INTERACTION OF LASER RADIATION WITH MATTER

Effect of laser irradiation of nanoparticles in aqueous uranium salt solutions on nuclide activity

A.V. Simakin, G.A. Shafeev

Abstract. **This paper presents an experimental study of the effect of laser irradiation of aqueous uranyl chloride solutions containing gold nanoparticles on the activity of the uranium series radionuclides ^{234}Th, ^{234m}Pa, and ^{235}U. The solutions were exposed to femtosecond Ti:sapphire laser pulses and to the second or third harmonic of a Nd:YAG laser (150-ps pulses) at a peak intensity in the medium of $\sim 10^{12}$ W cm^{-2}. The activities of the radionuclides in the irradiated solutions were shown to differ markedly from their equilibrium values. The sign of the deviation depends on the laser wavelength. The measured activity deviations can be interpreted as evidence that laser exposure of nanoparticles accelerates the alpha and beta decays of the radionuclides. The observed effects are accounted for in terms of a mechanism that involves resonant enhancement of optical waves by metallic nanoparticles.**

Keywords: laser irradiation of nanoparticles, nuclide activity, local field enhancement.

1. Introduction

High-intensity laser beams may initiate nuclear transformations in solid targets in vacuum when pico- and femtosecond pulses are used and the peak power on the target is $\sim 10^{18}$ W cm^{-2} [1–4]. Such beams produce relativistic electrons and protons because these are accelerated in the plasma generated by the intense light. Another approach to the laser initiation of nuclear processes is laser irradiation of nanoparticles in a liquid. Each nanoparticle can be regarded as a target which is optically thin, in contrast to bulk targets. Because its dimensions are small compared to the laser wavelength, there is weak or no reflection from the nanoparticle. Owing to the plasmon resonance of electrons in a metal nanoparticle, its absorption cross section may considerably exceed its geometric cross section, and the optical field may be considerably enhanced near the nanoparticle. In a laser beam, nanoparticles melt and even ionise at sufficiently high light intensities. The spectrum of the plasma forming during IR laser exposure of gold nanoparticles in water at a peak intensity of 10^{12} W cm^{-2} contains lines of atomic gold, which suggests that the plasma temperature is at least 5 eV. Laser exposure of mercury nanodroplets in D_2O under such conditions enabled the ^{196}Hg → ^{197}Au transmutation [5]. Presumably, thermal neu-

trons needed for this transmutation originated from the deuterium nuclei in the heavy water, but the neutron generation mechanism remains unclear.

It is of interest to apply this approach to the initiation of nuclear reactions in unstable elements, such as thorium and uranium. Nanoparticles of these metals are, however, difficult to prepare because they are reactive with water. In view of this, a different approach was proposed: laser radiation is absorbed by nanoparticles of a chemically inert metal, e.g. gold, whereas unstable elements are present in solution in the form of a dissolved salt. This approach was used to initiate nuclear transformations in ^{232}Th [6, 7]. Laser exposure of Au nanoparticles in aqueous $Th(NO_3)_4$ solutions at a picosecond laser intensity of $\sim 10^{12}$ W cm^{-2} was shown to be accompanied by changes in the activity of both the ^{232}Th and ^{137}Cs impurity. A similar approach was used to initiate nuclear processes in aqueous uranium salt solutions in the presence of gold nanoparticles. Laser exposure of the aqueous solutions was accompanied by nonequilibrium gamma-emission at photon energies of 53–56 eV, with a characteristic decay time of ~ 30 min [8, 9]. The emission was tentatively attributed to the short-lived isotope ^{214}Pb, situated at the end of the ^{238}U series. In this paper, we report an experimental study of the influence of laser exposure at different wavelengths on the activity of uranium series nuclides in the aqueous solutions in the presence of gold nanoparticles.

2. Experimental

In our experiments, we used uranyl chloride, UO_2Cl_2, of natural isotopic composition (0.7% ^{235}U). The gamma activity of samples before and after laser exposure was measured by an Ortec-65195-P semiconductor gamma spectrometer with an accuracy of $\pm 5\%$. The activity of radionuclides was determined as the area under the corresponding peaks in the gamma spectrum. The main isotope ^{238}U shows no gamma activity and alpha-decays with a half-life longer than 10^9 yr. The ^{235}U isotope alpha-decays to ^{231}Th with a half-life longer than 10^8 yr.

The influence of laser exposure can be quantified with good accuracy by measuring the activities of the strongest peaks of the nuclides present in the solution. These include ^{234}Th, ^{234}Pa and ^{235}U. The activity of a given radionuclide is the number of decays per unit time. Because the spectrum of gamma photons emitted by a radionuclide is its signature, its concentration in a sample can be evaluated from its gamma activity.

This paper examines the effect of laser exposure at an incident intensity of 10^{12} to 10^{13} W cm^{-2} on a gold target immersed in a uranyl chloride solution and exposed to the

A.V. Simakin, G.A. Shafeev Wave Research Center, A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia; e-mail shafeev@kapella.gpi.ru

second (532 nm) or third (355 nm) harmonic of a neodymium laser (pulse duration of 150 ps) or to femtosecond Ti:sapphire laser pulses (800 nm, pulse duration of 180 fs). The target was laser-ablated in a pure aqueous uranyl chloride solution, which was initially free of gold nanoparticles. The laser energy density deposited on the target surface was several times the ablation threshold, so that a suspension of gold nanoparticles was produced in the aqueous solution [10]. In a number of cases, nanoparticles were produced by laser ablation of a gold target in water. The resultant nanoparticle suspension (concentration of $\sim 10^{15}$ cm^{-3}) was mixed with a uranyl chloride solution just before laser exposure. Figure 1 shows the positions of the emission lines of the laser sources relative to the absorption spectrum of the aqueous uranyl chloride solution containing gold nanoparticles. The second harmonic (532 nm) lies within the plasmon resonance band of gold nanoparticles in water (530 nm). The other two laser wavelengths (800 and 355 nm) are away from the plasmon resonance of Au nanoparticles. In addition, in the concentration range studied, pure aqueous uranyl chloride solutions have an appreciable optical density at the third-harmonic wavelength of the neodymium laser. Au nanoparticles also absorb the third harmonic by virtue of interband transitions in gold [11].
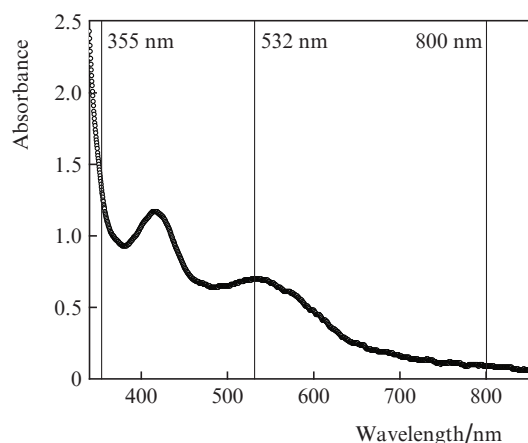

Figure 1. Positions of the emission lines of the three laser sources relative to the absorption spectrum of the aqueous uranyl chloride solution containing gold nanoparticles (open circles). The thickness of the cuvette was 10 mm.

3. Experimental results

3.1. Femtosecond Ti:sapphire laser

Laser exposure of the target has a pronounced effect on the activity of the nuclides present in the solution. Changes occur at all the gamma photon energies characteristic of a given nuclide. As an example, Fig. 2 illustrates the effect of laser exposure on the ^{234}Th activity. The activity is seen to markedly decrease. At the same time, it depends little on whether the exposure was performed in heavy or light water. The half-life of ^{234}Th is 24 days, so its activity just after the exposure was even lower than that in Fig. 2.

Figure 3 illustrates the influence of laser exposure on the activity of the nuclides in question. After the laser exposure, the activity was measured twice, which allowed us to examine its relaxation to the equilibrium state. The activities of the three nuclides are seen to decrease. After the exposure, the ^{234}Th
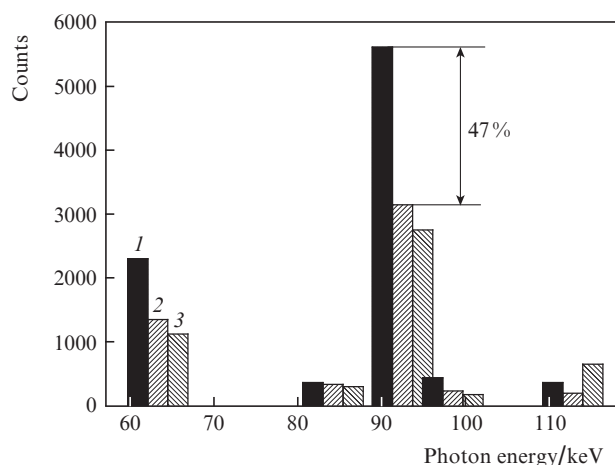

Figure 2. Peak intensities (counts over 10^4 s) for ^{234}Th (*1*) before and (*2, 3*) after laser exposure in H$_2$O and D$_2$O, respectively. Pulse repetition rate, 1 kHz; thickness of the solution layer over the target, ~ 2 mm; exposure time, 60 min; peak power density incident on the target, $\sim 10^{13}$ W cm^{-2}. The gamma spectra of the irradiated samples were taken two weeks after the exposure.

and ^{234}Pa activities gradually approach their initial level, whereas the ^{235}U activity varies insignificantly. This is due to the continuing spontaneous alpha decay of ^{238}U to ^{234}Th and then to ^{234}Pa. Note that the above data qualitatively correlate with results for aqueous uranium salt solutions exposed to 150-ps 1064-nm Nd:YAG pulses [9].
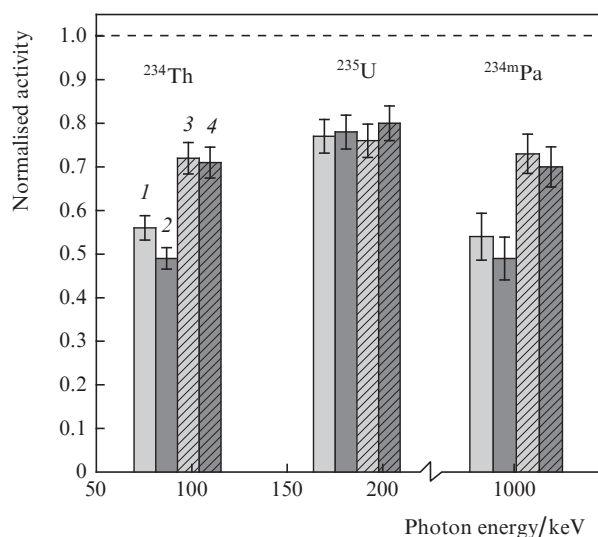

Figure 3. ^{234}Th (92.5 keV), ^{235}U (186.5 keV) and ^{234m}Pa (1001 keV) activities after laser exposure in (*1, 3*) D$_2$O and (*2, 4*) H$_2$O normalised to the respective activities before the exposure. The gamma activity was measured (*1, 2*) 35 and (*3, 4*) 64 days after the exposure. The dashed line indicates the activity before the exposure.

When there are no external influences, each nuclide of the ^{238}U series has an equilibrium activity, determined by its half-life. ^{235}U belongs to another decay series and, when alpha-decaying to ^{231}Th, it has an equilibrium activity. The ^{234}Th to ^{235}U activity ratio in uranium of natural isotopic composition is constant under secular equilibrium conditions. The $A_{234\text{Th}}/A_{235\text{U}}$ activity ratio in solutions after 800-nm femto-

second laser exposure is presented in Fig. 4. Laser exposure markedly reduces this ratio, which then gradually reverts back to its initial level. The deviation of the activity ratio from its equilibrium value is essentially independent of water composition (H_2O or D_2O).
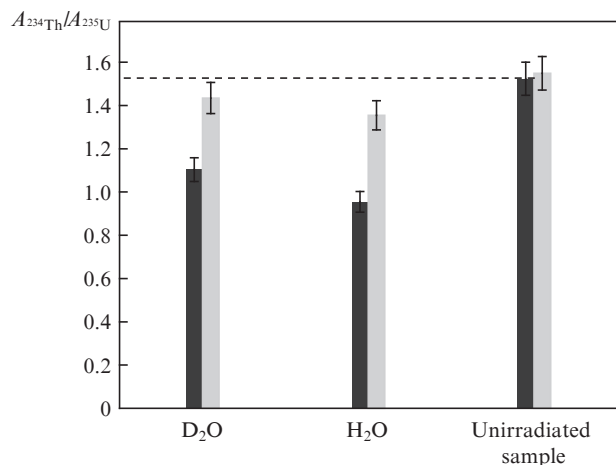

Figure 4. Effect of laser exposure of a gold target in an aqueous uranyl chloride solution on the ratio of the ^{234}Th and ^{235}U activities at 92.5 and 185 keV, respectively. The activity was measured 18 (black columns) and 64 days (grey columns) after the exposure. The activity of the un-irradiated sample was measured 47 days apart. The dashed line indicates the equilibrium ratio.

3.2. Picosecond Nd:YAG laser

3.2.1. Second harmonic (532 nm)

The exposure of a gold target to the second harmonic, which lies within the plasmon resonance of gold nanoparticles, in aqueous uranyl chloride solutions is also accompanied by a considerable deviation of nuclide activities from their equilibrium values. Figure 5 plots the activities of the three main nuclides in irradiated solutions against UO_2Cl_2 concentration. As seen, the ^{234}Th and ^{234m}Pa activities in the irradiated solutions markedly exceed those in the unirradiated solution, and the deviation of the activities increases with increasing concentration. At the same time, the ^{235}U activity in the same irradiated solutions coincides with its equilibrium value to within the present measurement accuracy.

3.2.2. Third harmonic (355 nm)

UV laser exposure of a gold target in an aqueous uranyl chloride solution leads to a considerable deviation of the $A_{^{234}Th}/A_{^{235}U}$ ratio from its equilibrium value. This activity ratio is shown in Fig. 6 as a function of uranium salt concentration in solution. From the data in Fig. 5, one can understand why this ratio varies with solution concentration. Laser exposure sharply reduces the ^{234}Th activity, whereas the ^{235}U activity changes little. That the activity ratio approaches its equilibrium value at high uranium salt concentrations seems to be caused by the fact that the solution absorbs the laser radiation while it travels towards the target. As a result, the rate of gold nanoparticle generation decreases with increasing salt concentration, and laser exposure has a weaker effect on the nuclide activities. Figure 7 shows normalised activities of
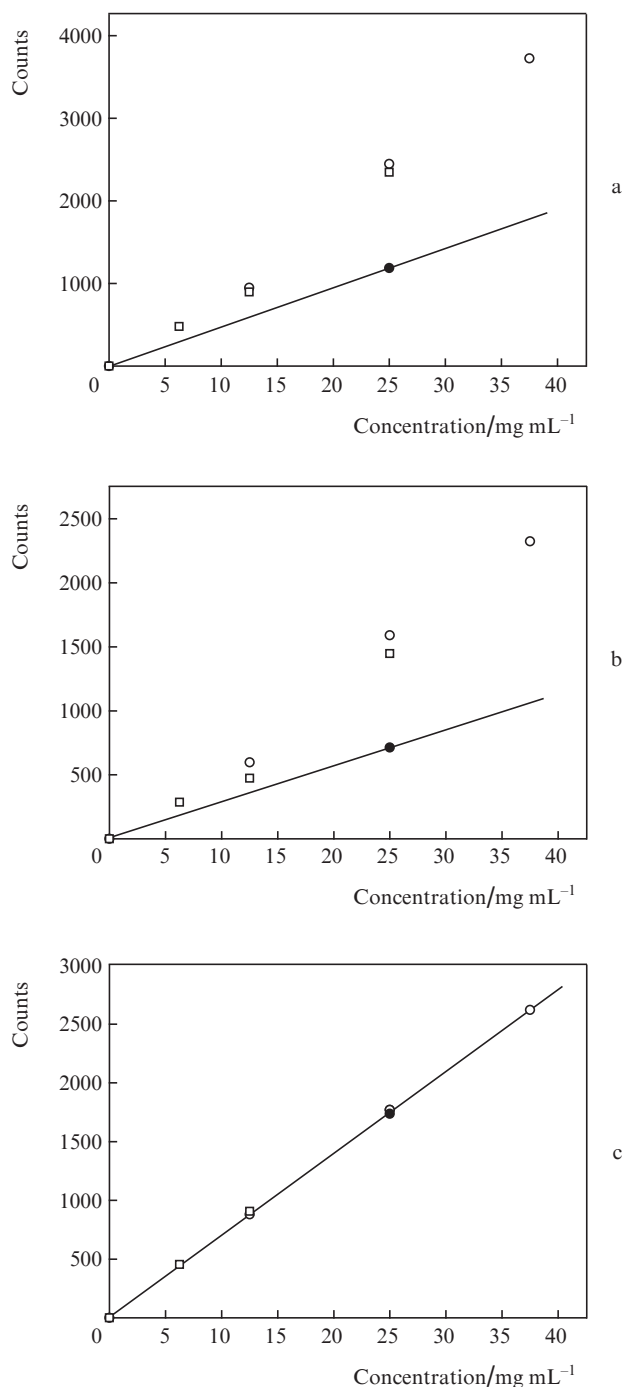

Figure 5. (a) ^{234}Th, (b) ^{234m}Pa and (c) ^{235}U activities (counts over 10^4 s) as functions of uranium salt concentration for uranyl chloride solutions in D_2O (o) and H_2O (□) containing gold nanoparticles and exposed to the second harmonic of a neodymium laser. The straight lines are drawn through the nuclide activities before the exposure (●).

the three nuclides in irradiated solutions at the lowest salt concentration. As in the case of 800-nm Ti:sapphire laser exposure, the Nd:YAG third harmonic reduces the nuclide activities, especially that of ^{235}U. The ^{234m}Pa activity in the irradiated sample was zero to within the present experimental uncertainty. It reached a measurable level only two months after the laser exposure. Moreover, the gamma spectra of irradiated samples contained peaks of nuclides (e.g. ^{214}Pb) that had not been detected before the laser exposure.
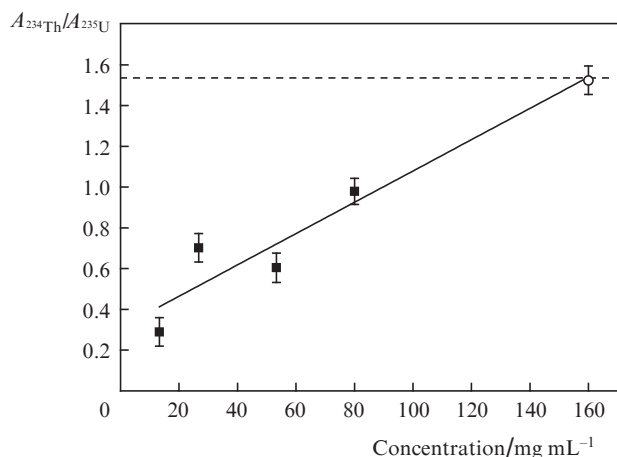
Figure 6. ^{234}Th/^{235}U activity ratio as a function of uranyl chloride concentration in D_2O after 36 000 pulses. The dashed line shows the equilibrium activity ratio, and the open circle represents the activity of the unirradiated sample.
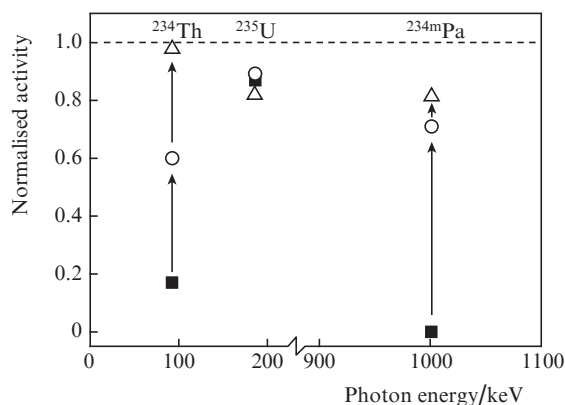

Figure 7. Normalised ^{234}Th (92.5 keV), ^{235}U (186.5 keV) and ^{234m}Pa (1001 keV) activities after laser exposure of a gold target. The activities are normalised to their values before the exposure. The measurements were made 28 (■), 66 (○) and 131 days (△) after laser exposure (36 000 pulses) in water at the uranyl chloride concentration of 13.3 mg mL^{-1}. The dashed line indicates the activity before the exposure. The vertical arrows show the change in activity between the measurements. The size of the symbols represents the experimental error.

Note that laser exposure had little effect on the ^{235}U activity.

4. Discussion

The present results demonstrate that laser exposure of gold nanoparticles in aqueous solutions of uranyl chloride of natural isotopic composition has a significant effect on the equilibrium activities of nuclides in the ^{238}U and ^{235}U series. No products other than those belonging to the ^{238}U series were detected after laser exposure to within the accuracy in our gamma-activity measurements. The sign of the deviation of uranium family radionuclide activities from their equilibrium values depends on the laser wavelength. At wavelengths away from the plasmon resonance of gold nanoparticles (800 and 355 nm), the ^{234}Th, ^{234m}Pa, and ^{235}U activities decrease to below their equilibrium values. Exposure to the Nd : YAG

second harmonic (532 nm), which is in resonance with gold nanoparticles, increases the ^{234}Th and ^{234m}Pa activities almost twofold (Fig. 5), whereas the ^{235}U activity in the same samples remains at its equilibrium level. The ^{238}U decay chain is

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta} {}^{234m}Pa \xrightarrow{\beta} {}^{234}U \xrightarrow{\alpha} \ldots .$$

The increase in ^{234}Th and ^{234m}Pa activities upon laser exposure attests to an accelerated ^{238}U alpha decay. The ^{234}Th activity follows the rate equation

$$\frac{d[^{234}Th]}{dt} = [^{238}U]\exp\left(-\frac{t}{t_{238_U}}\right) + k_1[^{238}U]$$

$$- k_2[^{234}Th] - [^{234}Th]\exp\left(-\frac{t}{t_{234_{Th}}}\right),$$

where the square brackets denote the nuclide concentration. The increase in activity is due to spontaneous ^{238}U alpha decay with a half-life t_{238_U} (negligible compared to the laser exposure time) and spontaneous ^{234}Th beta decay with a half-life $t_{234_{Th}}$ (also negligible). The rate constants k_1 and k_2 are determined by laser exposure. At a laser wavelength of 532 nm, the ^{234}Th activity increases through ^{238}U decay more rapidly than it decreases as a result of the laser exposure of the ^{234}Th nuclei. It may be that 800- and 355-nm laser exposures also increase the rate of ^{238}U alpha decay, but the decay rates of ^{234}Th and ^{234m}Pa are higher in this case, and their activities in the irradiated samples are lower than those in the unirradiated samples. To gain greater insight into this effect, the alpha activity of the ^{238}U should be measured, which can be done at considerably lower uranium salt concentrations in comparison with this study.

The mechanism underlying the influence of laser exposure on the rate of nuclear decays is not yet fully understood. Most likely, the electric field of an incident wave influences the potential in the electron shell. An important point is that the optical field is enhanced by the plasmon resonance of the electrons in nanoparticles. According to surface-enhanced Raman scattering data in the literature [12–14], the electric field of a laser wave can be enhanced at nanoparticles by a factor of 10^4 to 10^8, with a maximum at the plasmon resonance frequency. The field of the optical wave is enhanced by a factor of 10^2 to 10^4, which corresponds to a light intensity of 10^{16} to 10^{18} W cm^{-2} near the nanoparticles. The corresponding electric field strength ($E_{las} \sim 10^{10}$ V cm^{-1}) is comparable to the intra-atomic field strengths. Note that a laser beam of such intensity would be incapable of propagating through a liquid or air because of various nonlinear processes. Under the conditions of this study, this intensity is reached only near a nanoparticle, at a distance of the order of its radius (20–30 nm).

An electric field oscillating at the laser frequency may change both the height and width of the potential barrier to alpha particles, thereby influencing the probability of their tunnelling from the nuclei of uranium series nuclides. Indeed, the height and width of the barrier to alpha decays are governed by a superposition of the Coulombic potentials of the nucleus and all electrons in the atom. The polarisation of the electron shell of an atom by light changes the self-consistent intra-atomic field at the nucleus and distorts the potential barrier. The tunnelling probability is an exponential function of barrier parameters, so it is extremely sensitive to even slight changes in these parameters. Therefore, the effect of laser

exposure on nuclear decays has no intensity threshold, and a lower peak laser intensity in a medium can be compensated for in part by increasing the number of laser pulses. In particular, a measurable deviation of the activity of ^{238}U series nuclides is produced when a uranium salt solution containing gold nanoparticles is exposed to a copper vapour laser beam at an intensity of $\sim 10^{10}$ W cm^{-2} [9]. This laser source (the wavelength 510.6 nm corresponds to the plasmon resonance of gold nanoparticles) has a high repetition rate (10–15 kHz), which allows one to observe a significant deviation of nuclide activities from their equilibrium values at comparable exposure times.

Similarly, an electric field accelerates beta decays of ^{234}Th and ^{234m}Pa (^{238}U series). As shown for ^{187}Re [15], the beta decay probability is several orders of magnitude higher when the atom is fully ionised. Under the conditions of this study, it also cannot be ruled out that the electron shell of the uranyl ion experiences multiple ionisation in the field of the wave enhanced by the nanoparticles, producing changes in barrier height and uranium alpha decay probability.

Thus, laser exposure of gold nanoparticles in aqueous uranium salt solutions considerably accelerates alpha and beta decays of uranium series nuclides at a laser intensity of $\sim 10^{12}$ W cm^{-2}. As a result, the nuclide activities differ markedly from their equilibrium values. The deviation from equilibrium is largest when the laser wavelength lies within the plasmon resonance band of gold nanoparticles. It seems likely that the increased radionuclide decay rate is due to the optical field enhancement by the nanoparticles, which changes the height of the potential barrier to alpha-particle tunnelling. The results of this study are of practical interest for developing a new approach to radioactive waste deactivation.

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