Fourier transform infrared spectroscopy with visible light

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Abstract: Nonlinear interferometers allow spectroscopy in the mid-infrared range by detecting correlated visible light, for which non-cooled detectors with higher specific detectivity and lower dark count rates are available. We present a new approach for the registration of spectral information, which combines a nonlinear interferometer using non-degenerate spontaneous parametric down-conversion (SPDC) with a Fourier-transform spectroscopy concept. In order to increase the spectral coverage, we use broadband non-collinear SPDC in periodically poled LiNbO$_3$. Without the need for spectrally selective detection, continuous spectra with a spectral bandwidth of more than 100 cm$^{-1}$ are achieved. We demonstrate transmission spectra of a polypropylene sample measured with 6 cm$^{-1}$ resolution in the spectral range between 3.2 µm to 3.9 µm.

1. Introduction

Mid-infrared spectroscopy is one of the most important techniques for chemical analysis of organic compounds. It finds a wide range of applications in industry and science. However, the detectors available for the mid-infrared range suffer from lower specific detectivities and higher dark count rates than detectors used for the visible or near-infrared range, and often require cryogenic cooling [1].

Nonlinear interferometers have recently sparked interest for their applications in quantum imaging [2, 3], optical coherence tomography [4, 5] and spectroscopy [6–8], allowing for measurements in the mid-infrared range by detecting entangled visible photons. They rely on spontaneous parametric down-conversion (SPDC), which can be described as the decay of a pump photon into two photons, called signal and idler, inside a nonlinear crystal. Signal and idler photons are correlated, and the sum of their frequencies is equal to the pump frequency. For an efficient emission, pump, signal and idler photons have to be phase matched. If the emission of two identical SPDC sources is overlapped, interference is observable in both, signal and idler beams. This has been described by Zou, Ou and Mandel as induced coherence without induced emission [9] and is a direct consequence of the indistinguishability of the two photon pairs emitted by the identical sources. The interference pattern depends on the transmission and phase acquired by all three beams between the SPDC sources [10].

Recently, the application of this effect for mid-infrared spectroscopy has been demonstrated in several publications [6–8]. Hereby, different interferometer geometries were used: A Mach-Zehnder set-up, consisting of two identical nonlinear crystals placed in a row [6, 7], and a Michelson configuration, formed by a single nonlinear crystal with all beams passing the same crystal twice [8]. So far, two different methods for obtaining the spectral information of the mid-infrared idler from the correlated visible light have been demonstrated. As a first scheme, the signal light was analyzed with a spectrometer or spectrograph, which yielded a spectral resolution of 20 cm$^{-1}$ [6] or 5.2 cm$^{-1}$ [8]. In the second method, the absorption coefficient and refractive index of a sample was determined from the change of the interference fringes of the signal light with a numerical algorithm. However, this limited the spectral resolution to the natural linewidth of SPDC, which in that case was 80 cm$^{-1}$ [7].

In our work, we obtain the mid-infrared idler spectra via a Fourier-transform of the visible signal
interference pattern obtained while moving one interferometer mirror, allowing for simultaneous broadband measurements. The spectral bandwidth is increased by using non-collinear SPDC in periodically poled lithium niobate. Spectrally selective detection is not required, in analogy to classical Fourier-transform spectroscopy. Therefore, spectral resolution is limited only by the maximum optical path difference between the interferometer arms [1]. Additionally, a priori knowledge is not required, neither of the absorption and refractive properties of the sample nor of the exact phase matching conditions of the SPDC process. In contrast to previous works, this allows measuring continuous spectra with both, a high bandwidth of more than $100 \text{ cm}^{-1}$ and a good resolution of $6 \text{ cm}^{-1}$ in a single setting.

2. Methods

2.1. Setup

A sketch of the experimental setup comprising a nonlinear interferometer in Michelson-geometry is shown in figure 1(a). As pump source we use a laser with 532 nm emission wavelength, a spectral linewidth of less than 1 MHz, and up to 2 W output power (Coherent Verdi V2). The pump beam passes an optical isolator and is focused to a beam waist of 120 µm at the center of the nonlinear crystal. Reflected by the dichroic mirror $DM_c$, the pump passes through the nonlinear crystal, creating signal and idler photons via SPDC. As a nonlinear medium we use 5% MgO-doped periodically poled lithium niobate (PPLN). The crystal is 20 mm long, 0.5 mm thick and contains 21 channels with different poling periods which are each 0.5 mm wide. The poling periods range from 6.2 µm to 11.8 µm in 0.3 µm steps. The crystal temperature is stabilized using a Peltier element.

Behind the crystal, the beams are split using the dichroic mirror $DM_i$ which reflects visible and near-infrared light and transmits mid-infrared light. The transmitted idler beam is collimated with a $\text{CaF}_2$ lens ($L_i$) with 50 mm focal length. The plane mirror $M_i$ placed in 50 mm distance to the lens reflects the idler light, effectively forming a 4f relay optic imaging back into the crystal center. The end mirror is mounted on a piezo positioning system with a maximum displacement of 800 µm in beam direction and a position resolution of 1.8 nm. A spectroscopic sample can be placed in the collimated idler light in front of the plane mirror. The signal and pump beams are reflected on the dichroic mirror $DM_i$ into a second 4f optical path of equal length, where they are collimated by a lens $L_{ps}$ and reflected by a (fixed) plane mirror $M_{ps}$.

The back-travelling pump beam causes a second SPDC process, which is indistinguishable from the first SPDC emission if the beams are correctly aligned. Behind the crystal, the pump light is again reflected by the dichroic mirror $DM_i$ and then removed by the optical isolator to prevent damage to the pump laser source. The signal beam is transmitted by the dichroic mirror $DM_s$ and passes spectral filters, which remove residual pump, idler, and ambient light. The interference pattern of the signal light is then detected by a silicon sCMOS camera (Andor Zyla 4.2).

2.2. Phase matching considerations

The SPDC emission is governed by the phase mismatch $\Delta k$ between the pump, signal and idler waves. Efficient emission is only possible with small phase mismatch, which can be controlled by the crystal poling period and temperature. For a poling period of $\Lambda$, the phase mismatch can be calculated by its longitudinal ($z$) and vertical ($x$) components (with respect to the pump beam direction):

$$\Delta k_z = k_p - 2\pi/\Lambda - k_s \cos(\theta_s) - k_i \cos(\theta_i)$$
$$\Delta k_x = k_s \sin(\theta_s) - k_i \sin(\theta_i)$$
$$\Delta k = \sqrt{\Delta k_x^2 + \Delta k_z^2}$$

(1)
Hereby, \( k_{p,s,i} = 2\pi n_{p,s,i}/\lambda_{p,s,i} \) denotes the length of the wave vector for refractive index \( n_{p,s,i} \) and wavelength \( \lambda_{p,s,i} \) of pump, signal and idler light, respectively. The internal emission angles \( \theta_{s,i} \) for signal and idler beams are defined with respect to the pump beam direction.

Figure 1(b) shows calculated curves of phase-matched (\( \Delta k = 0 \)) signal emission wavelengths depending on the internal signal emission angle \( \theta_s \) for three different poling periods and crystal temperatures. A signal wavelength range of 615 nm to 640 nm with a pump wavelength of 532 nm corresponds to idler wavelengths ranging from \( \approx 3.9 \mu m \) to \( 3.2 \mu m \), which is an interesting spectral range for the analysis of organic compounds, due to the strong C-H fundamental vibration bands. The phase matching curves show that by imaging over a large emission angle range, one is able to obtain a broad spectral bandwidth. It is to be noted, that the idler emission angle \( \theta_i \) is bigger than the signal emission angle \( \theta_s \), since \( \theta_i \approx \lambda_i/\lambda_s \cdot \theta_s \). Both external emission angles are further increased due to refraction on the crystal facet.

### 2.3. Measurement Procedure and Analysis

The poling period and crystal temperature are set for efficient near-collinear emission at the targeted idler wavelength range. The idler mirror is displaced in beam direction, which varies the path length difference between the signal and idler interferometer arms. A camera image of the signal interference pattern is recorded for each 400 nm step of displacement. Up to the maximum displacement of 800 \( \mu m \), which results in an optical path difference of 1.6 mm, 2000 camera images are taken.

The interference pattern of a measurement taken with a poling period of 10.6 \( \mu m \) and a crystal temperature of 70°C is shown in Fig. 2(a). The interference fringes exhibit a near circular pattern. We attribute the missing interference contrast in vertical direction to the narrow crystal aperture in vertical direction. Marked with colored dots are five positions with different distances to the center of the interference pattern. From phase matching considerations, we expect the corresponding idler emission wavelength to shift to longer values with increasing emission angle.

Figure 2(b) shows the detected intensity at five different positions on the camera sensor (marked with the corresponding color in Fig. 2(a)) depending on the idler mirror displacement. At near-collinear emission (violet curve), the interferogram shows high modulation contrast along the whole displacement range. With increasing distance to the center, the point with
Interference pattern, single pixel interferograms, and Fourier transformed spectra of the reference measurement with 10.6 µm poling period and 70 °C crystal temperature:

(a) Camera image of the signal interference pattern at 400 µm displacement, rotated counterclockwise by 90°.

(b) Interferograms of selected camera pixels. Measured intensity at the positions marked with dots of the same color in (a) along the idler mirror displacement, shifted for clarity.

(c) Spectra (power spectral density) of the interferograms shown in (b), obtained by discrete Fourier transform.

The highest interference contrast shifts towards larger displacement values. This is caused by a larger path difference between signal and idler beam for increasing emission angles. Additionally, for increasing distance to the center, the envelope of the interferogram becomes narrow. This indicates that a larger spectral bandwidth is overlapped and interfering, which lowers the coherence length. The reason behind this can be seen in the phase matching curve shown in Fig. 1(b): With an increasing emission angle, the phase matching curve becomes steeper, thus a small angle element (as the one measured by one camera pixel) includes a larger wavelength range.

In our measurement approach, the spectral information is obtained purely by Fourier transform of the displacement-dependent interferograms. For this, partial spectra are calculated from the interferogram of each camera pixel by a discrete Fourier Transform (DFT) based on the Fast Fourier Transform (FFT) algorithm. This is demonstrated on the interferograms from Fig. 2(b), the Fourier transformed spectra are plotted in Fig. 2(c) in the same color. With increasing distance from the center (violet to dark red), the partial spectra shift to longer wavelengths in accordance with the phase matching conditions (Fig. 1(b)). The increasing width of the spectra, which is also visible in the interferograms, is also a consequence of phase matching. For the near-collinear interferogram (violet), side bands are visible in the Fourier transformed spectrum. These are caused by the finite displacement range of the interferogram, which results in a rectangular window function.

A complete spectrum is then calculated by the sum over the Fourier transform of all camera pixels. The black line in Fig. 3(a) shows the reference spectrum calculated from the sum of the Fourier transform of all camera pixels in the interference pattern shown in Fig. 2(a). The spectrum has a peak in intensity at 3.25 µm wavelength, which is the phase matched collinear idler wavelength (see Fig. 1(b)). For larger wavelengths, the spectral intensity decreases. This can be attributed to the larger emission angles, which are prone to imaging errors and reduced mode overlap, which lowers interference contrast.

To determine the transmission spectrum of a sample, the measurement procedure described above is then repeated with a sample introduced into the collimated idler beam. For demonstration purposes we chose a polypropylene film (thickness ≈120 µm), which has an absorption band around 3.4 µm. The sample spectrum is shown in Fig. 3(a) as a green line. For the whole
wavelength range, a reduced intensity of the sample spectrum is visible. We restrict both reference and sample spectrum to the non-collinear spectral range where no side bands of the Fourier transformed spectra occur. Since the measurement sample is passed twice inside the interferometer, the transmission $T$ is then calculated from the reference $I_r$ and sample $I_s$ spectrum by:

$$T = \sqrt{\frac{I_s}{I_r}}$$  \hspace{1cm} (2)

A reference intensity threshold at 2% of the maximum reference intensity was chosen to limit the evaluated spectral ranges for transmission measurements. These measurements are repeated for the three phase matching configurations shown in Fig. 1(b). For qualitative and quantitative comparison, the transmission of the polypropylene sample is also measured in a Fourier transform infrared (FTIR) spectrometer (Bruker Vertex 80). This reference FTIR spectrum is recorded with 64 scans at a resolution of 0.5 cm$^{-1}$.

### 3. Results

Figure 3(b) shows the transmission spectra of the thin polypropylene film. The black line represents the measurement of the sample taken with the commercial FTIR spectrometer (Bruker Vertex 80). The transmission spectra measured with the nonlinear interferometer are shown as colored lines (poling periods and crystal temperatures according to the color code). The spectra show good agreement to the FTIR measurement, they are continuous and have a spectral coverage of more than 100 cm$^{-1}$ each. In our setup, the spectral resolution is determined by the idler mirror displacement. Thus, the spectral resolution is limited to $\approx 6$ cm$^{-1}$, which is comparable to the resolution demonstrated in Ref. [8]. Since the spectral information in our measurement approach is obtained from a spatial-domain Fourier transform, the spectral resolution can be increased by larger mirror displacement.

### 4. Conclusion

Without the use of spectral selection or beforehand knowledge of the signal and idler wavelengths, good agreement of the measured transmission spectrum with a conventionally measured reference spectrum was achieved. Hereby, the measurement scheme is closely related to Fourier transform infrared spectroscopy, using a Michelson interferometer and the same numerical algorithm.
However, in our setup the infrared information is measured with the correlated visible light of spontaneous parametric down-conversion. This allows the usage of a silicon based detector and a visible laser light source, which circumvents the usage of expensive, cryogenically cooled infrared detectors. The demonstrated measurement technique can easily be applied to the whole infrared transparency range of lithium niobate; possibly it could be extended to the terahertz regime [11,12]. The usage of other nonlinear materials allows the extension of the technique to the far infrared. It is expected that the presented approach, comprising the combination of nonlinear interferometers and Fourier transform analysis, will provide easily applicable spectroscopy methods for wide fields in industry and science.

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**Disclosures**

The authors declare no conflicts of interest.

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