

Quantum Mechanics and Raman Spectroscopy Refute Greenhouse Theory

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Abstract

Greenhouse theory's premise – nitrogen and oxygen are not greenhouse gases as they do not emit and absorb infrared radiation – presents a paradox; it contradicts both quantum mechanics and thermodynamics – where all matter above absolute 0^0 Kelvin radiates IR photons. It was hypothesised these gases do radiate IR photons at quantum mechanics predicted spectra, and these spectra are observed by IR spectroscopy's complement instrument, Raman Spectroscopy; and N_2 spectra can be demonstrated to absorb IR radiation by experiment, and application of the N_2 - CO_2 laser. It was found the gases do possess quantum predicted emission spectra at 2338cm^{-1} and 1556cm^{-1} respectively, both well within the IR range of the EMS, and are only observed – and their temperatures accurately measured – by Raman Spectrometers. Raman spectrometers make IR spectroscopy redundant: they measure, more accurately, the Keeling curve, and have application with meteorological Lidars and planetary atmospheric analysis. The N_2 - CO_2 Laser showed – contrary to current greenhouse theory – N_2 absorbs electrons or (IR) photons at its – metastable 'long lasting' – said spectra mode. It was argued atmospheric CO_2 , as a law, is heated by the same mechanism as the N_2 - CO_2 laser: nitrogen (first) and the entire atmosphere absorbs IR radiation directly from the Sun, just as it heats H_2O on the ocean surface. With these findings, greenhouse theory as it stands is wrong – all gases are GHGs – and is in need of review.

Key Words: Greenhouse effect, Raman Spectroscopy, Quantum Mechanics, N_2 , O_2 , N_2 - CO_2 Laser, Spectroscopy

Table of Contents

1	Introduction.....	5
2	Methods.....	6
2.1	IR Spectra Prediction of N₂ and O₂ by Quantum Mechanics.....	6
2.2	Observing N₂ and O₂ with Raman Spectroscopy	6
2.2.1	Raman spectroscopy	6
2.2.2	No Confusion between Raman Spectroscopy and the Raman Effect	7
2.2.3	Approach and Scope of the RER.....	7
2.2.4	Operation of the Raman Exhaust Report (RER).....	7
2.2.5	Setup:.....	8
2.2.6	The Laser:.....	8
2.2.7	Temperature Measurement.....	8
2.3	Raman Lidar for Remote Sensing of CO₂ Leakage at an Artificial Carbon Capture and Storage Site.....	9
2.4	Evidence of N₂'s 2338 cm⁻¹ IR Absorption: the N₂-CO₂.....	10
2.4.1	N ₂ -CO ₂ Laser: A Practical Application of 'Radiated N ₂ at 2338 cm ⁻¹	10
2.4.1.1	The CO ₂ -N ₂ Laser	11
3	Results	11
3.1	N₂ and O₂ IR Spectra Predicted by Quantum Mechanics	11
3.2	Atmospheric IR and Raman IR Spectra Lines	12
3.3	Raman Gas Vibrational Modes Observation	13
3.3.1	N ₂ 2338cm Raman Vibrational Mode Spectra.....	14
3.3.2	O ₂ 1556 cm ⁻¹ Vibration Mode and Concentration.....	15
3.3.3	H ₂ O 3652 cm ⁻¹ Vibrational Mode	16
3.3.4	CO ₂ 1338 cm ⁻¹ Vibrational Mode (and Temperature).....	17
3.4	Gas Temperature Measurement by Raman Spectroscopy	18
3.4.1	N ₂ Temperature.....	18
3.4.2	Raman CO ₂ Temperature	20
3.5	Gas Concentrations by Raman Spectroscopy.....	21
3.5.1	H ₂ O Concentrations.....	21
3.5.2	CO ₂ Concentration	22
3.5.3	N ₂ /O ₂ Ratio.....	23
3.5.4	NO.....	24
3.6	RER Conclusion	24
3.7	Raman lidar sensing of CO₂ leakage - Results.....	25
3.8	N₂-CO₂ Laser Results	26
3.9	Natural N₂-CO₂ Lasers.....	27
3.9.1	'Blackbody CO ₂ Laser' Showing N ₂ Heated by Sunlight.....	28
3.9.2	Experimental Setup.....	29
4	Discussions.....	30
4.1	The Laws and Physics Central to Radiation Theory	30
4.1.1	Planck's Law	30
4.1.2	Boltzmann Constant	30
4.1.3	The Stefan-Boltzmann Law.....	30
4.1.4	Kirchhoff's Law of thermal radiation.....	31
4.1.5	Spectroscopy:.....	31
4.1.6	Quantum Mechanics Schrödinger Equation.....	31
4.2	Quantum Mechanics IR Spectra Predictions.....	31
4.3	Spectra Observation by Raman Spectroscopy.....	32
4.4	Temperature Measurement by Raman Spectroscopy.....	32
4.4.1	Temperature Detector Equivalence	32

4.4.2	Raman Temperature Measurements and the Boltzmann Constant	32
4.4.3	Raman Measurements and the Stefan Boltzmann Law	33
4.4.4	N ₂ and O ₂ and Planck's Law	33
4.4.5	Equivalence – Dual Modes H ₂ O	33
4.4.6	The Significance of Equipartition and Degrees of Freedom and Normal Modes	33
4.4.6.1	CO ₂ 's 1338 cm ⁻¹ and the Principle of Equipartition	33
4.4.7	Raman Spectroscopy and the Blackbody Curve.....	34
4.5	Raman lidar sensing of CO₂ leakage - Discussions [7].....	34
4.6	Other Applications of Raman Spectroscopy.....	35
4.6.1	Measuring Atmospheric Gas Concentrations (Keeling Curve) with Raman	35
4.6.2	Raman Solar System Space Probe Applications.....	36
4.6.2.1	Venus	36
4.6.3	Onboard (Raman) Lidar Detects Turbulence, Volcanic Ash Near and Far Photonics Spectra.....	37
4.6.4	Raman LIDAR and the Atmosphere.....	38
4.6.4.1	Lidar can reveal the temperature of the atmosphere:.....	39
4.6.5	Other Uses for Raman Spectroscopy.....	41
4.7	Radiating N₂: N₂-CO₂ LASER – Discussions.....	41
4.7.1	Stimulated and Spontaneous Emission	42
4.7.2	The CO ₂ Laser, and the Question of Radiation?	42
4.7.3	Is Discharge of Electrons Radiation?	42
4.7.4	Frank-Hertz Experiment.....	42
4.7.5	Collisions Implausible: Convection Paradox.....	42
4.7.6	Implications for IR Spectroscopy.....	43
4.7.7	N ₂ and Kirchhoff's Law	43
4.7.8	Metastable N ₂ and the Greenhouse Atmosphere.....	43
4.7.9	Metastable N ₂ from 'Collisions' and not Radiation	43
4.7.10	IR Photon Absorbing Atmospheric N ₂ : An Atmospheric Law of Physics.	44
4.8	Blackbody Emission Spectra with Raman N₂, O₂, and CO₂ 's Non-IR Modes [42]	44
4.9	Raman and IR Spectroscopy Complementary Instruments and Spectra	45
4.9.1	Other Molecules with Dual Raman thermoelectric	46
4.9.1.1	Ethanol.....	47
4.9.2	CO ₂ 's 1338 cm ⁻¹ Raman Active mode showing on IR spectra.....	48
4.9.3	N ₂ O's Shared IR and Raman Modes	49
4.9.4	Ozone O ₃ IR and – inferred by – Raman	50
4.10	H₂O: Dual Raman and IR Active	51
4.10.1	H ₂ O's 3652 cm ⁻¹ : IR and Raman Modes Equivalent.....	51
4.10.2	Contravention of the Rule of Mutual Exclusion	52
4.10.3	Solar IR Insolation Radiation Heats Water	53
4.10.3.1	Other 'IR' Active Thermoelectric spectra of H ₂ O	53
4.11	Augmenting the IR Spectroscopy and Raman Atmosphere	54
4.11.1	The Augmented Fourier Greenhouse Atmosphere spectrum	54
4.11.2	The Implications of Raman Spectroscopy on Current GH Theory	56
4.12	Strengths and Limitations.....	57
4.12.1	N ₂ Absorbing in the 'Hot' Thermosphere and the Aurora.....	57
4.12.2	IR Absorption and Thunder Creation: Lightning Heating the Air	57
4.12.3	IR Absorption and the Incandescent Light Bulb.....	57
4.12.3.1	Non-TE/IR Non-Raman Argon.....	57
4.12.4	Non-Radiant and Non-Conductive N ₂ and O ₂ Heat Capacity Paradox.....	57
4.12.5	Standard (bottle) Greenhouse Experiments, and SHC Measurement.....	58
4.12.6	Real Measurement of Gas Heat Capacity: Equivalent to GH Demonstrations	60

4.12.6.1	Measurement of GHGs Specific Heat proves non-GHGs absorb IR	60
4.12.7	Vibrational Behaviour and Specific Heat Capacity	60
4.13	What is Next?	61
5	Conclusions	62
6	Acknowledgements.....	63
7	References.....	64
8	Appendix.....	72
8.1	Other Uses for Raman	72
8.1.1	CO ₂ 's 1388cm ⁻¹ Excitation: The Dicke effect	72
8.1.2	Medical – anaesthetic RASCAL – Capnography Application.....	72
8.1.3	Geology CO ₂ 1388 cm ⁻¹	72
8.1.4	Automobile Emission Testing.....	73
8.2	Understanding Raman Backscatter and the Low Wavenumbers.....	73
8.2.1	Raman Laser to Wavenumber Correction Calculation	75
8.3	Raman spectra for Non-GHGs and GHGs	75
8.3.1	O ₂ and N ₂	75
8.3.2	O ₂ Spectra.....	77
8.3.3	N ₂ 2338 cm ⁻¹	77
8.3.4	O ₂ 1556.....	78
8.3.5	CH ₄	78
8.3.6	H ₂	80
8.3.7	H ₂ O Raman	80
8.3.8	H ₂ O TE IR.....	81
8.3.9	Ge Germanium.....	81
8.4	Thermal Image with Raman	82

1 Introduction

The current 'standard' model of greenhouse (GH) theory – first developed in the mid 19th Century, before 20th century quantum mechanics – claims the entire thermal-radiation behaviour of the atmosphere is explained by 1-2% of its constituent gases, the special greenhouse gases (GHGs). They are assumed to be the only gases to absorb infrared (IR) radiation; the non-GHGs nitrogen (N₂) and oxygen (O₂) – 99% of the dry atmosphere – do not absorb or emit any IR radiation, at any temperature. Any heat transferred to the non-GHGs comes only from collision with the special GHGs after these are heated from the Earth's surface – there is no heat gained by them directly from the Sun's irradiance.

[1][2]

Notwithstanding these, and the other gases, are very poor thermal conductors, this GH theory of the atmosphere appears to be in direct contradiction with modern quantum mechanics: by Planck's law of radiation all matter above absolute zero Kelvin absorbs and emits infrared radiation, and this should apply N₂ and O₂. This poses a catastrophe – an 'IR catastrophe' – as opposed to the 'UV'. While the science maybe said to be 'settled', as it is claimed to be; it appears the physics and chemistry are not. Either quantum mechanics is wrong, or GH theory is wrong?

By quantum mechanics, all atoms or molecules possess predicted absorption-emission spectra lines (or modes) in the IR range of the electromagnetic spectrum (EMS) by which they radiate. These predicted spectra-bands are observed by one of two types of IR spectrometers: either IR, or Raman spectrometers – and some modes are by both.

It was hypothesised N₂ and O₂ are too GHGs, they obey to the laws of radiation physics. The only reason separating them from the special GHGs is the instrument measuring them, and the fact they do not register with IR spectroscopy. N₂ and O₂ should have IR spectra bands, and these bands should be able to be observed by spectrometers. Further to this, these facts should be applied in a demonstration or real life application to absorb and emit IR photons. By measurement and by practical application they too are GHGs – there are no special GHGs.

This investigation was a review of the 'science' surrounding the non-GHGs and quantum mechanics, followed by practical applications and experiments of Raman IR spectroscopy and the said gases. It reviewed its application in atmospheric studies. To show the gases absorb at IR spectra frequencies the operation of the N₂-CO₂ laser was studied.

Without evoking any of the arguments posited in the current ensuing 'great' political-climate debate surrounding GH theory, this paper aims to address the problem by looking at the 'first principles' physics (4.1). The paper points to the problem being GH theory as it stands is based on 19th Century IR spectroscopy and neglects modern quantum mechanics and the laser based instruments – derived themselves from quantum knowledge. If the non-GHGs are equivalent to the special GHGs, and it is found that it is the instruments that are special; GH theory is wrong or incomplete. From first principles 0th and 1st Laws of

Thermodynamics all gases should transfer their energy towards equilibrium, where previous to this N_2 and O_2 were exempt.

2 Methods

No experiment as such was undertaken, but rather a first principles review of literature, theory, application, and instruments with respect to the hypothesis. The following order of methods in this section is maintained in the results and discussions section.

1. The quantum mechanics IR spectra were researched;
2. Two experiments using Raman spectroscopy to observe these IR spectra was reviewed: The Raman Exhaust Report (RER); and the ‘..Raman Lidar for Remote Sensing of CO₂ Leakage at an Artificial Carbon Capture and Storage Site’
3. An IR absorption application of predicted N_2 spectra was reviewed: the N_2 -CO₂ laser;

2.1 IR Spectra Prediction of N_2 and O_2 by Quantum Mechanics

A review of the literature was undertaken with respect to the predictions made by quantum mechanics of IR spectra of the said gases.

2.2 Observing N_2 and O_2 with Raman Spectroscopy

A review the literature surrounding the observation of the IR emission spectra modes of atmospheric molecules was made. Raman Spectrometers – the complement instrument of ‘IR’ spectrometers – were found to observe the modes of the non-GHGs.

2.2.1 Raman spectroscopy

“That branch of spectroscopy concerned with Raman spectra and used to provide a means of studying pure rotational, pure vibrational and rotation-vibration energy changes in the ground level of molecules. Raman spectroscopy is dependent on the collision of incident light quanta with the molecule, inducing the molecule to undergo the change.” [3]

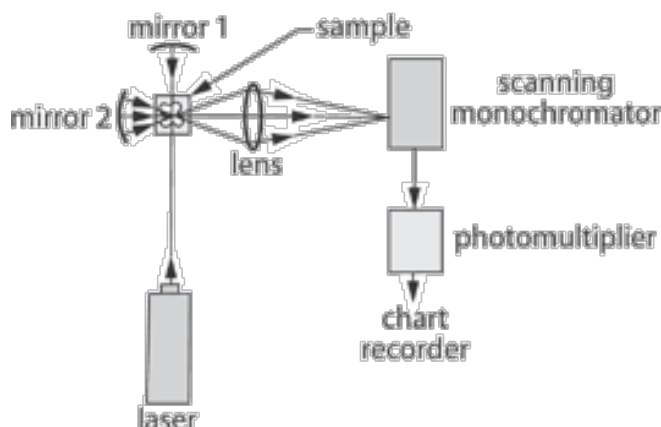


Figure 1 Raman Spectroscopy Configuration.

No direct primary experiment was undertaken in this investigation. Among others, a report of a previously conducted Raman spectrometer application was

referred to. This report called the: FIELD TESTS OF A LASER RAMAN MEASUREMENT SYSTEM FOR AIRCRAFT ENGINE EXHAUST EMISSIONS - 1974 [4]. For the purposes of this investigation 'The Raman Exhaust Report' was termed the RER. The operation of this Raman device (the RER) should correspond to our understanding of quantum mechanics and thermodynamics in that it will measure the predicted vibrational modes of each and every molecule it can, and; also measure the corresponding temperature/energy. Finally, the RER application should invoke questions at the fundamentals of physics: if N_2 and O_2 do radiate, how is it so – if it is assumed by GH theory not to? How have they become so hot so quickly from collision (conduction) alone when they are assumed they do not absorb any IR heat-energy.

2.2.2 No Confusion between Raman Spectroscopy and the Raman Effect

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

Appendix 8.2 addresses this discrepancy between the Raman 'Spectroscopy' and the Raman 'Effect'.

Raman spectroscopy shows these modes are real (Figure 7), and we shall soon learn they correspond to IR radiation.

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

2.2.3 Approach and Scope of the RER

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

2.2.4 Operation of the Raman Exhaust Report (RER)

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

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

“Laser induced Raman and fluorescent measurements were made in the exhaust of a T53-L13A gas turbine engine with a new field portable instrument devised specifically for gas turbine exhaust emission measurements. The gas turbine exhaust was analysed by conventional instruments for CO, CO₂, NO, NO₂, total hydrocarbons, smoke and temperature, and these data were used as a “calibration” standard for the evaluation of the laser Raman instrument, (p. v). “

2.2.5 Setup:

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

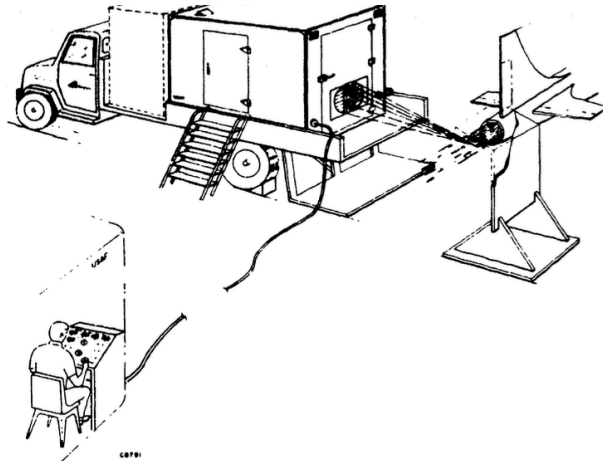


Figure 28 Schematic of Laser Raman Aircraft Engine Exhaust Emissions Measurement System

Figure 2. RER Setup. Pg. 46 [5]

“The gas analysis equipment used as a comparative standard for the laser Raman consisted of detectors similar to those specified by the SAE. They consisted of infrared detectors for CO, CO₂, and NO, a flame ionization detector for total hydrocarbons, and a polarographic detector for NO and NO₂ as shown in the schematic of Figure 14. Thus, NO was measured by two different detectors. A list of the instruments used and their ranges is given in Table I.” (P.20)

2.2.6 The Laser:

“The laser transmitter was an Avco Model C5000 pulsed nitrogen laser operating at a wavelength of 3371 Å (337.1 cm⁻¹).” (p.4)

2.2.7 Temperature Measurement

“Raman spectroscopy can be used to determine the temperature of a material when other more direct means are either impractical or not possible. The material’s temperature can affect the peak position of Raman bands. When a Raman band shifts significantly with temperature, the monitoring of the peak position can be the most straightforward manner of determining temperature provided the Raman spectrometer has sufficient spectral resolution. Another method is to determine the temperature from the ratio of the Stokes and anti-Stokes signal strengths of a given Raman band. The latter method requires the ability to detect light at wavelengths longer and shorter than that of the laser and an accurate measurement of the wavelength-dependent instrument response function.” [6]

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

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

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

“Raman spectra at elevated temperatures were obtained from the exhaust of a propane/air burner. Figure 18 shows the measured spectrum of the nitrogen Raman band at 3658Å at a temperature of 1000 K and measured with a thermocouple in the burner exhaust.” Pg. 32 [5]

2.3 Raman Lidar for Remote Sensing of CO₂ Leakage at an Artificial Carbon Capture and Storage Site

Raman lidar was used to detect CO₂ leakage: *Development of Raman lidar for remote sensing of CO₂ leakage at an artificial carbon capture and storage site [7].*

The apparatus, methods and the techniques are standard ‘Raman spectroscopy’ as described in this paper and shown below on in Figure 3. CO₂ concentration mixing ratios were measured.

“Since N₂ is present at a constant rate in dry air, the N₂ Raman signal, PN₂, is used as a measure of dry air [13]. The CO₂ mixing ratio can be derived from the normalization signal, which is the quotient of the CO₂ Raman signal divided by the N₂ Raman signal.” Page 3.

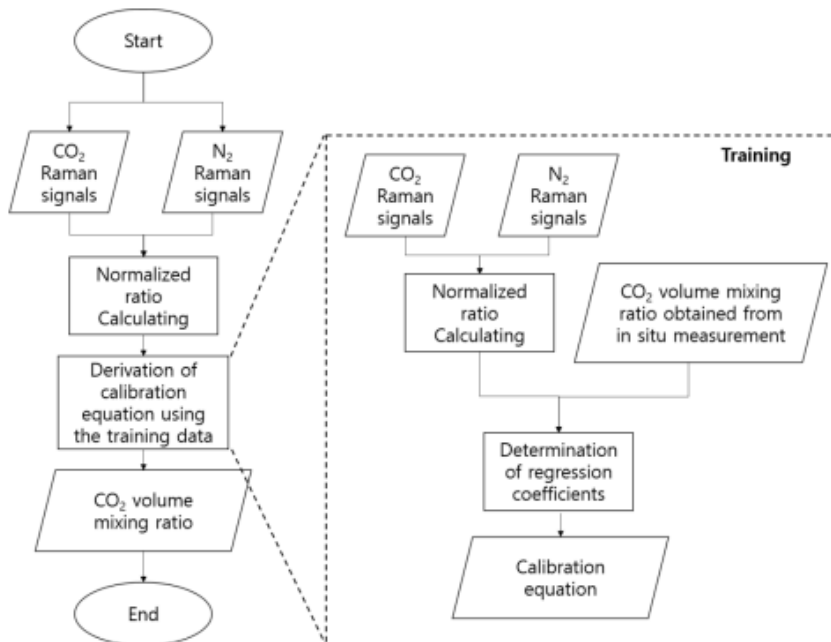


Figure 1. Flow chart for calculating the CO₂ volume mixing ratio using the Raman lidar system.

Figure 3 Show Raman spectroscopy process towards Concentration Ratios N₂ and CO₂

In an experiment the Raman Lidar was setup (Figure 4) to measure CO₂ concentrations from a mock gas leak. Results were compared to an 'IR' thermoelectric CO₂ measuring instrument (CO₂ in situ).

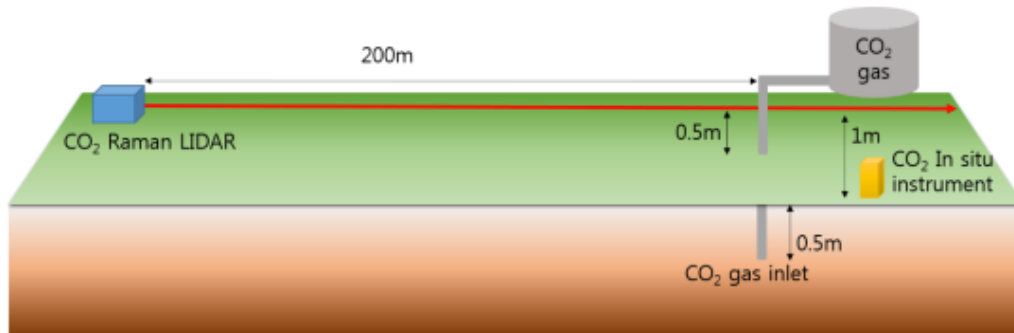


Figure 7. Schematic representation of the Eumseong Environmental Impact Evaluation Test Facility for the seepage of geologically stored CO₂.

Figure 4. Raman Lidar CO₂ 'leakage' Experiment.

An experiment was also setup to measure the CO₂ output from car on a motorway over a distance of 750 metres (Figure 19).

2.4 Evidence of N₂'s 2338 cm⁻¹ IR Absorption: the N₂-CO₂

For the Raman theory – of a radiating 'non-GHG' atmosphere – to have any validity, there should be instances that show coherence with the theory. The following are instances where the non-GHG modes are radiated, and in total compliance with quantum mechanics offer such examples: the CO₂ laser and absorbing thermosphere N₂ molecules – where there is only radiation as a transfer of heat-energy.

2.4.1 N₂-CO₂ Laser: A Practical Application of 'Radiated N₂ at 2338 cm⁻¹

The CO₂ Laser offers a pragmatic real-life application – or kind of experiment – invoking and testing both of the key atmospheric gases in question, N₂ and CO₂, revealing their real relationship between them when they are radiated – though it is not currently interpreted as so. After an understanding of the CO₂ Laser process it could be assumed – contrary to standard belief – N₂ in the atmosphere is the gas that affects – and actually forces – the CO₂.

All theory surrounding the CO₂ Laser points to the role of N₂ has in 'pumping' the CO₂ as an essential part of the process; so much so – it is explained in all textbooks – the laser will not operate without this 'absorbing/emitting' property of N₂ when radiated. The relationship is so close these lasers are technically termed **N₂-CO₂ Lasers**. A closer look at the physics behind the laser reveals N₂'s true nature, and its absorption property at its **2338cm⁻¹** mode; a property absolutely ignored in atmospheric 'GH' theory. It is as if the scientist describing the CO₂ laser are oblivious of the ramifications this knowledge would mean to GH theory; that they are using the very same mechanics – both physics and chemistry – that the Raman measurements point to in the atmosphere; only here the gas is excited at the said modes.

2.4.1.1 The CO₂-N₂ Laser

Lasers all have the following key components:

1. An active medium – for the CO₂-N₂ laser it is the CO₂ and N₂ that are of interest;
2. Energy input/ pumping source/ high voltage discharge
3. Optical Feedback, this is not of interest in the investigation
4. Population inversion, this is essential – more electrons must be in an excited state than lower state; this is very important.

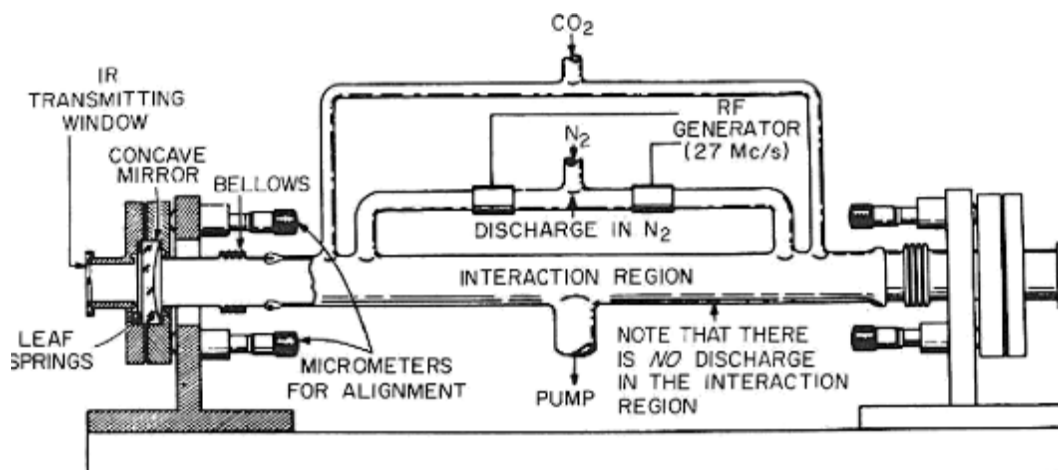


Fig. 1.1. System developed by Patel (1964b) demonstrating laser emission due to transfer of vibrational energy from N₂ to CO₂.

Figure 5. The CO₂ Laser [8]

"Infrared laser emission from CO₂ was first reported by Patel (1964) and others in pulsed discharges through pure CO₂. In this system N₂ is excited in a rf discharge to form vibrationally excited N₂ molecules which stream into an interaction region to mix with unexcited CO₂. The CO₂ is then vibrationally excited through the reaction which occurs efficiently." Pg. 1 [8]

3 Results

The results will follow in the order they are presented in the methods section.

3.1 N₂ and O₂ IR Spectra Predicted by Quantum Mechanics

N₂ and O₂'s modes are predicted at the frequencies **2360 cm⁻¹** and **1580 cm⁻¹** respectively – well within the infrared band of the electromagnetic spectrum, [9]. These modes are identified in the context of temperature, many papers reveal these predicted vibration functions [10], [11], [12]. Table 1 (below) is one example: and shows the predicted wavenumber where ω_e (column 3) of N₂ and O₂'s predicted modes at 2360 cm⁻¹ and 1580 cm⁻¹. In the RER these predicted modes are revealed by Raman Spectroscopy in Figure 8 and Figure 9.

Table 1. Table of predicted N₂ and O₂ vibration modes derived from the Schrodinger equation [9].

The third column from the left shows the vibration mode wavenumbers. Note H₂ is predicted (and also Raman observed).

Molecular Data and Statistical Weights of the <i>J</i> Levels for some Linear Molecules ^a								
Molecule	Molecular data					Nuclear spin	Statistical weight (<i>g_n</i>)	
	<i>B_e</i> (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	α_e (cm ⁻¹)	<i>r_e</i> (Å)		<i>J</i> (even)	<i>J</i> (odd)
¹ H ₂	60.80	4395	117	2.99	0.742	1/2	1	3
² H 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
¹ H ³⁵ Cl	10.59	2990	52.05	0.302	1.275	...	1	1
¹² C ¹⁶ O ₂ ^b	0.3906 (<i>B₀</i> = 0.3895)				1.162 (<i>r₀</i> = 1.163)	0	1	0
					1.202 (CC)			
¹² C ₂ ¹ H ₂ ^b	1.1838 (<i>B₀</i> = 1.1769)				(<i>r₀</i> = 1.207) 1.059 (CH) (<i>r₀</i> = 1.059)	1/2	1	3

^a Reference (1).

^b Reference (6).

570 / Journal of Chemical Education

3.2 Atmospheric IR and Raman IR Spectra Lines

Table 2 below shows all the emission spectra modes for the atmospheric gases, derived solely from the radiation physics principles listed above (4.1). The modes are both IR and the Raman. The outstanding issue from this table, and the central issue to this paper, is that the listed Raman Modes or Spectra (also shown on the spectrogram Figure 31) are not considered to behave as so-called 'IR-active' modes; in that they do not radiate or emit any IR radiation – further contravening with the above principles of physics. These are the Raman modes of they are know as non CO₂'s **1338 cm⁻¹**, H₂O's **3652 cm⁻¹** and CH₄'s two **2914 cm⁻¹** and **1303 cm⁻¹**. These Raman modes, among others, are shown clearly in Figure 6 in normal atmosphere by Raman spectroscopy.

Table 2. Atmospheric Gases with their Respective IR Range Vibrational Modes . Modes

highlighted in red are of particular interest; they, through the law of equipartition show all modes are the equivalent – and it as the detectors of them that are different.

Molecule	Vibration Mode or Band: wavenumber (frequency)	IR and Raman Properties	Mode Type
H ₂ O	3652 cm ⁻¹ (2.74μm)	IR and Raman	Symmetric
	1595 cm ⁻¹ (6.25μm)	IR and Raman	Asymmetric
	3756 cm ⁻¹ (2.66μm)	IR and Raman	Asymmetric
CO ₂	1388 cm ⁻¹ (7.2μm)	IR and Raman	Symmetric
	2349 cm ⁻¹ (4.257μm)	IR	Asymmetric
	961 cm ⁻¹ (10.6μm)	IR	Asymmetric

	667 cm^{-1} (14.992 μm)	IR	Asymmetric
CH ₄	3020 cm^{-1} (3.312 μm)	IR	Asymmetric
	2914 cm^{-1} (3.431 μm)	Non IR; Raman	Symmetric
	1508 cm^{-1} (6.5 μm)	IR	Asymmetric
	1303 cm^{-1} (7.7 μm)	Non IR; Raman	Symmetric
N ₂	2338 cm^{-1} (4.2 μm)	Non IR; Raman Active	Symmetric
O ₂	1556 cm^{-1} (6.25 μm)	Non IR; Raman Active	Symmetric
O ₃	1103 cm^{-1}	IR (Raman Active?)	
	701 cm^{-1}	IR	
	1042 cm^{-1}	IR	

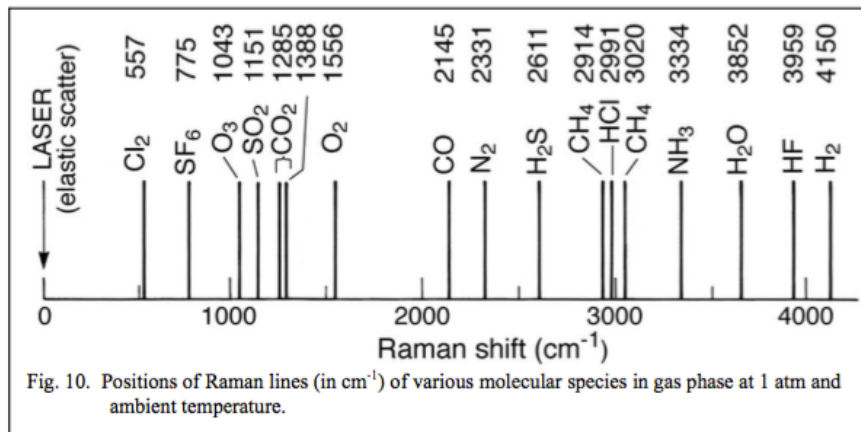


Figure 6. The Raman Atmosphere. Spectrograph of the Earth's Atmospheres gases and their Raman modes. [13] Notice these frequencies (of the molecules) are not (from the table above) IR in nature, and are not symmetric in nature.

3.3 Raman Gas Vibrational Modes Observation

The Raman active vibrational modes of atmospheric gases N₂, O₂ and CO₂ were observed at the (above) predicted wave numbers and shown as a report in Figure 7 below:

"..infrared and Raman spectra: the interaction of the molecule with electromagnetic radiation. The interaction of the electric vector of the electromagnetic radiation with the molecule will give rise to infrared absorption and inelastic scattering (Raman) spectra..."pg. 12 [14]

"Raman data were obtained which could be used to accurately measure the mole fractions of the major species in the flow, i.e. N₂, O₂, and CO₂ over the entire range of engine operation conditions from idle to full power. These Raman measurements were compared with the expected values of the specie concentrations as calculated from the measured fuel:/air ratio of the various operating conditions." (P.2) [15]

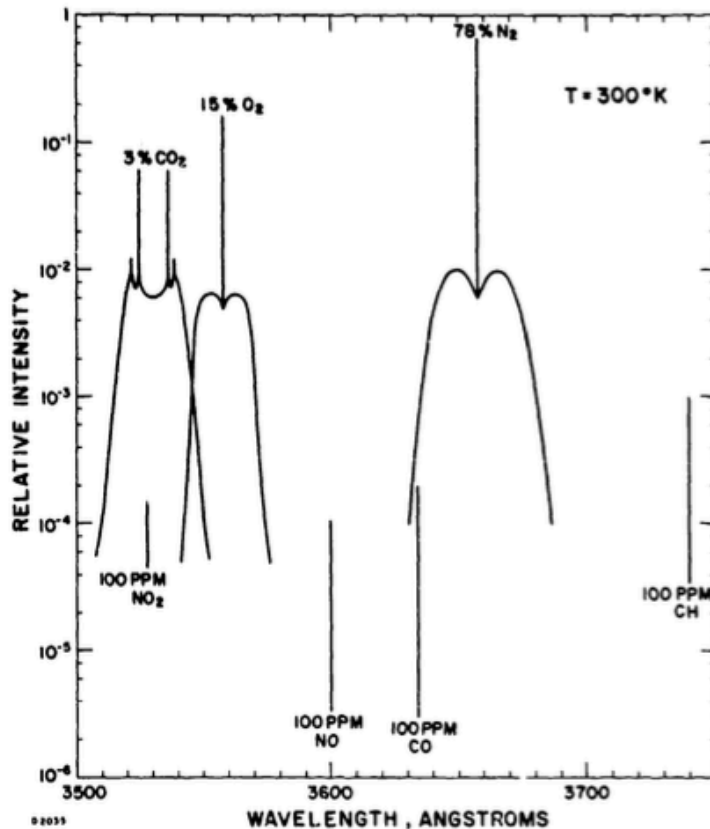


Figure 3 Typical Raman Spectrum from Room Temperature Combustion Gases Using a 3371 Å Laser Source

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

Notice not only the wave numbers for the different gases are shown but also their respective concentrations.

The following figures show Raman Spectra in detail:

"Initial tests were conducted in air at the AVCO Everett Laboratories to verify the predicted performance of the laser Raman field unit. Figures 18, 19, and 20 show spectra obtained in the spectral regions that correspond to vibrational transitions in N_2 , NO and H_2O at 2330 cm^{-1} , 1876 cm^{-1} and 3652 cm^{-1} that will produce Raman lines at 3658 , 3600 , and 3844 Å , respectively." Pg. 43

3.3.1 N_2 2338cm Raman Vibrational Mode Spectra

The Raman spectra of N_2 molecule's 2338 cm^{-1} mode is shown below in Figure 8.

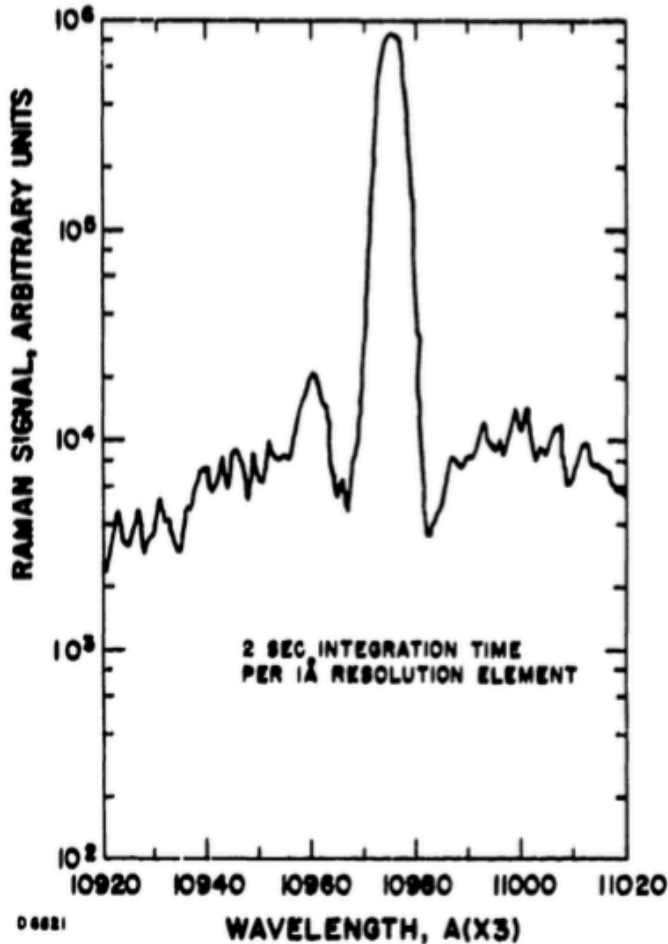


Figure 18 Ambient Air Nitrogen Vibrational Raman Line at 2330 cm^{-1}

Figure 8. 'Figure 18' N_2 2330 cm^{-1} Raman Spectra. Pg. 32 [15]

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

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

"Raman measurements were made of the O_2 concentrations in the T-53 engine exhaust. These measurements show excellent agreement when compared with the expected values of the concentration on the basis of the measured fuel/air ratio from the operating engine. Typical data of the O_2 vibrational Raman line in the hot exhaust gases are shown in Figure 31. The system was calibrated in the field for effective cross section and system transfer function by using the O_2/N_2 ratio obtained from ambient air and by assuming that air is 21% O_2 and 78% N_2 on a mole basis. " (P.43)

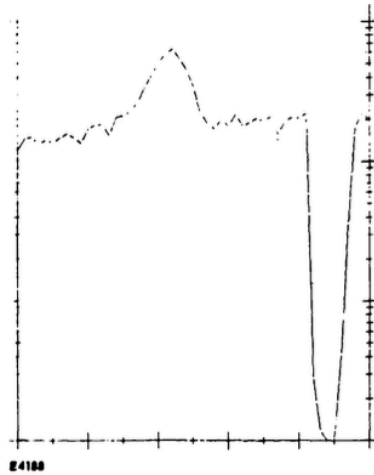


Figure 31 Typical Spectral Data of O₂ in Hot Exhaust Gases

Figure 9. O₂ 1556 cm⁻¹ Raman Spectra. Pg. 41 [15]

3.3.3 H₂O 3652 cm⁻¹ Vibrational Mode

H₂O's Raman mode was observed; its spectra is shown in Figure 10 below.

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

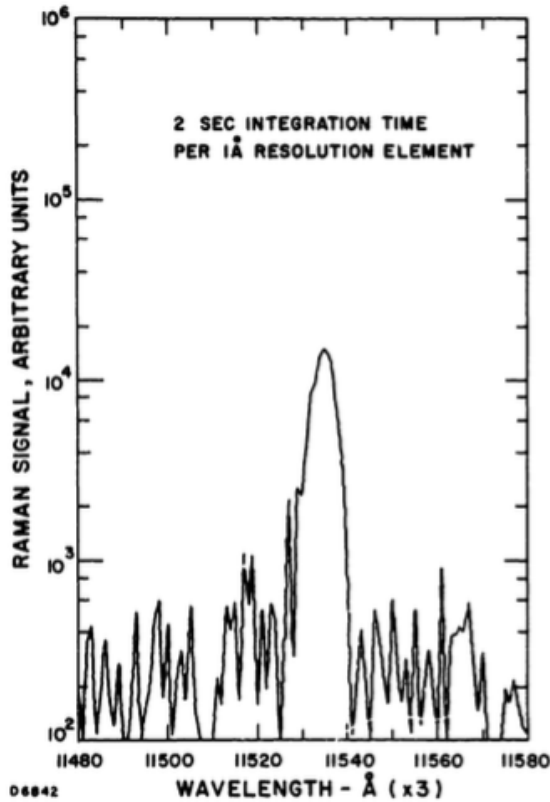


Figure 20 Atmospheric Water Vapor Vibrational Raman Line at 3652 cm⁻¹

Figure 10. H₂O 3652 cm⁻¹ Raman Spectra. Pg. 34 [15]

3.3.4 CO₂ 1338 cm⁻¹ Vibrational Mode (and Temperature)

Carbon dioxide's predicted 1338 cm⁻¹ mode was observed and its spectra are shown in Figure 11 below.

"A further example of a room temperature Raman spectrum is shown in Figure 17, which is the spectrum of the CO₂ doublet at 1285 cm⁻¹ and 1388 cm⁻¹ wave numbers."

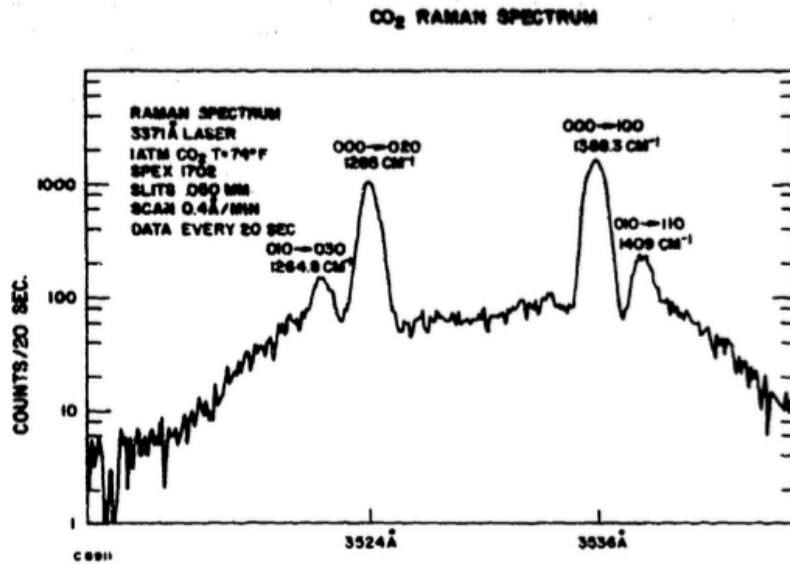


Figure 17 Experimental Raman Spectrum of Carbon Dioxide at Room Temperature

Figure 11. CO₂ 1338 Raman Spectra [5]

"Of special interest is the appearance of secondary peaks at 1265 cm⁻¹ and 1409 cm⁻¹ wave numbers which correspond to transitions from the lowest excited vibrational level of CO₂, the 010 level. This level is appreciably populated even at room temperature. Measurement of the ratio of the secondary to the primary peak is a sensitive means of temperature measurement throughout the temperature range of interest for turbine exhausts as will be shown later in this report." [5] (P.32)

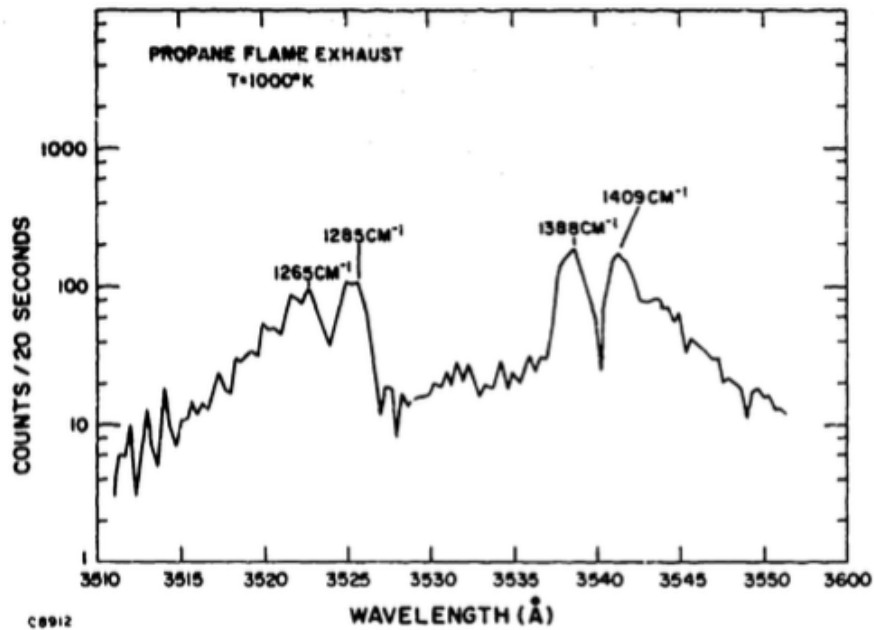


Figure 20 Experimental Raman Spectrum of Carbon Dioxide at -1000°K in a Propane/Air Burner Exhaust

Figure 12. CO₂ Spectra. Pg. 33 [5]

3.4 Gas Temperature Measurement by Raman Spectroscopy

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

*"The temperature profiles obtained in this way (Raman) are plotted in Figure 37 and appear quite reasonable. Thermocouple measurements in the exhaust stream gave an average of 7250 K for the 7% power point and 8900 K for the 100% power point, which is good agreement with the Raman data. **Since it is not subject to thermocouple heat loss corrections, the laser Raman data is inherently a more reliable and accurate' thermometer than a thermocouple.** Further work is required however to definitely establish the precision of the laser Raman method as a hot gas temperature measurement technique. (p. 54)"*

3.4.1 N₂ Temperature

"Accurate temperature profiles were obtained in the T-53 exhaust using laser Raman scattering from nitrogen via the density method. The spectral analysis of "hot bands" was found to be a less accurate method in the T-53 exhaust because of the high level of laser induced fluorescence. Although the feasibility has now been demonstrated, further work is required to quantify the precision of the laser Raman method for temperature measurements in aircraft engine exhaust streams." (Pg. 59)[15]

"The sensitivity of the method is shown in Figure 27, which is a plot of the ratio of the Raman scattering at 3634 Å to the Raman scattering at 3658 Å for pure nitrogen as a function of temperature. Over the expected range of turbine exhaust operation, i. e. 9000K to 12000 K. the uncertainty in the ratio is 9% per 100°K or about 1% per 11K temperature uncertainty- an attainable value using the

(010)/(000) CO2 Raman ratio method as.. discussed. Since the Raman intensity in the $\Delta J = -2$ side band of N_2 (with circular polarization) corresponds to about an apparent level of 1000 PPM of CO a 1% measurement of the side band intensity would enable detection and measurement of 10 PPM CO. This is difficult, requiring an S/N of 100 at low signal levels, but can in principle be done.” (P.41)[5]

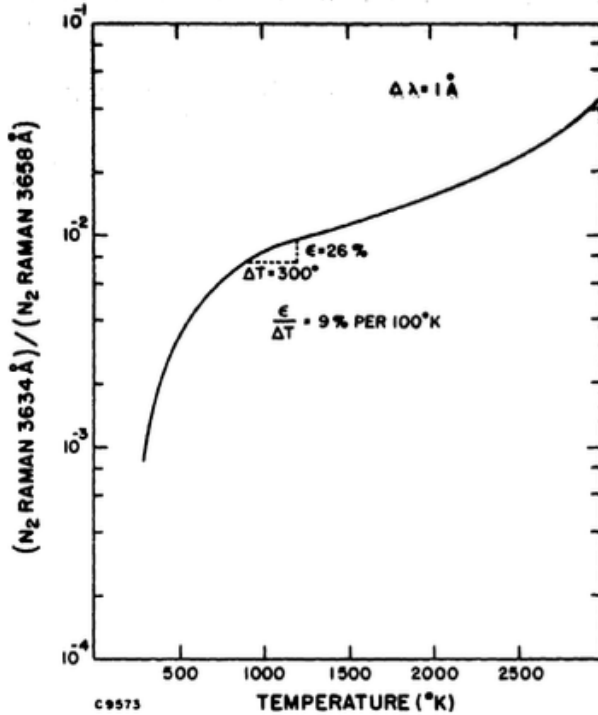


Figure 27 The Computed Ratio of Nitrogen Raman Scattering ($\Delta J=2$) at $\lambda = 3624 \text{ \AA}$ to Nitrogen Raman Scattering ($\Delta J=0$) at $\lambda = 3658 \text{ \AA}$

Figure 13. N_2 Prediction to Observation. Temperature measurement of a Non GHG by Raman spectrometer at N_2 's 2330 cm^{-1} predicted mode. Pg.43 [5]

“5. TEMPERATURE SENSITIVITY

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

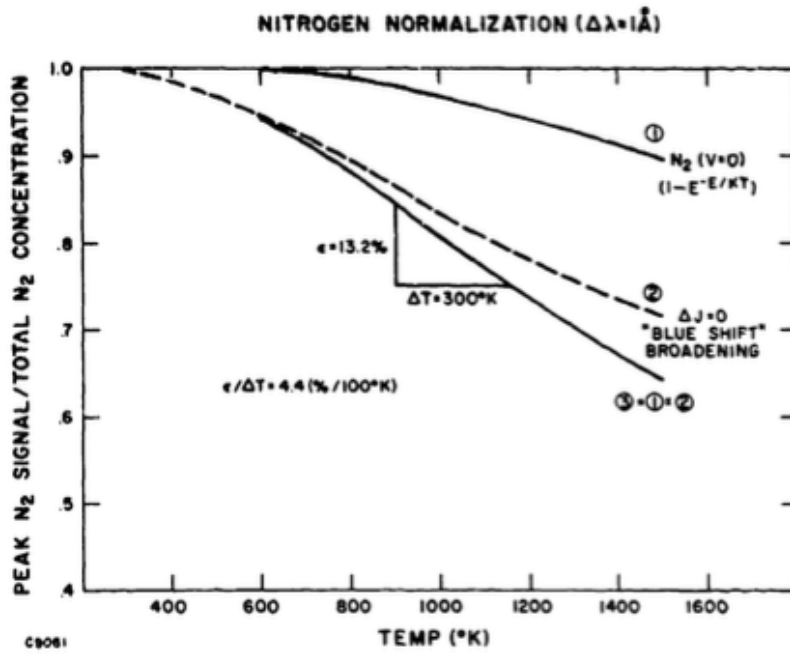


Figure 21 Computed Nitrogen Normalization Error as a Function of Temperature for a Detector with a Resolution of 1 Å

Figure 14. N₂ Temp. Pg.34 [5]

3.4.2 Raman CO₂ Temperature

“Figure 22 shows the estimated ratio of the peak (000) CO₂ signal to the total CO₂ concentration as a function of temperature.

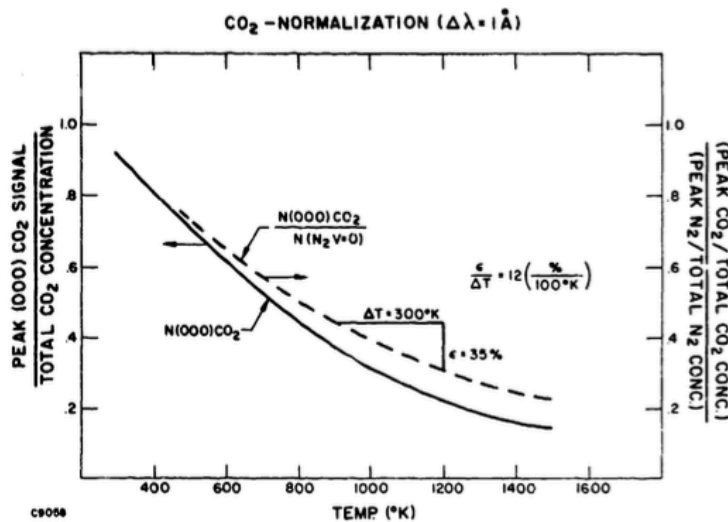


Figure 22 Computed Carbon Dioxide Normalization Error as a Function of Temperature for a Detector with a Resolution of 1 Å

Figure 15. CO₂ Temperature Measurement by Raman Spectrometer. Pg 35[5]

From the above, it is apparent that an independent method of temperature measurement is a desirable adjunct to a laser Raman turbine exhaust measurement system. The use of the CO₂ Raman spectrum seems to be a reasonable means to satisfy this requirement. **In particular the measurement of the ratio of the (000) CO₂ peak to the (010) CO₂ peak seems especially well suited for a temperature determination.**

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

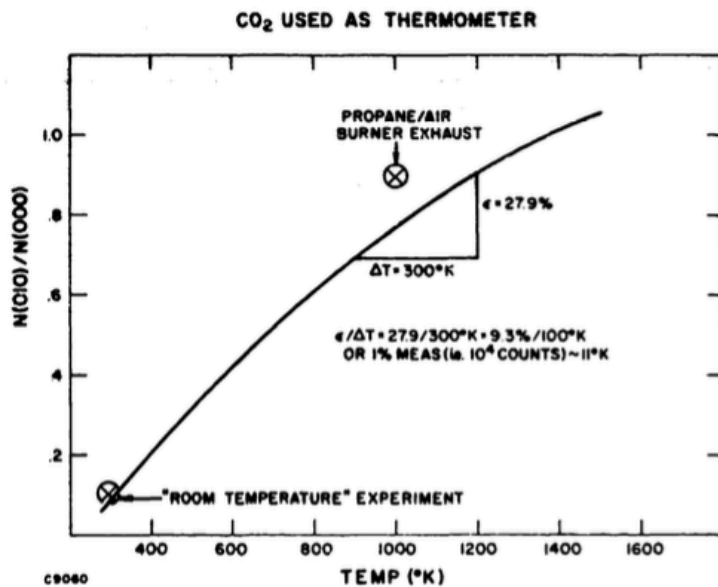


Figure 23 The Computed Temperature Dependence of the Ratio of the Raman Scattering from the 010 Level of CO₂ to the Raman Scattering from the 000 Level of CO₂. Two Experimental Points are shown.

Figure 16. CO₂ as Thermometer – by Raman Spectroscopy. Pg. 37 [5]

The disagreement of the high temperature data point with respect to theory is probably caused by a combination of noise and the positioning error of the thermocouple used to measure the temperature vs. the position of the laser focal point in the propane burner exhaust. More careful experiments to verify this theoretical curve and/or to calibrate the functional relationship of $N(010)/N(000)$ vs temperature should be conducted. " [5](P.32)

3.5 Gas Concentrations by Raman Spectroscopy

Gas concentrations for the following atmospheric gas were measured:

3.5.1 H₂O Concentrations

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

<i>Power Setting</i>	<i>Raman Measurement</i>	<i>Calculated From F/A</i>
<i>(1)</i>	<i>(2)</i>	<i>(3)</i>
7%	0.0274	0.0372
30%	0.0216	0.0416
100%	0.0226	0.0567

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

3.5.2 CO₂ Concentration

“The response of the laser Raman instrument to CO_2 was calibrated at the beginning of the test program with a T53 engine by using the previous conventionally measured CO_2 concentration from this engine at the 60% power setting. ... These data are displayed in Figure 33, which shows the volume percent CO_2 as a function of the percent shaft horsepower of the engine.” Pg. 59 [15]

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

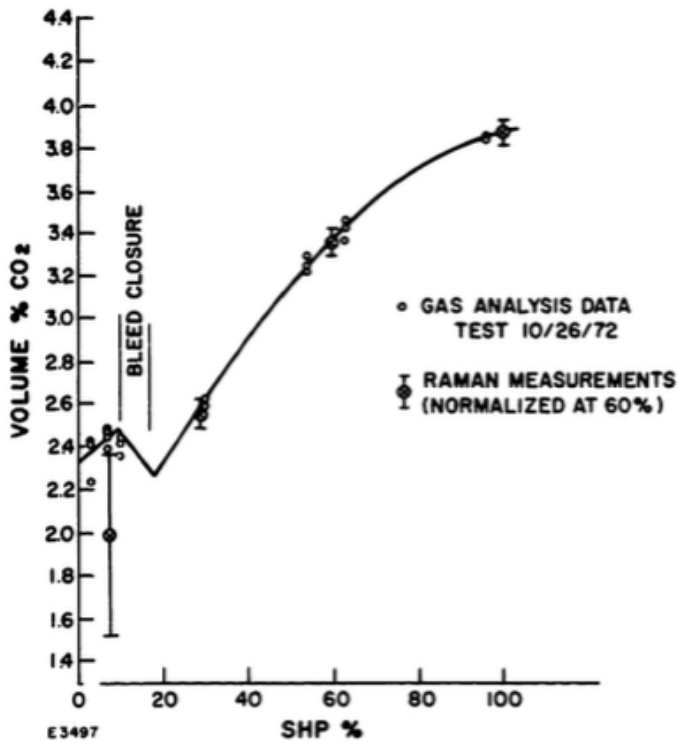


Figure 33 Volume % CO₂ as Measured from Raman Scattering vs Shaft Horse Power (SHP), %

Figure 17. CO₂ Raman vs IR. Raman measurements taken at 1338 cm⁻¹ match the IR 2349 cm⁻¹ mode. Pg.50 [15]

3.5.3 N₂/O₂ Ratio

"The ratio of the corrected O₂ to N₂ Raman signals can then be used to obtain the O₂/N₂ mole ratio. The system was calibrated in the field for effective cross section and system transfer function by using the O₂/N₂ ratio obtained from ambient air and by assuming that air is 21% O₂ and 78% N₂ on a mole basis. The results of the oxygen measurements are shown in Figure 32 where the O₂/N₂ mole ratio is calculated from the fuel/air ratio of the operating T-53 engine, using an approximate value of hydrogen/carbon mole ratio of 2.0. Perfect agreement would cause the data to fall in the line connecting zero with the point labeled "air".

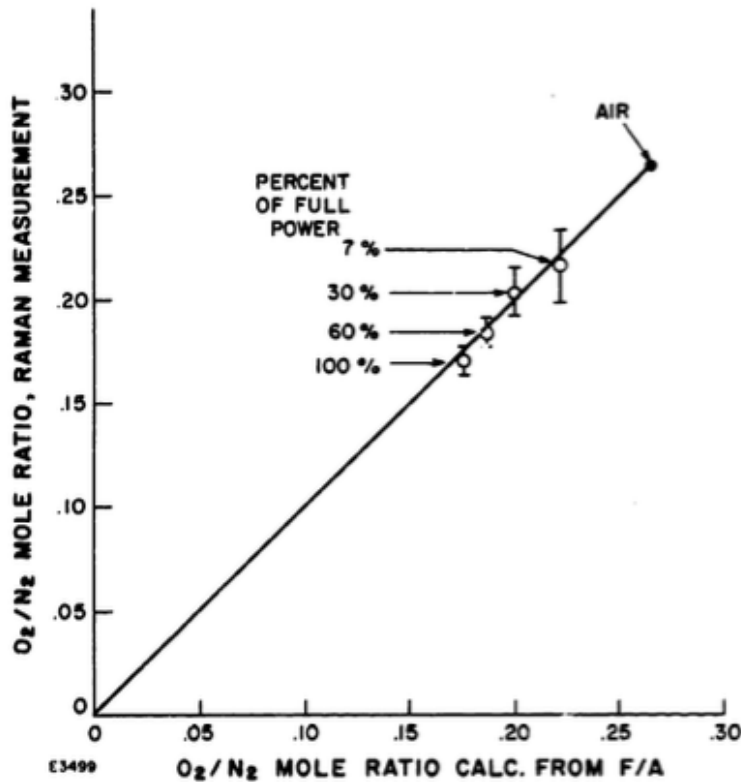


Figure 32 O₂/N₂ Mole Ratio for T-53 Engine Raman Measurement vs Calculated Value

Figure 18. N₂ O₂ Concentration Raman Measurements. Pg. 49 [15]

3.5.4 NO

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

3.6 RER Conclusion

The following is the conclusion to the Raman exhaust report:

1. Excellent agreement of (Raman) O₂ and CO₂ measurements with conventional exhaust gas measurements and correlations with engine fuel-air ratio.
2. Excellent agreement with smoke number measurements, with a calibration at one point only.
3. Good agreement of temperature profile measurements with thermocouple data.
4. Total hydrocarbons were detected and compared to flame ionization measurements to within a factor of +2 over a range of three decades of concentration.

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

3.7 Raman lidar sensing of CO₂ leakage - Results

The Lidar detected CO₂ at its Non-GHG Spectra Mode and Non-GHG N₂ as shown in Figure 19.

Figure 6b shows the Raman signals of CO₂ and N₂ as a function of distance from the lidar system and the motorway. The increased CO₂ Raman signals found at 400 m and 750 m from the lidar system represent the locations of a local motorway (A) and the Gapcheondosi Expressway (B), respectively. The enhanced Raman signals of CO₂ at locations A and B in Figure 6b imply that the lidar system is capable of detecting spatially resolved Raman signals of CO₂ emitted from motor vehicles. The Raman lidar obtained clear and stable Raman scattering signals of N₂ and CO₂ at a distance of 900 m from the lidar system. Page 7.

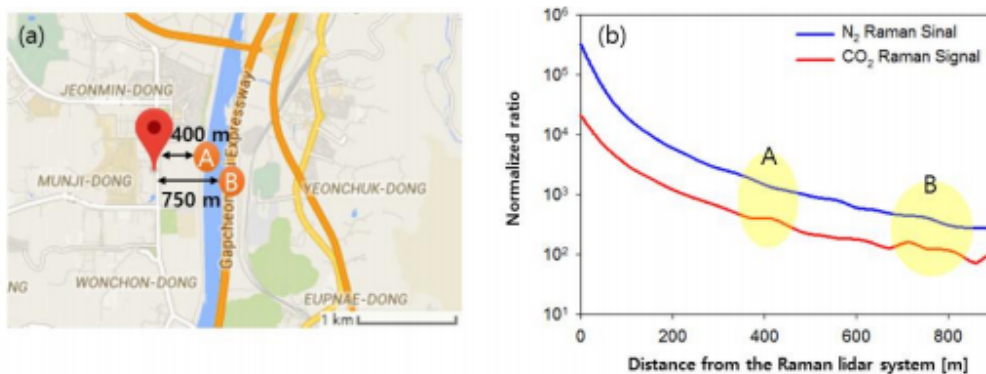


Figure 6. (a) Study area in Daejeon, Korea; (b) N₂ and CO₂ Raman signals measured by the Raman lidar system.

Figure 19 Raman Lidar Detecting CO₂ at its Non-GHG Spectra Mode and Non-GHG N₂.

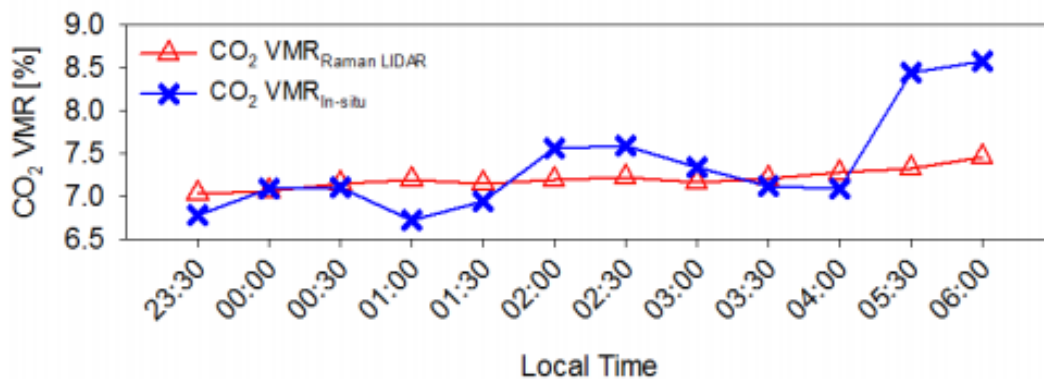


Figure 8. Time series of CO₂ VMR_{In-situ} and CO₂ VMR_{Raman LIDAR} on November 23, 2017.

Figure 20 Raman vs. IR Thermoelectric technology.

In Figure 20 the Raman CO₂ measurement raises steadily, not showing the erratic radios of the ground level detector.

3.8 N₂-CO₂ Laser Results

The following is an excerpt from a paper on how a CO₂ laser operates from the book LASER PHYSICS by PETER W. MILONNI JOSEPH H. EBERLY page 51 [16]. It is a typical description of how the CO₂ laser directly implicates N₂'s 2338 cm⁻¹ mode. I have posted the direct text to show this is standard knowledge. It is important to look out for are the Wavenumbers of the gases: particularly, N₂'s 2330 cm⁻¹ and CO₂'s 1388 cm⁻¹ and their role in the laser process.

"The electric-discharge carbon dioxide laser has a population inversion mechanism similar in some respects to the He-Ne laser: the upper CO₂ laser level is pumped by excitation transfer from the nitrogen molecule, with N₂ itself excited by electron impact. The relevant energy levels of the CO₂ and N₂ molecules are vibrational-rotational levels of their electronic ground states. We discussed the vibrational-rotational characteristics of the CO₂ molecule in Section 2.5, and indicated in Fig. 2.10 the relative energy scales of the three normal modes of vibration, the so-called symmetric stretch, bending, and asymmetric stretch modes (Fig. 2.9). Like all diatomic molecules, N₂ has a single "ladder" of vibrational levels corresponding to a single mode of vibration (Fig. 2.7) (2338 cm⁻¹). In Fig. 11.9 we show the CO₂ and N₂ vibrational energy level diagrams side by side. Figure 11.9 shows that the first excited vibrational level ($v = 1$) of the N₂ molecule lies close to the level (001) of CO₂. Because of this near resonance, there is a rapid excitation transfer between N₂ ($v = 1$) and CO₂(001), the upper laser level. N₂ ($v = 1$) is itself a long-lived (metastable) level, so it effectively stores energy for eventual transfer to

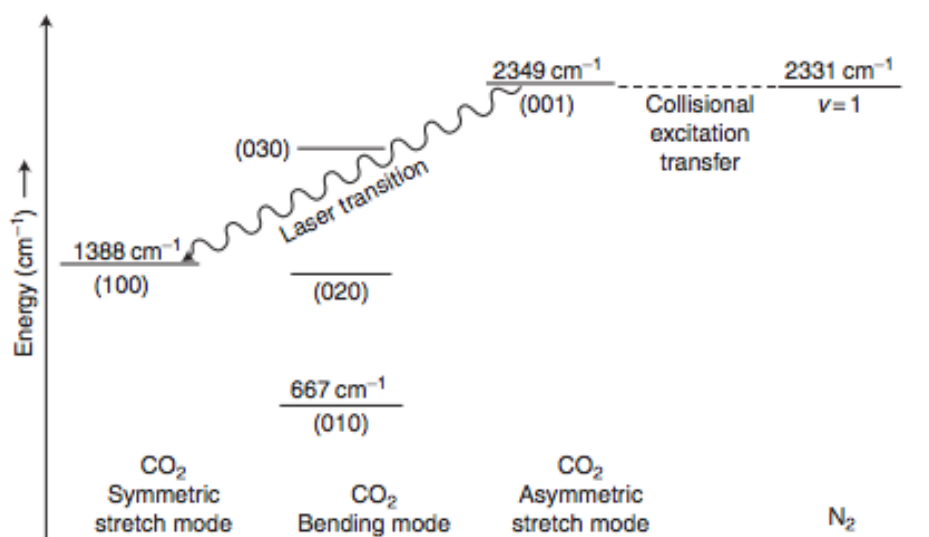


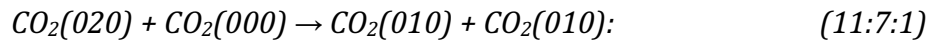
Figure 11.9 Vibrational energy levels of CO₂ and N₂. The energies are given in cm⁻¹, a unit corresponding to a frequency $(\text{cm}^{-1}) \approx 3.0 \times 10^{10}$ Hz, or an energy $h\nu \approx 1.2 \times 10^{-4}$ eV.

Figure 21 Vibrational Energy Levels of CO₂ and N₂. The claim of this paper is the quantum mechanism for the CO₂ laser should be universal and stand for the atmosphere also.

CO₂(001); it is also efficiently pumped by electron-impact excitation. As in the case of the He-Ne laser, therefore, advantage is taken of a fortuitous near

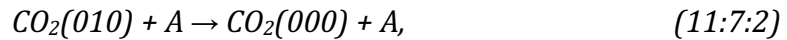
resonance between an excited state of the lasing species and an excited, long-lived collision partner. Laser action in CO₂ lasers occurs on the vibrational transition (001) → (100) of CO₂. This transition has a wave number around (2349–1388) cm⁻¹ $\frac{1}{4}$ 961 cm⁻¹ (Fig. 11.9), or a wavelength around (961 cm⁻¹) 21 $\frac{1}{4}$ 10.4 mm in the infrared. The laser wavelength depends also on the rotational quantum numbers of the upper and lower laser levels. For the case in which the upper and lower levels are characterized by J $\frac{1}{4}$ 19 and 20, respectively, the wavelength is about 10.6 mm, the most common CO₂ laser wavelength. The (100) and (020) vibrational levels of CO₂ are essentially resonant. This “accidental degeneracy” results in a strong quantum mechanical coupling in which states in effect lose their separate identities.

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

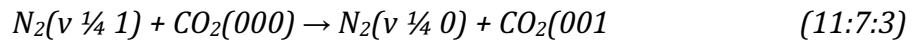


For practical purposes, then, the stimulated emission on the (001) → (100) vibrational band takes CO₂ molecules from (001) to (010). The (010) level thus acts in effect like a lower laser level that must be rapidly “knocked out” in order to avoid a bottleneck in the population inversion.

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



where A represents some collision partner. The VT de-excitation of (010) effectively depopulates the lower laser level and also puts CO₂ molecules in the ground level, where they can be pumped to the upper laser level by the VV excitation transfer



In high-power CO₂ lasers the lifetime of the CO₂(010) level may be on the order of 1 ms due to collisions of CO₂ with He, N₂, and CO₂ itself. Of course, the VT process (11.7.2) is exothermic and results in a heating of the laser medium; some of the other VT and VV processes in the CO₂ laser have the same effect. This heating of the laser medium is a very serious problem in high-power lasers. In the next section we will see how it may be overcome. Electron impacts excite CO₂ as well as N₂ vibrations. “

3.9 Natural N₂-CO₂ Lasers

NASA and others have discovered natural lasers on the likes of Mars and Venus [17] and below [18] is demonstrated how they – in the similar way as the laboratory ones – operate. Again this repeats the role of radiation has on atmospheric gases.

“000 to 101 followed by a resonant collisional energy transfer of a V3 quantum to another CO₂ molecule (2349cm⁻¹), which is similar to the laboratory CO₂ laser (Fig 8.6).”

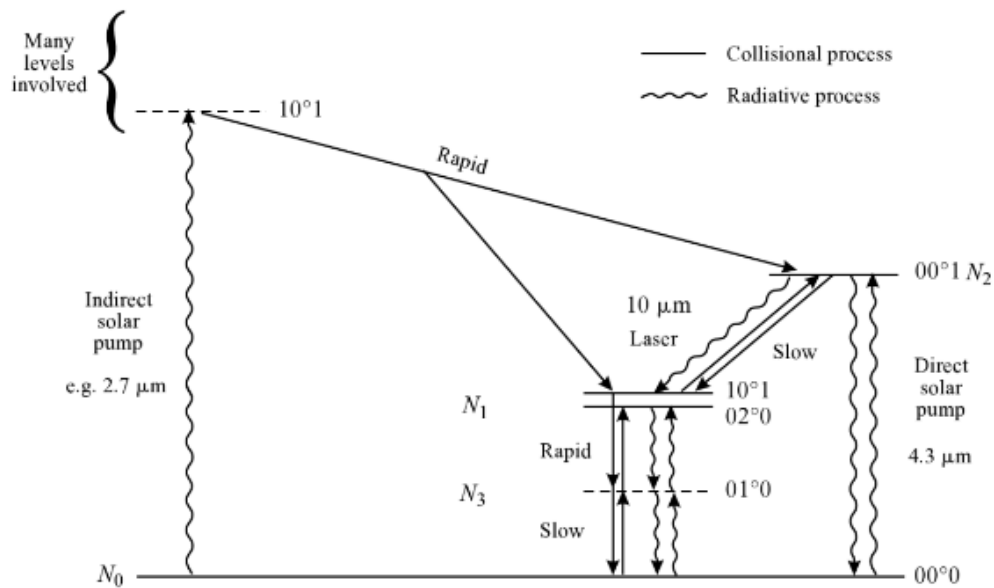


Fig. 8.6 Molecular physics of a natural CO₂ laser. Radiative and collisional processes affecting the pumping of this laser in the mesospheres of Mars and Venus are identified.

Figure 22 Natural CO₂ Lasers. Showing CO₂ lasers are natural and that N₂ is implicated at its respective vibration mode.

3.9.1 'Blackbody CO₂ Laser' Showing N₂ Heated by Sunlight

It is very difficult to directly show N₂ is directly radiated by the sun's energy, absorbing IR photons; however, the following experiment shows indirect confirmation of the hypothesis: N₂ is 'heated' (and heats) – i.e. absorbs (and emits) – by sunlight.

The extract below is taken directly from the 'NASA Technical Paper': [A Blackbody-Pumped CO₂-N₂ Transfer Laser](#), by Young and Higdon [19].

"One laser concept that may achieve such efficiencies is the blackbody-pumped CO₂ transfer laser. Such a system is called a fluid-mixing or transfer gas-dynamic laser and is shown in conceptual form in figure 1.

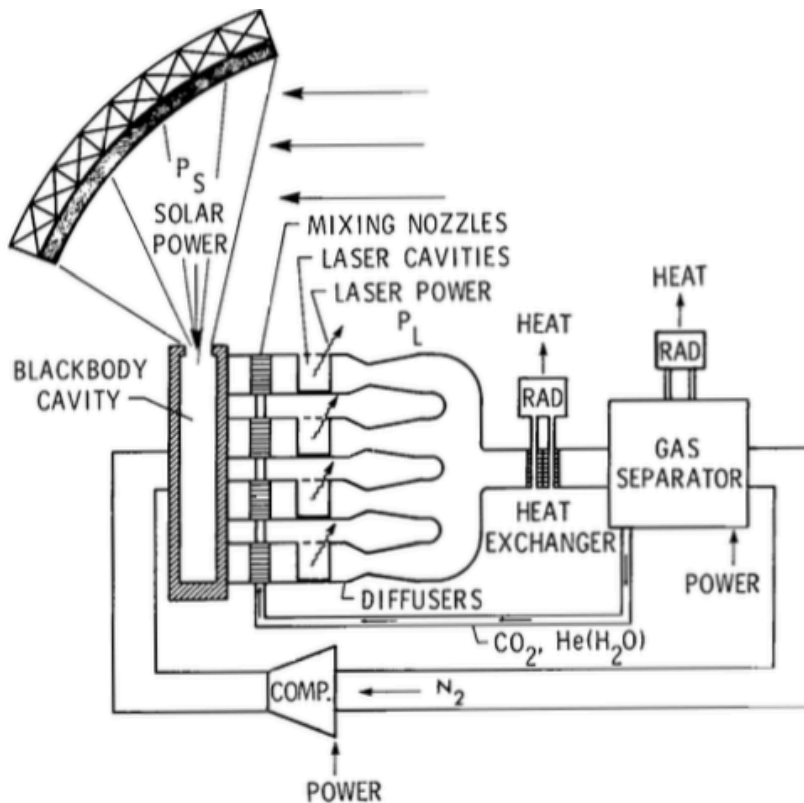


Figure 1. A conceptual design of a space-based blackbody N_2 - CO_2 transfer laser.

Figure 23. Demonstrating N_2 Excitation from the Sun.

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

3.9.2 Experimental Setup

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

4 Discussions

I found N_2 and O_2 do have spectra in the IR range of the electromagnetic spectrum. These spectra are predicted by the quantum mechanics Schrodinger equation, and these spectra, along with their respective temperatures, are only observed and measured by Raman Laser Spectroscopy – IR spectroscopy's known complement instrument. It was further found, by the application and operation of the N_2 - CO_2 laser N_2 absorbs radiation – whether by (radiation) of electrical discharge or by photons, at the predicted and observed spectra. These findings contradict and collapse GH theory, as we understand it. With Raman Spectroscopy we are not 'IR' colour blind to the non-IR colours.

The standard reason given for this discrepancy between the GHGs and non-GHGs is clear: spectra-modes without an electric dipole moment are assumed not to absorb, and as N_2 and O_2 only have one spectra mode in the IR, so this rules them out. I, argue this interpretation is wrong. I have found the Raman active modes IR. H_2O for instance was found to be both IR and Raman active, and argon's mode, on the other hand, was found to be neither 'IR' or Raman active – but none the less shares a comparable specific heat capacity, so something is missing there too.

The following discussion first addresses the direct question of this paper and then expands to address issues arising from the findings – what really are the special GHGs? While this section will focus directly on the above RER experiment results, it will– using principles and applications known to physics – also broaden to address the implications of this work on thermoelectric and Raman spectroscopy application and theory, and our general understanding of climate and other related areas. It will also bring in applications of Raman and thermoelectric devices, and applications of atomic radiation theory, all in support of this papers hypothesis.

4.1 The Laws and Physics Central to Radiation Theory

Before discussing the experiment, it may be important to show and remind ourselves of the physics at stake when it is assumed matter does not radiate IR. The following is a list the physics behind radiation theory. It was tested whether these apply to the atmospheric molecules – whether or not they are GHGs.

4.1.1 Planck's Law

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

4.1.2 Boltzmann Constant

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

4.1.3 The Stefan-Boltzmann Law

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

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

The Stefan-Boltzmann law, a fundamental law of physics, explains the relationship between an object's temperature and the amount of radiation that it emits. This law (expressed mathematically as $E = \sigma T^4$) states that all objects with temperatures above absolute zero (0K or -273°C or -459°F) emit radiation at a rate proportional to the fourth power of their absolute temperature. E represents the maximum rate of radiation (often referred to as energy flux) emitted by each square meter of the object's surface. The Greek letter “ σ ” (sigma) represents the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{W/m}^2\text{K}^4$); and T is the object's surface temperature in Kelvin. The W refers to watt, which is the unit used to express power (expressed in joules per second).” [20]

4.1.4 Kirchhoff's Law of thermal radiation

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

4.1.5 Spectroscopy:

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

4.1.6 Quantum Mechanics Schrödinger Equation

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

4.2 Quantum Mechanics IR Spectra Predictions

All modes, particularly for this investigation N_2 and O_2 , are predicted by the quantum mechanics and the Schrödinger equation – the centrepiece of modern atomic physics. This prediction is consistent with standard quantum mechanics and emission spectra understanding. This equation predicts the atomic vibrational mode frequencies for all matter, including the atmospheric gases

In the IR of the EMS the modes are divided into ‘IR active’ and Raman Active’.

GH theory totally ignores these Raman modes of the diatomic molecules, and the 'Raman active' modes within the so-called GH gases. N_2 and O_2 are not the only molecules affected by this assumption. The **1338 cm^{-1}** mode of CO_2 itself is also out; so too are all of water's (H_2O) modes, particularly its 3652 cm^{-1} , and also two of CH_4 's modes, 2914 cm^{-1} and 1303 cm^{-1} – all for the same assumed reason: no electric dipoles at those modes. This is not a coincidence; that they have been divided and one group dismissed – it is a mistake.

4.3 Spectra Observation by Raman Spectroscopy

In accordance with the quantum mechanics predictions, the Raman Spectrometer – itself a product mechanics – observed these predicted spectra. The IR spectroscopy complimentary instrument observes – just as it was explained too in all demonstration of it, and this known to all chemists – the IR modes it cannot.

4.4 Temperature Measurement by Raman Spectroscopy

It has been demonstrated throughout this paper thermoelectric detectors cannot measure the temperature of N_2 or O_2 above absolute zero Kelvin, but here it is demonstrated clearly Raman spectroscopy can not only detect the modes, they can also measure the temperature of the molecule from the intensity or kinetic energy of the mode signal. This fact alone should make Raman spectroscopy the fundamental GH-detecting instrument.

4.4.1 Temperature Detector Equivalence

From Raman RER experiment it is demonstrated the two detectors used within the IR range of the EMS, Raman and thermoelectric, are equivalent in terms of the vibrational and temperature behaviour of the molecule. H_2O 's 3659 cm^{-1} mode is equivalent, (as above section 4.4) thus the detectors of IR and Raman are equivalent. What is more, the temperature was measured from CO_2 's Raman active 1338 cm^{-1} mode alone (3.4.2); and this value compared well and calibrated 'favourably' by Raman's complimentary instrument the thermoelectric IR detector – Figure 41 above. From this, it can be implied all modes and thus molecules, are equivalent; they are only separated or discriminated by the detector 'observing' them. The RER shows temperature measurement of all atmospheric gases can be made reliably and accurately from the Raman vibrational modes alone; the Raman detector on its own could measure and quantify the 'special GHGs' (thermoelectric gases). As evidence to this Raman instruments is used as an instrument of choice on solar system space probes – more on this in a following section.

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

4.4.2 Raman Temperature Measurements and the Boltzmann Constant

By the Boltzmann constant, the observation of these and all vibrational modes at the said predicted frequencies, and their respective temperature measurement thereof, implies these modes are moving and thus are radiating IR. By observation, from this experiment, these modes are radiating – IR heat –

consistent with thermodynamics and quantum mechanics; if they were not there would be a contradiction.

4.4.3 Raman Measurements and the Stefan Boltzmann Law

As both N₂ and O₂ – independently – show a temperature value, as measured by Raman laser detectors, they must be said to be radiating in accordance to the Stefan-Boltzmann law. The Stefan-Boltzmann law is a central pillar to radiation theory, and states the following: expressed mathematically as

$$E = \sigma T^4.$$

This Raman signal is in total contrast to current GH theory – where it is not allowed. This misconception can only be due to the Raman detectors measuring the N₂ and O₂, and the TE/IR detectors not measuring it. This finding has direct significance to blackbody radiation theory and suggests it is incomplete, requiring updating with respect to the Raman observations made here, and everywhere in the fields of modern chemistry and physics.

4.4.4 N₂ and O₂ and Planck's Law

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

4.4.5 Equivalence – Dual Modes H₂O

Some modes appear to be both thermoelectric and Raman active for some molecules, H₂O the best example. This indicates that although most substances do not share this (for CO₂ for example), substances must be understood to be radiating from their predicted modes, whether they are IR-thermoelectric or Raman active. If there is a mode; there is, quantum mechanics, radiation – emission and absorption, all in accordance with the physics.

4.4.6 The Significance of Equipartition and Degrees of Freedom and Normal Modes

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

*"In classical statistical mechanics, the equipartition theorem relates the temperature of a system to its average energies. The original idea of equipartition was that, in thermal equilibrium, energy is shared equally among all of its various forms; for example, the average kinetic energy per **degree of freedom** in translational motion of a molecule should equal that in rotational motion.[21]"*

The following address this equipartition by showing many IR spectra are identified by both Raman the thermoelectric (IR) spectroscopy.

4.4.6.1 CO₂'s 1338 cm⁻¹ and the Principle of Equipartition

Notwithstanding this mode is present on 'IR' spectrograph Figure 37 and Figure 39, CO₂'s third QM predicted vibration mode or vibrational spectra – the mode not included in GH theory – is observed at 1338 cm⁻¹ by the RER (Figure 11) in the IR of the EMS: only with Raman spectrometers. This mode is not observed with IR thermoelectric detectors as it does not have an electric dipole moment and thus does not generate an electromotive force – more on this in a following

section. By the Principle of Equipartition[21], this Raman vibrational mode should be emission equivalent to the TE/IR (GHG) modes and assumed so. If it were not for Raman spectroscopy this mode would only be predicted and not observed. That there is a mode implies there is vibration, and through the Boltzmann constant this vibration implies a temperature equivalent IR emission and absorption proportional to the vibrational energy of the mode – as all spectra lines do.

4.4.7 Raman Spectroscopy and the Blackbody Curve

As Raman spectroscopy can show you both position and temperature of an atomic mode, it should have made the blackbody – thermoelectric – spectrum redundant, or at least updated it, see Figure 31. All the modes on can be shown to respond to radiation in compliance with the Stephan Boltzmann Law – where temperature rises to the 4th power, with irradiance. If the temperature of an object in isolation results in IR radiation, and Kirchoff's law holds, IR spectroscopy is not alone as a measure of this objects temperature, it should include Raman spectroscopy. Raman spectrometers are the complementary instrument to thermoelectric IR spectroscopy; they 'see' what thermoelectrics cannot. IR observes. Raman spectrometers are now the instrument of choice on most space probes. The 'Raman effect' led to one of the earliest confirmations of quantum theory;

"Raman optical spectra made vibrational information more convenient accessible – where these were previously available only from infrared spectra, which were difficult to obtain." Pg. 143 [22]

Raman Laser Spectrometers exploit the Raman effect (this fact is often confused with the Raman effect itself) to reveal, and observe, not only the quantum mechanics predicted emission spectra, but also, importantly for this study, the temperature of these spectra. The exception to this rule is H₂O, where the spectra are both IR and Raman (active) as we shall see below.

4.5 Raman lidar sensing of CO₂ leakage - Discussions [7]

The introduction lines of the paper cannot be overlooked without comment:

"The average temperature of Earth has increased by 0.8 °C since the beginning of the twentieth century, garnering worldwide interest [1]. This global warming is reported to be caused by an increase in the concentrations of greenhouse gases (e.g., CO₂, CH₄, N₂O, O₃, and CFCs) produced by human activities such as fossil fuel combustion, industrial processes, and deforestation."

The authors are concerned about the GHGs but seem unaware or oblivious they are using Raman Laser detectors that expose and exploit the non-IR spectra – the non- GHG deriving spectra modes.

In this experiment the Raman lidar is used to detect CO₂ leakage: this is the most unlikely of possibilities, unthinkable before the development of laser Raman technology. This experiment totally rebuts the claim the non-GHG do not absorb or emit IR or have emission spectra. It is clearly shown by practical application the said gases have spectra and radiate at their quantum predicted positions. The experiment also reveals properties of CO₂, namely its molecular

weight: the gases do not appear to defuse in the atmosphere but rather due to its density sink into the earth.

4.6 Other Applications of Raman Spectroscopy

The following are applications of Raman spectroscopy revealing N₂ and O₂ (and CO₂'s Raman 1338 cm⁻¹) Radiating IR. More examples are listed in Appendix 8.1.

4.6.1 Measuring Atmospheric Gas Concentrations (Keeling Curve) with Raman

*“..Raman scattering can be used to determine the nature of the molecular sample and is known as Raman spectroscopy. **Additionally, the intensity of the measured Raman lines is proportional to the molecular composition.** This means that Raman spectroscopy cannot only be done qualitatively, but also for **quantitative analysis**. It is routinely used in a range of applications for the compositional analysis of solid and liquid samples. The advancement of photonics technology has seen an increase in the popularity of Raman spectroscopy of gases in recent years. It has the additional advantage that it is a non-contact, inline multi-species gas analysis technique.”[23]*

The fact that Raman devices can measure gas concentrations – as demonstrated in the RER, section 3.5 in this paper – has implications on the measurement of GH gas concentrations in general. Indeed it has been found even the Keeling curve of GH gases – namely CO₂ – need not be measured by TE/IR thermoelectrics alone. The GH gases can be measured by Raman Lasers, just as they are on Solar system space probes; this is demonstrated in the following papers.

A Raman scattering method for precise measurement of atmospheric oxygen balance

Abstract

*Quantitative measurements of Raman scattering intensities from N₂, O₂, and CO₂ under ambient atmospheric conditions are given. The atmosphere was illuminated with 20,489 cm⁻¹ Ar⁺ laser radiation. These scattering intensities are sufficiently strong to **allow measurement of O₂/N₂ and CO₂/N₂ concentration ratios in the atmosphere to a precision of 0.3 and 0.006 ppm total atmosphere, respectively, by means of scattered photon counting over a 174-hour integration period. **The Raman technique represents an improvement in precision over existing techniques by almost two orders of magnitude**, and a substantial but less easily determined improvement in accuracy by using the transition probabilities of a monomolecular reference gas as a standard, rather than the properties of a mixed gas standard as is done in current measurements. [24]***

Analysis of influence of atmosphere extinction to Raman Lidar monitoring CO₂ concentration profile*

*“Lidar (Light detection and ranging) system monitoring of the atmosphere is a novel and powerful technique tool. The Raman lidar is well established today as a leading research tool in the study of numerous important areas in the atmospheric sciences. **In this paper, the principle of Raman lidar technique measurement CO₂ concentration profile is presented...**” [25]*

NDACC are using Raman Lidar to measure H₂O, with N₂ as “a reference molecule having a well-known mixing ratio throughout the altitude range considered” [26]

This process is also discussed by the IEEE under: LIDAR FOR ATMOSPHERIC TRACE GAS DETECTION [27], and in a paper “Relative Raman Cross Section for N₂, O₂, CO, CO₂, SO₂, and H₂S” [28]: where an (inferred) argon ion laser (5145Å) is used to identify the gases.

Also see appendix 7.8 for more on atmospheric Raman Lidar.

4.6.2 Raman Solar System Space Probe Applications

On modern-day solar system space probes Raman detectors are becoming the detector of choice: it makes sense, the detect oxygen and CH₄ – accidental part indicators of the existence of life – and CO₂, and N₂. In the review ‘**Remote Raman Spectroscopy of Minerals at Elevated Temperature** 2012’ [29]

Raman was extensively evaluated for its obvious complementary merits.

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

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

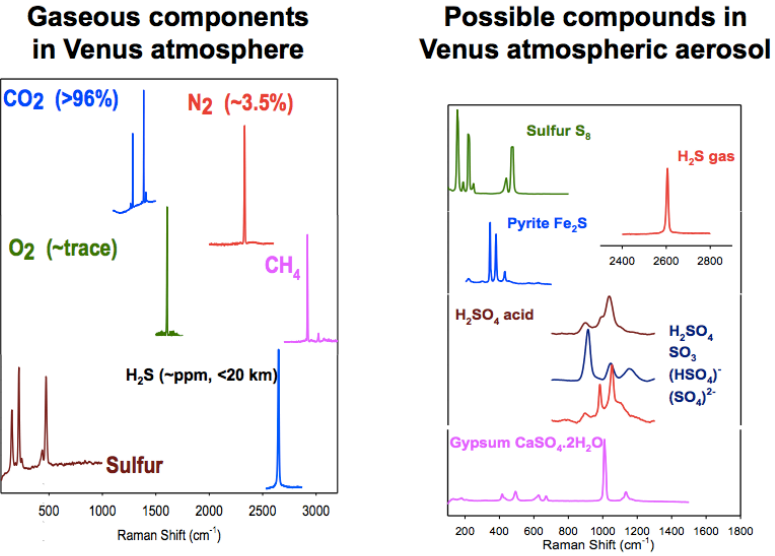
“Raman spectroscopy is not directly equivalent to infrared (IR) spectroscopy, as the strengths of individual features can be quite different between IR and Raman spectroscopy due to different selection rules. The activity of Raman vibrational modes is a function of the change in polarizability during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

4.6.2.1 Venus

Below (Figure 24) is a Raman spectra of Venus’s atmosphere. Notice CO₂ is measured at its 1338 cm⁻¹ mode. If the detection of CO₂ through this mode is good enough for Venus, why not for planet Earth? If TE/IR were used on Venus, no N₂ or O₂ would be measured – at any temperature.



Gas phase (Raman lines)



Alian Wang, WSU

Figure 24. Venus Atmosphere ‘Raman Lines’ Showing molecules with their respective modes in Venus’s atmosphere. [30]

4.6.3 Onboard (Raman) Lidar Detects Turbulence, Volcanic Ash Near and Far Photonics Spectra

Here it is demonstrated Raman Lidar can ‘read the air’, all on quantum mechanics Raman spectroscopy. This is something IR- thermoelectrics spectroscopy cannot do. This application is not allowed by GH theory. N₂ and O₂ are assumed not to emit or radiate. Here they are obeying the physics, and contradicting GH theory. The measured modes are in the IR, just as with the RER above.

Short- and midrange (Raman) lidar systems for planes can deliver strong data for automatic correction maneuvers, while long-range systems that track potentially dangerous atmospheric conditions miles away are still being researched.”

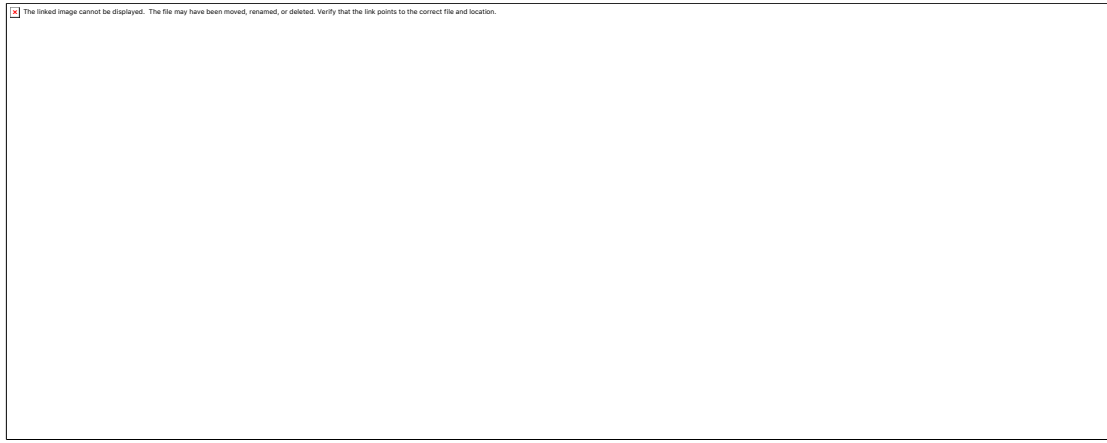


Figure 25 Raman Lidar Laser future aircraft application.

“Other air data, such as density, temperature, pressure and humidity, can be derived from molecular scattering (direct detection) only. Promising approaches exploit .. scattering processes such as Raman scattering. There, the molecules are excited by the laser beam to rotate or vibrate.

*The energy transfer to or from the molecules leads to a characteristic frequency shift of the backscattered light. **Temperature measurements with 1K accuracy and humidity measurements with 1 percent accuracy** (under relatively high humidity conditions) are straightforward to achieve. But a major challenge remains: measuring the air pressure and air density at the required 0.3 percent accuracy level.”*

4.6.4 Raman LIDAR and the Atmosphere

While I have shown N₂ and O₂ both have vibration modes that satisfy the prediction made of them (2330 and 1556cm⁻¹ respectively) different and lower wavenumber observations of them are made by using Lidar.

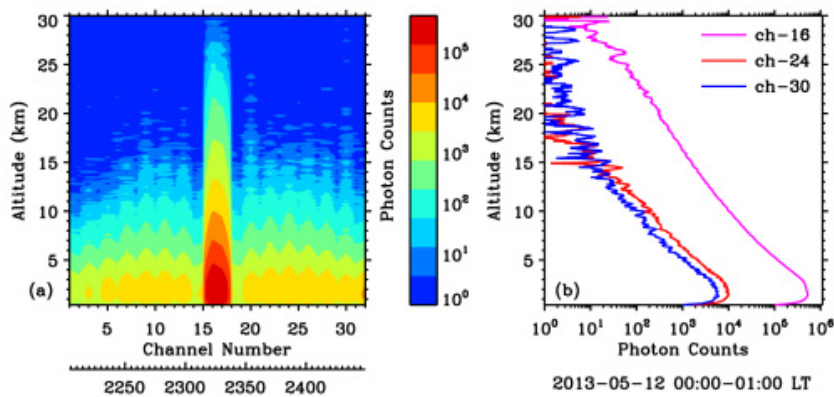


Fig. 3 (a) Altitude-dependent atmospheric N₂ Stokes vibrational-rotational Raman spectra derived from the spectrally resolved Raman lidar measurement at Wuhan during 0000-0100 LT on 12 May 2013. (b) Signal intensity profiles for the 16th (Q branch; magenta), 24th (S branch, $J = 6$; red) and 30th (S branch, $J = 12$; blue) channels, respectively.

Figure 26. Diagram showing N₂ by Lidar, altitude and wavenumber, more evidence to N₂ 2349cm⁻¹ vibration mode. [31]

In the diagram below N₂, O₂, and H₂O are shown with their Raman scatter wavelength – 580, 607, and 660nm from the incident laser 532nm align with the their respective wavenumbers, 1553, 2330, and 3652 cm⁻¹.

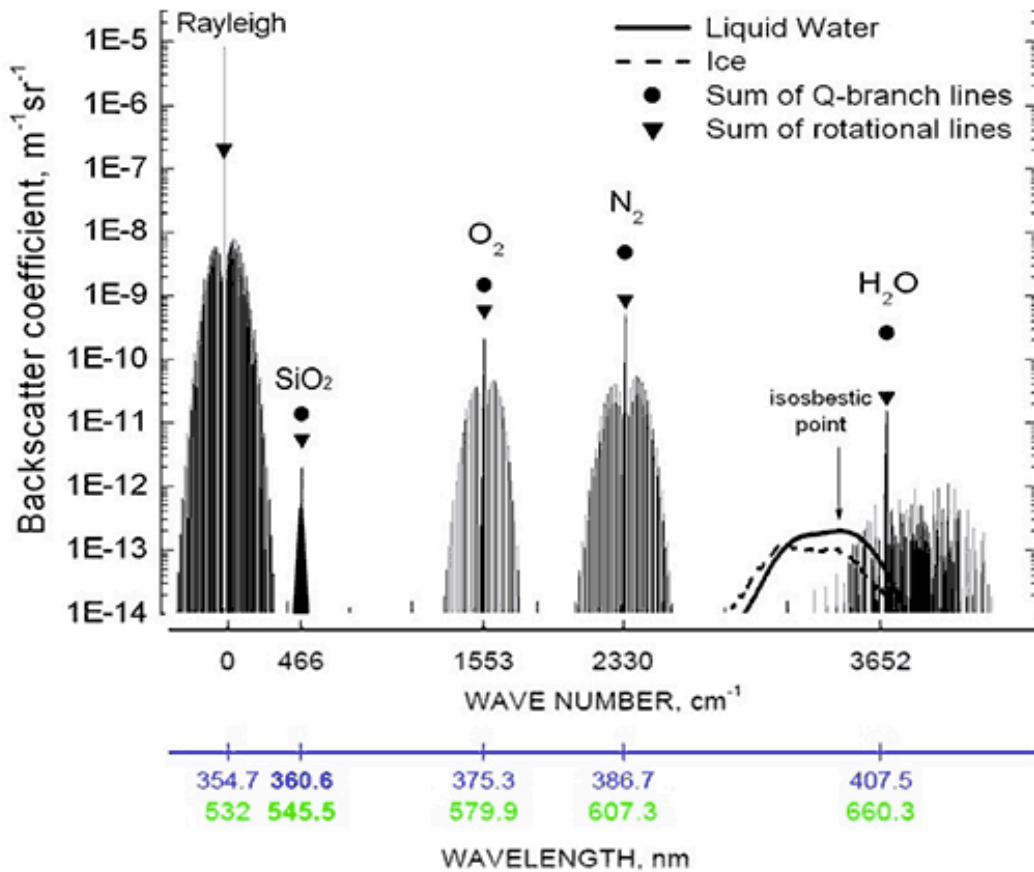


Figure 27. Showing N2 O2 H2O with Raman Number 112]

4.6.4.1 Lidar can reveal the temperature of the atmosphere:

“The RL measures atmospheric temperature using the ratio of two signals from the lidar’s rotational Raman (RR) channels. The RR channels sense Raman-shifted backscatter arising from rotational energy state transitions in atmospheric N2 and O2 molecules due to excitation at the laser wavelength of 354.7 nm (Di Girolamo et al. 2004, Behrendt et al. 2004, Radlach et al. 2008).” [33].

6.0 Example Plots

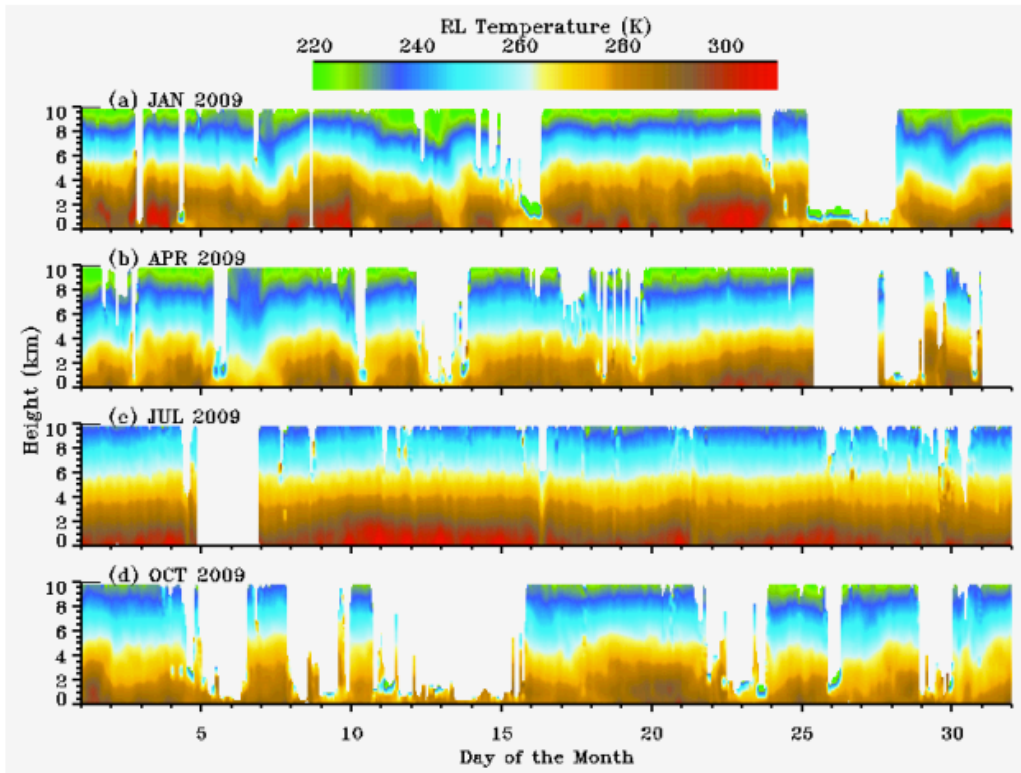


Figure 4. Sample output from the RLPROFTEMP VAP covering four selected months. Results are shown for (a) January 2009, (b) April 2009, (c) July 2009, and (d) October 2009.

Figure 28. Raman Atmosphere Profiles [33]

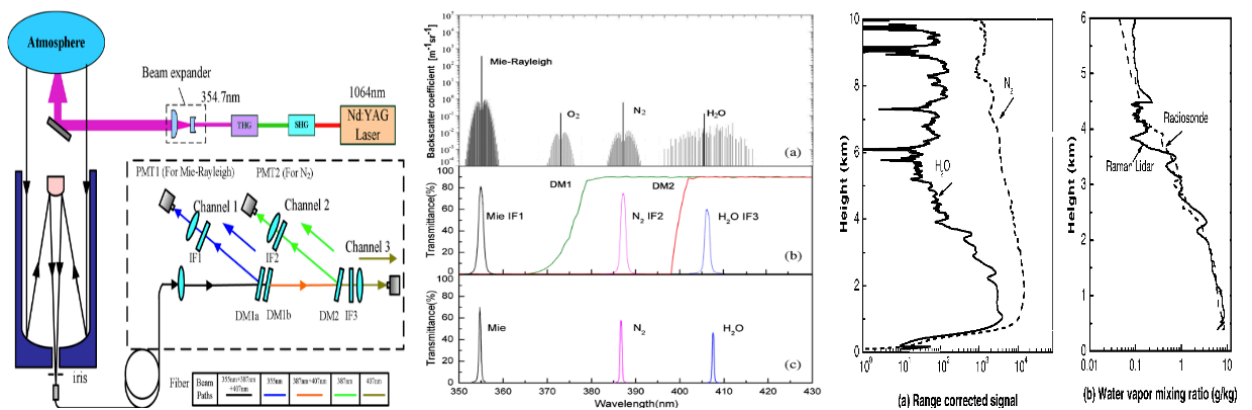


Figure 29. Raman Lidar [34]

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

“An airborne Lidar to measure methane, water vapor, and temperature on board NASA’s flying laboratory, the DC-8, has been developed at Goddard Space Flight Center. Methane and water are measured using Raman (inelastic) scattering, while temperatures are determined from both Rayleigh (elastic) scattering and nitrogen

Raman. Methane's long stratospheric lifetime (approximately a decade) makes it an ideal conserved tracer to track the motions of streamers or filaments of air as they peel off the polar vortex. Temperature measurements allow a calculation of the quasi-conserved quantity, potential temperature, which is useful in following the motions of large air parcels. The water measurement allows stratospheric water transport across the subtropical boundary to be studied.” [34] “ Page 273”

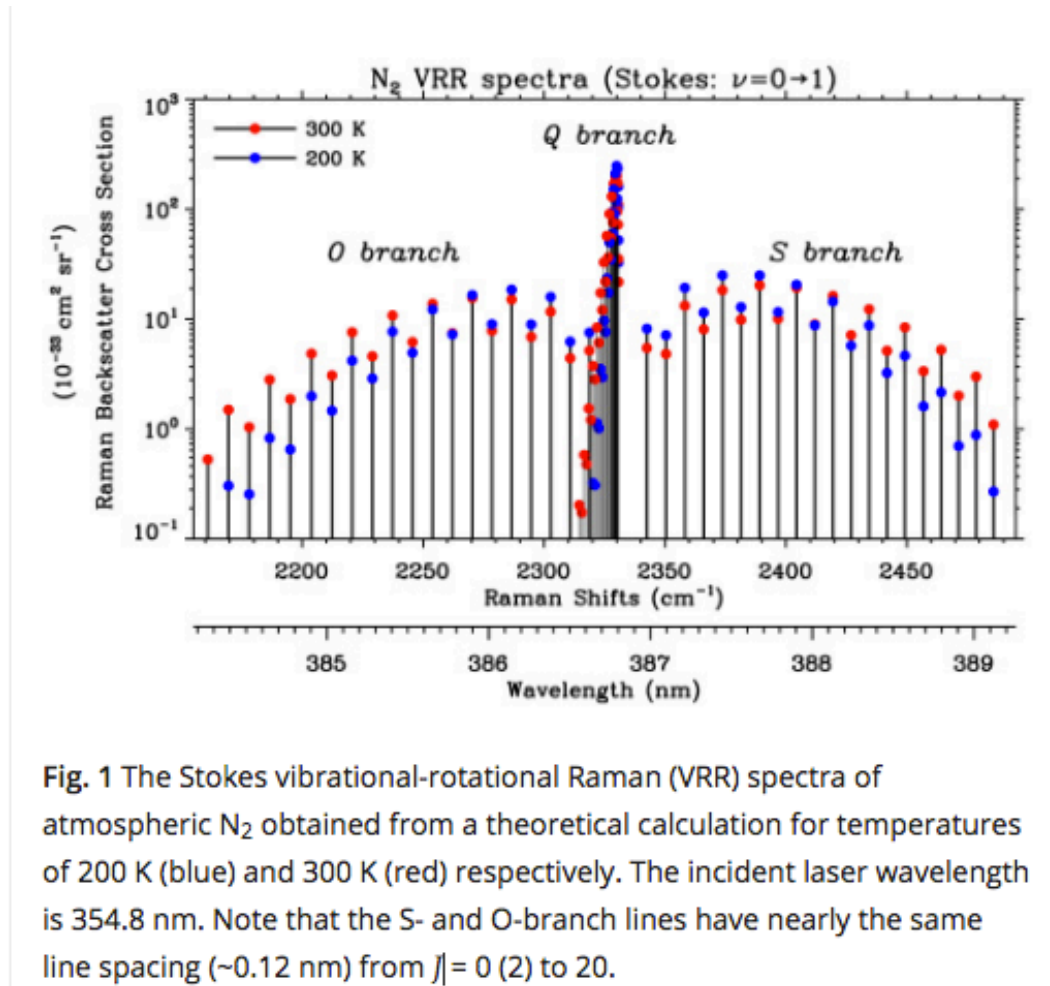


Figure 30. Atmospheric N₂ by Raman Lidar at laser stimulation 354.8nm. Notice the wavenumber of 2330cm⁻¹ is shown and also temperature is deduced. [31]

4.6.5 Other Uses for Raman Spectroscopy

See Appendix 8.1 for other uses for Raman; including: measuring automobile emissions; Raman SCattering AnaLyzer (RASCAL), Geology CO₂ 1388 cm⁻¹; CO₂'s 1388cm⁻¹ Excitation, and the 'Dicke effect' (see appendix).

4.7 Radiating N₂: N₂-CO₂ LASER – Discussions

Here, with the N₂-CO₂ laser, it is shown N₂ – a non-GHG that should not be able to absorb any (IR) radiation from any 'particle' whether photon or electron – is first excited or energised (heated up) at it's **2338** cm⁻¹ mode so as to further excite (heat up) the CO₂ molecules **2349** cm⁻¹ mode. This is in total contradiction to GH theory where N₂ is assumed not to absorb any radiation. This application shows

it is N₂ that directly affects, and excites the CO₂ molecule – though they do claim it is by collision and not radiation.

4.7.1 Stimulated and Spontaneous Emission

'Stimulated' and 'Spontaneous' Emission are quantum mechanical features, and together point to the absorption and emission of photons of light. In the case of the CO₂ laser, it is the 'stimulated' and 'spontaneous' emission and absorption of IR photons between N₂ and CO₂ molecules. It, on its own, stands as a proof of emission and absorption of N₂ of light photons.

4.7.2 The CO₂ Laser, and the Question of Radiation?

The Laser demonstrates how different substances are excited when 'fired upon' by electrons through an electrical discharge in a cathode ray tube. The important question for this investigation is: does this 'firing upon' constitute as radiation – as a transfer of energy? This is important because N₂ is assumed not to absorb radiation.

4.7.3 Is Discharge of Electrons Radiation?

The following are quotes from the first lines of Wikipedia:

"Thermal radiation is electromagnetic radiation generated by the thermal motion of charged particles in matter." [35]

Do the 'discharged electrons' used to excite the N₂ at its **2338 cm⁻¹** constitute 'charged particles' (from the above definition)?

"In physics, a charged particle is a particle with an electric charge. It may be an ion, such as a molecule or atom with a surplus or deficit of electrons relative to protons. It can be the electrons and protons themselves, as well as other elementary particles, like positrons." [36]

It can be deduced cathode rays are a form of radiation. From this, the fired electrons are charged particles, and they radiate thermal (IR) energy – the N₂ at its **2338 cm⁻¹** mode absorbs this energy.

4.7.4 Frank-Hertz Experiment

To support this claim non-IR modes radiate, the **Frank-Hertz experiment** shows electrons – from a variable electrical discharge – affect a gas molecule to reveal its emission spectra mode – the spectra predicted by the quantum mechanical Schrödinger equation. It can be shown to work for all gases. Even without radiation – it is assumed to be by 'collision' – the Frank-Hertz experiment shows N₂ absorbs, and thus emits. From this it is plausible energy is transferred from its excited **2338 cm⁻¹** to CO₂'s **2349 cm⁻¹** from emission from its mode.

4.7.5 Collisions Implausible: Convection Paradox

If excitation were by collisions alone, it would imply conduction as a means of energy transfer: again, it can be shown this is unlikely as N₂ has a very low conduction coefficient of 0.024k – so this form of transfer is unlikely.

4.7.6 Implications for IR Spectroscopy

To conclude from the CO₂ Laser and show the implications of it on IR spectroscopy; the symmetric vibrational modes of N₂ and O₂, and CO₂'s **1388** cm⁻¹ – assumed '**non-IR active**' as they do not, emit or absorb IR radiation due to their lack of a dipole – has been refuted. The 'symmetric stretch' N₂ mode excites the CO₂, having been radiated. Not only does the N₂'s symmetric mode vibrate from radiant excitation, heating and so forcing the CO₂ up an energy level, but CO₂'s own symmetric vibration (at **1388** cm⁻¹) is affected – or necessarily implicated in the process by the equipartition principle in what can arguably only be by radiation (by photon collision). Atmospheric CO₂ has this same **1388** cm⁻¹ symmetric mode, but there is no mention of this in atmospheric spectra, or its effect on climate forcing; it is assumed not to be part of the standard model, and this will need to change.

4.7.7 N₂ and Kirchhoff's Law

Kirchhoff's Law states 'good absorber, good emitter'. As it can be shown N₂ is absorbing charged electron particles from the electron discharge as if from radiation, in compliance with quantum mechanics: by Kirchhoff's Law it is equally, by definition, a said to be a 'good emitter'.

4.7.8 Metastable N₂ and the Greenhouse Atmosphere

I shall first define metastable and then discuss it in terms of N₂ and CO₂.

*"Metastable state, in physics and chemistry, particular excited state of an atom, nucleus, or other system that **has a longer lifetime than the ordinary excited states** and that generally has a shorter lifetime than the lowest, often stable, energy state, called the ground state. A metastable state may thus be considered a kind of temporary energy trap or a somewhat stable intermediate stage of a system the energy of which may be lost in discrete amounts. In quantum mechanical terms, transitions from metastable states are "forbidden" and are much less probable than the "allowed" transitions from other excited states." [37]*

N₂ is said to be **Metastable** – long-lasting (absorption) – and this property is central to the CO₂ laser; the (greenhouse) gas CO₂ is not said to be metastable.

This metastable N₂ has ramifications on greenhouse theory, as N₂ is the Earth's atmosphere's major constituent gas. This is not to say the atmosphere is a laser (though this is discussed by experts for other planets); it is only to say N₂ has this property when excited, and this is supported by experiment [38],[39] and may be assumed to be a property in the troposphere atmosphere also. Meschad – on the topic of planetary lasers and metastable N₂ – says:

"The occupation of the upper laser level is possible directly, but is much more favourable with the addition of nitrogen. Metastable N₂ levels not only can discharge but also can transfer the energy to the CO₂ molecules very profitably as well." (Pg. 274 [40])

4.7.9 Metastable N₂ from 'Collisions' and not Radiation

All explanations of metastable N₂ in the context of the CO₂ laser do not point to radiation; but rather support the non-radiating N₂ hypothesis, where it is all explained by collisions.

“ Electron collisions excite date nitrogen molecules to their vibrational level. Once in this level, the nitrogen molecules are metastable, they cannot really lose energy radiatively and can only return to the ground state as a result of collisions. Because into nitrogen is what is called a homo nuclear diatomic is it vibrates it has no dipole moment, and a direful moment is needed for spontaneous emission to occur. The population of N₂ molecules builds up and these molecules transport fare their excitation to CO₂ molecules, thereby populating the upper CO₂ laser level.” (P.220)[41]

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

The reason given for this metastable N₂ assumption is that it does not emit photons when excited; this, I believe this needs to be reviewed, and is, on its own, a repeat of the mistakes made in GH theory where diatomics (N₂ and O₂) are assumed not to radiate. I believe, based on the discoveries from this investigation, it is a ‘throwback’ to a lone reliance on ‘IR’ – thermo-electric – radiation theory that is the problem. N₂ can be shown (as it has been attempted in this paper) to emit IR photons. If it is that N₂ does emit and absorb radiation the assumption N₂ is metastable because it does not emit suggests radiation theory is incomplete.

4.7.10 IR Photon Absorbing Atmospheric N₂: An Atmospheric Law of Physics

The experiment shows – consistent with quantum mechanics theory – electron excitation is equivalent to solar photon excitation (as discussed throughout this paper). As a consequence, concentrated IR photons can be assumed to heat the N₂ by the same physics as the CO₂ Laser; only there is no electrical discharge. What is more, the experiment shows CO₂ is ‘pumped’ or stimulated by N₂ in this process: this behaviour constitutes a law of physics and so it must be for the atmosphere. Again, this process is not allowed in current GH theory.

4.8 Blackbody Emission Spectra with Raman N₂, O₂, and CO₂ ‘s Non-IR Modes [42]

Because N₂, O₂, and CO₂ (2349cm) are not measured by IR spectrometry there has been an attempt to explain and reconcile their absence on the blackbody radiation spectrum (derived alone by IR detectors). Their spectra positions are shown below on the IR blackbody ‘Planck curve’ emission spectrum of the atmosphere (red line Figure 31). Their respective position said to cause their low radiance justifying their respective weakness in absorption (Table 3). This inclusion of the non-GHGs is made in an *ad hoc* manner, and at the expense of the existence of Raman spectroscopy (IR’s complementary) and quantum theory – the modes are after all predicted by quantum mechanics. Non- GHG modes N₂, O₂, and CO₂ are shown, and their calculated irradiance presented in Table 3. It is

from this analysis their effect (absorption/emission) is said to be very poor, even negligible.

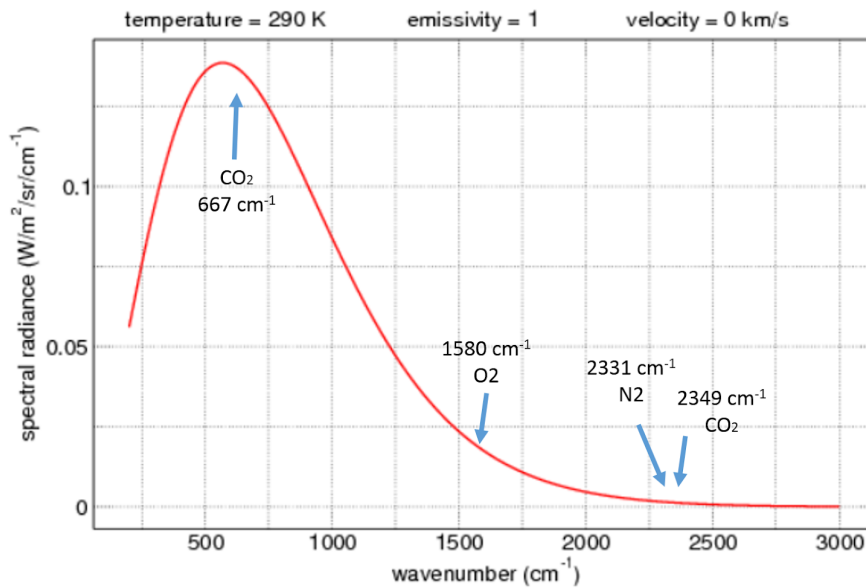


Figure 31. Blackbody Emission Spectrum with Non- GHG modes N₂ O₂ and CO₂. The solar blackbody emission spectra (red) is used to show the output of the non- GHG modes of N₂ O₂ and CO₂

Table 3. Non- GHG modes N₂ O₂ and CO₂ Irradiance by Wavenumber (frequency).

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

The fact is, and what is really neglected is these modes are only detected by Raman spectrometers – the focus of this paper; and when this fact is included it should make the Planck blackbody curve redundant.

4.9 Raman and IR Spectroscopy Complementary Instruments and Spectra

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

Raman and Infrared are Complementary Techniques

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

The infrared and Raman spectrum of styrene/butadiene rubber.

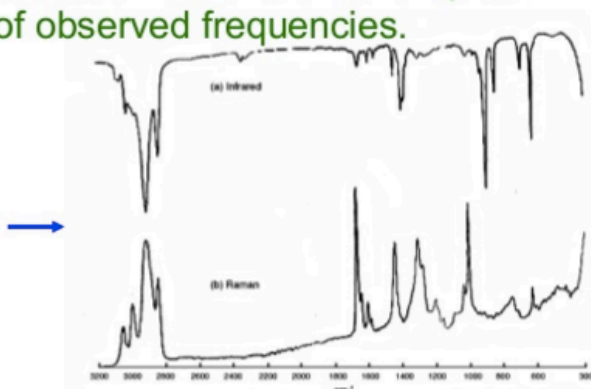
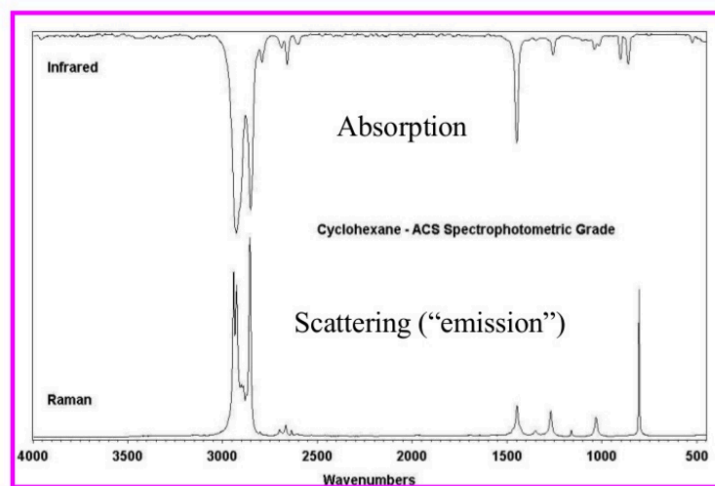


Figure 32. Complementary IR and Raman Spectroscopy. Infrared above; Raman below[43]

4.9.1 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. [44]

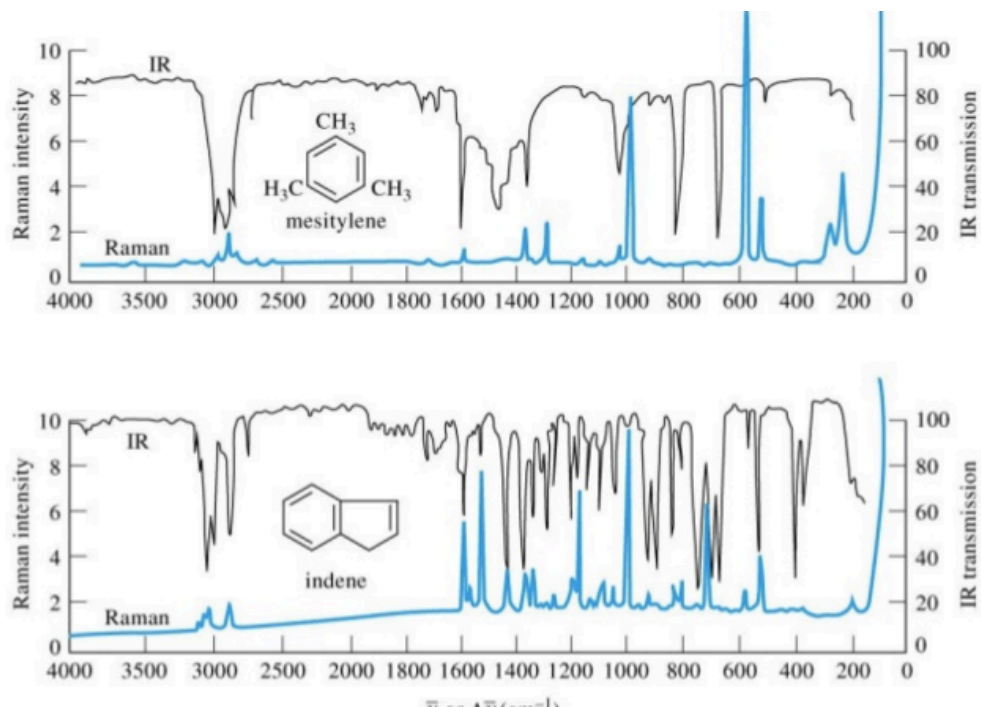


Figure 34 Demonstrating Dual Raman and IR Thermoelectric Modes of Mesitylene and Indene.

4.9.1.1 Ethanol

The following is an interesting (Raman image) reference: Ethanol has both and shared Raman and thermoelectric modes. Figure 35 clearly shows matching spectra measure measurement from both Raman and thermoelectric; and finally CO₂ to an informed chemist is both Raman and IR-thermoelectric (Figure 36).

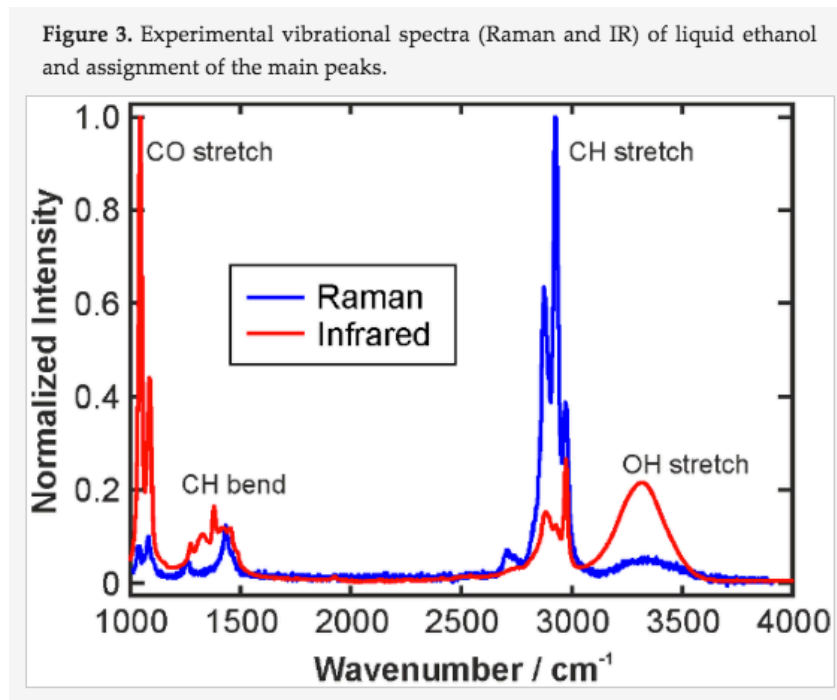


Figure 35. Ethanol Sharing Both Raman and Thermoelectric. [45]

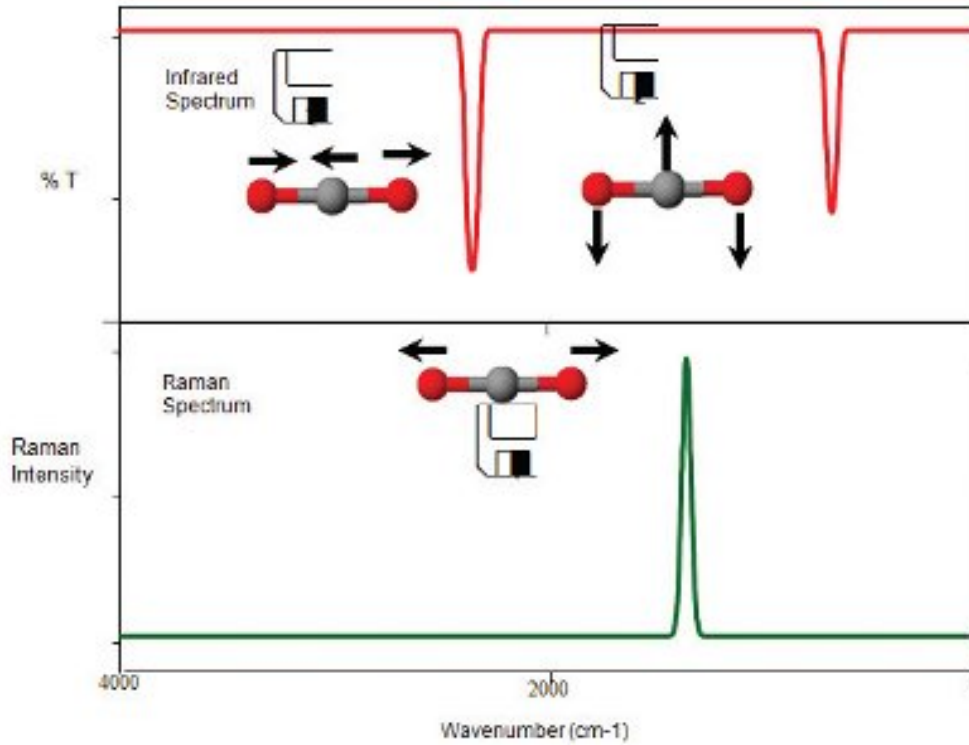


Figure 36. Schematic of CO₂ Raman and IR Spectra. “In gas phase spectra of CO₂, two infrared modes are observed at 2350 and 667 cm⁻¹ (red) and a single Raman band at ~1388 cm⁻¹ (green). (The latter band is actually a doublet due to quantum mechanical resonance effects, which is beyond this discussion).” [46]

4.9.2 CO₂'s 1338 cm⁻¹ Raman Active mode showing on IR spectra.

In Figure 37 and Figure 38 [47], and Figure 39 [48] and it is clearly shown CO₂'s 1338cm⁻¹ Raman Active spectra mode on IR (thermoelectric) spectrograms. This strengthens the case this mode is equivalent.

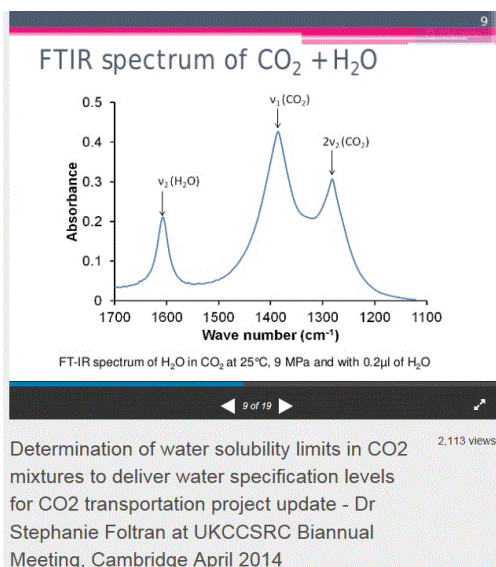


Figure 37. CO₂'s 1338cm⁻¹ Raman Mode showing on IR (thermoelectric)

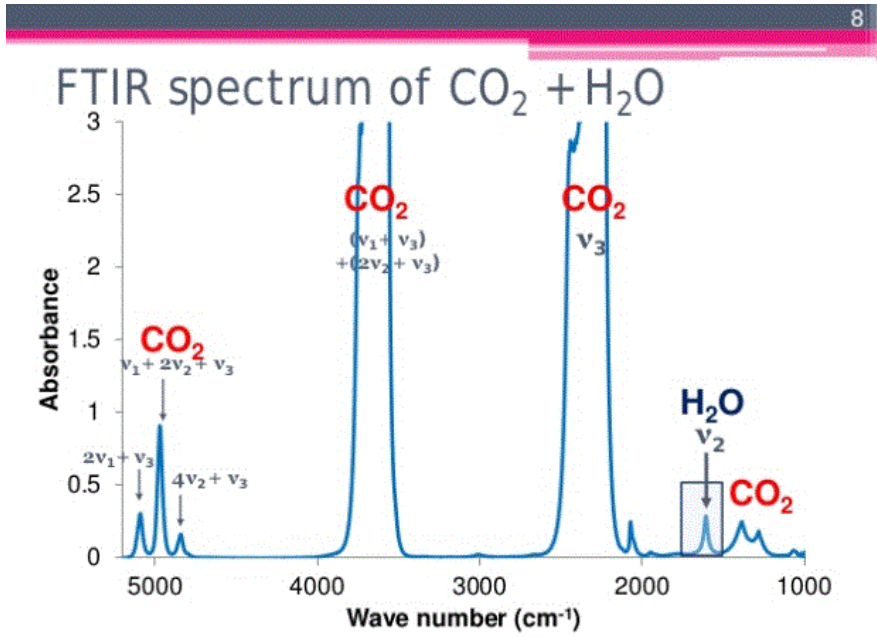
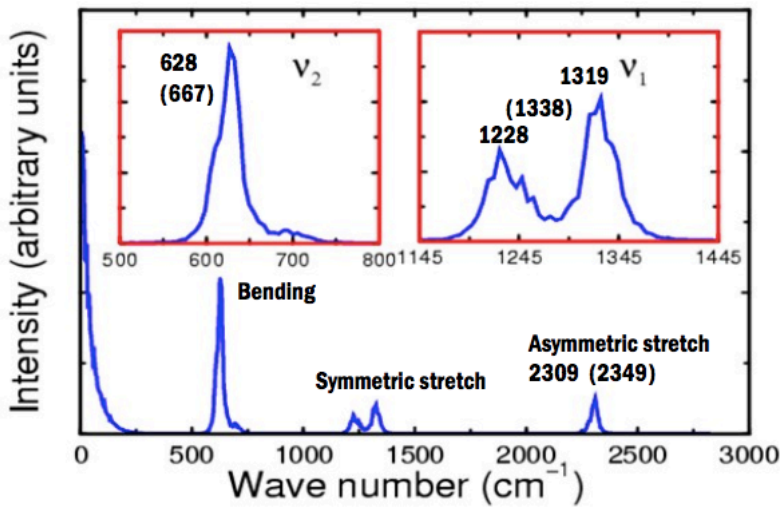


Figure 38 CO2's 1338cm-1 Raman Mode showing on IR (thermoelectric).



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

Figure 39. CO2's 1338cm-1 Raman Mode showing on IR (thermoelectric).

4.9.3 N₂O's Shared IR and Raman Modes

Just as with H₂O N₂O, another strong so called GHG also shares modes with Raman, though the Raman is weak as shown in Table 4. [49]

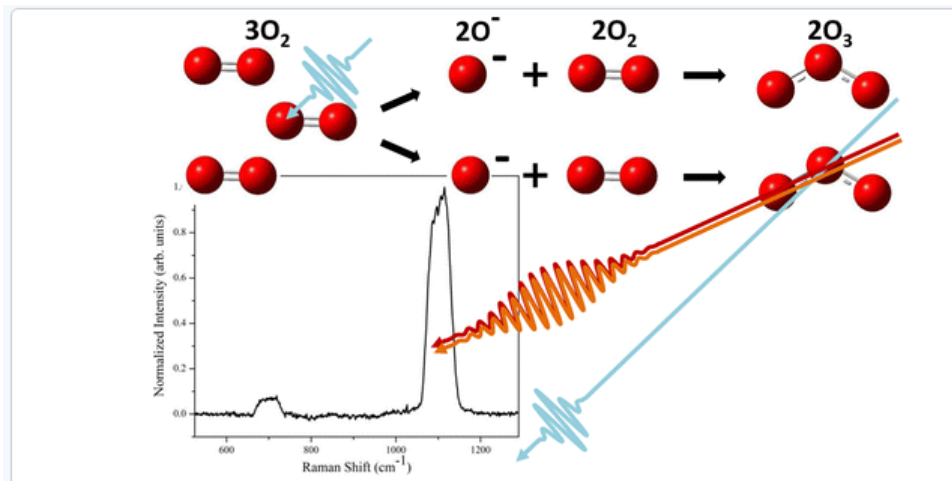
Table 4. N2O IR Raman Equivalence.

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

4.9.4 Ozone O₃ IR and – inferred by – Raman

Ozone is a greenhouse gas; it has IR spectra, and these spectra are observed. It's Spectra band at and around 1000cm^{-1} observed on the general atmosphere emission spectra Figure 31 it is in the same position as CO₂'s 960cm^{-1} . This CO₂ spectra position is – interestingly – the same as the output frequency of the CO₂ laser.

Ozone is also able to be detected Raman spectroscopy, or at least inferred by Raman Spectroscopy.



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 40 O₃ Raman Spectrograph Showing its 1103cm^{-1} [50]

The following are a collection of findings defending this claim. Firstly, a paper was found with the title: *Monitoring O₃ with solar-blind Raman Lidars* [51] which speaks for itself, and then one by the title of: *Ozone and Water Vapor Measurements by Raman Lidar in the Planetary Boundary Layer*[52].

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 [53]

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).

4.10 H₂O: Dual Raman and IR Active

Water has a special property significant to vibrational mode theory, it is both Raman active and 'IR' active at: 1590 cm⁻¹, 3652cm⁻¹, and 3790cm⁻¹ and this is revealed in the Raman Exhauste Report in Figure 10.

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

The Raman observation of H₂O's 3652 cm⁻¹ vibrational mode is significant as this mode is both TE- 'IR active' (as shown in Figure 41 below) and Raman active; it is a 'dual' Raman-TE mode. This mode is an absolute demonstration, observation, and the practical application, via the Principle of Equipartition, that these modes are equivalent. This also shows the detectors are equivalent. What is separating our understanding of the modes will be addressed when we look at how the IR modes are derived. This discovery has massive ramifications on the outcome of this investigations conclusion, and radiation physics as a whole – water has a dual means of absorption and emission.

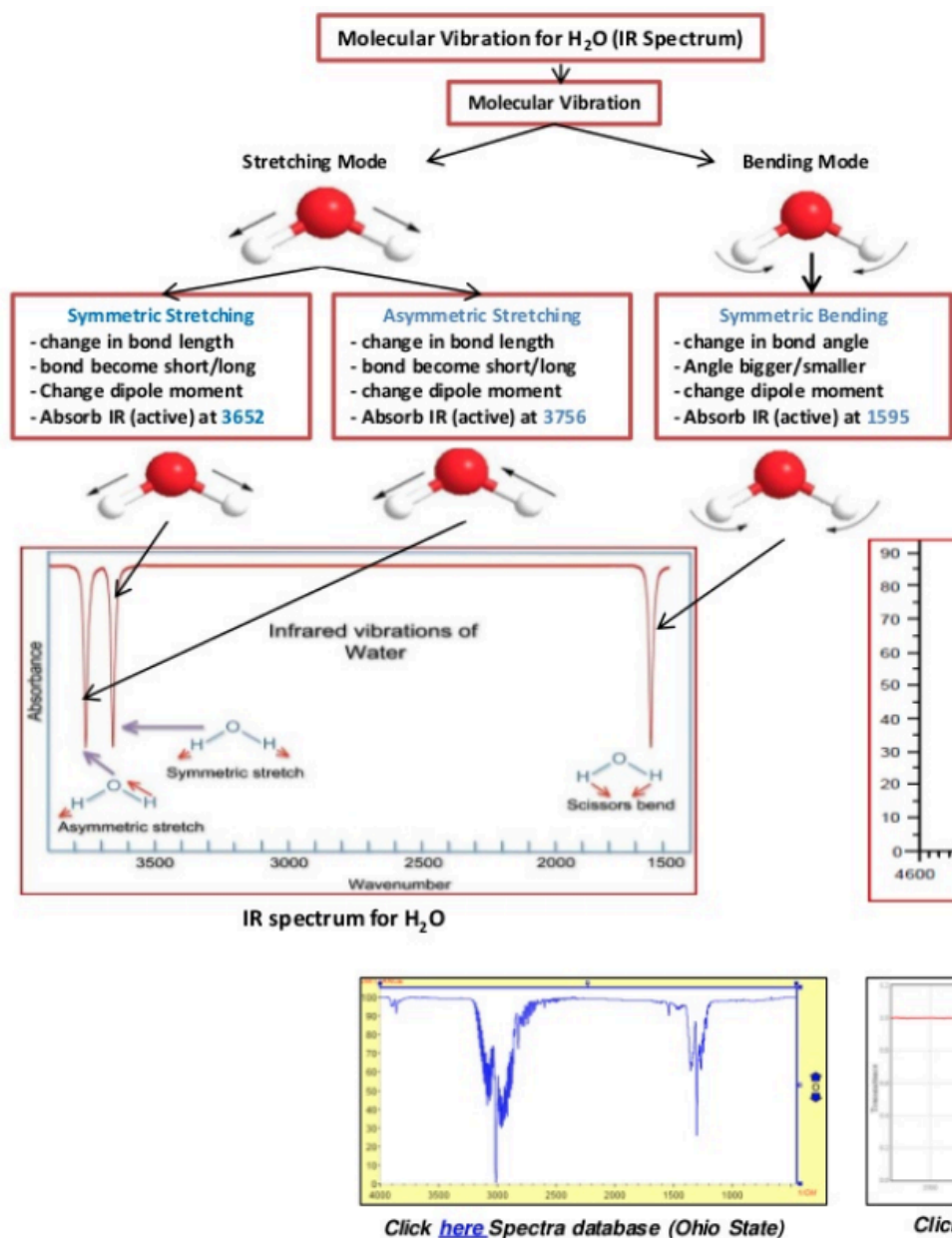


Figure 41. H₂O IR (thermoelectric) Vibration Modes and Respective Spectrum. Notice the 3652cm⁻¹ is clearly shown to be IR. [54]

4.10.2 Contravention of the Rule of Mutual Exclusion

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

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

Band H ₂ O	Infrared	Raman
v1 - symmetric stretching (3652cm ⁻¹)	strong	strong
v2 - asymmetric stretching (3755cm ⁻¹)	very strong	weak
v3 - bending (1595cm ⁻¹)	very strong	weak

(Source, online lecture notes).

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

4.10.3 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 [55] From this it can be deduced the air (‘the ocean of if) absorbs IR photons just as an ocean of water does. The question is why is this principle not so for the atmospheric gases? The answer is, as claimed here, the air does, absorb with its Raman and TE modes.

4.10.3.1 Other ‘IR’ Active Thermolectric spectra of H₂O

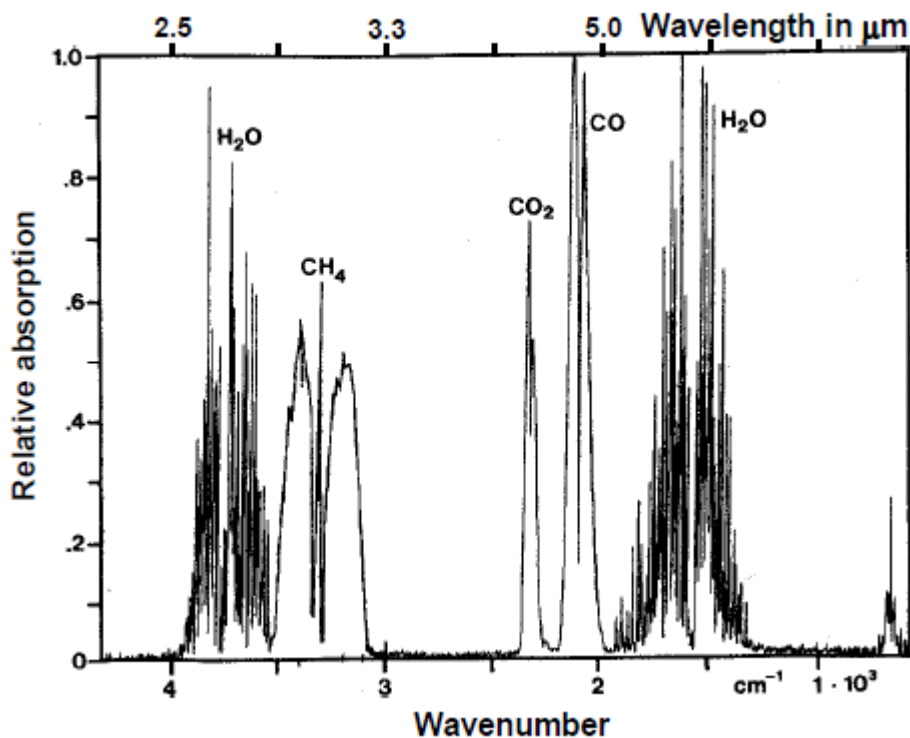


Figure 42. IR of H₂O and others.

4.11 Augmenting the IR Spectroscopy and Raman Atmosphere

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

Figure 43 below is a schematic of the predicted and observed Raman vibrational modes in the Earth’s atmosphere at different electromagnetic frequencies.

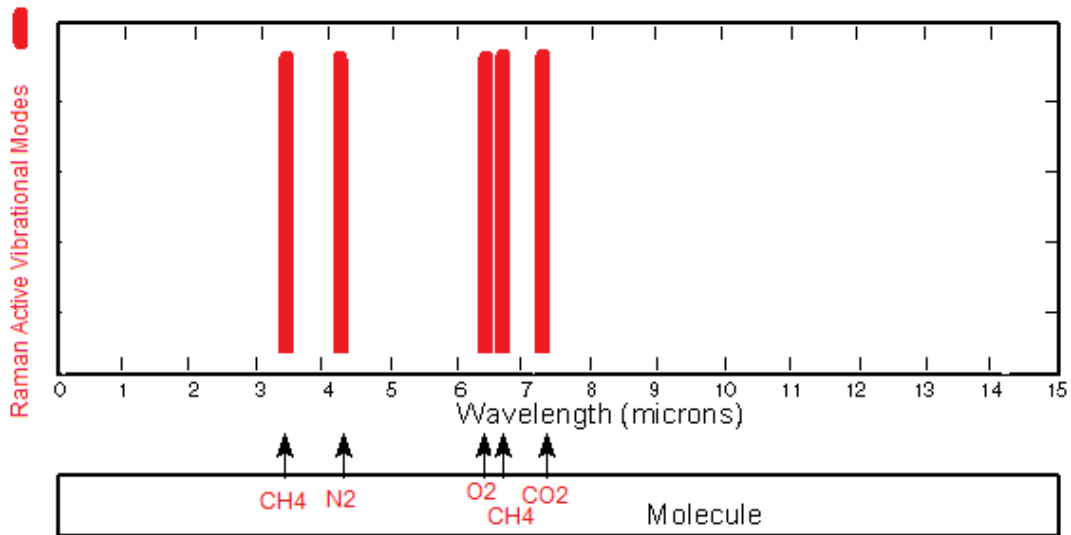


Figure 43. Raman Vibrational Modes of the Atmosphere. Predicted and Raman measured vibrational modes of (some) atmospheric gases CH₄, CO₂, N₂ and O₂.

4.11.1 The Augmented Fourier Greenhouse Atmosphere spectrum

Combining thermoelectric and Raman Spectrographs (Figure 44 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.

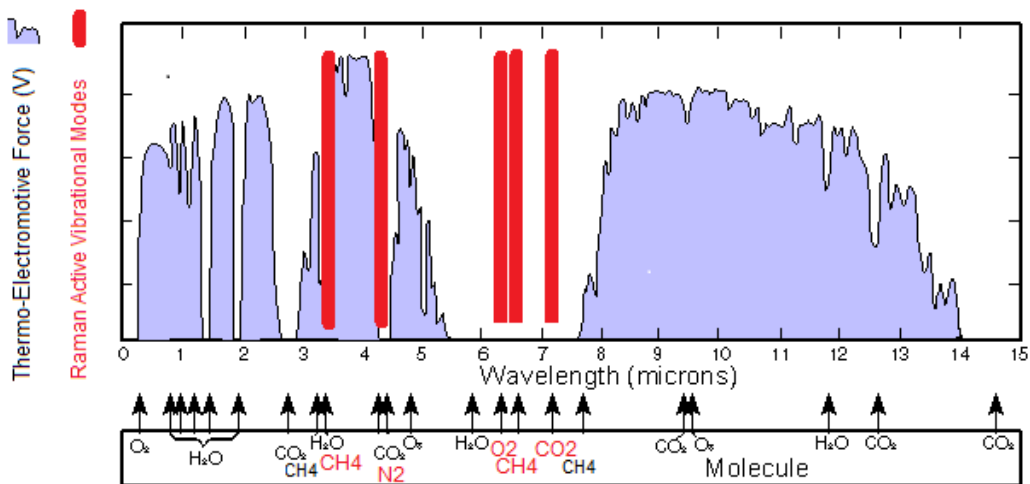


Figure 44. The Augmented Greenhouse Atmosphere. Combining Thermoelectric spectra with Raman spectra to reveal the complement of atmospheric vibrational modes and the greenhouse atmosphere of planet Earth.

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

Below (Figure 45) is a diagram of the Fourier Atmosphere as read from complementary instruments thermoelectric and Raman.

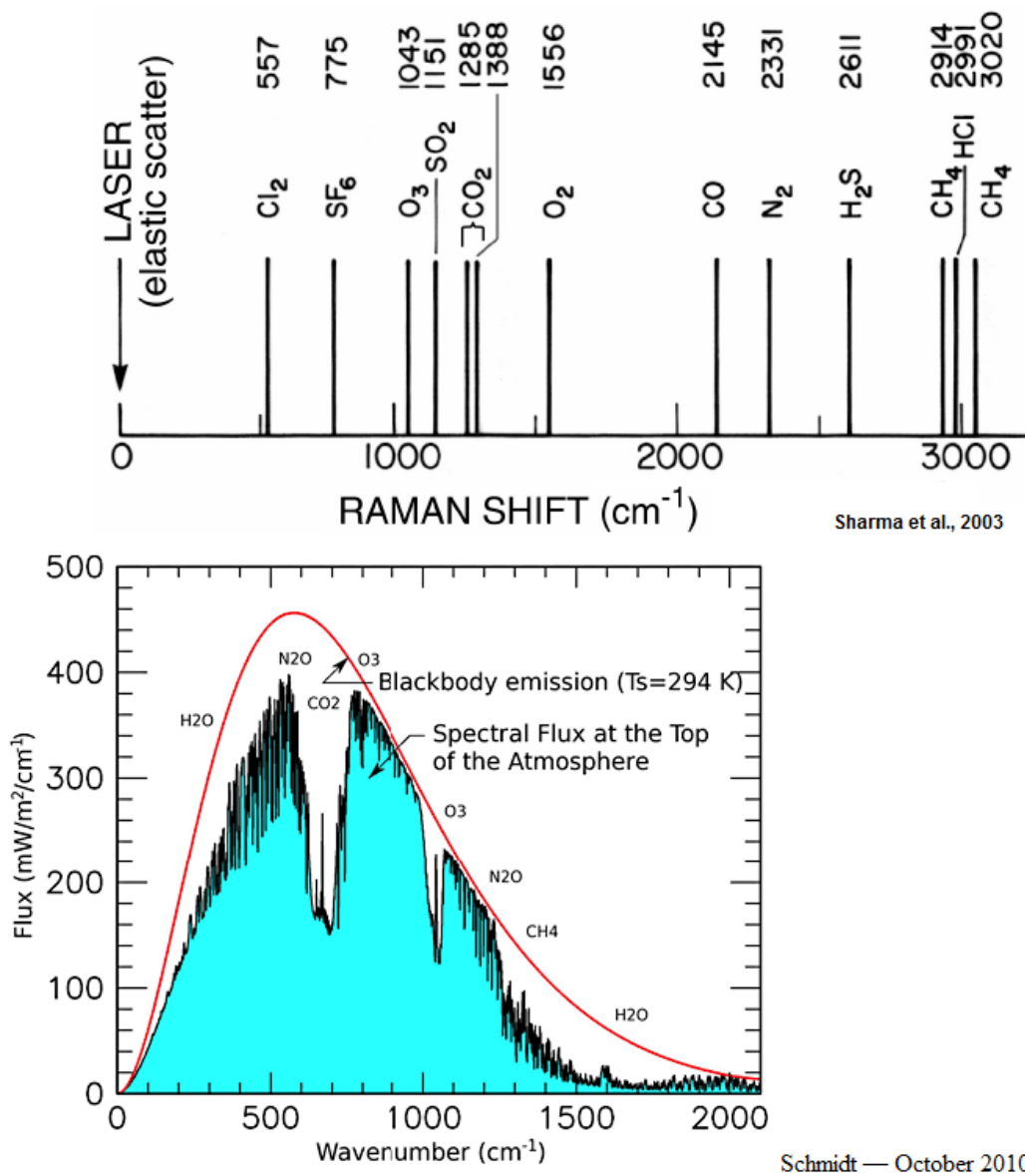


Figure 45 'IR' Thermolectric with Raman Atmosphere. Combining the two methods of accounting for constituent gases, namely N_2 O_2 H_2O , CH_4 O_3 and more, to complete the Fourier Greenhouse Atmosphere.

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

4.11.2 The Implications of Raman Spectroscopy on Current GH Theory

The current model assumes and is dependent upon the premise the non-GHGs do not absorb or emit any IR radiation[56], at any temperature; if they did, standard GH model would collapse. As it stands; if the simple question is asked; does that air gain heat from the sun? The obvious and intuitive answer as it is heated (directly) by the sunlight; but this is not the answer by GH theory. The GHGs are assumed by GH theory (Figure 46) to be the only gases to absorb 'outgoing long-wave' infrared (IR) radiation which has been in turn re-radiated back (up) from the Earth's surface after been absorbed by the Sun – by 'insolation'. IR-heat radiation is not directly absorbed by the Sun in the atmosphere itself[1][2]. This paper has overturned this assumption. The Sun's radiance does not pass 'through the clear atmosphere' as assumed in the schematic below; if it does it interacts on the way.

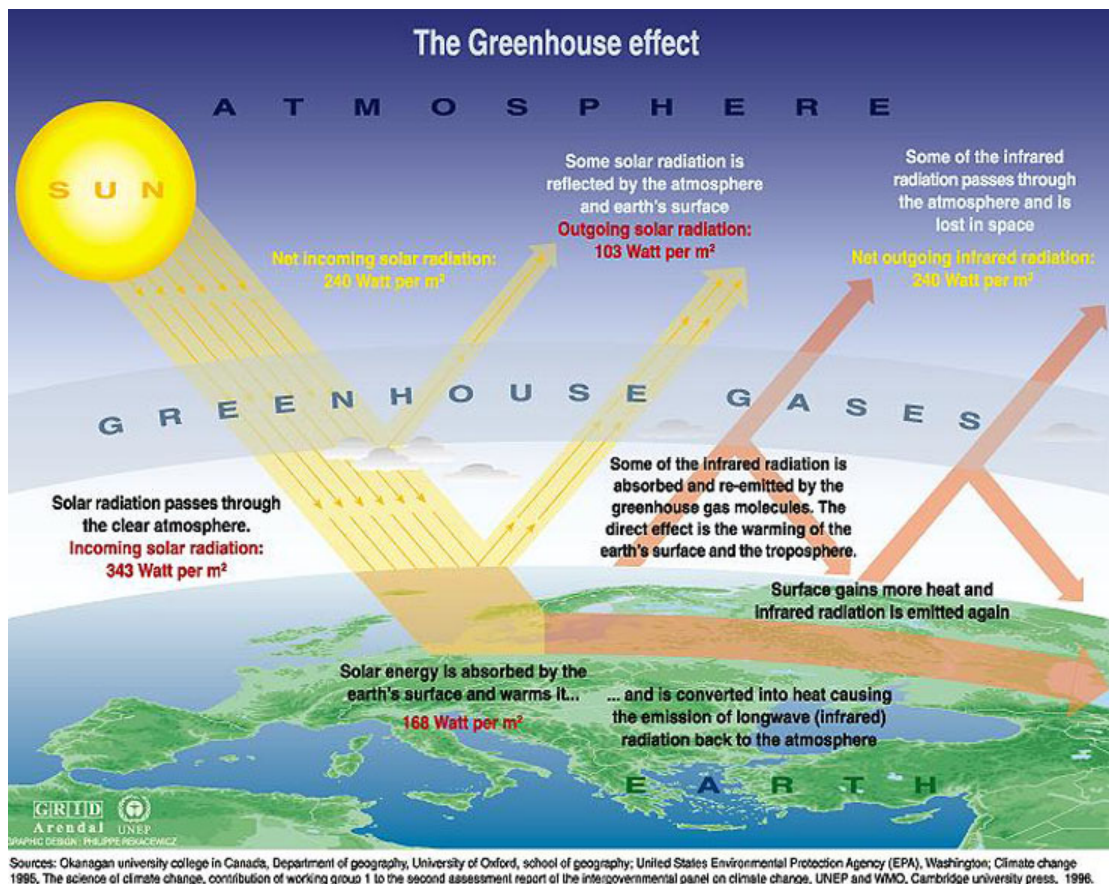


Figure 46. 'Natural Greenhouse effect[57]. The standard GH model where the atmosphere does not absorb any solar radiation and it is the 'special' GHGs that absorb and emit 'longwave (infrared) back to

the atmosphere after been heated from the Earth's surface. This claim is totally challenged in this paper: all the atmosphere absorbs, directly from the sun, and from the surface.

4.12 Strengths and Limitations

The following has been derived from, and is in anticipation of, reviewers' questions and criticisms.

The following are instances atmospheric N₂ absorbs IR photons.

4.12.1 N₂ Absorbing in the 'Hot' Thermosphere and the Aurora

N₂ and O₂ are excited by charged particles in the thermosphere and temperatures for these molecules reach up to 2000°C; it is **Raman** devices that are used to measure this temperature – in the lower thermosphere [58]. This is added proof that N₂ and O₂ are directly affected by IR photon radiation: if they absorb, they emit also. It can also shown charged particles heat the N₂ atmosphere during an aurora: further evidence of absorption.

4.12.2 IR Absorption and Thunder Creation: Lightning Heating the Air

From lightening radiation, the air is heated to 5 to 7 times the temperature of the sun. This radiation is consistent with N₂ absorption of IR photons and may stand as a 'natural' demonstration or experiment of the hypothesised.

4.12.3 IR Absorption and the Incandescent Light Bulb

While looking for supporting evidence of IR absorbing N₂ and O₂ and noticing the hot air is moving around the outside of the bulb when on. I wondered; what if the bulb were filled with air or N₂, what would result, a pressure increase? It turns out bulbs are filled with gas – mostly Argon (Ar) and small percentage N₂[59]. Neither of these gases are IR (thermoelectric), and they are said to warm inside the bulb by conduction. However, given the pressure inside the bulb is 70% of an atmosphere (to deal with the pressure problem) and Ar and N₂ are both very poor thermal conductors (argon even less than N₂ at 0.016 W/m K [60]), it is plausible the gases heat mostly – if not all – by radiation, as I have claimed.

4.12.3.1 Non-TE/IR Non-Raman Argon

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

4.12.4 Non-Radiant and Non-Conductive N₂ and O₂ Heat Capacity Paradox

How do N₂ and O₂ have a heat capacity if they do not radiate or have a strong nominal conduction value, when the fact is they do have a heat capacity?

Not withstanding the above (4.1.4), N₂ and O₂ both also have nominal – similar to other gases – heat capacities. This energy is only further transferred by means of convection and conduction mixing; and this presents another paradox: if most of the air does not transfer heat by radiation, and only by conduction and

convection, how is this accomplished when the air is a known as a poor thermal conductor of heat-energy, and is, in fact, a thermal insulator, with a thermal conduction value of near zero: 0.024 W/m K [60]. How can conduction, and related convection, stand alone as the means of heat transfer in the atmosphere? Without radiation and conduction, the atmosphere should not exist the way it does. The reality is; the atmosphere seems to behave in total accordance with the 0th, and 1st laws of thermodynamics, and also the Stefan-Boltzmann Law of radiation.

The discrepancy between the GHGs and the non-GHGs presents another paradox associated IR radiation theory, and it is to do with the gases respective specific heat capacities (SHC). All the atmospheric gases have specific heat capacities (as shown in Table 5, column two) which says they transfer energy by one type of the three types of transfer of heat directly. The paradox sits with how the non-GHGs N₂ and O₂, as assumed by GH theory, are also – like all other atmospheric gases – very poor conductors of heat (column 3) with values of near 0. This leaves only convection, but this is improbable due to the former types being poor or exempt (as addressed below in 4.8.5). The question is: how can these Non-GHG gases, specifically N₂ and O₂, have specific heat capacities if they cannot transfer heat energy without radiation as assumed or conduction as known?

Table 5. Comparing Gas Specific Heat Capacity with Thermal Conductivity and Radiation

Properties. Source: 'engineeringtoolbox.com.

Atmospheric Gas	Specific Heat Capacity -C _p - kJ(kgK)	Thermal Conductivity -k- w/(mK)	Assumed to Absorb IR Radiation? Yes/No
Ar	0.520	0.016	No
N ₂	1.04	0.024	No
O ₂	0.919	0.024	No
CO ₂	0.844	0.0146	Yes
CH ₄	2.22	0.003	Yes
He	5.19	0.142	No
Air	1.01	0.0262	Only the GHGs

The only way to reconcile this paradox is to assume radiation absorption – as demonstrated throughout this investigation – does take place with the non-GHGs, and presumably does so at their respective Raman modes.

4.12.5 Standard (bottle) Greenhouse Experiments, and SHC Measurement

One of the most popular demonstrations of the greenhouse gasses is the 'greenhouse bottle experiment'[61] where CO₂ in one bottle and air in another is radiated by thermal radiation and temperature through time recorded (Figure 56). The CO₂ bottle temperature rises highest as shown below. However, with knowledge of specific heat theory and the specific heat capacities of the respective gases – not withstanding the difference between constant volume (as assumed in the demonstrations) and constant pressure; I claim is this not an experiment demonstrating the specific heat capacity of air and CO₂, where CO₂ has a low heat capacity relative to air – as described in the next subsection.



Figure 47. Greenhouse Gas Bottle Demonstration [62]. Bottles with CO₂ and air are radiated and temperature measured – CO₂ in blue. Is this not an experiment to measure the heat capacities of the respective gases?

Below is an image taken from a specific heat capacity demonstration; if two more boxes were added showing the effect of air (C_p 1.01) and CO₂ (0.8), it would be understandable the CO₂ would have a higher temperature, concurring with GH demonstrations.

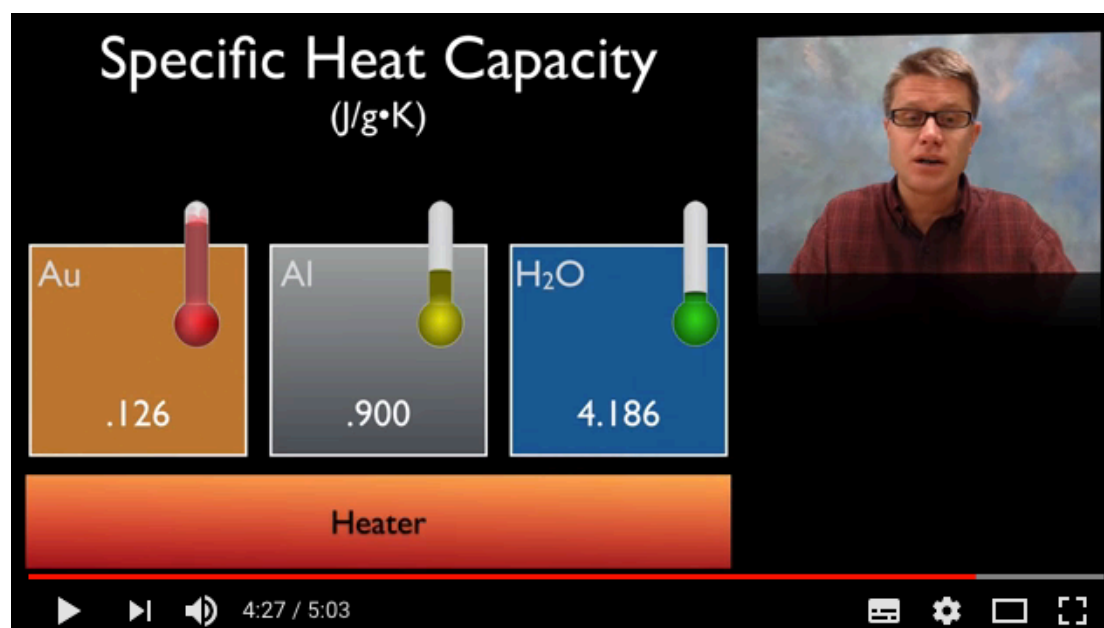


Figure 48. Specific Heat Capacity. The lower the heat capacity, the higher the temperature from single heat source.

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

In the standard experimental method to measure gaseous heat capacities an 'electric heater' element is used to heat the gas. The apparatus and method is inseparable from the above GH demonstrations – they are equivalent[63]. The electric heater implies radiation, as conduction is so low. And as a result of this radiation absorption, there will be convection. The closest solid to share the conduction properties of air – with a conduction value of 0.017 – is Aerogel – and is used on spacecraft for these properties. It is said to be 'extraordinary' with respect to this property.

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

As it is assumed the GHGs absorb IR heat radiation in Specific Heat measurement – at their respective TE/IR and Raman modes as presented in this investigation – it is equally plausible the non-GHGs, on the same principles, are absorbing IR heat radiation at their respective Raman modes, proportional to the resulting and measured specific heat capacities. Support for this claim is found with CO₂ and CH₄; both are poor thermal conductors (as with 'air') and both are IR (thermoelectric) emitters. From this investigation, and the equipartition principle, all their modes (TE and Raman) are equivalent; and so this must be so for the non-GHGs N₂ and O₂ also.

4.12.7 Vibrational Behaviour and Specific Heat Capacity

It is interesting to read when investigating the fundamental knowledge behind Specific Heat of matter: it is said to be 'by the vibrational behaviour of molecules' – as described earlier in this investigation – including the 'degrees of freedom' that determines the specific heat capacity of a substance. This adds further weight to including the Raman modes to radiation theory. Molecules such as N₂

and O_2 vibrate, they have degrees of freedom, and they have specific heats – so they must radiate IR also, at their Raman modes.

4.13 What is Next?

There are unanswered questions from this work that need to be addressed: why do N_2 and O_2 not show up in IR Spectroscopy? With respect to this question the following text is a (typical) chemistry explanation – as to why N_2 and O_2 are not GHG's:

“ 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. So N_2 has no dipole, and an EM photon passes by without being absorbed. Similarly, for O_2 .” [64]

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

5 Conclusions

It was found N_2 and O_2 , and all of the atmospheric gases, consistent to quantum mechanic's Schrödinger equation, have predicted spectra bands or modes – at 2338 cm^{-1} and 1556 cm^{-1} respectively – in the IR range of the EMS and these modes are observed by IR spectroscopies complement – and the one GHG deriving – instrument; Raman spectrometers. Consistent with radiation theory, by Raman Spectroscopy the temperature of the atom or molecule was measured at these predicted spectra. Raman instruments measurements concur with standard physical principles – including the Boltzmann constant – to the extent they can measure temperature and gas concentration to an equal of the greater degree of precision than it's similar thermoelectric counterpart. It was found modern Raman spectroscopy technology can measure the concentrations of the all the gases constituents of the atmosphere, equivalent to, and may stand as a substitute to, the current Keeling curve 'IR' spectrographic method. It is for this reason it is one of the instruments of choice on solar system space probes.

Further to this, it was shown, by practical application, the N_2 molecule absorbs IR photons in the operation of the (solar) N_2 - CO_2 laser: all dependent upon of it's quantum predicted 2338 cm^{-1} absorption mode. When the N_2 is radiated by electron discharge, or photons, it was also found to be long lasting 'metastable' absorption – essential in the laser process – and this heat-energy gained (pumped) is transferred directly to CO_2 's close mode at 2349 cm^{-1} . From this understanding of the IR absorption-emission properties of N_2 , at its one absorption mode, it can be inferred N_2 absorbs in the atmosphere infrared photons **by law**, by the identical process as demonstrated as in its role in the N_2 - CO_2 Laser. In this process, solar insolation – of IR photons – accounts for changing air temperature. By the photon absorption process of N_2 , it can be said, it is the N_2 that affects the CO_2 . This finding is totally inconsistent with greenhouse theory; however, it has the quantum physics and the quantum application – not to mention the real constituent volume of the gas – directly supporting it. This may well explain how air instantly rises in temperature – in the process of thunder production – to some '3 times the temperature of the surface of the sun', and how N_2 molecule reaches the temperature of 27000K in the thermosphere. It can be concluded the atmosphere absorbs IR radiation from the sun by (solar) insolation directly and warms the air just as it does the H_2O of the oceans and the like are, rather than indirectly, as it is currently assumed. It can also be concluded from this work it is not the gases that are special but rather it is the instruments that measure them. In support of this it was found all three of H_2O 's IR radiating modes (section 4.10.1), the modes pointing to them being GHGs, particularly the 3652 cm^{-1} mode, are both – or dual – Raman and IR active. CO_2 's only Raman active mode at 1388 cm^{-1} must be temperature equivalent – by the equipartition principle – to it's complementary 'IR active' modes – measured at 2349 cm^{-1} and 667 cm^{-1} (section 4.4.6.1). This says the detectors are equivalent: both can and should measure the temperature of these molecules. Modern Raman spectroscopy is so accurate – it does not suffer the emissivity problem – it should make 19th Century IR spectroscopy redundant. This finding has implications also on the IR (alone) derived 'blackbody spectrum'. It was concluded here this curve needs updating and may even be redundant with Raman Laser technology.

In respect to heat capacities, it was discussed Raman spectra properties also correspond to the nominal heat capacities of the said gases where with IR theory alone they are both non-absorbent and non-thermal conductive.

With this inclusion of the quantum mechanics to atmospheric models – and the direct mechanics behind Raman spectroscopy – it was revealed the current understanding of the ‘greenhouse’ atmosphere is fallacious, and built on outdated methods and equipment. Raman spectroscopy makes IR spectroscopy redundant. Quantum mechanics holds, not GH theory; all matter does radiate. It should finally be concluded all gases are GHGs; just as first posited by Joseph Fourier (and maybe others) ca. 1828. The non-GHGs should be known as the Raman gases; and together they all should constitute as the GHGs. There are no special gases. With this new understanding, all gases comply with the 0th and 1st Laws of Thermodynamics – transferring energy towards equilibrium where previous to this N₂ and O₂ were exempt. Any extrapolation based on IR spectroscopy technology alone – without reference to Raman spectroscopy – interpreting these as the only special ‘IR absorbent’ GHGs should be seen as inadmissible – not only in climate and atmospheric theory, but also any radiation theory. Climate models will need to be updated to take account of the – currently well understood method by all chemists – Raman spectroscopy.

6 Acknowledgements

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

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8 Appendix

8.1 Other Uses for Raman

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

Investigating whether CO₂'s 1388cm⁻¹ is excited in any way by radiation – it should not as this mode, like N₂ and O₂'s is 'Raman active' and not 'IR active' and thus, by current assumptions, should not transmit photon energy – it was found this mode is affected 'where the spectral exchange and Dicke effect play a noticeable role' [65]. The Dicke effect: 'refers to the Doppler broadening of a spectral line due to collisions the emitting species (atom or molecule) experiences with other particles' (photons) ;...the atom changes velocity and direction many times during the emission and absorption of the photon[66].

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

OPTICAL PROPAGATION IN GASES 299

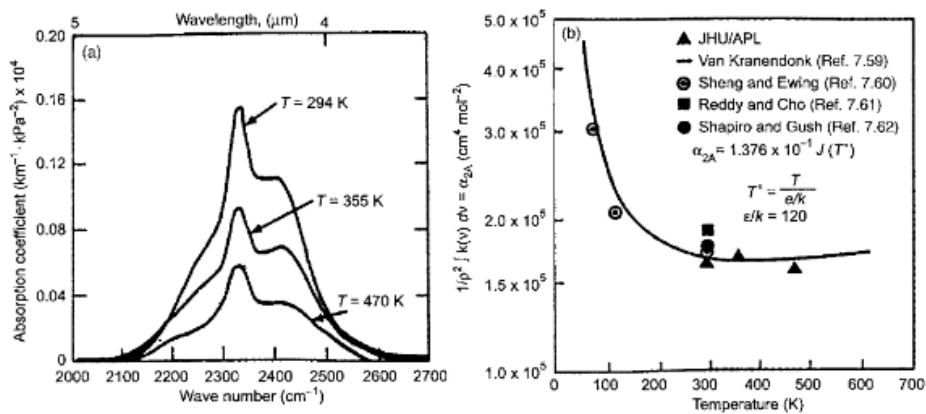


Fig. 7.21 Collision-induced absorption in the fundamental vibration band of N₂. (a) Band shape at various temperatures and (b) integrated intensity versus temperature (Thomas, Ref. 7.50).

[67]

8.1.2 Medical – anaesthetic RASCAL – Capnography Application

"In 1988 a Raman scattering instrument was introduced for clinical use. The Raman SCattering AnaLYzer (RASCAL)...for O₂, CO₂, N₂, N₂O; both identify and quantify these gases." *"This device is no longer marketed"*[68].

These Raman devices have since advanced and are used.

"These analysers have fast response times. They can analyze multiple anesthetic agents with good accuracy (greater than infrared spectroscopy, approaching mass spectrometry)" [69].

8.1.3 Geology CO₂ 1388 cm⁻¹

In the following study: "Quantification of dissolved CO₂ in silicate glasses using micro-Raman spectroscopy" CO₂ is identified at its IR 1388 (or near about) cm⁻¹ mode.

'we propose the calibration accuracy is better than ± 0.4 wt% CO₂ for our data set'[70]

8.1.4 Automobile Emission Testing.

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

The from the USA EPA: *"Raman LIDAR is self-calibrating to atmospheric oxygen and nitrogen, eliminating requirements for periodic calibration with test gases."*[71]

"The results indicate an excellent ability to identify and quantify the test species. By analyzing the sensitivity of these Phase I laboratory experiments, we estimate that the Compact UV Raman LIDAR system will be capable of achieving better than 120 parts per million (PPM) sensitivity for NO, 40 ppm for N₂ and CO, and 10 ppm for NO₂ and hydrocarbons."

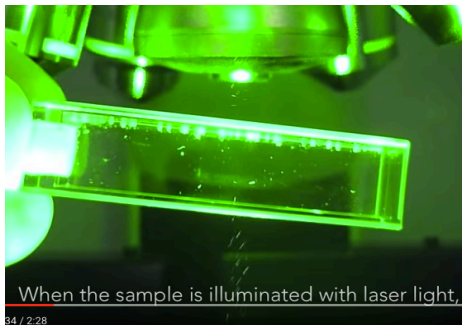


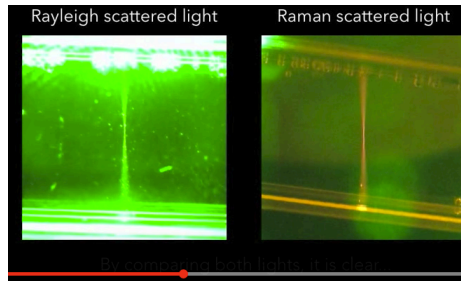
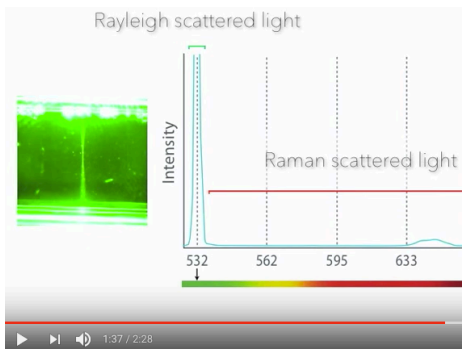
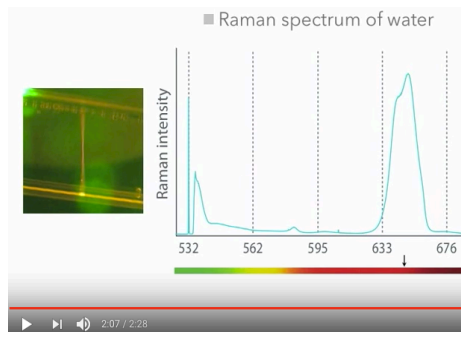
Truth be known, Raman can equally detect and quantify CO₂ (by its Raman 1388 cm⁻¹ mode) as revealed in the following study. However, before we go there, in the study 'Rotational Raman Spectroscopy for the Remote Sensing of Carbon Dioxide' [72] they concluded: "No Raman peaks were observed, so that the usefulness of rotational Raman for the remote sensing of CO₂ was not demonstrated."

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

In the book 'Automotive Exhaust Emission Testing..' they acknowledged the (potential) use of Raman "Both methods (IR and Raman) are complementary" [73] pg. 128; however, it did not go onto show the use of Raman.

8.2 Understanding Raman Backscatter and the Low Wavenumbers

It has been quoted to me that these lower Lidar wavenumbers – at 580nm and 607nm respectively – are inconsistency with my theory and show N₂ and O₂ in the atmosphere do not vibrate – emit and absorb – in the IR range of the EMS as these modes or bands are in the visible range of the EMS; I have researched these lower modes and found they indeed reveal the IR modes – they need correction. The reason the Lidar wavenumbers are quoted low is because they are quoted in relation or reference to the laser frequency of the Lidar laser. They work on the 'Raman backscatter'. When adjusted for, the differences are corrected (up) and correspond the predicted wavenumbers. This is demonstrated in the youtube presentation below[74] where in the last moments it is said: ". By using wavenumber, we see the excitation of water, independent of the excitation wavelength".

<p>A</p>  <p>When the sample is illuminated with laser light,</p> <p>0:34 / 2:28</p>	<p>B</p>  <p>This is Rayleigh scattered light</p> <p>0:39 / 2:28</p>
<p>C</p>  <p>Here is a filter that blocks green light.</p> <p>0:46 / 2:28</p>	<p>D</p>  <p>Rayleigh scattered light Raman scattered light</p> <p>0:58 / 2:28</p>
<p>E</p>  <p>Rayleigh scattered light</p> <p>Intensity</p> <p>Raman scattered light</p> <p>532 562 595 633 676</p> <p>1:37 / 2:28</p>	<p>F</p>  <p>Raman spectrum of water</p> <p>Raman intensity</p> <p>532 562 595 633 676</p> <p>2:07 / 2:28</p>
<p>G</p>	

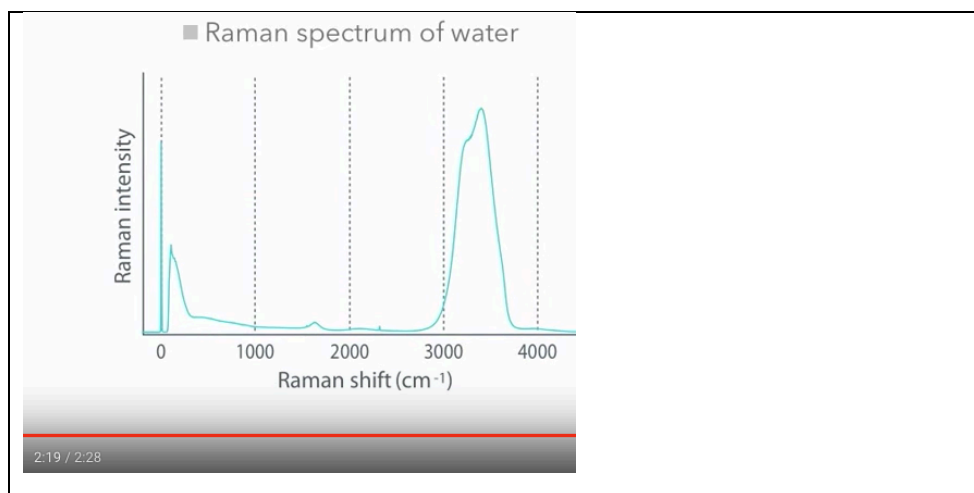


Figure 49. Raman Lidar wavenumber discrepancy Explained. Screen shots of a Youtube presentation [74] showing how green 532nm laser light is shone (A) onto water in the case Raleigh light is revealed (B and E), but when filtered Raman red 660nm light is revealed (D and F). When this adjusted for wavenumber (cm^{-1}) H_2O 's vibration band 3652cm^{-1} is revealed.

8.2.1 Raman Laser to Wavenumber Correction Calculation

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

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

Calculate the oxygen Raman wavelength:

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

With an excitation wavelength at 532 nm the oxygen Stokes line will appear at $1/532 \text{ nm} - 1556 \text{ cm}^{-1} = 18797 \text{ cm}^{-1} - 1556 \text{ cm}^{-1} = 17241 \text{ cm}^{-1} = 580 \text{ nm}$

Calculate the signal strength:

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

This means that the signal is $1000 \times \frac{1}{4} \times 1.41 = 352 \text{ counts}$



Figure 50. Scattering to Wavenumber calculation for Nitrogen. Nitrogen's 1556 cm^{-1} predicted and observed (with Raman spectroscopy) vibration mode is corrected for the 532nm laser. [75]

8.3 Raman spectra for Non-GHGs and GHGs

8.3.1 O_2 and N_2

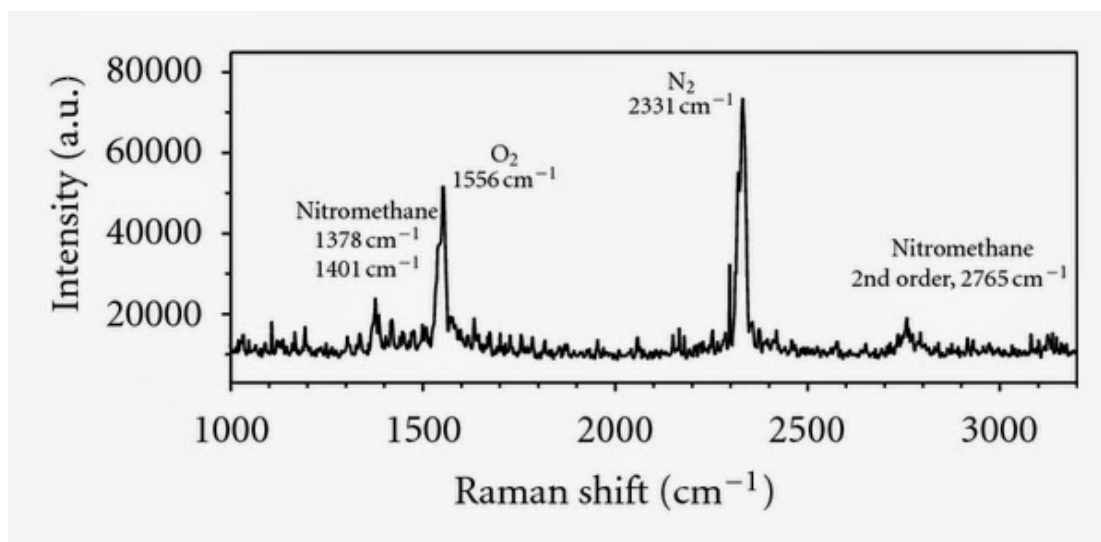


Figure 51. [76]

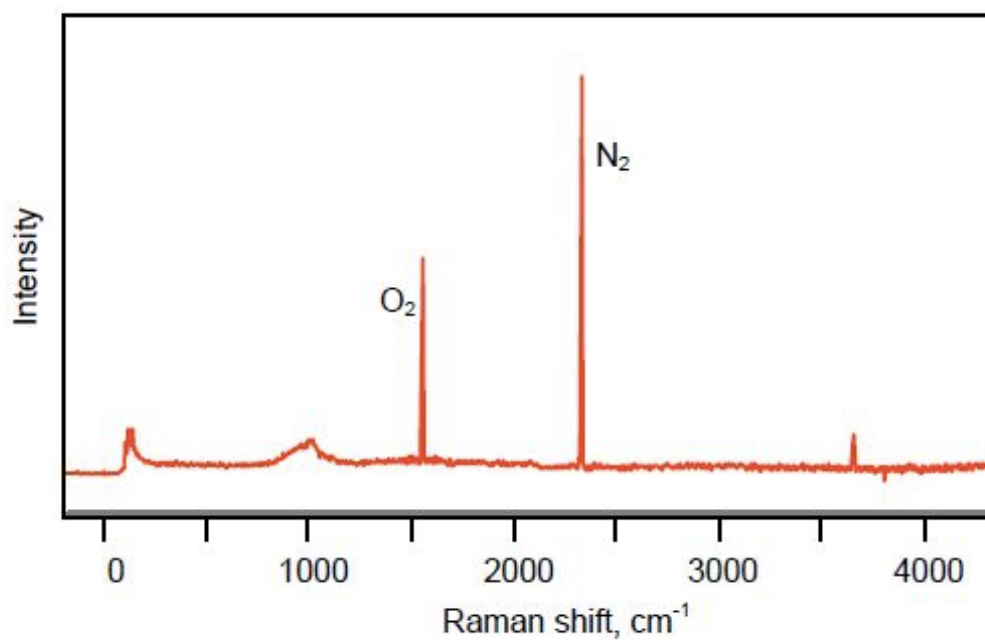


Figure 52. Raman spectrum of air, with the oxygen and nitrogen bands marked. [77]

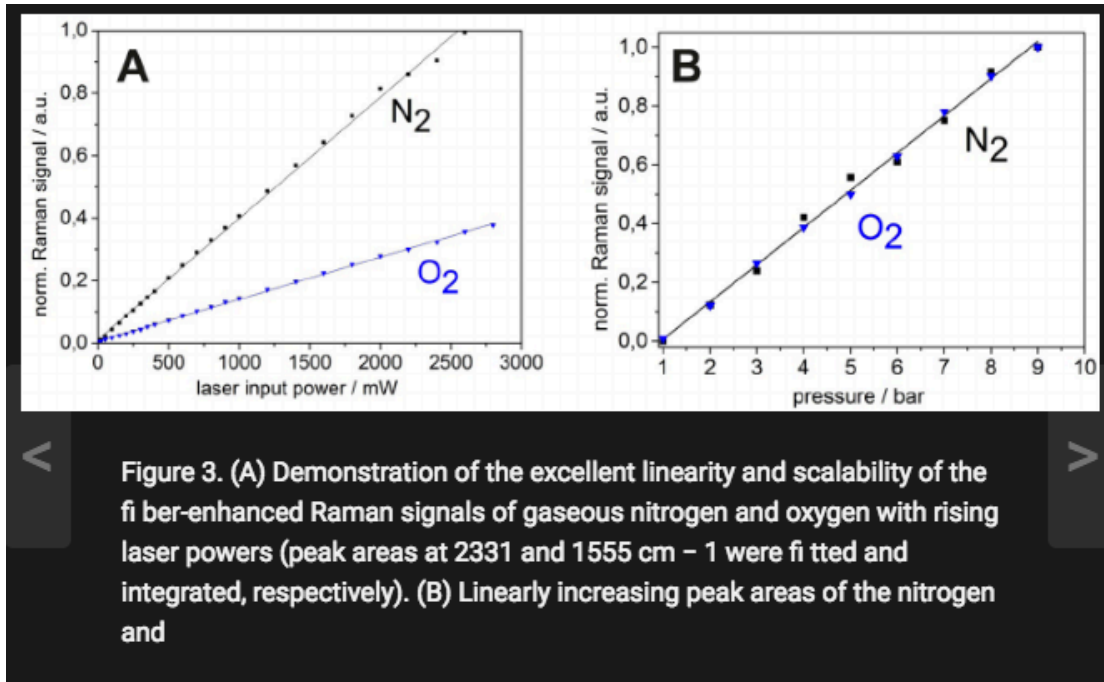


Figure 53. The above three images above: [78]

8.3.2 O₂ Spectra

300 OPTICAL PROPAGATION IN LINEAR MEDIA

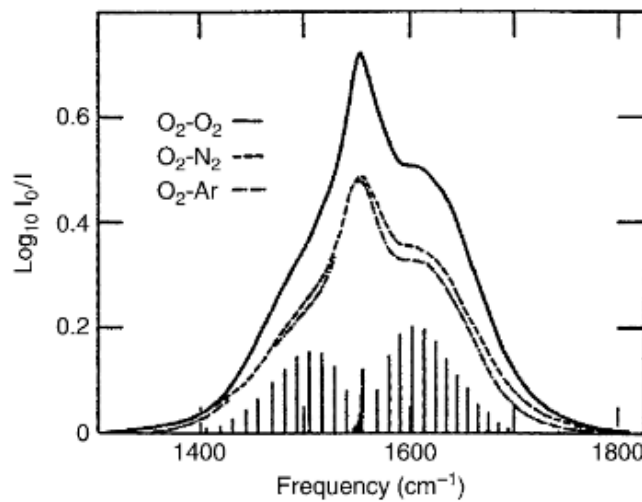


Fig. 7.22 The fundamental absorption band of oxygen for a path length of 40 meters. The densities are: pure oxygen 9.59 Amagats; oxygen–nitrogen mixture, $\rho_{O_2} = 1.09$ Amagats, $\rho_{N_2} = 56$ Amagats; oxygen–argon mixture, $\rho_{O_2} = 1.12$ Amagats, $\rho_{Ar} = 57.9$ Amagats (Shapiro and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

Figure 54. [67]

8.3.3 N₂ 2338 cm^{-1}

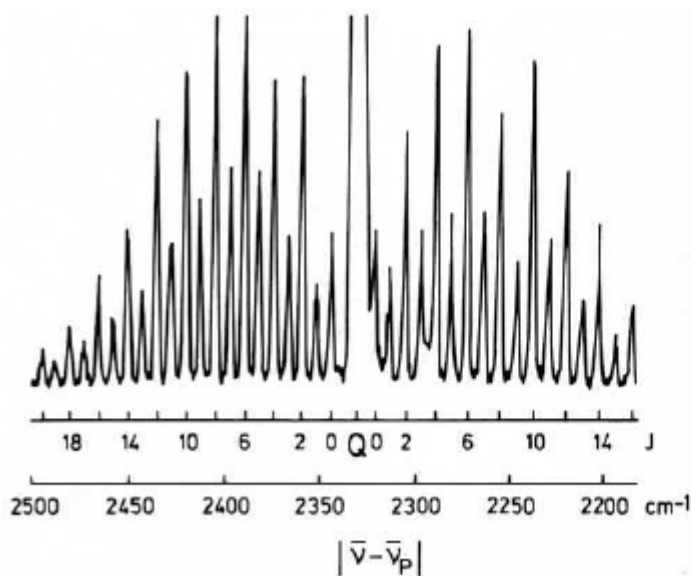


Fig. 12.11. The rotational-vibrational Raman spectrum of the nitrogen molecule, $^{14}\text{N}_2$. In the centre, at the position of the vibrational wavenumber $\bar{\nu}_e = 2330 \text{ cm}^{-1}$, the Q branch ($\Delta J = 0$) appears as a broad line. In $^{14}\text{N}_2$, with $I = 1$, an alternating intensity of the rotational lines with a ratio 1:2 is observed. After Hellwege

Figure 55. Raman peaks of N2 at the predicted 2330cm-1 – page 209 [79]

8.3.4 O₂ 1556

Figure 63 and 64 show Raman spectrograph peaks of N₂ at O₂ at the predicted 1556cm-1 and 2330cm-1 (pages 205 and 209 respectively) both within the infrared range of the electromagnetic spectrum.

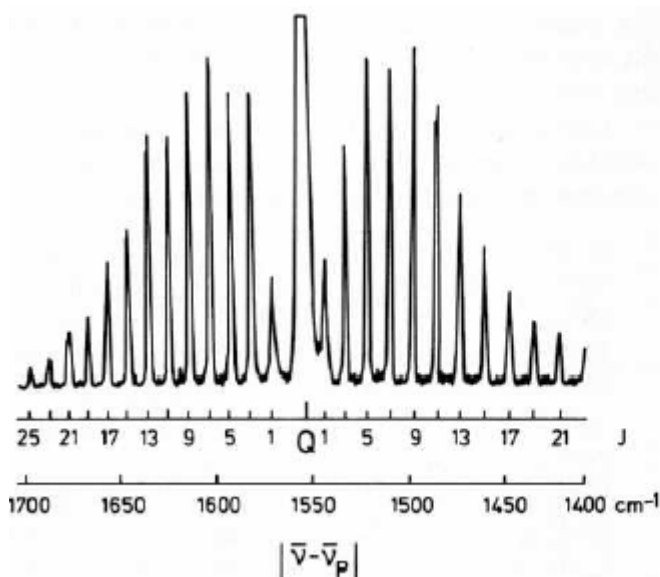


Fig. 12.7. A section of the rotational-vibrational Raman spectrum of oxygen, $^{16}\text{O}_2$. This is a vibrational line (Stokes line) with its accompanying rotational lines. In the centre, at the energy of the vibrational wavenumber $\bar{\nu}_e = 1556 \text{ cm}^{-1}$, we see the Q branch ($\Delta J = 0$) as a broad line. For $^{16}\text{O}_2$ ($I = 0$), the lines with even J are missing; cf. Sect. 12.4. After Hellwege

Figure 56. Raman peak of O₂ at the predicted 1556cm-1 [79] – page 205.

8.3.5 CH₄

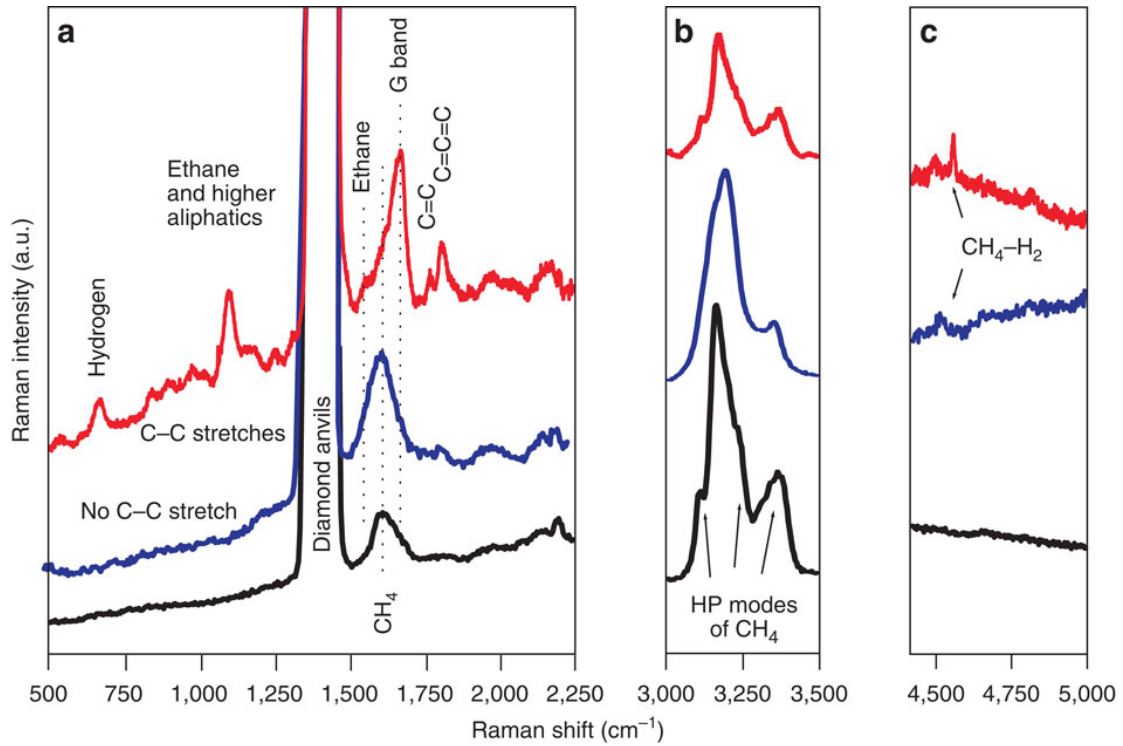


Figure 57. Synthesis in LH DAC at 48 GPa. Black line shows CH₄ Raman spectrum before heating. Blue line shows Raman spectrum collected at 1,445 K with evident CH₄ dissociation. Red line shows Raman spectrum of reaction products collected after heating to 2,000 K. The labels near the curves suggest the assignment of the Raman bands. HP modes of CH₄ refer to vibrations caused by partial orientational ordering of methane HP phase. Panels a–c show different parts of the spectral range.[80]

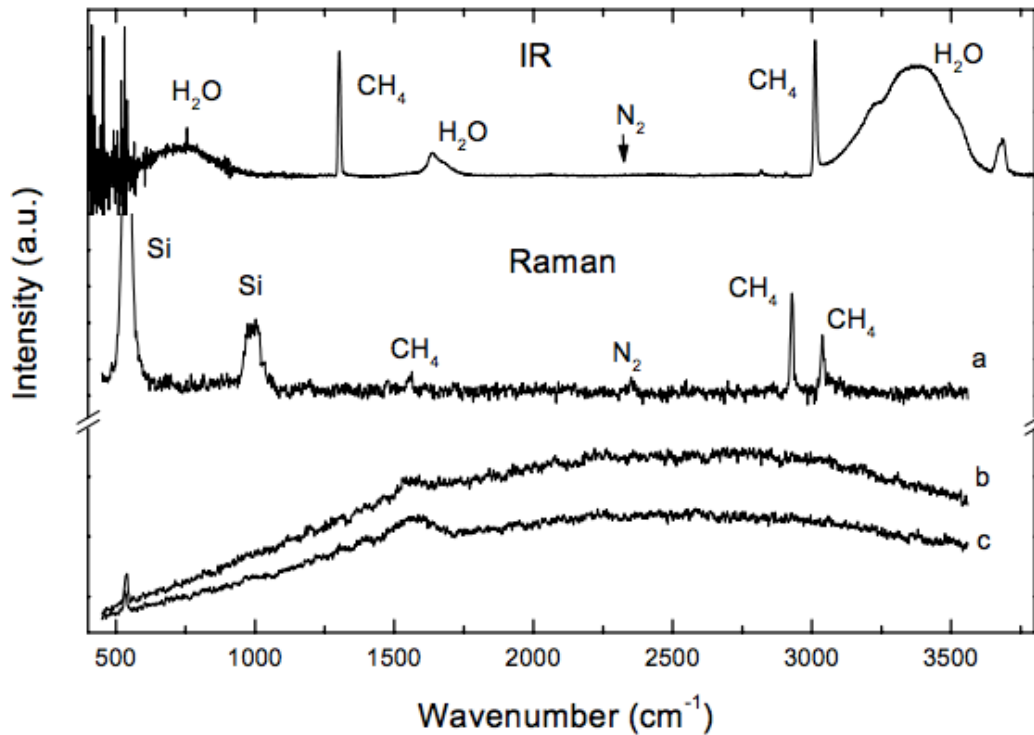


Figure 58. IR (top curve) and Raman spectra of the mixture H₂O:CH₄:N₂ before (curve a) and after (curves b and c, corresponding to doses of 378 eV/16 amu and 825 eV/16 amu respectively) irradiation with He⁺ (30 keV) ions at low temperature (12 K). In spectra b and c the ice features are undetectable 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 [81].

8.3.6 H₂

Hydrogen gas is assumed a non-GHG as it has similar properties to the other non-GHGs; however, it is predicted at 4342cm⁻¹ (table 2) and observed by Raman spectrometers as below Figure 59.

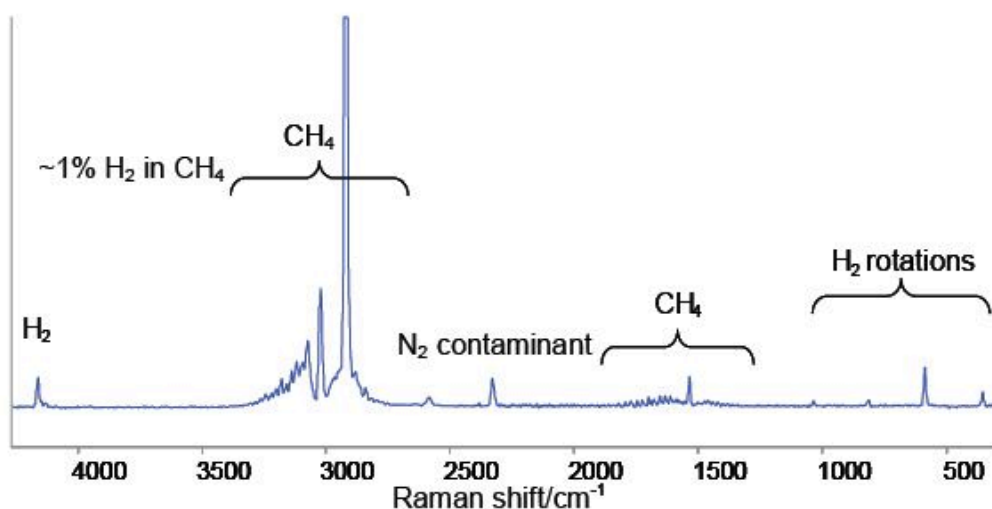


Figure 2. Raman spectrum of 1% H₂ in CH₄. The sharp bands below 1040cm⁻¹ are the pure rotational transitions of the H₂ molecule.

Figure 59. CH₄, H₂, with N₂ Raman Spectra. [82]

8.3.7 H₂O Raman

Earth atmospheric temperatures are too warm for H₂O's Raman signatures to show. The predicted vibrational modes are shown below.

KOLESOV: RAMAN INVESTIGATION OF H₂O MOLECULES IN HEMIMORPHITE

1359

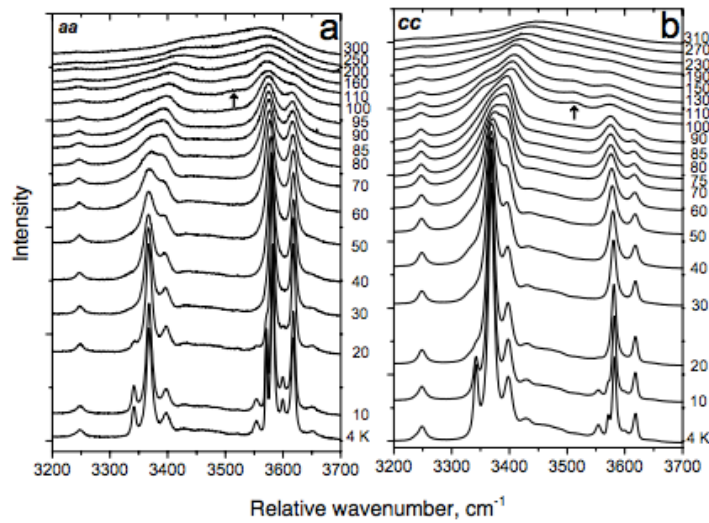
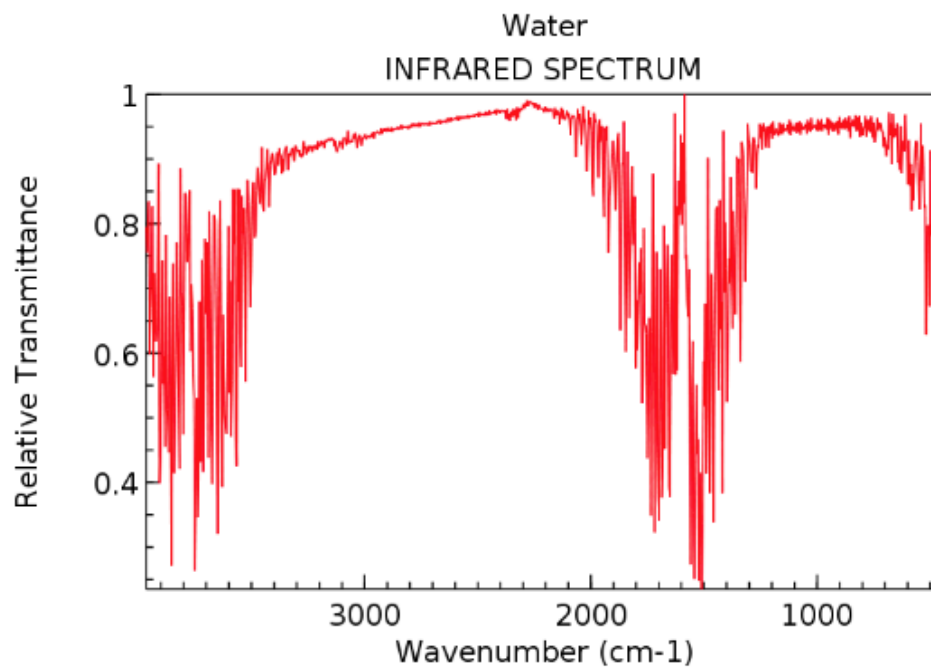


FIGURE 5. Temperature evolution of the polarized spectra showing the O-H and H₂O stretching modes in hemimorphite; (a) *aa*-spectra and (b) *cc*-spectra. The appearance of the new band at around 3500 cm⁻¹ at $T \geq 100$ K is shown by the arrow.

Figure 60. [83]

8.3.8 H₂O TE IR



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

Figure 61. H₂O IR Spectra Showing 3652cm Band.

8.3.9 Ge Germanium

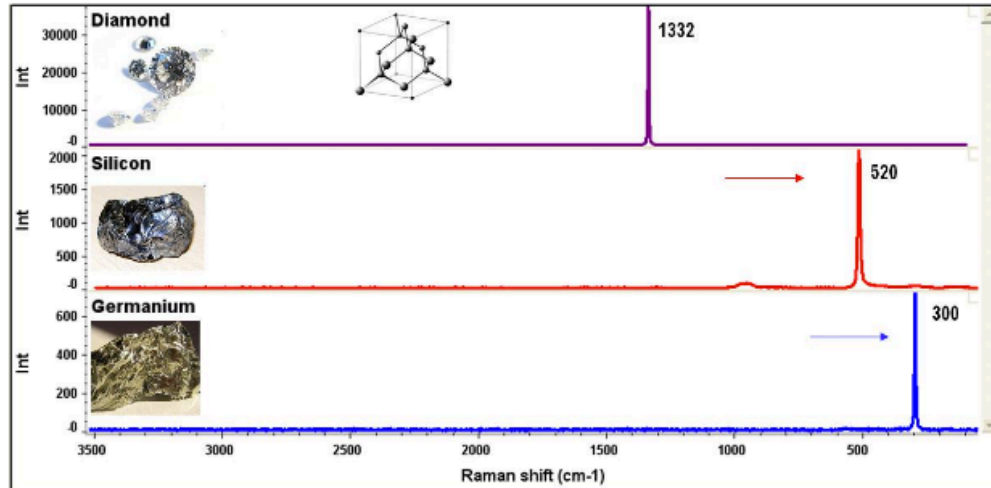


Figure 1: Raman spectra of diamond, crystalline silicon, and crystalline germanium

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

Figure 62. [84],[85]

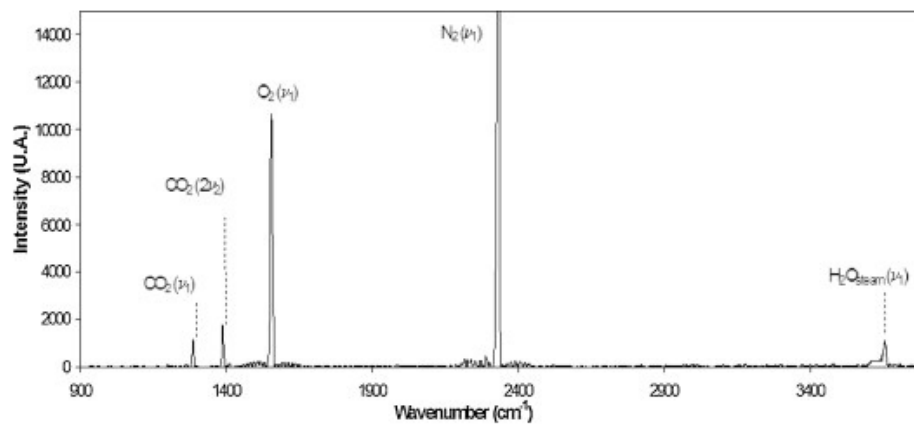
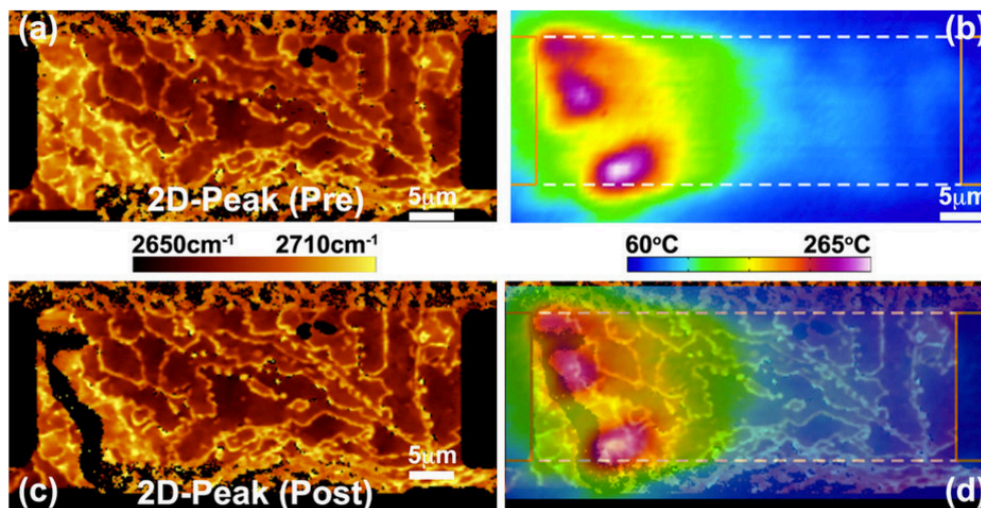


Figure 2. A typical Raman spectrum measured at the site in this study. Key peaks: H_2O vapor (3657cm^{-1}), N_2 (2331cm^{-1}), O_2 (1555cm^{-1}), and CO_2 (Fermi dyad at 1388 and 1285cm^{-1}).

Figure 63. Raman Spectra of N_2 , O_2 , CO_2 and H_2O together. [86]

8.4 Thermal Image with Raman

The following is a thermal image derived from Raman spectroscopy.



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

Figure 64. [87]