

Centre position (in wavenumber) of Raman bands of gases in fluid inclusions

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I have been using the Raman spectrometer a lot during the last decades to analyse fluid inclusions. All I want to know are properties of objects and physical parameters that can be directly observed either with an organic detector (my eyes and brain) or with a dead detector (camera). For fluid inclusions, this means that I want to know what they look like, how big they are, what shape they have, how they are distributed, but also what is the composition of the phases inside an inclusion, and what is their density.

A proper fluid inclusion study must include all these aspects. For the composition and density we need help from highly sophisticated machines that detect things that my senses cannot spot or are not suitable to feel or see. These machines are called "microthermometer" or "Raman spectrometer".

In 2010 I started to think about the possibility to use a Raman spectrometer for measuring the density of gases or fluids within fluid inclusions, after reading the work of Jean Dubessy, Jeffery Seitz and Jill Pasteris.

Of course, I already knew that you could use a microthermometer to calculate the density of fluids in inclusions by measuring the homogenization temperature of liquid and vapour phases. And this would be a great meter to check the results from a Raman spectrometer doing the same thing. Other scientist must have thought this simple thought already before I got this idea, but the problem was how to get a natural fluid inclusion with a suitable simple composition. Some guys solved this problem by using very little tubes, filled with a gas that they pump into it, or by measuring through a window in a chamber that could be pressurized with a known gas. And some even used synthetic fluid inclusions.

Synthetic fluid inclusions eh, what?

Well, take a seat, relax, and try to understand. That is what I told my grandmother last time I had to explain her about my job. Synthesis is a combination of separate parts into a whole or into a system, and "synthetic" also means artificially made (my grandmother is great in dictionaries, she knows it all). I have made those inclusions artificially, myself, in the kitchen (we also call it laboratory). And those inclusions contain exactly that gas mixture that I have selected to be included (more or less). No grandmother, I cannot select laughing gas, but CO₂ will do just fine. But I always need water, without water nothing works. Inclusion is an object that is being brought in, in what? To make a long story short: in quartz. You can find this natural material everywhere, and it has always lots of natural inclusions. Those crystals that are very clear (usually found in museums) can be used to make synthetic fluid inclusions. You can make the crystal grow at high temperature and pressure, and during this process you synthesize inclusions (which is actually imperfect growth). And it even grows faster in little cracks in the crystal.

But to get back to what I want to say, first of all, why would you use a Raman spectrometer if you can calculate the density with a microthermometer, which is a much simpler machine? What can a Raman spectrometer do what a microthermometer cannot?

Optics!

My organic detector (remember: my eyes and brain) may not have enough resolution to observe a homogenization of vapour and liquid phases with the microthermometer, because the object is too small or because the homogenization takes place into the vapour phase.

How is the Raman spectrometer detecting a gas density?

Not directly, it is measuring the wavelength of light, which was scattered from an object, and which has therefore changed its energy with specific light quanta. The energy change of the light depends on the chemical bonds within a molecule, but also on the density of a gas mixture.

Wow, not so fast! ... what are you talking about?

If I irradiate CO₂ with a light source that has a well-defined energy (hurray for the invention of the LASER!!!, do you remember who invented it?), then part of this energy is lost to vibrations and rotations in the molecules. The scattered light has lost packages of energy that correspond to a specific temporary movement in the molecules. This is causing a little change in wavelength of the photons. The scattered light with variable wavelengths is diffracted (spatially separated) and each wavelength is detected by a camera at different positions (different pixels). However, most of the photons are scattered without energy loss, and can be used as a perfect reference.

There once was a guy (I think his name was Max) who showed us how we can relate energy, wavelength, and wavenumbers of photons in simple equations. And another guy (his name was Chandrasekhara, you know ... Raman, ... maybe "Chuck" is easier to use) found out about how to use these physical effects to determine the nature of phases. Within the scattered light, the difference in wavenumber between elastic (Rayleigh) and inelastic (Stokes) scattering is a fingerprint of the material that has been illuminated. In other words: analyze the scattered light and you know what it is.

Gases are usually well-defined simple molecules, which reveal narrow peaks in a Raman spectrum. The vibration modes of gases such as CH₄, N₂ and CO₂ result in a variety of peak positions (relative wavenumbers), which depend on temperature, pressure and density of the gases. In other words, the way in which a free molecule can vibrate depends on how well it can move within a system of many molecules.

Wait a minute: system, phases, components, that sounds familiar.

Yes, you are right: the Gibbs phase rule. Or, how many independent parameters do I have in a system with one component and one phase? Remember that these parameters can be temperature, pressure, and density, but also energy or relative wavenumber.

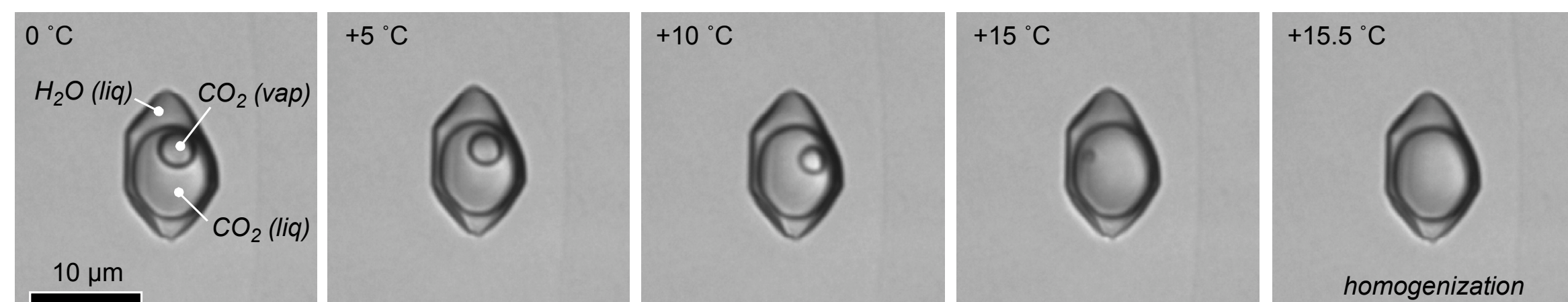
In fluid inclusion research in the 1990's, Jeffery Seitz, Jill Pasteris and I-Ming Chou noticed that the peak position of CH₄ and other gases shifted with pressure at constant temperature. I guess that other physicists and chemists already found out about this long before that (as usually in geosciences). But this is where the final part of my little story starts.

This final part is all about resolution, accuracy, uncertainty, error, precision, reproducibility, calibration ... did I leave something out?

OK, there we go. The shift of the peak position of gases is very small and can hardly be detected by modern spectrometers (the ones you can buy on the marketplace). The determination of peak positions over the last decades is a perfect example of how you may confuse "accuracy" and "precision", and the problems with calibration.... So, say hallo to Pandora.

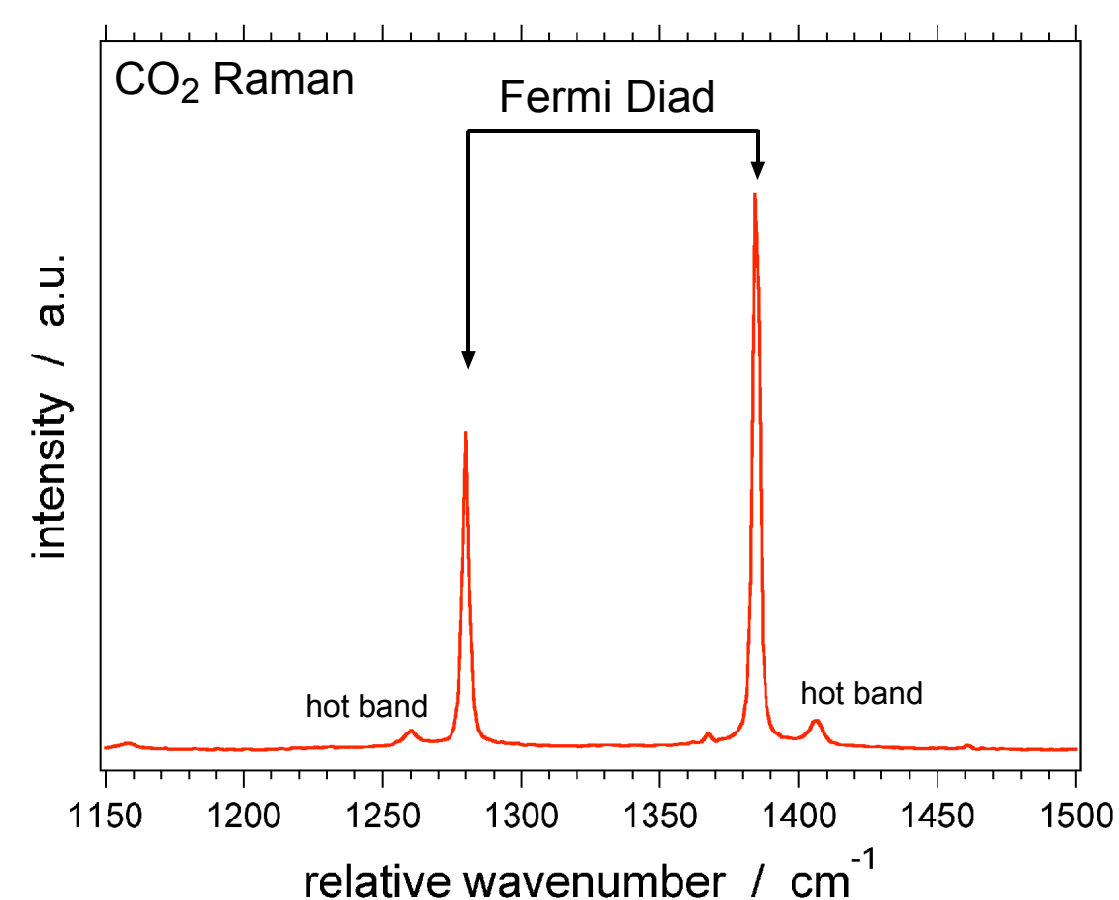
The shift in the peak position was also describe for CO₂, and several groups designed as many simple equations to calculate the density of CO₂ from its Raman spectrum. I was thinking (already in 2010, see my poster at the ECROFI XXI), lets measure a CO₂-rich fluid inclusion with a microthermometer, calculate the density from the homogenization temperature of liquid and vapour CO₂, and measure its Raman spectrum, and calculate from this the density according to all these equations for comparison, and see what we get.

Microthermometry:



The homogenization temperature of +15.5 °C (in the liquid phase) corresponds to a density of 0.8168 g·cm⁻³. The microthermometer has an accuracy of 0.1 °C in this temperature range, and a precision of 0.1 °C. Therefore, the uncertainty in density calculation is ± 0.001 g·cm⁻³.

Raman spectroscopy:



The splitting of the Fermi Diad is a function of CO₂ density. How large is the splitting of the Fermi Diad? and how do you measure it?

If you fit the lower and upper peak of the Fermi Diad to distribution curve (combination of Lorentzian and Gaussian): the splitting is 104.6567 cm⁻¹

Which gives us the following densities according to these pubs:

- Rosso and Bodnar (1995) = 0.7939 ± 0.02 g·cm⁻³
- Yamamoto and Kagi (2006) = 0.9062 g·cm⁻³ (precision = 0.01)
- Fall et al. (2011) = 0.8457 ± 0.013 g·cm⁻³
- Wang et al. (2011) = 0.8462 g·cm⁻³ (s = 0.0253)

I have checked the splitting on other machines, and I seem to get similar results: 104.47 and 104.74 cm⁻¹. Why do I get nearly the same value everywhere which is so different from what is published?

Now, there is a surprise. How can these numbers be so different, did I make a mistake? The methods are so simple that it is not possible to miscalculate. The results are not within the given uncertainties of each study. That means, I have to dig in really deep to find out about this differences. And most of all, none of this work can be used before we can clear this up.

I am a great fan of Sherlock Holmes (or should I say Arthur Conan Doyle), and this is exactly a case for him. With many so-called hidden facts and a minimum of information we have to solve this case. The "mystery" in this case is CALIBRATION. Reading each of these papers, I have to find out from the written text how the spectra were measured. The problem is that none of these papers are actually given precise information about this, and there are only a few superficial remarks. So, I need my experience, as a user of a Raman spectrometer, to deduce and interpret the handling.

How do you calibrate a Raman spectrometer?

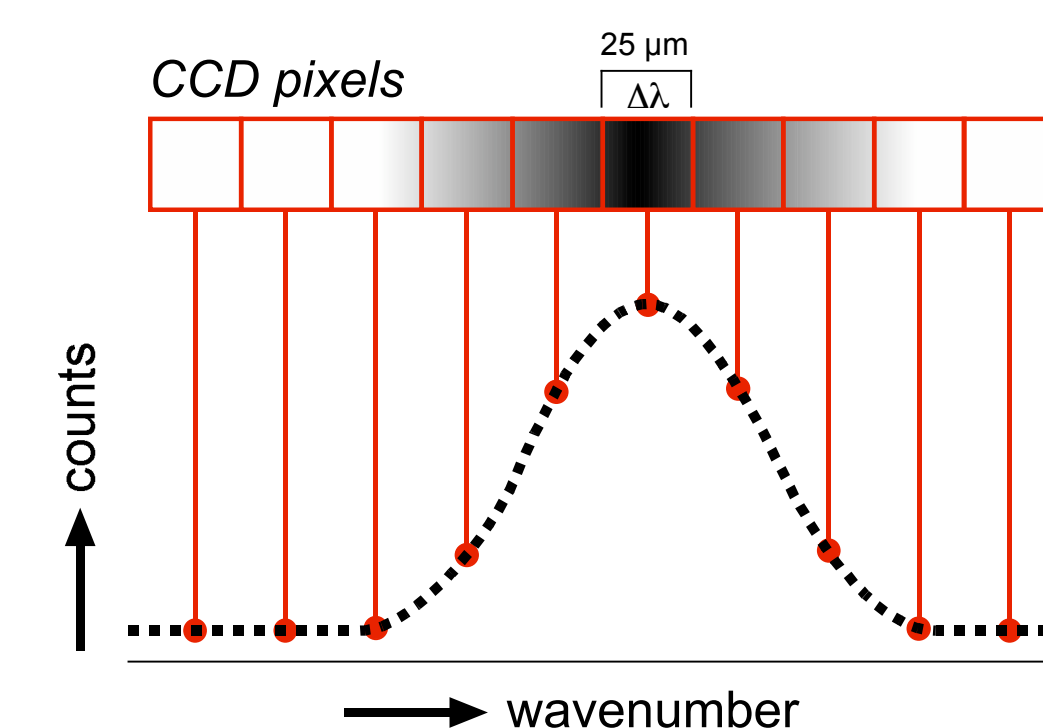
The literature is only given limited information. They mention a "low" accuracy if you use a know Raman band of a specific substance, for example "cyclohexane". The advantage of this is that any drift in your laser frequency has no effect on your measurement. On the other hand, they mention a "high" accuracy by using an emission line of noble gases, for example Neon or Argon. Now, emission lines are not Raman shifts, so there is a little problem with your meter. They never mention a number for "low" and "high".

We have to assume that we can estimate of all these standards the exact peak position (in wavenumbers) of their Raman signal. But, how exact exactly? What does a signal looks like?

Nowhere in literature you can find anything about the shape of emission lines and Raman shifts of standard materials in a Raman spectrograph. A physician would say that an emission line has the shape of a Lorentzian distribution curve in a spectrum. No way, well at least my observations are telling me a different story. There is software, that you can use to fit an array of pixels to a variety of distribution functions, and these emission pixels have to be fitted to a combination of Gaussian and Lorentzian.

"Fitting" is the word, meaning: a logical mathematical function with at least 4 parameters is able to reproduce the pixel intensities. Something like a parallel universe.

Lets explain a little bit about "pixels": a pixel is the smallest controllable element of a camera. The pixel has a specific size, and the photon that falls within the area defined by one pixel will be converted to electrons (photoelectric effect, oh thank you Albert). Remember that photons with different frequencies are directed to different pixels due to diffraction (the gratings). In the end, in an array of pixels, each pixel will receive photons of only one specific small range of wavelengths (or wavenumbers).



You could say, the pixel with the highest intensity represents the position of the peak position. But one pixel is given you a range of wavenumbers, for example, 1.67 cm⁻¹ and 0.45 cm⁻¹ if I use a better camera or settings. For example, the pixel with the number 1101.0487 cm⁻¹ has the highest intensity. The pixel before is 1099.5983 and after 1102.4989 cm⁻¹. So, this pixel detects photons from 1100.3235 to 1101.7738 cm⁻¹.

The accuracy of this simple detection can never be better than the size of a pixel.

What is the trick everybody uses to be able to illustrate an uncertainty, error, variance, etc ... of 0.03 cm⁻¹?

The answer is: FITTING with distribution curves (imagine again this parallel universe).

BUT: nobody has used this for emission lines, and a variety of distribution functions (and there are many) give the same variety in results.

From descriptions in literature, one can only imaging how they did it for emission lines: the pixel with the highest intensity (I guess). Hamaguchi was the only one who mentioned a small correction if the two adjacent pixels had unequal intensities, but at that time (the 1980's) they only used "eye determination", and how accurate can that be?

We can now conclude that in the parallel universe, in the world of Alice and Willy Wonka, the uncertainty in each measurement is 0.03 cm⁻¹, but in the real world we still have the pixel-size.

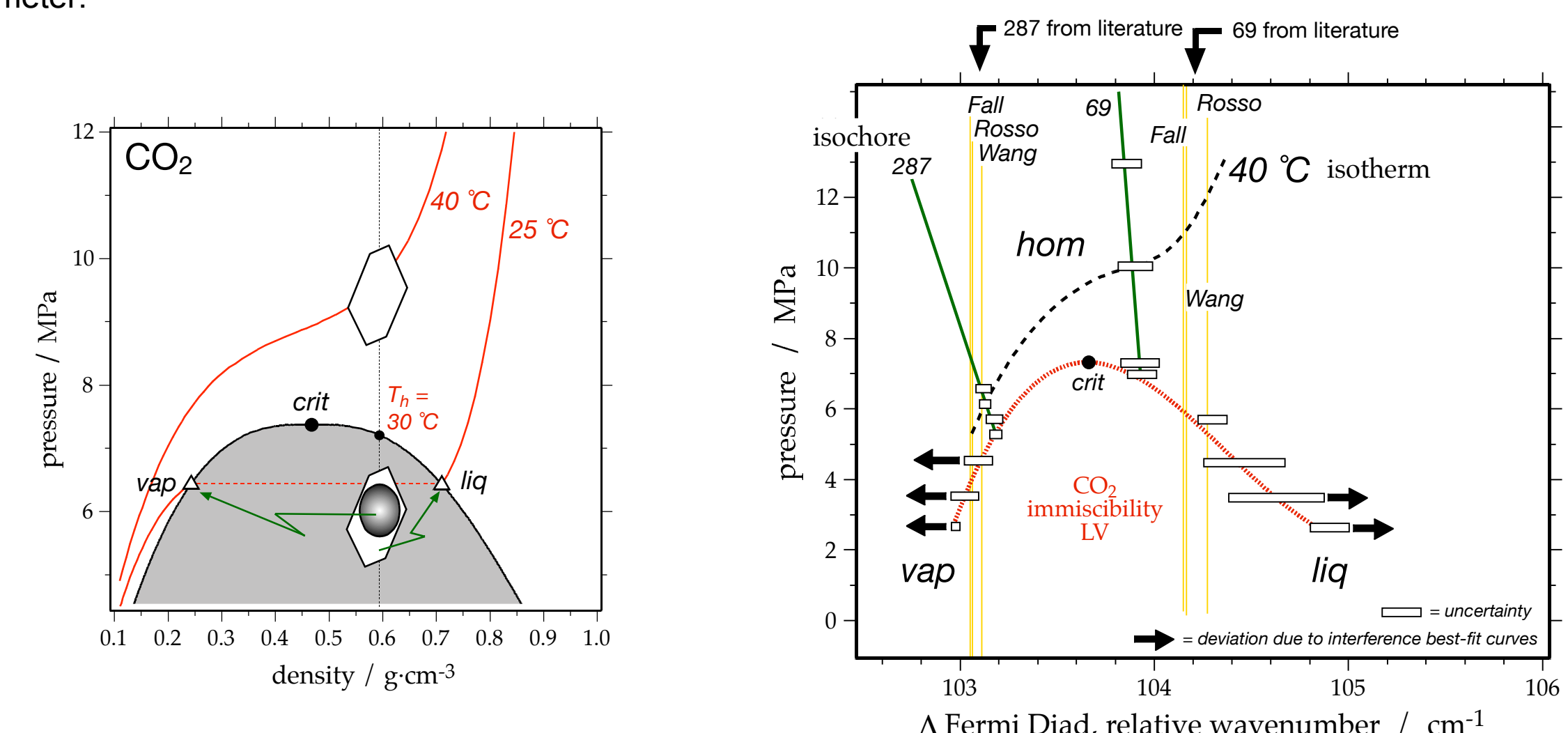
There is only one way of having a lower error (uncertainty, accuracy, name it as you want) than the pixel-size: "centre position of detector". Yes, there are so many variables and parameter with such a Raman spectrometer, there are lots of possibilities to do experiments.

The light is scattered and diffracted in all directions, and the camera can only get a part of this. Usually the meter allows you to move the detector or gratings physically, to be able to analyze all the possible wavenumbers in a large range of angles of diffraction. By moving, you change the number of each pixel. You can move in very small steps, which is only about one-tenth of the wavenumber range per pixel. For example, I can move the detector over 0.13 cm⁻¹ at 1300 cm⁻¹ (pixel size is 1.4132 cm⁻¹). By taking about ten steps within one pixel, the position with the highest intensity with detector movement is than selected as the peak value. With this sub-pixel movement, I can reduce the error to about 10% of a pixel size. That is it, no more.

So, what went wrong in all these publications?

If a publication claims an uncertainty of 0.03 cm⁻¹, and another publication cannot reproduce the same numbers, but also claims a similar uncertainty, than something is very wrong. And on top of that, if I want to use this information, and I (just a simple user of published material) find out that both results do not correspond with my observations, than I start to wonder.

Each of the studies that published equations to relate the wavenumber difference of the CO₂ Fermi Diad and the density of CO₂ only use one parameter. The density is a function of wavenumber difference, or vice versa. Now, remember what Gibbs did to us: in a unary system (pure CO₂) within one phase (a homogeneous vapour or liquid phase) we have the freedom to vary two parameters. Or in terms of our little problem: the wavenumber difference must be a function of temperature and density, or density and pressure, etc..... (Remember my poster at the ECROFI XXI, 2011). So, these published functions must have a large uncertainty, if they only use one parameter.



Something else, which I forgot to tell: what about refractive index?

Now, this is another fundamental part, which needs a little bit of attention. Nobody has ever published anything about the effect of refractive index on Raman spectra. The companies that sell these meters do not tell you anything about it. We are measuring in air because I like to breathe while I measure. Now we start a chain reaction: air slows down the speed of light, air reduces the wavelength of light, but the number of waves per meter remains the same, the frequency and wavenumber remain constant (well, Max would say nearly constant, but he was a theoretical physicist). The relationship between wavelength (that is what you actual measure with your Raman meter) and wavenumber (that is what is displayed in your graph) is changing. Who much? Bingo: refractive index.

My grandmother told me that a refraction index is not a constant number, hé. It depends on, eh, temperature, pressure, eh, air humidity, carbon dioxide content of air, and absolute wavelength. My grandmother is very smart, she has a cat (mozart), brown with darker stripes, she loves that cat.

A Raman spectrum in wavenumbers displays the difference between the laser source and the scattered light. That means we have to multiply this wavenumber number with the refractive index of air. This number is close to 1, so we just simply forget about it (and hoppa, we are back in the parallel universe).

Really? lets do a little thought experiment. The relative wavenumbers of the Fermi Diad of CO₂ would be 0.32 cm⁻¹ higher if we neglect the refractive index of air. And this corresponds to about 30% difference in CO₂ density according to these equations. Wow.

What does this matter if we systematically apply this error, so we get a systematic error. Max would say: are you crazy! You can related as many numbers with each other as you like, but it would be nice if they had a physical meaning (do not take this personally dear mathematicians).

I have been writing about CO₂ all the time, but what about CH₄? Well, it is the same story, but a little bit worse.

For those of you who cannot see the trees anymore in the wood, let me summarize this little story. Everything that has been published about the relationship between Raman spectra and gas density must be revised, scrutinized, modified, corrected, re-examined, The solution of it all is combining the meters.

Finally, I hope you have enjoyed my little story

Cheers

I would like to thank my grandmother, her cat, Max and Albert, and many greetings to Bruce.