Fourier Transform Infrared Spectroscopy Measurements of Metallic Ag on Consumer-grade Mylar Film in the Mid-Infrared

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We perform fourier transform IR measurements in the mid-infrared on consumer-grade photograph film of two exposures. We show that certain modes experience a shift and an amplification at greater exposure.

I. INTRODUCTION

Fourier transform infrared (FTIR) spectroscopy is a method of characterizing a source's spectrum while maintaining a high signal-to-noise ratio. It has wide-ranging applications and is an integral tool in modern spectroscopic science.

The basic design of a FTIR spectrograph is laid out in Fig. 1. Instead of measuring the intensity of many monochromatic sources of varying wavelength, the FTIR spectrograph measures the *aggregate* intensity of a time-varying *combination* of wavelengths. This is achieved by moving the secondary mirror in a Michelson interferometer back and forth. This causes interference between the two split beams at the detector. Exactly which wavelengths interfere and by what amount varies with time.

When the two beams are recombined, as its name implies, the instrument performs a Fourier transform to take that time-varying information into frequency space[1]. This method has several key benefits over the monochromatic method. First, it is easier to produce a continuously varying combination of wavelengths (through the interference of the two beams) than it is to continuously vary a single wavelength source. Second, the requirement that measurements be taken continuously significantly reduces the noise, resulting in a much cleaner signal[1].

While Michelson realized in the 1920's that such an instrument could be built from his interferometer, the computationally-intensive task of the Fourier transform prevented its construction. It was not for another fifty years, when not only had computers become powerful and miniaturized, but the Fast Fourier Transform algorithm had been rediscovered, that the first FTIR spectrograph was actually made[2].

In this experiment, mid-infrared (MIR) FTIR spectra were obtained of photographic film. Photographic film is a convenient starting point to look at different physical phenomena, particularly with an apparatus that measures absorbance. After all, film is designed to both let light pass and to be able to change the amount of light it lets through under different circumstances. Thus, it presents an ideal material in which to investigate spectra[3].

What follows is a look at the mathematical foundation of the Fourier transform method and a description of the process by which film changes under exposure.

A. A Brief Overview of Relevant Fourier Transform Analysis

Let us look briefly at how the method of the Fourier transform enables the operation of the FTIR spectrograph. Referring to Fig. 1, light from an infrared source is split in two by beamsplitter. One is sent to a fixed mirror and one to a movable mirror which introduces a time delay. At the detector, the beams interfere, allowing the temporal coherence of the light to be measured at each different time delay setting. By making measurements of the signal at many discrete positions of the movable mirror, the spectrum can be reconstructed using a Fourier transform of the temporal coherence of the light[1].

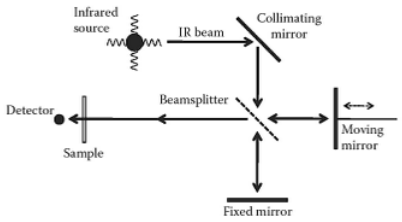

FIG. 1. Diagram of the FTIR spectroscope. The moving mirror produces a time-varying signal which can be converted into frequency space by means of a Fourier transform.[1]

So, how do we take the intensity of the interference of many wavelengths at different times and Fig. out the intensity of a single wavelength at all times? We begin with a relevant equation, the intensity I at the detector of a given wavelength ν for a given displacement δ of the moving mirror:

$$I(\delta, \bar{\nu}) = I(\bar{\nu})[1 + \cos(2\pi\bar{\nu}\delta)] \tag{1}$$

where $I(\bar{\nu})$ is the intensity of a wavelength we are interested in.

It is true that

$$I(\delta) = (\delta, \int_0^\infty I(\delta, \bar{\nu})d\bar{\nu}) \tag{2}$$

And, to plug in from equation 1, we have

$$I(\delta) = (\delta, \int_0^\infty I(\bar{\nu})[1 + \cos(2\pi\bar{\nu}\delta)]d\bar{\nu}) \tag{3}$$

Which is the very definition of the Fourier transform from the time domain to the frequency domain. (Where is the time domain? Remember that the displacement δ is implicitly dependent on time).[1]

B. A Brief Overview of Relevant Chemistry

Measurements were taken of two different exposures of grayscale photography film. The physical difference between these two exposures comes down to the reaction of silver halide molecules with light. Photographic film is created by coating a mylar (Biaxially-oriented polyethylene terephthalate or BoPET) sheet with an emulsion of AgBr in gelatin. Exposing this film to light, then, causes two things to happen: One, Ag^+ is reduced to metallic Ag in the presence of bromide which can be oxidized photochemically (i.e., a photon, with energy $h\nu$ in equation 4 ejects an electron from bromide). Second, the although the bromide salts of silver, AgBr, have very low aqueous solubility, many complex ions of Ag^+ do dissolve in water[3]. Modern silver-based photography relies on oxidation-reduction chemistry to capture the image. The media-specific solubility of silver bromide salts make the initial image permanent. The main reactions are:

$$\mathrm{Br^-} + (\mathrm{h}\nu) \longrightarrow \mathrm{Br} + \mathrm{e^-} \tag{4}$$

$$\mathrm{Ag^+} + (\mathrm{e^-}) \longrightarrow \mathrm{Ag} \tag{5}$$

The small number of Ag metal atoms formed act as a catalyst and sensitizes the surrounding bromide salt so that, in the presence of a developer (a reducing agent) the sensitized AgBr is reduced, to produce black metallic Ag in the area exposed to light. In areas that were not exposed to light, the developer will turn white[3].

For this reason, film that has been exposed for a longer time should have more metallic Ag. Any normal modes of metallic Ag, should, therefore, be more noticeable in the more exposed film under FTIR analysis.

What follows is a description of the experimental design. Then, section III will present the data. Section IV contains the analysis and section V concludes.

II. EXPERIMENTAL DESIGN

The experiment was performed with a Bruker IFS 66v/S spectrometer with a 993K blackbody source[4] (peak wavelength of approximately 2918nm). The resolution was 4 $\mathrm{cm^{-1}}$ and the range of wavelengths probed was 2000 $\mathrm{cm^{-1}}$ to 500 $\mathrm{cm^{-1}}$. A background spectrum (Fig. 2) was performed with a sample plate aperture of 7mm. The film used was Kodak 400 TMax black-and-white film. The background spectrum was divided from both the less-exposed (LE) and the more-exposed (ME) spectra.

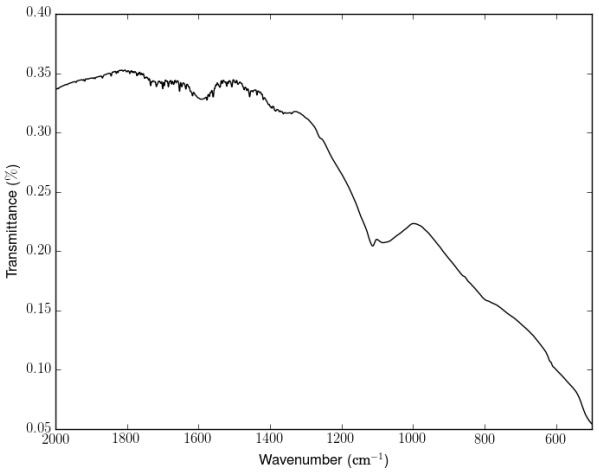

FIG. 2. The background spectrum. The features in the upper left correspond to water lines.

III. DATA

Two spectra of photographic film were taken. The first was of the LE film. Fig. 3 shows the spectrum with the background. A peak-finding algorithm was written (the code of which is made available in appendix A) and it was optimized to find the 10 peaks highlighted in Fig. 3 and explicitly stated in Table I. The spectrum of the ME film was then taken (Fig. 4), and the same peaks were found (Table I).

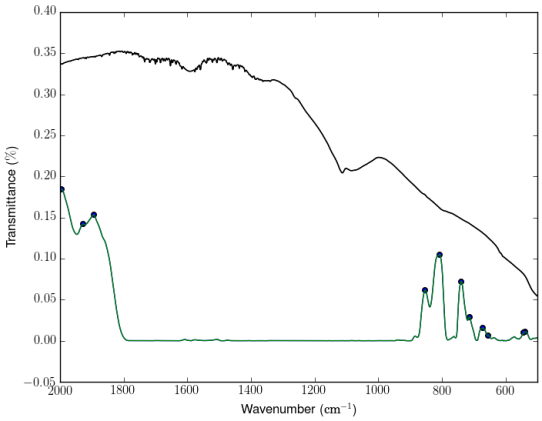

FIG. 3. The MIR FTIR spectrum of the LE film. The dots are the numerically calculated peaks and the black line at the top is the background.

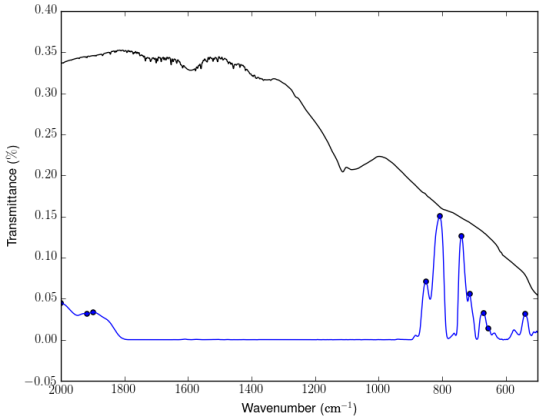

FIG. 4. The MIR FTIR spectrum of the ME film. The dots are the numerically calculated peaks and the black line at the top is the background.

TABLE I. The wavenumbers of corresponding peaks in each spectrum.

LE peak (cm^{-1}) (± 0.0005 cm^{-1})	ME peak (cm^{-1})	Δ (LE-ME) (± 0.0007 cm^{-1})
538.0422	538.0422	0.0000
653.7502	654.7145	-0.9642
671.1065	670.1422	0.9642
713.5327	713.5327	0.0000
739.5670	739.5670	0.0000
808.0276	808.0276	0.0000
852.3823	851.4180	0.9642
1894.7186	1897.6112	-2.8927
1927.5026	1917.8601	9.6423
1994.9989	2003.3032	-5.0011

IV. ANALYSIS AND DISCUSSION

As shown in Fig. 5 and Tables I and II, the peaks change significantly between the two different exposures. Actually determining which compounds are responsible for which lines has proven extremely difficult. For one, a search of the literature did not turn up any MIR spectra for metallic Ag. Second, although the mylar absorbs across much of the MIR, leaving a flat region between 1800cm^{-1} and 900cm^{-1}[5]. This happens to be where the gelatin has the most absorption[6], so we get almost no signature from the gelatin.

However, some arguments can be made about what is happening based on a qualitative analysis of Fig. 5. The peaks at around 2000cm^{-1} are of considerably lower intensity in the ME film than in the LE film. This might indicate that these peaks are due to the mylar, which would be transmitting far less for the darker, more exposed film.

We see, too, that all of the peaks to the right of about 900cm^{-1} are *higher* in the more exposed film. This indicates that these might be due to the metallic Ag, of which there is a higher concentration in the darker film. Thus, there would be more individual Ag atoms to excite in a normal mode.

TABLE II. The intensities of corresponding peaks in each spectrum.

LE transmittance (%) (± 0.0005 %)	ME transmittance (%)	Δ (LE-ME)
0.1844	0.0444	0.1400
0.1421	0.0317	0.1103
0.1532	0.0335	0.1197
0.0615	0.0708	-0.0093
0.1051	0.1503	-0.0453
0.0722	0.1266	-0.0544
0.0289	0.0555	-0.0266
0.0152	0.0322	-0.0169
0.0064	0.0138	-0.0074
0.0108	0.0313	-0.0204

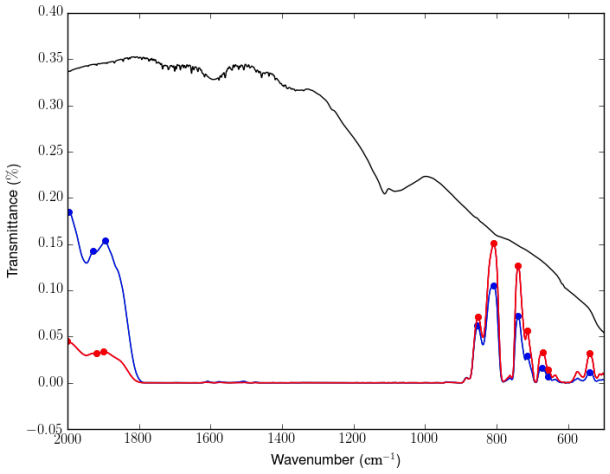

FIG. 5. Comparison of the two spectra. LE in blue, ME in red. The peaks have changed radically in intensity and have been shifted.

V. CONCLUSION

MIR FTIR spectra were obtained for consumer-grade photography film. Many features were observed, and these were identified with a customized peak-detection algorithm. Some features were observed to amplify in intensity with the more-exposed film, which was interpreted as being indicative of the presence of metallic Ag.

[1] P. Griffiths and J. Haseth, *Fourier Transform Infrared Spectroscopy*, (John Wiley & Sons, New York, 1986)

[2] P. Atkins and J. Paula, *Physical Chemistry*, (Oxford University Press: Oxford, UK.,1996)

[3] G. Christian, *Analytical Chemistry*, (Wiley, New York, 2003)

[4] Bruker Corporation, Bruker 66v/S Specifications, (Bruker Corp., Berlin, 1996)

[5] L. Ding, L. Shao, and Y. Bai, RSC Adv. **42**, 4, 2014

[6] K. J. Payne and A. Veis, Biopolymers, **27**, 11, 1988

Appendix A: peakfinder.py

```
import numpy as np
from math import pi, log

"""
peakfinder.py:  finds peaks and troughs (max and min) in spectra data

inputs-
y_axis: list-like record of the spectra data
x_axis (optional): list-like record of the x-axis.  Could be wavenumber, whatever.
If not provided, x_axis is taken to be the index of y_axis.
howfar: parameter which indicates how far ahead the script should look for the
next peak.  Too low is inefficient, too high will miss peaks.
delta: parameter which indicates an average peak width.

returns-
[spect_peaks,spect_mins], 2 2x2 lists of x,y points corresponding to
the peaks and troughs.
"""

#checks sanity of input data
def datasanitize_peakfinder(x_axis, y_axis):
    if x_axis is None:
        x_axis = range(len(y_axis))

    if len(y_axis) != len(x_axis):
        raise (ValueError,
                'Input vectors y_axis and x_axis must have same length')

    y_axis = np.array(y_axis)
    x_axis = np.array(x_axis)
    return x_axis, y_axis

def peakfinder(y_axis, x_axis = None, howfar = 2, delta=0):
    spect_peaks = []
    spect_mins = []
    toss = []

    x_axis, y_axis = _datasanitize_peakfinder(x_axis, y_axis)
    # store data length for later use
```

```
length = len(y_axis)


if howfar < 1:
    raise ValueError, "howfar must be '1' or above in value"
if not (np.isscalar(delta) and delta >= 0):
    raise ValueError, "delta must be a positive number"

  mn, mx = np.Inf, -np.Inf


for index, (x, y) in enumerate(zip(x_axis[:-howfar],
                                   y_axis[:-howfar])):
    if y > mx:
        mx = y
        mxpos = x
    if y < mn:
        mn = y
        mnpos = x

    if y < mx-delta and mx != np.Inf:
        if y_axis[index:index+howfar].max() < mx:
            spect_peaks.append([mxpos, mx])
            toss.append(True)
            mx = np.Inf
            mn = np.Inf
            if index+howfar >= length:
                break
            continue

    if y > mn+delta and mn != -np.Inf:

        if y_axis[index:index+howfar].min() > mn:
            spect_mins.append([mnpos, mn])
            toss.append(False)
            mn = -np.Inf
            mx = -np.Inf
            if index+howfar >= length:
                break

try:
```

```
    if toss[0]:
        spect_peaks.pop(0)
    else:
        spect_mins.pop(0)
    del toss
except IndexError:
    pass

return [spect_peaks, spect_mins]
```