

Ultrafast Optical Spectroscopy of Spectral Fluctuations in a Dense Atomic Vapor

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Transient four-wave mixing experiments with 100 fs pulses in a dense potassium vapor probe the electronic energy fluctuations that lead to optical decoherence. Echo-peak shift experiments yield a biexponential two-time correlation function of energy level fluctuations. Molecular dynamics simulations show that the slow component is a many-body excitonic contribution arising from long-range resonant interactions. The decay of the correlation function occurs on comparable time scales in theory and experiment.

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The spectral shape of atomic absorption and emission lines is a manifestation of fluctuations. As they can be accurately measured and, in principle, be calculated, atomic line shapes have received much attention over the last century [1]. Despite the extensive work, open questions exist, particularly regarding line wings, where classic frequency-domain techniques face limitations, and for resonance broadening, which is a many-body problem due to the long-range interactions. Since the line wings correspond to short times, the development of ultrashort pulse techniques presents a new approach to the unresolved questions in our understanding.

The simple optical spectra of alkali metals make them attractive for spectroscopy. In a self-broadened alkali vapor, i.e., when the broadening is due to collisions between like atoms, and not due to collisions with a foreign perturber atom or Doppler broadening, excitations that are delocalized across multiple atoms may be physically significant. To describe such excitations, it is natural to invoke the concept of an exciton, although excitons are more familiar in the context of crystalline solids or molecules. Because of the random spacing between the atoms, an alkali vapor corresponds to a highly disordered exciton system with long-range dipole interactions.

In this Letter, we present experimental measurements of the time-domain nonlinear optical response of a dense potassium vapor and show that they are in qualitative agreement with an exciton model combined with stochastic frequency fluctuations obtained from molecular dynamics simulations. A more rigorous quantum simulation of the nonlinear optical response would require integration of the many-particle Schrödinger equation within the single- and two-exciton manifolds. Instead we have adopted a simpler approach. We use the exciton model merely to calculate the frequency fluctuations and use the resulting correlation function in a stochastic model of the nonlinear response. We find that excitonic effects induce a slowly decaying contribution to the frequency-fluctuation correlation function.

In time-domain studies, interparticle dynamics result in non-Markovian changes in coherence, providing a window into the structure and dynamics of the system. Nonlinear time-domain optical techniques have been used to study non-Markovian behavior due to changes in molecular structure, but the time scale of the motion is often close to that of the solvent dynamics and to the pulse-width limit [2,3]. The long dephasing time of an atomic system relative to the collision duration results in a distinct non-Markovian regime conducive to detailed comparison between theory and experiment. In particular, signatures of non-Markovian dynamics exhibited in two-pulse–four-wave mixing in a dense potassium vapor are well-represented by a stochastic theory of energy level fluctuations [4]. The theory requires calculation of a two-point correlation function of frequency fluctuations. For foreign gas broadening, the correlation function can be calculated using the binary collision approximation and considering the interaction of one pair of resonant and foreign atoms at a time. For a self-broadened vapor, collisions are long-range because of resonance effects, and thus the binary collision approximation does not hold and fails to capture the many-body nature of excitations. The fluctuations induced by long-range couplings are sums of many small contributions, which by the central limit theorem are expected to have Gaussian statistics, while binary collisions have Poisson statistics of individual phase-destroying events [5]. By taking resonance effects into account through the exciton formalism and a stochastic correlation function based on Gaussian statistics, we attribute a slow component of the correlation function of energy level fluctuations revealed by experiment to the presence of these long-range resonant interactions.

In the three-pulse–four-wave mixing experiment, also referred to as three-pulse photon-echo (3PE), three optical pulses interact with the atoms to create a background-free signal that is detected as a function of the delays between the pulses [6–8]. A schematic of the experiment and the relevant energy levels of potassium are shown in Fig. 1. A

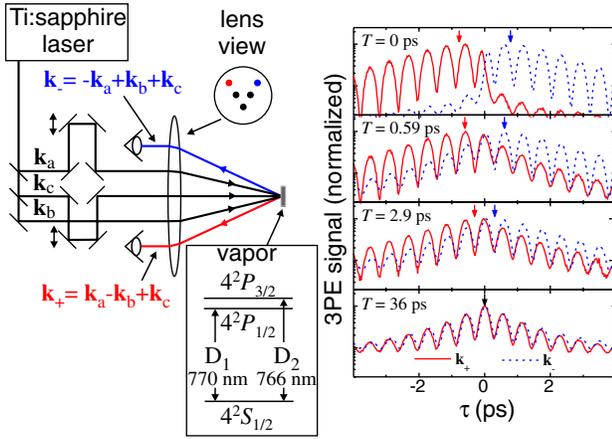


FIG. 1 (color online). The three-pulse photon-echo (3PE) experimental setup, with pulses labeled by their wave vectors, and the relevant energy levels of potassium. The signals are detected in reflection due to the short absorption length ($\sim \lambda/2\pi$) of the potassium vapor. At right, experimental 3PE signals at 600 °C versus the delay between the first two pulses, τ , for 4 values of the delay between the second and third pulse, T . The arrows indicate the peak of the signal without beats.

stretched-cavity mode-locked Ti:sapphire laser produces 160 fs pulses at a repetition rate of 26 MHz. Because of their broad bandwidth, the pulses are resonant with both the D_1 and D_2 lines of potassium. The output of the laser is split into three time-delayed pulses that are incident on the sample with wave vectors \mathbf{k}_a , \mathbf{k}_b , and \mathbf{k}_c . The first pulse excites a coherence between the ground and excited states. During the ensuing delay, τ , dephasing of the coherence occurs due to collisions. The second pulse converts the remaining coherence to a population grating. During the second delay, T , spectral redistribution occurs because of collisions, reducing the number of atomic superpositions that can rephase to emit a photon echo. The third and final pulse forms a coherence that radiates as the signals in directions $\mathbf{k}_- = -\mathbf{k}_a + \mathbf{k}_b + \mathbf{k}_c$ and $\mathbf{k}_+ = \mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c$, which are detected in reflection and are time-integrated versus the first delay τ for various fixed values of the second delay T . The potassium is held in a titanium vapor cell with a sapphire window for optical access. The temperature of the liquid potassium at the back of the cell is used to determine the density from phenomenological equations for the vapor pressure and the ideal gas equation [9].

The signals, examples of which are given in Fig. 1, exhibit quantum beating because of the simultaneous excitation of the D_1 and D_2 lines. The modulation envelope over the quantum beats peaks at a τ that corresponds to approximately the correlation time. The envelope peaks are designated by arrows in Fig. 1. By simultaneously measuring \mathbf{k}_- and \mathbf{k}_+ , zero delay is easily determined and drifts in it compensated. As T increases from zero, the range of τ over which the system emits a photon echo decreases because of collisions that randomize the phase, causing

the peak to shift toward $\tau = 0$. This shift as a function of T is referred to as the three-pulse photon-echo peak shift and has proven to be a useful probe of frequency fluctuations in numerous systems [2,3,10].

The statistics of the frequency fluctuations that result in decoherence are commonly represented by the two-time correlation function, $C(\tau) = \langle \delta\omega(\tau)\delta\omega(0) \rangle$, where $\delta\omega(t)$ is the amplitude of the fluctuation at time t , and the brackets denote an ensemble average [11]. The three-pulse photon-echo peak shift has been shown to correspond directly to the two-time correlation function of frequency fluctuations for two-level systems that contain both fast and slow dynamics [7,12,13]. Although this is not necessarily the case for a dense atomic vapor, the experimental results yield its qualitative form. For a pure potassium vapor, the experimental three-pulse photon-echo-peak shift is shown in Fig. 2(a) along with biexponential fits for a series of temperatures and densities. The values of T were chosen at integer multiples of the beat period to maximize the signal, and thus any oscillatory behavior at the beat period as a function of T would not have been detected [14]. As temperature and density increase, the initial decay rate increases and a slow exponential component of the peak shift decreases in amplitude relative to the initial fast component. This biexponential behavior could indicate the

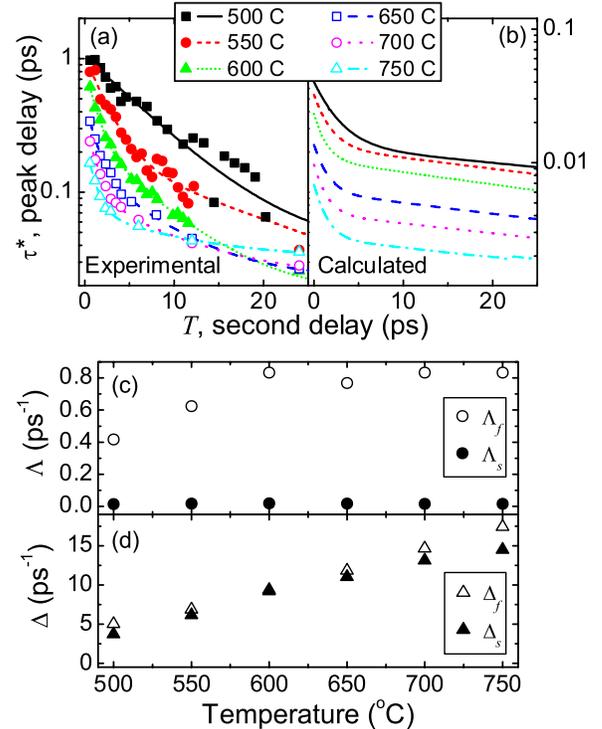


FIG. 2 (color online). (a) Experimental 3PE peak shifts for a series of temperatures and densities. (b) Calculated peak shifts from molecular dynamics simulations in an exciton picture. (c) Decay rates and (d) strengths for fast and slow components obtained from biexponential fits to theoretical correlation functions.

presence of two collision mechanisms, such as both binary (hard) and many-body (soft) collisions. The many-body effects would arise from the long-range attraction due to resonance effects [15].

To take resonance effects into account and gain a more complete description of the system response, we calculate peak shifts based on correlation functions derived from molecular dynamics trajectories in an exciton picture [16]. The calculation requires four steps: first, we simulate trajectories of an ensemble of atoms; second, we determine the resonant couplings based on distances between atom pairs for each snapshot of the trajectory; third, we diagonalize the Hamiltonian to obtain the exciton energies and calculate the correlation functions; and fourth, we calculate the peak shifts within a stochastic model of the three-pulse–four-wave mixing response [11].

Dynamic trajectories for a simulation unit cell containing 20 potassium atoms in the gas phase were generated from the $1^1\Sigma_g^+$ ground-state potential energy surface of K_2 [17] using the molecular dynamics package GROMACS [18]. Twenty runs of 600 ps were performed with a resolution of 0.02 ps for a series of temperatures and densities, with the box sizes scaled to include the same number of atoms for each temperature. Simulations performed with 40 atoms were found to be similar to those with 20 atoms; thus 20 atoms were used. The resonant couplings arise from the attractive or repulsive nature of atomic interaction, so interatomic potential energy surfaces represent the amplitude and range of the transition frequency fluctuations for the case of pairwise interaction and were used to determine the couplings.

The exciton formalism is more commonly used in condensed matter, for example, in semiconductors and molecular crystals, as well as for other disordered systems for which resonant interactions are important. In semiconductors, an exciton is a bound electron-hole pair, while in molecules it is an excitation distributed across molecular constituents. For a dense atomic vapor, an exciton is similar to the molecular case, known as a Frenkel exciton. This formalism accounts for the distribution of excitations over multiple atoms. The Frenkel exciton Hamiltonian $\hat{H}_S = \sum_m \Omega_m \hat{B}_m^\dagger \hat{B}_m + \sum_{m,n}^{m \neq n} J_{m,n} \hat{B}_m^\dagger \hat{B}_n$, where Ω_m is the excitation energy of atom m and $J_{m,n}$ is the resonant exciton coupling between atoms m and n . For each snapshot of the trajectory, the resonant exciton couplings $J_{m,n}$ for all atom pairs were determined from the difference between the $1^1\Sigma_u^+$ excited-state potential energy surface and the $1^1\Sigma_g^+$ ground-state surface of K_2 [17]. All other surfaces dissociating to $4s + 4p$ were not taken into account, nor were transitions from the $1^3\Sigma_u^+$ ground state. Quartic couplings, which result in two-exciton states, were assumed to be large such that the two-exciton states were spectrally shifted out of resonance and could be safely neglected in the simulations. If the elements of the eigenvectors for each snapshot changed by greater than 0.3 cm^{-1} as compared with those of the previous snapshot, the eigenvectors were

reordered to minimize the number of elements that underwent such a change, though there remained avoided crossings within eigenvectors that could not be reconciled frame-to-frame. The fluctuating one-exciton energies obtained from diagonalizing the Hamiltonian were then used to calculate the correlation functions of frequency fluctuations $C(\tau_j) = \langle \sum_{i=0}^N \delta\omega(t_i - \tau_j) \delta\omega(t_i) \rangle$, within the laser bandwidth ($\sim 200 \text{ cm}^{-1}$), where $\delta\omega$ is the difference between the one-exciton energy levels and Ω_m . The brackets denote an ensemble average over all the one-exciton states, and N is the number of frames in the trajectory for calculating $C(\tau)$. The correlation functions were averaged over all runs for a series of temperatures and densities.

For comparison with experiment, echo-peak shifts were calculated using the correlation functions produced by the exciton model. Each $C(\tau)$ was fit to a biexponential, with four fitting-parameters corresponding to the amplitudes $\Delta_f(\Delta_s)$ and decay rates $\Lambda_f(\Lambda_s)$ of the fast (slow) component. These parameters, shown in Figs. 2(c) and 2(d) were used as the amplitudes and decay rates of two stochastic correlation functions. A stochastic correlation function models excited-state frequency fluctuations as Gauss-Markov processes, in which the modulation of the i to j transition $\delta\omega_{ij}$ obeys $\langle \delta\omega_{ij}(t_1) \delta\omega_{ij}(t_2) \rangle = \Delta_{ij}^2 \exp(-\Lambda_{ij}|t_2 - t_1|)$ and $\langle \delta\omega_{ij}(t) \rangle = 0$, where Δ_{ij} corresponds to the root-mean-squared amplitude of the frequency fluctuations, and Λ_{ij}^{-1} is their time scale. The stochastic model gives a line shape function $g_{ij}(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta\omega_{ij}(\tau_1 - \tau_2) \delta\omega_{ij}(0) \rangle = (\Delta_{ij}^2 / \Lambda_{ij}^2) \times [\exp(-\Lambda_{ij}t) + \Lambda_{ij}t - 1]$. To calculate the peak shifts from the fast and slow correlation functions, the response functions derived for a two-level system with delta-function pulse durations using the cumulant expansion for the case of a single stochastic correlation function were used [4,19], with g_{ij} the sum of the line shapes of the fast and slow correlation functions. The sum of the response functions from the stochastic theory [4,20] yields the polarization. The signal is calculated by numerically time-integrating the intensity for a sequence of time delays between pulses.

The calculated peak shifts, shown in Fig. 2(b), exhibit similar changes in the ratio of slow-to-fast exponential amplitudes as a function of temperature and density as experimental peak shifts. We note that there are no adjustable parameters in the theory. To determine the origin of the biexponential behavior of the correlation function, we replaced the excited-state potential energy surface used to calculate the one-exciton couplings with a shorter-range potential, shown in Fig. 3(a), which was chosen to preserve the integrated potential energy change of the long-range potential. This change resulted in a single fast exponential decay, as shown in Fig. 3(b), revealing that the slow decay is due to long-range resonant interactions.

To experimentally check this conclusion, 220 Torr argon buffer gas was introduced into the cell and echo-peak shift data were taken at 600 °C. As shown in Fig. 4, the effect of

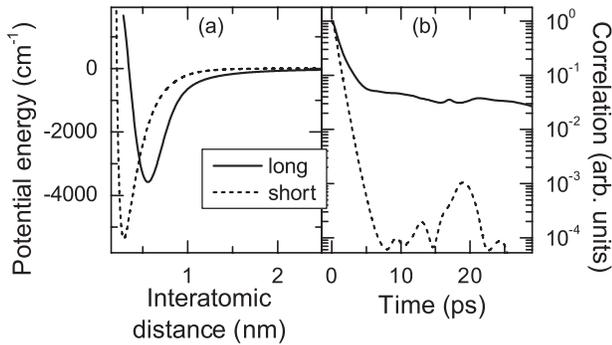


FIG. 3. (a) Potential energy surfaces used to calculate (b) the correlation functions of energy level fluctuations for long- (solid) and short-range (dashed) attraction.

introducing argon is similar to increasing both the density and temperature of a pure potassium vapor, increasing the decay rate and suppressing the slow component relative to the fast. This supports our attribution of the slow component of the correlation function to long-range interactions.

The agreement between theory and experiment is quite good considering the number of assumptions and the fact that there are no adjustable parameters. The main approximations are the use of only ground-state atoms in the dynamics simulation and the inclusion of only one of the dipole-allowed potential energy surfaces dissociating to $4s + 4p$ (ignoring the fine structure and hyperfine splitting) in calculating the exciton Hamiltonian. Considering only ground-state atoms means we do not take into account the sensitivity of the experiment to the frequency fluctuations of excited atoms. Agreement of the theoretical results with experiment at low temperature is less satisfactory, which may imply that the range of the potential is less than that represented by the potential energy surface used in the calculation. It is expected that theoretical improvements would result in qualitatively similar behavior as a function of temperature and density.

From three-pulse–four-wave mixing experiments and correlation functions of energy level fluctuations derived

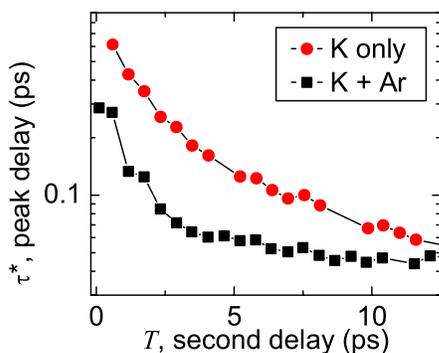


FIG. 4 (color online). Experimental echo-peak shifts for potassium vapor with (square) and without (circle) buffer gas.

from first principles, we attribute the slow exponential component of three-pulse photon-echo-peak shift data to long-range resonant attractions in a dense atomic vapor. This work shows that first principle simulations using currently available potential energy surfaces are capable of modelling the dynamics. Alkali vapors provide an ideal model for other disordered excitonic systems such as molecular aggregates, semiconductors, and photosynthetic complexes. The present analysis can be extended to these systems as well.

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