THRESHOLD LASER INTENSITIES FOR INTERACTION PROCESSES OF LASER RADIATION WITH GOLD NANOPARTICLES

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The achievement of some threshold temperature of nanoparticle means that such processes as explosive evaporation of adjacent to GN (gold nanoparticle) liquid, melting, evaporation or fragmentation of GNs, optical breakdown and plasma formation can be induced in nanoparticles and in adjacent media (tissues). These characteristic temperatures and laser intensities are very important for investigations in laser nanotechnologies, laser nanomedicine and will be estimated.
The threshold laser intensities (fluences) can be determined from equations [1,2]. Simplified equations can be formulated in the cases of "long" and "short" pulses. If the condition of "short" pulse $t_p << \tau_T$, where t_p - pulse duration, τ_T - thermal relaxation time, is obeyed and the loss of heat from the particle by heat conduction during the time t_p can be ignored, we find for value of I_{th} [1,2]:

$$I_{th} \approx \frac{4c_0\rho_0(T_{th}-T_\infty)r_0}{3K_{ab}t_p} \quad (1)$$

"Long" laser pulses with pulse duration t_p that exceed the thermal relaxation time τ_T, $t_p > \tau_T$, cause heating of both the particle and the surrounding medium and we have from [1,2]:

$$I_{th} \approx \frac{4k_\infty(T_{th}-T_\infty)}{K_{ab}r_0} \quad (2)$$

The dependence I_{th} on t_p has been disappeared in (2). The threshold energy density of laser pulse is determined by $E_{th} = I_{th}\, t_p$ and in the case of $t_p < \tau_T$ E_{th} does not depend on t_p (1), but for the case $t_p > \tau_T$ E_{th} is proportional t_p (2). These expressions can be used for approximate estimations of I_{th}. Analogous equations and solutions for small spheroidal particles are presented in [3].
The results of direct numerical calculations demonstrate that selective thermal denaturation of tissue proteins around GNs occurs as a result of GN heating by short pulses with durations in the range 1 μs > t_p > 10 ns to minimal temperatures $T_D \sim$ 450-510 K, whereas in the case of pulses of durations 1 ns > t_p > 1 ps, this happens as a result of heating to temperatures $T_D \sim$ 620-850 K. This dependence of the threshold temperatures on the pulse duration t_p is due to strong temperature dependence of thermal denaturation rate and also due to the fact that the denaturation reaction occurs during a characteristic time, i.e. the

shorter the pulse, the higher temperature of a particle should be realized which results in thermal denaturation of over 50% protein molecules inside thin layer adjoining to GN.

The results of analytical estimations and direct numerical calculations demonstrate that explosive boiling of water in water-contained tissues adjoining the radiation-heated surface of a GN occurs when the bulk of GN is heated to the threshold temperature T_V. Value of T_V for GN was approximately selected equal $T_V \sim$ 620-670 K for pulse duration in the range t_p = 1 μs – 10 ns, and $T_V \sim$ 820 – 1000 K for t_p =1 ns – 1 ps. These values were confirmed by computer simulation of explosive evaporation around heating nanoparticles under laser pulse action. Values of gold melting and boiling were chosen from [4] and they are equal T_M = 1337 K and T_B = 3150 K respectively. We suppose that T_* was approximately equal characteristic temperature of optical breakdown $T_* \sim 110^4$ K.

Figure presents the dependencies of threshold laser intensities I_{th} for wavelength 532 nm: I_D - for selective denaturation of proteins adjoining to GN, I_V - explosive evaporation of water adjacent to GN, I_M - melting and I_B - boiling of nanoparticle gold and I_* - optical breakdown initiated on GN on radius r_0 of spherical GN in the range 5-100 nm for pulse durations $1\cdot10^{-8}$, $1\cdot10^{-10}$, $1\cdot10^{-12}$ s on the base of equations (1,2) and some experimental data [5-10].

The dependencies I_{th} on r_0 are complicated because of real dependence of efficiency factor of absorption K_{ab} on r_0 for concrete laser wavelength and metal of particle [11,12]. Values of characteristic times τ_T for nanoparticles with radiuses in the range $5 < r_0 < 100$ nm are in the range $3.2\cdot10^{-11} < \tau_T < 1.28\cdot10^{-8}$ s.

Condition of "long" pulse, $t_p > \tau_T$, for pulse duration $t_p = 1\cdot10^{-8}$s is valid for range $5 < r_0 < 80$ nm, and dependence of I_{th} (lines 1, Fig.) on r_0 for mentioned range of r_0 is approximately described by (2). Lines 1 in Fig. for $t_p = 1\cdot10^{-8}$ s have the decreasing values for $5 < r_0 < 40$ nm and approximately constant values for $40 < r_0 < 100$ nm taking into account the dependence of K_{ab} on r_0.

For intermediate pulse duration $t_p = 1\cdot10^{-10}$ s (lines 2 in Fig.) the dependencies of I_{th} on r_0 have complicated form with decreasing values for $5 < r_0 < 30$ nm and increasing values for $40 < r_0 < 100$ nm and minimum at some value of r_0. It is interesting to note that in this case the characteristic value I_{th} is equal for two values of GN radius r_0 taking into account decreasing and increasing parts of each line 2.

Condition of "short" pulse, $t_p < \tau_T$, is fulfilled for pulse durations $t_p = 1\cdot10^{-12}$ s < τ_T for all range of r_0: $5 < r_0 < 100$ nm and dependencies of I_{th} have approximately constant values for $5 < r_0 < 30$ nm and monotonously increasing values for all range in accordance with (1) (see Fig. taking into account the dependence of K_{ab} on r_0).

These results can be used for different laser wavelengths λ on the base of calculated values of K_{ab} (λ) for GNs, e.g. see K_{ab} (λ) in [11,12] and equation

$$I_{th}(\lambda) = \frac{K_{ab}(\lambda = 532nm)}{K_{ab}(\lambda)} I_{th}(\lambda = 532nm).$$

We compare some experimental data with calculated results. Next experimental parameters were used in papers [5,6] - wavelength – 532 nm, rectangular shape laser pulse with 7 ns duration, laser intensity between ~ $2\cdot10^6$ and $1\cdot10^8$ W/cm^2. GNs with radiuses of between 2.5 and 25 nm were placed in liquid solutions. When the intensity was 4 10^6 W/cm^2, only the shape of the GNs

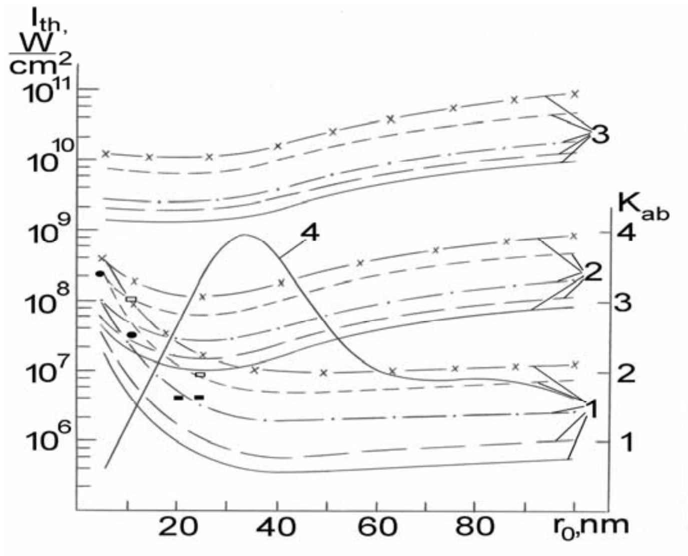

Figure. The dependencies of threshold laser intensities for selective denaturation of proteins adjoining to GN I_D (——), explosive evaporation of water adjacent to GN I_V (− − −), melting I_M (− · − · −) and boiling (evaporation) I_B (----) of GN and optical breakdown initiated on GN I_* (-x-x-x-) on radius of nanoparticle r_0 in the range 5-100 nm for pulse duration $t_p = 1\cdot10^{-8}$ (1), $1\cdot10^{-10}$ (2), $1\cdot10^{-12}$ (3) s and the dependence of K_{ab} on r_0 for laser wavelength 532 nm (4) [11,12]. Experimental data for laser intensities I_{th} are presented for GNs and laser wavelength 532 nm: t_p = 7 ns, r_0 = 20, 25 nm – melting (■) and for 25 nm - evaporation(□) [5,6], t_p = 10 ns, r_0 = 10 nm – evaporation (□) [7], t_p= 18 ps, r_0= 10 nm - evaporation (□) [8], t_p = 10 ns, r_0= 5 nm – fragmentation (●) [9], t_p = 6 ns, r_0= 20 nm – fragmentation (●) [10].

with r_0 ~ 20 - 25 nm was changed and became spherical. This value is the threshold intensity for melting and spheroidization of particles and coincides with the threshold of I_m in Fig. When the intensity was $I_0 \sim 8\cdot10^6$ W/cm^2 the change was clearly observed [5,6] and the diameter of particles was decreased. This value can be viewed as evaporation threshold, first of all, for particles with maximal values of radius r_0 = 20 – 25 nm. This experimental value of I_0 is practically coincides with threshold value of intensity I_B (see Fig.).

Treatment of gold nanoparticles with radiuses r_0 = 7.5 – 10 nm by ultrashort laser pulses with duration 18 ps, wavelength 532 nm, energies up to 1.5

mJ/pulse was investigated in [8]. Threshold experimental intensity, causing evaporation and decreasing of radius, is approximately equal $1{\cdot}10^9$ W/cm^2 and is in accordance with theoretical value in Fig.

Formation of gold nanonetworks and small nanoparticles by action of intense laser pulses on initial gold nanoparticles was investigated in [7]. Next experimental parameters – wavelength 532 nm, pulse duration $t_p \sim 10$ ns and intensity $1{\cdot}10^8$ W/cm^2 and more, initial radius of gold particles ~ 10 nm were used. Characteristic time for particle with radius 10 nm is equal about $\tau_T \sim 610^{-10}$ s < t_p and can be used quasi-stationary approximation for estimations. GNs were evaporated under laser irradiation with intensity $1{\cdot}10^8$ W/cm^2 and more. This value $I_0 \sim 1{\cdot}10^8$ W/cm^2 is a little bit higher than data for theoretical threshold intensity I_B for evaporation of particles with $r_0 = 10$ nm in Fig.

Photofragmentation of GNs with initial radius $r_\infty = 5$ nm was experimentally investigated in [7] under laser pulse 532 nm with $t_p = 10$ ns, threshold fluence 1 J/cm^2 and intensity $1{\cdot}10^8$ W/cm^2. These experimental dots are presented at Fig. and close to theoretical results according to evaporation and optical breakdown that can induce the fragmentation of GNs. Photofragmentation of phase-transferred GNs by intense laser pulses with 532 nm and $t_p = 6$ ns was experimentally investigated in [10]. Threshold fluence leading to fragmentation was equal 130 mJ/cm^2 pulse or $I_{th} = 2.1{\cdot}10^7$ W/cm^{2}pulse.

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