

Planar Array Infrared Emission Spectroscopy

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Planar array infrared spectroscopy (PA-IR) is shown to be a powerful new approach to infrared emission spectroscopy (IRES). A proof-of-concept study of selected polymers indicates that PA-IRES allows acquisition of emission spectra with a high signal-to-noise ratio at temperatures as low as 80 °C. It is shown that a time resolution below 20 ms is readily achievable for time-resolved characterization of single non-repeatable events. The possibility of recording spatially resolved emission spectra is also demonstrated, and potential applications of this novel technique are finally described.

Infrared emission spectroscopy (IRES) is an important technique in fields such as astronomy and astrophysics^{1,2} and for the standoff analysis of plumes of pollutants or potential threats in the context of military operations or homeland security.³ IRES also finds uses in laboratory settings, for instance, for studying thermally excited materials or chemically excited species during reactions.^{4–7} Transient emission infrared spectroscopy (TIRS) has also been used for on-line monitoring of industrial processes.^{8–10}

Emission and absorption spectroscopies are related through Kirchhoff's law, which states that the emittance (ϵ) of a sample is equal to its absorptance (α).¹¹ For any non-scattering material, the sum of the emittance (or absorptance), transmittance (τ), and reflectance (ρ) is equal to unity: $\epsilon(\nu) + \tau(\nu) + \rho(\nu) = 1$. For a perfect blackbody material, $\alpha(\nu) = \epsilon(\nu) = 1$ and $\tau(\nu) = \rho(\nu) = 0$, so that no sample can emit more light, at any wavelength, than a perfect blackbody. In contrast, a perfectly reflective metal has $\rho(\nu) = 1$ and thus does not contribute to the luminance spectrum, while an ideal transparent material does not emit because its transmittance is unity. Most real materials lie between these extreme cases. For thin or dilute samples, $\alpha(\nu)$ and $\epsilon(\nu)$ vary between 0 and 1 and are wavelength-dependent, thus enabling the measurement of characteristic absorption or emission spectra.

As in the case of absorption IR spectroscopy, applications of IRES spectroscopy rely on the use of Fourier transform IR (FT-IR) spectrometers. FT-IR spectroscopy provides well-documented advantages as compared to dispersive instrumentation: multiplex, high-throughput, and frequency precision advantages. The throughput advantage is especially interesting for IRES measurements because the temperature of the sample is often relatively low (e.g., 100–200 °C; 373–473 K), so that the luminance is much less than that of a conventional infrared source (typically, 1400 K). Commercial FT-IR spectrometers are often available with input beam ports that allow collection of IRES spectra, but they suffer from some limitations. For instance, FT-IR spectrometers use an interferometer that is sensitive to strong mechanical vibrations or shocks, which can limit their applicability for challenging field applications. In addition, recording low-intensity emission spectra generally requires a long acquisition time, a limiting factor for studies of transient species and for kinetics studies. Even if the signal is very intense, it is still necessary to perform a full moving-mirror scan to obtain a spectrum. This not only limits the accessible time resolution but also requires the assumption that no spectral changes occur during the scan.¹²

Recently, we have combined a 2-D focal plane array (FPA) infrared camera with an infrared spectrograph in a so-called planar

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array infrared (PA-IR) spectrometer.^{13,14} This instrument can record 700 cm⁻¹ spectra across the 4000–950 cm⁻¹ range with a sub-10 ms time resolution. A potential advantage of PA-IR spectroscopy for emission measurements is that it can be constructed as a no-moving parts instrument, making it much less sensitive to harsh environments than interferometers. In this work, we have thus explored the potential of PA-IR spectroscopy for emission infrared spectroscopy.

EXPERIMENTAL PROCEDURES

PA-IRES Measurements. The PA-IR spectrograph used in this work was adapted from that described in detail previously.¹³ This spectrograph contains a 300 μm slit, a reflection grating with 50 grooves/mm, and a 256 × 256 mercury-cadmium-telluride (MCT) FPA (Santa Barbara Focalplane, Goleta, CA). Emission measurements were performed by replacing the infrared source with the sample to be studied. IRES spectra of thin polymer films were recorded using a transmission heated cell (ThermoElectron, Waltham, MA), which allowed precise temperature control from room temperature up to 200 °C. The samples were deposited on a highly reflective aluminum plate. Blackbody spectra were approximated by recording the emission of a metal plate covered by a thick layer of flat black paint maintained at the same temperature as the sample. It should be realized that the emittance of this plate is less than unity and thus that it does not constitute a true blackbody emitter. Unless otherwise noted, all spectra were recorded in 1 s acquisitions. The absorption spectrum of a polystyrene film was also recorded in the transmission mode to calibrate the frequency axis of the instrument, as well as to correct the spectral images for slit curvature. The blackbody emission at 120 °C was used as a source for these absorption measurements. The procedure described by Pelletier et al. was used to bin multiple pixel rows of the FPA and improve the signal-to-noise ratio in the data.¹⁴

Spectrum Calculation. The emittance of a sample at a temperature T_1 can, in principle, be simply determined as the ratio of the luminance of a sample, $L_S(v, T_1)$, over that of a reference blackbody, $L_B(v, T_1)$, at the same temperature. In practice, it is necessary to take into account the response function of the spectrometer and the stray light originating from the different parts of the instrument when a liquid nitrogen-cooled detector is used.¹¹ This is generally accomplished by measuring the luminance of the sample and of the reference blackbody at a second (lower) temperature, T_2 . Finally, it is common practice in PA-IR spectroscopy to record a dark background spectrum, $D(v)$, which is the spectrum obtained when the entrance slit of the monochromator is closed, to correct for stray light reaching the FPA (sensitive to DC light from the environment) and for any offset in the response of individual camera pixels. The final emission spectrum of a sample at temperature T_1 is thus calculated as

$$\epsilon(v) = \frac{[L_S(v, T_1) - D_S(v, T_1)] - [L_S(v, T_2) - D_S(v, T_2)]}{[L_B(v, T_1) - D_B(v, T_1)] - [L_B(v, T_2) - D_B(v, T_2)]}$$

Because the dark background correction is applied on both the sample and the blackbody spectra, the emission spectrum is almost identical whether the measurements at temperature T_2 are considered or not.

RESULTS AND DISCUSSION

Figure 1 shows spectral images recorded for a polystyrene (PS) film in the absorption and emission modes, respectively. Pixel shifting correction and dark background subtraction were applied to those images. In both cases, light colors represent a higher intensity reaching the detector, and the horizontal scale covers a spectral range from approximately 1750 to 1000 cm⁻¹. In the absorption mode image of Figure 1A, a high-intensity envelope is observed due to the blackbody that acts as a broadband infrared source, and the dark vertical bands are due to absorption of the infrared light by the PS sample. Some very shallow and narrow bands are also present due to water vapor absorption since the spectrometer was not purged in any of the experiments presented here. This image is thus similar to a standard single beam spectrum recorded using an FT-IR spectrometer. In contrast, higher intensity appears in the emission image of Figure 1B at the frequencies where PS emits, and a low-intensity background is observed at other frequencies.

It can be observed that the emission and absorption bands appear at the exact same horizontal pixel (wavenumber) positions. Indeed, the infrared emission process involves the same energy levels as the standard absorption phenomenon. While absorption involves the transition of a vibration from a low-energy level (typically the ground level) to a higher one, IRES measures the radiation emitted by the relaxation of vibrators from an excited energy level to a lower energy state. Since the selection rules are the same for both processes, similar chemical information can be extracted from absorption and emission spectra.¹¹ A difference between Figure 1A and Figure 1B is the absence of water vapor bands in the emission image since the vast majority of water molecules are found in their ground state at room temperature and thus cannot emit infrared radiation. However, water vapor in the optical path can still absorb the infrared light emitted by the PS sample at frequencies where they overlap, which is why IRES measurements are often carried out with purged instruments.

Figure 1C shows the emittance and absorptance spectra of the polystyrene film recorded at 120 °C. As observed in the spectral images, the band shapes and positions are very similar between the two spectra. This proves that characteristic spectra can be recorded in the emission mode with a PA-IR spectrograph. The intensity of the bands always lies between 0 and 1, as expected. However, quantitative differences are obvious between the two spectra, with weaker bands appearing with a higher relative intensity in the emittance spectrum. This mostly originates from the imperfect nature of the blackbody used as a reference. In fact, using a blackbody spectrum recorded at about 30 °C above the sample temperature makes the emittance and absorptance very similar, as shown by the dotted line in Figure 1C. Fully quantitative work could thus be realized by using a calibrated commercial

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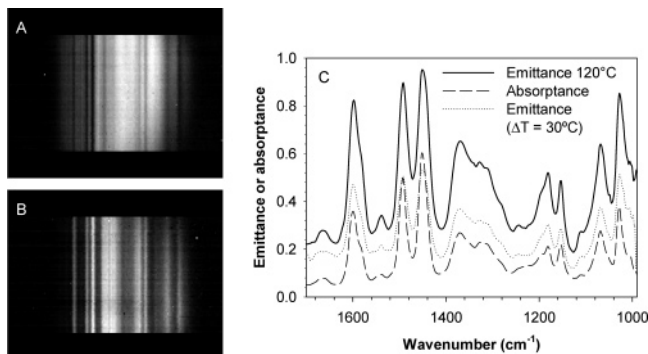


Figure 1. Spectral images of a polystyrene film recorded in (A) the absorption mode and (B) the emission mode at 120 °C. The horizontal axis covers the 1750 to 1000 cm^{-1} range, and light tones indicate high infrared radiation intensity. (C) Comparison of the absorbance (dashed line) and emittance spectra calculated using a blackbody spectrum recorded at either 120 °C (full line) or 150 °C (dotted line) for the emittance spectra.

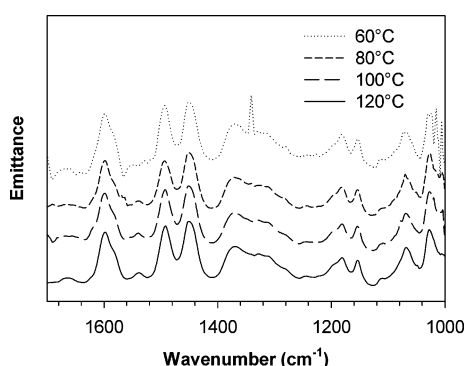


Figure 2. Emittance spectra of a polystyrene film recorded at temperatures from 60 to 120 °C.

blackbody source. It can be noted that no self-absorption is observed in Figure 1C because the temperature of the film was homogeneous across its thickness. When the surface of the sample is colder than its bulk, chemical groups from the upper layer that are in their vibrational ground state can absorb photons emitted from the underlying material, leading characteristic bands to show a truncated intensity profile.

The signal-to-noise (S/N) ratio of the emission spectrum is excellent and appears comparable to that of silicon grease spectra recorded at similar temperatures using an FT-IR spectrometer with 1024 scans.¹¹ In contrast with FT-IR spectroscopy, the emitted light has to go by a 300 μm slit at the entrance of the PA-IR monochromator, thus reducing the instrument throughput. This is nevertheless compensated for by the fact that the second dimension of the FPA detector allows binning of multiple pixel rows. In these measurements, 68 line spectra were acquired simultaneously (Figure 1B) and averaged, thus improving the S/N ratio by a factor of approximately 8 as compared to what could be expected for a 1-D array and making it similar to that of an FT-IR spectrometer.

Considering the S/N ratio obtained for a sample maintained at 120 °C, the possibility of recording spectra at lower temperatures was explored. Figure 2 compares the PS emission spectra recorded at temperatures ranging from 120 to 60 °C. It is clear that the sample temperature does not influence the peak positions and intensities. This is the expected result from calculations using

eq 1, in which the sample emittance is ratioed against that of a blackbody at the same temperature. Good quality spectra are obtained at a temperature as low as 80 °C, well below the melting point and/or the glass transition temperature of several important polymers such as PS, poly(ethylene terephthalate) (PET), polycarbonate, etc. PA-IRES spectra of PET and other polymers were also acquired (not shown) and present a similar noise level. The spectrum at 60 °C shows a larger noise level, and a sharp spike is evident at 1340 cm^{-1} , due to the small intensity difference between the sample emission signal and the dark background intensity reaching the FPA detector. This spectrum nevertheless still allows for easy identification of the sample and could be used in a qualitative way.

It can be observed that the noise level in Figure 2 increases mostly at both ends of the spectrum when the temperature is decreased. The noise at frequencies above 1600 cm^{-1} is due to a very limited number of vibrators in the excited state. A simple Boltzmann distribution calculation indicates that 1.7% of the vibrators emitting at 1100 cm^{-1} are in the excited state at 120 °C, as compared to only 0.28% for those giving rise to the 1601 cm^{-1} band (aromatic C–C stretching). At 60 °C, these populations drastically decrease to 0.9% and a mere 0.09%, respectively. For this reason, emission measurements in the high frequencies (such as in the C–H stretching region from 2800 to 3200 cm^{-1}) are usually performed at temperatures of at least 150 °C using a nitrogen-cooled detector. On the basis of this, higher S/N levels are expected at lower frequencies, which is the case down to approximately 1100 cm^{-1} . In contrast, the noise level significantly increases below 1000 cm^{-1} because of the reduced detectivity of the FPA, which possesses a spectral bandwidth limited to 950 cm^{-1} . The use of a microbolometer FPA, responsive in the 8–14 μm range, could in principle extend the useful low-frequency range of PA-IRES to 715 cm^{-1} .

When a sufficient S/N ratio can be obtained in a short time at a temperature (or excitation level) of interest, emission spectroscopy can be used to perform kinetic studies. For instance, the thermal degradation of various polymers was followed using continuous-scan FT-IR emission spectroscopy by recording spectra in as little as 13 s.⁶ One of the intrinsic advantages of a PA-IR spectrograph as compared to FT-IR spectrometers for the study of non-repeatable phenomena (that cannot be followed using step-scan measurements) is that its time resolution is dictated only by the frame rate of the FPA and not by the time needed for the reciprocating motion of a moving mirror. Depending on the FPA, frame rates typically range between 17 ms and 600 μs . This time resolution was used in previous studies to follow the reorientation dynamics of liquid crystals exposed to an external electric field.^{13,15}

To evaluate the possibility of performing kinetic PA-IRES studies with similar low-millisecond time resolutions, measurements were performed using limited time averaging. Figure 3 shows PS spectra recorded at 120 °C in 100, 10, and 2 camera frames, corresponding to acquisition times of 870, 87, and 17.4 ms, respectively. The S/N ratio of these spectra clearly indicates that sub-20 ms acquisition times are easily achievable. Such a time scale should prove useful for rapid dynamic emission studies involving non-repeatable events. For instance, Griffiths and co-

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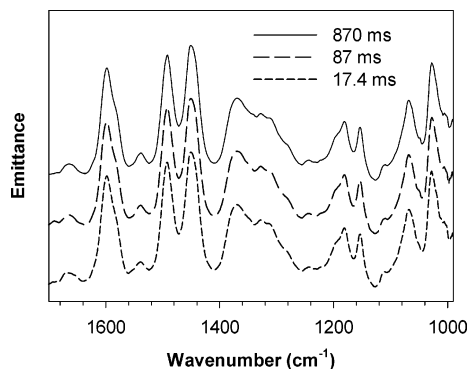


Figure 3. Emittance spectra of a polystyrene film recorded at 120 °C with acquisition times ranging from 870 to 17.4 ms.

workers have used an ultra-rapid scanning FT-IR spectrometer in the absorption mode to study the spark-initiated combustion of alkanes with a 7 ms time resolution.¹² In that work, the emission of infrared radiation by the excited species actually saturated the detector and made measurements impossible for a certain time following the spark. The use of PA-IRES would allow studying such excited species with a similar time resolution but without loss of information due to saturation of the detector since, in contrast with FT-IR, there is no high-intensity centerburst in a PA-IR measurement.

Another IRES application for which ultra-fast time resolution would be beneficial is the so-called transient infrared spectroscopy (TIRS) technique.^{8–10} In a TIRS experiment, a moving sample is exposed to a hot (cold) stream of air, thus generating a thin surface layer warmer (colder) than the bulk of the sample. This allows recording emission spectra (hot stream) or absorption spectra (cold stream) of the thin surface layer without the need for a physical contact (such as in attenuated total reflectance spectroscopy) or saturation of the signal due to large thicknesses. TIRS has been applied to the on-line characterization of materials such as polymer extrudates, wood chips, etc. In TIRS, long measurement times directly convert to poor spatial or sample resolution, as a large quantity of material is sampled during each spectrum. The application of a highly sensitive and rapid PA-IR spectrometer to TIRS measurements could thus significantly improve the efficiency of this monitoring technique.

A final characteristic of PA-IR spectroscopy is the possibility of using the second dimension of the FPA to record spatially resolved spectra. In previous work, this was an advantage when simultaneously recording spectra of two orthogonally polarized beams¹³ and measuring spectra in two different spectral ranges.¹⁴ Figure 4A shows that PA-IR spectroscopy also enables recording emission spectra of multiple samples in a single experiment. This spectral image was recorded by simply stacking three polymer samples in the field of view of the camera. Three resolved spectral bands are observed along the vertical axis, enabling the independent characterization of each sample. Figure 4B shows the three emittance spectra calculated from Figure 4A. Although those were known samples, the specificity of infrared spectroscopy allows easy identification of PS (top), isotactic polypropylene (middle), and PET (bottom).

The spatial resolution along the vertical axis of Figure 4A was approximately 150 μm , and the total vertical field of view was approximately 15 mm. This field of view was limited by the

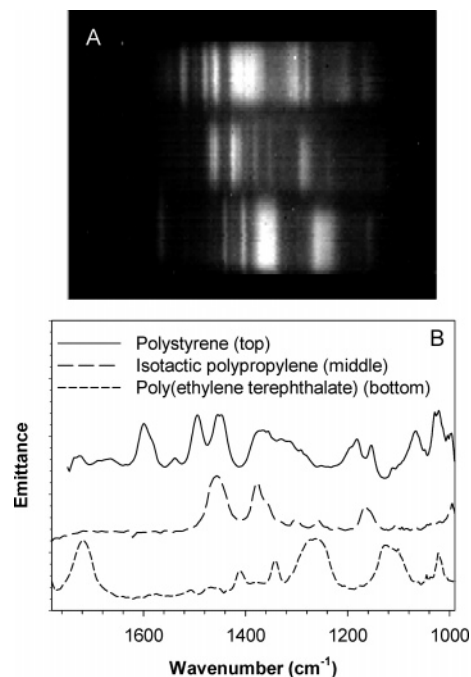


Figure 4. Spatially resolved PA-IRES spectral image recorded for a stack of three polymer samples (A) and the corresponding emittance spectra (B).

diameter of the collecting mirror and not by the size of the FPA, which could have covered 38 mm. Using appropriate optical magnification, it is, in principle, possible to improve the spatial resolution to 10 μm , although optical imperfections in the spectrograph and throughput considerations would be limiting factors. As a matter of fact, it would probably be more interesting to demagnify the image to acquire spectra over a larger field of view. The combination of a high time resolution with such 1-D spatial resolution could allow, for instance, real-time imaging and monitoring of a warm moving sample, such as rolled films or items on a conveyer belt.

It could also be possible to collect hyperspectral images of samples, such as gas plumes or other potentially threatening gaseous species, using a PA-IR spectrograph. Indeed, in addition to the spectral dispersion, the instrument already provides a 1-D spatial resolution along the height of the slit. Spatial resolution along the second dimension could be obtained by either (i) translating the spectrometer perpendicular to the slit axis, for instance, in a low-altitude surveillance aircraft or (ii) by using an additional mirror that would raster the field of view perpendicular to the slit axis. In the latter case, it would also become possible to record time-resolved hyperspectral images. This modification would, however, introduce a moving part in the spectrograph, potentially affecting its ruggedness.

CONCLUSION

The results obtained in this work suggest that PA-IR spectroscopy could become a powerful tool for performing infrared emission spectroscopy. Its advantages, as compared to FT-IR spectrometers, are acquisition times as short as 17 ms, its ruggedness, and the possibility of acquiring spatially resolved information. Its most significant drawbacks are a reduced frequency precision and the compromise between spectral bandwidth

and spectral resolution. This novel approach could prove extremely valuable for emission spectroscopy applications in which sensitivity, time, and spatial resolution are important, such as thin films analysis, kinetic studies, and real-time monitoring.

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