Bond Length and Bond Dissociation Energy of Nitrogen Molecule

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The nature of a chemical bond involves attraction and repulsion between atoms in achieving a certain intermolecular distance at equilibrium. Understanding this nature would give full insights to many of the electronic properties of diatomic molecules. This work is an attempt to estimate the bond length and bond dissociation energy (BDE) of nitergen molecule, N_2, at 0 K. The energetics of the molecular separation of N_2 is plotted thru computational calculations of its total energies at different intermolecular distances. Results revealed an intermolecular distance of 1.10 Å with a potential of 1015.42 kJ/mol. The calculated bond BDE from computations is 987.20 kJ/mol which is close to the standard values in literature.

1. Introduction

When 2 atoms are relatively far apart in manner where no electrostatic interaction occurs between them, we expect to have an intermolecular potential kept at minimal. It is when the 2 atoms brought closer together that the changes in the said potential become significant due to the attractive and repulsive forces between them. When attractive forces are dominant, the potential would be lowered to a negative quantity until such that the repulsive forces begin to dominate, thus its potential would then start to increase whenever these atoms are further pushed closer.

This kind of potential can be approximated by the Mie potential, V_M which is given by the difference of two terms

$$V_M = \frac{C_n}{r^n} - \frac{C_m}{r^m}$$

where n>m and r is the intermolecular distance between 2 atoms. The first term embodies short-range repulsion behavior and the second term long-range attractive behavior.

A special kind of Mie potential is called the Lennard-Jones potential, V when n = 12 and m = 6 where the constants $C_n = 4\varepsilon\sigma^{12}$ and $C_m = 4\varepsilon\sigma^6$. The resulting equation would be

$$V = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The two parameters in the Lennard-Jones potential have the following physical interpretation: ε is the depth of the potential well and σ is the distance at which V = 0. As such, ε is a measure of how strongly the molecules attract each other, r is the distance of separation between both particles and σ is a measure of the size of the molecules. A typical Lennard-Jones plot follows the total energy curve depicted in Figure 1 which has similar curve to the Born-Oppenheimer approximation of molecular potential energy curve, in which makes Lennard-Jones plot a good approximate but a simpler guesstimate from the complex Schrödinger equation for internuclear separations. This simplified potential is useful for assessing several properties in diatomic molecules.[1,2]

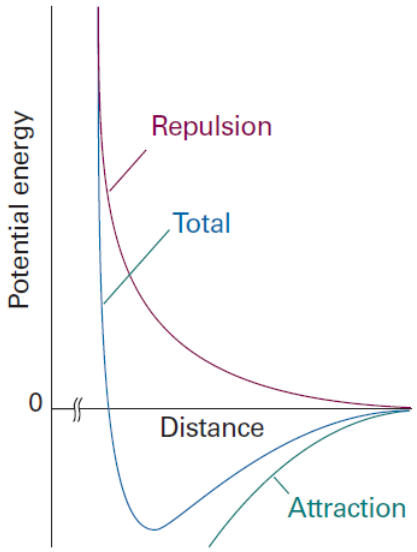

Figure 1. A typical intermolecular potential energy curve taken from [1]

The diatomic in focus is the nitrogen molecule, N_2. This molecule is common and abundant, making up 78.1% of the earth's atmospheric volume. Although it is less abundant in the earth's crust, it is essential to the organisms, especially plants, as it is converted into nitrogen compounds (i.e. ammonia, nitrite and nitrate) which would then be essential the growth of many plants and animals. The nitrogen compound interchange between

atmosphere, geosphere and biosphere forms what is known as the nitrogen cycle. Series of chemical reactions needed in this cycle would need energetic processes where the bond between the abundant N_2 molecules needs to be broken first.

In this study, the potential energy as a function of distance of separation between the atoms of a diatomic molecule would be plotted using Lennard-Jones equation using computational analysis. With this plot, the stable bond length and the bond dissociation energy of the N_2 molecule can be estimated. Estimating these values in computational analysis is vital in further understanding of physical and thermodynamic properties of the said essential molecule at a molecular level.

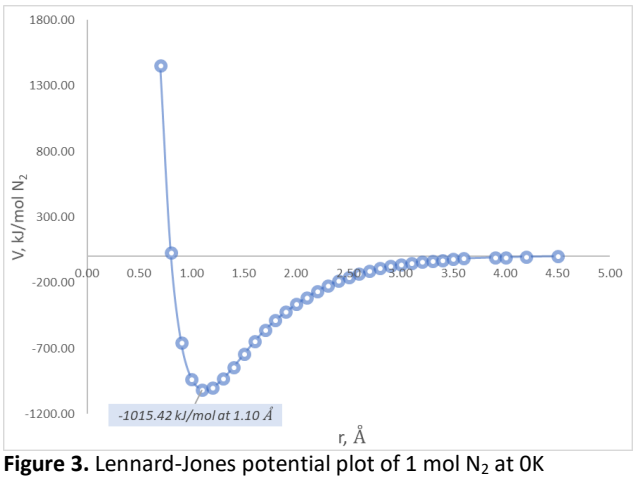

Figure 3. Lennard-Jones potential plot of 1 mol N_2 at 0K

2. Results and Discussion

Quantum espresso package and Burai GUI (Version 1.3) were mainly used for the computational calculations.

A large cubic super cell (20x20x20 $Å^3$) representation of N_2 molecule is constructed, which represents 1.5 units of N_2 molecule, with one of the atoms placed at (0,0,0) coordinate whereas the is other placed at (1,0,0) coordinate as shown in Figure 1 where no electrostatic interaction between N_2 molecules is expected. Different static calculations at 0K for different intermolecular distances, r, (starting at 0.7 Å with minimum increments of 0.1 Å until 4.5 Å) of N_2 were performed to generate total energies.

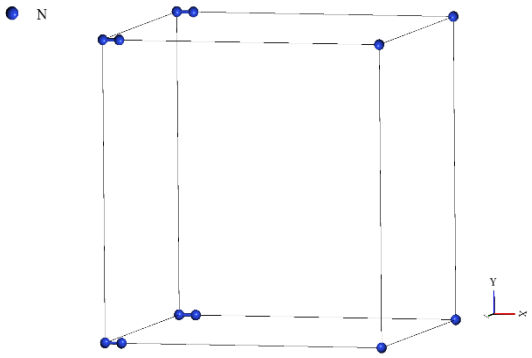

Figure 2. Constructed nitrogen molecule supercell

Results of these calculations were plotted in Figure 3 with V, calculated as kJ per mole of N_2, as a function of r, in Å. The lowest potential in the graph is -1015.42 kJ/mol. Having the lowest potential, the 2 nitrogen atoms is said to be in equilibrium with attractive and repulsive forces hence the intermolecular distance of 1.10 Å is best considered as the stable bond length of N_2. The magnitude of ε occurs at a distance r with the lowest potential, V. Thus, the best estimate of the Lennard-Jones potential parameters ε and r would be 1015.42 kJ/mol and 1.10 Å respectively.

The ε value can be used to approximate the bond dissociation energy (BDE), corrected with reported zero-point vibrational energy (ZPVE) of N_2 of 28.2148 kJ/mol [3], which is calculated to be 987.20 kJ/mol.

The calculated BDE and bond length of this study are comparable, with less than 5% deviations, to the standard values with experimental basis [4,6] and to the DFT study on diatomic molecules by Esterhuysen and Frenking as shown in Table 1 [5].

Table 1. Comparison of Bond Lengths and Bond Dissociation Energies of Nitrogen Molecule in Different Studies

Parameter	*This study*	Literature Values[a]	Deviation from Literature
Bond Length, Å	1.10	▪ 1.0976 [4] ▪ 1.105 [5]	▪ 0.219% ▪ 0.452%
BDE, kJ/mol	987.20	▪ 941.69 [6] ▪ 957.30 [5]	▪ 4.83% ▪ 3.12%

a – values are based from references in [].

Given the intermolecular distance of 1.10 Å, nitrogen would have a radius of 0.55 Å. This is actually lower than the reported covalent radius of nitrogen of 0.71 Å [7]. Covalent radius of an atom is a measure of the size of an atom that forms part of one covalent bond. This study, along with other experimental results, mean that the nitrogen molecule exhibits a higher order covalent bond formation to become stable. In fact, the bond order (BO) for nitrogen molecule in molecular orbital theory studies is 3 in comparison to oxygen (BO = 2) and fluorine (BO = 1) molecules [8].

3. Conclusion

Using Quantum espresso package and Burai GUI (Version 1.3) as computational tools, the nitrogen molecule exhibit Lennard-Jones behavior as shown in Figure 2 graph, where the calculated ε and r are 1015.42 kJ/mol and 1.10 Å respectively. The bond dissociation energy of 987.20 kJ/mol and bond length of 1.10 Å are calculated in this study, which are comparable to standard values and related studies.

Computational Model

DFT calculations will be implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons will be described using the projector augmented wave (PAW) method. Plane wave basis sets will be employed with an energy cut-off of 400 eV. The surface Brillouin zone integrations will be performed on a grid of 1x1x1 Monkhorst-Pack k-points using Methfessel-Paxton smearing of =0.2 eV.

Notes and references

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