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T_2 selective scanning vibrational echo spectroscopy

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Abstract

Experiments are presented on a mixture of tungsten hexacarbonyl ($W(CO)_6$) and (acetylacetonato)dicarbonylrhodium(I) ($Rh(CO)_2acac$) in liquid dibutylphthalate (DBP) in which the spectrum of the asymmetric CO stretching modes (~ 2000 cm^{-1}) is taken by continuously scanning the frequency of a ps vibrational echo pulse sequence and observing the vibrational echo intensity. While the absorption spectrum shows a large solvent background with DBP vibrational peaks, the vibrational echo spectrum is background free and contains only the $W(CO)_6$ and $Rh(CO)_2acac$ peaks. When the delay between the vibrational echo pulses is changed, the ratio of the $W(CO)_6$ and $Rh(CO)_2acac$ peaks changes because of differences in their homogeneous dephasing times.

1. Introduction

Infrared vibrational absorption spectroscopy is a useful method for obtaining information about bonding, anharmonicity, solvent interactions, and dynamics of molecules in condensed phase systems. In the mid infrared region of the spectrum, there are usually a large number of absorbances. These arise from fundamental, overtone, and combination band transitions of molecular vibrations. Moderate sized molecules can have spectra with a large number of peaks. Systems of large molecules in complex solvents can have spectra that are so crowded that clean observation of the spectral feature of interest can become difficult. In principle, the solvent spectrum can be subtracted out by taking a background spectrum with the solvent alone. However, when the species of interest is in low concentration, in some cases accurately performing background subtraction can be difficult [1].

Proteins and other biological molecules can have spectral bandwidths which are wide compared to the spacing between the bands, making structural assignments and quantitative IR absorption spectroscopy measurements difficult [2,3]. Mathematical techniques can be used to narrow an absorption line [4]. However, such techniques lose information on line widths and shapes, reducing the usefulness of pure mathematical methods.

The vibrational echo is a coherent pulsed infrared technique that can extract the vibrational homogeneous line shape even from a massively inhomogeneously broadened vibration line. Vibrational echoes

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have been applied to the study of liquids, glasses, and proteins [5–9]. Recently, a new method, vibrational echo spectroscopy (VES), which is a utilization of vibrational echoes to measure spectra rather than dynamics, has been described theoretically and demonstrated experimentally [10]. VES is a form of two-dimensional vibrational spectroscopy. The two independently variable parameters are time delay between the infrared (IR) pulses that create the echo signal and the center frequency of the IR. Using VES it is possible to suppress unwanted background and peaks in a vibrational spectrum.

The development of the NMR spin echo in 1950 [11], changed the nature of magnetic resonance spectroscopy. The spin echo, a coherent pulsed technique, is the precursor of the sophisticated pulse methods that are widely used today. In VES, background suppression is in some respects analogous to NMR background suppression techniques [12,13]. Coherent sequences of pulses are used to remove unwanted spectral features in both types of spectroscopy.

In the following, the first continuously scanned VES spectra are presented. The spectrum of the asymmetric CO stretching modes (~ 2000 cm^{-1}) of tungsten hexacarbonyl ($W(CO)_6$) and (acetylacetonato)dicarbonylrhodium(I) ($Rh(CO)_2$acac) in liquid dibutyl phthalate (DBP) is recorded by continuously scanning the frequency of a ps vibrational echo pulse sequence and observing the vibrational echo intensity. While the absorption spectrum shows a large solvent background with DBP vibrational peaks, the vibrational echo spectrum is background free and contains only the $W(CO)_6$ and $Rh(CO)_2$acac peaks. When the delay between the vibrational echo pulses is changed, the ratio of the $W(CO)_6$ and $Rh(CO)_2$acac peaks changes because of differences in their homogeneous dephasing times, T_2s. Thus, it is possible to suppress the solvent absorption and emphasize one peak over another using VES.

2. Experimental procedures

Infrared vibrational echo experimental method has been described in detail previously [7]. Unlike a vibrational echo experiment, in which the frequency is fixed and the time between the pulses is scanned, VES requires a tunable source of infrared pulses. In the experiments presented below vibrational echo spectra were taken with the Stanford Free Electron Laser (FEL) [7]. It should also be possible to perform VES experiments using conventional laser systems based on optical parametric amplifiers to down convert visible or near IR light into the IR.

The FEL produces a ~ 2 ms macropulse at a ~ 5 Hz repetition rate. Each macropulse consists of ~ 1 ps micropulses at a repetition rate of 11.8 MHz (84.7 ns). The micropulse energy at the input to experimental optics is ~ 0.5. To avoid sample heating problems, micropulses are selected out of each macropulse at a repetition rate of 50 kHz by Ge acousto-optic modulator single pulse selectors. This pulse selection yields an effective experimental repetition rate of ~ 1 kHz, and an average power < 0.5 mW.

The two pulses for the VES experiment were obtained using a 10%R beam splitter. The 10% beam is single pulse selected using an Ge AOM and sent through a computer-controlled stepper motor delay line. The remaining portion (second pulse in the vibrational echo pulse sequence) is single pulse selected by a second Ge AOM. The first AOM selects pulses at 25 kHz, i.e., half the rate of the second pulse, permitting subtraction of scattered light background generated by the stronger pulse. The two pulses were focused using an off-axis parabolic reflector for achromatic focusing to ~ 100 μm diameter and crossed in the sample. The VES signals were measured with an InSb detector, gated integrators, digitized, and recorded by computer.

The experiments were conducted in the frequency range around ~ 2000 cm^{-1}. The frequency of the FEL is determined by energy of the electron beam that enters the wiggler [14]. Normally, this wavelength is fixed and stabilized by a feed back system that uses a monochromator to monitor the FEL wavelength and control the electron beam energy to stabilize the wavelength. This active frequency stabilization allows wavelength drifts to be limited to < 0.2 cm^{-1}. In the VES experiments, the FEL is continuously scanned over the frequency range of interest, ~ 120 cm^{-1}. This was accomplished by slowly scanning the monochromator used in the frequency feed back stabilization system. As the monochromator is scanned, the feed back system adjusts

the electron beam energy to maintain the center of the FEL wavelength at the monochromator wavelength setting. The $\sim 120\ \mathrm{cm}^{-1}$ scan required ~ 5 min. A second monochromator was used to measure the spectrum of the FEL pulse and to determine the wavelength at the beginning and the end of the scans. An IR autocorrelator was used to measure the duration of the pulses.

When the FEL is used to perform a vibrational echo experiment, the wavelength is set, and various parameters of the FEL, such as the cavity length, are adjusted to optimize the operating characteristics at the chosen wavelength. When the wavelength was scanned for the VES experiments, the pulse characteristics changed somewhat over the scan. The changes in the intensity of the FEL were recorded and, using the I^3 dependence of the vibrational echo signal, the intensity changes were normalized out of the data [10]. However, changes in bandwidth and pulse duration were not corrected for. Over the scanned range the pulse duration and the bandwidth changed $< 20\%$. These changes could be reduced or eliminated by a system that adjusted the cavity length as the laser is scanned.

Careful studies of power dependence and repetition rate dependence of the vibrational echo data on the molecules studied have been performed previously. It was determined that there were no heating or other unwanted effects when vibrational echo experiments were performed with the available pulse energies at the sample of ~ 200 nJ and a repetition rate of 50 kHz during each macropulse.

The sample consisted of $W(CO)_6$, concentration 5×10^{-4} M, and $Rh(CO)_2$acac concentration 1×10^{-3} M, in DBP. The solution was placed in a cell composed of CaF_2 flats with a 400 μm path length. The experiments were conducted at room temperature. The absorption spectrum of the sample was taken with an FT-IR spectrometer. The concentrations of the $W(CO)_6$ and $Rh(CO)_2$acac were adjusted so that their absorbances were approximately the same.

3. Results and discussion

A detailed theoretical calculation of the VES signal, model calculations, and comparison to the absorption spectrum have been given previously [10]. The vibrational echo signal from a solution composed of a number of species including the solvent and solutes is a function of a large number of parameters, which must be included in the calculation. These are the optical frequency, the finite pulse duration, and the homogeneous and inhomogeneous widths, concentrations, and transition dipole matrix elements for each species.

An IR vibrational echo experiment can be described as a third order non-linear experiment using diagrammatic perturbation theory. For a single transition of one species, the total third order polarization is the sum of the third order polarizations from each of the four diagrams [15,16]:

$$P^{(3)}_{\mathrm{tot}} = \sum_{N=\mathrm{I}}^{\mathrm{IV}} P^{(3)}_N \tag{1}$$

Two of the diagrams (echo diagrams) represent rephasing paths. These give rise to what is normally considered an echo. If the homogeneous T_2 is long compared to the pulse duration, vibrational echo signal occurs when the pulses are separated in time. There are also two diagrams (grating diagrams) that represent non-rephasing paths. These only contribute to the signal when the pulses are overlapped in time. Since a VES spectrum can be taken with $t = 0$, all four diagrams need to be considered. To calculate the vibrational echo observable for a fixed laser frequency, ω_1, $P^{(3)}$ must be integrated over the inhomogeneous line, $g(\omega_{\mathrm{ba}})$ and then the modulus square of the result must be integrated over all time since the observable is the integrated intensity of the echo pulse [15,16],

$$I_{\mathrm{s}}(\tau, \omega_1) \propto \int_{-\infty}^{\infty} \mathrm{d}t_{\mathrm{s}} \left| \int_0^{\infty} \mathrm{d}\omega_{\mathrm{ba}}\, g(\omega_{\mathrm{ba}})\, P^{(3)}_{\mathrm{tot}}(\omega_{\mathrm{ba}}, \tau, \omega_1) \right|^2 . \tag{2}$$

τ is the separation between the two laser pulses. The numerical calculation of the vibrational echo spectrum with realistic laser pulse envelopes and realistic material properties involves a five dimensional integral. This is the situation for a single transition of a

single species. In general, there are two or more spectroscopic lines with independent $P^{(3)}$. The contribution from each transition of each species must be summed at the polarization level

$$I_s(\tau,\omega_1) \propto \int_{-\infty}^{\infty} \mathrm{d}t_g \times \left| \sum_{i,j} \left[\int_0^{\infty} \mathrm{d}\omega_{ab}^{i,j}\, g_{i,j}\left(\omega_{ab}^{i,j}\right) P^{(3)}_{tot,i,j}\left(\omega_{ab}^{i,j},\tau,\omega_1\right) \right] \right|^2, \quad (3)$$

where i is the label for the species and j is the label for the jth transition of the ith species [10]. It is necessary to distinguish between transitions on different species since the species may have different concentrations as well as the transitions having distinct line shapes, $g_{i,j}(\omega_{ab}^{i,j})$, and transition dipole matrix elements [10].

For fixed τ, if ω_1 is scanned, $I_s(\tau,\omega_1)$ is the vibrational echo spectrum. In VES, line selectivity can be achieved because nearby transitions can have different homogeneous dephasing times or substantially different transition dipole moments [10]. Absorption is proportional to $m\mu^2$ while the echo signal is proportional to $m^2\mu^8$, where m is the concentration of the species and μ is the transition dipole matrix element. If the background is composed of a very high concentration of weak absorbers (m large, μ small) and the spectral features of interest are in low concentration but are strong absorbers (m small, μ large), the background absorption can be substantial, but the vibrational echo spectrum can suppress the background and enhances the relevant peaks. This situation can occur, for example, if the background arises from combination bands and overtones of the solvent while the relevant peaks are low concentration fundamentals.

If the background or unwanted peak absorptions have homogeneous dephasing times, T_2^bs, short compared to the T_2s of the lines of interest, then VES can use the time evolution of the system to discriminate against the unwanted features. The time, τ, between the pulses in the vibrational echo sequence is set such that it is long compared to T_2^b but short compared to T_2. The vibrational echo signal from the background will have decayed to zero while the signal from the desired peaks will be non-zero.

Fig. 1 displays the absorption spectrum and the VES spectrum of $W(CO)_6$ and $Rh(CO)_2$acac in DBP. The upper trace is the absorption spectrum. The peak at 1976 cm^{-1} is the asymmetric CO stretching mode of $W(CO)_6$ and the peak at 2012 cm^{-1} is the asymmetric CO stretching mode of $Rh(CO)_2$acac. The vertical axis is in absorbance units for the upper trace. The DBP has a very broad absorption in the region giving a background absorbance (optical density) of ~ 0.5. In addition there is at least one solvent peak at ~ 1948 cm^{-1}. The lower trace is the VES spectrum. For the VES spectrum, the vertical axis is in arbitrary units. Two features are immediately clear. First, the background is zero, and second, the solvent peak at 1948 cm^{-1} is not visible.

As discussed above, there are two mechanisms by which VES can eliminate background and spectral peaks, T_2 selectivity and transition dipole matrix element selectivity. The VES scan in Fig. 1 was taken with $\tau = 0$. Nonetheless, there can still be T_2 selectivity. The pulses have finite duration, ~ 1 ps. The vibrational echo signal arises from three interactions with the fields, the first interaction is with the first pulse and the second and third interactions are

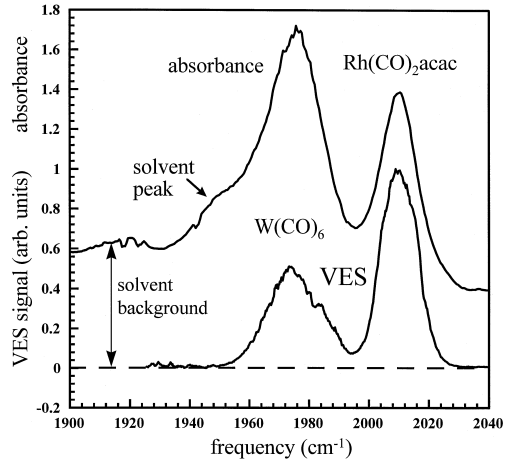

Fig. 1. Absorption spectrum (upper trace) and VES spectrum (lower trace) of the asymmetric CO stretching modes of $W(CO)_6$ and $Rh(CO)_2$acac in the solvent dibutylphthalate at room temperature. The vertical axis is in absorbance units for the upper trace. For the VES spectrum, the vertical axis is in arbitrary units. In the VES spectrum, the solvent background is eliminated.

with the second pulse. The interactions do not have to be time coincident, only time ordered, i.e., the second interaction must come after the first, and the third interaction must come after the second. A transition with a T_2 that is longer than the pulse will produce a polarization that involves the integral of the time ordered interactions throughout the pulses. Since the intensity of the signal is related to the absolute value squared of the polarization, the signal grows dramatically during the duration of the pulse. However, if T_2 is very short, the three interactions must occur almost simultaneously, and the polarization does not increase integrally throughout the pulse, greatly reducing the signal.

While T_2 selectivity may contribute to the elimination of the solvent background, it is clear that in this sample transition dipole matrix element selectivity will eliminate the background. Using round numbers, the DBP concentration is ~ 10 M and its absorbance is ~ 1. The metal carbonyl concentrations are $\sim 10^{-3}$ M and their absorbances are ~ 1. Therefore, the metal carbonyl extinction coefficients are $\sim 10^4$ larger than the solvents and their concentrations are $\sim 10^4$ smaller than the solvents. In terms of the extinction coefficient, ε, and the concentration, m, the VES signal, $I_s \propto m^2\varepsilon^4$. Therefore, I_s should be on the order of $\sim 10^8$ greater for the metal carbonyls than for the DBP solvent. The result is the observed zero solvent background spectrum.

Fig. 2 illustrates T_2 selectivity between the metal carbonyl peaks. Two scans were taken, one with zero delay and one with 1 ps delay between the vibrational echo excitation pulses. The two spectra have been normalized to make the $Rh(CO)_2$acac peaks the same size. The change in the relative peak heights is clear.

Vibrational echo experiments have been used to measure the homogeneous T_2s of both solutes in DBP below room temperature [5,8]. The T_2s are not known accurately at room temperature, but estimates based on the low temperature measurements indicate that the absorption lines are substantially inhomogeneously broadened at room temperature. In principle, it is possible to take a series of spectra like those shown in Fig. 2 with different delays. Plotting the peak heights (without normalization to one peak) as a function of delay would yield the homogeneous T_2 for each peak. However, in most cases it would be preferable to obtain T_2 by fixing the frequency on a particular peak and scanning the pulse separation to record an echo decay curve.

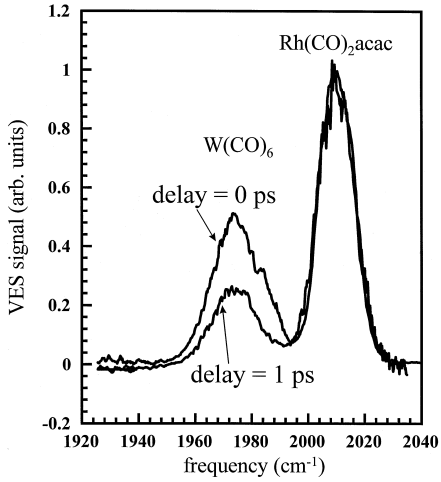

Fig. 2. Two VES spectra of the asymmetric CO stretching modes of $W(CO)_6$ and $Rh(CO)_2$acac in the solvent dibutylphthalate at room temperature taken with delay times of 0 ps and 1 ps between the excitation pulses in the vibrational echo pulse sequence. The spectra are normalized at the peak of the $Rh(CO)_2$acac spectra. When the delay is increased, the relative sizes of the $W(CO)_6$ and $Rh(CO)_2$acac peaks change because the $W(CO)_6$ homogeneous dephasing time is shorter than that of $Rh(CO)_2$acac.

As can be seen from the spectrum, $W(CO)_6$ has a shorter T_2 than $Rh(CO)_2$acac in DBP at room temperature. With a longer delay, it would be possible to eliminate the $W(CO)_6$ peak completely from the spectrum. Subtracting the 1 ps trace from the 0 ps trace can eliminate the $Rh(CO)_2$acac peak. Fig. 2 shows that it is possible to manipulate peaks that appear in the VES in addition to eliminating a broad solvent background.

4. Concluding remarks

The data presented above demonstrates that it is possible to use vibrational echo spectroscopy to take a true scanning vibrational spectrum. The spectra were taken with an FEL, which is configured for stable fixed frequency operation. As described in Section 2, the frequency stabilization system of the FEL was manipulated to cause the FEL to scan its

wavelength. As can be seen from the data, spectra can be taken with quite good signal-to-noise ratio in a single scan in ~ 5 min.

VES experiments require a tunable source of IR pulses. These can be obtained from a commercially available Ti:Sapphire based OPA system, which has recently been used to perform vibrational echoes at ~ 5 μm on the CO stretch of CO bound to the protein hemoglobin. Such OPA systems can produce several μJ pulses at 1 kHz repetition rate from 1 μm to 10 μm. It is possible to scan an IR OPA under computer control. However, there can be problems with bandwidths from IR OPAs. VES, like any spectroscopy, has a resolution that is ultimately limited by the laser pulse bandwidth. IR OPAs that produce fs pulses can be very efficient (pulse energies > 10 μJ). It is more difficult to produce ps or longer pulses with narrow bandwidths. Condensed phase vibrational lines typically have widths of ~ 10 cm^{-1} or greater, although very narrow lines can be ~ 5 cm^{-1} wide. Current, commercially available IR OPAs can readily produce 20 cm^{-1} bandwidth pulses, and it seems clear that there is room for reducing this bandwidth further.

In the early days of NMR, an experiment required a massive amount of home-build equipment. Today, complete, highly sophisticated NMR instruments are available as commercial instruments. The VES experiments presented above are a step toward extension of methods like those used in NMR to vibrational spectroscopy. We are at the point where the laser equipment necessary to perform VES is commercially available. It is possible that in the future, fully commercial short pulse IR spectrometers will make coherent pulse sequence vibrational spectroscopy an everyday tool in the fields of chemistry, physics, biology, medicine, and materials science.

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