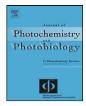


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#### **Invited Review**

# Ultrafast photon echo experiments in condensed phase: Detection of solvation dynamics, coherent wavepacket motions and static inhomogeneity

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#### ABSTRACT

Three-pulse photon echo (3PPE) experiment has been applied to liquids, amorphous, and biological systems to elucidate the origin of the spectral line-broadening mechanism of optical transitions. 3PPE is a third-order nonlinear coherent optical process which is a part of the degenerate four-wavemixing (DFWM) technique. Originally it was developed to determine electronic dephasing time in low-temperature glass and/or amorphous systems and simultaneously applied to solvation dynamics and/or spectral diffusion in condensed phase. Moreover, when a sufficiently short femtosecond laser pulse is utilized, it could also induce and control intramolecular coherent nuclear wavepacket motions. In the present review, we introduce the development and application of 3PPE spectroscopy in condensed phase, together with its basic background.

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**Yutaka Nagasawa** started his research work on timeresolved resonance Raman spectroscopy in 1988 when he was a master course student in Waseda University. Then he moved to the Graduate University for Advanced Studies and worked on ultrafast electron transfer by femtosecond fluorescence up-conversion spectroscopy in Prof. K. Yoshihara's group. After getting a Ph. D. degree in 1994, he became a postdoctoral researcher at Prof. G. R. Fleming's group in the University of Chicago and performed femtosecond photon echo experiments. At 1997, he returned to Japan at Osaka University as an assistant researcher and since then he collaborated with Prof. T. Okada and Prof. H. Miyasaka in the field of ultrafast spectroscopy. At 2003,

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#### 1. Introduction

Compared to the sharp and distinct spectra in the gas phase, spectra in the condensed phase are usually broad and featureless [1–7]. In the low-pressure gas phase where the collision of molecules is rare, the spectrum reflects the energy differences between quantum mechanical electronic and/or vibrational/rotational states of molecules while the width of narrow spectral lines is affected mostly by the Doppler broadening. On the other hand, in a condensed phase where the molecular density is rather high, a guest molecule is surrounded by host molecules (a solute is surrounded by solvent molecules) and hence the environment provided by the host is somewhat different for each guest, i.e. inhomogeneous broadening of the spectrum is inevitable. Moreover, at higher temperatures, thermal fluctuation causes the molecules to collide frequently with each other and thus the environment also perpetually changes, resulting in a motional (homogeneous) broadening of the spectrum. It can be said that broad and featureless spectrum due to the coupling of transition frequency to the bath degrees of freedom is the essential physicochemical characteristic of the condensed phase. Investigation of line-broadening and spectral diffusion mechanisms is a fundamental study that can lead to better understanding of the molecular nature of the condensed phase [1–8].

The mechanism of spectral line-broadening is also important from a chemical point of view. Thermal fluctuation and inhomogeneity of the organic solvents are important factors that determine the course of a chemical reaction, i.e. collision with solvent molecules activates the reactant to cross the reaction barrier and also reduces the energy to stabilize the product [9–12]. Solvent–solute interactions allow coupling of states and open a reactive channel which is not available for an isolated molecule. In polar solvents where electric charges and/or dipoles are stabilized by solvation, thermal fluctuation can be the driving force for a reaction accompanying significant charge redistribution. Therefore, in the field of electron transfer (ET) reaction, the relation between the ET rate and the solvent relaxation time is extensively studied [13–16].

A coherent third-order nonlinear spectroscopy, photon echo, can be employed to investigate electronic dephasing process which is responsible for the line-broadening in condensed phase. Photon echo is performed with two or three optical pulses and it extracts dynamic homogeneous contribution from inhomogeneously broadened spectrum and the pure electronic dephasing time,  $T_2$ , can be obtained [2,17]. The unique feature of photon echo is that the echo signal is delayed from the last incident pulse and, in the inhomogeneous limit, the delay is equivalent to the interval between the first and second pulses. This feature is often explained by analogy of the "foot race scenario" in the case for two-pulse photon echo (2PPE) where several runners run around a circular track [18–21].

Runners lined up at a starting line take off simultaneously with a bang of a starting gun (analogous to the first pulse). After some time, runners will be distributed randomly around the circular track due to the different speeds of each runner (inhomogeneity in speed). With a second gun fire (the second pulse), all of the runners immediately turn around and start running toward the opposite direction. If each runner maintains a constant speed throughout the entire process, all of the runners will cross the starting line exactly in line again with the interval between the second gun fire and crossing the line being exactly the same with that between the first and second gun fires. At the starting line, the group is "rephased" and the inhomogeneity in speeds is nullified no matter how fast or slow each individual runs.

However, this is an idealistic case and speeds of the runners may change during the actual process, i.e. the runners may get tired or stumble on a rock. If there is some fluctuation in the speed, the runners will not cross the starting line exactly in a line but with a spread in positions (imperfect rephasing). Greater spread in positions will arise if the runners run out for a longer time, because there will be greater chance for the speed to fluctuate. In the same manner, the photon echo process can rephase the inhomogeneously distributed transition frequencies of molecules, while random fluctuations of the frequency induce irreversible dephasing. Therefore, photon echo spectroscopy is capable of monitoring the coupling of optical transition to the bath degrees of freedom in the condensed phase.

In this article, development and application of photon echo spectroscopy is reviewed in the following manner: To begin with, brief experimental and theoretical backgrounds are described and subsequently more detailed experimental results are introduced. Development of three-pulse photon echo peak shift (3PEPS) technique and its application to solvation dynamics are reviewed [8,22–25], and finally control of intramolecular wavepacket motions by three-pulse photon echo (3PPE) spectroscopy are introduced [26–29].

#### 2. Principles of photon echo experiment

#### 2.1. Experimental background

One way to observe dynamics of thermal fluctuation in condensed phase is to monitor the time-evolution of an inhomogeneously broadened spectrum of a molecule by creating a photo-induced nonequilibrium state, i.e. spectral hole-burning (HB) [1–7]. When adequately strong narrow-band laser is utilized, a hole can be induced in the spectrum by photo-elimination of a small portion of molecules in a certain environment which is resonant with the laser. Time-evolution of the hole-spectrum could provide information about thermal fluctuation although the timeresolution of this method is limited by the bandwidth of the laser. The best spectral resolution will be provided by a single-mode cw laser although it could be only applied to low temperature glassy samples where static inhomogeneity is dominant [1-7]. To monitor the thermal fluctuation in room temperature solutions, femtosecond time resolution is required which accompanies a broad excitation spectrum due to the time-energy uncertainty principle. In such a case, hole-spectrum becomes equivalent to the ground state bleach observed in the time-resolved transient absorption spectroscopy which is usually overlapped with the stimulated emission and the bandwidth analysis becomes irrelevant [30.31].

Photon echo experiment is a time domain analogue of spectral HB which is performed with either two or three optical pulses. In the case of three-pulse photon echo (3PPE) experiment, the first two pulses are the pump pulses that burn a hole while the third pulse probes the condition of the hole [18,32–34]. The typical pulse configuration for 3PPE setup is shown in Fig. 1a [22,27,35–37]. When the pump pulses arrive simultaneously at the sample, the

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