Augmenting 19th Century Thermoelectric Greenhouse Theory with 20th Century Quantum Mechanics Raman Spectroscopy: Towards a Coherent Radiation Theory of the Atmosphere

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Abstract

Current greenhouse theory is incomplete: it does not include Raman spectroscopy and is incorrectly based on the special group of 'Tyndall' greenhouse gases, which are really the thermoelectric (TE-IR) gases, as detected only by thermoelectric transducers. It's premise: 'the non-GHGs Nitrogen and Oxygen do not absorb or emit infrared radiation' presents a paradox, it contradicts both quantum mechanics and thermodynamics – where all matter above absolute 0^0 Kelvin radiates IR photons. These (above) molecules possess quantum predicted emission spectra within the IR range of the EMS – at 2338cm^{-1} and 1556cm^{-1} respectively – but are only observed, and temperatures from them measured, by Raman Spectrometers, 'IR spectrometers' complement instrument. This was investigated by quantum and thermoelectric theory and application. A report of Raman spectrometer measurements on jet engine outlet temperatures and gas concentrations was referring to, and the following conclusions made: 1) all Raman modes (the non-GHGs) are temperature/radiation equivalent to 'IR- active modes with respect to – and complying with – the Boltzmann and Planck's constant, and quantum spectroscopy theory; 2) in support, H_2O's 3659cm^{-1} mode is both TE-IR and Raman equivalent – supporting the 'equipartition' principle; and CO_2's temperature can be measured by both instruments independently through its shared modes; 3) the special (1%) greenhouse gases, discovered by Tyndall in ca. 1859, are really the thermoelectric gases, detected only by receiving (non-radiating) thermo-electric transducers; 4) 'IR' spectroscopy is also based on these thermoelectric transducers, and as a consequence 'IR' spectrographs show only the spectra modes with electric dipoles and not Raman; 5) N_2, when radiated at it's 2338cm^{-1} mode, is (long lasting) metastable, and is essential to the operation of a CO_2 Laser: from this mechanism, it was concluded – contrary to current greenhouse theory – atmospheric CO_2 is heated by the same mechanism; 6) all the atmosphere absorbs heat directly from the Sun – just as with the oceanic euphotic layer.

Key Words: greenhouse gases, John Tyndall, climate change, Raman Spectroscopy, thermoelectrics, Seebeck effect, emission spectroscopy

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1 Introduction

The current 'standard' model of greenhouse (GH) theory – developed in the 19th Century; before 20th century quantum mechanics – claims the entire thermal-radiation behaviour of the atmosphere is explained by 1-2% of its dry constituent gases. These special greenhouse gases (GHGs), as they are termed, explain all past, present, and future climate change. These 1% GHG's – of which Methane (CH_4) is 1.7 parts in a million volume – are assumed to be the only gases to absorb 'outgoing long-wave' infrared (IR) radiation, which has been in turn re-radiated back (up) from the Earth's surface after been absorbed by the sun – by 'insolation'. Radiation heat is not directly absorbed by the sun in the atmosphere itself[1][2]. The model also assumes, and is dependent upon the premise, the non-GHGs nitrogen (N_2) and oxygen (O_2) – 99% of the dry atmosphere – both do not absorb or emit IR radiation, at any temperature – if they did, model collapses.

1.1 An IR Catastrophe

While the maybe science is 'settled', as it is said to be; it appears the physics is not. Apart from being unintuitive, 'the air not absorbing the suns energy directly', the above (non-GHG) assumption presents a paradox, a catastrophe – an IR catastrophe – as it contradicts many key principles of physics, namely it quantum mechanics and thermodynamics where all matter by above the temperature of absolute zero Kelvin is assumed to radiate electromagnetic heat-energy in the IR range of the electromagnetic spectrum (EMS). Either the physics of quantum mechanics is wrong, or GH theory is wrong?

1.1.1 Principles the Laws Central to Radiation Theory

Before setting a hypothesis, I would like to list the exact physics at stake. Atmospheric molecules – whether or not GHGs – must concur with the following accepted Principles the laws central to radiation theory:

1.1.1.1 Spectroscopy:

*"The study of the interaction between electromagnetic radiation (**h**ν) and matter is called spectroscopy; where radiation is emission or transmission of energy in the form of waves or particles through space or through a material medium. Interaction takes place by absorption and by emission, and is explained by quantum mechanics. **Emission spectroscopy** is a spectroscopic technique which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state. Each element emits a characteristic set of **discrete wavelengths** according to its electronic structure, and by observing these wavelengths the elemental composition of the sample can be determined. Emission spectroscopy developed in the late 19th century and*

efforts in theoretical explanation of atomic emission spectra eventually led to quantum mechanics."

1.1.1.2 Quantum Mechanics Schrödinger Equation

From quantum mechanics – the fundamental physics theory in which describes nature on the smallest scales of energy levels of atoms and subatomic particles – this equation, the Schrödinger equation, is used to calculate the predicted vibrational modes or absorption-emission spectra of atoms and molecules.

1.1.1.3 Planck's Law

*"**Planck's law** describes the spectral density of electromagnetic radiation emitted by a black body in thermal equilibrium at a given temperature T."*

1.1.1.4 Boltzmann Constant

The Boltzmann constant is a fundamental constant of the universe, which links the kinetic energy movement of molecules in a gas with temperature. By the Boltzmann constant, the observation of these and all vibrational modes at the said predicted frequencies, and their respective temperature measurement thereof, implies these modes are moving and thus are radiating IR.

1.1.1.5 The Stefan-Boltzmann Law

The Stefan-Boltzmann law is a central pillar to radiation theory, and states the following:

"All objects actually emit radiation if their temperature is greater than absolute zero. Absolute zero is equal to zero Kelvin, which is equal to -273°C or -460°F. An object that absorbs and emits all possible radiation at 100 percent efficiency is called a blackbody.

*The Stefan-Boltzmann law, a fundamental law of physics, explains the relationship between an object's temperature and the amount of radiation that it emits. This law (expressed mathematically as E = σT4) states that all objects with temperatures above absolute zero (0K or -273°C or -459°F) emit radiation at a rate proportional to the fourth power of their absolute temperature. E represents the maximum rate of radiation (often referred to as energy flux) emitted by each square meter of the object's surface. The Greek letter "**σ**" (sigma) represents the Stefan-Boltzmann constant ($5.67 \times 10^{-8} W/m^2K^4$); and T is the object's surface temperature in Kelvin. The W refers to watt, which is the unit used to express power (expressed in joules per second)." [3]*

1.1.1.6 Kirchhoff's Law of thermal radiation

For an arbitrary body emitting and absorbing thermal radiation in thermodynamic equilibrium, the emissivity is equal to the absorptivity. Good emitter; good absorber.

1.1.1.7 Specific Heat

Not withstanding the above, N_2 and O_2 both also have nominal – similar to other gases – heat capacities. This energy is only further transferred by means of convection and conduction mixing; and this presents another paradox: if most of the air does not transfer heat by radiation, and only by conduction and convection, how is this accomplished when the air is a known as a poor thermal conductor of heat-energy, and is, in fact, a thermal insulator, with a thermal conduction value of near zero: 0.024 W/m K) [4]. How can conduction, and related convection, stand alone as the means of heat transfer in the atmosphere? Without radiation and conduction, the atmosphere should not exist the way it does. The reality is; the atmosphere seems to behave in total accordance with the 0th, and 1st laws of thermodynamics, and also the Stefan-Boltzmann Law of radiation.

1.2 Deriving the Original GHGs

Again before setting a hypothesis, how our understanding of the GHG's was developed must be presented. The GH atmosphere is derived solely from detectors first developed during the early 19th Century: the thermo-electric (TE) thermo-pile transducer. This fact offers a window into and explanation to the problem. The modern derivatives of these TE transducers are used in thermal imaging cameras and IR spectrometers, and all have the same thing in common; they convert thermal energy into electro-motive force (emf) via the Seebeck effect. In 1859, John Tyndall used the thermopile to analyse and derive what he thought were, and what are still today believed to be, the 'greenhouse gases' – as first posited by Joseph Fourier – of the atmosphere.

1.3 Atmospheric Thermoelectric and Raman IR Spectra Lines

Table 1 shows the thermoelectric-IR modes and the Raman modes of the atmospheric gases derived solely from the radiation physics listed above (1.1.1). The outstanding issue from this table, and the central issue to this paper, is that the listed Raman Modes or Spectra (also shown on the spectrogram figure 1), are not considered to behave as so-called 'IR-active' modes in that they do not radiate or emit IR radiation – thus further contravening with the above principles of physics. These are the Raman modes of N_2's **2338cm^{-1}**, O_2's **1556 cm^{-1}**, CO_2's **1338 cm^{-1}**, H_2O's **3659 cm^{-1}** and CH_4's two **2914 cm^{-1}** and **1303 cm^{-1}**.

Table 1. Atmospheric Gases with their Respective IR Range Vibrational Modes

Molecule	Vibration Mode or Band: wavenumber (frequency)	Thermoelectric (TE) and Raman Properties	Mode Type
H_20	3652 cm^{-1} (2.74μm)	TE (IR) and Raman	Symmetric
	1595 cm^{-1} (6.25μm)	TE (IR)	Asymmetric
	3756 cm^{-1} (2.66μm)	TE (IR)	Asymmetric
CO_2	1388 cm^{-1} (7.2μm)	Non-TE (Non IR); Raman	Symmetric
	2349 cm^{-1} (4.257μm)	TE (IR)	Asymmetric
	667 cm^{-1} (14.992μm)	TE (IR)	Asymmetric
CH_4	3020cm^{-1} (3.312μm)	TE (IR)	Asymmetric
	2914cm^{-1} (3.431μm)	Non-TE (Non IR); Raman	Symmetric

	1508cm^{-1} (6.5μm) 1303cm^{-1} (7.7μm)	TE (IR) Non-TE (Non IR); Raman	Asymmetric Symmetric
N_2	2338 cm^{-1} (4.2μm)	Non-TE (Non IR); Raman Active	Symmetric
O_2	1556 cm^{-1} (6.25μm)	Non-TE (Non IR); Raman Active	Symmetric

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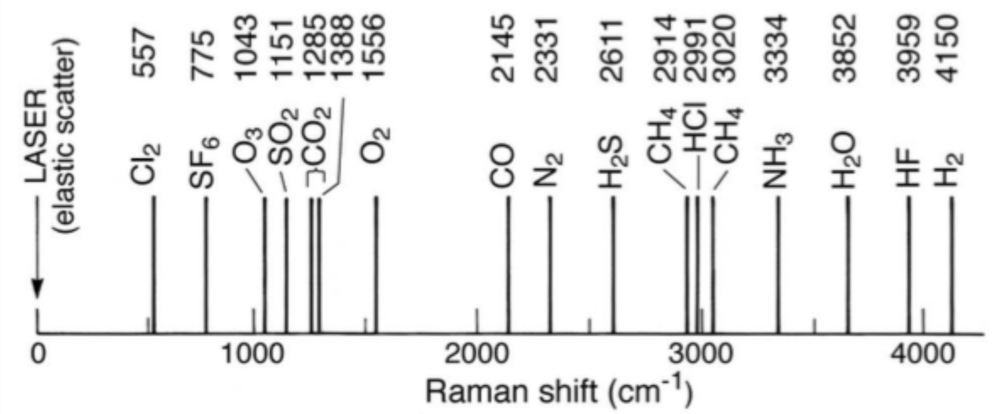


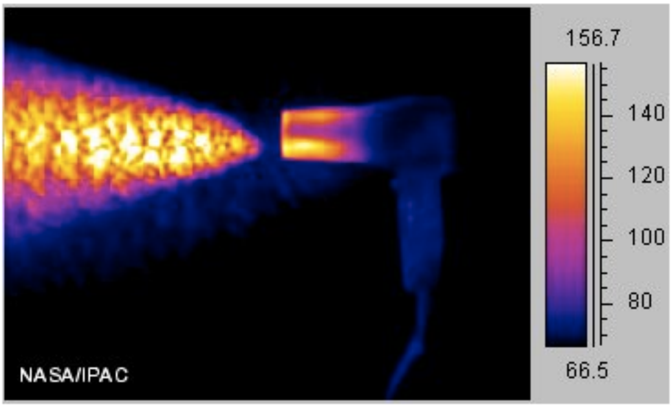
Fig. 10. Positions of Raman lines (in cm^{-1}) of various molecular species in gas phase at 1 atm and ambient temperature.

Figure 1. The Raman Atmosphere. Spectrograph of the Earth's Atmospheres gases and their Raman modes. [5] Notice these frequencies (of the molecules) are not (from the table above) thermoelectric in nature, and are not symmetric in nature.

1.4 Problems with TE-IR: The Hairdryer Gap Paradox

The illustrate the problem of TE transducers – as claimed above in 1.2 – the thermal radiation image below of an operating hairdryer emphasises and offers insight into this thermal discrimination the leads to the (above) 'IR catastrophe'. From the thermal image, it can be made out the hair dryer is operating as its body is of a moderate (blue) temperature and its outlet a red to yellow (indicated) temperature.

The discrimination is revealed with the conspicuous '**gap**' (of no apparent heat) between the hot 'flow' patch – to the left of the dryer – and the (glowing) hairdryer outlet? Why does this gap show no hot air coming directly out at the outlet, when there appears to be a hot flow after? In principle, the hairdryer operates by radiation from its radiating electrical elements. These elements should radiate the air, and the air should – by quantum mechanics – absorb this energy.



Hair dryer creates IR
(Picture courtesy of NASA)

Figure 2. The Hair Dryer 'Gap' Paradox. A thermo-electric produced thermogram of an operating hair dyer blowing hot air – of temperature around 60C – onto a surface. Why is the blown air not glowing at the temperature of the outlet and the surface? Why the 'gap'? The answer lies in understanding thermoelectric materials.

But this is not how the image is interpreted by radiation physics. It is assumed the air is heated instead by forced-convection or conduction; however, it cannot be heated by conduction (the air is a thermal insulator, as stated above), and it cannot be by convection for the same reason. This leaves only radiation. In fact, it must be by radiation; and if this is true, where has the physics gone wrong? Why is this hot air not explained by radiation with the dryer, and – similarly – with the standard model of the atmosphere? See section 4.5.5 for an explanation to this paradox.

1.5 Thermal Measurements by Raman Spectroscopy

Returning to the hairdryer paradox described above in figure 2, this investigation will show the hot air temperature 'gap' can be measured by Raman instruments or a combination of Raman and IR/thermoelectric instruments.

To show pragmatically the IR emission spectra modes of atmospheric molecules are equivalent and only different by their respective detectors – due to whether they have an electric property or not – no direct primary experiment was undertaken in this investigation, but rather a report of a previously conducted Raman spectrometer application was referred to. This report called the: FIELD TESTS OF A LASER RAMAN MEASUREMENT SYSTEM FOR AIRCRAFT ENGINE EXHAUST EMISSIONS - 1974 [6], is referred to and termed for purposes of this investigation 'The Raman Exhaust Report' (RER).

With the RER the hot air expelled from a jet engine was analysed by Raman laser instruments and compared to TE/IR measurements. Essentially it is a scaled up version of the hairdryer; only the TE GHGs are included. Importantly, the RER shows an instrument measuring the non-TE/GHGs with improved accuracy. The rationale being: if Raman devices are good enough to use for a practical application like a jet engine, it should be good enough for the entire atmosphere.

Below is a FLIR thermal image of an operational jet engine produced by TE transducers – the same technology as used to derive the GHGs. The bright white-hot plum image suggests – correctly – hot GHGs are expelled; what is missing – again just as with the hairdryer paradox (above) – is the 'hot' N_2 and O_2. In the case of this FLIR image the plum can only be bright because of the presence of TE GHG molecules – CO_2, H_2O and the like. What result would we achieve if Raman were used to measure all the gases temperatures?

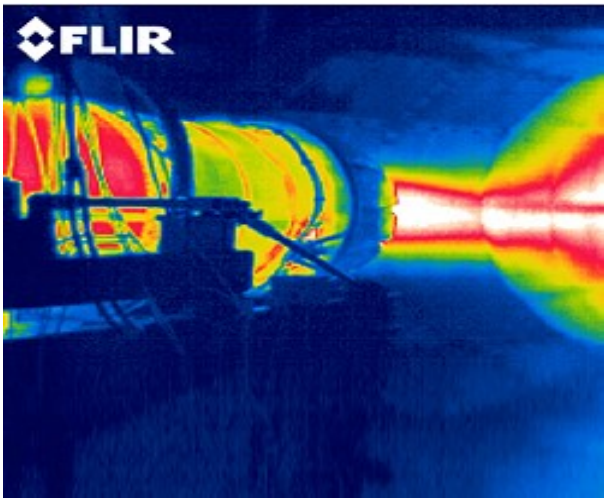


Figure 3. FLIR Image of an operating jet engine [7]. The bright 'hot' plum an only correspond to the GHGs within it.

The operation of this Raman device (the RER) should correspond to our understanding of quantum mechanics and thermodynamics in that it will measure the predicted vibrational modes of each and every molecule it can, and; also measure the corresponding temperature/energy.

Finally, the RER application should invoke questions at the fundamentals of physics: if N_2 and O_2 do radiate, how is it so – if it is assumed by GH theory not to? How have they become so hot so quickly from collision (conduction) alone when they are assumed they do not absorb any IR heat-energy. The simple answer, and truth is they do emit and radiate – perfectly.

1.6 Hypothesis

Without evoking any of the arguments posited in the current ensuing 'great' political-climate debate surrounding GH theory, this paper aims to address the problem by looking at the 'first principles' physics (1.1.1). The paper points to the problem being our 'primitive' use and misunderstanding of radiation in atmospheric sciences, namely modern quantum mechanics and the Laser instruments derived from it, and particularly, how it is used to form the foundational premise of the standard model of GH theory.

1. It was hypothesised the non-GHGs – N_2 and O_2 and the 'Raman' modes of the GHGs (Table 1) – all comply with standard radiation physics (1.1.1): they radiate IR at their respective (QM predicted) emission spectra, equivalent to the IR modes. What separates the gases is whether they

(mostly the diatomic) are Raman or thermoelectric with respect to their IR emission spectra. There are no special GHGs; only special instruments.

2. The non-GHGs modes, unlike the 'Tyndall-GHGs' [8], do not have an electric dipole moment due to their symmetric vibration; so do not generate an electromagnetic force (EMF) by the thermo-electric transducers ('IR' detectors) – the same transducers used to measure them. To measure these Raman modes, Raman laser instruments – IR-thermoelectric spectrometers complementary instrument – must be used. The Raman 'non-GHGs' are special in that they share a non-thermoelectric (non-TE) symmetric vibration nature. Raman spectrometers – by measuring the Raman modes – can measure temperature just as the IR-thermoelectric spectrometers can – they are equivalent. With an understanding of Raman spectroscopy, these TE-IR spectrometers should not be used in isolation in atmospheric radiation theory.
3. What Tyndall discovered in ca. 1959 was the thermoelectric –TE – properties of the atmospheric gases; of which CO_2 and the other 'Tyndall Gases' are TE, and N_2 and O_2 are not. Thermoelectric transducers discriminate – by their process – all substances on their ability to generate electricity, and especially the gases in which the Tyndall experiment demonstrated. The modern use of these TE transducers produce – what are termed (incorrectly) – 'IR' spectrographs. They are better termed TE-IR spectrometers. These TE-IR spectrometers do not radiate the samples as claimed, but rather graph the emf difference between the sample and a reference IR-heat source, and in so doing, correctly produce the TE spectra bands ('IR' vibrational modes, table 1) as predicted by quantum mechanics. As N_2 and O_2 are not TE, their modes are not produced, and as consequence of this, N_2 and O_2 are assumed not to radiate IR as the other 'GHGs'. With Raman spectrometers it is shown N_2 and O_2 both share the same thermal properties as the current special GHGs in that they absorb and emit infrared radiation. By this, N_2 and O_2 and the other gases all directly absorb (and emit) IR radiation (by means of insolation) from the sun.
4. From understanding of the IR absorption-emission properties of N_2, at its one absorption mode, it is further hypothesised N_2 absorbs infrared photons by the identical process as demonstrated as in its role in the CO_2 Laser. In this process – explained by quantum mechanics – N_2 is a pumping – metastable – medium. It is the CO_2 molecule that is stimulated by the excited N_2. From this, assuming electron discharge is equivalent to photon radiation; solar insolation – of IR photons – accounts for changing air temperature. It will also account for the high temperatures reached by N_2 during a lightning strike producing thunder where the excitation causes the temperature of the air to reach some five times the surface temperature of the sun, and the 2700^0K molecule temperature of N_2 in the thermosphere.
5. From an understanding thermoelectric and Raman physics, the GHGs thus should be known as the thermoelectric gases (TEGs); the non-GHGs – the non-TEGs – as the Raman gases; and together they all constitute as the GHGs – as first posited by Joseph Fourier in 1828.

1.6.1 Hypothesis Essentials

To prove my theory correct, it was required to show:

1. All vibration modes of all the atmospheres gases, predicted by quantum mechanics, can be observed by either thermoelectric IR spectrometers, or Raman IR spectrometers. Raman Active (symmetric stretch) non-GHGs N_2 and O_2's mode's are observed at **2338 cm^{-1}** and **1556 cm^{-1}** respectively (both within the IR range of the electromagnetic spectrum (EMS)) by Raman IR spectrometers (section 4.1);
2. Vibrational modes – with respect to measured temperature, and concentration – are equivalent, in accordance with the Principle of Equipartition of Energy (sections 4.2);
3. Raman Active modes must also demonstrate or imply radiation emission and absorption of IR photons – in accordance with Kirchoff's and Stewarts Laws (sections 4.7.7);
4. CO_2's only Raman active mode at **1388 cm^{-1}** must be shown to be temperature equivalent to its complementary 'IR active' modes – measured at **2349 cm^{-1}** and **667**cm^{-1} (section 4.1.2).
5. H_2O's modes (both Raman active and IR active) must show radiation (temperature) equivalence (section 4.1.3).
6. Further to 5., it was required to show N_2's **2338 cm^{-1}** mode absorbs and emits radiation in the IR range of the EMS, in a real-life application (the CO_2 laser), directly affecting CO_2's **2349 cm^{-1}** 'IR' mode (Section 4.7.1)
7. Further to 6., it will be required to show this phenomenon holds for photons – and not only electron discharge (section 4.7.1.5);
8. What is termed 'IR spectroscopy' only reveals the thermo-electric modes, and a gas with any one of those modes is termed a GHG. (Section 4.4);
9. All IR detectors do not radiate the sample, they are receiving thermoelectric transducers; they produce an electromotive force (EMF) and, report the difference in EMF between the sample and the control heat source (section 4.3.7).

To prove this hypothesis I shall firstly draw upon practical application and respective physics theory, and then follow up with a detailed explanation as to where greenhouse theory has gone wrong. I shall also add supporting evidence where needed.

1.7 Approach and Scope of this Investigation

While this paper will evaluate Raman spectrometers for their equivalence to TE/IR spectrometers – with respect to testing the atmosphere gases – it will also explain where and how 'physics' has misconceived the standard 'special' GHGs. To prove the hypothesis, the Raman vibrational modes of the atmospheric gases will be evaluated for their respective IR radiative propensity. An already performed experiment – where 'hot' air is measured using both IR/TE transducers and Raman spectrometers for its thermal properties – is referred to, along with applications of thermoelectric, and quantum theory.

2 Methods

2.1 Raman Exhaust Report (RER)

The RER directed a high power Nitrogen laser Raman spectrometer into the outlet flow of an operating (T-53) jet engine to measure the gas temperature, and concentration. To calibrate and compare measurements made by the Raman laser; 'conventional' thermoelectric - IR spectrometers (table 1 p.25) and thermocouples were used.

The following are extracts from the report pertaining to the Raman method and could be repeated in any other gaseous context.

2.1.1 From the RER abstract:

"Laser induced Raman and fluorescent measurements were made in the exhaust of a T53-Ll3A gas turbine engine with a new field portable instrument devised specifically for gas turbine exhaust emission measurements. The gas turbine exhaust was analysed by conventional instruments for CO, CO_2, NO, NO_2, total hydrocarbons, smoke and temperature, and these data were used as a "calibration" standard for the evaluation of the laser Raman instrument, (p. v). "

2.1.2 The Laser:

"The laser transmitter was an Avco Model C5000 pulsed nitrogen laser operating at a wavelength of 3371 Å (337.1 cm^{-1})." (p.4)

2.1.3 Temperature Measurement

"The temperature of the T53 exhaust was measured by means of the N2 Raman density method whereby the temperature is assumed to be inversely proportional to the density of nitrogen, with a constant static pressure. "

2.1.4 Setup:

The laser beam was pointed at and through the jet outlet as shown in the reports figure 28 (p. B46)

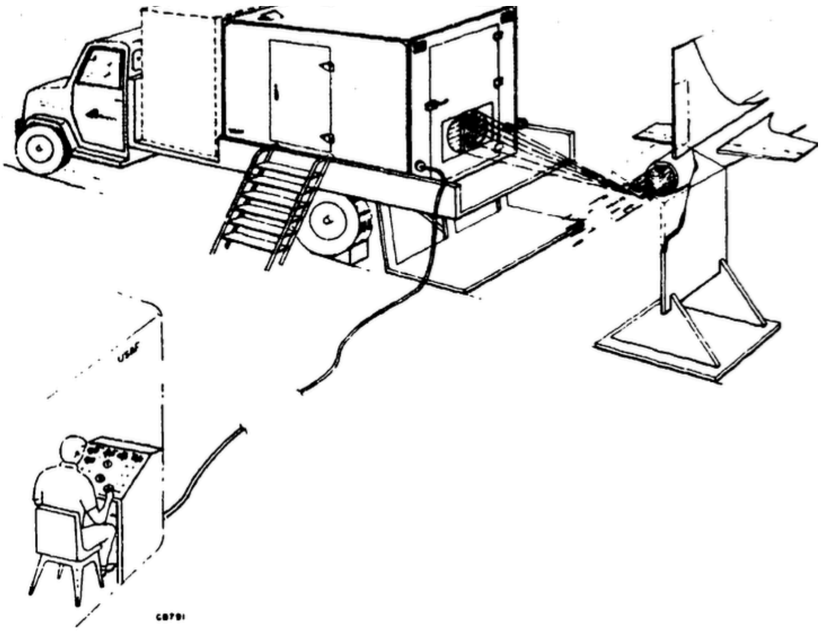


Figure 28 Schematic of Laser Raman Aircraft Engine Exhaust Emissions Measurement System

Figure 4. RER Setup. Pg. 46 [9]

"The gas analysis equipment used as a comparative standard for the laser Raman consisted of detectors similar to those specified by the SAE. They consisted of infrared detectors for CO, CO_2, and NO, a flame ionization detector for total hydrocarbons, and a polarographic detector for NO and NO_2 as shown in the schematic of Figure 14. Thus, NO was measured by two different detectors. A list of the instruments used and their ranges is given in Table I." (P.20)

2.1.5 Temperature Measurement

Temperature measurements were made from the Raman laser unit and from conventional thermoelectric devices.

"Room temperature experiments were conducted in room air to measure for nitrogen.."

"Raman spectra at elevated temperatures were obtained from the exhaust of a propane/air burner. Figure 18 shows the measured spectrum of the nitrogen Raman band at 3658Å at a temperature of 1000 K and measured with a thermocouple in the burner exhaust." Pg. 32 [9]

3 Results

Before revealing the direct results of the Raman Exhaust Report (RER), a short recap on the purpose of the experiment: I was testing the non-GHGs – N_2 and O_2's 2338 cm^{-1} and 1556 cm^{-1} vibrational modes – with IR spectroscopies complementary instrument – Raman spectroscopy – for equivalence with modes of the GHGs.

Results draw directly from the Reports comments:

3.1 Raman Gas Vibrational Modes Observation

The Raman active vibrational modes of atmospheric gases N_2, O_2 and CO_2 were observed at the predicted wave numbers as shown and figure 5 below:

"Raman data were obtained which could be used to accurately measure the mole fractions of the major species in the flow, i.e, N_2, 0_2, and $C0_2$ over the entire range of engine operation conditions from idle to full power. These Raman measurements were compared with the expected values of the specie concentrations as calculated from the measured fuel:/air ratio of the various operating conditions." (P.2) [10]

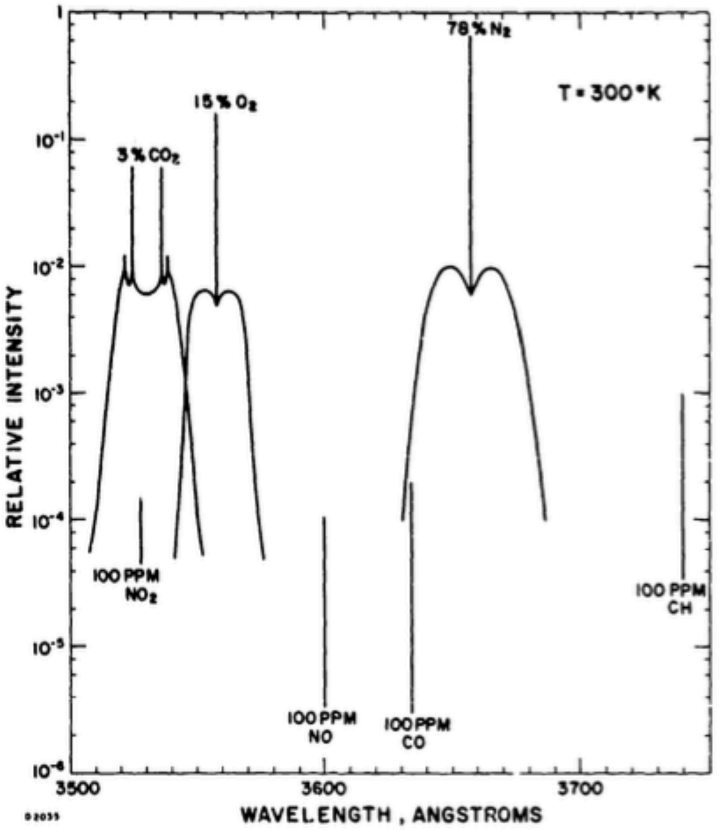


Figure 3 Typical Raman Spectrum from Room Temperature Combustion Gases Using a 3371 Å Laser Source

Figure 5. RER Raman Atmosphere Spectra. Pg. 7 [9]

Notice figure 5 shows not only the wave numbers for the different gases but also their respective concentrations.

The following figures show Raman Spectra in detail:

"Initial tests were conducted in air at the AVCO Everett Laboratories to verify the predicted performance of the laser Raman field unit. Figures 18, 19, and 20 show spectra obtained in the spectral regions that correspond to vibrational transitions in N_2, NO and H_20 at 2330 cm^{-1}, 1876 cm^{-1} and 3652 cm^{-1} that will produce Raman lines at 3658, 3600, and 3844 Å, respectively." *Pg. 43*

3.1.1 N2 2338cm Raman Vibrational Mode Spectra

The Raman spectra of N_2 molecule's 2338 cm^{-1} mode is shown below in figure 6.

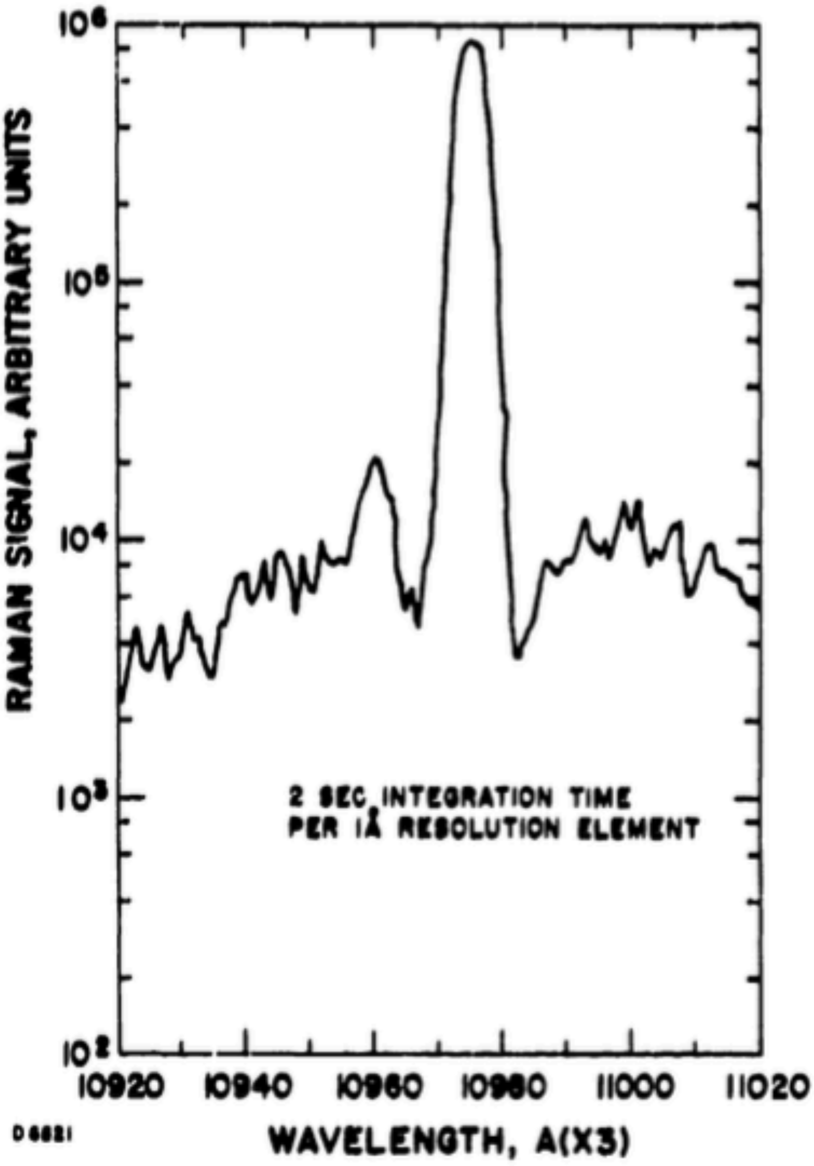


Figure 18 Ambient Air Nitrogen Vibrational Raman Line at 2330 cm^{-1}

Figure 6. 'Figure 18' N_2 2330 cm^{-1} Raman Spectra. Pg. 32 [10]

3.1.2 O_2 1556 cm^{-1} Vibration Mode and Concentration

O_2 was not the molecule of attention; however, the Raman spectra were observed to calculate concentration levels.

"Raman measurements were made of the 0_2 concentrations in the T-53 engine exhaust. These measurements show excellent agreement when compared with the expected values of the concentration on the basis of the measured fuel/air ratio from the operating engine. Typical data of the O_2 vibrational Raman line in the hot exhaust gases are shown in Figure 31. The system was calibrated in the field for effective cross section and system transfer function by using the $0_2/N_2$ ratio

obtained from ambient air and by assuming that air is 21% 0_2 and 78% N_2 on a mole basis. " (P.43)

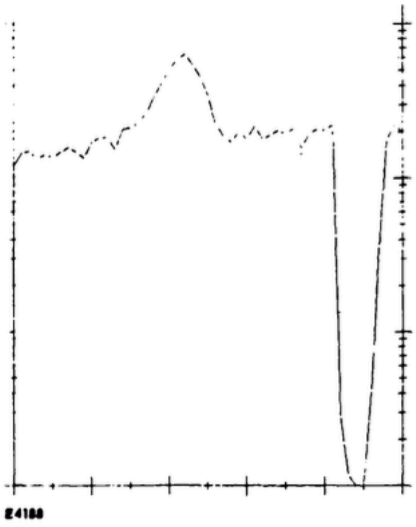


Figure 31 **Typical Spectral Data of O_2 in Hot Exhaust Gases**

Figure 7. O_2 1556 cm^{-1} Raman Spectra. Pg. 41 [10]

3.1.3 H_2O 3652 cm^{-1} Vibrational Mode

H2O's Raman mode was observed; its spectra is shown in figure 8 below.

"Water vapor detection is shown in Figure 20 (below), where a signal/noise ratio of about 100 at a relative concentration of about 1% of the atmospheric nitrogen signal is observed." (P. 31)

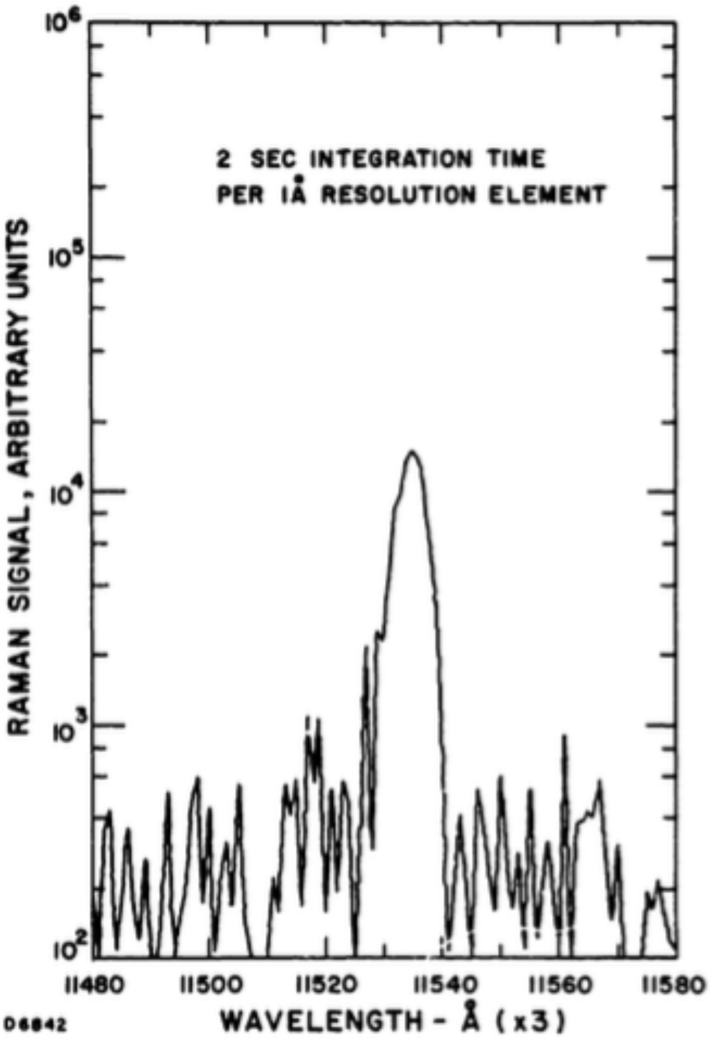


Figure 20 Atmospheric Water Vapor Vibrational Raman Line at 3652 cm^{-1}

Figure 8. H_20 3652 cm^{-1} Raman Spectra. Pg. 34 [10]

3.1.4 CO_2 1338 cm^{-1} Vibrational Mode (and Temperature)

Carbon dioxide's predicted 1338 cm^{-1} mode was observed and its spectra are shown in figure 9 below.

"A further example of a room temperature Raman spectrum is shown in Figure 17, which is the spectrum of the CO_2 doublet at 1285 cm^{-1} and 1388 cm^{-1} wave numbers."

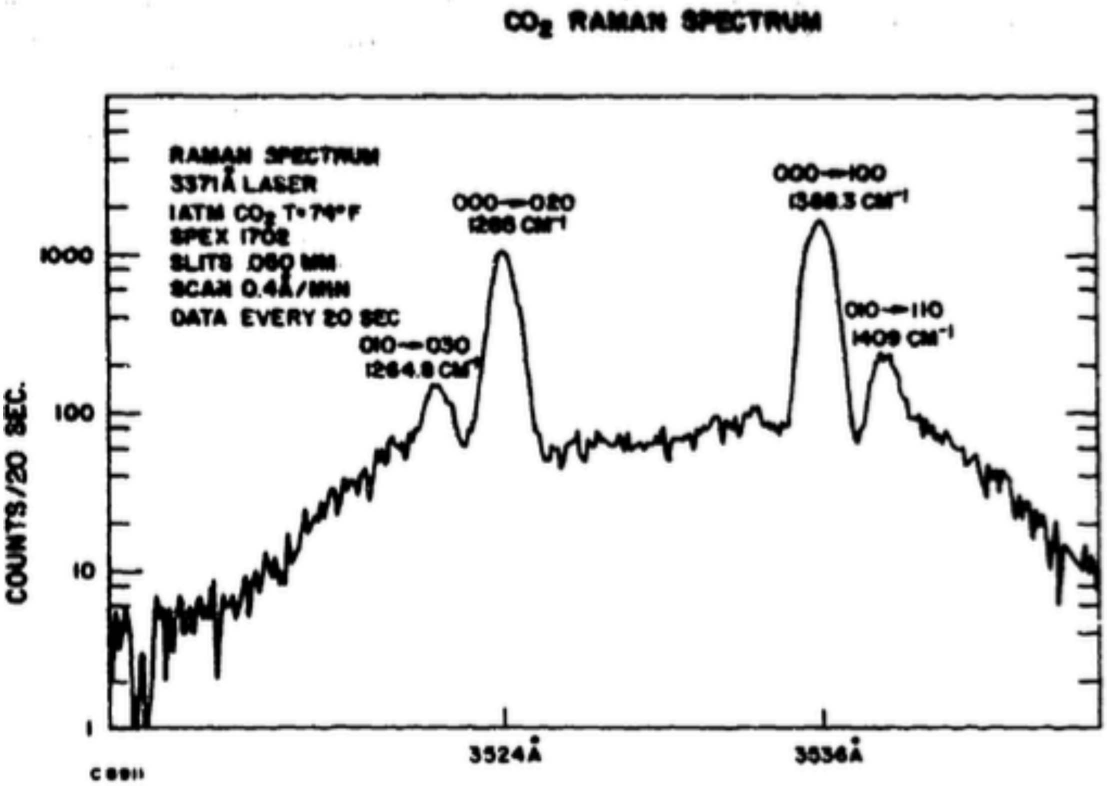


Figure 17 **Experimental Raman Spectrum of Carbon Dioxide at Room Temperature**

Figure 9. CO2 1338 Raman Spectra [9]

"Of special interest is the appearance of secondary peaks at 1265 cm^{-1} *and 1409 cm*$^{-1}$ *wave numbers which correspond to transitions from the lowest excited vibrational level of* CO_2*, the 010 level. This level is appreciably populated even at room temperature. Measurement of the ratio of the secondary to the primary peak is a sensitive means of temperature measurement throughout the temperature range of interest for turbine exhausts as will be shown later in this report."* [9] (P.32)

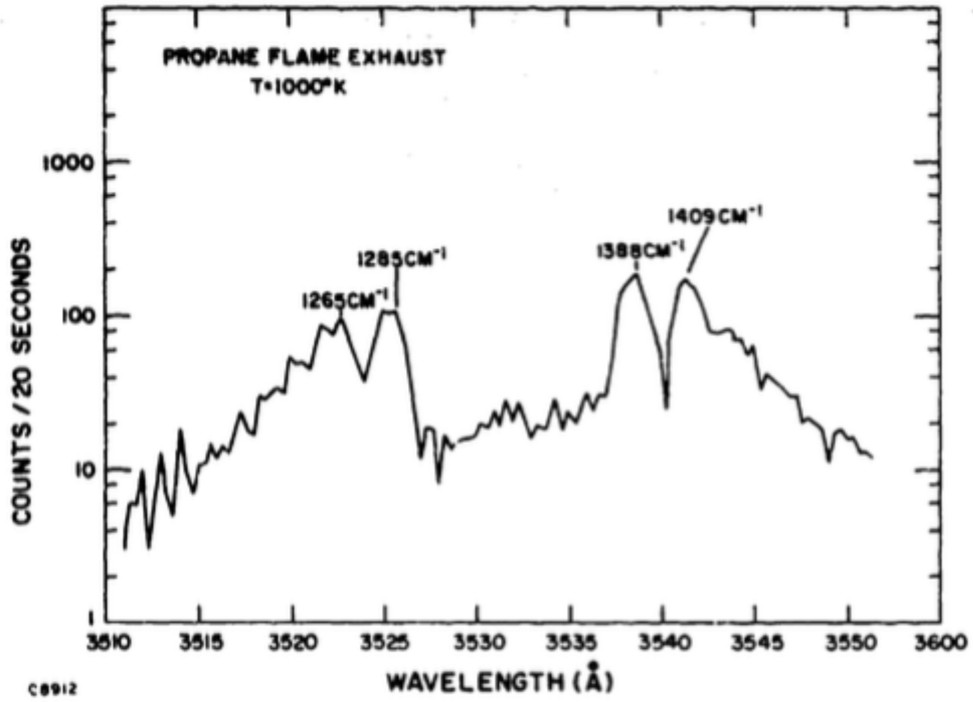


Figure 20 Experimental Raman Spectrum of Carbon Dioxide at ~1000°K in a Propane/Air Burner Exhaust

Figure 10. CO2 Spectra. Pg. 33 [9]

3.2 Gas Concentrations by Raman Spectroscopy

Gas concentrations for the following atmospheric gas were measured:

3.2.1 H2O Concentrations

"The water vapor Raman data that was obtained from the exhaust of the T-53 engine is shown in the following tabulation: "

Power Setting	*Raman Measurment*	*Calculated From F/A*
(1)	*(2)*	*(3)*
7%	*0.0274*	*0.0372*
30%	*0.0216*	*0.0416*
100%	*0.0226*	*0.0567*

The Raman Measurement values in (2) are the ratios of the peak value of the water Raman signals in the 3652 cm^{-1} *band to the peak value of the nitrogen Raman signals at 2330 cm*$^{-1}$*. The system was calibrated - using the ambient air values. The calculated values used the same F/A data as was used in the above* O_2 *and* CO_2 *comparisons and included a slight correction for the ambient air water vapor."(P.51)*

3.2.2 CO2 Concentration

"The response of the laser Raman instrument to $C0_2$ was calibrated at the beginning of the test program with a T53 engine by using the previous conventionally measured C02 concentration from this engine at the 60% power setting. ... These data are displayed in Figure 33, which shows the volume percent CO_2 as a function of the percent shaft horsepower of the engine." Pg. 59 [10]

"Similar Raman measurements were made of the CO_2 concentration in the T53 turbine engine exhaust and are shown in Figure 33 (below). ***The Raman data were normalized to the (IR) gas analysis data at the 60% power point****. Absolute CO2 calibrations using the atmosphere were not conducted in the field because of the uncertainty in the C02 concentration of the air in the Bridgeport, Connecticut industrial area." (P.48)*

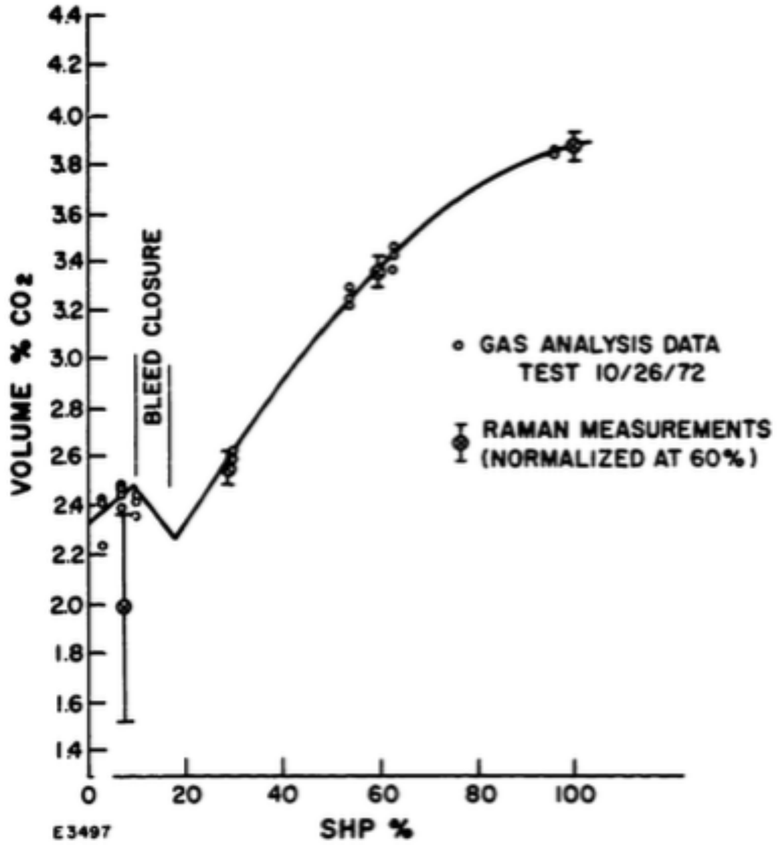


Figure 33 Volume % CO_2 as Measured from Raman Scattering vs Shaft Horse Power (SHP), %

Figure 11. CO2 Raman vs IR/thermoelectric. Raman measurements taken at 1338 cm-1 match the IR thermoelectric 2349 cm-1 mode. Pg.50 [10]

3.2.3 N_2/O_2 Ratio

"The ratio of the corrected 0_2 to N_2 Raman signals can then be used to obtain the $0_2/N_2$ mole ratio. The system was calibrated in the field for effective cross section

and system transfer function by using the O_2/N_2 ratio obtained from ambient air and by assuming that air is 21% O_2 and 78% N_2 on a mole basis. The results of the oxygen measurements are shown in Figure 32 where the $0_2/N_2$ mole ratio is calculated from the fuel/air ratio of the operating T-53 engine, using an approximate value of hydrogen/carbon mole ratio of 2. 0. Perfect agreement would cause the data to fall in the line connecting zero with the point labeled "air".

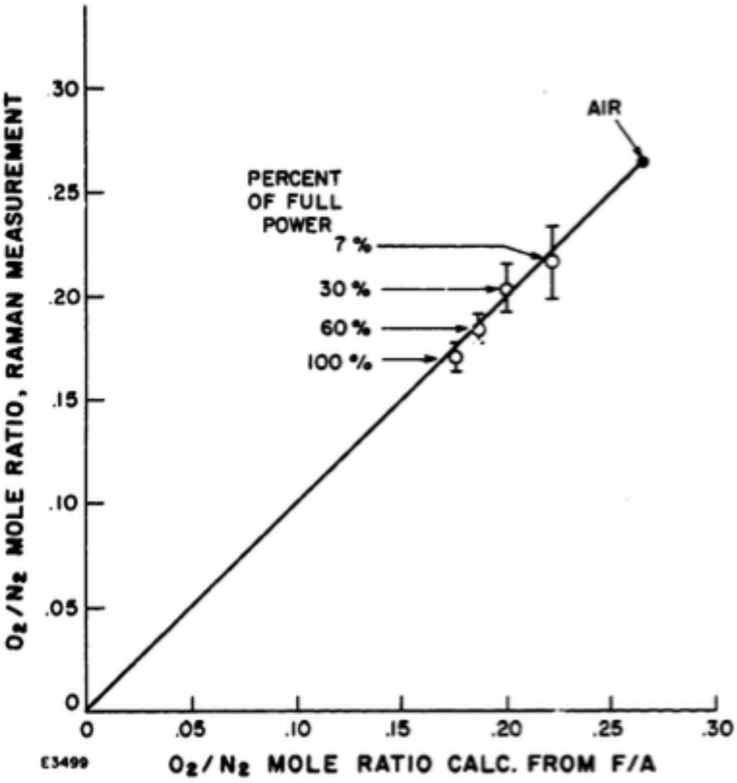


Figure 32 O_2/N_2 Mole Ratio for T-53 Engine Raman Measurement vs Calculated Value

Figure 12. N_2 O_2 Concentration Raman Measurements. Pg. 49 [10]

3.2.4 NO

"An attempt was made to detect nitric oxide (NO) in the T53 exhaust using the 1876 cm^{-1} vibrational Raman transition. The T53 engine typically produces 100 ppm of NO when operating at full power. Because the fluorescence level in the T53 at full power was about 100 times greater than the expected signal from NO, the required integration times for detection were longer than the test time available." (p. 51)

3.3 Temperature Measurement by Raman Spectroscopy

Temperature measurements were made from Raman Active modes of the atmospheric gases, as follows:

"The temperature profiles obtained in this way (Raman) are plotted in Figure 37 and appear quite reasonable. Thermocouple measurements in the exhaust stream gave an average of 7250 K for the 7% power point and 8900 K for the 100% power point, which is good agreement with the Raman data. ***Since it is not subject to***

thermocouple heat loss corrections, the laser Raman data is inherently a more reliable and accurate' thermometer than a thermocouple*. Further work is required however to definitely establish the precision of the laser Raman method as a hot gas temperature measurement technique. (p. 54)"*

3.3.1 N_2 Temperature

"Accurate temperature profiles were obtained in the T-53 ***exhaust using laser Raman scattering from nitrogen*** *via the density method. The spectral analysis of "hot bands" was found to be a less accurate method in the T-53 exhaust because of the high level of laser induced fluorescence. Although the feasibility has now been demonstrated, further work is required to quantify the precision of the laser Raman method for temperature measurements in aircraft engine exhaust streams." (Pg. 59)[10]*

"The sensitivity of the method is shown in Figure 27, which is a plot of the ratio of the Raman scattering at 3634 Å to the Raman scattering at 3658 Å for pure nitrogen as a function of temperature. Over the expected range of turbine exhaust operation, i. e. 9000K to 12000 K. the uncertainty in the ratio is 9% per 100°K or about 1%per 11K temperature uncertainty- an attainable value using the (010)/(000) CO2 Raman ratio method as.. discussed. Since the Raman intensity in the AJ = -2 side band of N_2 *(with circular polarization) corresponds to about an apparent level of 1000 PPM of CO a 1% measurement of the side band intensity would enable detection and measurement of 10 PPM CO. This is difficult, requiring an S/N of 100 at low signal levels, but can in principle be done." (P.41)[9]*

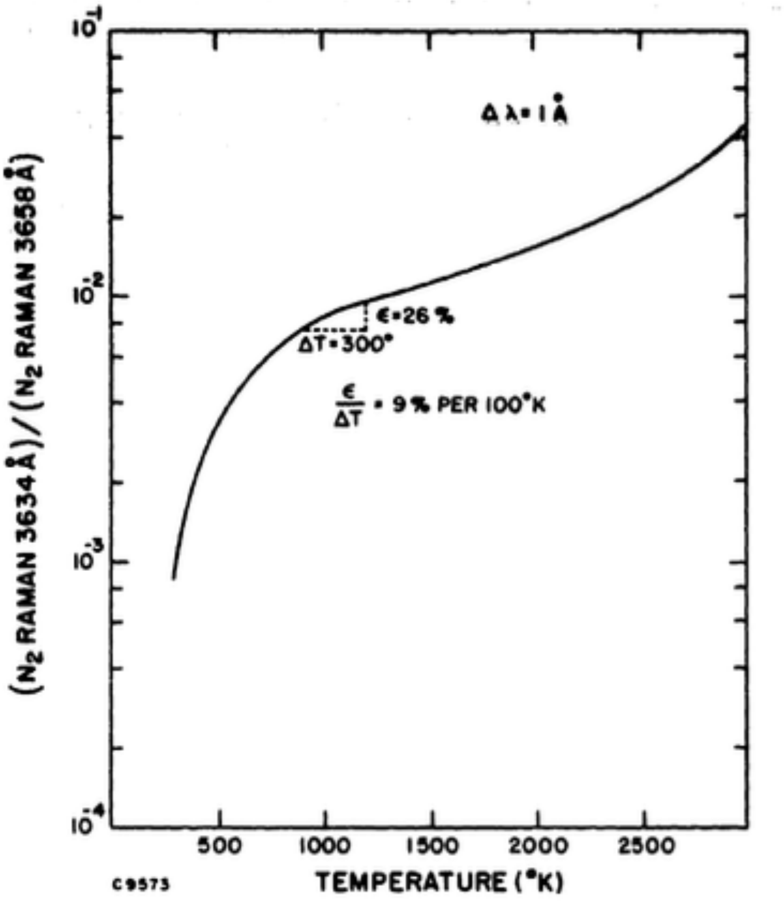


Figure 27 The Computed Ratio of Nitrogen Raman Scattering $(\Delta J=2)$ at $\lambda = 3624$ Å to Nitrogen Raman Scattering $(\Delta J=0)$ at $\lambda = 3658$ Å

Figure 13. N_2 Prediction to Observation. Temperature measurement of a Non GHG by Raman spectrometer at N_2's 2330 cm^{-1} predicted mode. Pg.43 [9]

“5. TEMPERATURE SENSITIVITY

The effects of increasing temperature become important to the laser Raman turbine exhaust analysis system in many ways. Foremost is the effect on the ratio of the peak Raman signal intensity of a particular species to the actual concentration of that species. The tacit assumption in previous work has usually been that the Raman signal is proportional to species concentration. However, over the temperature range of interest this proportionality constant is somewhat temperature dependent. “

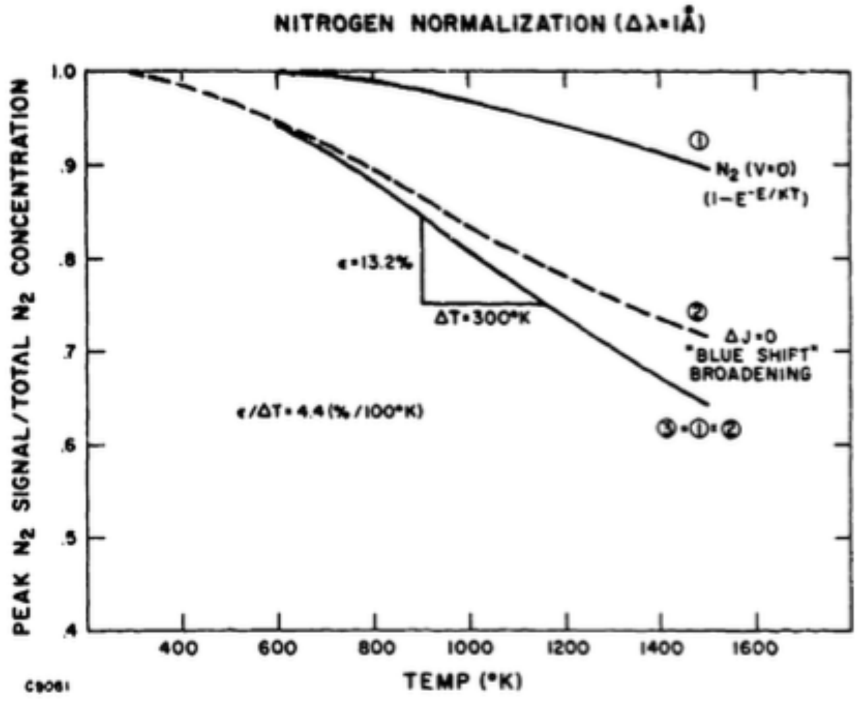


Figure 21 Computed Nitrogen Normalization Error as a Function of Temperature for a Detector with a Resolution of 1 Å

Figure 14 N_2 Temp. Pg.34 [9]

3.3.2 Raman CO_2 Temperature

"Figure 22 shows the estimated ratio of the peak (000) CO_2 signal to the total CO_2 concentration as a function of temperature.

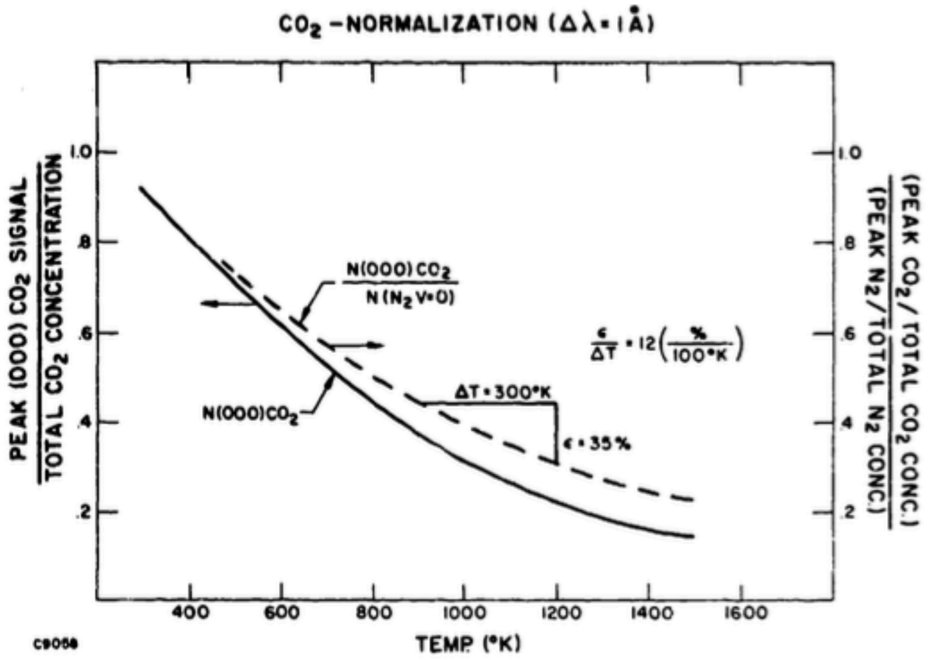


Figure 22 Computed Carbon Dioxide Normalization Error as a Function of Temperature for a Detector with a Resolution of 1 Å

Figure 15. CO_2 Temperature Measurement by Raman Spectrometer. Pg 35[9]

From the above, it is apparent that an independent method of temperature measurement is a desirable adjunct to a laser Raman turbine exhaust measurement system. The use of the CO_2 Raman spectrum seems to be a reasonable means to satisfy this requirement. ***In particular the measurement of the ratio of the (000) CO_2 peak to the (010) CO_2 peak seems especially well suited for a temperature determination.***

Also shown in Figure 23 are two experimental points representing a room temperature determination which agreed exactly with the theoretical curve and a higher temperature data point obtained from the propane/air burner exhaust CO2 spectra.

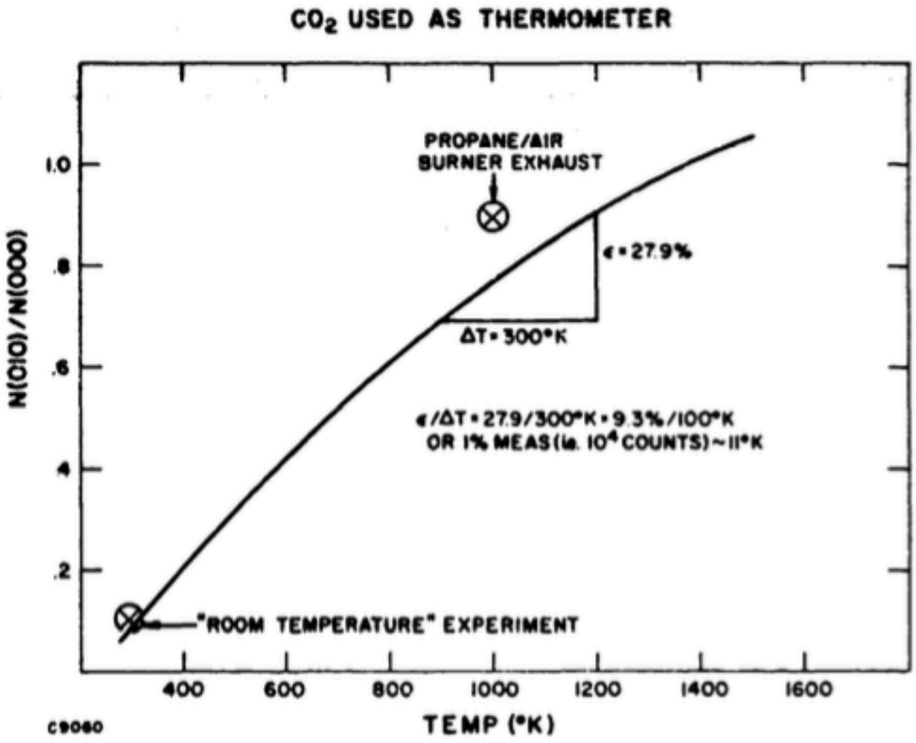


Figure 23 **The Computed Temperature Dependence of the Ratio of the Raman Scattering from the 010 Level of CO_2 to the Raman Scattering from the 000 Level of CO_2. Two Experimental Points are shown.**

Figure 16. CO_2 as Thermometer – by Raman Spectroscopy. Pg. 37 [9]

The disagreement of the high temperature data point with respect to theory is probably caused by a combination of noise and the positioning error of the thermocouple used to measure the temperature vs. the position of the laser focal point in the propane burner exhaust. More careful experiments to verify this theoretical curve and/or to calibrate the functional relationship of N(010)/N(000) vs temperature should be conducted. " [9](P.32)

3.4 RER Conclusion

The following is the conclusion to the Raman exhaust report:

1. *Excellent agreement of (Raman) 02 and CO2 measurements with conventional exhaust gas measurements and correlations with engine fuel-air ratio.*

2. *Excellent agreement with smoke number measurements, with a calibration at one point only.*

3. *Good agreement of temperature profile measurements with thermocouple data.*

4. *Total hydrocarbons were detected and compared to flame ionization measurements to within a factor of +2 over a range of three decades of concentration.*

5. *Water vapor has been detected in exhausts under all conditions. Calibration requires fundamental water cross-section data as a function of temperature, which is not now available. "*

4 Discussions

While this section will focus directly on the above RER experiment results, it will– using principles and applications known to physics – also broaden to address the implications of this work on thermoelectric and Raman spectroscopy application and theory, and our general understanding of climate and other related areas. It will also bring in applications of Raman and thermoelectric devices, and applications of atomic radiation theory, all in support of this papers hypothesis. This is a very difficult issue to put into order; my best attempt was made.

More reference and background to Raman Spectroscopy can be found at Appendix from 8.2.

4.1 Quantum – Schrödinger equation – Predicted and Raman Observed Vibration Modes

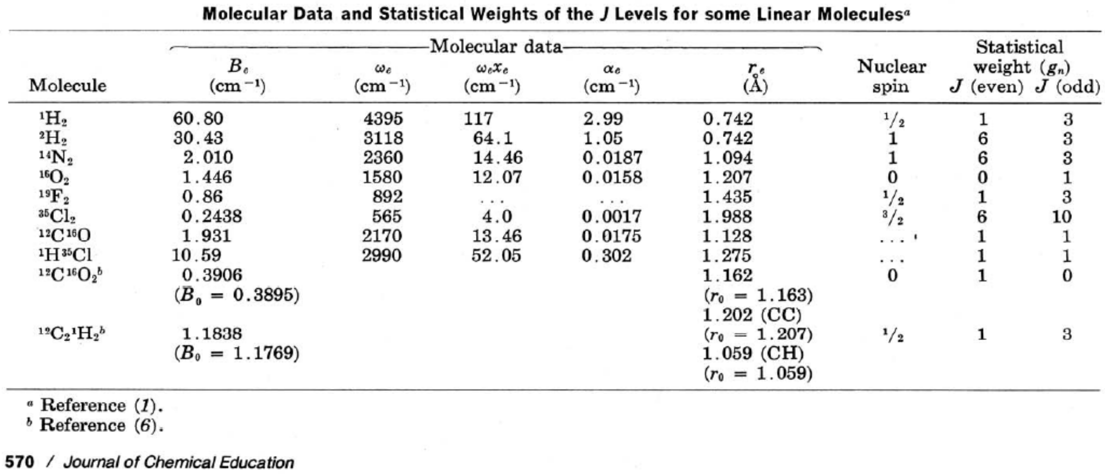
The RER observes and applies the predicted vibrational modes viewed in Table 1.

"..infrared and Raman spectra: the interaction of the molecule with electromagnetic radiation. The interaction of the electric vector of the electromagnetic radiation with the molecule will give rise to infrared absorption and inelastic scattering (Raman) spectra…"pg. 12 [11]

4.1.1 N_2 and O_2

These modes – particularly N_2 and O_2 – are predicted by quantum mechanics Schrödinger equation – the centrepiece of modern atomic physics. This prediction is consistent with standard quantum mechanics and emission spectra understanding. This equation predicts the atomic vibrational mode frequencies for all matter, including the atmospheric gases. N_2 and O_2's predicted modes are observed at the frequencies **2360 cm^{-1}** and **1580cm^{-1}** respectively – well within the infrared band of the electromagnetic spectrum, [12]. These modes are identified in the context of temperature, many papers reveal these predicted vibration functions[13], [14],[15]. Table 2 (below) is one example: and shows the predicted wavenumber where ω_e (column 3) of N_2 and O_2's predicted modes at 2360 cm^{-1} and 1580 cm^{-1}.

Table 2. Table of predicted N_2 and O_2 vibration modes derived from the Schrodinger equation [12]. The third column from the left shows the vibration mode wavenumbers. Note H_2 is predicted (and also Raman observed).



Molecular Data and Statistical Weights of the *J* Levels for some Linear Molecules[a]

Molecule	Molecular data					Nuclear spin	Statistical weight (g_n)	
	B_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	α_e (cm^{-1})	r_e (Å)		J (even)	J (odd)
$^1H_2$	60.80	4395	117	2.99	0.742	$^1/_2$	1	3
$^2H_2$	30.43	3118	64.1	1.05	0.742	1	6	3
$^{14}N_2$	2.010	2360	14.46	0.0187	1.094	1	6	3
$^{16}O_2$	1.446	1580	12.07	0.0158	1.207	0	0	1
$^{19}F_2$	0.86	892	. . .	. . .	1.435	$^1/_2$	1	3
$^{35}Cl_2$	0.2438	565	4.0	0.0017	1.988	$^3/_2$	6	10
$^{12}C^{16}O$	1.931	2170	13.46	0.0175	1.128	. . .	1	1
$^1H^{35}Cl$	10.59	2990	52.05	0.302	1.275	. . .	1	1
$^{12}C^{16}O_2$[b]	0.3906 (B_0 = 0.3895)				1.162 (r_0 = 1.163)	0	1	0
$^{12}C_2{}^1H_2$[b]	1.1838 (B_0 = 1.1769)				1.202 (CC) (r_0 = 1.207) 1.059 (CH) (r_0 = 1.059)	$^1/_2$	1	3

[a] Reference (*1*).
[b] Reference (*6*).

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GH theory totally ignores these modes of the diatomic molecules, and the 'Raman active' modes within the so-called GH gases (CO_2's 1338 cm^{-1} and CH_4's 2914 cm^{-1} and 1303 cm^{-1}). Raman spectroscopy shows these modes are real, and we shall soon learn they correspond to IR radiation theory.

4.1.2 CO_2's 1338 cm^{-1} and the Principle of Equipartition

CO_2's third QM predicted vibration mode or vibrational spectra – the mode not included in GH theory – is observed at 1338 cm^{-1} by the RER in the IR of the EMS: only with Raman spectrometers. This mode is not observed with IR thermoelectric detectors as it does not have an electric dipole moment and thus does not generate an electromotive force – more on this in a following section. By the Principle of Equipartition[16], this Raman vibrational mode should be emission equivalent to the TE/IR (GHG) modes and assumed so. If it were not for Raman spectroscopy this mode would only be predicted and not observed. That there is a mode implies there is vibration, and through the Boltzmann constant this vibration implies a temperature equivalent IR emission and absorption proportional to the vibrational energy of the mode – as all spectra lines do.

4.1.2.1 The Significance of Equipartition to Degrees of Freedom and Normal Modes

"In classical statistical mechanics, the equipartition theorem relates the temperature of a system to its average energies. The original idea of equipartition was that, in thermal equilibrium, energy is shared equally among all of its various forms; for example, the average kinetic energy per ***degree of freedom*** *in translational motion of a molecule should equal that in rotational motion.[16]"*

Normal modes (IR spectra bands) are derived from how many degrees of freedom a molecule has; and it says they are equal in their output. So it is significant; they are equal in terms of heat-energy radiation.

4.1.3 H_2O's 3652 cm^{-1}: IR/TE and Raman Modes Equivalent

The Raman observation of H_2O's 3652 cm^{-1} vibrational mode is significant as this mode is both TE- 'IR active' (as shown in figure 17 below) and Raman active; it is a 'dual' Raman-TE mode. This mode is an absolute demonstration, observation, and the practical application, via the Principle of Equipartition, that these modes are equivalent. This also shows the detectors are equivalent. What is separating our understanding of the modes will be addressed when we look at how the IR modes are derived. This discovery has massive ramifications on the outcome of this investigations conclusion, and radiation physics as a whole – water has a dual means of absorption and emission.

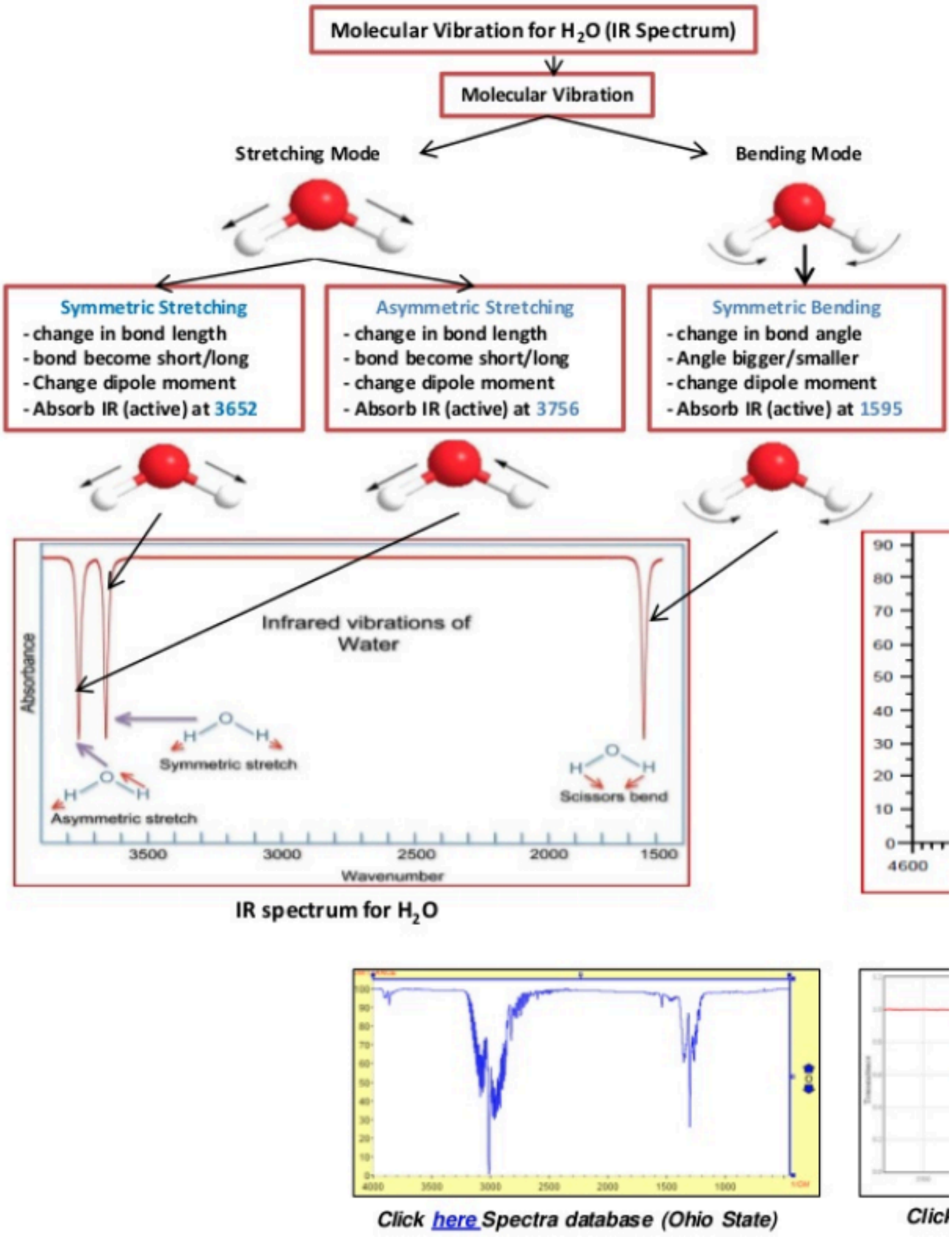


Figure 17. H_2O IR (thermoelectric) Vibration Modes and Respective Spectrum. Notice the 3652cm^{-1} is clearly shown to be IR. [17]

4.1.3.1 Contravention of the Rule of Mutual Exclusion

It appears the above H_2O 3652 cm^{-1} mode is a contravention of the rule of mutual exclusion, where "*no normal modes can be both Infrared and Raman active in a molecule that possesses a centre of symmetry*". However, H_2O is a special exception as described below.

"The fact that H_2O does not obey the rule of mutual exclusion indicates that the H_2O molecule is not centrosymmetric (it is bent). As expected, the v1 symmetric stretch is also strongly Raman active.

Band H_2O	**Infrared**	**Raman**
v1 - symmetric stretching (3652cm^{-1})	strong	strong
v2 - asymmetric stretching (3755cm^{-1})	very strong	weak
v3 - bending (1595cm^{-1})	very strong	weak

(Source, online lecture notes).

Does this mean H_2O offers the best example and application of the law of equipartition? Explanation is beyond the scope of this investigation.

4.1.3.2 Solar IR Insolation Radiation Heats Water

In the euphotic zone of water bodies: "*almost all of the (IR) radiation is absorbed converting electromagnetic energy into heat. Most of this absorption is carried out by water molecules with the first 50 metres".* Pg. 38 [18] From this it can be deduced the air ('the ocean of if) absorbs IR photons just as an ocean of water does. The question is why is this principle not so for the atmospheric gases? The answer is, as claimed here, the air does, absorb with its Raman and TE modes.

4.2 Temperature Measurement – by Raman

IR thermoelectric detectors cannot measure the temperature of N_2 or O_2 at any above absolute zero Kelvin, but here; Raman spectroscopy can not only detect the modes, they can also measure the temperature of the molecule also from the intensity or kinetic energy of the mode signal.

4.2.1 Raman Spectroscopy and the Raman Effect – No Confusion

For clarification purposes: by using the word 'Raman' is not to assume a Raman effect mechanism leading to thermal heating of the atmosphere. Pre-publishing reviewers made claims to this effect. To counter this, this paper claims Raman Spectrometers identify the predicted molecular vibrational modes of the 'non-GHGs' in the IR range of the EMS, and also the different parameters measured – such as temperature. Raman spectrometers exploit the Raman effect with their lasers. The vibrational modes of the atmosphere are described and predicted by QM and are observed by Raman Spectroscopy.

4.2.2 Temperature Detector Equivalence

From Raman RER experiment it is demonstrated the two detectors used within the IR range of the EMS, Raman and thermoelectric, are equivalent in terms of the vibrational and temperature behaviour of the molecule. H_2O's 3659 cm^{-1} mode is equivalent, (as above section 4.1) thus the detectors IR and Raman are equivalent. What is more, the temperature was measured from CO_2's Raman active 1338 cm^{-1} mode alone (3.3.2); and this value compared well and calibrated 'favourably' by Raman's complimentary instrument the thermoelectric IR detector – figure 17 above. From this, it can be implied all modes and thus molecules, are equivalent; they are only separated or discriminated by the detector 'observing' them. The RER shows temperature measurement of all atmospheric gases can be made reliably and accurately from the Raman vibrational modes alone; the Raman detector on its own could measure and quantify the 'special GHGs' (thermoelectric gases). As evidence to this Raman instruments is used as an instrument of choice on solar system space probes– more on this in a following section.

From the above equivalences, we can say a GH atmosphere without this Raman vibrational mode knowledge is incomplete: these Raman temperature observations are not – as it stands today – used or discussed in GH theory and they should.

4.2.3 Raman Temperature Measurements and the Boltzmann Constant

By the Boltzmann constant, the observation of these and all vibrational modes at the said predicted frequencies, and their respective temperature measurement thereof, implies these modes are moving and thus are radiating IR. By observation, from this experiment, these modes are radiating – IR heat – consistent with thermodynamics and quantum mechanics; if they were not there would be a contradiction.

4.2.4 Raman Measurements and the Stefan Boltzmann Law

As both N_2 and O_2 – independently – show a temperature value, as measured by Raman laser detectors, they must be said to be radiating in accordance to the Stefan-Boltzmann law. The Stefan-Boltzmann law is a central pillar to radiation theory, and states the following: expressed mathematically as E = σT4.

This Raman signal is in total contrast to current GH theory – where it is not allowed. This misconception can only be due to the Raman detectors measuring the N_2 and O_2, and the TE/IR detectors not measuring it. This finding has direct significance to blackbody radiation theory and suggests it is incomplete, requiring updating with respect to the Raman observations made here, and everywhere in the fields of modern chemistry and physics.

4.2.5 N_2 and O_2 and Planck's Law

The above claim also pertains to Planck's Law. Planck's law – with the addition of the Raman-IR modes, suggesting they are 'blackbody' emitters – will require amending.

4.3 Thermoelectrics: Deriving the 'Standard' GHGs

From the Raman Exhaust Experiment we can deduce all the modes of atmospheric molecules emit and absorb IR radiation in accordance with quantum mechanics – they are all GHGs. We need now to explain how it is we have come to believe in a special – select – set of 'GHGs' derived by TE/IR alone – totally ignoring the quantum mechanics predicted and observed Raman modes? This section of discussions directly addresses this question.

To show the role of thermoelectric transducers have played in GH theory – I first want to first show their direct role in the fundamental 1859 GH experiment, and then show how thermopiles work. This will be followed by an analysis of the current modern technology applications of this technology, in such things as non-contact IR thermometers, and thermal imaging cameras. I will end this section by connecting thermo-electrics to infrared spectroscopy, where I shall show how and where – consistent with all their properties – these spectrometers only show one part of reality – the thermoelectric electric atmosphere. In this section I will need to show what TE/IR spectrometers produce, how they produce, and importantly what they do not produce – and explain why not. I need to show they are inadmissible (as they are currently used) as an instrument if used on their own, and without their known complement – Raman spectrometers. By the end of this section, we shall understand they are best-termed TE-IR spectrometers – as hypothesised – from the fact their output is purely produced by their thermoelectric measurements.

4.3.1 Historical Order of IR Spectroscopy

Before we start, a quick look at the order and history of discoveries and claims; it reveals a lot on its own. The developmental history of IR-thermo-electric spectroscopy, and as a direct consequence the GHGs is all 19th Century, pre-quantum mechanics knowledge; the Raman active – non-GH gases – modes are all the domain of the 20th Century quantum mechanics – and are indeed on their own identified only by quantum technology, lasers.

It should be made clear this investigation should not undo the merits of TE-IR spectroscopy per say; it rightly reveals part of the IR atmosphere. Science should have been searching for the other ‘part’, and questioning the extrapolation made from its incompleteness. Also, it should be noted that Tyndall (and others) did not know why these gases were special; it took quantum mechanics to explain that, and that was yet to come for them in the mid 19th Century.

How the thermopile operates will be covered in the next section.

4.3.2 The Tyndall Experiment: the Thermo-electric, Transducer Derived GH Atmosphere

In 1859 John Tyndall [19],[20] published his analysis of the atmospheric gases using the newly developed thermopile transducer and galvanometer [21],[22],[23],[24],[25]. Previous to this experiment the entire atmosphere was thought to consist of – as posited by Joseph Fourier in 1828 – only ‘heat trapping’ gases; all acting as a ‘greenhouse’, and insulating the earth. Tyndall redefined this group of all gases to consist of ‘small’ group of special gases that specifically – by his experiment – absorb and emit infrared [26] thermal radiation.

Below (figure 18) is the setup of Tyndall’s experiment: he isolated all the atmospheric gases between a heat source and a thermopile, and analysed them for their change in electric flow – measured by the galvanometer.

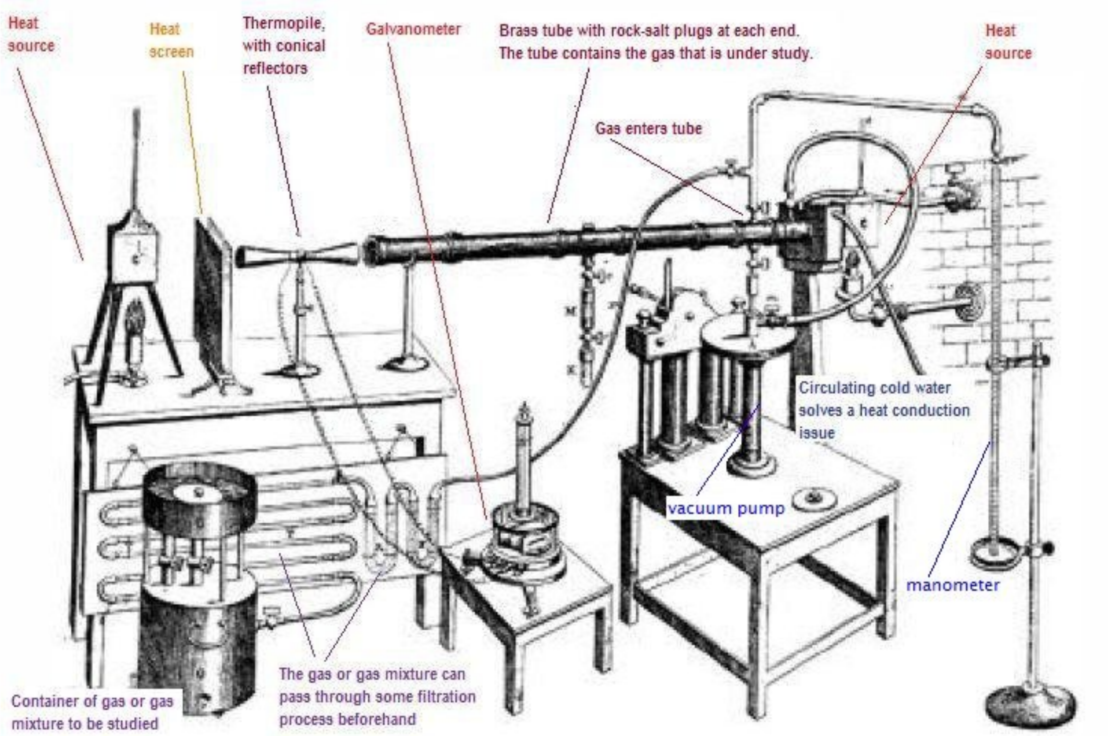


Figure 18. Tyndall's 1859 Setup For Measuring Radiant Heat Absorption By Gases. The apparatus clearly shows thermopile, galvanometer and heat source. [21]

Tyndall noted – from the gases that moved the galvanometer – N_2 and O_2 did not appear to be affected by the heat source; while others, including H_2O, CO_2, CH_4, NO_2, and O_3 did. He concluded from this the latter group of gases absorbed the thermal radiation; while the former did not. From this, the latter group is today known as the GHGs: and the former – N_2 and O_2 – as the non-GHGs, and these non-GHGs were thus assumed to be transparent to thermal radiation.

This discovery – on its own – sounds convincing and plausible, even special; but with knowledge of thermopiles, thermoelectrics and the Seebeck effect – not to mention modern quantum mechanics and the (above) Raman instruments – it is not.

4.3.2.1 Tyndall IR Thermoelectric Misconception

To reiterate – based on the following facts about thermoelectrics – I claim what John Tyndall really discovered, by the thermopile transducer, are not the 'special' heat-trapping gases but rather only the gases of the atmosphere that are thermoelectric (TE) – the gases that generate electricity via the Seebeek effect and TE transducers. If we were to generate electricity with a thermoelectric- pile transducer from hot gases, which we could, we would source the same apparatus as Tyndall's experiment above. However, while it is possible to generate electricity from these select gases, the amount is so small it is uneconomic; if this were not so, we'd be doing it. More on this in the coming sections.

4.3.2.2 *Unrecognised Seebeck effect in MS Word*

It should be pointed out before going further: the mere typing of the words 'thermoelectrics' and 'Seebeck' triggers the spellcheck of my MS Word word-processor, suggesting this knowledge is not at all disseminated as other science. Similarly, few – if any – of modern general (university and school) science textbooks have the topic thermoelectrics in them – it was from physics online the knowledge for this investigation was found.

4.3.3 TE (Thermoelectric)/ IR Spectroscopy

The next set of instruments in the thermoelectric transducer family to also exploit thermoelectrics, and also misinterpret what they detect, are termed 'IR' spectrometers'. They are at the centre to the field of what is termed incorrectly 'IR spectroscopy'; they are more correctly termed TE (Thermoelectric)/ IR Spectroscopy. They are the modern instruments that define the said special GH gases, and without this assumption, would be assumed all the gases trap heat – just as posited by Joseph Fourier in the early 19th Century.

TE/IR spectrometers are the modern version of the Tyndall experiment – and they (I claim) share the same flaws as the Tyndall experiment, in that they discriminate on N_2 and O_2. They – whatever the thermoelectric detector method – share the same properties or problems of the TE/IR cameras and TE/IR thermometers, and CO2 sensors: they do not measure all matter, they discriminate on what is not TE. They imply these gases do not interact with 'light', and thus are not greenhouse gases. As this must be wrong – if not impossible – understanding TE/IR spectrometers will help us understand where we have gone wrong forming this paradox.

One truth about them is they are incorrectly thought to be the only proof of how radiating light – in the form of IR electromagnetic photons from the Sun – interacts with matter, and in particularly – for this investigation – the atmospheric gases..

4.3.3.1 *TE/IR Spectrographs*

TE/IR spectrometers measure or record the entire infrared range of the electromagnetic spectrum frequency by frequency by comparing a sample to a reference heat source. They reveal – as can be seen in the spectrograph below (figure 19) – the quantum mechanics predicted vibrational modes or emission spectra that possess 'asymmetric electric dipole moments' such as (there are others): H_20's **3652 cm^{-1}** (2.74μm), **1595 cm^{-1}** (6.25μm), and **3756 cm^{-1}** (2.66μm); CO_2 's **2349 cm^{-1}** (4.257μm), and **667 cm^{-1}** (14.992μm); CH_4's **3020cm^{-1}** (3.312μm), **1508cm^{-1}** (6.5μm), and O_3's 1103 **cm^{-1}**, 701 **cm^{-1}**, and 1042 **cm^{-1}.**

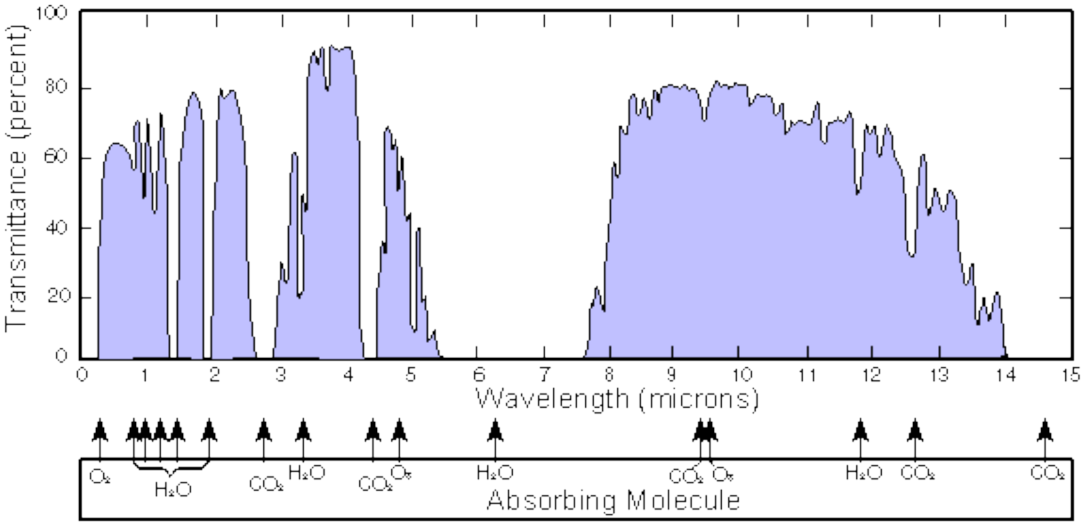


Figure 19. Infrared Spectrograph of the atmosphere [27]. This spectrogram does not take into account Raman modes and thermoelectric principles. See 4.4.4 for a correct interpretation of this spectrograph.

4.3.4 The IR Dipole Misconception

Here is the crux of the problem. The above modes all have one thing in common, defining them as 'IR active' and part of a GHG molecule, and that is they all have asymmetric modes with '**electric dipole**' movements. Standard GH theory definitions clearly state this; however, when it is understood the thermoelectric transducers receive these 'thermal' - 'electric' signals, only from these modes, just like a radio receives electromagnetic 'radio' signals, common sense prevails. Those modes that do not have electric diopole moments are not received and incorrectly interpreted as non-thermal/ non-GHG. The following highlights this current understanding:

Diatomic molecules are observed in the Raman spectra but not in the IR spectra. This is due to the fact that diatomic molecules have one band and no permanent (electric) dipole, and therefore one single vibration. An example of this would be O_2 or N_2.[15]

For some reason the 'electric' in these 'electric dipoles' definition is interpreted to explain the thermal in the 'GH' atmosphere, and this is wrong. Of course, if we want to observe these non-TE modes, Raman Laser is the solution.

In section 4.5.4 below I describe how the spectrograph is really produced.

4.3.5 TE/IR – Transducing – Spectrometer Configuration

To show the dispersive TE/IR spectrometers are the same in principle as the CO_2 sensor (explained below) and Tyndall experiment setup, and only measure electricity production from the radiated heat, we need to look at the component parts of the instrument and deduce how it works. The following schematics (figures 20 and 21) show the working of a typical dispersive IR spectrometer [28] and the Fourier Transform IR (FTIR) spectrometer. I shall demonstrate both these share the same principles: transducer detectors, heat source, separate sample and empty reference/control tubes or cells; but differ in that they have a 'splitter' that can split and read output from a specific band of the electromagnetic spectrum, and by this create a graph – a spectrograph – as shown above.

4.3.5.1 The dispersive IR Spectrometer:

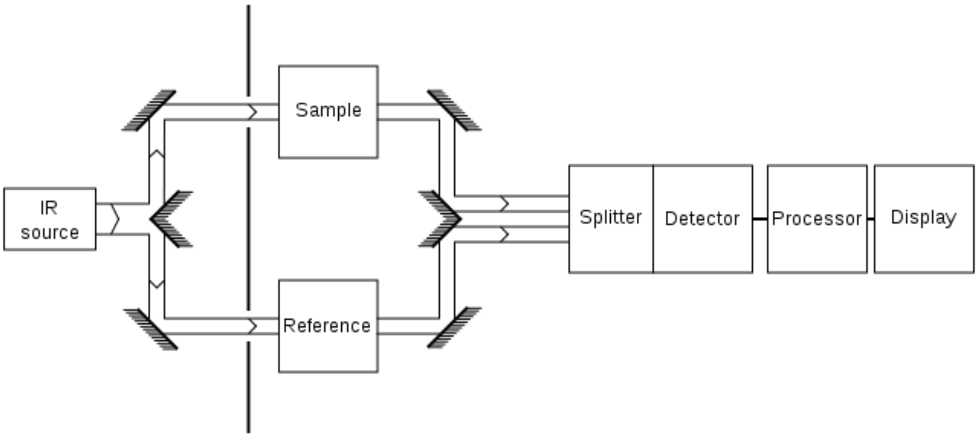


Figure 20. Operations Schematic of Dispersive Spectrometer [29], [28]. Notice the splitter and the division from the reference (control) and the sample.

Just as with the CO_2 sensor, the IR (heat) source of the dispersive 'IR spectrometer' is heated to a considerable temperature – some 1500°C (3:40 [30] – with this high temperature the relatively low temperature of the sample will stand out. Also, notice glass is not used to prepare samples, but Sodium Chloride (NaCl) salt plates or Potassium Bromide (KBr) are used. These slides or plates are said to be transparent to IR radiation; but, this is not so – and is misleading, it is that they are non-thermoelectric, or are at least, less so.

4.3.5.2 The Fourier Transform IR (FTIR) spectrometer

The FTIR has a different configuration, but the main features remain: 'sample compartment', 'source' (heat source), and 'detector'.

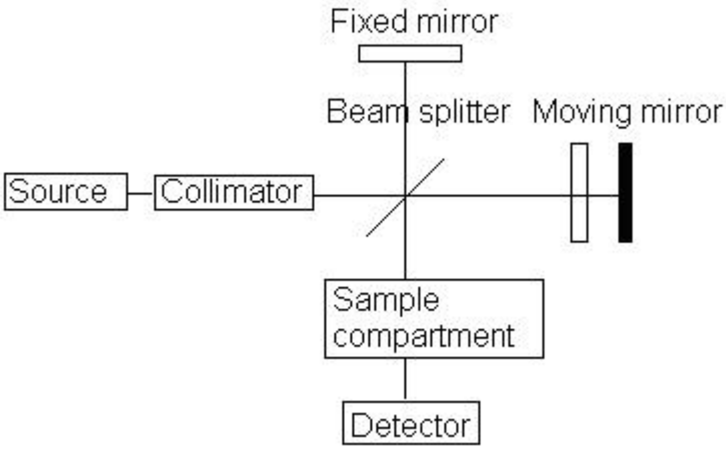


Figure 21. Operations Schematic of Fourier Transform IR (FTIR) spectrometer [29].

4.3.6 All 'IR Spectrometers' Detectors are Thermoelectric (TE/IR) Transducers

It can be shown – contrary to standard belief – all 'IR spectrometers' [31] use thermoelectric transducers[32] [33].

"Thermo detectors mainly classified into: (1) ***thermopile*** *detectors that change in electromotive force, (2)* ***bolometers*** *that that change resistance, (3)* ***pyroelectric*** *detectors that change in dielectric surface charge, (4)* ***diodes*** *that change in voltage."* Pg 2 [34]

With the likes of, for example, Mercury Cadmium Telluride (**MCT**) spectrometers, it can (also) be inferred –by the similarity of their respective output – they too are TE detectors. All show the same results and do not detect non-thermoelectric vibration modes of N_2, O_2, CO_2 and CH_4 and so on. They also do not fully detect solid Germanium or CL_2. This includes Golay cells where they as they are included as transducers – slide 16 [35].

The photodiodes are used as a detector of UV light, presented on a spectrograph. The detector differs from the thermopile in that it, as far as can be found, does not discriminate between molecules as with the thermopile. Evidence of this is in the how samples can be in glass and plastic [36]; this is not possible for IR spectroscopy as explained.

A final note to this section; all spectrometers are named after what band of electromagnetic spectrum is radiated in – microwave, UV and so on – IR is also named for the same reason. The problem arises when it is understood there are two methods of detecting all the samples vibrational bands, Raman and thermoelectric. For this reason, I suggest the names TE/IR and Raman IR.

4.3.7 The Misconception, and Fallacy of 'IR Spectrometers' Radiating the Sample

'IR/TE spectrometers' – and all other 'IR' technology - share the standard assumption the sample gases are radiated with IR light (heat), and as a result the – what is termed – an 'IR spectrograph' (shown) is produced revealing the said (above) corresponding absorption/emission spectra at the said modes; and hence, because of the thermal radiation, we have the name 'IR spectroscopy'. This assumption is most likely inferred from the following is a standard definition of spectroscopy; pointing to it being a study of light (photons) radiating a sample:

*"**Absorption spectroscopy** refers to **spectroscopic** techniques that measure the **absorption** of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field."[37]*

Samples may be radiated for the many types of spectrometers: gamma, X-ray, UV, visible, and microwave; however for 'IR' is not so, as we shall now investigate.

4.4 The Thermo-electric 'Detectors': How Transducers Function

To develop our knowledge further we need to first understand how the Tyndall GH deriving apparatus works and how they are connected to modern knowledge and instruments. In the case of GH theory and other so-called IR radiation areas, it is not deduced correctly: thermopiles and the like transduce an IR heat signal into electricity – hence the term 'thermo-electrics' infrared. But, as we shall see in this section, just as with the TE-IR spectrographs, they do not transduce everything.

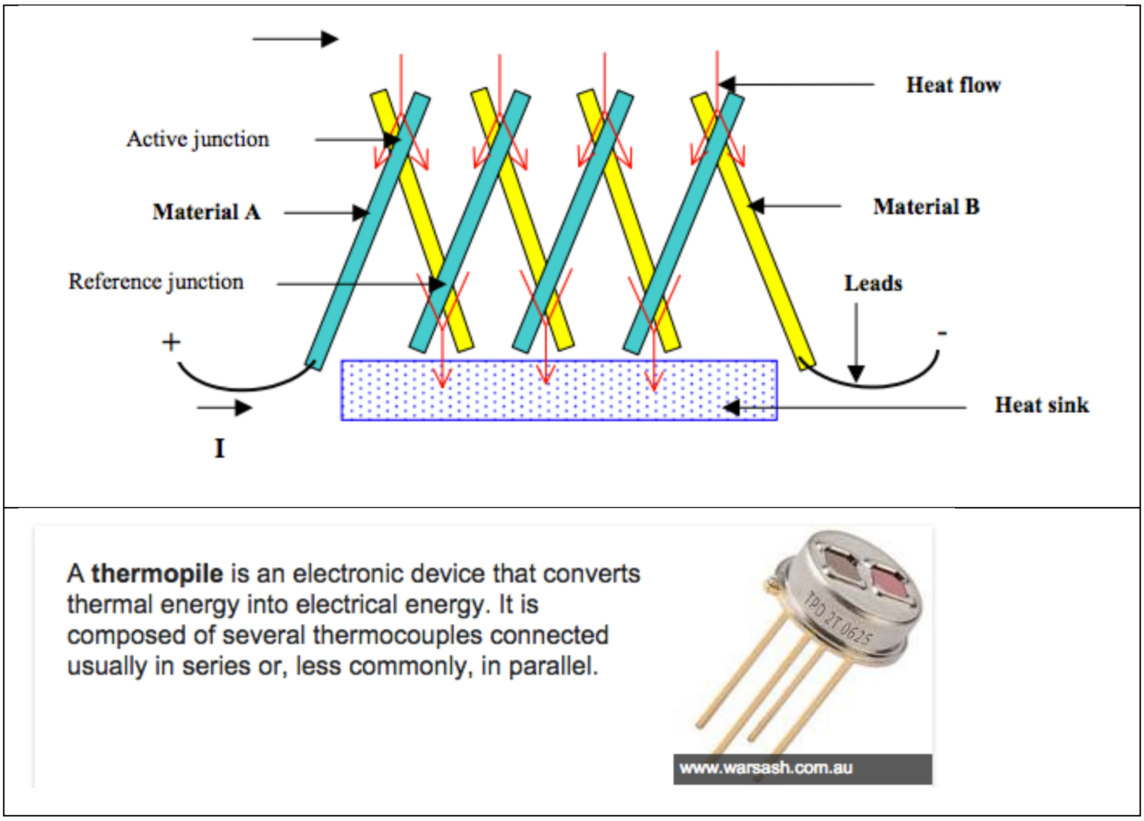
4.4.1 The Seebeck Effect, and the Thermocouple and Thermopile [38]

In 1821, Thomas Seebeck [39] discovered electricity current was produced when two metals – of different kinds – are joined at one end and were exposed to 'hot objects. He discovered what to be known as the thermocouple [40]): with a device to measure the electric current – or electromotive force (EMF) – the electric current produced was found proportional to the IR Temperature (**T**) as given by the following equation

$$\boldsymbol{E_{EMF}} = -\boldsymbol{S\nabla T} \tag{1}$$

where the **S** is the Seebeck coefficient (also known as thermo-power). This discovery is said to be one of the most important breakthroughs in the history of science and engineering: we could accurately measure temperature for the first time.

Thermopiles are many thermocouples connected together in series (figure 22).



A **thermopile** is an electronic device that converts thermal energy into electrical energy. It is composed of several thermocouples connected usually in series or, less commonly, in parallel.

Figure 22 Thermopiles. Above, schematic of a thermopile [41] ; below, The Modern thermopile. [42]

4.4.2 The Thermopile a Heat to Electricity Transducer

The thermopile is a transducer: it converts one form of energy – IR radiation – into another – electricity. The voltage output relationship is shown below in the figure below: as temperature rises, voltage output increases.

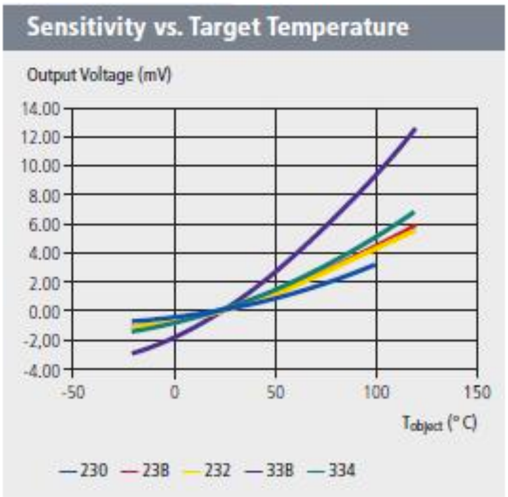


Figure 23. Thermopile Voltage output by Temperature

4.4.3 Thermoelectric Substances

In the context of TE transducers, TE substances refer to - unlike current reference – the substances detected; and not the substances used to detect.

Before we go deeper into the chemistry as to why some substances are TE while others are not, an important starter: while all substances radiate IR heat – by the laws of quantum mechanics and thermal dynamics – not all substances are thermoelectric. This may seem trivial; however, in the light of modern climate science – and where it has lead us – it is not. What Tyndall's experiment revealed are only **the gases** that generate electricity via the thermopile, not the other phases of matter. Had he equally tested the solids and liquids for the same property, he would have found similar patterns amongst these.

4.4.3.1 TE Solids and Gases

While most solids are TE, only some substances – like water and ice – transduce a near perfect electric signal to correspond with the real temperature of the substance: shiny metals conversely deliver a very poor signal and require a near 100% correction. This correction factor between thermoelectric transduction and the real temperature is what is termed the *emissivity* of a substance; this subject 'matter' is open to further research as a consequence of this investigation.

4.4.3.2 Greenhouse Liquids and Solids – Water and Glass

By GH reasoning, where it is deduced – by thermoelectric transducers – the GHGs are transparent to the visible spectrum, and 'opaque to the IR', Water should be known as a GH liquid, and transparent *glass* a GH solid. They are both transparent to the visible, and also said to be opaque to the IR. Of course, the reality is – as deduced by this investigation – water and glass are TE and no more special than other matter, even if they are not claimed to be. Thermoelectric glass is the reason Tyndall did not use glass to contain the gases in his experiment; he instead used (presumably non-TE) salt crystal. It is also why IR thermal cameras do not use it.

4.4.3.3 Non-TE Gases, Solids and Liquids

While the atmospheric gases N_2, and O_2 – as reasoned in this investigation – are non- TE, so too are Hydrogen (H_2), Helium (He) and possibly Argon, and all for the same physical reasons, as we shall come to see. Interestingly liquid Oxygen is non-TE just as its gaseous form; it will not generate an EMF at any temperature. Non-TE solids include Germanium (Ge), Sodium Chloride (NaCl) – or salt plates (as used in Tyndall's experiment); Potassium Bromide (KBr); and to some extent the plastics.

As a final word for the gases: it is no coincidence these non-TE gases above are known as – in the case of GH theory – 'the non-GHGs'; and we must remind ourselves they are (wrongly) assumed not to absorb IR heat; when the fact is they are simply non-TE, and have been misinterpreted.

4.4.4 Thermoelectric Interpretation of the Atmosphere

I contest, as stated above in 4.3.7, the assumption IR spectrometers radiate samples, and claim the spectrographs show the thermoelectric dipole moments or emission spectra of the said (atmospheric) gases – within the EMS. They are only gases able to be detected by the thermoelectric transducer/sensors. The thermoelectric infrared (TE/IR) spectrograph of the IR atmosphere is shown (below): the only difference from the former interpretation is the spectrograph is produced by the difference between transduced – measured in thermal EMF voltage – sample (IR radiation) and a reference source's IR (1500^0C) radiation.

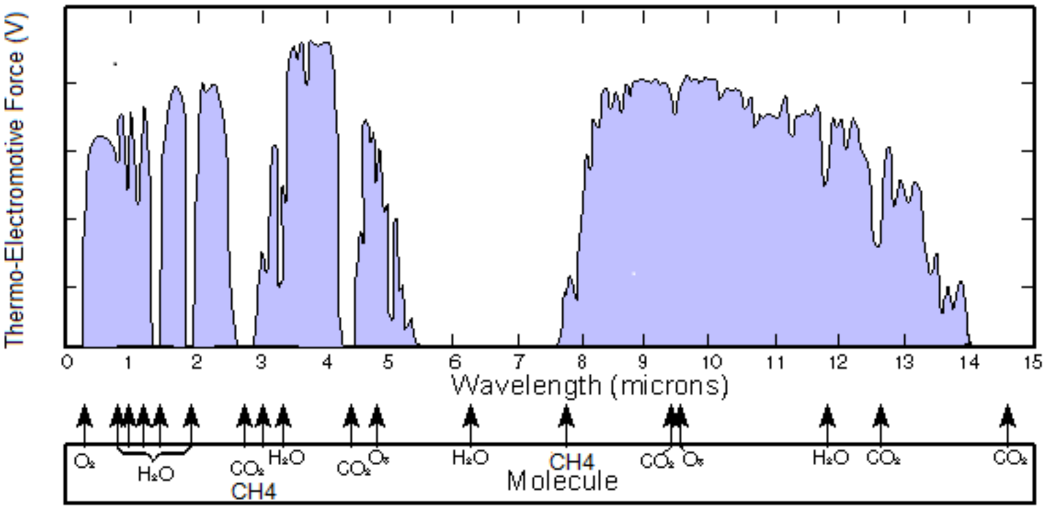


Figure 24. Thermo-electromotive Force and the Electromagnetic Spectrum. Thermoelectric vibration modes identified by thermoelectric transducers; currently known as the greenhouse atmosphere. The Raman modes are missing.

The black line in the absorption interpretation is explained by 'intensity' or 'transmittance' – inferring the samples are radiated; with the thermoelectric interpretation it shows the measured electricity production (EMF) from the heat source – at that particular frequency or wavenumber – and the dips show lower voltage, as the heat radiation from these sample gases measured is at a considerably lower energy (temperature) than the control heat source; i.e. it is cooler.

It should be noted: 'IR spectrometers' need to be purged of the thermoelectric (greenhouse) gases before use; this is to be sure only the heat source is measured and not any other thermoelectric gas.

It should be made clear the above modes do absorb and emit IR radiation as claimed – this is not contested in this investigation; the point of this paper is to say they are not the only modes to do this. Notwithstanding this, it does not mean the instrument operates as assumed: the samples are not radiated, just as the glass is not radiated in the above hand /glass IR thermometer demonstration. Also, if they did radiate the sample, then – by the law of equipartition all matter should interact with the (IR) 'light', and all modes – whether TE/IR or TE Raman.

4.4.4.1 Spectroscopy Beer-Lambert Law

Below (figure 25) is a schematic shows how spectrometers produce what they display. Again, the samples are not being radiated as such; but rather the detectors measure the difference between the reference radiation and the sample radiation.

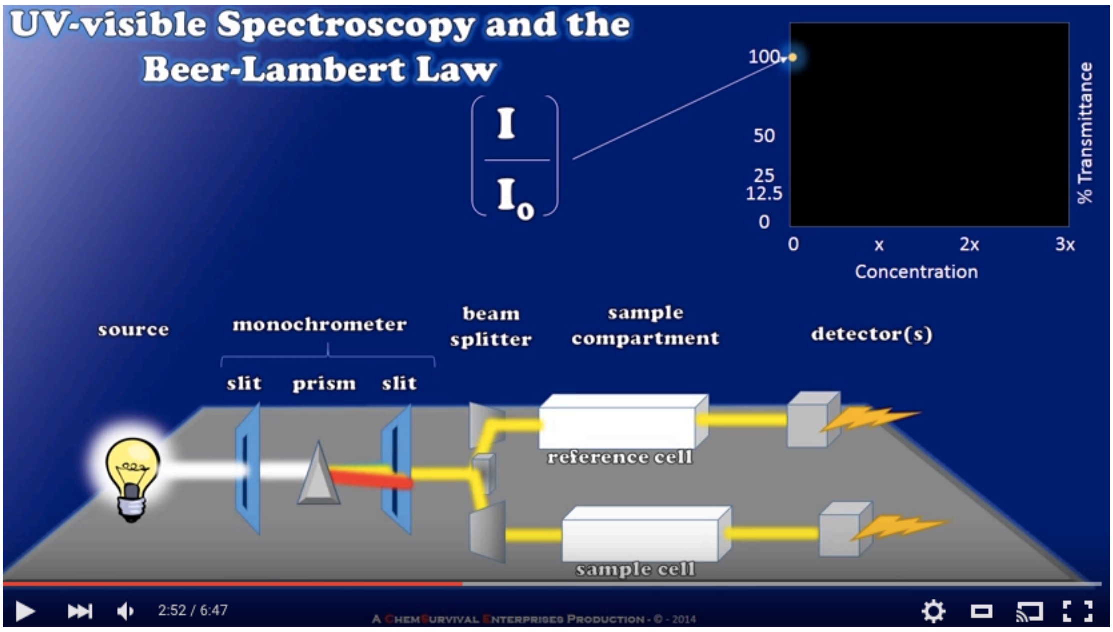


Figure 25. UV Spectrometer [43]

Spectrographs are said to be determined in terms of **transmittance** (T) through the sample by the following equation:

$$T = I / I_0$$

where **I** is said to be the **light intensity** after it passes through the sample, and $\mathbf{I_0}$ is the **initial light intensity**. Again, this interpretation ignores the role of thermoelectric transducers, and the TE properties of the substances measured.

4.4.4.2 *Blackbody Measurement*

The control tube, or reference cell, of the 'IR' spectrometer, will measures only the electricity produced from – what is termed – a 'black body' heat source, and nothing else, and not the common air in the tube (mostly N_2 and O_2). This is because the 'air' is not thermoelectric.

4.4.5 Analysis of the CO_2 Thermoelectric Emission Absorption Spectra

Below is TE/IR spectrograph for CO_2: it clearly shows CO_2's absorption bands that are shared electric dipole moments – at **2349cm^{-1}** and **667cm^{-1}**; however, what it does not show, is CO_2's 3rd symmetric (no electric dipole moment) band at **1388cm^{-1}** – thought there is a small hint of it in the figure at that wavenumber.

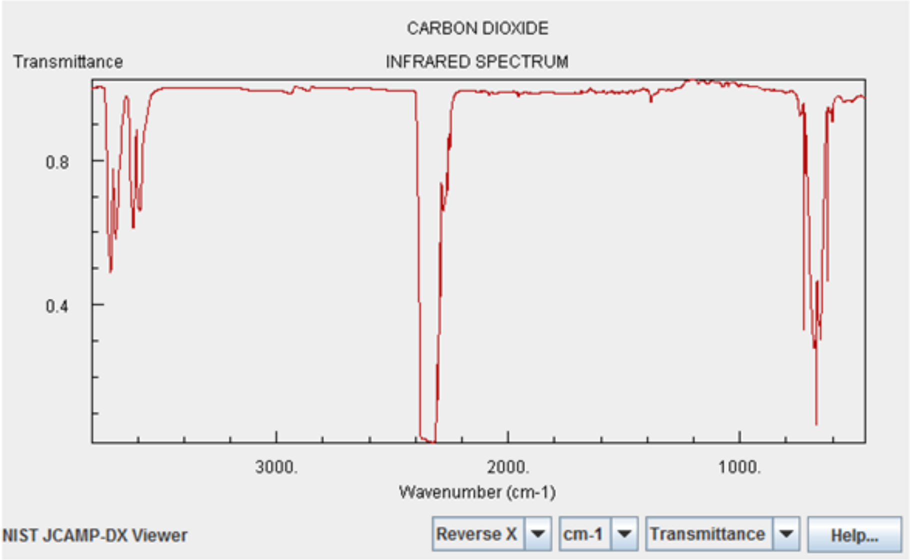
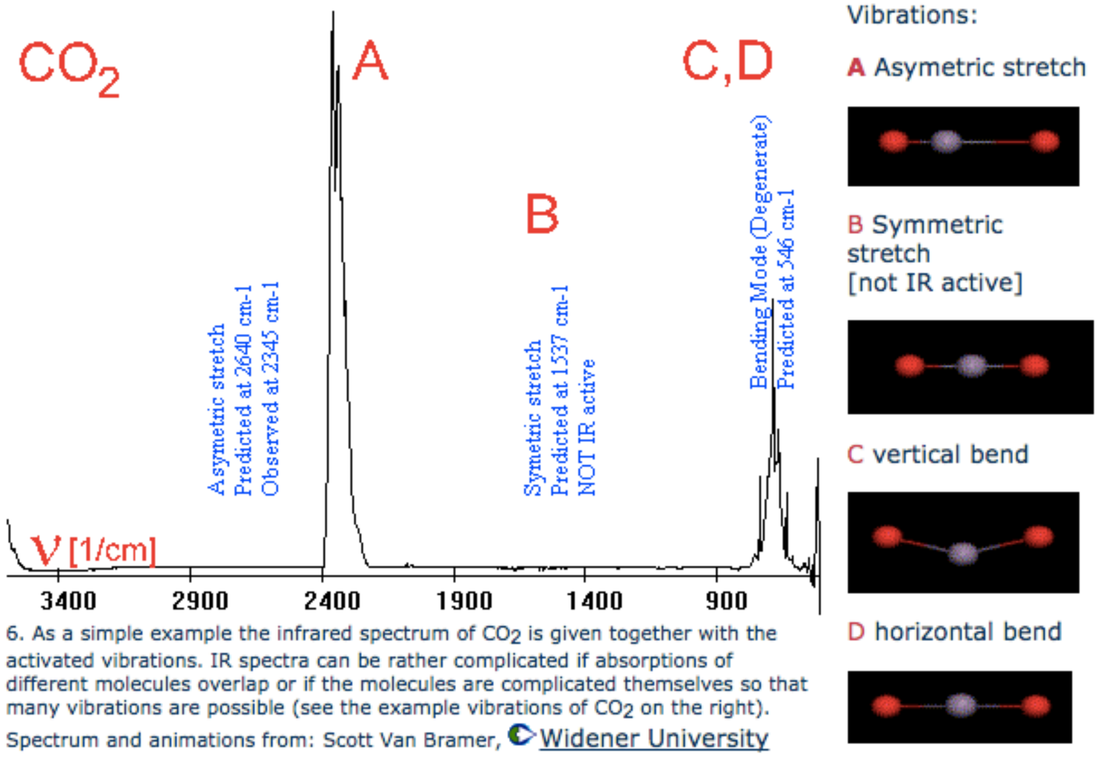


Figure 26. CO_2 transmission spectra. [44]

And below is the inverse diagram of the above spectrograph showing the absorption bands of the molecule. Again, the strength of the 'greenhouse' gas CO_2 is shown. Note the absence of the symmetric vibration modes (B) in the spectrograph and only the presences of asymmetric vibration modes A, C, and D



6. As a simple example the infrared spectrum of CO_2 is given together with the activated vibrations. IR spectra can be rather complicated if absorptions of different molecules overlap or if the molecules are complicated themselves so that many vibrations are possible (see the example vibrations of CO_2 on the right).

Spectrum and animations from: Scott Van Bramer, Widener University

Figure 27. CO_2 Thermoelectric IR Spectra. Showing CO_2's IR active vibrational modes and one non-IR active. [51] 1538 cm-1 clearly shown absent; incorrectly indicated as 'not IR active' when it is more correctly non-thermoelectric due to symmetric stretch.

4.4.5.1 Atmospheric CO_2 TE/IR Spectra

The figure (28) below shows the effect of CO_2 gas when added (in clockwise) into the sample cell of the TE/IR spectrometer: the greater the concentration, the greater the 667 cm^{-1} band is indicated. The thermo-electric explanation for this is the CO_2 add is at a lower temperature that of the 1500°C reference cell and thus generates a lower EMF at this band. The more the concentration, the greater the offsetting EMF production; but not enough to out-produce the reference heat source.

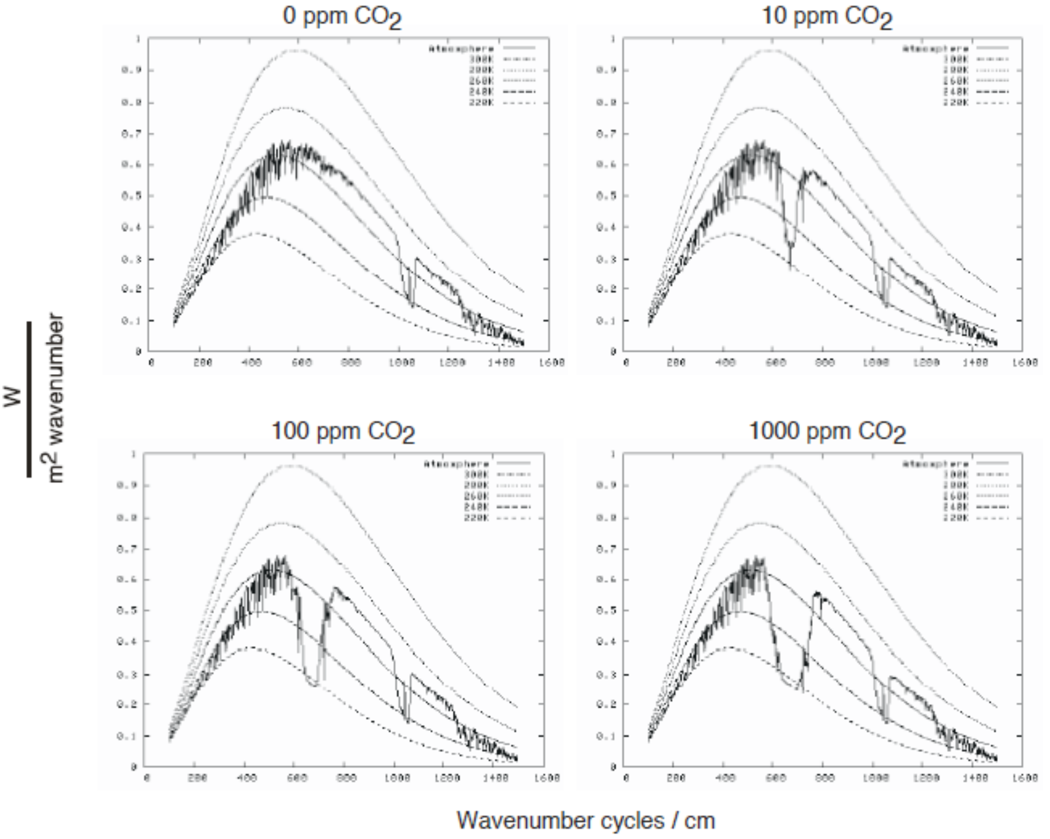


Figure 28. Thermoelectric Spectra of CO_2 at $667cm^{-1}$. Increased CO_2 concentration – from 0 ppm to 1000 ppm – produces thermal EMF revealing CO_2's 667 TE band.

Note the CO_2 EMF is not equal to the heat source just as the candle flame can still be seen in the image figure 8c (Stewart demonstration) with high concentration CO_2.

4.5 Modern Applications of the 19th Century Thermopile

Today, the thermoelectric thermopile Tyndall and modern instruments use is ubiquitous and can be found in hardware such as the handheld non-contact IR thermometer, early thermal imaging cameras, and early IR spectrometers. These new technologies all have the same problems Tyndall's discovery in that they register or discriminate the same properties of the substances measured.

We shall now look at each of these instruments and identify the same problems.

4.5.1 The Non-Contact IR Thermometer

The regular non-contact IR thermometer (IR thermometer) shares the same core technology, the thermopile, as used to derive the GHGs, and so it offers an easy to use and relatively cheap device (20 U.S dollars, 2018) to learn and understand the special GHGs. The IR thermometer measures IR radiation from 8 to 14 microns on the electromagnetic spectrum (EMS), in what is termed the atmospheric window [27]. They measure the temperature of most substances quite well, but they must be adjusted for the emissivity of the respective substances; for instance, when used to measure the temperature of shiny metals they do not show the real temperature by some 90% revealing a flaw or issue with the thermopile that must be addressed.

4.5.2 The IR thermometer and the Hand-Glass Demonstration

Figure 29 below shows how the IR thermometer discriminates between different substances, in this case, glass and air. The interpretation of what is happening in this demonstration is right at the core of radiation theory: is it the device is detecting IR thermal radiation or is it generating electricity from special substances? Does glass (specially) absorb IR radiation or is it – compared to the 'air' – thermoelectric?

Firstly, (frame A of figure 29) the IR thermometer is pointed at my hand: the temperature of my hand – as indicated – is measured at around 32.9 °C; then (frame B) it is pointed at a 3mm thick pane of glass, and the temperature indicated of the glass is around 21.2 °C.

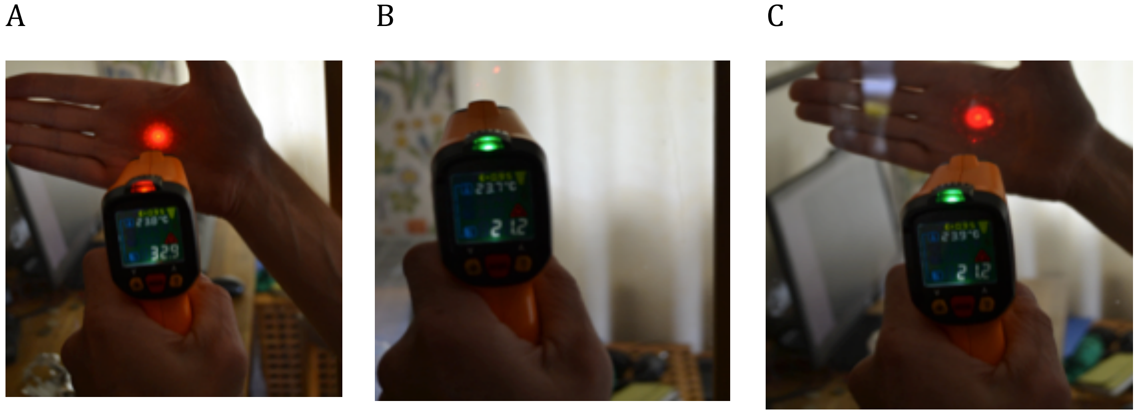


Figure 29. Non-contact thermoelectric thermometer 'transparent glass demonstration. Frame A, hand temperature measured directly as 32.9°C and the ambient temperature 23.8 (red light indicates wrong emissivity match); frame B, the temperature of glass measured as 21.2° C (green light indicates correct emissivity match); and Frame C, hand temperature through glass measures at 21.2 °C (the temperature of the glass). Notice the temperature of the 'air' is not measured with the instrument, but the glass and the hand.

Lastly (in frame C) the gun is pointed at my hand with the glass in between. Before knowing the indicated temperature the question is: will the IR thermometer measure the temperature of my hand – through the glass, or will it measure the temperature of the glass? Most answer, when asked, it is the hand that is measured. This is wrong. When the same visibly transparent glass is placed between my hand and the device, it does not measure my hand's temperature, but the temperature of the glass; in fact the instrument does not detect my (indicated) 32.9°C hand at all, but shows the same temperature as frame B, 21.2°C. My hand – through the glass – is visible to the eye, but is invisible, or opaque, to the IR thermometer. Right here, there is a divide in interpretation of what's happening: one by radiation and greenhouse reasoning where the glass is absorbing – as if it is radiated by a beam of IR photons – the IR radiation from my hand; and the other by thermoelectric (TE) reasoning – the glass is thermoelectric and is generating a current proportional to the radiant temperature (or energy).

The fact is the glass is TE as explained in the section above: glass is a thermoelectric substance.

There is another question that can be posited from this demonstration – which will help to understand the derivation of greenhouse and current radiation theory – and that is: what is not being measured? Or, what is not mentioned, in frame A other than my hand and the detector? It is the ambient air* (temperature) between my hand and the detector. (* assumes= 100% N_2 and O_2 mix)

While being visibly transparent, air*; (as claimed in this paper) is non-TE – unlike the (similarly) visibly transparent glass in frame B and the of the said GHGs. There is a paradox here and it is the air* in this demonstration (and universally) does – of course – have an 'ambient' temperature; however, an IR thermoelectric thermometer cannot, and will not, measure the air* temperature – whether at ambient room temperature (if the room temperature were measured by a regular thermometer), or whether outside – in extreme sub 0°C, or conversely, high temperatures.

Returning to frame A (figure 4): what if the same demonstration was undertaken in a bath of GH (or TE) gas – say CO_2? What would the detector measure then? Of course, it will measure the temperature of the CO_2, and not my hand – just in the same way it measured the glass in frame C. If we can describe and understand CO_2 to be TE we should equally be able to describe and understand glass to be 'a GH solid'.

The outstanding question from this demonstration – that is addressed directly in this paper – is whether or not the air* absorbs and emits IR photons: the Raman Exhaust Report shows it does.

4.5.3 CO_2 Sensors

Regular CO_2 concentration sensors use a thermopile transducer – exploiting the Seebeck effect (though this is not how they are explained in most references [46],[47], [48], [49]). In general, the operation is similar to the IR thermometer and the hand-glass demonstration above in figure 3, and demonstrations in figures 5 and 6. Instead of measuring the temperature of my hand through the glass, the CO2 sensor is more controlled. To measure the concentration of a sample, the sample is let in between a constant reference heat source, and the thermopile detector. Then a ratio calculation of the difference in signal between a sample and a reference heat source is computed. In principle, a 100% sample of CO_2 will transduce more than the heat source and in effect block out the heat source by 100%.

4.5.4 'IR' Thermal Imaging Cameras

Using the same principle as the 'spot measuring' IR thermometer, the IR thermal imaging camera measures an array of thermoelectric 'spots', able to be viewed – with modern screen technology. 'IR' cameras originality used a thermopile thermoelectric detectors [50][51]; modern array detectors are more sophisticated, but all are based on either voltage, resistance or current, 'production' when heated by IR radiation. The principle is the same, and the proof of this is all detectors measure the same substances – as Tyndall – in the same way; they equally cannot measure the likes of N_2 and O_2. It is, for this reason, I will term them as thermoelectric IR cameras or TE/IR cameras. Maybe someday they will be correctly named thermoelectric imagery.

Unlike traditional light sensing cameras, the TE/IR camera – as with the 'IR thermometer' cannot use glass for its lenses – as glass is TE, or as it is said to be, opaque to IR radiation. Instead, the lenses (figure 30 below) are made of one of the few non-TE substances that is solid, Germanium (Ge). Germanium is said to be – just as with N_2 and O_2 and air' – 'transparent' to IR radiation, Pg. 5 [52] and [53],[54]: a thermoelectric interpretation may say it is simply non-, or at least less, thermoelectric. In frame A the presenter holds a piece of glass between the camera and a heat source, revealing the 'opaque' property of glass in the camera image; in frame B he holds a germanium camera lenses, and in frame C, places a lenses between the camera and the heat source revealing the transparent property of Germanium to the camera.

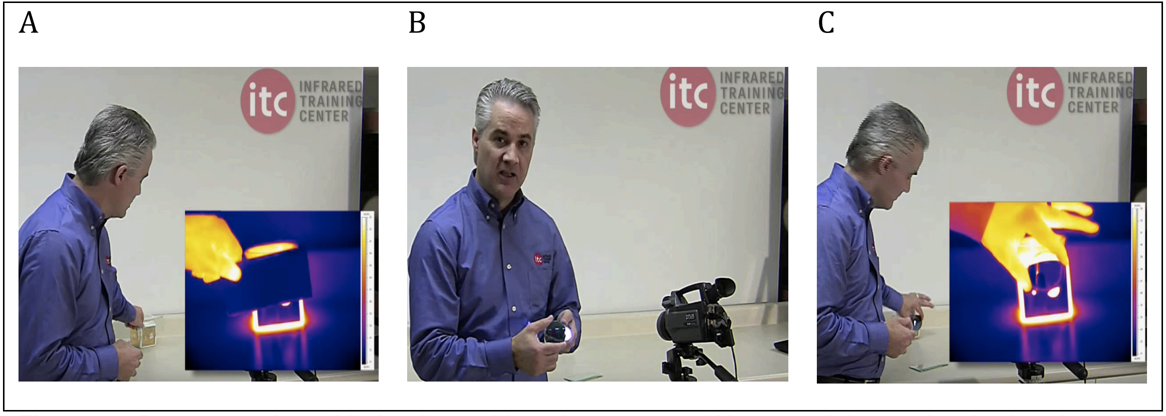


Figure 30. Demonstrating with the thermal imaging camera: (A) 'opaque' thermoelectric glass in front of the heat source; (B) visibly opaque germanium in hand; (C) 'transparent' non-thermoelectric germanium placed in front of heat source [55].

Germanium presents the same paradox of TE detectors to the air: they do not measure temperature. But what if the germanium was hot? I could heat up a lump of germanium to a dangerous temperature, but unlike a regular thermometer, TE/IR thermometers, or TE/IR cameras, would not register its temperature – and its danger; just as it does not register the temperature of the (hot) 'air'.

4.5.4.1 The Germanium Sauna

As a thought experiment: imagine a 'hot' sauna made entirely made of germanium: what temperature would an IR thermometer or camera measure if measured within the sauna? It would indicate – unlike the traditional thermometer – the temperature outside the sauna: it would 'see' right through the walls (apart, of course, for the water vapour and other trace gases, and the people inside). As a thermometer, it would be useless. As silly as this may sound, this scenario – which could be created, though it would be expensive – is exactly what a TE/IR camera does in the free ±300K° atmosphere; it only detects the objects that are thermoelectric.

4.5.4.2 Greenhouse Gases and Thermography

To Show the effects different gases have on thermoelectric transducers; in another (Youtube clip, figure 31 below) demonstration using the thermal imaging camera –'thermoelectric' camera – Infrared absorption of a greenhouse gas: two concealed glass cylinders are shown (frame A): the cylinder on the in the left is filled with 'air', and on the right the cylinder is filled with "a greenhouse gas" – presumably CO2. Frame B shows the left-hand glass full of air to be "transparent to IR radiation", and in Frame C, the GHG is shown to be opaque. Again, with knowledge of thermoelectrics this conclusion is an illusion, and wrong – the air is not thermoelectric.

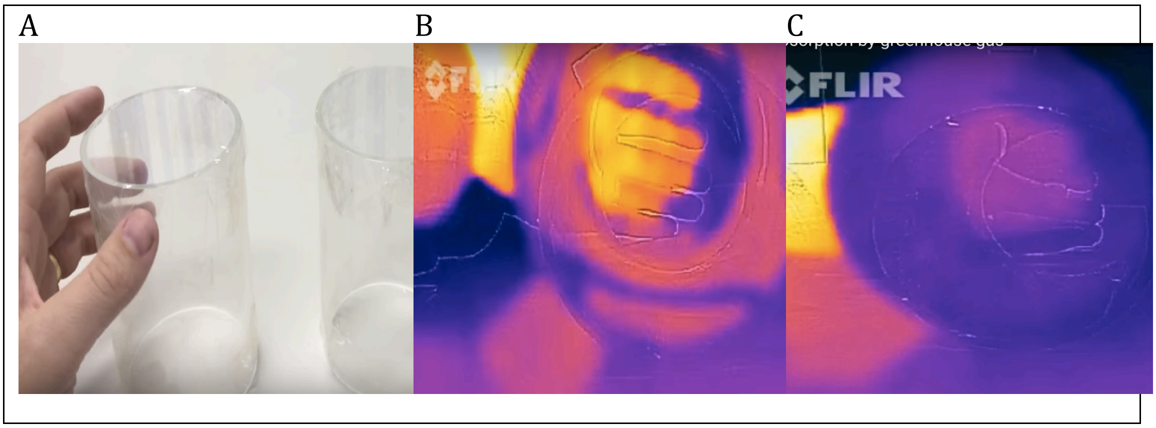


Figure 31. Thermal Imaging camera Greenhouse gas demonstration. (A), two glasses, one fill with air (mostly N2 and O2) and the other with a GHG, presumably CO2; (B), the first glass is non-thermoelectric, wrongly said to be 'transparent to IR'; and C, the GHG is thermoelectric, wrongly said to be opaque to IR. [56]

To defend this claim; firstly, notice the glass cylinders of 'air' and GHG are contained using a thin plastic 'kitchen' wrap: this is not for convenience, thin plastic is known to be "transparent to IR radiation" or, in keeping thermoelectrics, is more correctly interpreted as being non-thermoelectric. This containment problem has significant to the Tyndall experiment (above) as he had too had the same problem containing the gases in his mid 19th Century experiment, and used rock salt crystal (which is still used in laboratories today). The point being he did not use glass. Secondly, the appears not to have a temperature; but the 'air' does have (must have) a temperature – else it is contravening thermodynamics and quantum mechanics as it is matter and so must be radiating. By thermoelectrics, the thermopile is generating electricity off the radiation of the TE gas, and as the TE gas in the line of sight of the camera detector, it is the incident TE gas, and not the background hand of the demonstrator, that is measured.

So far I am only using end-use instruments; later I will get into the physics and chemistry behind these instruments: what we will see is this is only half the story.

4.5.4.3 Non-Thermoelectric Liquid Oxygen

In another simple and normally trivial video demonstration on thermography (figure 32), liquid oxygen – at a temperature of less than 90K – is interpreted to be transparent to infrared (below); however, with the knowledge of thermoelectrics what has been demonstrated is liquid oxygen (also – like the oxygen gas) is not thermoelectric, and the magnet in the Dura cup is.

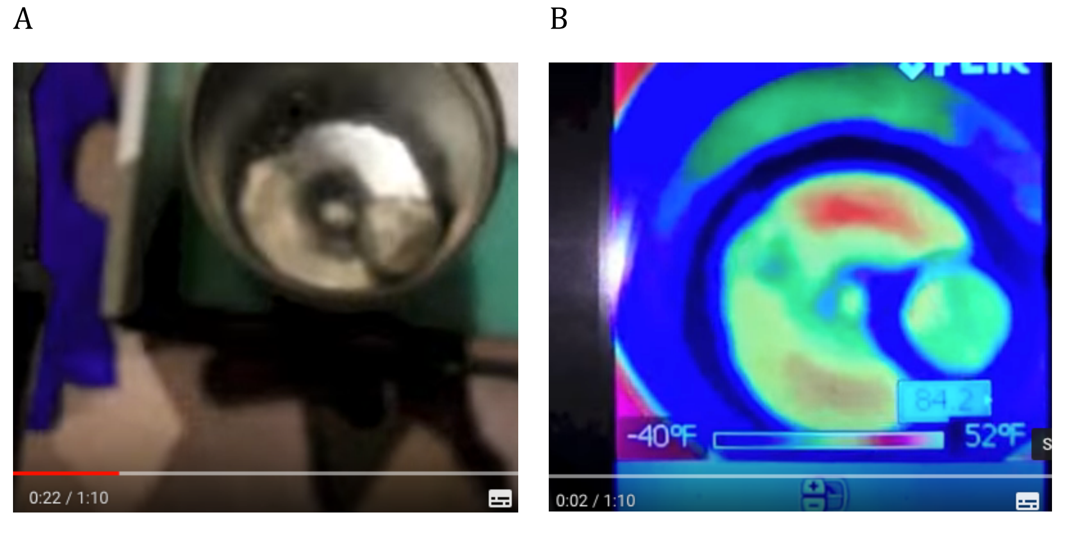


Figure 32 Thermal imaging camera liquid oxygen demonstration. Frame a visible, showing a magnet in a cup of (90K) liquid oxygen; and in frame B a thermoelectric infrared image, again showing the magnet, and importantly not showing the liquid oxygen. [57]

If it were any other liquid, with the exception of liquid nitrogen, the image of the magnet would not be shown in the FLIR image. The conclusion of these demonstrations is oxygen does not show with thermoelectric transducers.

4.5.4.4 The BBC Dr. Stewart GHG Demonstration

In BBC's documentary: 'The Climate Wars'[58], Dr Stewart demonstrates the greenhouse effect using a thermal imaging camera; unbeknown to Dr Stewart – it appears – is he is literally reconstructing of the original 1859 Tyndall experiment only with modern materials and technology (as shown in Figure 33 below). The thermal imaging camera (frame B) stands in for the single thermopile, and thin plastic (frame a) at either end of the 'glass' tubes contains the gases.

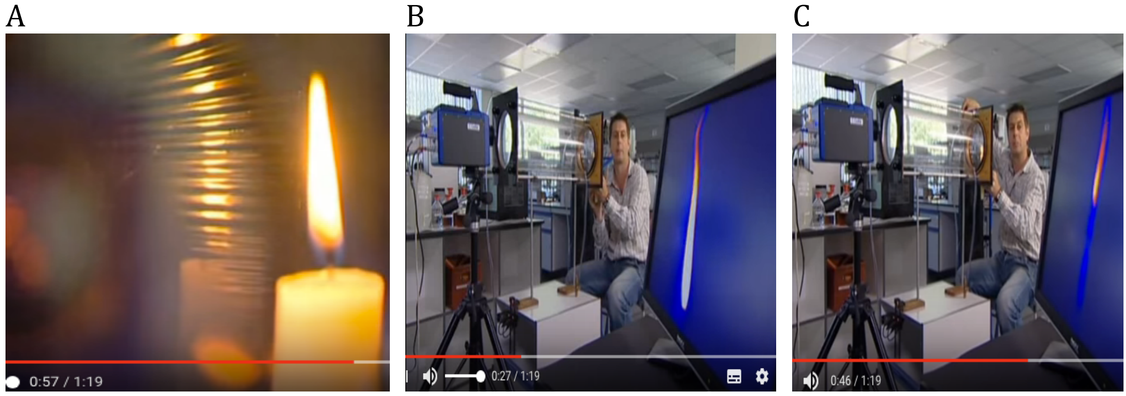


Figure 33. Dr Stewart YouTube clip [58], [59]. Demonstrating the greenhouse effect. Frame A shows the gas contained behind thin plastic, B. thermal image of a flame through 'air'; and C. CO2 'blocking' the flame out.

An image of the candle is seen on a screen via the TE/IR camera link (frame A), and as the heavier than air CO_2 is released into the sealed cylinder the bright candle image from the camera disappears – from the bottom up – and is replaced by the blue colour screen (frame C). Dr Stewart concludes – just as John Tyndall did: *"The CO2 absorbs the infrared or is essentially trapping the heat from the candle."*

If this claim is true, the claim must be said and understood in full knowledge of (the above) thermoelectric theory and practical application of infrared instruments – including thermal imaging cameras and thermopiles. If in the experiment the electricity generating ability of the said (and inferred) gases and solids – via the Seebeck Effect – were disclosed and understood – i.e. an understanding of how the thermal imaging camera discriminates between IR active and IR inactive substances at the particular spectrum range observed – a totally different conclusion would be drawn, and Dr Stewart's conclusion wrong.

With this been said, the alternative interpretation and conclusion of both the Tyndall experiment and the modern laboratory 'Stewart' experiment (above) may read as follows. The first thermal image (frame B) shows the bright flicking candle. This is due to the 'air' (close to 100% N_2 and O_2) within the tube, the thin plastic sheet at either end of the tube, the air between the camera and the tube, and finally the lenses of the camera (most probably made of Germanium) all being non-thermoelectric/non-TE. Only the incident flame is thermoelectric, and hence – given the camera display is calibrated for the hot flame and not its background radiation – the flame's image is displayed. The next scene (frame C) shows the flame image slowly to a blue colour as the CO_2 gas is released into the tube: it is the incident CO_2 that now generates electricity proportional to the temperature.

4.5.5 The Hairdryer Paradox Explained

With a first principles knowledge of thermoelectrics, an explanation can be found to this discrepancy, which will lead us to a hypothesis. The thermal 'outlet blast' image blown onto a surface implies this surface is of a thermoelectric nature, and the air is not. If there were no surface there at all, or if the surface were of solid – not thermoelectric – Germanium, maybe salt crystal (more on this later), no heat by the thermoelectric detector would be detected. As a matter of interest, one may ask: how would the thermogram appear if the hairdryer were: (1) was fed only with CO_2; and, (2) if the dryer were submerged in a 'bath' of only CO_2? Reasoning by thermoelectrics, for the former (1), it would show a plume of 'bright-hot' outflow; and for the later (2), no discernable image would be observed as it will be the incident temperature CO_2 measured by the thermoelectric detector.

4.5.5.1 *White Body Cavity /Air Experiment*

To further to emphasise this flaw with thermoelectric detectors as the hair dryer paradox attempts, suppose the following experiment. In the tradition of 'blackbody radiation', fill a cavity made of shiny gold (an assumed perfect white body IR 'reflector'), with N_2 and O_2 ('air'), and radiate IR photons (heat) from a centrally positioned electric element. This should pose a paradox as all these ingredients do not absorb IR; leaving us with the question, what would happen to the temperature of the gases, and the gold? As shiny gold has one to the lowest emissivities possible (of 0.025), and 'air' (as it is assumed) does not absorb, current assumptions would suggest no heating of the gases and the gold. A pragmatic, common sense view would suggest the converse – the gases and gold would heat somewhat proportional to the energy radiated.

4.5.6 Paradoxes Associated with Emissivity

Emissivity is not without contradiction, for instance it assumes shiny metals hardly radiate; and snow and ice are near-perfect black bodies. Emissivity is a definitive measure of radiation of matter and has a value ranging from the value of 0 to 1: but seen here, it too presents deep paradoxes. The following is outside the scope of the study, but requires a mention as it was found while researching this paper emissivity is not the only used in direct association with thermoelectric detectors, but it is itself determined by thermoelectric thermopile detectors. If there is a mistake made in radiation physics by using thermoelectrics in isolation, this is only compounded by using thermoelectrics to define the problem with thermoelectrics.

As strange as this may sound, it is all-true; and further reconciling this problem will be the topic of another study. Notwithstanding this, this study has led the author to conclude emissivity is no more than a correction factor between the real temperature of an object and the thermoelectric indicated temperature (itself determined by the Seebeck effect and not accurate).

4.6 Other Applications of Raman Spectroscopy: Revealing IR Radiating N_2 and O_2 (and CO_2's Raman 1338 cm^{-1})

The following are some of the few applications of Raman monitoring.

More examples are listed in Appendix 8.1.

4.6.1 Measuring Atmospheric Gas Concentrations (Keeling Curve) with Raman

The fact that Raman devices can measure gas concentrations – as demonstrated in the RER – has implications on the measurement of GH gas concentrations.

Indeed it has been found and suggested even the Keeling curve of GH gases – namely CO2 – need not be measured by TE/IR thermoelectrics alone, which they are today. The GH gases can be measured by Raman Lasers, just as they are on Solar system space probes; this is demonstrated in the following paper:

A Raman scattering method for precise measurement of atmospheric oxygen balance

Abstract

Quantitative measurements of Raman scattering intensities from N_2, O_2, and CO_2 under ambient atmospheric conditions are given. The atmosphere was illuminated with 20,489 cm^{-1} Ar^+ laser radiation. These scattering intensities are sufficiently strong to ***allow measurement of O_2/N_2 and CO_2/N_2 concentration ratios in the atmosphere to*** *a precision of 0.3 and 0.006 ppm total atmosphere, respectively, by means of scattered photon counting over a 174-hour integration period.* ***The Raman technique represents an improvement in precision over existing techniques by almost two orders of magnitude****, and a substantial but less easily determined improvement in accuracy by using the transition probabilities of a monomolecular reference gas as a standard, rather than the properties of a mixed gas standard as is done in current measurements. [60]*

Analysis of influence of atmosphere extinction to Raman Lidar monitoring CO_2 concentration profile*

"Lidar (Light detection and ranging) system monitoring of the atmosphere is a novel and powerful technique tool. ***The Raman lidar is well established today as a leading research tool in the study of numerous important areas in the atmospheric sciences. In this paper, the principle of Raman lidar technique measurement CO_2 concentration profile is presented…****" [61]*

NDACC are using Raman Lidar to measure H_2O, with N_2 as "*a reference molecule having a well-known mixing ratio throughout the altitude range considered*" [62]

This process is also discussed by the IEEE under: LIDAR FOR ATMOSPHERIC TRACE GAS DETECTION [63], and in a paper "Relative Raman Cross Section for N_2, O_2, CO, CO_2, SO_2, and H_2S"[64]: where an (inferred) argon ion laser (5145Å) is used to identify the gases.

Also see appendix 7.8 for more on atmospheric Raman Lidar.

4.6.2 Raman Solar System Probe Applications

On modern-day solar system space probes Raman detectors are becoming the detector of choice: it makes sense, the detect oxygen and CH_4 – accentual part indicators of the existence of life – and CO_2, and N_2. In the review '**Remote Raman Spectroscopy of Minerals at Elevated Temperature** 2012' [65]

Raman was extensively evaluated for it obvious complementary merits.

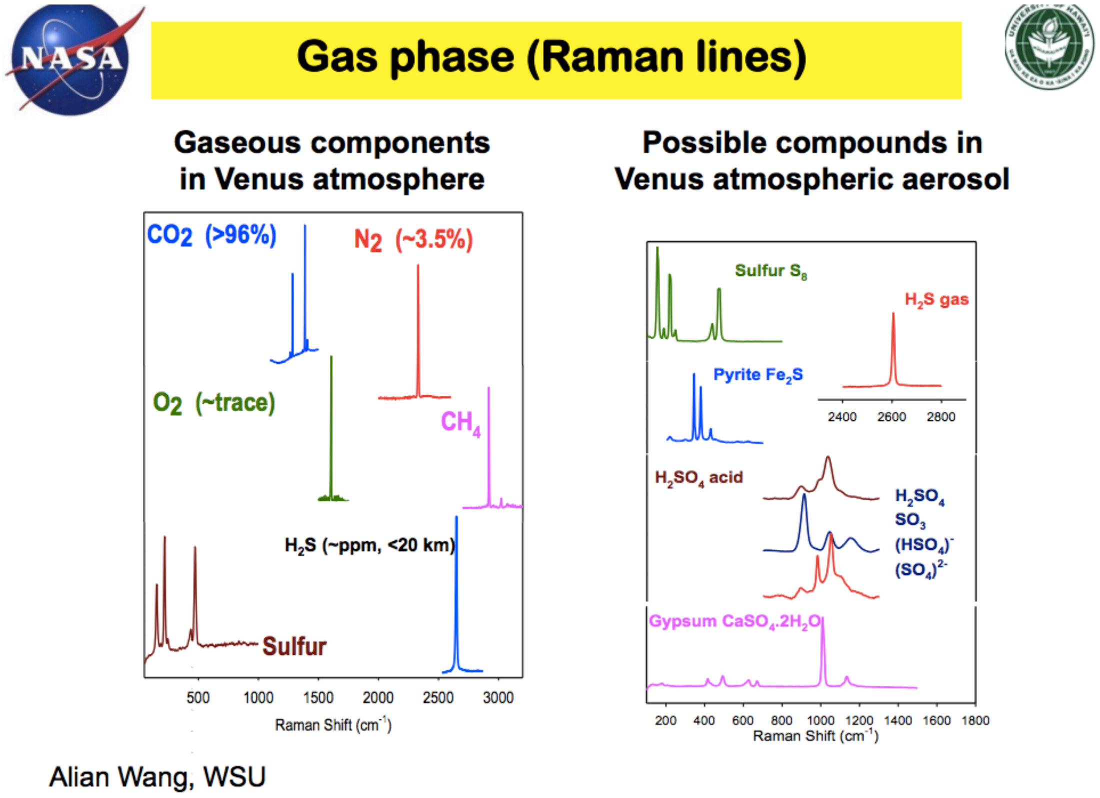
"..thus, using strictly visible light sources and receivers Raman spectroscopy ***can yield complementary information*** *about the vibrational transitions observed in infrared emission or reflection spectra."*

This statement was followed by a standard misunderstanding (as interpreted for this research) between Raman and TE/IR: the following is not consistent with the findings of this paper.

> *" Raman spectroscopy is not directly equivalent to infrared (IR) spectroscopy, as the strengths of individual features can be quite different between IR and Raman spectroscopy due to different selection rules. The activity of Raman vibrational modes is a function of the change in polarizability during the vibrational mode, whereas the activity of infrared modes is associated with the change in permanent dipole moment during a normal mode of molecular vibration. Raman spectra of samples contain a wealth of information that can be used to identify minerals and chemical compounds based on the vibrational frequencies, relative intensities, and number of bands in the spectra."*

4.6.2.1 Venus

Below (figure 34) is a Raman spectra of Venus's atmosphere. Notice CO_2 is measured (at it's 1338 cm^{-1} mode. If this mode is good enough for Venus, why not Planet Earth? If TE/IR were used on Venus, no N_2 or O_2 would be measured – at any temperature.



Gas phase (Raman lines)

Gaseous components in Venus atmosphere

Possible compounds in Venus atmospheric aerosol

Alian Wang, WSU

Figure 34. Venus Atmosphere 'Raman Lines' Showing molecules with their respective modes in Venus's atmosphere. [66]

4.6.3 Other Uses for Raman Spectroscopy

See Appendix 7.1 of other uses for Raman; including: measuring automobile emissions; RAman SCattering AnaLyzer (RASCAL), Geology CO_2 1388 cm^{-1} ; CO2's 1388cm-1 Excitation, and the 'Dicke effect' (see appendix).

4.7 Evidence of Raman and TE-IR Modes (N_2's 2338 cm^{-1}) Radiating IR

For the Raman theory – of a radiating 'non-GHG' atmosphere – to have any validity, there should be instances that show coherence with the theory. The following are instances where the non-GHG modes are radiated, and in total compliance with quantum mechanics offer such examples: the CO_2 laser and absorbing thermosphere N_2 molecules – where there is only radiation as a transfer of heat-energy.

4.7.1 CO_2 Laser: A Practical Application of 'Radiated N_2 at 2338 cm^{-1}

The CO_2 Laser offers a pragmatic real-life application – or kind of experiment – invoking and testing both of the key atmospheric gases in question, N_2 and CO_2, revealing their real relationship between them when they are radiated – though it is not currently interpreted as so. After an understanding of the CO_2 Laser process it could be assumed – contrary to standard belief – N_2 in the atmosphere is the gas that affects – and actually forces – the CO_2.

All theory surrounding the CO_2 Laser points to the role of N_2 has in 'pumping' the CO_2 as an essential part of the process; so much so – it is explained in all textbooks – the laser will not operate without this 'absorbing/emitting' property of N_2 when radiated. The relationship is so close these lasers are technically termed **N_2-CO_2 Lasers**. A closer look at the physics behind the laser reveals N_2's true nature, and it absorption property at its **2338**cm^{-1}mode; a property absolutely ignored in atmospheric 'GH' theory. It is as if the scientist describing the CO_2 laser are oblivious of the ramifications this knowledge would mean to GH theory; that they are using the very same mechanics – both physics and chemistry – that the Raman measurements point to in the atmosphere; only here the gas is excited at the said modes.

4.7.1.1 The CO_2-N_2 Laser

Lasers all have the following key components:

1. An active medium – for the CO_2-N_2 laser it is the CO_2 and N_2 that are of interest;
2. Energy input/ pumping source/ high voltage discharge
3. Optical Feedback, this is not of interest in the investigation
4. Population inversion, this in essential – more electrons must be in an excited state that lower state; this is very important.

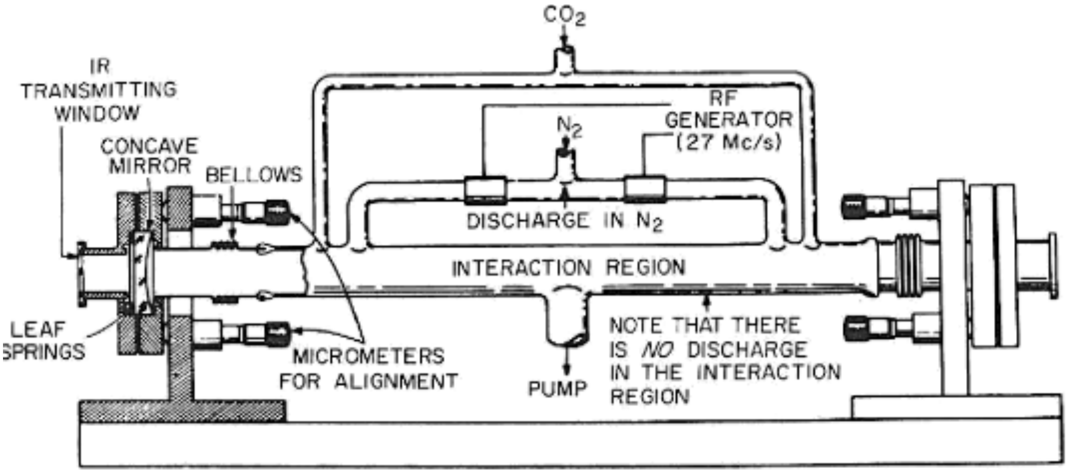


Fig. 1.1. System developed by Patel (1964b) demonstrating laser emission due to transfer of vibrational energy from N_2 to CO_2.

Figure 35. [67]

"Infrared laser emission from CO_2 was first reported by Patel (1964) and others in pulsed discharges through pure CO_2. In this system N_2 is excited in a ef discharge to form vibrationally excited N_2 molecules which stream into and interaction region to mix with unexcited CO_2. The CO_2 is the in vibrationally excited through the reaction which occurs efficiently. " Pg. 1 [67]

The following is an exert from a paper on how a CO_2 laser operates from the book LASER PHYSICS by PETER W. MILONNI JOSEPH H. EBERLY page 51 [68]. It is a typical description of how the CO_2 laser directly implicates N_2's **2338** cm^{-1} mode. I have posted the direct text to show this is standard knowledge. It is important to look out for are the Wavenumbers of the gases: particularly, N_2's **2330** cm^{-1} and CO_2's **1388** cm^{-1} and their role in the laser process.

*"The electric-discharge carbon dioxide laser has a population inversion mechanism similar in some respects to the He –Ne laser: the upper CO_2 laser level is pumped by excitation transfer from the nitrogen molecule, with **N_2 itself excited by electron impact**. The relevant energy levels of the CO_2 and N_2 molecules are vibrational-rotational levels of their electronic ground states. We discussed the vibrational-rotational characteristics of the CO_2 molecule in Section 2.5, and indicated in Fig. 2.10 the relative energy scales of the three normal modes of vibration, the so-called symmetric stretch, bending, and asymmetric stretch modes (Fig. 2.9). Like all diatomic molecules, N_2 has a single "ladder" of vibrational levels corresponding to a single mode of vibration (Fig. 2.7) (**2338**cm^{-1}). In Fig. 11.9 we show the CO_2 and N_2 vibrational energy level diagrams side by side. Figure 11.9 shows that the first excited vibrational level (v ¼1) of the N_2 molecule lies close to the level (001) of CO_2. Because of this near resonance, there is a rapid excitation transfer between N_2 (v ¼ 1) and CO2(001), the upper laser level. **N_2 (v ¼ 1) is itself a long-lived (metastable) level, so it effectively stores energy for eventual transfer to***

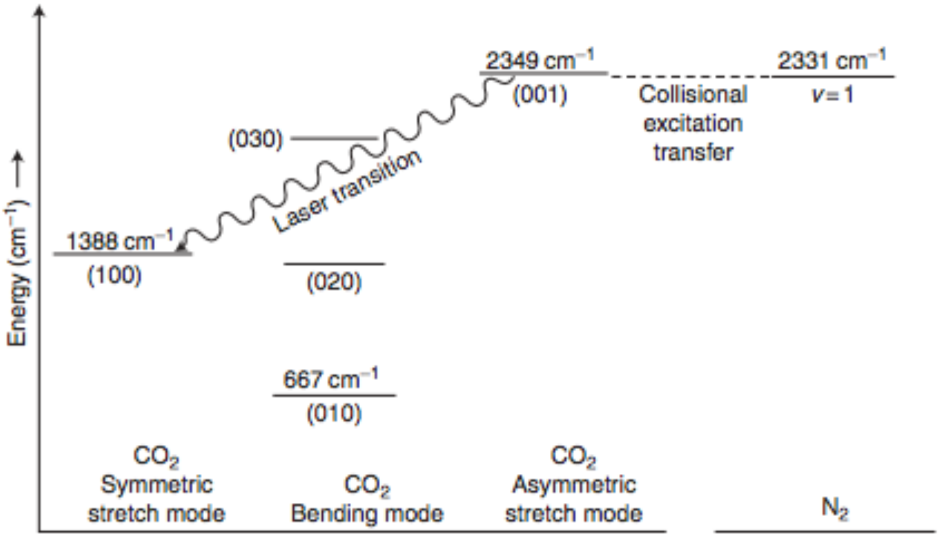


Figure 11.9 Vibrational energy levels of CO$_2$ and N$_2$. The energies are given in cm^{-1}, a unit corresponding to a frequency $(c)(1\ \text{cm}^{-1}) \approx 3.0 \times 10^{10}$ Hz, or an energy $h\nu \approx 1.2 \times 10^{-4}$ eV.

Figure 36.

CO$_2$(001); it is also efficiently pumped by electron-impact excitation. As in the case of the He–Ne laser, therefore, advantage is taken of a fortuitous near resonance between an excited state of the lasing species and an excited, long-lived collision partner. Laser action in CO$_2$ lasers occurs on the vibrational transition (001) → (100) of CO2. *This transition has a wave number around (**2349–1388**) cm^{-1} ¼ 961 cm^{-1} (Fig. 11.9), or a wavelength around (961 cm^{-1}) 21 ¼ 10.4 mm in the infrared. The laser wavelength depends also on the rotational quantum numbers of the upper and lower laser levels. For the case in which the upper and lower levels are characterized by J ¼ 19 and 20, respectively, the wavelength is about 10.6 mm, the most common CO$_2$ laser wavelength. The (100) and (020) vibrational levels of CO$_2$ are essentially resonant. This "accidental degeneracy" results in a strong quantum mechanical coupling in which states in effect lose their separate identities.*

Furthermore the (010) and (020) levels undergo a very rapid vibration-to-vibration (VV) energy transfer:

$$CO_2(020) + CO_2(000) \rightarrow CO_2(010) + CO_2(010): \qquad (11:7:1)$$

For practical purposes, then, the stimulated emission on the (001) → (100) vibrational band takes CO$_2$ molecules from (001) to (010). The (010) level thus acts in effect like a lower laser level that must be rapidly "knocked out" in order to avoid a bottleneck in the population inversion.

Fortunately, it is relatively easy to de-excite the (010) level by vibration-to-translation (VT) processes:

$$CO_2(010) + A \rightarrow CO_2(000) + A, \qquad (11:7:2)$$

where A represents some collision partner. The VT de-excitation of (010) effectively depopulates the lower laser level and also puts CO_2 *molecules in the ground level, where they can be pumped to the upper laser level by the VV excitation transfer*

$$N_2(v \text{ ¼ } 1) + CO_2(000) \rightarrow N_2(v \text{ ¼ } 0) + CO_2(001 \qquad (11:7:3)$$

In high-power CO_2 *lasers the lifetime of the* $CO_2(010)$ *level may be on the order of 1 ms due to collisions of* CO_2 *with He,* N_2*, and* CO_2 *itself. Of course, the VT process (11.7.2) is exothermic and results in a heating of the laser medium; some of the other VT and VV processes in the* CO_2 *laser have the same effect. This heating of the laser medium is a very serious problem in high-power lasers. In the next section we will see how it may be overcome. Electron impacts excite* CO_2 *as well as* N_2 *vibrations. "*

4.7.1.2 Stimulated and Spontaneous Emission

'Stimulated' and 'Spontaneous' Emission are quantum mechanical features, and together point to the absorption and emission of photons of light. In the case of the CO_2 laser, it is the 'stimulated' and 'spontaneous' emission and absorption of IR photons between N_2 and CO_2 molecules. It, on its own, stands as a proof of emission and absorption of N_2 of light photons.

4.7.1.3 Radiating N_2: CO_2 LASER – Discussions

Here, with the CO_2 laser it is shown N_2 – a non-GHG that should not be able to absorb any (IR) radiation from any 'particle' whether photon or electron – is first excited or energised (heated up) at it's **2338** cm^{-1} mode so as to further excite (heat up) the CO_2 molecules **2349** cm^{-1} mode. This is in total contradiction to GH theory where N_2 is assumed not to absorb any radiation. This application shows it is N_2 that directly affects, and excites the CO_2 molecule – though they do claim it is by collision and not radiation.

4.7.1.4 The CO_2 Laser, and the Question of Radiation?

The Laser demonstrates how different substances are excited when 'fired upon' by electrons through an electrical discharge in a cathode ray tube. The important question for this investigation is: does this 'firing upon' constitute as radiation – as a transfer of energy? This is important because N_2 is assumed not to absorb radiation.

4.7.1.5 Is Discharge of Electrons Radiation?

The following are quotes from the first lines of Wikipedia:

"Thermal radiation is electromagnetic radiation generated by the thermal motion of charged particles in matter. " [69]

Do the 'discharged electrons' used to excite the N_2 at its **2338** $\mathbf{cm^{-1}}$ constitute 'charged particles' (from the above definition)?

"In physics, a charged particle is a particle with an electric charge. It may be an ion, such as a molecule or atom with a surplus or deficit of electrons relative to protons. It can be the electrons and protons themselves, as well as other elementary particles, like positrons." [70]

It can be deduced cathode rays are a form of radiation. From this, the fired electrons are charged particles, and they radiate thermal (IR) energy – the N_2 at its **2338** cm^{-1} mode absorbs this energy.

4.7.1.6 Frank-Hertz Experiment

To support this claim non-TE-IR modes radiate, the **Frank-Hertz experiment** shows electrons – from a variable electrical discharge – affect a gas molecule to reveal its emission spectra mode – the spectra predicted by the quantum mechanical Schrödinger equation. It can be shown to work for all gases. Even without radiation – it is assumed to be by 'collision' – the Frank-Hertz experiment shows N_2 absorbs, and thus emits. From this it is plausible energy is transferred from its excited **2338** $\mathbf{cm^{-1}}$ to CO_2's **2349** $\mathbf{cm^{-1}}$ from emission from its mode.

4.7.1.7 Collisions Implausible: Convection Paradox

If excitation were by collisions alone, it would imply conduction as a means of energy transfer: again, it can be shown this is unlikely as N_2 has a very low conduction coefficient of $0.024k$ – so this form of transfer is unlikely.

4.7.1.8 Implications for IR Spectroscopy

To conclude from the CO_2 Laser and show the implications of it on IR spectroscopy; the symmetric vibrational modes of N_2 and O_2, and CO_2's **1388** cm^{-1} – assumed '**non**-IR active' as they do not, emit or absorb IR radiation due to their lack of a dipole – has been refuted. The 'symmetric stretch' N_2 mode excites the CO_2, having been radiated. Not only does the N_2's symmetric mode vibrate from radiant excitation, heating and so forcing the CO_2 up an energy level, but CO_2's own symmetric vibration (at **1388** cm^{-1}) is affected – or necessarily implicated in the process by the equipartition principle in what can arguably only be by radiation (by photon collision). Atmospheric CO_2 has this same **1388** cm^{-1} symmetric mode, but there is no mention of this in atmospheric spectra, or its effect on climate forcing; it is assumed not to be part of the standard model, and this will need to change.

4.7.1.9 N_2 and Kirchhoff's Law

Kirchhoff's Law states 'good absorber, good emitter'. As it can be shown N_2 is absorbing charged electron particles from the electron discharge as if from radiation, in compliance with quantum mechanics: by Kirchhoff's Law it is equally, by definition, a said to be a 'good emitter'.

4.7.1.10 Metastable N_2 and the Greenhouse Atmosphere

I shall first define metastable and then discuss it in terms of N_2 and CO_2.

"Metastable state, in physics and chemistry, particular excited state of an atom, nucleus, or other system that ***has a longer lifetime than the ordinary excited states*** *and that generally has a shorter lifetime than the lowest, often stable, energy state, called the ground state. A metastable state may thus be considered a kind of temporary energy trap or a somewhat stable intermediate stage of a system the energy of which may be lost in discrete amounts.*
In quantum mechanical terms, transitions from metastable states are "forbidden"

and are much less probable than the "allowed" transitions from other excited states." [71]

N_2 is said to be **Metastable** – long-lasting (absorption) – and this property is central to the CO_2 laser; the (greenhouse) gas CO_2 is not said to be metastable.

This metastable N_2 has ramifications on greenhouse theory, as N_2 is the Earth's atmospheres major constituent gas. This is not to say the atmosphere is a laser (though this is discussed by experts for other planets); it is only to say N_2 has this property when excited, and this is supported by experiment [72],[73] and may be assumed to be a property in the troposphere atmosphere also. Meschad – on the topic of planetary lasers and metastable N_2 – says:

'The occupation of the upper laser level is possible directly, but is much more favourable with the addition of nitrogen. Metastable N_2 levels not only can discharge but also can transfer the energy to the CO_2 molecules very profitably as well." (Pg. 274 [74])

4.7.1.11 Metastable N_2 from 'Collisions' and not Radiation

All explanations of metastable N_2 in the context of the CO_2 laser do not point to radiation; but rather support the non-radiating N_2 hypothesis, where it is all explained by collisions.

" Electron collisions excite date nitrogen molecules to their vibrational level. Once in this level, the nitrogen molecules are metastable, they cannot really lose energy radiatively and can only return to the ground state as a result of collisions. Because into nitrogen is what is called a homo nuclear diatomic is it vibrates it has no dipole moment, and a direful moment is needed for spontaneous emission to occur. The population of N_2 molecules builds up and these molecules transport fare their excitation to CO_2 molecules, thereby populating the upper CO_2 laser level." (P.220)[75]

Here again we have problem, a paradox: does 'collision' – by electrons or photons, at this level – constitute radiation? I say it does, but if it does, this is a striking and damning revelation, totally contradicting GH theory. Equally, if it doesn't, it stands is a contradiction to quantum mechanics: where all matter is said to radiate, including accelerated electrons.

The reason given for this metastable N_2 assumption is that it does not emit photons when excited; this, I believe this needs to be reviewed, and is, on its own, a repeat of the mistakes made in GH theory where diatomics (N_2 and O_2) are assumed not to radiate. I believe, based on the discoveries from this investigation, it is a 'throwback' to a lone reliance on 'IR' – thermo-electric – radiation theory that is the problem. N_2 can be shown (as it has been attempted in this paper) to emit IR photons. If it is that N_2 does emit and absorb radiation the assumption N_2 is metastable because it does not emit suggests radiation theory is incomplete.

4.7.1.12 Natural CO_2 Lasers

NASA and others have discovered natural lasers on the likes of Mars and Venus [76] and below [77] is demonstrated how they – in the similar way as the laboratory ones – operate. Again this repeats the role of radiation has on atmospheric gases.

*"000 to 101 followed by a resonant collisional energy transfer of a V3 quantum to another CO2 molecule (**2349**cm^{-1}), which is similar to the laboratory CO2 laser (Fig 8.6)."*

Basics of collisionally pumped astrophysical lasers **123**

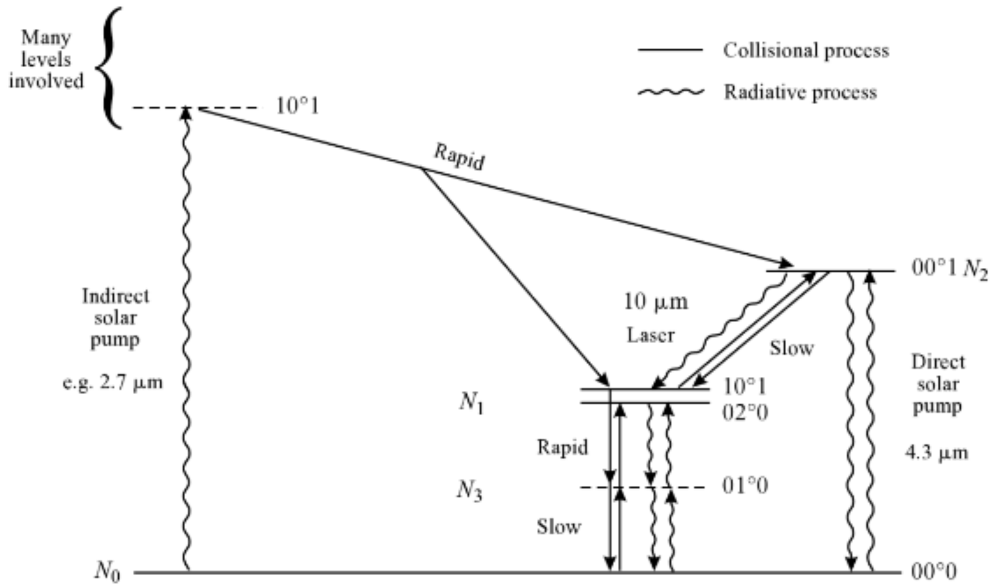


Fig. 8.6 Molecular physics of a natural CO_2 laser. Radiative and collisional processes affecting the pumping of this laser in the mesospheres of Mars and Venus are identified.

Figure 37.

4.7.2 'Blackbody CO_2 Laser' Showing N_2 Heated by Sunlight

It is very difficult to directly show N_2 is directly radiated by the suns energy, absorbing IR photons; however, the following experiment shows indirect confirmation of the hypothesis: N_2 is 'heated' (and heats) – i.e. absorbs (and emits) – by sunlight.

The extract below is taken directly from the 'NASA Technical Paper': A Blackbody-Pumped CO_2-N_2 Transfer Laser, by Young and Higdon [78].

"One laser concept that may achieve such efficiencies is the blackbody-pumped CO_2 transfer laser. Such a system is called a fluid-mixing or transfer gas-dynamic laser and is shown in conceptual form in figure 1.

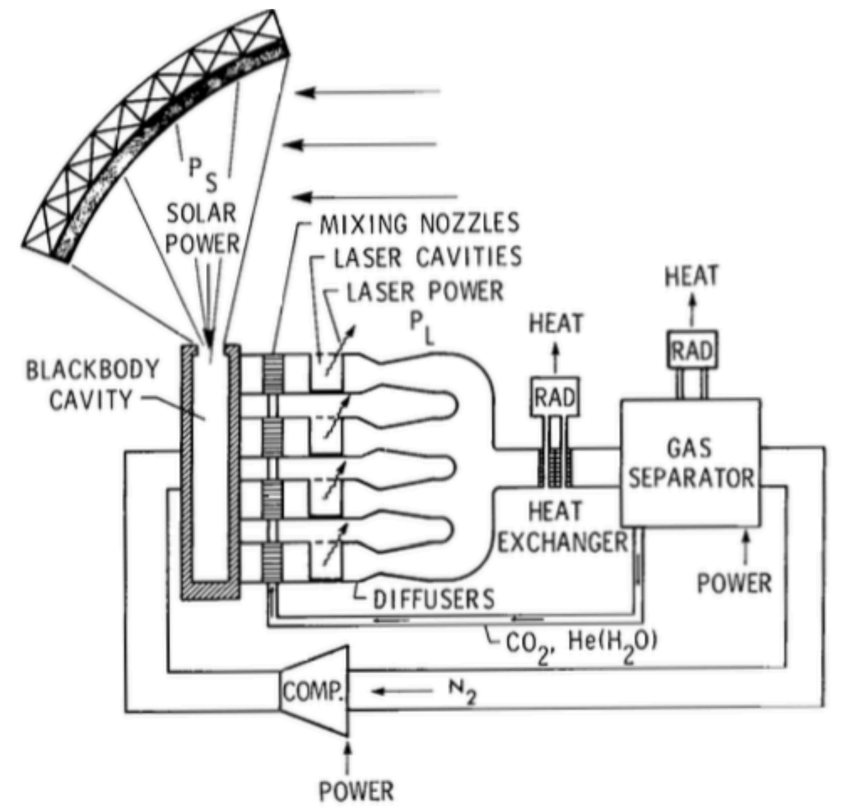


Figure 1. A conceptual design of a space-based blackbody N_2-CO_2 transfer laser.

Figure 38. Demonstrating N_2 Excitation from the Sun.

In this system, a black body cavity is heated by collected sunlight ('solar power') to a temperature of approximately 2000 K. ***Nitrogen gas passing through the cavity is heated to the blackbody temperature.*** *The vibrationally excited N_2 then passes through a nozzle into a low-pressure laser cavity. Here CO_2 and He are mixed with the vibrationally excited N_2. A coincidence between N_2 (v=1)* ***(2338*** *cm^{-1}) and the 001 asymmetric longitudinal mode (****2349 cm^{-1}****) of CO_2 allows rapid transfer of the N_2 (v = 1) vibrational energy into the CO_2 001 upper laser level. Lasing commences between the 001 and the 100 levels at 10.6 microns. "*

4.7.2.1 Experimental Setup

"Standard purity N_2 flowed through a quartz tube within an electrically heated, which in the present experiment simulates a solar-heated blackbody cavity. The oven temperature and pressure were monitored. The gas velocity was slow enough (226 cm/sec) to allow the N_2 temperature to come into equilibrium with the oven temperature... CO_2 and He were then mixed with the vibrationally excited N_2 to cause a transfer of energy from the N_2 (v= 1) to the CO_2 upper laser level. "

4.7.2.2 Absorbing N_2: A New Law of Physics?

The experiment shows – consistent with quantum mechanics theory – electron excitation is equivalent to solar photon excitation (as discussed throughout this paper).

As a consequence, concentrated light photons heat the N_2 by the same physics as the CO_2 Laser; only there is no electrical discharge. Again, this process is not allowed in current GH theory. What is more, the experiment shows CO_2 is 'pumped' or stimulated by N_2 in this process: this behaviour constitutes a law of physics.

4.7.3 N_2 Absorbing in the 'Hot' Thermosphere and the Aurora

N_2 and O_2 are excited by charged particles in the thermosphere and temperatures for these molecules reach up to 2000^0C; it is **Raman** devices that are used to measure this temperature – in the lower thermosphere [79]. This is added proof that N_2 and O_2 are directly affected by IR photon radiation: if they absorb, they emit also. It can also shown charged particles heat the N_2 atmosphere during an aurora: further evidence of absorption.

4.7.4 IR Absorption and Thunder Creation: Lightning Heating the Air

From lightening radiation, the air is heated to 5 to 7 times the temperature of the sun. This radiation is consistent with N_2 absorption of IR photons and may stand as a 'natural' demonstration or experiment of the hypothesised.

4.7.5 IR Absorption and the Incandescent Light Bulb

While looking for supporting evidence of IR absorbing N_2 and O_2 and noticing the hot air is moving around the outside of the bulb when on. I wondered; what if the bulb were filled with air or N_2, what would result, a pressure increase? It turns out bulbs are filled with gas – mostly Argon (Ar) and small percentage N_2[80]. Neither of these gases are IR (thermoelectric), and they are said to warm inside the bulb by conduction. However, given the pressure inside the bulb is 70% of an atmosphere (to deal with the pressure problem) and Ar and N_2 are both very poor thermal conductors (argon even less that N_2 at 0.016 W/m K [4]), it is plausible the gases heat mostly – if not all – by radiation, as I have claimed.

4.7.5.1 Non-TE/IR Non-Raman Argon

In this discussion of IR absorbing gases, Ar presents itself as an odd one out. It is nether a GHG (it is not thermoelectric), nor a Raman-active gas. This is said to be due to it vibrational behaviour as an atom alone. However, Ar has a specific heat capacity of 0.520 (kJ/kg K) compared to air of 1.01, and does, (be it low) conduct heat. The dismissing of it radiating IR may be due to the said detectors being unable to detect its behaviour, just as thermoelectric-IR cannot detect Raman modes. Again, if it does not radiate IR, this is in contradiction to quantum physics.

4.8 Heat Capacity-Radiation Paradox

The discrepancy between the GHGs and the non-GHGs presents another paradox associated IR radiation theory, and it is to do with the gases respective specific heat capacities. All the atmospheric gases have specific heat capacities (Table 3, column two), which says one type of transfer of heat-energy directly affects them. The paradox sits with the – assumed not to absorb IR heat energy by radiation – non-GHGs which are also, like all the other gases, very poor conductors of heat (column 3). This leaves only conviction; but this is improbable due to the former being poor or exempt (addressed below in 4.8.5). The question is: how can these gases have specific heat capacities if they cannot transfer heat energy – with out radiation or conduction,as known, and assumed? The only way to reconcile this paradox is to assume radiation absorption – as demonstrated in this investigation –does take place for the non-GHGs, and presumably at their respective Raman modes.

Table 3. Comparing Gas Specific Heat Capacity with Thermal Conductivity and Radiation Properties. Source: 'engineeringtoolbox.com.

Atmospheric Gas	Specific Heat Capacity -C_p- kJ(kgK)	Thermal Conductivity -k- w/(mK)	Assumed to Absorb IR Radiation? Yes/No
Ar	0.520	0.016	No
N_2	1.04	0.024	No
O_2	0.919	0.024	No
CO_2	0.844	0.0146	Yes
CH_4	2.22	0.003	Yes
He	5.19	0.142	No
Air	1.01	0.0262	Only the GHGs

4.8.1 Standard (bottle) Greenhouse Experiments, and SHC Measurement

One of the most popular demonstrations of the greenhouse gasses is the 'greenhouse bottle experiment'[81] where CO_2 in one bottle and air in another is radiated by thermal radiation and temperature through time recorded. The CO_2 bottle temperature rises highest as shown below. However, with knowledge of specific heat theory and the specific heat capacities of the respective gases – not withstanding the difference between constant volume (as assumed in the demonstrations) and constant pressure; I claim is this not an experiment demonstrating the specific heat capacity of air and CO_2, where CO_2 has a low heat capacity relative to air – as described in the next subsection.

Figure 39. Greenhouse Gas Bottle Demonstration [82]. Bottles with CO2 and air are radiated and temperature measured – CO2 in blue. Is this not an experiment to measure the heat capacities of the respective gases?

Below (figure 40) is an image taken from a specific heat capacity demonstration; if two more boxes were added showing the effect of air (Cp 1.01) and CO_2 (0.8), it would be understandable the CO_2 would have a higher temperature, concurring with GH demonstrations.

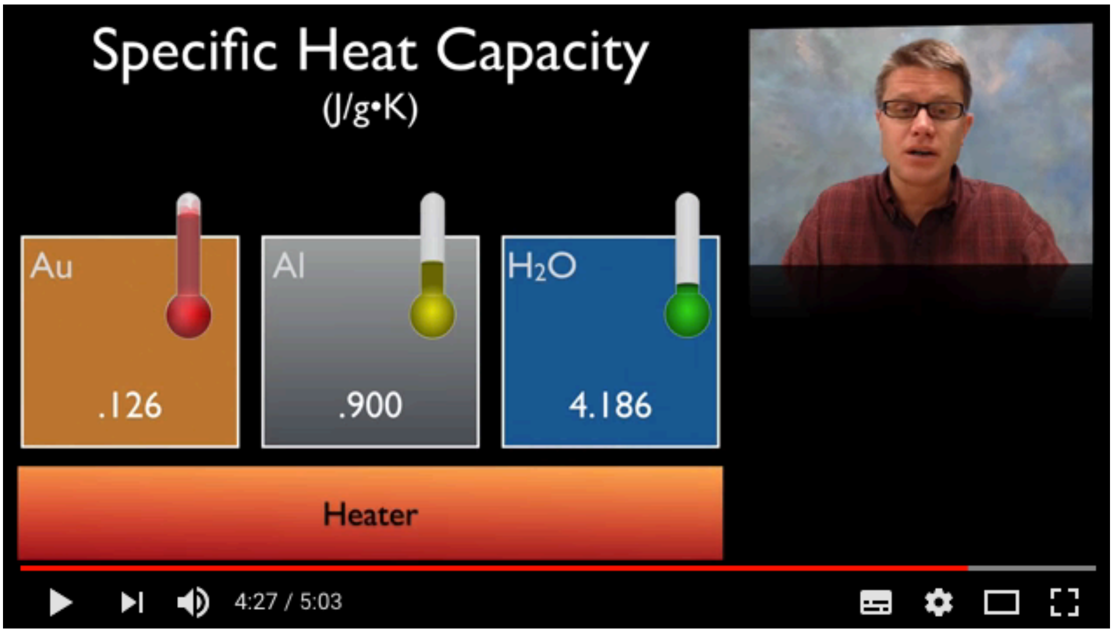


Figure 40. Specific Heat Capacity. The lower the heat capacity, the higher the temperature from single heat source.

4.8.2 Real Measurement of Gas Heat Capacity: Equivalent to GH Demonstrations

In the standard experimental method[83], to measure gaseous heat capacities uses an 'electric heater' element to heat the gas: the apparatus and method is inseparable from the above GH demonstrations – they are equivalent. Does this electric heater imply radiation, conduction, and as a result of these, convection? The answer, given the limited choices, must be yes. The closest solid to share the conduction properties of air with a conduction value of 0.017 and is said to be 'extraordinary' with respect to this, is Aerogel – and is used on spacecraft for these properties.

4.8.2.1 Measurement of GHGs Specific Heat proves non-GHGs absorb IR

As it is assumed the GHGs absorb IR heat radiation in Specific Heat measurement – at their respective TE/IR and Raman modes as presented in this investigation – it is equally plausible the non-GHGs, on the same principles, are absorbing IR heat radiation at their respective Raman modes, proportional to the resulting and measured specific heat capacities. Support for this claim is found with CO_2 and CH_4; both are poor thermal conductors (as with 'air') and both are IR (thermoelectric) emitters. From this investigation, and the equipartition principle, all their modes (TE and Raman) are equivalent; and so this must be so for the non-GHGs N_2 and O_2 also.

4.8.3 Vibrational Behaviour and SHC

It is interesting to read when investigating the fundamental knowledge behind Specific Heat of matter: it is said to be by the vibrational behaviour of molecules – as described earlier in this investigation – including the 'degrees of freedom' that determines the specific heat capacity of a substance. This adds further weight to including the Raman modes to radiation theory. Molecules such as N_2 and O_2 vibrate, they have degrees of freedom, and they have specific heats – so they must radiate IR also, at their Raman modes.

4.8.4 Further Paradoxes Associated with Convection – is it all Radiation

The above work on specific heat highlights another paradox to do with the transfer of heat energy: how does a gas or liquid convect without conduction or radiation? Is convection dependent on conduction and/or radiation? Is convection separate and special from the other two it is associated with?

"Convection is the heat transfer due to bulk movement of molecules within fluids such as gases and liquids. Convection takes place through advection, diffusion or both. " Wikipedia.

Further to the 'hairdryer paradox' presented in the introduction (figure 1), the transfer of heat energy here claimed as convection must really only be by radiation. Advection and diffusion are too slow with respect to the numbers (of molecules) involved, and that (again) conduction with the said gases is poor. This area needs review and further investigation.

4.9 Augmenting the Thermoelectric and Raman Atmosphere

Finally, to bring together, augment, the IR-Raman modes with the TE-IR modes. Raman spectroscopy spectra, as identified and used in the Raman Exhaust

Report, show the predicted N_2 and O_2 vibrational modes of these abundant molecules. These 'Raman' modes along with the TE/IR modes of the EMS, can now be brought together – augmented – to complete the GHGs.

Figure 41 below is a schematic of the predicted and observed Raman vibrational modes in the Earth's atmosphere at different electromagnetic frequencies.

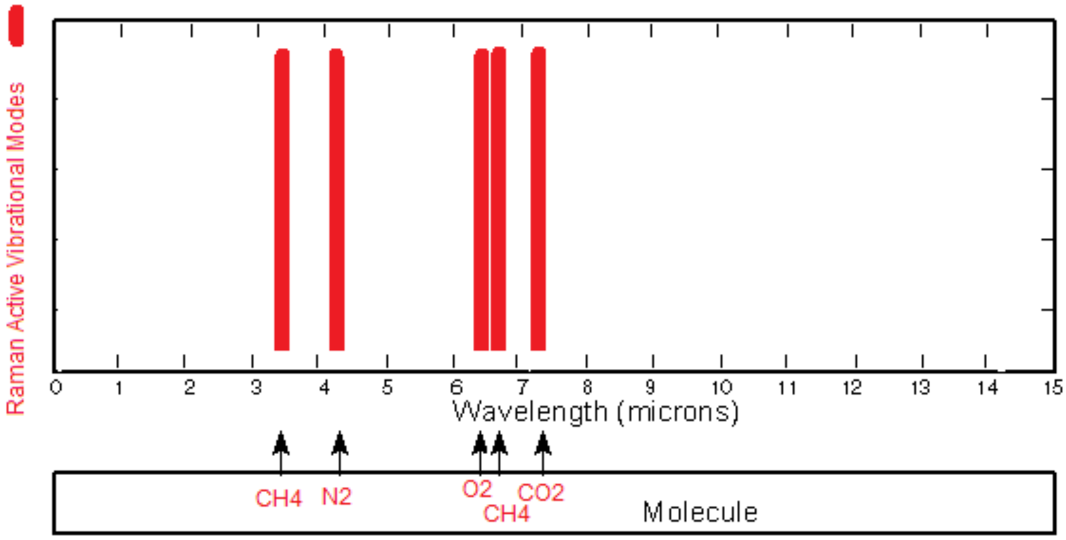


Figure 41. Raman Vibrational Modes of the Atmosphere. Predicted and Raman measured vibrational modes of (some) atmospheric gases CH4, CO2, N2 and O2.

4.9.1 The Augmented Fourier Greenhouse Atmosphere spectrum

Combining thermoelectric and Raman Spectrographs (figure 42 below) reveals all the predicted and observed vibrational modes of the atmosphere. The augmented atmospheric spectrum now accounts for the hidden 'dark' 98% of gases in the atmosphere.

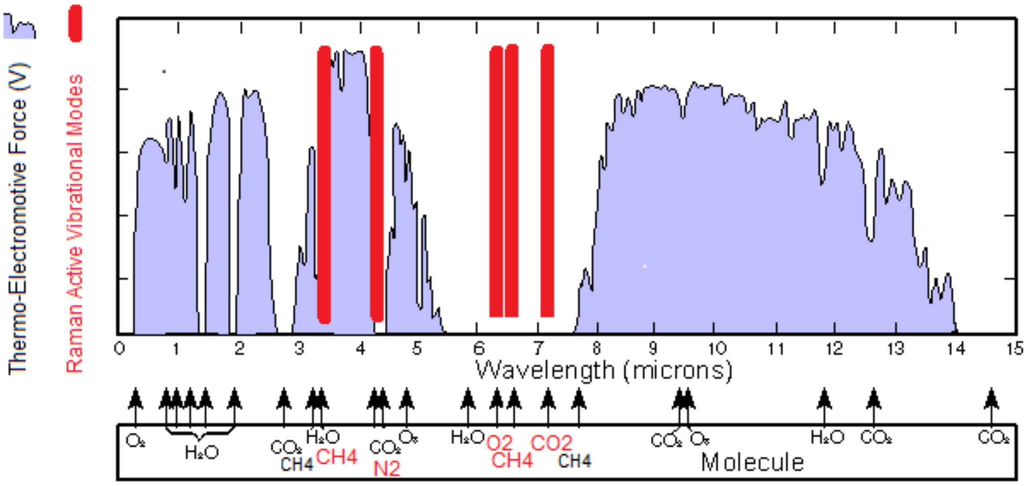
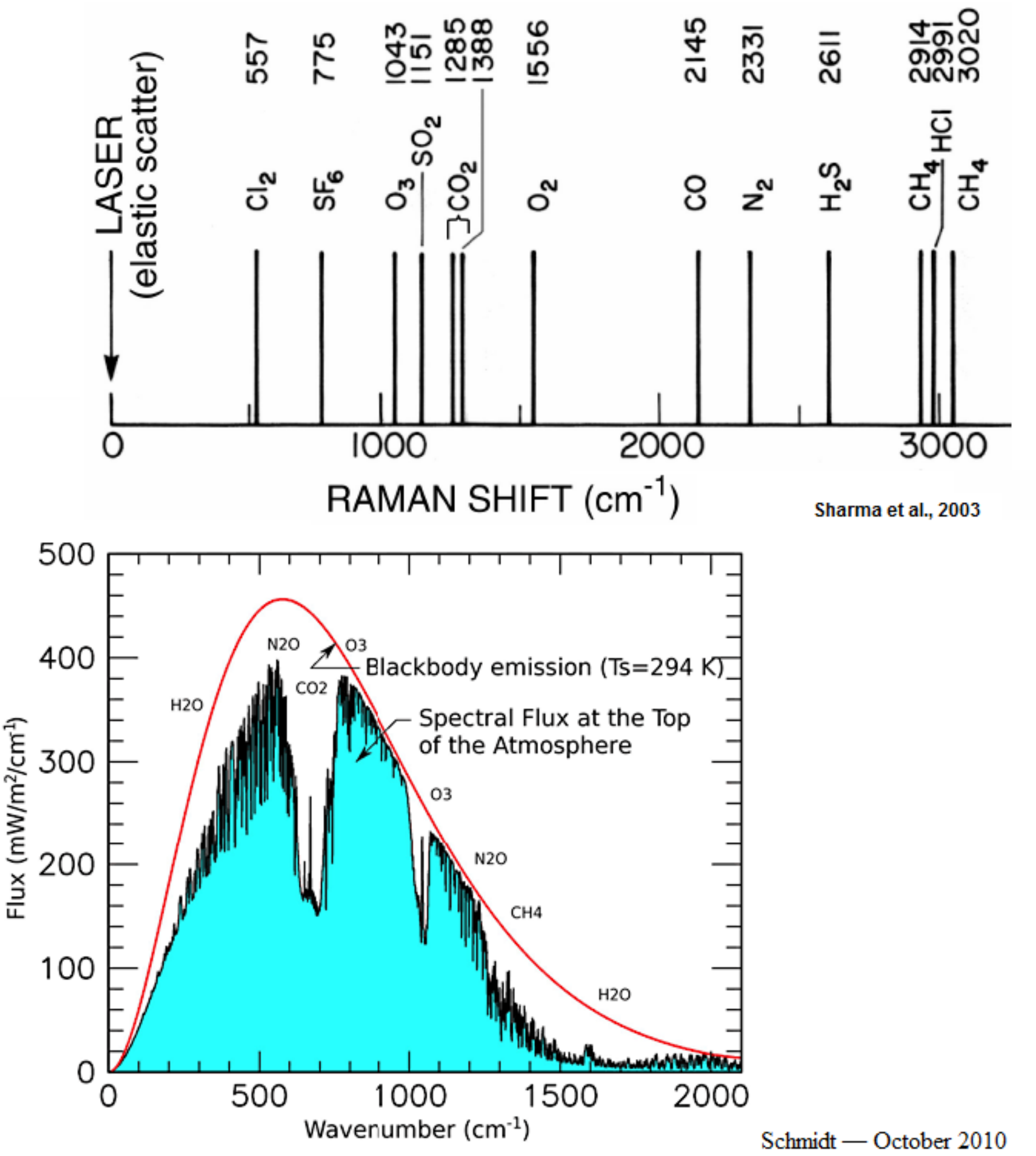


Figure 42. The Augmented Greenhouse Atmosphere. Combining Thermoelectric spectra with Raman spectra to reveal the complement of atmospheric vibrational modes and the greenhouse atmosphere of planet Earth.

In recognition of the first person to posit a 'greenhouse' atmosphere – before the advent of thermoelectrics and Raman Quantum mechanics – the augmented atmosphere maybe known as the Fourier Atmosphere: where all gases are greenhouse gases.

Below (figure 43) is a diagram of the Fourier Atmosphere as read from complementary instruments thermoelectric and Raman.



Sharma et al., 2003

Schmidt — October 2010

Figure 43 'IR' Thermoelectric with Raman Atmosphere. Combining the two methods of accounting for constituent gases, namely N_2 O_2 H_2O, CH_4 O_3 and more, to complete the Fourier Greenhouse Atmosphere.

Together the IR-Raman and IR-TE modes cover all the vibration modes of the atmospheric gases, and in so doing explain how it is the air absorbs and emits infrared radiation.

5 Conclusions

Without referring to any climate politics or climate records, this investigation showed the science of climate 'is far from settled [2], but is, in fact, wrong at its foundations. This was a first principles investigation to ascertain the validity of the fundamental premises and assumptions of greenhouse theory: is it only the 'special' "greenhouse gases" that absorb and emit infrared radiation, and remaining the non-greenhouse gases N_2 and O_2 do not, the answer was not in favour. While it is not discussed in physics today, this assumption, as it stands, is a contradiction of quantum mechanics – where all matter above absolute zero is assumed to radiate infrared radiation; in this study the solution was found. The hypothesis of the study was clear: N_2 and O_2, at their predicted 2338 cm^{-1} and 1556 cm^{-1} modes respectively, both do radiate and are too GHGs, and the reason for the discrepancy lies with a misinterpretation of the fundamental greenhouse experiment – the Tyndall experiment. Tyndall only really discovered the gases that are thermoelectric, as measured by, and as he used, thermoelectric thermopile transducers. The 19th Century Tyndall experiment, and resulting greenhouse theory, was before the time of modern 20th Century quantum theory, and the emergent technology developed from it, namely and specific to this investigation the modern laser-based Raman spectrometer – IR spectroscopy's complement instrument. The investigation aimed to reconcile the contradiction by augmenting Raman spectroscopy with current 'greenhouse theory'. To do this current vibrational physics and chemistry theory was reviewed, and a number of related real-life practical applications – that appear to contradict the status quo position – identified.

Primarily the investigation referred to a report where a Raman spectrometer measured temperature and molecule emission concentrations of N_2 and O_2 and others – directly from a jet engine exhaust plume's quantum spectra. It was found from this report N_2 and O_2's Raman vibrational modes, and the other Raman active modes including CO_2's 1338 cm^{-1} mode (which is not able to be detected by thermoelectric IR spectroscopy) are equivalent (by the equipartition principle), and comply with standard quantum-mechanics radiation and thermodynamics theory. N_2 and O_2 are greenhouse gases; they absorb, and they emit IR radiation – it is only they are not thermoelectric. Raman instruments measurements concur with standard physical principles – including the Boltzmann constant – to the extent they can measure temperature and gas concentration to an equal of the greater degree of precision than it's similar thermoelectric counterpart. It is not the gases that are special; it is the instruments. In support of this it was found all three of H_2O's IR radiating modes, particularly the 3652 cm^{-1} mode, are both – or dual – Raman and thermoelectric/IR active, which says the detectors are equivalent – temperature can be measured by both.

As an aside, and with respect to IR spectroscopy, this investigation uncovered it is only Raman IR spectrometers that actually radiate their samples: thermoelectric instruments transduce thermal radiation into emf and 'report' of graph the difference between the sample and reference heat source. Raman instruments, it was shown, do not have the problem of emissivity, and that this is solely an infrared-thermoelectric instrument problem. It was concluded emissivity is a limitation of the thermoelectric transducer to generate complete emf from a substance, and is not a real property of radiation. Also, as Raman and thermoelectric modes being equivalent, it was concluded Raman modes, and thus N_2 and O_2, are the best 'blackbody' radiators as they have an emissivity of 1. This discovery of including the 'Raman modes' in atmospheric radiation theory will challenge and possibly overturn current blackbody theory in general; where contradictions are also abound – such as water and snow being assumed near perfect (emissivity) absorbers.

It was also concluded spectrographic thermoelectric infrared modes (current IR active modes) differ only – and in terms of their current part in determining the GHGs – by their possession (or not) of an electric dipole moment, and hence their respective emf generation. All the so-called 'IR modes' – special only to the special greenhouse gases – are actually no more than the thermoelectric modes, and should be termed the 'thermoelectric IR modes' or TE/IR modes in short.

With knowledge of thermoelectrics and the GHGs, it should come as no coincidence – and be common sense – the only property separating the GHGs from the non-GHGs is whether or not the gas has a mode with an electric dipole, and the emf potential of this fact. One does not need to be an expert to understand that the possession of an electric dipole ('IR active') pertains directly to the thermo-electric modes able to generate electricity by the thermoelectric transducers – termed detectors. Conversely, the modes without these electric modes are the non-thermoelectric and wrongly termed 'non-GHGs'. These Tyndall gases should be termed the thermoelectric gases (TEGs).

The CO_2 Laser was found to be a practical application in support of (solar) IR absorbing N_2 (and O_2). From the quantum mechanics behind, and the application of the CO_2 Laser, and particularly from the direct interplay between N_2 and CO_2 in it, was claimed atmospheric N_2 molecule not only absorbs (IR) photons at its 2338cm^{-1} mode, but the energy absorbed is 'long living' metastable and is 'passed onto' the CO_2's 2349cm^{-1} mode. With photon absorption, it is N_2 that affects the CO_2. This finding is totally inconsistent with greenhouse theory; however, it has the physics and the application – not to mention the real constituent volume of gas – behind it. It was shown N_2 freely absorbs at this wavenumber – outside the laboratory – and may well explain how air instantly rises in temperature – in the process of thunder production – to some 3 times the temperature of the surface of the sun – where it is said now the air 'absorbs' photons, and electrons from electron excitation – all in compliance of quantum mechanics. It was concluded the atmosphere absorbs IR radiation from the sun by (solar) insolation directly and warms the air just as it does the oceans and the like are, rather than indirectly, as it is currently assumed.

In respect to heat capacities, it was discussed Raman and thermoelectric properties also correspond to the nominal heat capacities of the said gases.

With this new understanding of the quantum mechanics of the atmosphere – and the direct mechanics behind Raman spectroscopy – it was revealed a current fallacious understanding of the 'greenhouse' atmosphere. Any extrapolation based on thermoelectric technology alone – without reference to the Seebeck effect and Raman spectroscopy – and interprets the special GHGs alone as the IR absorbent gases, should be seen as inadmissible not only in climate and atmospheric theory, but also any radiation theory. Climate models will need to be updated to take account of the – currently well-understood – Raman modes and knowledge, and conclude all gases as greenhouse gases, as first posited by Joseph Fourier (and maybe others) ca. 1828. With this new understanding, all gases comply with the 0th and 1st Laws of Thermodynamics – transferring energy towards equilibrium where previous to this N_2 and O_2 were exempt.

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8 Appendix

8.1 Other Uses for Raman

8.1.1 CO2's 1388cm-1 Excitation: The Dicke effect

Investigating whether CO_2's 1388cm^{-1} is excited in any way by radiation – it should not as this mode, like N_2 and O_2's is 'Raman active' and not 'IR active' and thus, by current assumptions, should not transmit photon energy – it was found this mode is affected 'where the spectral exchange and Dicke effect play a noticeable role' [84]. The Dicke effect: 'refers to the Doppler broadening of a spectral line due to collisions the emitting species (atom or molecule) experiences with other particles' (photons) ;…the atom changes velocity and direction many times during the emission and absorption of the photon[85].

This is clear evidence this mode is active and they do radiate.

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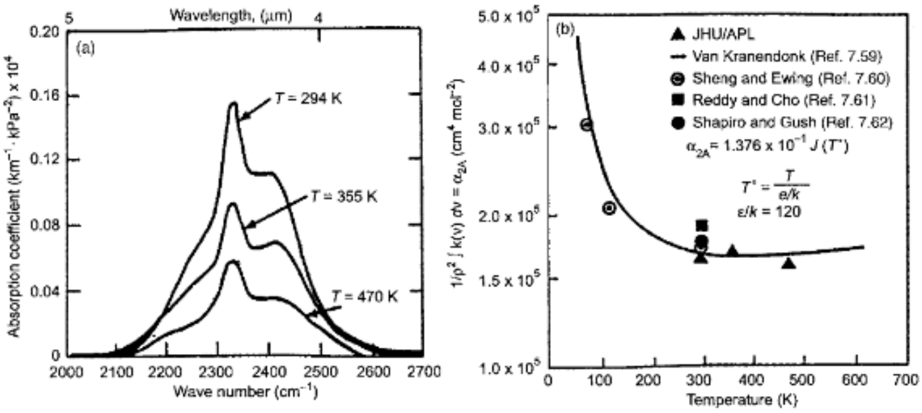


Fig. 7.21 Collision-induced absorption in the fundamental vibration band of N_2. (a) Band shape at various temperatures and (b) integrated intensity versus temperature (Thomas, Ref. 7.50).

[86]

8.1.2 Medical – anaesthetic RASCAL – Capnography Application

"In 1988 a Raman scattering instrument was introduced for clinical use. The RAman SCattering AnaLyzer (RASCAL)…for O_2, CO_2, N_2, N_2O; both identify and quantify these gases." "This device is no longer marketed"[87].

These Raman devices have since advanced and are used.

'These analysers have fast response times. They can analyze multiple anesthetic agents with good accuracy (greater than infrared spectroscopy, approaching mass spectrometry)' [88].

8.1.3 Geology CO_2 1388 cm^{-1}

In the following study: "Quantification of dissolved CO_2 in silicate glasses using micro-Raman spectroscopy" CO_2 is identified at its IR 1388 (or near about) cm^{-1} mode.

'we propose the calibration accuracy is better than ±0.4 wt% CO2 for our data set'[89]

8.1.4 Automobile Emission Testing.

Raman is an accepted instrument in measuring automobile emissions; it is so by exploiting the 'radiative' behaviour of the non- GHGs. This is a contradiction.

The from the USA EPA: *"Raman LIDAR is self-calibrating to atmospheric oxygen and nitrogen, eliminating requirements for periodic calibration with test gases."[90]*

"The results indicate an excellent ability to identify and quantify the test species. By analyzing the sensitivity of these Phase I laboratory experiments, we estimate that the Compact UV Raman LIDAR system will be capable of achieving better than 120 parts per million (PPM) sensitivity for NO, 40 ppm for N_2 and CO, and 10 ppm for NO_2 and hydrocarbons."

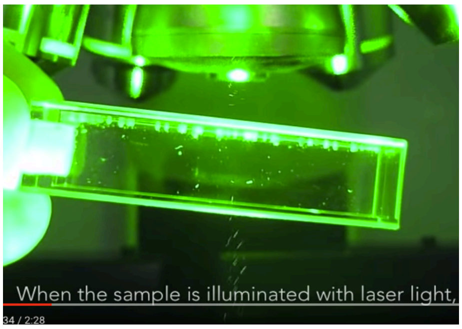
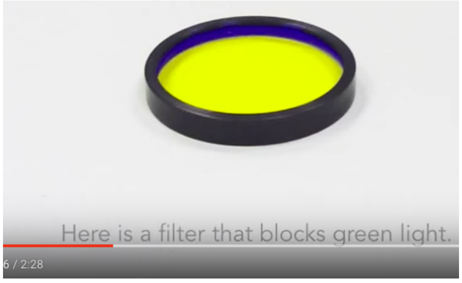
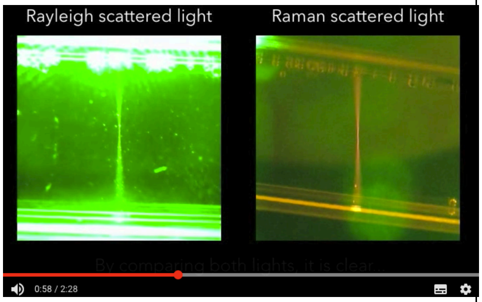
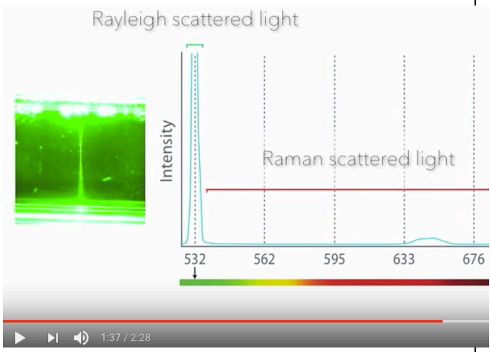
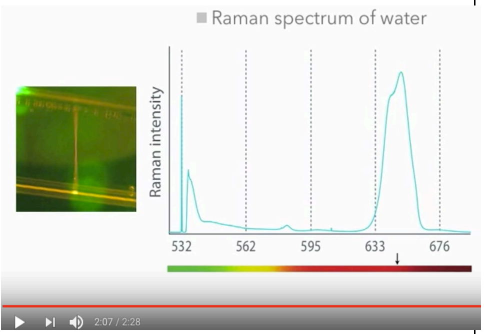
Truth be known, Raman can equally detect and quantify CO_2 (by its Raman 1388 cm^{-1} mode) as revealed in the following study. However, before we go there, in the study 'Rotational Raman Spectroscopy for the Remote Sensing of Carbon Dioxide' [91] they concluded: "No Raman peaks were observed, so that the usefulness of rotational Raman for the remote sensing of CO_2 was not demonstrated."

This maybe so for 'remote' solutions; however, it does not match the many results from other studies.

In the book 'Automotive Exhaust Emission Testing..' they acknowledged the (potential) use of Raman "Both methods (IR and Raman) are complementary" [92] pg. 128; however, it did not go onto show the use of Raman.

8.2 Understanding Raman Backscatter and the Low Wavenumbers

It has been quoted to me that these lower Lidar wavenumbers – at 580nm and 607nm respectively – are inconsistence with my theory and show N_2 and O_2 in the atmosphere do not vibrate – emit and absorb – in the IR range of the EMS as these modes or bands are in the visible range of the EMS; I have researched these lower modes and found they indeed reveal the IR modes – they need correction. The reason the Lidar wavenumbers are quoted low is because they are quoted in relation or reference to the laser frequency of the Lidar laser. They work on the 'Raman backscatter'. When adjusted for, the differences are corrected (up) and correspond the predicted wavenumbers. This is demonstrated in the youtube presentation below[93] where in the last moments it is said: ". By using wavenumber, we see the excitation of water, independent of the excitation wavelength".

A	B
 When the sample is illuminated with laser light, 	 This is Rayleigh scattered ligh
C	D
 Here is a filter that blocks green light. 	 By comparing both lights, it is clear
E	F
 	
G	

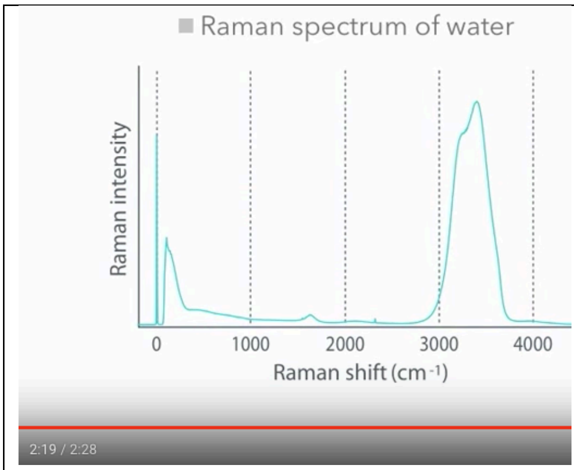
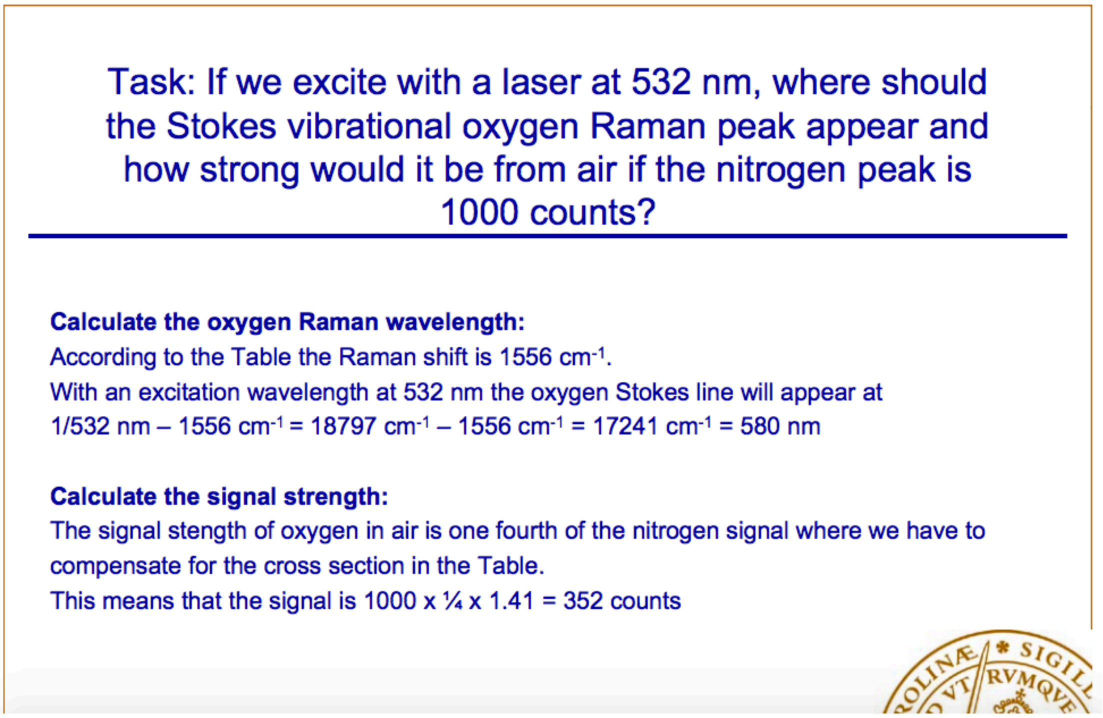


Figure 44. Raman Lidar wavenumber discrepancy Explained. Screen shots of a Youtube presentation [93]showing how green 532nm laser light is shone (A) onto water in the case Raleigh light is revealed (B and E), but when filtered Raman red 660nm light is revealed (D and F). When this adjusted for wavenumber (cm-1) H2O's vibration band 3652cm-1 is revealed.

8.2.1 Raman Laser to Wavenumber Correction Calculation

A demonstration and method of the calculation needed to correct from the low wavelength produced by Raman Lidar and Laser to the real wavenumber vibrational bands (in this case, O_2) was found. This is evidence the often quoted low wavenumbers must be corrected or understood to be relative to the incident Raman laser frequency and not the real vibration mode.



Task: If we excite with a laser at 532 nm, where should the Stokes vibrational oxygen Raman peak appear and how strong would it be from air if the nitrogen peak is 1000 counts?

Calculate the oxygen Raman wavelength:

According to the Table the Raman shift is 1556 cm^{-1}.

With an excitation wavelength at 532 nm the oxygen Stokes line will appear at

1/532 nm – 1556 cm^{-1} = 18797 cm^{-1} – 1556 cm^{-1} = 17241 cm^{-1} = 580 nm

Calculate the signal strength:

The signal stength of oxygen in air is one fourth of the nitrogen signal where we have to compensate for the cross section in the Table.

This means that the signal is 1000 x ¼ x 1.41 = 352 counts

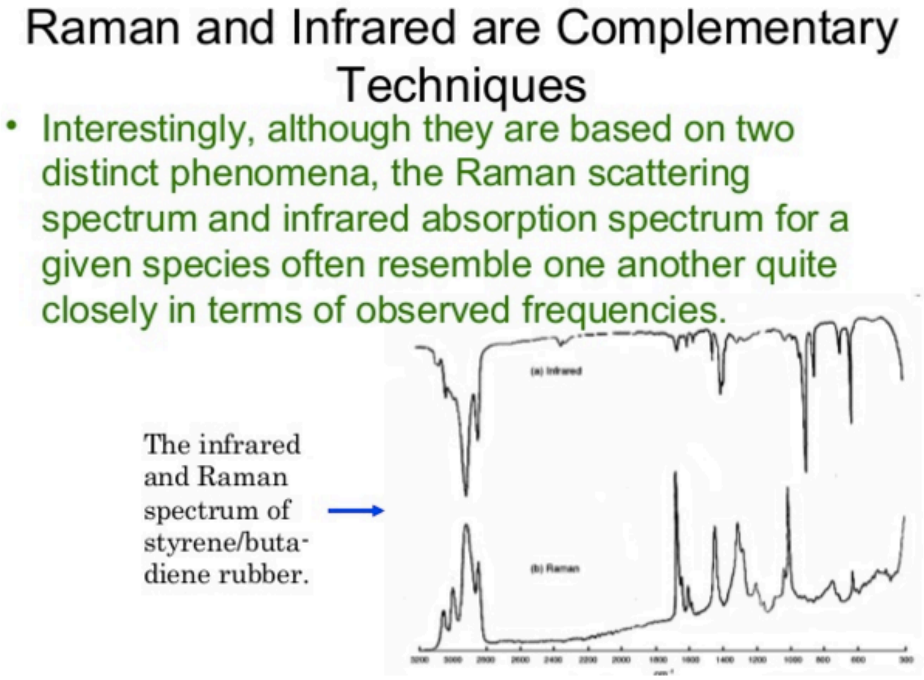
Figure 45. Scattering to Wavenumber calculation for Nitrogen. Nitrogen's 1556 cm-1 predicted and observed (with Raman spectroscopy) vibration mode is corrected for the 532nm laser. [94]

8.3 Raman and Thermal Electric IR Equivalence – Dual Modes

Some modes appear to be both thermoelectric and Raman active. This indicates that although most substances do not share this (CO2 for example); these substances must be understood to be radiating. If there is a mode; there is radiation – emission and absorption.

8.3.1 Raman Complementary to IR Thermoelectric

It is well understood by chemists Raman is a complement to 'IR' spectroscopy: no one has made brought them together with regards to the infrared atmosphere.



Raman and Infrared are Complementary Techniques

- Interestingly, although they are based on two distinct phenomena, the Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely in terms of observed frequencies.

The infrared and Raman spectrum of styrene/butadiene rubber.

Figure 46. Complementary IR and Raman Spectroscopy. Infrared above; Raman below[95]

8.3.2 H_2O is both Raman and IR (thermoelectric) Active

Water has a special property significant to vibrational mode theory, it is both Raman active and 'IR' active at: 1590 cm^{-1}, 3690cm^{-1}, and 3790cm^{-1}.

'IR' Active Thermoelectric spectra of H_2O

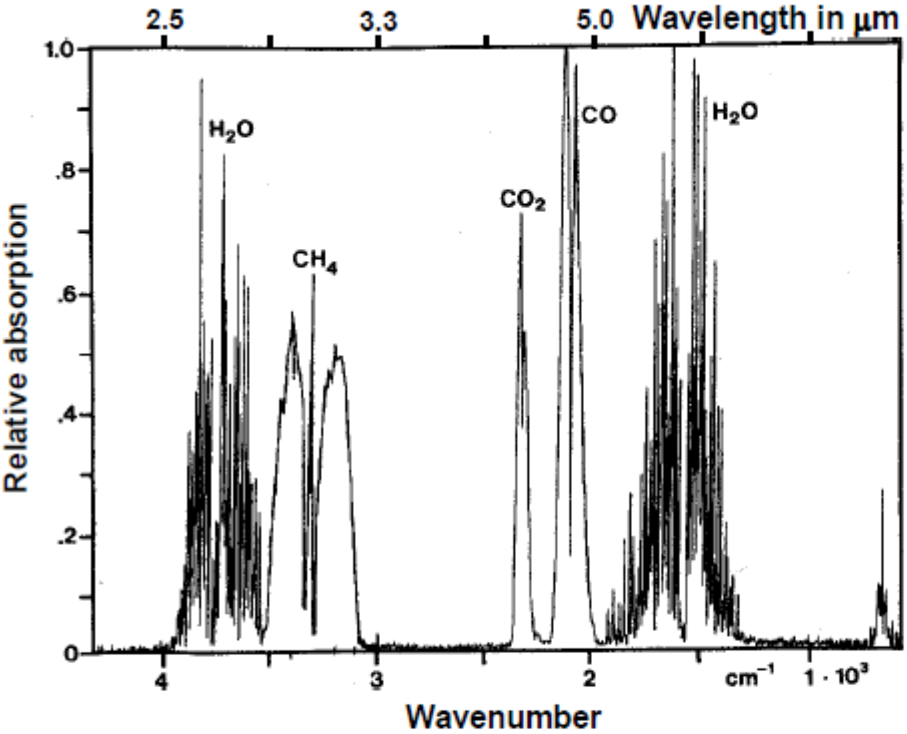


Figure 47. TE IR of H_2O and others.

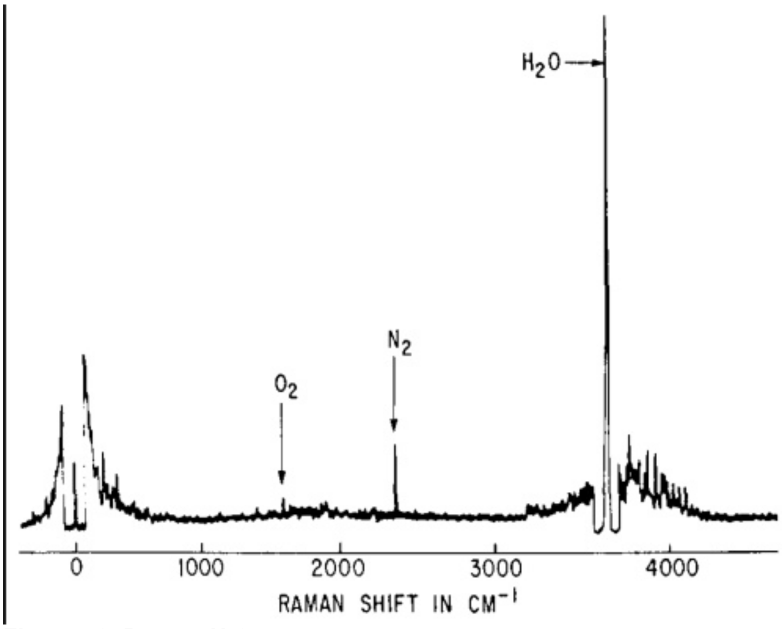
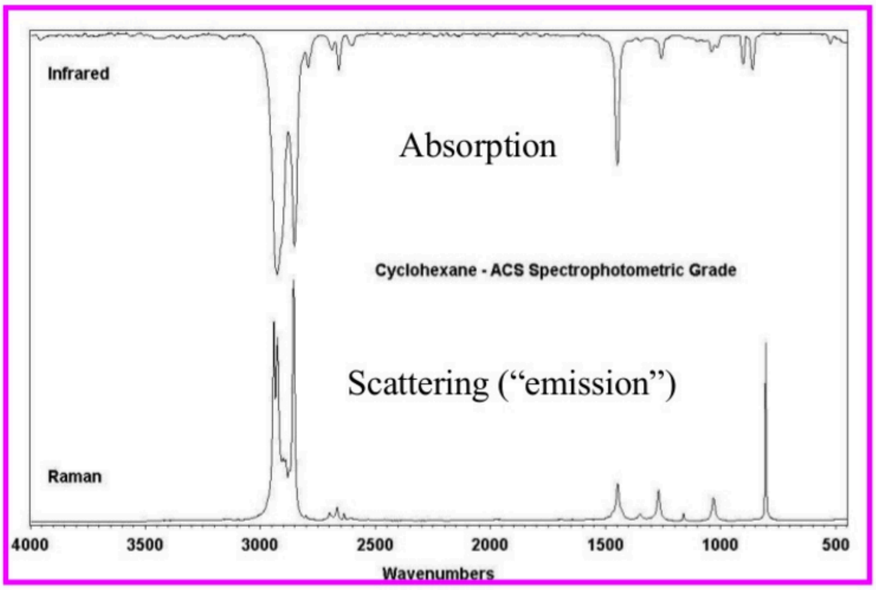


Figure 48. Raman H_20.

8.3.3 Other molecules with duel Raman thermoelectric.



A molecule can be characterised (and identified) based on the position and intensity of the spectral peaks by either FT/IR or Raman spectroscopy

Figure 49. [96]

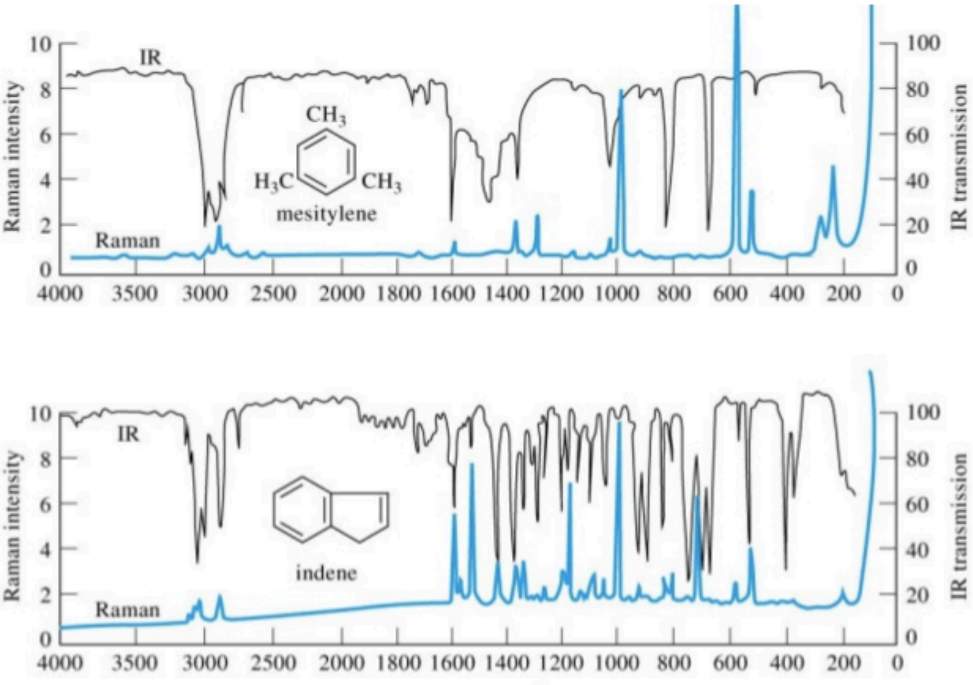


Figure 50

8.3.4 Ethanol

The following is an interesting (Raman image) reference: Ethanol has both and shared Raman and thermoelectric modes. I’ll drink to that.

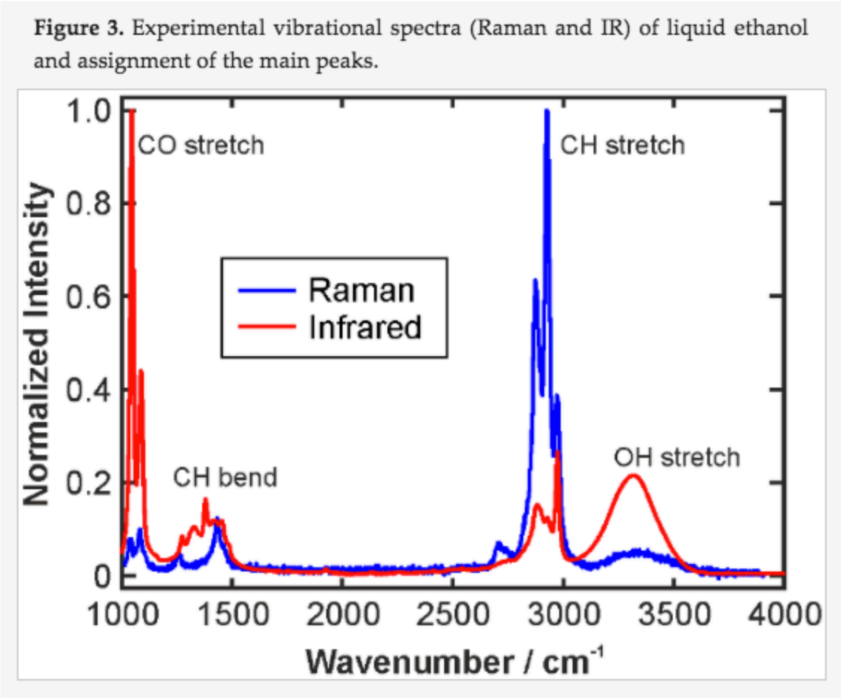


Figure 3. Experimental vibrational spectra (Raman and IR) of liquid ethanol and assignment of the main peaks.

Figure 51. Ethanol Sharing Both Raman and Thermoelectric. [97]

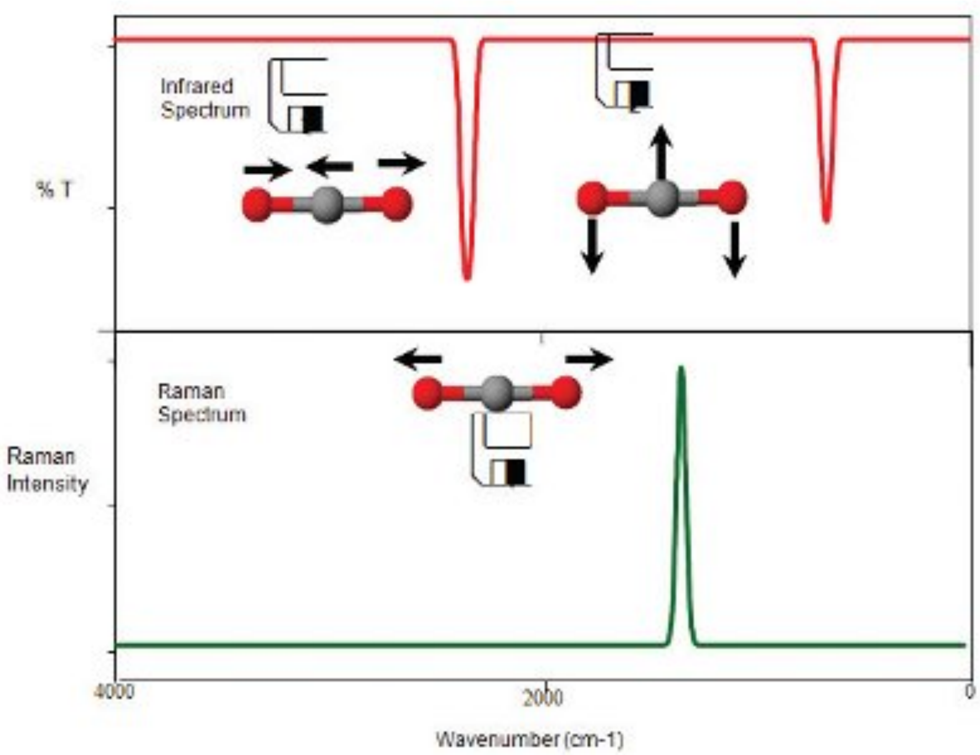


Figure 52. Schematic of CO2 Raman and IR Spectra. “In gas phase spectra of CO2, two infrared modes are observed at 2350 and 667 cm-1 (red) and a single Raman band at ~1388 cm-1 (green). (The latter band is actually a doublet due to quantum mechanical resonance effects, which is beyond this discussion).” [98]

8.4 Raman spectra for Non-GHGs and GHGs

8.4.1 O_2 and N_2

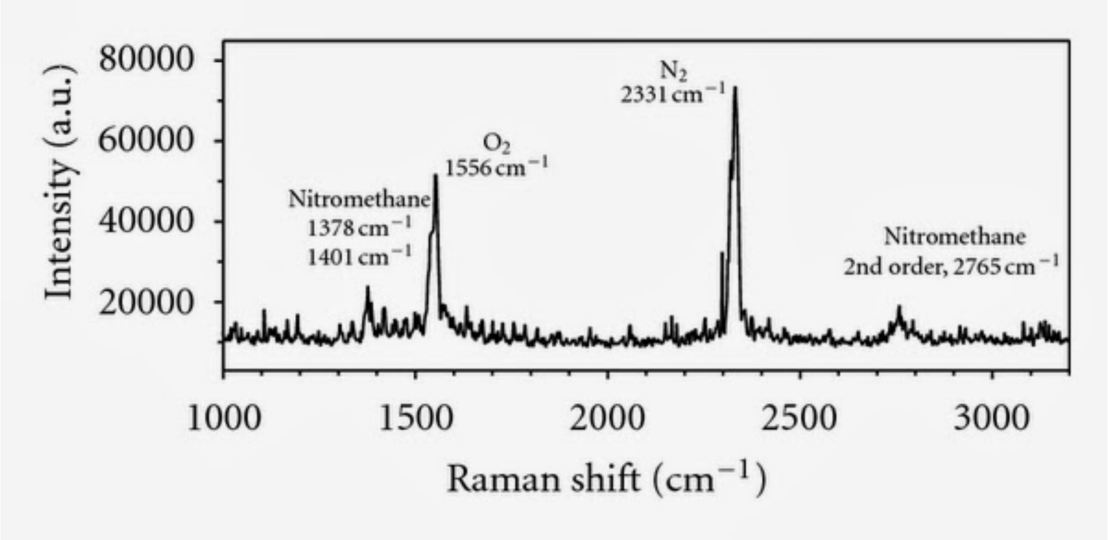


Figure 53. [99]

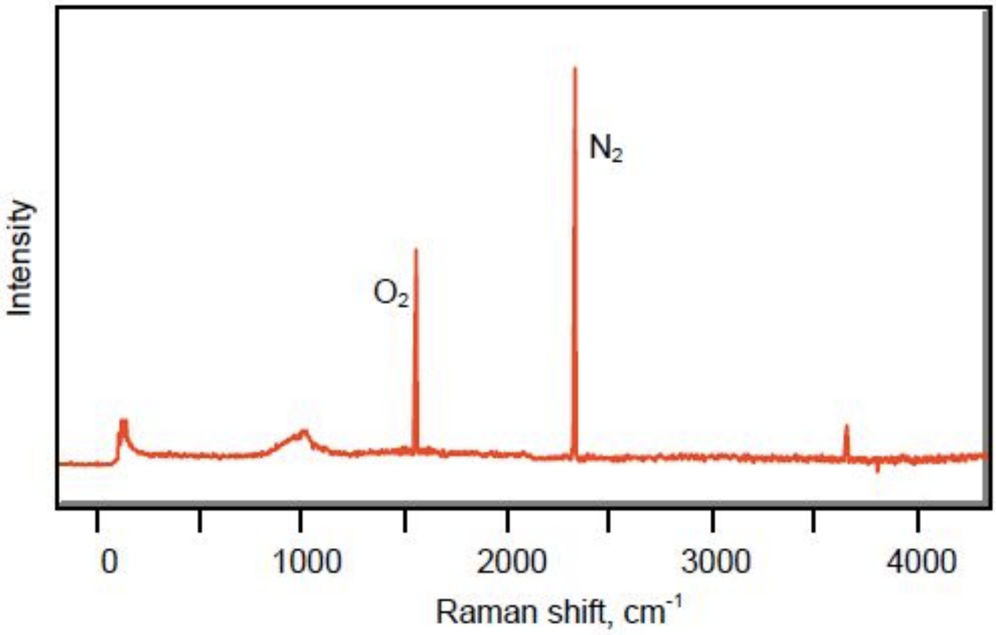


Figure 54. Raman spectrum of air, with the oxygen and nitrogen bands marked. [100]

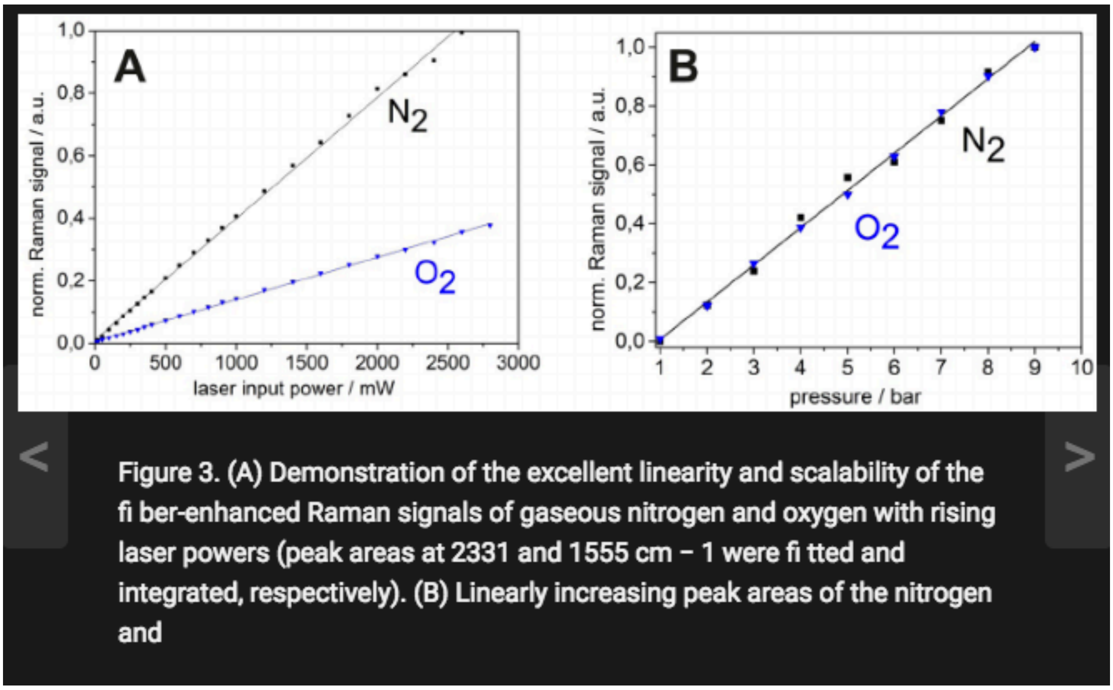


Figure 3. (A) Demonstration of the excellent linearity and scalability of the fi ber-enhanced Raman signals of gaseous nitrogen and oxygen with rising laser powers (peak areas at 2331 and 1555 cm − 1 were fi tted and integrated, respectively). (B) Linearly increasing peak areas of the nitrogen and

Figure 55. The above three images above: [101]

“It has to be noted that monoatomic gas molecules, such as nitrogen, N2, or oxygen, O2, are not affected by IR radiation and can therefore not be detected by this means. Otherwise the mentioned atmospheric greenhouse effect would be extremely severe and probably we would not exist in the current life form”. [49]

8.4.2 O_2 Spectra

300 OPTICAL PROPAGATION IN LINEAR MEDIA

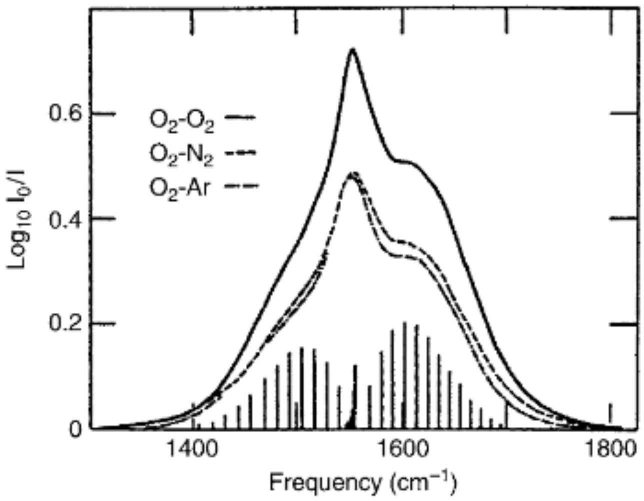


Fig. 7.22 The fundamental absorption band of oxygen for a path length of 40 meters. The densities are: pure oxygen 9.59 Amagats; oxygen–nitrogen mixture, $\rho_{O_2} = 1.09$ Amagats, $\rho_{N_2} = 56$ Amagats; oxygen–argon mixture, $\rho_{O_2} = 1.12$ Amagats, $\rho_{Ar} = 57.9$ Amagats (Shapiro and Gush, Ref. 7.62, with permission). (Note: 1 Amagat is the STP ratio of pressure in atm to temperature in K.)

Figure 56. [86]

8.4.3 N2 2338 cm^{-1}

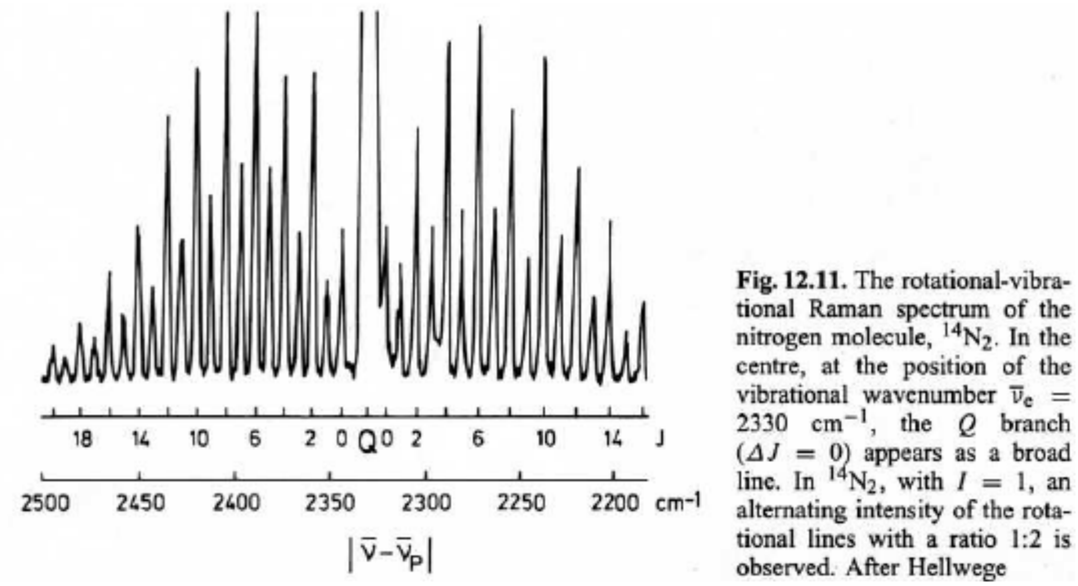


Fig. 12.11. The rotational-vibrational Raman spectrum of the nitrogen molecule, $^{14}N_2$. In the centre, at the position of the vibrational wavenumber $\bar{\nu}_e = 2330\ cm^{-1}$, the Q branch ($\Delta J = 0$) appears as a broad line. In $^{14}N_2$, with $I = 1$, an alternating intensity of the rotational lines with a ratio 1:2 is observed. After Hellwege

Figure 57. Raman peaks of N2 at the predicted 2330cm-1 – page 209 [102]

8.4.4 O_2 1556

Figures 6 and 7 below show Raman spectrograph peaks of N_2 at O_2 at the predicted 1556cm-1 and 2330cm-1 (pages 205 and 209 respectively) both within the infrared range of the electromagnetic spectrum.

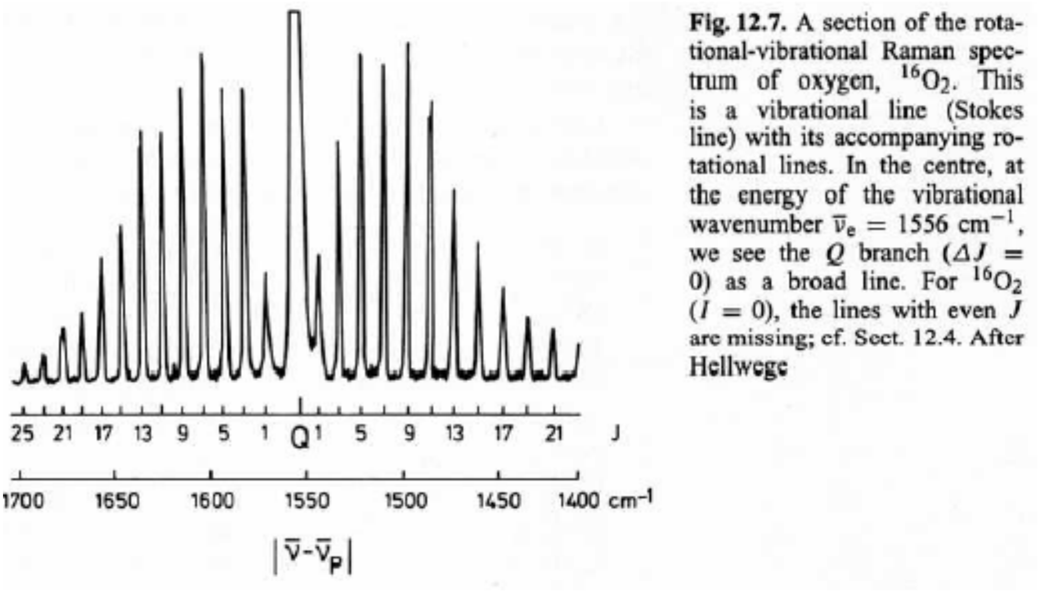


Fig. 12.7. A section of the rotational-vibrational Raman spectrum of oxygen, $^{16}O_2$. This is a vibrational line (Stokes line) with its accompanying rotational lines. In the centre, at the energy of the vibrational wavenumber $\bar{\nu}_e = 1556\ cm^{-1}$, we see the Q branch ($\Delta J = 0$) as a broad line. For $^{16}O_2$ ($I = 0$), the lines with even J are missing; cf. Sect. 12.4. After Hellwege

Figure 58. Raman peak of O_2 at the predicted 1556cm-1 [102] – page 205.

8.4.5 CH_4

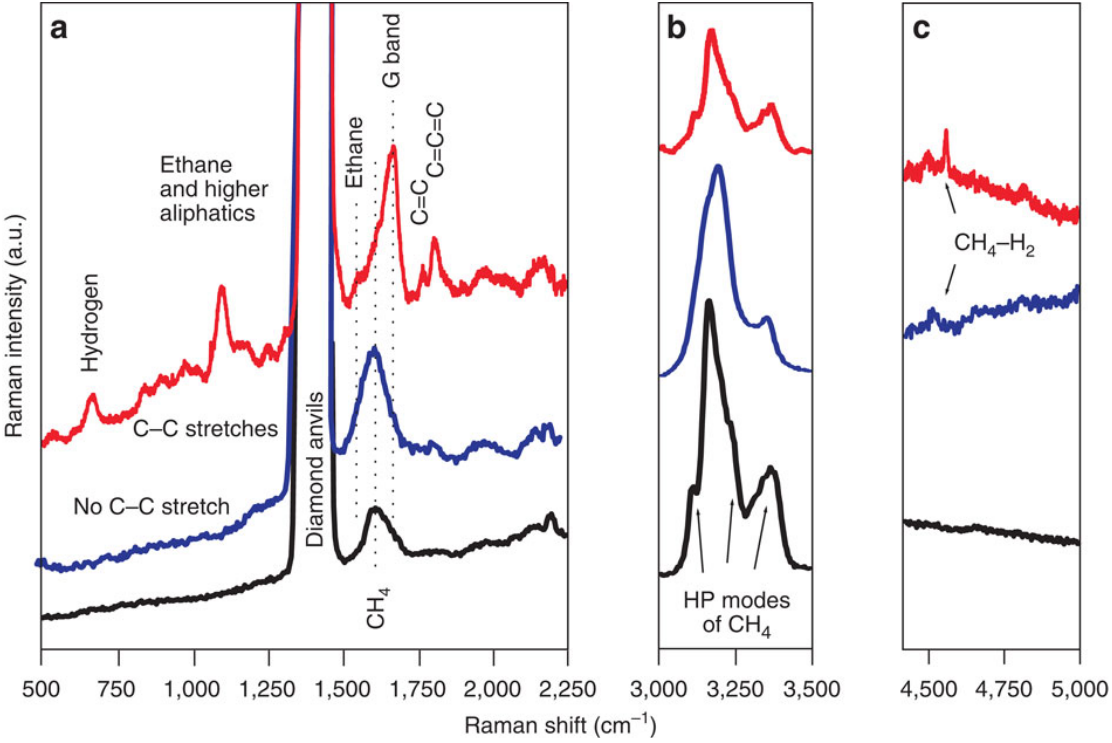


Figure 59. Synthesis in LH DAC at 48 GPa. Black line shows CH4 Raman spectrum before heating. Blue line shows Raman spectrum collected at 1,445 K with evident CH4 dissociation. Red line shows Raman spectrum of reaction products collected after heating to 2,000 K. The labels near the curves suggest the assignment of the Raman bands. HP modes of CH4 refer to vibrations caused by partial orientational ordering of methane HP phase. Panels a–c show different parts of the spectral range.[103]

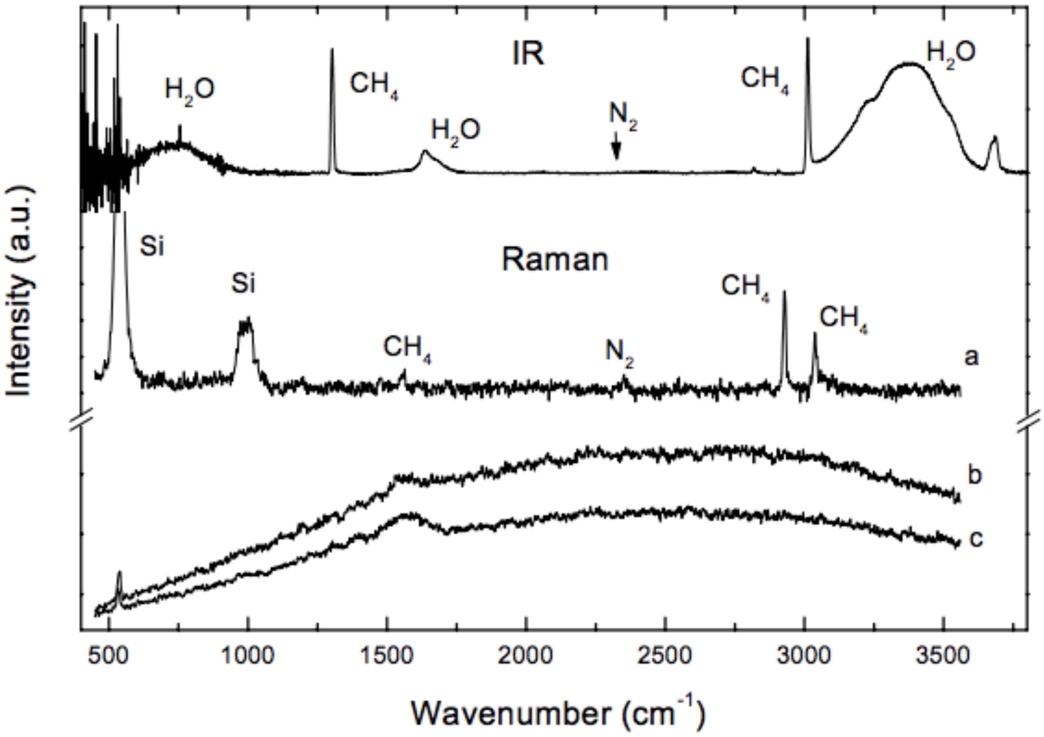


Figure 60. IR (top curve) and Raman spectra of the mixture H2O:CH4:N2 before (curve a) and after (curves b and c, corresponding to doses of 378 eV/16 amu and 825 eV/16 amu respectively) irradiation with He+ (30 keV) ions at low temperature (12 K). In spectra b and c the ice features are undetectable because of the intense fluorescence background. The arrow in the IR spectrum indicates the position of the N≡N symmetric stretching mode, which cannot be observed. Fig. 3 [104].

8.4.6 H_2

Hydrogen gas is assumed a non-GHG as it has similar properties to the other non-GHGs; however, it is predicted at 4342cm^{-1} (table 2) and observed by Raman spectrometers as below figure 65.

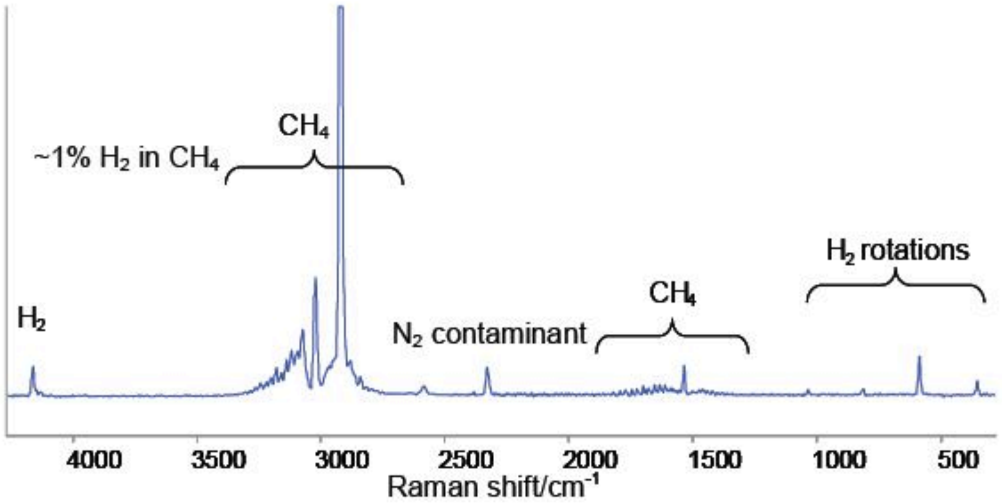


Figure 2. *Raman spectrum of 1% H_2 in CH_4. The sharp bands below 1040cm^{-1} are the pure rotational transitions of the H_2 molecule.*

Figure 61. CH_4, H_2, with N_2 Raman Spectra. [105]

8.4.7 H_20 Raman

Earth atmospheric temperatures are too warm for H_20’s Raman signatures too show. The predicted vibrational modes are shown below.

KOLESOV: RAMAN INVESTIGATION OF H_2O MOLECULES IN HEMIMORPHITE 1359

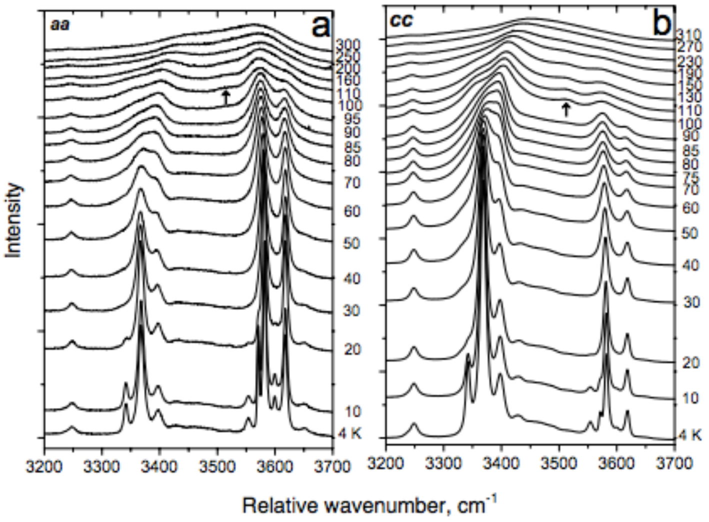
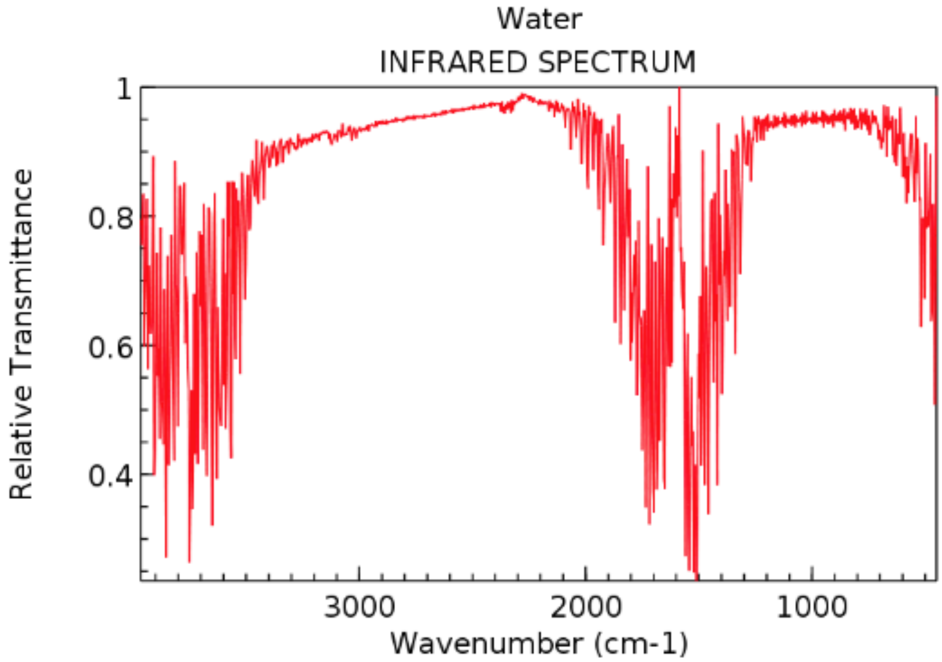


FIGURE 5. Temperature evolution of the polarized spectra showing the O-H and H_2O stretching modes in hemimorphite; (a) *aa*-spectra and (b) *cc*-spectra. The appearance of the new band at around 3500 cm^{-1} at $T \geq 100$ K is shown by the arrow.

Figure 62. [106]

8.4.8 H_2O TE IR



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Figure 63. H2O IR Spectra Showing 3652cm Band.

8.4.9 Ge Germanium

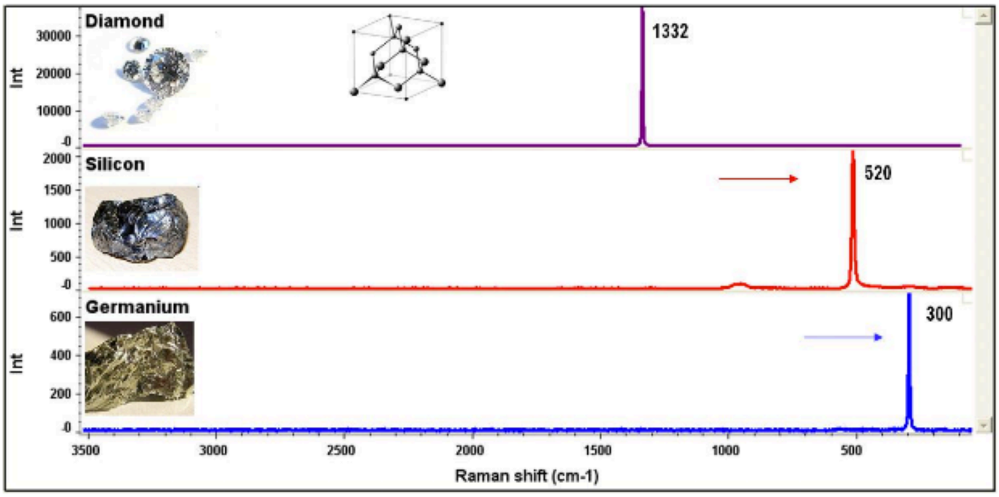


Figure 1: Raman spectra of diamond, crystalline silicon, and crystalline germanium

Figure 1: Raman spectra of diamond, crystalline silicon, and crystalline germanium.

Figure 64. [107],[108]

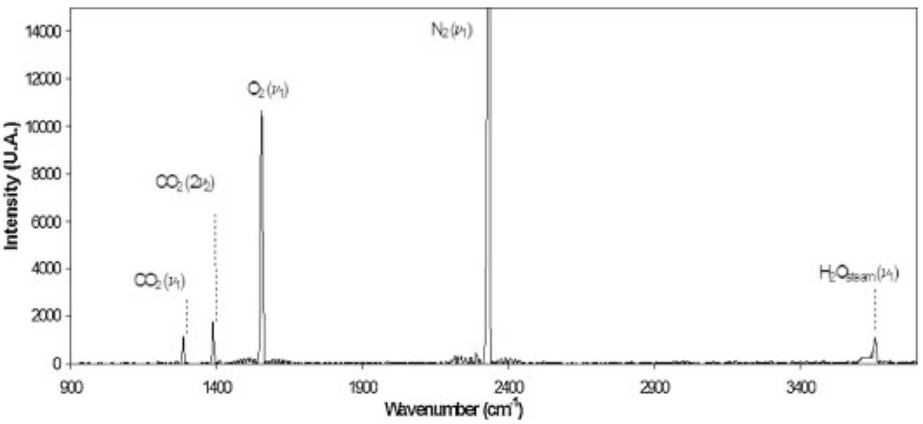


Figure 2. *A typical Raman spectrum measured at the site in this study. Key peaks: H_2O vapor (3657cm^{-1}), N_2 (2331cm^{-1}), O_2 (1555cm^{-1}), and CO_2 (Fermi dyad at 1388 and 1285cm^{-1}).*

Figure 65. Raman Spectra of N2, O2, CO2 and H20 together. [109]

8.5 The following text is a (typical) chemistry explanation as to why N_2 and O_2 are not GHG's [110]:

"N2 and O2 have no dipole, so they are not greenhouse gases. Nitrogen (N2) is symmetrical AND made of identical atoms. Even with rotation or vibration, there is no unequal sharing of electrons between one N atom and the other. So N_2 has no dipole, and an EM photon passes by without being absorbed. Similarly, for O2."

8.5.1 Greenhouse and Non-greenhouse (thermoelectric and non-thermoelectric) wavenumbers

In detail, from the table (1), each molecule has a specific (calculated) number of modes (degrees of freedom): N_2 and O_2 have 1 each, at 2331 cm^{-1} and 1556 cm^{-1} respectively. CO_2 has 3 degrees of freedom – 2 IR thermoelectric (at 2349 cm^{-1} and 667 cm^{-1}) and 1 non-thermoelectric (at 1338 cm^{-1}); CH_4 has 6 degrees of freedom: 4 thermoelectric and 2 non thermoelectric; and H_2O has 3 degrees of freedom – 2 thermoelectric (at 1595cm-1 and 3756cm-1), and 1 non-thermoelectric (at 3652cm-1).

8.5.2 Mode Type, Thermoelectric or Raman,

The mode type (shown in column 4 table 1) is to me the crux of the greenhouse problem: greenhouse theory posits it is these mode-types that specifically determine what is, or what is not a greenhouse gas. It also assumes the non-thermoelectric modes do not 'thermally radiate. This cannot be true. I argue there has been a misconception: the non-thermoelectric modes have been ignored and discriminated, but if they are real, they are there (as we shall soon see) and they do radiate.

8.5.3 Electric Dipole Moments

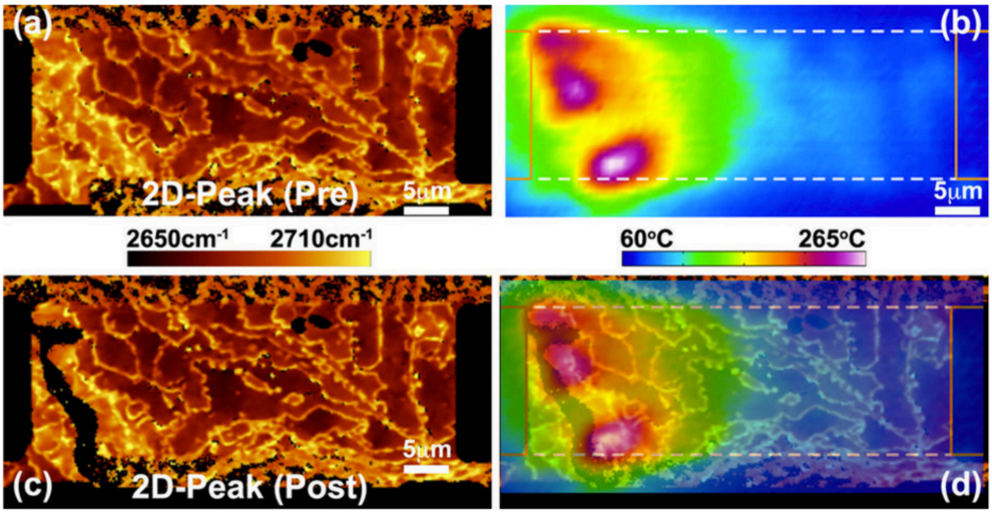
If a molecule has a vibration mode other than a symmetric mode it possesses an electric dipole moment. This electric dipole moment is a key word here: if an electric dipole moves, it generates electricity (with thermo-electric transducers); if not, they do not. As can be seen, the thermoelectric (IR active/ greenhouse gas) modes of all the gases have all types of modes (**stretch, wag, and so on)**. It is the non-greenhouse gases that have symmetric modes. Symmetric directly implies – to be clear – no electric dipole: no electricity generated by the thermo-electric transducers, and it is for this reason they do not show up – at any temperature. This where the problem lies; and this is where it ends.

If a molecule has only one of these electric (dipole) modes, it is enough to call it a greenhouse gas. N_2 and O_2 have no electric dipole modes and so are (correctly) not detected, but incorrectly termed non-greenhouse gases as this does not mean they are not radiating. CO_2 also has one electric dipole mode that are also missing from this IR spectrograph, and CH_4 two.

To reiterate: if a mode or gas possesses an electric dipole moment (or movement) – revealed simply from a movement of the dipole – it is a greenhouse gas. These modes will show on a spectrograph like **figur**e above.

8.6 Thermal Image with Raman

Find the thermal image and write it up.



(a) Raman image of 2D-mode peak position before self-heating. Variation in peak position indicative of multilayer boundaries and mobility reductions are evident near left contact. **(b)** IR measured temperature distribution while dissipating 325 mW of power. **(c)** Raman image of 2D-mode peak position after failure. **(d)** Overlay of **(b,c)** indicating that the failure is co-located with regions of most severe heating. The grounded electrode is on the right-hand side.

Figure 66. [111]

8.7 Raman LIDAR and the Atmosphere

While I have shown N_2 and O_2 both have vibration modes that satisfy the prediction made of them (2330 and 1556cm-1 respectively) different and lower wavenumber observations of them are made by using Lidar.

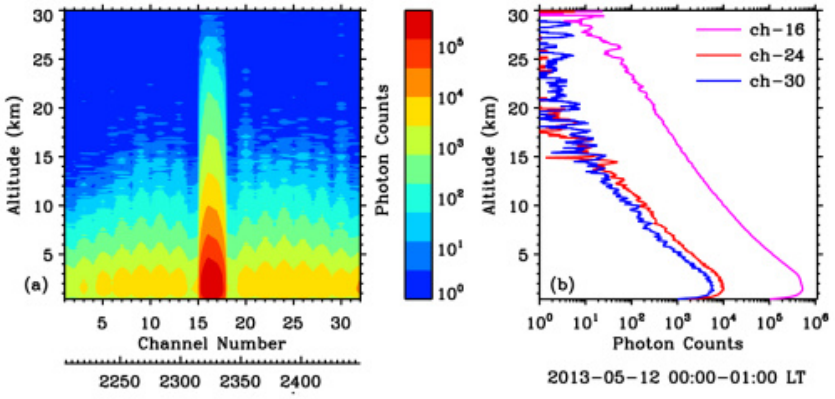


Fig. 3 (a) Altitude-dependent atmospheric N_2 Stokes vibrational-rotational Raman spectra derived from the spectrally resolved Raman lidar measurement at Wuhan during 0000-0100 LT on 12 May 2013. (b) Signal intensity profiles for the 16th (Q branch; magenta), 24th (S branch, *J* = 6; red) and 30th (S branch, *J* = 12; blue) channels, respectively.

Figure 67. Diagram showing N2 by Lidar, altitude and wavenumber, more evidence to N2 2349cm-1 vibration mode. [112]

In the diagram below N_2, O_2, and H_2O are shown with their Raman scatter wavelength – 580, 607, and 660nm from the incident laser 532nm aline with the their respective wavenumbers, 1553, 2330, and 3652 cm^{-1}.

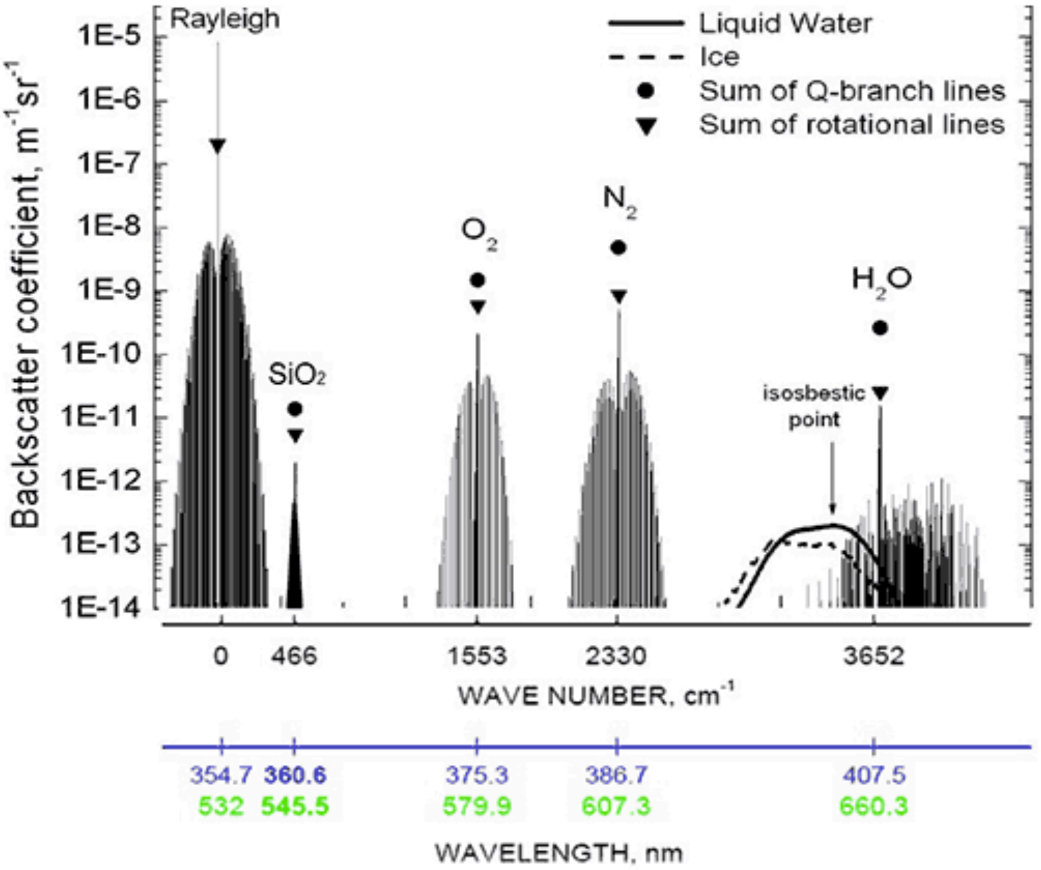


Figure 68. **112]**

Lidar can reveal the temperature of the atmosphere:

"The RL measures atmospheric temperature using the ratio of two signals from the lidar's rotational Raman (RR) channels. The RR channels sense Raman-shifted backscatter arising from rotational energy state transitions in atmospheric N2 and O2 molecules due to excitation at the laser wavelength of 354.7 nm (Di Girolamo et al. 2004, Behrendt et al. 2004, Radlach et al. 2008)." [114].

6.0 Example Plots

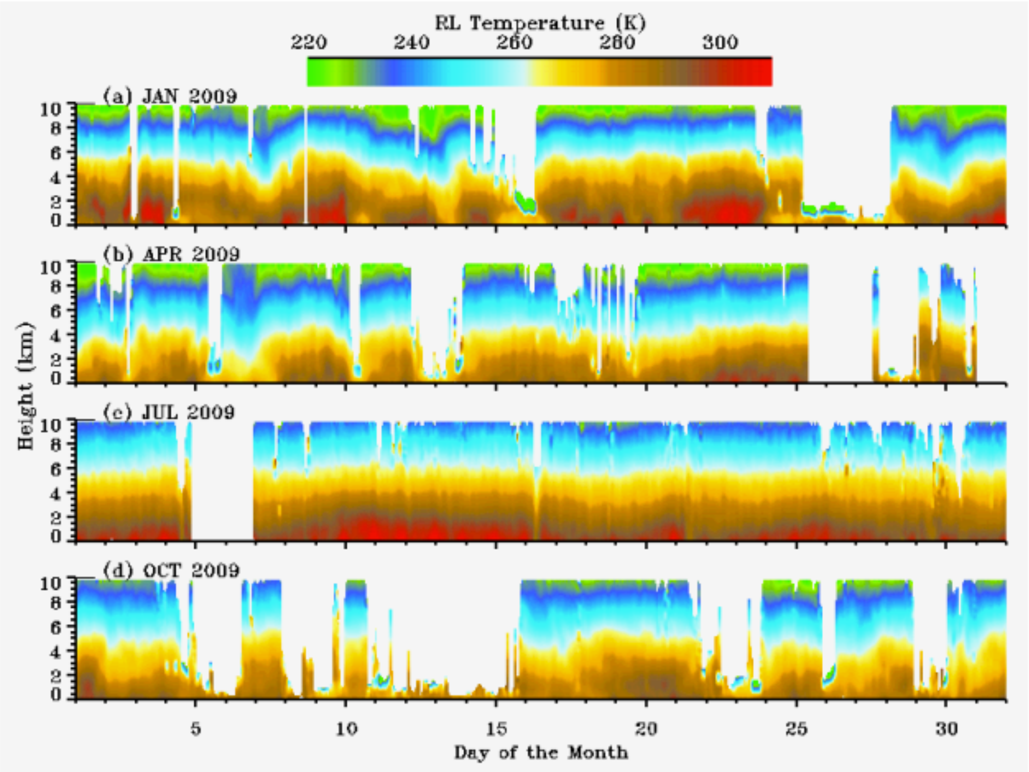


Figure 4. Sample output from the RLPROFTEMP VAP covering four selected months. Results are shown for (a) January 2009, (b) April 2009, (c) July 2009, and (d) October 2009.

Figure 69. [114]

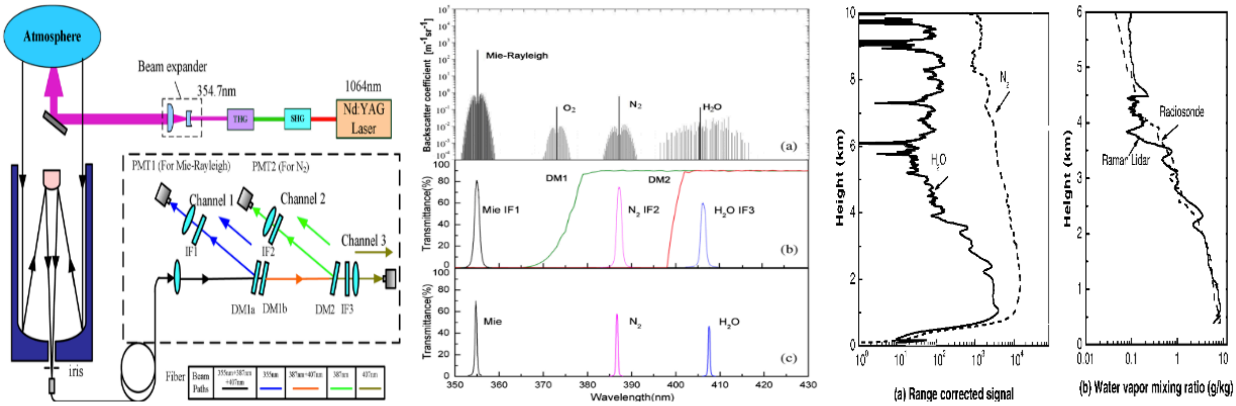


Figure 70. [115]

In another example, Raman uses methane and Nitrogen to measure temperature.

"An airborne lidar to measure methane, water vapor, and temperature on board NASA's flying laboratory, the DC-8, has been developed at Goddard Space Flight Center. Methane and water are measured using Raman (inelastic) scattering, while temperatures are determined from both Rayleigh (elastic) scattering and nitrogen Raman. Methane's long stratospheric lifetime (approximately a decade) makes it an ideal conserved tracer to track the motions of streamers or filametns of air as they peel off the polar vortex. Temperature measurements allow a calculation of the quasi-conserved quantity, potential temperature, which is useful in following the motions of large air parcels. The water measurement allows stratospheric water transport across the subtropical boundary to be studied." [115] " Page 273"

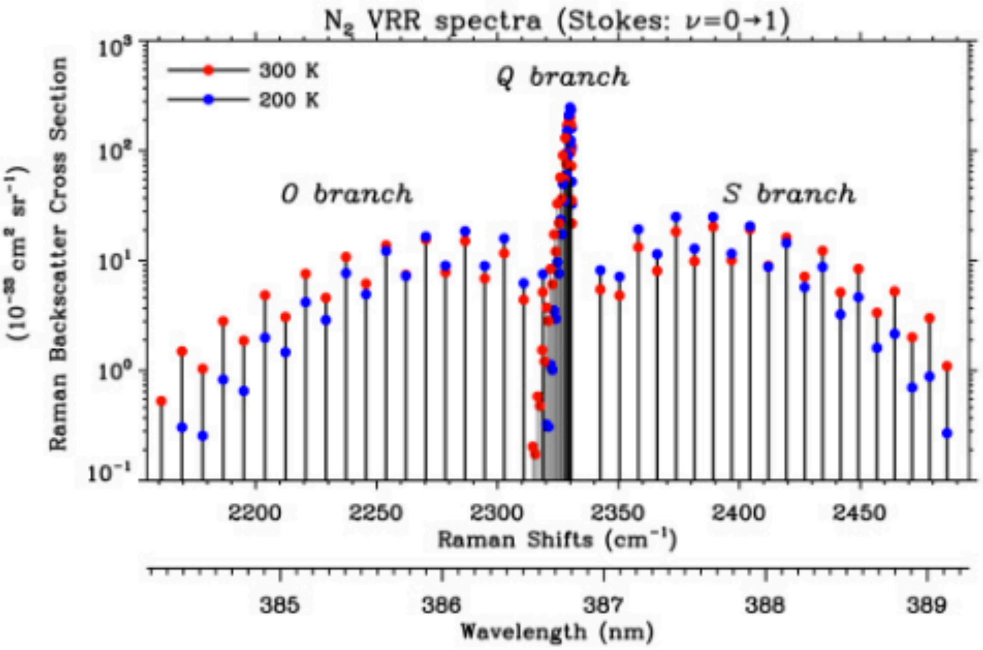


Fig. 1 The Stokes vibrational-rotational Raman (VRR) spectra of atmospheric N_2 obtained from a theoretical calculation for temperatures of 200 K (blue) and 300 K (red) respectively. The incident laser wavelength is 354.8 nm. Note that the S- and O-branch lines have nearly the same line spacing (~0.12 nm) from J|= 0 (2) to 20.

Figure 71. Atmospheric N2 by Raman Lidar at laser stimulation 354.8nm. Notice the wavenumber of 2330cm-1 is shown and also temperature is deduced. [112]

8.8 Animals that can see IR

Humans do not see the infrared, but some other animals can – pit snakes are the best example. These snakes have pits that house 'detectors' and their vision is said to be just or much like a thermal camera – at least that is how it is described by experts. If this is so, then the question is: are they are exploiting thermoelectricity and the Seebeck effect? I have found no reference to this; but, they seem to be able to see animal heat, but not - interestingly – the temperature of the air. My question here is whether snakes – like us with our thermopiles – see all the IR? No, they do not – they see only the thermoelectric as far as one can tell. It appears they are as limited – or discriminant – as we are. They, like us, are exploiting a property of substances – thermoelectricity.

Some tests that may clear things would be: can the snake see 'hot' objects through glass? The thermal camera cannot and a no answer to this would suggest they are thermoelectic. The hypothesis they are.

It is interesting that fish – for the most part – cannot detect IR or use it directly: this makes seen as water is a thermoelectric substance. The question that would be interesting