Non-Markovian Dynamics in a Dense Potassium Vapor

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Transient four-wave mixing experiments on a dense potassium vapor, which has a dephasing time long compared to the collision duration, reveal distinct signatures of non-Markovian dynamics. Theoretical fits assuming stochastic fluctuation of the excited-state frequencies confirm that the two-time correlation function has a finite temporal width.

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In broadening of resonances, the non-Markovian regime corresponds to time scales when phase memory during interactions must be taken into account. The issue of non-Markovian dynamics appears in the general problem of quantum dissipative systems, and thus arises in many fields [1]. The transition from non-Markovian to Markovian dynamics is determined by the correlation time. For times less than the correlation time, non-Markovian dynamics lead to nonexponential decoherence [2]. However, if the dephasing time is comparable to the correlation time, the transition from non-Markovian to Markovian dynamics is not distinct, preventing comparison between the two regimes. This is often the case in molecular liquids, which also suffer from limitations due to the temporal resolution of the experiments [3–5]. This is not the case for a dense atomic vapor, in which phase-interrupting interactions can be ascribed to collisions between atoms and the correlation time is the collision duration. Resonant interactions between like atoms result in extended collision durations, and the dephasing time for an atomic vapor is longer than the collision duration. The combination of these important qualities leads to experimentally accessible regimes of non-Markovian and Markovian atomic interaction. We study the phase relaxation dynamics of a dense potassium vapor using the two-pulse photon echo technique, also known as transient four-wave mixing (TFWM) [6]. The TFWM signal exhibits signatures characteristic of both Markovian and non-Markovian dynamics, which can be modeled assuming stochastic modulations of the transition frequency of the atoms during collisions [7]. Since the signatures of non-Markovian dynamics appear at short time scales, a time-domain technique, such as TFWM, is preferred because it is most sensitive to the fastest dynamics. In contrast, non-Markovian dynamics appear in the wings of the spectral line shape, where the signal is weak and may be influenced by other resonances, which hinders frequency domain investigations [8]. Studying such a model system allows us to improve the understanding of more complex systems to which the stochastic model is applied. The interactions in such systems are commonly studied using the three-pulse photon echo peak shift technique, which can map the correlation function of frequency fluctuations directly [9], as was done recently, for example, to investigate hydrogen bond dynamics via the OH-stretching frequency in water [10,11]. The stochastic model does not take into account memory in the bath, as occurs, for example, in semiconductors due to electron-LO-phonon scattering [12]. The effects of memory in the bath can be described in a microscopic model and result in oscillatory dephasing [13,14].

The clear transition from non-Markovian to Markovian dynamics in an atomic vapor results from a distinct separation of time scales. At very short times the motion of the atoms can be neglected; thus, the ensemble can be considered inhomogeneously broadened due to dipole-dipole interactions over the varying interatomic distances. At intermediate times comparable to the collision duration between atoms, the relaxation dynamics are dominated by the perturbations of the transition frequency of the atoms as they collide. The collision can be thought of as the transient formation of a dimer, here K_2, where the transition frequencies are modified according to the potential energy surfaces at small internuclear spacings [15]. Thus the collision duration is determined by the velocity of the atoms and the range of the interatomic potential. These early time scales represent the regime of non-Markovian dynamics. On time scales much greater than the collision duration, the system is homogeneously broadened due to atomic motion, i.e., the atoms can be considered to traverse the attractive range of the internuclear potential infinitely fast. These time scales correspond to the Markovian regime.

The major broadening mechanisms in an atomic vapor with no buffer gas are Doppler broadening and resonance broadening, where resonance broadening is due to dipole-dipole interactions between excited and unexcited atoms of the same species (also known as self-broadening). We choose densities ($N \gtrsim 10^{17}$ cm^{-3}) such that resonance broadening dominates and Doppler broadening can be neglected. At these densities, collisions are no longer strictly binary [16]. In addition, in the case of resonance broadening it has been shown that many-body effects are important even at low densities because of the long-range nature of the resonant interaction [17]. Because of these difficulties, the effect of resonance broadening on the line shape is still an open question [18]. Nonlinear optical time-domain techniques prove useful because they are able to separate broadening mechanisms in time. The corresponding theory of the nonlinear response must span both inhomogeneous and homogeneous temporal regimes, which is accomplished by allowing the transition frequency of the atoms to be modulated during collisions according to an assumed two-time correlation function of frequency fluctuations [7].

In self-diffracted TFWM, two pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ interact nonlinearly in a sample, resulting in a background-free signal in direction $2\mathbf{k}_2 - \mathbf{k}_1$, which is time integrated by a detector. The loss of coherence of the system is probed by varying the delay between the pulses. In the experimental setup, shown in Fig. 1(a), pure potassium vapor, with no buffer gas, is contained in a cell made from corrosion-resistant titanium with a sapphire window for optical access. To keep the potassium from condensing onto the sapphire window, higher temperature is maintained at the window than at the back of the cell. The temperatures are varied from 500 °C to 750 °C, corresponding to number densities from 3×10^{17} cm^{-3} to 6×10^{18} cm^{-3} [19]. Pulses 70 fs long are focused onto the interface between the sapphire window and the potassium vapor. A TFWM signal also occurs in reflection for an optically thin sample [20]. We detect this reflected signal because the absorption length of the potassium vapor is on the order of the wavelength of the incident light at these densities, and thus it is effectively thin, which minimizes reshaping of the excitation pulses and reabsorption of the signal. The broad laser spectrum excites both the potassium D_1 and D_2 lines, which are well separated, resulting in quantum beats at the difference frequency. This is in contrast to molecular vibronic spectra, which often contain multiple, overlapping transitions [5]. In this experiment the dephasing time, collision duration, and pulse width are all well separated; at 700 °C, the collision duration is approximately 0.5 ps, which is much less than the time between collisions of 2 ps and greater than the pulse duration of 70 fs. This results in unusually well-separated contributions from homogeneous and inhomogeneous broadening as compared to molecules in the condensed phase. We also note that we do not need to be concerned with contributions from other time orderings that occur during pulse overlap.

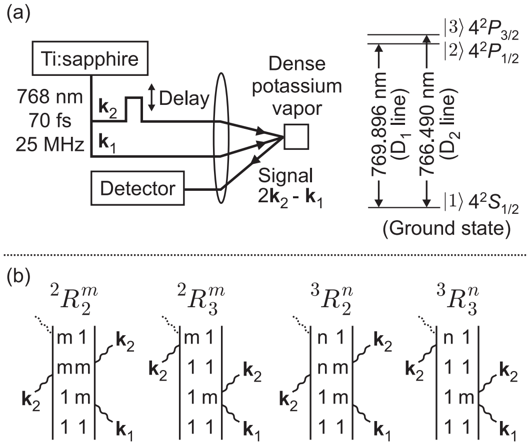

FIG. 1. (a) Transient four-wave mixing experiment setup and the optically active energy levels of potassium. The experiment is performed in reflection due to the short absorption length of the potassium vapor. (b) The relevant double-sided Feynman diagrams; with $m, n = 2, 3$; $m \neq n$.

The TFWM signal contains signatures of both non-Markovian and Markovian dynamics. In the Markovian, or long-time, limit, the perturbations of the resonance frequency can be considered as delta functions in time and the system homogeneously broadened. The corresponding TFWM signal decays exponentially due to the collisions between atoms. In the non-Markovian, or short-time, limit, the collisions are considered to occur in a finite time and the two-time correlation function of the excited-state frequency fluctuations determines the evolution of the signal. This corresponds to a constant TFWM signal at small delays, representing the finite time needed for collisions to occur. In reality there is a rise of the signal from zero delay due to the integration up to the full area of the real-time signal (a photon echo) [21]. Thus in the TFWM signal the dynamical signatures are well separated (see Fig. 2) as an initial rise of the signal caused by the integration of the photon echo, a flat signal at short delays due to non-Markovian scattering, and exponential dephasing due to pure homogeneous broadening. The extra dip near zero delay results from the signal following the integration of the pulse, which has a finite duration.

The TFWM signal can be calculated more rigorously for our system using a stochastic model for the dipole-dipole interaction between atoms [2,7,22]. Indeed, the well-defined signatures outlined above provide an important opportunity to test this theoretical description of dephasing, which is frequently employed in molecular systems

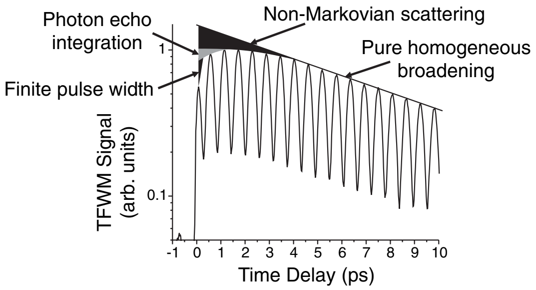

FIG. 2. Experimental TFWM signal for potassium vapor at 500 °C (number density ≈ 10^{17} cm^{-3}) with dynamical signatures labeled. Quantum beats are due to the excitation of both the potassium D resonance lines.

[5]. Calculating the optical response in the non-Markovian regime requires a modification of the optical Bloch theory, which allows for only phenomenological exponential dephasing terms. This is done by assuming a stochastic modulation of the resonance frequency during a collision. Thus the modulation of the i to j transition, $\delta\omega_{ij}$, is assumed to obey the two-time correlation function

$$\langle \delta\omega_{ij}(t_1)\delta\omega_{ij}(t_2)\rangle = \Delta_{ij}^2 \exp(-\Lambda_{ij}|t_2 - t_1|) \qquad (1)$$

and $\langle \delta\omega_{ij}(t)\rangle = 0$, where Δ_{ij} corresponds to the root-mean-squared amplitude of the frequency fluctuation and Λ_{ij} is its inverse correlation time. The angle brackets denote an ensemble average over the stochastic process. In this manner we account for the modulation of the transition frequency in both inhomogeneous and homogeneous regimes; however, this model does not include the effects of resonance broadening nor do we consider fluctuations in the dipole moment. Using this model, the TFWM signal can be calculated via the polarization:

$$S(\tau) = \int_{-\infty}^{\infty} |P^{(3)}(t,\tau)|^2 dt, \qquad (2)$$

where the polarization is determined by convolution of the response function of the system with the incident fields. We consider a system of three-level atoms [see level diagram in Fig. 1(a)]. The nonlinear response functions are calculated using a cumulant expansion [2], resulting in a dependence on the two-time correlation function of Eq. (1) via the line shape function

$$\begin{aligned} g_{ij}(t) &= \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta\omega_{ij}(\tau_1 - \tau_2)\delta\omega_{ij}(0)\rangle \\ &= \frac{2\Delta_{ij}^2}{\Lambda_{ij}^2}[\exp(-\Lambda_{ij}t) + \Lambda_{ij}t - 1]. \end{aligned} \qquad (3)$$

The response functions for the two possible interaction pathways corresponding to 2- and 3-level physics [see Fig. 1(b)] within the assumption that the pulses can be represented as delta functions in time are

$$\begin{aligned} {}^2R_2^m &= {}^2R_3^m \\ &= \mu_{1m}^4 \exp(i\omega_{1m}\tau - i\omega_{1m}t)\exp\{-[2g_{1m}^*(\tau) \\ &\quad + g_{1m}(t) + g_{1m}^*(t) - g_{1m}^*(t+\tau)]\}, \\ {}^3R_2^n &= {}^3R_3^n \\ &= \mu_{1m}^2\mu_{1n}^2 \exp(i\omega_{1m}\tau - i\omega_{1n}t)\exp\bigg\{-\frac{1}{2}[3g_{1m}^*(\tau) \\ &\quad - g_{1m}^*(\tau+t) + g_{1m}^*(t) - g_{1n}^*(\tau+t) + g_{1n}^*(\tau) \\ &\quad + g_{1n}^*(t) + 2g_{1n}(t) + g_{mn}^*(t+\tau) - g_{mn}^*(\tau) \\ &\quad - g_{mn}^*(t)]\bigg\}, \end{aligned} \qquad (4)$$

where μ_{ij} is the dipole moment of the i to j transition. In the notation of the R's the first superscript represents 2- or 3-level physics. For 2-level physics, the subscript represents an excited-state (2) or ground-state (3) population to second order. For 3-level physics, the subscript represents a Raman coherence (2) or ground-state population (3) to second order. The second superscript is the final excited state that forms a coherence with the ground state at third order. The sum of the response functions gives the polarization in Eq. (2) that is then numerically integrated to obtain the TFWM signal.

Theoretical results match quite well with the experimental results via least-squares fits, as shown in Fig. 3. The discrepancy near zero delay is due to the assumption of delta-function pulses in time, which does not allow for finite pulse width effects. One of the fit parameters, Λ_{ij}, corresponds to the decay rate of the correlation function and determines the time scale of the deviation of the TFWM signal from exponential behavior at short delays. To confirm these signatures data were taken as a function of temperature, and as expected Λ_{ij} increases with increasing temperature, as shown in Fig. 4(a). This represents a decreasing collision duration. The magnitude of the excited-state frequency fluctuations is represented by the parameter Δ_{ij}, which is also plotted in Fig. 4. The ratio $\kappa = \Lambda_{ij}/\Delta_{ij}$ is of order 1, which means that the broadening mechanism is intermediate and not in either the homogeneous or inhomogeneous limits. The excellent fit between theory and experiment demonstrate that the stochastic model adequately describes the dynamics. Thus a model that includes a microscopic description of the bath [13,14]

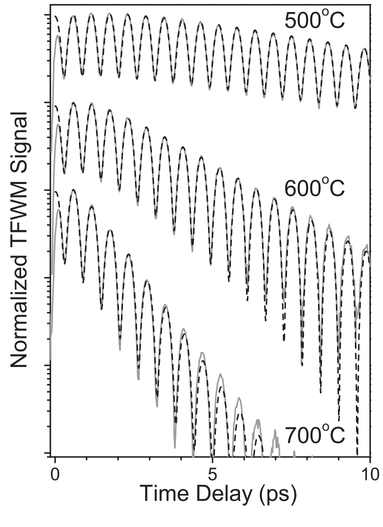

FIG. 3. Typical experimental TFWM signal (solid gray lines) for potassium vapor at 500 °C ($N \approx 3.4 \times 10^{17}$ cm^{-3}), 600 °C ($N \approx 1.3 \times 10^{18}$ cm^{-3}), and 700 °C ($N \approx 3.7 \times 10^{18}$ cm^{-3}), with curves offset for clarity. The dashed lines are least-squares fits assuming a stochastic modulation of the electronic transition frequency during collisions.

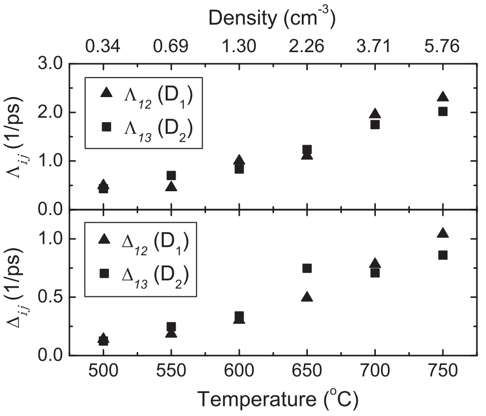

FIG. 4. Theoretical fitting parameters Λ_{ij}, the time scale of the excited-state frequency fluctuations, and Δ_{ij}, their magnitude, for the D_1 (square) and D_2 (triangle) lines.

is not needed, which is consistent with the fact that we do not see oscillatory dephasing. The stochastic model does not include resonance broadening effects; thus, differences will exist in comparison with a foreign-gas broadened vapor in which the interaction range and therefore the collision duration is relatively small. The deviation of the inverse collision duration from square-root dependence on temperature may indicate the importance of many-body (nonbinary) interactions. This can be explored experimentally by introducing a buffer gas to the potassium vapor, which would decrease the interaction range and bring the system to the Markovian, homogeneously broadened limit. In doing this we anticipate the ability to determine signatures unique to resonance broadening. In addition, further insight can be gained with a three-pulse echo peak shift experiment, which would enable the mapping out of the correlation function of the system [9,23,24].

In summary, we have explored with transient four-wave mixing the non-Markovian dynamics of a dense potassium vapor, which has the unusual quality of a long dephasing time compared to the collision duration. This clear separation of dynamics has provided an opportunity to compare theory and experiment in a system for which it may be possible to calculate the correlation function of transition frequency fluctuations, representative of the complete dynamics of the system, from first principles, which, to the best of our knowledge, has not been done. With further experiments using the echo peak shift technique and the introduction of a buffer gas we anticipate greater insight into resonance broadening effects and the ability to determine the correlation function of the system.

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