Holographic detection of nonradiative transitions in oxygen molecules: digital and classical approach

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Abstract. The paper presents a novel approach to detect and monitor nonradiative transitions in singlet oxygen molecules in water by means of holographic recording of thermal disturbances. The approach is realized experimentally using classical and digital holographic techniques. Advantages and disadvantages of each of the techniques are considered.

1. Introduction

Singlet oxygen, the oxygen molecule in its first excited state $\alpha \Delta g$, is one of the active oxygen species which is of paramount importance for a wide variety of biophysical and biochemical processes in nature and living organisms in particular. In medicine it is a key agent in photodynamic therapy (PDT) used for treatment of malignant tumors, some pathogenic diseases, dermatopathies etc.

The most commonly used method for singlet oxygen formation is its photosensitized generation. The detection of singlet oxygen is usually based on the processes associated with its deactivation. The radiative transition from the excited singlet to the ground triplet state of the oxygen molecule $\alpha \Delta g \rightarrow X^3\Sigma_g$ is strongly forbidden by several selection rules that results in the extremely low phosphorescence intensity at 1270 nm. Nonradiative transitions play a key role in the deactivation of singlet oxygen [1]. The nonradiative deactivation of excited oxygen molecules via surrounding molecules causes temperature gradients which may be detected by the techniques sensitive to refractive index variations. Photoacoustic and photorefractive approaches have already been applied for detection of deactivation processes in singlet oxygen ([see e.g. 2]) and have demonstrated their efficiency in providing important information on the process efficiency, quantum yield and temporal characteristics. In the present paper singlet oxygen was detected by means of two holographic techniques based on the recording of phase distributions of a probe laser beam. These techniques are widely used nowadays to obtain information on spatial distributions of refractive index variations caused by different processes.

Various methods of phase reconstruction are developed by now. The classical approach is based on the recording and subsequent optical reconstruction of holograms and holographic interferograms. Some methods are based on the application of specific devices, such as Shack-Hartmann wavefront sensors. Another approach utilizes the wavefront reconstruction from digital holograms. Each of the
approaches exhibit advantages and disadvantages defining their application domains. In this paper we present results of wavefront reconstruction using classical and digital (DH) holographic techniques along with their comparison.

2. Experimental arrangement

In the experiments singlet oxygen was generated in an aqueous solution of Radachlorin photosensitizer [3] by the 50 mW laser diode emitting at 405 nm in the absorption band of Radachlorin. Laser radiation was directed vertically onto the solution surface in the water cell with the excitation area of about 1 mm in diameter (Fig. 1, a). The recording was performed in the perpendicular direction using pulsed Ruby laser (694 nm, 20 ns) in the case of classical arrangement (Fig. 1, b) and CW HeNe laser (633 nm) in digital recording arrangement (Fig. 1, c). In the latter case the Videoscan 205 digital camera with 4.65x4.65 μm pixel size was used for hologram recording.

Phase reconstruction from classically recorded holographic interferograms was performed using the “Fringe Analyzer” software, Mathcad 14 had been used for temperature mapping. As a result of the processing temperature maps of the recorded areas were reconstructed. The phase retrieval from digitally recorded holograms was performed using the two-step complex-wave retrieval algorithm.

Figure 1. Schematics of the experimental setups. Excitation channel layout (a), classical holographic interferometry arrangement (b), digital holography arrangement (c).
developed in [4]. Note that the recently suggested modification of this algorithm [5] provides data retrieval from even highly noisy or modulated by speckle structures digital holograms.

The major distinction of DH arrangement from the classical approach is a relatively strict constraint on the angle formed by the object and reference beams which defines the interference fringe width. From one hand this angle must be smaller than that defined by the Nyquist theorem. On the other hand many reconstruction algorithms (e.g. [4, 6] impose a requirement on the reference wave phase: in the recording plane it should vary much faster than that of the object wave. This condition holds when the angle between the reference and object waves is sufficiently big (usually a few tenths of degree). Another specific aspect of DH is the necessity to reconstruct two digital holograms recorded before and in the presence of the disturbance. The difference of phase distributions of object waves recorded by these holograms represents the sought phase retardation induced by the disturbance.

Note that digital cameras also pose some limitations to experimental realizations. First of all modern digital cameras can not provide frame rate sufficient for recording processes in nanoscale time frame with high spatial resolution. Also due to their high sensitivity a presence of strong extraneous radiation which may result from physical processes occurring with the object under study may hinder hologram recording. In the classical realization such spurious radiation may worsen the quality of each hologram. However at the reconstruction stage only object waves corresponding to the coherent recording radiation are formed, and the quality of the resulting optically reconstructed interferogram does not deteriorate much.

3. Data processing

The processing procedure of classically recorded interferograms includes measurements of fringe shifts with consecutive calculations of phase, refractive index and finally of temperature variations. In the digital approach phase distributions are obtained first from each hologram and then the resulting distribution of phase retardation is calculated as a difference of the two phase distributions taken at the desired time moments. Temperature variations are then calculated from these distributions.

Note that in both realizations integral phase retardation distributions along the recording beam path are obtained from the recorded holograms. To obtain a phase distribution in some cross section an inverse problem is to be solved. In the case of cylindrical symmetry the inverse Abel transform is usually applied. For more correct reconstruction of the initial distribution in a discrete case as many as possible readings should be used for calculations. In DH their number is defined by the pixel size of the recording photosensitive array. In classical holographic interferometry, regardless of the initial higher resolution, only a limited number of readings can be taken which is due to much lower density of the resulting interference fringes.

4. Results and discussion

Figure 2 (a-c) presents holographic interferograms of thermal disturbances induced in 1% Radachlorin solution in water by 405-nm laser excitation of 10s, 15s and 20s duration, respectively. Interferograms were recorded in the classical holographic arrangement. The temperature maps obtained as a result of their processing are shown in Fig. 2 (d-f). Figure 3 presents temperature maps obtained from digitally recorded holograms for 0.17%, 0.35% and 0.7% Radachlorin solution in water at 5s, 10s and 15s excitation durations. The comparison of the results obtained using these two techniques shows a good correspondence of the data retrieved by the two holographic approaches.

Note that the released heat is directly connected to the number of excited oxygen molecules, giving thus an opportunity to obtain information on the spatial distribution of oxygen molecules in the medium under study.
5. Conclusions

Thus it was shown that both the classical and digital holographic approaches provide reliable (and similar) data on the process under study. Classical holographic interferometry is more suitable to retrieve information on fast developing processes since conventional holographic materials allow hologram recording with pulsed lasers on nano- or even picosecond time scale. Digital holography on the other hand, although providing recording on microsecond time scale, allows one to monitor the process evolution and provides an opportunity to compare phase distributions recorded at any selected time moments.

Mention also that generally speaking the suggested approach is demonstrated to be promising for recording and monitoring of nonradiative deactivation processes in optically transparent media.
Figure 3. Temperature maps reconstructed from a set of digital holograms recorded at various concentrations of the photosensitizer solution (indicated over each column) and various excitation durations: 5 s – first row, 10 s – second row and 15 s – third row.

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