

Investigation of the Effects of Various Model Chemistries on Bond Parameters and Solvent Effects on Energy Barrier of the Reaction $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$

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I. Introduction

Computational chemistry [1] is a branch of chemistry that uses the principles of computer science to assist in solving chemical problems. It uses the results of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. The programs used in computational chemistry are based on many different quantum chemical methods that solve the molecular Schrodinger equation associated with molecular Hamiltonian.

We use ab-initio method for finding transition state of a bimolecular reaction. Ab-initio methods [2] is an approach to calculate energy and many other properties of molecule and it is obtained by solving Schrodinger equation. The simplest type of ab-initio electronic structure calculation is the Hartree - Fock (HF) scheme, an extension of molecular orbital theory, in which the correlated electron-electron repulsion is not specifically taken into account ; only its average effect is included in calculation.

Gaussian is a computational chemistry software program [3] which is used in this study. Starting from the basic laws of quantum mechanics, Gaussian predicts the energies, molecular structures and vibrational frequencies of molecular systems, along with numerous molecular properties derived these basic computation types. It can be used to study molecules and reactions under a wide range of conditions, including both stable species and compounds which are difficult or impossible to observe experimentally such as short lived intermediates and transition structures. Gaussian 03 version is used in this study.

II. AB- Initio Method- An Overview

2.1 Introduction

The aim of ab initio molecular orbital theory is to predict the properties of atoms and molecules. It is based on the fundamental laws of quantum mechanics [4,5]. Different mathematical transformations and approximation techniques are necessary to solve the equations that build up this theory. We review this theory briefly.

2.2 The Schrodinger Equation

For an isolated N-electron atomic or molecular system within the Born-Oppenheimer approximation, the electronic Schrodinger equation is given by

$$\hat{H}_{elec} \Phi_{elec}(r) = E_{elec} \Phi_{elec}(r) \dots\dots\dots 2.1$$

where $E_{elec} = E_{elec}(\{R_A\})$ is the electronic energy, $\Phi_{elec} = \Phi_{elec}(\{r_i\}, \{R_A\})$, is the wave function which describes the motion of electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates, as does the electronic energy. By a parametric dependence we mean that, for different arrangements of the nuclei Φ_{elec} is a different function of the electronic coordinate. \hat{H}_{elec} is the electronic Hamiltonian operator describing the motion of N electrons in the field of M point charges:

$$\hat{H}_{elec} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \dots\dots\dots 2.2$$

The total energy E_{tot} is the electronic energy E_{elec} including the nuclear repulsion energy according to the following equation:

$$E_{tot} = E_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \dots\dots\dots 2.3$$

2.3 The Hartree-Fock Approximation

The Hartree-Fock approximation[6,7] is a mean field approximation, where an electron is thought to move in the average field due to all other electrons present in the system. On the basis of the variation theory, the lowest value of \hat{E} is approximated as E_0 identified as the electronic energy for the selected nuclear configuration.

$$E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle \dots\dots\dots 2.4$$

where $\psi_0 = |\chi_1, \chi_2, \dots, \chi_N\rangle$ is a single Slater determinant. By minimizing E_0 with respect to the spin orbitals, it is possible to derive Hartree-Fock equation, which is basically an eigenvalue equation of the type,

$$\hat{f}_i(i) \chi_i(x_i) = \varepsilon_i \chi_i(x_i) \dots\dots\dots 2.5$$

where the $\hat{f}_i(i)$ is an effective one electron operator called the Fock operator [8] having the following form,

$$\hat{f}_i(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i) \dots\dots\dots 2.6$$

Here $v^{HF}(i)$ is the average potential experienced by the i-th electron due to the presence of other electrons in the system. The essence of the Hartree-Fock approximation [9] is to replace the complicated many-electron problem by one electron problem in which the electron-electron repulsion is treated in an average way. The Hartree-Fock potential, $v^{HF}(i)$, term depends on the spin orbital of other electrons i.e., the Fock operator depends on its own eigenfunctions. Thus Hartree-Fock equation is non-linear and has to be solved iteratively.

The Hartree-Fock calculations can be closed-shell calculations with all paired electrons or open shell calculations with some unpaired electrons. In closed-shell restricted Hartree-Fock (RHF) calculations [10] all the electrons are paired so that the spatial orbitals are doubly occupied. In unrestricted Hartree-Fock (UHF) calculations the orbitals need not be doubly occupied. The HF equations might be solved numerically according to the suggestion of Roothaan and Hall . A set of known spatial basis functions (for example, atomic orbital basis functions) is introduced and the unknown molecular orbitals are expanded in the linear expansion:

$$\psi_i = \sum_{\mu}^K C_{i\mu} \phi_{i\mu} \dots\dots\dots 2.7$$

The problem of calculating the HF molecular orbitals is then reduced to the problem of calculating a set of expansion coefficients. Substituting the above equation into the HF integrodifferential equation therefore gives $\mathbf{FC} = \mathbf{SC}\varepsilon$ where \mathbf{F} , \mathbf{S} , \mathbf{C} and ε are Fock matrix, overlap matrix, square matrix of the expansion coefficients, and the diagonal matrix of the orbital energies ε_i , respectively.

2.4 Ab-initio Method

The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular Schrodinger equation associated with the molecular Hamiltonian. Methods that do not include any empirical or semi-empirical parameters in their equations-being derived directly from theoretical principles, with no inclusion of experimental data are called Ab-initio method[11]. This does not imply that the solution is an exact one; they are all approximate quantum mechanical calculations. It means that a particular approximation is rigorously defined on first principles (quantum theory) and then solved within an error margin that is qualitatively known beforehand. If numerical iterative methods have to be employed, the aim is to iterate until full machine accuracy is obtained. The simplest type of ab-initio electronic structure calculation[12] is the Hartree-Fock (HF) scheme, an extension of molecular orbital theory, in which the correlated electron-electron repulsion is not specially taken into account; only its average effect is included in the calculation.

2.5 Gaussian 03

Gaussian 03 version in the Gaussian series of electronic structure program is used for this study. Gaussian 03[13,14] is used by chemists, chemical engineers, biochemists, physicists and others for research in established and emerging areas of chemical interest. Starting from the basic laws of quantum mechanics,

Gaussian predicts the energies, molecular structures, and vibrational frequencies of molecular systems, along with numerous molecular properties derived from these basic computation types.

2.6 Geometry optimizations

molecular system varies with small changes in its structure is The geometry of a molecule determines many of its physical and chemical properties. This is why it is very important that we understand the geometry of a molecule when running computations. In computational chemistry we are specifically concerned with optimizing bond angles (degrees), bond lengths (angstroms) and dihedral angles (degrees). Geometry optimization[15,16] is either an energy minimization or a transition state optimization. The aim of geometry optimization is to generate the lowest energy structure of a molecule from an arbitrary starting state. The way the energy of a molecular system varies with small changes in its structure is specified by its potential energy surface. A potential energy surface is a mathematical relationship linking molecular structure and the resultant energy. For a diatomic molecule, it is a two- dimensional plot with the internuclear separation on the X-axis and the energy at that bond distance on the Y-axis, producing a curve. For larger systems, the surface has as many dimensions as there are degrees of freedom within the molecule.

2.7 Potential Energy Surface(PES)

Potential energy surface[17,18] is the potential interaction energy of nuclei in a molecular system. It is a function of the nuclei internal coordinates (bonds, angles and dihedral angles). If a molecule has N atoms, it has three degrees of freedom for translational motions of the whole molecule and two or three overall rotational motions if it has a linear or non-linear structure, respectively. Thus the potential energy surface has a (3N-5) or (3N-6) dimensions. The simplest potential energy surface is the potential curve of a diatomic molecule that is a function of only the bond distance.

There are minima on the potential surface. A minimum is the bottom of a valley on the potential surface. From such a point, motion in any direction- a physical metaphor corresponding to changing the structure slightly- leads to a higher energy. A minimum can be a local minimum, meaning that it is the lowest point in some limited region of the potential surface, or it can be the global minimum, the lowest energy point anywhere on the potential surface. Minima occur at equilibrium structures for the system, with different minima corresponding to different conformations or structural isomers in the case of single molecules, or reactant and product molecules in the case of multicomponent systems.

Peaks and ridges correspond to maxima on the potential energy surface. A peak is a maximum in all directions. A point which is a maximum in one direction and a minimum in the other is called a saddle point. For example, the saddle point is a minimum along its ridge and a maximum along the path connecting minima on either side of the ridge. A saddle point corresponds to a transition structure connecting the two equilibrium structures.

Potential energy surface is calculated by solving the Schrodinger equation using the Born-Oppenheimer approximation which assumes the electron motions can be separated from the nuclear motions for a large number of geometrical structures. Since the Schrodinger equation can only be solved approximately for multi- electron systems, depending on the level of approximation (method/basis set) used, locations of these stationary points (minimum or transition state) may vary from their 'true' structures.

III. Model Chemistries, Basis Set Effects And Solvent Effects

3.1 Model Chemistries

The theoretical philosophy underlying Gaussian is characterised by the following principle. A theoretical model should be uniformly applicable to molecular systems of any size, and type, up to a maximum size determined only by the practical availability of computer resources. The Schrodinger equation can be approximated much more closely for small systems than for large ones. However, using different levels of theory for different size molecules makes comparing results among systems unreliable.

A theoretical model should be uniquely defined for any given configuration of nuclei and electrons. This means that specifying a molecular structure is all that is required to produce an approximate solution to the Schrodinger equation. No other parameters are needed to specify the problem or its solution.

A theoretical model ought to be unbiased. It should rely on no presuppositions about molecular structure or chemical processes which should make it inapplicable to classes of systems or phenomena where these assumptions did not apply. It should not in general invoke special procedures for specific types of molecules.

The implementation of such a model theoretically is termed a theoretical model chemistry, or simply model chemistry. Once a theoretical model has been defined and implemented, it should be systematically tested on a variety of chemical system, and its results should be compared to known experimental values. Once a

model demonstrates that it can reproduce experimental results, it can be used to predict properties of systems for which no data exist.

Gaussian includes many different model chemistries. Model chemistries are characterised by the combination of theoretical procedure and basis set. Every calculation performed with Gaussian must specify the desired theoretical model chemistry in addition to specifying molecular systems to consider and which results to compute for it.

A model chemistry generally consists of the combination of a theoretical method with a basis set. Each such unique pairing of method with basis set represents a different approximation to Schrodinger equation. Results for different systems generally may only be compared and tested by comparing their on the same systems to one another and to the result of experiments.

In general computational cost and accuracy increases as we move to the higher level methods. Choosing a model chemistry almost always involves a trade off between accuracy and computational cost. More accurate methods and basis sets make run longer[19].

3.2 Basis Set

A basis set is a mathematical representation of the molecular orbitals within a molecule. The basis set can be interpreted as restricting each electron to a particular region of space. The basis set is a set of atomic functions used to construct LCAO-MOs. A complete set of basis function must be used to represent spin orbitals exactly.

An infinite basis set is not computationally feasible hence a finite basis set is always used. A key computational consideration should be to keep the number of basis functions low. Larger basis set impose fewer constraints on electrons and more accurately approximate exact molecular orbitals. They require correspondingly more computational resources.

Standard basis set for electronic structure calculations use linear combination of Gaussian functions to form the orbital. Gaussian offers a wide range of predefined basis sets, which may be classified by the number and types of basis functions, that they contain. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbitals. These basis functions are themselves composed of a linear combination of Gaussian functions; such basis functions are referred to as contracted functions, and the component Gaussian functions are referred to as primitives. A basis function consisting of a single Gaussian function is termed uncontracted.

3.3 Basis Functions

Most molecular quantum-mechanical methods begin the calculation with the choice of a basis set. The use of an adequate basis set is an essential requirement for success of the calculation.

In principle, a complete set of basis functions must be used to represent spin orbitals exactly and the use of an infinite number of functions would result in Hartree-Fock energy equal to that given by the variational expression. This limiting energy is called the Hartree-Fock limit. The HF limit is not the exact ground state energy of the molecule because it still ignores effects of electron correlation. Because an infinite basis set is not computationally feasible, a finite basis set is always used, and the error due to the incompleteness of the basis set is called the basis set truncation error. The difference between the Hartree-Fock limit and computed lowest energy in an HF SCF calculation is a measure of the basis set truncation error. A key computational consideration therefore will be to keep the number of basis functions low (to minimize the number of two electron integrals to evaluate) to choose them cleverly (to minimize the computational effort for the evaluation of each integral) but nevertheless achieve a small basis set truncation error [20].

In principle, the atomic orbitals can be chosen to be hydrogen like wave functions, or even Hartree-Fock orbitals, for the atoms. However, neither of these is often used, as their complicated functional form (with lots of nodes near the nucleus for high n and small l functions) makes them cumbersome for evaluating integrals.

3.4 Different Basis Sets

3.4.1 Minimal Basis Set

Minimal basis set contain minimum number of basis functions needed for each atom. It is a representation that contains just the number of functions that are required to accommodate all the filled orbitals in each atom. For example,

H:1S

C:1S,2S,2P_x,2P_y,2P_z

Minimal basis set use fixed size atomic type orbitals. The STO-3G is a minimal basis set; (although it is not the smallest possible basis set). It uses three Gaussian primitives per basis function, which accounts for the 3G in its name. "STO" stands for "Slater type orbitals" and the STO-3G basis set results in wave function

and energies that are not very close to the Hartree-Fock limit. To construct the primitive and the contracted Gaussians a set of basis functions is chosen and an atomic SCF calculation is performed resulting in an optimized set of exponent for the basis functions, which can then be used in molecular structure calculations. This simplest type of basis set is a minimal basis set in which one function is used to represent each of the orbitals of elementary valence theory. A minimal basis set is a representation that strictly speaking, contains just the number of functions that are required to accommodate all the filled orbitals in each atom. A minimal set normally includes all the atomic orbitals in the shell. A minimal basis set would indicate one function each for H and He (for the 1s orbital); five basis function each for Li to Ne (for the 1s,2s and three 2p orbitals) nine functions each for Na to Ar and so on. For instance a minimal basis set for H₂O consists of seven functions and includes two basis functions to represent the two hydrogen 1s orbitals and one basis function each for the 1s,2s,2p_x,2p_y and 2p_z orbitals of oxygen. A calculation with such a minimal basis set results in wave functions and energies that are not very close to the HF limits. Accurate calculations need more extensive basis sets.

One approach to the construction of a contracted Gaussian set is to make a least squares fit of N primitive Gaussians to a set of STOs that have been optimized in atomic SCF calculation. For example, an atomic SCF calculation is performed on C using STOs to find the contracted Gaussians best representing the 1s,2s,2p STOs and then contracted Gaussians are used in a subsequent SCF calculation on methane. The expansion of an STO in N=3 giving a set of contracted Gaussians referred to as STO-3G.

It is found that at least three Gaussian functions are required to properly represent each STO and the STO-3G basis set is the absolute minimum that should be used in an ab-initio MO calculations. In fact there is often little difference between the results obtained with the STO-3G basis set and the large minimal basis sets with more Gaussian functions, although for hydrogen bonded complexes STO-4G can perform significantly better. The STO-3G basis set does perform remarkably well in predicting molecular geometries though this is due in part to fortuitous cancellations errors. Of course the computational effort increases the number of functions in the Gaussian expansions.

The minimal basis set are well known to have several deficiencies. These are particular problems with compounds containing atoms at the end of a period such as oxygen or fluorine. Such atoms are described using the same number of basis functions as the atoms at the beginning of the period, despite the fact that they have more electrons. A minimal basis set only contains one contraction per atomic orbital and as the radial exponents are not allowed to vary during the calculations the functions can not expand or contract in size in accordance with the molecular environment. The third drawback is that a minimal basis set can not describe non-spherical aspect of the electronic distribution[21]. For example, for a second row element such as carbon, the only functions that incorporate any anisotropy are the 2p_x, 2p_y and 2p_z functions. As the radial components of these functions are required to be the same, no one component (x, y or z) can differ from another.

3.4.2 Double Zeta Basis Set

The problems with minimal basis sets can be addressed if more than one function is used for each orbital. A basis set which doubles the number of functions in the minimal basis set is described as a double zeta basis (DZ) ie, basis set generated from a sum of two STO with different orbital exponents. A DZ basis set for H₂O consist of fourteen functions. Thus a linear combination of a contracted function and a diffuse function gives an overall result that is intermediate between the two. The basis set coefficients of the contracted and the diffuse functions are automatically calculated by the SCF procedure which thus automatically determines whether a more contracted or a more diffuse representation of that particular orbital is required. Such an approach can provide a solution to the anisotropy problem because it is then possible to have different linear combinations for the p_x, p_y and p_z orbitals. In a triple zeta basis set (TZ), three basis functions are used to represent each of the orbitals encountered in elementary valence theory.

3.4.3 Split Valence Basis Set

The first way that a basis set can be made larger is to increase the number of basis functions per atom. Split valence basis sets such as 3-21G and 6-31G, have two sizes of functions for each valence orbital. For example, Hydrogen and Carbon are represented as H:1S, 1S' C:1S, 2S, 2S' 2P_x, 2P_y, 2P_z, 2P_x', 2P_y', 2P_z' Where primed and unprimed orbitals differ in size.

The Double Zeta basis set, form all molecular orbitals from linear combinations of two sizes of functions for each atomic orbital. Similarly triple set valence basis sets like 6-311G, use three sizes of contracted functions for each orbitals.

An alternative to the DZ basis approach is to double the number of functions used to describe the valence electrons, but to keep a single function for the inner shells. The rationale for this approach is that the core orbitals unlike the valence orbitals do not affect chemical property very much and vary only slightly from one molecule to another. Such a basis set that describes the inner shell electrons by a single Slater orbitals and

the valence shell electrons by a sum of Slater orbitals are commonly referred to as split valence basis set (SV) [22, 23, 6, 24]. It is a compromise between the inadequacy of a minimal basis set and the computational demands of DZ and TZ basis sets. The notation used for SVDZ basis sets is exemplified by 3-21G. In this basis set three Gaussian functions are used to describe the core orbitals. The valence electrons are also represented by three Gaussians, the contracted part by two Gaussians and the diffuse part by one Gaussian. The most commonly used SV basis set are 3-21G, 4-31G and 6-31G. For example, an atomic SCF calculation on carbon using contracted Gaussians, there is one contracted function representing 1s orbital, two representing the 2s orbital and two each for the three 2p orbitals.

3.4.4 Polarized Basis Sets

Split valence basis sets allow orbitals to change size, but not to change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example, polarized basis sets add d functions to carbon atoms and f functions to transition metals and some of them add p functions to the hydrogen atoms.

Examples; 6-31G(d); It is 6-31G basis set with d functions added to heavy atoms. This basis set is also known as 6-31G*. Another popular polarized basis set is 6-31G(d, p) also known as 6-31G**, which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms. Another improvement to STO-nG basis sets involves using polarization functions [21]. These are also Gaussians, but the orbital angular momentum l is one (or more) larger than is appropriate for the orbital being described. Thus in describing a 2p orbital on an atom, a polarization function would have 3d character. The purpose of a polarization function is to describe distortion of the orbital by the other atomic centres away from what would be expected for a spherically symmetric atomic environment. In using Gaussian orbitals, it is typical to denote basis sets that allow for polarization functions using an asterisk (*), so a split-valence-plus-polarization basis might be 6-31G* (if a polarization function is to be added to atoms other than hydrogen) or 6-31G** (if polarization functions are to be added for hydrogen as well) [6, 24]. A more explicit notation that differentiates between the orbital angular momentum used for hydrogen atoms with that for heavier atoms is 6-31G(kp,ld), where k and l are integers that indicate the number of (for hydrogen) and d (for other atoms) polarization functions included in this basis.

3.4.5 Diffuse Functions

Diffuse functions are large size versions of S and P type functions. They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for electrons are relatively far from nucleus, molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, descriptions of absolute acidities and so on.

The 6-31+G(d) basis set is the 6-31G(d) basis set with diffuse functions added to heavy atoms. The double plus version 6-31++G(d) adds diffuse functions to hydrogen atoms as well. Diffuse functions on hydrogen atom seldom makes a significant difference in accuracy [6, 24].

3.4.6 High Angular Momentum Basis Sets

Even larger basis sets are now used. Such basis sets add multiple polarization functions per atom to the triple zeta basis set. For example, the 6-31G(2d) basis sets adds two d functions per heavy atom instead of just one, while the 6-311++G(3df,3pd) basis set contains three sets of valence region functions, diffuse functions on both heavy atoms and hydrogen and multiple polarization functions; three d functions and one f function on heavy atoms and three p functions and one d function on hydrogen atoms. Such basis sets are useful for describing the interactions; between electrons in electron correlation methods; they are not generally needed for Hartree-Fock calculations.

Some large basis sets specify different sets of polarization functions for heavy atoms depending upon the row of periodic table in which they are located. For example, the 6-311+(3df,2df,p) basis set places three d functions and one f function on heavy atoms in the second and higher rows of the periodic table, and it places two d functions and one f function on first row heavy atoms and one p function on hydrogen atoms.

3.4.7 Basis Sets For Post-Third Row

Basis sets for atoms beyond the third row of periodic table are handled somewhat differently. For these very large nuclei, electrons near the nucleus are in an approximate way, via effective core potentials. This treatment includes some relativistic effects, which are important in these atoms. The large basis sets and LANL2DZ basis sets are the best known of these [25]

3.5 Methods

The Gaussian program contains a hierarchy of procedures corresponding to different approximation methods. The ones we will be concerned with most often in this work are listed below:

Hartree-Fock Self Consistent-HF

Second order Moller-Plesset Perturbation Theory-MP₂

Quadric CI-QCISD (T)

More accurate methods become correspondingly more expensive computationally.

3.6 Selection Of Appropriate Theoretical Method

3.6.1 Hartree – Fock Method

Hartree – Fock method provides a reasonable model for a wide range of problems and molecular systems. However Hartree – Fock theory also has limitations. They arise principally from the fact that Hartree – Fock theory does not include a full treatment of the effects of electron correlation. The energy contributions arising from electrons interacting with one another. For systems and situations where such effects are important, Hartree-Fock results may not be satisfactory.

A variety of theoretical methods have been developed which include some effects of electron correlation. Such methods are referred to as post-SCF methods because they add correlation corrections to the basis Hartree-Fock model. Hartree-Fock theory is very useful for providing initial, first level predictions for many systems. It is also reasonably good at computing the structures and vibrational frequencies of stable molecules and some transition states.

3.6.2 The MP_n Methods

The MP₂ method was one of the least expensive ways to improve on Hartree-Fock and it was thus often the first correlation method to be applied to new problems. MP₂ geometries are usually quite accurate. In general, the more unusual the electronic structure a system has, the higher level of theory that will be needed to model it accurately [25, 6, 24, 26]. Higher level MP orders are available for cases where the second order solution of MP₂ is inadequate.

3.7 Reaction Field Models Of Solvation

One family of models for systems in non- aqueous solution are referred to as self consistent reaction field (SCRf) methods. These methods all model the as a continuum of uniform dielectric constant. The solute is placed into a cavity within the solvent [28]. SCRf approaches differ in how they define the cavity and reaction field. The simplest SCRf model is the Onsager reaction field model [29]. In this method, the solute occupies a fixed spherical cavity of radius within the solvent field. A dipole in the molecule will induce a dipole in the medium, and the electric field applied by the solvent dipole will in turn interact with the molecular dipole, leading to net stabilization.

The influence of solvents on the rates of reactions was discovered by Berthelot & Gilles. Let us examine the influence of solvents on the following 3 reactions.

1. (C₂H₅)₃N + C₂H₅I → (C₂H₅)₄N⁺ I⁻
2. N₂O₅ → N₂O₃ + O₂
3. (CH₃CO)₂O + C₂H₅OH → CH₃COOC₂H₅ + CH₃COOH

The rate constant for the 1st reaction varied from 0.00018 in hexane to 0.133 in benzyl alcohol and 70.1 in nitrobenzene. The rate constant of the 2nd reaction was more or less the same in different solvents while the influence of solvents on the rate constant of the 3rd reaction was almost the reverse of the 1st reaction.

Solvents influence the reaction rates in 3 different manners.

Polarity of solvent: If the reaction is one in which the products are more polar than the reactants then a polar solvent accelerates the reaction. In reaction (1) the product being a salt is more polar than the reactants which are comparatively less polar. So the reaction is accelerated in the presence of polar solvents like benzyl alcohol. On the other hand if the reactants are more polar than the products like reaction (3), a polar solvent decreases the reaction rate. In general a polar solvent hastens the reaction in the direction of increasing polarity. When both reactants and products are non polar, polarity of solvents will have no influence on the rate of the reaction and the rate is independent of the nature of the solvent which is what happened in reaction (2).

Influence of solvation: If either the reactant or the product or the activated complex interacts with the solvent, there may be considerable influence on the rate of the reaction. When the reactants interact with the solvent and are solvated leading to lowering the potential energy of the reactants then the activation energy increases lowering the reaction rate. On the other hand if the activated complex interacts with the solvent and is solvated lowering the potential energy, the activation energy decreases and the rate of the reaction increases. If both the activated complex as well as reactants is solvated, the influence of solvent on the rate may not be considerable. The influence of solvation of products will not have any influence on the rate unless it is a reversible reaction.

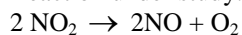
Dielectric constant of the solvent: The work done in bringing 2 charges q₁ & q₂ from infinity to r is given by, $W = q_1 \cdot q_2 / D r$ where D is the dielectric constant of the medium and r is the distance between the charges. So in the case of ionic reactions taking place in the presence of solvents, the dielectric constant of the solvent plays a major role. The more the value of D, the more is the ionization. This work is equal to the electrostatic

contribution to the increase of Gibb's free energy from the initial to the transition state. If the signs on the charges are same, then work done is positive; if they are different, then it is negative. The logarithm of the rate constant of an ionic reaction varies inversely with the dielectric constant at a given temperature.

IV. Experimental Methods

4.1 Introduction

Reaction under study:



This study requires the following calculations:

1. Optimization of reactant, NO_2
2. Optimization of products, NO and O_2
3. Finding the transition state for the reaction
4. The change in molecular parameters with change in basis sets and methods
5. Finding the activation energy for the reaction
6. Finding the effect solvent on energy barrier

4.2 Optimization of reactant and products

The Opt keyword in the route section request optimization, using different basis sets. In Gaussian, the molecule specification for a geometry optimization can be given in any format desired. This study requires geometry optimization of reactants, products and transition structure.

4.3 Finding the transition state for the reaction

The Freq keyword in the route section requests a frequency job, using the basis set. The frequency calculations are valid only at the stationary points on the potential energy surface. Thus frequency calculations should be performed on optimized structures. So it is necessary to run a geometry optimization prior to doing a frequency calculation. Frequencies computed with a different basis set or procedures have no validity. Geometry optimization converge to a structure on the potential energy surface where the forces on the system are essentially zero. The final structure may correspond to a minimum on the potential energy surface, or it may represent a saddle point. Ordinary transition state structures are characterized by one imaginary frequency since they are first order saddle points.

4.4 The change in molecular parameters with change in basis sets and methods

The experimental bond lengths for NO_2 , NO AND O_2 are 1.19\AA , 1.15\AA and 1.21\AA respectively. The experimental bond angle for NO_2 is 134.3° . First we optimized the structure of reactant products using different basis sets. Determine the basis set required to predict the above structure accurately. Perform the optimizations at the HF, MP_2 and MP_3 level of theory. From this also find the method required to predict the structure accurately.

4.5 Finding the activation energy for the reaction

Since we have verified that the transition structure connects the reactant and products, we can now compute the activation energy for the reaction. Predict the energy of reactant and transition structure in different solvent using Onsager model. For Onsager model calculations, the energy in solution marked as total energy in the output. This value is the same as that given in the regular SCF output for HF calculations. The difference in energies between transition structure and reactant gives the activation energy.

4.6 Finding the effect solvent on energy barrier

Predict the energy difference between the transition structure and reactant for the reaction, $2 \text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ in different solvent. The experimental activation energy for the above reaction is 111.0 KJ/Mol . The predicted activation energy for different media is given in the table 10. This table indicates that the activation energy is decreases in more polar solvent.

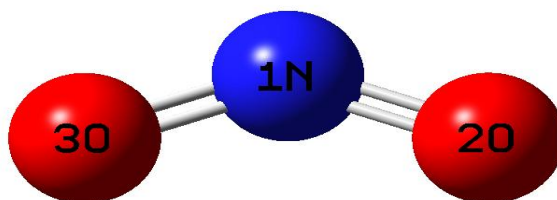
INPUT DATA – REACTANT USING DIFFERENT BASIS SET DOUBLE SPLIT VALENCE BASIS SET – 3-21G

#T UHF/3-21G Opt Freq Test

NITROGEN DIOXIDE

0,2

N
O 1 1.19
O 1 1.19 2 134.3



POLARISATION FUNCTION – 6-31G(d)

#T UHF/6-31G(d) Opt Freq Test

NITROGEN DIOXIDE

0,2
N
O 1 1.19
O 1 1.19 2 134.3

INPUT DATA – REACTANT USING DIFFERENT METHODS

HF – METHOD

#T UHF/6-31G(d,p) Opt Freq Test

NITROGEN DIOXIDE

0,2
N
O 1 1.19
O 1 1.19 2 134.3

MP2 METHOD

#T UMP2/6-31G(d,p) Opt Freq Test

NITROGEN DIOXIDE

0,2
N
O 1 1.19
O 1 1.19 2 134.3

MP3 METHOD

#T UMP3/6-31G(d,p) Opt Freq Test

NITROGEN DIOXIDE

0,2

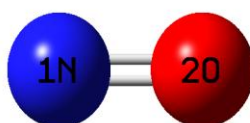
N

O 1 1.19

O 1 1.19 2 134.3

INPUT DATA – PRODUCTS

NITROGENMONOXIDE



#T UHF/6-311+G(d,p) Opt Freq Test

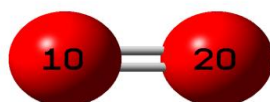
NITROGEN MONOXIDE

0,2

N

O 1 1.15

OXYGEN



#T RHF/6-311+G(d,p) Opt Freq Test

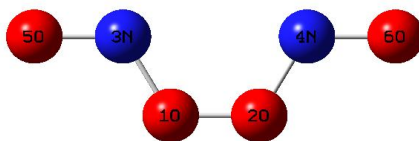
OXYGEN

0,1

O

O 1 1.

INPUT DATA – TRANSITION STATE



#T RHF/6-311+G(d,p) Opt Freq Test

TS RN

0,1

O

O 1 ROO

N 1 RON 2 AON

N 2 RON 1 AON 3 0.0

O 3 RNO 1 AONO 2 180.0

O 4 RNO 2 AONO 1 180.0

ROO=1.3

RON=1.4

AON=120.0

RNO=1.3

AONO=120.0

INPUT DATA FOR FINDING ENERGY IN SAME MODEL FOR DIFFERENT SOLVENT

*ACETONITRILE-ONSAGER MODEL

#T UMP2/6-31+G(D) Test SCRF=Dipole

NITROGEN DIOXIDE ACETONITRILE

0,2

N

O 1 1.19

O 1 1.19 2 134.3

3.02 35.9

*CYCLOHEXANE-ONSAGER MODEL

#T RMP2/6-31+G(D) Test SCRF=Dipole

NITROGEN DIOXIDE CYCLO HEXANE

0,1

N

O 1 1.19
O 1 1.19 2 134.3

3.02 2.0

V. Results And Discussions

Informations obtained from the output data are the following.

COMPARISON OF BOND LENGTH (A⁰) IN NO₂ MOLECULE USING VARIOUS MODEL CHEMISTRIES

Experimental bond length=1.19 A⁰

TABLE:1

BASIS SET	HF	MP2	MP3
STO-3G	1.2842	1.2980	1.2480
3-21G	1.2374	1.2713	1.2041
6-31G(d)	1.1945	1.2169	1.1643
6-311G(d,p)	1.1945	1.2169	1.6435
6-311+G(d,p)	1.1800	1.2029	1.1559
6-311+G(2d,p)	1.2050	1.2056	1.1565

COMPARISON OF BOND ANGLE (°) IN NO₂ MOLECULE USING VARIOUS MODEL CHEMISTRIES

Experimental bond angle=134.3°

TABLE:2

BASIS SET	HF	MP2	MP3
STO-3G	127.4878	129.0615	130.2162
3-21G	134.235	133.6181	136.2713
6-31G(d)	134.2950	133.7109	136.0447
6-311G(d,p)	134.2950	133.7109	136.0447
6-311+G(d,p)	134.6052	133.9456	136.3873
6-311+G(2d,p)	133.8598	133.9859	136.3947

COMPARISON OF BOND LENGTH (A⁰) IN NO MOLECULE USING VARIOUS MODEL CHEMISTRIES

Experimental bond length=1.15 A⁰

TABLE: 3

BASIS SET	HF	MP2	MP3
3-21G	1.131	1.131	1.20
6-31G(d)	1.146	1.1416	1.127
6-311G(d,p)	1.146	1.1416	1.127
6-311+G(d,p)	1.1307	1.1345	1.177
6-311+G(2d,p)	1.132	1.1370	1.168

COMPARISON OF BOND LENGTH (A^0) IN O_2 MOLECULE USING VARIOUS MODEL CHEMISTRIES

Experimental bond length= 1.21 A^0

TABLE: 4

BASIS SET	HF	MP2	MP3
STO-3G	1.315	1.3148	1.221
3-21G	1.313	1.486	1.241
6-31G(d)	1.213	1.274	1.165
6-311G(d,p)	1.213	1.274	1.165
6-311+G(d,p)	1.195	1.248	1.154
6-311+G(2d,p)	1.201	1.257	1.157

COMPARISON OF PROCESSING TIME IN NO_2 MOLECULE USING VARIOUS MODEL CHEMISTRIES

TABLE :5

BASIS SET	HF	MP2	MP3
STO-3G	2 seconds	4 seconds	11 seconds
3-21G	2 seconds	5 seconds	20 seconds
6-31G(d)	4 seconds	25 seconds	18 seconds
6-311G(d,p)	2 seconds	24 seconds	16 seconds
6-311+G(d,p)	9 seconds	1 minute 30 seconds	2 minute 50 seconds
6-311+G(2d,p)	38 seconds	3 minute 4 seconds	3 minute 2 seconds

COMPARISON OF PROCESSING TIME IN O₂ MOLECULE USING VARIOUS MODEL CHEMISTRIES

TABLE: 6

BASIS SET	HF	MP2	MP3
STO-3G	2 seconds	2 seconds	7 seconds
3-21G	1 seconds	3 seconds	8 seconds
6-31G(d)	5 seconds	6 seconds	13 seconds
6-311G(d,p)	3 seconds	5 seconds	12 seconds
6-311+G(d,p)	4 seconds	11 seconds	21 seconds
6-311+G(2d,p)	5 seconds	19 seconds	43 seconds

COMPARISON OF PROCESSING TIME IN NO MOLECULE USING VARIOUS MODEL CHEMISTRIES

TABLE: 7

BASIS SET	HF	MP2	MP3
3-21G	2 seconds	3 seconds	14 seconds
6-31G(d)	3 seconds	9 seconds	26 seconds
6-311G(d,p)	2 seconds	8 seconds	30 seconds
6-311+G(d,p)	5 seconds	23 seconds	60 seconds
6-311+G(2d,p)	7 seconds	46 seconds	2 minute 4 seconds

TOTAL ENERGY OF THE REACTANT (HARTREES) IN VARIOUS MEDIUM

TABLE: 8

MEDIUM	ONSAGER MODEL
GAS PHASE	-408.0711768
CYCLOHEXANE	-408.071174
ACETONITRILE	-408.0710
DMSO	-408.0710467

TOTAL ENERGY OF THE TRANSITION STATE (HARTREES) IN VARIOUS MEDIUM

TABLE: 9

MEDIUM	ONSAGER MODEL
GAS PHASE	-407.8942217
CYCLOHEXANE	-407.8942343
ACETONITRILE	-407.8942547
DMSO	-407.8942551

ENERGY BARRIER OF THE REACTION IN VARIOUS MEDIUM
EXPERIMENTAL VALUE=111.0KJ/MOI

TABLE: 10

MEDIUM	ONSAGER/HF (KJ/MOL)
GAS PHASE	111.039
CYCLOHEXANE	111.3848
ACETONITRILE	110.9076
DMSO	110.9367

COMPARISON OF RESULTS OF INVESTIGATION WITH EXPERIMENTAL RESULTS

TABLE: 13

PARAMETER	FORWARD REACTION	METHOD
ACTIVATION ENERGY(KJ/Mol)	111.039	ONSAGER/HF

Results of calculations given in the above tables. In tables 1, 2, 3 and 4 different model chemistries are compared and tested by comparing their results on the same systems to one another and to results of experiments. Here we investigated the basis set effects of model chemistry on the molecules. For NO₂, NO and O₂ 6-31G(d) /HF give accurate result. Adding an additional polarization function yields a more accurate values within less time. It does not significantly affect the results. HF method is used for all systems because these are simple molecular systems. HF provides reasonable model for a wide range of problems and molecular systems within short time. So this method is computationally inexpensive. MPn methods are used for complex systems and more time consuming that is computationally expensive.

When we consider the energy barrier of the reaction, the onsager/HF values are in pretty good agreement with the experimental data. When we consider the same reaction in different solvent, the change in energy difference produced by the solvent- then also the HF model is in the closest agreement with the experimental value. It indicates that the energy difference between TS and reactant decreases in more polar solvents. Among these solvents, acetonitrile has energy barrier less than other solvents and speed up the reaction.

VI. Conclusion

All the geometries predicted with 6-31G (d) basis set are quite accurate for the reaction $2 \text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$. Adding additional polarization function yields a more accurate structure. 6-311G (d,p) thus appears to achieve the basis set limit for this model chemistry.

Onsger/HF model does a much better job of reproducing the observed energy barrier for above reaction. The energy difference between TS and reactant decreases in more polar solvents. Among these solvents, acetonitrile has energy barrier less than other solvents and speed up the reaction.

References

- [1]. A. Hinchliffe, Computational Chemistry (Wiley, New York, 1988).
- [2]. J.B. Foresman, "Ab Initio Techniques in Chemistry: Interpretation and Visualization" Chapter 14 in What Every Chemist Should Know About Computing, Ed. M.L. Swift and T.J. Zielinski.
- [3]. James B. Foresman and Eelen Frisch, Exploring Chemistry with Electronic Structure Methods, second Ed.
- [4]. A. Szabo, N.S. Ostlund, Modern Quantum Chemistry, McGraw-Hill (1982).
- [5]. L.I. Schiff, Quantum Mechanics (McGraw-Hill, New York, 1968).
- [6]. I.N. Levine, Quantum Chemistry, 4th ed. (Prentice-Hall, Englewood Cliffs, NJ, 1991).
- [7]. Schaefer, Henry F. III (1984). Quantum Chemistry. Oxford: Clarendon Press.
- [8]. J. Simons An introduction to Theoretical Chemistry, Cambridge (2003).
- [9]. A. Szabo, N.S. Ostlund, Modern Theoretical Chemistry, McGraw-Hill (1982).
- [10]. K.I. Ramachandran, G Deepa and Krishnan Namboori. P.K. Computational Chemistry and Molecular Modeling Principles and applications.
- [11]. Richards, W.G. Walker T.E.H and Hinkley R.K. (1971). A bibliography of ab initio molecular wave functions.
- [12]. W.J. Hehre, L. Random, P.V.R. Schleyer, and J.A. Pople, Ab Initio Molecular Orbital Theory (Wiley, New York, 1986).
- [13]. Computational Chemistry, David Young, Wiley-Interscience, 2001. Appendix A. A. 2.4B pg 336, Gaussian.
- [14]. http://www.gaussian.com/g_tech/g_ur/m_citation.htm
- [15]. T. Clark A Handbook of Computational Chemistry, Wiley, New York (1985).
- [16]. J. Almlof, K. Korsell, and K.Faegri, Jr., J. Comp. Chem.3, 385 (1982).
- [17]. H.B. Schlegel, "Geometry Optimization on Potential Energy Surfaces", in Modern Electronic Structure Theory, Ed. D.R. Yarkony, 2 vols. (World Scientific Publishing: Singapore, 1994).
- [18]. C. Peng, P.Y. Ayala, H.B. Schiegel and M.J. Frisch, J Comp. Chem.17, 49 (1996).
- [19]. M. Haserand R. Ahlrichs, J. Comp. Chem. 10, 104 (1997).
- [20]. Donald A. McQuarrie, Quantum Chemistry, 2003, 9.
- [21]. Peter Atkins and Julio de Paula, Physical Chemistry, Ed. 2002, 14.
- [22]. Guy H. Grant and W. Graham Richards, Computational Chemistry.
- [23]. P.O. Sullivan, L. Forni and B.K. Hodnett, Ind. Eng. Chem. Res. 40, 1471 (2001).
- [24]. P.W. Atkins and R.S. Friedman, Molecular Quantum Chemistry (1997), 271.
- [25]. S. Sato, K. Hirose, M. Kitamura and N. Tojimatt Ishi, J. Am. Chem. Soc. (1987).
- [26]. Joseph P. Adams, J. Roy. Soc. Chem. 44, 135 (2000).
- [27]. Van Duijnen, P. Th, A.H. Juffer, J.P. Dijkman, J. Mol. Sstructure. (Theo. Chem) 260, 195 (1992).
- [28]. R.P. Frutos and D. M. Spero, Tetrahedron Lett. 39, 2475 (1998).
- [29]. Minh Tho Nguyen, G. Raspoet and L.G. Vanquickenborne, J. Am. Chem. Soc.119, 2553 (1997).

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