Laser interferometric investigations on some physical properties of Natural bio- gases

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Abstract. In this work a Mach-Zehnder interferometer system [MZIS] was constructed and illuminated by using [He-Ne] laser. And a gas flow system [GFS] was strictly designed and constructed that was connected to [MZIS], this gas flow system was controlled by both temperature range between 313 to 348 K and pressure range from 60-90 cm-Hg. The [MZIS] and [GFS] were linked and used for determining the refractive index of Methane [CH₄] and Nitrogen [N₂] gases as a function of pressure n[p]T and temperature n[T]P. The variety of refractive index of gases regarding the pressure factor at steady temperature (dn/dp)T was resolved. Likewise, the variety of refractive index of gases regarding to temperature at steady pressure factor [dn/dT]P was determined. By applying both Maxwell’s and Clausius-Mosotti equations, some physical parameters of Methane and Nitrogen gases, which related to refractive index, like as optical permittivity, dielectric susceptibility, Specific refractivity, Molar refractivity, and Molecular radius were estimated. In addition, the volume expansion values of the investigated gas samples were evaluated. Theoretically, by using Gaussian 09 program we had got some chemical parameters for Methane and Nitrogen.

1. Introduction
We described the main dielectric properties of Methane and Nitrogen and the relation between them with refractive index and their variation with pressure and temperature. We need to provide an accurate experiment, which give us the behavior of the gas at different temperatures and pressures. Some of these experiments show that the optical behavior of gases related to gas density. A modified Lorentz –Lorenz mode was used to provide theoretical values of the refractive indices of some gas hydrate at pressure between 2 and 15 Mpa, and temperature range from 0 c to 12°c by O. Bonnefoy et al [1]. Also M. Musso et al [2] measured the refractive index of liquid Sulphur dioxide SO₂ by using a Michelson interferometer.

K. Betzler et al [3] used a simple approach for detecting parallel sample refractive indices for shifting the pattern of interference when the sample is rotated in one arm of a Mach-Zehnder interferometer.
D.L. Khokhlov [4] considered the problem of the interference of a single particle in the two-path experiment by using the Mach-Zehnder interferometer with a single photon. Also, Rui Wang et al [5] used a Mach-Zehnder interferometer to measure a refractive index sensing structure by an integrated circuit with a hybrid silica polymer waveguide which have thermo-optic effects.

1.1 Characteristics and Uses of Methane gas

Methane is a chemical compound with the chemical form CH₄. It is the simplest alkane, [about 87% by volume] of natural gas and perhaps the most abundant organic substance on earth [6]. As a result, it has proven to be a desirable fuel. Steam reformation is used in the chemical industry to convert methane to synthesis gas, which is a mixture of carbon monoxide CO and hydrogen H₂. Methane can be produced in a variety of ways, including biological, industrial, and geological. The geological path is separated into two categories: organic (thermally generated, or thermogenic) and inorganic (abiotic). Thermogenic methane forms from the separation of natural material at elevated temperatures. Methane is generated abiotically, that is, without biological activity, from inorganic molecules. Methane is manufactured via the Sabatier process on the industrial way, using hydrogenated carbon dioxide CO₂. Methanogens in the colon can use CO₂ and H₂ to produce methane as a byproduct in the biological route [8]. The generation of methane gas in 30-62 percent of people by enteric bacteria has been based on several studies on the association between production of methane and intestinal problems such as constipation, bowel syndrome, diverticulosis and colon cancer [9].

Methane’s bioactivity is unquestionably not a new concept in medicine. Studies have shown that methane can decrease bowel movements by changing intestine neuromuscular capacities and decreasing peristaltic pace and increasing the abundance of pig ilea withdrawal [10].

Methane is classified as basically harmless by the United States’ Occupational Safety and Hazards Administration. When it comes to employing this gas as a medicinal agent, this appears to be excellent news. Furthermore, because of its physical capacity to penetrate membranes and diffuse into organelles, methane has good diffusion characteristics [11]. The fundamental cause of many diseases is extreme Oxidative Stress which is a major source of devastating reactive oxygen species with the mitochondrial respiratory chain, but antioxidants have limited therapeutic effect, which may be attributable to their impermeability [12].

When methane enters the nucleus and mitochondria, nuclear DNA and mitochondrial protection suggest that methane has a defense effect against infections caused by oxidative pressure. There are two routes of transport that have been feasible for studies, including the inhalation of methane gas and injection with the high-salt saline, and Methane is able to shed cells and organs against irritation, oxidation, and apoptosis [13].

The use of inflammable gas and biogas to power the immediate use of methane for energy purposes can be considered. In gas power stations, for example, natural gas is used as fuel. In contrast to steam generating stations, steam boilers in gas generating stations are disregarded and so chemicals may be converted into electricity more efficiently. Moreover, 45% less carbon dioxide is emitted by gas power plants than by coal fired power stations [14]. Typical examples for usage of biogas are electric heat generation in modified gas boilers or electricity and heat simultaneous generation in linked units. Energy components, especially low-temperature cells, as Proton Exchange Membrane Fuel Cells ((PEMFC) are another important use of methane which are frames that endure for a long time in the tho80-100°C range [15].
The potential of methane for climate change and global warming has recently been addressed. Methane concentrations in the atmosphere were stable until around 100 years ago, when they began to grow. Methane has a global warming potential of 25 compared to CO\textsubscript{2} over a 100-year period, according to estimates from 1992 [although accepted statistics are likely an underestimate [16].

1.2 Characteristics and Uses of Nitrogen gas

Nitrogen is the major element of the atmosphere (78.03% by volume, 75.5% by weight). Nitrogen gas is harmless, noncorrosive, and nonflammable. It is colorless, odorless, and tasteless. Nitrogen is non-combustible and does not support life. It is inert unless heated to extremely high temperatures, at which point it forms nitrides with some of the more active metals like lithium and magnesium. It can also react with oxygen to generate nitrogen oxides, and it can combine with hydrogen to generate ammonia in the presence of catalysts [17].

Nitrogen is used as a plant fertilizer. Terrestrial plants absorb N, chiefly in the roots from soil, though N can be absorbed from the leaves when urea etc. is applied by a foliar spray. Plants are unable to utilize N\textsubscript{2} on their own. Some leguminous and non-leguminous plants, on the other hand, use N\textsubscript{2} through an interdependent relationship with bacteria in the soil, such as rhizobia or diazotrophic endophytes. Mineralization of organic matter, breakdown of organic waste, and chemical fertilizers are all sources of inorganic nitrogen compounds. Ammonium [NH\textsubscript{4}+] and nitrate [NO\textsubscript{3}−] are the most common inorganic forms of nitrogen in soils, while organic N molecules like amino acids can also be absorbed [18].

In medical dentistry, nitrous oxide is the most commonly utilized inhalation general anesthetic, and it is also commonly utilized in emergency rooms and ambulatory surgery centers but, it should be combined with alternative inhalation and/or blood vessel agents in deep sedative/general anesthetic techniques. Nevertheless, as a one agent, it is quite safe for hesitant dental patients and it is excellent for giving little and moderate sedation [19].

Oxidation of specific materials is a result of usage of heat in the presence of oxygen. It can cause discoloration and the formation of a carbon layer on the cut edge, affecting the completed product's look or preventing any coating or paint finish from adhering to the oxidized surface. Nitrogen gas plays an important role as it prevents oxidization of the cut edge by permitting the laser to work in an oxygen-free environment [20].

In particular types of laser cutting machines, nitrogen is equally used as 'cleansing gas,' which can be used to confirm the laser-beam guidance from the resonator to the cutting head that can in a way or other change the power or shape of the beam. The right nitrogen gas pressure, purity and flow may be achieved, with optimal cost savings and efficiency for customers depending on the capacity and thickness of the laser and on the type of material to be cut. The thickness of laser-cut material ranges from a few millimeters to more than twenty-five millimeters [21].

2. Interferometry

Interference was defined as the outcome of the superposition of two beams or waves at distinct sites that add constructively or destructively. It was quickly discovered that the two waves must have a constant phase difference between them, implying coherence, in order to form the observed pattern of interference fringes. If the phase difference among two waves is not constant, the degree of coherence must be determined that shows how distinctly visible is the interference pattern [22].

There are two typical methods for splitting a single beam of light into two beams. The beam is split in the first technique by passing it through apparatus set side by side; this method, known as division of wave front, is only useful for modest sources. The other method, known as division of
amplitude, involves splitting the beam at one or more partially reflecting surfaces, where one part of
the light is reflected and the other is transmitted [23].

Interferometers, which use large path differences between two interfering beams to produce interference, provide some very interesting and useful applications of the interference phenomenon as the determination of refractive index, refractive index distribution, refractive index variation with temperature, pressure, and refractive index variation with both temperature and pressure were investigated [24]-[29].

The Mach-Zehnder is a mainly simple device for showing interferences by amplitude division. A beam splitter divides into two parts and then recombines it with a second beam splitter, which then reflects the floor mirrors and finally emerges into a correct collection lens. The efficacy of an interferometer of the Mach-Zehnder will depend on the equivalent path length of the two beam routes before it is recombined so that the four reflecting surfaces are generally positioned around their centers in a parallelogram corner [30] as shown in the Fig.1.

The MZI system standard optical targets can be mentioned below:
1- The path difference can be recognized at zero in the system, so as to limit the number of bands and thereby maximize the intensity.
2-The system absorbs a small light which causes two beams to emerge around 50% of the light that reaches the final image plane.
3-With no disturbance in either beam, the direction and spacing of the fringes obtained in the source and final image planes, as well as the fringe number at a specific point in the fringe plane, are the only essential modifications.

For the above advantages of MZI, we constructed and used it in this work for measuring the refractive indices of biogases and their variation with both temperature and pressure.

3. Spectroscopy and quantum chemical calculation
Spectroscopy is the study of electromagnetic waves' interactions with matter. The structure and behavior of molecules of various sizes can be studied using infrared spectroscopy [IR]. IR spectroscopy is a low-cost, quick, and powerful technique that has long been a common tool among analytical chemists. Also, it uses in a wide variety of fields, ranging from pharmaceuticals applications, to food sciences to medicinal applications and even to entomology [31]-[34].

Ultraviolet-Visible spectroscopy examines changes in the molecular energy levels resulting from electron transfer from non-bonding orbitals. The π-electron system, conjugated unsaturation, aromatic compounds, and conjugated non-bonding electron systems are all commonly covered. This absorption spectroscopy uses electromagnetic radiations among 190nm to 800nm and is split into Ultraviolet (UV, 190-400nm) and visible (VIS, 400-800nm) regions [35].

Theoretical simulations of the researched molecules were carried out in order to determine some quantum chemical characteristics derived from our molecules' structure [36]. We used the density functional theory DFT (B3LYP) method with the 6-31G basis (d) for this purpose, and the calculations were done with Gaussian software 09W [37],[38].

The various molecular quantum parameters such as energy gap \( \Delta E_{\text{gap}} \), chemical potential \( \mu \), electronegativity \( \chi \), the chemical hardness \( \eta \) and the chemical softness \( \sigma \) are expressed by the following relations [39]-[43]:

\[
\Delta E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}} \tag{1}
\]

\[
\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \tag{2}
\]
Where $E_{\text{HOMO}}$ is the energy of the highest occupied molecular orbital and $E_{\text{LUMO}}$ is the energy of the lowest unoccupied molecular orbital.

3. Experimental Technique

The Helium-Neon laser with 632.8nm in wavelength is suitable for use as light source in our laser interferometer experiment. The gas cell was built in the form of two fixed cylindrical glass cells. As illustrated in Fig.1. The gas under investigation was filled in the inner cylinder, and the outer cylinder was utilized to heat the inner cylinder (gas cell). A calibrated thermocouple is fixed through them for measuring the interior temperature of the gas's cell. The outside cylinder we constructed for heating up the temperature of the gas under investigation that used as a container of heating liquid water surrounding the cell of the gas. The temperature of the gas might be measured. The accuracy of temperature change was about ± 1°C. The temperature range changed from 313 to 348 K.

![Figure 1](image.png)

**Figure 1.** The constructed set-up used to measure the gas's refractive index.

We must change the pressure of the gas inside the cell to analyze the effect of pressure on the gas under investigation. In Fig.2, the change and control of gas pressure inside the cell is depicted schematically. The gas pressure inside the cell was controlled by two 100 mL syringes with a
moveable piston controlled by two tiny screws. With an Hg-manometer, the amount of gas inside the
gas cell was controlled.
The evacuation system was split into two sections (the rotary and the diffusion). The rotary has three
ranges for pressure range the first from 1 to $10^1$ mbar, the second from $10^1$ to $10^2$ mbar, and the third
from $10^2$ to $10^3$ mbar. After the rotary reached to the range of $10^{-3}$ mbar we could use the diffusion.
The diffusion has three ranges for pressure, range one from $10^{-2}$ to $10^{-5}$ mbar, the second ranges from
$2 \times 10^{-5}$ to $10^{-6}$ and the third from $2 \times 10^{-6}$ to $10^{-7}$.
The number of fringes that traverse the field of view is changed by varying the gas pressure within
the cell. By counting the number of changed fringes $\Delta N$ crossing the field of view by varying the pressure
$p$ in the gas cell, we can calculate the refractive index at any arbitrary pressure from the equation [44];

$$n(P_s) = \frac{\lambda \Delta N}{t \Delta p} P_s + 1 \quad (6)$$

Where; $n(P_s)$ is the refractive index at pressure $P_s$; $\lambda$ is the wavelength of the laser light, $t$ is
the length of the cell, $(\Delta N)$ is the varying in the number of fringes count and$(\Delta p)$, is the change in
the pressure.

4. Theoretical Background

4.1. Permittivity and Dielectric Susceptibility

The value of permittivity $\varepsilon$ is a dimensionless parameter it is one of the most important dielectric
parameters, which plays a major role in the description of substance properties. In theory of the
propagation of electromagnetic waves in a matter, the velocity of according to Maxwell's propagation
is determined from the relation [45];

$$v = \frac{1}{\sqrt{\varepsilon_r \mu_r}} = \frac{c}{\sqrt{\varepsilon_r \mu_r}} \quad (7)$$

Here, $\mu_r$ is the relative permeability of medium, $\mu_r$ is the permeability in vacuum has value
$4 \pi \times 10^{-7}$ Hm$^{-1}$, $\varepsilon_r$ is the relative permittivity in medium and $\varepsilon_r$ is the permittivity in vacuum has value
$8.854 \times 10^{-12}$ F/m. For the nonmagnetic dielectric materials, $\mu_r \approx 1$

$$v = \frac{c}{\sqrt{\varepsilon_r}} \quad (8)$$

Using equation (7) and (8), one got the relation between dielectric constant and the refractive
index, assuming $\varepsilon_r = \varepsilon$

$$\varepsilon = \varepsilon_r^2 \quad (9)$$

In general, the dielectrics contain linear and non-linear dielectrics. In case of linear dielectrics,
the relation between the value of polarization and the intensity of electric field [46] is given by:

$$P = k_e \varepsilon_0 E \quad (10)$$

Where $k_e$ is the dielectric susceptibility and the product $k_e \varepsilon_0$, F/m, is known as the absolute
dielectric susceptibility.
The quantity [47]

$$D = \varepsilon_r E + P \quad (11)$$

Is called electric displacement (electric induction).

Also, there is a relationship between the electric displacement and intensity of an electric field

$$D = \varepsilon \varepsilon_0 E \quad (12)$$

From equations (10), (11), and (12) we can get the relation between dielectric susceptibility and
permittivity

$$k_e = \varepsilon - 1 \quad (13)$$

4.2. Specific and Molar Refractivity

From the Clausius- Mostti equation (46), (48)
Where, \(N = N_A \frac{P}{RT}\), here \(N_A\) is Avogadro's number, \(R\) is the gas universal constant and \(\alpha\) is the polarizability. The quantity \(\frac{\varepsilon-1}{\varepsilon+2}\) is known as specific refractivity \([A_{sp}]\) of a gas

\[
A_{sp} = \frac{\varepsilon-1}{\varepsilon+2}
\]

By multiplying both sides of equation (15) by \(\frac{M}{\rho}\) we can get

\[
\frac{\varepsilon-1}{\varepsilon+2} \frac{M}{\rho} = \frac{N_A \alpha M}{3\varepsilon \rho}
\]

Where \(M\) is the molecular mass of a gas, \(\rho\) is the density of a gas, and \(\frac{\varepsilon-1}{\varepsilon+2} \frac{M}{\rho}\) is known as molar refractivity \(\Pi\).

4.3. Molecular Radius \(r\) and Volume Expansion \(\beta\)

When a conducting sphere of radius \(r\) is placed in an electric field \(E\) the induced moment \(P\) is determined by

\[
P = r^3 E
\]

But

\[
P = \alpha E
\]

From these two equations \(\alpha = r^3\)

From equation [14], by substituting \([\varepsilon = 1/4\pi]\) we get

\[
\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi N \alpha}{3}
\]

In case of cgs electrostatic units (without \(4\pi\varepsilon_0\)), equation (19) becomes [47]

\[
\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi N_A \alpha}{3N_A r^3}
\]

There is a relation between the thermo-optic coefficient \([dn/dT]\) and the volume expansivity \(\beta\) given by Murphy and Albert [50] as

\[
\frac{dn}{dT} = \frac{-3n[n^2-1]}{2[2n^2+1]} \beta
\]

5. Results and Discussion

5.1. Experimental calculations

We devoted to the experimental measurements of the refractive index and its variation with pressure and temperature for Methane and Nitrogen gases. Fig. 2.(a, b) implies that the refractive index of CH\(_4\) and N\(_2\) increase by increasing the pressure at constant temperature and selected wavelength 633nm. This is because by increasing of gas's pressure, the density of the gas increases; this leads the refractive index to increase. As shown in Table.1, the pressure coefficient values \((dn/dp)_{T}\) for methane and nitrogen decrease by increasing the temperature.
Figure 2. Refractive Index against Pressure for Methane CH$_4$ (a) and for Nitrogen N$_2$ (b) at constant Temperature.

Table 1. The values of pressure coefficient (dn/dp)$_T$ for methane and nitrogen gases at different temperature.

| T K  | 348  | 343  | 338  | 333  | 328  | 323  | 318  | 313  |
|------|------|------|------|------|------|------|------|------|
| (dn/dp)$_T$ | 4.842 | 4.920 | 5.079 | 5.214 | 5.394 | 5.612 | 5.818 | 6.121 |
| CH$_4$$\times 10^{-6}$ | 4.102 | 4.302 | 4.333 | 4.471 | 4.619 | 4.647 | 4.844 | 5.017 |

Figure 3. Refractive index against Temperature for Methane CH$_4$ (a) and for Nitrogen N$_2$ (b) at constant pressure.

Table 2. The values of the thermo-optical coefficient for methane and nitrogen gases at different pressures

| PCm Hg | 60  | 65  | 70  | 76  | 80  | 85  | 90  |
|--------|-----|-----|-----|-----|-----|-----|-----|
| (dn/dT)$_p$ | -2.133 | -2.228 | -2.590 | -2.597 | -2.790 | -2.800 | -3.214 |
| CH$_4$$\times 10^{-6}$ | -1.266 | -1.347 | -1.566 | -1.623 | -1.748 | -1.897 | -1.935 |
From that figure the refractive index $n$ decreases by increasing the temperature $T$ at constant pressure $p$. This was reasonable because when the temperature of the gas increases, the density of the gas decreases, which leads to decrease the refractive index.

The values of the thermo-optical coefficient $(dn/dT)_p$ that shown in Table.2 describe how the gas can converge or diverge the incident laser beam according to the sign of $(dn/dT)_p$ [51]. If the sign of the thermo-optical coefficient $(dn/dT)_p$ was positive, the gas converges the incident laser beam. If negative, the gas diverges the incident light. In our case the gases diverge the incident laser beam.

We calculated the refractive index $n$ in the range of temperature 313-348 K and pressure from 60 to 90 Cm-Hg by using H$_2$-N$_e$ laser with wavelength 633 nm. The calculated value of refractive index of Methane gas ranged from 1.000331 to 1.000426 from 348K to 313K at 76 Cm Hg or atmosphere pressure. Also, the Nitrogen gas has a refractive index $n$ ranged from 1.000251 to 1.000309 from 348K to 313K at 76 Cm Hg as shown in Fig. 2, 3.

![Figure 4](image1.png) **Figure 4.** Dielectric Constant against Pressure for Methane CH$_4$ (a) and for Nitrogen N$_2$ (b) at constant Temperature.

![Figure 5](image2.png) **Figure 5.** Dielectric Susceptibility against Pressure for Methane CH$_4$ (a) and for Nitrogen N$_2$ (b) at constant Temperature.
Figures 6 and 7 (a), (b) imply the relation between the dielectric constant $\varepsilon$, dielectric susceptibility $K_e$, and specific refractivity $A_{sp}$ of Methane and Nitrogen gases respectively with the pressure $P$ at constant temperature $T$. These figures show that, by increasing the pressure of the gas at constant temperature, the permittivity, dielectric susceptibility, and specific refractivity increase. Tables 3, 4 show the calculated values of dielectric constant, dielectric susceptibility and specific refractivity of Methane, Nitrogen gases with respect pressure at constant temperature. These values decrease with increase the temperature.
Fig. 7, 8 and 9 (a), (b) show the decreasing of dielectric constant $\varepsilon$, dielectric susceptibility $k_e$ and specific refractivity $A_{sp}$ by increasing the temperature of the gas at constant pressure for methane and nitrogen gases. Tables. 5, 6 show the calculated values of dielectric constant, dielectric susceptibility and specific refractivity of Methane and Nitrogen with respect to temperature at constant pressure. These values increase with increase the pressure.

Table 3. The values of $(d\varepsilon/dp)_T$, $(dk_e/dp)_T$ and $(dA_{sp}/dp)_T$ for Methane at different temperature.

| T K  | 348  | 343  | 338  | 333  | 328  | 323  | 318  | 313  |
|------|------|------|------|------|------|------|------|------|
| $(d\varepsilon/dp)_T$ CH$_4$$\times$$10^{-5}$ | 0.968 | 0.984 | 1.016 | 1.043 | 1.079 | 1.123 | 1.164 | 1.225 |
| $(dk_e/dp)_T$ CH$_4$$\times$$10^{-5}$ | 0.968 | 0.984 | 1.016 | 1.043 | 1.079 | 1.123 | 1.164 | 1.225 |
| $(dA_{sp}/dp)_T$ CH$_4$$\times$$10^{-6}$ | 3.228 | 3.279 | 3.386 | 3.476 | 3.596 | 3.741 | 3.878 | 4.080 |
Table 4. The values of \((\frac{d}{dp})_T\), \((\frac{d k}{dp})_T\) and \((\frac{d A_{SP}}{dp})_T\) for Nitrogen at different temperature.

| T K  | 348 | 343 | 338 | 333 | 328 | 323 | 318 | 313 |
|------|-----|-----|-----|-----|-----|-----|-----|-----|
| \((\frac{d}{dp})_T\) | 8.404 | 8.606 | 8.669 | 8.944 | 9.241 | 9.297 | 9.690 | 10.037 |
| \(N_2 \times 10^{-6}\) | | | | | | | | |
| \((\frac{d k}{dp})_T\) | 8.404 | 8.606 | 8.669 | 8.944 | 9.241 | 9.297 | 9.690 | 10.037 |
| \(N_2 \times 10^{-6}\) | | | | | | | | |
| \((\frac{d A_{SP}}{dp})_T\) | 2.734 | 2.810 | 2.862 | 2.926 | 3.026 | 3.056 | 3.163 | 3.249 |
| \(N_2 \times 10^{-6}\) | | | | | | | | |

Table 5. The values of \((\frac{d}{dT})_p\), \((\frac{d k}{dT})_p\) and \((\frac{d A_{SP}}{dT})_p\) for Methane at different pressure.

| P cm Hg | 60 | 65 | 70 | 76 | 80 | 85 | 90 |
|---------|----|----|----|----|----|----|----|
| \((\frac{d}{dT})_p\) | -4.2678 | -4.4586 | -5.1827 | -5.1971 | 5.5831 | -5.6029 | -6.4315 |
| \(CH_4 \times 10^{-6}\) | | | | | | | |
| \((\frac{d k}{dT})_p\) | -4.2678 | -4.4586 | -5.1827 | -5.1971 | 5.5831 | -5.6029 | -6.4315 |
| \(CH_4 \times 10^{-6}\) | | | | | | | |
| \((\frac{d A_{SP}}{dT})_p\) | -1.4220 | -1.4855 | -1.7267 | -1.7315 | -1.8601 | -1.8664 | -2.1425 |
| \(CH_4 \times 10^{-6}\) | | | | | | | |

Table 6. The values of \((\frac{d}{dT})_p\), \((\frac{d k}{dT})_p\) and \((\frac{d A_{SP}}{dT})_p\) for Nitrogen at different pressure.

| P cm Hg | 60 | 65 | 70 | 76 | 80 | 85 | 90 |
|---------|----|----|----|----|----|----|----|
| \((\frac{d}{dT})_p\) | -2.533 | -2.848 | -3.134 | -3.362 | -3.558 | -3.796 | -3.872 |
| \(N_2 \times 10^{-6}\) | | | | | | | |
| \((\frac{d k}{dT})_p\) | -2.533 | -2.848 | -3.134 | -3.362 | -3.558 | -3.796 | -3.872 |
| \(N_2 \times 10^{-6}\) | | | | | | | |
| \((\frac{d A_{SP}}{dT})_p\) | -0.8443 | -0.9491 | -1.044 | -1.120 | -1.192 | -1.264 | -1.290 |
| \(N_2 \times 10^{-6}\) | | | | | | | |

From equations (20), (21) we calculated the values of molecular radius and volume expansion of Methane, Nitrogen gases at \(P=76\) cm Hg, \(T=313\) as shown in table. 7.

Table 7. The values of molecular radius and volume expansion of Methane gas at \(P=76\) cm Hg and \(T=313\) K.

| Gas        | Molecular radius [r] Å | Volume expansion \(\beta\) |
|------------|------------------------|---------------------------|
| Methane \([CH_4]\) | 1.401                  | 0.0060985                 |
| Nitrogen \([N_2]\)  | 1.223                  | 0.005255                  |

5.2 Theoretical Calculations

All calculations were obtained with the Gaussian 09 program package. The structure optimizations were carried out at the DFT/6-31G(d) level of theory. The DFT method that was a significant improvement over Hartree-Fock is B3LYP. Generally, the B3LYP functional is faster than the most Post Hartree-Fock techniques and usually is a comparable method [52].

The \(CH_4\) and \(N_2\) molecular structures are optimized using DFT/B3LYP level theory and from which the HOMO (Highest Occupied Molecular Orbital) energy, LUMO (Lowest Unoccupied Molecular Orbital) energy and energy gap \(E_g\) are calculated as shown in Fig.10.
HOMO energy is often associated with the molecule’s ability to give away its electrons to suitable vacant orbital, the low values of HOMO energy for Methane and Nitrogen indicated to difficulty of giving electrons to an acceptor having a vacant orbital molecular. On the other hand, LUMO gives information on the acceptance of electrons in the molecule. Methane and Nitrogen molecules have high value of LUMO energy which means disability to accept electrons from occupied orbital [52].

![Graphical presentation of the highest occupied HOMO and lowest unoccupied molecular LUMO orbitals for CH₄ (a) and N₂ (b).](image)

**Figure 10.** The graphical presentation of the highest occupied HOMO and lowest unoccupied molecular LUMO orbitals for CH₄ (a) and N₂ (b).

| Parameter          | Methane [CH₄] | Nitrogen [N₂] |
|--------------------|---------------|---------------|
| $E_{\text{HOMO}}$ [eV] | 1.4512        | -1.1712       |
| $E_{\text{LUMO}}$ [eV] | -10.8042      | -11.637       |
| E.G. [eV]          | 12.255        | 10.466        |
| $\mu$              | -4.6765       | -6.4044       |
| $\chi$             | -6.1277       | -5.2331       |
| $\rho$             | 0             | 0             |
| $\xi$              | 4.6765        | 6.4044        |
| $\eta$             | -0.1632       | -0.1911       |
| Molecular charge   | 0             | 0             |

**Table. 8** Calculated $E_{\text{HOMO}}, E_{\text{LUMO}}$ levels, energy gap $E_{\text{g}}$, dipole moment $\rho$ and chemical hardness $\eta$, other quantum parameters chemical as electronegativity $\chi$, chemical potential $\mu$ and chemical softness $\sigma$ values of the studied Methane and Nitrogen molecules obtained by B3LYP/6-31G(d) level.

![Optimized structures of (a) Methane CH₄, (b) Nitrogen N₂ which have been obtained by using B3LYP/6-31G(d)β level of theory.](image)

**Figure 11.** Optimized structures of (a) Methane CH₄, (b) Nitrogen N₂ which have been obtained by using B3LYP/6-31G(d)β level of theory.
The value of molecular charge equal zero which means the methane and nitrogen molecules is neutral as shown in Fig.11. The dipole moment $\rho$ is the parameter most used to describe the polarity of a molecule [53]. It is defined as the charge product in the atom and the distance among two polar covalent bonds. Dipole moment of zero point to that there is no partial charge on either end of a covalent bond. On the other hand, chemical hardness $\eta$ and softness $\sigma$ are important chemical properties for measuring molecular stability and reactivity [52]; the results of these two parameters are also listed in Table.8. Methane and Nitrogen molecules have good chemical stability because of the increase in the hardness values and decrease in softness values.

In the infrared spectrum of methane there are two strong bands as shown in Fig.12, the fundamental frequencies, $v_3$ at 3020.3 cm$^{-1}$, and $v_4$ at 1306.2 cm$^{-1}$. Because of the symmetry of the molecule, the other two fundamentals $v_1$ at 2914.2 cm$^{-1}$ and $v_2$ at 1526 cm$^{-1}$ are not active in the infrared, although these frequencies may appear in combination bands with the other frequencies and their overtones, to give bands in the near infrared [54].

![IR Spectrum](image)

**Figure 12.** IR Spectrum of Methane which have been obtained by using B3LYP/6-31G(d) level of theory.

![UV-V spectrum](image)

**Figure 13.** UV-V spectrum of Methane (a) and Nitrogen (b) which have been obtained by using B3LYP/6-31G(d) level of theory.

Chemical bonds are the forces that hold the atoms in a molecule together. The chemical forces that hold the atoms together are considered to be like to those utilized by massless springs. In a Cartesian coordinate system, each mass requires three coordinates to define the molecule's position in space, using coordinate axes x,y,z. Thus, the molecule has three independent degrees of freedom of movement. There will be a total of 3N degrees of freedom of movement for all the atoms in a molecule if a molecule has N atom. We get 3N-6 internal motions for a nonlinear molecule and 3N-5
for a linear molecule after subtracting the translational and rotational degrees of freedom from the 3N degrees of freedom. These interior vibrations are known as the normal modes of vibration. Consequently simple diatomic molecule has only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N₂, the band is detected only in Raman spectrum not in IR spectrum. More intricate molecules with numerous bands have a more complicated vibrational spectrum, i.e. big molecules have several peaks in their IR spectrum [55]. By utilizing functional, B3LYP and applying the 6-31G [d] basis set, the UV-VIS spectra for Methane and Nitrogen gases were calculated. The calculated maximum absorption wavelength of Methane and Nitrogen molecules are 87, 98 nm respectively as shown in Fig.13.

6. Conclusion:
In the present text we had built an optical system to measure the refractive index of both Nitrogen and methane gases at different temperature and pressure. Some related physical properties were calculated. These calculated parameters are the optical permittivity (dielectric constant), dielectric susceptibility, specific refractivity, molar refractivity, molar radius volume expansion coefficient were estimated. In addition, both CH₄ and N₂ molecular structures are optimized using DFT/B3LYLB level theory and from which the HOMO energy, LUMO energy and energy gap E₉ were calculated with the Gaussian 09 program package. The structure optimizations were carried out at the DFT/6-31G(d) level of theory. The DFT method that was a significant improvement over Hartree-Fock is B3LYP. Generally, the B3LYP functional is faster than the most Post Hartree-Fock techniques and usually is a comparable method. Methane and Nitrogen molecules have good chemical stability because of the increase in the hardness values and decrease in softness values. Also, the IR-spectrum of both methane and nitrogen gasses were investigated theoretically.
Longevity

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