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Vibrational dynamics in condensed matter probed with linac based FELs

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Abstract

The super-conducting linac pumped free electron laser (FEL) at Stanford has been used to study the vibrational dynamics of molecules in liquids and glasses. A variety of experiments have been performed, including the world's first vibrational photon echo experiments in liquids and glasses and polarization selective pump-probe experiments. In this paper vibrational photon echo experiments are described and characteristics of the FEL important to these experiments are discuss. Vibrational photon echo experiments were performed on the asymmetric CO stretching mode of tungsten hexacarbonyl (1976 cm^{-1}) in the organic glass dibutylphthalate as a function of temperature using sub-picosecond infrared pulses. The echo decays display pronounced beats and are bi-exponential. The beats and bi-exponential decays arise because the bandwidth of the transform limited FEL pulses exceeds the vibrational anharmonicity, leading to the excitation and dephasing of a multilevel coherence. From the beat frequency, the anharmonicity is determined to be 14.7 cm^{-1}. From the bi-exponential decay components, the temperature-dependent homogeneous vibrational dephasing rates of both the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions are determined.

1. Introduction

In liquids and other condensed phase systems, vibrational spectra can have contributions from inhomogeneous broadening which mask the homogeneous vibrational lineshape [1,2]. Third-order coherent Raman experiments measure the free induction decay of the spontaneous Raman line, and cannot distinguish or eliminate contributions from inhomogeneous broadening [3]. For this reason, higher order Raman experiments, such as the Raman echo, are required to distinguish inhomogeneity in vibrational transitions [3–8].

As an alternative to these non-resonant techniques, resonant third order experiments, such as the vibrational photon echo, can be used to determine the homogeneous linewidth of a vibrational transition [1,2]. Unlike Raman experiments, resonant infrared experiments allow significant transfer of population to the excited vibrational state. Thus, when the bandwidth or Rabi frequency of the excitation source exceeds the anharmonicity of the vibrational transition, population can be further excited to higher vibrational levels [9–11]. Such experiments permit multilevel vibrational dynamics to be observed [10,11]. Resonant experiments have the additional distinct advantage of being able to separate pure dephasing and lifetime contributions to the homogeneous vibrational linewidth [1], both of which can contribute significantly [1,12].

Here, we report the results of sub-picosecond infrared vibrational photon echo experiments, conducted with the Stanford super-conducting linac pumped free electron laser (FEL), in which the excitation bandwidth exceeds the vibrational anharmonicity. These experiments are the first to determine the homogeneous vibrational linewidth for both the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions. Furthermore, this measurement accurately determines the vibrational anharmonicity, which cannot be done by linear absorption spectroscopy.

Temperature dependent measurements were made on the asymmetric CO stretching mode of tungsten hexacarbonyl [$W(CO)_6$] in the organic glass dibutylphthalate (DBP) from 10 K to 150 K. The results show vibrational dephasing dynamics with dramatically different temperature dependences, indicating different line broadening mechanisms. Furthermore, the echo decays show that the absorption line is massively inhomogeneously broadened over this temperature range.

In a vibrational photon echo experiment, two IR pulses tuned to the molecular vibration of interest, are crossed in the sample. The first pulse creates a coherent superposition state that begins to dephase due to inhomogeneous broadening. A second pulse, delayed by time τ, initiates rephasing of the inhomogeneous contributions to the vibrational transition. This rephasing results in a macroscopic polar-

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ization that is observed as an echo pulse at time 2τ. The echo emerges from the sample in a unique direction given by wave vector matching conditions. The integrated intensity of the echo pulse is measured as a function of τ. For the case in which the laser bandwidth is narrow with respect to the vibrational anharmonicity, such that the vibrational coherence involves only the $v = 0 \rightarrow 1$ transition, the process is modeled well by a two level system, and the decay of the echo intensity measures the homogeneous vibrational dephasing time T_2. For a Lorentzian homogeneous lineshape with linewidth $\Gamma = 1/\pi T_2$, the echo decays as

$$I(\tau) = I_0 \exp(-4\gamma_{10}\tau), \tag{1}$$

where $\gamma_{10} = 1/T_2$ for the $v = 0 \rightarrow 1$ transition.

When the bandwidth of the excitation pulses exceeds the vibrational anharmonicity, population can be excited to higher vibrational levels. The extent of vibrational uppumping is limited only by the magnitude of the vibrational anharmonic frequency splitting, Δ, relative to the laser bandwidth, Ω, or the Rabi frequency. For the case where $\Delta \approx \Omega$, short pulse excitation will create a three level coherence involving the $v = 0$, 1 and 2 vibrational levels. Extending a treatment of photon echoes in harmonic vibrational systems [13], Fourkas has derived an expression for the photon echo decay for a three level system with anharmonicity [14]. For a finite pulse bandwidth where the E-field differs at the frequencies of the two transitions, the Fourkas result can be extended, and the decay is given by

$$\begin{aligned} I(\tau) = \exp(-2\gamma_{10}\tau)\big[& E_{10}^2 \exp(-2\gamma_{10}\tau) \\ & + E_{21}^2 \exp(-2\gamma_{21}\tau) \\ & - 2E_{10}E_{21} \exp(-(\gamma_{10}+\gamma_{21})\tau) \cos(\Delta\tau)\big]. \end{aligned} \tag{2}$$

This equation is based upon an on-resonance assumption with excitation E-field amplitudes E_{10} and E_{21} for the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions, respectively. Eq. (2) shows that the echo signal envelope decays in proportion to the dephasing rates of the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions, with exponentially damped beats observed at the frequency splitting, Δ. For the narrow bandwidth case ($E_{21} \approx 0$), Eq. (1) is recovered.

2. Experimental procedures

The infrared photon echo experiments reported here were performed with ~ 0.7 ps (~ 20 cm^{-1} bandwidth) IR pulses at 5.06 μm (1976 cm^{-1}) generated by the Standford superconducting-accelerator-pumped free electron laser. FEL pulses are generated as transform-limited Gaussian pulses. The FEL emits a 2 ms macropulse at a 10 Hz repetition rate. Each macropulse consists of ~ 1 μJ micropulses at a repetition rate of 11.8 MHz.

To avoid severe sample heating problems and to assure that the sample has returned to the initial condition prior to the application of the next pulse sequence, it is necessary to select single micropulses from the FEL macropulse. It cannot be emphasized enough the importance of being able to control the micropulse repetition rate to permit a wide variety of experiments to be performed properly. With the Stanford FEL, single pulse selection is made possible by the 85 ns separation between micropulses. A germanium acousto-optic single pulse selector was developed which permits pulses to be selected at any repetition rate. The experiments were conducted at 50 kHz during the macropulse, giving an overall repetition rate of 1 kHz. Also essential for there experiments is stabilization and continuous measurement, of the FEL wavelength and the duration and functional form of the optical pulse. In addition, methods for optical alignment, detection equipment, and specialized software are required to successfully perform photon echo and other experiments.

During one 3 ms macropulse, the RMS variation in power is only 1.8%. This is typical operation. Since the FEL must be tuned into a relatively narrow vibrational line, wavelength stability is essential. The variation is minimized by a feedback stabilization system. The RMS variation is only 0.009%. At 2000 cm^{-1}, this is ~ 0.2 cm^{-1}. This variation should be compared to the transform limited bandwidth of the pulse, which is ~ 20 cm^{-1}. In addition, constant monitoring of the pulse duration using autocorrelation gives the pulse duration and pulse shape. All of the relevant information is provided directly to the user and this information is constantly updated.

To perform the echo experiments, the two pulses for the echo pulse sequence are obtained with a ZnSe beam splitter. The data was taken with pulse energies of 15 nJ for the first pulse and 100 nJ for the second pulse. The pulse energy of the second pulse gives a peak Rabi frequency, estimated from $|(\boldsymbol{\mu}\cdot\boldsymbol{E})/\hbar|$, of approximately 15 cm^{-1}. The more intense pulse was chopped at 25 kHz by a second AOM. The photon echo signal and an intensity reference signal were measured with two HgCdTe detectors sampled by two gated integrators. The reference detector was used for shot intensity windowing; all data with pulse intensities outside of a 10% window were discarded. Carefully performed power and repetition rate dependences demonstrated that the data is free of power and heating artifacts.

Vibrational photon echo data were taken on the triply degenerate T_{1u} asymmetric CO stretching mode of $W(CO)_6$. Data were taken on 4×10^{-3} M solutions of $W(CO)_6$ in DBP (99.9%). The absorption bandwidth is 26 cm^{-1} at all temperatures.

3. Results and discussion

Fig. 1 shows photon echo decays for several temperatures in the glass, as well as fits to Eq. (2). These decays

are consistent with the expected decay of a three level vibrational coherence. The decays are modulated at a 2.3 ps frequency, which is constant within error over all temperatures. Based on the average of several data sets, the vibrational anharmonic splitting is $\Delta = 14.7 \pm 0.3$ cm^{-1}. This splitting is in accord with the value of 15 ± 1 cm^{-1} recently obtained by Heilweil and co-workers from observation of the $v = 1 \rightarrow 2$ and $v = 2 \rightarrow 3$ transitions using transient infrared absorption [11]. The agreement between the anharmonicity obtained from the beat frequency and that obtained by transient absorption confirms the interpretation of the beats as arising from the multilevel coherence of an anharmonic oscillator.

Fits to the echo decay data also provide the rates of homogeneous dephasing for the two transitions involved in the multilevel coherence. Fig. 2 shows the homogeneous dephasing times for the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions at temperatures between 10 K and 150 K. These dephasing times, at all temperatures, are long compared to the inverse of the absorption linewidth and indicate a massively inhomogeneously broadened line.

At low temperatures, the dephasing rate, or homogeneous linewidth, of the $v = 1 \rightarrow 2$ transition is more than

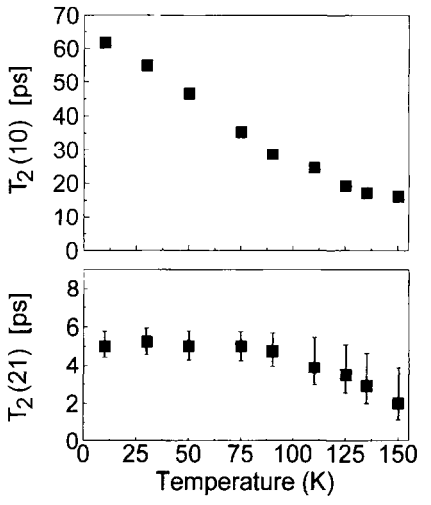

Fig. 2. Decay times $T_2(10) = 1/\gamma_{10}$ and $T_2(21) = 1/\gamma_{21}$ for temperatures between 10 K and 150 K obtained from fits to Eq. (2). Error bars for $T_2(10)$ are on the order of the size of the squares. Error bars for $T_2(21)$ show the influence of the small uncertainties in both $T_2(10)$ and Δ on the accuracy of the determination.

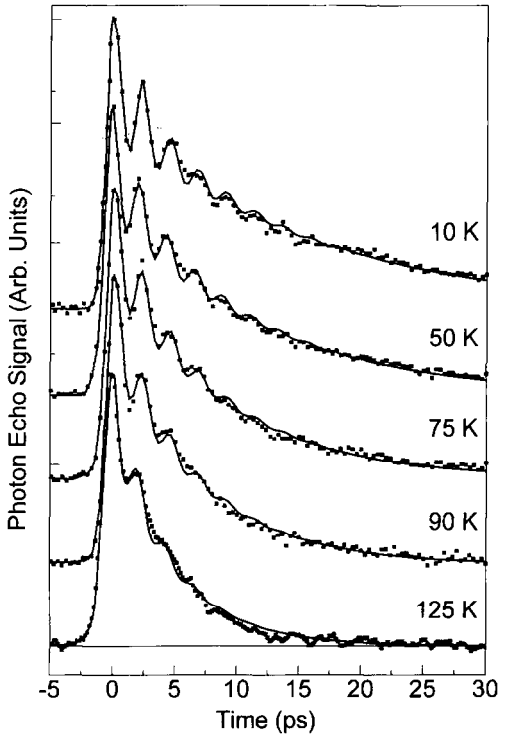

Fig. 1. Photon echo decays and fits for the asymmetric CO stretching mode of $W(CO)_6$ in di-butylphthalate at several temperatures in the glass. Fits are to Eq. (2) and represent the homogeneous dephasing of the three level coherence with beating at the anharmonic vibrational frequency splitting.

10 times that of the $v = 0 \rightarrow 1$ transition. Temperature dependent photon echo studies of $W(CO)_6$ in other glasses [1,2,12] indicate that the 10 K homogeneous line is dominated by lifetime broadening. The lack of temperature dependence of the homogeneous linewidth of the $v = 1 \rightarrow 2$ transition between 10 K and ~ 100 K suggests that the width arises from lifetime broadening since pure dephasing is temperature dependent. The $v = 0 \rightarrow 1$ dephasing can display temperature dependent pure dephasing over this same temperature range because the $v = 0 \rightarrow 1$ lifetime is much longer than the $v = 1 \rightarrow 2$ lifetime.

The temperature dependence of the $v = 0 \rightarrow 1$ dephasing is similar to that observed in other glasses [1,2] measured with photon echo experiments using the FEL. The rate of dephasing increases by a factor of ~ 6 over the temperature range studied. If the 10 K point is assumed to be the temperature independent vibrational lifetime and is subtracted out of the homogeneous linewidth, the remaining linewidth, due to pure dephasing, has a power law temperature dependence, $\Gamma \propto T^{\alpha}$ with $\alpha = 1.8$. This power law temperature dependence is representative of other measurements of the homogeneous linewidth in glasses, made with photon echoes [15] and infrared hole-burning [16,17]. A comparison of these results with those for two other glassy systems and the behavior in the three liquids will be presented in another publication [15]. As seen from the $v = 0 \rightarrow 1$ data, the $v = 1 \rightarrow 2$ dephasing rate begins to increase at higher temperatures as the pure dephasing rate approaches the upper level lifetime.

As evident from Eq. (2), at higher temperatures where $\gamma_{10} + \gamma_{21} \geq \Delta$ and $1/\gamma_{21}$ approaches the pulse width, an

accurate determination of γ_{21} cannot be made without proper convolution. When $\gamma_{21} > \Delta$, the decay of the $v = 1 \rightarrow 2$ coherence appears as part of an oscillation of less than one cycle near $t = 0$. The discussion and interpretation of higher temperature data, including convolution with the proper echo response function [18] for the decay of a three-level coherence with the three field interactions of the photon echo, is the subject of continuing work. It was possible to determine γ_{10} all the way to room temperature. It was found that the vibrational line in the liquid even at room temperature is massively inhomogeneously broadened [15].

4. Concluding remarks

This work presents the first measurements of homogeneous dephasing of a multilevel vibrational coherence in a condensed phase system. The infrared photon echo experiment, with excitation bandwidth wider than the vibrational anharmonicity, allows the determination of vibrational dephasing of both the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions, an accurate determination of the vibrational anharmonicity, and the removal of inhomogeneous contributions to the vibrational lineshape. These experiments suggest that performing this sort of Fourier transform spectroscopy with even shorter femtosecond pulses may make it possible to investigate more of the anharmonic potential of a vibrational mode by exciting many vibrational levels.

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