

The Greenhouse Gases and Infrared Radiation Misconceived by Thermoelectric Transducers

Blair D. Macdonald

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Abstract

Greenhouse theory has at its foundation a special group of trace gases and molecules. Together these gases are claimed to be the only ones that absorb infrared radiation. The assumption that the remaining gases, nitrogen and oxygen, do not absorb or emit infrared radiation presents a paradox; it contradicts both quantum mechanics and the laws of thermodynamics which prescribes that all matter above absolute zero degrees Kelvin radiates infrared photons. In this study the role of thermoelectric detectors as used to determine the 'infrared atmosphere' was investigated. This study hypothesises that current greenhouse theory has misinterpreted the significance of those special greenhouse gases (CO₂ etc.) since they and their spectral 'modes' are detected only by thermoelectric transducers: that they are the thermoelectric gases. It was concluded that the special (1%) greenhouse gases, discovered by Tyndall in ca. 1859, are really only those detected by thermo-electric transducers. 'IR' spectroscopy is also based on these thermoelectric transducers, and as a consequence 'IR' spectrographs show only the spectral modes with electric dipoles and not Raman modes. All current Blackbody radiation theory is determined from thermoelectric measurements alone and requires revision in light of complementary modern Raman laser Spectroscopy measurements. From this thermoelectric understanding in conjunction with modern Raman Spectroscopy, it was concluded that current greenhouse theory is incomplete and misconceived. All of the atmosphere radiates IR radiation in compliance with the said laws. The only thing separating the gases are the instruments detecting them.

Key Words: Greenhouse effect, Tyndall Experiment, climate change, Raman Spectroscopy, thermoelectrics, Seebeck effect, emission spectroscopy

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1 Introduction

With respect to the infrared (IR) atmosphere, the total gases are divided between what are termed the 'IR' gases – the greenhouse gases (GHGs) – and Non-IR gases – the non- greenhouse gases (non-GHGs).

The GHGs constitute 1-2% of the dry atmosphere and account for the entire atmospheric IR thermal-radiation behaviour; explaining all climate, on all time scales. This leaves the remaining constituents, (less H₂O) the non-GHGs – nitrogen (N₂) and oxygen (O₂) – out, as they are assumed not to absorb or emit any IR radiation, at any temperature[1]. This foundational premise to GH theory holds both N₂ and O₂ are 'transparent' to 'Shortwave' IR light because they do not – with respect to their molecular vibration behaviour – share a dipole moment. An electric dipole moment. These non-GHGs only receive their IR (heat) energy via 'collisions' with the special IR absorbing GHGs [2][3] after they themselves have been radiated by the Earth's surface with 'Longwave' IR radiation. These very odd and counter-intuitive assumptions should still be at the centre of the climate debate. The science, the physics, it not settled – as claimed. As it stands, these assumptions present a contradiction to standard physics. Notwithstanding air's near-zero thermal conductivity property (0.024 W/m K), Planck's and Stefan-Boltzmann's Laws (T⁴) of radiation and standard quantum mechanics, no less, all state all 'matter' above absolute zero Kelvin absorb and emit IR (photon) radiation. How is it N₂ and O₂ exempt of these laws; placing them s likes to the cosmos's paradoxical 'dark energy' and 'dark matter'?

I think the quantum physics holds and there has been a mistake or oversight somewhere to cause this misconception. Finding a solution to this is the goal of this paper.

What we do know is this: all the quantum mechanics predicted spectra in the IR come in two 'flavours', and the same is true for the atmosphere; they are IR active and Raman active. Accordingly, the IR is observed by IR spectrometers, and the Raman by Raman spectrometers. The Raman spectrometers can accurately measure temperature and gas concentrations so they are not only complements to IR spectrometers, they are, substitutes to the IR spectrometers.

These IR spectrometers all have one thing in common: they all employ thermoelectric transducers of different types as their detectors. Raman, on the other hand, exploits the 'Raman effect' to detect their spectra, with the use of laser. We also know IR spectrometers only detect spectra with electric dipole moments – as stated above; and for Raman, though this is not true in all cases, observe only the contrary. In a related study I wrote called *Quantum Mechanics and Raman Spectroscopy Refute Greenhouse Theory [4]* I found Raman spectroscopy proves these so-called non-GHGs are really GHGs.

Bringing this together, in this investigation, it was hypothesised the reason for the IR discrepancy between the atmospheric gases is the 'IR' detectors used. The IR gases and their spectra modes are only detected by the thermoelectric transducer. These transducers receive an electric signal given off from the 'electric dipole'. They do not radiate the sample with IR photons as claimed. What John Tyndall really discovered with the thermopile in 1859, in the first and fundamental GHG deriving experiment [5] (pg. 111) was not the special IR absorbing GHGs as claimed, but rather, the special thermoelectric gases. Further to this, and staying with the thermopile; all the so-called 'IR' radiation knowledge is misconceived for being properties of the 19th-century thermo-electric transducer. This especially pertains to the paradoxes associated with what is termed *emissivity* (ϵ), central to the Stefan-Boltzmann equation $E = \epsilon\sigma T^4$, and the shape and interpretation of what is termed the *blackbody radiation curve*, shown by the red line Figure 1 below. Both, in this paper, are hypothesised to be properties or problems of the thermopile; they are directly associated with the electricity production of different substances at different temperature – no more than that.

To emphasise this, Figure 1 below shows the thermopile derived 'blackbody' curve for an object temperature of 290 K. It is hypothesised this curve shifts to the left (Wein's Law) as the temperature rises due to higher emf output at higher temperatures. This thermoelectric thermopile derived red- shift (my term) has led to the Long-wave absorption and Short-wave emission discrepancy and discrimination of in-between spectra frequencies.

Further to the latter, it was hypothesised N₂'s and O₂'s single non- 'IR' spectra modes, along with CO₂'s one non-IR spectra mode at 2349cm⁻¹ are misrepresented by this *ad hoc* positioning on this curve. Raman spectroscopy and application of the N₂/CO₂ laser shows they are 'strong' and dominate[4], contrary to Table 1.

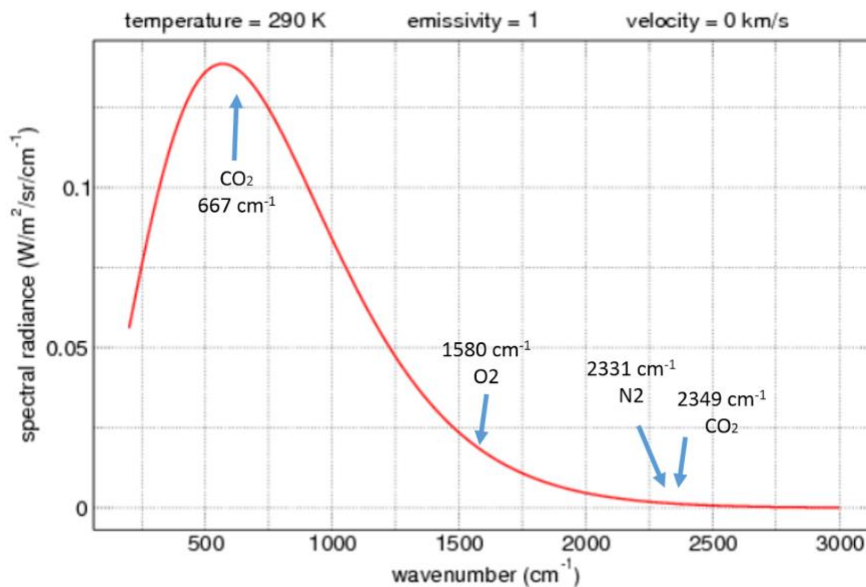


Figure 1. Blackbody Emission Spectrum with Non- GHG modes N₂ O₂ and CO₂. The solar blackbody emission spectra (red) is used to show the output of the non- GHG modes of N₂ O₂ and CO₂

Table 1. Non- GHG modes N₂ O₂ and CO₂ Irradiance by Wavenumber (frequency).

	Vibrational Freq	Radiance W/m ² /sr/cm ⁻¹
CO ₂	Bend/ 667 cm ⁻¹	0.134
CO ₂	Asym Stretch/ 2349 cm ⁻¹	0.001
O ₂	1580 cm ⁻¹	0.018
N ₂	2330 cm ⁻¹	0.001

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. The paper points to the problem being with our misconception of the GHGs. GH theory as it stands is based on 19th Century thermoelectrics (IR spectroscopy) and neglects modern quantum mechanics and the Laser instruments – derived from it. The two,

quantum mechanics and thermoelectrics, together will change our understanding of the atmosphere and more.

2 Methods

No direct experiment as such was undertaken in this investigation but rather a mixture of direct demonstration from and first principles review of the literature, theory, and application, of the instruments and detectors with respect to the hypothesis. To ascertain the IR modes are really only the emf or thermoelectric modes the following was undertaken:

1. Source all the quantum mechanics predicted spectra of the atmospheric gases in the IR range of the EMS and determine which are said to be 'IR' and which are Raman. Is there a pattern matching their respective type to their detection;
2. Source how the chemistry atomic theory that determines whether a spectra mode is IR-active or Raman-active. Test for the hypothesis 'IR Active' asymmetric vibration and electric dipole properties and its relationship to the GHGs.
3. Review the Seebeck effect and its thermo-electric derived transducers and their role in determining the GHGs.
4. Source the instruments or detectors that determine the IR modes and GH gases. Are they thermoelectric by their nature?

3 Results

The following are physics facts with respect to the GHGs and IR radiation.

3.1 Thermo-electric Transducer and the Tyndall Experiment: the - GH Atmosphere

In 1859 John Tyndall [6],[7] published his analysis of the atmospheric gases using the newly developed thermopile transducer and galvanometer [8],[9],[10],[11],[12]. Below (Figure 2) 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.

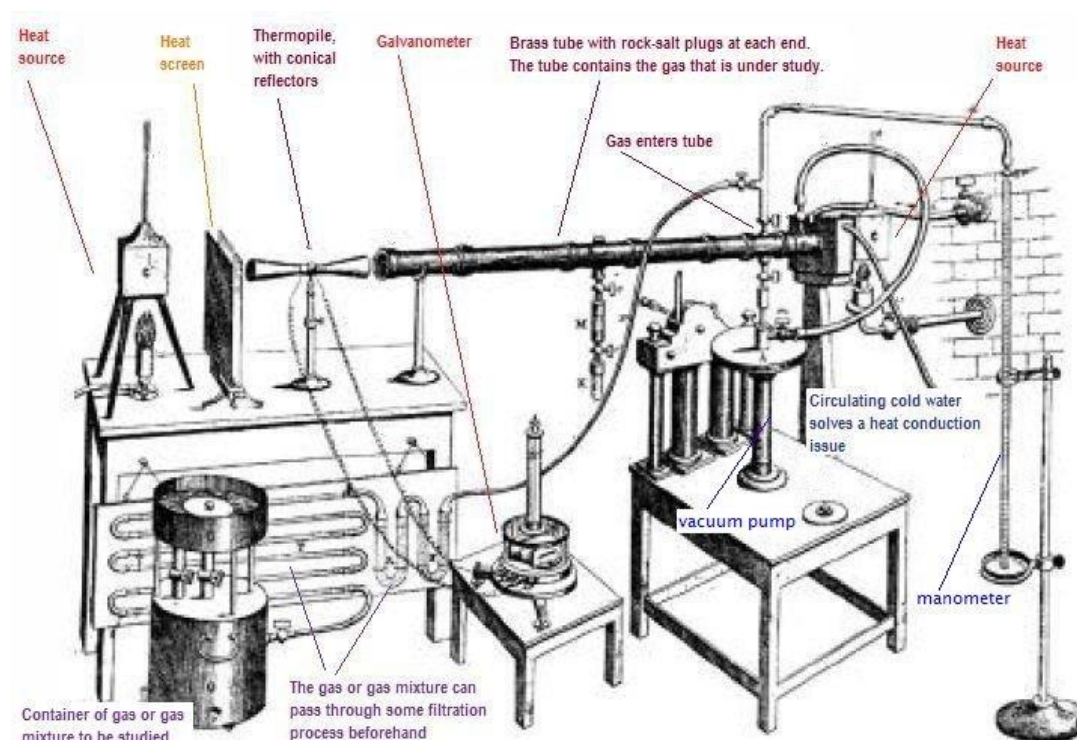


Figure 2. Tyndall's 1859 Setup for Measuring Radiant Heat Absorption by Gases. The apparatus clearly shows thermopile, galvanometer and heat source. [8]

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.

Not the ends of the brass tube containing the gases were plugged with rock salt; we shall come to see why this it and why it is significant in the next section.

The Quantum Mechanics Predicted Spectra of the Atmospheric Gases in the IR Range of the EMS

Table 2 below shows all the quantum mechanics predicted emission spectra modes for the atmospheric gases. The modes are both 'IR' and the 'Raman active'.

Table 2. Atmospheric Gases with their Respective IR Range Vibrational Modes. Modes highlighted in red are of particular interest; they, through the law of equipartition show all modes are the equivalent – and it as the detectors of them that are different.

Molecule	Vibration Mode or Band: Wavenumber (frequency)	IR (Thermoelectric) and IR Raman Spectroscopy Properties	Mode Type
H ₂ O	3652 cm ⁻¹ (2.74μm)	IR and Raman	Symmetric
	1595 cm ⁻¹ (6.25μm)	IR and Raman	Asymmetric
	3756 cm ⁻¹ (2.66μm)	IR and Raman	Asymmetric
CO ₂	1388 cm ⁻¹ (7.2μm)	IR and Raman	Symmetric
	2349 cm ⁻¹ (4.257μm)	IR	Asymmetric
	667 cm ⁻¹ (14.992μm)	IR	Asymmetric
CH ₄	3020 cm ⁻¹ (3.312μm)	IR	Asymmetric
	2914 cm ⁻¹ (3.431μm)	Non IR; Raman	Symmetric
	1508 cm ⁻¹ (6.5μm)	IR	Asymmetric
	1303 cm ⁻¹ (7.7μm)	Non IR; Raman	Symmetric
N ₂	2338 cm ⁻¹ (4.2μm)	Non IR; Raman Active	Symmetric
O ₂	1556 cm ⁻¹ (6.25μm)	Non IR; Raman Active	Symmetric
O ₃	1103 cm ⁻¹ (9.1μm)	IR (Raman Active?)	-
	1042 cm ⁻¹ (9.6μm)	IR	-
	701 cm ⁻¹ (14.3μm)	IR	-
N ₂ O	2224 cm ⁻¹ (4.5μm)	IR	-
	1285 cm ⁻¹ (7.8μm)	IR	-
	589 cm ⁻¹ (17μm)	IR	-

3.2 Electric Dipoles and the Determination of the 'IR-active Modes and GH Gases

*“The major atmospheric constituents, nitrogen, oxygen, and argon, are not greenhouse gases because molecules containing two atoms of the same element such as N₂ and O₂ and monatomic molecules such as argon (Ar) have **no net***

change in the distribution of their electrical charges when they vibrate. Hence they are almost totally unaffected by infrared radiation.”

*“It has to be noted that monoatomic gas molecules, such as nitrogen, N_2 , or oxygen, O_2 , 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”. [13]*

“ N_2 and O_2 have no dipole, so they are not greenhouse gases. Nitrogen (N_2) 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. N_2 has no dipole, and an EM photon passes by without being absorbed. Similarly, for O_2 .”

“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 .”[14]

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. 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. See Figure 10 below for the vibrational behaviour of the CO_2 molecule; the symmetric stretch in non-IR active.

3.3 ‘IR’ Detectors: the Seebeck Effect and the Thermopile

In 1821, Thomas Seebeck [15] 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 [16]): 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

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

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 3).

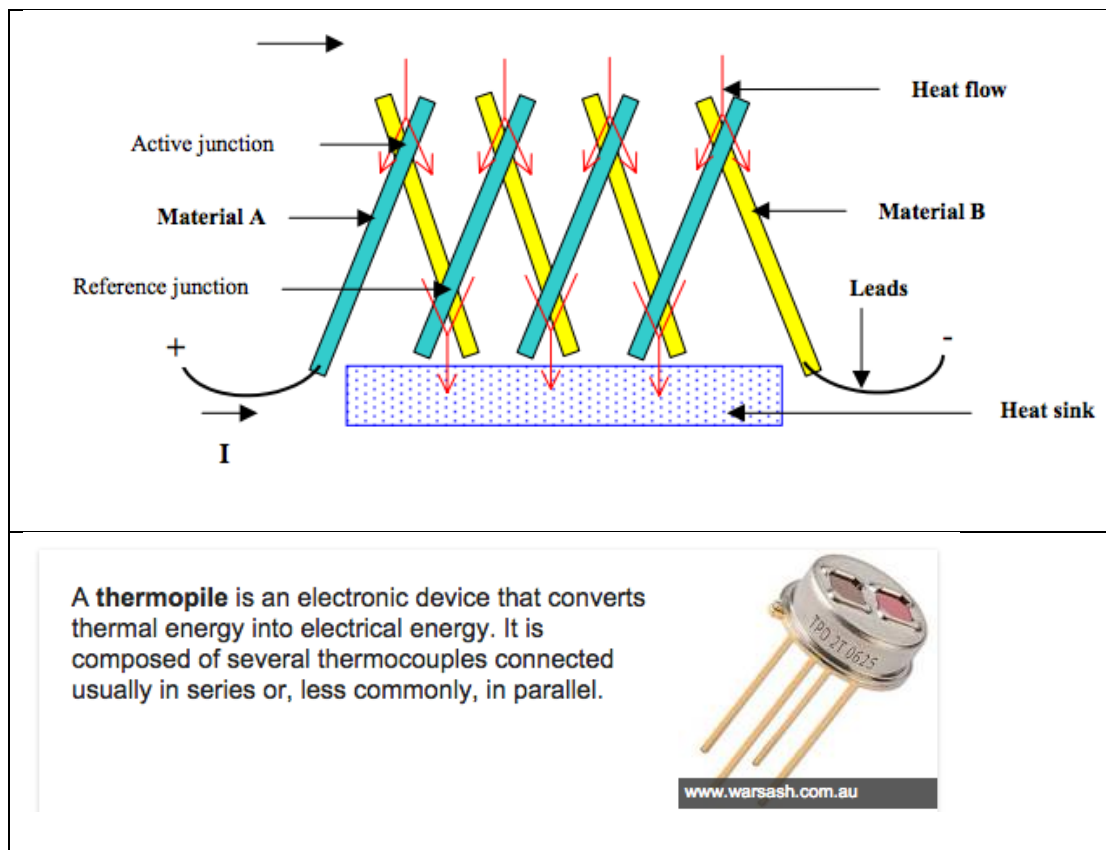


Figure 3 Thermopiles. Above, schematic of a thermopile [17] ; below, The Modern thermopile. [18]

3.3.1 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 Figure 4 below: as temperature rises, voltage output increases.

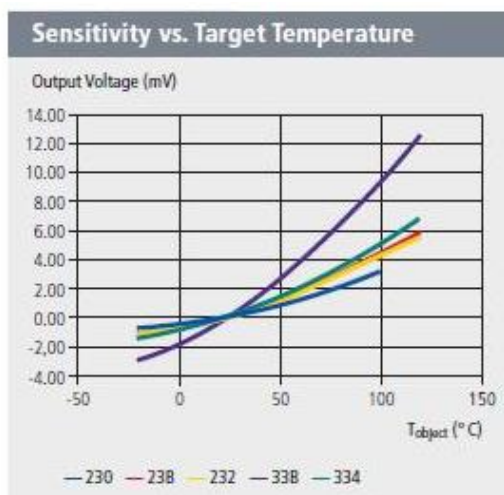


Figure 4. Thermopile Voltage output by Temperature

3.4 Thermoelectrics and 'IR Spectroscopy'

Other instruments to use the thermoelectric transducer and also exploit thermoelectrics are termed 'IR' spectrometers'.

To show the dispersive IR spectrometers are the same in principle as the CO₂ 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 (Figure 5 and Figure 6) show the working of a typical dispersive IR spectrometer [19] 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.

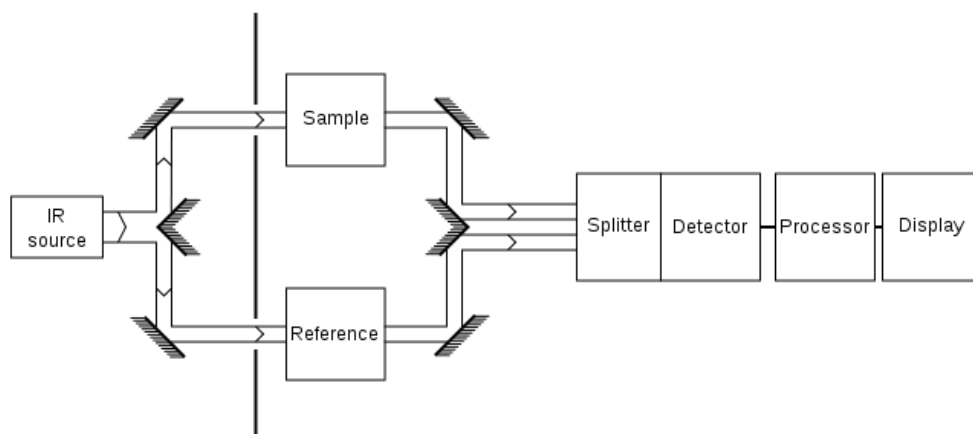


Figure 5. Operations Schematic of Dispersive Spectrometer [20], [19]. Notice the splitter and the division from the reference (control) and the sample.

3.4.1 The dispersive IR Spectrometer:

Just as with the CO₂ sensor, the IR (heat) source of the dispersive 'IR spectrometer' is heated to a considerable temperature – some 1500°C [3:40 [21] – with this high temperature the relatively low temperature of the sample will stand out. Again, if the CO₂ sample was heated to the same temperature as the reference cell temperature, no CO₂ would be detected – just as with 4.4 above. 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.

3.4.2 The Fourier Transform IR (FTIR) spectrometer

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

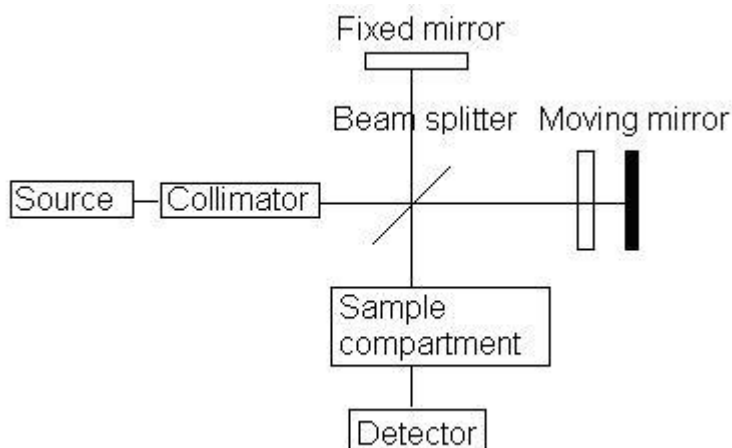


Figure 6. Operations Schematic of Fourier Transform IR (FTIR) spectrometer [20].

3.4.3 Spectroscopy Beer-Lambert Law

Below (Figure 7) is a schematic that shows how spectrometers produce what they display. Again, the samples are not being radiated at all; but rather the detectors measure the difference in EMF between the reference hot light source radiation and the sample EMF generated from the samples (relatively low) temperature radiation.

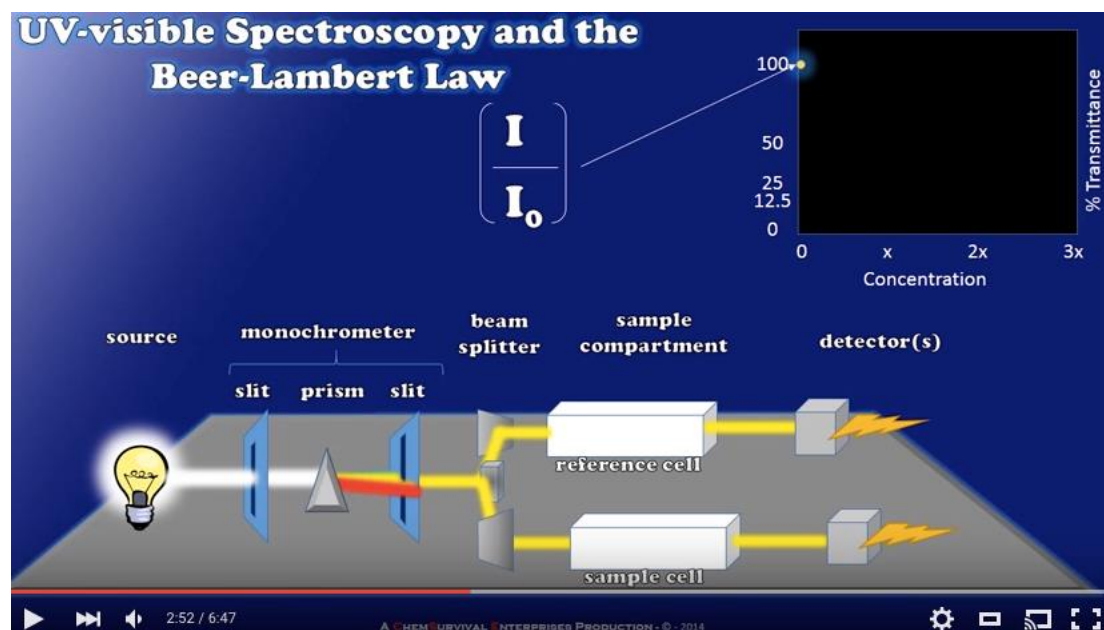


Figure 7. UV Spectrometer. Showing the heat source, the two cells, the reference and the sample. [22]

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 **I₀** is the **initial light intensity**. Again, this interpretation ignores the role of thermoelectric transducers – producing an EMF – and the thermoelectric properties of the substances measured.

3.4.4 All 'IR Spectrometers' Detectors are Thermoelectric (IR) Transducers

It can be shown – contrary to standard belief – all 'IR spectrometers' [23] use thermoelectric transducers[24] [25].

*“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 [26]*

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 IR detectors. All show the same results and do not detect non-thermoelectric vibration modes of N₂, O₂, CO₂ and CH₄ and so on. They also do not fully detect solid Germanium or CL₂.

3.5 Vibrational Modes and Radiation Theory and Spectroscopy

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 8) – the quantum mechanics predicted vibrational modes or emission spectra that possess 'asymmetric electric dipole moments' such as (there are others): H₂O's **3652 cm⁻¹** (2.74μm), **1595 cm⁻¹** (6.25μm), and **3756 cm⁻¹** (2.66μm); CO₂ 's **2349 cm⁻¹** (4.257μm), and **667 cm⁻¹** (14.992μm); CH₄'s **3020cm⁻¹** (3.312μm), **1508cm⁻¹** (6.5μm), and O₃'s **1103 cm⁻¹**, **701 cm⁻¹**, and **1042 cm⁻¹**.

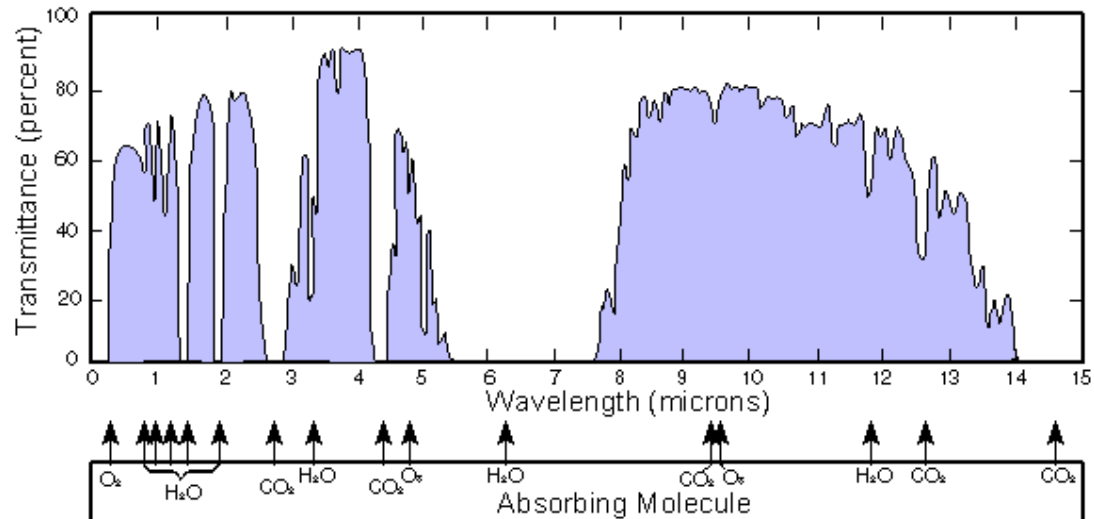


Figure 8. Infrared Spectrograph of the atmosphere [27]. This spectrogram does not take into account Raman modes and thermoelectric principles. See 4.4.4 for a correct interpretation of this spectrograph.

3.5.1 Analysis of the CO₂ Thermoelectric Emission Absorption Spectra

Below is a IR spectrograph for CO₂: it clearly shows CO₂'s absorption bands that are shared electric dipole moments – at **2349cm⁻¹** and **667cm⁻¹**; however, what it does not show, is CO₂'s 3rd symmetric (non-electric dipole moment) band at **1388cm⁻¹** – though there is a small hint of it in the figure at that wavenumber.

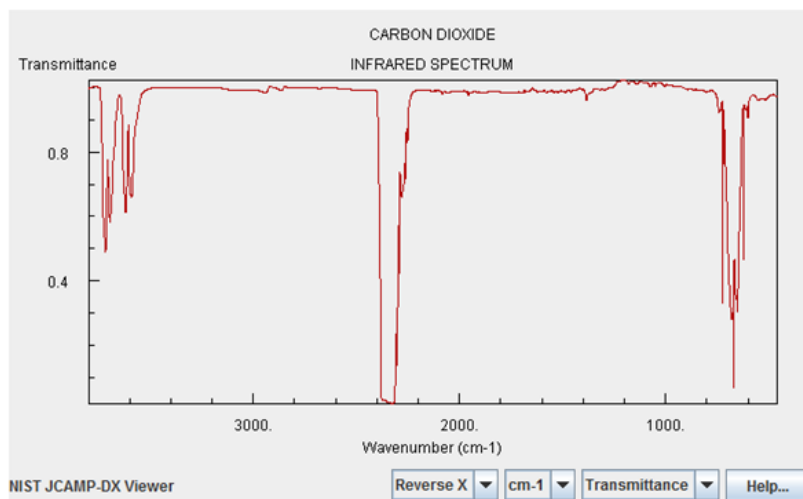


Figure 9. CO₂ transmission spectra. [28] Here the differential between the reference 1500°C heat source and the ambient temperature CO₂ gas is clearly shown. Predicted absorption bands are shown, however, this indication would decrease if the temperature of the CO₂ were equal to the reference heat source.

And below is the inverse or 'negative' diagram of the same above spectrograph showing the same absorption bands of the molecule. Again, the strength of the

'greenhouse' gas CO₂ 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.

Notice there is not 100% 'transparency': this suggests, again, some of the heat source shows through. If the CO₂ were heated to the same temperature as the reference heat source temperature (some 1500°C), no CO₂ would be detected.

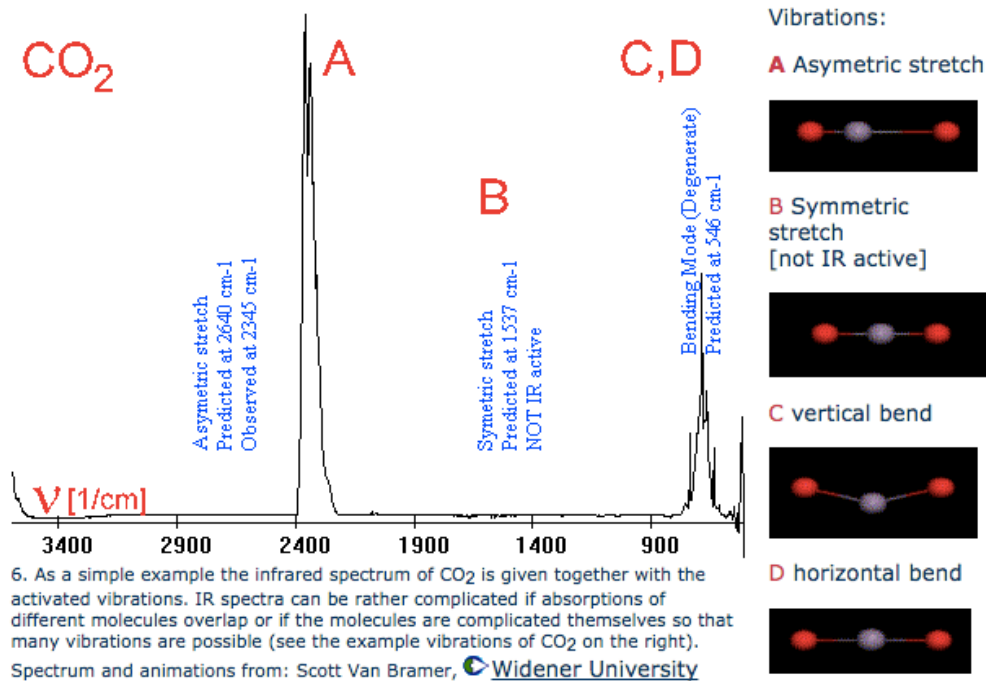


Figure 10. CO₂ Thermoelectric IR Spectra. A 'negative' image of the above image (Figure 32) showing CO₂'s IR active electric dipole vibrational modes and one non-IR active. [51] 1538 cm⁻¹ clearly shown absent; incorrectly indicated as 'not IR active' when it is more correctly non-thermoelectric due to symmetric stretch.

3.6 Thermopiles and the Solar Blackbody – Planck Curve

Solar Blackbody curves (Figure 29) are derived by the Seebeck effect and the thermopile; they are a thermoelectric measurement of the electromagnetic spectrum. Figure 11 shows the experiment deriving what is termed the 'blackbody' radiation curve, with its apparatus and resulting curve. It shows the effect – the 'red' shift to the right – of lowering the temperature of the emission bulb. It was also found most modern instruments used to produce the atmospheres blackbody spectrums – pyranometers[30] and pyrgeometers –also use the thermopile transducer to produce the curve.

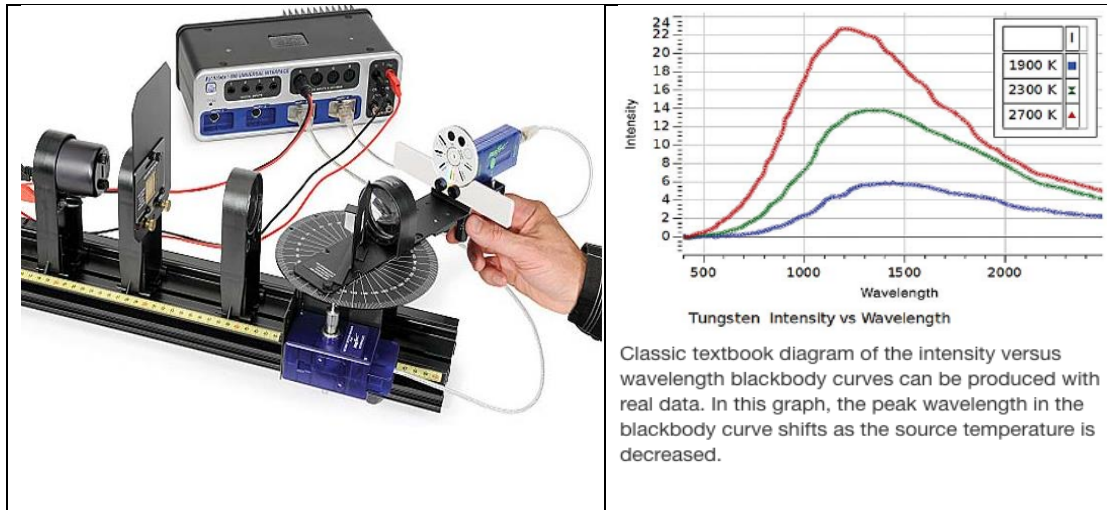


Figure 11. Thermopile Experiment Deriving the Blackbody Spectrum. “The spectrum of an incandescent light bulb is scanned by hand using a prism spectrophotometer, which measures relative light intensity as a function of angle. A Broad-Spectrum Light Sensor is used with a prism so the entire spectrum from approximately 400 nm to 2500 nm can be scanned without the overlapping orders caused by a grating. The wavelengths corresponding to the angles are calculated using the equations for a prism spectrophotometer. The relative light intensity can then be plotted as a function of wavelength as the spectrum is scanned, resulting in the characteristic blackbody curve. The intensity of the light bulb is reduced, reducing the temperature, and the scan is repeated to show how the curves nest with a shift in the peak wavelength.” [31]

4 Discussions

The following discussions on the topic of the atmosphere and radiation theory, in general, have never been undertaken before. While normally it would be simple to come a conclusion after an experiment, in this case, this is not so. While the conclusion is simple, the facts surrounding the question are difficult and complex and as a result of this it has been very difficult to order the discussions; what comes first, and what comes next? Everything I have found – from this investigation – is interconnected, so the order or priority, due to the scale of this misconception, is unclear. I decided to first address the thermal electric properties of a molecule, and their relationship to the thermoelectric transducer – and go from there. I then expand to address issues arising from the findings – what really are the special ‘Tyndall’ GHGs? I will show, by first principles review, they are the gases that are thermoelectric – they generate and EMF (electricity) by the Seebeck effect driven thermoelectric transducers. My findings have implications on all radiation theory, including the derivation of the blackbody radiation curve.

4.1.1 “Seebeck effect” Unrecognised by Spellchecks, and not in Physics Texts

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 vocabularies. 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.

4.2 The Misconception in Vibrational Theory

This discussion refers to 3.5. Right from the beginning,

Table 2 column 4 is at the crux of the confusion and misconception. The so-called IR modes of a molecule all have one thing in common when defining them as ‘IR active’ and part of a GHG molecule: they all have **asymmetric vibration modes** resulting from an ‘**electric dipole**’ movement. Standard GH theory definitions

clearly state this dipole behaviour; however, when it is understood how these modes are detected only by thermoelectric transducers receiving 'thermo' - 'electric' signals just like a radio receives electromagnetic 'radio' signals, common sense prevails. These modes and gases are the electric gases. Those modes that do not have electric dipole moments are not received by the radiating electric transducer receiver and are as a result incorrectly interpreted as being non-thermal and thus non-GHG. 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 at those modes. Raman spectroscopy shows they are. CO_2 also has one mode missing from this IR spectrograph, and CH_4 two, but again, these modes are Raman active. 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-IR modes, Raman Laser is the solution.

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 thermo-electric gas of the greenhouse gases. These modes will show on a thermoelectric spectrograph. This does not mean they the other modes or gases are not radiating: we need both Raman spectrometers and thermoelectric spectrometers to see the complete IR atmosphere.

In section 0 below I describe how the spectrograph is really produced.

4.3 Thermoelectric Interpretation: Vibrational Modes and Radiation

Theory and Spectroscopy

This discussion refers to the section on modes 3.5. So-called IR spectrometers are the modern version of the Tyndall experiment – and they (I claim) share the same flaws as the Tyndall experiment 4.7, in that they discriminate on N_2 and O_2 . They – whatever the thermoelectric detector method – share the same properties or problems of the IR cameras and IR thermometers, and CO_2 sensors 4.5: they do not measure all matter, they discriminate on what is not thermoelectric, not on what radiates IR photons. They imply these non- GHG

gases do not interact with 'light' and thus are not greenhouse gases. As this must be wrong – if not impossible – understanding IR spectrometers will help us understand where we have gone wrong forming this paradox. They are the modern instruments that still define the said special GH gases and it should be said without them it would be assumed all the gases trap heat – just as posited by Joseph Fourier in the early 19th Century.

4.3.1 Addressing the Misconception and Fallacy 'IR Spectrometers' Radiate their Sample

IR thermoelectric spectrometers' – and all other 'IR' technology - share the standard assumption: 'the sample gases are radiated with IR light (heat)', and as a result of this assumption the – what is termed – 'IR spectrograph' (shown) is produced revealing the corresponding absorption/emission spectra at the said modes. 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.”[32]*

Samples may be radiated for the many types of spectrometers: gamma, X-ray, UV, visible, and microwave; however, for 'IR' this is not so, it is instead – as we shall now investigate – a measure derived from temperature differentials between the sample and the heat source as shown above in 4.4.

I contest this claim, as stated above; 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.

It should be made clear this investigation should not undo the merits of IR spectroscopy per se; 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.

4.3.2 The Naming of the Type of Spectroscopy

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. This is where the problem is, it is in the language. The problem arises when it is understood there are two methods of detecting all the samples infrared vibrational bands, Raman and IR thermoelectric. For this reason, I suggest the names thermoelectric-IR or TE-IR and Raman IR.

Thermoelectric transducers on their own, in isolation, have led to a misinterpretation of what they really detect – the thermoelectric spectra of atoms and molecules and substances in general. They are at the centre to the field of what is termed ‘IR spectroscopy’. This term, by first principles, is incorrect; they are more correctly termed thermoelectric Spectroscopy (TE) as opposed to what they are currently thought of, ‘IR’.

4.3.3 Thermoelectric Spectrograph Misconceived as IR Spectroscopy

The thermoelectric infrared (IR) spectrograph of the IR atmosphere is shown (Figure 12): the only difference from the traditional interpretation is the spectrograph is produced by the difference in temperature between transduced – measured in thermal EMF voltage – of the sample and a reference source’s IR (1500°C) radiation. This is the same in principle as demonstrated in section 4.4.

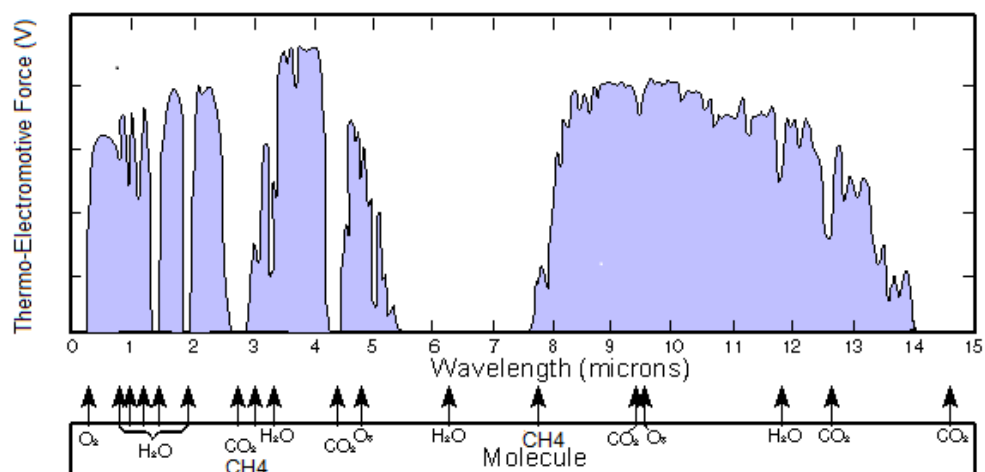


Figure 12. Thermo-electromotive Force and the Electromagnetic Spectrum. Thermoelectric vibration modes identified by thermoelectric transducers; currently known as the greenhouse atmosphere. The non-electric (dipole) Raman modes are unable to be detected. The black line traces the thermo-EMF (electricity produced) relative to the EMF produced from a 1500°C reference heat source.

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 radiation for the heat source – at that particular frequency or wavenumber – and the ‘dips’ show lower voltage produced, 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.

4.3.4 IR Thermoelectric Spectrometers Do Show Predicted Spectra Modes

It should be made clear: all 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 hand /glass IR thermometer demonstration, section 4.4. Also, if the sample was radiated, it – by the law of equipartition – all

matter should interact with the (IR) 'light', and all modes – whether IR thermoelectric or IR Raman.

Again, if the GHG were heated to the same temperature as the reference temperature, no gases would be detected because the EMF from the gases and reference would be equal – just as with 4.4.1.

It should be made clear this investigation should not undo the merits of 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.

4.3.5 Historical Order of IR Spectroscopy

A look at the order and history of IR and quantum discoveries and claims 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.

4.4 Thermoelectric Thermopile 'Hand-Glass' Demonstration

Figure 13 below demonstrates the crux of the thermoelectric problem: how the IR non-contact thermometer, with its thermopile, 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. As presented throughout this paper there is a dichotomy: is it the device detecting IR thermal radiation as claimed, or is it the device is generating electricity from special substances? Does glass (specially) absorb IR radiation, or is it – unlike the 'air' – thermoelectric? When reading this let my hand represent the heat source in Tyndall's experiment described above in 4.1.1.

In frame A of Figure 13 the IR thermometer is pointed at my hand. The temperature of my hand – as indicated – is measured at around 32.9 °C; then in

frame B it is pointed at a 3mm thick pane of glass where the temperature indicated of the glass is around 21.2 °C. Lastly, in frame C, the 'IR thermometer' is pointed at the glass with my hand behind – the glass is in between. Before doing this, ask what will be the indicated temperature? 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. It is the glass that is measured.

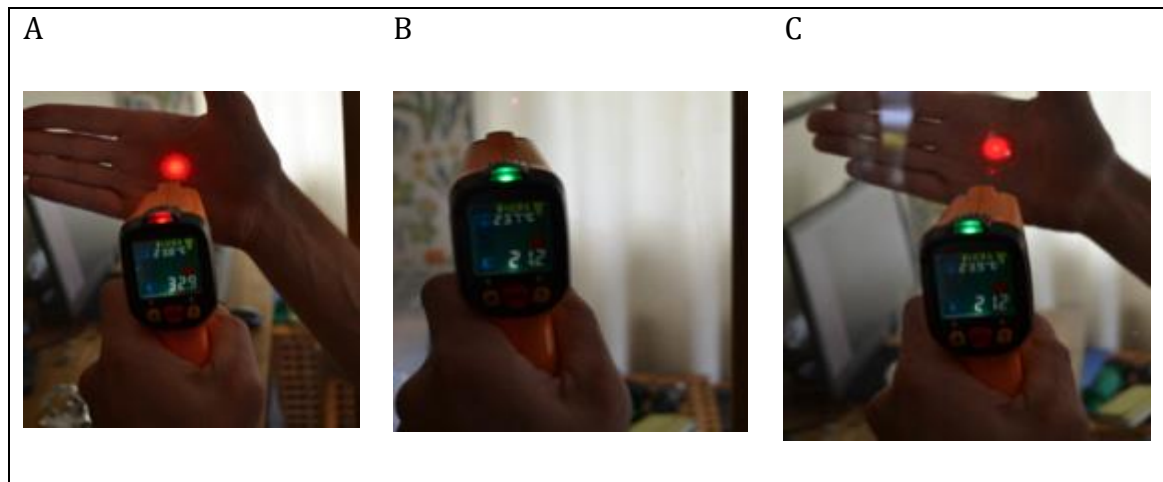


Figure 13. Non-contact thermoelectric thermometer 'transparent' glass demonstration. Frame A, hand temperature measured directly as 32.9°C and the ambient temperature 23.8 (red light indicates wrong emissivity match); frame B, the temperature of glass measured as 21.2° C (green light indicates correct 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.

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.

This experiment is currently interpreted as it being my hand – through the glass – is visible to the eye, but is invisible, or opaque, to the IR radiation. Right here is where there is a divide in interpretation: one by radiation and thermoelectrics, and with-it greenhouse reasoning where the glass is absorbing as if it were

radiated by a beam of IR photons – the IR radiation from my hand; the other interpretation by thermoelectric (IR) reasoning sees the glass as being thermoelectric and is generating a current proportional to the radiant temperature (or energy) – the Seebeck Effect.

The fact is the glass is thermoelectric 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 us to understand the derivation of greenhouse and current radiation theory – and that is the question of 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% N₂ and O₂ mix)

While being visibly transparent, air*; (as claimed in this paper) is non-IR – unlike the (similarly) visibly transparent solid glass in frame B, and that 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 this air temperature – whether at ambient room temperature, where the room temperature may be measured by a regular thermometer, or whether outside in extreme sub 0°C or conversely at high temperatures.

Returning to frame A (Figure 13): what if the same demonstration was undertaken in a bath of GH (or IR) gas – say CO₂? Just as with the hair dryer paradox 4.8.1. What would the detector measure then? Of course, it will measure the temperature of the CO₂, and not my hand – just in the same way it measured the glass in frame C. If we can describe and understand CO₂ as being thermoelectric we should equally be able to describe and understand glass to be ‘a GH solid’.

4.4.1 Temperature Differentials Measured by Thermoelectrics and Thermal Equilibrium

From the above demonstration (Figure 13) we see a key insight into all thermoelectric applications: what they detect and graph is the temperature differential between a heat source temperature (my hand in the above) and the temperature of the sample (the glass). What if I was to touch the glass with my hand and bring the temperature of the glass to thermal equilibrium, equal with the temperature my hand? The glass would not be detected. It would be as if it were only my hand being measured. The implications of this insight become very important in the following sections where it is described how the thermopile is used to detect and to produce spectrographs. In all of the following descriptions, if the temperature of the sample is the same as the temperature of the heat source then the sample will not be discerned.

4.5 Modern Applications for Thermoelectric Transducers

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 problems they share.

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.

4.5.2 CO₂ Sensors

Regular CO₂ concentration sensors use a thermopile transducer – exploiting the Seebeck effect (though this is not how they are explained in most references [33],[34], [35], [13]). In general, the operation is similar to the IR thermometer and the hand-glass demonstration above in Figure 13. 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 (hot) reference heat source is computed. In principle, a 100% sample of CO₂ will transduce EMF more than the hot heat source and in effect look like it is blocking out the heat source by 100%. Because the air (N₂ and O₂) do not generate and EMF at any temperature, if the CO₂ was heated to the same temperature as the reference's heat sauce no CO₂ would be detected – just as with 4.4 above.

4.5.3 Thermoelectric Imagery; 'IR' Thermal Imaging Cameras

Using the same principle as the 'spot measuring' IR thermometer, with modern screen technology the IR thermal imaging camera measures a complete array of thermoelectric 'spots' or pixels in one view. 'IR' cameras originality used a thermopile thermoelectric detectors [36][37]; however, modern array detectors are more sophisticated, but all are still based on EMF, either voltage, resistance or current, 'production' when heated by IR radiation – the principle is the same. The proof of them being the same is all detectors measure the same substances – as Tyndall – in the same way; they equally cannot measure the likes of N₂ and O₂. It is for this reason I will term them as thermoelectric-IR cameras or IR cameras. Maybe someday they will be correctly named thermoelectric imagery.

4.6 Thermoelectric Substances

In the context of thermoelectric transducers, thermoelectric substances refer to – unlike current understanding – the substances that produce an EMF, due to their molecular vibrational behaviour 4.2. The problem lies with the chemistry, the vibrational modes, as to why some substances are assumed IR while others are not. To repeat, 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 led 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. One only has to take a look at

Table 2 to see this pattern of electric dipole and GHG modes.

4.6.1 Thermoelectric ‘Greenhouse Liquids and Solids’ – Water and Glass

By GH reasoning, where it is deduced – by thermoelectric transducers – the GH Gases are transparent to the visible spectrum, and ‘opaque to the IR’; water too should be known as a GH liquid and with this visible transparent *glass* a GH solid. All three are similar in that they are 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, and the GHGs are thermoelectric and are 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-thermoelectric) salt crystal. It is also why thermoelectric thermal cameras do not use glass, and cannot see through water. More on this in 4.5.3.

4.6.2 Non-Thermoelectric/ Non-IR Gases, Solids and Liquids

While the atmospheric gases N_2 , and O_2 – as reasoned in this investigation – are non- thermoelectric, so too are Hydrogen (H_2), Helium (He) and possibly Argon, and all for the same physical reasons. Interestingly liquid Oxygen is non-TE just as its gaseous form – see 4.7.5; it will not generate an EMF at any temperature. Non-TE solids include Germanium (Ge) – see 4.6.3, 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 of no coincidence these non-TE gases are known as – in the case of GH theory – ‘the non-GHG’s’; and we must remind ourselves they are (wrongly) assumed not to absorb and emit IR heat; when the fact is they are simply non-TE, and have been misinterpreted. What is more, they

all have specific heat capacities: which says they absorb and emit IR radiation (more on this in my complementary paper [4] 4:12:3 where I examine heat capacity determination).

4.6.3 Thermoelectric Demonstration: Glass and Germanium

Unlike traditional light sensing cameras, the IR camera, as with the 'IR thermometer', cannot use glass for its lenses as glass is IR opaque. Instead, the lenses (Figure 14 below) are made of one of the few non-IR 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 [38] and [39],[40]. A thermoelectric interpretation: it is simply non-thermoelectric, or at least less so. 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 lens, and in frame C, he places a lens between the camera and the heat source revealing the transparent property of Germanium to the camera.

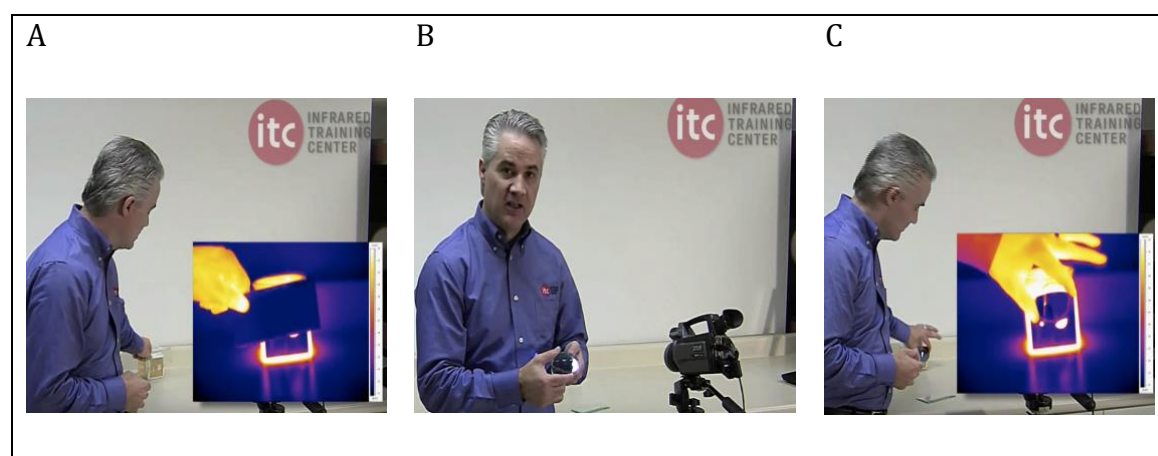


Figure 14. Non-Thermoelectric Germanium. (A) 'Opaque' thermoelectric glass in front of the heat source; (B) visibly opaque germanium in hand; (C) 'transparent' non-thermoelectric germanium placed in front of heat source [41].

Solid Germanium presents the same paradox, in principle, just as the non-GHG air does: to the thermoelectric IR detectors temperature is not at all measurable – no emf is produced. To expand on this paradox, the following thought experiment may be useful. What if the Germanium was hot? One could heat up a lump of Germanium to a dangerous temperature, but unlike a regular thermometer, IR thermometers, or IR cameras, would not register this

temperature – and its danger; just as they do not register the temperature of (hot) ‘air’.

4.6.4 The Germanium Sauna

As another 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 an IR camera does in the free $\pm 300\text{K}^\circ$ atmosphere; it only detects the objects that are thermoelectric.

4.6.5 Ge Germanium Raman Spectra

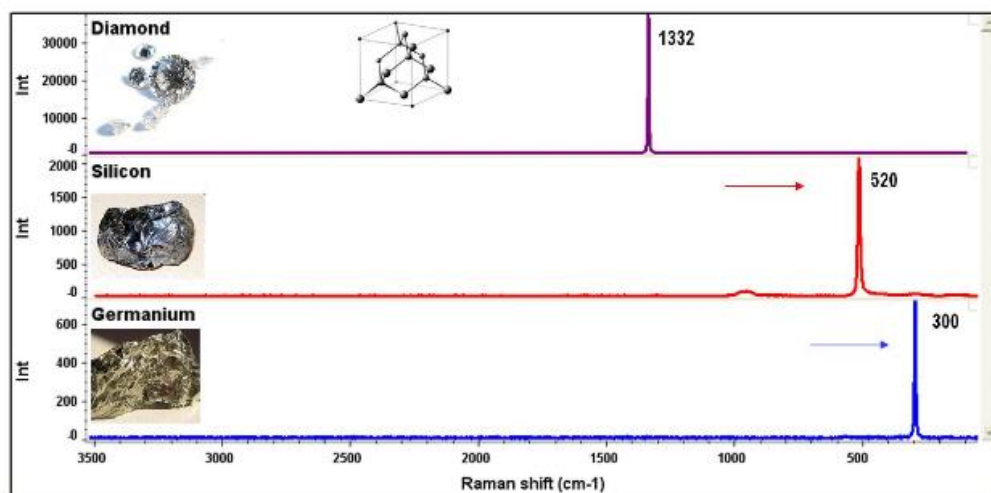


Figure 1: Raman spectra of diamond, crystalline silicon, and crystalline germanium

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

Figure 15. Showing the spectra of Germanium, the only non-thermoelectric solid [42],[43]. The spectra are identified only by Raman and is well with the IR range of the EMS.

4.6.6 Germanium and Emissivity and Spectrographs

As it turns out, Germanium does not show well at all on thermoelectric spectrographs, and it does not have, similar to N_2 and O_2 , an emissivity. It does not ‘appear’ to emit radiation. No, it is not thermoelectric. However, Germanium

does have a Raman spectrum, with a spectra mode at 300 cm^{-1} as shown in Figure 15.

4.7 The Tyndall Experiment and the Thermo-electric Transducer: the – ‘TE’ Atmosphere

Here I shall discuss the role the thermoelectric technology has played in our understanding of the atmosphere.

4.7.1 Tyndall IR Thermoelectric Misconception

Based on the facts about thermoelectrics 3.3 it has been found in the investigation, and I claim what John Tyndall really discovered – using the thermopile transducer – are not the ‘special’ set of heat-trapping gases but rather only the gases of the atmosphere that are thermoelectric (TE) – the gases that generate electricity via the Seebeck effect and IR transducers. If we were to generate electricity with a thermoelectric- pile transducer from hot gases, which we could (see TEGS 0), 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 would be doing it.

Tyndall’s 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. Previous to Tyndall’s 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 [44] thermal radiation.

4.7.2 Thermoelectrics: The BBC Dr Stewart GHG Demonstration

In BBC’s documentary: ‘The Climate Wars’ [45], Dr Stewart is said to demonstrate the greenhouse effect using a thermal imaging camera; but, unbeknown to Dr Stewart, he is literally reconstructing of the original 1859 Tyndall experiment only with modern materials and technology (as shown in Figure 16 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 stands in for the rock salt to contain the gases.

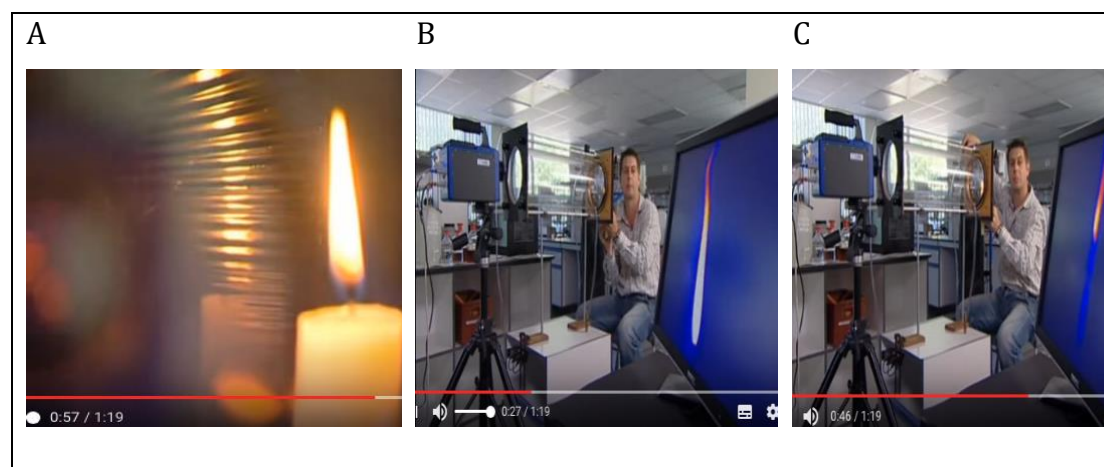


Figure 16. Dr Stewart YouTube clip. [45], [46] Demonstrating the greenhouse effect. Frame A shows the gas contained behind thin plastic, B. thermal image of a flame through 'air'; and C. CO₂ 'blocking' the flame out. Notice a light-blue image in the lower flame remains in C; this may be attributed to the temperature differential between the gas and the candle. If the CO₂ were colder it may disappear; and conversely, if the CO₂ were as hot as the flame the screen would turn yellow.

An image of the candle is seen on a screen via the IR camera link (frame A), and as the heavier than air CO₂ 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 (incorrectly) – 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.

4.7.3 Thermoelectric Interpretation of the Stewart Demonstration

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% N₂ and O₂) 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-IR. 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 CO₂ gas is released into the tube: it is the incident CO₂ that now generates electricity proportional to the temperature.

Again, if the CO₂ were heated to the same temperature as the reference candle temperature, no CO₂ would be detected – just as with 4.4 above.

4.7.4 The Greenhouse Gases and Thermoelectric Thermography

To Show the effects different gases have on thermoelectric transducers; in another (YouTube clip, Figure 17 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. Again, if the CO₂ was heated to the same temperature as the reference hand temperature no CO₂ would be detected – just as with 4.4 above.

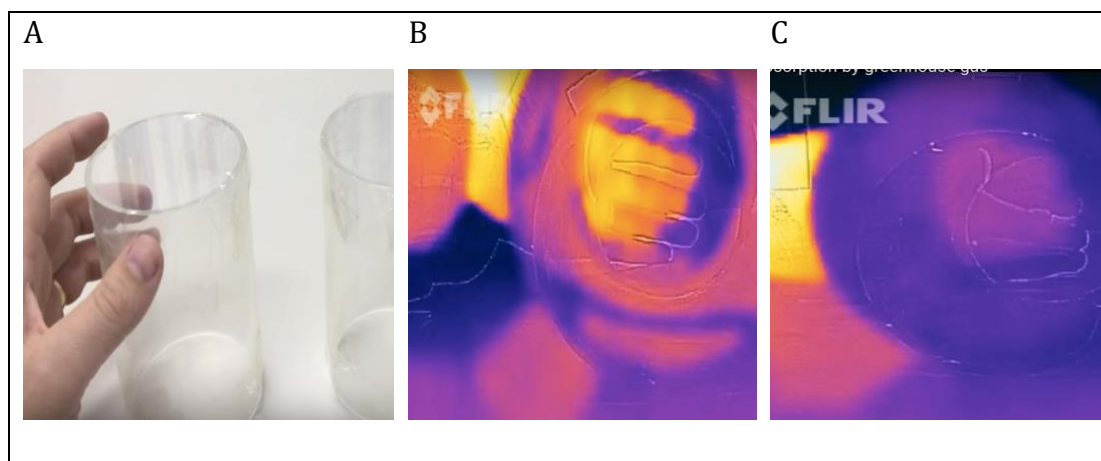


Figure 17. Thermal imaging camera Greenhouse gas demonstration. (A), two glasses, one fill with air (mostly N₂ and O₂) and the other with a GHG, presumably CO₂; (B), the first glass is non-thermoelectric, wrongly said to be 'transparent to IR'; and C, the GHG is thermoelectric, wrongly said to be opaque to IR. [47]

To further 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 air 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 IR gas, and as the IR gas in the line of sight of the camera detector, it is the incident IR gas and not the background hand of the demonstrator, that is measured.

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

4.7.5 Non-Thermoelectric Liquid Oxygen Thermography

In another simple and normally trivial video demonstration on thermography (Figure 18), liquid oxygen – at a temperature of less than 90K – is interpreted to be 'transparent' to infrared; however, with a knowledge of thermoelectrics what

has been demonstrated is liquid oxygen (just like the oxygen gas) is not thermoelectric, and the magnet in the Dura cup is.

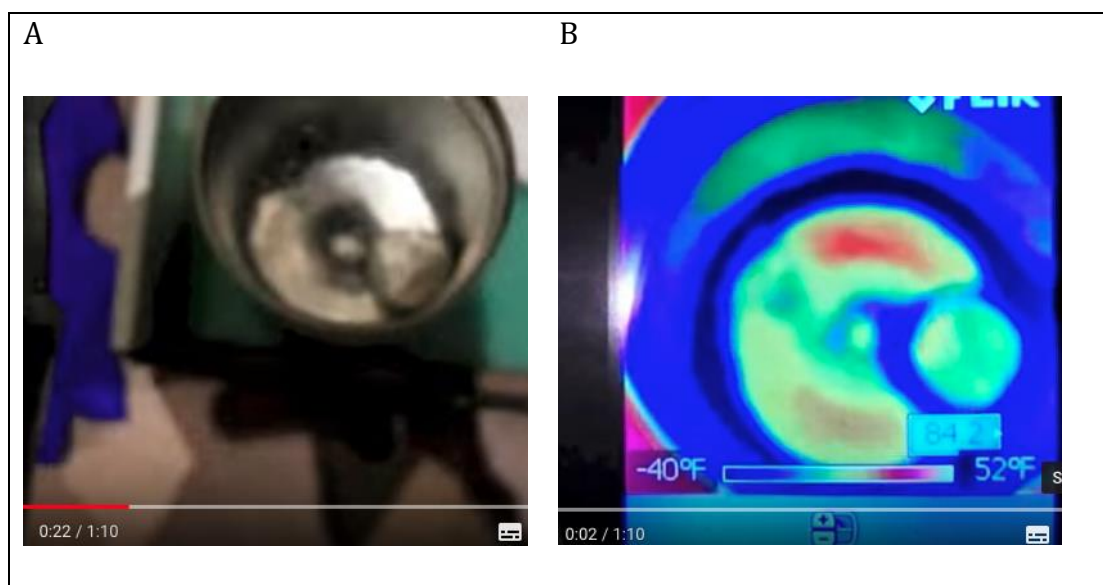


Figure 18. Thermal imaging camera liquid oxygen demonstration. [48] Frame a visible, showing a magnet in a cup of (90K) liquid oxygen; and in frame B a thermoelectric infrared image, again showing the magnet, and importantly not showing the liquid oxygen. If the liquid were water or other only its temperature would be shown.

If it were any other liquid in the Dura, with the exception of liquid nitrogen, the magnet would not show in the FLIR image; only the liquid in question would. And what if instead of a magnet or another object it was a piece of Germanium, the ‘camera’ would equally not show it. The conclusion of these demonstrations is oxygen does not show with thermoelectric transducers – this does not mean oxygen does not have a temperature and thus, by Stefan’s Law, does not radiate.

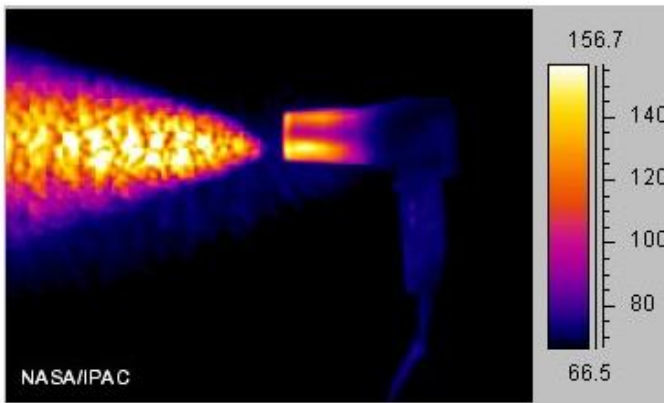
4.8 Thermoelectric Paradoxes and Anomalies

The following is a set of Paradoxes and Anomalies all associated with the thermoelectric thermopile and the like.

4.8.1 The Hairdryer Gap Paradox

To illustrate the problem of thermoelectric transducers the thermal radiation image below of an operating hairdryer emphasises offers insight into this thermal discrimination that leads to the ‘IR catastrophe’. From the thermal image (Figure 19), 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 19. The Hair Dryer ‘Gap’ Paradox. A thermo-electric produced thermogram of an operating hair dryer 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 4.8.2 for an explanation to this paradox.

4.8.2 The Hairdryer Paradox Explained

With a first principles knowledge of thermoelectrics, an explanation can be found to this discrepancy, which will lead us to the same hypothesis as presented in this paper. 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 CO₂; and, (2) if the dryer were submerged in a ‘bath’ of only CO₂? Reasoning by thermoelectrics, for the former (1), it would show a plume of ‘bright-hot’ outflow; and for the later (2), no discernible image would be observed as it will be the incident temperature CO₂ measured by the thermoelectric detector.

4.8.3 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 N₂ and O₂ (‘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.

4.8.4 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, so a negative response or answer to this would suggest they are thermoelectric. The hypothesis being they are.

It is interesting that fish – for the most part – cannot detect IR or use it directly: this makes sense as water is a thermoelectric substance and so all the EMF is generated from the incident molecules.

4.9 The Thermoelectric Derived Misconception of Emissivity: a Paradox Associated with Thermopiles

Emissivity – *is a property that relates how well a material radiates infrared energy compared to a perfect material at the same temperature* – has to be one of the most paradoxical concepts and physics: there is no other concept in physics that gets the 'hands waving' quite like this one. Fundamentally it should be about the ability for a substance to emit and absorb IR heat, 'dark' objects vs 'light' objects, but it is not. I believe it is not about IR emission all; but rather, the ability or inability of the thermoelectric transducer (the thermopile) to transduce.

As we can see below Table 3 emissivity has a value ranging from the value of 0 to 1: for instance, it assumes shiny metals radiate next to 0, and conversely and paradoxically snow and ice are near-perfect black bodies with an emissivity of near 1. Something is wrong, and hence the arm waving.

Table 3. Emissivity measurements for many surfaces. Compiled in many handbooks and texts [49].

Material	Emissivity
Aluminum foil	0.03
Aluminum, anodized	0.9 ^[11]
Asphalt	0.88
Brick	0.90
Concrete, rough	0.91
Copper, polished	0.04
Copper, oxidized	0.87
Glass, smooth (uncoated)	0.95
Ice	0.97
Limestone	0.92
Marble (polished)	0.89 to 0.92
Paint (including white)	0.9
Paper, roofing or white	0.88 to 0.86
Plaster, rough	0.89
Silver, polished	0.02
Silver, oxidized	0.04
Snow	0.8 to 0.9
Water, pure	0.96

4.9.1 Possible Cause of the Discrepancy: Emissivity Similar to Reflectivity of Shiny Metals

One reason emissivity has been misconceived by thermopiles may lie with the property shiny metals have low emissivities (high reflection) and also really do have high reflectivity as revealed in the NASA report '*Solar Absorptance and Thermal Emittance of Some Common Spacecraft Thermal-Control Coating*, [50] pages 11 and 12. So the two measures fit together here where it intuitively should. But as I have shown, they do not with it comes to the colours of substances and the likes of water and snow.

4.9.2 Emissivity and Thermoelectric Thermal Cameras

Figure 20 below shows the problems associated with emissivity when using thermoelectric thermal cameras. A and B show colour is not an emissivity causal factor. Firstly, it must be assumed the cup is at a state of thermal equilibrium. Where it is well understood the albedo of an object is determined by the colour of the object – light colours for high albedo, and dark for low – here emissivity shows no difference in absorption and emission whatsoever with the colour. This can only be attributed to a measurement problem – a detector problem – as all practical applications of colour and radiation suggest albedo theory is correct and emissivity is not.

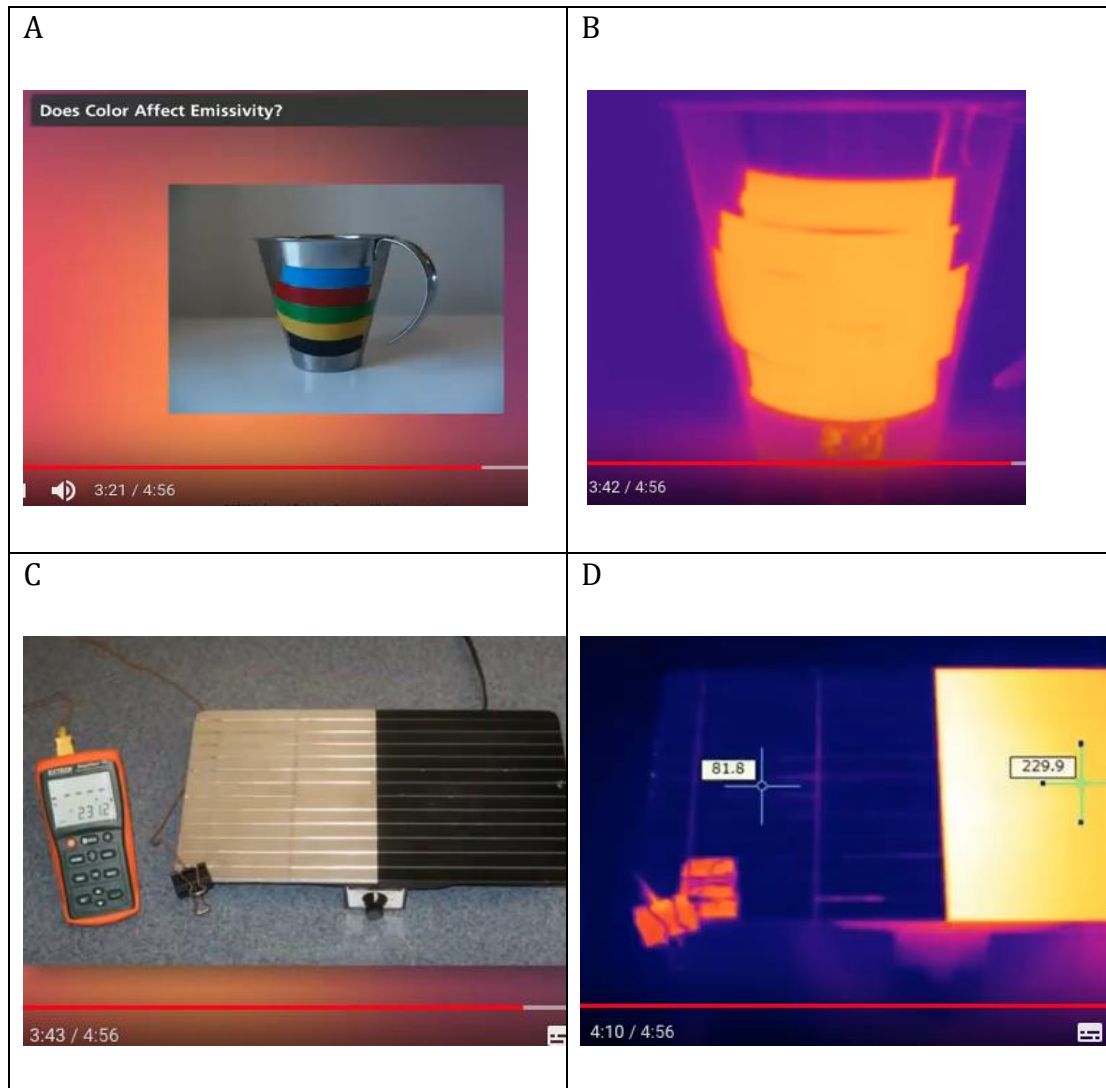


Figure 20. Demonstrating Paradoxes Associated with Thermoelectrics. [51] A and B show colour, unlike albedo, does not determine the emissivity of a substance. C and D show the surface type does determine the emissivity. All of these inconsistencies are claimed to be properties all radiation; however, in this paper, they are claimed to be a property of the detector.

C and D offer a further insight into the emissivity problems associated with different surfaces. Again, the object – the plate – is in the thermal equilibrium, both black side and shiny side, as indicated by a temperature of 231.2 degrees F. The shiny side is said to have a low emissivity, and the dark black a high. This demonstration is close to reality where it is understood shiny metals do actually reflect more than the dark objects; however, this is not entirely what is demonstrated here. Recall that all matter with a temperature radiates IR – that is quantum mechanics: the shiny side with a very low emissivity, near 0, suggests no radiation rather than just low. The dark side a closer to accurate reading with reality.

I contend all this is demonstrating is the ability or inability of the thermoelectric-transducer detector to receive radiation and convert it to a thermal emf, voltage. This phenomenon invites further investigation as this area is paradoxical: why is it the reception from shiny metals so low with thermopiles?

4.9.3 Emissivity, Blackbodies and the Stefan-Boltzmann Law a Thermopile Misconception

The *Stefan-Boltzmann law* states all substances above absolute zero emit infrared (IR) – or thermal – radiation with an intensity proportional to temperature. Initially, the law assumes all substances are perfect ‘blackbody’ emitters, however, most substances do not reach this upper limit, and the difference between this theoretical (blackbody) radiation and the actual emitted is called emissivity.

The following diagram Figure 21 shows the disparity between blackbody emissivity calculated and emf derived curves. The real radiation body is derived by a thermopile so traces the emf production at each wavelength.

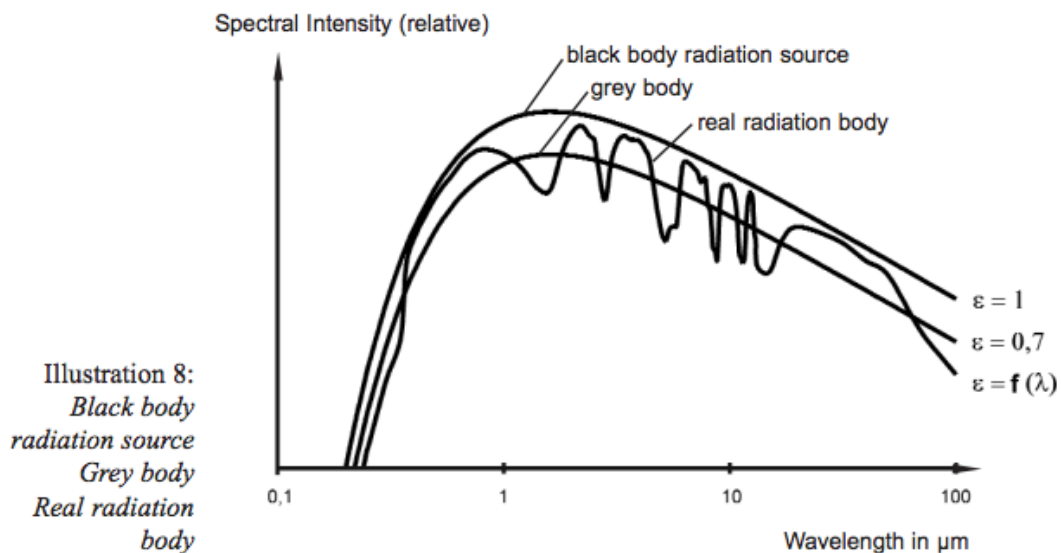


Figure 21. Black body and Real Radiation (emf) curve.

The initial Stefan- Boltzmann equation for blackbody radiation is written as

$$E = \sigma T^4 \tag{1}$$

where E is the radiant heat energy emitted from a unit area in one second, T is the absolute temperature (in degrees Kelvin), and the Greek letter sigma (σ) represents the constant of proportionality, called the Stefan–Boltzmann constant. Only the equation for *grey body* radiation includes emissivity:

$$E = \epsilon \sigma T^4 \tag{2}$$

where ϵ = the emissivity coefficient of the object (one - 1 - for a black body).

4.9.4 Measurement of Emissivity - by Thermopiles

One of the most extraordinary overlooked, bad pieces of science must be the knowledge surrounding the understanding of emissivity. Emissivity is only associated with thermoelectric devices, but it turns out the measurement of the coefficient itself is measured directly by a thermoelectric thermopile. This says it is a property of the thermopile and not of the substance measured. It is a correction factor. The following diagram, Figure 22, [52] shows how emissivity is measured and reveals it is only a correction factor between the temperature of an object, measured by a thermocouple, and emf-temperature produced from the thermopile. From a thermoelectric perspective emissivity has little to nothing to do with the IR (heat) emission properties of a substance – an iterated throughout this paper.

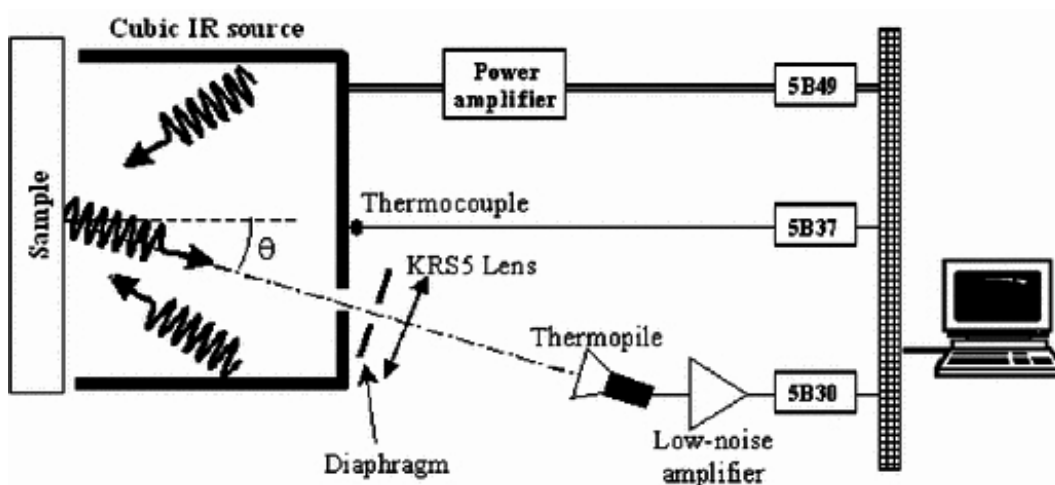


Figure 22 Measurement of Emissivity. The emissivity is measured by the thermocouple for its real temperature and by the thermopile (for its heat radiation).

This study has led me to conclude ***emissivity is no more than a correction factor between the real temperature of an object and the indicated EMF deduced thermoelectric temperature (itself determined by the Seebeck effect)***. Emissivity only applies to thermoelectric devices and is itself measured by thermoelectric devices. Emissivity may well in time turn out to be one of the saddest mistakes in the history of physics.

4.9.5 Why N₂ O₂ and Germanium have no Emissivity

A final word on emissivity: what does this mean for N₂ and O₂, the gases in question? As it stands N₂, O₂ and Germanium have no nominal emissivity to speak of. By an understanding of emissivity, their respective emissivity's must be 0 as they, as it is assumed, do not emit or absorb IR radiation; the same goes for Germanium. However, from studies by Raman Laser Spectroscopy they do emit and absorb at their predicted spectra, and thus their 'emissivity' is only a thermoelectric property, not a radiation property.

4.10 The Misconception of Greenhouse Theory 'Back Radiation'

Back radiation is described as the IR radiation emitted back to the atmosphere by GHGs after it is first absorbed by the Earth's surface by shortwave radiation.

"The amount of heat radiated from the atmosphere to the surface (sometimes called "back radiation") is equivalent to 100 percent of the incoming solar energy. The Earth's surface responds to the "extra" (on top of direct solar heating) energy by raising its temperature. "

As this is a said property of only the GHGs and not the non-GHGs it is safe to conclude this is a product of the thermoelectric properties of the said gases – as revealed in this examination and others[53]. This conclusion is supported with the demonstration of back radiation by a non-contact thermometer in Figure 23. The 'thermometer' reads a higher temperature when pointed at a cloud compared with the blue sky. In fact the blue sky reading can be so cold an 'error' message is displayed.



Figure 23. Misconceived Demonstration of ‘Back Radiation’ by a non-contact thermometer. [54] It appears the cloud is radiating (right) and the ‘blue-sky’ (not) not. Knowledge of thermoelectrics reveals the air does not produce an emf from the radiation in comparison with water vapour.

4.10.1 Explaining the Back-Radiation Misconception

In concurrence with the finding of this paper, the non-contact thermometer is receiving and transducing the IR radiation from only the H₂O cloud. The signal is converted to electricity and this output calibrated to the real temperature of the cloud. The device gives an approximate value only. The blue-sky ‘air’ is of such as high concentration N₂ and O₂ that no signal is received by the thermopile. Back radiation is – again – a misconception of thermoelectric transducers. If a Raman laser were beamed into the cloud and the surround ‘air’ the temperature would be similar, if not the same – ignoring any latent heat release from phase change.

4.11 The Solar Blackbody IR Spectra Misconceived for the Thermoelectric Spectrum

The blackbody curve (as shown in Figure 1) is central to our understanding of emission spectra – and responsible for the ultraviolet catastrophe, and subsequent birth of quantum mechanics is a direct product and result of thermoelectrics; it is produced by the thermopile (Figure 11) [31],[55]. If modern thermoelectric IR detector substitutes are used, they produce similar results. The thermopile is still the detector of choice in most pyranometers[30] and pyrgeometers, the instrument used to produce the atmospheres blackbody

spectrum. The following is an examination of the role thermopiles have with the derivation of the so-called 'blackbody' radiation curve.

4.11.1 Explaining the Imperfect Blackbody Curve – as opposed to the 'perfect'

The 'perfect' blackbody curve – laid down by Planck, Wein, Stefan and others in the late 19th Century – is a mathematical construct derived on results from a thermopile output. As the thermopile does not transduce a perfect signal of matter the curve is incomplete and the difference between the constructed skewed bell shape curve and the real signal is the emissivity (as discussed above 4.9.3). Accordingly, from this 'construct' it is assumed (incorrectly) no matter is a perfect blackbody. It is only snow and water, paradoxically considering their albedo, that come the closest to perfect absorbing-emitting 'black bodies'. Why this central claim is 'incorrect' can be reasoned by the limitations of the thermopile and its inability to transduce a perfect EMF from the IR signal – the temperature of the sample gases are lower than the Sun, and so some of the solar heat radiation leaks through. See the section: *'Thermoelectric Thermopile 'Hand-Glass' Demonstration'*, for a full demonstration and explanation to the claims.

4.11.2 Blackbody Curve, Thermoelectrics and the Birth of Quantum Mechanics

Concerning the role of thermopiles and thermoelectrics have in the birth of quantum mechanics, and its process or application in the mapping of the Cosmic Microwave Background (CMB) and the like, it is thought, at this time of writing, to be of no consequence of their respective validity of the instrument – they do serve a purpose; but their conclusions questionable give the all give the same skewed bell shape curve. Quantum mechanics is well-established and evidence of it is found elsewhere since; and as for the CMB, it has shown the universe is a perfect blackbody, there is no emissivity discrepancy there. Beyond the scope of this investigation the author is inspired to do further research.

4.12 Revealing the 'IR Blackbody Spectrum Curve' Misconception through Thermo-electric Generators (TEGs)

While writing this paper I wondered if it were possible to use thermoelectric transducers to produce Green Energy from carbon dioxide. It turns out this dream is almost a truth, it is done; thermoelectric generators (TEGs) have been

combined with photovoltaic (PV) cells to do just that. When I learnt this, I wondered if there had been any research done on the output of the TEG by wavelength. My hypothesis was the curve should look exactly like the atmospheric blackbody radiation spectra as in Figure 1 and Figure 11 because they are the same detector, they are produced by the Seebeck effect.

4.12.1 Smoking Gun: Proof Atmospheric Blackbody Emission Spectra are IR Produced

Modern ‘green tech’ solar TEGs exploit the Seebeck effect to transduce and generate electricity. The significance of this fact becomes important when understanding the blackbody emission spectra, where I claim it is nothing else but the production of EMF (electricity) at each and every frequency – from the TEG transducer. This would be evidence of the true role and properties of thermoelectric transducers, indirect from radiation theory. It is a practical application that would demonstrate the thermopiles limitations.

The following is what I found. Firstly a schematic, Figure 24, showing a curve almost identical in shape to the emission spectra.

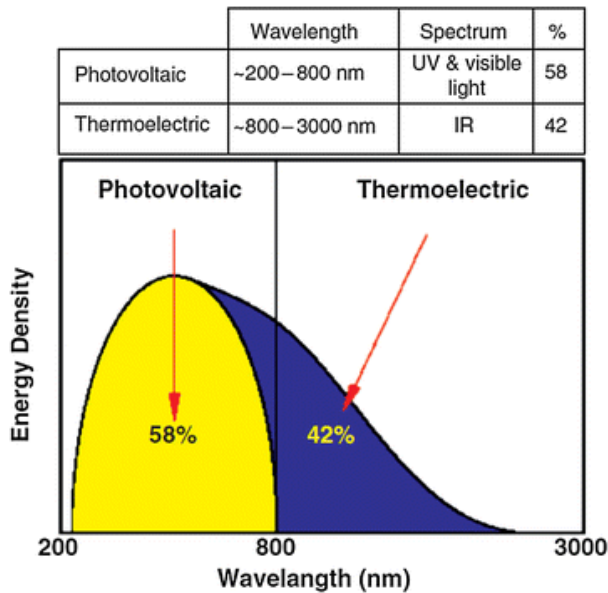


Figure 24. Simplified solar spectrum and energy ratios to be used within the PV cell and the TEG [56]. This schematic shows a shape and profile similar to the IR generated Solar irradiance spectrum – by no coincidence.

I then found a paper to back up this schematic. Figure 25 shows the AM1.5 spectrum and the efficiency of the TEG comparison to the PV. It is Figure 26 that

is the real smoking gun; it shows evidence all atmospheric blackbody emission spectra are derived from Seebeck effect-thermoelectric transducers. The efficiency (output over input) of the TEG decreases with wavelength after a maximum at 500nm, identical in shape and form to the said. The TEG is not efficient at wavelengths above 1100nm because the transducer does not generate EMF at those wavelengths. This is coherent with the blackbody curve.

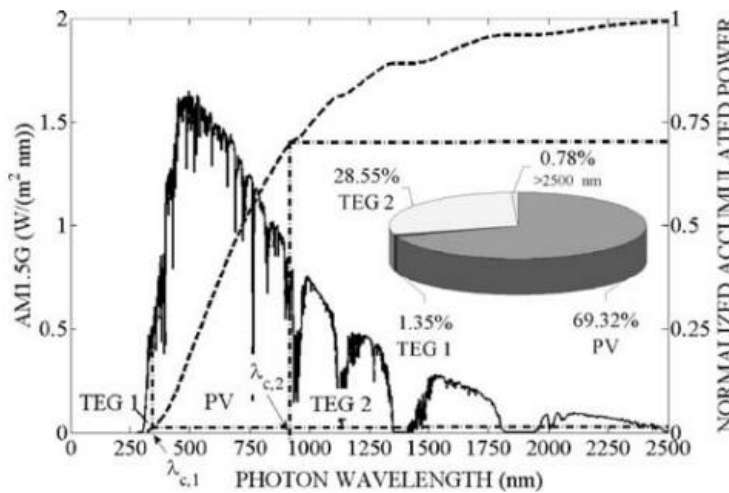


FIG. 1. Segmentation of AM1.5G spectrum in three regions for a mc-Si:H solar cell and solar TEG with 4% efficiency. Normalized accumulated radiation power. Pie chart: converted power fraction of each module.

Figure 25. Photovoltaic and TEGs and IR Generated AM1.5G solar irradiance spectrum[57]. In this diagram is shown the IR generated AM1.5G solar irradiance spectrum and the efficiency of the green technology PV-TEGs at each wavelength. This is circular reasoning.

This alone does not settle the issue: one can still argue the curve is a property of the Sun's irradiance and not the transducer at all. I would argue this is wrong, and it is a false dichotomy to argue this as this blackbody emission spectra shape it not unique to the Sun, but, in general, and known to all radiation and known as the blackbody spectrum. The scientists working with solar TEGs are only thinking about the output of their invention, and are oblivious, I think, to the connection between the blackbody emission spectra and their results. This is clear from the following figure, Figure 26.

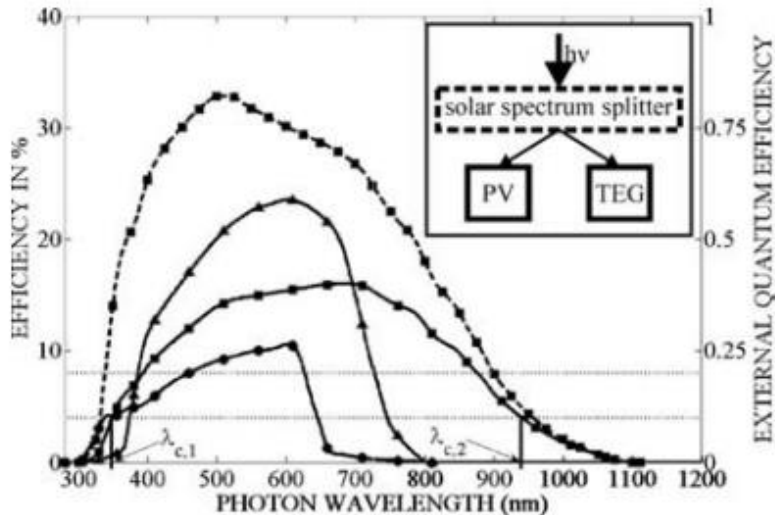


FIG. 2. Schematic diagram of the PV-TE hybrid system. EQE (dashed line) and spectral conversion efficiency (solid lines) of a-Si:H (▲), mc-Si:H (■), and polymer (●), assumed solar TEG efficiency of 4% and 8% (dotted lines).

Figure 26. PV and TEG Efficiency by Wavelength [57]. The efficiency (input over output) of the TEG is the same shape as the IR Generated AM1.5G solar irradiance spectrum, and has the same wavelength output. This is because they are the same – they are both produced by the thermo-electric Seebeck effect. This shows the solar irradiance spectrum is a TEG curve, and in general, all blackbody spectra curves are no more than that, and are not what is claimed.

The main point is that these Solar TEGs are about electricity production; emission spectra are not and never have been. What I am saying is the emission spectra are electric has demonstrated by the solar TEGs.

I argue this (shape) is a property of the detector, the transducer. I would also claim we know from Raman spectroscopy, as demonstrated in this paper, and by the equipartition principle, molecules outside this range do absorb energy at frequencies greater than ones shown (1100nm).

4.13 The Misconception of Wein’s Law as a Property of the Thermopile

With respect to Figure 11, it was shown at the temperature of the heat source increased the maximum of the output curve ‘red’ shifted (my words) – to the right. This is known as Wein’s displacements law, and, by its current understanding, is demonstrated below in Figure 27 and Figure 28.

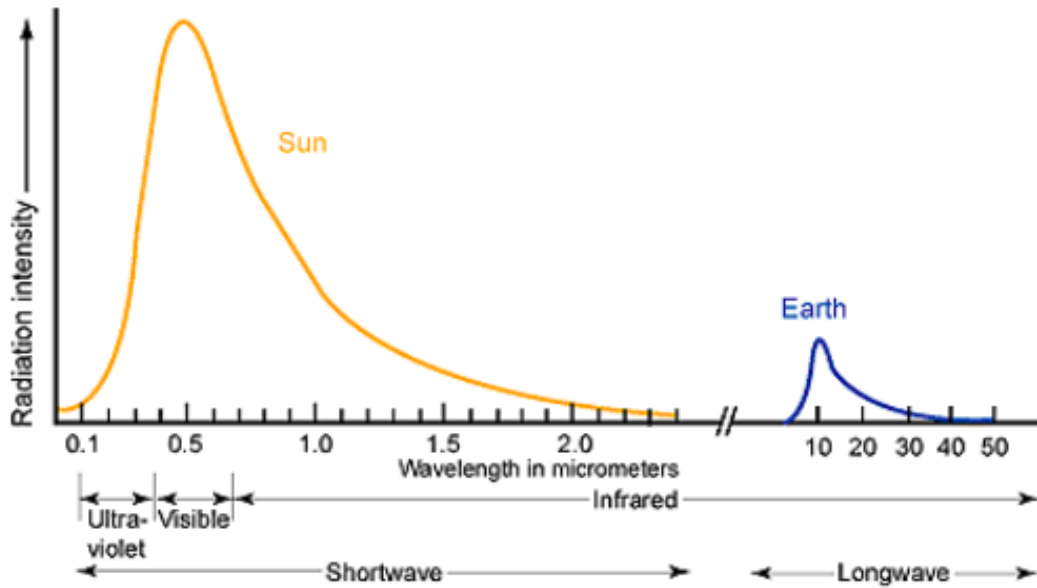


Figure 27. Thermoelectric ('Blackbody') Curves' for Sun and Earth[58]. The thermopile produces a curve dependent on intensity; the Sun being more than the Earth. This has been misconceived as the only representation of thermal radiation.

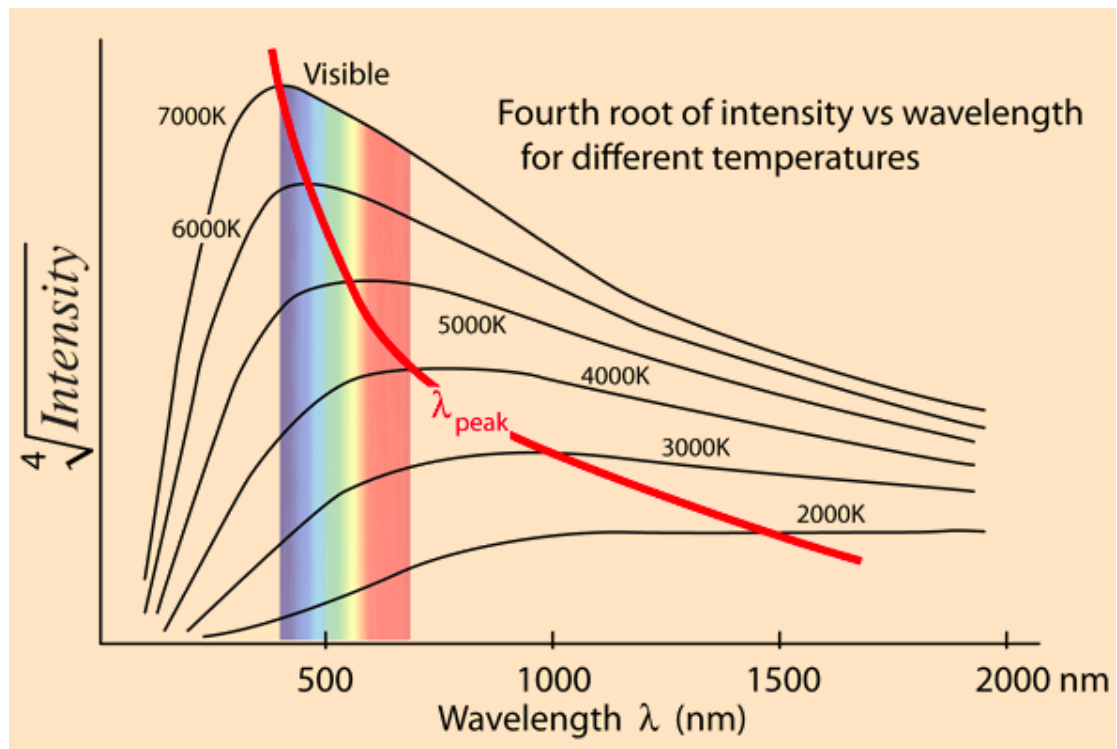


Figure 28. Demonstrating Wien's Law [59] As the temperature of an object falls the blackbody curve maximum of 'peak' shifts to the right. In this study this result is a property of the thermopile and not radiation.

While this bell-shaped curve is not disputed; the interpretation of it being the sole IR radiation curve is. And the assumption gained from it that the Earth absorbs only shortwave IR radiation and emits only longwave from is also disputed here. Given that the curve is produced by the thermopile transducer, it is really and only the thermoelectric curve of a radiating object. The bell-shaped curve is a property of the thermopile; and it seems the more intense the 'heat' source, the more left shift the curve max. This has led us to, I believe, a misconception of the emission and absorbance of the predicted spectra on the flanks of this bell-shaped curve. For instance, N₂ and O₂ are on the far right flank of the solar emission spectra (Figure 1), and are well off to the left of the Earth surface spectra (Figure 29); and so have been interpreted as being from 'very poor', to 'non-emitters'. Raman spectrometers results of these quantum predicted spectra show the contrary; they are perfect emitters and perfect absorbers and respond to IR photons of all intensities.

The implications of the claim made here are not lost on the author: the blackbody curve is at the core of all radiation theory and quantum mechanics. In the 'light' of modern quantum mechanics and specifically laser-based Raman spectroscopy, its key assumption may need review. The great radiation scientists of the 19th century did not have the knowledge we have today. They did not have Quantum mechanics and Raman Laser spectroscopy. Even if these discoveries led to quantum mechanics, it does not mean it is correct. Today quantum predicted spectra are observed by both Raman Laser and IR thermoelectric spectrometers.

4.13.1 Solar Blackbody IR Spectra and the Addition of CO₂

Figure 29 below shows (clockwise) the effect of increasing the concentration of CO₂ gas to a (thermopile deduced) solar blackbody spectrum. It appears the greater the concentration the greater the absorption at the CO₂'s 667 cm⁻¹ spectral band. The thermoelectric explanation for this increasing drop or decline in the spectra line is the temperature of the CO₂ added is at a lower temperature than that of the background Sun reference and the cool CO₂ added generates a less EMF than the hot solar background at this band. The more the concentration

the greater the offsetting EMF production; but not enough to out-produce the solar reference heat source, just like the candle shows through in Figure 29-C.

Again, if the CO₂ was heated to the same temperature as the solar reference temperature or something near it, no CO₂ would be detected – just as with 4.4.1 above.

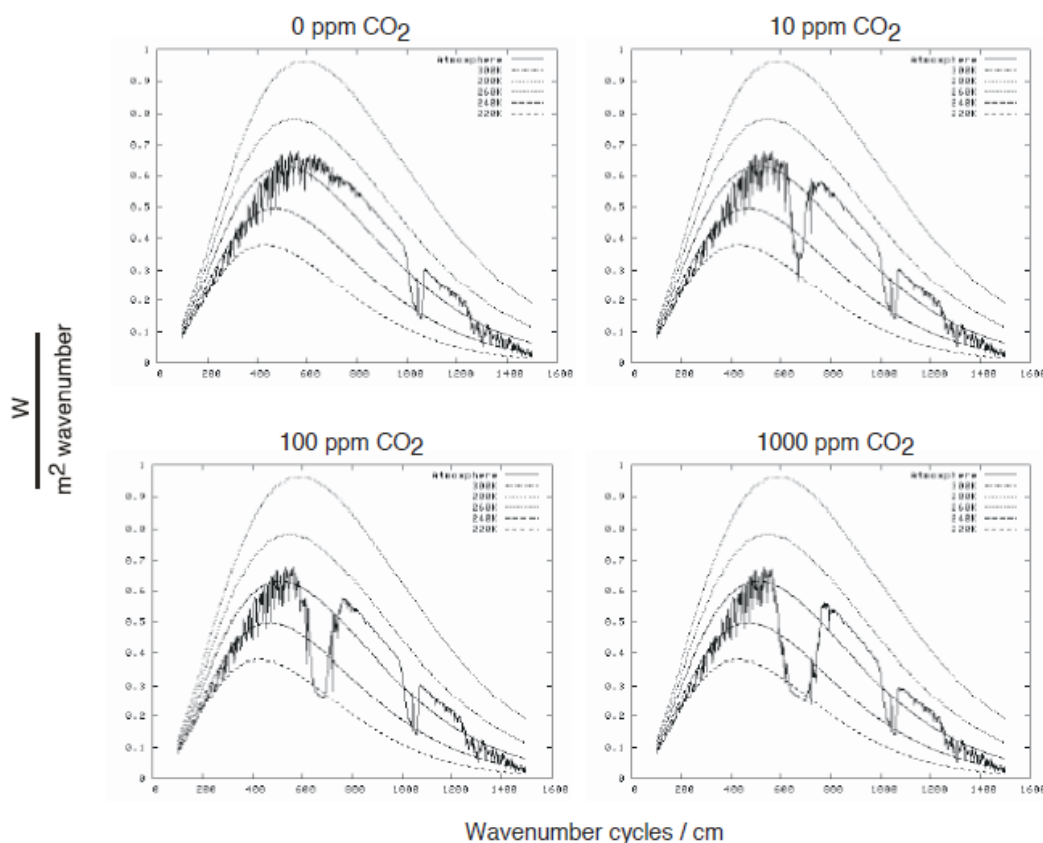


Figure 29. Thermoelectric Spectra of CO₂ at 667cm⁻¹. Increased CO₂ concentration – from 0 ppm to 1000 ppm – produces thermal EMF revealing CO₂'s 667 IR band.

Note the CO₂ EMF is not equal to the heat source: just as the candle flame can still be seen in the image Figure 16-C (Stewart BBC demonstration) with high concentration CO₂ the background heat source still has some dominance.

4.13.1.1 New development.

Looking at the derivation of the IR thermoelectric spectrogram, Figure 45; could it be that there is a 'background spectra' produced where upon all other measurements are compared against.

4.13.2 Solar Blackbody IR Spectra 'Hanging CO₂ Paradox' at different Temperatures

There remains a paradox to the author; how is it the following spectrographs change with temperature and the CO₂ 667cm⁻¹ does not? Why do spectra hang when the curve falls around it and changes with temperature as in Figure 30 and Figure 31 below?

For Figure 30 the changes in the curves from looking down (a) and (b) looking down can be explained by an understanding the thermopile. If we point a thermopile at the sky there is no reading of temperature; if we point down to the ground, a fair, but not perfect temperature is measured. This along would explain the dropout between the CO₂ modes in (b).

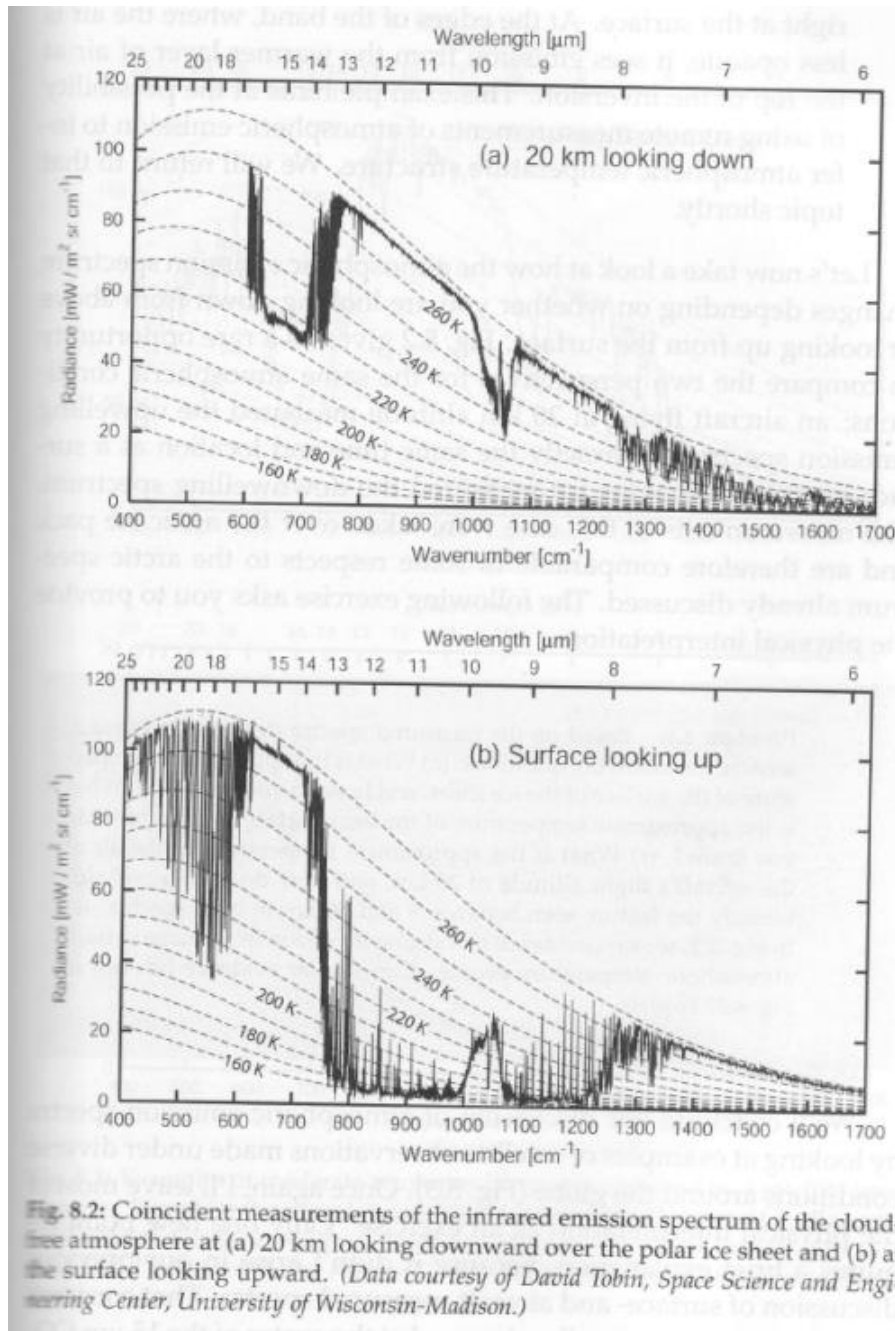


Fig. 8.2: Coincident measurements of the infrared emission spectrum of the cloud-free atmosphere at (a) 20 km looking downward over the polar ice sheet and (b) at the surface looking upward. (Data courtesy of David Tobin, Space Science and Engineering Center, University of Wisconsin-Madison.)

Figure 30 Thermoelectric Spectra; (a) Looking Up, and (b) Looking Down [60].

Explaining Figure 31's dramatic changes of blackbody curve shape at different locations on Earth, we need to understand that while thermopile derived IR spectrographs do show the emission spectra of CO₂ and other molecules, they also respond to temperature. At lower temperatures, the emf from the thermoelectric detector will be low, so indicated curve around these spectra is correspondingly low. It should follow that at low temperatures the CO₂ 667 cm⁻¹ also drops; as it does from extremes of (a) to (b).

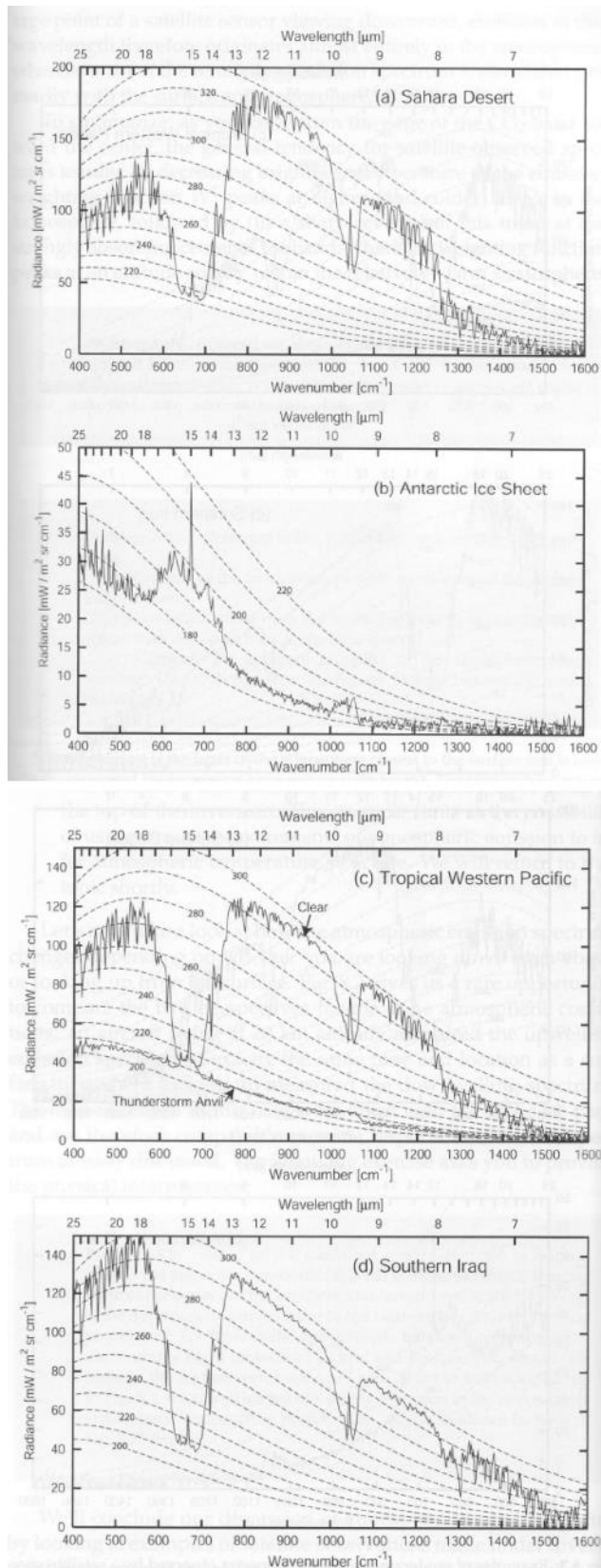


Fig. 8.3: Examples of moderate resolution IR spectra observed by a satellite spectrometer. Except for the curve labeled "thunderstorm anvil" in panel (c), all spectra were obtained under cloud-free conditions. (Nimbus-4 IRIS data courtesy of the Goddard EOS Distributed Active Archive Center (DAAC) and instrument team leader Dr. Rudolf A. Hanel.)

Figure 31. Thermoelectric spectra for different Locations on Earth. [60]

4.14 Showing Raman and IR-Thermoelectric Spectrometers are Complementary Instruments

In a separate working paper, I have researched the role Raman spectrometers have in identifying the 'Raman-active' spectra IR thermoelectric instruments cannot. The paper is called Quantum Mechanics and Raman Spectroscopy Refute Greenhouse Theory[4].

It is well understood by chemists Raman spectroscopy is a complement to 'IR' spectroscopy; it completes the IR picture. No one has brought them together with regards to the infrared atmosphere. This complementarity is revealed clearly below in Figure 32, Figure 33, and Figure 34, where some spectra modes are even identified by both Raman and thermoelectrics.

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.

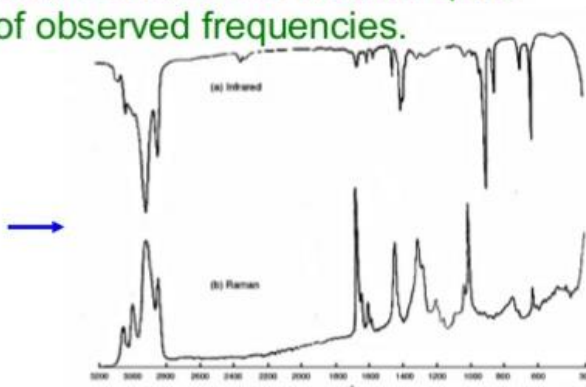
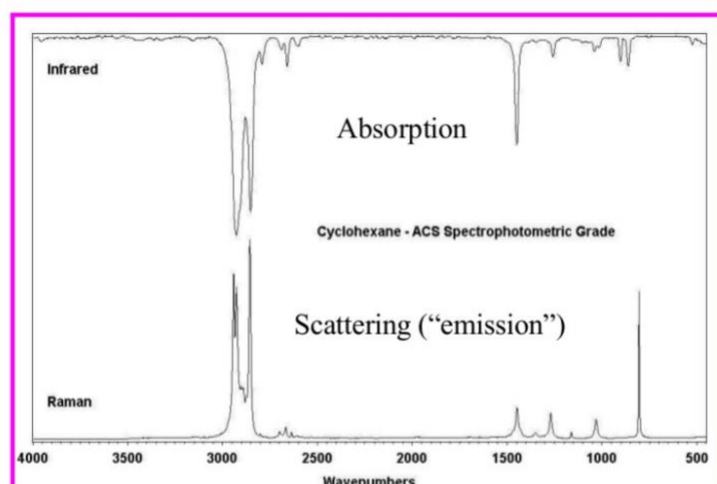


Figure 32. Complementary IR and Raman Spectroscopy. Infrared above; Raman below[61]

Other Molecules with Dual 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 33. Demonstrating Dual Raman and IR Thermoelectric Modes of Cyclohexane. [62]

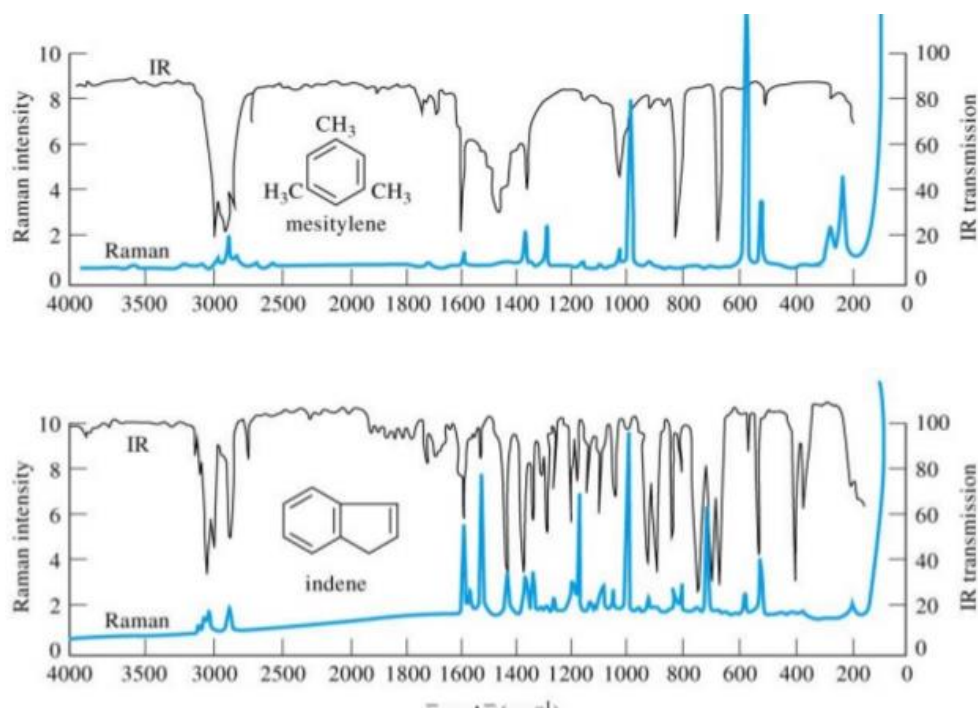


Figure 34 Demonstrating Dual Raman and IR Thermoelectric Modes of Mesitylene and Indene.

4.14.1 Ethanol

The following is an interesting (Raman image) reference: Ethanol has both and shared Raman and thermoelectric modes. Figure 35 clearly shows matching spectra measure measurement from both Raman and thermoelectric, and finally, CO₂ to an informed chemist is both Raman and IR-thermoelectric.

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

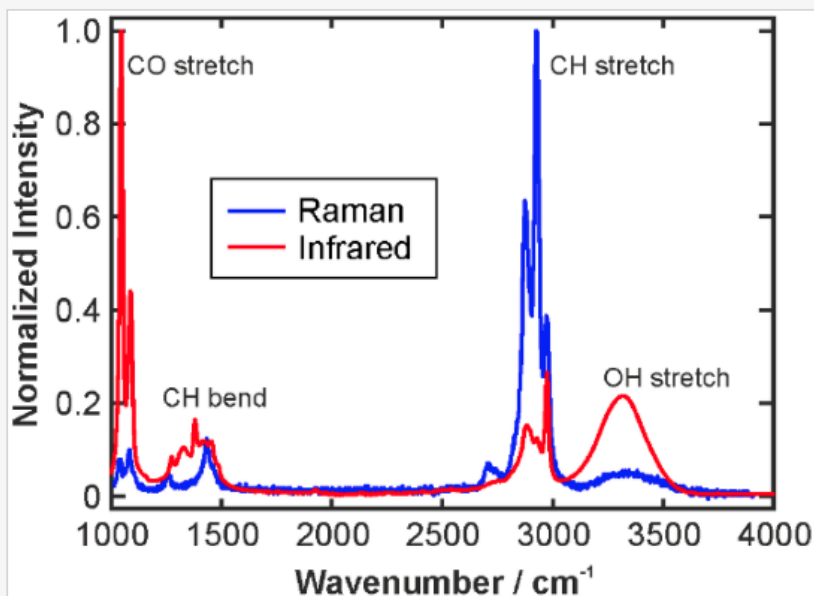


Figure 35. Ethanol Sharing Both Raman and Thermoelectric. [63]

4.14.2 CO₂'s 1338 Raman Active mode showing on IR spectra.

Figure 36 and Figure 37[64], and Figure 38 [65] clearly show CO₂'s 1338cm⁻¹ Raman Active spectra mode on IR (thermoelectric) spectrograms. This strengthens the case the mode is equivalent.

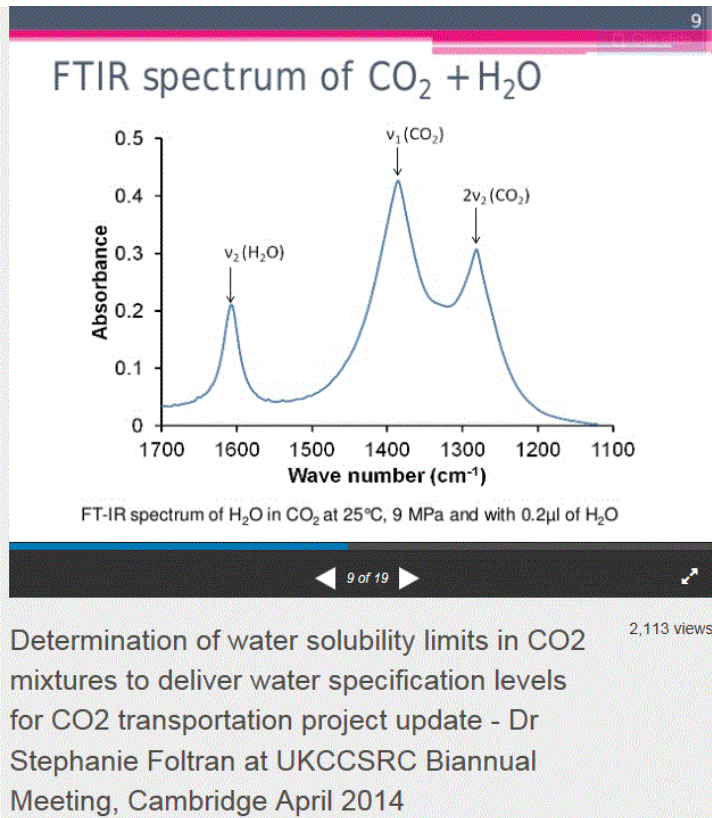


Figure 36. CO₂'s 1338cm⁻¹ Raman Mode showing on IR (thermoelectric)

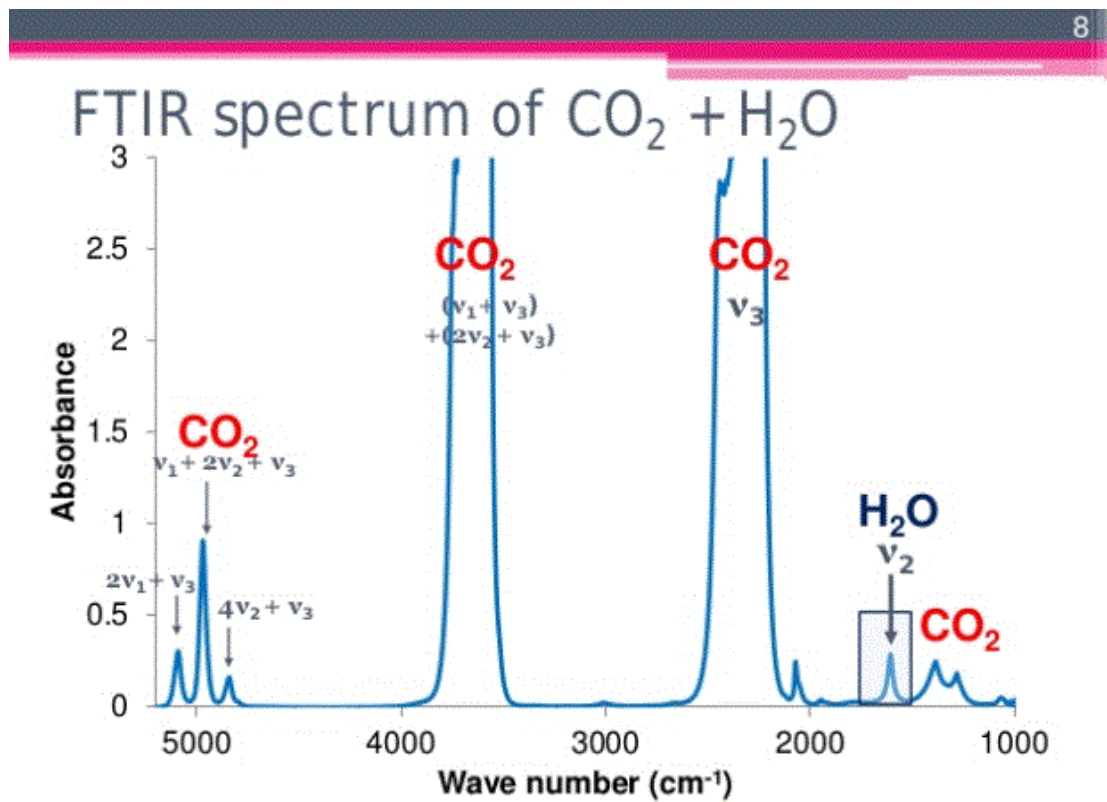
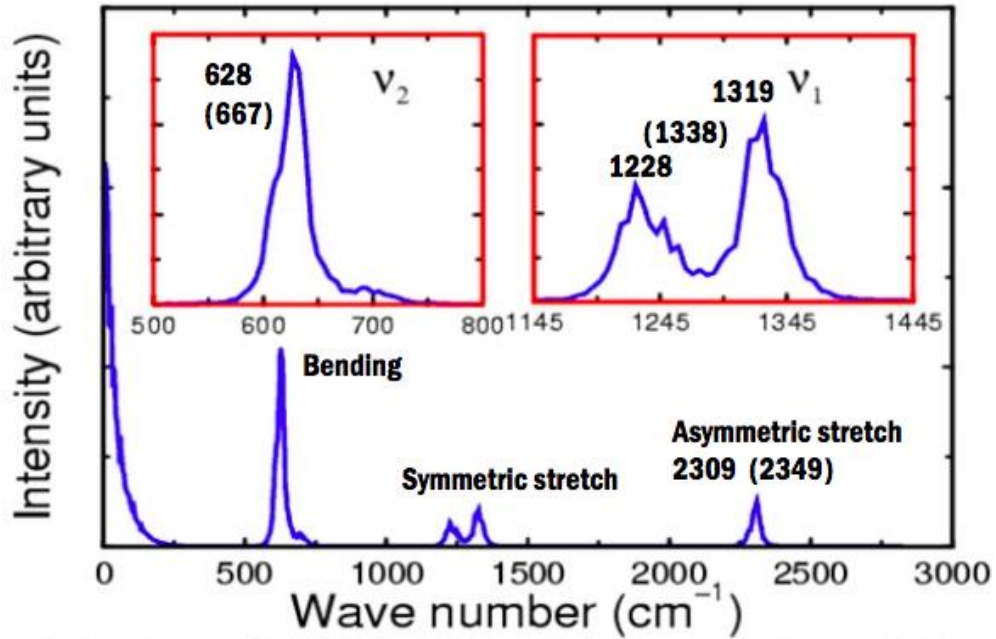


Figure 37. CO₂'s 1338cm⁻¹ Raman Mode showing on IR (thermoelectric).



Numbers in brackets are for 'ISOLATED' CO₂. Splitting in symmetric stretch is due to 'FERMI RESONANCE'

Figure 38. CO₂'s Raman Active Mode on IR Thermoelectric Spectrogram.

4.14.3 H₂O (and N₂O): Spectra 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, 3652cm⁻¹, and 3790cm⁻¹.

4.14.4 H₂O's 3652 cm⁻¹: IR/IR and Raman Modes Equivalent

The Raman observation of H₂O's 3652 cm⁻¹ vibrational mode is significant as this mode is both IR- 'IR active' (as shown in Figure 39 and Figure 40 below) and Raman active; it is a 'dual' Raman-IR mode. This mode is an absolute demonstration, observation, and practical application, via the Principle of Equipartition, that these modes are equivalent.

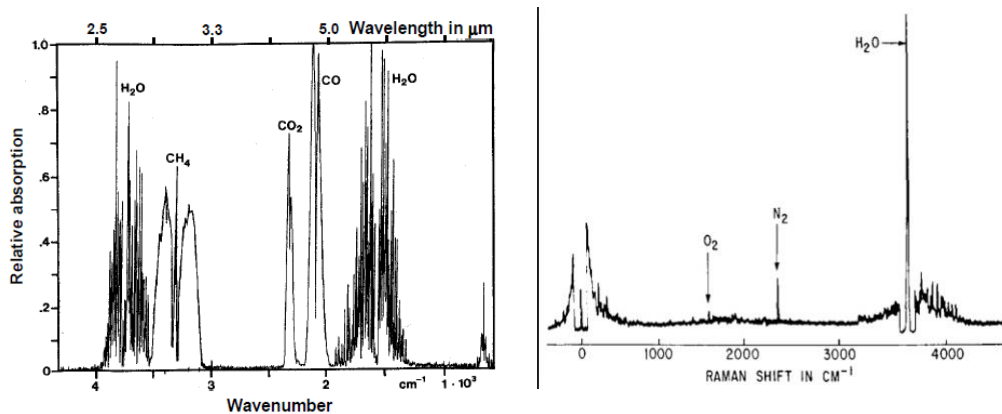


Figure 39. H₂O Thermoelectric (IR) and Raman Spectra. Left 'IR' and Right Raman; showing H₂O's 3562cm⁻¹ mode and others.

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 investigation's conclusion, and radiation physics as a whole – water has a dual means of absorption and emission.

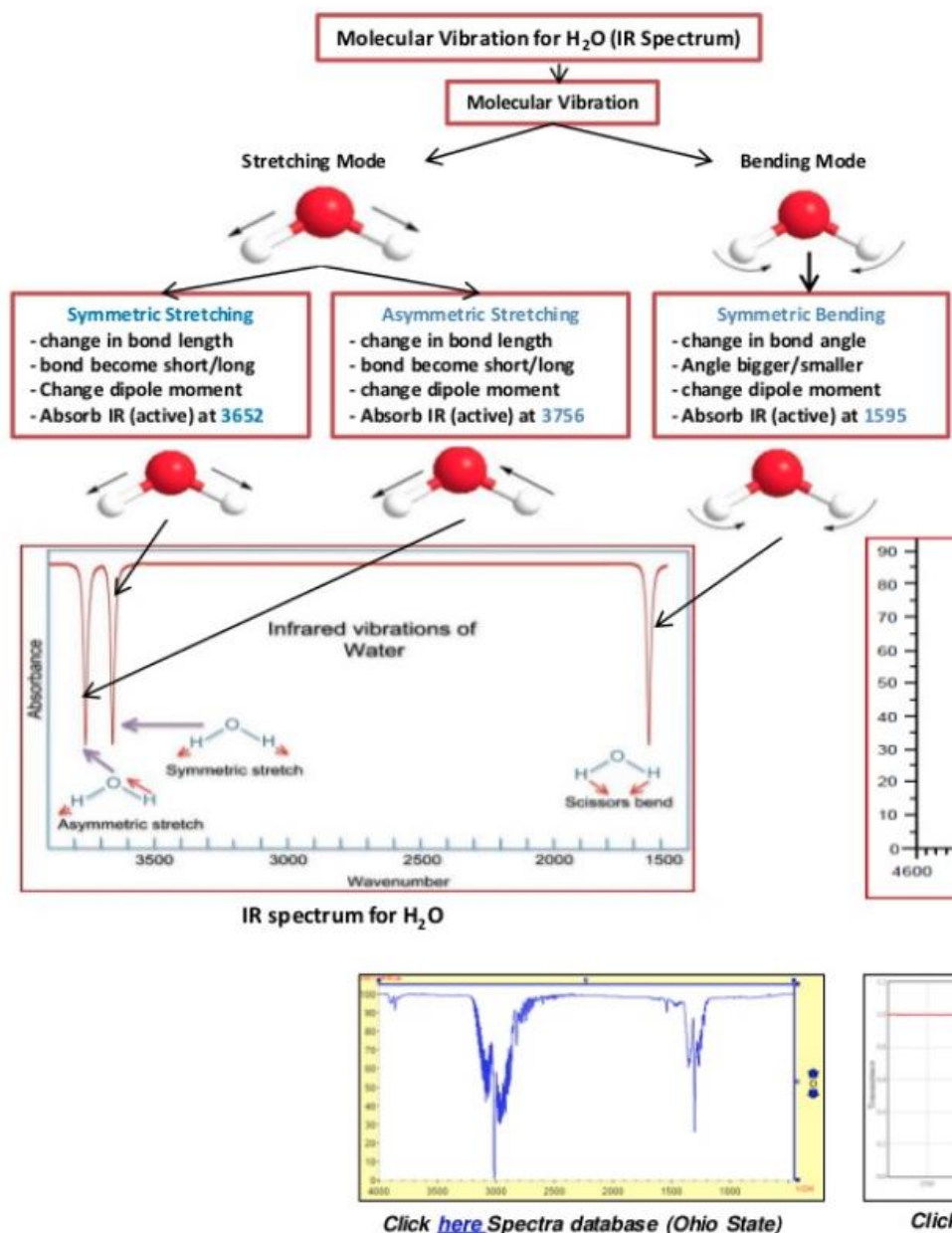


Figure 40. H₂O IR (thermoelectric) Vibration Modes and Respective Spectrum. Notice the 3652cm⁻¹ is clearly shown to be IR. [66]

4.14.5 Contravention of the Rule of Mutual Exclusion

It appears the above H₂O 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, H₂O is a special exception as described below.

“The fact that H₂O does not obey the rule of mutual exclusion indicates that the H₂O molecule is not centrosymmetric (it is bent). As expected, the v₁ symmetric stretch is also strongly Raman active. “

Band H ₂ O	Infrared	Raman
v ₁ - symmetric stretching (3652cm ⁻¹)	strong	strong
v ₂ - asymmetric stretching (3755cm ⁻¹)	very strong	weak
v ₃ - bending (1595cm ⁻¹)	very strong	weak

(Source, online lecture notes).

Does this also mean H₂O offers the best example and application of the law of equipartition? Where the mode is both. Explanation of this is beyond the scope of this investigation.

4.14.5.1 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 [67] 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 IR modes.

4.14.6 N₂O’s Shared IR and Raman Modes

Just as with H₂O, N₂O is another strong so-called GHG. It also shares modes that are Raman active, though the Raman is weak as shown in Table 4 [68] and no IR Raman spectrograms of it have been produced to knowledge.

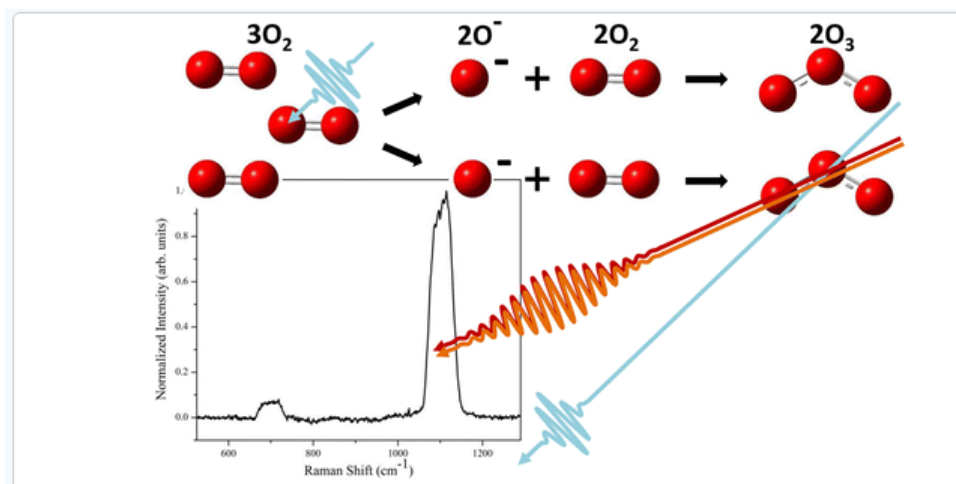
Table 4. N₂O IR Raman Equivalence.

$\bar{\nu}$ (cm ⁻¹)	Infra-red	Raman
589	Strong PQR contour	-
1285	Very strong PR contour	Very strong polarized
2224	Very strong PR contour	strong depolarized

4.14.7 Ozone O₃ IR and - inferred by - Raman

Ozone is a greenhouse gas; it has IR spectra, and these spectra are observed. It's Spectra band at around 1000cm⁻¹ observed on the general atmosphere emission spectra Figure 1. It shares the same position as CO₂'s 960cm⁻¹. This CO₂ spectra position is the same as outputted by the CO₂ laser.

Ozone is also able to be detected Raman spectroscopy, or at least inferred by Raman Spectroscopy. The following are a collection of findings defending this claim.



The filament-assisted impulsive Raman spectra of ozone, nitric oxide, and nitrogen dioxide are presented. The Raman response as a function of ozone concentration scales as N^2 , where N is the number of oscillators in the interaction region. The system described has a detection limit of ~300 ppm for gas-phase ozone. Ozone produced via the strong field chemistry occurring within the filament pump was also detected. The measurements reveal spectral interference in the Raman features. Simulations show the spectral fringing results from interference of the Raman signal with pump-induced cross-phase modulation. The fringes are used to classify the symmetric mode of the low concentration filament-generated ozone.

Figure 41 O₃ Raman Spectrograph Showing its 1103cm⁻¹ [69]

Firstly, a paper was found with the title: *Monitoring O₃ with solar-blind Raman Lidars* [70] which speaks for itself, and then one by the title of: *Ozone and Water Vapor Measurements by Raman Lidar in the Planetary Boundary Layer*[71].

The following is said:

To retrieve the ozone concentration profile, we take advantage of the simultaneous spontaneous Raman backscattering on the molecules of nitrogen (N₂) and oxygen (O₂) that have different ozone absorption cross-sections. Thus with a modified DIAL technique, the ozone concentration can be measured without most of the interference from poorly known backscatter by particles. Water vapor mixing ratio profile can also be obtained with a set of three Raman backscattered signals, simultaneously detected, from the molecules of H₂O, N₂ and O₂. The main advantage of this Raman system is its essential independence to the wavelength dependent backscatter problems as induced by aerosols, and the fact that the N₂ and O₂ concentrations are well known as well as the Raman cross-sections of interest. Although the Raman cross-sections are two or three orders of magnitude lower than the elastic backscattering cross-sections, they are compensated by the proportionally much higher concentrations of O₂, N₂ and H₂O compared to trace gases like O₃.

Backing this up a paper titled Tropospheric ozone profiles by DIAL at Maïdo Observatory (Reunion Island): system description, instrumental performance and result comparison with ozone external data set [72]

Comparisons with 11 ground-based Network for Detection of Atmospheric Composition Change (NDACC) Fourier transform infrared (FTIR) spectrometer measurements acquired during the daytime in a ±24 h window around lidar shooting show good agreement between data sets with a D of 11.8 % for the 8.5–16 km partial column (LIO3T higher than FTIR), and comparisons with 39 simultaneous Infrared Atmospheric Sounding Interferometer (IASI) observations over Reunion Island show good agreement between data sets with a D of 11.3 % for the 6–16 km partial column (LIO3T higher than IASI).

4.15 Augmenting the Thermoelectric and Raman Atmosphere

Finally, to bring together, augment, the IR-Raman modes with the IR modes. Raman spectroscopy spectra, as identified and used in the Raman Exhaust Report, show the predicted N₂ and O₂ vibrational modes of these abundant molecules. These ‘Raman’ modes along with the IR modes of the EMS, can now be brought together – augmented – to complete the GHGs.

Figure 42 below is a schematic of the predicted and observed Raman vibrational modes in the Earth’s atmosphere at different electromagnetic frequencies.

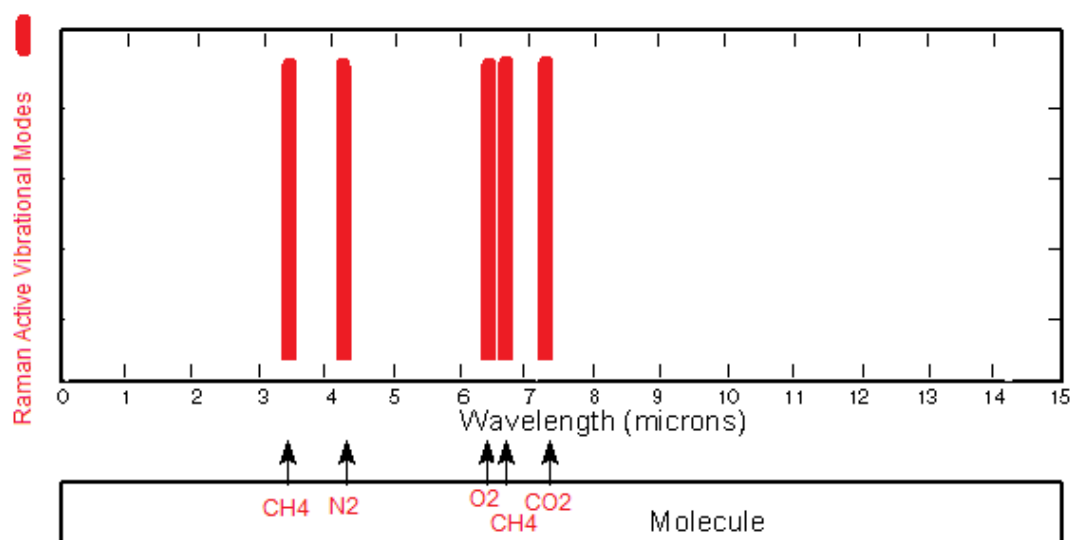


Figure 42. Raman Vibrational Modes of the Atmosphere. Predicted and Raman measured vibrational modes of (some) atmospheric gases CH₄, CO₂, N₂ and O₂.

4.15.1 The Augmented Fourier Greenhouse Atmosphere spectrum

Combining thermoelectric and Raman Spectrographs (Figure 43 below) reveals all the predicted and observed vibrational modes of the atmosphere. The augmented atmospheric spectrum now accounts for the hidden 98% of gases in the atmosphere.

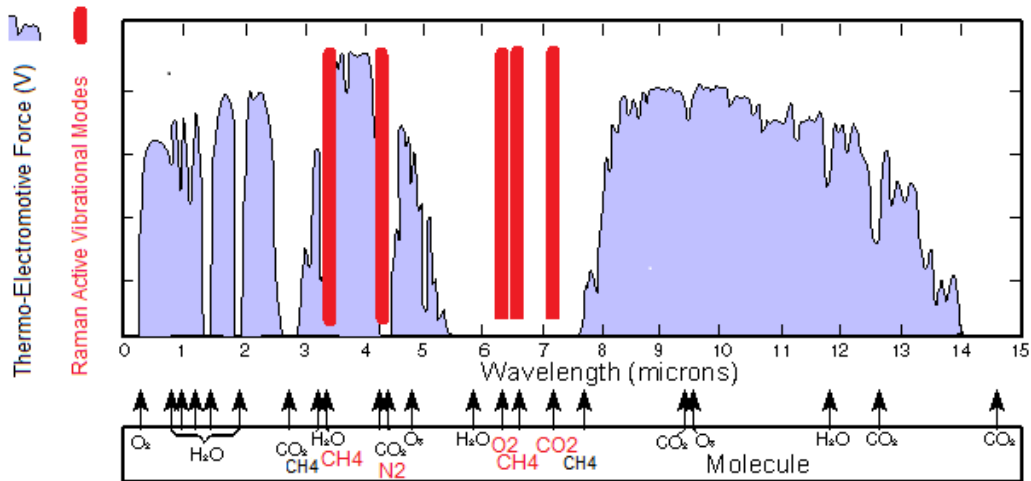


Figure 43. The Augmented Greenhouse Atmosphere. Combining Thermoelectric spectra with Raman spectra to reveal the complement of atmospheric vibrational modes and the greenhouse atmosphere of planet Earth.

4.15.2 Addressing Raman Spectra between Solar and Earth 'Blackbody Curves

Continuing with the above, Figure 44 shows all the (important) predicted IR spectra (red thermoelectric, purple both Raman-active and TE, and blue Raman-active only from

Table 2) and the Sun's and Earth's blackbody radiation curves (*b - b*).

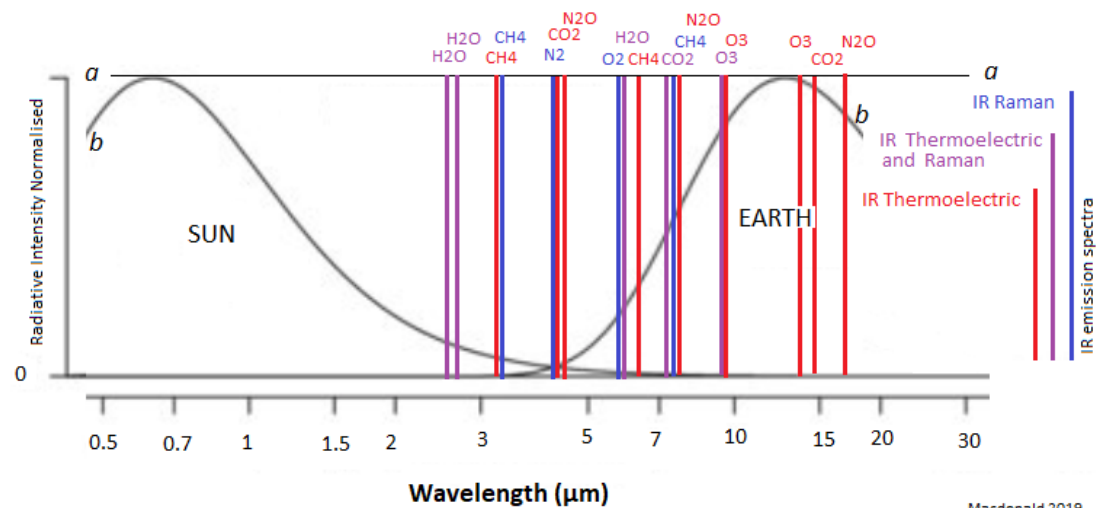


Figure 44. Quantum Predicted IR Spectra with Sun and 'Earth Blackbody' Curves. Spectrogram shows positions and type of the predicted IR emission spectra of gas molecules within the EMS matching the normalised – thermoelectric derived 'Blackbody' curves (*b - b*) – Planck intensity curve' (*a - a*).

The blackbody curves are assumed to be envelope curves: any energy values outside them are unattainable. However, from Raman spectroscopy the observations and quantitative properties (temperature etc.) taken from the Raman spectra lines (both purple and blue spectra lines) this claim is refuted. As a result of the augmentation of Raman-active modes with thermoelectric modes are can exist outside the blackbody domains. This is in total contradiction to current GH theory.

As the Raman-active spectra behave as IR radiators in accordance with quantum mechanics; they all have the potential to output – in terms of intensity – at the ($a - a$) 'Wein law' Line. This claim challenges Radiation theory as we know it. In conclusion; the so-termed blackbody radiation curves are a misconception of thermoelectrics and are refuted with Laser Raman Spectroscopy.

4.15.2.1 New Developments to Wein's Law Claim

Looking at the derivation of the IR thermoelectric spectrogram, Figure 45; it is shown that the blackbody curve peaks at and around CO₂'s 2349 cm⁻¹ mode with a temperature of around 1500K. From this the it can be assumed the so called blackbody curves are independent of how they are understood and are a function of temperature.

4.16 New Developments Since First Publication

The following are new developments that support my hypothesis. I have added them here so as not to change the figure and contents numbering of my original publication.

4.16.1 IR-Thermoelectric Spectroscopy and Blackbody Curves

So far, I have presented how IR thermoelectric spectroscopy and blackbody curves are the product of thermoelectrics; the following figure will strengthen these claims. Figure 45 shows the derivation of a sample spectrum. The 'processed sample spectrum' on the right is derived from the difference between 'background spectrum' and the 'raw sample spectrum'.

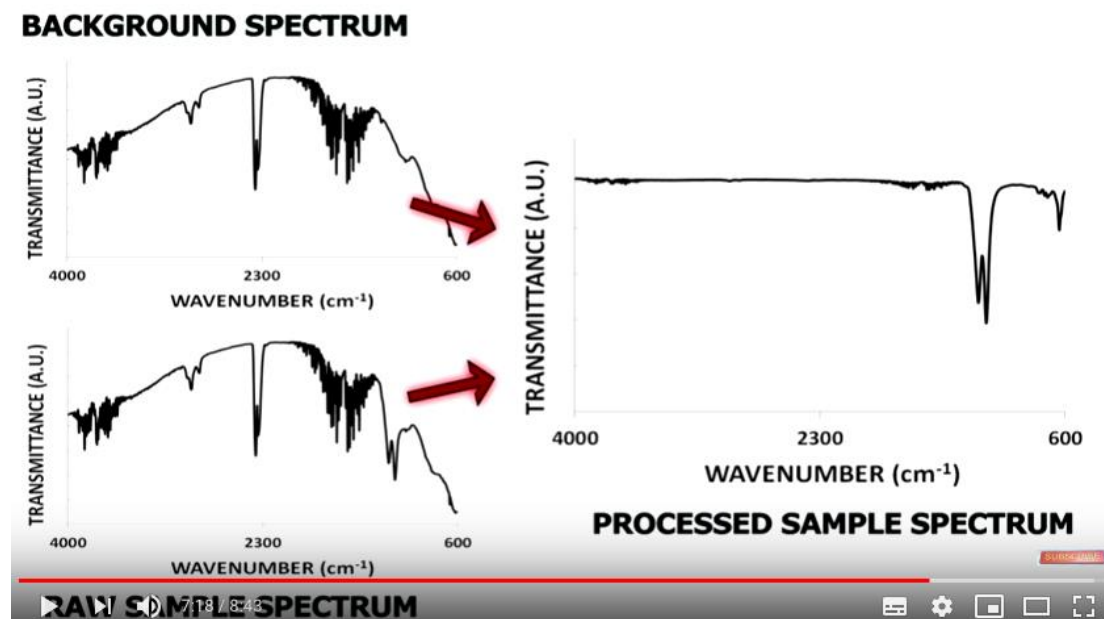


Figure 45. IR Spectrograms Showing Blackbody Curve and CO₂. [73]

Three important points for this study should be noted: the bell shape curves on the left peaking around the 2300cm⁻¹; the position of the CO₂ 2349 cm⁻¹; and the straight-line curve of the processed sample. The peak of the curve should correspond to the heat element temperature of around 1500K. This peak is outside both the Earth's and Sun's peak positions show in Figure 44.

4.16.2 1960's Spectroscopy Film Showing all CO₂'s Spectra are Equivalent

In support the above claim, an introduction film from 1962: [Molecular Spectroscopy](#) from University of California [74] describes and demonstrates the three vibrational modes of the CO₂ molecule. In it they demonstrate harmonic vibration of the molecules using a basic ball and spring scale model with a harmonic vibration generator, Figure 46 (A and B). The three vibrational modes of CO₂ without any separation or discrimination of them are all identified (C): at 7.05×10^{13} (corresponding to the 1338 cm⁻¹ mode), 4.16×10^{13} (corresponding to the Raman Active 2349 cm⁻¹ mode) and 2×10^{13} (corresponding to the 667cm⁻¹).

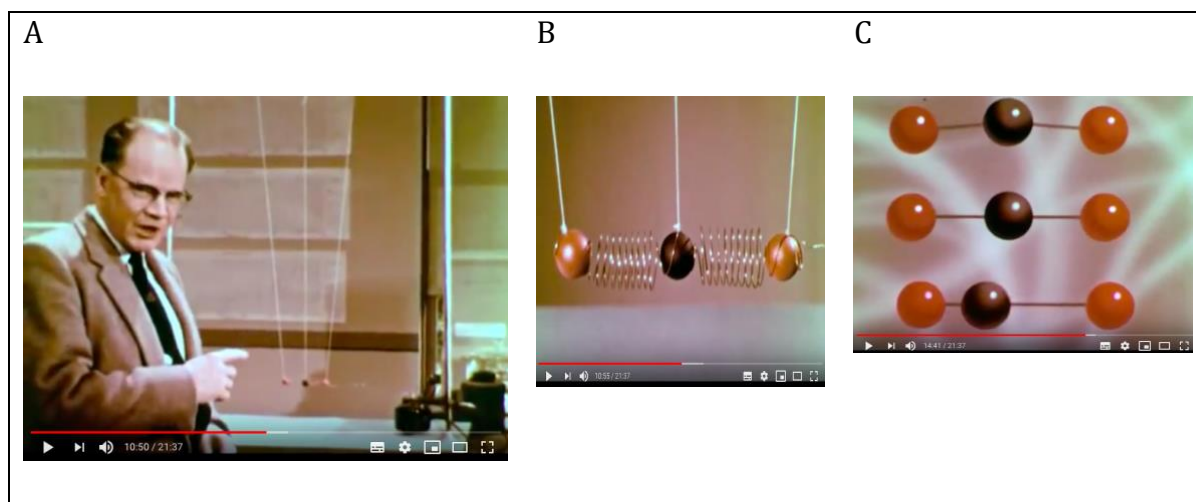


Figure 46. Demonstration of Harmonic Vibration of all of CO₂'s Modes. Frame A, a model the CO₂ molecule is vibrated by frequency producer at different frequencies; frame B, close up of the spring and ball model attached to the devise on the right; and Frame C, the film showing – in an age before Raman Spectroscopy – all CO₂'s modes and their positions.

The significance of this is that at the time of this film there appears to be no understanding of the Raman active modes, only the said IR (thermoelectric) modes – which the film goes on to describe. The point I am making is this is proof the modes are equivalent, they resonate at their respective vibrational positions, and that one only needs a modern Raman spectrometer to observe the third. It is clearly stated in the film the diatomic – N₂ and O₂ – share the same properties of resonance.

4.16.3 Venus's Blackbody Curve 'Maxing Between the Earth's and the Sun's

Continuing with Section 4.13 – The Misconception of Wein's Law as a Property of the Thermopile – I was thinking about how the blackbody 'Planck function' curves shift with different temperatures (curve bb, Figure 44). The Earth's 'max' is at and around 270 Kelvin and so discriminates all other spectra outside this curve. I wondered what this would mean for Venus's atmosphere; it is hotter.

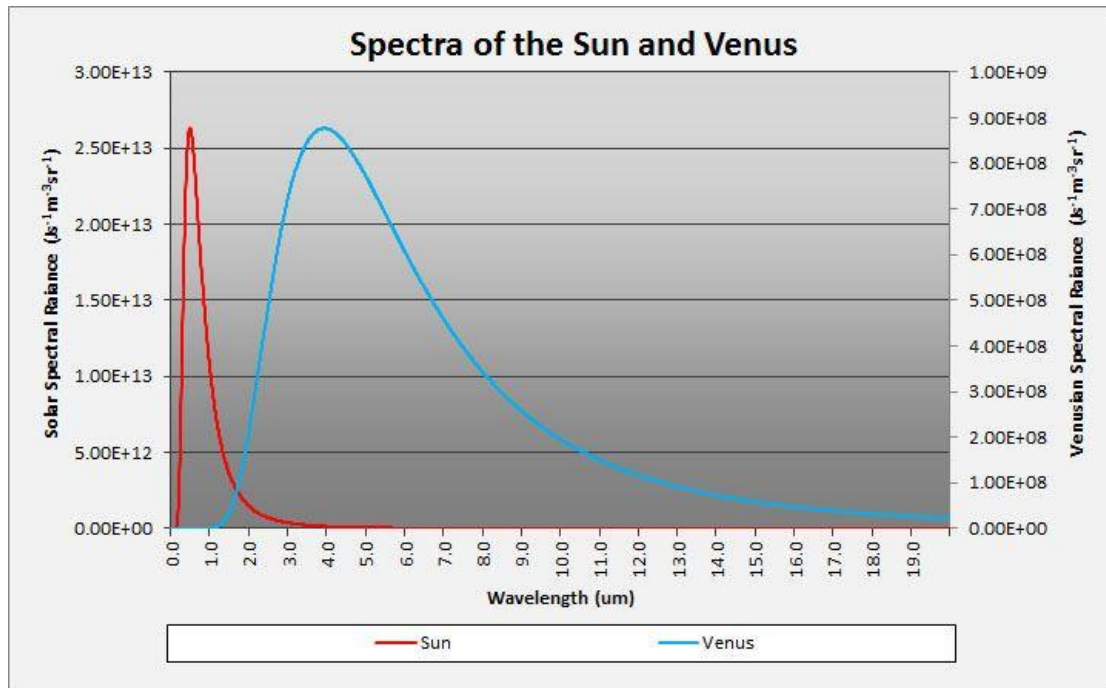
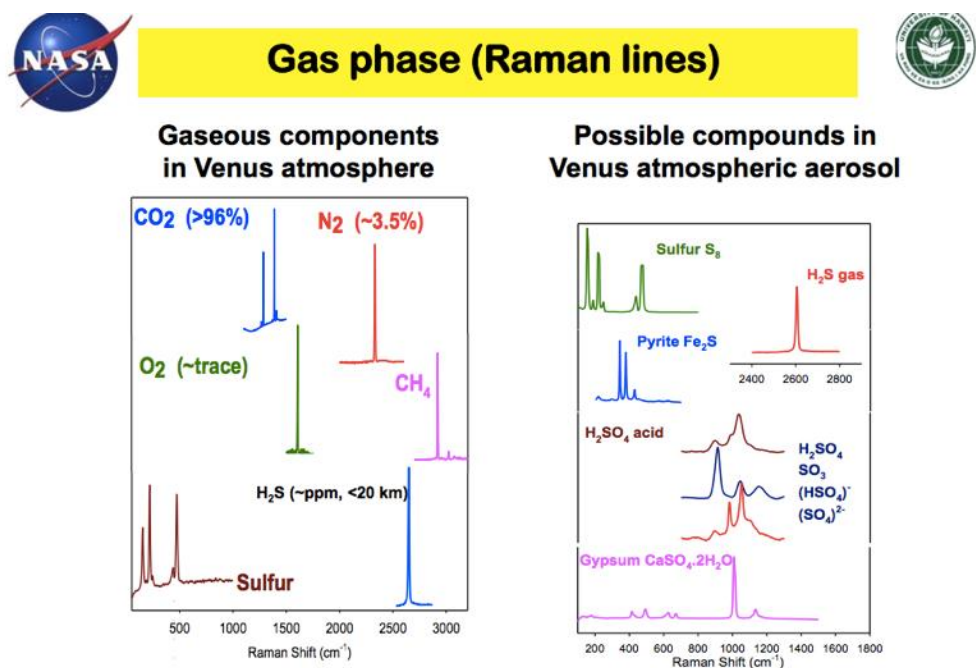


Figure 47. Venus's Blackbody Radiation Curve Peaking Between Sun and Earth. [75] The point of showing this curve is that it lays where the Earth and the Sun's emission spectra are ignored as they are outliers. Presumably for Venus, they are not.

Venus is hotter and so the blackbody curve will shift to the left. It's blackbody curve peaks at and around 4 microns; right between the Sun's and the Earth's; discriminating – now – the Earth's spectra. And it now absorbs the spectra the Earth is said not to – including, to name the important, CO₂'s 1338 cm⁻¹, N₂'s 2338cm⁻¹, and H₂O's 3652cm⁻¹.



Alian Wang, WSU

Figure 48. Planet Venus's Raman Spectra measurements. Raman spectra in left diagram correspond to Raman spectra in Figure 44.

In light of the accurate Raman spectrometric measurements – taken from IR spectra – of Venus's gas composition and concentration (Figure 48), the Blackbody curves are discriminatory, trivial, and misconceived. To clarify my point: if an N_2 molecule – or any other said molecule – was radiated to a temperature of Venus or Earth, then they would absorb corresponding to the Raman results and not the thermoelectric blackbody results. This claim can be and should be tested.

5 Conclusions

It was found IR radiation theory as we currently understand it, and the derivation of the GHGs, is misconceived; it is only the thermo-electric aspect of IR radiation, and as a result is incomplete. My work exonerates CO_2 and the other so-called GHGs from any special role in the climate as claimed. The detection of all so-called 'IR' spectroscopy spectra is really and only the thermo-electric side of the spectroscopy, and this includes the determination of the GHGs. It was found that the detectors of IR radiation are thermo-electric-pile transducers; they convert IR radiation into electricity proportional to the intensity of IR

radiation, but not all substances share this property, nitrogen and oxygen that best examples of these, but, solid Germanium shares the same non-thermoelectric property. Thermopiles were used by John Tyndall, the father of the special GHGs, in 1859. What he really only discovered are the thermoelectric gases; the gases made up of at least one thermoelectric IR spectra mode. These transducers receive the IR radiation signal from the electric dipole modes or spectra of the sample molecules. Those spectra that do not have electric spectra have been misconceived as non-IR radiating and as a result, N_2 and O_2 – as they only have one spectra each in the IR range of the EMS – have been misconceived as not radiating IR. Modern Raman laser Spectrometers measure their predicted spectra positions, and the temperature of these molecules implying they are, by Stefan's Law of radiation, radiating – as all matter is assumed to do.

It was also found the so-called 'Blackbody' radiation spectrum curve, central to GH and IR radiation theory is derived by thermoelectric transducers and thus, as demonstrated with green tech TEGs, is a curve of emf production at each frequency with respect to the temperature of the object. This discovery has implications on the claims of longwave absorption and shortwave emission of the Earth claim. In the 'light' of Raman data, this claim and central theory demands review. As it is it is wrong. The blackbody curves discriminate unnecessarily active Raman measured spectra.

It was also found that so-called IR spectrometers, while they do show a molecules quantum predicted spectra – the thermo-electric ones at that – they do not radiate their samples with IR photons as claimed, and it is only Raman IR spectrometers that radiate their samples with such. They instead measure and graph the difference in temperatures between the 'cooler' sample and 'hotter' reference heat source as transduced from thermal radiation into EMF.

It was also found the concept of emissivity is solely an infrared-thermoelectric instrument problem and really a limitation of the thermoelectric transducer to generate complete EMF from a substance, and is not a real property of radiation at all. Raman modes, and thus N_2 and O_2 , are the best 'blackbody' radiators as they have, by Raman measurement, an emissivity of 1. Further to this, it was

found, by analysing H₂O's 3652 cm⁻¹ mode – and others – ‘Raman’ IR and thermoelectric IR modes are equivalent, consistent to the equipartition law. 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.

With this new thermoelectric understanding – which ignores the quantum mechanics of the atmosphere – the direct mechanics behind the current understanding of the ‘greenhouse’ atmosphere, based alone on thermoelectrics is fallacious. Quantum mechanics and Stefan’s and Planck’s Laws hold; all matter above absolute 0 Kelvin radiates. N₂ and O₂ behave like all other matter, the only thing separating the gases in the IR are the instruments measuring them. 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 N₂ and O₂ were exempt.

6 Acknowledgements

Aside from the support from family colleagues and friends, due to the nature of the investigation, I do not have anyone to acknowledge directly for this work; I have been totally unsupported. I can and should thank the pre-publication reviewers, the sceptics of my theory, some from the sceptic side of the climate debate. Thank you, Barry James.

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