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Multilevel vibrational dephasing and vibrational anharmonicity from infrared photon echo beats

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Abstract

Vibrational photon echo experiments were performed on the asymmetric CO stretching mode of tungsten hexacarbonyl in glassy dibutylphthalate as a function of temperature using sub-picosecond infrared pulses (1976 cm^{-1}) from a free electron laser. The echo decays display pronounced beats and are bi-exponential. The beats and bi-exponential decays arise because the bandwidth of the pulses exceed 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 vibrational dephasing of both the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions are determined.

1. Introduction

The advantage of measuring vibrational spectra using Fourier transform spectroscopy is demonstrated by the greatly enhanced resolution that can be achieved compared to spectral dispersion techniques. Vibrational spectral characteristics, such as peak splittings and linewidths, can also be obtained with time domain experiments using short pulse, broad bandwidth excitation. This principle has been widely exploited with non-resonant coherent Raman experiments in the condensed phase, such as coherent anti-Stokes Raman [1] and Raman-induced Kerr effect experiments [2,3]. The time decay of a broad bandwidth coherence experiment is related to the Fourier transform of the spectral information within the excitation frequency bandwidth.

Although such experiments permit the measurement of multiple vibrational modes located within the excitation bandwidth, in liquids and other condensed phase systems, vibrational spectra can have contributions from inhomogeneous broadening which mask the homogeneous vibrational lineshape [4,5]. Third-order coherent Raman experiments measure the free induction decay of the spontaneous Raman line, and cannot distinguish or eliminate contributions from inhomogeneous broadening [6]. For this reason, higher-order Raman experiments, such as the Raman echo, are required to distinguish inhomogeneity in vibrational transitions [6–8].

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 [4,5]. 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

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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 their use in separating pure dephasing and lifetime contributions to the homogeneous vibrational linewidth [4], both of which can contribute significantly [4,12].

In this Letter, we report the results of sub-picosecond infrared vibrational photon echo experiments 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 T_{1u} asymmetric CO stretching mode of tungsten hexacarbonyl [$W(CO)_6$] in the organic glass dibutylphthalate (DBP). The temperature dependence of vibrational dephasing of both the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions is followed from 10 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 an ensemble of coherent superposition states that begin to dephase because of 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 polarization 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 system 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. The homogeneous dephasing time has contributions from the pure dephasing time T_2^* and vibrational lifetime T_1, related by $1/T_2 = 1/T_2^* + 1/2T_1$.

When the bandwidth of the excitation pulses exceed the vibrational anharmonicity, then population can be excited to higher vibrational levels. The extent of vibrational up-pumping 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. The expected photon echo signal can be described for an unequally spaced three-level system using a semiclassical perturbative treatment of the third-order nonlinear polarizability in the Bloch limit [13,14]. The three-level system is spaced by the frequencies ω_{10} and ω_{21}, where $\omega_{10} = \omega_{21} + \Delta$, and $\Delta \ll \omega_{10}$ and ω_{21}. Here Δ represents the anharmonic vibrational energy splitting. The transition frequencies ω_{10} and ω_{21} lie within the bandwidth of the pulses. For such a model, three-independent resonant pathways exists for the rephasing of the echo pulse. In addition to the two that exist for a rephasing of an echo in a two level system [14], a third pathway accounts for the possibility of rephasing the coherence created by the first pulse on the $v = 1 \rightarrow 2$ transition. For a finite pulse bandwidth, where the E-field amplitude differs at ω_{10} and ω_{21}, the decay is given by

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

Here, E_{10} and E_{21} are excitation E-field amplitudes for the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions, respectively. The phase factor in Eq. (2) does not arise from the derivation ($\phi = 0$), but has been added to aid in fitting the data, as discussed below. 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. The dephasing rates for the two transitions, γ_{10} and γ_{21}, are phenomenological; no model has been assumed for the coupling of these modes to the bath. For the narrow bandwidth case ($E_{21} \approx 0$), Eq. (1) is recovered. A similar expression has been obtained for a harmonic oscillator with equally spaced levels [15]. Since $\Delta = 0$, no beats are observed. This treatment was extended for a three-level model with $\Delta \neq 0$, but with infinite bandwidth pulses, i.e. $E_{10} = E_{21}$ [16].

Eq. (2) bears close similarity to the decay of a femtosecond coherent anti-Stokes Raman (CARS) signal with two discrete Raman transitions under the excitation bandwidth [1]. The CARS signal involves $v = 0 \rightarrow 1$ coherences only, and decays as the term in the brackets in Eq. (2), with dephasing times given for each Raman transition and beating observed at the frequency splitting. However, the decay of a multilevel vibrational coherence observed in the resonant photon echo is dictated by the decay of the $v = 0 \rightarrow 1$ coherence, as given by the exponential factor in front of Eq. (2). In addition, the CARS signal represents the free induction decays of the vibrational lines including any inhomogeneity, while the photon echo measures the true homogeneous lineshapes.

2. Experimental procedures

The infrared photon echo experiments were performed with ≈ 0.7 ps (≈ 20 cm^{-1} bandwidth) IR pulses at 5.06 μm (1976 cm^{-1}) generated with the Stanford superconducting-accelerator-pumped free electron laser (FEL). The pulses are transform-limited with a Gaussian envelope. Frequency stabilization allows wavelength drifts to be limited to $< 0.01\%$, or < 0.2 cm^{-1}. 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. The micropulse repetition rate was reduced to 50 kHz by a germanium AOM single pulse selector, yielding an experimental repetition rate of ≈ 1 kHz. The two pulses for the echo pulse sequence were obtained with a ZnSe beam splitter. The pulse time coincidence ($t = 0$) was determined by autocorrelation in $AgGaSe_2$. 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. Careful studies of the power dependence and repetition rate dependence 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 sample was sealed with a 400 μm teflon gasket between two CaF_2 flats in a copper housing, and the temperature was controlled using a closed-cycled He refrigerator. The sample temperature was measured to ± 0.2 K. Absorption spectra of the T_{1u} mode show that the band position shifts to the red by ≈ 1 cm^{-1} between 80 and 300 K, which is small compared to the FEL bandwidth of 20 cm^{-1}. The room temperature vibrational line is centered at 1975 cm^{-1} (5.063 μm). The absorption bandwidth is 26 cm^{-1} at all temperatures.

3. Results and discussion

Fig. 1 shows photon echo decays for asymmetric CO stretching mode of $W(CO)_6$ in DBP for several temperatures in the glass taken at 5.06 μm, as well as fits to Eq. (2). These decays are essentially 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 $\Delta = 14.7$ cm^{-1} ± 0.3 cm^{-1}. This splitting is in accord with the value of 15 cm^{-1} ± 1 cm^{-1} recently obtained by Heilweil and co-workers from observation of the $v = 1 \rightarrow 2$ and $v = 2 \rightarrow 3$ transitions of the asymmet-

ric CO stretching mode of $W(CO)_6$ in hexane 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 the anharmonic oscillator.

The echo decay data also provide the homogeneous dephasing times for the two transitions involved in the multilevel coherence. The results are displayed in Fig. 2. The homogeneous dephasing times for the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions are given for temperatures between 10 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. The error bars given for γ_{21} reflect the influence of the magnitude of γ_{10}, the amplitude of the beats, and the magnitude of γ_{21} relative to Δ in determining the upper level dephasing rates.

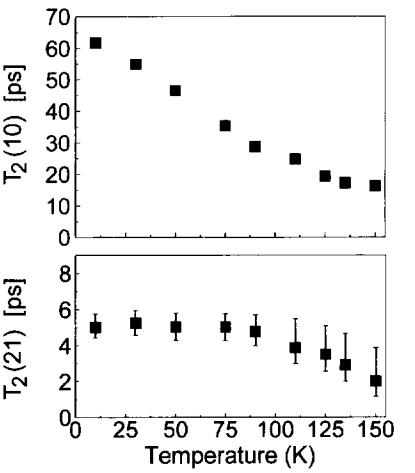

Fig. 2. Decay times $T_2(10) = 1/\gamma_{10}$ and $T_2(21) = 1/\gamma_{21}$ for temperatures between 10 and 150 K obtained from fits to Eq. (2). Error bars for $T_2(10)$ are on the order of the size of the squares. Error bars for $T_2(21)$ show the influence of the small uncertainties in $T_2(10)$ and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

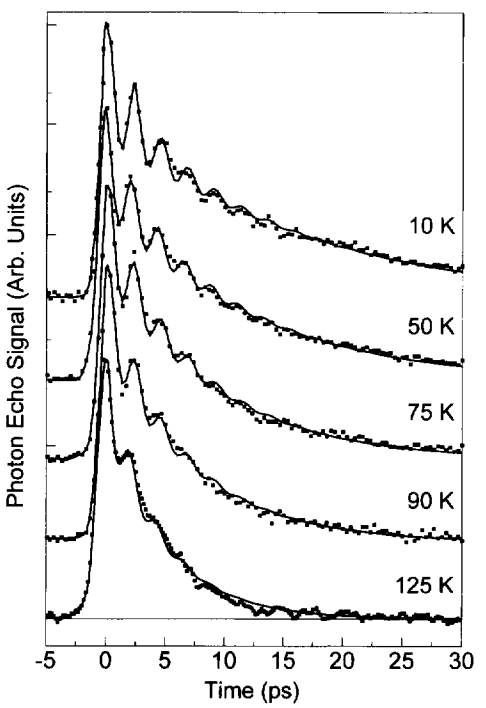

Fig. 1. Photon echo decays and fits for asymmetric CO stretching mode of $W(CO)_6$ in dibutylphthalate at several temperatures in the glass. Fits are to Eq. (2) and represent the homogeneous dephasing of the three level coherence with beating at the anharmonic vibrational frequency splitting.

In fitting the data, the phenomenological phase factor ϕ in Eq. (2) was varied in addition to the other parameters. While the data can be fit with $\phi = 0$, the fitting routine consistently returned values of $\phi \approx \pi/2$ at all temperatures. Although the fit is improved by varying ϕ, this does not significantly effect the values of the reported parameters. The error bars in Fig. 2 include the uncertainty in ϕ.

The simplest models for the dependence of the vibrational lifetime of a $v \rightarrow v + 1$ transition on the vibrational quantum number v predict that the rate of vibrational relaxation will scale linearly with v [17]. A linear dependence occurs if the density of bath states and the strength of coupling to the bath for the relaxation process are assumed to be independent of v. Then the action of a lowering operator for a $v \rightarrow v - 1$ relaxation brings out a factor of $\sqrt{v}$. The relaxation rate scales as the square of this matrix element, yielding a linear dependence. If the vibrational dephasing is dominated by vibrational lifetime relaxation, the linewidth for $v \rightarrow v + 1$ transitions would also increase linearly with v. This relationship appears to exist in transient infrared spectra of a hydrogen-bonded polymer [18]. However the relaxation behavior can be dramatically different [11,19]. Detailed consideration of the density of states, thermal occupation of the receiving modes, and variation

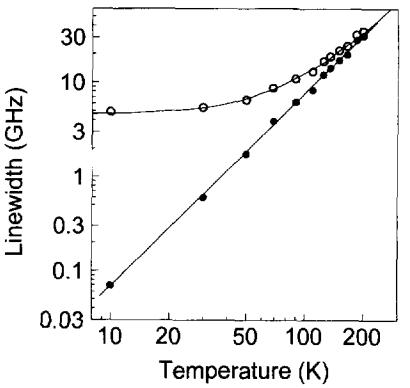

Fig. 3. Homogeneous linewidth of $W(CO)_6$ in DBP between 10 and 200 K. The homogeneous linewidth $(1/\pi T_2)$ is shown in open circles, and the corresponding data with the low temperature lifetime of $T_1(0\ K) = 33$ ps removed are shown with solid circles. The data fit has a power law temperature dependence ($\Gamma \propto T^{\alpha}$) with a power law of $\alpha = 1.9 \pm 0.1$.

in the strength of coupling to the bath with v can determine the v dependence of the relaxation rate in anharmonic systems [20].

At low temperatures, the dephasing rate, or homogeneous linewidth, of the $v = 1 \rightarrow 2$ transition is more than 10 times that of the $v = 0 \rightarrow 1$ transition. Temperature-dependent photon echo studies of $W(CO)_6$ in other glasses [4,5,12] indicate that the low temperature $v = 0 \rightarrow 1$ 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 and ≈ 100 K strongly suggests that the width arises from lifetime broadening since pure dephasing is temperature dependent. The $v = 0 \rightarrow 1$ dephasing displays 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.

In Fig. 3, the rates of dephasing of the $v = 0 \rightarrow 1$ transition are plotted as the homogeneous linewidth. The rates of dephasing increase by a factor of ≈ 6 over the temperature range studied. If the 10 K point is assumed to be the temperature independent vibrational lifetime ($\Gamma_0 = 1/2T_1$) 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 $\alpha = 1.9$. The temperature-dependent contribution to pure dephasing with the power law fit is also shown in Fig. 3. This power law temperature dependence is representative of other measurements of the homogeneous linewidth in glasses, made with photon echoes [21] and infrared hole-burning [22,23]. 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 [21].

Although it is temperature independent at lower temperatures, the rate of dephasing for the $v = 1 \rightarrow 2$ transition begins to increase above 80 K. This occurs as the rates of pure dephasing T_2^* become significant relative to the lifetime contribution $2T_1$. It can be seen from Fig. 2 that the $v = 1 \rightarrow 2$ dephasing begins to increase at the temperature where the $v = 0 \rightarrow 1$ dephasing becomes non-negligible compared to the low temperature $v = 1 \rightarrow 2$ dephasing. This may suggest that the rates of *pure* dephasing for the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions have similar magnitudes and temperature dependences.

As is evident from Eq. (2), at higher temperatures where $\gamma_{10} + \gamma_{21} \geqslant \Delta$ 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 of the material response with the true pulse E-field envelopes for the decay of a three level coherence with the three field interactions of the photon echo, is the subject of continuing work.

The data displayed in Fig. 1 was taken with the center of the laser bandwidth slightly to the blue of the absorption peak. As the excitation source is tuned to the red of the peak, the magnitude of the E-field at the $v = 1 \rightarrow 2$ transition frequency increases. Fig. 4 shows photon echo data taken at 10 K for excitation frequencies of 5.07, 5.08 and 5.09 μm. The peak absorption frequency is at 5.063 μm. These increments (0.01 μm $\approx 4\ cm^{-1}$) are small compared to the laser bandwidth of 20 cm^{-1}, yet result in pronounced differences in the form of the echo decay. Notice that these decays differ from the 10 K data in Fig. 1 taken at 5.06 μm. Excitation on the blue side of the line gives the behavior described by Eq. (2). As the excitation frequency is shifted to the red, the amplitude of the oscillations decreases, and the rise-time to the peak echo signal shifts to longer

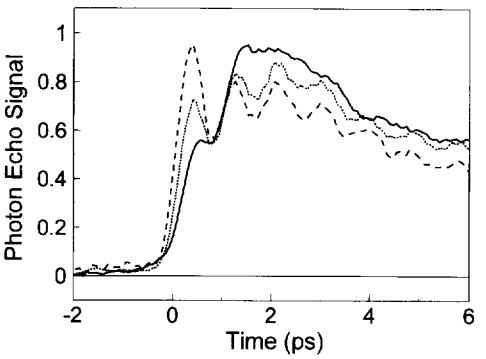

Fig. 4. Photon echo decays as a function of excitation wavelength near $t = 0$ at 10 K. Excitation wavelengths are 5.07 μm (– – –), 5.08 μm (· · ·), and 5.09 μm (———), which are small increments relative to the laser bandwidth. The peak absorption wavelength is 5.063 μm. Note that all of these decays differ from the 10 K data in Fig. 1 taken at 5.06 μm. Data has been normalized to the peak signal.

delay times. In addition, the amplitude of the initial beat is decreased. However, the phase and frequency of the oscillations are independent of the excitation wavelength. At long times ($\tau > 1/\gamma_{21}$), all decays are exponential and relax with γ_{10}, as with the 10 K data in Fig. 1. The longest wavelength excitation in Fig. 4 represents a frequency directly between the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions.

Eq. (2) cannot account for the observed behavior. The change in frequency would come into Eq. (2) only by changing the magnitudes of the two E fields, E_{10} and E_{21}. It is possible that the observed behavior occurs because of coherent excitation of the $v = 2 \rightarrow 3$ transition. Then, the decay must be described in terms of a four level coherence, and interference terms in the evolution of the coherence will occur at both the 14.7 cm^{-1} splitting of the adjacent vibrational transitions and the 29.4 cm^{-1} splitting between the $v = 0 \rightarrow 1$ and $v = 2 \rightarrow 3$ transitions. This high frequency beating, when convolved with a 0.7 ps pulse, will be washed out to give a featureless profile.

In general, phase factors are not expected for time reversal experiments such as the photon echo in the low flip angle, delta function excitation limit. However, in these experiments, the Rabi frequency is approximately equal to the laser bandwidth, and the experiment may not be considered in the low power limit. The failure of Eq. (2) to account for the frequency dependence displayed in Fig. 4 and the necessity of employing a phase factor in the data analysis could arise because Eq. (2) is derived for low power conditions.

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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