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ELTECdata #138

Computing the Relationship of Pyroelectric Detector Output to Gas Concentration

We are often asked what the relationship is between the changes in detector output and the gas concentration. The question is simple but the answer is complex. Here is an attempt to quantify the situation.

BEER'S LAW

$$A = \text{Absorbance} = \log_{10} \frac{I_o}{I_t} = \log_{10} \frac{1}{T}$$

Absorbance = optical density = OD

$$T = \text{transmittance} = \frac{I_t}{I_o}$$

Percent transmittance = 100T

Where I_o = ingoing optical intensity (original intensity)
 I_t = transmitted intensity

But A is directly proportional to the concentration of the gas and the pathlength through the gas. Thus,

$$A = \epsilon c L$$

Where ϵ = the extinction coefficient in liters mole⁻¹ cm⁻¹ (M⁻¹cm⁻¹) (molar absorptivity)
L = pathlength in centimeters (cm)
c = concentration in moles liter⁻¹ (M)

1 mole is the gram formula or gram formula weight

1 mole has 6.022 x 10²³ molecules, which is Avogadro's number

1 mole of a gas occupies approximately 22.4 liters (1,000 cc is 1 liter) at STP ((standard pressure and temperature, which are 0°C (273K) and 760 mm Hg (1 atmosphere))

BOUGUER-LAMBERT LAW

There is another approach called the Bouguer-Lambert Law. Here one envisions the optical radiation passing through an infinitely thin layer (dx) of absorptive "material" and thus loses some energy (-dl).

The "loss" is proportional to the initial energy (I_o), the thickness (dx), and some proportionality constant called the absorptivity (a). Thus,

$$-dl = I_o a dx \quad \text{or} \quad \frac{dl}{I_o} = -l dx$$

which integrates to $\ln \frac{I_T}{I_o} = -ax$

which becomes the very familiar form $\frac{I_T}{I_o} = e^{-ax}$

And since transmittance (T) is the ratio of I_T/I_o, then T = e^{-ax}

In Beer's Law we had two coefficients (ϵ and c) prefixing the thickness (l) and now we have only one. This can be valid only by making the concentration 100%. To do this we gather all the absorbent gas in our pathlength into a pure column of gas

and that column has a length of x. Thus the pathlength (l) of Beer's Law is NOT the thickness (x) of the Bouguer-Lambert Law and the direct proportionality has become the Law of Growth or as Lord Kelvin called it, the Compound Interest Law.

ABSORPTANCE $1 - T = 1 - e^{-ax}$ (note: Absorptance is not Absorbance)

Note: Reflectance is not taken into account when the above is used for solids and liquids, remember that only internal transmittance is considered.

For a gas, 1/22.4 mole per liter converts to a million ppm because concentration is 100%.

To convert from mole-based numbers to atm.cm (atmospheric centimeters, the "length" of a column of gas referenced to 1 cm of pure gas at STP per square centimeter - a unit commonly used in atmospheric transmission studies), use the following:

$$1 \text{ atm.cm} = \frac{\text{molecular.weight grams/sq.cm}}{2.24 \times 10^4}$$

Note that in the above system, since water is not a gas it is expressed as "pr cm" (precipitable centimeters) which equates to 3.34×10^{22} molecules/cm².

ABSORPTION and the PYROELECTRIC DETECTOR

The output of the pyroelectric detector is linear with respect to absorbed optical power. Thus, if there is no out-of-band radiation, the peak-to-peak detector output (from modulated or pulsed source) is directly proportional to A which is the common base (base-10 or Briggsian) logarithm of the ratio of the initial optical radiation level to that of the transmitted optical radiation. Or, to the log of the detector output with no absorbing gas in the chamber to that of the output with x moles of absorbing gas in the chamber. If the optical filter on the detector is broader than the absorbing gas bandwidth (in micrometers or reciprocal centimeters), our original equation becomes

$$A = \log \frac{V_i}{V_g + V_{\text{extra}}}$$

where V_i = detector voltage output under initial conditions (no gas in chamber)
 V_g = that part of the detector output directly attributable to gas transmission (the voltage corresponding to the in-band radiative power minus the power absorbed by the gas)
 V_{extra} = detector output from out-of-band radiation

V_{extra} = (after manipulating the equation) becomes

$$V_{\text{extra}} = \frac{V_i}{10^A} - V_g$$

And now we face the problem of somehow factoring out this extraneous signal.

It would seem that with 100% gas concentration and a long pathlength that one would reach a point where increasing the pathlength no longer made a difference in detector output. That point could be considered total absorption and the remaining voltage would be the "extra" or an offset that could be subtracted from the signal. (Of course this assumes perfectly parallel light rays from the source and no trace of aerosol to scatter light).

But:

An examination of a high resolution spectrogram clearly shows that our absorption band is not a neat step function, but a myriad of absorption peaks and valleys. See the detailed carbon monoxide spectrogram (attached) from Harris & Bertolucci, Symmetry & Spectroscopy, 1989/1978, Dover, page 122.

Thus our absorption band is, at best, an integral through an interval which is x% absorptive and 100% - x% transmissive. And the V_{extra} is some combination of out-of-band radiation, secondary radiation (which may be from 0 to 180 degrees out-of-phase), light leakage and transmission through the actual (alleged?) absorption band.

All of which is not to deny computability, but to caution against reliance on simplistic approaches. Use whatever data is available and obtain a detailed spectrum to better estimate the best bandpass and at least a rough estimate of bandpass transmission. The better your computational predictions, the better will be your ability to discern and identify problems.

See the absorption and spectral data on methane from pages 5-81 and 5-93 of The Infrared Handbook as examples of helpful information.

Note: Considering the time and expense of your development effort, you may wish to investigate the USF HITRAN-PC program for prediction of absorption. HITRAN-PC is distributed by Ontar Corporation: Phone (508) 689-9622; Fax (508) 681-4585.

ABSORBANCE and EXTINCTION COEFFICIENT calculations

1. Go to NIST Chemistry WeBook (<http://webbook.nist.gov/chemistry/>) and get to the infrared transmission scan for the gas of interest.
2. Change the ordinate (y-axis) to ABSORBANCE.
3. Use left-click to blow up section of scan of interest. (Note that 10,000 divided by Wavenumber equals micrometers).
4. "Save" or somehow capture this modified scan so you can print it out.
5. Choose appropriate strong absorbance band and then shop-around until you find an interference filter (bandpass) that is available and close to what you would really like.
6. The Half Power Bandwidth of the filter is "x" to "y" micrometers. The actual significant absorption of the gas within band may only be "x + a" to "x to b" or the filter may be sufficiently narrow so that the band is full. Estimate the mean weighted average absorption of the band within the filter band. This is your absorbance - perhaps 0.02 to 0.8 or even 3. (If the gas absorption band doesn't fill the filter band, the "open" part of the filter will act like an "offset").
7. Take the molecular weight of the gas in grams (e.g. for CO₂ it is 44). Divide by 22.4 liters. This is 100% concentration expressed as moles per liter.
8. Thus in the formula $A = \epsilon c L$, you now have "A" from step 6 and "c" from step 7. For "L", use 1.
9. Now solve for the extinction coefficient "e".
10. From this point on keep "e" as calculated in step 9. Take whatever percent of "c" in step 7 that is of interest in your application. Use 1 centimeter and see what you get for Absorbance. If you get something like 0.003, you're going to get an extremely small signal - unless you have a white-hot ingot of steel as an infrared source.
11. Point of information: Very, very few people ever go through these computations - even if they have problems.

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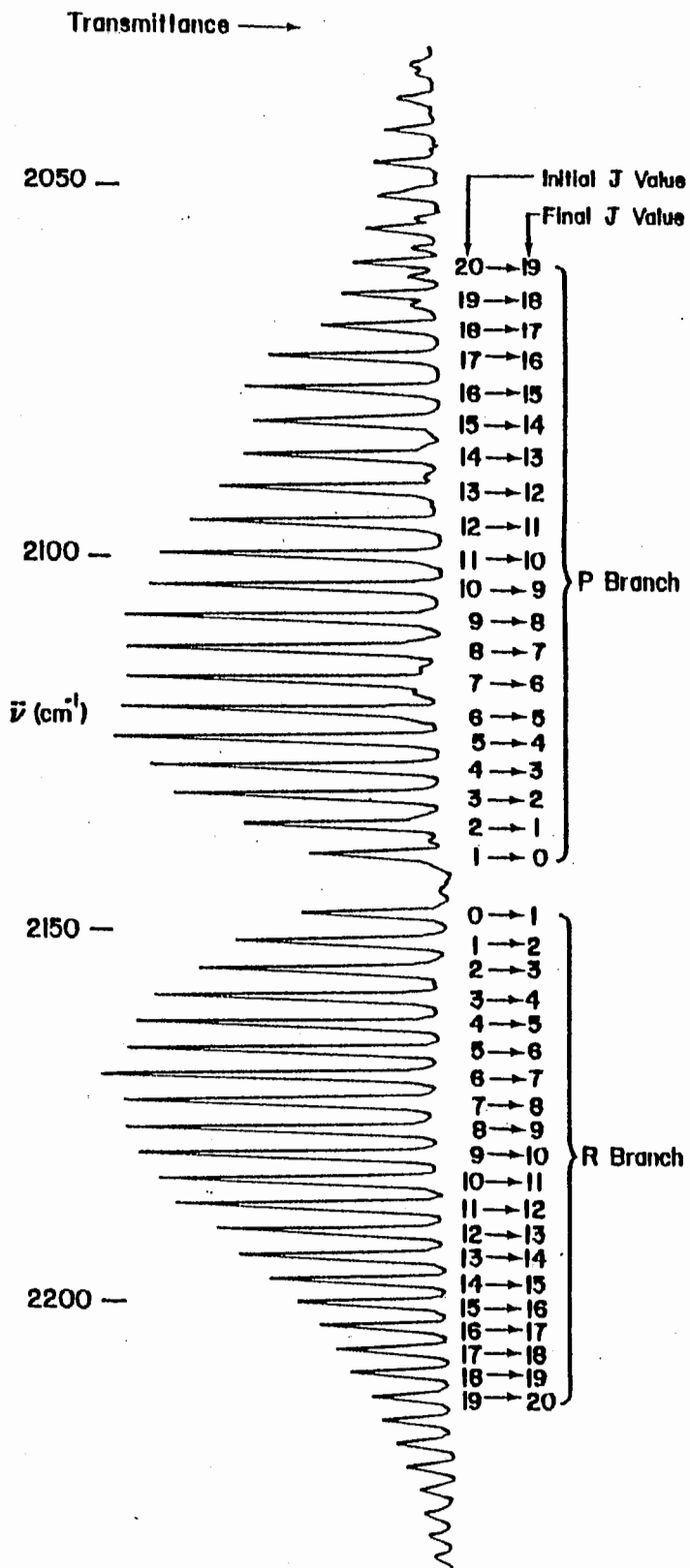
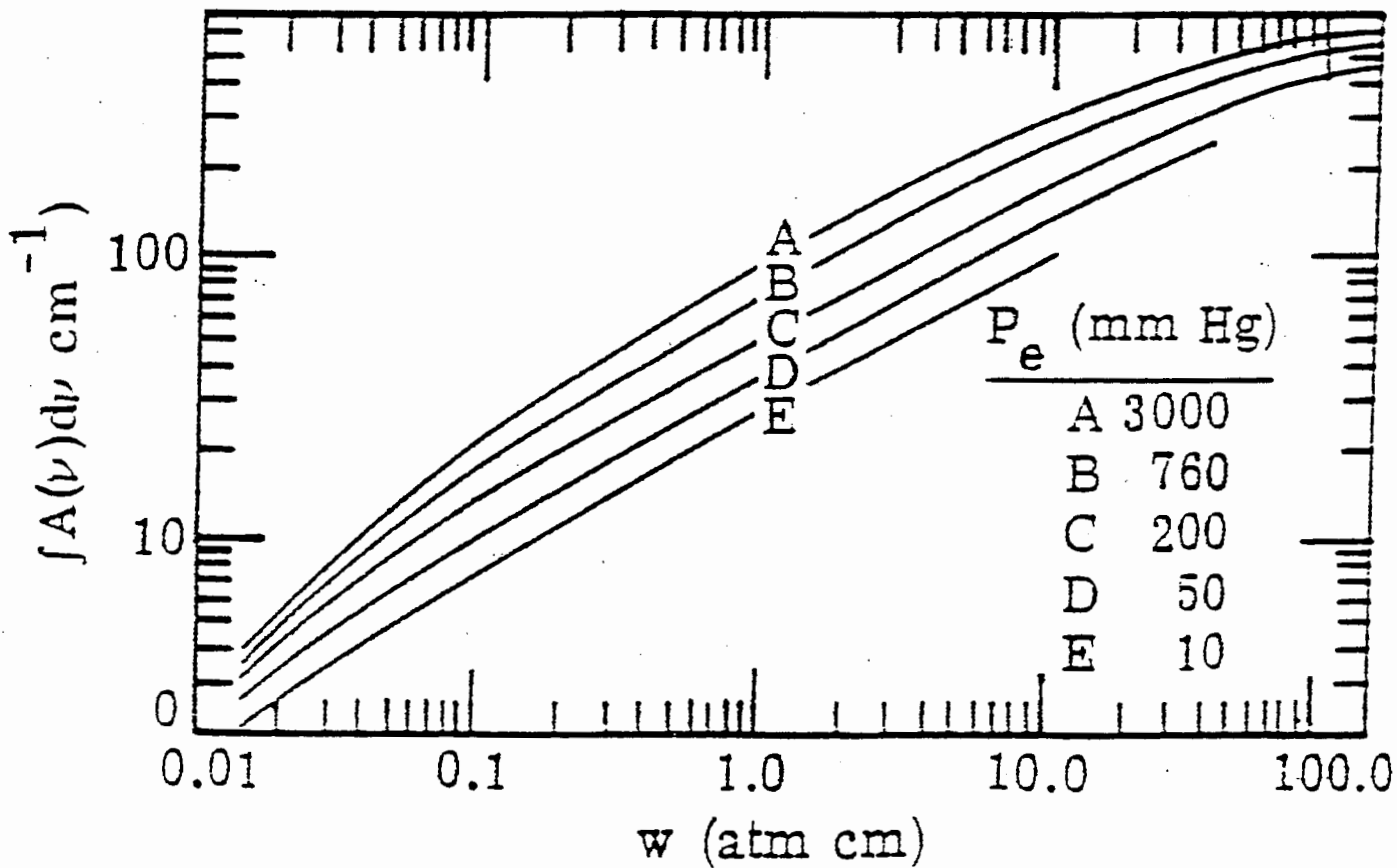


Fig. 3-19. High resolution infrared spectrum of gaseous carbon monoxide.



(a) $3.3 \mu\text{m}$ (3020 cm^{-1}) CH_4 band.

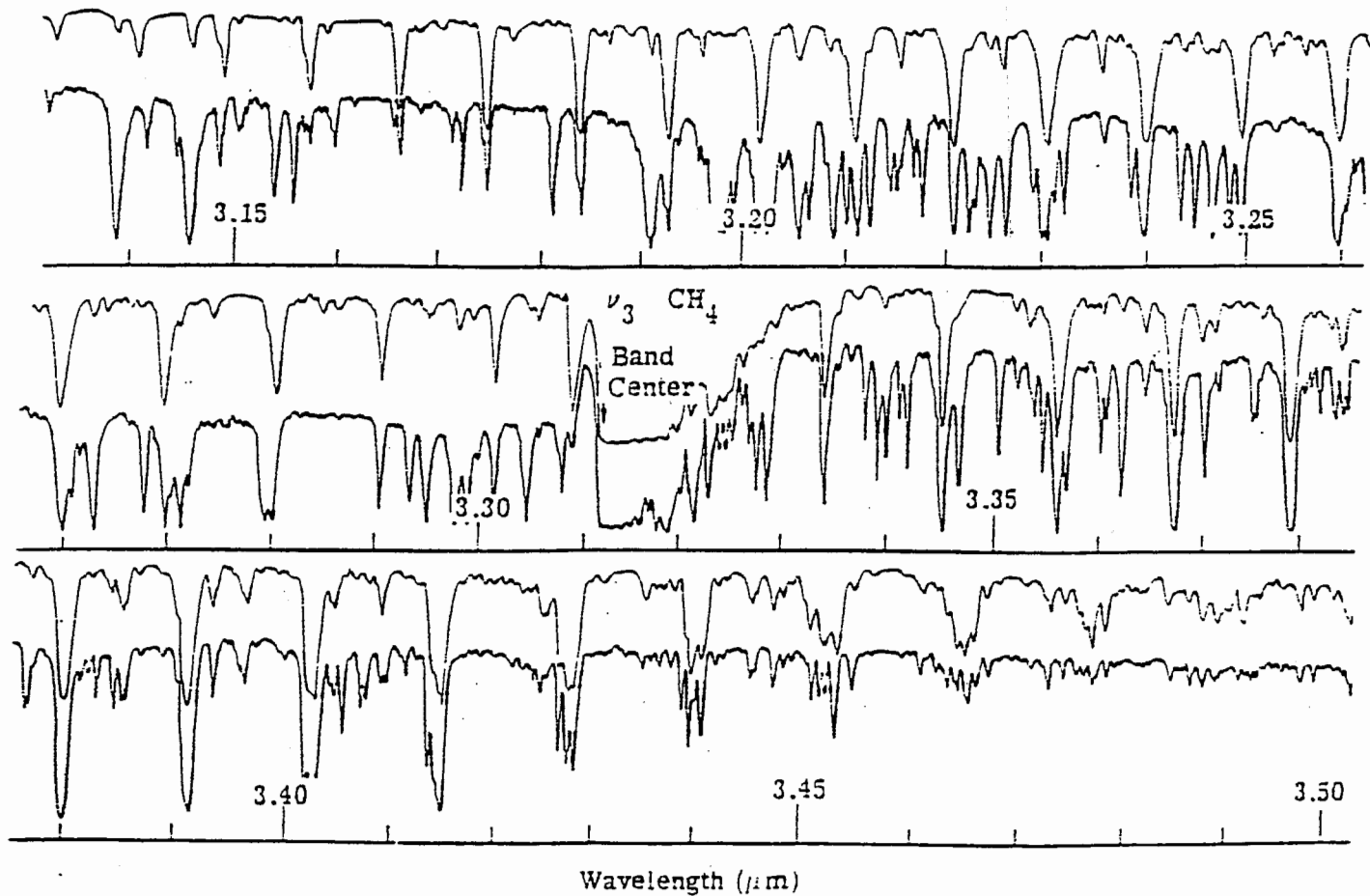


Fig. 5-35. Solar spectrum from 3.15 to 3.5 μm (lower curve) and laboratory spectrum of CH_4 (upper curve).