Fourier Transform Infrared (FTIR) Spectroscopy

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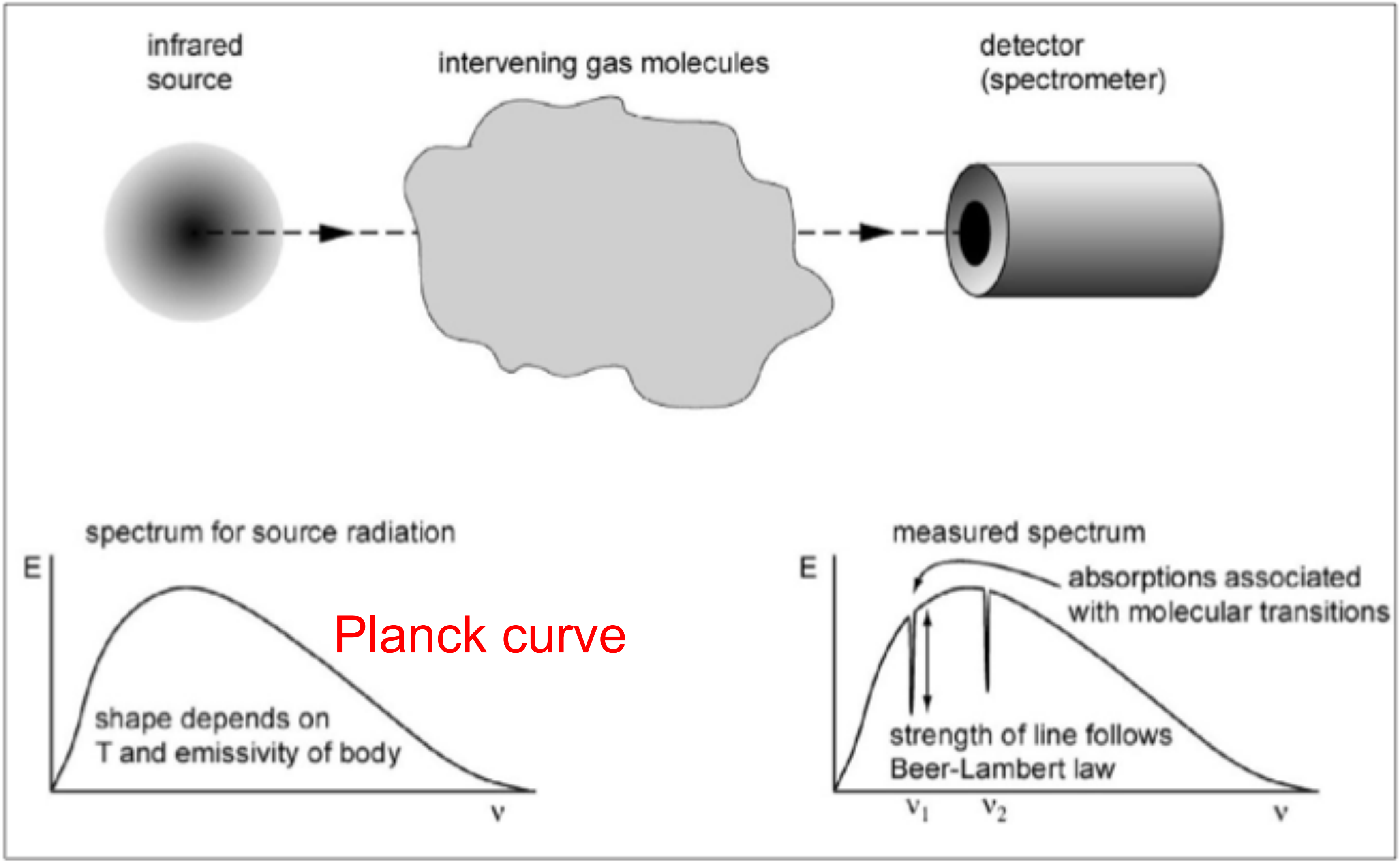
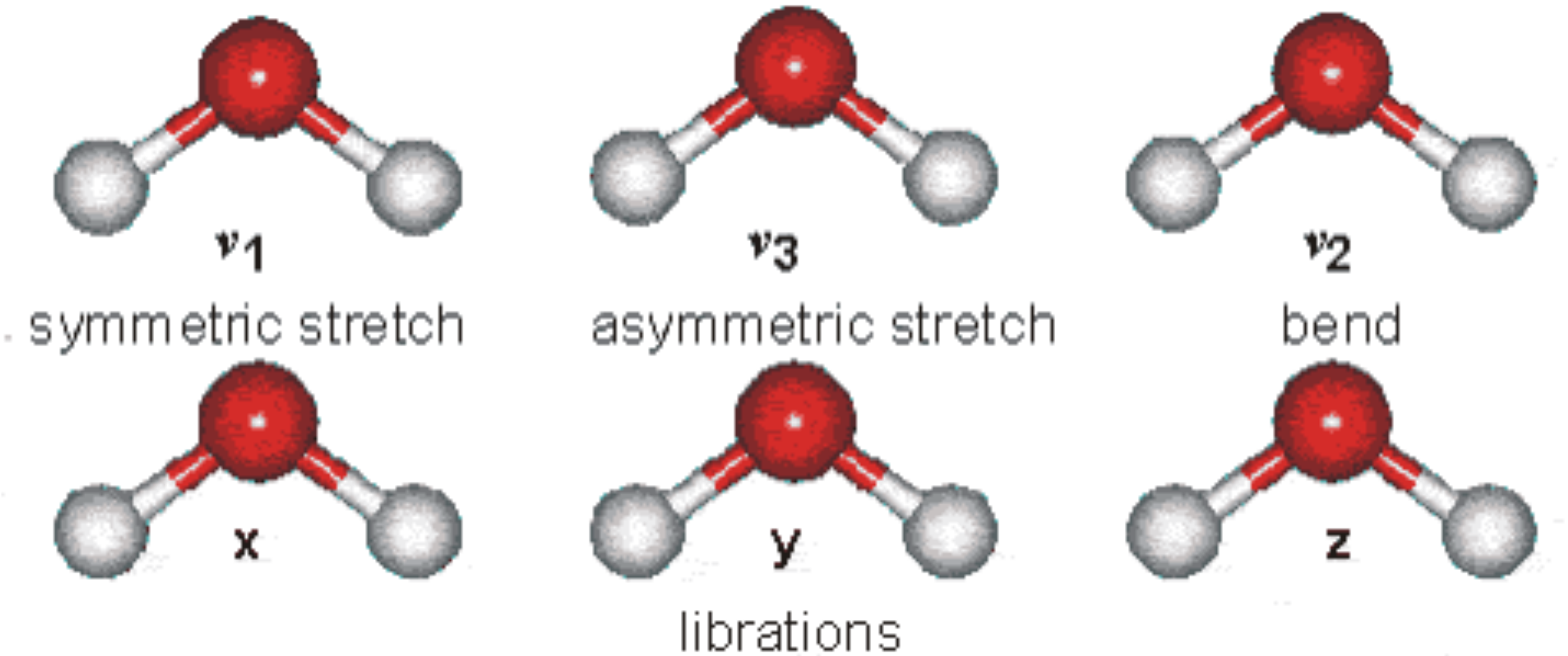
- Basis of many IR satellite remote sensing instruments
- Ground-based FTIR spectrometers also used for various applications

Absorption spectroscopy



Absorption of EM radiation



Molecular absorption processes

- Electronic transitions
  - UV and visible wavelengths
- Molecular vibrations
  - Thermal infrared wavelengths
- Molecular rotations
  - Microwave and far-IR wavelengths

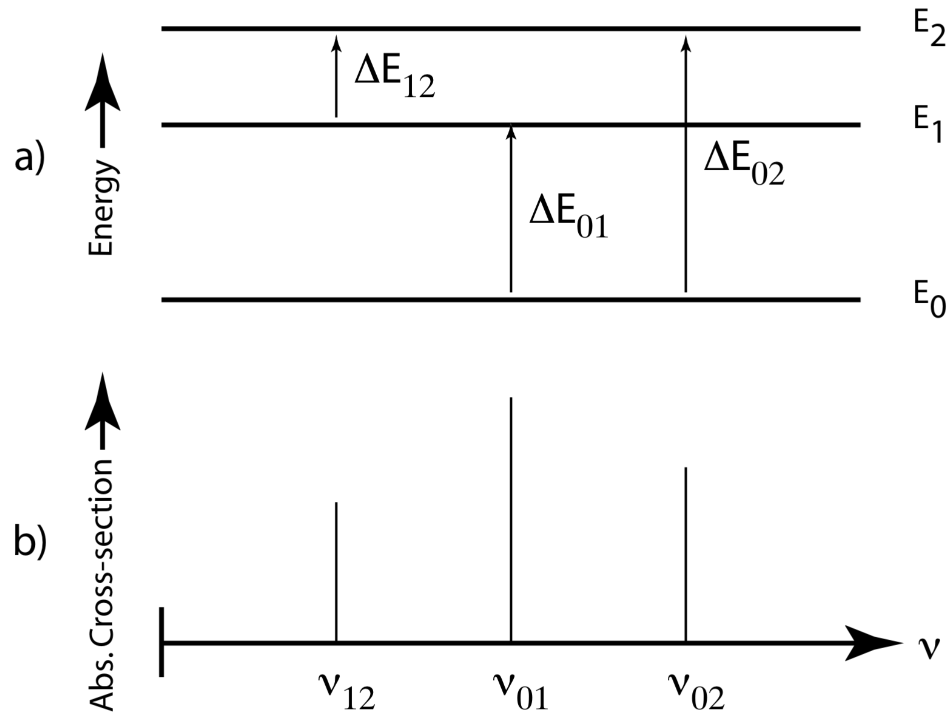
$\sim 10^{-18}$ J

Increasing energy

$\sim 10^{-23}$ J

- Each of these processes is quantized
- *Translational kinetic energy of molecules is unquantized*

Absorption spectra of molecules



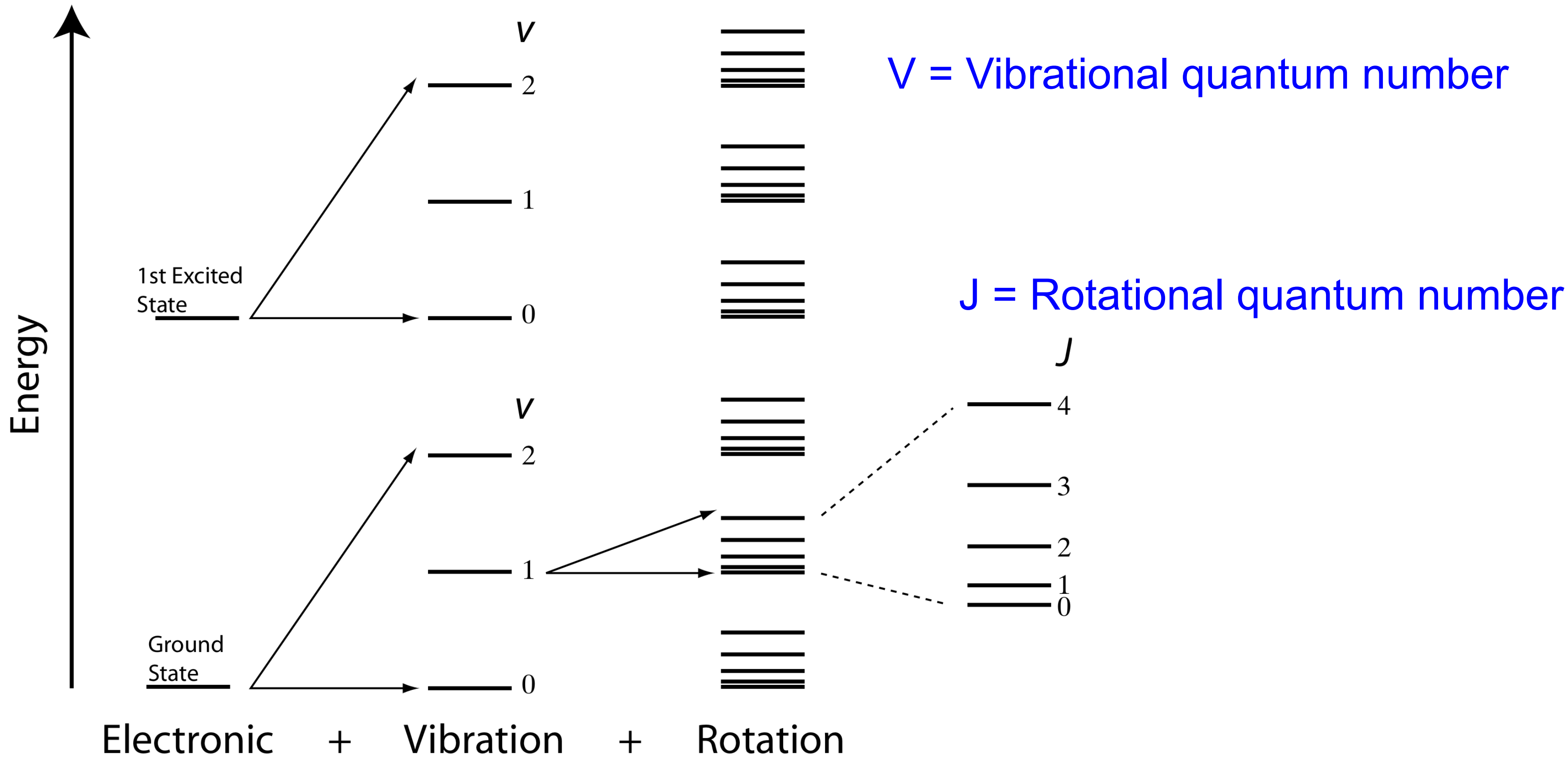
Hypothetical molecule with three allowed energy levels

$$\nu_{ij} = \Delta E_{ij}/h$$

(a) allowed transitions
(b) positions of the absorption lines in the spectrum of the molecule

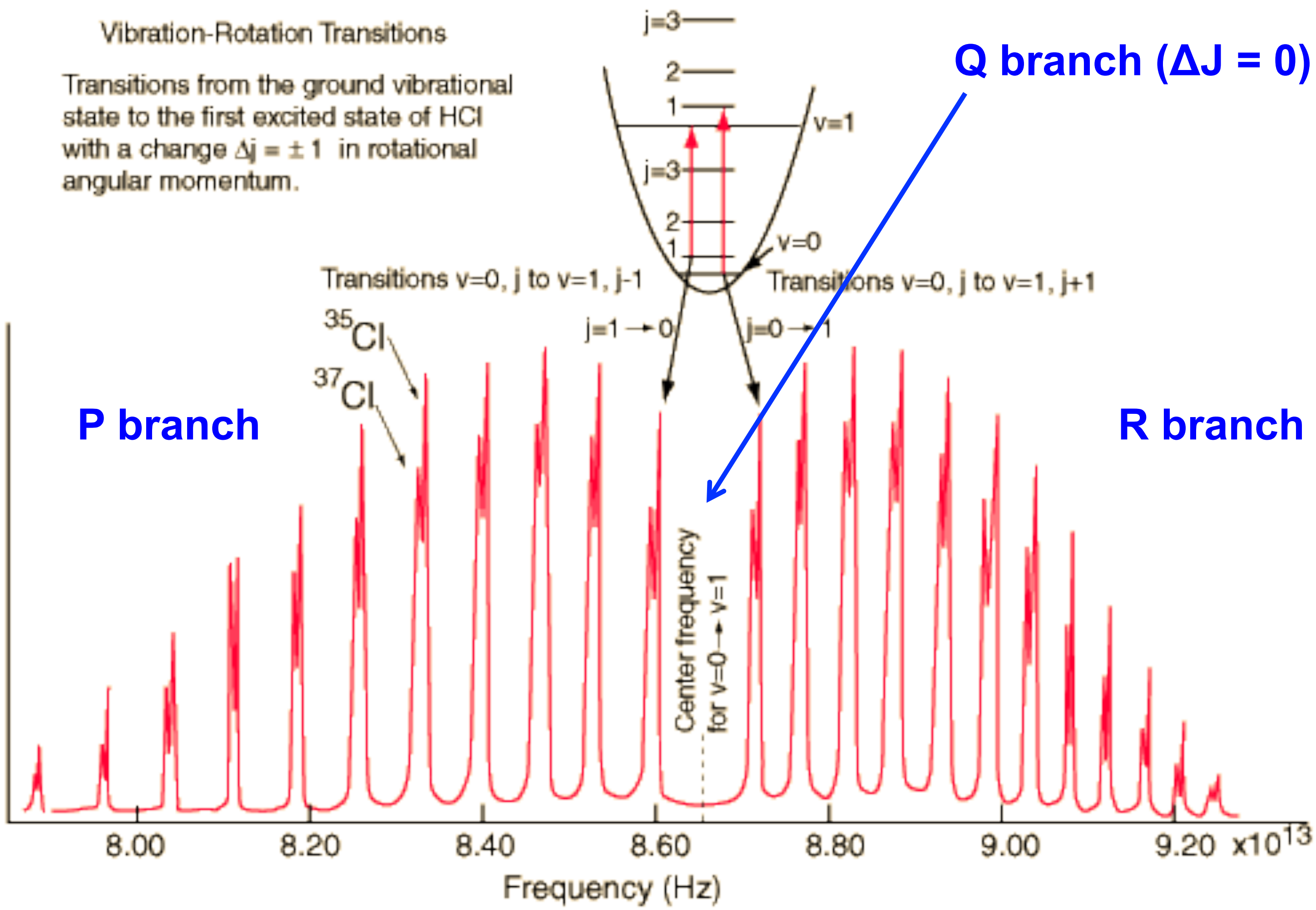
- Line positions are determined by the *energy changes of allowed transitions*
- Line strengths are determined by the *fraction of molecules that are in a particular initial state required for a transition*
- Multiple degenerate transitions with the same energy may combine

Absorption spectra of molecules



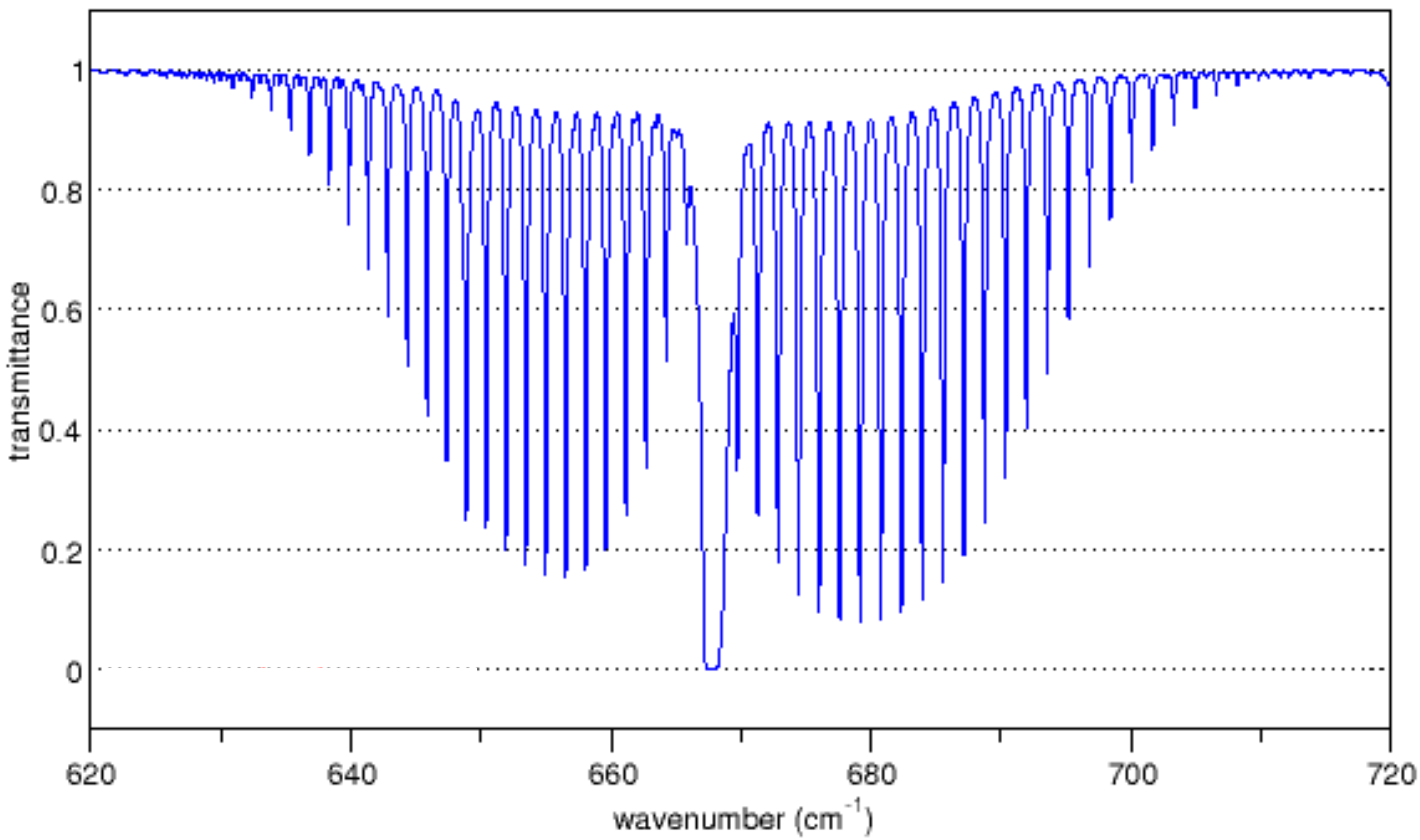
- Electronic, vibrational and rotational energy levels are superimposed
- The absorption spectrum of a molecule is determined by all allowed transitions between pairs of energy levels, and whether the molecule exhibits a sufficiently strong electric or magnetic dipole moment (permanent or otherwise) to interact with the radiation field

Hydrogen chloride (HCl) absorption lines

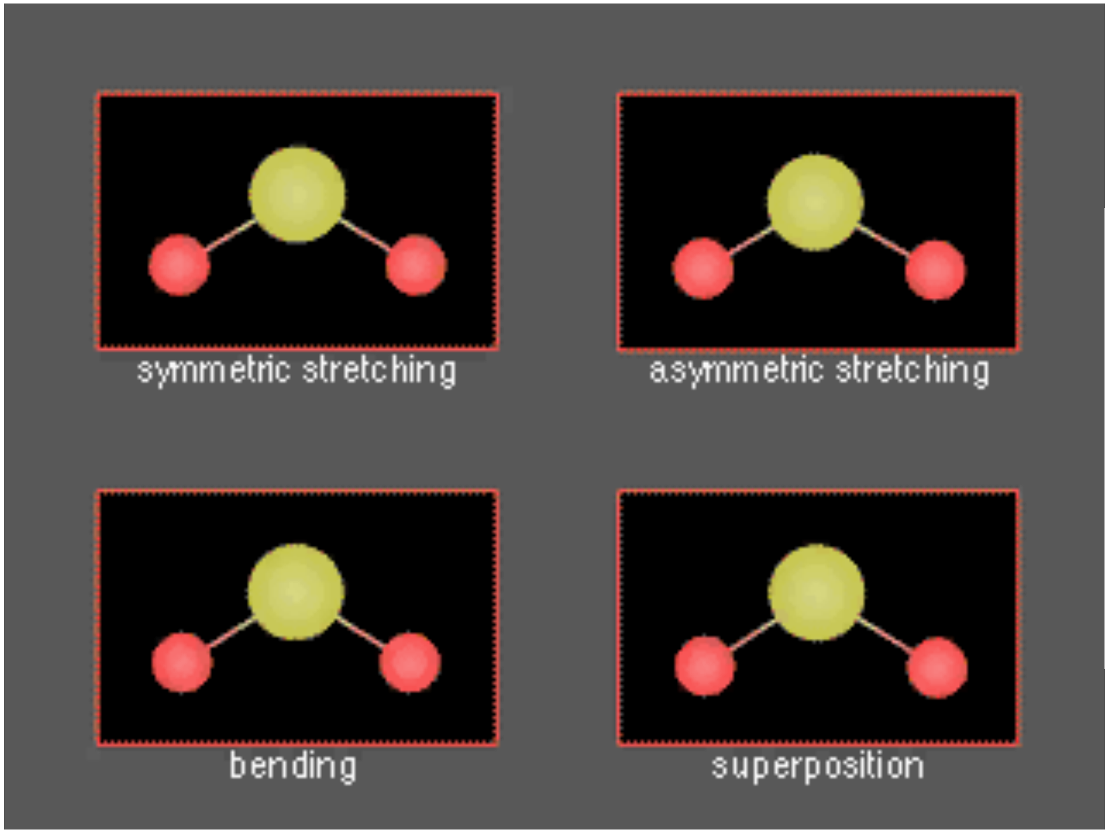


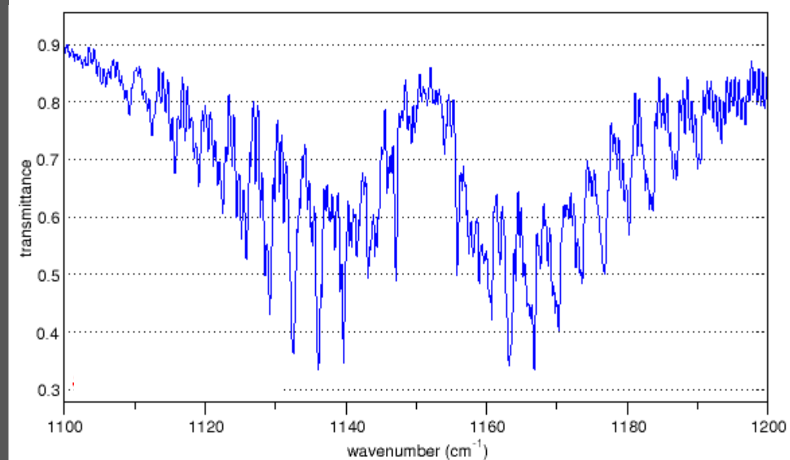
• Vibrational-rotational absorption spectrum of HCl: shows affect of two chlorine isotopes with slightly different mass

Transmittance spectrum for CO_2



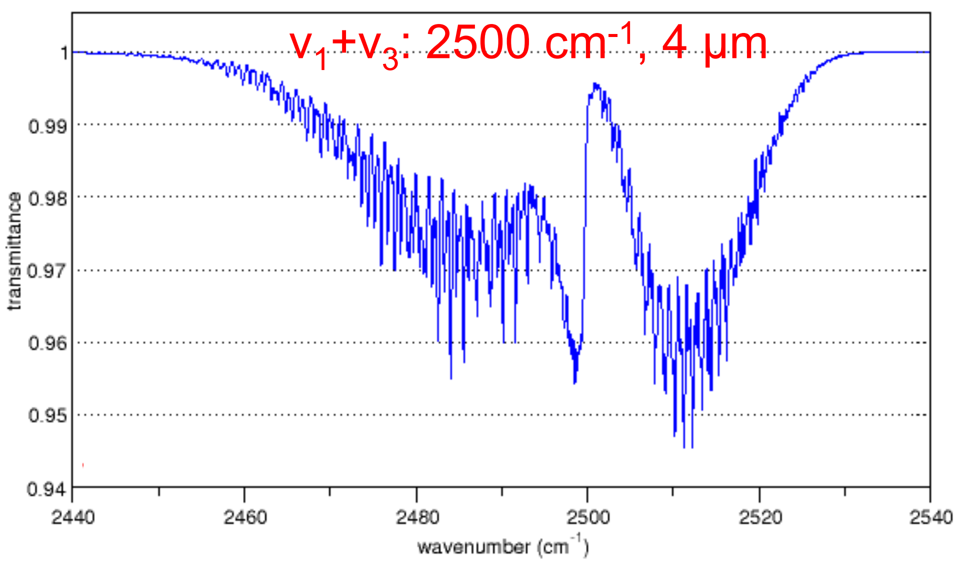
Sulfur dioxide (SO_2)

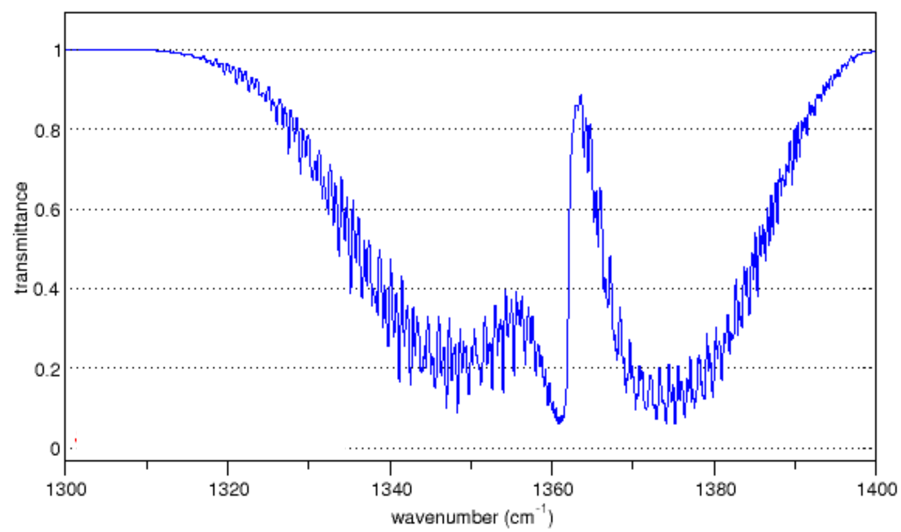




ν_1: 1151 cm^{-1}, 8.6 μm

ν_3: 1361 cm^{-1}, 7.3 μm

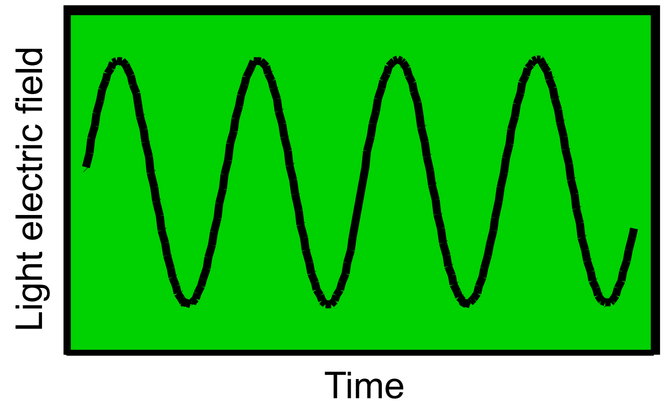


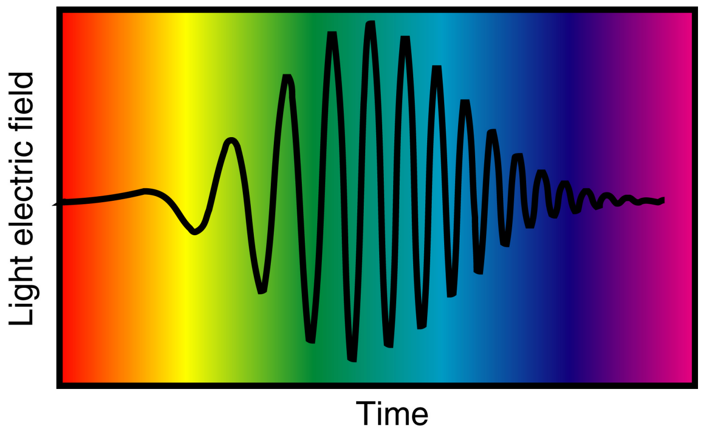


Measuring the spectrum of an EM wave

Remote sensing requires measurements of the frequencies (or wavelengths) present in an EM wave, i.e., the spectrum of the wave.

Plane waves have only one frequency, ω.





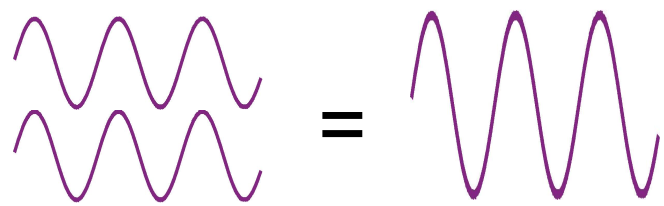
This light wave has many frequencies. And the frequency increases in time (from red to blue).

Spectra can be measured using dispersive instruments, or an interferometer. Interferometers offer a multiplex and throughput advantage.

Interference

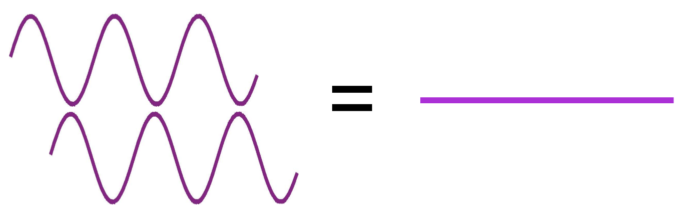
- Consequence of the wave properties of light
- Coherence required for interference: only occurs if two waves have the same frequency and polarization

Waves that combine **in phase** add up to relatively high irradiance.



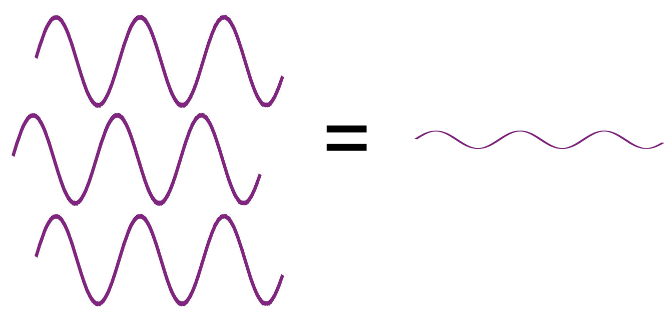
Constructive interference (**coherent**)

Waves that combine **180° out of phase** cancel out and yield zero irradiance.



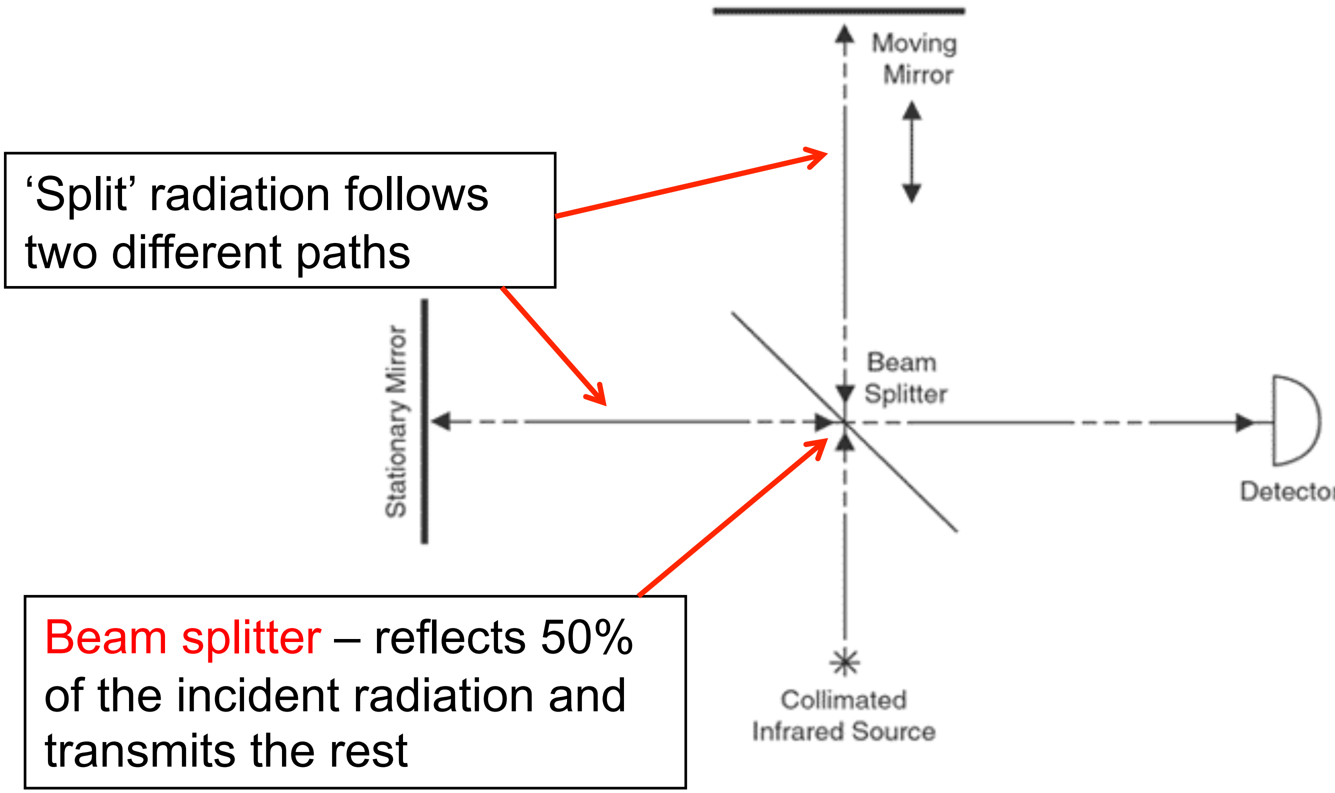
Destructive interference (**coherent**)

Waves that combine with **lots of different phases** nearly cancel out and yield very low irradiance.



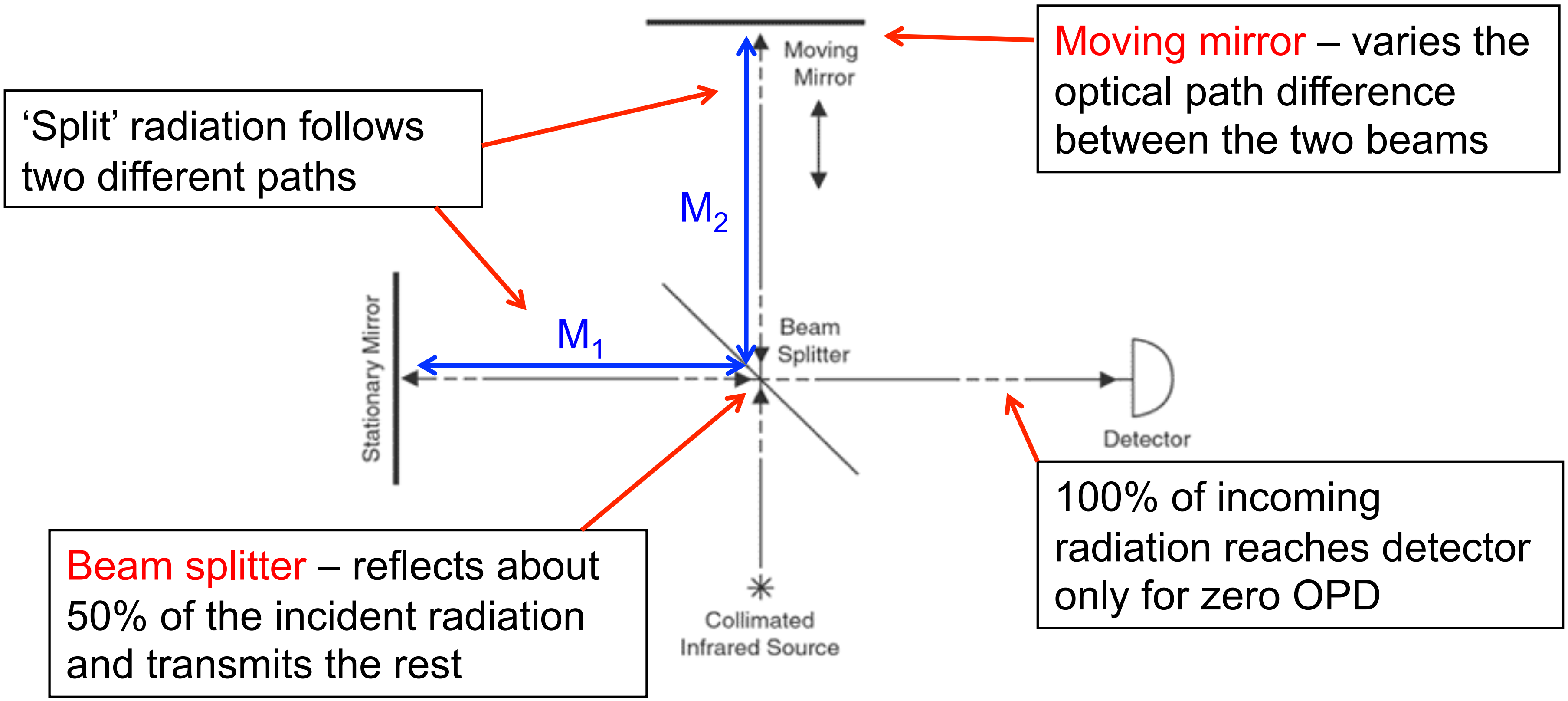
Incoherent addition

Michelson Interferometer



- A *Michelson Interferometer* (Albert Michelson, 1891) uses interference to generate a spectrum (variation of intensity with wavelength for a source of EM radiation) – *used widely in remote sensing, particularly in the infrared*
- Consists of a beam splitter, a stationary mirror and a moving mirror

Michelson Interferometer

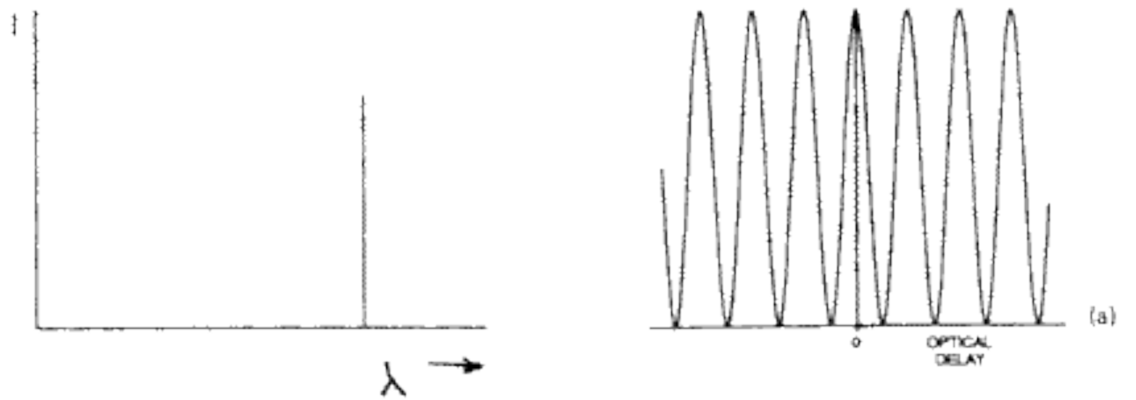


- If $M_1 = M_2$, there is no optical path difference (OPD), and hence radiation is recombined at the beam splitter *in phase* (constructive interference).
- If $M_1 \neq M_2$, radiation recombining at the beam splitter is *phase shifted* and may undergo destructive interference (depending on wavelength)

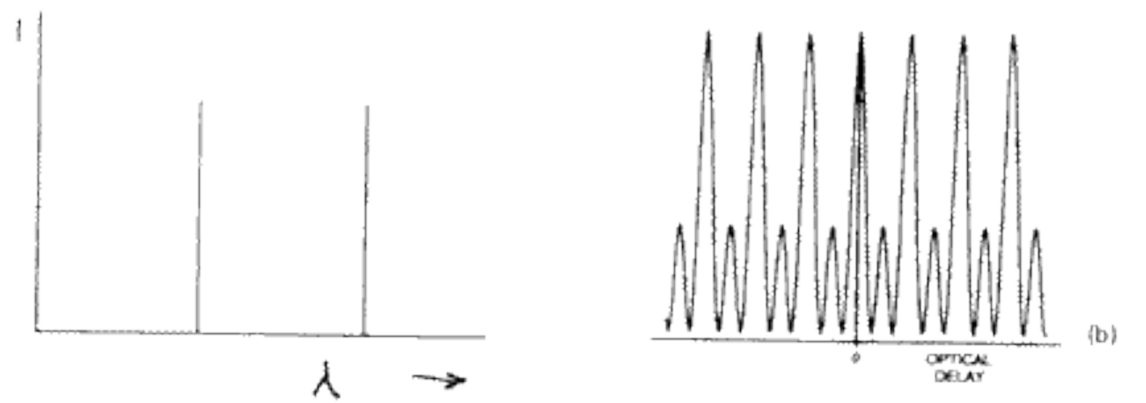
Interferometer signal

- Constructive interference: OPDs equal to integer numbers of λ
- Destructive interference: OPDs equal to integer numbers of half-λ
- OPD is measured very accurately using a laser

Single wavelength: for a mirror moving at constant velocity, the detector signal varies sinusoidally with OPD (a *cosine function* – with maxima at zero OPD and integer multiples of λ)



Two wavelengths: superposition of cosine functions for the two wavelengths



And so on for all wavelengths present in the incident radiation…

Interferograms

- The end result is an '*interferogram*'.
- An interferogram has every infrared frequency (or λ) 'encoded' in it.
- Characterized by a 'center burst' at zero OPD and a complex pattern of waves around it.

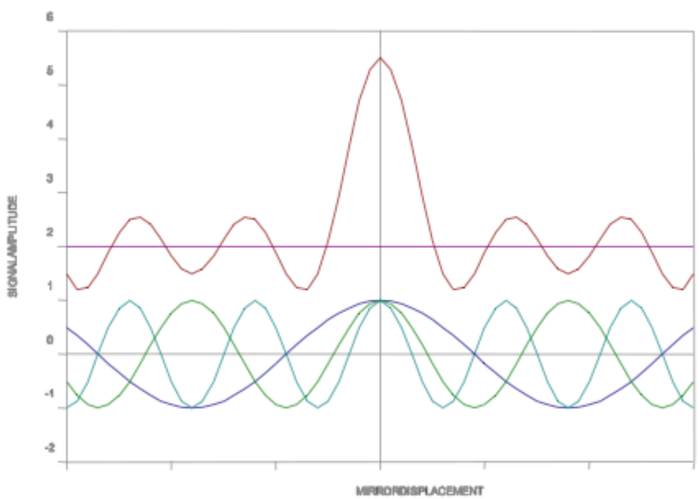
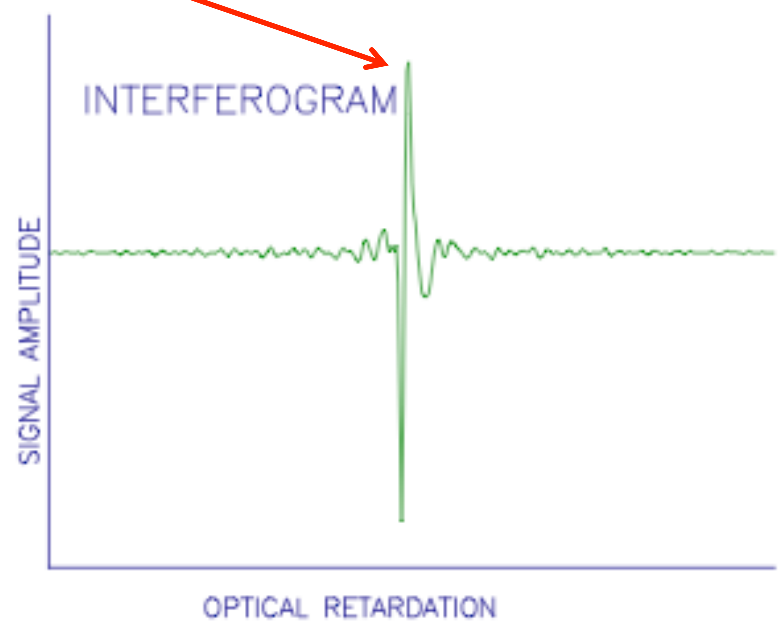


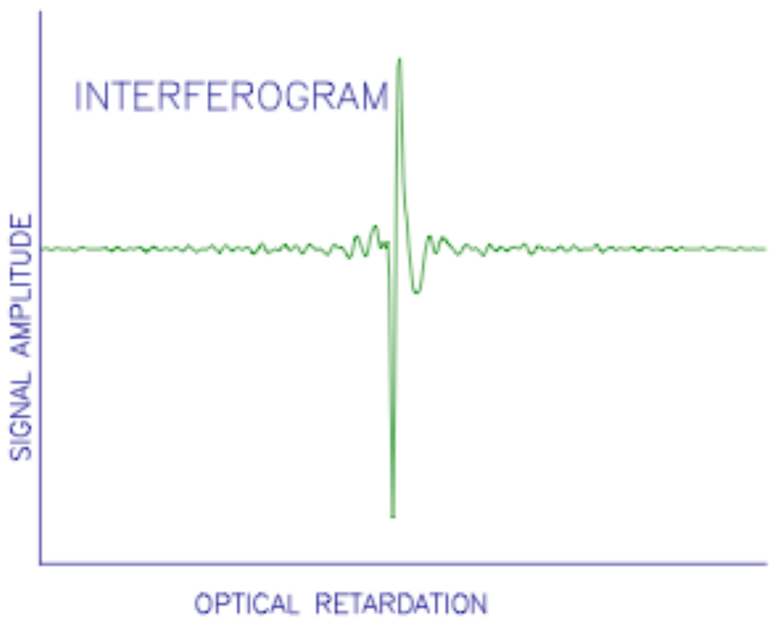
Figure 5. A simplified interferogram (offset by 2 units) from a light wave consisting of three discrete frequencies. This signal is the sum of the 3 cosine waves separately.

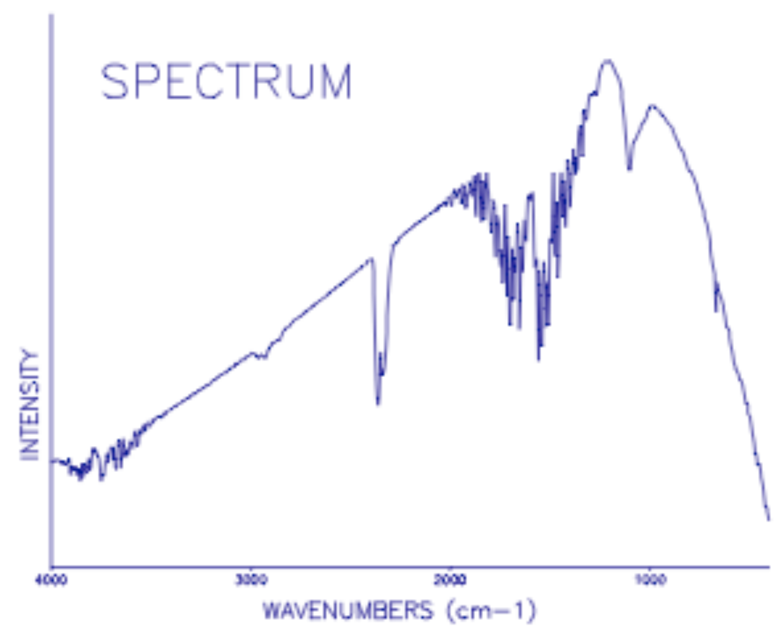


Interferograms

- The interferogram is not recognizable as a spectrum.
- The interferogram is a function of time whereas a spectrum is a function of frequency (or wavelength).
- To produce a spectrum we compute the *cosine Fourier Transform* of the interferogram – essentially a 'frequency analyzer' extracting the component frequencies from the interferogram.

Cosine Fourier Transform →





The Fourier Transform and its Inverse

The Fourier Transform and its Inverse:

$$F(\omega) = \int_{-\infty}^{\infty} f(t) \exp(-i\omega t)\, dt$$

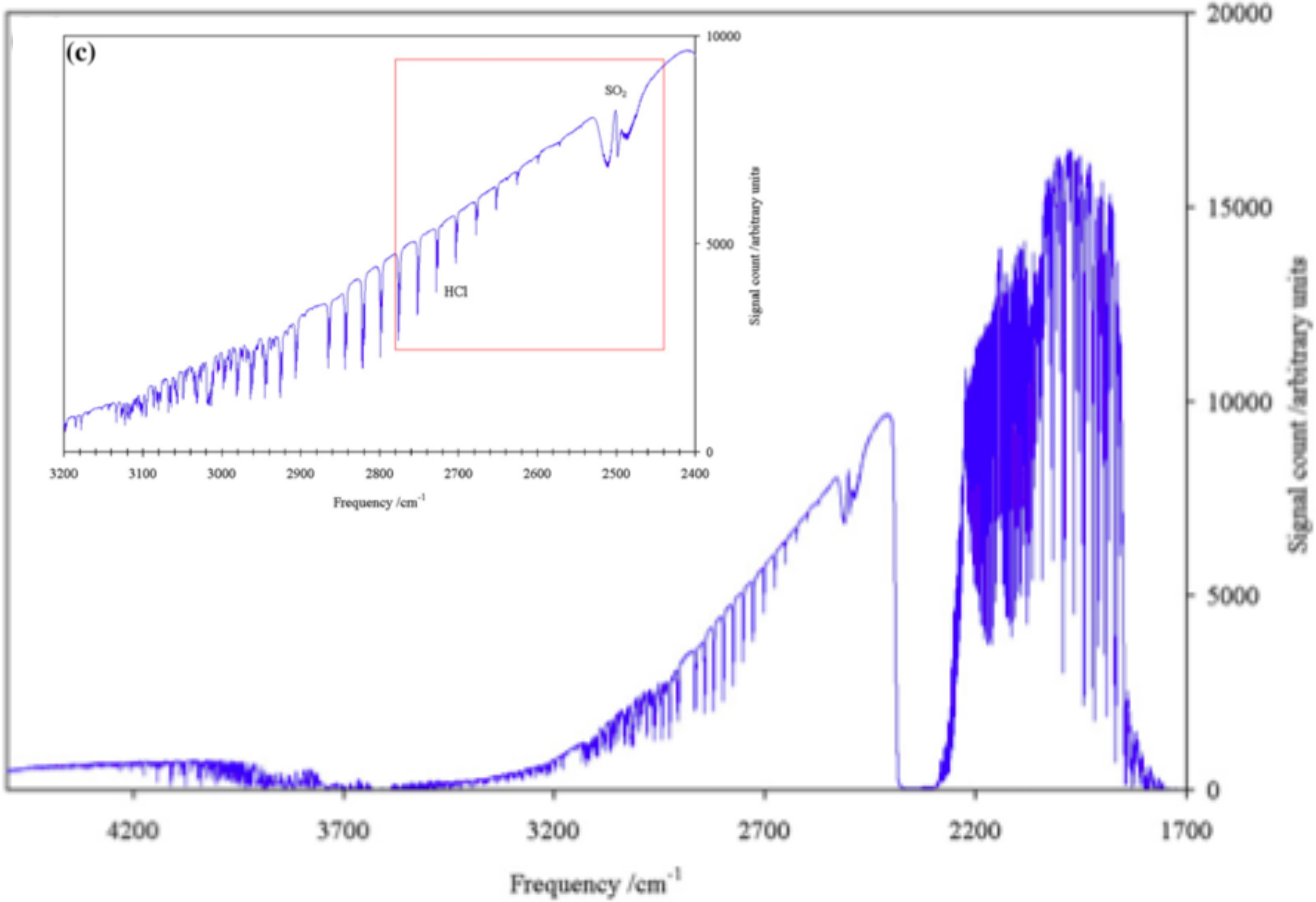
Fourier Transform

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \exp(i\omega t)\, d\omega$$

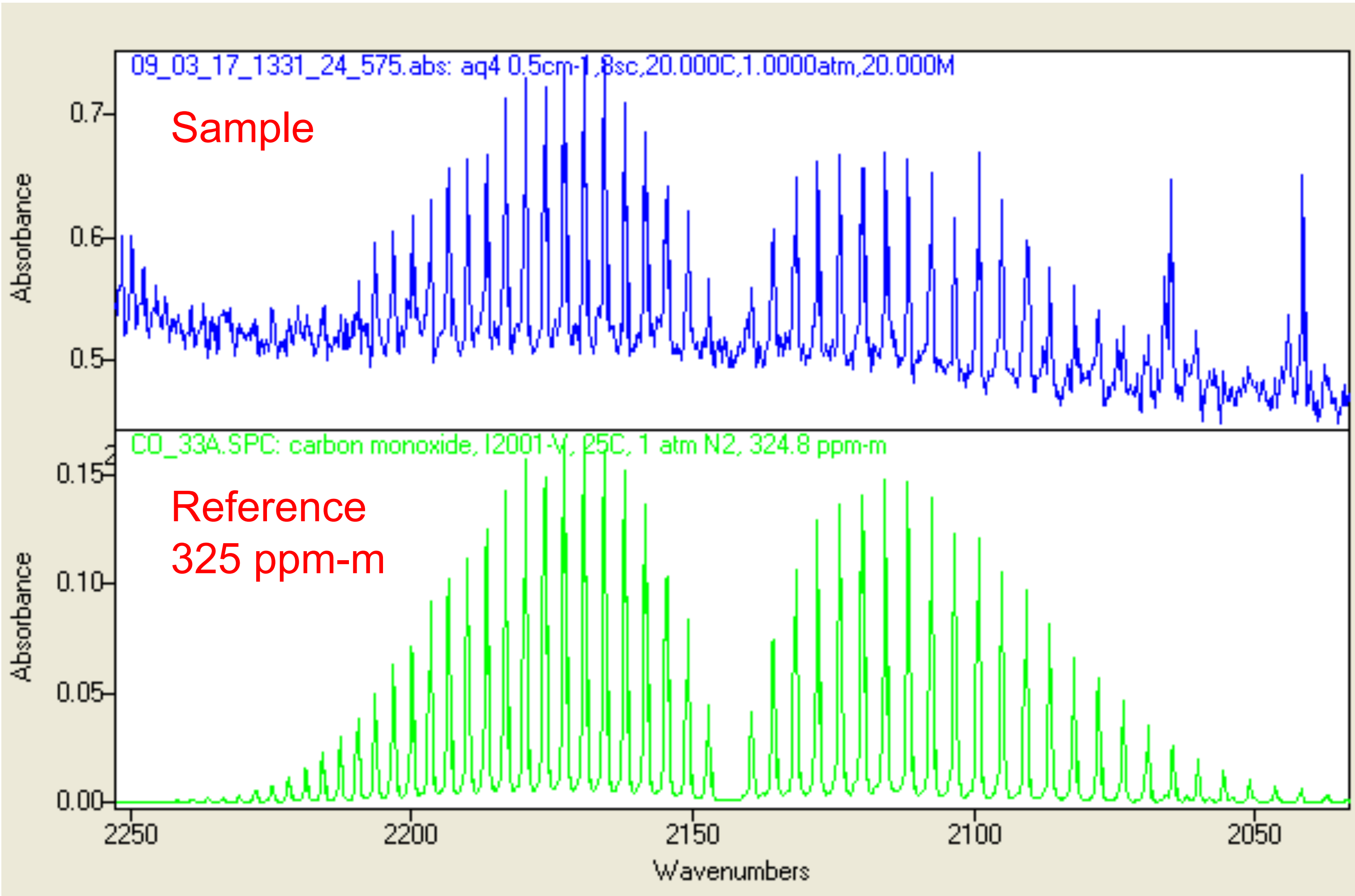
Inverse Fourier Transform

Allow transformation from the time domain (t) to the frequency domain (ω) and back.

Transmission spectrum



Absorbance spectra



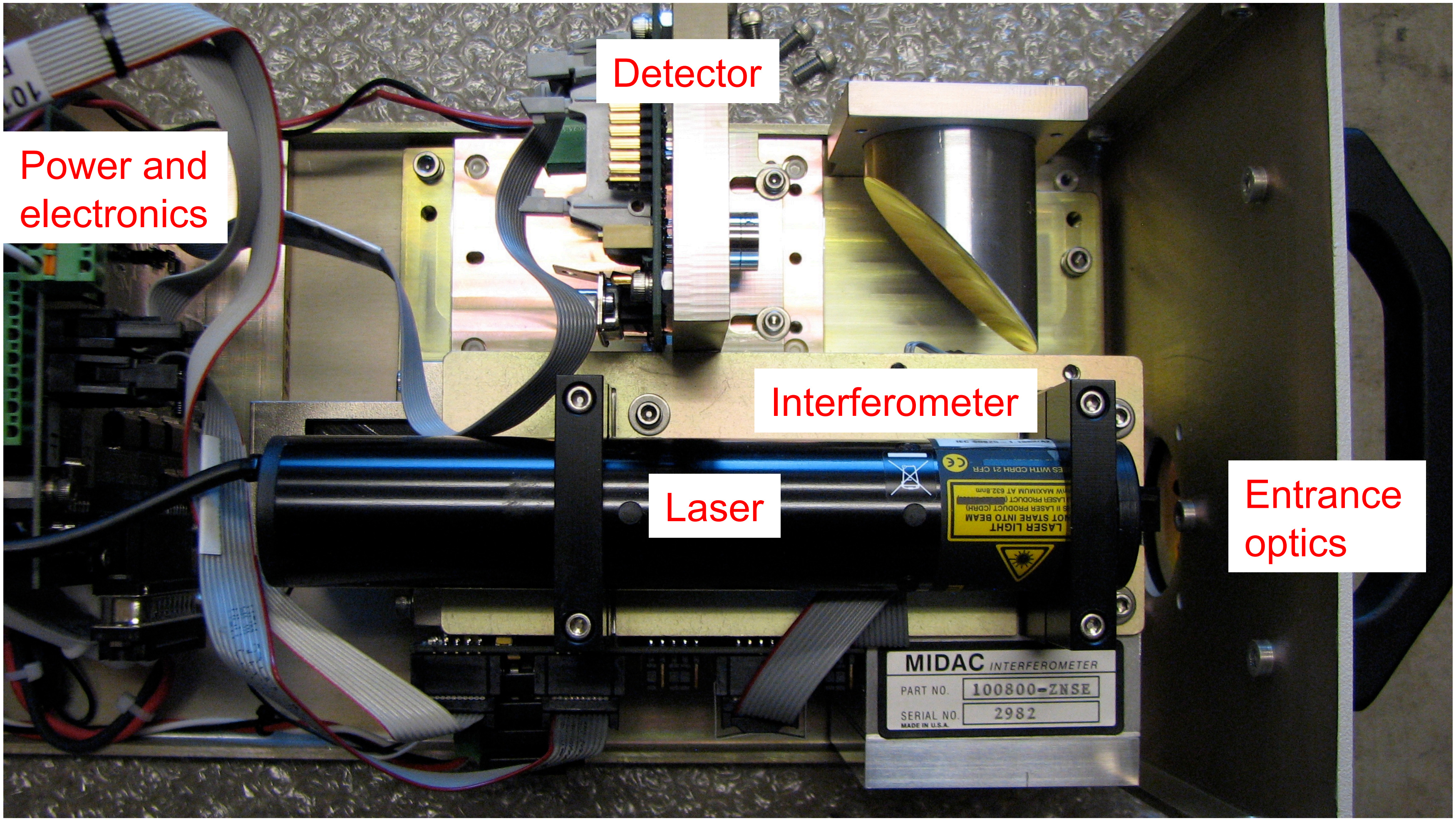
4.4 µm

4.9 µm

MIDAC FTIR components

- MIDAC M4406-S emission spectrometer, 0.5 cm^{-1} resolution
- 10” Newtonian telescope
- ZnSe (Zinc Selenide) optics and window (transmission range 0.5-22 μm)
- Gold-coated optics (improved reflectance in IR)
- Michelson interferometer
    - Maximum OPD = 2 cm (spectral resolution = 1/OPD)
- HeNe laser (λ = 633 nm) – monitors optical path difference
- Mercury-Cadmium-Telluride (MCT; HgCdTe) detector
    - Sensitive from ~2000-5000 cm^{-1} (~2-5 μm)
    - Thermoelectrically cooled (Peltier Effect)
- Indium-Antimonide (InSb) detector
    - Sensitive from ~1800-6000 cm^{-1} (~1.6-5.6 μm)
    - Liquid nitrogen cooled
- 20” IR source for active measurements

MIDAC FTIR components



FTIR deployment modes (absorption)

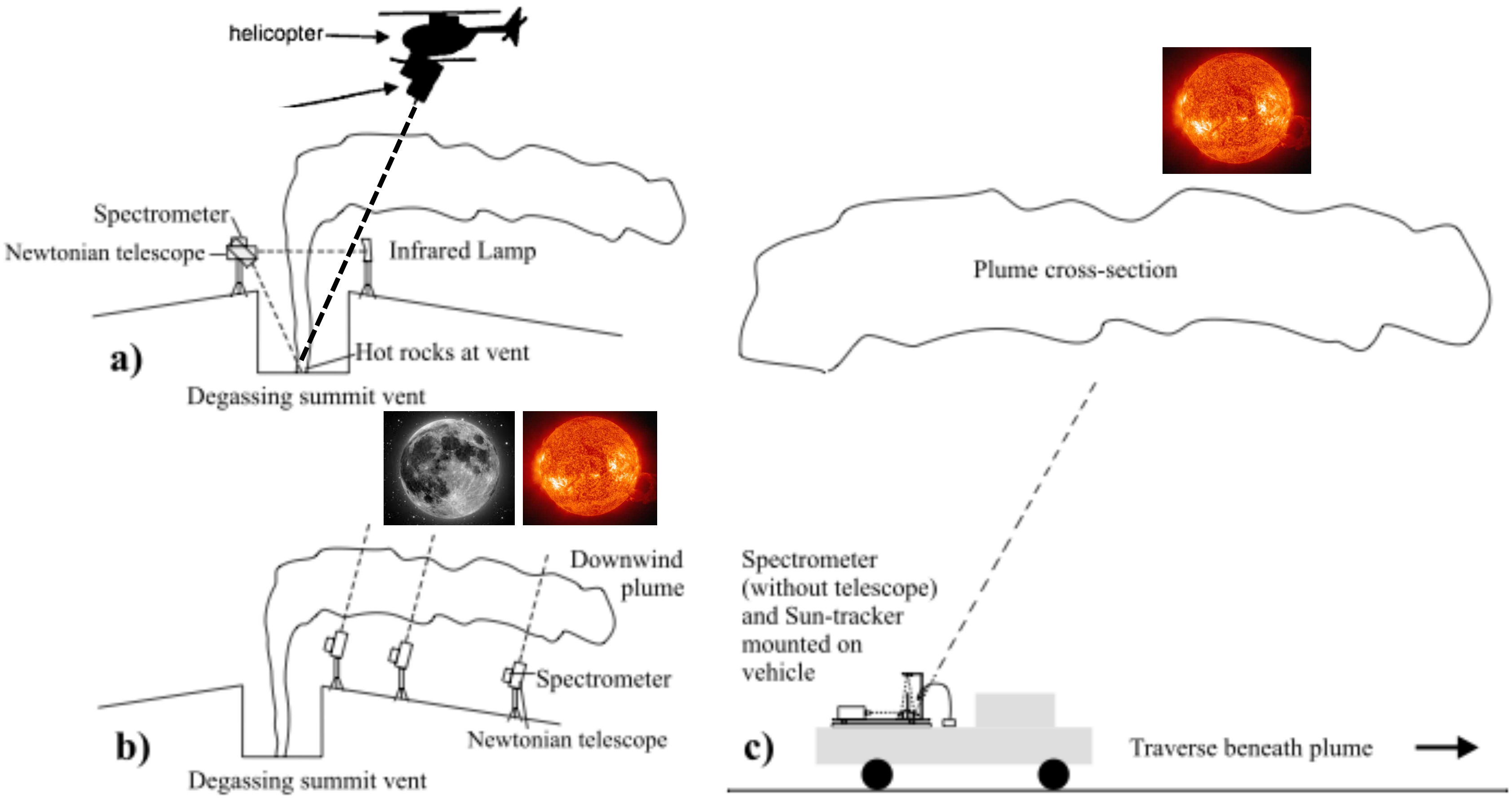


Fig. 2. Diagrams showing modes of FTS deployment. (a) and (b) are from Oppenheimer et al. (1998). (a) Infrared lamp or hot rocks used as source over a specified pathlength. (b) Sun used as infrared source. Both the lamp and Sun can be used as IR sources at the summit or at different distances downwind from the volcano. A Newtonian telescope is used to collimate the light into the spectrometer. (c) Sun used as infrared source and a Sun-tracker allows cross-sectional traverses beneath the plume. This can also be used in a fixed position instead of using the Newtonian telescope.

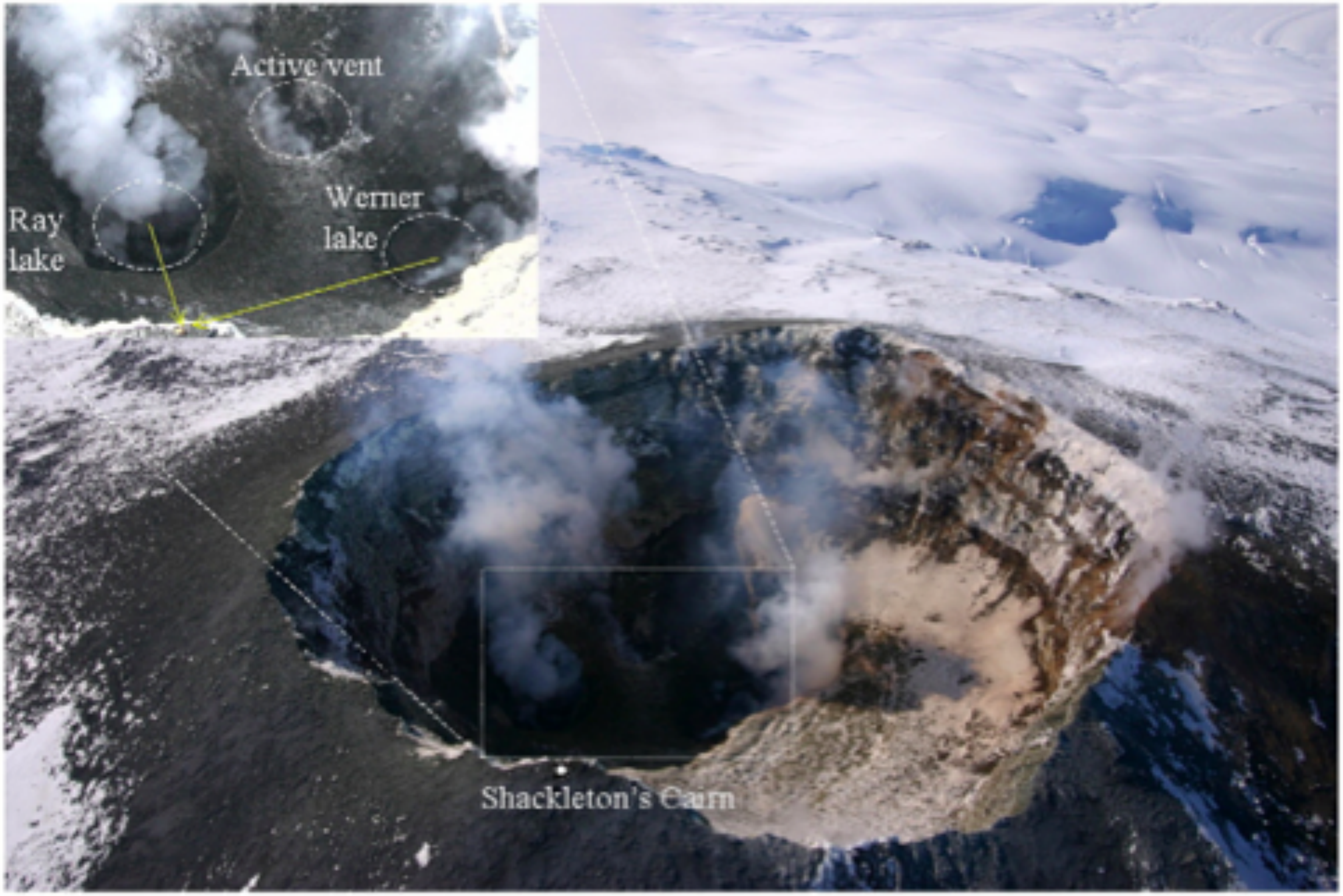

Nyiragongo, DR Congo
FTIR

FTIR at Erta ‘Ale (Ethiopia)

Fig. 2. Photograph of Erta 'Ale lava lake from the observation site on the north eastern rim of the central pit. The black circle approximates the 1.5 m 'footprint' of the FTIR spectrometer.

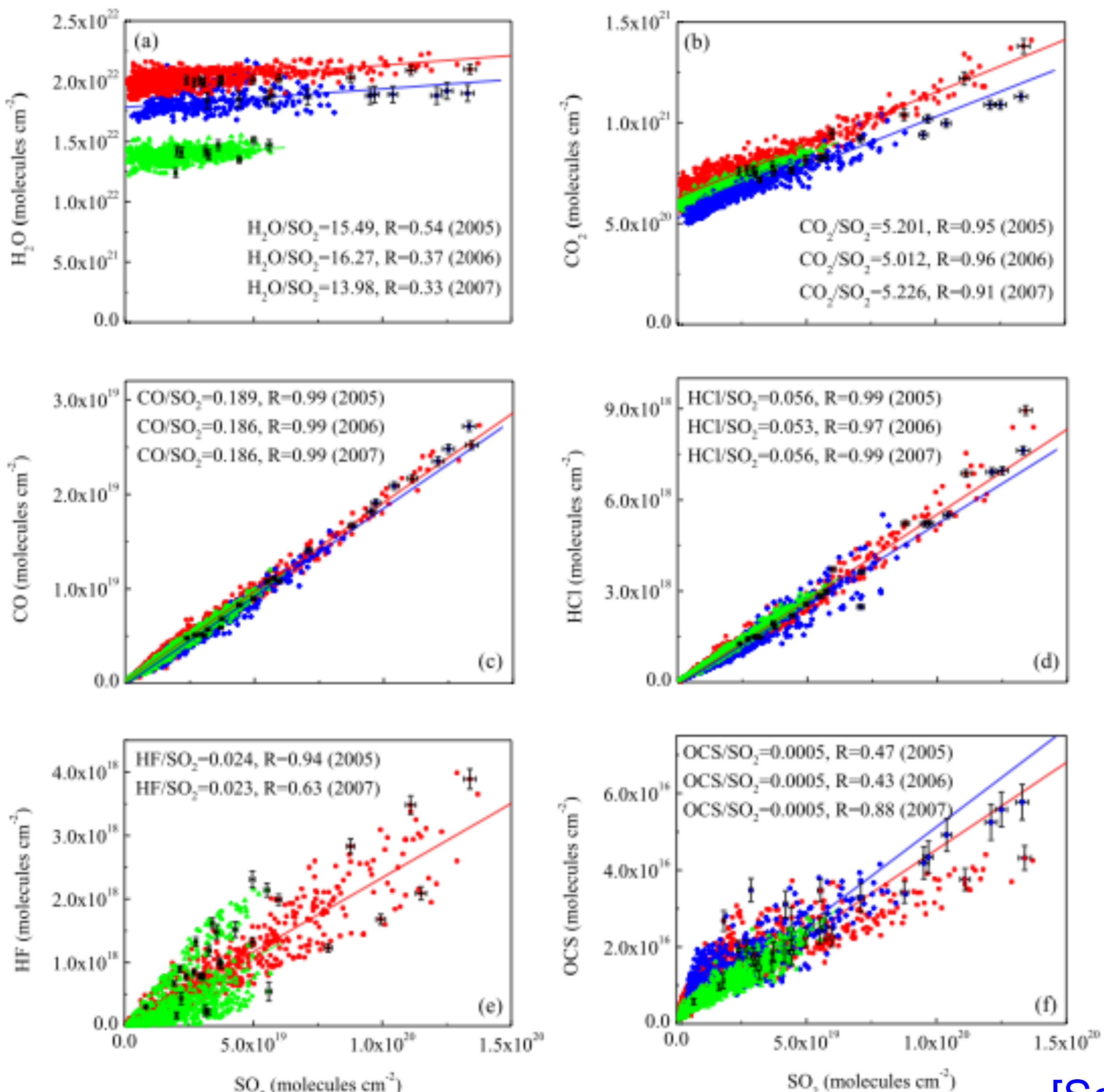
[Sawyer et al., 2008]

FTIR at Erebus (Antarctica)



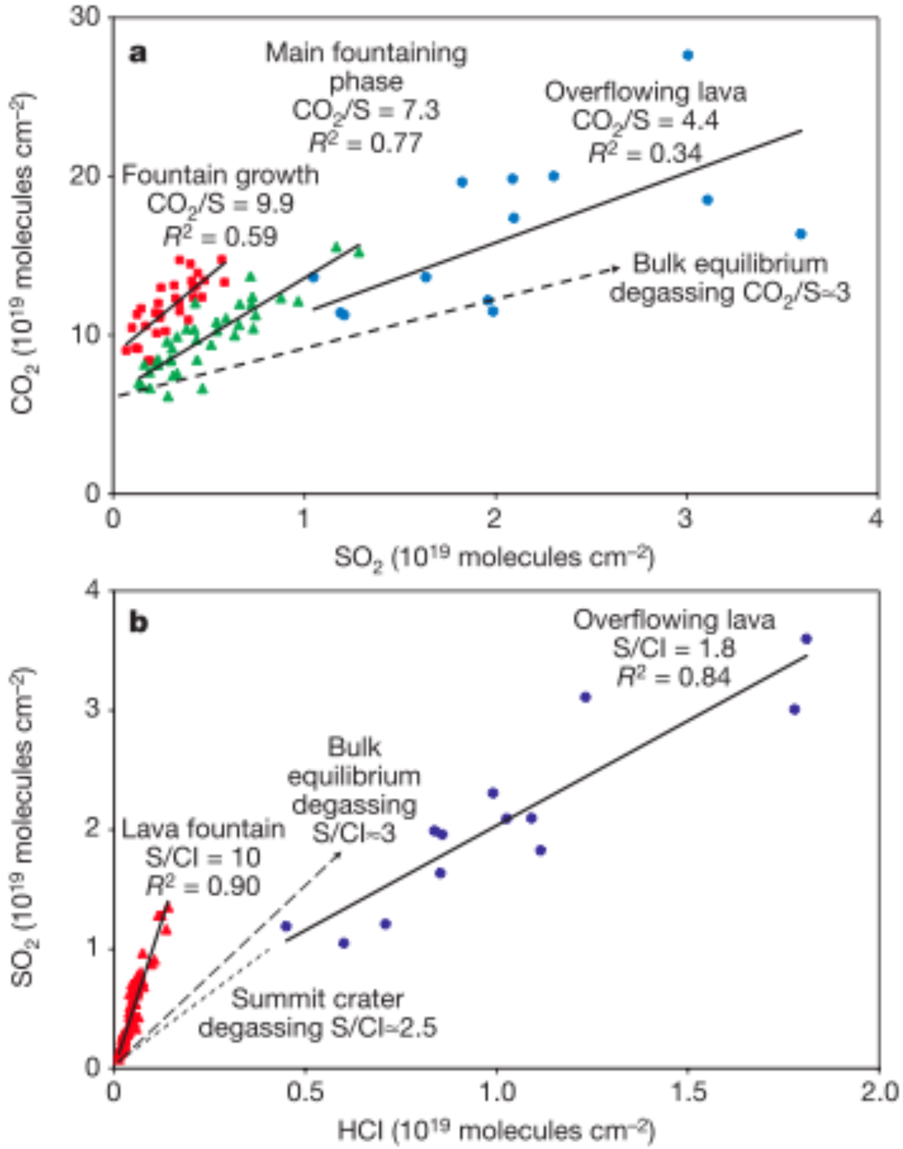
[Oppenheimer et al., 2008]

Gas ratios at Nyiragongo, 2005-2007



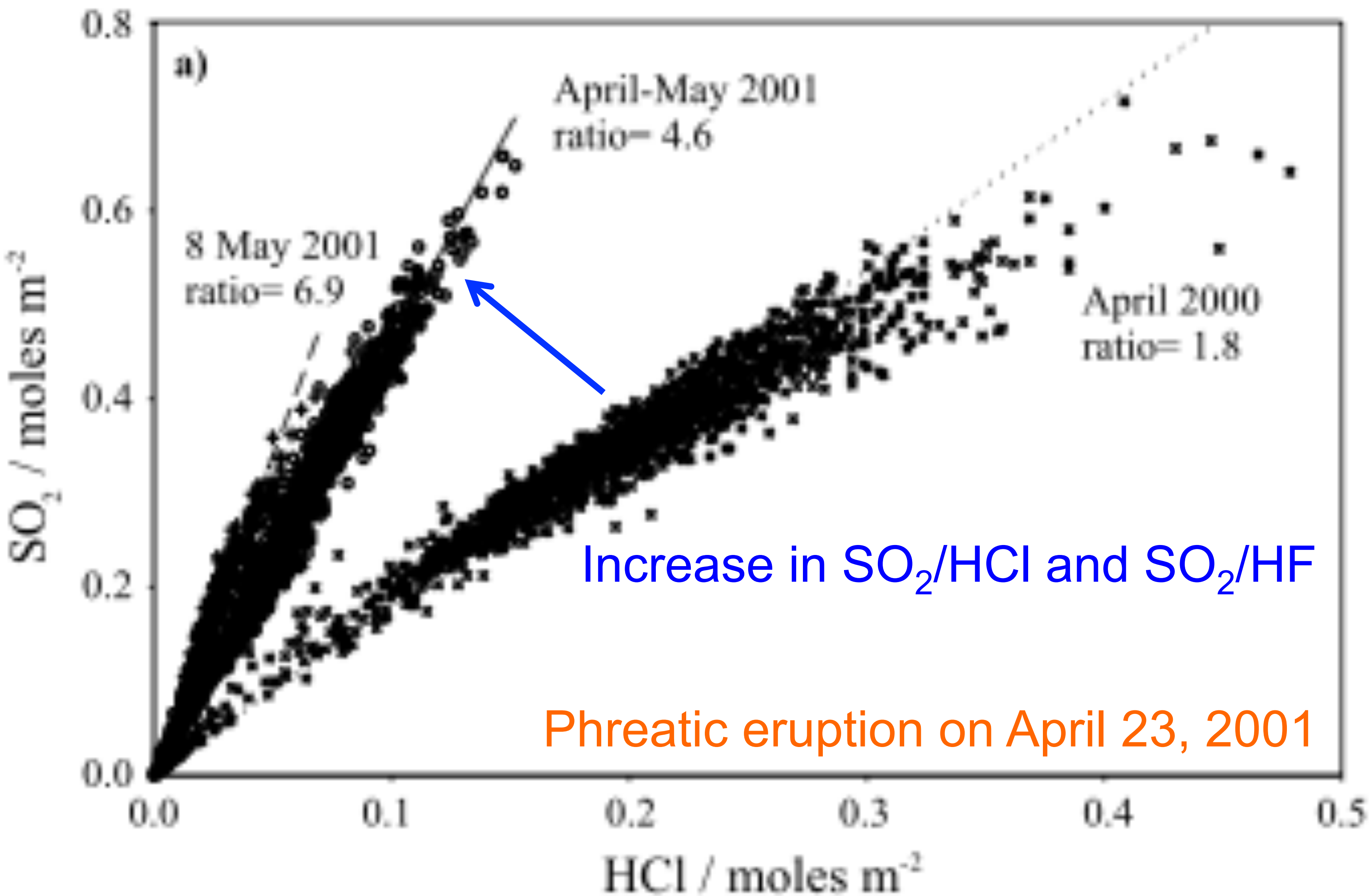
[Sawyer et al., 2008]

Gas ratios at Etna



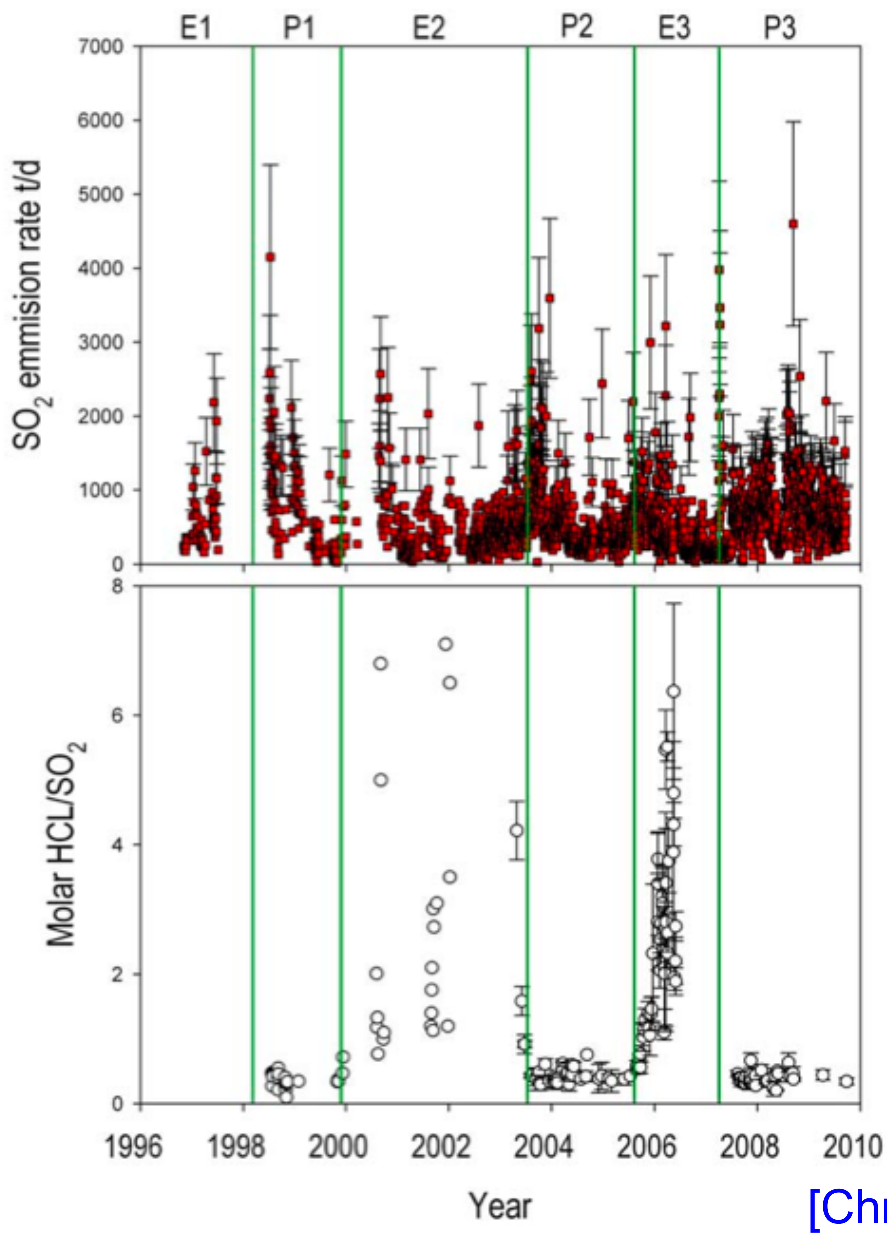
[Allard et al., 2005]

Change in gas ratios prior to eruption at Masaya



[Duffell et al., 2003]

Dome growth and HCl/SO_2 at Soufriére Hills volcano



E = lava effusion
P = pause

[Christopher et al., GRL, 2010]

Nocturnal volcanic plume studies

SO_2/HCl (night) = 2.2±0.28 (±1σ). SO_2/HCl (day) = 1.6±0.02 (±1σ).

[Burton et al., 2001]