate constant on the trap with depth E_1 seven times as much, as on the trap with depth E_2.

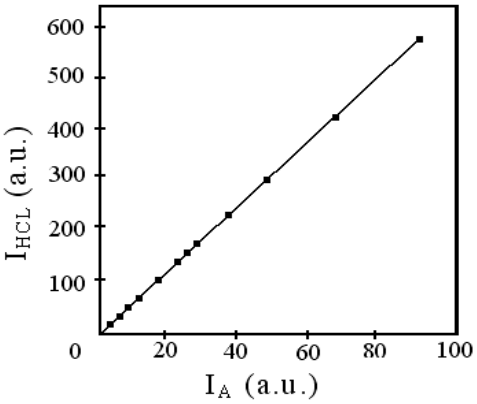

Fig. 3. The dependence of I^e_{HCL} on the afterglow intensity I_A. T = 180–320 K

4. Discussion

The kinetic mechanism of HEHA without description of processes of luminescence and emission includes following stages:

I. $R + L \xrightarrow{v_1} RL$;

II. $R + RL \xrightarrow{v_2} R_2^v L$;

III. $R_2^v L + Z \xrightarrow{(1-\alpha)k_1} R_2 + L + Z$;

IV. $R_2^v L + Z \xrightarrow{\alpha k_1} R_2 + L + Z^*$;

V. $R_2^v L + Z^* \xrightarrow{(1-\beta)k_2} R_2^{v-v_1} L + Z$;

VI. $R_2^v L + Z^* \xrightarrow{\beta k_2} R_2^{v-v_1} L + Z^*$;

VII. $R_2^{v-v_1} L + Z \xrightarrow{(1-\Theta)k_5} R_2 + L + Z$;

VIII. $R_2^{v-v_1} L + Z \xrightarrow{\Theta k_5} R_2 + L + Z^*$;

IX. $Z^* \xrightarrow{k_3} Z$;

X. $hv + Z \xrightarrow{k_4\beta} Z^*$.

Here Z is the centre of equilibrium accommodation of reaction energy; Z^* is the trap, filled with electron. In stage IX the thermal emptying of traps occurs, and in process X they are populating at the expense of light.

Let us make the substitutions for concentrations at the moment of time t: $R_2^v L \to N_2^v$, $Z \to m_s$, $hv \to \Phi$. From the model the rate of reaction is:

$$w = w_p\left[1 + \frac{\alpha k_2 N_2^v + (k_2/k_1)\Phi k_4\beta}{N_2^v(1-\beta-\Theta)k_2 + k_3}\right].$$

Here $w_p = N_2^v m_s \alpha k_1$ is the rate, which is determined by the equilibrium channel of accommodation of reaction energy. At a high T (large k_3) the second addend tends to 0 and $w = w_p$. In the field of a low T ($k_3 \to 0$) and a high Φ the second addend, which is associated with electron accommodation, can be significantly greater than 1, and $w > w_p$. During the ex-

periment the rate of recombination of H-atoms on ZnS,CdS-Ag has been increased two times as much at the UV light irradiation.

An elementary mechanism of electronic accommodation is related to the formation of the vibrationally excited molecule H_2^vL (Fig. 3). Simultaneous transitions through several vibrational levels are possible even at the first order of decomposition of the quadruple moment of a molecule to internuclear distance due to the anharmonicity of the $(H\text{-}H)^V$ bond vibration in H_2^vL [12]. Due to the quadruple (H_2^vL) – dipole (electron in the trap) interaction, the energy released at the acts of vibrational relaxation of H_2^vL can be directly switched over to the excitation energy of an electron in the trap and its transfer to the conducting band. The rate of the vibrational-electronic transition:

$$\Gamma_{V-E} = A\frac{\left[\dot{D}(R)\right]^2}{R^8}\exp\left(-\frac{EP}{\hbar\omega_0}\right), \qquad (1)$$

where $\dot{D}(R)$ is the derivative of the quadruple moment over the internuclear distance in the H_2 molecule; A is a constant; $\hbar\omega_0$ = 0,545 eV is the energy of the vibrational quantum $(H\text{-}H)^V = 1$; the parameter P takes into account the anharmonicity of the $(H\text{-}H)^V$ bond; and E is the excitation energy of the center. At $E = E_1$, $E_2 \le 0{,}5$ eV and $R \le 3$ Å, the $\Gamma_{V\text{-}E}$ value corresponds to the probability of the electronic accommodation (arrow 2 in Fig. 4) close to 1. The relation of rates, which was obtained from (1) for E = 0,17 eV and E = 0,4 eV, is equal to 2 and has been slightly different from experimental value.

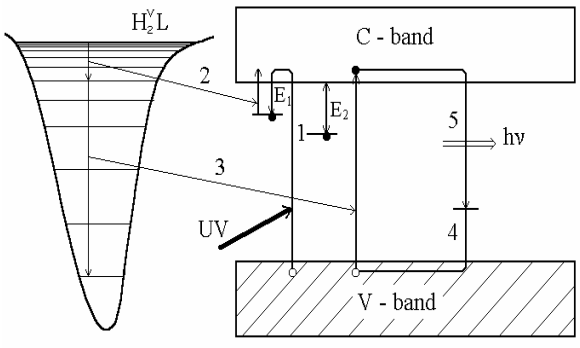

Fig. 4. The scheme of electronic transitions on the surface during H-atoms recombination and irradiation by UV light

5. Conclusion

The increase of the speed of electronic accommodation of energy of the chemical reaction by 5 orders of magnitude at UV excitation and the results of measuring γ show, that there exists the efficient electronic channel of accommodation, which on wide-band solids can be commensurable with the phonon one, and that with the help of ionizing radiation it can be possible to control the reaction speed.

The effective cross-section of HEHA is such, that on the clean surface of metals $m_s^e \sim 10^{15}$ cm^{-2} the accommodation of energy of H_2^v should occur by electronic channel at a very high speed and the processes of energy relaxation should not restrict the reaction and affect its speed.

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