

Three-Pulse Photon Echo in a Dense Potassium Vapor

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Abstract. Time-integrated three-pulse photon echo (3PE) and time-resolved 3PE measurements in a dense potassium vapor reveal clear signatures of non-Markovian dynamics. We pursue a molecular dynamics simulation to study the resonance effects contributing to the response.

Relaxation phenomena in condensed phase systems often occur in time scales on the order of a picosecond or less. In these short time regimes, the dynamics depart from Markovian behavior, meaning phase memory during interactions must be taken into account. Nonlinear time-domain optical techniques have been used in molecular systems to study non-Markovian changes in molecular structure [1], but the time scales of the local structural transitions is often close to that of the solvent interactions and the pulse-width limit can be an issue. In a time-integrated three-pulse photon echo (3PE) and time-resolved 3PE experiment, we have observed the non-Markovian dynamics of a simple atomic system whose dephasing time is large compared to the collision duration, allowing clear separation of time scales. While the measured echo peak shift qualitatively supports the use of an exponential correlation function in the current theory [2], at the densities studied ($>10^{17}\text{cm}^{-3}$) collisions are no longer merely binary. The current theory describes foreign atom broadening and does not include resonance effects. Thus we are currently pursuing a molecular dynamics simulation to include resonance effects through an exciton picture. Potassium vapor is an ideal system in which to study disordered excitons due to its electronic simplicity and its easily adjusted density and temperature.

In the three-pulse photon echo (3PE) technique, three optical pulses interact nonlinearly in a sample, resulting in a background-free signal that is time-integrated by a slow detector (Fig. 1). The first pulse excites a coherence between the ground and excited states. During the ensuing delay τ , dephasing occurs due to collisions. Then the second pulse arrives and converts the remaining coherence to excited-state or ground-state population. During the second delay T , loss of population and spectral redistribution occurs due to natural decay and collisions, and the system's ability to rephase and form a photon echo decreases. The third and final pulse forms a third-order coherence that radiates as the signal. The time-integrated 3PE is measured by scanning the first delay τ for various fixed values of the second delay T , with negative delay corresponding to the conjugate pulse coming second. In the time-resolved version of 3PE (time-gated 3PE), a reference

pulse is correlated with the emitted 3PE signal at a particular τ and T in a BBO crystal for up-conversion, resulting in a time-resolved scan of the nonlinear response versus the delay between the signal and the reference, t .

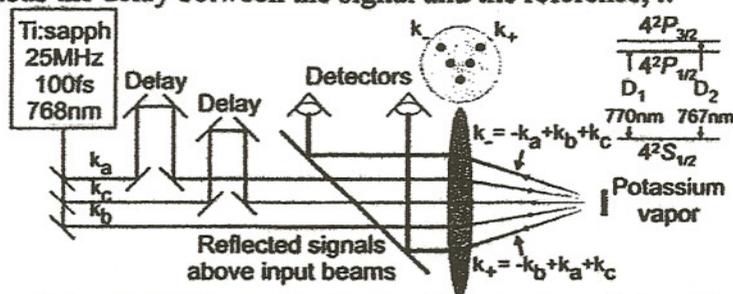


Fig. 1. The time-integrated 3PE experiment setup. The signals are detected in reflection due to the small absorption length ($\sim \lambda/2\pi$) of the potassium vapor.

As exhibited by the data shown in Fig. 2(a), and considering only the k signal for simplicity, for $\tau > 0$ the overall signal versus τ (ignoring the quantum beating due to simultaneous excitation of both excited states) rises, peaks, and then exponentially decays. Across the peak, the real-time signal changes from a photon echo to free polarization decay, corresponding to the crossover from non-Markovian to Markovian dynamics. As T is increased, the system's ability to form a photon echo decreases, and thus the crossover approaches $\tau = 0$ (Fig. 2(b)). The presence of the photon echo is clearly seen in the time-resolved signal (Fig. 3).

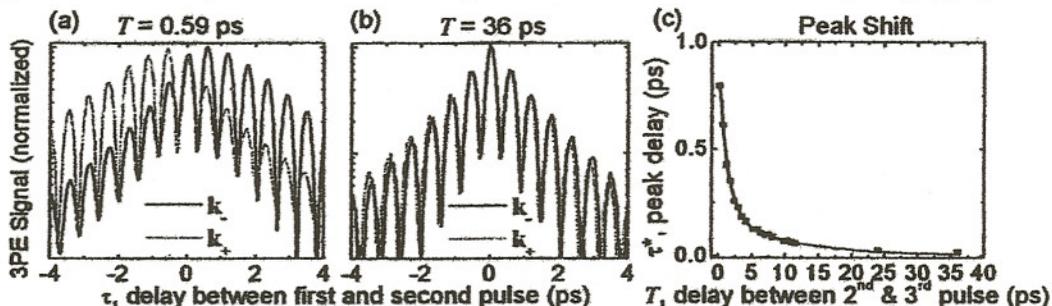


Fig. 2. Experimental signals at 600°C ($1.3 \times 10^{18} \text{ cm}^{-3}$). (a) 3PE for $T = 0.58 \text{ ps}$. The non-exponential behavior at small τ is due to non-Markovian dynamics. (b) 3PE for $T = 36 \text{ ps}$. The echo peaks have shifted to $\tau = 0 \text{ ps}$ due to the loss of rephasing capability. (c) 3PEPS and bi-exponential fit (solid line).

For some molecular systems the three-pulse echo peak shift (3PEPS) reveals the two-time correlation function of frequency fluctuations directly [3]. However, this is only possible due to a theoretical simplification arising from the presence of both fast and slow modulation in the system. For a dense atomic vapor, such simplifications do not necessarily occur, but a qualitative form for the correlation function can be found from the 3PEPS. The experimental peak location versus T is exponential at lower temperatures and thus qualitatively supports the use of an exponential correlation function in modeling two-pulse experiments, as was done in [4]. The peak shift is bi-exponential above 500°C (Fig. 2(c)). It is not yet clear

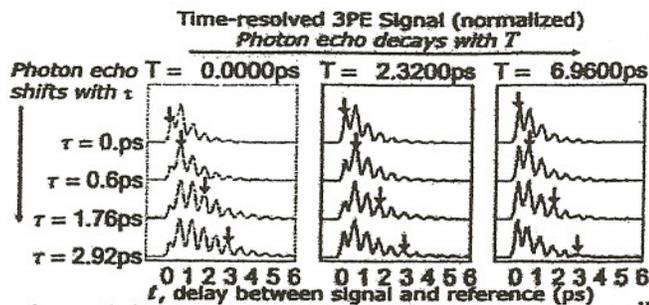


Fig. 3 (a) Experimental time-resolved 3PE signals at 600°C ($1.3 \times 10^{18} \text{ cm}^{-3}$). Small arrows point to $t = \tau$, the photon echo location for perfect rephasing. Photon echo strength clearly decreases with increasing T .

whether this represents the presence of two collision mechanisms, such as both binary (hard) and many-body (soft) collisions, or contributions from higher order powers of the correlation function [5]. The current theory does not account for resonance broadening, which dominates at these high densities [6]. To take resonance effects into account and gain a more complete description of the system response, we are currently performing molecular dynamics simulations in an exciton picture, with the signals calculated via the SPECTRON computational package [7,8]. This will provide insight into the non-Markovian dynamics of disordered excitonic systems in general and a resonance-broadened vapor in particular.

In summary, we have explored the non-Markovian dynamics of a dense potassium vapor with time-integrated and time-resolved 3PE. Studying such a simple system with unusually well-separated dephasing time and collision duration lends insight into the signatures of non-Markovian effects. In addition, future molecular dynamics simulations will shed light on the effects of many-body interactions in disordered excitons. Understanding the nonlinear response of this simple system should provide insight into other disordered excitonic systems such as molecular aggregates, semiconductors and biological systems. VOL and STC acknowledge the support of the NSF JILA Physics Frontier Center. SM acknowledges the support of the Chemical Sciences, Geosciences and Biosciences Division Office of Basic Energy Sciences, U.S. Department of Energy.

References

- 1 see, for example, T. Joo *et al.*, *J. Chem. Phys.* **104**, 6089-6108 (1996).
- 2 S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, (Oxford, NY, 1995).
- 3 E. T. J. Nibbering *et al.*, *Phys. Rev. Lett.* **66**, 2464-2467 (1991).
- 4 V. O. Lorenz and S. T. Cundiff, *Phys. Rev. Lett.* **95**, 163601 (2005).
- 5 D. A. Farrow *et al.*, *J. Chem. Phys.* **118**, 9348-9356 (2003).
- 6 J. A. Leegwater and S. Mukamel, *Phys. Rev. A* **49**, 1:146-155 (1994).
- 7 S. Mukamel, *Annu. Rev. Phys. Chem.* **51**:691-729 (2000).
- 8 W. Zhuang *et al.*, *J. Phys. Chem. B* **108**, 18034-18045 (2006).