Experimental Evidence of Transmutation of Hg into Au under Laser Exposure of Hg Nanodrops in D_2O

G. A. Shafeev[a]**, F. Bozon-Verduraz**[b]**, and M. Robert**[c]

[a] *Wave Research Center, Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *ITODYS, UMR CNRS 7086, Université Paris-7, 75251 Paris Cedex 05, France*
[c] *Laboratoire d'Electrochimie Moléculaire, UMR CNRS 7591, Université Paris-7, 75251 Paris Cedex 05, France*
E-mail: shafeev@kapella.gpi.ru

Abstract — Laser irradiation of suspensions of Hg nanodrops in D_2O induces partial transformation of Hg into Au. The Hg–Au conversion depends on the characteristics of the laser source used (Cu vapor, femtosecond Ti:sapphire, 90-ps Nd:YAG, 350-ps Nd:YAG) and on the initial Hg isotopic composition. For Hg of natural isotopic composition, the conversion gives the ^{196}Hg content close to initial (0.15 %). Starting with ^{196}Hg-enriched (52 %) Hg, the conversion yields 10 %. This transmutation is assigned to the generation of thermal neutrons during laser exposure of Hg nanodrops in D_2O. Possible mechanisms of neutron release are discussed.

INTRODUCTION

Excitation of nuclei in plasma produced by femtosecond laser radiation has been reported recently for both ^{181}Ta and ^{201}Hg nuclei [1, 2]. Laser plasma may contain hot electrons necessary for excitation of nuclear levels, which further decay with emission of γ-photons. A detailed review of the initiation of nuclear reactions in plasma produced on solid targets by ultrashort laser pulses, typically femtosecond, has been published recently [3]. This transformation (transmutation) may occur upon absorption of particles (e.g., neutrons) that do not need to overcome the potential barrier and can penetrate a nucleus due to their neutrality. X-rays with MeV energies have been observed under ablation of a Ta target in vacuum by femtosecond laser radiation with an estimated intensity of 10^{18} W cm^{-2} [4]. In this intensity range, electrons in the laser-produced plasma acquire relativistic velocities. These photons induce subsequent fission of a Be target and generation of thermal neutrons. It was proposed in [4] to use photoinduced neutron emission for transmutation of Hg into Au. In denser environment, e.g., in aqueous solutions of various salts exposed to femtosecond laser radiation, characteristic X-rays with

energies of about 10 keV are observed [5, 6]. Recent study of the so-called wake-field acceleration showed that a sufficiently intense laser beam propagating through a plasma may separate ions and electrons and thus induce a high electric field in which electrons acquire energies in the GeV range [7]. These energies exceed the binding energy of some nuclei and, therefore, may result in direct excitation of nuclear energy levels. Therefore, the energy required for initiation of nuclear reactions lies within the energy range of modern lasers.

Laser exposure of bulk targets has a serious drawback: shielding of the laser beam from the target by the plasma formed above it. Indeed, laser radiation is reflected from the plasma as soon as the plasma electron frequency exceeds the laser frequency. At the same time, nanoparticles are optically thin at the wavelengths of most generally used lasers. Despite small size (about 10 nm), these nanoparticles can effectively absorb laser radiation. The efficiency of this interaction is a function of numerous experimental parameters, such as the particle size, detuning of the laser frequency from the position of the plasmon resonance in nanoparticles, etc. However, in most cases

nanoparticles are optically thin (i.e., are almost transparent at the laser wavelength). Hence, the time required to reach nanoparticle temperature under laser exposure is shorter than the laser pulse duration as soon as the latter exceeds the electron-phonon relaxation time. The temperature of nanoparticles inside the laser beam is proportional to the peak laser power. Estimations show that the temperature of Au nanoparticles inside the Cu-vapor laser beam with a peak intensity of 10^8 W cm^{-2} is several kK, and this temperature changes linearly with the laser intensity [8–10]. In this case, the liquid surrounding nanoparticles turns into a vapor having a high temperature and pressure, and eventually into plasma that perfectly is confined around it. Laser initiation of neutron emission may open new possibilities for transmutation of elements, synthesis of desired isotopes, disposal of nuclear waste, etc. The medium chosen in this work is a suspension of nanoparticles in deuterium-containing liquids. This choice follows from our recent results on the interaction of laser radiation with nanoparticles immersed in liquids (colloidal solutions) [8–10]. One may expect that, at sufficiently high laser intensities, high-energy levels of the material and environment of nanoparticles become highly excited and initiate new processes. We have chosen a suspension of Hg in D_2O as a model system for laser-assisted transmutation of Hg into Au since the neutron-binding energy in D is the lowest [11].

EXPERIMENTAL

Two types of Hg were used: (i) Hg of analytical purity with a natural isotopic composition and (ii) enriched Hg containing 55.6 % ^{196}Hg and 41.4 % ^{199}Hg, with a much lower content of other isotopes. The latter type was obtained by selective photochemical reaction of Hg with oxygen [12].

Four types of laser sources were used:

(i) A Cu-vapor laser with wavelengths 510 and 578 nm, pulse width 20–30 ns, repetition rate 10 kHz, and energy per pulse up to 100 μJ. The intensity at the focal point in the suspension was estimated to be 2×10^8 W cm^{-2}.

(ii) A femtosecond Ti:sapphire laser with wavelengths either 810 or 405 nm (frequency-doubled mode), energy per pulse up to 900 μJ at 810 nm, pulse duration 120 fs, repetition rate 1 kHz, and beam peak intensity in the liquid 2×10^{12} W cm^{-2}.

(iii) A Nd:YAG laser with pulse duration 90 ps, wavelength 1.06 μm, energy per pulse up to 40 mJ,

repetition rate 10 Hz, and estimated peak intensity 10^{13} W cm^{-2}.

(iv) A Nd:YAG laser with pulse duration 350 ps, wavelength 1.06 μm, energy per pulse 350 μJ, repetition rate 300 Hz, and peak intensity 10^{10} W cm^{-2}.

Prior to laser exposure of Hg suspensions, a Hg drop was dispersed in a liquid in a cylindrical glass cell using a standard ultrasonic bath. Then the obtained suspension was divided into two parts, one of which was used as the initial suspension for further analysis and the other was subjected to laser exposure. In some cases, the dispersion of Hg drops in D_2O was obtained by exposure to a focused laser beam through the glass wall of the cell. This technique facilitates the primary dispersion of Hg and its final dispersion in an ultrasonic bath. Laser exposure was carried out either through the free liquid surface or through a cell wall which is almost transparent at the laser wavelengths used.

Analysis of the Hg suspensions was carried out using atomic absorption spectroscopy (*Hitachi*). The suspension was atomized either electrothermally or in an inductively coupled plasma. The concentration of elements was measured from their absorption or emission, respectively. Prior to measurements, the suspension was treated with aqua regia to dissolve any solid components including Au. The sensitivity of metal detection is typically 3 μg l^{-1}. The laser-exposed samples was analyzed several weeks after the exposure to exclude detection of any unstable Au isotopes that might have been formed, since they decay back to Hg within several days.

RESULTS

Using either a Cu-vapor laser (8-h exposure) or a Ti:sapphire laser (2-h exposure), no Au content was detected within the accuracy of measurements. The absorption peak at 470 nm [11], which is observed in the spectra of the exposed suspensions in both cases, is tentatively assigned to HgO. Another peak in the range 270–290 nm [11] is also present in the spectrum of the initial suspensions recorded prior to their laser exposure. This peak is assigned to the plasmon resonance of Hg nanoparticles, which is close to the theoretical position of 290 nm reported for 10-nm Hg nanoparticles in H_2O [13]. Therefore, at the initial stages, exposure of Hg suspensions to laser radiation leads to the formation of Hg nanoparticles about 10 nm in size.

After an exposure to 90-ps Nd:YAG laser radiation, the suspension precipitates very slowly, unlike
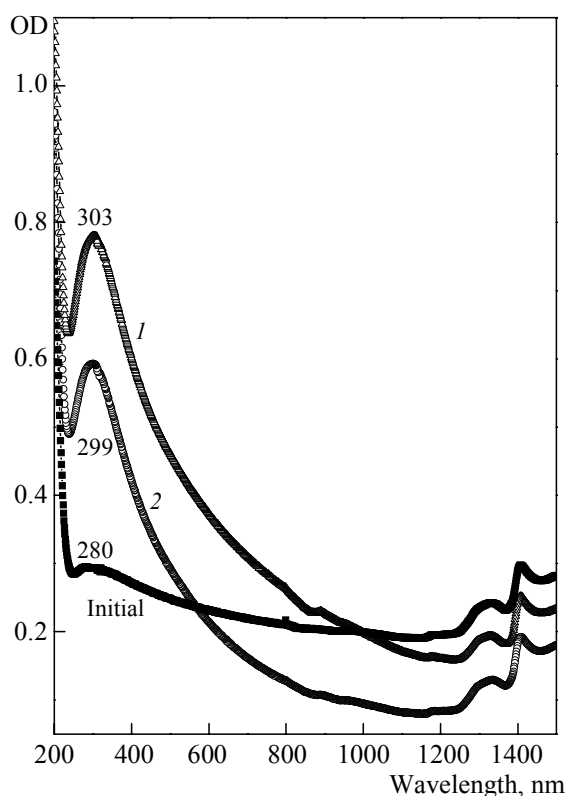
Optical density of a Hg suspension in D_2O exposed to 90-ps Nd:YAG laser radiation: (*1*) the part near the bottom of the cell after 24-h sedimentation and (*2*) the colloid remaining in the liquid after the 24-h sedimentation.

a freshly prepared suspension in an ultrasonic bath. After 1-day sedimentation, the liquid separated into two parts, the one located near the bottom and the other remaining in the suspension (the figure, Table 1). The analytic data listed in Table 1 show the formation of Au.

The optical spectra of these parts are shown in the figure. The peak observed at 299–303 nm is much more intense than the initial peak at 280 nm that is attributed to the plasmon resonance of Hg nanoparticles (as previously). This feature and the broad shoul-

Table 1. Analysis of Hg samples of natural isotope composition exposed to 90-ps Nd:YAG laser irradiation during 60 min.

Sample	Hg in D_2O initial	Hg in D_2O sample 1	Hg in D_2O sample 2
Hg, mg l^{-1}	35	23	8
Au, mg l^{-1}	0.009	0.1	0.024
Au/Hg ratio	0.00026	0.0043	0.003

der toward higher wavelengths could indicate a contribution of the Au plasmon resonance (is usually recorded near 520 nm) or Au–Hg alloys.

The formation of Au from a suspension of Hg with the natural isotope abundance occurs also if D_2O is mixed with deuterated dimethylsulphoxide $(CD_3)_2SO$ in 1:1 ratio.

Experiments with the 350-ps Nd:YAG laser irradiation were carried out on two types of Hg samples, either of natural isotopic composition or enriched with ^{196}Hg. The latter sample is designated below as ^{196}Hg. The results of the analysis of the Hg suspension of natural isotope composition in D_2O are similar to those obtained with the 90-ps laser. The formation of Au in the exposed suspensions of Hg in D_2O is confirmed analytically, though Au/Hg ratio is generally lower.

The results of the analysis for Hg enriched with ^{196}Hg are given in Table 2. Note that Au content is found under laser exposure of a Hg drop immersed into D_2O for about 10 min in order to disperse the metal. Four-hour laser exposure increases the Au content to almost 10 %. The last sample (after sedimentation) was taken from the entire cell, including Hg deposited on its inner walls.

DISCUSSION

Hg is a mixture of isotopes with various atomic masses A, and the abundance of stable isotopes in natural Hg is as follows: $A = 196$ (0.15 %), 198 (10.02 %), 199 (16.84 %), 200 (23.13 %), 201 (13.22 %), 202 (29.79 %), and 204 (6.85 %). The only stable isotope of Au is ^{197}Au. Fast neutrons induce transmutation of natural Hg into unstable Au isotopes that transform back to Hg within few days through β-decay. In nuclear physics, transmutation of elements is an ordinary process, and transmutation of Hg into Au under bombardment of a Hg target with fast neutrons was observed as early as in 1941 [14]. Another possibility of transmutation of Hg into Au is interaction of ^{196}Hg with slow (thermal) neutrons: $^{196}Hg + n \rightarrow {}^{197}Hg + \gamma$, where γ stands for a γ-photon. The cross section of this (n, γ) reaction is 3.08×10^{-25} m^2, which exceeds by several orders of magnitude the cross sections of (n, γ) reactions with other Hg isotopes (~10^{-27} m^2), except for ^{199}Hg [15]. However, the latter transforms into a heavier Hg isotope rather than into ^{197}Au. ^{197}Hg decays within 23.8 h into ^{197}Au through electron capture from its own K shell [15]: ^{197}Hg ($Z = 80$) + e$^-$ $\rightarrow {}^{197}Au$ ($Z = 79$). This process was also realized in 1947 using Chicago cyclotron facilities.

Table 2. Exposure of ^{196}Hg suspension in D_2O to 350-ps Nd:YAG laser radiation. The results are averaged over four different exposures.

Sample	^{196}Hg/D_2O initial	^{196}Hg/D_2O exposed Hg drop	^{196}Hg/D_2O 4-h exposure (averaged over four samples)	^{196}Hg/D_2O after sedimentation
Au, mg l^{-1}	0.0073	0.38	0.23	0.17
Hg, mg l^{-1}	20	8.94	2.31	12.6
Au/Hg	0.00036	0.0425	0.10	0.0135

Analysis of Hg suspensions in D_2O shows partial transformation of Hg into Au for picosecond laser irradiation with pulse widths from 90 to 350 ps. For natural Hg, the Au/Hg ratio is close to the natural ^{196}Hg/Hg ratio due to the large cross section of neutron capture by this isotope. In the ^{196}Hg-enriched sample (55.6%) exposed to this laser radiation, the Au/Hg ratio is much larger, up to 0.10. With respect to the ^{196}Hg content in this sample, the transformation is almost twice more intense (0.2). Assuming the measurements of the Au content in Hg samples to be precise and reliable, we may conclude that the observed transformation is only possible if the laser exposure of Hg in D_2O is accompanied by emission of thermal neutrons. Apparently, these neutrons are produced from D_2O, as is confirmed by the shift of its vibrational overtones. Indeed, the Raman spectrum of the liquid after exposure to 350-ps laser irradiation indicates the presence of HDO molecules, which are absent in the initial liquid. No traces of H_2O were found within the accuracy of measurements. Formation of HDO molecules might be attributed to neutron release from D_2O. The neutrons are released for any isotope composition of Hg, and the use of ^{196}Hg instead of natural Hg only enhances the effect of transmutation. In this sense, the main result of this work is the production of thermal neutrons under laser exposure of metallic nanoparticles in D_2O, while the Hg-Au transformation is a probe reaction confirming this process.

An interesting feature is the relatively high Au content obtained at the stage of laser-assisted dispersion of a Hg drop prior to irradiation. In this stage, the concentration of Hg nanodrops inside the laser beam is much higher than when nanodrops are dispersed in the entire volume of the liquid.

The lower peak intensity of the 350-ps Nd laser (10^{10} W cm^{-2}) as compared to that of the 90-ps one (10^{13} W cm^{-2}) may result in a comparable amount of Au in an exposed Hg/D_2O suspension after longer exposure. Indeed, the typical number of laser pulses of a 350-ps laser is about 10^6, while this value is about 10^4 for the more powerful 90-ps laser. This means that only a small fraction of generated X-ray photons have energies sufficient for neutron release. At the same time, about 10^8 pulses of a Cu-vapor laser at an intensity of 10^8 W cm^{-2} are not sufficient to produce any measurable amount of Au.

We suggest the following mechanism of neutron release. Laser radiation ionizes nanoparticles and the shell around them. Collisions of hot electrons with nanoparticles lead to the generation of X-rays. The energy of some X-ray photons should exceed the binding energy of a neutron in D to causes its release. This hypothesis explains the absence of Au–Hg transformation under femtosecond laser irradiation. Indeed, in this case the suspension is ionized after the laser pulse as soon as all excited electrons in nanoparticles are thermalized. A longer pulse, e.g., of picosecond duration, produces laser plasma and then heats it.

The reflection of the incident laser radiation by the plasma is the main drawback of laser heating of bulk targets. As soon as the electron density reaches the critical value, the target is shielded from the laser beam. This reflection is insignificant for nanosized materials since the plasma optical density around each nanoparticle is too small to cause reflection of laser radiation. Therefore, the interaction of laser radiation with the plasma surrounding each nanoparticle in the laser beam may continue even if the electron density in it exceeds that corresponding to the plasma frequency. Due to the small size of a nanoparticle, the density of X-ray photons around it is extremely high, and neutron generation from the surrounding D_2O can be efficient even when the number of X-ray photons of necessary energy is small. The advantage of nanosized targets over bulk ones for generation of high-energy photons was underlined in [3]. It was suggested in [3] that the main role of the small size of the target (porous Si) components is the increase in their

specific surface. In our opinion, laser exposure of metallic nanoparticles is also characterized by local enhancement of the electric field of laser radiation. This effect is well known from surface-enhanced Raman scattering observations.

The collapse of gas bubbles [16] around nanoparticles might contribute to both their temperature and pressure, though in our case the main contribution to the increase in the temperature of Hg nanodrops is due to the direct absorption of the laser beam energy. Metallic nanoparticles may serve as a source of electrons via field emission. The nanoparticle radius is small, and even a small potential difference with respect to the surrounding liquid (for example, due to the specific adsorption of some ions from the liquid) would result in a strong electric field extracting electrons from it. The high temperature of the nanoparticles exposed to laser radiation enhances the electron emission even more. Observation of neutron release at a moderate laser intensity of 10^{12}–10^{13} W cm^{-2} is tentatively assigned to the enhancement of the electromagnetic field induced by the laser radiation at Hg nanoparticles.

The next step in studying the transmutation of Hg into Au, described above, should be direct observation of neutrons from the laser-exposed suspension of Hg nanodrops in D$_2$O. Preliminary measurements using a Cramal 31 calibrated neutron counter indicate the presence of neutrons in suspensions of various nanoparticles (Au, C, etc.) in D$_2$O exposed to 90-ps Nd:YAG laser radiation. The neutron flux exceeds the background noise by a factor of four and is typically about 30 µS (micro-Sivert) after a 30-min exposure. Further measurements including detection of X-rays from laser-irradiated nanoparticles are in progress.

CONCLUSION

The observed transmutation of Hg into Au under laser exposure of Hg nanodrops suspended in D$_2$O indicates production of thermal neutrons. This production occurs at moderate intensities of picosecond laser pulses (about 10^{12} W cm^{-2}). It is suggested that neutrons are released from deuterium under absorption of high-energy X-ray photons generated in the plasma shell surrounding nanoparticles under laser irradiation. The local enhancement of the laser field may be due to the presence of Hg nanodrops.

ACKNOWLEDGEMENTS

REFERENCES

1. A. V. Andreev, R. V. Volkov, V. M. Gordienko, P. M. Mikheev, A. B. Savel'ev, E. V. Tkalya, O. V. Chutko, A. A. Shashkov, and A. M. Dykhne, "Excitation of Tantalum-181 Nuclei in a High-Temperature Femtosecond Laser Plasma," JETP Lett. **69**(5), 371 (1999).

2. A. V. Andreev, V. M. Gordienko, A. B. Savel'ev, E. V. Tkalya, and A. M. Dykhne, "Excitation of Nuclei in a Hot, Dense Plasma: Feasibility of Experiments with ^{201}Hg," JETP Lett. **66**(5), 331 (1997).

3. A. V. Andreev, V. M. Gordienko, and A. B. Savel'ev, "Nuclear Processes in a High-Temperature Plasma Produced by an Ultrashort Laser Pulse," Quantum Electron. **31**(11), 941 (2001).

4. H. Schwoerer, P. Gibbon, S. Düsterer, R. Behrens, C. Ziener, C. Reich, and R. Sauerbrey, " MeV X Rays and Photoneutrons from Femtosecond Laser-Produced Plasmas," Phys. Rev. Lett. **86**(11), 2317 (2001).

5. K. Hatanaka, T. Miura, and H. Fukumura, "Ultrafast X-Ray Pulse Generation by Focusing Femtosecond Infrared Laser Pulses onto Aqueous Solutions of Alkali Metal Chloride," Appl. Phys. Lett. **80**(21), 3925 (2002).

6. K. Hatanaka and H. Fukumura, "X-Ray Generation from Optical Transparent Materials by Focusing Ultra-Short Laser Pulses," in *Three-Dimensional Laser Microfabrication: Principles and Applications*, Ed. by H. Misawa and S. Juodkazis (Wiley-VCH, 2006), Ch. 9, p. 199.

7. A. Pukhov and J. Meyer-ter-Vehn, "Laser Wake Field Acceleration: the Highly Non-Linear Broken-Wave Regime," Appl. Phys. B. **74**, 355 (2002).

8. S. I. Dolgaev, A. V. Simakin, V. V. Voronov, G. A. Shafeev, and F. Bozon-Verduraz, "Nanoparticles Produced by Laser Ablation of Solids in Liquid Environment," Appl. Surf. Sci. **186**, 546 (2002).

9. F. Bozon-Verduraz, R. Brayner, V. V. Voronov, N. A. Kirichenko, A. V. Simakin, and G. A. Shafeev, "Production of Nanoparticles by Laser-Induced Ablation of Metals in Liquids," Quantum Electron. **33**(8), 714 (2003).

10. G. A. Shafeev, E. Freysz, and F. Bozon-Verduraz, "Self-Influence of a Femtosecond Laser Beam upon Ablation of Ag in Liquids," Appl. Phys. A. **78**, 307 (2003).

11. G. A. Shafeev, F. Bozon-Verduraz, and M. Robert, Preprint No. 45, GPI RAN (Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Apr. 12, 2006).

12. Yu. V. Vyazovetskii and A. P. Senchenkov, "Production of Highly Enriched Mercury Isotopes by a Photochemical Method," Tech. Phys. **43**(1), 60 (1998).

13. J.A. Creighton and D.G. Eadon, "Ultraviolet–Visible Absorption Spectra of the Colloidal Metallic Elements," J. Chem. Soc. Faraday Trans. **87** (1991) 3881.

14. R. Sherr, K. T. Bainbridge, and H. H. Anderson, "Transmutation of Mercury by Fast Neutrons," Phys. Rev. **60**, 473 (1941).

15. *Handbook on Physical Data*, Ed by I. S. Grigoriev and E. Z. Meilikhov (Energoatomizdat, Moscow, 1991) [in Russian].

16. R. P. Taleyarkhan, C. D. West, J. S. Cho, R. T. Lahey, Jr., R. I. Nigmatulin, and R. C. Block, "Evidence for Nuclear Emissions During Acoustic Cavitation," Science. **295**, 1868 (2002).