The Greenhouse Gases and Infrared Radiation Misconceived by Thermoelectric Transducers

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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. This study investigated the role of thermoelectric detectors in determining the 'infrared atmosphere'. This study hypothesises that the current greenhouse theory has misinterpreted the significance of those special greenhouse gases (CO_2, 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 the 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 is 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

The total gases in the infrared (IR) atmosphere are divided between what is 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 climates on all time scales. This leaves the remaining constituents (less H_2O), the non-GHGs – nitrogen (N_2) and oxygen (O_2) – out, as they are assumed not to absorb or emit any IR radiation at any temperature[1]. This foundational premise to GH theory holds that both N_2 and O_2 are 'transparent' to 'Shortwave' IR light because they do not – concerning 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 have been radiated by the Earth's surface with 'Longwave' IR radiation. These odd and counter-intuitive assumptions should still be at the centre of the climate debate. The science and the physics are 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 (T^4) of radiation and standard quantum mechanics, no less, all state all 'matter' above absolute zero Kelvin absorb and emit IR (photon) radiation. How are N_2 and O_2 exempt from these laws, placing them like the cosmos's paradoxical 'dark energy' and 'dark matter'?

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

We do know 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 a laser. We also know IR spectrometers only detect spectra with electric dipole moments – as stated above; 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]*, Raman spectroscopy proved that 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 thermoelectric transducer only detects the IR gases and their spectra modes. These transducers receive an electric signal emitted from the 'electric dipole'. They do not radiate the sample with IR photons, as claimed. What John Tyndall 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* $(\boldsymbol{\varepsilon})$, central to the Stefan-Boltzmann equation $\boldsymbol{E} = \boldsymbol{\varepsilon}\sigma T^4$, 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 temperatures – 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 N_2's and O_2's single non- 'IR' spectra modes, along with CO_2'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 N_2/CO_2 laser shows they are 'strong' and dominate[4], contrary to Table 1.

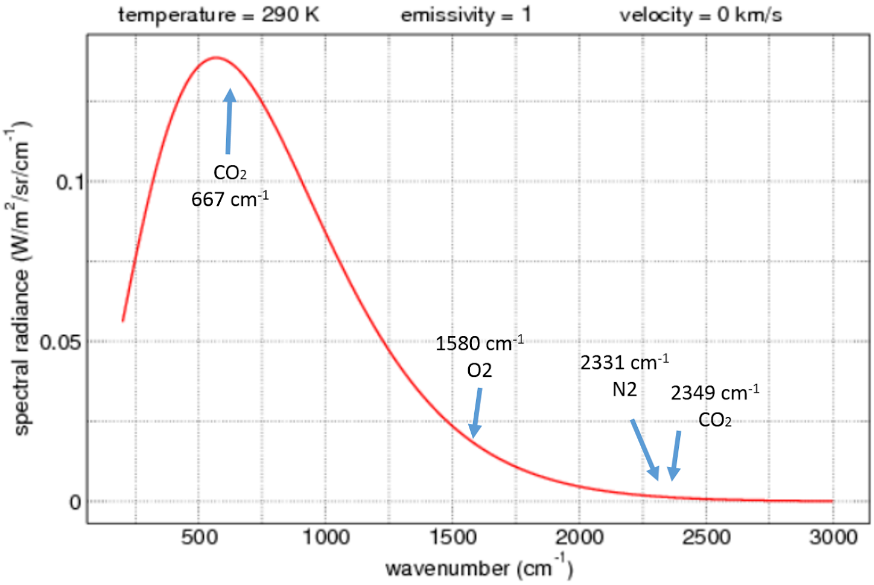


Figure 1. Blackbody Emission Spectrum with Non- GHG modes N_2 O_2 and CO_2. The solar blackbody emission spectra (red) is used to show the output of the non- GHG modes of N_2 O_2 and CO_2

Table 1. Non- GHG modes N_2 O_2 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' of physics. The paper points to the problem with our misconception of 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, will change our understanding of the atmosphere.

2 Methods

No direct experiment was undertaken in this investigation; rather, it was 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 whether the IR modes are 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 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 Seebeek effect and its thermo-electric derived transducers and their role in determining the GHGs.
4. Source the instruments or detectors determining the IR modes and GH gases. Are they thermoelectric by their nature?

3 Results

The following are physics facts concerning 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 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.

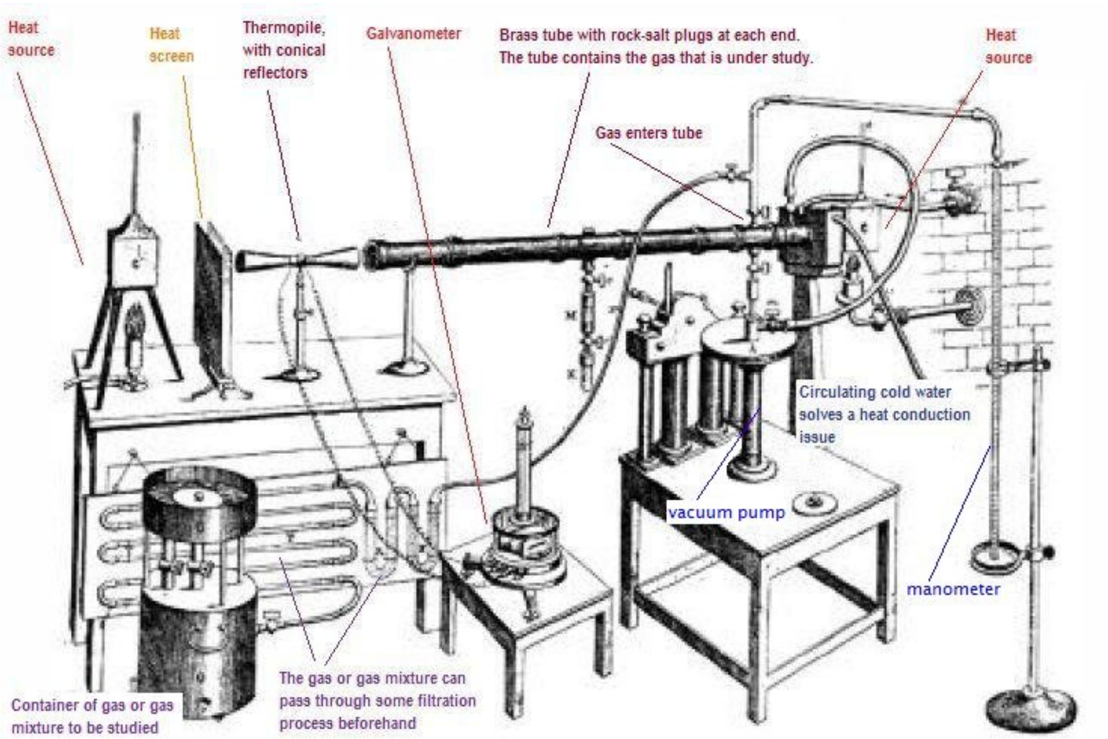


Figure 2. Tyndall's 1859 Setup for Measuring Radiant Heat Absorption by Gases. The apparatus clearly shows a thermopile, galvanometer and heat source. [8]

Tyndall noted that 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_20, CO_2, CH_4, NO_2, and O_3, did. He concluded from this that the latter group of gases absorbed the thermal radiation, while the former did not. From this, the latter group is known today 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. The ends of the brass tube containing the gases were not plugged with rock salt; we shall see why this 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; the law of equipartition shows that all modes are equivalent—and it is the detectors of them that are different.

Molecule	Vibration Mode or Band: Wavenumber (frequency)	IR (Thermoelectric) and IR Raman Spectroscopy Properties	Mode Type
H_20	**3652 cm^{-1} (2.74µm)** **1595 cm^{-1} (6.25µm)** **3756 cm^{-1} (2.66µm)**	**IR and Raman** **IR and Raman** **IR and Raman**	**Symmetric** **Asymmetric** **Asymmetric**
CO_2	**1388 cm^{-1} (7.2µm)** **2349 cm^{-1} (4.257µm)** **667 cm^{-1} (14.992µm)**	**IR and Raman** **IR** **IR**	**Symmetric** **Asymmetric** **Asymmetric**
CH_4	**3020 cm^{-1} (3.312µm)** **2914 cm-1 (3.431µm)** **1508 cm^{-1} (6.5µm)**	**IR** **Non IR; Raman** **IR**	**Asymmetric** **Symmetric** **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) 1042 cm-1 (9.6μm) 701 cm-1 (14.3μm)	IR (Raman Active?) IR IR	- - -
N_2O	2224 cm^{-1} (4.5μm) 1285 cm-1 (7.8μm) 589 cm-1 (17μm)	IR IR 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 keyword: 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.

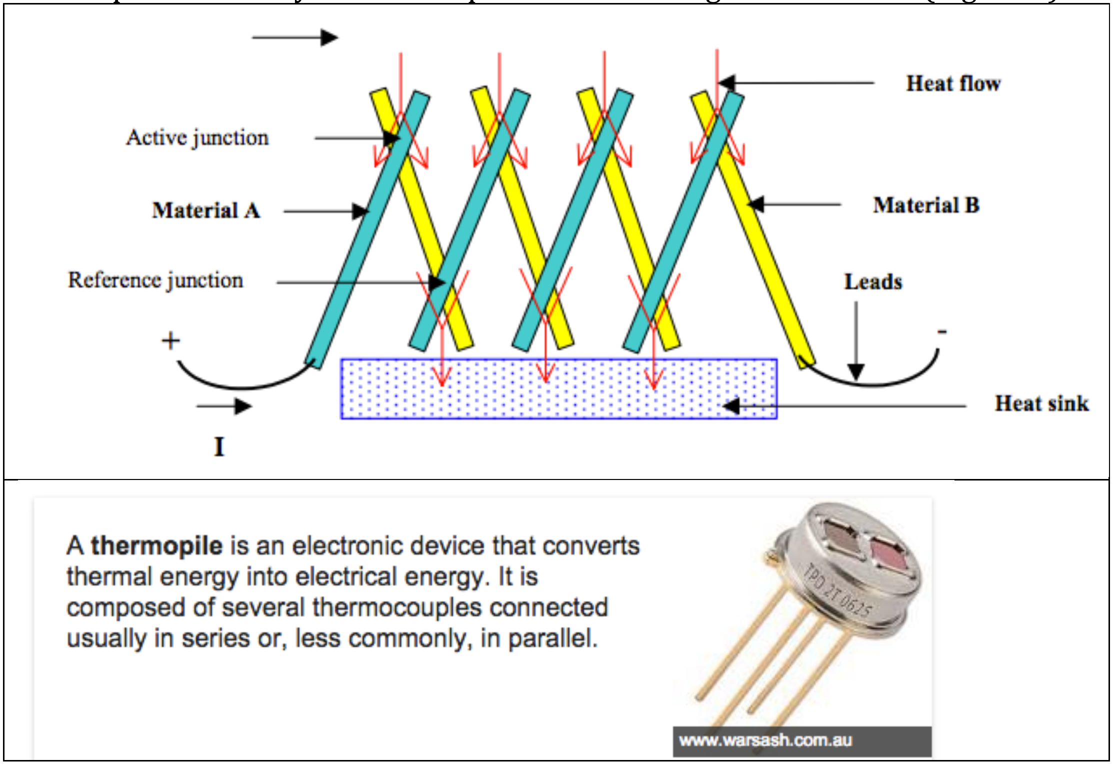
3.3 'IR' Detectors: the Seebeck Effect and the Thermopile

In 1821, Thomas Seebeck [15] discovered electricity current was produced when two different kinds of metals 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

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

where 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).



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

Figure 3 Thermopiles. Above, a 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: as temperature rises, voltage output increases.

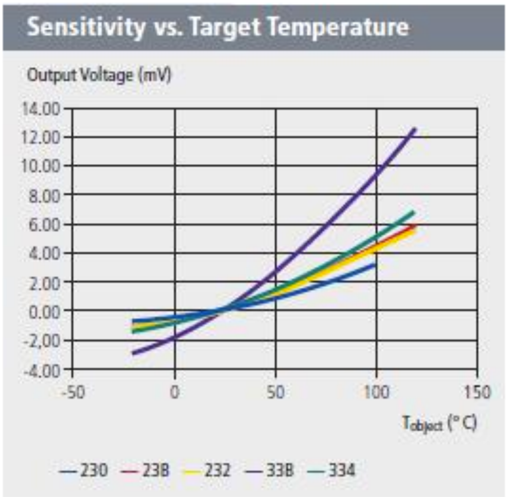


Figure 4. Thermopile Voltage Output by Temperature

3.4 Thermoelectrics and 'IR Spectroscopy'

Other instruments that use the thermoelectric transducer and exploit thermoelectrics are called 'IR' spectrometers.

To show the dispersive IR spectrometers are the same in principle as the CO_2 sensor (explained below) and Tyndall experiment setup and only measure electricity production from the radiated heat, we need to look at the 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.

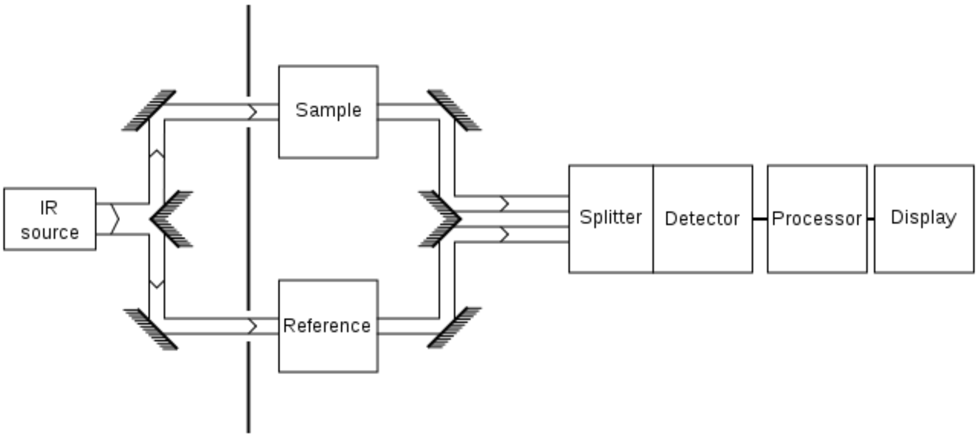


Figure 5. Operations Schematic of Dispersive Spectrometer [20], [19]. Notice the splitter and the division from the reference (control) and the sample.

3.4.1 The dispersive IR Spectrometer:

Just as with the CO_2 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 CO_2 sample were heated to the same temperature as the reference cell temperature, no CO_2 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'.

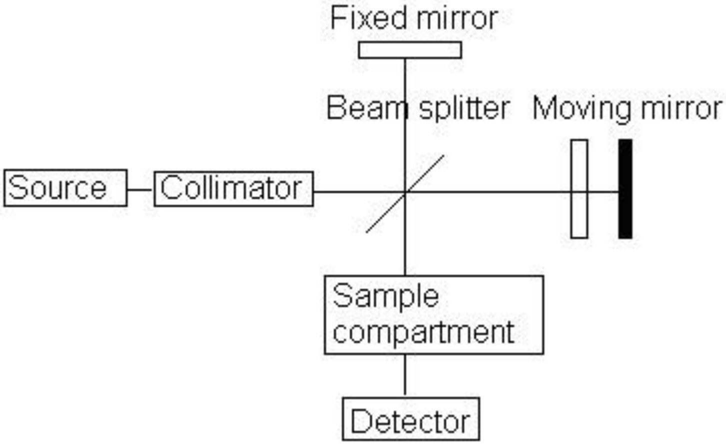


Figure 6. Operations Schematic of Fourier Transform IR (FTIR) spectrometer [20].

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; 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.

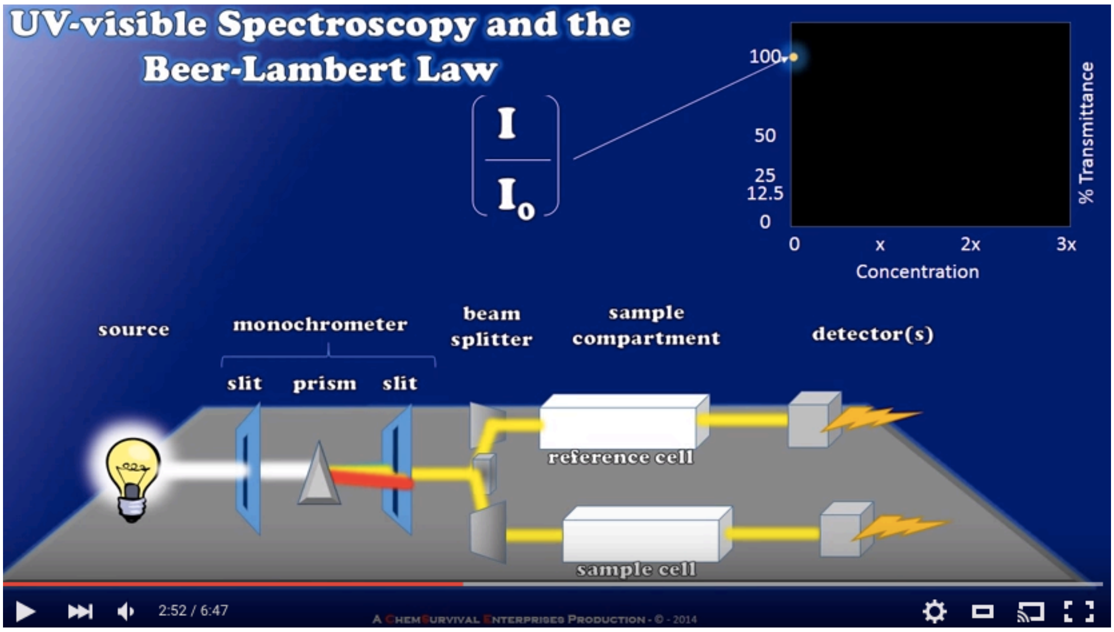


Figure 7. UV Spectrometer. Showing the heat source, the two cells, the reference and the sample. **[22]**

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

$$T = I / I_o$$

where **I** is said to be the **light intensity** after it passes through the sample, and **I_o** is the **initial light intensity**. Again, this interpretation ignores the role of thermoelectric transducers – producing an EMF – and the measured thermoelectric properties of the substances.

3.4.4 All 'IR Spectrometer' 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 – that they, too, are IR detectors. All show the same results and do not detect non-thermoelectric vibration modes of N_2, O_2, CO_2, CH_4, etc. They also do not fully detect solid Germanium or CL_2.

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): H_20’s **3652 cm^{-1}** (2.74μm), **1595 cm^{-1}** (6.25μm), and **3756 cm^{-1}** (2.66μm); CO_2 ‘s **2349 cm^{-1}** (4.257μm), and **667 cm^{-1}** (14.992μm); CH_4’s **3020cm^{-1}** (3.312μm), **1508cm^{-1}** (6.5μm), and O_3’s 1103 **cm^{-1}**, 701 **cm^{-1}**, and 1042 **cm^{-1}.**

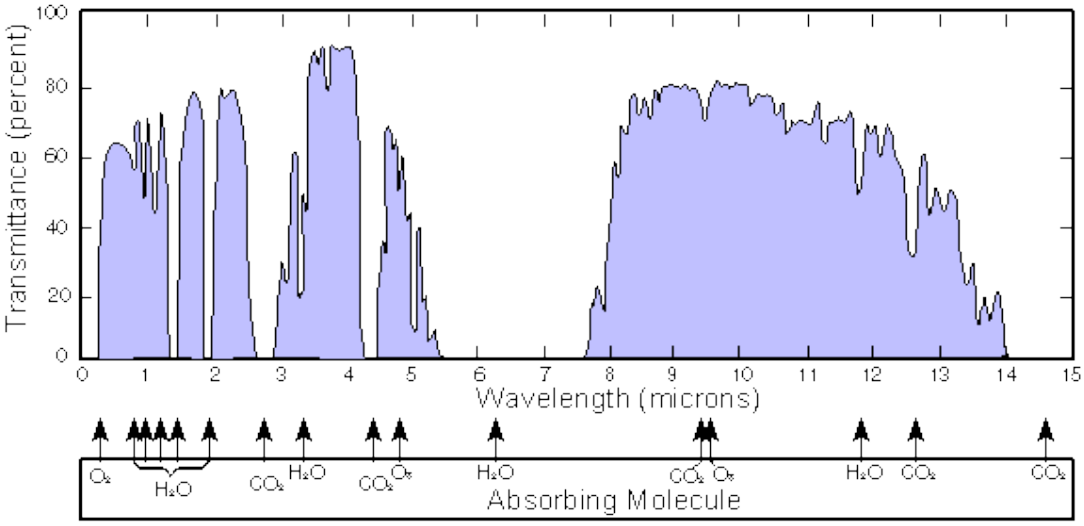


Figure 8. Infrared Spectrograph of the atmosphere [27]. This spectrogram does not take into account Raman modes and thermoelectric principles. See 4.4.4 for a correct interpretation of this spectrograph.

3.5.1 Analysis of the CO_2 Thermoelectric Emission Absorption Spectra

Below is an IR spectrograph for CO_2: it clearly shows CO_2’s absorption bands that are shared electric dipole moments – at **2349cm^{-1}** and **667cm^{-1}**; however, what it does not show, is CO_2’s 3rd symmetric (non-electric dipole moment) band at **1388cm^{-1}** – thought there is a small hint of it in the figure at that wavenumber.

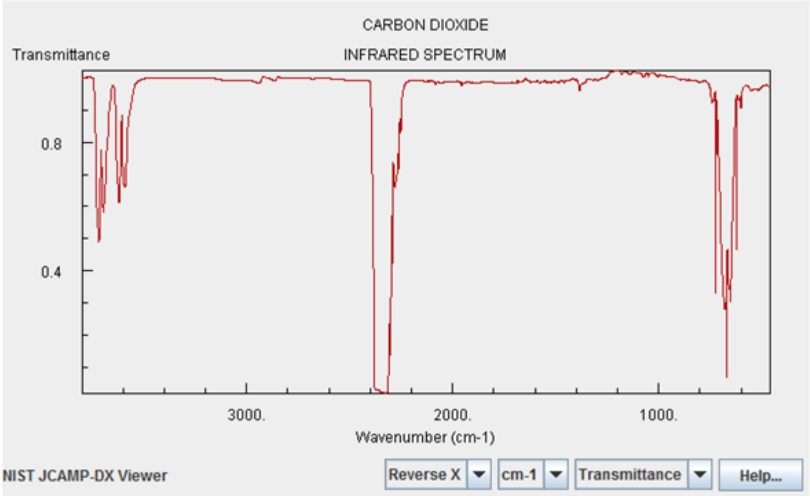
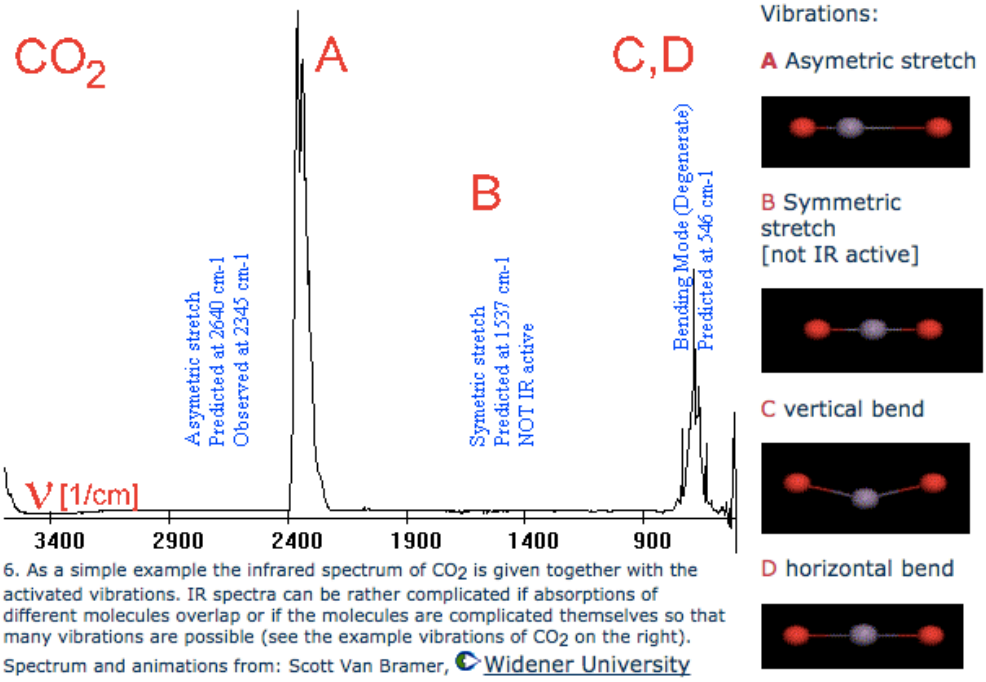


Figure 9. CO_2 transmission spectra. [28] Here the differential between the reference 1500°C heat source and the ambient temperature CO_2 gas is clearly shown. Predicted absorption bands are shown, however, this indication would decrease if the temperature of the CO_2 were equal to the reference heat source.

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 CO_2 is shown. Note the absence of the symmetric vibration modes (B) in the spectrograph and only the presence 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 CO_2 were heated to the same temperature as the reference heat source temperature (some 1500°C), no CO_2 would be detected.



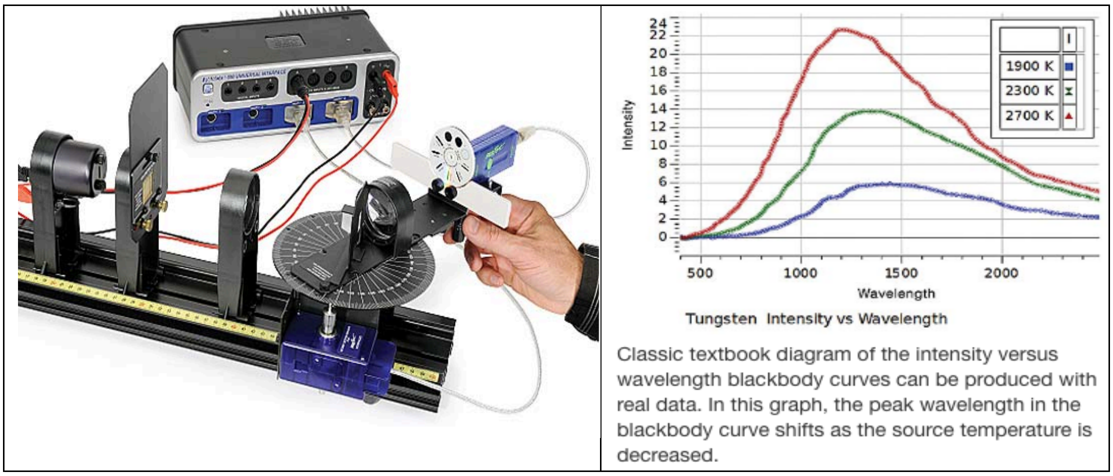
6. As a simple example the infrared spectrum of CO_2 is given together with the activated vibrations. IR spectra can be rather complicated if absorptions of different molecules overlap or if the molecules are complicated themselves so that many vibrations are possible (see the example vibrations of CO_2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

Spectrum and animations from: Scott Van Bramer, Widener University

Figure 10. CO_2 Thermoelectric IR Spectra. A 'negative' image of the above image (Figure 32) shows CO_2's IR active electric dipole vibrational modes and one non-IR active. [51] 1538 cm^{-1} is clearly shown as absent; it is 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 from the Seebeck effect and the thermopile, 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 atmosphere's blackbody spectrums – pyranometers[30] and pyrometers –also use the thermopile transducer to create the curve.



Classic textbook diagram of the intensity versus wavelength blackbody curves can be produced with real data. In this graph, the peak wavelength in the blackbody curve shifts as the source temperature is decreased.

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 atmosphere and radiation theory, in general, have never been undertaken before. While usually it would be simple to conclude an experiment, this is not so in this case. While the conclusion is simple, the facts surrounding the question are difficult and complex, and as a result of this, it has been 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 first to 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 are the special 'Tyndall' GHGs? By first principles review, I will show that they are thermoelectric gases – they generate EMF (electricity) by the Seebeck effect-driven thermoelectric transducers. My findings have implications for all radiation theories, 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—modern general university and school science textbooks have the topic thermoelectrics in them—it was from physics online that 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 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 electric gases. The radiating electric transducer receiver does not receive those modes that do not have electric dipole moments 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 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, which 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 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 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. Whatever the thermoelectric detector method, they share the same properties or problems as the IR cameras, IR thermometers, and CO_2 sensors 4.5: they do not measure all matter; they discriminate on what is not thermoelectric, not 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 in 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,– 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 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. I assume IR spectrometers radiate samples, and I claim the spectrographs show the thermoelectric dipole moments or emission spectra of the said (atmospheric) gases within the EMS. They are the 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 the band of the electromagnetic spectrum in which they are radiated—microwave, UV, and so on—and 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 that 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 detect – the thermoelectric spectra of atoms and molecules and substances in general. They are at the centre of the field of '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 as '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 that the spectrograph is produced by the difference in temperature between the transduced—measured in thermal EMF voltage—of the sample and a reference source's IR (1500⁰C) radiation. This is the same in principle as demonstrated in section 4.4.

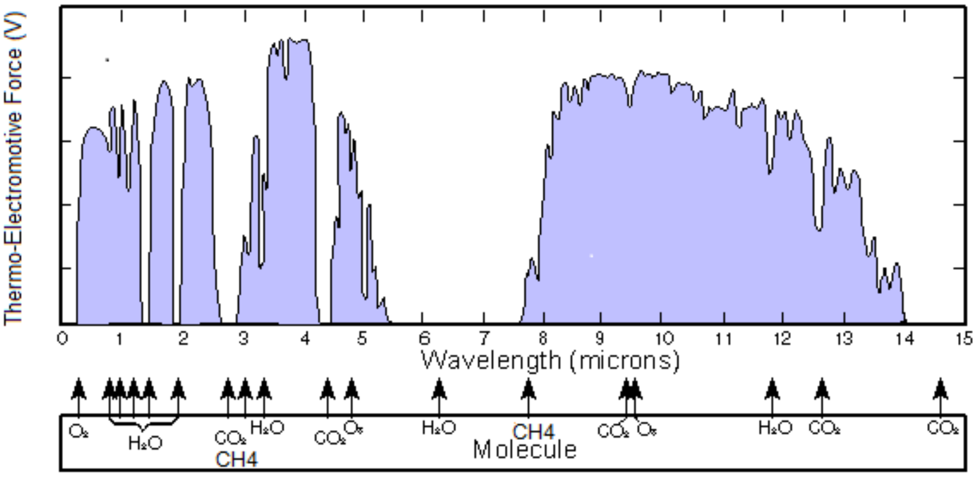


Figure 12. Thermo-electromotive Force and the Electromagnetic Spectrum. Thermoelectric vibration modes identified by thermoelectric transducers are currently known as the greenhouse atmosphere. The non-electric (dipole) Raman modes cannot be detected. The black line traces the thermo-EMF (electricity 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 a cooler temperature.

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 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 that this investigation should not undo the merits of IR spectroscopy; 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 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 generating electricity from special substances? Does glass (specially) absorb IR radiation, or is it thermoelectric, unlike the 'air'? 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 the indicated temperature will be. Will the IR thermometer measure the temperature of my hand – through the glass – or will it measure the temperature of the glass? Most answers, when asked, are measured by the hand. This is wrong. It is the glass that is measured.

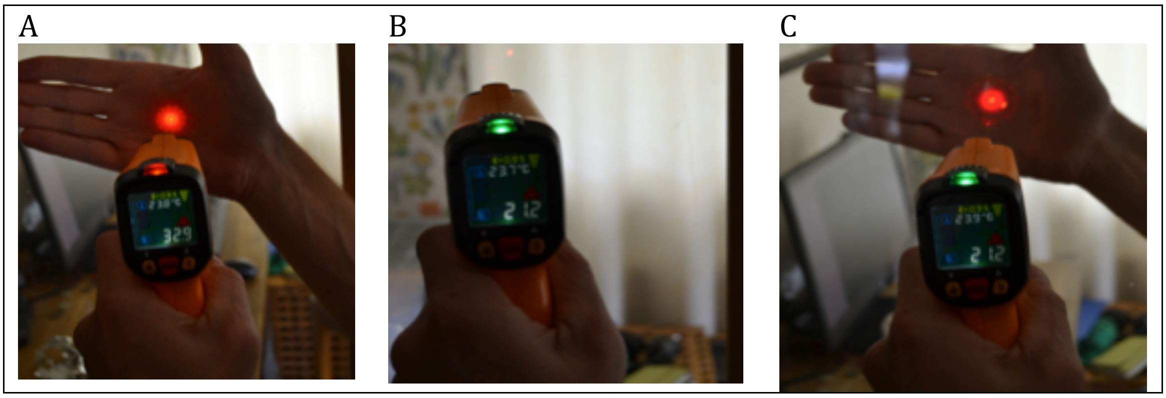


Figure 13. Non-contact thermoelectric thermometer 'transparent' glass demonstration. Frame A, the hand temperature was measured directly as 32.9°C and the ambient temperature 23.8 (red light indicates wrong emissivity match); frame B, the temperature of glass was measured as 21.2 °C (green light indicates correct emissivity match); and Frame C, hand temperature through glass measures at 21.2 °C (the temperature of the glass). Notice that the 'air' temperature is not measured with the instrument but with 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. The instrument does not detect my (indicated) 32.9°C hand 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 a beam of IR photons radiated it – 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.

Glass is a thermoelectric substance, as explained in the section above.

Another question can be posited from this demonstration – which will help us 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? The ambient air* (temperature) between my hand and the detector. (* assumes= 100% N_2 and O_2 mix)

While 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 a regular thermometer may measure the room temperature, 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 GH (or IR) gas bath – say CO_2? 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 CO_2, and not my hand – just in the same way it measured the glass in frame C. If we can describe and understand CO_2 as being thermoelectric we should equally be able to describe and understand glass as '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 sauce temperature (my hand in the above) and the temperature of the sample (the glass). What if I were to touch the glass with my hand and bring the temperature of the glass to thermal equilibrium, equal to the temperature of my hand? The glass would not be detected. It would be as if only my hand were being measured. The implications of this insight become very important in the following sections, which describe how the thermopile is used to detect and 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 are ubiquitous and can be found in hardware such as handheld, non-contact IR thermometers, early thermal imaging cameras, and early IR spectrometers. These new technologies all have the same problems in Tyndall's discovery in that they register or discriminate the same properties of the substances measured. We shall now look at each of these instruments and identify the 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, used to derive the GHGs. So, it offers an easy-to-use and relatively cheap device (20 U.S. dollars, 2018) for learning and understanding special GHGs. The IR thermometer measures IR radiation from 8 to 14 microns on the electromagnetic spectrum (EMS), in 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 CO_2 Sensors

Regular CO_2 concentration sensors use a thermopile transducer – exploiting the Seebeck effect (though this is not how they are explained in most references [33],[34], [35], [13]). The operation is generally 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 CO_2 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 CO_2 will transduce EMF more than the hot heat source, and, in effect, it looks like it blocks out the heat source by 100%. Because the air (N_2 and O_2) do not generate an EMF at any temperature, if the CO_2 was heated to the same temperature as the reference's heat sauce, no CO_2 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 originally used 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 their being the same is that all detectors measure the same substances – as Tyndall – in the same way; they equally cannot measure the likes of N_2 and O_2. For this reason, I will call them 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 and vibrational modes, as to why some substances are assumed to be IR while others are not. 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. Tyndall's experiment revealed only **the gases** that generate electricity via the thermopile, not the other phases of matter. He would have found similar patterns if he had equally tested the solids and liquids for the same property. One only has to take a look at

Table 2 shows 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 a GH solid with this visible transparent glass. All three are similar in that they are transparent to the visible and also said to be opaque to the IR. Of course, as deduced by this investigation, the reality is water and glass, and the GHGs are thermoelectric and no more special than other matter, even if they are not claimed to be. Thermoelectric glass is why Tyndall did not use glass to contain the gases in his experiment; instead, he used (presumably non-thermoelectric) salt crystal. This 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, 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-GHGs'; 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. Instead, the lenses (Figure 14 below) are made of one of the few solid non-IR substances, 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 the heat source [41].

Solid Germanium presents the same paradox, in principle, just as the non-GHG air does: to the thermoelectric IR detectors, the temperature is not measurable – no EMF is produced. To expand on this paradox, the following thought experiment may be helpful. What if the Germanium was hot? One could heat 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? Unlike the traditional thermometer, it would indicate the temperature outside the sauna: it would 'see' right through the walls (apart, of course, from 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 ±300K° atmosphere; it only detects the objects that are thermoelectric.

4.6.5 Ge Germanium Raman Spectra

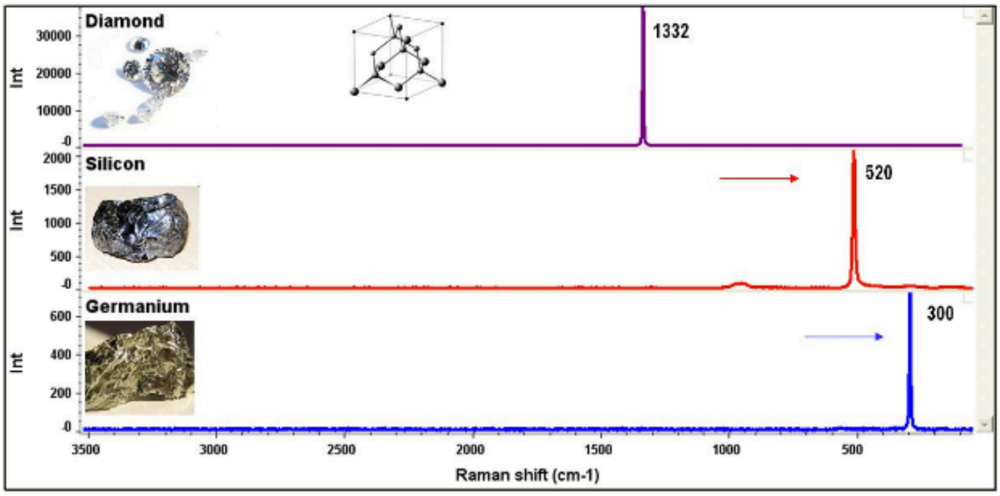


Figure 1: Raman spectra of diamond, crystalline silicon, and crystalline germanium

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]. Raman identified the spectra only and are well within the IR range of the EMS.

4.6.6 Germanium and Emissivity and Spectrographs

As it turns out, Germanium does not show well on thermoelectric spectrographs, and it does not have an emissivity similar to N_2 and O_2. 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 thermoelectric technology's role 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. I claim what John Tyndall discovered – using the thermopile transducer – are not the ‘special’ set of heat-trapping gases but rather only the thermoelectric gases of the atmosphere (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 tiny 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 a ‘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 reconstructing the original 1859 Tyndall experiment only with modern materials and technology (as shown in Figure 16 below). The thermal imaging camera (frame B) stands for the single thermopile, and thin plastic (frame a) at either end of the 'glass' tubes stands for the rock salt to contain the gases.

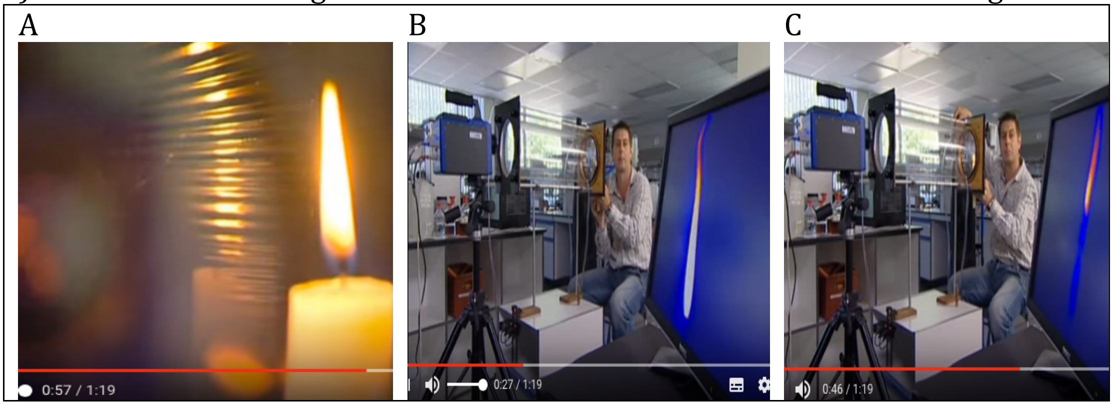


Figure 16. Dr Stewart's YouTube clip. [45], [46] Demonstrating the greenhouse effect. Frame A shows the gas contained behind thin plastic, B. thermal image of a flame through 'air', and C. CO_2 'blocking' the flame out. Notice a light-blue image in the lower flame remains in C; this may be attributed to the temperature differential between the gas and the candle. If the CO_2 were colder, it may disappear; 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). As the heavier-than-air CO_2 is released into the sealed cylinder, the bright candle image from the camera disappears – from the bottom up – and is replaced by the blue colour screen (frame C). Dr Stewart concludes (incorrectly) – just as John Tyndall did: *"The CO2 absorbs the infrared or is essentially trapping the heat from the candle."*

If this claim is valid, 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 different conclusion would be drawn, and Dr Stewart's conclusion wrong.

4.7.3 Thermoelectric Interpretation of the Stewart Demonstration

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

Again, if the CO_2 were heated to the same temperature as the reference candle temperature, no CO_2 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 CO_2. 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 CO_2 were heated to the same temperature as the reference hand temperature, no CO_2 would be detected – just as with 4.4 above.

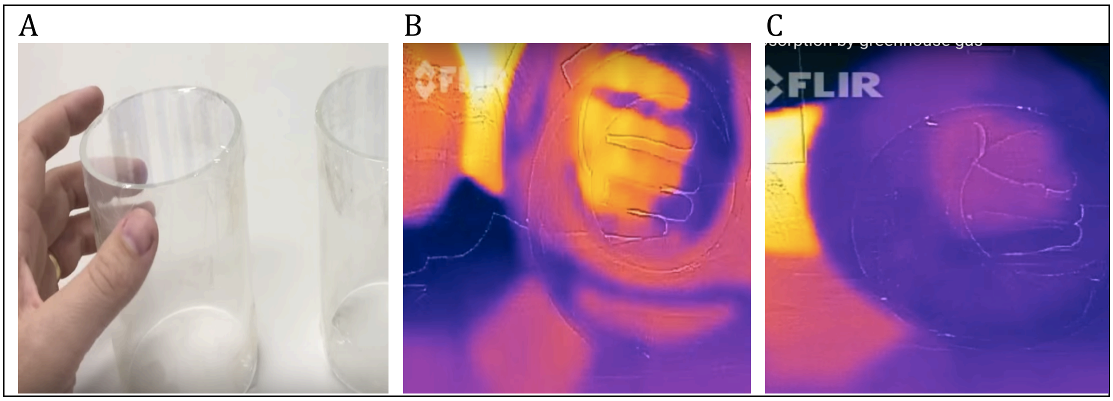


Figure 17. Thermal Imaging camera Greenhouse gas demonstration. (A), two glasses, one filled with air (mostly N2 and O2) and the other with a GHG, presumably CO2; (B) the first glass is non-thermoelectric, wrongly said to be 'transparent to IR'; and C, the GHG is thermoelectric, wrongly said to be opaque 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 is 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 is that he did not use glass. Secondly, the air appears not to have a temperature, but the 'air' does have (must have) a temperature; otherwise, 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 is 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 usually 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.

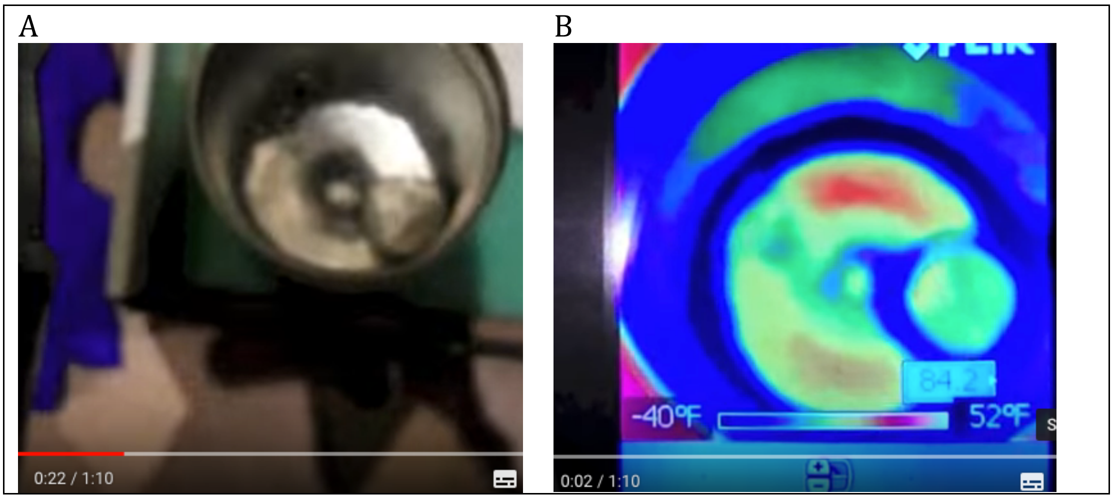


Figure 18. Thermal imaging camera liquid oxygen demonstration. [48] Frame A is visible, showing a magnet in a cup of (90K) liquid oxygen, and in frame B, a thermoelectric infrared image, again showing the magnet, and importantly, not the liquid oxygen. Only its temperature would be displayed if the liquid were water or something else.

If it were any other liquid in the Dura, except for 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? These demonstrations conclude that 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.

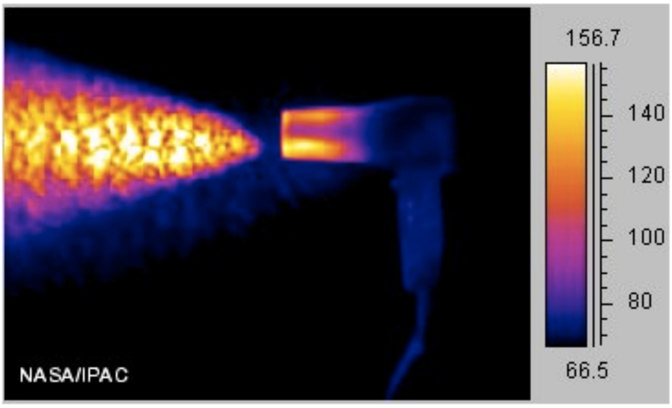
4.8 Thermoelectric Paradoxes and Anomalies

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 offers insight into this thermal discrimination that leads to the 'IR catastrophe'. From the thermal image (Figure 19), it can be made out that the hair dryer is operating as its body is at a moderate (blue) temperature and its outlet is at 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 dyer blowing hot air 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. It must be by radiation; if true, where has the physics gone wrong? Why is this hot air not explained by radiation with the dryer and – similarly – with the standard atmosphere model? See section 4.8.2 for an explanation of this paradox.

4.8.2 The Hairdryer Paradox Explained

With a first principles knowledge of thermoelectrics, an explanation can be found for this discrepancy, leading us to the same hypothesis presented in this paper. The thermal 'outlet blast' image blown onto a surface implies this surface is thermoelectric, and the air is not. If there were no surface 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) fed only with CO_2 and (2) if the dryer were submerged in a 'bath' of only CO_2? Reasoning by thermoelectrics, for the former (1), it would show a plume of 'bright-hot' outflow; and for the latter (2), no discernible image would be observed as it will be the incident temperature CO_2 measured by the thermoelectric detector.

4.8.3 White Body Cavity /Air Experiment

To further emphasise this flaw with thermoelectric detectors as the hair dryer paradox attempts, suppose the following experiment. In the tradition of 'blackbody radiation', fill a cavity made of shiny gold (an assumed perfect white body IR 'reflector') with N_2 and O_2 ('air') and radiate IR photons (heat) from a centrally positioned electric element. This should pose a paradox as all these ingredients do not absorb IR, leaving us with the question, what would happen to the temperature of the gases and the gold? As shiny gold has one of 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 experts describe it. If so, then the question is: are they 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. I question 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 clarify 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 is that they are.

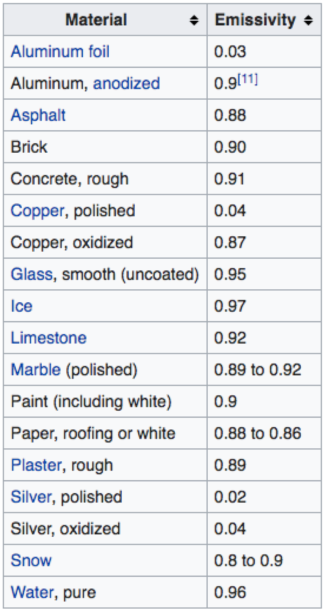
It is interesting that fish – for the most part – cannot detect IR or use it directly: this makes sense as water is a thermoelectric substance, so all the EMF is generated from the incident molecules.

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

Emissivity – *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 in* physics: there is no other concept in physics that gets the 'hands waving' quite like this one. Fundamentally, it should be about the ability of 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 at all but rather the ability or inability of the thermoelectric transducer (the thermopile) to transduce.

As shown below, Table 3 emissivity ranges from 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 thermopiles have misconceived emissivity may lie with the property that 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 they intuitively should. But as I have shown, they do not when 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 in 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.

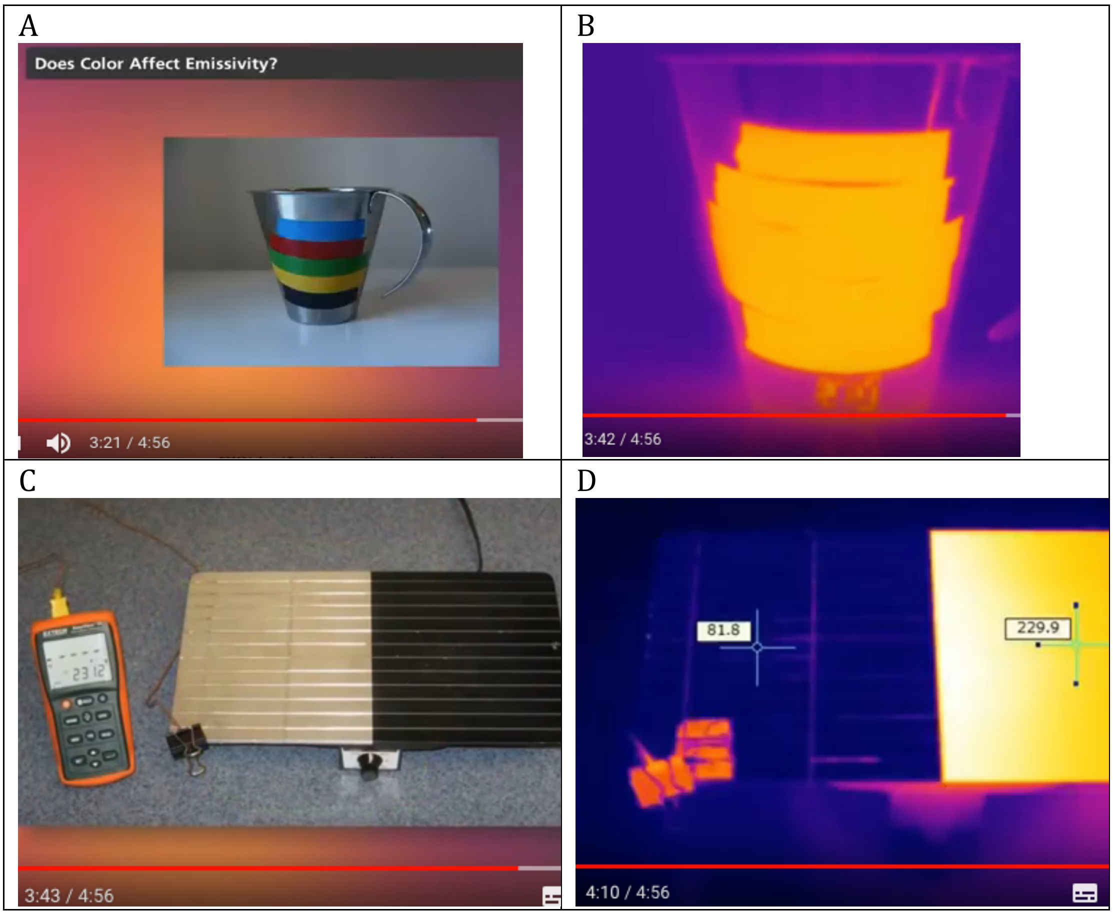


Figure 20. Demonstrating Paradoxes Associated with Thermoelectrics. [51] A and B show colour, unlike albedo, does not determine the emissivity of a substance. C and D show that the surface type determines the emissivity. All of these inconsistencies are claimed to be properties of all radiation; however,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

C and D offer further insight into the emissivity problems associated with different surfaces. Again, the object – the plate – is in the thermal equilibrium, both black and shiny sides, as indicated by a temperature of 231.2 degrees F. The shiny side is said to have a low emissivity, and the dark black is a high. This demonstration is close to reality, where shiny metals reflect more than 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 very low emissivity, near 0, suggests no radiation rather than just low. The dark side is closer to an accurate reading of reality.

I contend all this demonstrates 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 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 that 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 radiation is called emissivity.

Figure 21 shows the disparity between the calculated blackbody emissivity and EMF-derived curves. A thermopile derives the real radiation body and traces the EMF production at each wavelength.

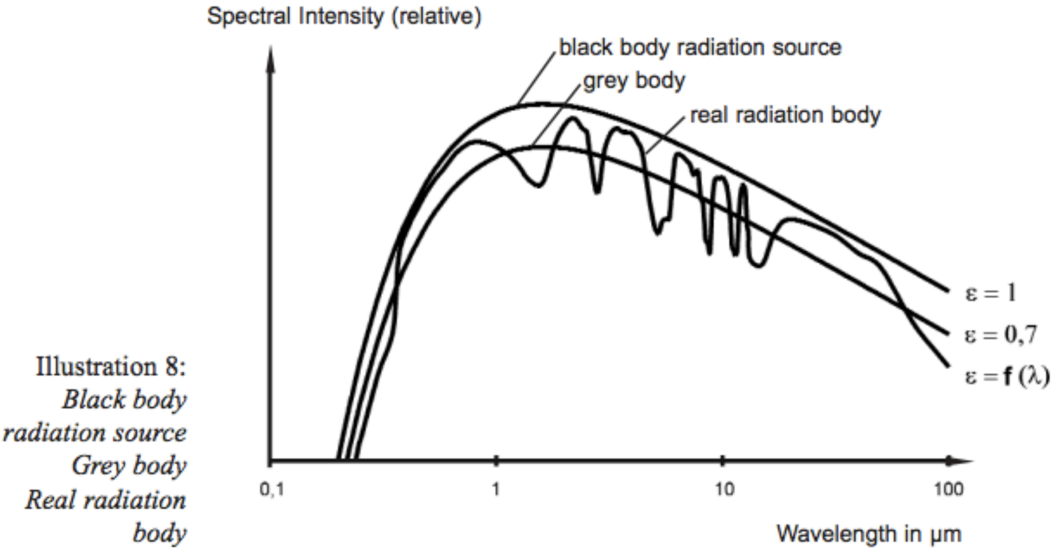


Figure 21. Black body and Real Radiation (emf) curve.

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

$$E = \sigma T^4 \qquad (1)$$

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:

$$E = \varepsilon\sigma T^4 \qquad (2)$$

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 extraordinarily overlooked pieces of bad 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, not the substance measured. It is a correction factor. The following diagram, Figure 22, [52]shows how emissivity is measured. It reveals it is only a correction factor between the temperature of an object, measured by a thermocouple, and the emf-temperature produced from the thermopile. From a thermoelectric perspective, emissivity has little to nothing to do with a substance's IR (heat) emission properties – an iterated throughout this paper.

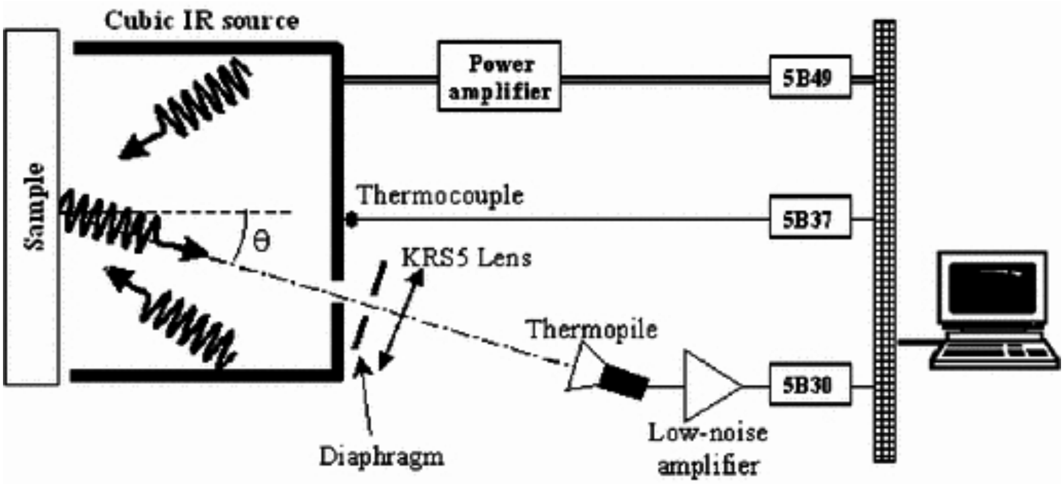


Figure 22 Measurement of Emissivity. The emissivity is measured by the thermocouple for it real temperature and by the thermopile (for its heat radiation).

This study has led me to conclude ***that emissivity is no more than a correction factor between an object's real temperature 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 be one of the saddest mistakes in the history of physics.

4.9.5 Why N_2 O_2 and Germanium have no Emissivity

A final word on emissivity: what does this mean for N_2 and O_2, the gases in question? N_2, O_2 and Germanium have no nominal emissivity to speak of. By understanding emissivity, their respective emissivity must be 0 as they, as it is assumed, do not emit or absorb IR radiation; the same goes for Germanium. However, studies by Raman Laser Spectroscopy show that they 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 by 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' is not. Knowledge of thermoelectrics reveals the air does not produce an emf from the radiation compared to 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 H_2O cloud. The signal is converted to electricity, and this output is calibrated to the real temperature of the cloud. The device gives an approximate value only. The blue-sky 'air' is of such a high concentration of N_2 and O_2 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 surrounding '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 pyrometers, the instrument used to produce the atmosphere's blackbody spectrum. The following is an examination of thermopiles' role in deriving 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 from 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) that no matter is a perfect blackbody. Only snow and water, paradoxically considering their albedo, come the closest to ideal 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 is lower than the Sun, so some of the solar heat radiation leaks through. See the section: *'Thermoelectric Thermopile 'Hand-Glass' Demonstration'* for a full demonstration and explanation of the claims.

4.11.2 Blackbody Curve, Thermoelectrics and the Birth of Quantum Mechanics

Concerning the role of thermopiles and thermoelectrics 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 has been found elsewhere since then. As for the CMB, it has shown the universe is a perfect blackbody, and there is no emissivity discrepancy there. Beyond the scope of this investigation, the author is inspired to do further research.

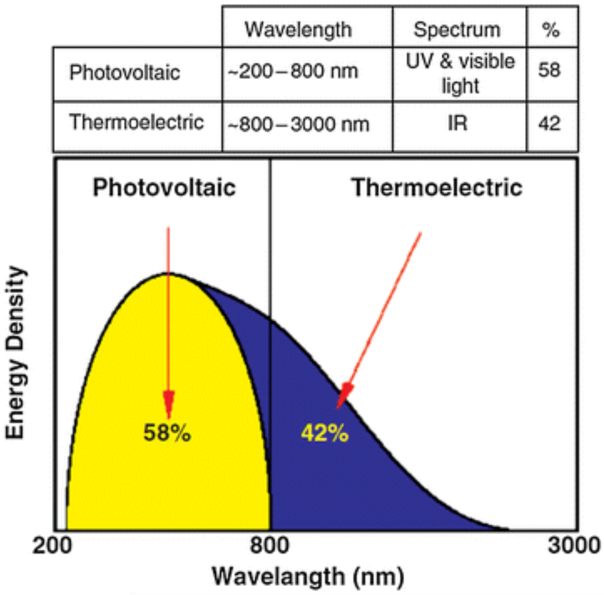
4.12 Revealing the 'IR Blackbody Spectrum Curve' Misconception through Thermo-electric Generators (TEGs)

While writing this paper, I wondered if it would be possible to use thermoelectric transducers to produce green energy from carbon dioxide. It turns out this dream is almost true; 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; the Seebeck effect produces them.

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 essential when understanding the blackbody emission spectra, where I claim it is nothing else but the production of EMF (electricity) at every frequency – from the TEG transducer. This would be evidence of thermoelectric transducers' proper role and properties, which are 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, shows a curve almost identical in shape to the emission spectra.



	Wavelength	Spectrum	%
Photovoltaic	~200–800 nm	UV & visible light	58
Thermoelectric	~800–3000 nm	IR	42

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. Figure 26 shows the real smoking gun; it shows evidence that 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 of 500nm, identical in shape and form to the said. The TEG is inefficient at wavelengths above 1100nm because the transducer does not generate EMF. This is coherent with the blackbody curve.

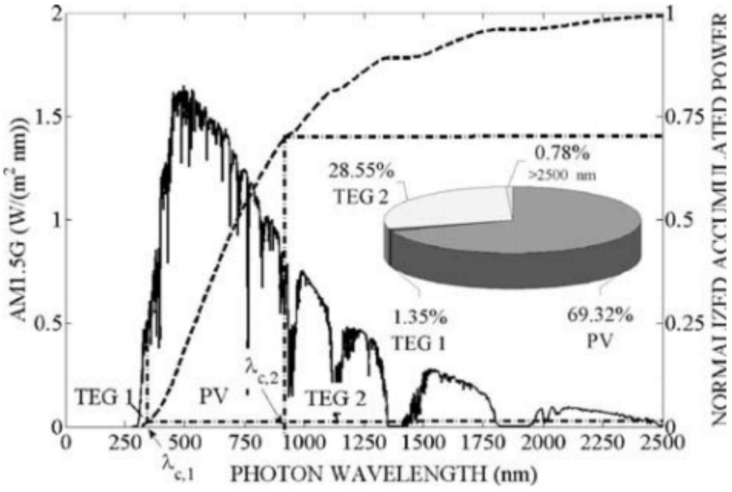


FIG. 1. Segmentation of AM1.5G spectrum in three regions for a mc-Si:H solar cell and solar TEG with 4% efficiency. Normalized accumulated radiation power. Pie chart: converted power fraction of each module.

Figure 25. Photovoltaic and TEGs and IR-generated AM1.5G solar irradiance spectrum[57]. This diagram shows 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 that the curve is a property of the Sun's irradiance and not the transducer. I would argue that this doesn't seem right, and it is a false dichotomy to claim this, as this blackbody emission spectra shape is not unique to the Sun but is generally known to all radiation, known as the blackbody spectrum. The scientists working with solar TEGs are only thinking about the output of their invention. They are oblivious, I think, to the connection between the blackbody emission spectra and their results. This is clear from the following figure, Figure 26.

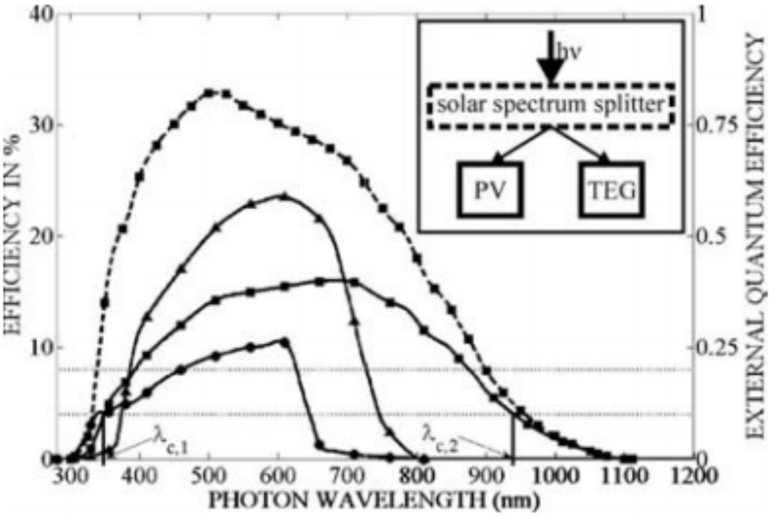


FIG. 2. Schematic diagram of the PV-TE hybrid system. EQE (dashed line) and spectral conversion efficiency (solid lines) of a-Si:H (▲), mc-Si:H (■), and polymer (●), assumed solar TEG efficiency of 4% and 8% (dotted lines).

Figure 26. PV and TEG Efficiency by Wavelength [57]. The TEG's efficiency (input over output) 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 –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 that the emission spectra are electric, as demonstrated by the solar TEGs.

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

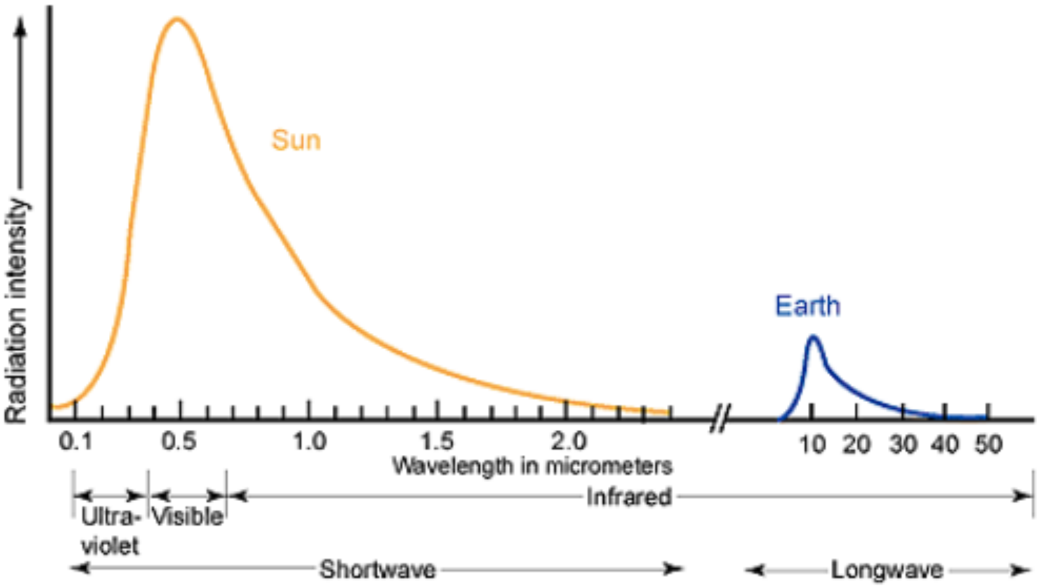


Figure 27. Thermoelectric ('Blackbody') Curves' for the Sun and Earth[58]. The thermopile produces a curve dependent on intensity, the Sun being more than the Earth. This has been misconceived as the only representation of thermal radiation.

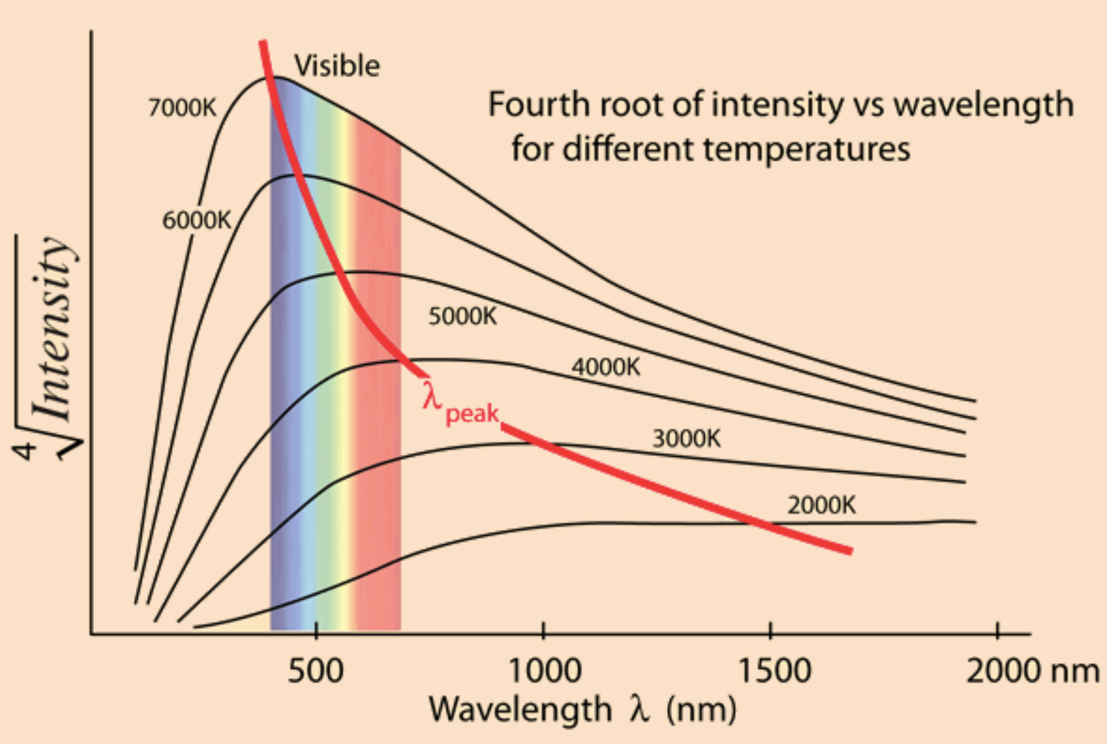


Figure 28. Demonstrating Wein's Law [59], As the temperature of an object falls, the blackbody curve maximum of 'peak' shifts to the right. This study's result is a property of the thermopile and not radiation.

While this bell-shaped curve is not disputed, the interpretation of it as the sole IR radiation curve is. The assumption gained from it that the Earth absorbs only shortwave IR radiation and emits only longwave radiation is also disputed here. Given that the thermopile transducer produces the curve, 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, N_2 and 0_2 are on the far right flank of the solar emission spectra (Figure 1) and are well off to the left of the Earth's surface spectra (Figure 29); and so have been interpreted as being from 'very poor', to 'non-emitters'. Raman spectrometer 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. Its fundamental assumption may need review in the 'light' of modern quantum mechanics and specifically laser-based Raman spectroscopy. 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, both Raman Laser and IR thermoelectric spectrometers observe quantum-predicted spectra.

4.13.1 Solar Blackbody IR Spectra and the Addition of CO_2

Figure 29 below shows (clockwise) the effect of increasing the concentration of CO_2 gas to a (thermopile-deduced) solar blackbody spectrum. The greater the concentration, the greater the absorption of CO_2 in the 667 cm^{-1} spectral band. The thermoelectric explanation for this increasing drop or decline in the spectra line is the temperature of the CO_2 added is at a lower temperature than that of the background Sun reference, and the cool CO_2 added generates a less EMF than the hot solar background at this band. The higher the concentration, the greater the offsetting EMF production, but not enough to out-produce the solar reference heat source, just like the candle shows in Figure 29-C.

Again, if the CO_2 were heated to the same temperature as the solar reference temperature or something near it, no CO_2 would be detected – just as with 4.4.1 above.

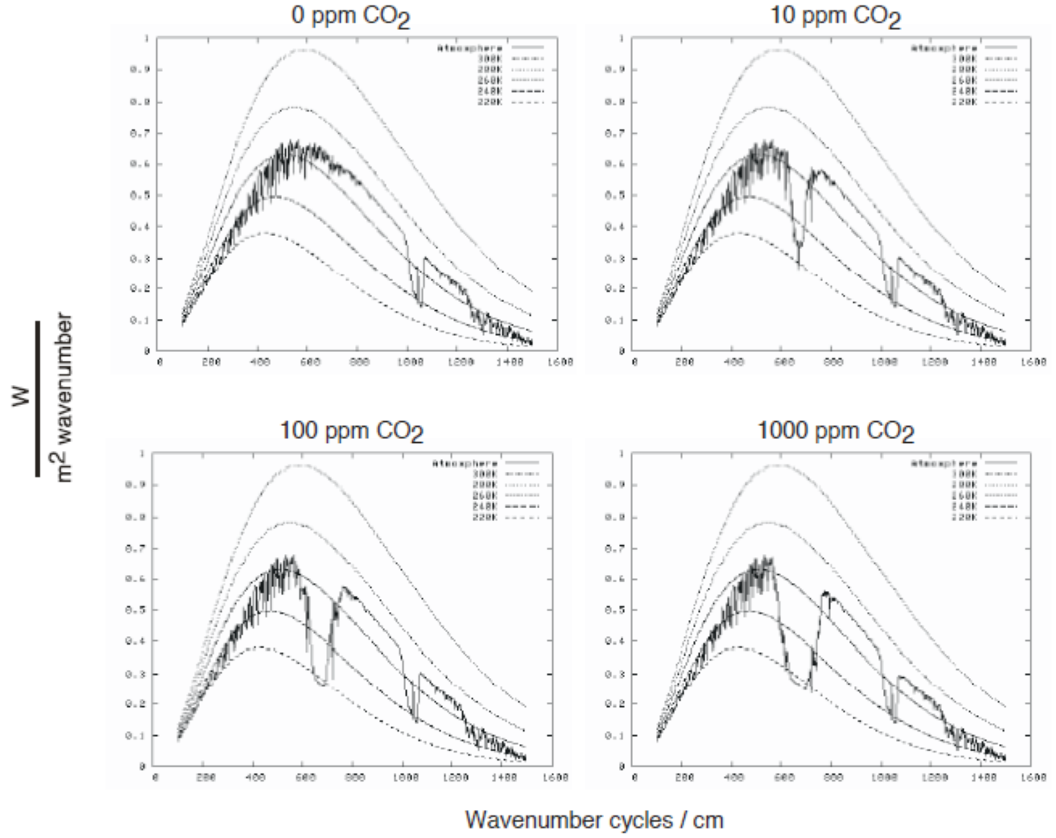


Figure 29. Thermoelectric Spectra of CO_2 at 667cm^{-1}. Increased CO_2 concentration – from 0 ppm to 1000 ppm – produces thermal EMF, revealing CO_2's 667 IR band.

Note that the CO_2 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 a high concentration of CO_2, 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 a 'background spectra' is produced where all other measurements are compared?

4.13.2 Solar Blackbody IR Spectra 'Hanging CO_2 Paradox' at different Temperatures

The author remains puzzled by a paradox: How do the following spectrographs change with temperature, while the CO_2 667cm^{-1} does not? Why do spectra hang when the curve falls around them 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 of the thermopile. If we point a thermopile at the sky, there is no temperature reading; if we point down to the ground, a fair but not perfect temperature is measured. This would explain the dropout between the CO_2 modes in (b).

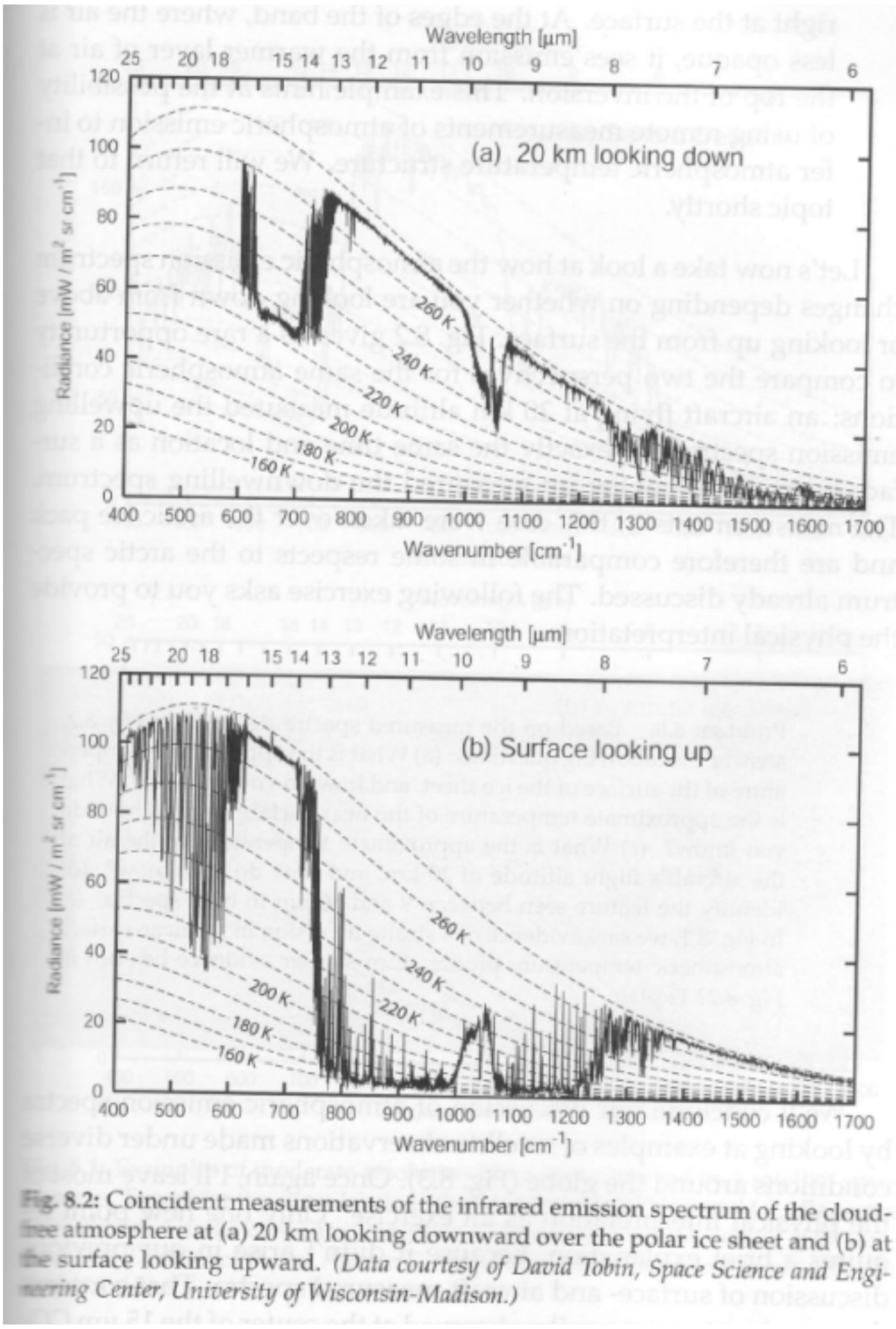


Fig. 8.2: Coincident measurements of the infrared emission spectrum of the cloud-free atmosphere at (a) 20 km looking downward over the polar ice sheet and (b) at the surface looking upward. *(Data courtesy of David Tobin, Space Science and Engineering Center, University of Wisconsin-Madison.)*

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

Explaining Figure 31's dramatic changes in the blackbody curve shape at different locations on Earth, we must understand that while thermopile-derived IR spectrographs show the emission spectra of CO_2 and other molecules, they also respond to temperature. At lower temperatures, the emf from the thermoelectric detector will be low, so the indicated curve around these spectra is correspondingly low. It should follow that at low temperatures, the CO_2 667 cm^{-1} also drops, as it does from extremes of (a) to (b).

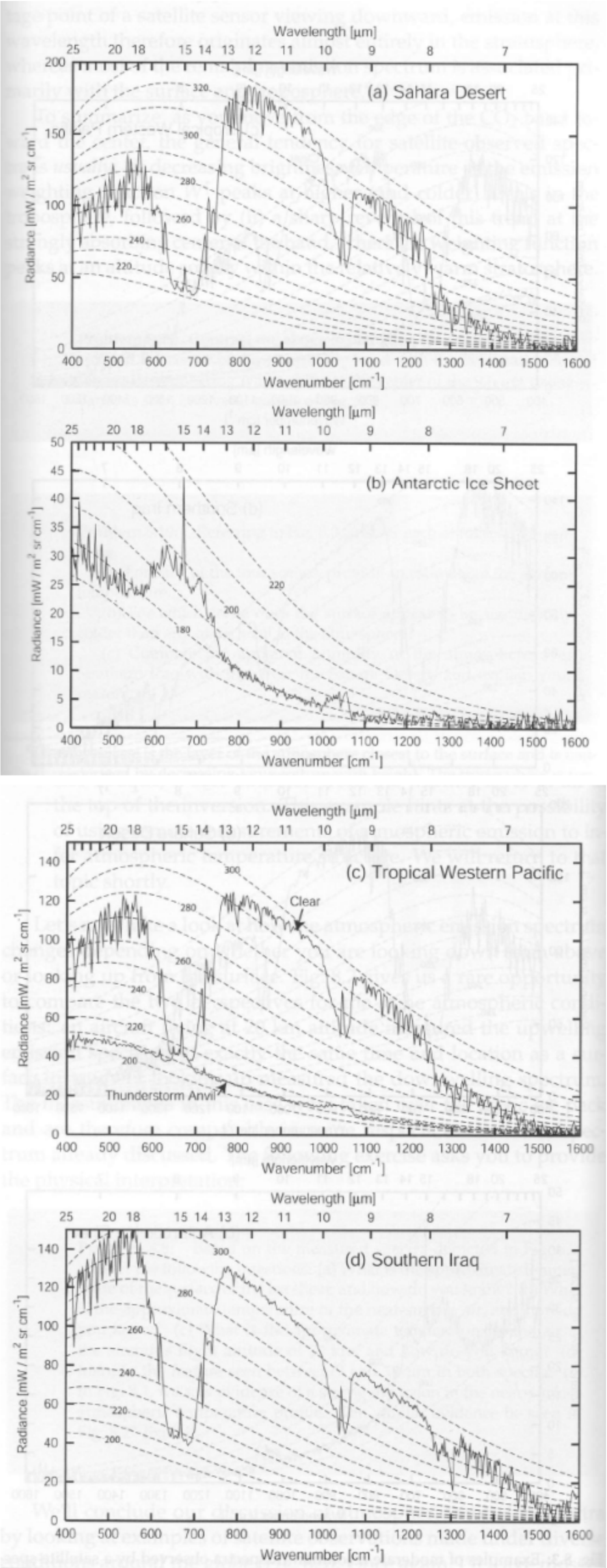


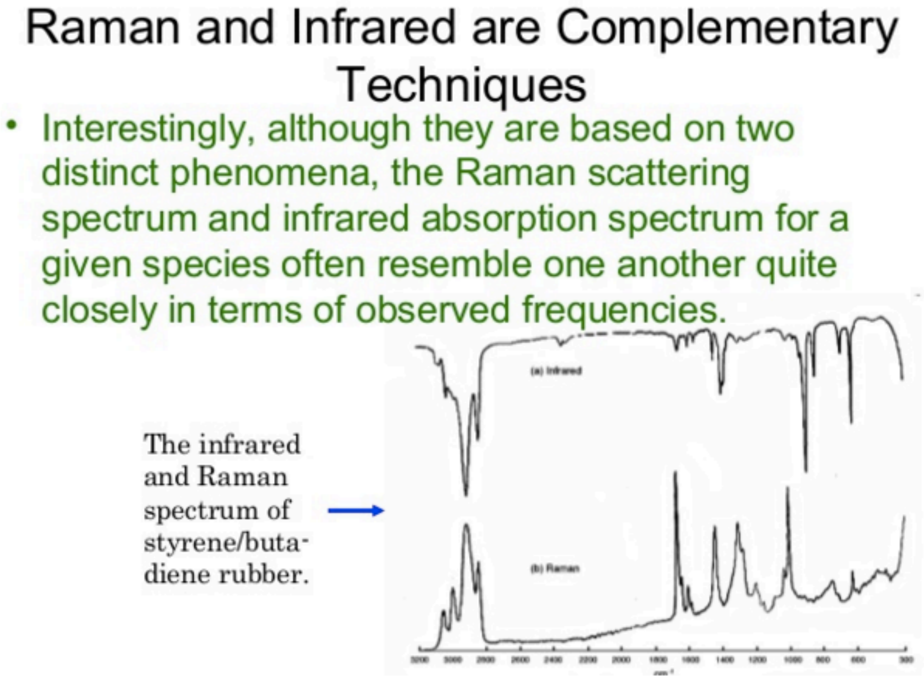
Fig. 8.3: Examples of moderate resolution IR spectra observed by a satellite spectrometer. Except for the curve labeled "thunderstorm anvil" in panel (c), all spectra were obtained under cloud-free conditions. *(Nimbus-4 IRIS data courtesy of the Goddard EOS Distributed Active Archive Center (DAAC) and 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 Raman spectrometers' role in identifying the 'Raman-active' spectra IR thermoelectric instruments cannot. The paper is called Quantum Mechanics and Raman Spectroscopy Refute Greenhouse Theory[4].

Chemists well understand that Raman spectroscopy complements 'IR' spectroscopy; it completes the IR picture. No one has brought them together regarding the infrared atmosphere. This complementarity is revealed clearly below in Figures 32, 33, and, where both Raman and thermoelectrics even identify some spectra modes.



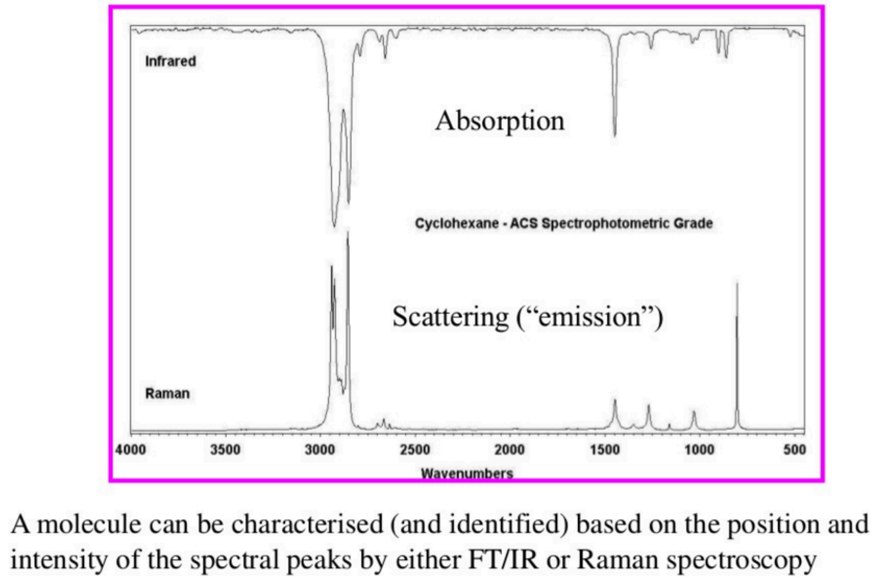
Raman and Infrared are Complementary Techniques

- 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]

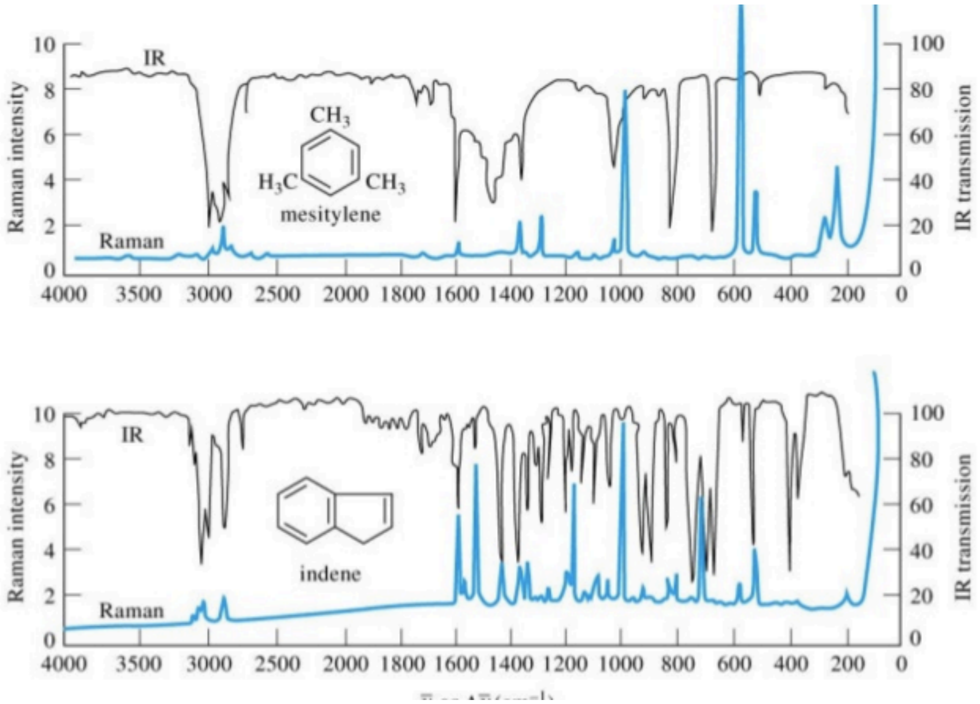


Figure 34 Demonstrating Dual Raman and IR Thermoelectric Modes of Mesitylene and Indene.

4.14.1 Ethanol

The following is an interesting (Raman image) reference: Ethanol has both shared Raman and thermoelectric modes. Figure 35 clearly shows the matching spectra measurement measurements from both Raman and thermoelectric. Finally, to an informed chemist, CO$_2$ is both Raman and IR-thermoelectric.

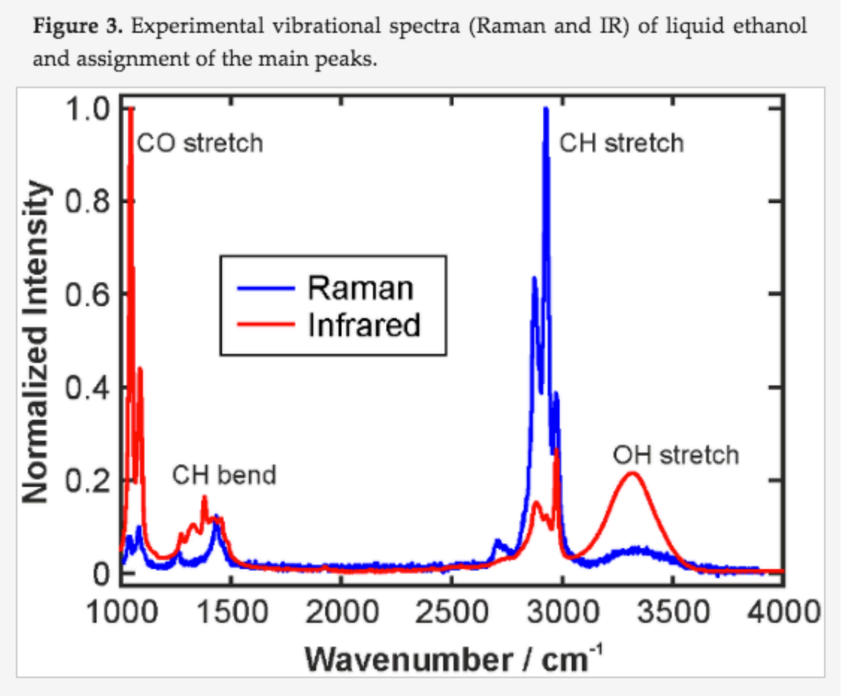
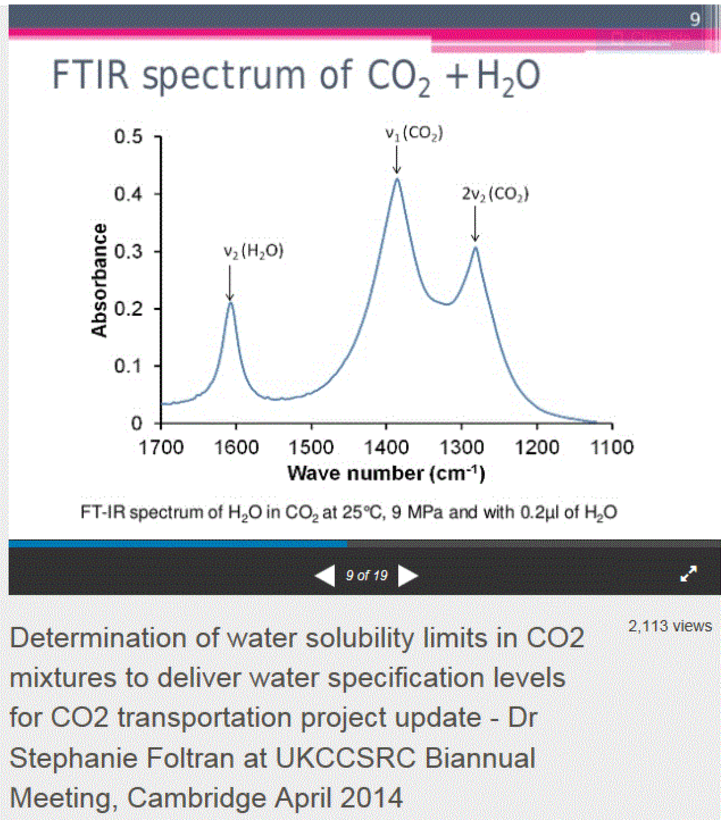


Figure 3. Experimental vibrational spectra (Raman and IR) of liquid ethanol and assignment of the main peaks.

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

4.14.2 CO$_2$'s 1338 Raman Active mode showing on IR spectra.

Figure 36, 37[64], and 38 [65] clearly show CO$_2$'s 1338cm^{-1} Raman Active spectra mode on IR (thermoelectric) spectrograms. This strengthens the case that the mode is equivalent.



FTIR spectrum of $CO_2 + H_2O$

FT-IR spectrum of H_2O in CO_2 at 25°C, 9 MPa and with 0.2µl of H_2O

Determination of water solubility limits in CO2 mixtures to deliver water specification levels for CO2 transportation project update - Dr Stephanie Foltran at UKCCSRC Biannual Meeting, Cambridge April 2014

Figure 36. CO_2's 1338cm-1 Raman Mode showing on IR (thermoelectric)

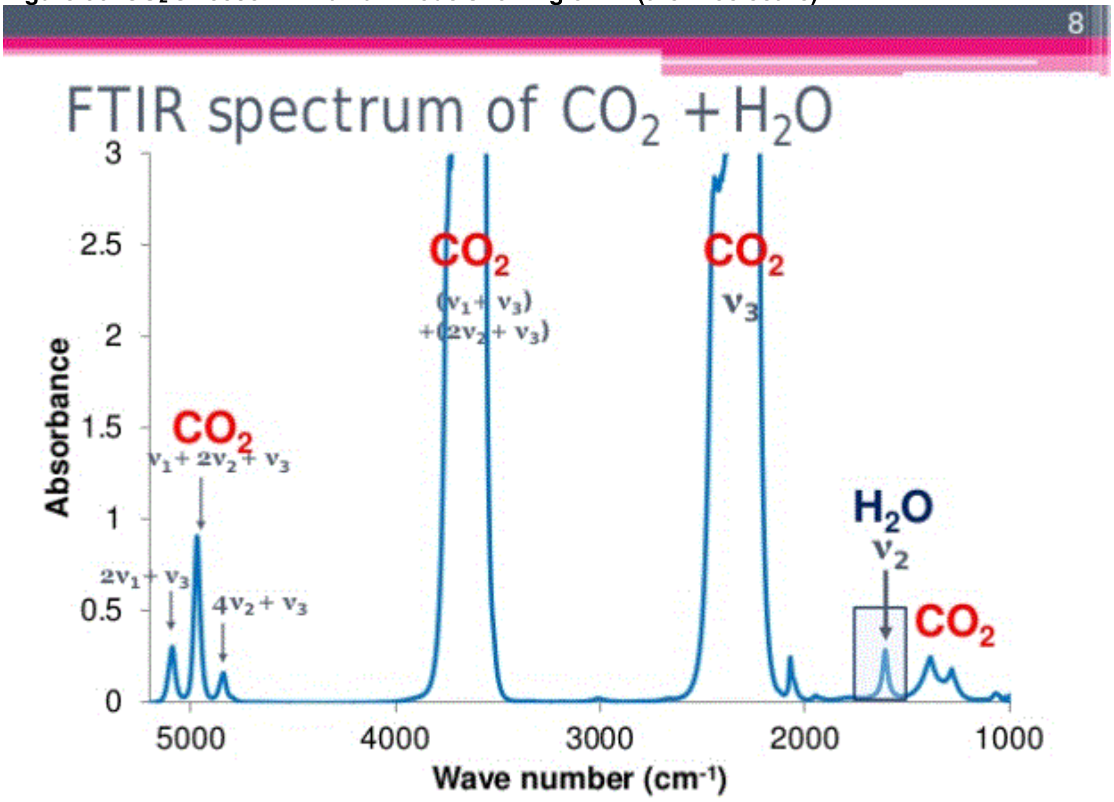
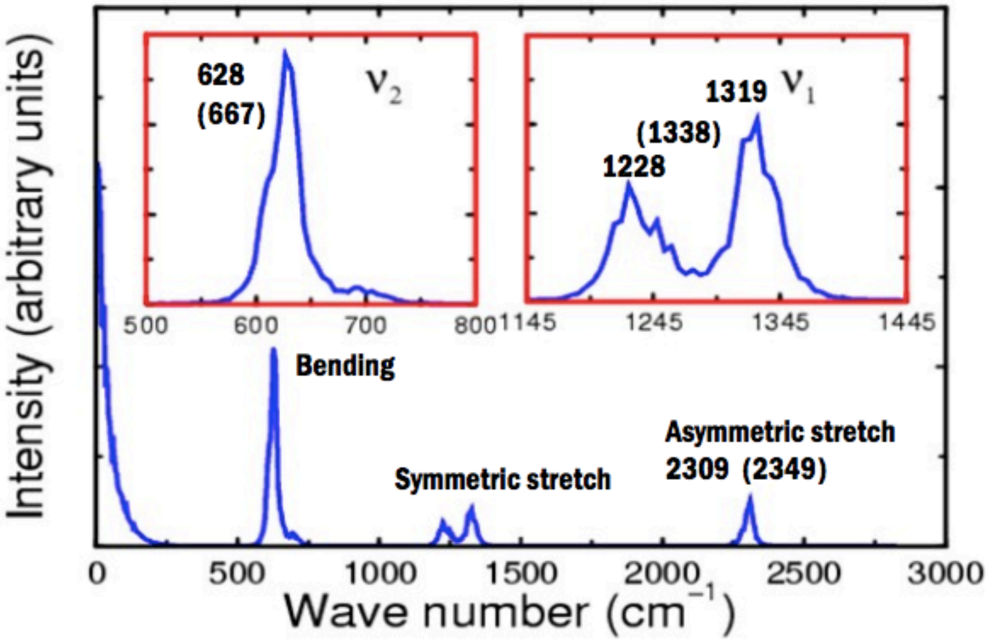


Figure 37. CO_2's 1338cm-1 Raman Mode showing on IR (thermoelectric).



Numbers in brackets are for 'ISOLATED' CO_2. Splitting in symmetric stretch is due to 'FERMI RESONANCE'

Figure 38. CO_2's Raman Active Mode on IR Thermoelectric Spectrogram.

4.14.3 H_2O (and N_2O): Spectra of 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}, 3652 $^{cm-1}$, and 3790 cm^{-1}.

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

The Raman observation of H_2O's 3652 cm^{-1} vibrational mode is significant as it is both IR- 'IR active' (as shown in Figure 39 and Figure 40 below) and Raman active, a 'dual' Raman-IR mode. This mode is an absolute demonstration, observation, and practical application via the Principle of Equipartition, and these modes are equivalent.

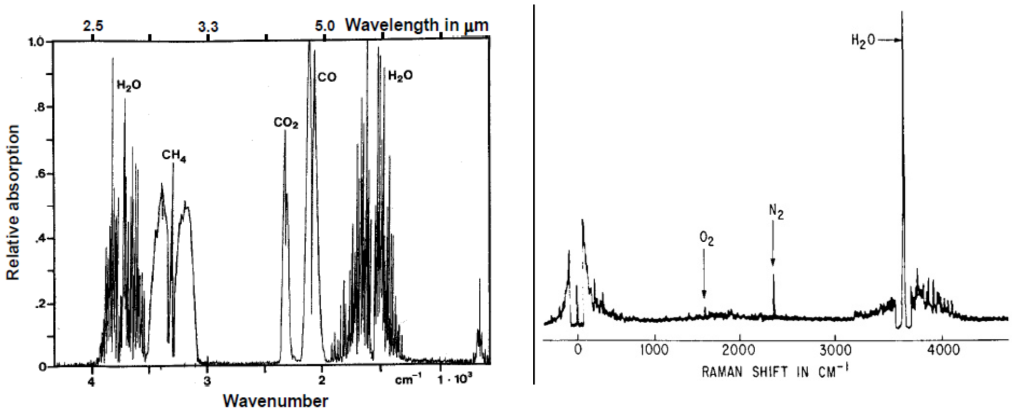


Figure 39. H_2O Thermoelectric (IR) and Raman Spectra. Left 'IR' and Right Raman, showing H_2O's 3562cm-1 mode and others.

This also shows that 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 for the outcome of this investigation and radiation physics as a whole—water has a dual means of absorption and emission.

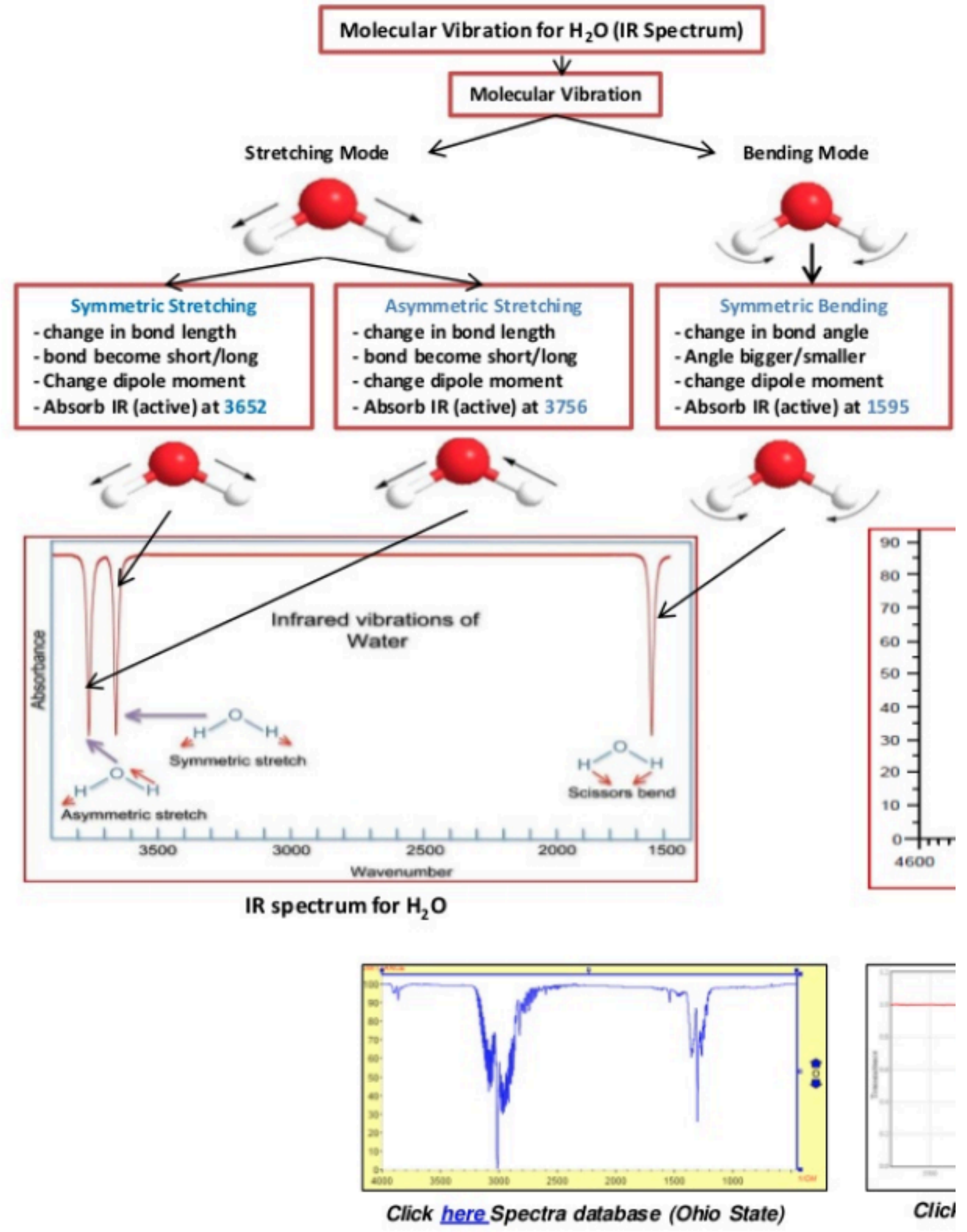


Figure 40. H_2O IR (thermoelectric) Vibration Modes and Respective Spectrum. Notice the 3652cm^{-1} is clearly shown to be IR. [66]

4.14.5 Contravention of the Rule of Mutual Exclusion

The above H2O 3652 cm-1 mode appears to be a contravention of the rule of mutual exclusion, where "*no normal modes can be both Infrared and Raman active in a molecule that possesses a centre of symmetry*". However, H_2O is a special exception, as described below.

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

Band H_2O	**Infrared**	**Raman**
ν1 - symmetric stretching (3652cm^{-1})	strong	strong
ν2 - asymmetric stretching (3755cm^{-1})	very strong	weak

ν3 - bending (1595cm^{-1})	very strong	weak

(Source, online lecture notes).

Does this also mean H_2O 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.

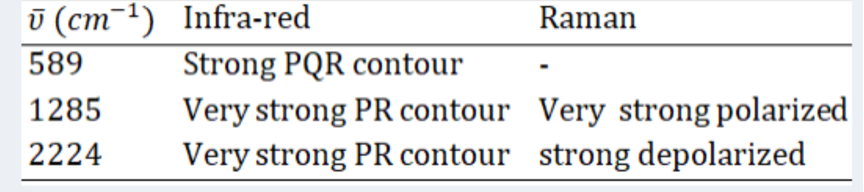
4.14.5.1 Solar IR Insolation Radiation Heats Water

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 that 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? As claimed here, the answer is that the air is absorbed by its Raman and IR modes.

4.14.6 N_2O's Shared IR and Raman Modes

Just as with H_2O, N_2O is another strong so-called GHG. It also shares Raman active modes, 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. N_2O IR Raman Equivalence.

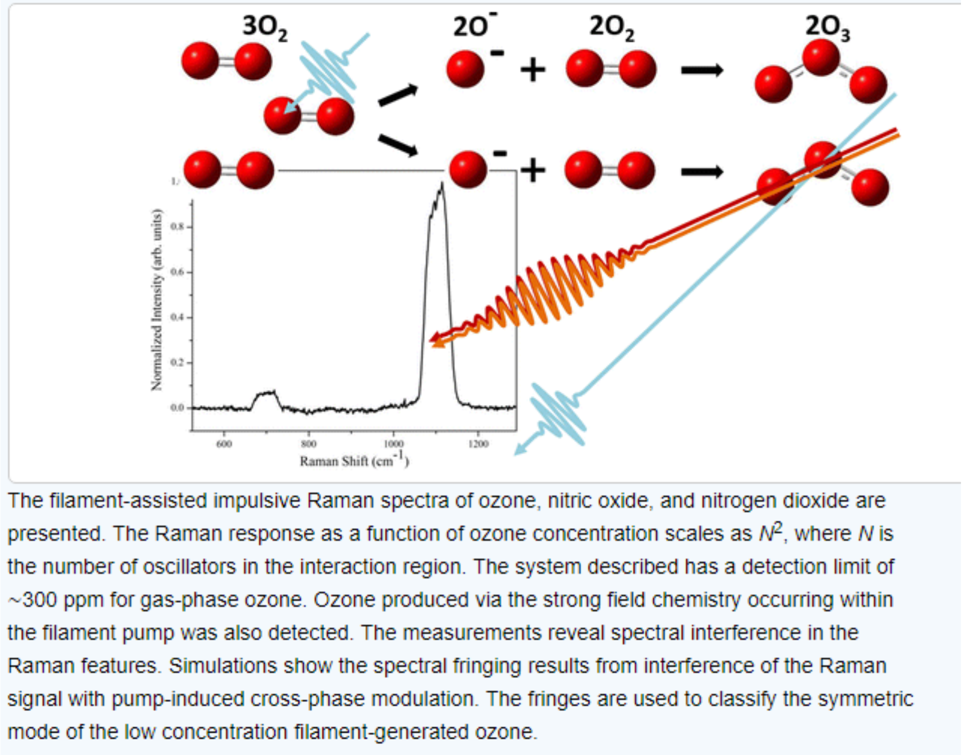


$\bar{\upsilon}\ (cm^{-1})$	Infra-red	Raman
589	Strong PQR contour	-
1285	Very strong PR contour	Very strong polarized
2224	Very strong PR contour	strong depolarized

4.14.7 Ozone O_3 IR and – inferred by – Raman

Ozone is a greenhouse gas; it has IR spectra, and these spectra are observed. Its Spectra band at around 1000cm-1 is observed in the general atmosphere emission spectra Figure 1. It shares the same position as CO_2's 960cm^{-1}. This CO_2 spectra position is the same as outputted by the CO_2 laser.

Ozone can also be detected by Raman spectroscopy or at least inferred by Raman Spectroscopy. The following is 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 O_3 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 with the title *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 combine and augment the IR-Raman modes with the IR modes. Raman spectroscopy spectra, as identified and used in the Raman Exhaust Report, show these abundant molecules' predicted N_2 and O_2 vibrational modes. These 'Raman' modes and the EMS's IR modes 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.

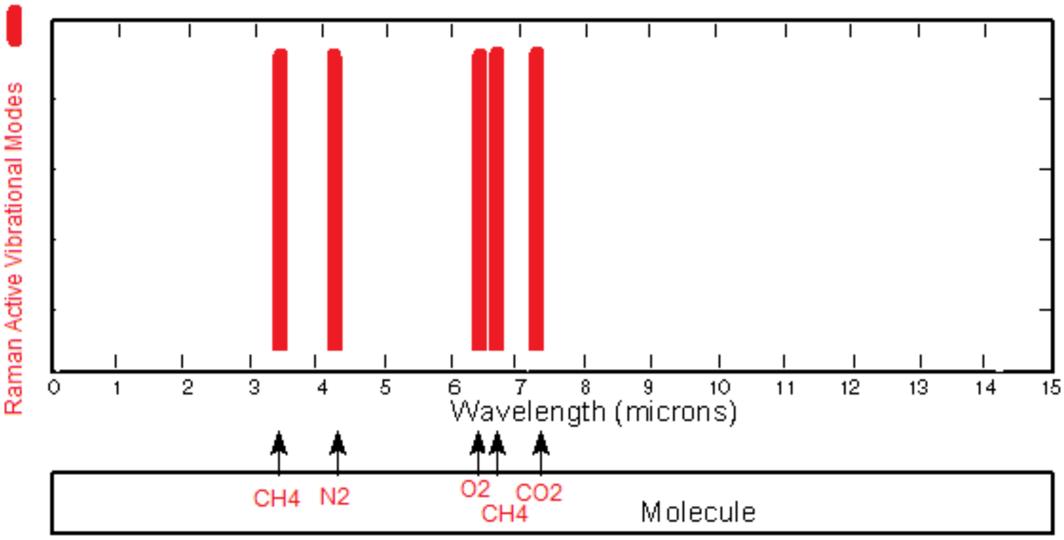


Figure 42. Raman Vibrational Modes of the Atmosphere. Predicted and Raman measured vibrational modes of (some) atmospheric gases CH4, CO2, N2 and O2.

4.15.1 The Augmented Fourier Greenhouse Atmosphere Spectrum

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

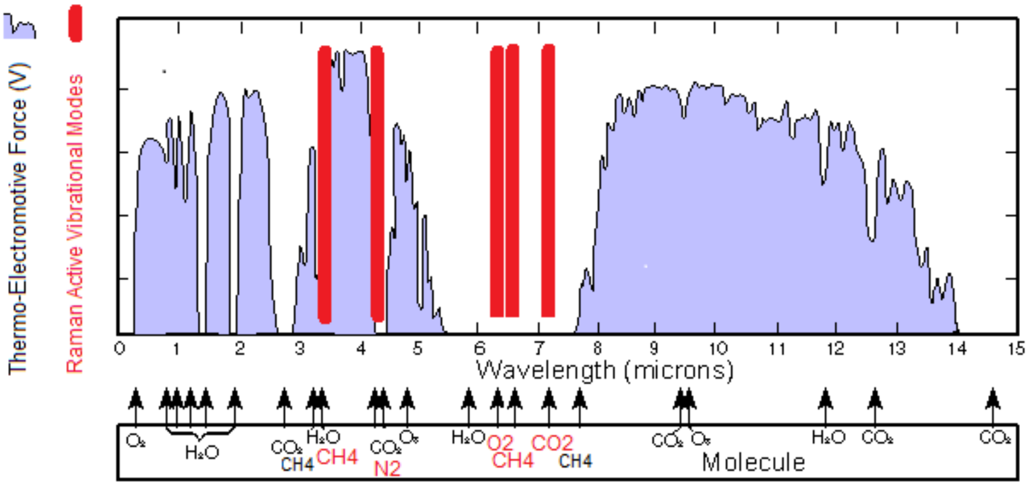


Figure 43. The Augmented Greenhouse Atmosphere. Combining Thermoelectric and Raman spectra will reveal the complement of atmospheric vibrational modes and the greenhouse atmosphere of planet Earth.

4.15.2 Addressing Raman Spectra between Solar and Earth's Blackbody Curves

Continuing with the above, Figure 44 shows all the (necessary) 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*).

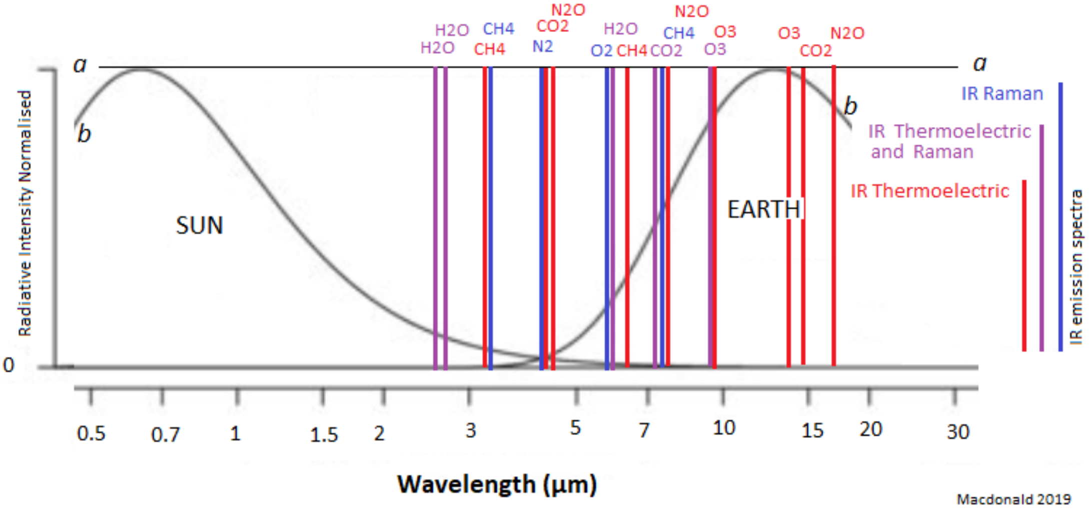


Figure 44. Quantum Predicted IR Spectra with Sun and 'Earth Blackbody' Curves. The spectrogram shows the positions and type of the predicted IR emission spectra of gas molecules within the EMS, matching the normalised—thermoelectric derived 'Blackbody' curves (b—b)—Planck intensity curve' (a—*a*).

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) are refuted. As a result of the augmentation of Raman-active modes with thermoelectric modes, they can exist outside the blackbody domains. This is in total contradiction to the current GH theory.

As the Raman-active spectra behave as IR radiators by quantum mechanics, they all can 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-called 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 CO_2's 2349 cm-1 mode with a temperature of around 1500K. From this, it can be assumed that 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 numbering of my original publication's figure and contents.

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 the ‘background spectrum’ and the ‘raw sample spectrum’.

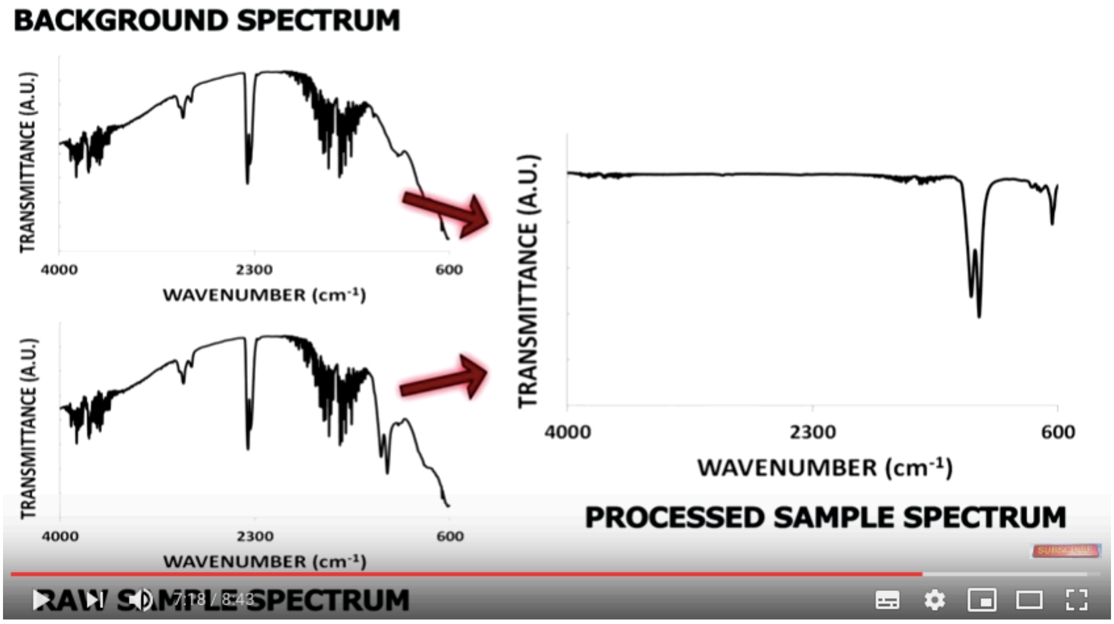


Figure 45. IR Spectrograms Showing Blackbody Curve and CO$_2$. [73]

Three important points for this study should be noted: the bell-shaped curves on the left peaking around 2300 cm-1, the position of the CO$_2$ at 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, as shown in Figure 44.

4.16.2 1960s Spectroscopy Film Showing all CO$_2$’s Spectra are Equivalent

In support of the above claim, an introduction film from 1962, Molecular Spectroscopy from the University of California [74], describes and demonstrates the three vibrational modes of the CO$_2$ molecule. In it, they demonstrate the 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 CO$_2$ without any separation or discrimination of them are all identified (C): at 7.05 x 10^{13} (corresponding to the 1338 cm^{-1} mode), 4.16 x 10^{13} (corresponding to the Raman Active 2349 cm^{-1} mode) and 2 x 10^{13} (corresponding to the 667cm^{-1}).

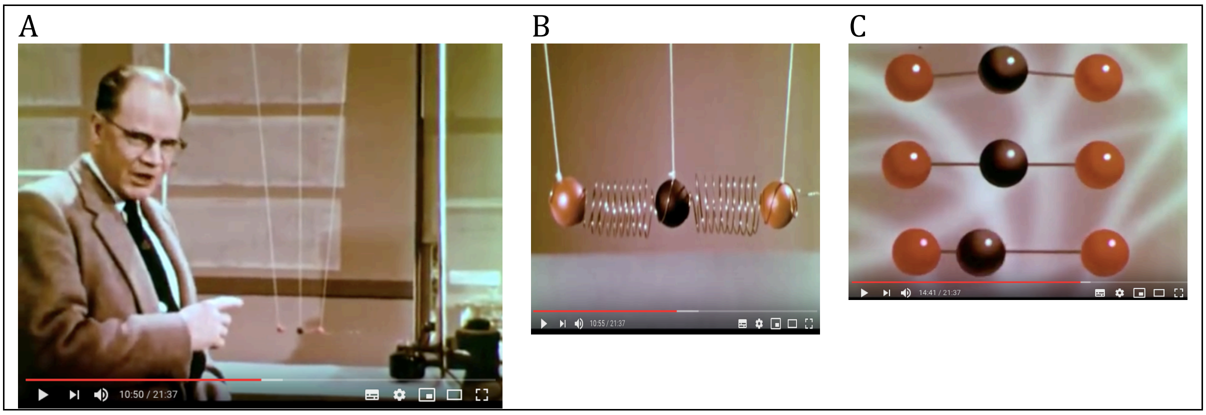


Figure 46. Demonstration of Harmonic Vibration of all of CO2's Modes. Frame A, a model of the CO2 molecule is vibrated by frequency producer at different frequencies; Frame B, a close-up of the spring and ball model attached to the device on the right; and Frame C, the film showing – in an age before 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 describes. The point I am making is proof that the modes are equivalent and 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 that the diatomic – N_2 and O_2 – share the same resonance properties.

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 considered how the blackbody 'Planck function' curves shift with different temperatures (curve bb, Figure 44). The Earth's 'max' is around 270 Kelvin and discriminates all other spectra outside this curve. I wondered what this would mean for Venus's atmosphere; it is hotter.

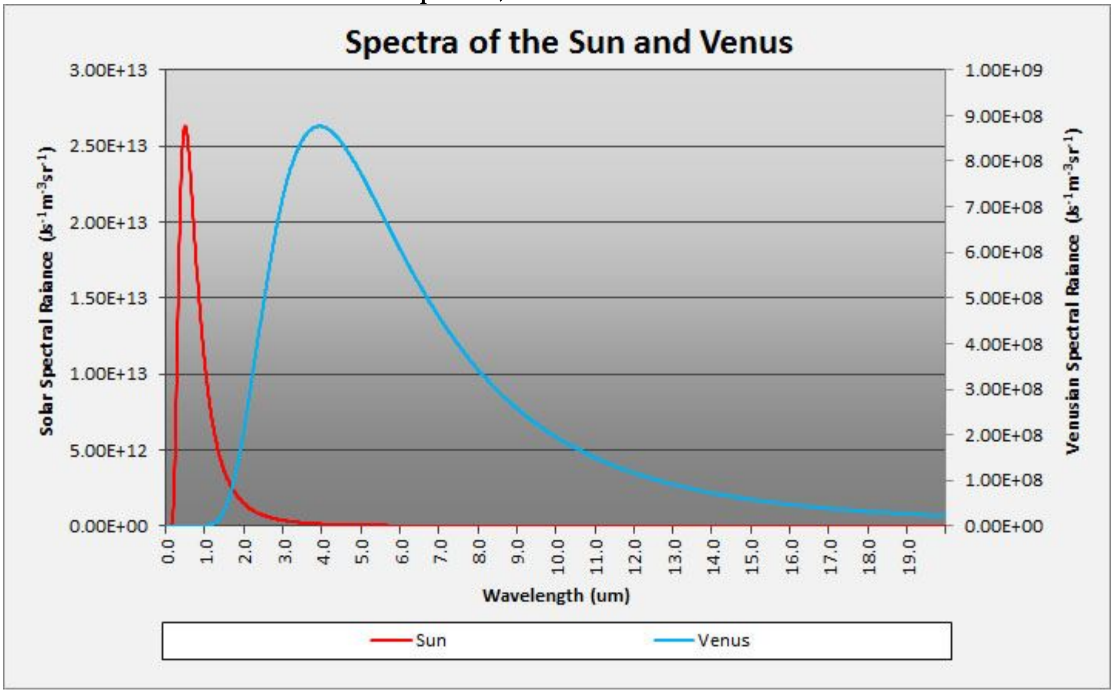


Figure 47. Venus's Blackbody Radiation Curve Peaking Between Sun and Earth. [75] The point of showing this curve is that it lies where the Earth and the Sun's emission spectra are ignored as they are outliers. Presumably, they are not for Venus.

Venus is hotter, so the blackbody curve will shift to the left. Its 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, CO_2's 1338 cm^{-1}, N_2's 2338cm^{-1}, and H_2O's 3652cm^{-1}.

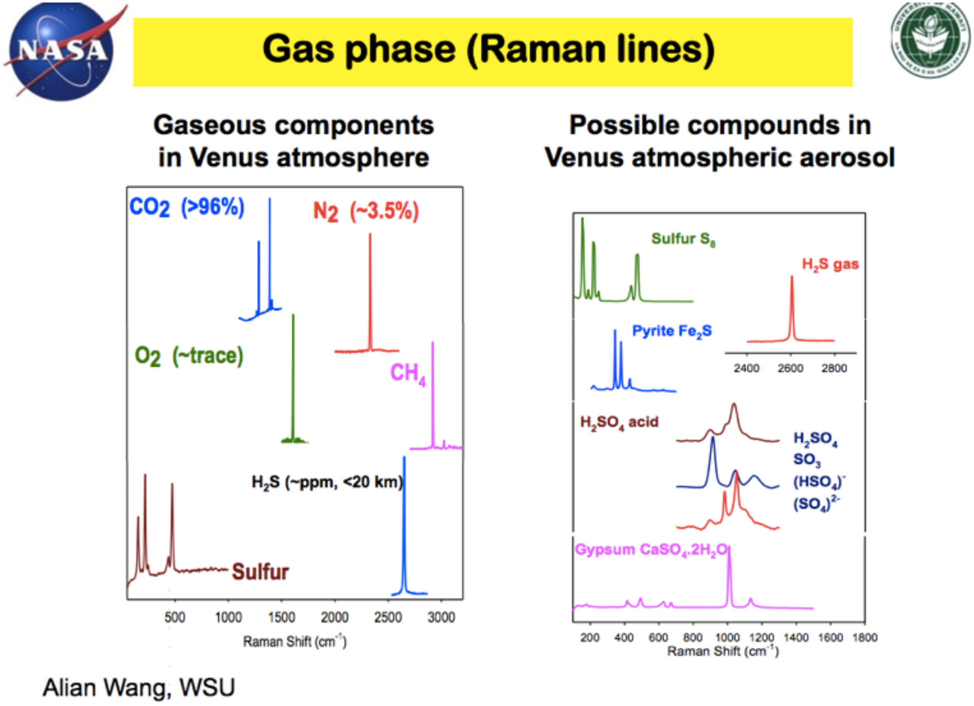


Figure 48. Planet Venus's Raman Spectra measurements. Raman spectra in the left diagram correspond to Raman spectra in Figure 44.

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 – were 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

IR radiation theory, as we currently understand it, and the GHGs' derivation 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 unique role in the climate, as claimed. The detection of all so-called 'IR' spectroscopy spectra is only the thermo-electric side of the spectroscopy, including determining 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 are the 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. He only discovered the thermoelectric gases comprising at least one thermoelectric IR spectra mode. These transducers receive the IR radiation signal from the sample molecules' electric dipole modes or spectra. 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 line 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 for the claims of longwave absorption and shortwave emission of the Earth claim. This claim and central theory demand review in the 'light' of Raman data. As it is, it is wrong. The blackbody curves discriminate unnecessarily active Raman-measured spectra.

It was also found that so-called IR spectrometers. At the same time, they show that molecule quantum predicted spectra – the thermo-electric ones– do not radiate their samples with IR photons as claimed, and only Raman IR spectrometers radiate their samples with such. Instead, they measure and graph the temperature difference between the 'cooler' sample and the 'hotter' reference heat source as transduced from thermal radiation into EMF.

It was also found that emissivity is solely an infrared-thermoelectric instrument problem and a limitation of the thermoelectric transducer to generate complete EMF from a substance. It is not a fundamental 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, it was found that by analysing H2O's 3652 cm-1 mode – and others – 'Raman' IR and thermoelectric IR modes are equivalent and consistent with the equipartition law. Including the 'Raman modes' in atmospheric radiation theory will challenge and possibly overturn current blackbody theory, where contradictions such as water and snow being assumed near-perfect (emissivity) absorbers also abound.

With this new thermoelectric understanding – which ignores the quantum mechanics of the atmosphere – the direct mechanics behind the current knowledge of the 'greenhouse' atmosphere, based alone on thermoelectrics, is fallacious. Quantum mechanics and Stefan's and Planck's Laws hold that all matter above absolute 0 Kelvin radiates. N_2 and O_2 behave like all other matter; the only things 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 interpreting the special GHGs alone as the IR absorbent gases should be seen as inadmissible in climate and atmospheric theory and in 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 an equilibrium where, previous to this, N_2 and O_2 were exempt.

6 Acknowledgements

Due to the nature of the investigation, I do not have anyone to acknowledge directly for this work, aside from the support from family, colleagues, and friends; I have been totally unsupported. I can and should thank the pre-publication

reviewers, the sceptics of my theory, and some from the sceptic side of the climate debate. Thank you, Barry James.

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