Dräger

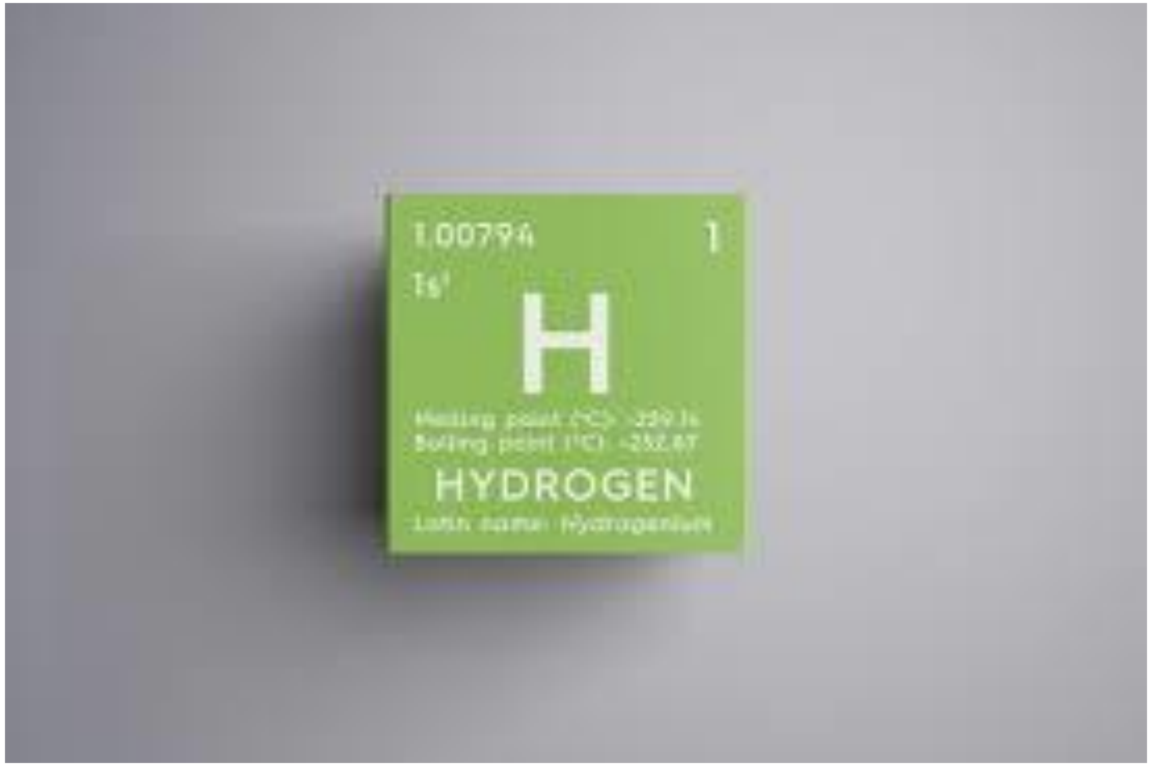
Hydrogen Safety

Megan Hine – Gas Detection

February 2022

Gases – and their properties

- Hydrogen

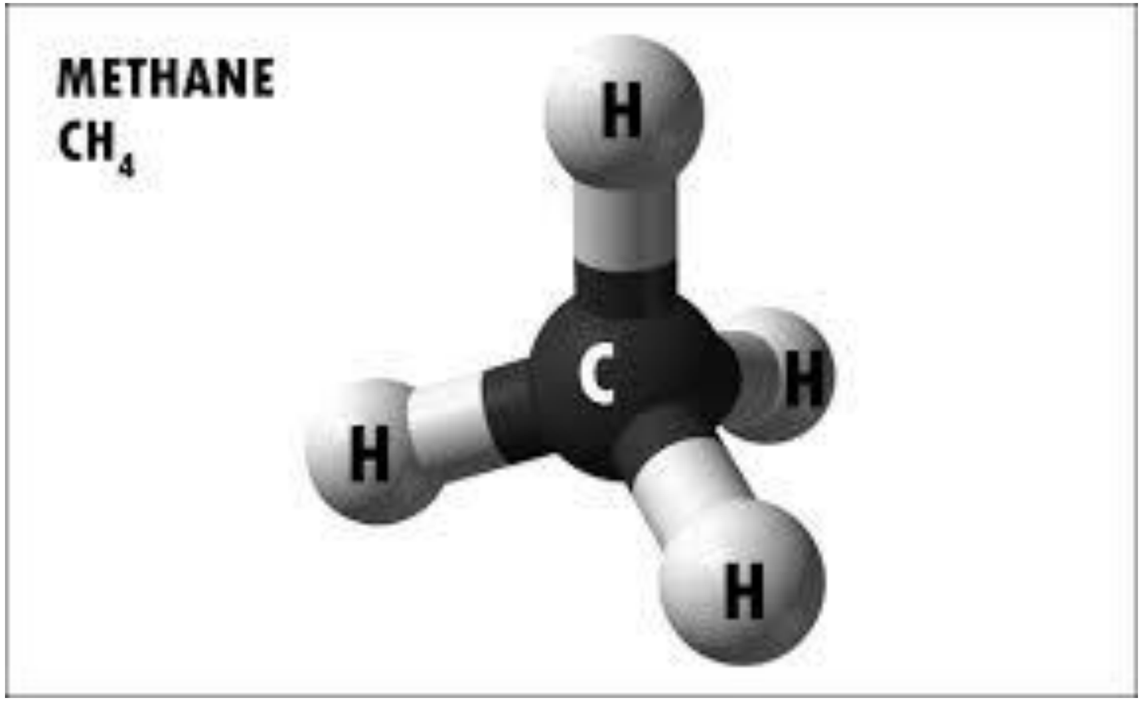


12 Key Facts:

- H_2 is 14x lighter than air
- Ignition energy is order of magnitude lower than methane (0.019 mJ)
- Molecule size ¼ of methane
- Hydrogen has low viscosity due to the small molecule size
- Hydrogen explosion velocity is 7x higher than gasoline and methane
- Hydrogen LEL 4% Vol
- Hydrogen UEL 75% Vol
- Hydrogen is odourless
- Pure hydrogen burns with an almost invisible blue flame
- Hydrogen flames have low radiant heat compared with hydrocarbon fires
- Commonly used in the fertilizer industry to manufacture ammonia
- Emits water (H20) as a by product of combustion

Gases – and their properties

- Methane



9 Key Facts:

- Lighter than air
- Density of 0.7057 by comparison to air
- Explosive gas
- LEL of 4.4% Vol
- UEL of 16.4% Vol
- Methane is Odourless
- Ignition energy 0.1 mJ
- Methane is not considered toxic
- Well understood

Hydrogen Flame Speed

		Propane	Methane	Gaseous Hydrogen	Ammonia
Formula	Unit	C3H8	CH4	H2	NH3
Flammability limits, gas in air	Vol. %	2.1 - 9.5	5 - 17	4 - 75	15 – 33.5
Flame speed	m/s	0.83	0.4	3.51	1.09
Minimum ignition energy	MJ	0.1	0.1	0.019	8
Boiling point	°C	-42	-161.6	-252.9	−33.4
Storage method		Comp. liquid	Comp. gas	Comp. gas	Comp. liquid

Hydrogen Safety

04 — 100% Hydrogen Point detection

100% Hydrogen

A challenging gas to detect!

No dipole moment means no IR detection. Why is this a problem?

- No ‘visual’ detection possible (YET)
  - No large area leak monitoring
  - No perimeter monitoring
- Accoustic (‘listening’) detection possible
  - Can cover large areas
  - Not gas specific
- Point (‘smell’) detection possible
  - Small area coverage
  - Susceptible to influence by ambient conditions

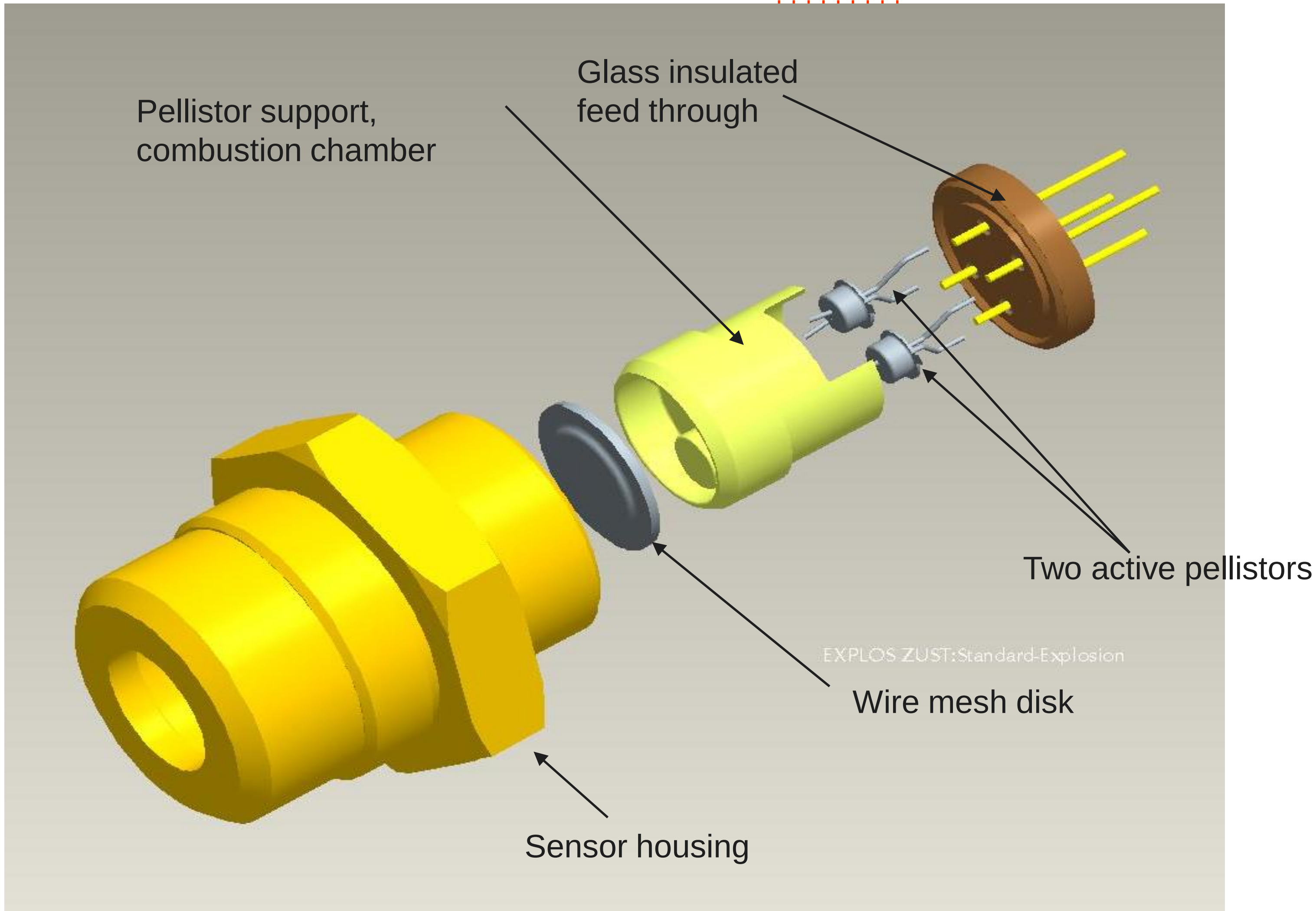
100% H2

Flammable Detection - Hydrogen

Gas detection is about assessing the risks.

No bonds in hydrogen which can absorb IR energy

- Wheatstone bridge variation
  - Designed to measure an unknown difference
  - Use heated pellistor to burn small qtys of gas



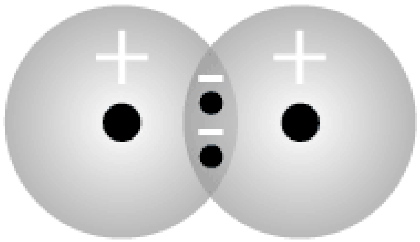
100% Hydrogen

A challenging gas to detect!

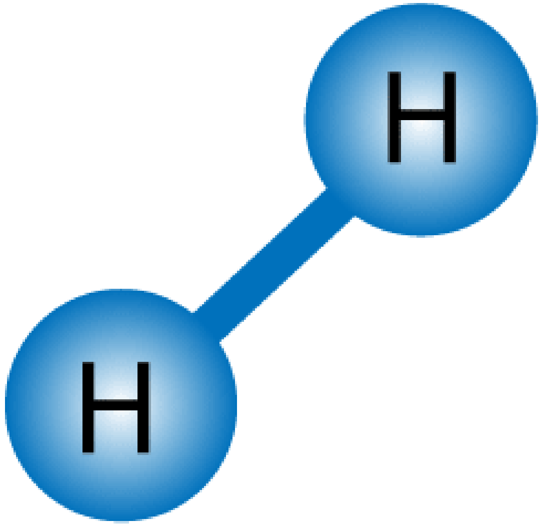
We use dipole moments to detect gases with infra-red

What is a Dipole Moment?

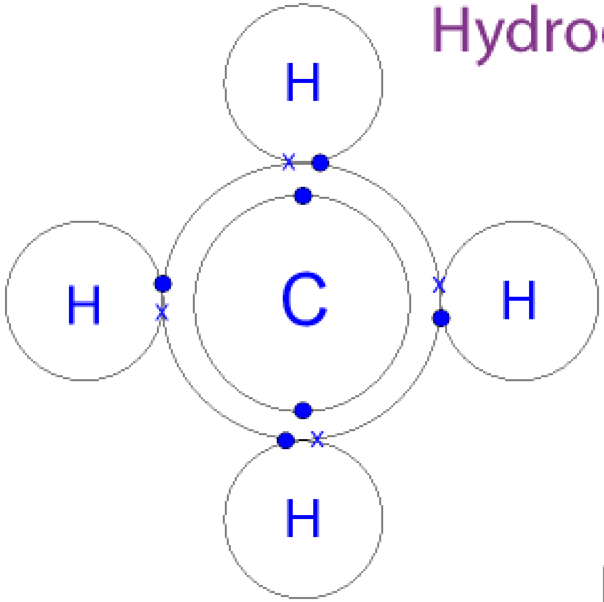
- Dipole moments can be permanent or temporary
- A dipole moment arises from differences in electronegativity
    - When atoms in a molecule share electrons **unequally** it creates a dipole moment
    - When atoms in a molecule share electrons **equally**, there is no dipole moment
- Dipole moments have a magnitude and direction

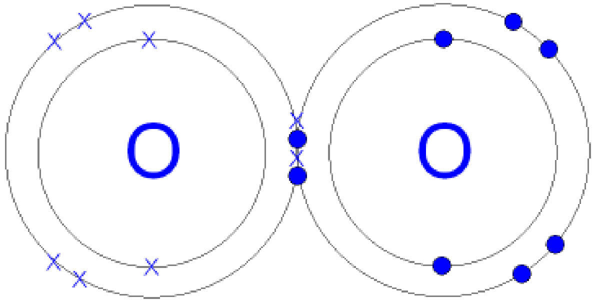


H:H

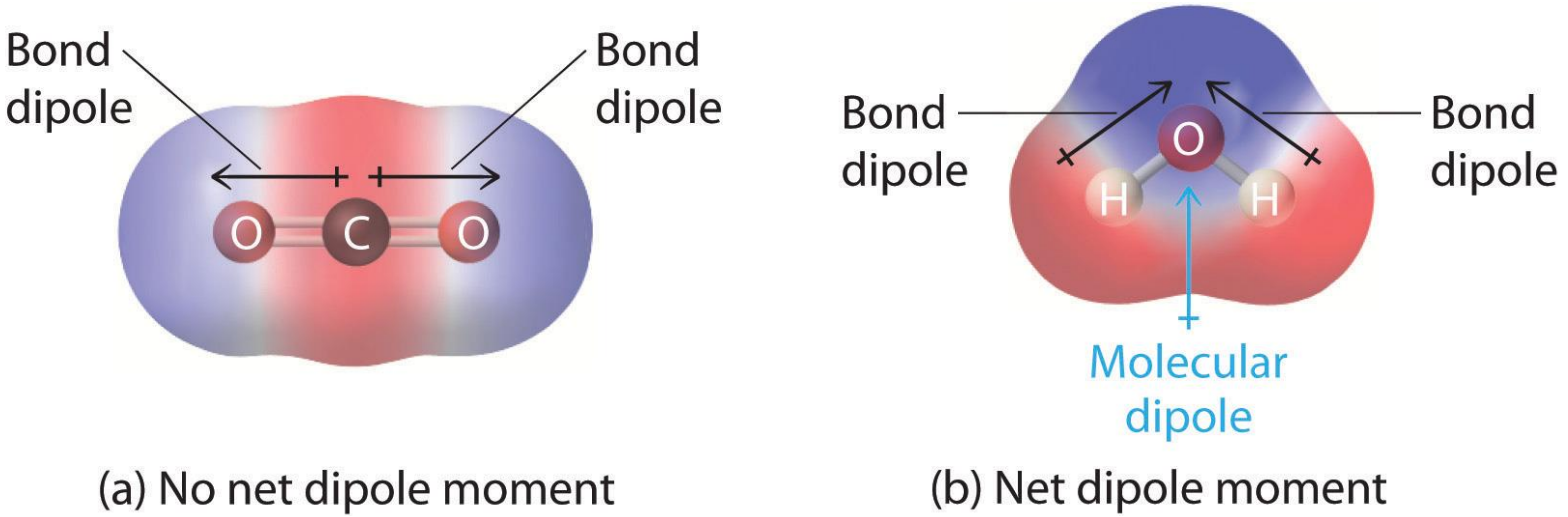


Hydrogen (H_2)





Dipole moments



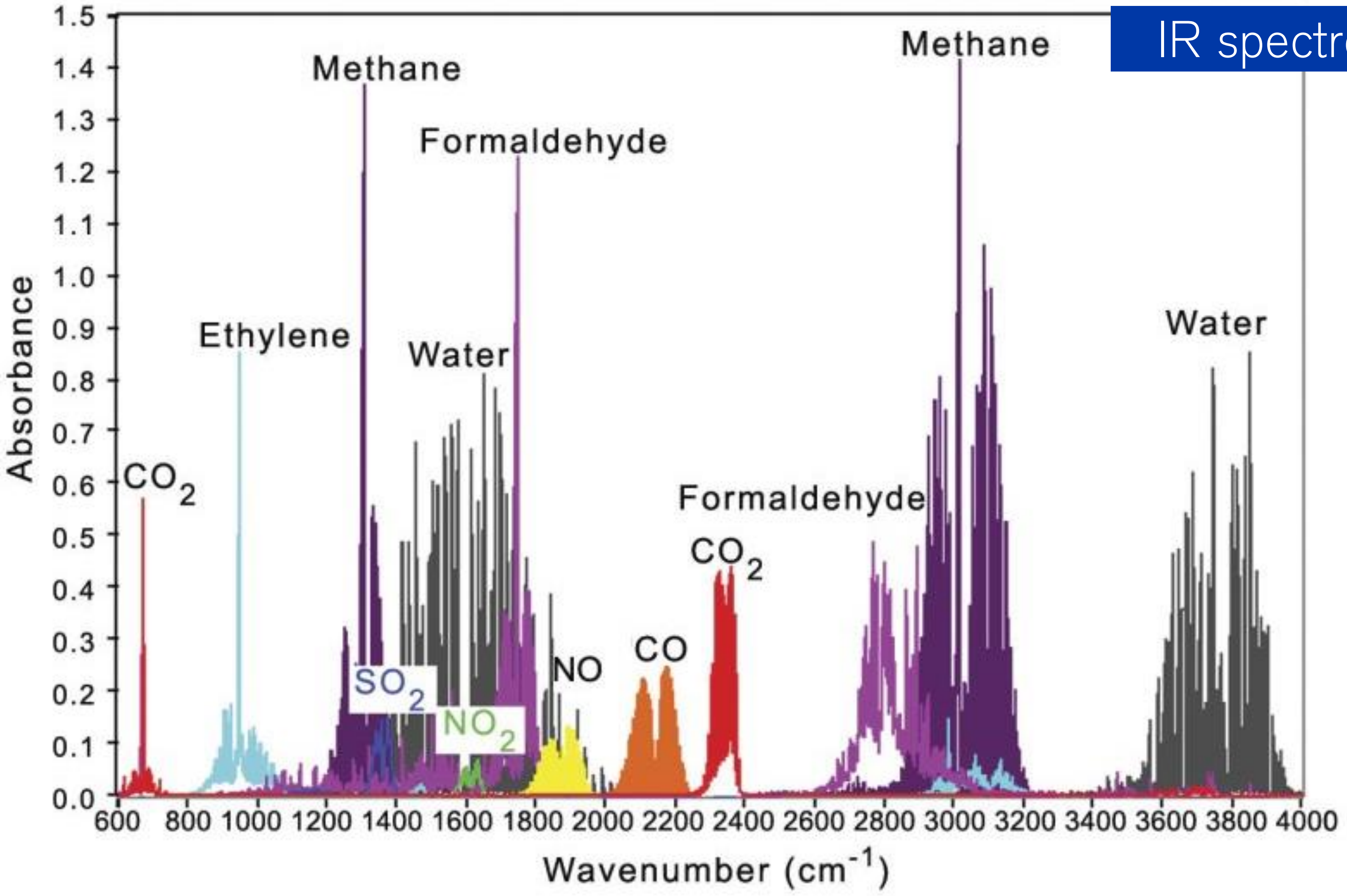
CO2 vs H20

100% Hydrogen

Why is CH_4 IR active and H_2 is not IR active?

- The criteria for a molecule to show IR spectra is that the dipole moment must **change** during the vibration of the molecule (described as IR active)
- CH_4 dipole moment is 0, but it **changes** during vibration so is **IR active**
- CO_2 dipole moment is 0, but it **changes** during vibration so is **IR active**
- CO dipole moment is 0.122 D and it **changes** during vibration so is **IR active**
- H_2 dipole moment is 0, it **does not change** during vibration so it is **IR inactive**
- N_2 dipole moment is 0, it **does not change** during vibration so it is **IR inactive**

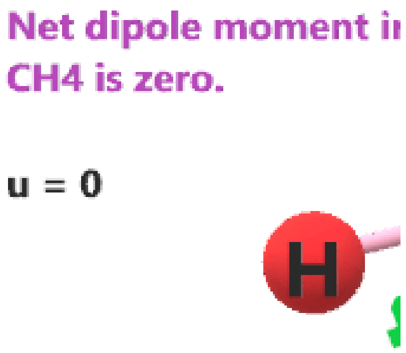
IR Spectroscopy



IR spectroscopy

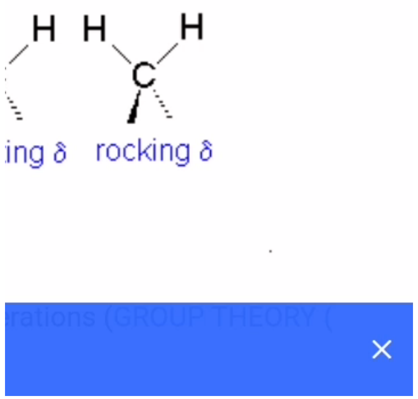
Dipole moments

CO_2 IR absorption vs Methane IR absorption



Why CH_4 absorbs more IR radiation than CO_2?
It is because CH_4 geometry is tetrahedral, while CO_2 is a linear molecule.

When IR radiation hits these molecules, they vibrate at particular frequencies that are characteristic of the strength of the bond, bond length, atomic masses, and vibration mode. The energy that each vibration mode (stretching, bending, and wagging) absorbs is determined by these factors — rotation falls into microwave frequencies, so does not apply here),



To put is simply, a tetrahedron has more vibration modes that an object with linear geometry has, and so tetrahedral molecules can absorb energy at a greater number of frequencies than linear molecules can.

Hydrogen Safety

02 —— 100% Hydrogen
Line of Sight

100% Hydrogen

Raman Spectroscopy

Raman spectroscopy, is the inverse of IR. Raman spectroscopy is based on scattering not absorbance.

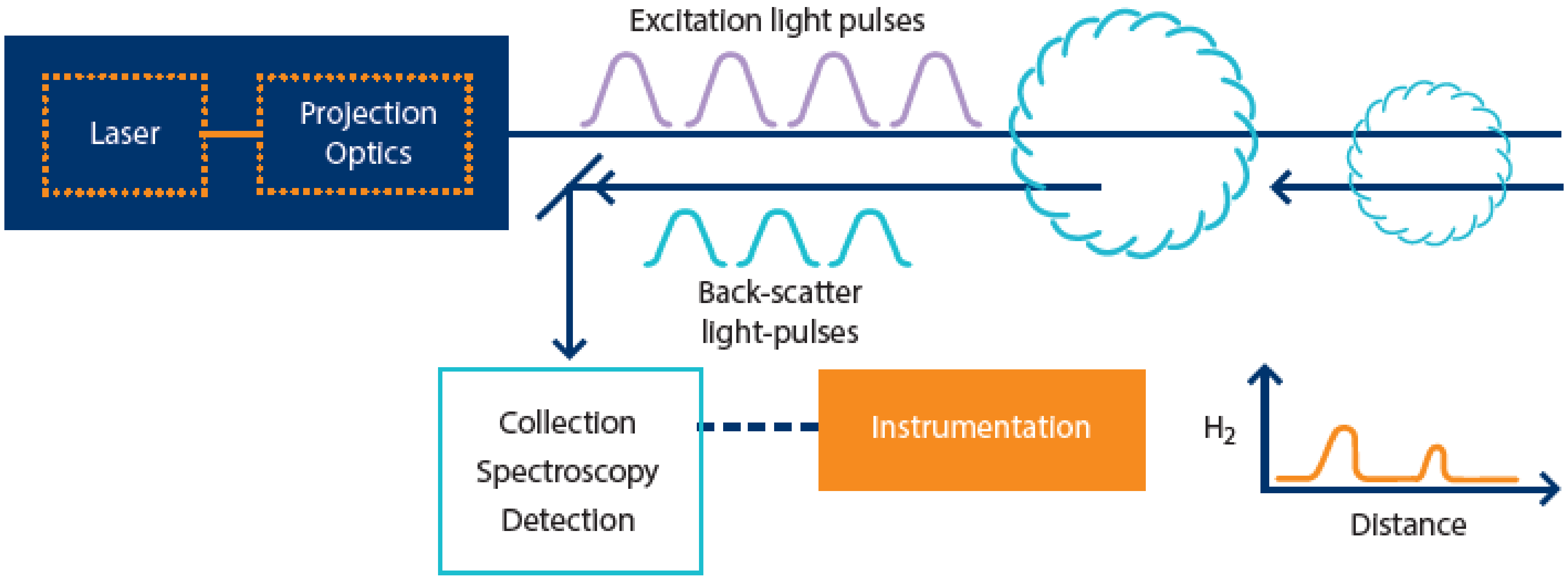
- IR active functional groups are Raman inactive.
- IR inactive functional groups are Raman active.

Hydrogen displays relatively strong interaction with light via Raman excitation. In Raman excitation, incident photons are scattered inelastically by a molecule to a different wavelength.

The shift in wavelength between the incident photon and scattered photon is characteristic of the molecule.

Fraunhofer UK

100% Hydrogen



Fraunhofer Centre for Applied Photonics have developed stand-off hydrogen detection system that relies upon the interaction of pulses of laser light with hydrogen and uses sensitive time-resolved sensors to detect the returned signal giving both concentration and location.

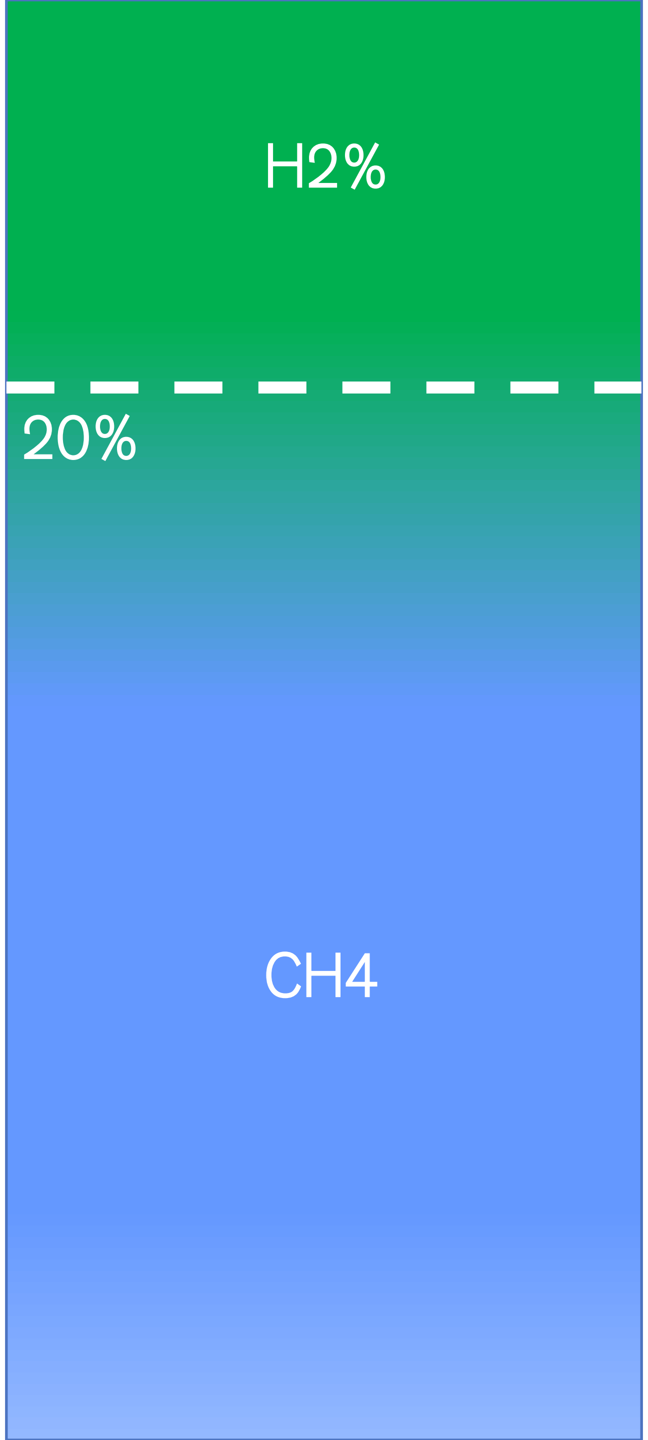
Hydrogen Safety

02 — Blends

Hydrogen Blends

Reducing carbon emissions by blending up to 20% Hydrogen with natural gas

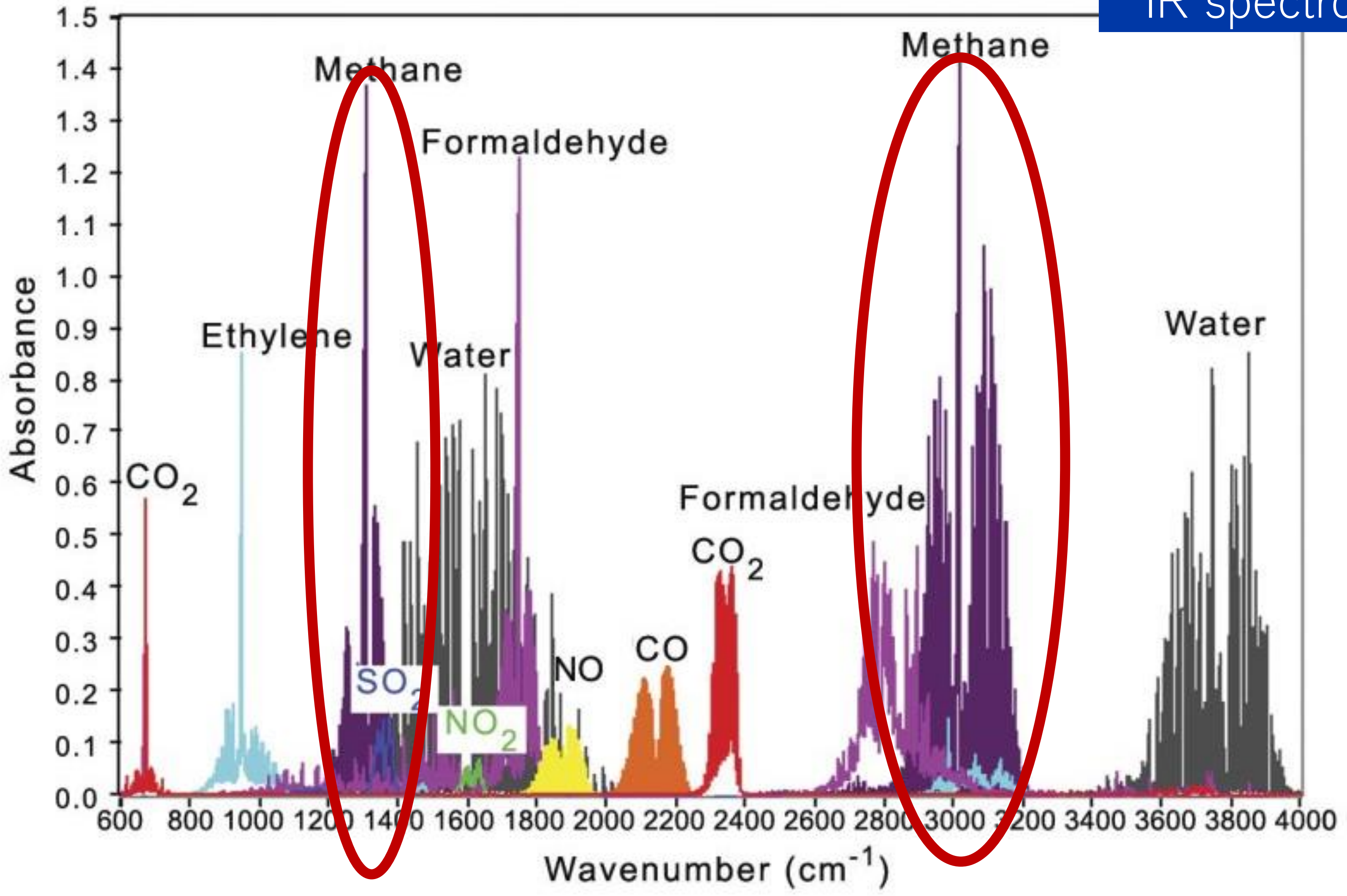
- Up to 20% H_2 does not affect the combustion efficiency of methane based combustion
- Above 20% starts to affect the combustion efficiency
- Blends still have a majority of methane in the composition
- Methane detection is still the best way to detect leaks



Preventing Explosion

Methane, infrared and hydrocarbon bonds

IR spectroscopy



Blending

Technical information: 38% Hydrogen 68% Natural Gas

Point detection: We offer the PIR7000 as an IR combustible gas detector. The PIR7000 is incapable of detecting hydrogen, however as the volume of natural gas (methane) is the larger volume present in the process, and the method of detection is more reliable (immune to poisoning and fail safe) this would be the preferred point detection method where CH4 is present. To account for the lower volume of CH4 we recommend lowering alarm set points.

Line of Sight detection: We offer the Pulsar 7000 as an IR combustible gas detector as above

See below extract from *GAS DETECTION OF HYDROGEN/NATURAL GAS BLENDS IN THE GAS INDUSTRY Copyright Cadent Gas Limited / Northern Gas Networks Limited, 2019*

Blending

Technical information: 38% Hydrogen 68% Natural Gas

GAS DETECTION OF HYDROGEN/NATURAL GAS BLENDS IN THE GAS INDUSTRY
Copyright Cadent Gas Limited / Northern Gas Networks Limited, 2019

Northern Gas Networks

*For catalytic-based detectors, the relative **difference is minimal and conservative from a safety perspective**, i.e., a blend would cause the instrument to alarm at a lower flammable gas level. **The opposite is true of an IR detector**, i.e., a blend would only cause the instrument to alarm at a higher flammable gas level. This does not preclude the use of IR technology but would mean **that recalibration of the LEL level would be needed**. Figure 2 highlights the minimal effect on LEL of the blend for catalytic-based instruments (A, B, C, E), and the greater effect on IR-based instruments (D) assuming the instruments' LEL ranges are set the same (i.e., 5.0 vol%).*

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Blending

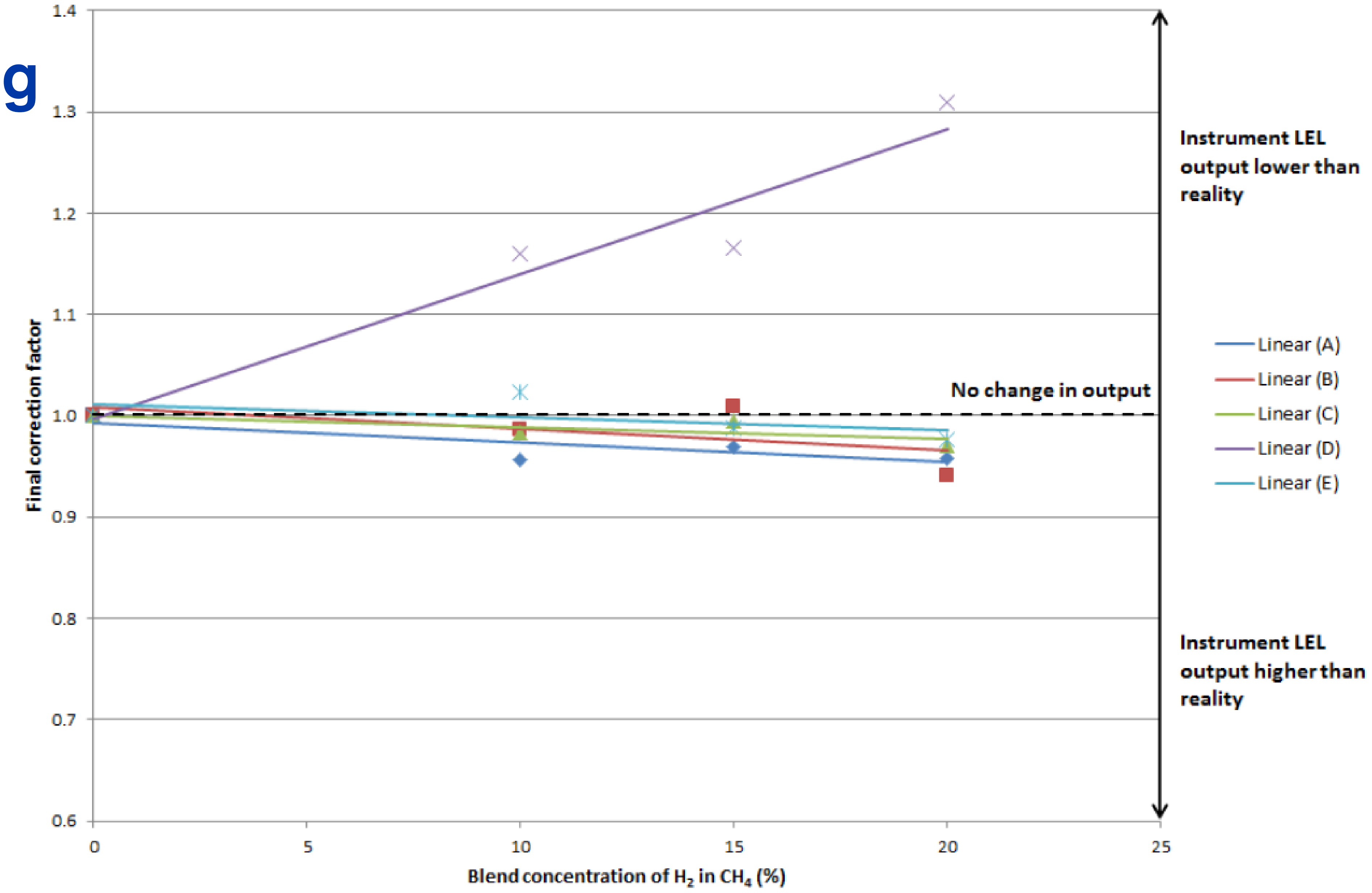

Figure 2: Flammable LEL correction factors based on H_2 content

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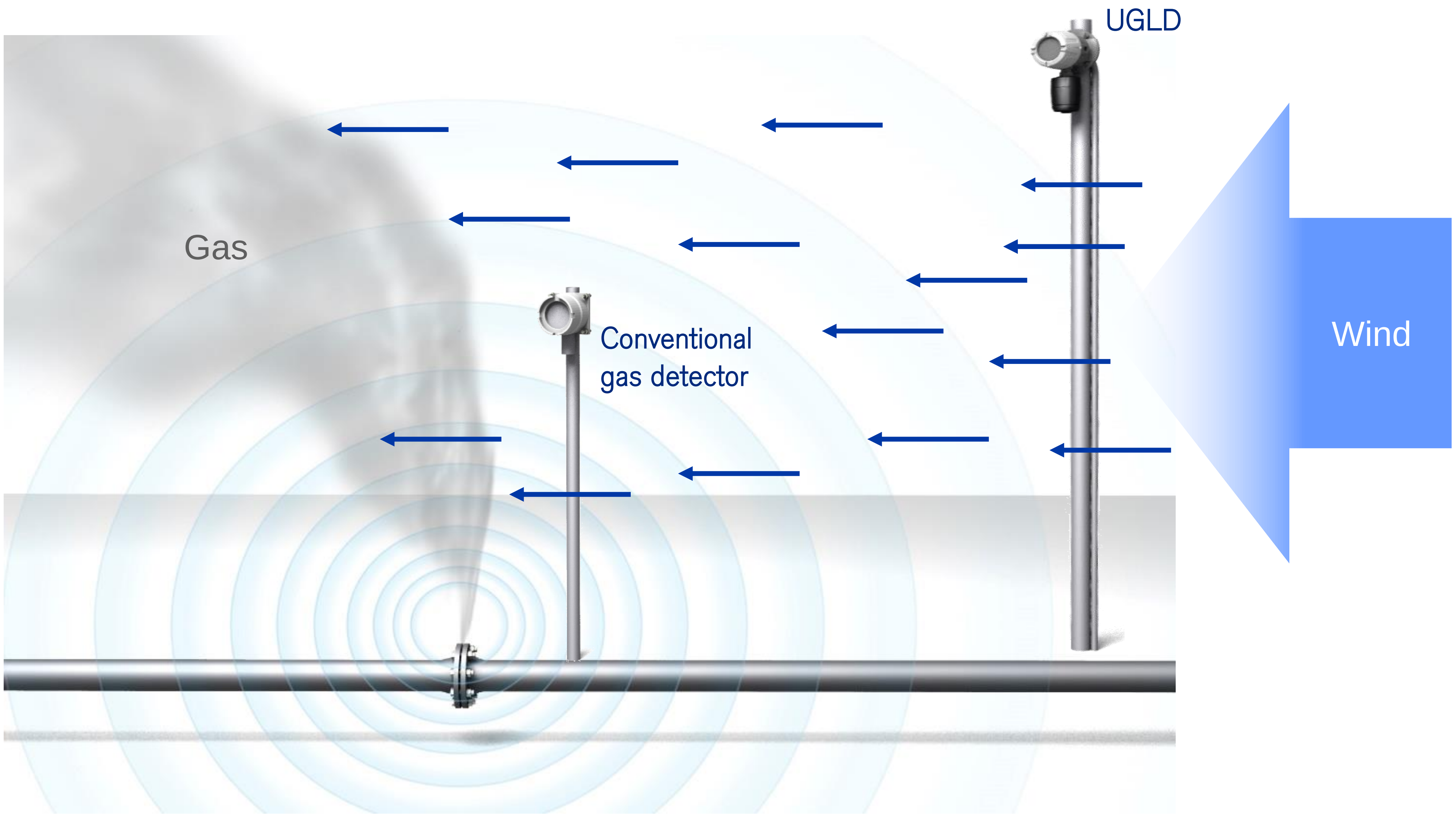
03 —— 100% Hydrogen

Accoustic detection

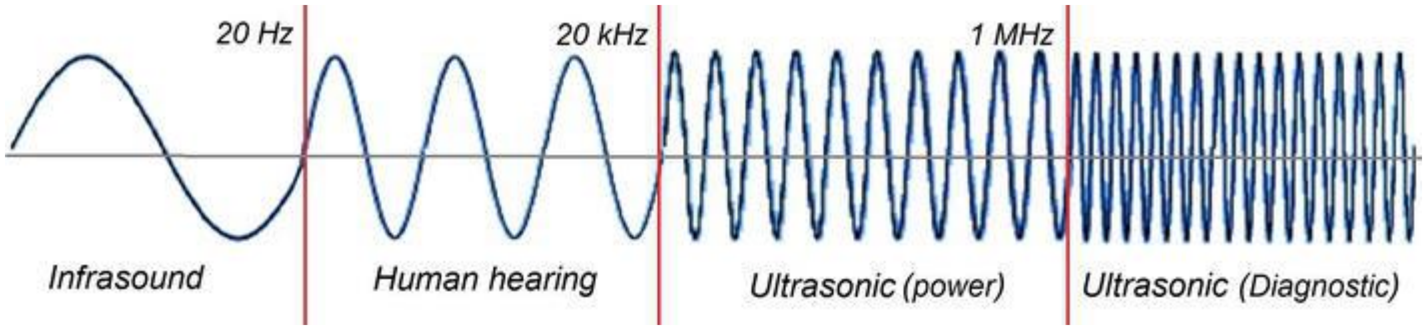
Why Ultrasonic Gas Leak Detection - UGLD



100% Hydrogen

What is ultrasonic sound?

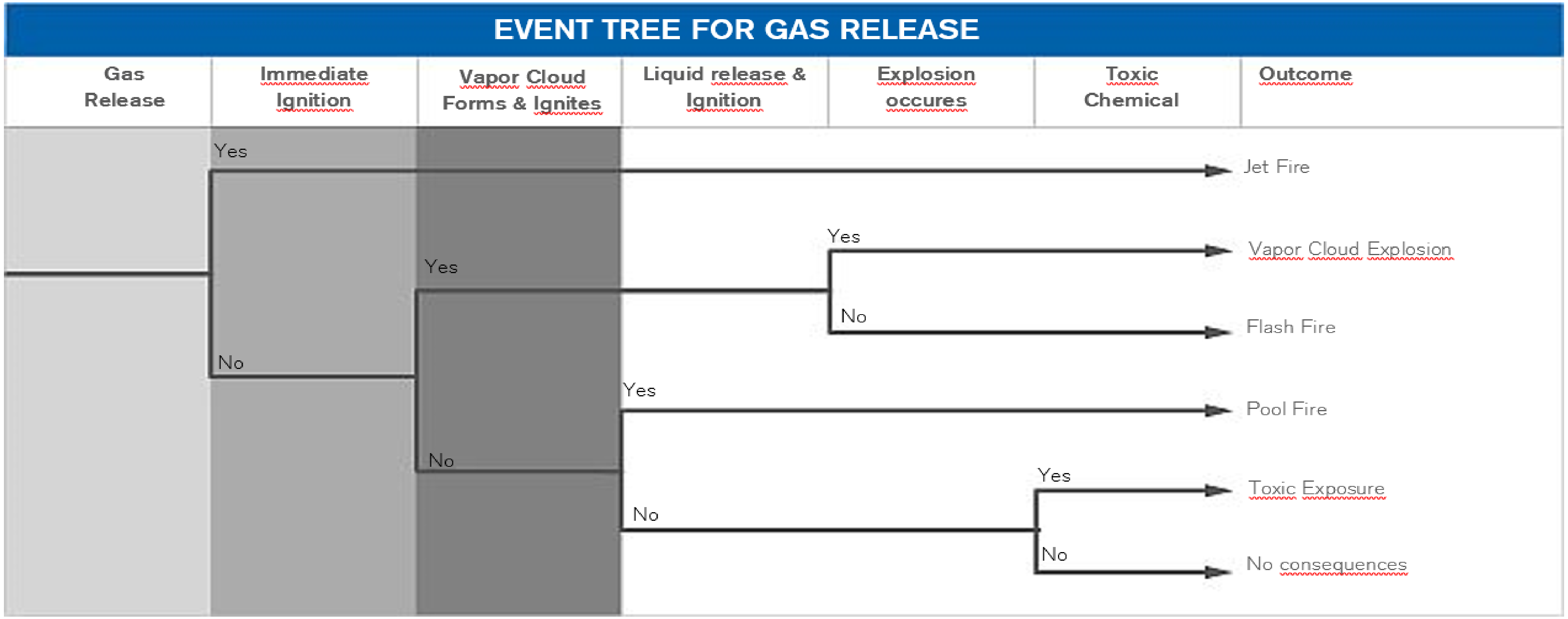
Ultrasonics sound waves are vibrations of frequencies greater than the upper limit of the audible range for humans—that is, greater than about 20 kilohertz.



100% H2

Safety and speed of detection

Deployment of early response to improve hazard management



UGLD respons

Conventional gas detector respons

100% Hydrogen

Limitations of UGLD

- It is not gas specific
- Not all gas releases are ‘unsafe’
- False alarm immunity is very specific to set up

Benefits of UGLD

- Very good in outdoor applications
- Extremely fast response
- No need to wait for an accumulation
- Not gas specific

100% H_2

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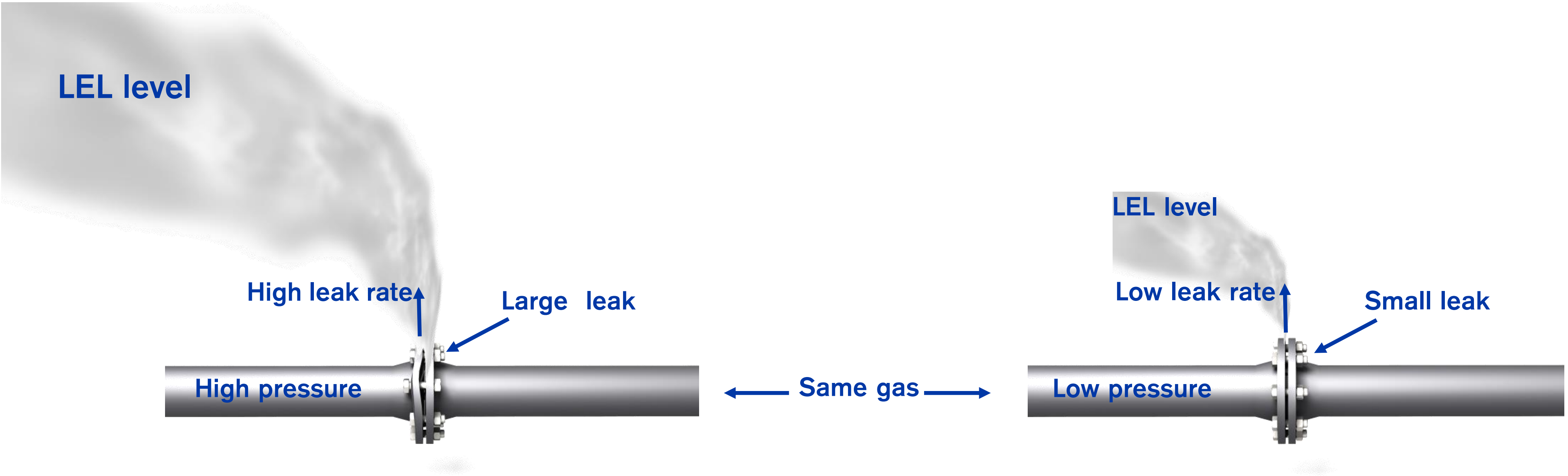
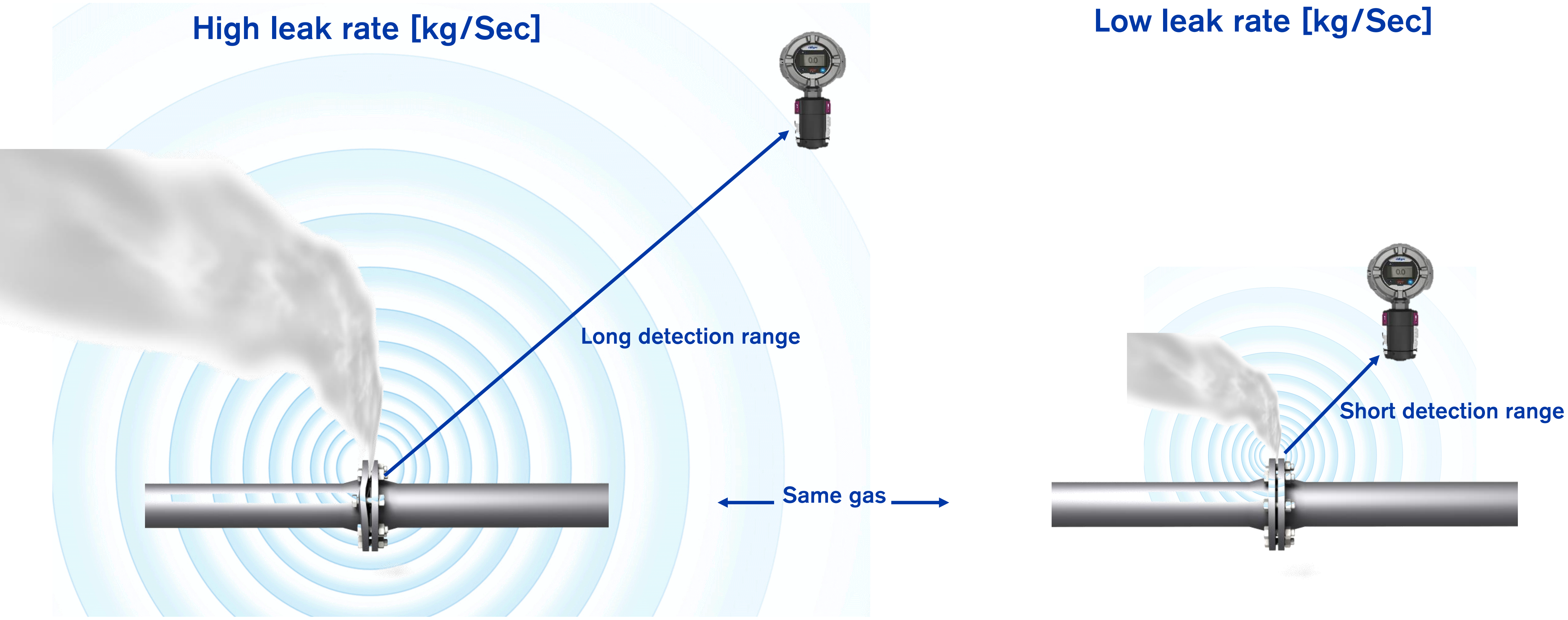
Gas concentration (LEL or ppm) versus Leak rate

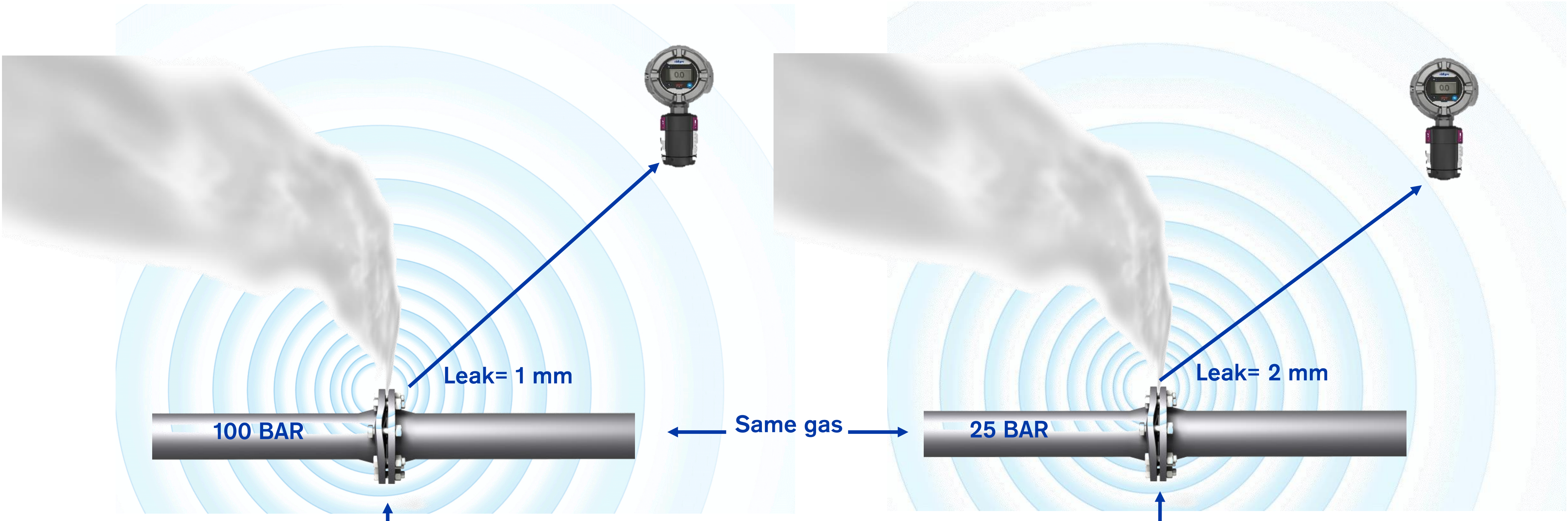


The Leak rate (massflow rate) is how much gas escapes through the leak in Kg/sec

Leak rate versus ultrasound



The leak rate will determine the gas cloud and the UGLD detection range



Same leak rate will result in same gas cloud formation, which result in same ultrasound level, and thereby same UGLD detection range

Hydrogen Safety

05 — Flame Detection

Flame detection
What is a flame?

- A **flame** is the visible portion of a fire

- Most flames consist of
  - – carbon dioxide
  - – water vapor
  - – oxygen
  - – nitrogen

N-Heptane Fire

Flame detection
What is a flame?

This mixture of reacting gases and solids usually emits

– **visible**
– **infrared**
– **ultraviolet** radiation

The frequency spectrum of which depends on the chemical composition of the burning material and its intermediate **reaction products.**

N-Heptane Fire

Flame detection
Different types of fuel

N-Heptane Fire

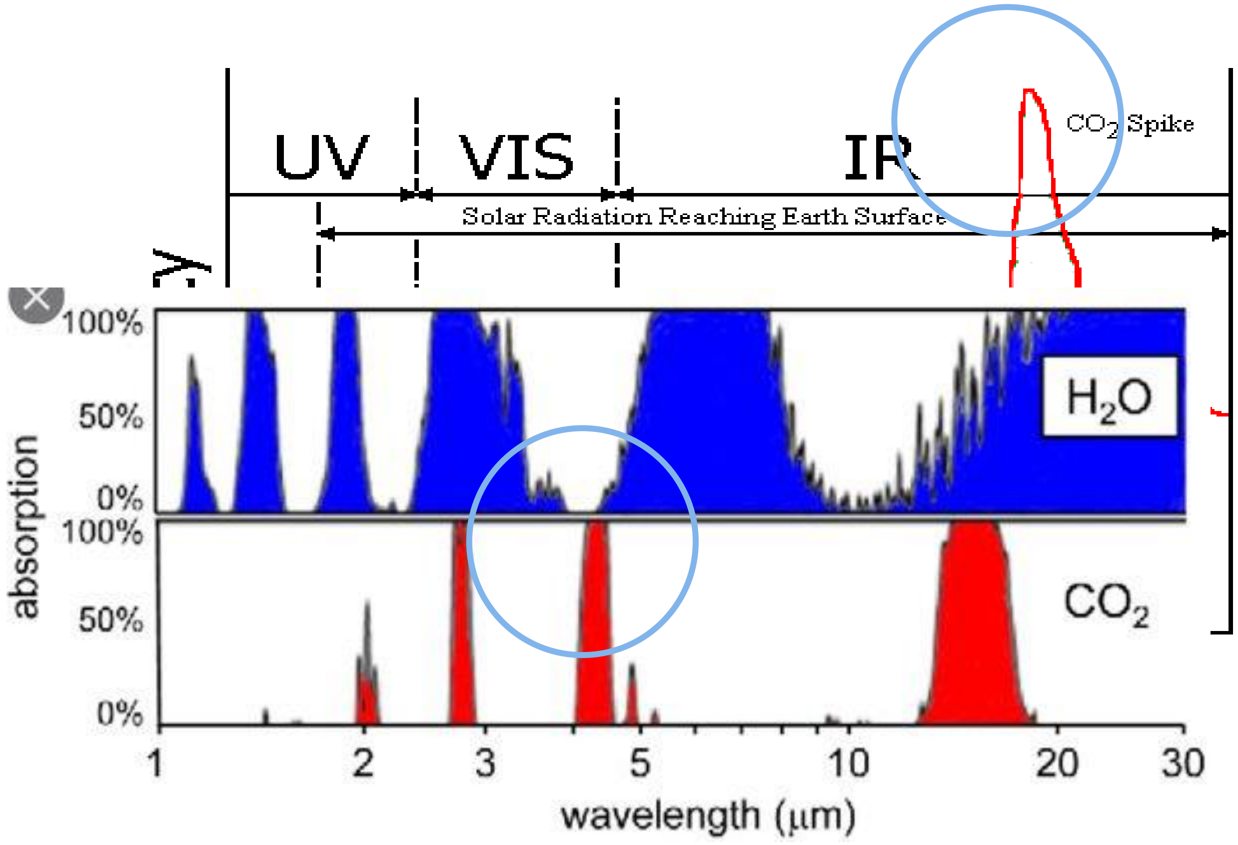
Methane Fire

Hydrogen Fire

Flame detection
What is different about hydrogen flames?

- **Hydrocarbon** fires emit vast amounts of carbon dioxide, water vapor, oxygen and nitrogen

- Most flame detectors therefore scan for a peak in the electromagnetic emissions at **4,3µm**



Flame detection
What is different about hydrogen flames?

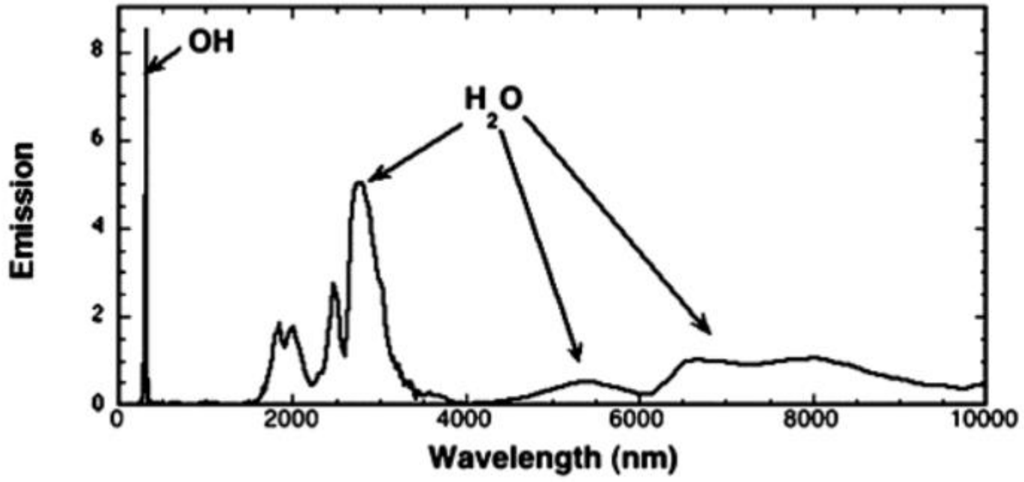
- To the human body and all our senses hydrogen and its flames are almost undetectable.

- Hydrogen flames
  – are **invisible** in daylight
  – emit **very little radiant heat**
  – are **odorless**

Flame detection
What is different about hydrogen flames?

Hydrogen flames do **not** emit CO_2

Hydrogen flames only emit hot H_2O
$2\ H_2 + O_2 \rightarrow 2\ H_2O$ + Energy



Flame detection
What flame detectors are suitable for hydrogen?

Visual flame detector

– Analyzes each pixel of a camera picture for visible indications of flames such as color, flicker and shape
– Only “sees” what the human eye can see

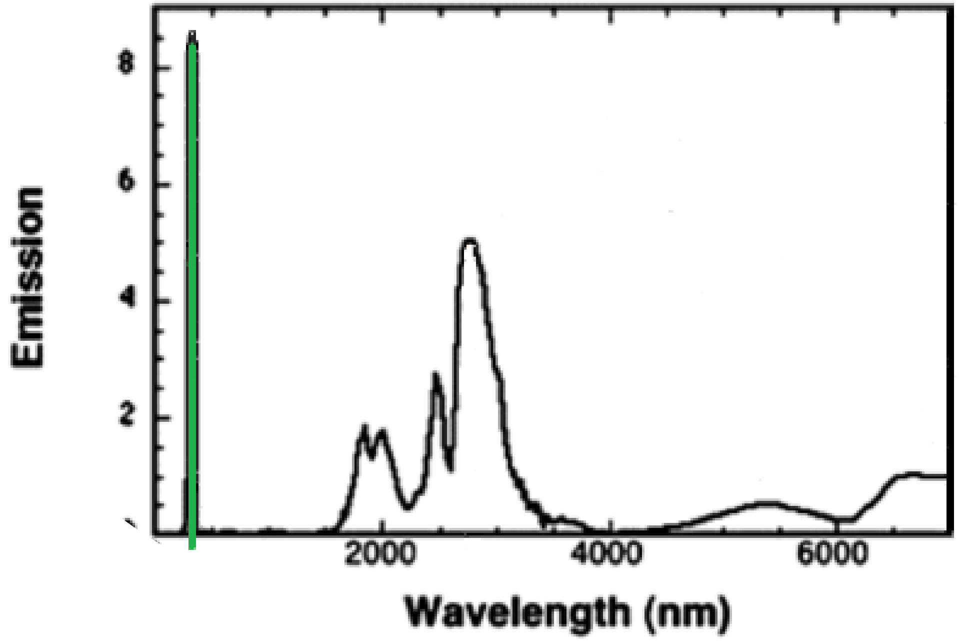
NOT suitable

Flame detection
What flame detectors are suitable for hydrogen?

UV detector

- Measures UV spectrum around 0,2µm
- Fast reaction time
- Very sensitive to false alarm sources

Suitable

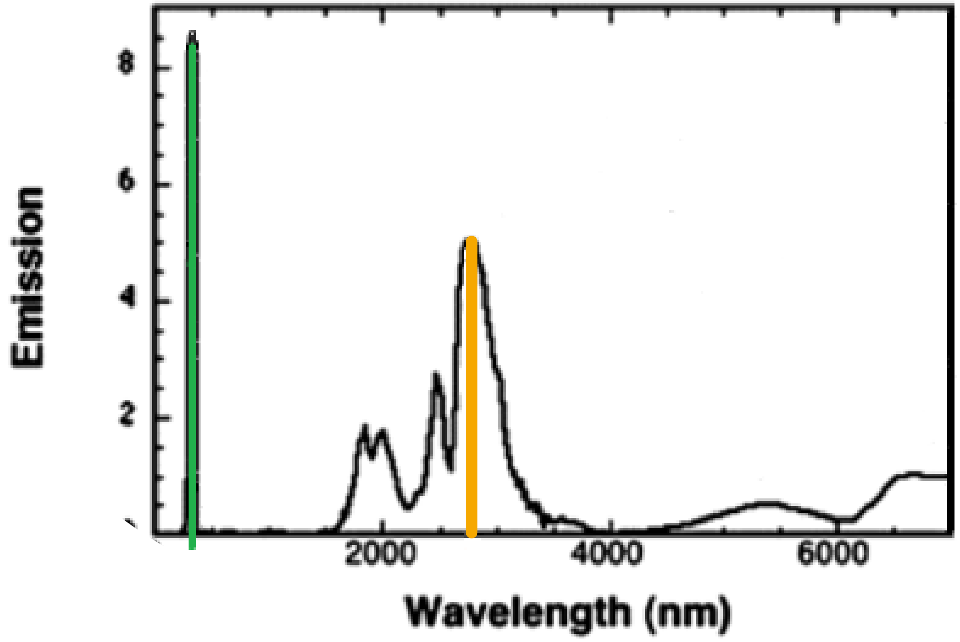


Flame detection
What flame detectors are suitable for hydrogen?

UV/IR detector

– Measures UV spectrum around 0,2µm and IR spectrum around 2,7µm
– Fast reaction time
– Sensitive to false alarm sources

Suitable

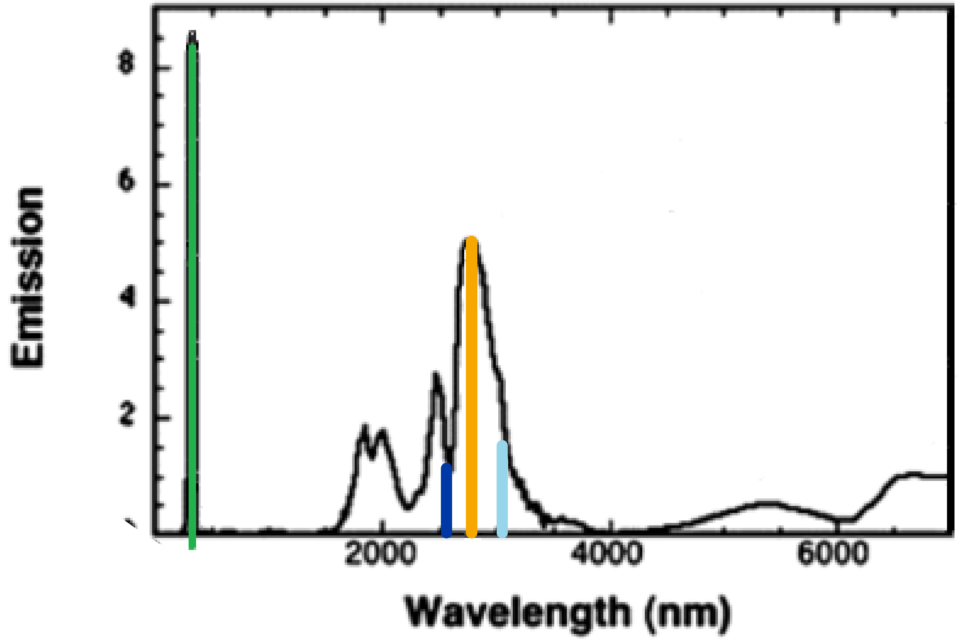


Flame detection
What flame detectors are suitable for hydrogen?

IR3 H_2 detector

– Measures three different IR wavelengths one measurement, two references
– Fast reaction time
– High immunity to false alarms

Optimal

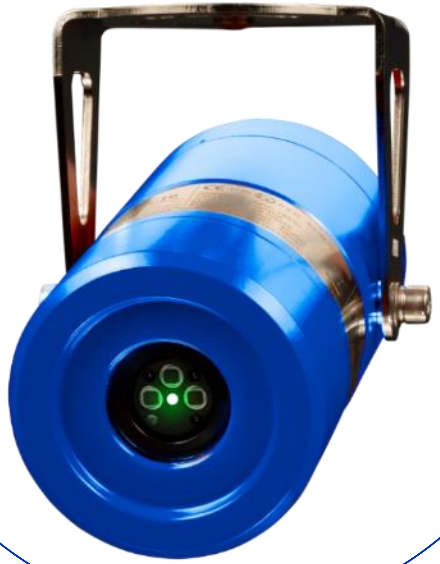


Dräger Flame 1750 H_2 – Key Features Introduction

Hydrogen flames
and in addition, most hydro-carbon flames at short distances

Fast reaction time
< 5 seconds (typical) for 100cm hydrogen plume fire from 40 m distance

All year availability
due to heated window against frost and fogging



Avoidance of false alarms
using three infrared sensors and sophisticated algorithms

Maximum coverage
Field of view of 90° horizontal and 90° vertical and max. detection range of 40m

Low maintenance
due to built-in self-test without optical mirror

IR 3

To be launched in Q4 2022

Hydrogen Safety

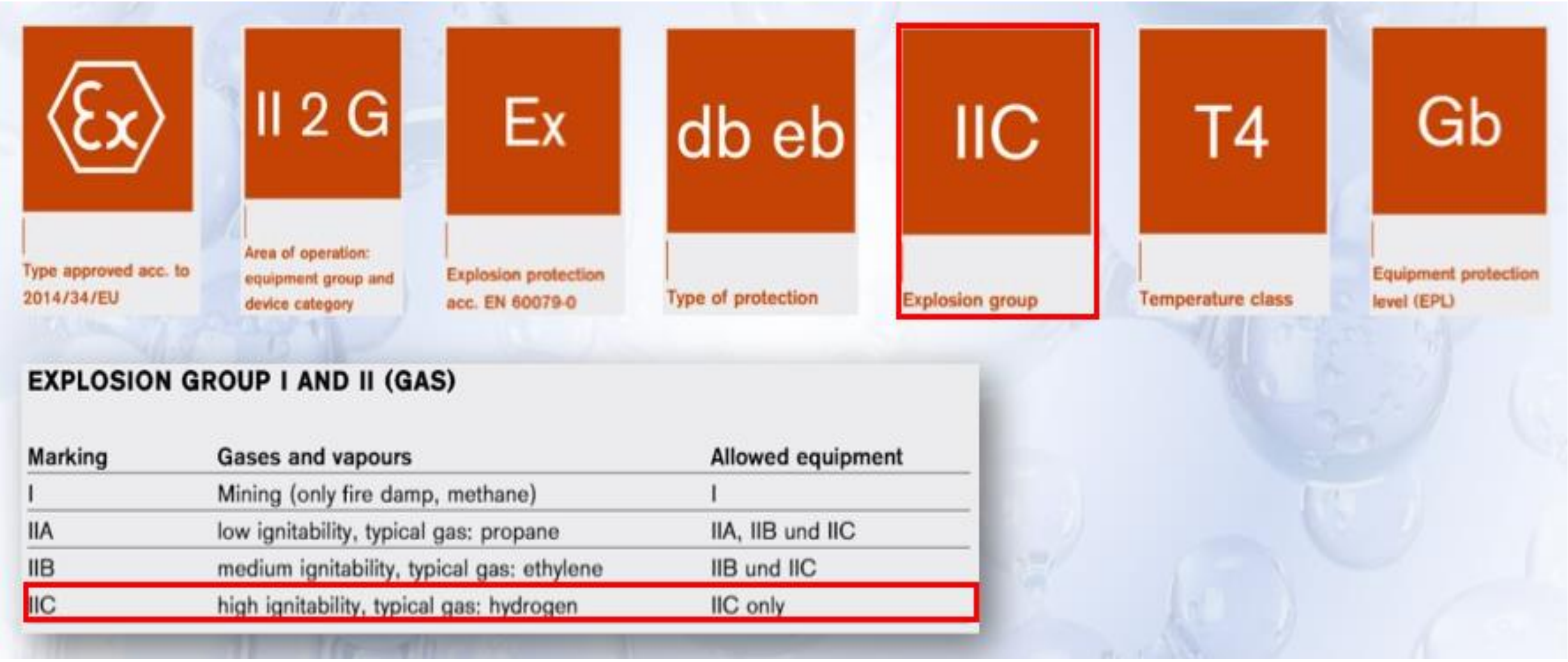
05 —— Explosion Protection

Preventing Explosion

Hazardous area approval | Ex-Protection considerations :

- Product Ex Certification – Gas Group changes from A to C
  - NOTE: This includes all other equipment for use in a Hydrogen atmosphere e.g. Breathing Apparatus
- Area Ex Certification – Zones sizes will probably increase

Hydrogen vs. Natural gas explosions are more intense AND also have greater LEL parameters and therefore likelihood. This in turn will influence HAZOP analysis findings which in turn may affect selected detector spacings and functional safety system requirements etc.



EXPLOSION GROUP I AND II (GAS)

Marking	Gases and vapours	Allowed equipment
I	Mining (only fire damp, methane)	I
IIA	low ignitability, typical gas: propane	IIA, IIB und IIC
IIB	medium ignitability, typical gas: ethylene	IIB und IIC
IIC	high ignitability, typical gas: hydrogen	IIC only

Another Possibility is IIB +H2
IIC covers Hydrogen and Acetylene & Carbon-disulphide. Most application don't have these additional gases.

Hydrogen Safety

06 — Alternative Detection Methods

Alternative detection methods – MPS Nevada Nano

Molecular property spectrometer – Nevada Nano sensor, currently used by Crowcon.

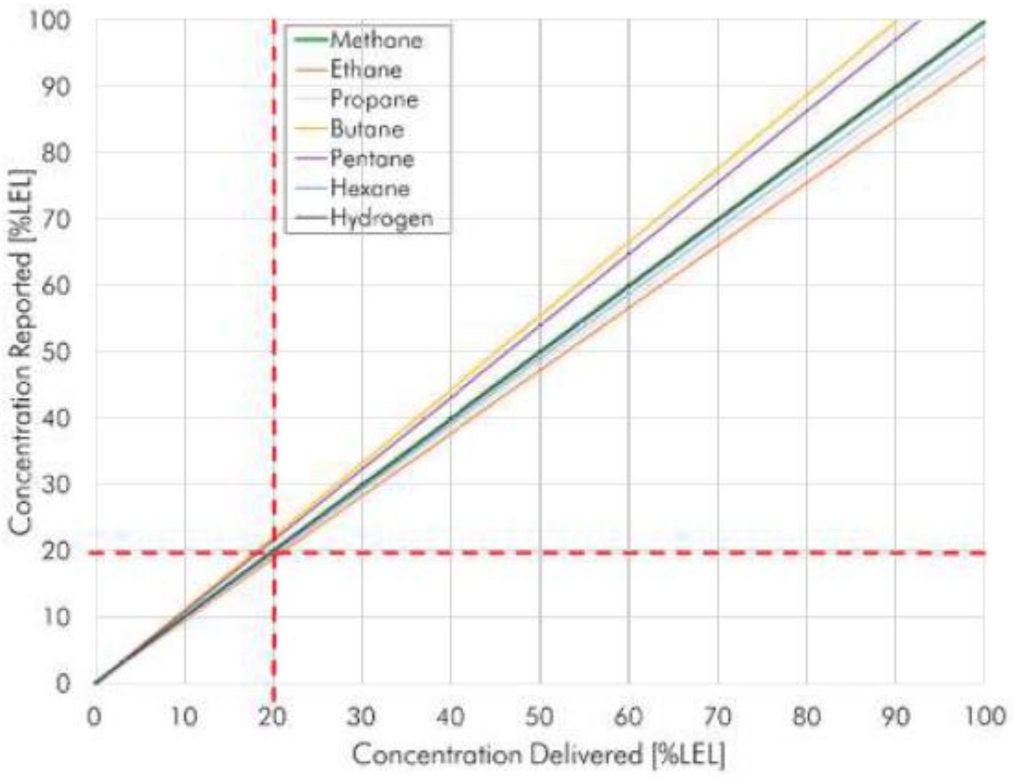
- Promising technology
- Works on density and then heats up the gas mixture and calculates energy required to heat the gas to a set temperature (specific heat – 1 degree at set pressure)

	Hydrogen	Natural Gas	LPG
Specific Heat, constant pressure (J/g-K)	14.89	2.22	1.56

Alternative detection methods – MPS Nevada Nano

Pros
- No field calibration
- Claim zero drift
- Can detect multiple gases

Cons
- The drift is managed with mathematical calculation. We tested the sensor, drift compensation of 10% LEL within 10 days exceeding requirements of EN 60079-29-1 by factor of 7
- Response time is slow: 30 seconds for multiple gases, 15 seconds for CH4 alone
- Not SIL rated, not performance approved



Thank you for your attention