Controlling the water nonlinear refractive index in the THz frequency range via temperature variation

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To create self-controlled radiation photonics systems, it is necessary to have complete information about the nonlinear properties of the materials used. In this paper, the vibrational mechanism of the giant low–inertia cubic nonlinearity of water in the terahertz frequency range is experimentally proven. Its dominance which manifests itself when the temperature of the liquid changes is demonstrated. The measured nonlinear refractive index in the THz frequency range for water jet at temperatures from 14°C to 21°C demonstrates a correlation with the theoretical approach, varies from 4 to $10^{-10}$ cm$^2$/W and is characterized by an inertial time constant of less than 1 ps.

I. INTRODUCTION

In recent years the area of nonlinear terahertz (THz) photonics develops intensively. This process results from recent investigation of high-intensity THz radiation sources [1], which might show applicability in communications [2], non-destructive evaluation [3, 4], light-control devices etc. [5–7].

THz sources of ultrafast pulses gave an opportunity to construct devices which can control radiation parameters due to nonlinear effects of pulses self-modulation [8–10]. However, there is still a problem with gaining high intensities, which is essential to observe nonlinear effects.

In 2015 authors of [11] supposed that dominant mechanism of nonlinearity in THz spectral range is based on anharmonic oscillations of atoms which the molecules of matter consist of. That theory predicted a giant nonlinear refractive index of some liquid and crystal materials in THz range [11, 12]. Later, various scientific groups reported experimentally obtained giant value of nonlinear refractive index in liquid water and some other liquids and crystals via different methods (e.g. z-scan, full-phase analysis) [13–17]. These discoveries proved for the theory of vibrational nonlinearity in THz range and opened wide perspectives for using nonlinear effects in ultrafast THz photonics.

The analytical formula for nonlinear refractive index contains thermal expansion coefficient in power of two, which depends on temperature. In the case of liquid water this coefficient equals to zero near 4°C, which must result in zero nonlinear refractive index at this temperature. The authors of [18] reported that the nonlinear response of liquid water at 1 THz is similar at 21°C and 4°C and, based on that result, declared that the theory of vibrational nonlinearity in THz range is the wrong one. However, it is worth noting that there is no reason to estimate the nonlinear response of the refractive index in the THz frequency range based on nonlinear absorption. Direct contribution to the nonlinear refractive index in THz frequency range comes from the resonant interaction of oscillations in the IR range (100 THz = 3 μm), and not in the THz. To experimentally demonstrate this statement, we conducted a series of experiments on temperature dependency of liquid water nonlinear refractive index measurements and compare it with the curve calculated via theory of vibrational nonlinearity. The measurements were provided by z-scan method with central frequency of single-cycle pulse at 0.75 THz. The results obtained show the possibility of controlling the nonlinear properties of water by changing its temperature and confirm the vibrational nature of the nonlinearity in the THz frequency range. This can be used to create devices for ultrafast THz photonics.

II. EXPERIMENTAL SETUP

The nonlinear refractive index $n_2$ of water temperature dependence verification consisted of a series of experiments based on the classical z-scan method [19] using a pulsed THz radiation source based on a lithium niobate crystal (see Supplemental material [20], Section A for details). The experimental setup is shown in Fig. 1.

The generation of a high-intensity THz field is carried out due to the effect of optical rectification in a MgO:LiNbO$_3$ crystal [21] of a femtosecond optical pulse with the following parameters: pulse energy 1 mJ, pulse duration 35 fs, center wavelength 790 nm and repetition rate 1 kHz. The intensity of THz radiation when focused by
a parabolic mirror with a focal length of 1 inch is 10^8 W/cm^2.

A distinctive feature of the experiment was the use of a liquid jet [22] rather than a cell, which, as shown in our previous works [13, 16], makes it possible to avoid the cumulative thermal effect that can affect the nonlinearity. The water temperature was controlled by a cooling unit in a jet formation system similar to that presented in [23], the temperature varying from 14°C to 24°C. The sensitivity of evaluation method and features of cooling system do not permit operating on temperatures below 14°C due to an increase in measurement error. To move along the radiation propagation axis, the nozzle was mounted on a linear translator. The measurement of the THz field distribution was carried out using the method of open and closed aperture [19], in order to exclude the influence of nonlinear absorption on the results.

### III. RESULTS AND DISCUSSION

Figure 2 shows the resulting z-scan curves obtained by dividing the data from a closed aperture case by the data with an open aperture case. These curves were normalized to the THz pulse energy in the linear propagation mode. The jet displacement range along the radiation propagation axis was 10 Rayleigh lengths. The Rayleigh length with the focusing parameters used is 0.96 mm.

As can be seen from Fig. 2, the peak-to-valley ratio changes drastically with water temperature. The higher it is, the greater the difference. Using the standard formula for calculating \( n_2 \) from the ratio [19], while satisfying the recommendations for working with few-cycle pulses [24], the values of \( n_2 \) for different temperatures were obtained. They are presented in Table I (see Supplemental material [20], Section B for details).

| \( t \) °C | 14  | 16  | 17  | 18  | 18.5 | 20  | 21  |
|----------|-----|-----|-----|-----|------|-----|-----|
| \( n_2 \), \( 10^{-10} \text{ cm}^2/\text{W} \) | 4.2 | 5.3 | 6.5 | 6.8 | 7.8  | 9.5 | 9.7 |

Using the mathematical model of the non-resonant vibrational contribution to the nonlinear refractive index [11] (see Supplemental material [20], Section C for details), the dependence of \( n_2(t) \) on temperature can be written as follows:

\[
  n_2^{\omega<\omega_0}(t) = \frac{3a^2m^2\omega_0^3\alpha_T(t)}{32n_0\pi^2N^2k_B} \left[ (n_0^{\omega<\omega_0})^2 - 1 \right]^3 - \frac{9}{32\pi NN_0\hbar\omega_0} \left[ (n_0^{\omega<\omega_0})^2 - 1 \right] (1)
\]

It can be seen that the only term in the expression [1] that depends on temperature is the thermal expansion coefficient \( \alpha_T(t) \), the values of which for water were obtained in [25].

Figure 3 shows the dependence of \( n_2 \) on temperature for water, calculated by the formula (1) according to the values of the thermal expansion coefficient \( \alpha_T(t) \) and superimposed on experimental data.

Experimental data sets were taken independently from each other to confirm the repeatability. The results obtained demonstrate that a decrease in water temperature leads to a decrease in the value of \( n_2 \), which is in full
agreement with the presented theoretical model. This confirms that the resulting cubic nonlinearity is of a vibrational nature.

IV. CONCLUSION

In the article, the temperature dependence of the nonlinear refractive index of water in the THz spectral range has been measured for the first time. It has been experimentally shown that, when the temperature changes from 14°C to 21°C, the nonlinear refractive index value of water in spectral range from 0.2 to 1 THz changes from $4 \times 10^{-10}$ cm$^2$/W to $10 \times 10^{-10}$ cm$^2$/W. Influence of cumulative thermal effect on the nonlinearity was avoided by the use of a liquid jet instead of a cell. Since the measurements of the nonlinear characteristic of water were carried out using the jet, each subsequent THz pulse interacted with a new region of the water jet, therefore, the inertia of the nonlinearity mechanism did not exceed 1 ps. It is theoretically shown that the measured dependence of the water nonlinear refractive index on temperature corresponds to the dependence for the squared coefficient of thermal expansion of water on temperature. This is a new and significant confirmation of the vibrational nature of the refractive index giant low-inertia nonlinearity of liquids in the THz range. This confirmation is of great importance for future development of devices for ultrafast THz photonics based on materials with such a high nonlinearity.

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