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Selective Laser Heating and Nonlinear Light Scattering in a Homogeneous Medium

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Abstract. Observation of light scattering on the laser-produced temperature inhomogeneities, the centres of which are connected with some absorbing molecules, is reported. The experimentally observed scattering intensity agrees well theory.

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Let us consider a transparent liquid that contains a small amount of molecules absorbing the light with the wavelength λ. Since with quenching collisions practically the whole absorbed energy is converted into heat, each absorbing molecule is a point source of heat. In the steady-state case the deviation of the temperature from the average temperature around the point source of heat is of the form: $\Delta T(r) = P/4\pi\kappa r$, P being the amount of heat released per unit time, and κ the thermal conductivity coefficient. We shall consider r to be minimum for which the following formula is applicable: $r_1 = 2.5/\sqrt[3]{n_1}$, n_1 being the liquid molecule concentration. For water $r_1 \approx 7.8 \times 10^{-8}$ cm. With the absorption cross-section $\sigma = 1.5 \times 10^{-15}\,\mathrm{cm}^2$ and the intensity of laser radiation of $I_0 = 1\,\mathrm{GW/cm}^2$ $P = \sigma I = 15$ erg/s, $\Delta T(r_1) \approx 260$ K. Considerable heating of the medium in the nearest vicinity of the absorbing molecule can give various results, particularly, peculiar nonlinear light scattering that can be an indicator of this phenomenon. Since a refractive index depends on temperature, each absorbing molecule is the centre of optical inhomogeneity, the quantity of which is proportional to an incident light intensity. In its physical content, the light scattering is due to these inhomogeneities differs qualitatively from both the nonlinear scattering on small particles [1] and the scattering to the thermal gratings produced by interference of two light beams [2]. The present paper reports on an observation of this new type of nonlinear light scattering in an optically homogeneous medium.

Theory

Let us estimate the quantity of the phenomenon. Let the concentration of absorbing molecules, n_{eff}, be such that an average distance between them would be $l = n_{\mathrm{eff}}^{-1/3} \ll \lambda$. Here we take into account the fact that not all molecules of an impurity participate in the process of absorption, and n_{eff} can be several orders smaller than the overall concentration n, because of inhomogeneous broadening and a non-unity statistical weight at the lower working level. The quantity l determines not only the distance between inhomogeneities but in the steady-state case also their size. The resonance-frequency drift of impurity molecules within the limits of the inhomogeneous linewidth results in the fact that the optical inhomogeneities appear and disappear when the molecule is in and out of resonance. Their average number remains constant. We shall therefore assume that the radiation scattered by different inhomogeneities is generated incoherently. In this case one may use the known formula for the Rayleight scattering of a linearly polarized light [3]:

$$I_S = I \frac{\pi^2}{\lambda^4 r^2} N \Delta\varepsilon^2 v^2 \sin^2\varphi\,, \tag{1}$$

where I, I_S are the intensities of incident and scattered light, N is the number of inhomogeneities in the observed volume V, $\Delta\varepsilon$ is the root-mean-square deviation of permittivity in the inhomogeneity, v is the inhomogeneity volume, φ is the angle between the vector of the incident radiation field and the observed direction. The quantity $B=N\Delta\varepsilon^2 v^2$ consists, in our case, of two parts. The first one corresponding to an ordinary molecular scattering is denoted by $B_0=VA$. The second part initiated by laser radiation is

$$B_i=Vn_{\mathrm{eff}}(\textstyle\int\Delta\varepsilon dV)^2$$

$$=Vn_{\mathrm{eff}}\left(\frac{d\varepsilon}{dT}\right)^2(\textstyle\int\Delta TdV)^2, \qquad (2)$$

where

$$\textstyle\int TdV=\frac{\tau\sigma I}{\delta\varrho} \quad \text{for} \quad \tau\ll l^2/4a$$

$$=\frac{l^2\sigma I}{2\kappa} \quad \text{for} \quad \tau\gg l^2/4a\,.$$

Here δ is the specific heat, ϱ is the liquid density, τ is the pulse duration of the incident light, σ is the cross-section of light absorption of a given wavelength, a is the thermal conductivity.

The $\int\Delta\varepsilon dV$ integral in (2) corresponds to one "average" inhomogeneity; the resulting effect is obtained by multiplication with the number of inhomogeneities Vn_{eff}. The solution of $\int\Delta TdV$ is derived from the solution of the heat-conduction equation for one point heat source. With short pulse duration ($\tau\ll l^2/4a$) the maximum inhomogeneity size is $(4a\tau)^{1/2}\ll l$ and the inhomogeneities do not overlap. In the stationary case ($\tau\gg l^2/4a$) the presence of inhomogeneities is allowed for in the following way. We assume the inhomogeneity to be a ball with radius l, the temperature inside the inhomogeneity being described by the expression $\Delta T(r)=P/4\pi\kappa r$ up to $r=l$. In the centre of the inhomogeneity the influence of neighbours on ΔT is negligible, as $l\gg r_1$.

Finally, (1) acquires the following form

$$I_S(I)=I\frac{\pi^2 V}{\lambda^4 r^2}A\sin^2\varphi[1+c(I)]\,, \qquad (3)$$

$$c(I)=\frac{1}{3}\frac{n_{\mathrm{eff}}}{A}\left(\frac{d\varepsilon}{dT}\right)^2\left(\frac{\tau\sigma I}{\delta\varrho}\right)^2$$

$$\text{for} \quad \tau\ll l^2/4a \qquad (4)$$

$$=\frac{n_{\mathrm{eff}}}{A}\left(\frac{d\varepsilon}{dT}\right)^2\left(\frac{l^2\sigma I}{2\kappa}\right)^2$$

$$\text{for} \quad \tau\gg l^2/4a\,. \qquad (5)$$

The additional factor 1/3 in (4) arises from time averaging from 0 to τ. The estimates for given conditions of our experiment will be presented below.

Experiments

The experiment has been made in the installation presented schematically in Fig. 1. A radiation source is the YAG:Nd laser operating at a repetition rate of 12.5 Hz and a wavelength of 0.53 µm in the regime of single transverse modes. The generation-pulse duration τ is 20 ns, the maximum energy in a pulse 1.2 mJ. The laser radiation is focused by a spherical or cylindrical lens into the cell with a water solution of iodine. The radiation intensity varies by a factor of 10^3 with a set of light filters. The maximum radiation intensity at the lens focus is 250 MW/cm². The scattered radiation intensity is recorded by a photomultiplier in the direction perpendicular to the direction of propagation of the laser radiation. The signal from the photomultiplier is observed by an oscillograph. The laser-radiation intensity is controlled by a photodiode.

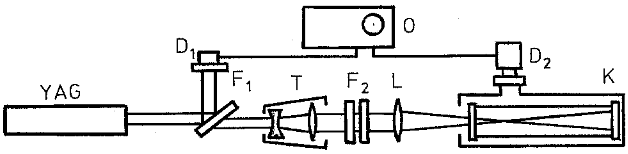

Fig. 1. Experimental arrangement

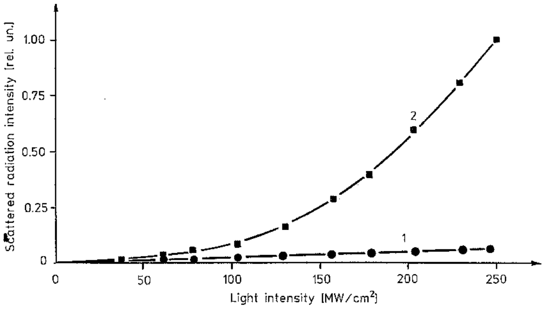

Fig. 2. Scattered versus incident radiation

In the experiment we have obtained the dependences of the intensity of the scattered radiation on that of the incident laser radiation $I_S(I)$ for a distilled water and a weak solution of iodine ($n=2.8\times10^{17}\,\mathrm{cm}^{-3}$) shown in Fig. 2. The linear dependence for distilled water corresponds to an ordinary Rayleight scattering. The continuous curve is drawn by the method of least squares based on (4). At the maximum intensity the coefficient c measured in this way is $c(I_{\max})\approx15$. The absorption factor, with the given iodine concentration, is $\alpha=0.21\,\mathrm{cm}^{-1}$, the absorption line halfwidth is $\Delta\omega=3.4\times10^{14}\,\mathrm{cm}^{-1}$ ($\Delta\lambda=50\,\mathrm{nm}$).

In the process of the experiment we also observed the dependence of the absorption factor of the solution on the incident radiation intensity. No saturation was observed.

With a cylindrical lens used, the scattering intensity is independent of the angle between the cylinder axis and the observation direction. A conclusion can be made that the observed scattering is not induced, as it follows from our model. This is the principal difference of the observed phenomena from the induced thermal scattering [4].

The above-described experiments were carried out in the solution passing through the filters with 0.8 μm pores. With the filters having 10 μm pores we observed, when studying the scattering, the following phenomenon. At the first moment after the laser has started operating, the scattering intensity is maximum, then for 0.2–0.3 s decreases and becomes a steady-state one. The steady-state value of the scattering intensity corresponds to the scattering intensity in a well-filtered solution. The dependence of the gain of the scattering intensity at the first moment on the intensity of incident laser radiation is practically a linear one. The duration of establishment of the steady-state value of the scattering intensity decreases with an increase in laser-radiation intensity. A flash-up in the intensity was observed when the cell with the solution was moved perpendicularly to the laser beam.

These facts appear to be explainable by an ordinary Rayleigh scattering on the complexes of 1–10 μm in size occurring in a poorly filtered solution. Under laser radiation these complexes are destroyed which results in establishment of the steady-state conditions.

Discussion of Results

First of all, we shall estimate the value of n_{eff}. Let us assume that the relaxation time for an iodine molecule in water is $\tau_r = 10^{-12}$ s. Accordingly, the homogeneous halfwidth is $\Gamma = 10^{12}\,\text{s}^{-1}$. The absorption factor is found from the formula:

$$\alpha = \frac{8\pi^2 |d|^2 n_{\text{eff}}}{\lambda \hbar \Gamma}, \tag{6}$$

where d is the dipole moment of an electronic transition, $n_{\text{eff}} = ng\Gamma/\Delta\omega$. Low-frequency oscillations typical of liquids and molecular crystals [3] are allowed for by using a statistical weight g. According to [5], for the electron $B \leftrightarrow X$ transition of an iodine molecule $d \approx 1D = 10^{-18}$ cm g s. Consequently, from (6) $n_{\text{eff}} = 1.4 \times 10^{14}\,\text{cm}^3$, which corresponds to $g = 0.17$. Further $l \approx 2 \times 10^{-5}$ cm, $l^2/4a = 65$ ns, $\sigma = \alpha/n_{\text{eff}} = 1.5 \times 10^{-15}\,\text{cm}^2$, $\sigma I = 3.75$ erg/s. Since $\tau < l^2/4a$, we use (5) to estimate c. Inserting $A = 10^{-24}\,\text{cm}^{-1}$ [Ref. 3, p. 121] and $(d\varepsilon/dT)^2 = 5.23 \times 10^{-8}\,\text{K}^{-2}$ we obtain $c(I_{\max}) = 7.8$ as compared to $c(I_{\max}) = 15$ experimentally measured. With allowance for the estimation character of the used formula, the agreement should be considered to be good. This allows the conclusion on the validity of the chosen model and on the availability of considerable temperature inhomogeneities around an iodine molecule that are in resonance with the laser radiation. In accordance with the estimates made and with $I = 250\,\text{MW/cm}^2$ ΔT in the centre of the inhomogeneity is 65 K, with an average water heating in the focus 0.4 K.

Conclusion

Absorption of the laser radiation by some molecules causing considerable local medium heating allows selective thermal chemical reactions, disruption of biomolecules and so on. We shall report later on the selective chemical reaction on the surface under the action of high-power laser radiation. The influence of local temperature fluctuations on chemical reactions during the radiation absorption was already discussed in [6].

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