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Waveguide-Enhanced 2D-IR Spectroscopy in the Gas-Phase

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A novel method for obtaining high quality 2D-IR spectra of gas-phase samples is presented. Time-resolved IR absorption spectroscopy techniques, such as 2D-IR spectroscopy, often require that beams are focused into the sample. This limits the exploitable overlapped path length through samples to a few millimeters. To circumvent this path length limitation, 2D-IR experiments have been performed within a hollow waveguide. This has enabled acquisition of high quality 2D-IR spectra of low concentration gas-phase samples, with more than an order of magnitude signal enhancement compared with the equivalent experiment in free space. The technique is described, with demonstration of its application to the 2D-IR spectroscopy of iron (0) pentacarbonyl.

OCIS Codes: (230.7370) Optical devices, waveguides; (300.6500) Spectroscopy, time-resolved; (300.6340) Spectroscopy, infrared (140.3490).

Introduction

Ultrafast time-resolved IR absorption spectroscopy is an excellent approach for studying dynamic structural changes. In particular, over the last 15 years, 2D-IR spectroscopy [1–3] has been successfully applied to studies of a range of structural dynamics [4,5] and energy transfer processes [6,7]. A wide range of approaches involve pulsed IR excitation and IR probing of samples providing detailed dynamical information about vibrational processes in molecules.

In the condensed-phase, 2D-IR spectroscopy has become a mature field, even extending its application to large biological systems [8–10]. However, the use of the technique to study gas-phase samples is still limited. When studying a chemical reaction, the role of the environment cannot be ignored [11,12]. In the case of condensed-phase 2D-IR experiments, one often considers whether energy transfer or ligand exchange processes are truly intra-molecular or solvent-mediated. Solution-phase experiments are usually performed under a variety of conditions (*e.g.* in different solvents) to resolve such ambiguity. The possibility to perform such experiments in the gas-phase offers an opportunity to remove solvent effects altogether.

Compared to the condensed-phase, gas-phase spectroscopy suffers from low sample concentrations and thus weak signal intensities. It is normally straightforward to increase the path length through the sample to regain signal intensity. However, transient pump – probe spectroscopy techniques like 2D-IR require that the beams be focused onto the sample in order to generate a sufficient population of excited state species to probe. This requirement to use focused beams (typically 100 μm diameter) limits the path length of a measurement to a few millimeters in the mid-IR. Previous IR pump – IR probe measurements have utilized sample heating to increase vapor pressures [13] or high IR pump energies to maximize the transient populations to be observed [14].

However, Quack and coworkers [15] overcame focusing limitations in near-IR pump – UV probe experiments by performing them in a hollow waveguide over a 500 mm path length.

To increase the effective path length of a gas-phase 2D-IR measurement to > 90 mm, we performed experiments inside a square hollow IR waveguide [16], made from polycrystalline macorTM ceramic. Signal intensity is enhanced by more than an order of magnitude as compared with unguided measurements, despite some laser intensity losses incurred by transport through the waveguide.

Iron (0) pentacarbonyl, $\text{Fe}(\text{CO})_5$, provides an ideal demonstration of the present technique as it has significant vapor pressure (21 Torr at 293 K), intense absorptions in the 2000 cm^{-1} region of the mid-IR spectrum and because there are previous solution-phase studies with which to compare [17].

Experimental

2D-IR spectra of $\text{Fe}(\text{CO})_5$ vapor were taken using a double-resonance approach [18], with a narrowband ($\sim 10 \text{ cm}^{-1}$, 2 ps duration) pump pulse and a broadband ($\sim 300 \text{ cm}^{-1}$, 50 fs duration) probe pulse. The IR pulses were generated from a 10 kHz repetition rate, dual ps/fs titanium sapphire amplified laser (Thales) described previously [19]. Synchronized ps and fs 800 nm outputs from the titanium sapphire laser pumped two optical parametric amplifiers (OPA, Light Conversion), with IR generation achieved through signal and idler difference frequency generation. Pump and probe pulses were combined at a 50 % beamsplitter, propagated collinearly, and focused to spot-sizes of $\sim 100 \mu\text{m}$ diameter in the gas cell containing the sample, as shown in figure 1. After propagating through the sample, the expanding IR beams were recollimated and directed to an IR spectrograph. In experiments where the waveguide was omitted from the gas cell, the position of the collimating lens was adjusted

accordingly. The two beams had orthogonal polarizations, so that the pump beam could be removed from the collinear probe beam after the sample by positioning a polarizer just before the spectrograph. Pump pulse energies were ~ 500 nJ, and the relative timing of the pump and probe pulses was computer-controlled by an optical delay line. 2D-IR scans were accumulated by computer-controlled scanning of the pump OPA wavelength and recording normalized pump on – pump off difference spectra at each position.

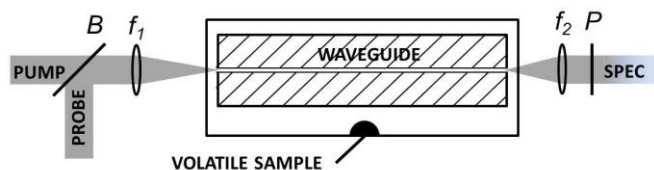


Figure 1. Experimental layout. The waveguide is placed inside a sealed cell, with CaF_2 windows, containing the sample. Pump and probe beams are combined at a beamsplitter (B) and focused (f_1) onto the waveguide entrance. After passing through the waveguide, the beams are collimated (f_2), the pump beam removed by a polarizer (P) and the probe beam sent to a spectrograph.

$\text{Fe}(\text{CO})_5$ vapor was prepared in the 100 mm long non-evacuatable gas cell (with CaF_2 windows on each end) by placing $\ll 1$ ml volume of a 2 mM solution of $\text{Fe}(\text{CO})_5$ in n -heptane. The vapor diffused throughout the cell within minutes, creating an optical density (OD) of 0.4 at the IR wavelengths of interest. The sample was diluted in heptane to reduce the vapor pressure, as a room temperature sample of pure $\text{Fe}(\text{CO})_5$ has an OD > 4 at this wavelength. The heptane vapor has no significant absorption in this spectral region. The waveguide was placed inside the gas cell and aligned onto the beam.

The waveguides used in this study had lengths of 84 or 97 mm. Results obtained using 300 μm wide waveguides of both lengths were compared, and <10 % difference in signal intensity observed. This probably reflects the inefficient transmission through the waveguides (see below), with the major pump contribution to the signal coming from the early part of the waveguide.

Results

Important considerations when taking measurements of samples inside the waveguide are: (i) the IR beams are propagated with minimum loss, (ii) time resolution is not lost due to excitation of multiple waveguide modes, (iii) polarization is preserved in the waveguide and that there is no perturbation of the spectrum or dynamics due to (iv) measurement in the waveguide compared to free gas or (v) due to surface effects.

(i) Previous tests on a 1 mm wide hollow waveguide with ~ 10 μm wavelength QCL lasers showed that, with correct mode matching, >98 % transmission is achievable [16], close to the expected theoretical transmission. The transmission scales with the guide width. At 5 μm , the maximum theoretical transmission through an 84 mm long hollow waveguide would be 96, 88, and 56 % for a 300, 200, and 120 μm guide width, respectively [20]. With the ultrafast lasers used here at ~ 5 μm wavelength, > 25

% was achieved. This additional loss suggests that high order hybrid modes are excited within the waveguide due to non TEM_{00} Gaussian beams, imperfect angular and axial coupling conditions, and increased scattering of the waveguide surfaces. Indeed, even though the arithmetic average surface roughness of the waveguide wall is ~ 0.5 μm , the maximum peak to valley roughness can be as high as ~ 5 μm . For the present demonstration, this loss of power through the waveguide reduces the observed signal strength as the compromised pump power reduces the excitation efficiency. However, the >10 -fold increase in signal intensity demonstrated below (fig. 2) demonstrates the principle of improvement in 2D-IR spectra, despite these transmission losses. With improved waveguide surface quality and spatial mode matching of the ultrafast laser to the waveguide, one may expect at least a further 2-fold improvement over the present results.

(ii) A time-resolved IR absorption cross-correlation of the IR pulses with synchronized 50 fs, 400 nm pulses in germanium was made before and after passage through the waveguide. The difference in the cross-correlation rise time was < 100 fs.

(iii) Polarizers before and after the waveguide confirmed the polarization to be preserved after passing through the waveguide at a level of $> 300:1$.

(iv) The flow of fresh sample through the waveguide is restricted compared with the open gas but we are not damaging the molecule by dissociation or generating long-lived excited states in these 2D-IR experiments. Repumping the same part of the sample at the 5 kHz repetition rate of the pump pulses is thus acceptable.

(v) A potential perturbation in the measurements could come from surface associated or condensed-phase sample in the waveguide. Significant condensation could occur if the waveguide temperature was lower than the sample temperature, or if there was high sample vapor pressure. In these experiments, all apparatus was maintained at 293K and the vapor pressure was very low (*cf.* a pure $\text{Fe}(\text{CO})_5$ sample). Calculated intensity distributions [15,16] predict that the amplitude of the laser beam at the edges of the waveguide is necessarily low. To confirm these assumptions, free gas 2D-IR spectra and kinetics were measured for $\text{Fe}(\text{CO})_5$ vapor and compared with the waveguide-enhanced 2D-IR spectra and kinetics. No discernible differences were observed in the data with or without the waveguide, except for a significant improvement in the signal to noise when the waveguide is used.

Figure 2 shows the enhancement in IR pump – IR probe difference spectra as the waveguide width is reduced. The signal intensity increases by a factor of ~ 15 between the free gas and the smallest (200 μm wide) waveguide. The FTIR spectrum of $\text{Fe}(\text{CO})_5$ vapor (fig. 3A) in the 2000 cm^{-1} region shows two main absorptions associated with the e' and a_2'' modes (with wavenumbers of 2013 and 2034 cm^{-1} , effectively equatorial and axial $\text{C} \equiv \text{O}$ stretch modes, respectively). When pumping at 2013 cm^{-1} (fig. 2A), a negative ‘bleach’ signal appears at this wavenumber, associated with loss of absorbance and increase of stimulated emission on the $v = 1-0$ transition, as $v = 0$ population is reduced and $v = 1$ population increased. The positive ‘transient’ signal shifted by ~ 15

cm^{-1} to lower wavenumber, is associated with the corresponding increase in the $\nu = 2-1$ absorption, as the $\nu = 1$ population is increased. The $\sim 15 \text{ cm}^{-1}$ shift reflects the increasing anharmonicity with increasing vibrational excitation. Some additional structure is evident, attributable to the partially resolved rotational band envelope and, potentially, to ladder climbing as $\nu = 1$ population can be further excited to $\nu = 2$. Figure 2B shows the equivalent difference spectrum when pumping the 2034 cm^{-1} band. Some weak excitation of the neighboring band is evident in figs. 2A and 2B, due to the $\sim 10 \text{ cm}^{-1}$ bandwidth of the pump laser.

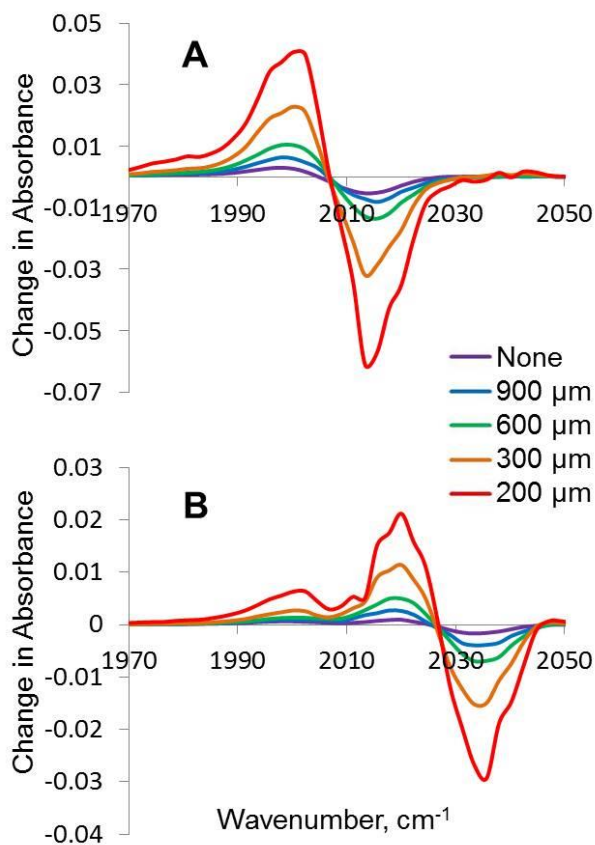


Figure 2. Normalised IR pump – IR probe difference spectra, illustrating the signal increase with decreasing waveguide width (shown in the legend, with None referring to the measurement with no waveguide present). All spectra were taken with 2 ps delay between pump and probe. **A:** pump at 2013 cm^{-1} . **B:** pump at 2034 cm^{-1} .

The 2D-IR spectra shown in figs. 3B and 3C were obtained by acquiring pump–probe spectra like those shown in fig. 2 while scanning the narrowband pump wavenumber. At minimum delay of 2 ps between the pump and probe, the bleach/transient pair associated with each band in the FTIR spectrum (fig. 3A) are clearly visible along the 2D-IR diagonal. On a timescale of ~ 100 ps, off-diagonal peaks appear due to exchange that occurs between the axial and equatorial $\text{C} \equiv \text{O}$ ligands, as seen in the 2D-IR spectrum recorded at 240 ps (fig. 3B). 2D-IR spectra of this exchange process in heptane solution were recorded also and found to compare well with previous

measurements in *n*-dodecane solution by Cahoon *et al* [17]. The 8 ps timescale measured in that work is more than an order of magnitude shorter than that recorded in the present gas-phase study, however. The present measurements were all performed in air at atmospheric pressure so, even in these gas-phase experiments, molecular collisions may be influencing the exchange kinetics at timescales > 100 ps. Future studies will employ a modified gas cell that allows accurate control of the gas pressure and a greatly reduced molecular collision frequency.

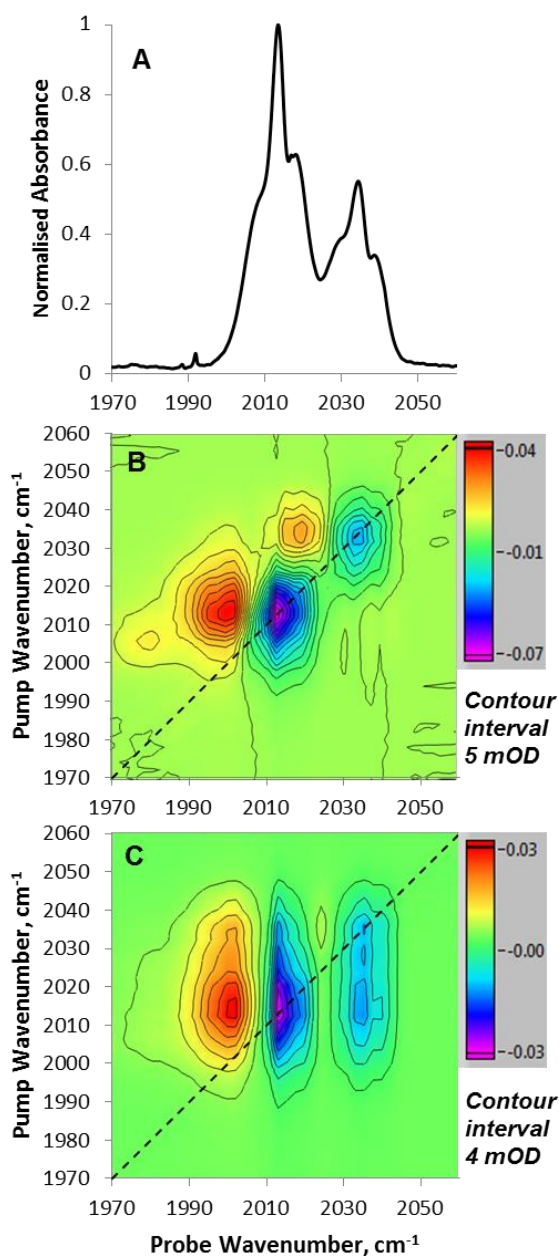


Fig. 3. **A:** FTIR spectrum of $\text{Fe}(\text{CO})_5$ vapor. **B:** Waveguide-enhanced 2D-IR spectrum of $\text{Fe}(\text{CO})_5$ vapor with 2 ps time delay between pump and probe. **C:** Waveguide-enhanced 2D-IR spectrum of $\text{Fe}(\text{CO})_5$ vapor with 240 ps time delay between pump and probe. Color gradient in 2D-IR spectra: blue (negative change in absorbance) to red (positive change in absorbance).

Summary

The waveguide-enhanced 2D-IR spectroscopy technique reported here is shown to enable >10-fold enhanced transient signal intensities as a result of the extended path-length of IR pump – IR probe overlap – a benefit that is not possible under normal gas-phase experimental conditions due to focusing limitations of mid-IR laser beams. The technique has been applied to gas-phase studies of ligand exchange dynamics in Fe(CO)₅, demonstrating substantial improvement in signal to noise ratio.

This method can be further applied to obtain high quality 2D-IR spectra in the gas-phase, with potential to improve data quality in low concentration gas-phase samples (*e.g.* gas phase dimers [14]), as well as providing scope for a range of structural dynamics and energy transfer studies.

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