

Conference Paper

Excitation of N_2 Molecules as a Density Modifier: A Theoretical Approach

Excitación de Moléculas de N_2 como un Modificador de su Densidad: Desde una Perspectiva Teórica

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Abstract

This work presents a theoretical exploration of modifying the volume and density of N_2 gas molecules so as to feed gas balloons and zeppelin airships for flying purposes. This research aims to develop a gas system with a lower density than their non-modified ground state gas by studying the properties associated with excited state levels and their differences from the fundamental one. Then, this approach is achieved by altering the micro-molecular or electronic properties of N_2 gas to assess the change at the macro-molecular level, such as volume and density. Density functional theory (DFT), time-dependent density functional theory (TD-DFT), and molecular dynamics (MD) computational methods are employed to look for the effects of excited N_2 molecules on volume and density at standard conditions. As a result, a density decrease of 2.77% is achieved for the eighth excited state molecule set compared to the ground state system, indicating the feasibility of this approach. Contrasting this system with the traditional hydrogen gas used in zeppelins, N_2 gas is a widely available, eco-friendly, and safe source (non-flammable) around Earth, strengthening its suitability as a source for high-tech applications.

Keywords: *gas, excited states, DFT, TD-DFT, MD, volume, density modification.*

Resumen

A través de este trabajo se presenta una exploración teórica acerca de la modificación del volumen y densidad del N_2 gas con el objetivo de alimentar globos aéreos o aeronaves Zeppelin para propósitos de vuelo. Este estudio apunta hacia el desarrollo de un sistema gaseoso de menor densidad mediante el estudio de propiedades asociadas a niveles excitados de energía, contrastando con el sistema no modificado en estado fundamental. Esta estrategia es conseguida mediante la alteración de las propiedades micro-moleculares o electrónicas del N_2 gas para evaluar cambios a nivel macromolecular, tales como el volumen y la densidad. Varios métodos computacionales, tales como la teoría de densidad funcional (DFT), la teoría de densidad funcional dependiente del tiempo (TD-DFT) y dinámica molecular (MD), son empleados para observar los efectos de moléculas excitadas de N_2 sobre el volumen y densidad de este gas a condiciones estándar. Como resultado, se consiguió un decremento de la densidad del gas en un 2.77 % para el sistema en octavo estado excitado, comparado con el sistema en estado fundamental; lo cual es indicativo de la factibilidad de esta estrategia. Al contrastar el sistema de estudio con gases tradicionales como el hidrogeno gaseoso usado en zeppelins, el N_2 gas es un recurso de amplia disponibilidad alrededor del globo, eco-amigable,

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y un material seguro (no flamable), lo cual lo hace un recurso ideal para aplicaciones de nuevas tecnologías.

Palabras Clave: *N₂, gas, estados excitados, DFT, TD-DFT, MD, volumen, modificación de densidad.*

1. Introduction

Humanity has made efforts since the beginning of time to explore and rule every possible environment of this planet, including the skies. Over the course of history, man has created a wide variety of tools to attempt flying, including kites, cloaks with stiffened edges, and wings that resemble birds. For instance, since antiquity, the Chinese have known that hot air rises and have used this idea to create a particular kind of tiny hot air balloon known as a sky lantern [1]. Said invention was recovered by the Frenches on November 21, 1783, in a hot air balloon made of paper and silk by the Montgolfier brothers. To further improve balloons, Henry Cavendish, an Englishman, found a suitable pathway to produce hydrogen, a gas lighter than air, 1776 by mixing sulfuric acid and iron filings. [2].

Gas balloons quickly rose to popularity as a means of air travel in the decades between 1830 and 1840, which encouraged constant improvements to their capabilities. This led to the development of the known airship design, which was used across the board, from transportation to combat during World War I [2]. In fact, gas balloons became the primary form of air travel, but flying was not just something everyone could afford due to the costs and time-consuming requirements of filling gas balloons. Since hot air ballooning was not very feasible then, the airships' primary fuel at that point was hydrogen gas [2]. Considering that hydrogen is one of the most flammable substances known to man, this led to the German zeppelin Hindenburg exploding on May 6, 1937, and engulfing Lakehurst, New Jersey skies in flames [2]. As a result, the era of the airships came to an end, at least within the transport field, making way for the airplane designs promoted concurrently by the Wright brothers in 1903 [1, 2].

As was previously stated, the gas used to fill the balloon structures was the primary issue with airships. A density of 0.0899 g/L at 20 °C, 1 atm, made hydrogen gas an appealing choice by then and current type-technologies. Currently, helium gas (He), which has a density of 0.1634 g/L at 20 °C, 1 atm, is a desirable alternative. However, because this last one is an uncommon gas, it is not readily available everywhere. The air, on the other hand, continues to be the most plentiful gas resource in the entire globe. The lingering question from this viewing point is whether air is a practical source for flight. The air mass-density relationship is an essential component of the atmosphere,



which varies in composition. About 78% of the gases that make up the atmosphere of the Earth are nitrogen, 21% are oxygen, and the remaining traces are water vapor, carbon dioxide, helium, argon, ozone, or other pollutants. Water vapor concentration varies greatly and is largely dependent on temperature, affecting altitude in the sky. The air is said to be dry when significant quantities of water vapor have been physically removed. At 273 K and a pressure of 101.325 kPa, pure, dry air has a 1.293 kg/m³ density. The composition of air is basically constant up to an altitude of at least 50 km, with the exception of the variability of water vapor [3].

The characteristics and properties of air vary according to the latitude, altitude, temperature, and amount of solar light available. Then, distinct behaviors can be expected and assessed when these variables are changed. Indeed, it is possible for heat activities, direct electron impacts, cascades from excited states, photoionization, and chemical reactions to excite and deexcite N_2 ground state levels. In nature, these procedures have been evidenced at the ionosphere since the energetic solar radiation knocks electrons off molecules and atoms, turning them into ions with a positive charge. As the thermosphere temperature varies between night and day and between the seasons, the numbers of ions and electrons do. [4]. From this point of view, multiple electronic events are involved under these conditions, although the energy cost to carry out them is artificially high. Despite the required energy costs, it is an efficient mechanism by which Earth adsorbs or reflects electromagnetic radiation of specific wavelengths in order to sustain life [5, 6].

Because of the increased vibrational temperature, N_2 contributes more to ionospheric processes such as decreasing electron density, developing high-altitude electron density troughs, and generating NO. Although the N_2 vibrational temperature cannot be measured directly in the thermosphere, other thermospheric data has to be assessed with varying degrees of success [7, 8]. Utilizing models based on species diffusion and observed positive ion concentrations under quiescent conditions, the N_2 vibrational temperature is higher than the kinetic temperature for the lower thermosphere. Vibrationally excited N_2 has been hypothesized to facilitate the formation of NO in the disturbed polar thermosphere as a result of the exothermic chemical reaction of O atoms with vibrational levels superior to 11 in the electronic ground state of molecular N_2 , in addition to its known effect on the electron density. Then, it appears that no analysis of the electron impact produced a vibrational distribution of N_2 has been reported that treats both the excited electronic states and the vibrational levels of the N_2 ground state consistently, despite the fact that a variety of excitation and environment models have been evaluated for producing an enhanced N_2 vibrational population [7, 8].



If these spontaneous events are seen from the perspective of N_2 activation pathways, this phenomenon has been studied extensively for over 80 years, although with other purposes. Principally, artificial approaches have focused on the design of suitable catalysts so as to obtain chemical derivatives of industrial interest for the agricultural field, organic synthesis, and food industry, among others. For instance, multiple developments have been developed from the perspective of low-temperature thermochemical catalysis and (photo)electrocatalysis [9], and special attention has been developed in the field of organometallic chemistry so as to replicate the biological activities of Nitrogenase enzymes. Thus, multiple works have driven out to weakening or even breaking the triple bond of N_2 and getting fixed nitrogen species for further uses.

Considering that molecular nitrogen is the main component of air, the overall air density can be described by this component. Considering that it is a resource of wide availability along the Earth's surface, N_2 can be stated as an almost infinite ecological gas resource. As an attempt to solve the density problem, by means of this work, the excitation of the N N bond is presented as an alternative to modifying the said property. Thus, the aim of this study is to present a possible alternative to change N_2 density for flying applications. The selected route to get said goal was modifying the N_2 bond length through the reach of an excited state. Consequently, an analysis of volume, density, and energy properties of the first and eighth excited state nitrogen molecule was executed in order to evaluate it as a suitable gas source candidate for flying purposes.

2. Computational Methods

Advanced computational methods were used better to understand the electronic and structural characteristics of N_2 molecules. Time-dependent density functional theory (TD-DFT) and molecular dynamics (MD) are two such methods that have become widely used in recent years. Through the use of TD-DFT, it is possible to examine the dynamic behavior of electrons in materials and investigate excited states and the characteristics that go along with them. On the other hand, MD models can offer insights into the structural dynamics of materials by monitoring the movements of atoms and molecules over time. Together, these potent computational tools have the potential to significantly improve the comprehension of how the henceforth system behaves under different circumstances. By means of this article, it will be used by both TD-DFT and MD to study and analyze the properties of the target molecule and gain new insights into its behavior.



2.1. TD-DFT

Understanding the behavior of materials under the impact of external energy sources like light or an electric field requires knowledge of excited-state properties and dynamics. Since the traditional version of density functional theory (DFT) implies that electrons are in the ground state, it is inappropriate for studying excited states. Time-dependent density-functional theory (TD-DFT), an extension of DFT that explicitly addresses excited-state properties, dynamics, and spectroscopy, was developed to offset this drawback. [11]. Calculating ab-initio electronic neutral excitations, which are samples in optical or energy-loss spectra, is possible using the extremely accurate TD-DFT theory. In principle, TD-DFT can be considered an alternative formulation of time-dependent quantum mechanics, with electron density as its primary variable, as opposed to the conventional approach, which depends on wave functions and the many-body Schrodinger equation. TD-DFT is an important instrument for studying excited-state properties and dynamics because this special method makes it possible to calculate excited states in materials more quickly and accurately. [12].

TD-DFT greatly streamlines the computations necessary for analyzing excited states in materials because it uses electron density as its fundamental variable. This makes TD-DFT an appealing choice for researchers in the area of materials science, allowing for more effective and precise computation of excited-state properties and dynamics [13]. The common method is to use the Kohn-Sham system, a hypothetical system of non-interacting electrons, to calculate the electron density. The resulting equations are regularly applied for quantitative analysis of systems containing numerous atoms and are comparatively easy to solve numerically. In this approach, the electrons in the Kohn-Sham system are subjected to an effective potential known as the time-dependent Kohn-Sham potential [14]. Although the exact form of this potential is unknown and must be approximated, the Kohn-Sham approach has proven to be a highly effective method for calculating excited-state properties and dynamics in materials [15].

Despite the limitations of TD-DFT, which may result in errors for certain types of excitations, it remains a valuable tool for studying the excited-state properties and dynamics of materials. In order to better understand the structure of the molecule under the influence of external energy, the current work examines the excited states of the molecular nitrogen gas based on the TD-DFT principles. Specifically, the study aims to provide information about the orbitals involved in electronic transitions during the excited-state dynamics of molecular Nitrogen. By using TD-DFT as a theoretical framework, this work provides valuable insights into the excited state properties and



dynamics of molecular nitrogen, which can have important implications in various areas of materials science.

2.2. Molecular dynamics (MD)

The behavior of complex systems at the atomic and molecular size is frequently studied through molecular dynamics simulations in various disciplines, such as materials science, biochemistry, and physics. The accuracy of the simulations depends on the quality of the chosen force field, which is often parameterized based on experimental data or quantum mechanical calculations. However, the assumptions and approximations used in the modeling process mean that even with the greatest force field, MD simulations may still have some limitations. [16]. To overcome some of these limitations, researchers have developed more advanced MD methods that incorporate quantum mechanical effects, such as density functional theory (DFT) and quantum mechanics/molecular mechanics (QM/MM) approaches [17]. These methods allow for a more accurate description of chemical reactions and other complex phenomena that classical force fields cannot capture alone.

Another important aspect of MD simulations is the choice of time step and integration scheme. The time step must be small enough to capture the fast atomic motions but not too small to result in excessive computational cost. That means that the integration scheme should be chosen carefully to ensure energy conservation and stability of the simulation [18]. For instance, MD simulations can be used to forecast macroscopic properties, such as diffusion coefficients, viscosity, and elastic moduli, that are challenging or impossible to measure experimentally and offer insights into a system's microscopic behavior. Additionally, by contrasting the simulation findings with experimental data, researchers can enhance the force field and other modeling parameters, producing more precise and prognosticative simulations. [19]. Overall, molecular dynamics simulations are a powerful tool for studying the behavior of complex systems at the atomic and molecular scale.

3. Calculations Methodology

3.1. Construction of molecular nitrogen structure

A nitrogen molecule was drawn using Avogadro software as the first stage. Once created, it was initially optimized by using Force Fields, in this instance, the universal force field (UFF). DFT calculations were used to optimize the structure further using



ORCA 4.2.1 software [20]. The CAM-B3LYP functional method is employed for the calculations. This effectively blends the hybrid qualities of B3LYP functional and the long-range correction put forth by Tawada et al. Indeed, the CAM-B3LYP functional has a short-range exchange interaction of 0.19 Hartree-Fock (HF) plus 0.81 Becke 1988 (B88) and a long-range exchange interaction of 0.65 HF plus 0.35 B88. The standard error function with parameter 0.33 provides a smooth description of the intermediate range. Dispersion correction factors, such as D3BJ, are also included. Once the optimizations were finished, the final coordinates were used for additional computations and for modeling the molecular orbitals of N_2 .

3.2. Calculation of the first excited state

This stage involves scanning the first 50 excited states of N_2 using the TD-DFT method. The scanning technology enables the identification of the global minima of the molecule in order to identify the most probable excited states to occur when the electrons in a nitrogen molecule are subjected to higher energy levels. Thus, this methodology involves exploring a molecule's potential energy surface (PES) by varying one or more internal coordinates while keeping the remaining coordinates fixed. In the case of the first 50 excited states of N_2 , a scan was performed on the PES in order to find the lowest energy state or the global minimum when this was promoted from the ground state PES to the excited PES. To acquire structural and energy information about the first excited state of N_2 , calculations are restricted to it instead of a whole scanning as before. It is noteworthy to note that these calculations are based on the N_2 optimized ground state structure that was earlier established at the same parameters mentioned in the previous section.

3.3. Other excited states

At the same as the previous calculations, other procedures are developed for other excited states of interest, following exactly the main process. In this work, only the first and eighth excited states were analyzed due to the highest probability and feasibility of these ones at the moment to be subjected to an energy stimulus.

3.4. MD simulations

MD simulations were developed for N_2 molecules in both their ground state and excited state, respectively. Sets of 50 molecules were built using the optimized structures from



each of the previous calculations in order to investigate their microscopical interactions and forecast the macroscopical properties of the *Nitrogen* system. Given that the aim is on the density of the N_2 gas in both its ground and excited states, an isothermal-isobaric (NPT) thermodynamic ensemble with parameters of 293 K and 1.01325 bar was established. Additionally, a $P1$ cubic cell with a length of 125 \AA [21] was used for the computations. For this calculation, used *CHARMM* Force Field was modified in order to introduce the *Nitrogen* triple bond length and force constant. For the whole calculation, it used *NAMD 2.14* software [23]. All analyses were studied using a time-step of 40 ns .

4. Results and Discussion

4.1. Structural aspects of ground and excited states:

Once the proposed insights were interpreted, the initial ground state bond length increase was driven out by the excitation of the N_2 molecules, as was expected. Therefore, the ground state bond length increases by 16.21% in the first excitation state. Compared to the fundamental one, there is an increase of 58.74% in the bond length of the eighth excited state. The N_2 molecules will then, as the initial premise, occupy a larger volume, leading to a reduction in the density value. However, it is essential to take into account the energy required to reach excited states since it is noticeable from Fig. 1 (a) the triple bond character of the Nitrogen molecule is considered one of the most difficult molecules to dissociate by artificial approaches [9, 10]. This last is caused principally by the nature of its bond composed of one σ (simple bond) and two π bonds (double and triple bond), complemented by the apolarity of the molecule resulting in the inertness of the system, and by consequence, its great stability under standard conditions. For this reason, the triple bond nature of Nitrogen is maintained even in Fig 1 (b), denoting the high energy requirements to overcome the barrier of triple bond and reducing it, changing its bond length as a result. But, in the case of Fig. 1 (c), the bond is reduced to a single bond character due to a higher energy supply capable of reducing the Nitrogen molecule.

Nevertheless, these changes demand excessive energetic supplies (energy radiation) so as to break some bonds causing at the same time the complete change of the electron density and also the increase of reactivity of the molecule with its surroundings. That is why this kind of phenomenon has been reported in the ionosphere of Earth, where the conditions of the UV radiation are able to lead to ionic or excited Nitrogen species. Given the induced activation of this molecule, these species are highly reactive, which in turn are involved in other mechanisms so as to reach equilibrium and decrease

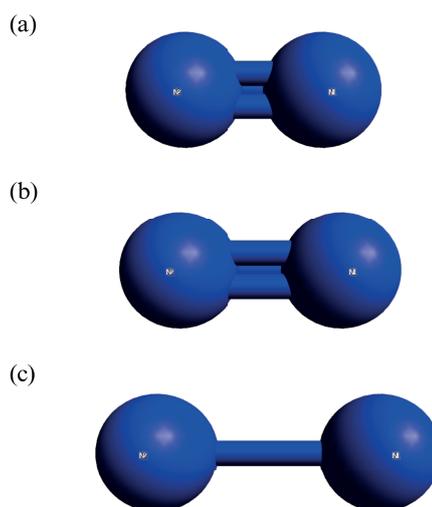


Figura 1

Nitrogen molecule structures. (a) Structure of ground state N_2 molecule. (b) Structure of first excited state N_2 molecule. (c) Structure of eighth excited state N_2 molecule.

their energy. Therefore, the effects of excitation on the physical and chemical properties of N_2 should be carefully considered, considering both the increase in volume and the potential changes in bond character and reactivity.

Tabla 1

Bond length of N_2 molecules structures.

State	Bond Length (Å)	Elongation (%)	Percentage
0	1.086	-	
1	1.262	16.21	
8	1.724	58.74	

4.2. Electronic transitions of N_2

From Figure 2 (a), it is observed that the absorption peaks of N_2 are located in the ultraviolet (UV) region of the electromagnetic spectrum, ranging from 20 to 130 nm. The energy required to excite the molecule to higher electronic states is also relatively high, approaching the X-ray radiation region. For example, as shown in Fig. 2 (b), it takes 9.523 eV to excite N_2 to the first electronic state, equivalent to radiation of 130.3 nm. In contrast, for the eight excited states shown in Fig. 2 (c), an energy of 16.178 eV is needed, corresponding to radiation of 76.7 nm. The UV region is typically divided into



three sub-regions: UV-A, UV-B, and UV-C. UV-A, also known as "blacklight" or "long wave" UV, has wavelengths between 200 and 320 nm and is the closest to visible light. Shorter wavelength, greater energy. Wavelengths in the far UV area range from 91 to 200 nm. Extreme UV radiation, which straddles the UV and X-ray spectrums, is the area of the ultraviolet spectrum with the shortest wavelength range and highest energies. Extreme UV light spans wavelengths between 10 and 30 nm. [24]

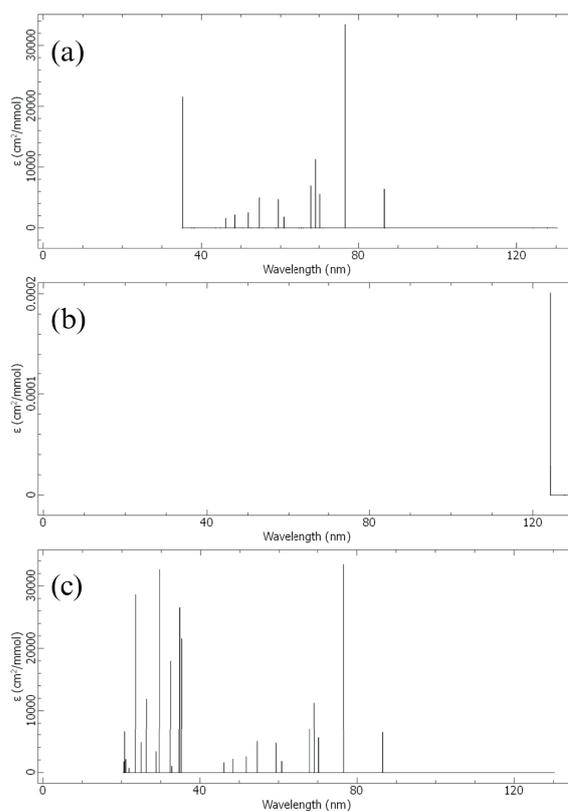


Figura 2

(a) UV absorption spectra of N_2 the molecule along the first 50 excited states. (b) UV absorption spectra of N_2 molecule along the first excited state. (c) UV absorption spectra of N_2 molecule along the eighth excited state.

Almost all UV radiation penetrating the Earth's atmosphere and reaching the surface is UV-A. UV-B waves, with wavelengths between 280 and 320 nm, carry more energy than UV-A waves and cause sunburn. The third subregion, UV-C, includes radiation with wavelengths between 100 and 280 nm, which have high energies and are very damaging to living creatures. UV-C is also called "short wave" UV or "germicidal" UV because it is sometimes used to sterilize laboratory equipment or to purify water by killing microbes [24]. Considering this overview of UV radiation, it is possible to know about the capabilities and potential of each one, as well as its free distribution in nature. Here, it is paramount to highlight that UV-B and UV-C are naturally distributed in the



outer layer of the atmosphere, so they cannot be obtained directed by humans from the surroundings against the case of UV-A radiation.

It is worth noting that normal air is largely opaque to UV radiation with wavelengths shorter than 200 nm, as oxygen in the atmosphere absorbs this radiation. The other contributor to the absorbance of UV radiation in the atmosphere is nitrogen, according to the theoretical results obtained in this study. The atmosphere acts as a shield, blocking the most dangerous, highest energy portions of the UV spectrum that reach our planet from the sun and other sources in space. Thus, it is clarified why it is difficult and energetically costly to excite nitrogen molecules at visible or near UV radiation wavelengths since it is an atmosphere component specifically designed to protect Earth from high-energy cosmic radiation.

4.2.1. Orbitals and electronic transitions involved

Analyzing the TD-DFT results of the first excited state of N_2 , it is observed that the transition involves a calculated value. It should be noted that the study was conducted in 1996, and some simplifications may have been introduced to facilitate the calculations, leading to this variation between the obtained results with the reported ones. After analyzing the TD-DFT results of the first excited state of N_2 , it is evident that the transition involved is of the π - π^* or n - π^* type based on the molecular orbitals involved (n = non-bonding orbitals).

Typically, such transitions are located in the 150-500 nm range. The transition involved in the first excited state of N_2 at 130.1 nm is not too far from the typical range. However, the presence of a triple bond in the molecule could contribute to the deviation from the normal range. To induce this type of transition, a radiation of the UV-C type, ranging from 100-280 nm, is required. However, natural radiation of this wavelength is limited to the outer atmospheric layers and cannot be directly utilized by solar rays, but the use of artificial radiation sources can counter this drawback. The promotion of an electron from either the π_x or y orbital to the π_x or π_y orbitals, respectively, with contributions of 0.497304 and 0.497006, respectively. This is illustrated in Fig. 3, where there and blue arrows indicate the electronic transitions, and the red and blue circles show the molecular orbitals involved.

As previously mentioned, the excitation of N_2 from the ground state to the first excited state requires an energy of 9.523 eV. Comparing these results with the reported spectroscopic transition states for the N_2 molecule, it is observed that the involved states are $X^1\Sigma_g^+$ (ground state) $B^3\Sigma_u^-$ and $a^1\Sigma_u^-$ (antibonding π orbitals), with the corresponding transitions $B^3\Sigma_u^- \leftarrow X^1\Sigma_g^+$ (Fig 4, blue arrow) and $a^1\Sigma_u^- \leftarrow X^1\Sigma_g^+$ (Fig

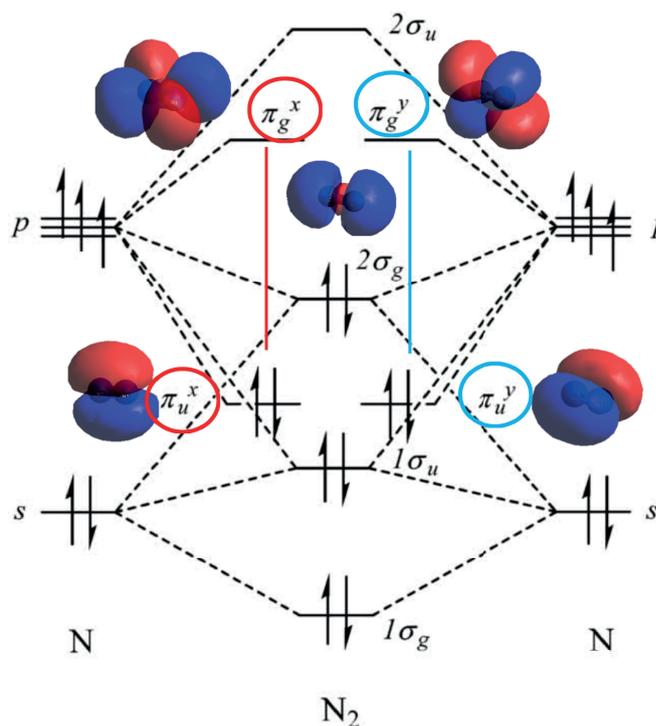


Figura 3

MO diagram of N_2 molecule with orbitals involved at the first excited state .

4, red arrow). The energy required for these transitions can be calculated from the diagram and has been reported as 10.41 eV [22–24], which differs by 9.31% from the calculated value. It should be noted that the study was conducted in 1996, and some simplifications may have been introduced to facilitate the calculations, leading to this variation between the obtained results with the reported ones.

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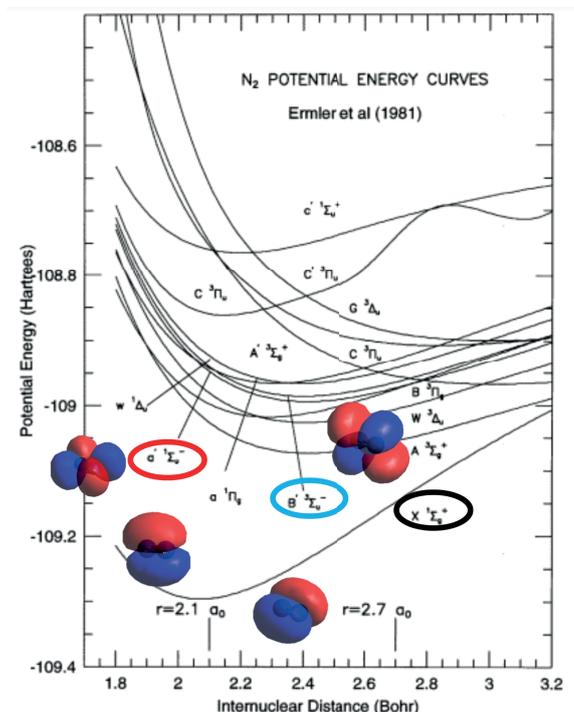


Figura 4

Potential energy curves computed by Ermler et al. (1981) for the lowest 13 valence states of N_2 . Red lines indicate the electronic transitions involved in the first excitation state of N_2 . Adapted from [22].

4.2.2. Oscillator strength

In spectroscopy, the oscillator strength is a dimensionless quantity that indicates the probability of absorption or emission of electromagnetic radiation during transitions between energy levels of an atom or molecule [25]. Therefore, the oscillator strength is an essential parameter that characterizes the efficiency of a particular transition in coupling to light at a given frequency. It provides information about the probability of an electronic transition occurring. Hence, if the oscillator strength of a transition is low, the likelihood of that transition occurring is also low. Conversely, if the oscillator strength of a transition is high, the transition is more probable. In the case of the two transitions discussed (first and eighth excited states), the first one has a low probability of occurring, and the second one requires a considerable amount of energy but a high probability of occurrence, making both transitions unsuitable for cheaper applications [26].

Table II shows the values of f_{osc} for different electronic states. It is worth noting that the first excited state has a f_{osc} value of zero, indicating a low probability of electronic transition. Similarly, several other states also have f_{osc} values between 0.20

**Tabla 2**

Absorption spectrum via transition electric dipole moments of N_2 the molecule for the first 15 excited states.

State	Energy (cm^{-1})	Wavelength (nm)	f_{osc}
1	76811.3	130.2	0.000000000
2	78276.8	127.8	0.000000000
3	78280.8	127.7	0.000000000
4	80420.1	124.3	0.000000007
5	80420.9	124.3	0.000000001
6	115663.6	86.5	0.221431053
7	115669.3	86.5	0.221531139
8	130486.2	76.6	1.164965420
9	140647.6	71.1	0.000000000
9	140647.6	71.1	0.000000000
10	142532.6	70.2	0.193221014
11	142539.5	70.2	0.191757468
12	144770.1	69.1	0.391866533
13	147292.8	67.9	0.239449991
14	147301.3	67.9	0.240636723
15	151555.3	66.0	0.000000000

to 0.40. However, the eighth state stands out with a f_{osc} value of 1.16, suggesting a high probability of electronic transition. The only issue is that this transition requires a considerable amount of energy (16.178 eV) or radiation of 76.6 nm, which falls in the extreme-UV radiation region and is higher than the typical UV-C radiation used [27].

4.3. Evaluation of gas density using MD simulation

The first stage of the study involved performing MD simulations for the ground state of the N_2 molecule using the conditions and parameters outlined in the Calculations methodology section. After running the simulation with a time-step of 40 ns, 50,000 values were obtained for the unit cell volume occupied by the set of molecules. For instance, a time-step for ground state MD simulation is shown in Fig. 5 (a). Only the last 30,000 data values were considered to stabilize the system, so an average value was determined, which provided an estimate of the system's density of molecules. Table III shows that the calculated density of the system of molecules was 1.173 g/L, which can be compared to the experimental data of 1.1606 g/L at 20°C and 1 atm. The deviation between the calculated and experimental values is 1.07%, which is relatively



low considering the approximate parameters and assumptions used in the Force Field employed for these calculations for the first time.

The same procedure used for calculating the density of the ground state system of N_2 molecules was applied to calculate the average volume of the unit cell occupied by the set of molecules and its corresponding density for the excited states. A sketch of a time-step for the first and eight excited states MD simulations are shown in Fig. 5 (b) and (c), respectively, from which, given the extra elongation of the nitrogen bonds drives out to the increase of the volume in the unit cell, and by consequence the decrease of the density. The results are reported in Table III, which shows a decrease in density of 0.31% for the first excited state and a decrease of 2.77% for the eighth excited state. The MD simulation was performed for the eighth excited state due to its high f_{osc} value, as mentioned previously.

Tabla 3

MD simulation results of N_2 . set of molecules.

State	Volume Av. (\AA^3)	Density (g/L)	Var with ground st.
0	1.984E+06	1.173	-
1	1.988E+06	1.170	0.21%
8	2.038E+06	1.141	2.77%

The results show that excitation of N_2 molecules to higher electronic levels leads to an increase in the volume occupied by the particles and a corresponding decrease in gas density [28], which was expected. When comparing the obtained density values with those reported for hydrogen and helium, it is noted that the density of excited state N_2 gas is still higher than these other gases [29]. However, the density values can vary with changes in temperature. In the early days of airships and gas balloons, hot air was used as a gas source, highlighting the potential for alternative gas sources.

4.4. Assessment of the buoyancy force of nitrogen gas

In order to be able to build a lifting apparatus, the buoyancy capacity associated with the gas source must be known. The mass a gas can lift depends upon the differences in densities between air and the specific gas ($\rho_{air} - \rho_{gas}$). The buoyancy force, in N, can be deduced through the inclusion of the gravitational constant g and the volume, so this force is expressed as follows:

$$F_b = (\rho_{air} - \rho_{gas}) \cdot g \cdot V(1)$$

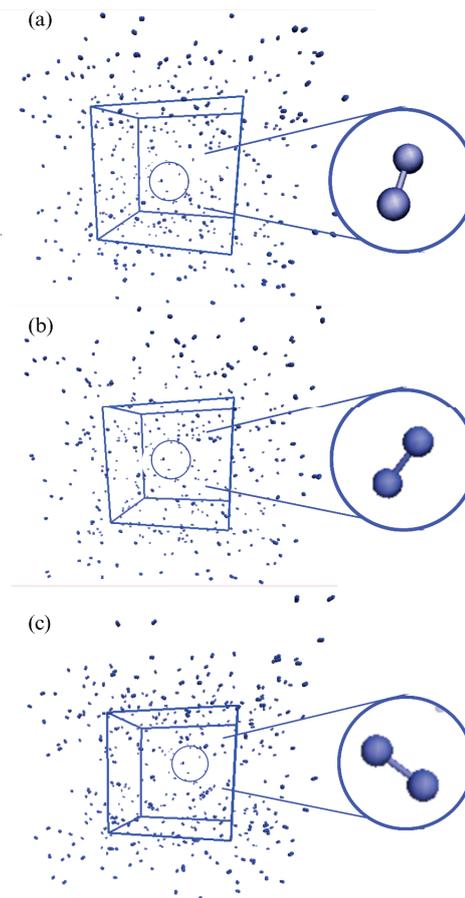


Figura 5

(a) MD simulation of 50 molecules of N_2 at ground state. (b) MD simulation of 50 molecules of N_2 at first excited state. (c) MD simulation of 50 molecules of N_2 at the eighth excited state.

The lighter the gas inside the balloon, the higher would be the lifting force. As a reference, the calculation can be made for hydrogen following the values provided in the introduction section:

$$F_b = (1.293 - 0.090) \cdot (9.81 \text{ m/s}^2) \cdot (1 \text{ m}^3) = 11.798 \text{ N(2)}$$

Following this approximation, for each m^3 of hydrogen a little more than 1kg could be lifted. The exact same calculations were done for nitrogen based on density values deduced from molecular dynamics simulations.

From these numbers, the buoyancy force associated with N_2 is approximately ten times smaller than in H_2 all cases which would result in transportation devices roughly ten times larger than the ones constructed upon hydrogen technology. For a human body of 60 kg, it would result in a balloon of 375 m^3 of N_2 (eighth excited state) without including any other equipment. In order to provide a comparison, the volume of the

**Tabla 4**

Weight lifted and buoyancy force associated with each type of gas.

Gas	Weight lifted (kg) by (1 m ³) of gas	Buoyancy force (N)
H ₂	1.203	11.798
N ₂ (ground state)	0.120	1.177
N ₂ (first excited state)	0.123	1.206
N ₂ (eighth excited state)	0.152	1.491

Hindenburg LZ-129 was 200000 m³, while a typical hot-air balloon is around 2000 m³. In these, the structure, the equipment, and the crew would occupy a large proportion of the lifting force. However, contrasting the results about N₂ is interesting: the eighth excitation brings approximately 27% of additional buoyancy force in reference to ground state N₂, which is not negligible and shows this excitation path as a viable strategy to generate lighter gas.

4.5. Specific potential in the Ecuadorian context

The study of alternative transportation strategies is becoming increasingly important in the current society, as humanity faces significant challenges such as climate change, air pollution, and increasing demands for transportation services. The use of eco-friendly and sustainable modes of transportation, such as airships and balloons, could help mitigate these challenges. The theoretical study presented here contributes to this goal by offering a new approach for modifying N₂ gas molecules to achieve desired macro-molecular properties. By investigating the excited state levels of N₂ molecules and their effects on gas volume and density, this study offers insights into the potential applications of this gas in various industries, including transportation. Furthermore, this study demonstrates the importance of theoretical research in developing new technologies and strategies for addressing pressing societal issues.

The results of this study have several potential applications, including as a lifting gas for airships and balloons. The modified N₂ gas with lower density could reduce the weight of airships and balloons, enabling them to carry larger payloads over longer distances. This could have significant implications for transporting goods and passengers, particularly in areas with low air traffic. With its relatively small number of airports and free skies in most parts of the country, Ecuador could be an interesting candidate to try this alternative flying transport strategy. With further development, this technology could be used to transport passengers or small parcels, improving the postal service of Ecuador. While the transport speed of airships would be slower than conventional planes, this



should be balanced with the ecological aspect, as this kind of transport based on air modification would be entirely pollution-free. Furthermore, the modified N_2 gas could have applications in chemical, pharmaceutical, and semiconductor manufacturing industries, where precise control of gas density is required. Finally, this gas could have implications for space exploration, as it could potentially be used in developing propulsion systems and gas storage for spacecraft.

5. Conclusions

This research established that when properties at the micro-molecular level are changed, the macro-molecular properties of Nitrogen gas molecules can be altered. In this instance, the increase in bond length caused by the excitation of electrons by their promotion from the ground state of the Nitrogen molecule to higher electronic states results in a change in the electron density and structure of the molecule. For instance, in the eighth excited state, the triple bond was broken into a single bond, potentially increasing the molecule's reactivity. However, this analysis was not included in the current research, which is important for activating nitrogen in catalysis. In a subsequent stage, the changes made at the microscopic level impact the volume of the set of molecules in the simulations' unit cell, increasing this value and reducing the density as originally predicted.

But even though the aim of the study was achieved, this method was not energetically advantageous due to the low f_{osc} values for the first excited states or the substantial amount of energy needed to produce the excitation of molecules to eight excited states, for example. Therefore, when evaluating the viability of this work for possible future applications or experimental analysis, it must be taken into account that in order to facilitate the aforementioned transitions, a UV radiation source with a wavelength that oscillates between 30 and 100 nm, associated with high energies near to the X-ray radiation, is required. Despite the achievements and drawbacks of the excitation of one of the most inert molecules on Earth, this theoretical methodology is proven to be a new alternative to modify the properties of gases which in principle constitutes a suitable alternative for flying purposes, but these insights also constitute paramount capabilities for other research areas, such as advanced engines, aerospace, weather analysis and monitoring, among others.



6. Further Remarks

As was mentioned in this study, simulation of the set of molecules was performed at standard conditions. However, it is suggested to study the behavior of the system at variable temperatures since this last parameter is a crucial modifier of the density of the gas system (Fig. 6), and also include gas collision theory basis to have a whole panorama of the interactions in real life.

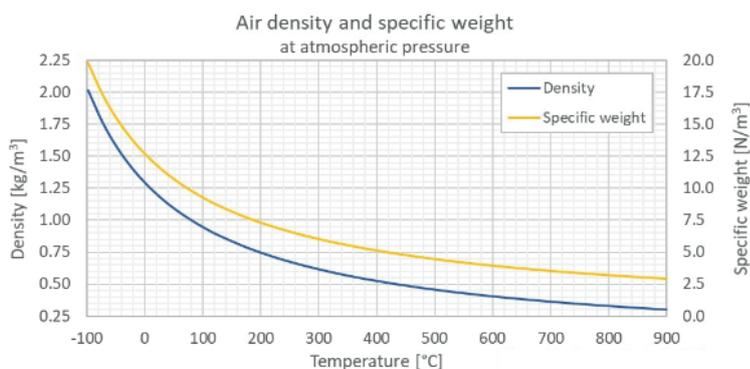


Figura 6

Air density and molecular weight at atmospheric pressure.

As another aspect, the force constant of the force field employed should be corrected for the corresponding excited states; in this study, it was assumed the same force constant for all the systems (ground and excited states), so this parameter may be one aspect of the introduction of some errors and deviations. Finally, further analysis must solve the problem of the Force Field's non-bonding parameters to obtain the most reliable MD simulation.

Conflicts of Interest

The authors declare no conflict of interest.

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