Reinterpreting and Augmenting John Tyndall's 1859 Greenhouse Gas Experiment with Thermoelectric Theory and Raman Spectroscopy

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Abstract

Climate science's fundamental premise – assumed by all parties in the great climate debate – says the greenhouse gases – constituting less than 2% of Earth's atmosphere; first derived by John Tyndall's in his 1859 thermopile experiment, and demonstrated graphically today by infrared IR spectroscopy – are special because of their IR (heat) absorbing property. From this, it is – paradoxically – assumed the (remaining 98%) non-greenhouse gases N_2 nitrogen and O_2 oxygen are non-heat absorbent. This paper reveals, by elementary physics, the (deceptive) role thermopiles play in this paradox. It was found: for a special group substances – all sharing (at least one) electric dipole moment – i.e. CO_2, and the other greenhouse gases – thermopiles – via the thermoelectric (Seebeck) effect – generate electricity from the radiated IR. Devices using the thermopile as a detector (e.g. IR spectrographs) discriminate, and have misinterpreted IR absorption for anomalies of electricity production – between the sample gases and a control heat source. N_2 and O_2 were found to have (as all substances) predicted vibrational modes (derived by the Schrodinger quantum equation) at 1556cm-1 and 2330cm-1 respectively – well within the IR range of the EM spectrum and are clearly observed – as expected – with Raman Spectroscopy – IR spectroscopy's complement instrument. The non-greenhouse gases N_2 and O_2 are relegated to greenhouse gases, and Earth's atmospheric thermoelectric spectrum was produced (formally IR spectrum), and was augmented with the Raman observations. It was concluded the said greenhouses gases are not special, but typical; and all substances have thermal absorption properties, as measured by their respective heat capacities.

Key Words: greenhouse gases, climate change, thermopiles, Raman, Seebeck effect, spectroscopy, John Tyndall

1   Introduction

While the debate over how concentrations of greenhouse gases (GHGs) [1] past, present, and predicted, have, do and will affect climate ensues, both proponents and sceptics appear to agree on one assumption: the foundational premise that the special GHG's – as first derived by John Tyndall in his 1859 thermopile and galvanometer experiment – are special because they absorb radiant heat[2]. Today, the same thermopile technology as used by Tyndall in his experiment is used in infrared (IR) spectrometers to produce spectrographs, and these are also used to interpret – in the same way as Tyndall – to support the IR (heat) absorption properties of the GHG's. Extrapolation of this (special) gas absorption assumption is foundational to climate theory; however, the absorption assumption presents paradoxes – even catastrophes:

1. How is it the atmosphere is warm at all – when less than 2% of it is comprised of the heat trapping GHG's, and the remaining 98% (N_2 and O_2) is not?
2. How can convective phenomena – such as the sea breeze – in the atmosphere be explained alone by these special (heat trapping) GHG's – where in direct topic related literature, they are not?

There seems to be – an even larger – question: where has the thermally 'dark' (from the cosmic 'dark energy' and 'dark matter') 98 % of the atmosphere gone? Is this the reality, or has there been a mistake? An oversight?

Since Tyndall's time, knowledge, applications, and instruments have developed – all using the thermopile. There is also a better, almost complete, understanding of the atom – both classically and quantum mechanically – that accommodates, and explains thermoelectric effects, and the heat capacities of substances. Devices combining computers with the thermopile have developed: the IR thermometer, thermal imaging cameras, and IR spectrographs. On top of this, a parallel and complimentary method to IR spectroscopy (measuring what IR spectroscopy cannot) has developed called Raman spectroscopy.

Upon closer inspection, the Tyndall experiment, and the use of IR spectroscopy, overlooks a number of essential details, which without disclosing, the

experiment – and demonstrations thereafter – is incomplete, and potentially flawed. They include: the thermoelectric properties of the gases and conversely, the physics of the thermopile itself – with its ability to produce electricity via the Seebeck effect; and the parallel Raman Spectroscopy.

With this knowledge taken into account, there appears to be a polarity – or discrepancy – between the possible interpretations of the Tyndall experiment. With these in mind, the experiment can either be interpreted as the current infrared absorption/transmittance interpretation (the 'IR' interpretation); or as the thermoelectric property of the gases measured by the thermopile – (the 'thermoelectric interpretation). In the true sense of a scientific polarity, both will attribute the vibrational behaviour of atoms to their outputs or measurements; and both will argue support by classical and quantum mechanical physics to their conclusions; but their explanations, in detail, will fundumentally be at odds – their conclusions used to different ends. The polarity is such, that the two together, cannot simultaneous be true.

The aim of this paper is to evaluate whether the current IR absorption interpretation – and its greenhouse extrapolation – is unfounded, in light of a (Seebeck) thermoelectric interpretation?

At stake with this investigation are the special GHG's; are they – by the laws of physics – special, or is it that they are typical? Are all gases in the atmosphere GHG's?

I have presented my argument in the following order:

 (2) a description of how the GHG's are derived;

(3), thermoelectricity, thermopiles and the Seebeck effect;

(4) thermopile devices;

(5) device interpretations – absorption vs. thermoelectricity;

(6) atomic theory – vibrational modes and quantum predictions of N_2 and O_2;

(7) Raman Spectroscopy observations of N_2 and O_2;

(8) heat capacity;

(9) discussions; and

(10) conclusions.

2   The Greenhouse Gases: The 1859 John Tyndall Thermopile Experiment

In 1859 John Tyndall (1820-1893) [3],[4] set about analysing the atmospheric gases using the newly developed thermopile and galvanometer [5],[6],[7],[8],[9]. Tyndall isolated the atmospheric gases between a heat source and a thermopile, and analysed them for their change in electric flow – measured by the galvanometer. He noticed some gases did not appear to be affected by the heat source. They did not change the galvanometer; while others did. He concluded – and this is where our reasoning branches to this day – that some gases absorbed the heat; while others did not. He inferred – from the gases that moved the galvanometer – the greenhouse gases, and they include (H_2O) water vapour, (CO_2) carbon dioxide, (CH_4) methane, (NO_2) nitrous oxide, and (O_3) ozone. On Earth, these gases constitute less than 2% of the Earth's total atmospheric volume; the remaining non-GHGs – (N_2) nitrogen and (O_2) oxygen – did not move the galvanometer, and were inferred not to be heat absorbent, and thus not greenhouse gases. The standard view can be summed as:

 "It has to be noted that monoatomic gas molecules, such as nitrogen, N2, or oxygen, O2, are not affected by IR radiation and can therefore not be detected by this means. Otherwise the mentioned atmospheric greenhouse effect would be extremely severe and probably we would not exist in the current life form". [10] Also see Appendix 11.4 for a similar supporting description.

3   Thermoelectrics

The IR absorption and transparency explanation or interpretation to why substances behave so differently – as deduced by Tyndall – I argue is misleading and is wrong. It does not take into account the underlying physics of the thermopile – thermoelectrics and the Seebeck effect.

3.1   The Thermopile and the Seebeck Effect [11]

In 1821, Thomas Seebeck [12] noted the electricity was produced when two wires – of different kinds – are joined at one end (to form a thermocouple) with a

device to measure electric current at the other. The electric current produced was proportional to the heat radiated. This discovery was important breakthrough in the history of temperature measurement. Thermopiles (figure 1 below) are many thermocouples connected together in series.
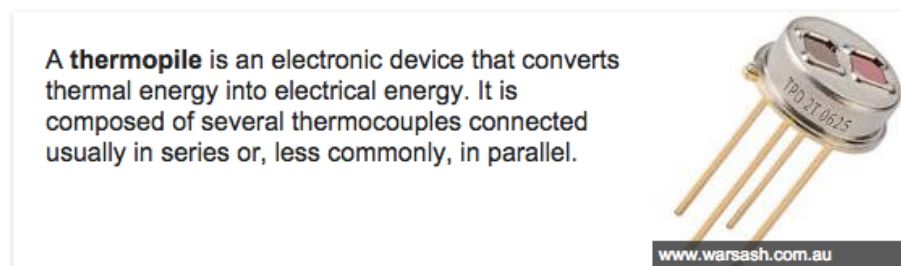

A **thermopile** is an electronic device that converts thermal energy into electrical energy. It is composed of several thermocouples connected usually in series or, less commonly, in parallel.

www.warsash.com.au

Figure 1. The Modern thermopile. An image from a typical internet search on the said topic. [13]

As all substances radiate IR energy, devices such as the IR thermometer and spectrograph exploit this radiation, using the thermopile to convert the radiation to electricity. The device calibrates the electrical current to display the temperature of the object. On the IR thermometer, the temperature of a substance is indicated, not the voltage generated. All devices using thermopile detector technology are bound by the thermoelectric laws of physics. Without the thermopile, these devices would not operate.

It is interesting, both the Seebeck effect and thermoelectric effect are noticeable by in absence in modern physics textbooks. References can only be found online, or in concise science dictionaries.

3.2   The Thermoelectric Substances

Just like some substances are magnetic, and will move a compass needle, and others are not; not all substances generate electricity with the thermopile. Thermoelectric substances – in general – include most solids and gases (including transparent glass). There are a number of gases that are thermoelectric – thermoelectric gases (TEG's) – including: H_2O, CO_2, CH_4, NO_2, and O_3.

3.3   Non Thermoelectric Substances (TES's)

Notably, as solids, the non-TES's include: Germanium (Ge); Sodium Chloride (NaCl) or salt plates; Potassium Bromide (KBr); and to some extent the plastics.

The non-TEG's include the atmospheric gases N_2, O_2, and possibly Hydrogen (H_2), and Helium (He).

3.4　Germanium

Germanium is almost 100% transparent to IR thermometers – just as glass is to our eyes [14],[15]. I could heat a lump of germanium to a dangerous temperature, but unlike the regular thermometer, the IR thermometer would not register the danger. Imagine a sauna – heated to sauna temperature – with walls made of IR transparent germanium: what temperature would a noncontact IR thermometer within the sauna measure? It would indicate – unlike the traditional thermometer – the outside temperature. It would 'see' right through the walls (apart of course for the water vapour and other trace gases would show). It would be useless.

These substances will no more register to a thermopile than plastic strings will amplify on an electric guitar. It just won't happen: it's physics. But, this is not to say, the strings will not play a tune: it is just that they are not electromagnetic and won't be registered by the pickups. We shall soon learn this analogy is a pretty close one for the non-TEG's as they – as the plastic strings still play tunes – hold heat.

4　Thermopile Devises

Tyndall's decedent thermopile apparatus is in today's ubiquitous handheld non-contact IR thermometer, thermal imaging camera, and IR spectrograph. They all share the same core technology, the thermopile: so we can all learn from the basic handheld device, to understand the complex machine.

4.1　The Non-Contact IR Thermometer

Today, non-contact IR thermometers (IR thermometers) are easily available, and cost around 30 US dollars. They generally measure IR radiation from 8 to 14 microns on the electromagnetic spectrum, in what is termed the atmospheric window [16]. When used to test the temperature of different substances, they reveal the (above) flaws in the thermopile: they, not surprisingly, measure the temperature some substances, but not all. They discriminate. For instance, as

shown in Figure 1 below, they will measure the temperature of my hand as around 31 °C (in frame A of figure 2); it will measure the temperature of glass when pointed at it (around 18 °C in frame B); but when the same visibly transparent glass is placed between my hand and the device, it will not measure my hand's temperature, but the temperature of the glass (again around 18 °C in frame C).
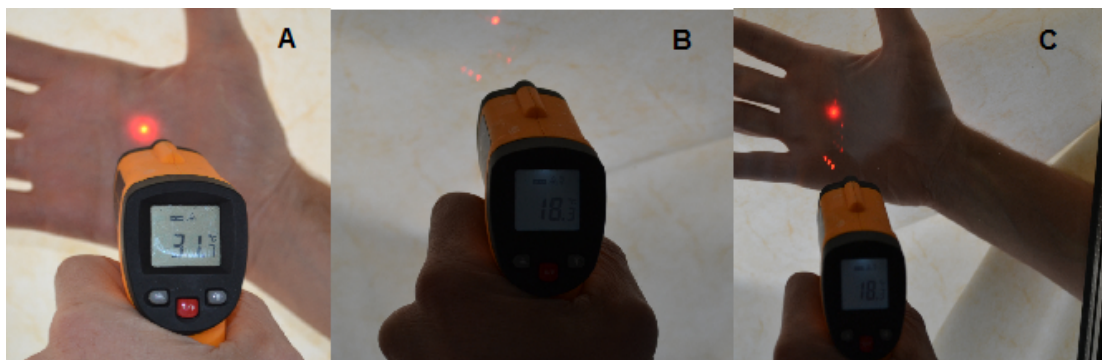

Figure 2. Non contact IR thermometer demonstration. Frame A, hand temperature measured directly as 31°C; frame B, the temperature of glass measured as 18° C, and Frame C, hand temperature through glass measures at 18 °C

While my hand, through glass, is visible to the eye, it is invisible to the IR thermometer. The significance of this paradox is essential to understanding the potential flaws of Tyndall's experiment, and the explanation as to why – revealed by atomic physics coming up in section 6 – decisive. As strange as this paradox may be, there is another – even stranger – paradox from this demonstration: what substance (between the device and my hand in frame A) is it the device not measuring when you point it at my hand? The answer is, the air in between. A non-contact IR thermometer will not measure the air temperature whether at room temperature (if the room temperature were measured by a regular thermometer), or whether outside – in extreme sub zero, or conversely, hot temperatures. Why are some substances visible to the device, while others are not – why the discrimination?

Again, the answer is coming, but before we get there, some more applications exploiting the thermopile.

4.2   CO₂ Sensors

Regular CO_2 concentration sensors use a thermopile detector, again exploiting the Seebeck effect (though this is not how they are explained in most references [17],[18], [19], [10]). Similar to my IR thermometer, measuring my hand temperature through the glass, the CO2 sensor is more controlled. To measure the concentration of a sample, the sample is let in between a constant heat source, and the thermopile detector. In principle, a 100% sample of CO_2 will block out the heat source by 100%: 50% by 50%. How this actually works, as I am coming too, is open to interpretation.

4.3   IR spectrometers

Spectrometers[20] in principle differ only slightly from the simple CO2 sensors: they share the same thermopile detector, heat source and sample and empty reference/control tubes; but differ in that they have a 'splitter' that can split and read output from a specific band of the spectrum, by this a graph – a spectrograph – is created as shown below in figure 3.
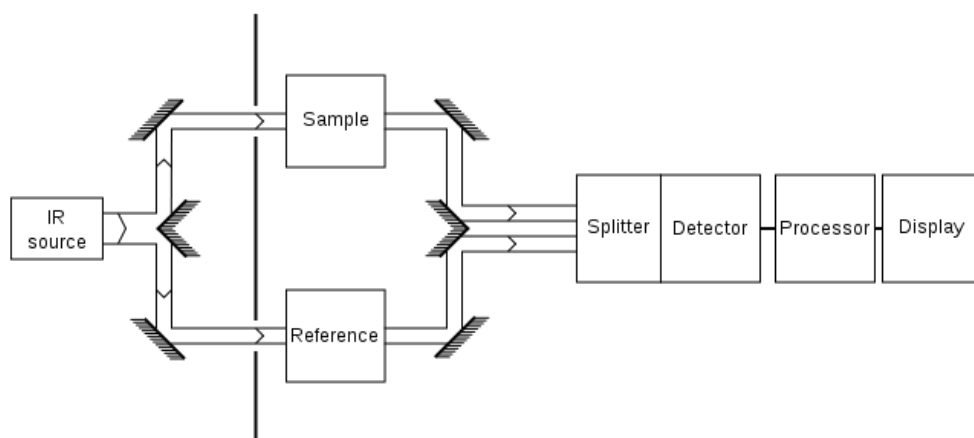

Figure 3 Schematic of Spectrograph [20]. Notice the spliter, and the division from the reference (control) and the sample.

The IR (heat) source is heated to a considerable temperature – some 1500 C (3:40 [21]). Samples are to be prepared between either Sodium Chloride (NaCl) salt plates or Potassium Bromide (KBr) as these substances will not show spectra lines. Interpretations of how they work – next.

5   Interpretations: IR (Absorption) vs. Thermoelectric

All of these devices have similar outcomes, they describe, and discriminate, but their explanations to why are un-unified; especially at the atomic level. I have found no reference that matches why the IR thermometer and the IR spectrograph discriminate; when they both use thermopiles. The explanation should clearly point to – they are one and the same.

Here we shall review the above devices in terms of two interpretations that can be made from devices using thermopiles:

1. IR absorption interpretation; or a
2. thermoelectric interpretation (TE).

5.1   IR thermometer.

5.1.1   Absorption Interpretation

The standard answer given is, it is the device reads what IR is absorbed (or emitted) by substances – i.e. the IR opacity or transparency of substances. To the device, the air – most of it – is said to be transparent to IR; that is, it does not absorb (or emit) IR radiation, where as other gases such as water vapour and carbon dioxide – just as with the IR opaque glass – do. But this explanation still leaves us with the paradox: why does the IR device not measure the air temperature while a regular thermometer will?

5.1.2   TE Interpretation

As described above in 3.1, it is all down to thermoelectricity.

5.2   CO2 sensor

5.2.1   Absorption Interpretation

This interpretation is the standard interpretation in all texts and demonstrations: the discrimination is due to the IR absorption properties of the CO_2 – the CO_2 molecule absorbs the IR (heat) emitted from the heat source. Using the 50% example: 50% is **absorbed**; the remaining must be non-CO2, and IR transparent.

5.2.2   TE Interpretation

The non-TEGs (N_2 and O_2) do not generate electricity by the thermopile; the thermopile generates electricity only from the radiation emitted from the constant heat source. The heat source is the measurement control. When the CO_2 is let into the sample tube, the thermopile generates a current from the CO_2 rather than the control heat source. If the CO_2 concentration of a sample is (for example), 50%, the CO_2 thermopile would detect a 50% drop in electric current, and so register and indicated 50% CO_2 concentration.

The energy emitted the CO2 sensor essentially has repeated, in a controlled setting, the same problem I set with the handheld non-contact IR thermometer (in section 3), where I had glass placed between the device and my (warm) hand. Recall the device measured the glass temperature, and not my hand. CO_2 is a TE substance just as the glass.

It is interesting the control heat source takes time to warm up. Why? Could it be that without the differential in temperature, between the heat source and the sample, there will be no anomaly measured – there would be no difference to detect. It would be like the glass being the same temperature as my hand – in the handheld IR thermometer example above.

5.3 Atmospheric IR spectrographs

Spectrometers produce spectrographs; again, do they represent IR absorption, or thermoelectric properties of atmospheric gases?

5.3.1 Absorption Interpretation

Just as with the CO2 sensor, atmospheric IR spectra produced by IR spectrometers are said to – or are interpreted – to depict the absorption and transmittance properties of the atmospheric gases. At different frequency bands there will be either absorption or transmittance of IR heat through the sample as
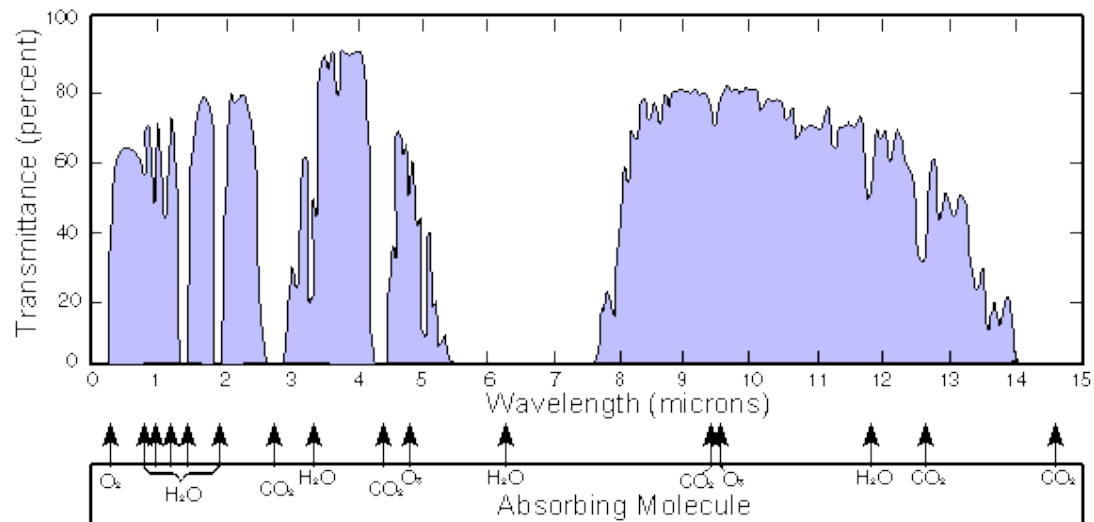
shown below in figure 4.

Figure 4. Infrared Spectrograph of the atmosphere [16].

The curve is inverted to emphasise transparency, where the dips are termed are accossiated with – as we will come to learn when we look at atomic theory – the molecular vibrational modes of the sampled gases. The spectrograph reveals the said GHGs. Notice the range from around 8 to 14 microns – termed 'the infrared window' – is mostly 'transparent'. It is the range non-contact IR thermometers exploit. Also notice the absence of N_2 and O_2. They are absent because they are said not to trap of absorb IR heat.   An N_2 and O_2 sample – on their own – would produce an IR spectrograph of near 100% transition.

5.3.2   TE Interpretation

Following thermoelectric laws associated with the thermopile, the graph (figure 5 below) is a reading of the thermo-electromotive force (electricity) produced (measured in Volts) from the sample (gases) at each frequency along the electromagnetic spectrum – before the reference (control) heat source. Only thermoelectric gases will be measured.
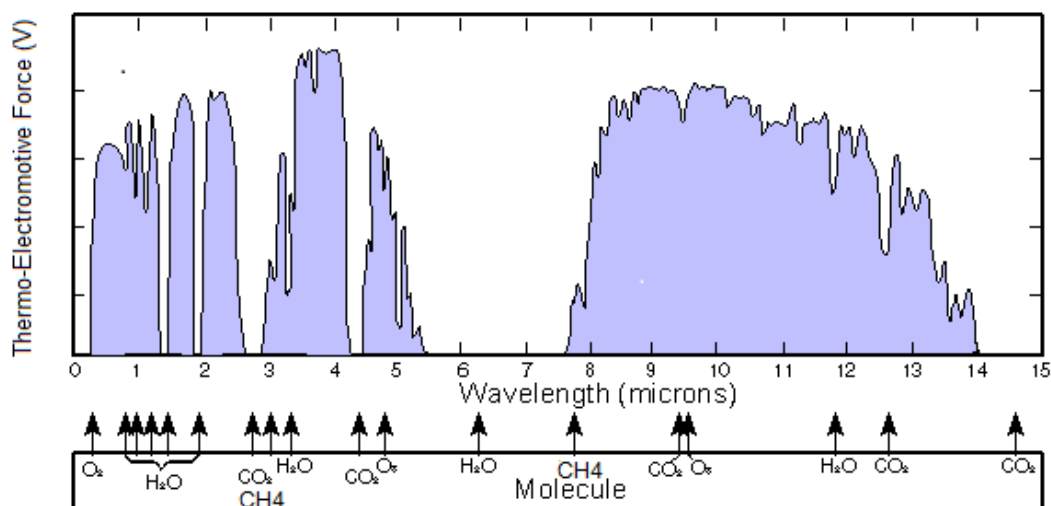
Figure 5. Thermoelectric Force and the Electromagnetic Spectrum.

The control tube, or cell, will show only the electricity produced from the 'black body' heat source and nothing else, as the common air in the tube (mostly N_2 and O_2) is not thermoelectric. The peaks thus show measured electricity production from the heat source – at that particular frequency or wavenumber – and the dips show lower voltage, as the heat radiation from these sample gases measured is at a considerably lower energy state than the control heat source; i.e. it is cooler.

A review of the Tyndall Experiment, by a thermoelectric interpretation, can be found at appendix 11.2

6   Atomic Theory

Here we shall look at the crux theories upon which the above thermopile device is based. Atomic theory is the foundation knowledge of all electromagnetic spectroscopy. It includes both classical vibration behaviour of molecules, and their quantum mechanical predictions. Again, just as above, there are two possible explanations or interpretations to how the atomic behaviour may produce spectrographs: IR absorption, or TE thermoelectric. At the time of writing, all explanations point towards IR absorption, however these explanations appear to be selective in what to include – and what they leave out

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– to fit their interpretation, and (unintentionally) leave out important known axioms that would give a TE credence.

Also, at the time of this writing, there are no direct references available to explain the GHG's and non-GHG's other than by their IR absorption properties. At no point is their any unification between thermopiles, thermoelectric effects and atomic theory.

I shall firstly show the IR absorption interpretation, and follow with the alternative TE explanation.

6.1   IR Absorption Interpretation

Current explanation of the greenhouse effect and IR absorption with IR spectroscopy will be presented. This is not instructional, but is intended to highlight key points.

6.1.1   Vibrational Modes

Central to the absorption or transparency properties of substances in IR spectroscopy is the different vibrational modes [22] of molecules. Whether or not a molecule absorbs IR radiation as shown by IR spectroscopy is determined directly by the excitation behaviour of the substances molecules, the vibrational modes of the substance. Vibrational modes can be either IR active, or IR inactive. By IR active or inactive is simply to say whether, or whether not, the Vibrational Mode absorbs IR radiation. IR inactive molecules are determined by their vibration mode: they have a symmetric stretch vibration, while the other IR active molecules have at least one asymmetric vibrational mode.

6.1.2   Degrees of Freedom

Degrees of Freedom are the amount of Vibrational modes a molecular can have. Most gases have more than one degree of freedom – for example CO_2 and H_2O – but some have only one – N_2 and O_2 are examples of this. The N_2 and O_2 molecules are both IR inactive so do not absorb IR radiation; while CO_2 has 3 degrees of freedom, 2 IR active and 1 IR inactive; and H_2O has 3 degrees of freedom, 2 IR active and 1 IR inactive.

6.1.3   Dipoles

If a vibrational mode has a dipole movement, IR radiation is absorbed; if not, no IR radiation is absorbed. N_2 and O_2 both have only one degree of freedom each: the one vibrational mode they have is IR inactive because there is no dipole movement – thus they are not GHGs. The other (remaining) atmospheric gases have at least one vibrational mode with dipole movement, so are IR active and thus termed GHGs.

6.2   Thermoelectric Interpretation

Whether or not a molecule shows up an IR spectrometer has nothing to do with the thermal absorption properties, but rather, its thermoelectric properties. My point could not be made more clearer than from the words said by expert lecturer Professor Adrian Lee explains – in an educational Youtube lecture [23] the thermoelectric reality of dipoles. (below). Transcript from 05:35 minutes. Notice he clearly separates the thermoelectric from thermal behaviour.

"The dipole moment for homo-nuclear diatomic is zero, no matter what the bond length is. During vibration its dipole movement stays zero, and it gradient stays zero, so therefore homonuclear diatonics (N_2 and O_2) cannot exhibit an infrared or vibrational spectrum. They are known as infrared inactive…. It does not mean homonuclear diatonics do not have vibrations levels, it just means one cannot use electromagnetic radiation to excite molecules from one vibrational state to another. In just the same way, one cannot excite a homonuclear diatonics from one rotation to another using microwave radiation, but these levels exist – the Schrodinger equation tells us what the energies of those levels are. How does a molecule change from one vibration level to another, simply by bumping in one another. Thermal energy will change the vibration state of the molecule. "

Molecule's vibrational functions can be predicted from classical and quantum equations. These functions (or frequency bands) are either IR active, or IR inactive – due to their respective possession of an electric dipole moment or lack of an electric dipole moment.

6.2.1   Vibrational Modes Dipoles, Degrees of Freedom, and the Gross Selection Rule

Whether, or whether not, a vibration function of a molecule registers on an IR spectrometer is determined by the type of its vibrational mode. Molecules that are IR active register because they have at least one asymmetric vibrational mode, and a dipole moment – that thermoelectrically excites. Conversely, molecules that are IR inactive will not show, as they fail the gross selection rule: they have a symmetric stretch vibration with no dipole moment to thermoelectrically excite.

N_2 and O_2 both have only one degree of freedom each with a vibrational mode that is IR inactive. Because of this they do not register on spectrographs. Molecules that have IR active vibrations with (electric) dipole movements are measured by a spectrometer – they include H_2O, CO_2, CH_4, NO_2, and O_3. Together known as the 'greenhouse gases'.

6.3   Quantum Equation Predictions

The Schrodinger equation calculates the predicted vibrational mode frequency bands for any atomic structure. These predicted vibrational modes are observed using thermopile technology. That a vibration mode of molecule does not show on thermopile spectrograph (i.e. N_2 or O_2) does not mean these molecules vibration modes do not exist.

6.3.1 N_2 and O_2 Quantum Equation Predictions

As Professor Lee implied in his explanation (above) the vibrational mode frequencies of N_2 or O_2 can be predicted by solving the Schrodinger equation. Many papers have been published using quantum mechanical equations to derive these predicted vibration functions[24], [25] ,[26]. Table 1 (below) shows the predicted wavenumber (ω_e column 3,) of N_2 and O_2: 2360cm-1 and 1580cm-1 respectively. These frequencies are well within infrared band of the electromagnetic spectrum[27], [28]. The hidden 'IR inactive' vibrational modes of GHG molecules, such as CO_2 and CH_4, are also able to be predicted by this calculation.

Table 1. Table of predicted N_2 and O_2 vibration modes derived from the Schrodinger equation [28].

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

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

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

If these predicted modes of N_2 and O_2 (and the IR inactive vibrational modes of molecules such as CO_2 and CH_4) do not show by 'IR spectroscopy', is there another way to reveal their presence? The answer is yes; a very well established test called Raman spectroscopy.

7 Raman Spectroscopy

During the time IR – thermopile based spectroscopy – technology was developing, a parallel – complementary – technology called Raman spectroscopy was also developing. Raman spectroscopy reveals the (predicted) symmetric vibrational modes that IR spectroscopy cannot. It detects the IR inactive, (the non-TEGs or TESs) [29]. An essential introduction, comparison, and evaluation of the two technologies is presented in a YouTube clip [30]. Supporting teaching exercises with questions on the IR and Raman relationship can be found at appendix 11.3 as evidence to their knowledge to experts.

7.1.1 Raman Spectroscopy and N_2 and O_2 Spectra

Figures 6 and 7 below show Raman spectrograph peaks of N_2 at O_2 at the predicted 1556cm-1 and 2330cm-1 [31] – pages 205 and 209 respectively – both within the infrared range of the electromagnetic spectrum.
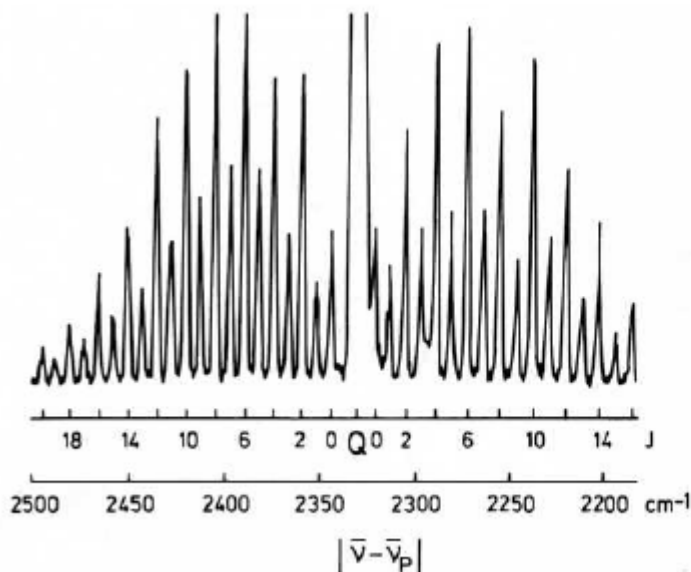
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Fig. 12.11. The rotational-vibrational Raman spectrum of the nitrogen molecule, $^{14}N_2$. In the centre, at the position of the vibrational wavenumber $\bar{v}_e = 2330$ cm^{-1}, the Q branch ($\Delta J = 0$) appears as a broad line. In $^{14}N_2$, with $I = 1$, an alternating intensity of the rotational lines with a ratio 1:2 is observed. After Hellwege

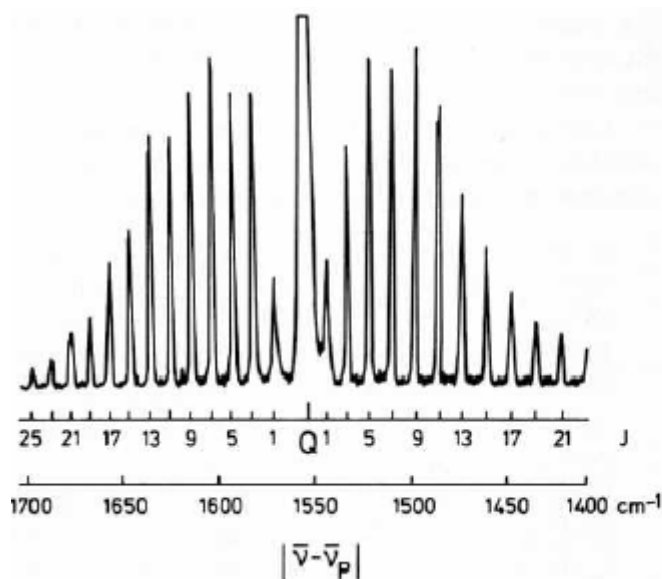**Figure 6 Raman peaks of N2 at the predicted 2330cm-1 – page 209 [31]**

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

Figure 7. Raman peak of O_2 at the predicted 1556cm-1 [31] – page 205.

Also see appendix 11.1 for a Raman spectra combining N_2 and O_2 observations in one.

7.1.2   Raman and IR Spectroscopy and CO_2 Spectra

Following the same rationale as for the N_2 and O_2 Raman spectral, it can be shown (figure 8 below) that Raman spectroscopy reveals the hidden (to IR

spectroscopy) symmetric stretch predicted at the 1388 cm-1 band of the spectrum.
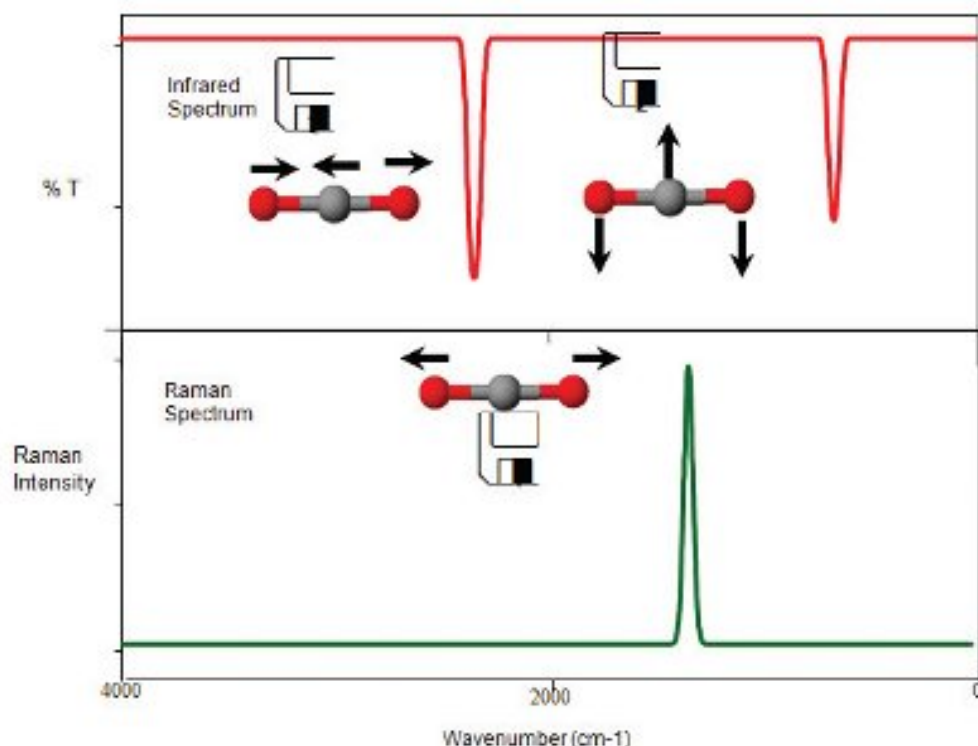

Figure 8. Schematic of CO2 Raman and IR Spectra. "In gas phase spectra of CO_2, two infrared bands are observed at 2350 and 667 cm^{-1} (red) and a single Raman band at ~1388 cm^{-1} (green). (The latter band is actually a doublet due to quantum mechanical resonance effects, which is beyond this discussion)." [32]

To support the above schematic, figure 4 in the paper titled: <u>Time-solved remote Raman study of minerals under supercritical CO2 and high temperatures relevant to Venus exploration</u> [33], shows conclusive "Raman doublet (1284 and 1388 cm−1) of CO2".

Vibrational modes of other said GHG's, revealed in Raman spectra, are shown in appendix 11.1.

8   Heat Capacity

Vibrational behaviour of molecules, as described above, determines the Specific Heat Capacity of a substance. Heat capacity is the true measure of heat absorption. All substances, including atmospheric gases, absorb and radiate infrared (IR) heat. When heat energy is applied to a substance, the ability for the

substance to absorb the heat energy and raise the temperature of the substance is known as the specific heat capacity[34]. The converse of emitting energy (cooling down) when released from the heat energy source is true. If – based purely on how the non-GHG's are currently defined – N_2 and O_2 are non-GHGs because they do not absorb heat, then this must imply they both have no specific heat capacity; this is, of course, not true. N_2 and O_2 not only have vibrational behaviour – as I have shown (above) in this paper, expressed in their respective absorption bands in the infrared; but also have respective specific heat capacities – as shown (alone with other gases) in the following table.

Table 2. Specific Heat Capacities and their constants [35].

Gas or Vapour	C_P (kJ/(kgK))
Air	1.01
Ar (Argon)	0.52
CO_2	0.844
He	5.19
H_2	14.32
N_2	1.04
O_2	0.919
Water Vapour	1.93
CH_4	2.22
N_2O	0.88

If energy is applied to CO_2, its temperature will – by its specific heat capacity – rise quickly, and conversely will fall quickly when the energy is released. Air on the other hand will take longer to warm, and water vapour longer still. A real life example of this is the regular sea and land breeze explanation.

9   Discussions

As the telescope has changed our view of the heavens, the application of – and theory behind – the regular non-contact IR thermometer will change our view of

how we understand the climate, particularly the role of the GHG's in climate forcing. What Tyndall – and his predecessors – neglected to mention, or reason, was the role of the thermopile and the thermoelectric properties of the different gases analysed. From molecular vibration understanding, we must be able to deduce the thermopile discriminates between substances with the IR thermometer and CO2 sensor for the same reasons it discriminates on the spectrograph – deriving the said GHG's.

While one paper does attempt to show N_2 and O_2 to be part (and only part) of the special greenhouse effect [36], the fact remains, instruments that use thermopile technology –as shown – do not measure the absorption and transparency properties of substances, but rather – only – the thermoelectric properties of the substances. Just as with the handheld IR thermometer, the IR spectrometer does not measure what it cannot 'see'. They cannot measure N_2 or O_2, but this does not mean those gases are not affected by thermal radiation, and are not 'heat trapping'. It is as if the non-TEG's are camouflaged or stealth.

9.1   Raman Observations

Raman spectroscopy spectra of N_2 and O_2 – figures 6 and 7 respectively – show the predicted (from the Schrodinger equations) vibrational modes of these abundant molecules – invisible to IR spectroscopy. These gases are predicted, and observed within the IR range of the EM spectrum, so are GHGs.

Figure 9 below is a schematic of the predicted and observed Raman vibrational modes in the Earth's atmosphere at different electromagnetic frequencies.
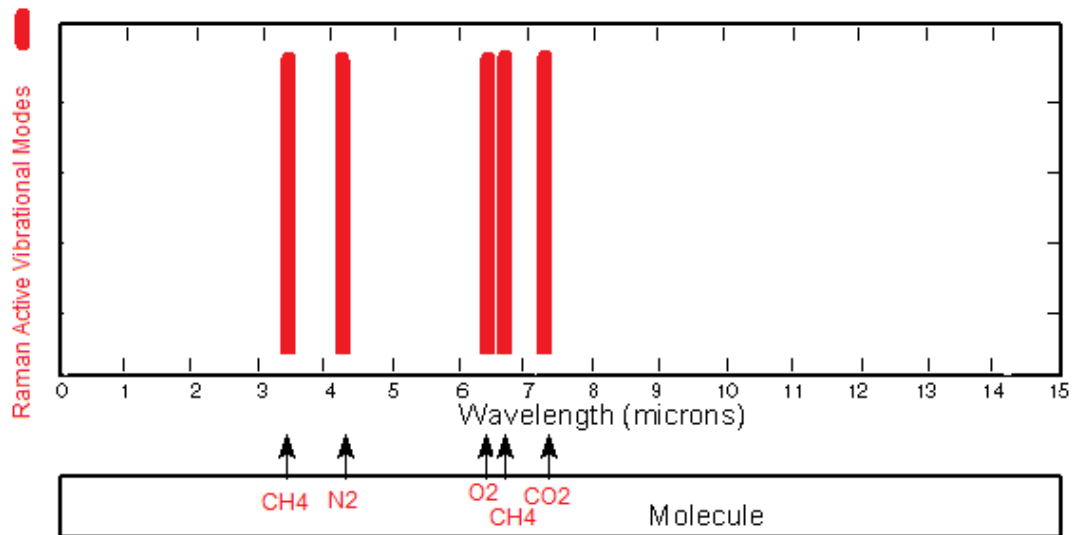
Figure 9. Raman Vibrational Modes of the Atmosphere. Predicted and Raman measured vibrational modes of (some) atmospheric gases CH_4, CO_2, N_2 and O_2.

With Raman spectroscopy we can view the total complement of GHGs – yellow box (3) in the demonstration (table 3) below – rather than a polarised view of (1) thermopiles, and (2) Raman spectrographs. If Raman spectroscopy was the only test we had to analyse the IR spectrum of substances, we may have equally have concluded that N_2 and O_2 are the (only) 'greenhouse' gases.

Table 3. Polarisation by instrument. (1) GHG's (vibrational modes) measured by thermopiles; ((2) GHG's by Raman; and (3) the reality, the full complement of GHG's*.

(1) GHG's by Thermopile	(2) GHG's by Raman	(3) GHG's
CO_2 H_2O CH_4 O_3	N_2 O_2 CH_4 CO_2	CO_2 H_2O N_2 O_2 CH_4 CO_2 CH_4 O_3

*Not a complete set of GHG's.

9.2   The augmented atmospheric spectrum

Combining thermoelectric (thermopile) and Raman Spectrographs (figure 10 below) reveals all the predicted and observed vibrational modes of the atmosphere. The augmented atmospheric spectrum now accounts for the hidden 'dark' 98% of gases in the atmosphere.
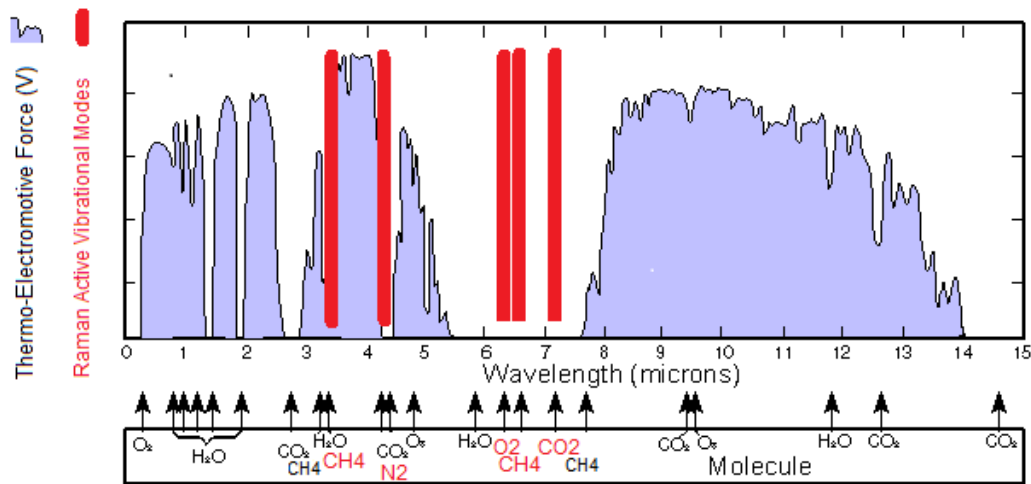
Figure 10. The Augmented Greenhouse Atmosphere. Combining Thermoelectric spectra with Raman spectral to reveal the complement of atmospheric vibrational modes, and the greenhouse atmosphere of planet Earth.

9.3   Implications

As the IR absorbing GHG's – as derived from IR thermopile technology – is the central premise to our universal understanding of the climate, the revelation presented in this paper is potentially – very – embarrassing for general science, especially given the availability of knowledge on thermoelectricity and the Seebeck effect all this time: all of which, is elementary science. It is a massive oversight. All extrapolations using the absorption claim will need to be reviewed. The special group of GHG's are not at all thermally special; they are though, thermoelectrically special. In light of the physics, and observational evidence: any attempt to explain the greenhouse gases without reference to the thermoelectric properties and their deriving apparatus – namely the thermopile – is paramount to scientific fraud.

10   Conclusions

This investigation has found there has been an oversight in interpretation of not only the 1859 Tyndall experiment, but also the thermal properties of atmospheric gases. The thermal absorption effects deduced from this experiment have been misinterpreted, and are really only thermoelectric (Seebeck effect) prosperities of the substances measured –by a thermopile device. The only gases

that can be measured by thermopile technology are the known 'greenhouse gases'; this is due to their asymmetric vibrational modes or dipole movement. The remaining gases N_2 and O_2 share symmetric vibrational modes (no dipole moment) and so are 'invisible' to the thermopile, even though they have thermal properties as represented by their respective heat capacities. The vibrational modes of N_2 and O_2 are revealed the Raman Spectroscopy, and both are well within the IR range of the electromagnetic spectrum. From this evidence, both N_2 and O_2 and another gases said to be a non-greenhouse gases are indeed greenhouse gases, and should be relegated so. The original said greenhouses gases are not thermally special, but typical. Complementing the thermoelectric (thermopile) spectroscopy with Raman spectroscopy reveals the total 'augmented' greenhouse atmosphere. Any extrapolation using thermopile technology to interpret gases as IR absorbent is inadmissible in climate theory without reference to the Seebeck effect and Raman spectroscopy. Climate models will need to take account for this change.

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11 Appendix

11.1 Raman spectra for Non GHGs and GHGs

11.1.1 O_2 and N_2 [37]
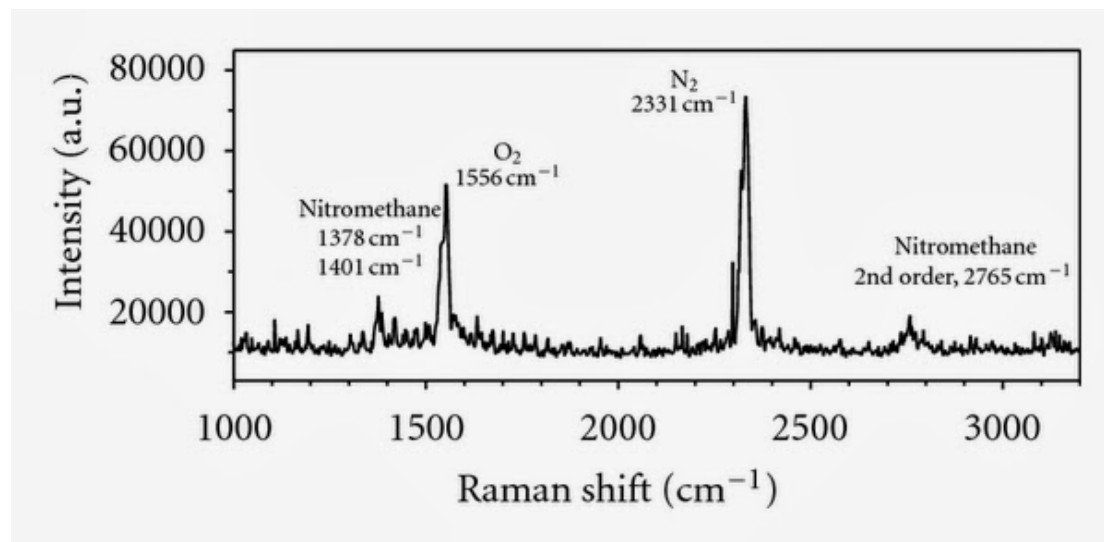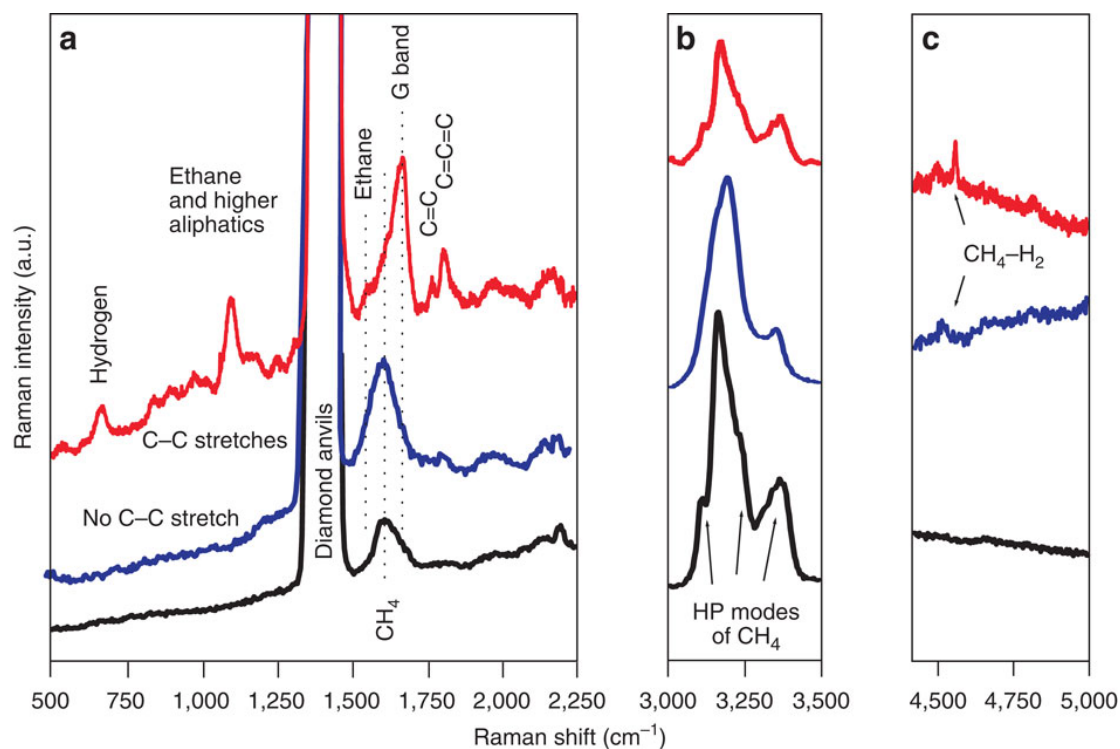

11.1.2 CH_4

Figure 11. Synthesis in LH DAC at 48 GPa. Black line shows CH_4 Raman spectrum before heating. Blue line shows Raman spectrum collected at 1,445 K with evident CH_4 dissociation. Red line shows Raman spectrum of reaction products collected after heating to 2,000 K. The labels near the curves suggest the assignment of the Raman bands. HP modes of CH_4 refer to vibrations caused by partial orientational ordering of methane HP phase[36]. Panels a–c show different parts of the spectral range.[38]
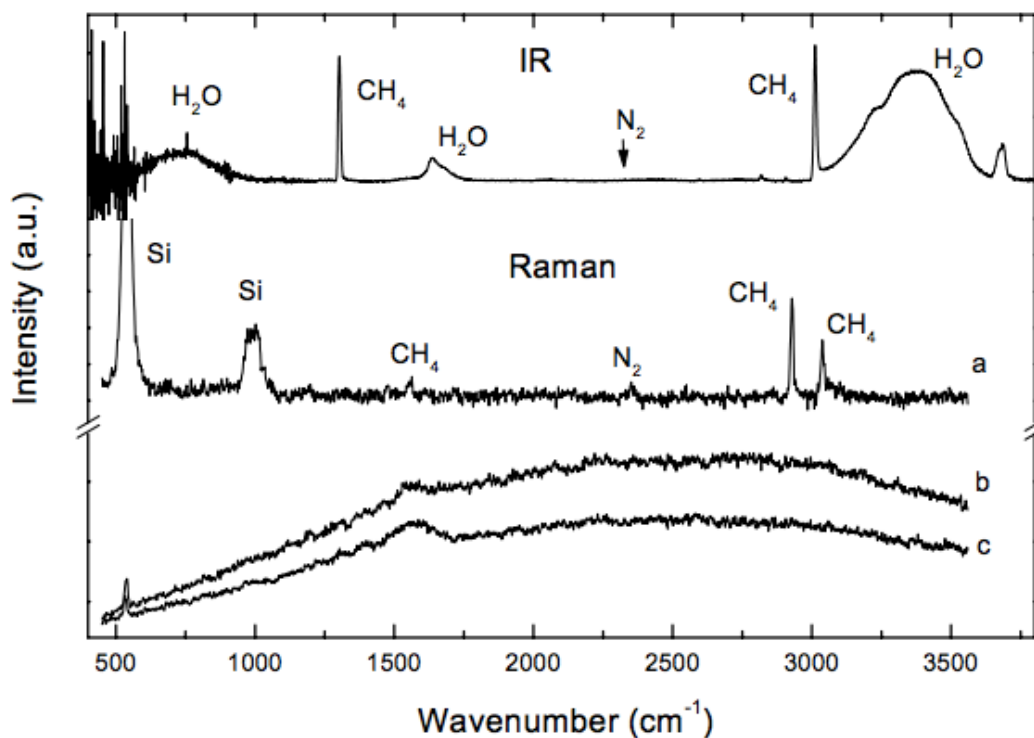
Figure 12. IR (top curve) and Raman spectra of the mixture H2O:CH4:N2 before (curve a) and after (curves b and c, corresponding to doses of 378 eV/16 amu and 825 eV/16 amu respectively) irradiation with He+ (30 keV) ions at low temperature (12 K). In spectra b and c the ice features are undetectable because of the intense fluorescence background. The arrow in the IR spectrum indicates the position of the N≡N symmetric stretching mode, which cannot be observed. Fig. 3 [39].

11.1.3 H_2O

Earth atmospheric temperatures are too warm for H_2O's Raman signatures too show. The predicted vibrational modes are shown below.
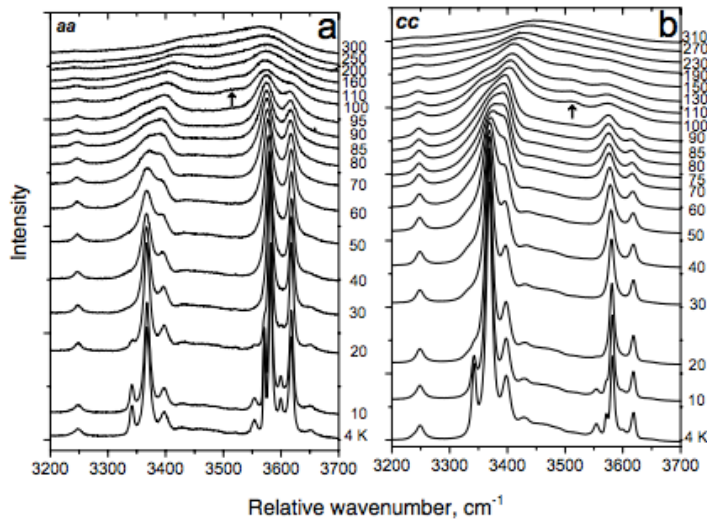
FIGURE 5. Temperature evolution of the polarized spectra showing the O-H and H₂O stretching modes in hemimorphite; (a) *aa*-spectra and (b) *cc*-spectra. The appearance of the new band at around 3500 cm⁻¹ at $T \geq 100$ K is shown by the arrow.

Figure 13. [40]

11.2 Thermoelectric Review of the Tyndall Experiment

A clip with Dr Stewart demonstrating the greenhouse gases is for intents and purposes is a reconstruction of the 1859 origin Tyndall experiment[41]. Modern materials and technology are used in place of the original (as shown in Figure 1 below): the thermal imaging camera stands in for the single thermopile, and thin plastic at either end of the tube.
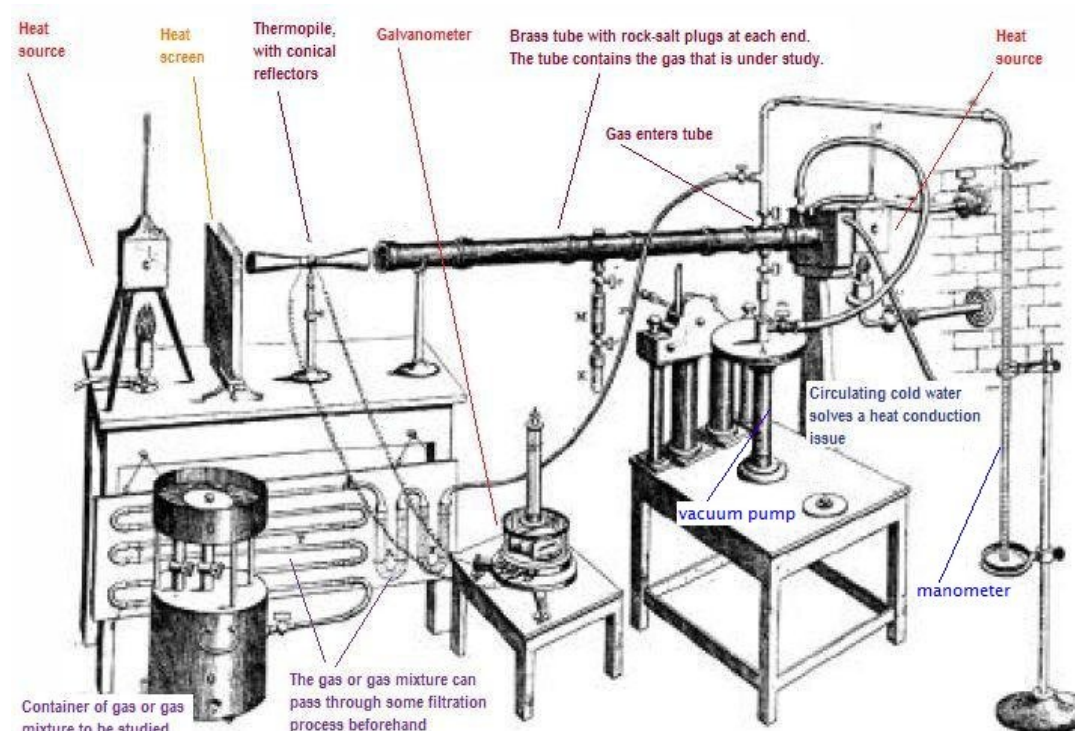
Figure 14. Tyndall's 1859 Setup For Measuring (Radiant Heat Absorption By) Gases. Reference [5]

The image of a flicking candle is seen first in the IR camera. As the CO_2 is released and fills the (sealed) cylinder, the bright candle image disappears and is replaced by a blue colour screen. Dr Stewart concludes just as John Tyndall did: "The CO_2 absorbs the infrared or is essentially trapping the heat from the candle."

If this claim is true, the claim must be said and understood in the knowledge of (the above) thermoelectric theory and practical application practice 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 particularly spectrum range observed – a totally different conclusion would be drawn.

With this been said, an alternative interpretation and conclusion of both the Tyndall experiment and the modern laboratory experiment (above) may read as

follows. The first thermal image 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 IR transparent (IR inactive or non-thermoelectric substances). The only substance able to generate electricity is the candle flame, and hence – given the camera display is calibrated for the hot flame and not its background radiation – the flame's image is displayed. The next scene shows the flame image slowly to a blue colour as the CO_2 gas is released into the tube.

11.3 Raman Spectroscopy Chemistry Tutorial

This following Chemistry tutorial note states clearly role of Raman spectroscopy as a shadow test for IR spectroscopy [42].

3. Are the stretching modes of the diatomic molecules O_2 and N_2 infrared active? Why or why not? Are the stretching modes of O_2 and N_2 Raman active? Why or why not?

The stretching mode of a homonuclear diatomic molecule does not lead to a change in the dipole moment of the molecule; hence, the stretching mode is **not IR active**. The stretching mode of a homonuclear diatomic molecule does lead to a change in polarization of the molecule; hence, the stretching mode is **Raman active**.

Another way to consider this is that since O_2 and N_2 possess centers of symmetry, the stretching mode must be Raman active because it is IR inactive.

11.4 The following text is a (typical) chemistry explanation as to why N_2 and O_2 are not GHG's [43]:

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