3. THEORETICAL BACKGROUND AND PRINCIPAL APPLICATIONS OF EMISSION FTIR SPECTROSCOPY

- **SOURCE REPLACED WITH A SAMPLE**

Atomic Emission Spectroscopy (AES)

IR emission spectroscopy IRES

IR emission experiment is not yet routine

ADVANTAGES: ("difficult" IR samples)

- **Highly absorbing samples (catalysts)**

- **Opaque porous samples (electrode surfaces)**

- **Black powdered samples (Pd-black)**

- **Very thick samples (bulk polymers, minerals)**

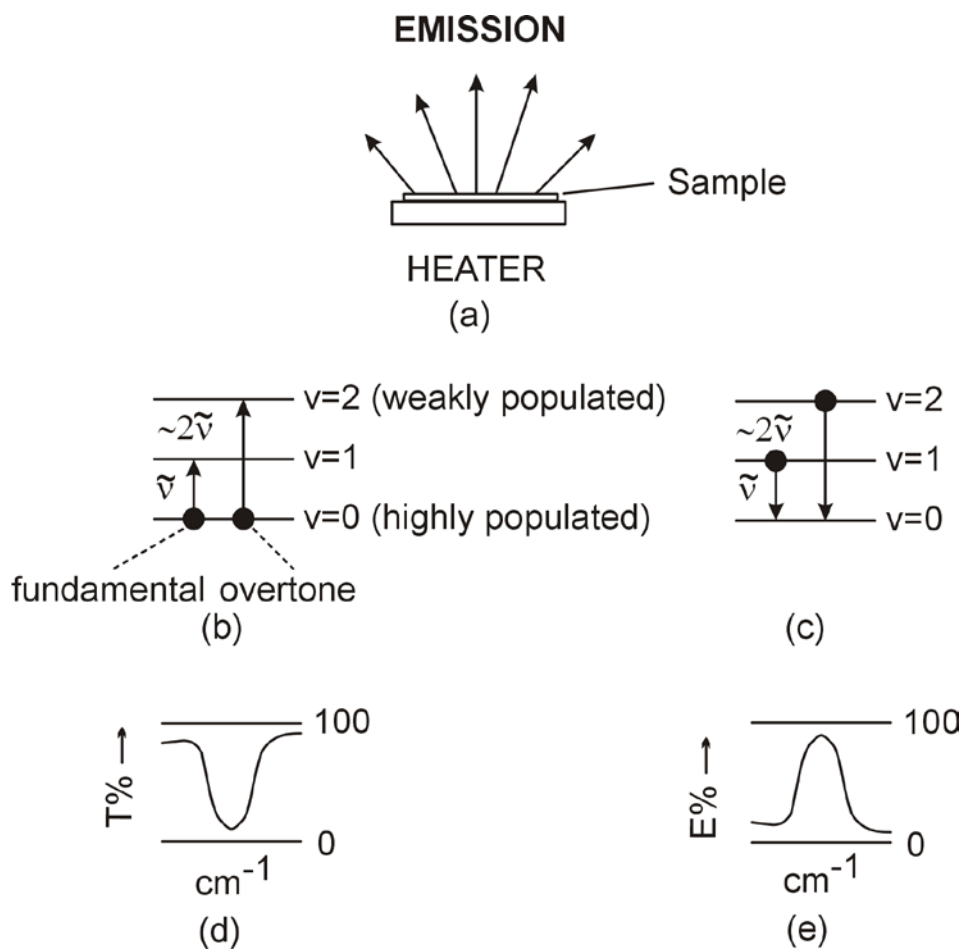- **Originally hot samples (catalysts, flames)**

EMISSION

Sample

HEATER

(a)

v=2 (weakly populated)

$\sim 2\tilde{v}$

v=1

$\tilde{v}$

v=0 (highly populated)

fundamental overtone

(b)

$\sim 2\tilde{v}$

v=2

$\tilde{v}$

v=1

v=0

(c)

T% →

100

0

cm^{-1}

(d)

E% →

100

0

cm^{-1}

(e)

**Illustration of the origins of absorption and emission spectra:**

(a) The emitting (heated) sample replacing the standard IR light source;

(b) Absorption of IR light by non-excited molecules (v = 0): fundamental ($\Delta v = 1$) and first overtone ($\Delta v = 2$) transitions;

(c) Emission of IR radiation by thermally excited (v = 1 and v = 2) molecules;

(d) Observed absorption band;

(e) Observed emission band.

"First" Emission Spectrum
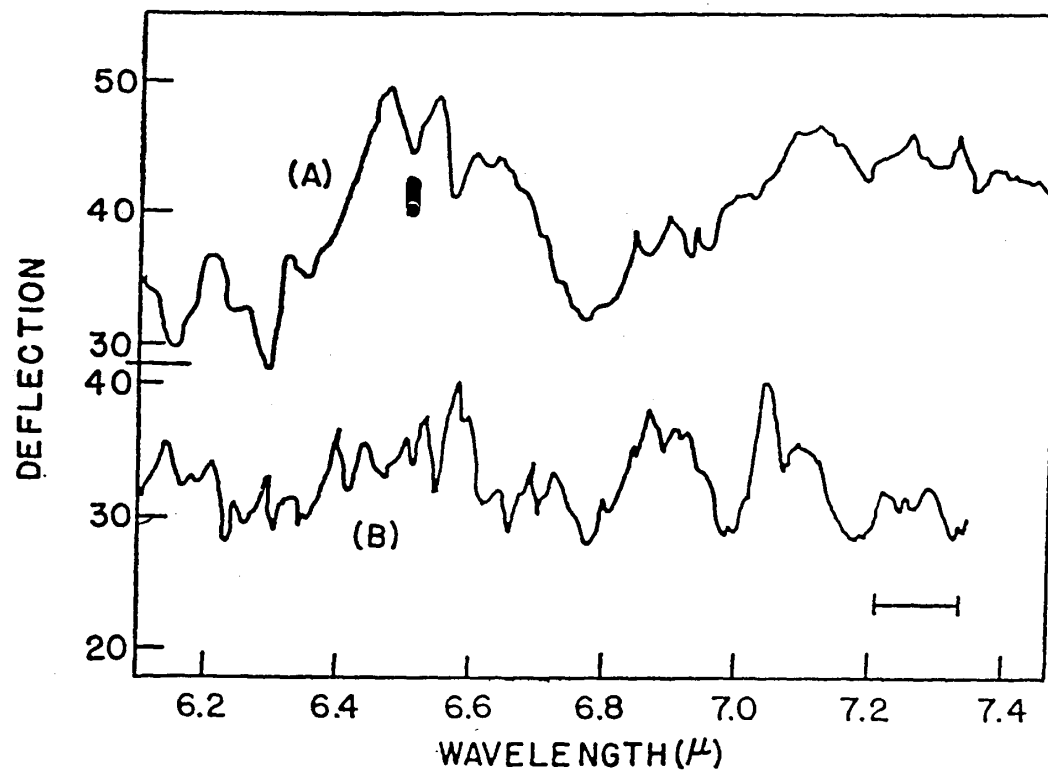
Emission spectrum of oleic acid chemisorbed on an aluminum rod (oxide-coated).

EISCHENS AND PLISKIN, ADVANCES IN CATALYSIS, VOL. X, P.1. (1958)
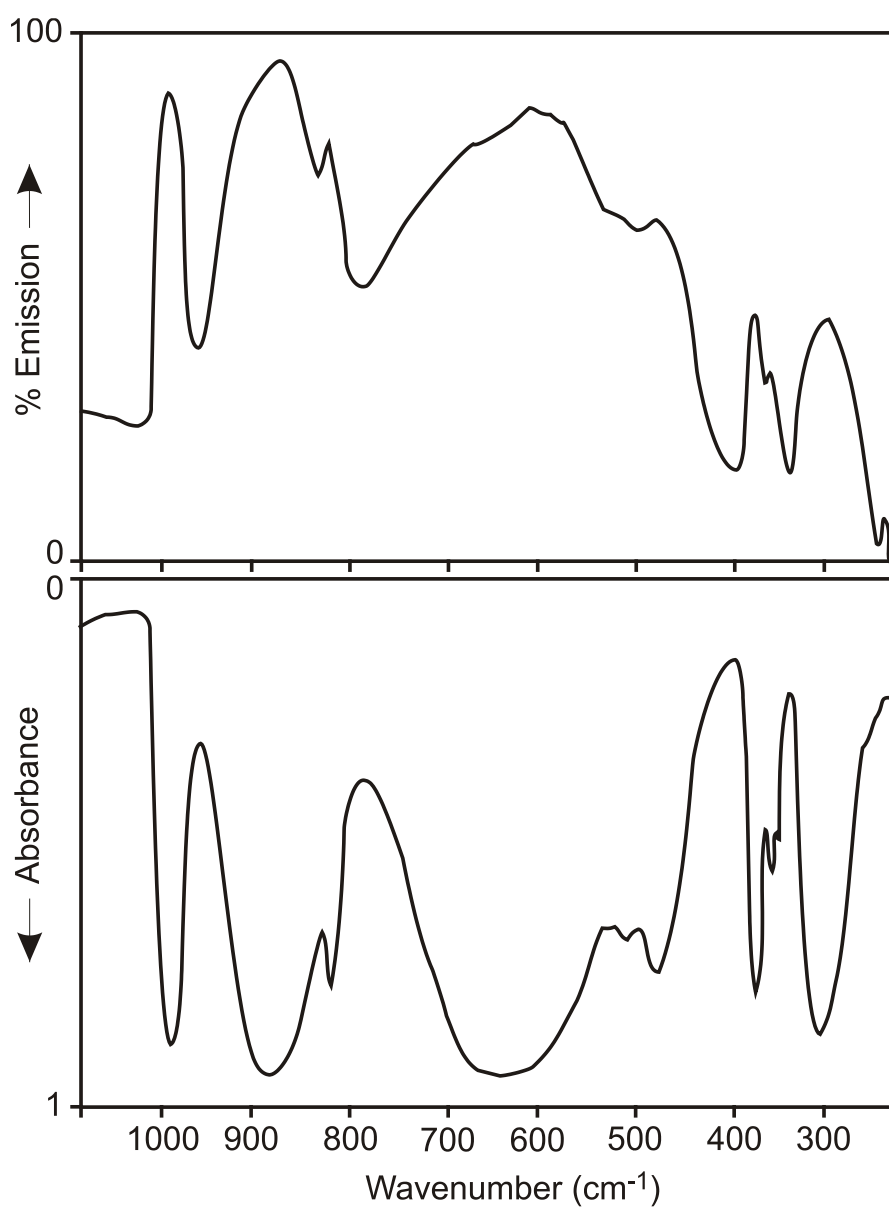
Comparison of the measured emission (upper trace) and absorption (lower trace) FTIR spectra of MoO₃ (in CsI pellet).

3.1. LAWS OF THERMAL RADIATION

EMISSION = HIGHER LEVEL $\xrightarrow{\text{transition}}$ LOWER LEVEL

THERMAL EXCITATTION

RADIANT ENERGY DENSITY $H = Q/V$

      Q - is the total radian energy

      V - in the volume

RADIATION OF VARIOUS WAVELENGTHS (**frequencies**)

$$H = \int_0^\infty H_\nu \, d\nu = \int_0^\infty H_{\tilde\nu} \, d\tilde\nu = \int_0^\infty H_\lambda \, d\lambda$$

H_ν, $H_{\tilde\nu}$ and H_λ **spectral radiant energy densities**

BLACKBODY RADIATION

In essence, all matter absorbs electromagnetic radiation falling on it is called a black body, means it is a perfect absorber. But when blackbody is in uniform temperature state, it emits back this absorbed energy and it is called as "blackbody radiation". Radiant energy of the blackbody is shown in Figure . As the temperature of the body becomes higher, the amount of radiant energy from a material becomes larger. The increase follows the Stefan-Boltzmann law and is proportional to the fourth power of the absolute temperature (T). It is shows as follows:

$$E = \sigma x T^4 = 5.6697.\ 10^{-12}\ xT^4\ W\ cm^{-2}$$

As the absolute temperature of the radiator rises, the maximum position of the curves shifts to the short wavelengths i.e. to the direction of the visible region. Wien's displacement law states that

$$\lambda_{max}\ x\ T = constant = 2897.8\ \mu K$$

For example, the peak maximum (λ_{max}) of a person with temperature of 36 degrees Celsius (309K) becomes 9.4 µm. The person emits infrared radiation with a maximum peak position wit about 9.4 µm. At the surface temperature of the sun (6000 K) the maximum is shifting to 0.48 µm, which is in the visible (blue) region of the spectrum (Fig.1).

In the IR radiation the energy is transferred purely in the form of heat which can be perceived by the thermo receptors in human skin as radiant heat.

Infrared or thermal radiation has been used effectively for millennia to treat certain diseases and "repair" discomforts. Heated saunas are only one of the oldest treatments to deliver infrared radiation in controlled environment and controlled "exposure" time.
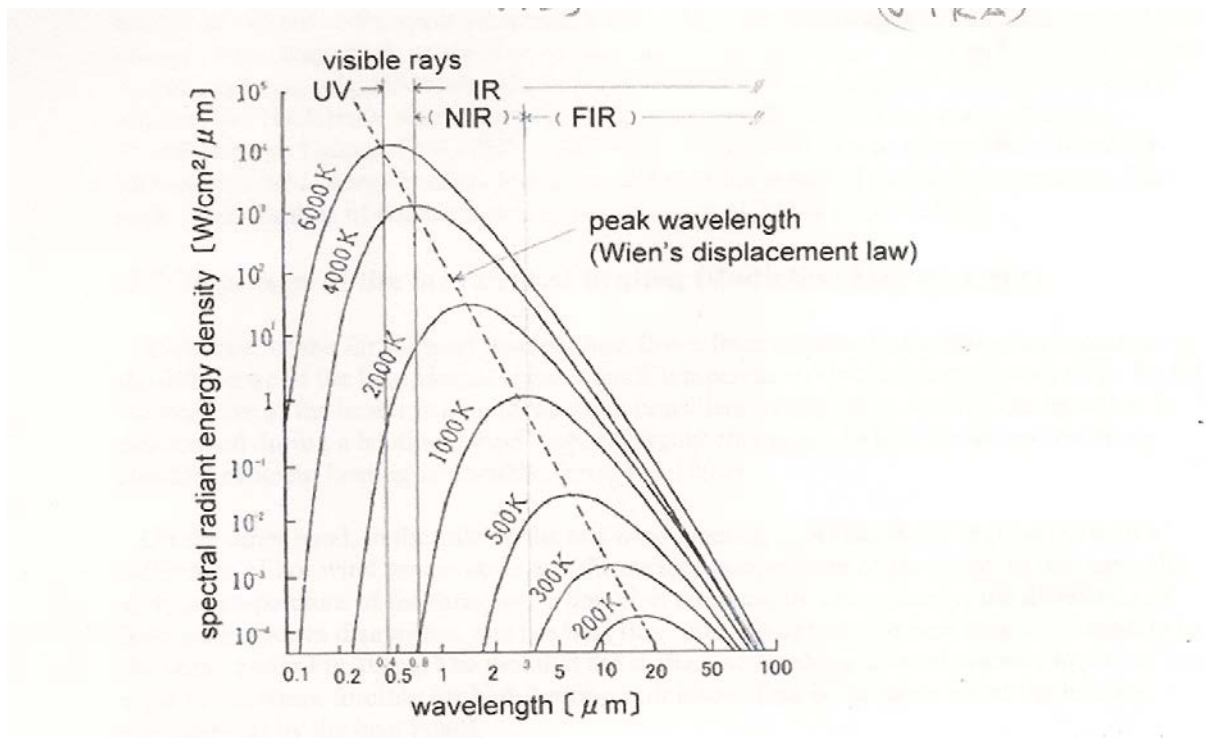
Radiant energy of blackbody at different temperatures (Planck's radiation law).

The absorptance of the blackbody

$$\alpha_{\tilde{v}} = 1 \text{ (In the whole spectral range)}$$

Stefan (1878), Boltzmann (1884) theory:

$H = \sigma T^4 = 5.6697 \cdot 10^{-12} \times T^4 \text{ W cm}^{-2}$

σ - in the S.-B. constant

$\sigma = 8\pi^5 k^4 / 15 c^3 h^3$

Rayleigh - Jeans law:

$$H_{\tilde{v}} = 2kT\ \tilde{v}^2$$

Wien's radiation law:

$$H_{\tilde{v}} = 2hc\,\tilde{v}^{\,3}e^{-h\tilde{v}\,/\,kT} \text{ ,}$$

Wien's displacement law:

$$\tilde{v}_{\text{max}} = \text{const x } T = 3.451 \text{ x } T \text{ cm}^{-1}$$

For $\tilde{v}$

$$\lambda_{\text{max}} = 2897.8/T \text{ } \mu\text{m}$$

Planck's law of blackbody radiation:

(a) $H_{\tilde{v}}(T) = \dfrac{2hc^2\tilde{v}}{e^{hc\tilde{v}/hT} - 1}$ **(in spectral element d $\tilde{v}$)**

Spectral radiant energy density

(b) $H_\lambda(T) = \dfrac{2hc^2}{\lambda^5(e^{hc/\lambda kT} - 1)}$ **(in spectral element d$_\lambda$)**
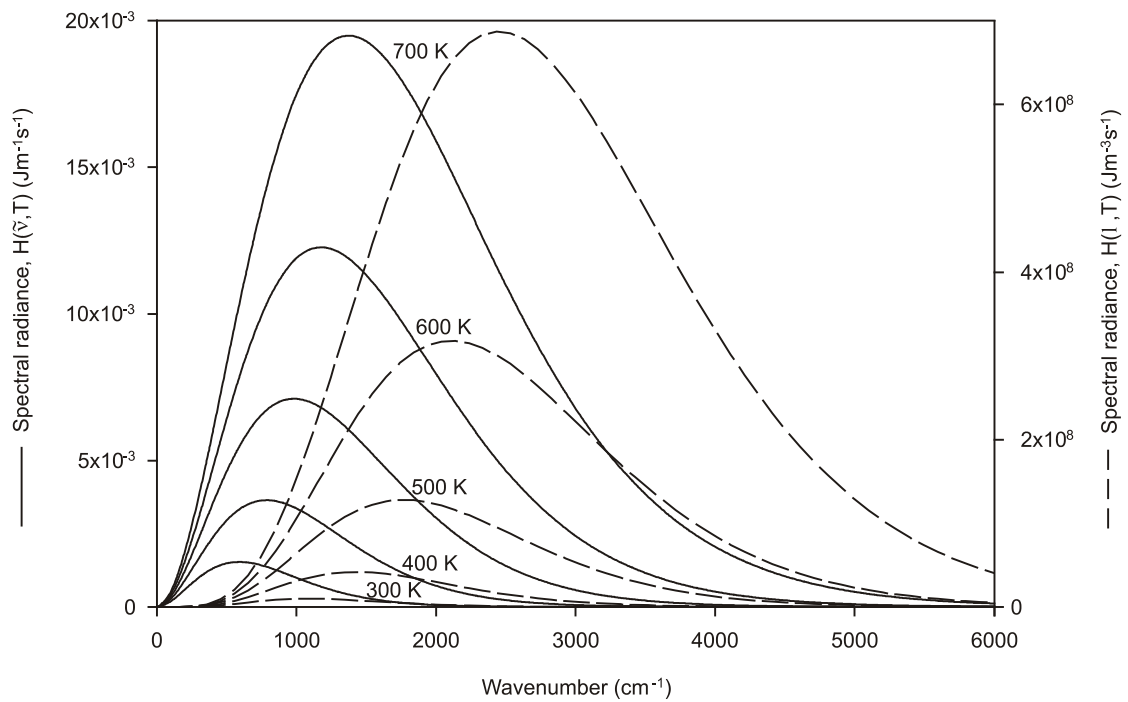
Theoretical blackbody radiation curves in the wavenumber representation (solid lines) and in the wavelength representation (dashed line) for five temperatures.

THERMAL EMISSION OF NON-BALCKBODIES

Kirchoff law:

$$\alpha + \rho + \tau \; = \; 1$$

α - absorptance

ρ - reflectance

τ - transmittance

Blackbody: α = 1

ρ = τ = 0

Reflecting mirror:

ρ = 1

α = τ = 0

KBr window:

τ = 1

α = ρ = 0

Greybody:

$$\left.\begin{matrix} \alpha \\ \rho \\ \tau \end{matrix}\right\} \; = 0 - 1.0$$

$$\varepsilon\,(\tilde{\nu}) = 1 - \tau\,(\tilde{\nu}) - \rho\,(\tilde{\nu})$$

3.2. Experimental methods of IR emission spectroscopy
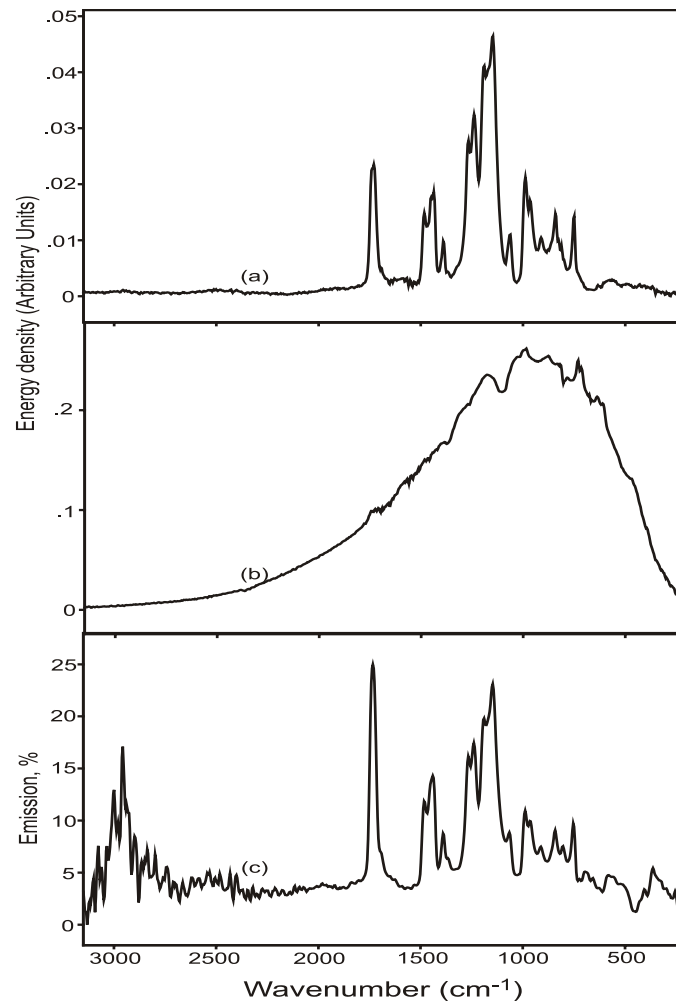
Procedure for production of the double beam emission (emittance) spectrum of PMMA film:

(a)   Single beam emission spectrum of 2.6 μm thick PMMA film on polished steel sample holder at 100 °C;

(b)   Blackbody reference emission spectrum at 100 °C;

Double beam emittance spectrum of PMMA obtained via rationing *a* to *b* (Resolution: 8 cm^{-1}, number of scans: 1024).
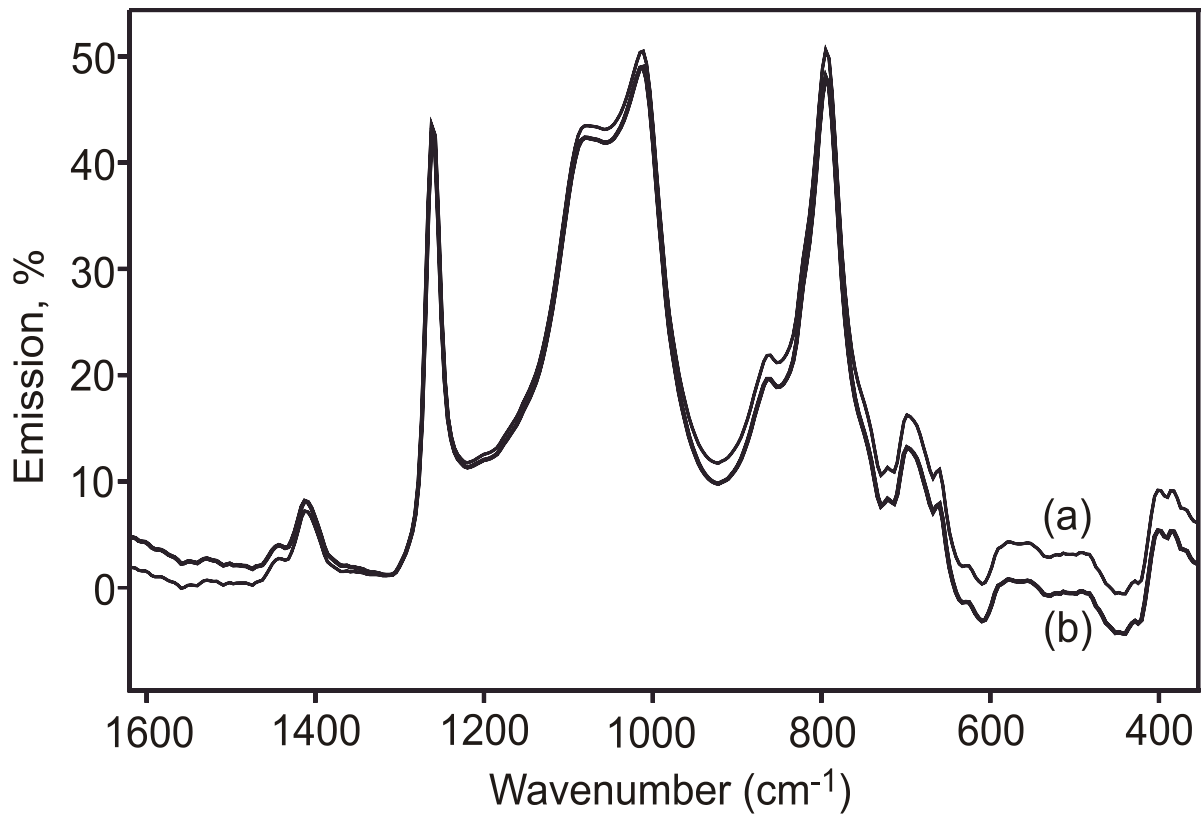
Emittance spectra of silicon grease (0.15 μm thick film) using a Peltier-thermostated DTGS detector (20 °C):

(a) With correction for background radiation;

(b) Without correction for background radiation (temperature: 150 °C, resolution: 8 cm⁻¹, number of scans: 1024).
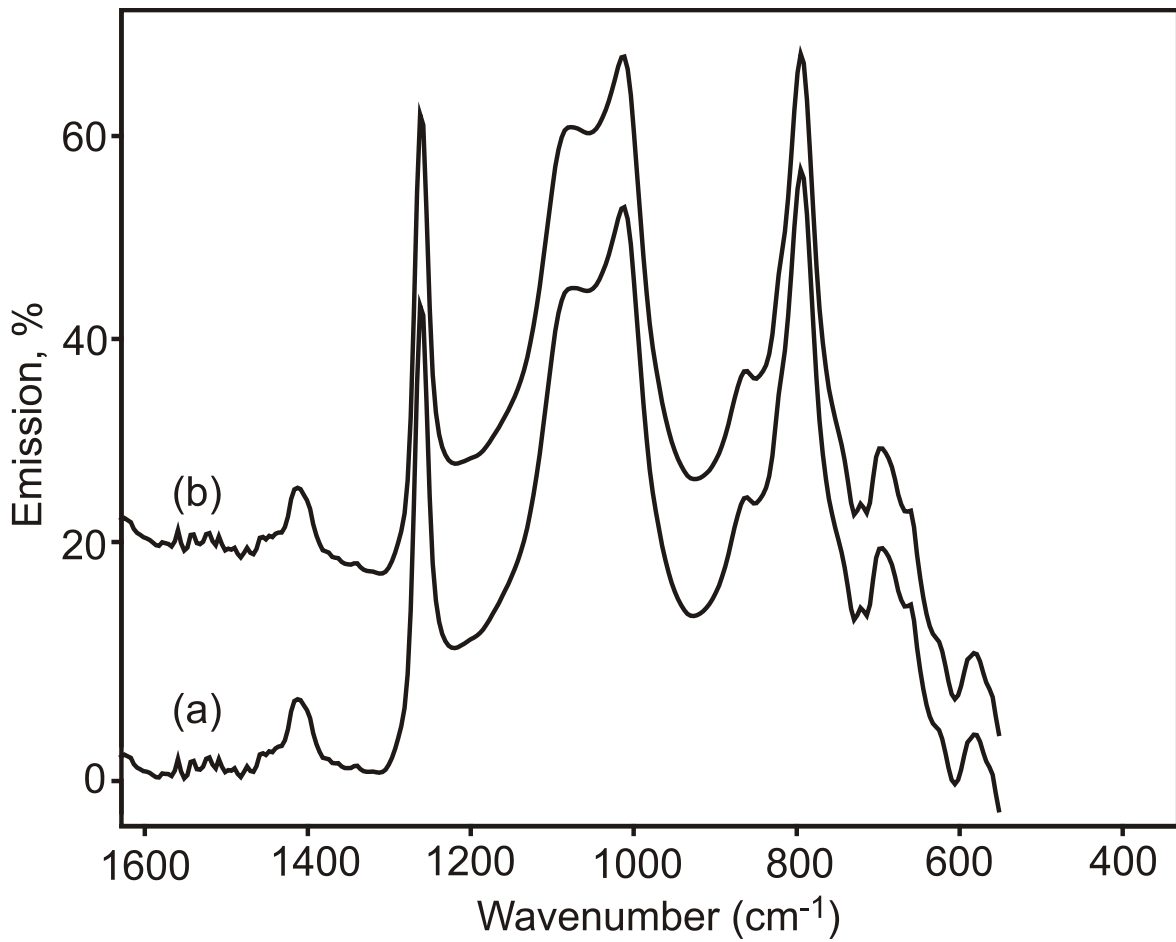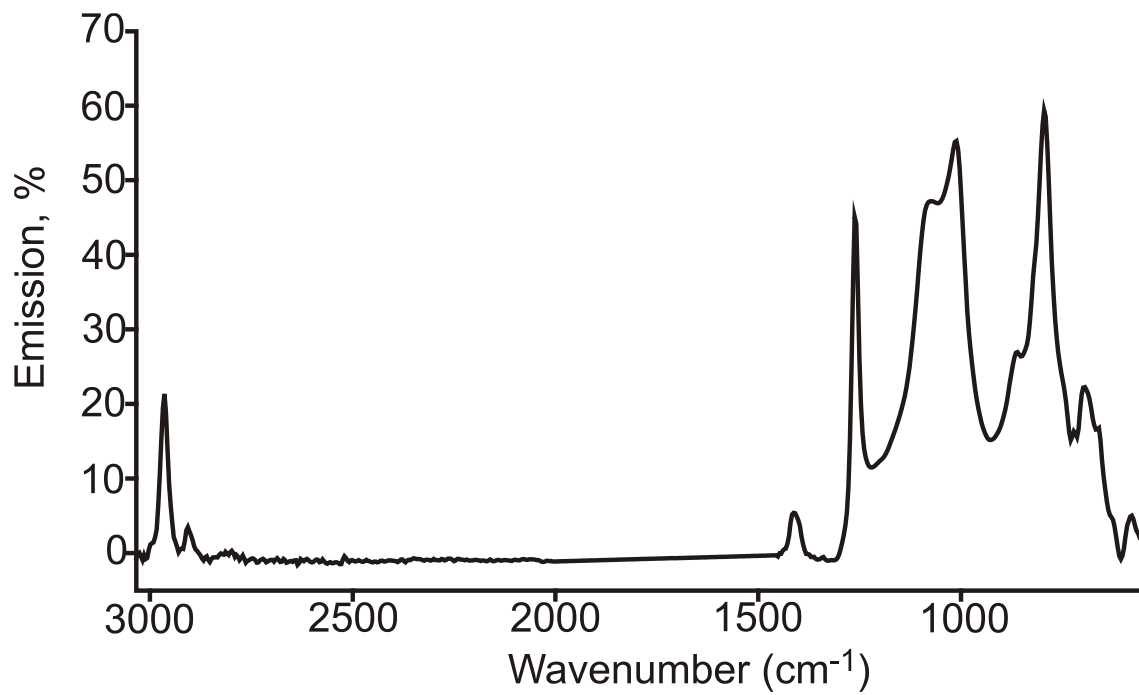
Emittance spectra of silicon grease (0.15 μm thick film) using a liquid-N₂-cooled MCT detector

(a) With correction for background radiation;

(b) Without correction for background radiation (temperature 150 °C, resolution 8 cm⁻¹, number of scans 1024).
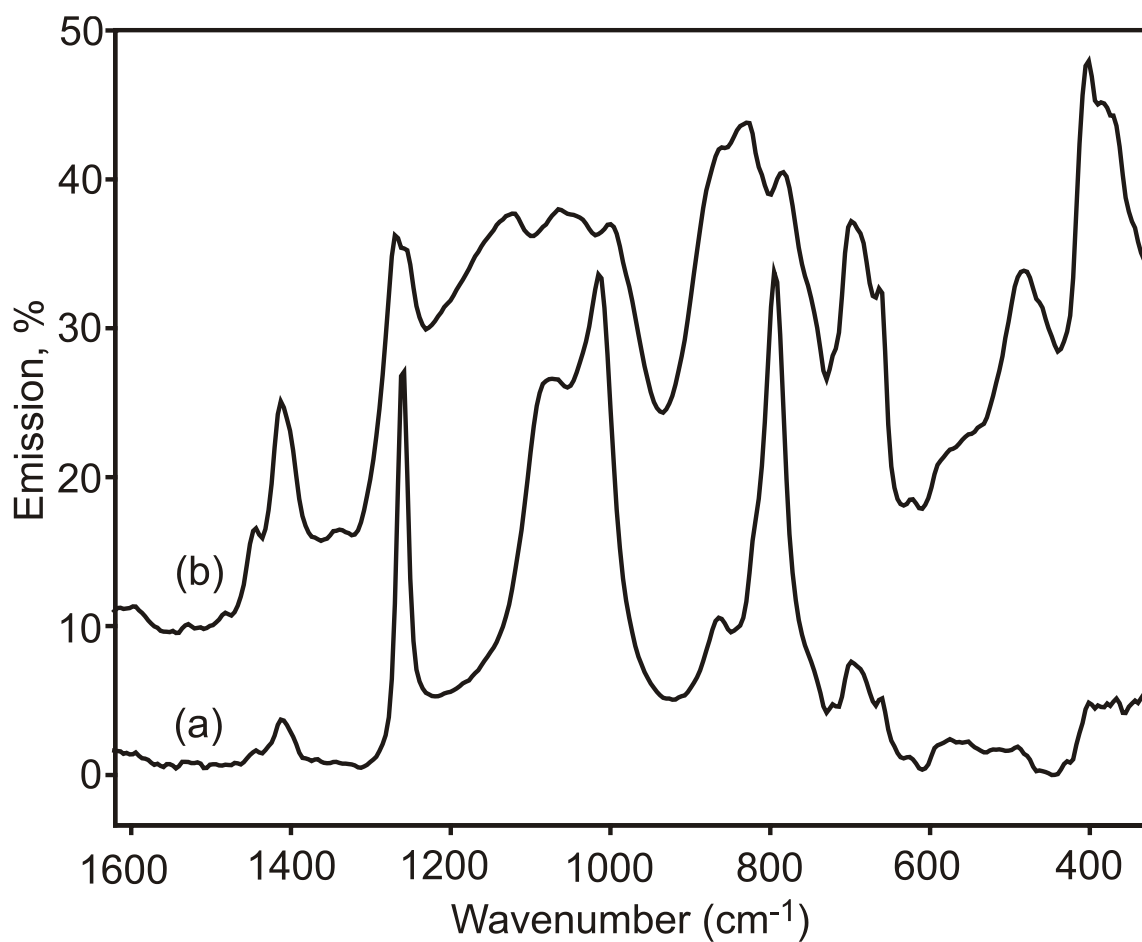
Emittance spectra of (a) 1.5 and (b) 95 μm thick silicon grease films recorded at 100 °C, 1024 scans, 8 cm^{-1} resolution.
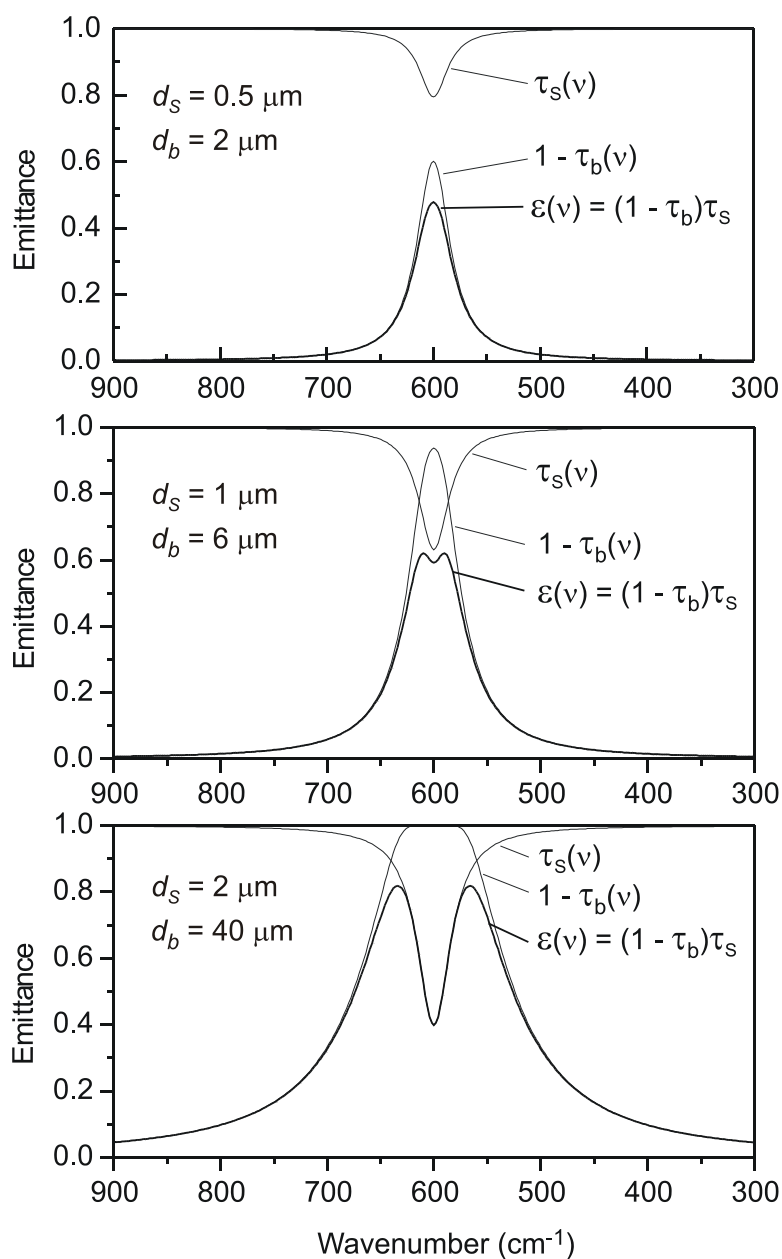
Simulation of the effect of self-absorption by a cooler surface layer (d_b and d_s are thicknesses of the emitting *bulk* and absorbing *surface* layers respectively). (Reprinted with permission from Keresztury, Mink, Kristóf, *Anal. Chem.* 67(20), 3782-3787 (1995). © 1995 American Chemical Society).
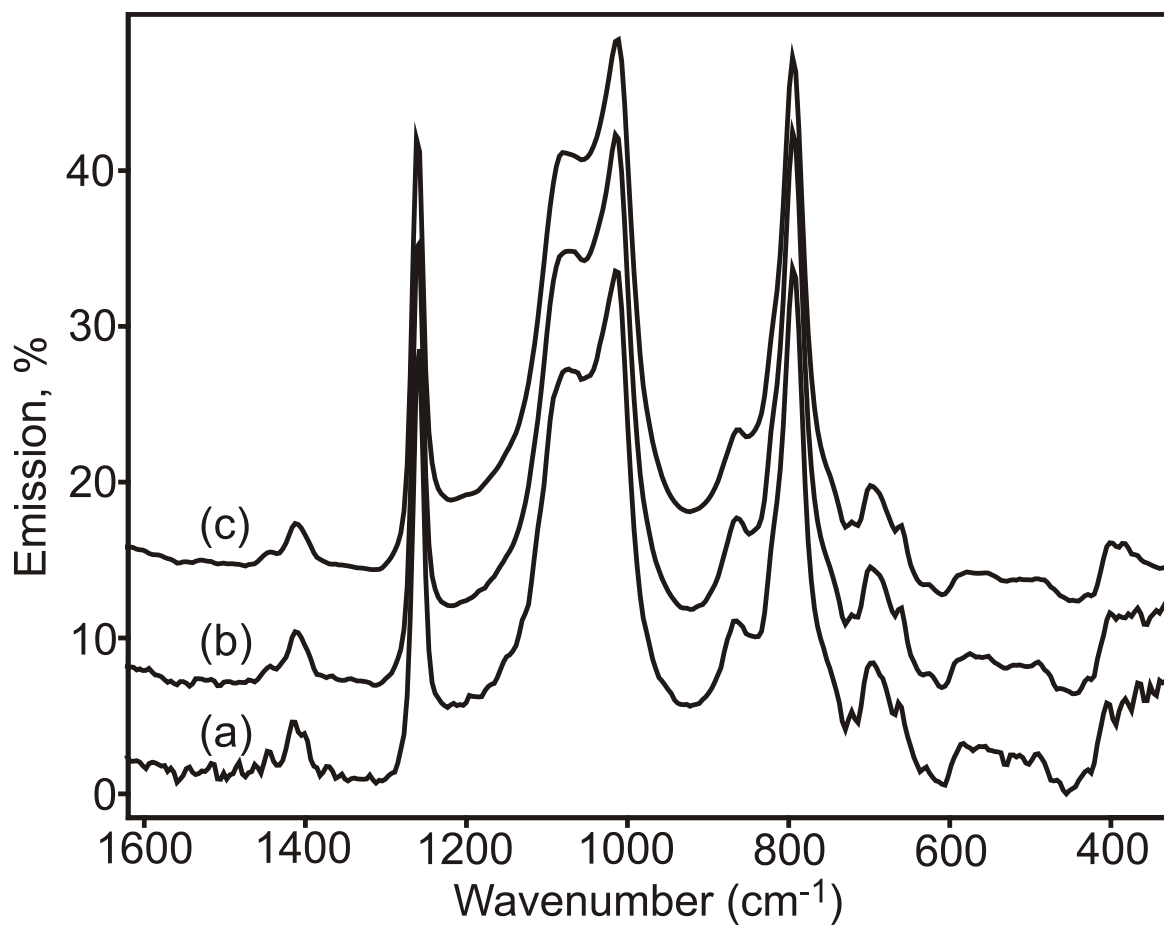
Emittance spectra of 1.5 μm thick silicon grease film recorded at (a) 60 °C, (b) 100 °C and (c) 170 °C, 1024 scans, 8 cm^{-1} resolution. (Spectra *b* and *c* are shifted upwards to avoid confusion.)

Emittance spectra of 1.5 μm thick silicon grease film recorded with MCT detector at 170 °C, 64 scans, 8 cm⁻¹ resolution.
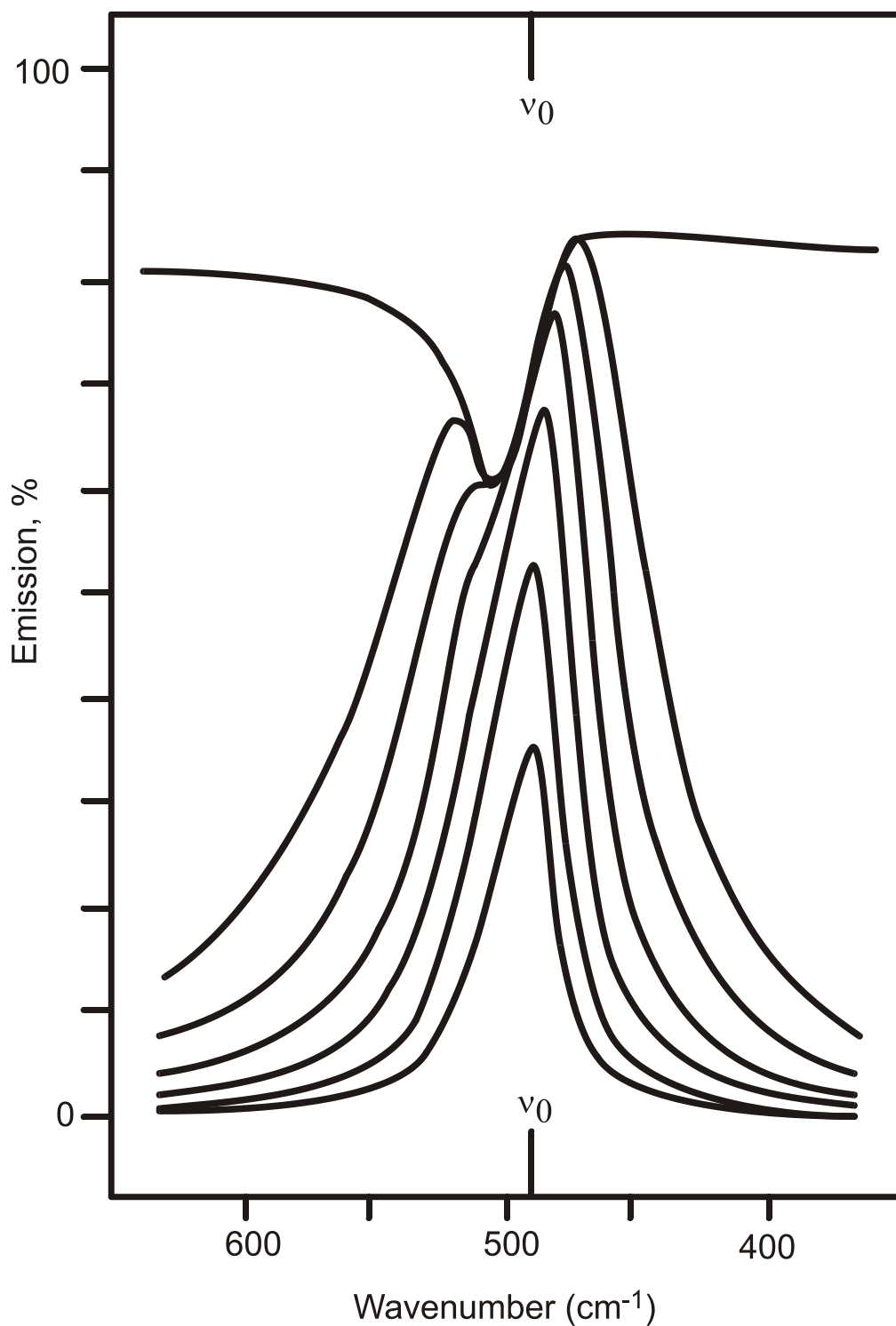
Simulation of the distortion due to surface reflectivity on emission bands of different intensities (Calculated on the basis of References 7 and 8).
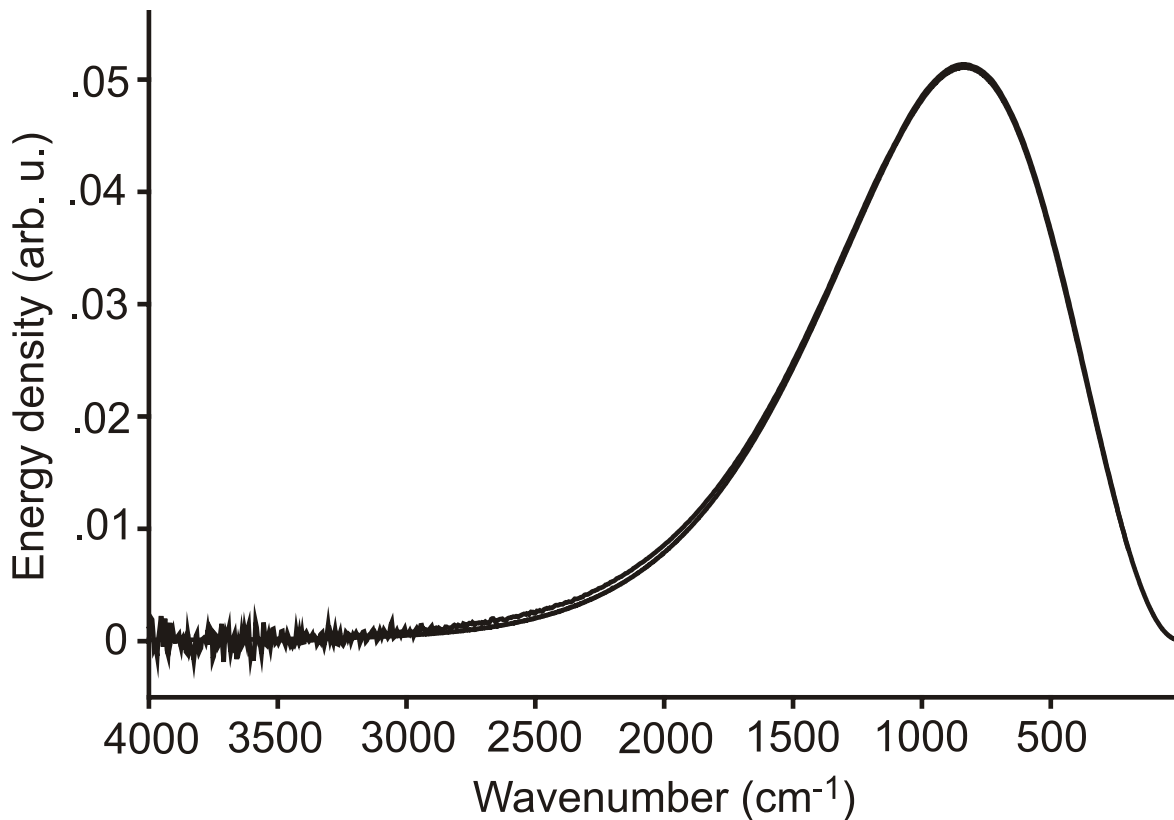
3.2.1. Detector temperature, response functions
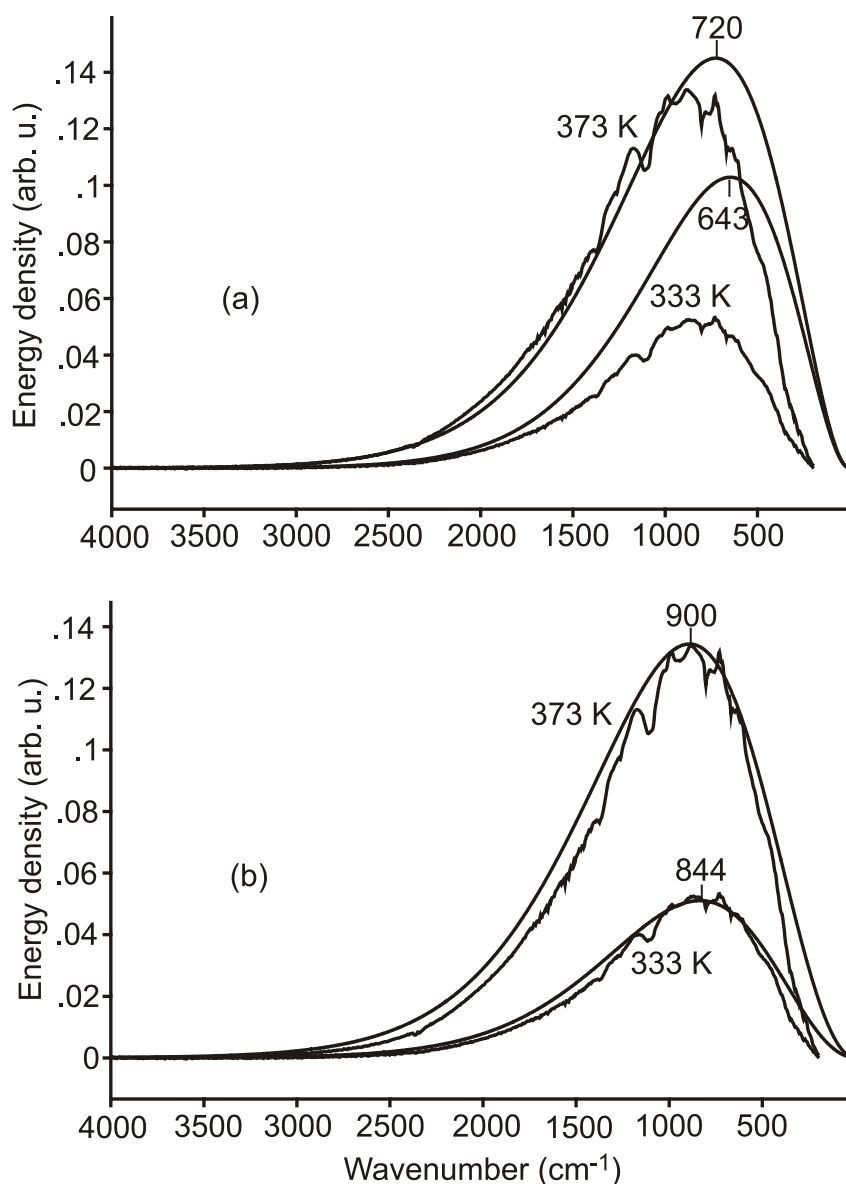
Comparison of blackbody emission spectra measured on a Bio-Rad FTS-175 spectrometer at 60 and 100 °C (with a Peltier thermostated DTGS detector at 20 °C) with uncorrected Planck functions (a) and with Planck functions corrected for detector temperature (b). The numbers 720, 643, 900 and 844 refer to the wavenumber position of the blackbody curve maxima.
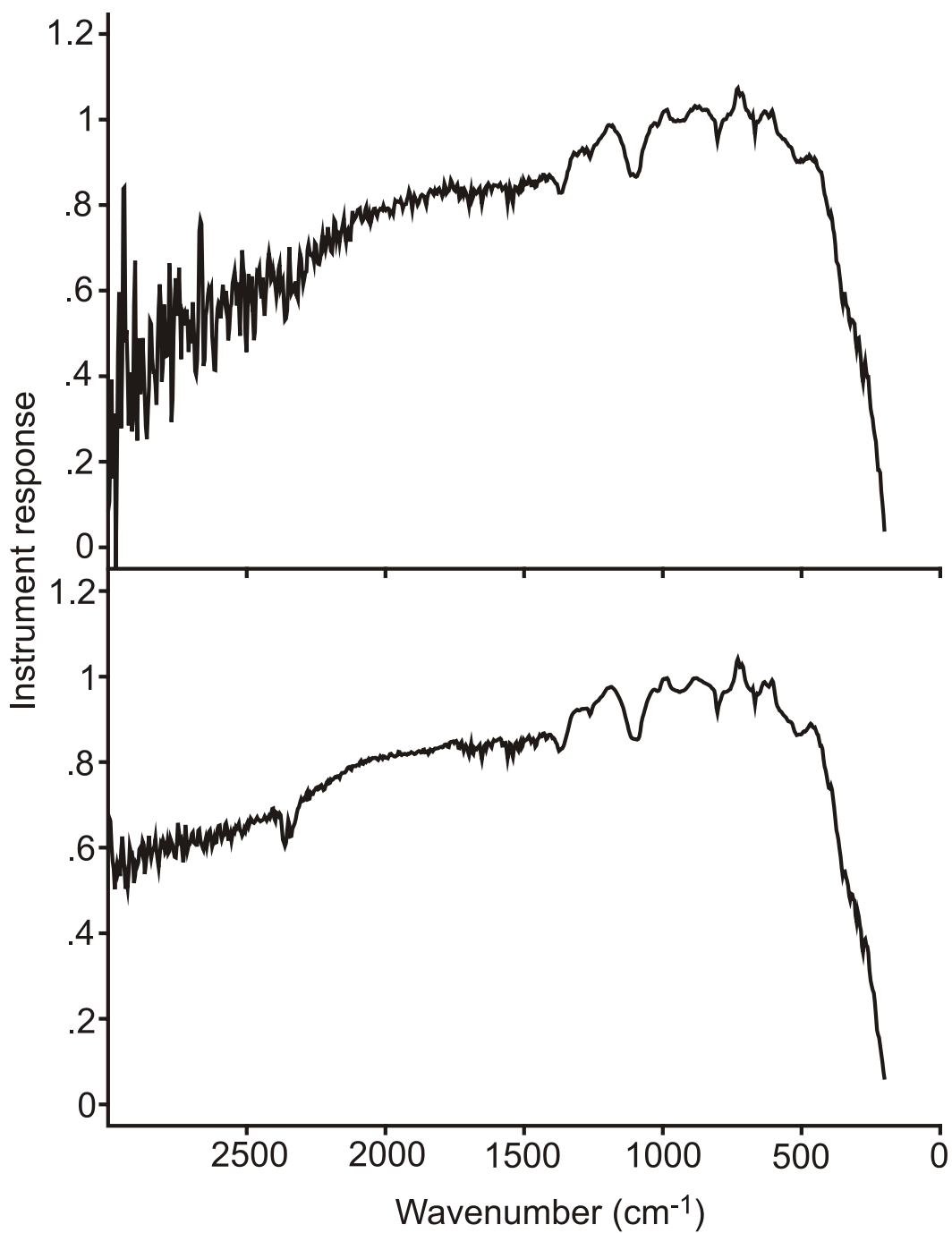
Instrument response functions obtained for the Bio-Rad FTS-175 spectrometer using a laboratory blackbody sample emitting at 100 (bottom) and 60 °C (top).

Emission spectrum of a laboratory blackbody sample at 60 °C measured with a room-temperature detector and corrected for instrument response (noisy curve) compared to the theoretical blackbody radiation curve corrected for detector temperature (smooth curve).

3.2.2. Optical arrangements of external emission ports

Emission accesory

IR source

Extra mirror for emission

Beamsplitter

Interferometer

Detector

Sample Compartment
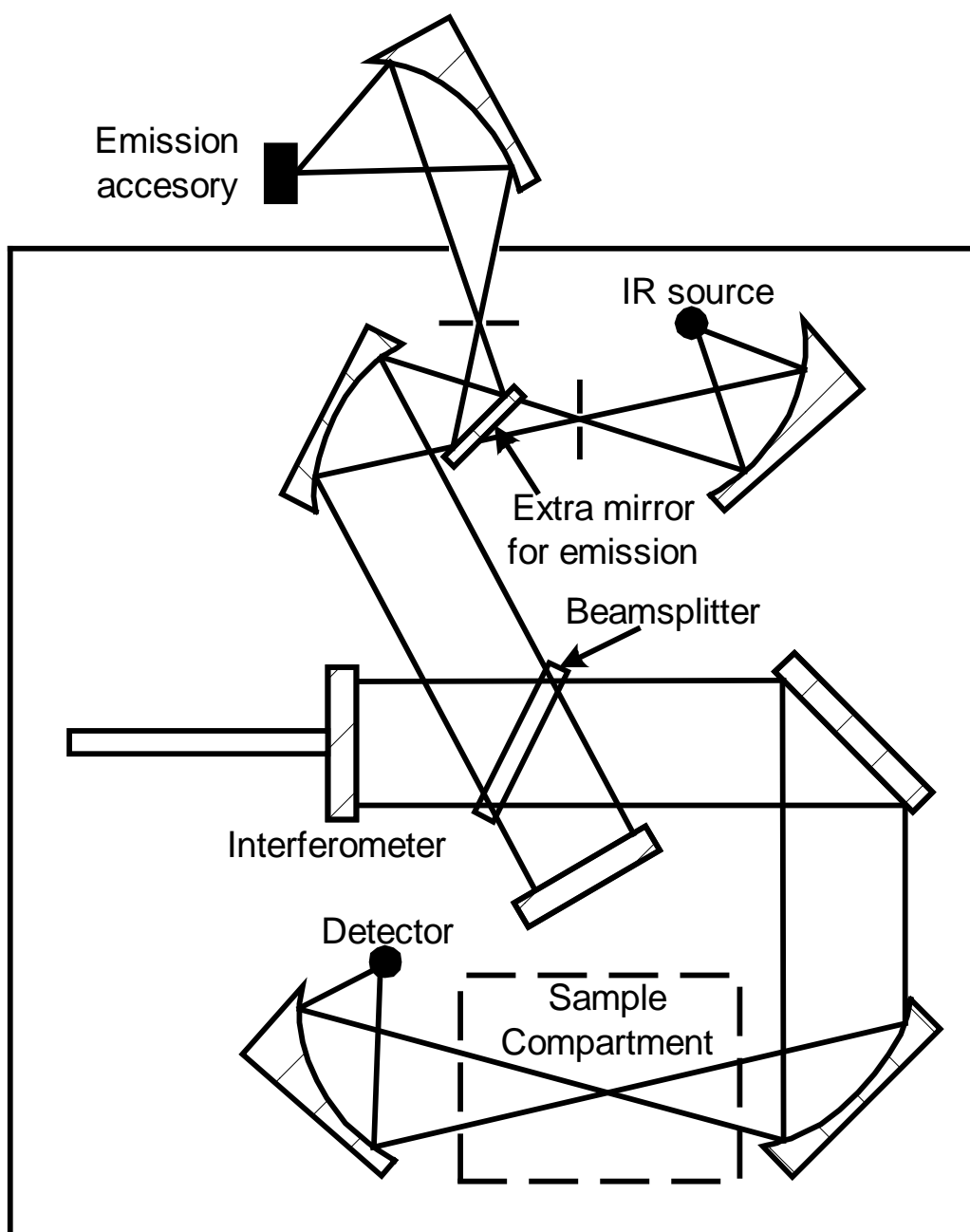
A schematic of the optical layout of the emission experiment realized by an auxiliary port.

IR source

Emission
sample holder

To
interferometer
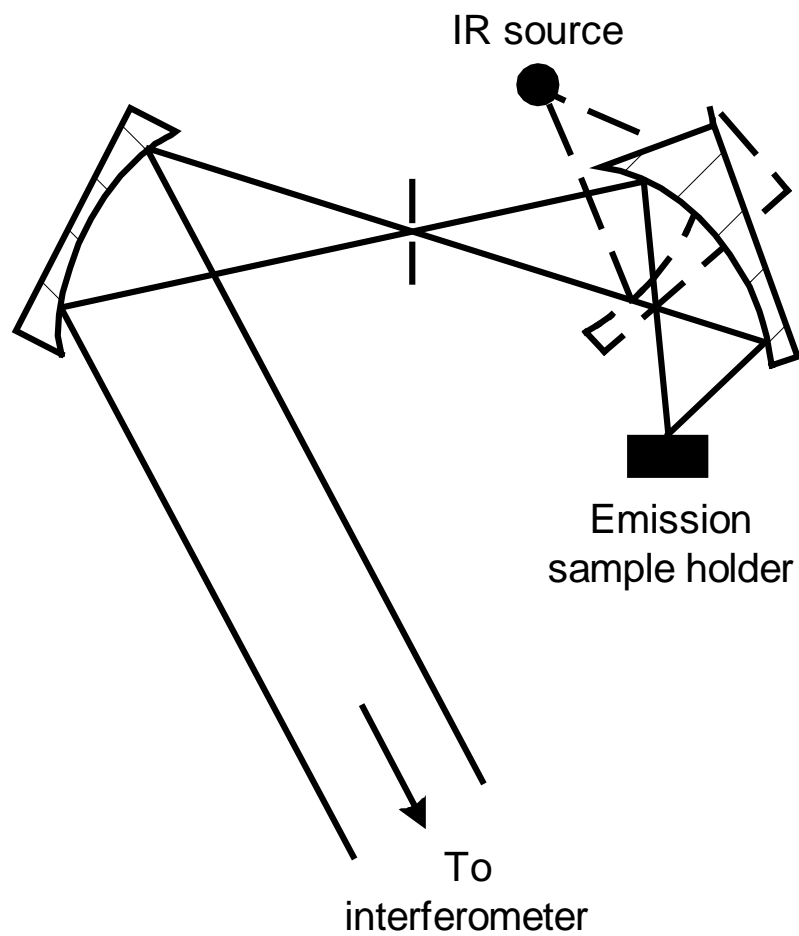
**A schematic of the dual-source assembly accepting
an emission sample holder.**
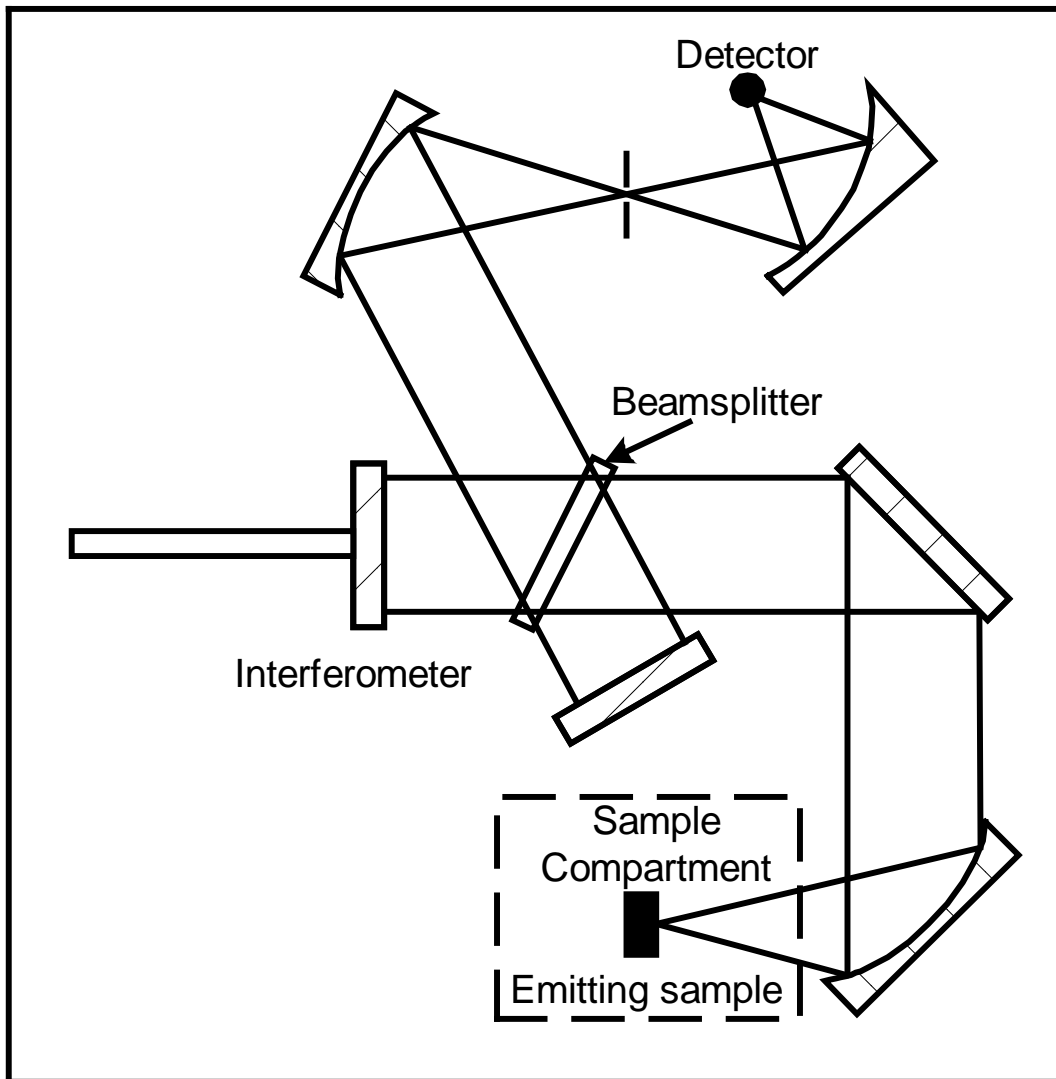
Emission experiment with the emission port situated in the sample position (in the sample compartment) and the detector replacing the usual IR light source.
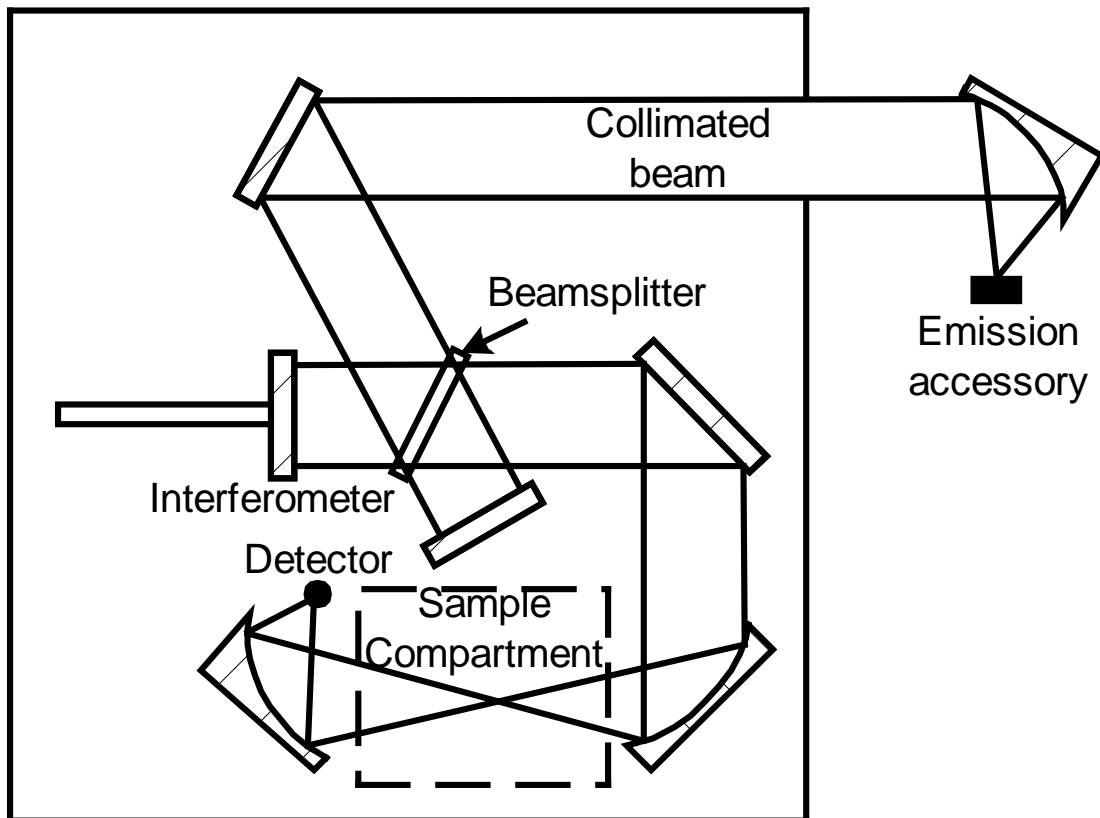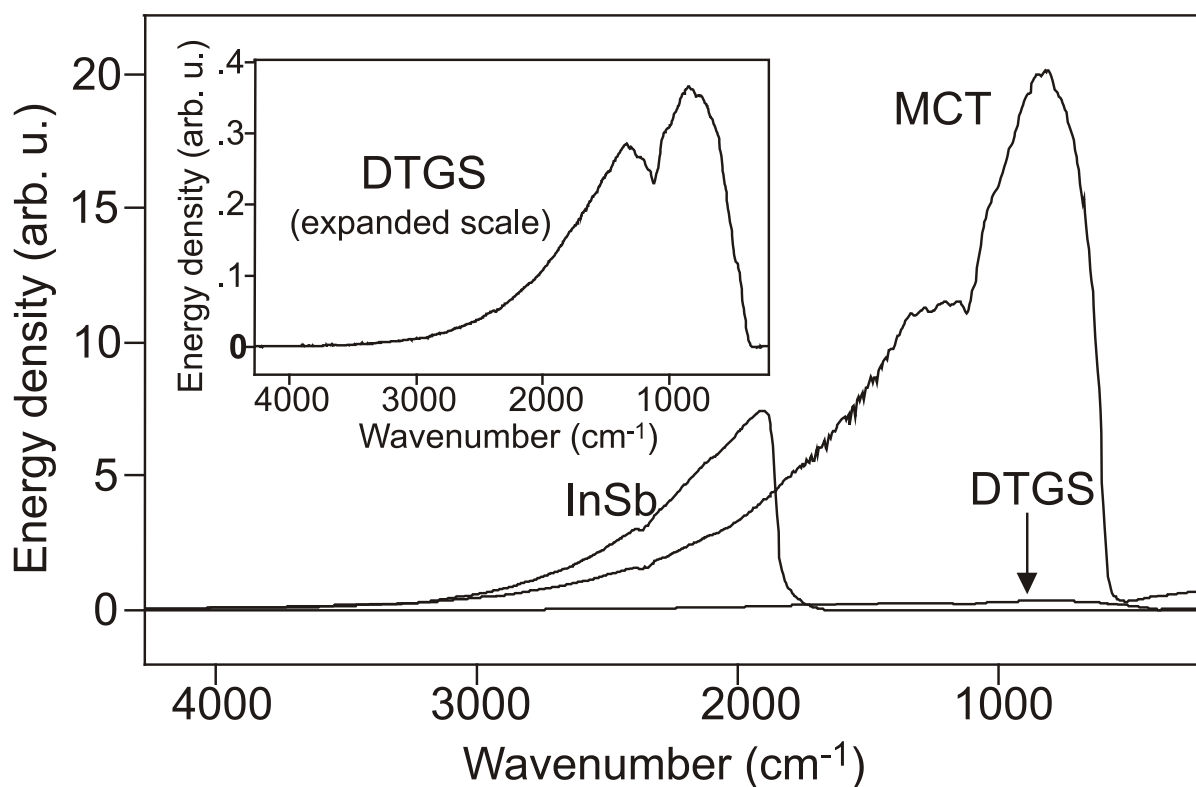
An auxiliary emission accessory is shown with parabolic collector (collimating mirror).

3.2.3. Self emission
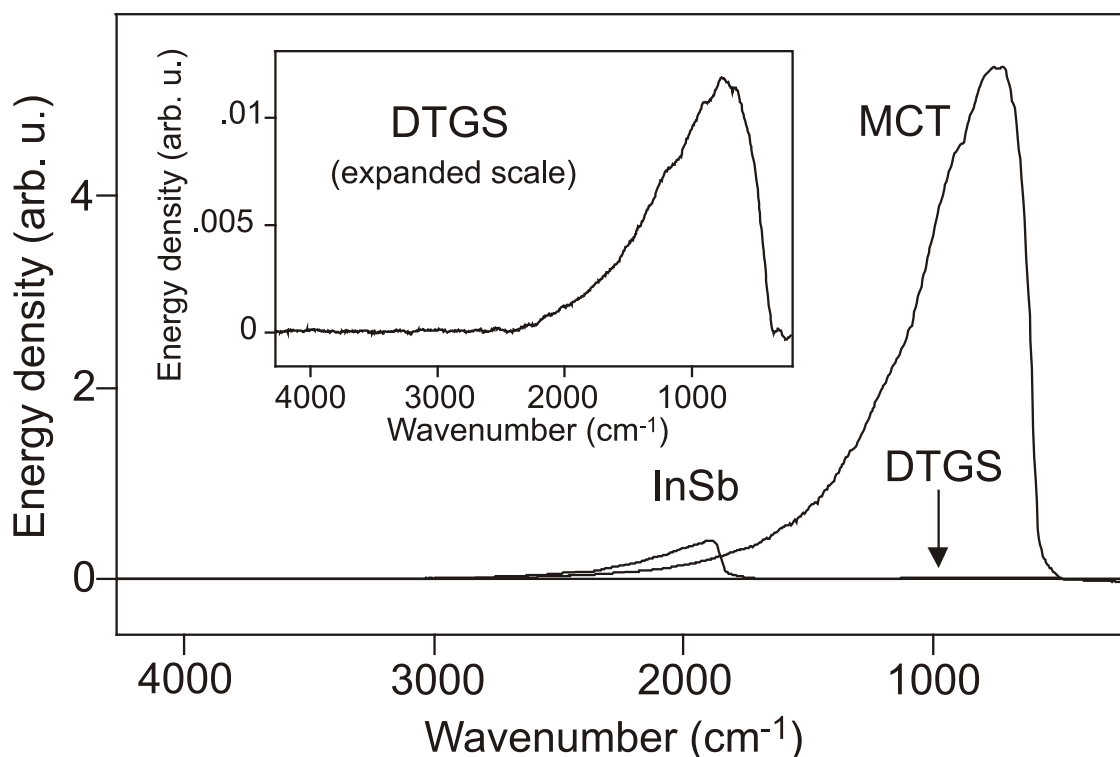
Comparison of single beam spectra of self-emission by an interferometer at room temperature recorded with different detectors (the DTGS detector is Peltier thermostated at 20 °C; all spectra taken with 16 scans, 8 cm⁻¹ resolution).
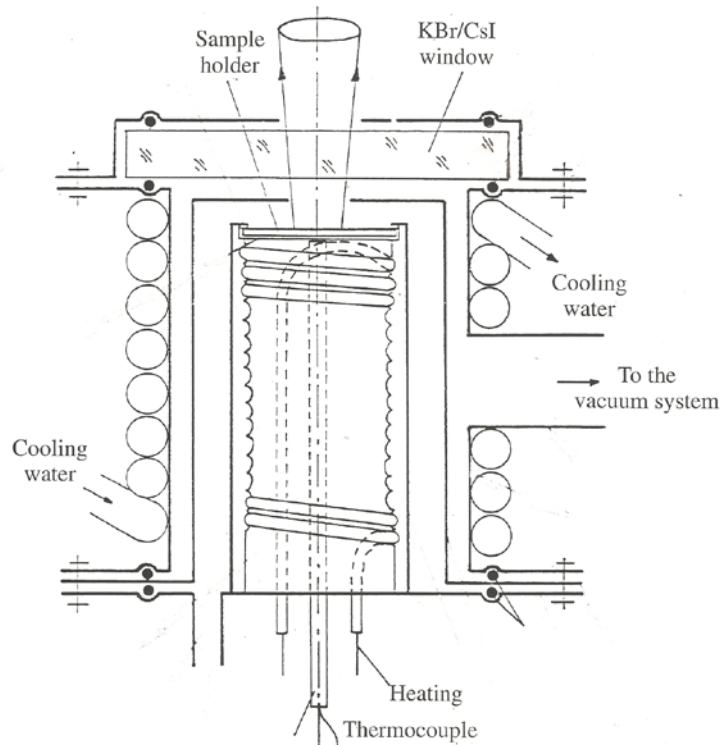
Comparison of blackbody emission spectra at 150 °C obtained using a Bio-Rad FTS-175 spectrometer equipped with different detectors (16 scans, 8 cm^{-1} resolution).
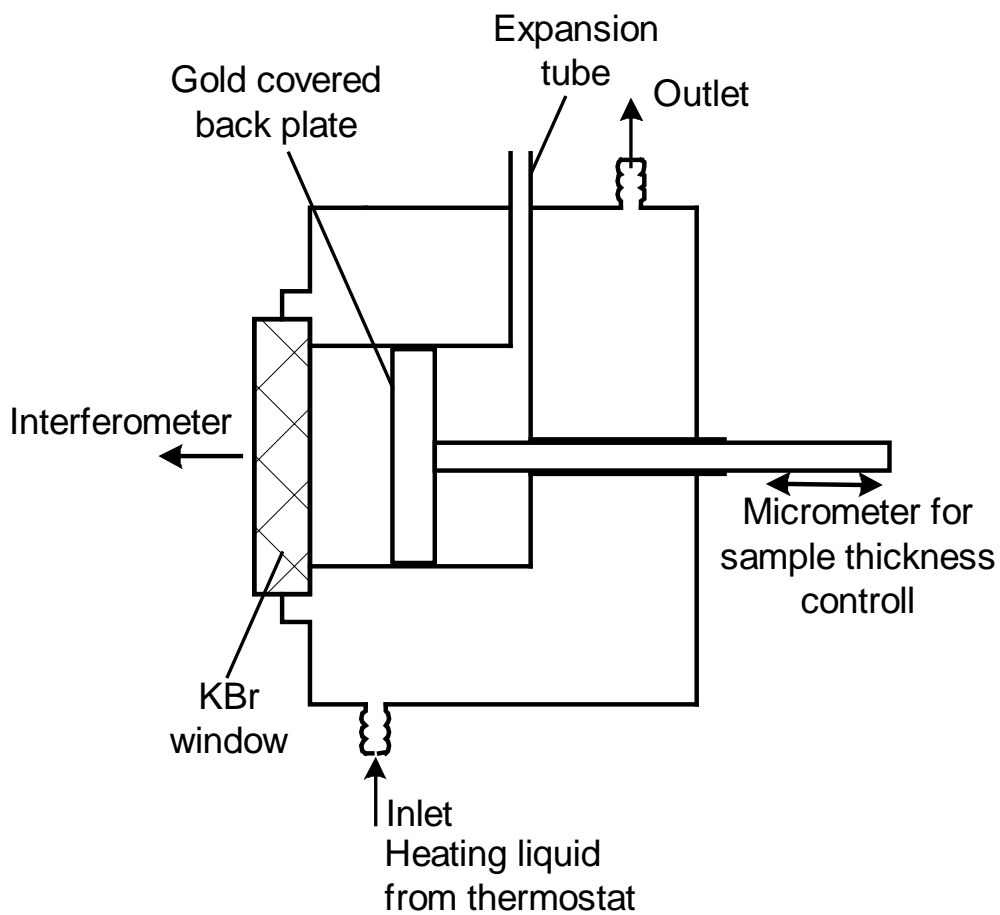
3.2.4. Emission cells
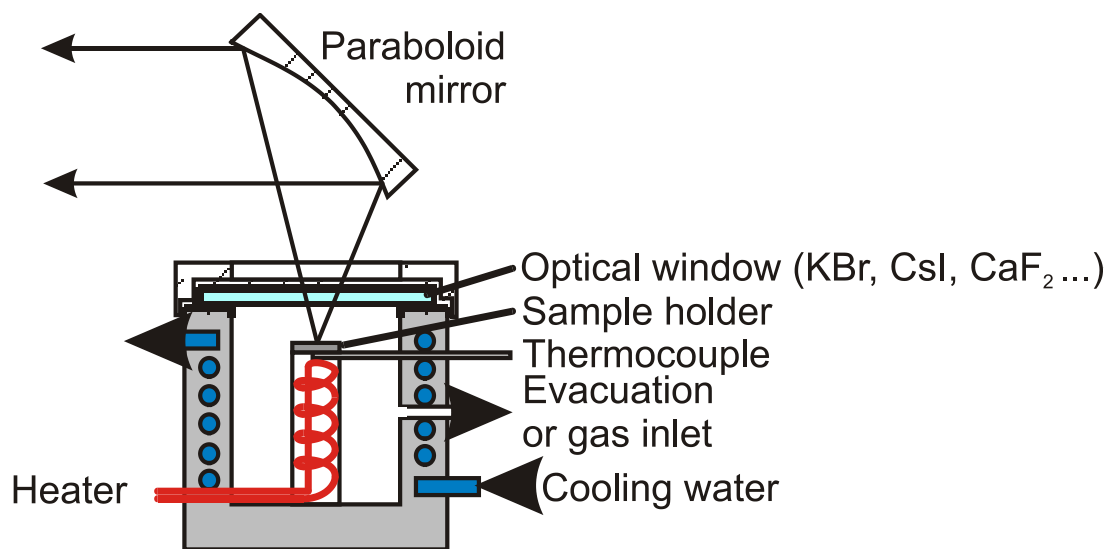
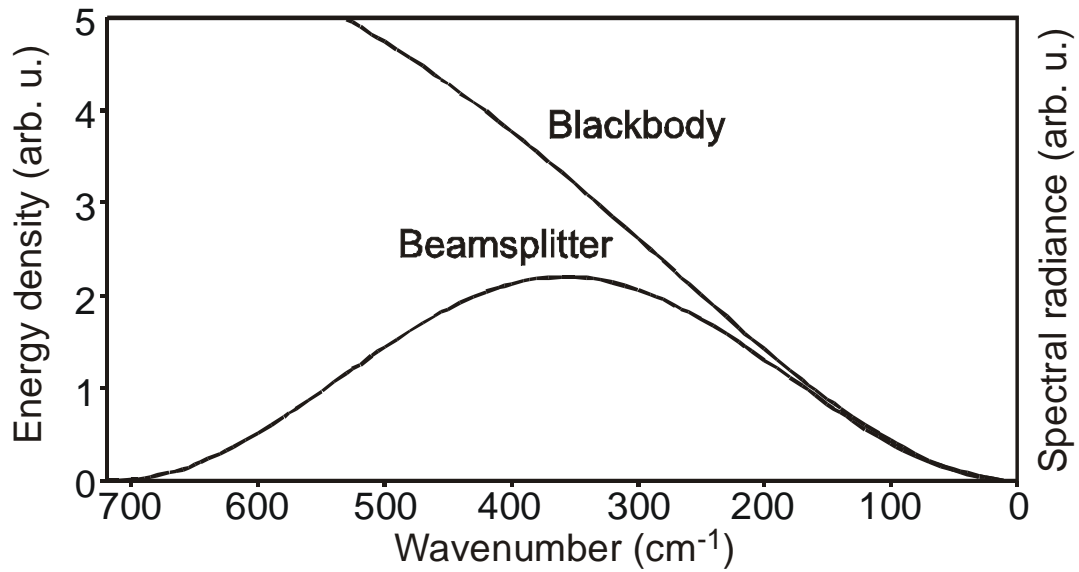**Cross-sectional view of an infrared emission cell suitable for *in situ* studies of catalysts.**

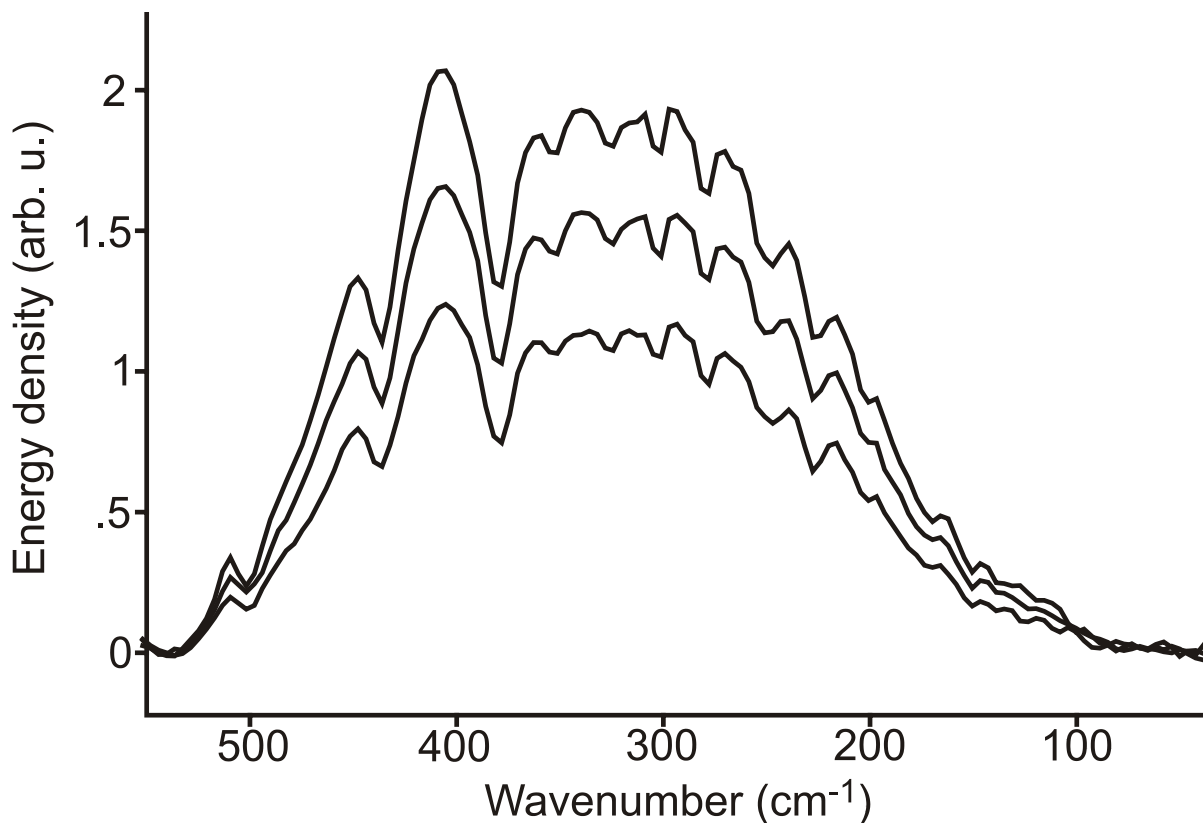**Cross-section of high vacuum emission cell for *in situ* study of catalysts.**

**Variable path length emission cell for liquids and solutions.**

3.3. Far IR emission spectroscopy

Comparison of spectral radiance of a blackbody heated to 140 °C and the 6.5 μm thick Mylar beamsplitter throughput in the far-infrared region.

Blackbody curves obtained in far-infrared region using a Bio-Rad FTS-175 spectrometer equipped with a DTGS detector and 6.5 μm thick Mylar beamsplitter. Blackbody temperatures were 140, 120 and 100 °C (from the top to the bottom).
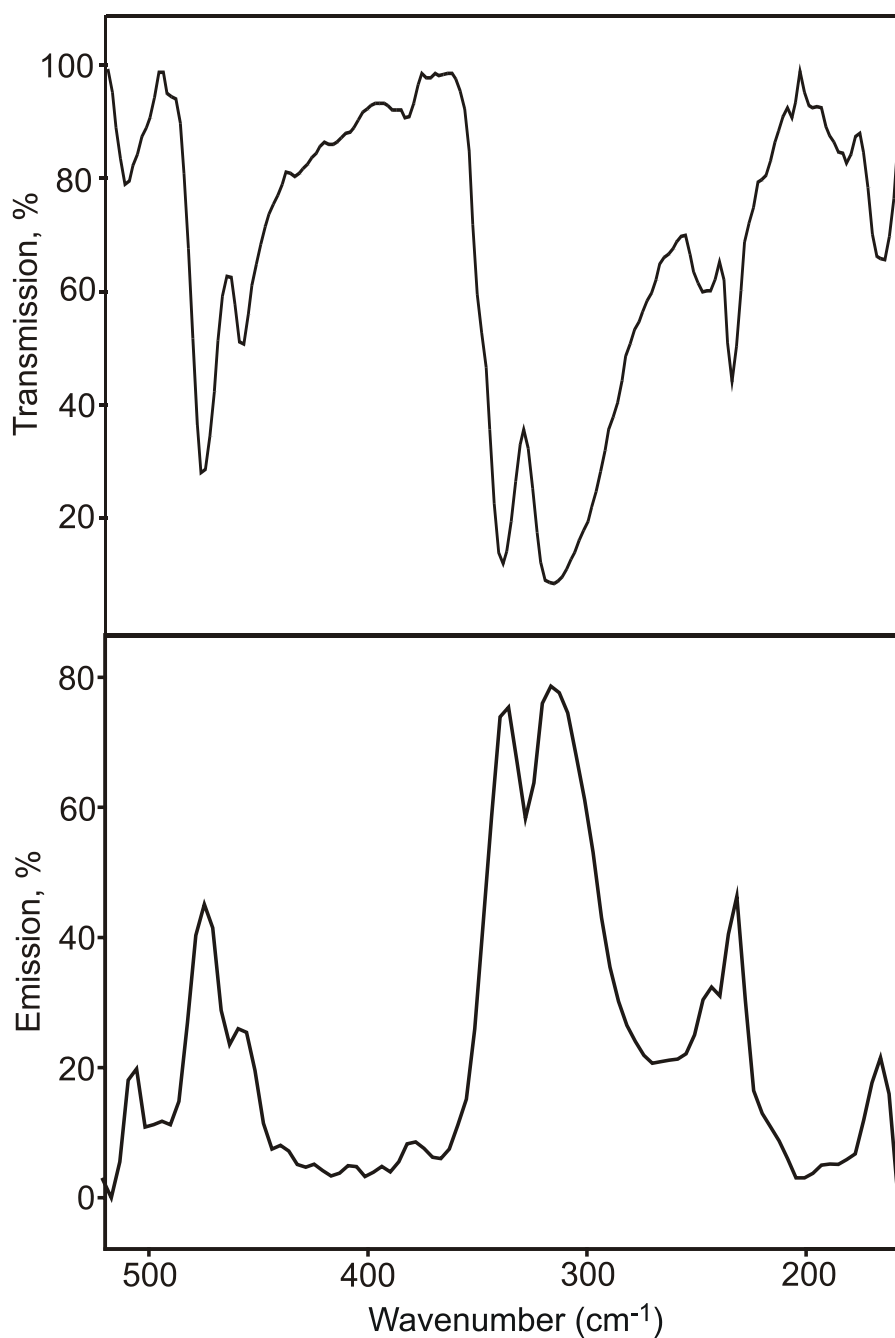
Far-infrared emission spectrum of (COD) PtCl₂ prepared as a nujol mull at 100 °C (COD – 1,5-cyclooctadiene ligand) (lower trace). The spectrum below 150 cm⁻¹ is very noisy. Emission spectrum of the same sample is shown in the upper trace (at 100 °C)

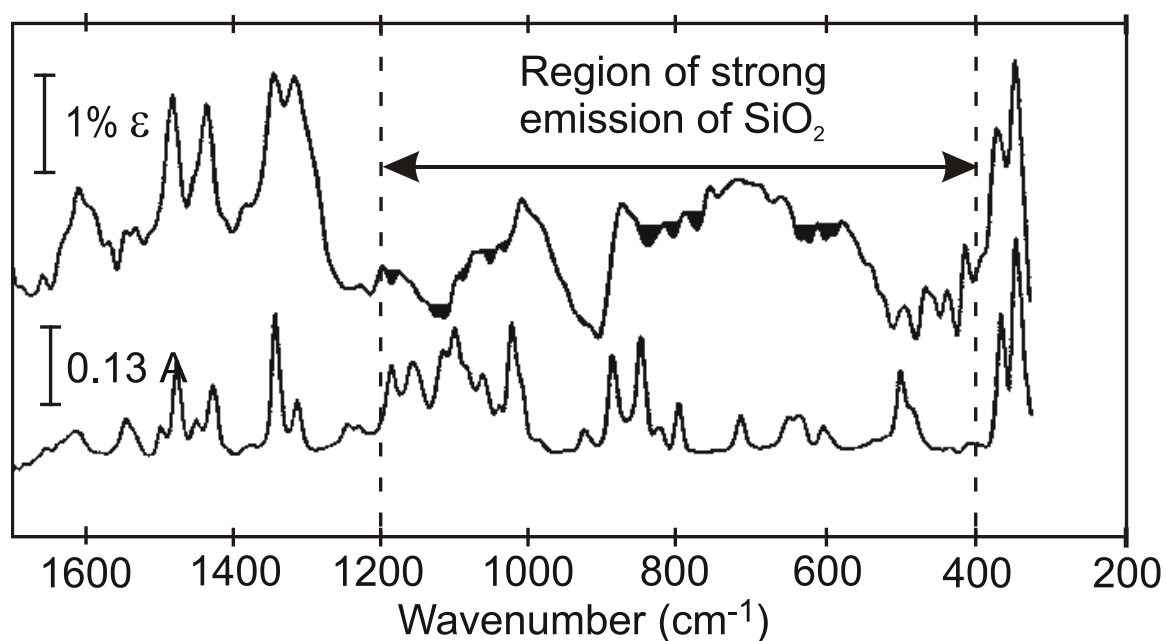# 3.4. Special examples
Subtrate-adsorbate vibrations
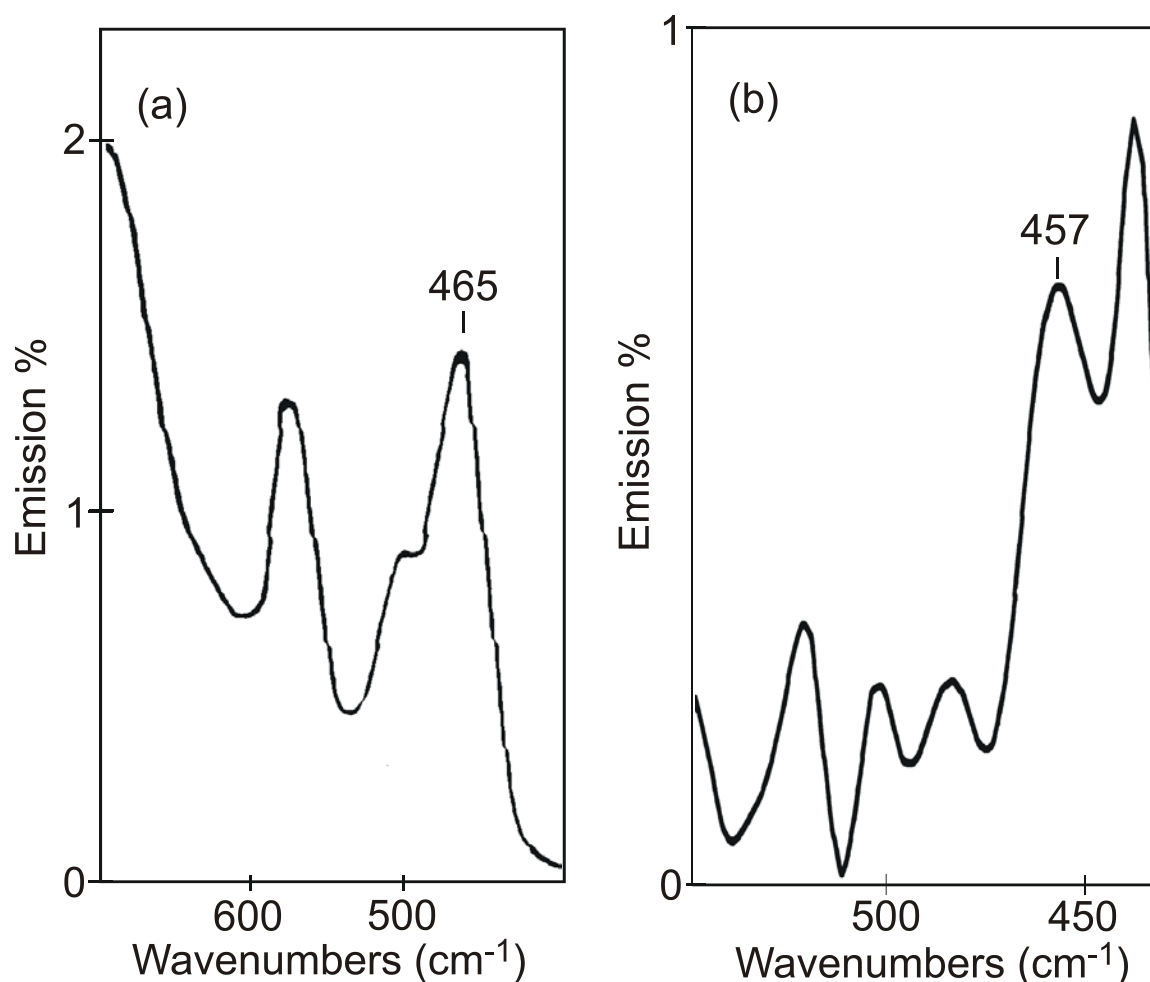
Infrared emission spectra of carbon monoxide adsorbed on supported platinum catalysts in the PtC stretching region.

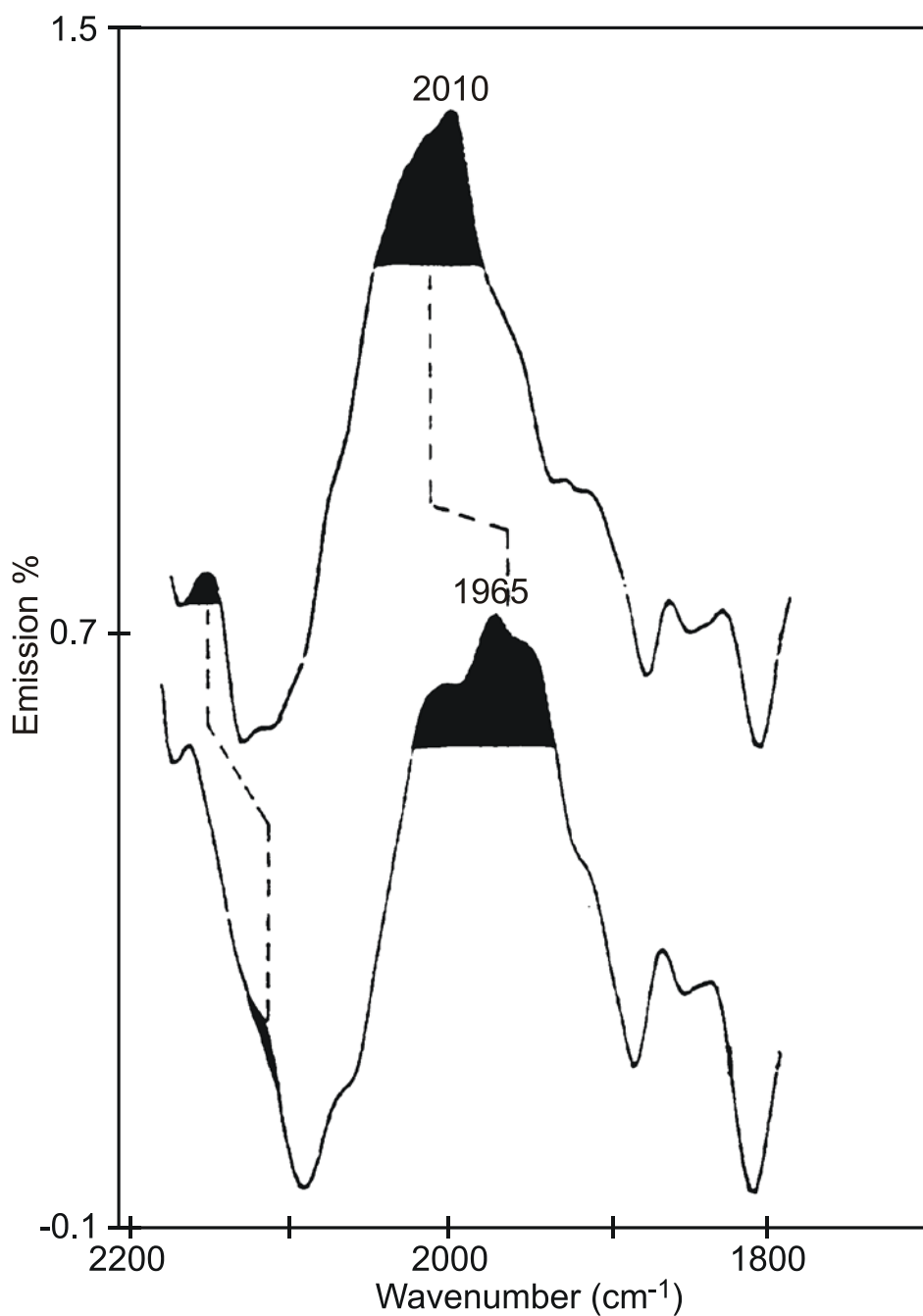**(a) Adsorption on Pt/NaY at 110 °C and 1300 Pa CO pressure.(Taken from Ref. 30)**

(b) Adsorption Pt/Al₂O₃ at 150 °C and 70 Pa CO pressure. (Taken from M.Primet, Ref. 31)

"EMISSION-ABSORPTION SPECTROSCOPY"

IR emission spectra of (COD)PtCl₂/SiO₂ measured at 100 °C (upper trace) and absorbance spectra of pure complex in CsI pellet (lower trace).

(Taken from Ref. 33)

Emission spectra of chemisrobed ^{12}CO (upper trace) and ^{13}CO (lower trace) on Pd powder at 80 °C. Specific surface area of Pd-black was 3.7 m^2/g, and the main particle size was 28-34 μm.

(Taken from Ref. 35)
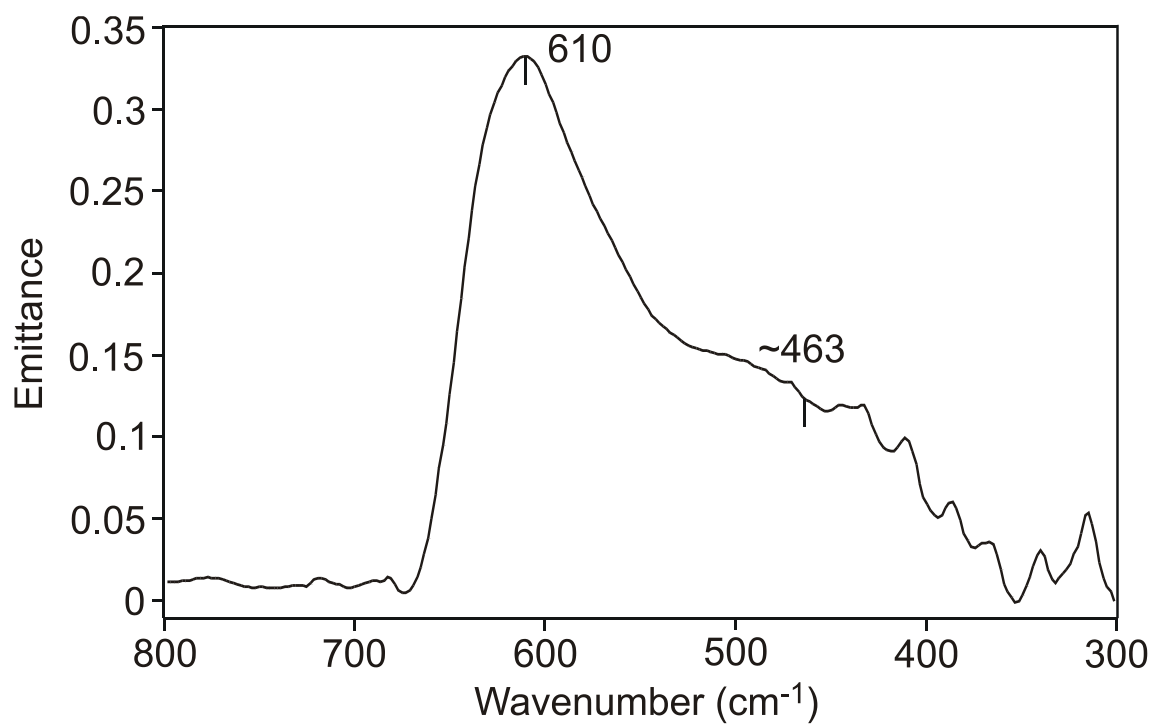
An IRES spectrum of a copper disc which was oxidized under atmospheric O_2 for 20 min at 400 °C. The spectrum was obtained at 100 °C.