

THEORETICAL INVESTIGATION INTO THE CAPTURE MECHANISM OF CARBONYL SULFIDE BY ORGANIC SOLVENTS: AN AB INITIO QUANTUM CHEMICAL APPROACH

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Abstract

The efficient removal of carbonyl sulfide (COS) from industrial gas streams is critical for environmental protection and catalyst preservation. In this work, an ab initio quantum chemical approach was employed to investigate the capture mechanisms and kinetics of twenty-four organic solvent mixtures composed of guanidine bases (BTMG, TBD) or amidine bases (DBU, DBN) paired with linear alcohols (C1–C6). Computational modeling performed at the ω B97X-D3/6-311++G(d,p) level, incorporating the polarizable continuum model (PCM), successfully validated the thermodynamic and kinetic feasibility of a proposed single-step termolecular reaction mechanism. The results demonstrate excellent alignment with established benchmarks for CO₂ capture in similar systems. Among all screened formulations, the BTMG/methanol system exhibited the lowest activation energy barrier and the highest reaction rate constant, rendering it the most effective candidate for COS sequestration, followed by TBD/1-propanol. For the amidine systems, DBU performed optimally with methanol and ethanol, while DBN showed the best compatibility with 1-propanol. These first-principles insights provide a robust theoretical foundation for the rational design of highly efficient, non-aqueous solvent mixtures for acid gas separation.

Keywords: Carbonyl sulfide (COS) capture; Ab initio; ω B97X-D3; Termolecular mechanism; Guanidine and Amidine bases; Organic solvent mixtures.

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الملخص

بعد الفصل الفعال لمركب كبريتيد الكربونيل (COS) من التدفقات الغازية الصناعية أمراً بالغ الأهمية لحماية البيئة وحفظ الحوافز من التسمم. في هذا العمل، تم استخدام منهج كيميائي كمي يعتمد على المبادئ الأولية (Ab Initio) لاستقصاء آليات الاحتجاز والخصائص الحركية لأربعة وعشرين خليطاً من المذيبات العضوية المكونة من قواعد الغوانيديين (BTMG) و (TBD) أو قواعد الأميديين (DBU) و (DBN) المقترنة بكحولات خطية (C1–C6). وأثبتت النمذجة الحسابية التي أجريت عند المستوى النظري ω B97X-D3/6-311++G(d,p)، مع إدراج نموذج الاستمرار المستقطب (PCM)، الجدوى الديناميكية الحرارية والحركية لآلية تفاعل جزيئي ثلاثي مقترحة تسير في خطوة واحدة. وتُظهر النتائج اتساقاً ممتازاً مع المعايير المرجعية المعتمدة لاحتجاز ثاني أكسيد الكربون (CO₂) في أنظمة مماثلة. ومن بين جميع التركيبات المفحوصة، سجل نظام BTMG/الميثانول أدنى حاجز لطاقة التنشيط وأعلى ثابت لمعدل التفاعل، مما يجعله المرشح الأكثر كفاءة لعزل مركب COS، يليه نظام TBD/1-بروبانول. أما بالنسبة لأنظمة الأميديين، فقد قدم DBU أداءً مثالياً مع الميثانول والإيثانول، بينما أظهر DBN التوافق الأفضل مع 1-بروبانول. توفر هذه الرؤى المستمدة من المبادئ الأولية أساساً نظرياً راسخاً للتصميم العقلاني لمخاليط المذيبات غير المائية عالية الكفاءة لفصل الغازات الحمضية.

الكلمات المفتاحية: احتجاز كبريتيد الكربونيل (COS)؛ المبادئ الأولية؛ B97X-D3؛ الآلية الجزيئية الثلاثية؛ قواعد الغوانيديين والأميديين؛ مخاليط المذيبات العضوية.

1. Introduction

In recent years, the mitigation of volatile sulfur compounds has emerged as a critical objective in environmental engineering and industrial gas purification. Among these contaminants, carbonyl sulfide (COS) represents a highly pervasive and hazardous pollutant found in natural gas, synthesis gas (syngas), coal gasification streams, and refinery gases. Unlike carbon dioxide (CO₂), COS is chemically more stable and less reactive, posing unique challenges for industrial gas sweetening processes. Furthermore, the release of COS into the atmosphere contributes significantly to the formation of stratospheric sulfate aerosols, which catalyze ozone depletion and exacerbate global climate change. Consequently, the efficient capture and removal of COS before fuel utilization or atmospheric release are imperative for both equipment protection preventing catalyst poisoning in downstream processes and environmental sustainability. Industrial technologies for COS removal typically rely on chemical absorption, physical scrubbing, or catalytic hydrolysis. While aqueous amine solutions (such as monoethanolamine, MEA) are widely used for acid gas capture, they often suffer from notable drawbacks when applied to COS, including irreversible solvent degradation, high energy penalties during thermal regeneration, and severe equipment corrosion. To overcome these limitations, research has shifted toward exploring alternative organic solvents, such as specialized alkanolamines, ionic liquids (ILs), and deep eutectic solvents (DESs). These organic frameworks offer highly tunable physical properties, lower vapor pressures, and enhanced thermal stabilities, making them promising candidates for efficient and sustainable COS sequestration.

Natural gas has grown in importance in the global energy matrix during the previous few decades, and its importance has been steadily increasing over time. The reason for this rise is that natural gas has gradually replaced coal and fuel oil as a more convenient and environmentally friendly alternative. Regardless, gas processing technologies play a part in its development since they can help with the extraction of inaccessible deposits [1]. Most gas fields contain considerable amounts of acid, carbon dioxide (CO₂), and sulfur compounds, such as hydrogen sulfide (H₂S) gas. It is true that sulfur compounds sour the gas, and if H₂S concentrations in natural gas exceed 5.7 mg/m³, it is difficult to use [2]. There are some procedures that have been utilized in the removal of H₂S and other acid gases. A process such as this is what is known as a "sweetening process". This is because this process aids in the process of removing the acid gas. In recent decades, acid gas treatment has grown in popularity. Since the implementation of increasingly rigorous environmental rules, the efficiency of acid gas removal (CO₂ and H₂S) has greatly increased; thus, greater research work in this field is required. Because much recent research has concentrated on CO₂ and H₂S removal, specialists have paid little attention to the removal of less reactive sulfur compounds such as carbon disulfide (CS₂), mercaptans, and carbonyl sulfide (COS), despite the fact that they are also present in several industrial gases. Normally, environmental specifications are stated in terms of total sulfur content rather than merely H₂S; however, eliminating other sulfur compounds is equally critical [3, 4]. Such sulfuric compounds are very toxic; hence, they can poison catalysts and they are extremely detrimental to industrial equipment and pipelines [3, 5]. To comply with environmental pollution prevention requirements, it is necessary that these contaminants in the gas streams, which were mentioned previously above, are removed and then handled in an environmentally appropriate manner. Reactive absorption, which frequently employs

alkanolamines as absorbents, is likely the most commonly chosen technology that is used in the removal of acid gas in gas processing operations [5–7].

Purpose of the Study, the present thesis focused on achieving the following goals: Understanding the process of removing COS using organic solvent mixtures. As well as, investigating and revealing kinetics of the reaction when COS absorption takes place in an organic solvent mixture. Finding an effective organic solvent to remove COS. Where, the aims of this study included investigating the COS absorption and its reaction kinetics in organic liquids [COS-binding organic liquids (COS-BOLs. To achieve these aims, specific objectives were set: Conducting a performance evaluation of a one-step reaction with the aim of obtaining reaction rate constants for the reaction that occurs between amidine or guanidine organic bases, which, in this research, comprised 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), 1,5-diazabicyclo [4.3.0]-non-5-ene (DBN), and 2-tert-butyl-1,1,3,3-tetramethylguanidine (BTMG), 1, 5, 7-triazabicyclo [4.4.0] dec-5-ene (TBD) and COS in the presence of linear alcohols.

2. Quantum Mechanics

Quantum mechanics calculations are used for clarifying the reaction mechanism, and highlighting the processes involved in it [8-11]. This is a benefit because it allows the opportunity to calculate chemical properties with or without experimental data. Recently, quantum mechanics has improved in terms of calculations and applications pertaining to computational chemistry, and such calculations have been successfully applied to research for assessing the molecular structures, reaction mechanisms, and spectroscopic characterizations and thermodynamics of the studied systems [11]. The mathematical expression for dynamical equations for particle velocity and mass is subdivided into four regimes (Figure 1).

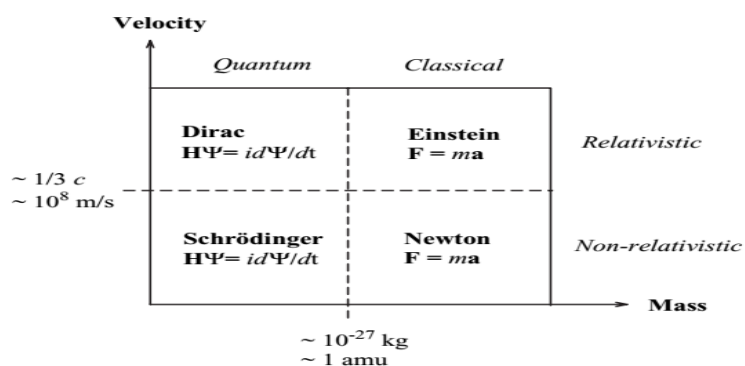


Figure 1: Domains of the dynamical equations [12].

Classical/deterministic mechanics is based on the integration of Newton's equations, which define the locations of the particles at certain times. Using this type of mechanics, it is possible to predict the location and time of solar eclipses with remarkable accuracy; however, quantum mechanics calculates both the time and location in terms of probability, and the probability function is determined by taking the square of the wave function, as shown below:

$$P(\mathbf{r}, t) = \Psi^2(\mathbf{r}, t). \quad (1)$$

Here, $\mathbf{r}$ represents the location/position, while t shows the time, and the wave function is denoted by Ψ , which is computed by solving the Schrödinger or Dirac equation (Figure 1) [12]. The electronic Schrödinger equation (time-independent) for an N -electron atomic or molecular system can be given as in the following equation:

$$H\Psi = E\Psi. \quad (2)$$

In this equation, the Hamilton operator (H) sums up the potential as well as kinetic energies, which can be termed as electronic energy. Here, H represents the Hamiltonian operator of a molecular system, which has N electrons and M nuclei. In this case, the wave function, Ψ_i , possesses all possible information regarding the i th state of the quantum system that is under study. It relies on X_M , which are the spatial coordinates of the nuclei and X_N (spatial and spin coordinates). Here, Ψ_i describes E_i , which is a numerical value of energy. Moreover, H is a differential operator as well, which shows the total energy, as shown below:

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (3)$$

In this equation, i and j denote the system electrons; A and B both run over the M nuclei; A , r , and R denote the inter-particle distances; and M_A denotes the mass of the nucleus. The Hamiltonian operator sums up all kinetic (T) and potential (V) energies.

$$H_{Schrodinger} = T + V \quad (4)$$

The Schrödinger equation shows results in the form of Eq. (1), which finds a the probability of a particle at time t and position $\mathbf{r}$. Light particles move at a mere fraction of the speed of light, and the Dirac equation is used in this case.

$$H\Psi = i \frac{\partial \Psi}{\partial t} \quad (5)$$

Here, the Hamiltonian operator is more complex.

$$H_{Dirac} = (c\alpha \cdot \mathbf{p} + \beta mc^2) + V \quad (6)$$

Both α and β exist in the form of 4×4 matrices, while the relativistic wave function is made up of 4 components that are both large and small, and each one of them has α and β spin functions that differ from the α and β matrices. Here, wave functions have two components: electronic (large components) and positronic (small components), whereas the α and β matrices couple components

such as these. When the limit $c \rightarrow \infty$, the Schrödinger equation forms when Dirac equation is reduced; hence, the wave function components are reduced into the α and β spin orbitals [12]. The physical properties of the system are described through a wave function; thus, factors (operators) are applied in quantum mechanics according to the studied physical properties. The probabilities and expectations allow a system to give a certain value/values for the physical property/properties. Both atoms and molecules have more weight when compared to electrons; hence, they basically behave like classical particles. Quantum mechanics, on the other hand, describes electrons as lighter and also mentions their particle properties [12]. A spin quantum number describes electrons, but it cannot be assigned to two electrons. Then, in the opposite spin, the MO is fixed for two electrons. Although the Schrödinger equation is accurate, it is over-complicated, that a H_2 atom is the greatest system it can analytically solve. For calculating the multi-particle system, Dirac and others conducted several approximations [13].

• Ab Initio Computation Methods

These methods require no approximation other than the one that was mathematically tested. In this context, a useful approximation for molecules is the Born-Oppenheimer approximation.

1. Born-Oppenheimer Approximation

This study theoretically deals with multi-molecular systems, which means that the wave functions for these systems are excessively complicated because the movements of the species are affected by both repulsion and attraction forces, which means that the particles are unable to travel independently [11]. It is common knowledge that nuclei move remarkably slower when compared to electrons because electrons are lighter; thus, separating electronic energies in fixed nucleic positions will be appropriate. Nucleic kinetic energy is independent of electrons, and the potential energy of electron-nuclear attraction is ignored; hence, nuclear-nuclear repulsion has constant potential energy. The term Born-Oppenheimer approximation is alternatively termed as clamped nuclei approximation because electrons move towards a fixed nuclei field; thus, H reduces into electronic Hamiltonian, H_{elec} [Eq. (4)].

$$H_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = T + V_{Ne} + V_{ee} \quad (7)$$

The Schrödinger equation is solved using H_{elec} , which has electronic energy E_{elec} and electronic wave function Ψ_{elec} .

$$H_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (8)$$

The total energy, E_{tot} , is the summation of repulsion energy and E_{elec} :

$$E_{nuc} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}},$$

2. Hartree-Fock Self-Consistent Field Method

There are some difficulties in solving and analyzing a Schrödinger equation, because defining the energy of a single electron is required, which exists in a field with all of the other electrons [13]. The HF-SCF process deals with this difficulty because it computes the energy of each electron. Initially, it estimates the total energies of the electrons, which are later used to compute the energy that exists in each electron. Then, the repetition of this recursive routine continues until convergence is assured. Correlation energy needs to be defined because it is the energy difference between the Hartree-Fock calculations and the Schrödinger equation [13]. Since the HF-SCF calculations are sufficiently accurate, and they adequately highlight the issues, they are applied in different problems. Moreover, the correlation energy is significant in defining the properties of the system [13].

3. Electron Correlation Methods

The HF-SCF process has a major deficiency, in which it assumes that every electron is under the average effect of the energy for the movement; hence, finding the particular position of a specific electron is not dependent on the other electrons' positions. In quantum chemical calculations, electron correlation can be handled using multiple approaches, of which the density functional theory (DFT) and Møller-Plesset perturbation theory are very important. DFT is explained in detail in the next section because it is applied in this research.

• Density Functional Theory

For the sake of simplicity and ease in processes, rather than working on wave functions, it is possible to work on physical observables to determine energy; moreover, this possibility existed in classical mechanics as well. Studying the Hamiltonian operator is sufficient to find the physical observable because it is dependent on both the nuclei's atomic number and its position ($\mathbf{r}$). On the other hand, the Hamiltonian operator depends on the total number of electrons, which makes it a useful choice for physical observation because it aids in computing the electron density (ρ) [11].

Electron Density

The given electronic system has a specific electron density, $\rho(\mathbf{r})$, in the given state. Its formula in terms of wave function is given below: The local maxima, in terms of electron density, is according to the positions of the nuclei; hence, the Hamiltonian operator can be defined by the atomic number. The density shows this information because the maximum electron density ($\mathbf{r}_A$) is the location of each nucleus (A). Here, r_A is the radial distance from A, $\bar{\rho}$ represents the spherically-averaged density, and Z_A is the atomic number of A. The DFT of the electronic structure allows for replacing the complex N -

$$N = \int \rho(\mathbf{r}) d\mathbf{r}. \quad (9)$$

$$\left. \frac{\partial \bar{\rho}(r_A)}{\partial r_A} \right|_{r_A=0} = -2Z_A \rho(\mathbf{r}_A) \quad (10)$$

First Hohenberg-Kohn Theorem: Proof of Existence

For N -electron system, Hohenberg and Kohn reported that the Hamiltonian operator can be completely fixed by the external potential (V_{ext}); hence, all of the ground state density $\rho(\mathbf{r})$ properties can be determined using N and the V_{ext} . In this case, the Hamiltonian operator is determined through $\rho(\mathbf{r})$. Moreover, the density integration shows a specific number of electrons, and the remainder of the process involves defining an operator to determine the V_{ext} in terms of the positions and charges of the nucle. In this case, ρ shows V_{ext} , and it is assumed that the V_{ext} s (V_a and V_b) are consistent and have a similar ground state density (ρ_0). In this case, the ground state wave functions are Ψ_a and Ψ_b , and H_a and H_b belong to them. The wave functions correspond to E_{0a} and E_{0b} , given that $E_{0a} \neq E_{0b}$. The only difference between H_a and H_b is the V_{ext} , so $H_a = T + V_{ee} + V_a$ and $H_b = T + V_{ee} + V_b$. With Hamiltonian operators H_a and H_b , V_a and V_b appear, while every Hamiltonian operator associates with the ground state Ψ_0 . It is further associated with the ground state E_0 . H_a is the expected value through Ψ_b , but it should be more than E_a , as given below:

$$E_{0a} < \langle \Psi_{0b} | H_a | \Psi_{0b} \rangle. \quad (11)$$

Rewriting this expression:

$$\begin{aligned} E_{0a} &< \langle \Psi_{0b} | H_a - H_b + H_b | \Psi_{0b} \rangle \\ &< \langle \Psi_{0b} | H_a - H_b | \Psi_{0b} \rangle + \langle \Psi_{0b} | H_b | \Psi_{0b} \rangle \\ &< \langle \Psi_{0b} | V_a - V_b | \Psi_{0b} \rangle + E_{0b}. \end{aligned} \quad (12)$$

If the system-independent parts in a Hohenberg-Kohn (HK) function, $F_{HK}(\rho_0)$, are combined:

$$E_0(\rho_0) = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + F_{HK}(\rho_0). \quad (13)$$

However, it is important to understand if the density that has been defined is in actuality the density of the ground state that is required.

Second Hohenberg-Kohn Theorem: Variational Principle

In this theorem, at the ground state, the functional $F_{HK}(\rho_0)$ drives the system energy, and it also drives the least energy when there is real ground state density ρ_0 . The variational principle can be written in the following form: The trial density $\tilde{\rho}(\mathbf{r})$ has its specific H and $\tilde{\Psi}$. Now, this wave function is taken as Ψ_{trial} . The true V_{ext} generates H . The desired results are achieved from the equation below:

$$E_0 \leq E(\tilde{\rho}) = T(\tilde{\rho}) + E_{Ne}(\tilde{\rho}) + E_{ee}(\tilde{\rho}). \quad (14)$$

$$\langle \tilde{\Psi} | \tilde{H} | \tilde{\Psi} \rangle = T(\tilde{\rho}) V_{ee}(\tilde{\rho}) + \int \tilde{\rho}(\mathbf{r}) V_{ext} d\mathbf{r} = E(\tilde{\rho}) \geq E_0(\rho_0) = \langle \Psi_0 | H | \Psi_0 \rangle. \quad (15)$$

The Kohn-Sham Approach

Kohn and Sham (KS), used the HF theory to bring the HK theorems into reality, and performed its calculations. It is necessary to develop the required imaginary system for N non-interacting electrons with the density of a real system. This system has a ground state wave function Ψ_0 that has been expressed through a single-slater determinant. This slater determinant is formed by the KS orbital (ϕ KS) to solve N single-particle equations. The ϕ KS variations determine the energy and density of the ground state on the basis of the variational principle. The single-electron KS operator is given below:

$$h_i^{KS} = -\frac{1}{2} \nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{xc} \quad (16)$$

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho}. \quad (17)$$

Here, E_{xc} is the V_{xc} expectation value and V_{xc} is a single-electron operator. The KS-energy contribution comes from the exchange correlation energy (E_{xc}), which includes the kinetic energy corrections, which emerge because of electron-electron repulsions, while the interaction correlations need corrections.

3. RESULTS AND DISCUSSION

An Ab Initio Quantum Chemical Approach to COS Capture by Organic Base Alcohol Systems

1. Computational approach and reaction systems

The quantum-chemical investigation examined the mechanism and energetic feasibility of carbonyl sulfide (COS) capture by combinations of organic bases and linear alcohols. Four nitrogen-containing organic bases were considered: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 2-tert-butyl-1,1,3,3-tetramethylguanidine (BTMG), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). These bases were investigated in combination with six linear alcohols: methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. The reactant, transition-state, and product geometries were level of theory. The computational treatment incorporated empirical dispersion corrections and implicit solvent effects, allowing the investigation to account for noncovalent interactions and the influence of the surrounding medium on the optimized structures and reaction energetics. The analysis focused on three complementary aspects of the COS-capture process: geometrical changes along the reaction pathway, redistribution of electronic charge, and the thermodynamic and kinetic characteristics of the resulting reactions. Examining these properties together provides a molecular-level basis for comparing the performance of the different base-alcohol combinations and identifying systems that combine favorable reaction energetics with relatively low activation barriers.

2. Geometrical changes and the proposed reaction mechanism

The optimized geometries provide evidence for a concerted reaction pathway involving simultaneous interactions among COS, the organic base, and the alcohol. The proposed mechanism involves proton transfer from the hydroxyl group of the alcohol to a nitrogen atom of the base, accompanied by the formation of a new covalent bond between the alcohol-derived oxygen atom and the carbon atom of COS. The resulting products are represented as a protonated organic base and an alkyl thiocarbonate anion. The changes in the O–H and N–H bond distances provide direct structural evidence for the proton-transfer process. In the COS/BTMG/methanol system, for example, the calculated H31–O26 distance increases from 0.990 Å in the reactant complex to 1.090 Å in the transition-state structure and 1.927 Å in the product. This progressive elongation indicates weakening and eventual cleavage of the original alcohol O–H bond. Simultaneously, the H31–N1 distance decreases from 1.801 Å in the reactant to 1.438 Å in the transition state and 1.018 Å in the product, consistent with the formation of a new N–H bond.

A similar pattern is observed for the other investigated base–alcohol combinations. In the optimized product structures, the H31–N1 distance is generally close to 1.02 Å, indicating the formation of a covalent bond between the transferred proton and the nitrogen center. These changes support the proposed conversion of the initially neutral base–alcohol assembly into an ion-pair product following COS incorporation. The structural evolution of the COS molecule provides further evidence of chemical transformation. Isolated COS is approximately linear, with an O–C–S bond angle close to 180°. During the reaction, this angle decreases substantially as the molecule interacts with the alcohol-derived oxygen atom. For the COS/BTMG/methanol system, the O27–C25–S28 angle decreases from 177.694° in the reactant to 149.821° in the transition state and 128.209° in the product. This pronounced bending is consistent with a change in the bonding environment around the COS carbon atom. The C25–O26 distance shows an even more direct indication of bond formation. In the COS/BTMG/methanol system, this distance decreases from 2.987 Å in the reactant to 1.902 Å in the transition state and 1.379 Å in the product. The substantial reduction in the carbon–oxygen separation supports the formation of a new covalent bond between COS and the deprotonated alcohol. Comparable structural changes occur in the other systems, although the extent of bending and the initial separation of the interacting atoms vary with the base–alcohol combination. Changes in the internal COS bond lengths also accompany the reaction. For the COS/BTMG/methanol system, the C25–O27 bond length increases from 1.152 Å in the reactant to 1.219 Å in the product, while the C25–S28 bond length increases from 1.563 to 1.726 Å. These changes indicate that COS incorporation alters the bonding environment of both the oxygen and sulfur atoms as the new carbon–oxygen bond develops. The structural analysis therefore supports a coordinated process involving O–H bond cleavage, N–H bond formation, COS bending, and formation of a new C–O bond. Taken together, these observations are consistent with the proposed single-step termolecular mechanism. Nevertheless, the geometrical evidence alone should be interpreted as support for the proposed pathway; definitive confirmation of a concerted mechanism normally requires appropriate transition-state characterization, including vibrational analysis and verification that the transition state connects the intended reactant and product structures.

3. Electronic charge distribution and product stabilization

The electronic structure analysis provides complementary evidence for the proposed COS-capture mechanism. Mulliken population analysis, Hirshfeld analysis, and natural population

analysis (NPA) were used to examine changes in the partial charges of the atoms directly involved in the reaction. Particular attention was given to the COS carbon atom (C25), the alcohol-derived oxygen atom (O26), the COS oxygen atom (O27), the sulfur atom (S28), the transferred hydrogen atom (H31), and the nitrogen atom (N1) of the organic base. The results indicate substantial electronic redistribution during COS capture. In the reactant complexes, the alcohol oxygen participates in the O–H bond, while the COS carbon remains separated from this oxygen by a relatively long distance. As the reaction proceeds, proton transfer changes the electronic environment of the alcohol-derived oxygen, while the formation of the C25–O26 bond modifies the charge distribution across the COS-derived fragment.

The Hirshfeld charges illustrate these changes. For the COS/BTMG/methanol system, the charge on O26 changes from $-0.292e$ in the reactant to $-0.125e$ in the product. A similar trend is observed for the COS/DBU/methanol system, where the corresponding value changes from $-0.317e$ to $-0.139e$. These changes are consistent with the altered bonding environment associated with proton transfer and COS incorporation. The COS oxygen and sulfur atoms also exhibit notable charge changes. For COS/BTMG/methanol, the Hirshfeld charge on O27 becomes more negative, changing from $-0.137e$ in the reactant to $-0.383e$ in the product. The sulfur atom likewise changes from $-0.046e$ to $-0.537e$. These results demonstrate that the reaction affects the electronic distribution across the COS-derived product rather than being limited to the formation of a single new bond. The calculated charge on C25 also changes during the reaction. In the COS/BTMG/methanol system, the Hirshfeld value decreases from $+0.216e$ to $+0.147e$. This reduction is consistent with the change in the carbon atom's bonding environment as the alcohol-derived oxygen becomes covalently attached. The associated changes in the C–O and C–S bond lengths further support the conclusion that COS undergoes substantial electronic and structural reorganization during capture. At the product-fragment level, the calculations identify protonated-base and alkyl thiocarbonate species. For the four methanol-based systems, the reported Hirshfeld charges of the protonated bases are $+0.757e$ for DBU–H⁺, $+0.810e$ for DBN–H⁺, $+0.773e$ for BTMG–H⁺, and $+0.730e$ for TBD–H⁺. The corresponding COS-containing fragments carry equal and opposite charges under the reported fragment analysis. The COS/DBN/methanol system exhibits the largest absolute fragment charge among these four examples, whereas COS/TBD/methanol exhibits the smallest. The comparison between charge-analysis methods is important. Mulliken charges generally show larger absolute values for charged fragments than Hirshfeld charges, while NPA provides another estimate of the electron distribution. Such differences are expected because the methods partition the molecular electron density differently. Consequently, the absolute numerical values should not be treated as interchangeable. The more robust interpretation is that the methods collectively indicate substantial electronic redistribution and the formation of oppositely charged product fragments. Overall, the charge analyses are consistent with a reaction in which proton transfer to the organic base and nucleophilic attachment of the alcohol-derived oxygen to COS produce an ion-pair structure. These findings complement the geometrical results and provide an electronic explanation for the formation of the predicted COS-capture products.

4. Thermodynamic feasibility of COS capture

The thermodynamic behavior of the investigated systems was assessed using the standard Gibbs free energy of reaction. According to the reported results, all 24 base–alcohol combinations have negative reaction free energies, ranging from -8.57 to -18.87 kcal mol⁻¹. Within the

thermodynamic framework used in the study, these negative values indicate that product formation is energetically favorable relative to the corresponding reactants under the modeled conditions. The most negative reported reaction free energy is associated with COS/TBD/1-propanol, for which is $-18.87 \text{ kcal mol}^{-1}$. This result identifies the TBD/1-propanol combination as the most thermodynamically favorable system among those investigated. COS/BTMG/methanol also exhibits a strongly favorable reaction free energy, reported as approximately $-18.1 \text{ kcal mol}^{-1}$ in the discussion and $-18.17 \text{ kcal mol}^{-1}$ in Table 1.

Table 1: Tabulation of the kinetic and thermodynamic properties of the systems used to capture the COS.

Thermodynamic & kinetic properties	System			
	COS/DBU/methanol	COS/DBN/methanol	COS/BTMG/methanol	COS/TBD/methanol
ΔG_{rxn}° (kcal/mol)	-12.61	-12.74	-18.17	-16.28
$\Delta^{\ddagger}G^{\circ}$ (kcal/mol)	9.23	10.71	8.49	10.13
k (s^{-1})	10.57×10^5	0.876×10^5	37.34×10^5	2.33×10^5
	COS/DBU/ethanol	COS/DBN/ethanol	COS/BTMG/ethanol	COS/TBD/ethanol
ΔG_{rxn}° (kcal/mol)	-13.05	-13.99	-16.50	-17.45
$\Delta^{\ddagger}G^{\circ}$ (kcal/mol)	8.83	11.24	10.97	11.12
k (s^{-1})	21.07×10^5	0.359×10^5	0.568×10^5	0.44×10^5
	COS/DBU/1-propanol	COS/DBN/1-propanol	COS/BTMG/1-propanol	COS/TBD/1-propanol
ΔG_{rxn}° (kcal/mol)	-10.93	-15.01	-18.12	-18.87
$\Delta^{\ddagger}G^{\circ}$ (kcal/mol)	10.06	10.61	13.47	8.71
k (s^{-1})	2.635×10^5	1.032×10^5	0.829×10^3	25.39×10^5
	COS/DBU/1-butanol	COS/DBN/1-butanol	COS/BTMG/1-butanol	COS/TBD/1-butanol
ΔG_{rxn}° (kcal/mol)	-10.16	-13.16	-16.23	-16.69
$\Delta^{\ddagger}G^{\circ}$ (kcal/mol)	11.68	11.64	10.37	11.90
k (s^{-1})	0.171×10^5	0.181×10^5	1.555×10^5	0.117×10^5
	COS/DBU/1-pentanol	COS/DBN/1-pentanol	COS/BTMG/1-pentanol	COS/TBD/1-pentanol
ΔG_{rxn}° (kcal/mol)	-9.40	-13.66	-14.49	-16.55
$\Delta^{\ddagger}G^{\circ}$ (kcal/mol)	12.54	10.97	9.07	11.88
k (s^{-1})	0.040×10^5	0.560×10^5	14.02×10^5	0.121×10^5

	COS/DBU/1-hexanol	COS/DBN/1-hexanol	COS/BTMG/1-hexanol	COS/TBD/1-hexanol
ΔG_{rxn}° (kcal/mol)	-8.57	-13.87	-14.11	-16.12
$\Delta^{\ddagger}G^{\circ}$ (kcal/mol)	12.69	10.62	10.48	12.49
k (s ⁻¹)	0.031×10^5	1.013×10^5	1.293×10^5	0.043×10^5

The thermodynamic results further indicate that the choice of alcohol affects the calculated reaction energetics. For the DBU-based systems, the reaction free energy becomes progressively less negative as the alcohol chain length increases, changing from -12.61 kcal mol⁻¹ for methanol to -8.57 kcal mol⁻¹ for 1-hexanol. This trend suggests that, within the DBU series, the shorter-chain alcohols are more favorable from a reaction-free-energy perspective. A similar, though not identical, pattern is observed in the BTMG series. The reported reaction free energy changes from -18.17 kcal mol⁻¹ for methanol to -14.11 kcal mol⁻¹ for 1-hexanol. However, the trend is not uniform across every base-alcohol combination. The TBD series, for example, includes particularly favorable values for ethanol and 1-propanol, at -17.45 and -18.87 kcal mol⁻¹, respectively. These differences indicate that the thermodynamic behavior cannot be explained by alcohol chain length alone; it depends on the specific combination of base and alcohol. The comparison between COS/TBD/1-propanol and COS/BTMG/methanol is especially informative. Although TBD/1-propanol has the most negative reaction free energy, BTMG/methanol exhibits the lowest reported activation free energy. The two systems therefore demonstrate different forms of favorable behavior: TBD/1-propanol is the most favorable in terms of the reported reaction thermodynamics, while BTMG/methanol has the strongest reported kinetic performance.

5. Activation free energies and predicted reaction rates

The kinetic comparison was based on the standard Gibbs free energy of activation, and the reaction rate constants reported in Table 1. The activation free energy describes the energetic barrier separating the reactant state from the transition state. Under comparable conditions and within the assumptions of the rate model, a lower activation free energy generally corresponds to a faster predicted reaction. Among the investigated systems, COS/BTMG/methanol exhibits the lowest reported activation free energy, at 8.49 kcal mol⁻¹. Its corresponding rate constant the highest value reported for the investigated combinations. This pairing of a relatively low barrier and a high predicted rate constant makes BTMG/methanol the strongest kinetic candidate in the present computational comparison. COS/TBD/1-propanol provides the second prominent result, with an activation free energy of 8.71 kcal mol⁻¹ and a reported rate constant. The small difference between its activation free energy and that of BTMG/methanol is consistent with the high predicted rate constant reported for the TBD-based system. In addition, its highly negative reaction free energy makes it a particularly interesting candidate when both reaction thermodynamics and kinetics are considered. These results show that favorable kinetic behavior is not restricted to a single base family. Although the BTMG/methanol combination has the highest reported rate constant, certain DBU-based systems also exhibit relatively low activation barriers. The alcohol identity therefore appears to play an important role in determining the predicted reaction rate, in combination with the chemical characteristics of the organic base. The combined kinetic and thermodynamic data therefore identify BTMG/methanol and TBD/1-propanol as the leading candidates in the present study, while DBU/ethanol, DBU/methanol, and BTMG/1-pentanol also show promising calculated

kinetic characteristics. The contrasting behavior of BTMG/methanol and BTMG/1-propanol further demonstrates why screening the complete base–alcohol combination is essential.

6. Comparison with previously reported COS-capture barriers

The reported activation free energies were also compared with values cited in the source document for previously investigated COS-capture systems. Experimental studies involving aqueous diethanolamine solutions reported reaction barriers of approximately 12.5 and 11.5 kcal mol⁻¹. Other experimental investigations using amine-containing systems in different solvents reported activation energies in the range of 11.1–19.7 kcal mol⁻¹. In a separate theoretical study of COS reactions with imidazole-2-ylidene carbene species, barrier heights of 15.1–27.3 kcal mol⁻¹ were reported. The present calculations identify several combinations with activation free energies below these cited ranges. In particular, the barriers calculated for COS/BTMG/methanol and COS/TBD/1-propanol are 8.49 and 8.71 kcal mol⁻¹, respectively. COS/DBU/ethanol and COS/BTMG/1-pentanol also exhibit reported barriers below 10 kcal mol⁻¹. These comparisons suggest that selected organic base–alcohol combinations may offer favorable reaction pathways for COS capture. A direct quantitative ranking requires harmonized calculation conditions or a consistent experimental protocol. Accordingly, the present results provide a promising computational basis for further investigation rather than definitive proof of superior practical performance.

7. Implications for selecting COS-capture systems

The results demonstrate that selecting a potential COS-capture medium requires simultaneous consideration of structural feasibility, electronic redistribution, reaction thermodynamics, and activation barriers. No single parameter fully characterizes the overall behavior of a candidate system. The geometrical analysis supports the formation of a covalent bond between COS and the alcohol-derived oxygen atom, while the charge analyses indicate the development of protonated-base and thiocarbonate-containing fragments. The negative reaction free energies indicate favorable product formation within the modeled reaction framework. Finally, the calculated activation free energies distinguish combinations that are predicted to react rapidly from those with less favorable kinetic behavior. On this basis, COS/BTMG/methanol emerges as the leading kinetic candidate because it combines the lowest reported activation free energy with the highest reported rate constant. COS/TBD/1-propanol is also highly promising because it combines a low activation barrier with the most negative reaction free energy in the investigated set. COS/DBU/ethanol provides another potentially attractive option because its reported barrier is relatively low and its predicted rate constant is comparatively high. By contrast, COS/BTMG/1-propanol should not be assumed to perform well simply because BTMG/methanol is highly favorable. Before these candidates can be recommended for practical gas treatment, further work is needed to examine their COS absorption capacities, selectivity in the presence of competing gases, viscosity, volatility, thermal stability, corrosivity, regeneration requirements, and recyclability. Experimental kinetic measurements would also be necessary to validate the calculated rate constants under controlled conditions. These considerations are essential for translating molecular-level predictions into meaningful process-level recommendations.

8. Overall interpretation

The ab initio results provide a consistent molecular-level explanation for COS capture by organic base–alcohol combinations. The optimized structures support a reaction pathway involving proton

transfer from the alcohol to the organic base, accompanied by the formation of a new carbon–oxygen bond between the alcohol-derived oxygen and COS. The resulting structural changes are accompanied by redistribution of electronic charge across the COS-derived fragment and the protonated base. Thermodynamically, all investigated reactions have negative reported Gibbs free energies, ranging from -8.57 to -18.87 kcal mol $^{-1}$. COS/TBD/1-propanol exhibits the most favorable reaction free energy, whereas COS/BTMG/methanol exhibits the lowest reported activation free energy of 8.49 kcal mol $^{-1}$ and the highest reported rate constant. The strong contrast between COS/BTMG/methanol and COS/BTMG/1-propanol further indicates that reaction performance depends on the specific pairing of the base and alcohol. Collectively, the findings establish a useful computational screening framework for identifying promising COS-capture systems. BTMG/methanol and TBD/1-propanol are the strongest candidates according to the reported kinetic and thermodynamic indicators, while selected DBU-based combinations also warrant further study. These conclusions remain predictions based on the computational model and should be tested experimentally before practical performance claims are made.

Figure 2&3 presents the optimized reactant, transition-state, and product geometries for the proposed reaction between carbonyl sulfide (COS), BTMG, and methanol. Comparison of the three structures provides a qualitative description of the molecular rearrangement associated with the proposed COS-capture pathway. In particular, the changes in the O–H and N–H distances can be used to assess proton transfer from methanol to the organic base, while the evolution of the C–O distance provides evidence for the formation of a new carbon–oxygen bond. Changes in the C–O and C–S bond lengths within the COS-derived species can further clarify the redistribution of bonding during product formation. These structural observations should be interpreted alongside the calculated reaction energies, activation free energy, atomic charge distributions, and transition-state verification results to establish a consistent mechanistic interpretation.

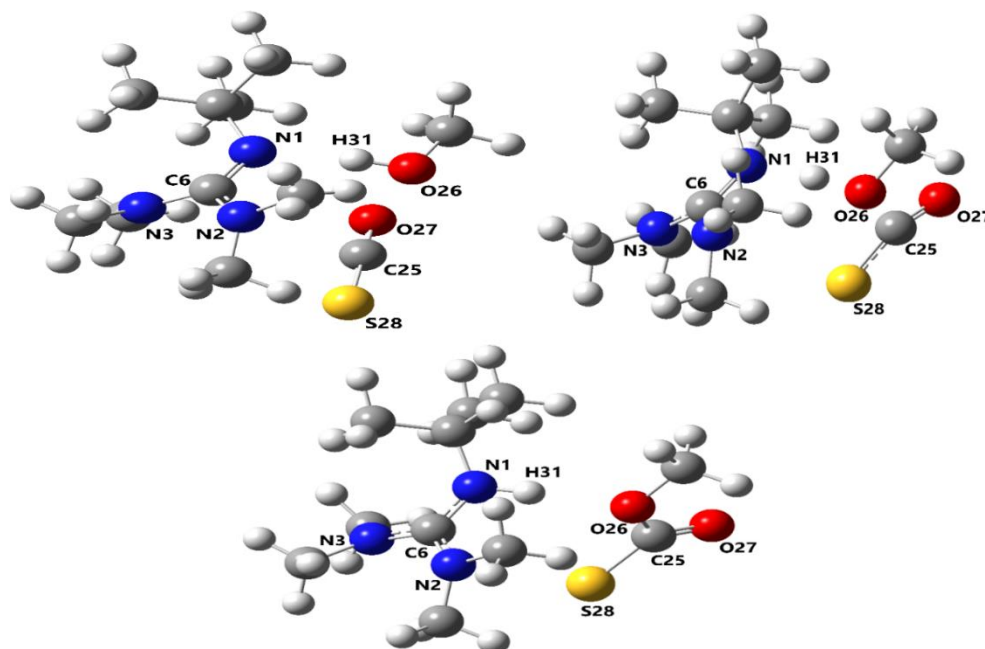


Figure 2: R (top), TS (middle), and P (bottom) structures of the COS/BTMG/methanol system.

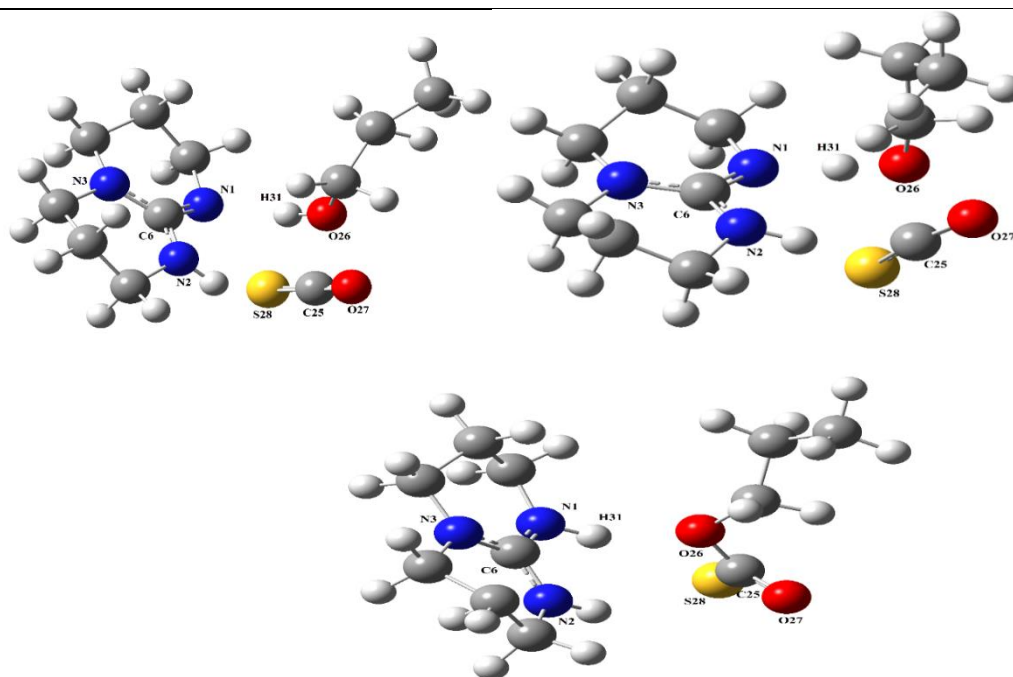


Figure 3: R (top), TS (middle), and P (bottom) structures of the COS/TBD/1-propanol system.

CONCLUSIONS

In this study, a comprehensive ab initio quantum chemical investigation was successfully executed to evaluate the performance and molecular mechanisms of twenty-four organic liquid mixture systems for carbonyl sulfide (COS) capture. The investigated formulations comprised guanidine-based bases (BTMG and TBD) and amidine-based bases (DBU and DBN) paired with a series of linear alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol). Electronic structure calculations performed at the high-level, theoretical level, integrated with the polarizable continuum model (PCM), rigorously validated the thermodynamic and kinetic feasibility of the proposed single-step termolecular reaction mechanism. The first-principles computational insights obtained herein strongly corroborate existing theoretical and empirical benchmarks for carbon dioxide (CO₂) capture using closely related organic mixtures. Furthermore, our high-level results demonstrate excellent consistency with previously reported B3LYP/6-31G(d) calculations documented for the baseline (CO₂)/DBU/1-propanol trapping system, thereby confirming the reliability of the applied quantum chemical framework.

The prospective screening yielded the following key structural insights for solvent optimization:

- **Optimal System Performance:** The BTMG/methanol mixture exhibited the lowest activation energy barrier among all twenty-four systems evaluated. Consequently, this formulation possesses the highest reaction rate constant, rendering it the most kinetically and thermodynamically viable candidate for efficient COS sequestration.
- **Secondary Guanidine Candidates:** Following the BTMG/methanol system, the TBD/1-propanol mixture was identified as the second most efficient capturing media based on its favorable potential energy surface parameters.
- **Amidine-Based Subsystems:** When employing DBU as the amidine base, both methanol and ethanol emerged as superior alcohol co-solvents, yielding enhanced kinetic pathways.

Conversely, 1-propanol proved to be the most structurally compatible and thermodynamically appropriate alcohol partner when paired with DBN.

Finally, the ab initio quantum chemical approach successfully decodes the microscopic interactions driving COS capture in multi-component organic liquid mixtures. The established reactivity trends and energetic benchmarks provide an invaluable theoretical foundation for the rational design and implementation of highly optimized, next-generation alkanolamine-free scrubbing technologies.

REFERENCES

1. A. Barreau, E. Blanchon Le Bouhelec, K. N. Habchi Tounsi, P. Mougin and F. Lecomte, "Absorption of H₂S and CO₂ in Alkanolamine Aqueous Solution: Experimental Data and Modelling with the Electrolyte-NRTL Model", *Oil & Gas Science and Technology*, vol. 61, no. 3, pp. 345–361, 2006.
2. K. Othmer, "Metathesis" in *Encyclopedia of Chemical Technology*, vol. 26. J. Peters, Ed. New York: McGraw-Hill, 2005, pp. 920–958.
3. F. Amararene and C. Bouallou, "Kinetics of Carbonyl Sulfide (COS) Absorption with Aqueous Solutions of Diethanolamine and Methyldiethanolamine", *Industrial and Engineering Chemistry Research*, vol. 43, no. 19, pp. 6136–6141, 2004.
4. G. Hinderaker and O.C. Sandall, "Absorption of Carbonyl Sulfide in Aqueous Diethanolamine", *Chemical Engineering Science*, vol. 55, no. 23, pp. 5813–5818, 2000.
5. S.C. Lee, M.J. Snodgrass, M.K. Park and O.C. Sandall, "Kinetics of Removal of Carbonyl Sulfide by Aqueous Monoethanolamine", *Environmental Science and Technology*, vol. 35, no. 11, pp. 2352–2357, 2001.
6. F. Yan, R. Kakuchi, K. Takahashi and H.J. Kim, "CS₂ Capture in the Ionic Liquid 1-alkyl-3-methylimidazolium Acetate: Reaction Mechanism and Free Energetics", *Physical Chemistry Chemical Physics*, vol. 20, no. 29, pp. 19339–19349, 2018.
7. P.D. Vaidya and E.Y. Kenig, "Kinetics of Carbonyl Sulfide Reaction with Alkanolamines: A review", *Chemical Engineering Journal*, vol. 148, no. 2–3, pp. 207–211, 2009.
8. S. Francisco, N. Technical Monitor and A. Aden, (2009, Mar.), "Survey and Down-selection of Acid Gas Removal Systems for the Thermochemical Conversion of Biomass to Ethanol with A detailed Analysis of an MDEA System Task 1: Acid Gas Removal Technology Survey and Screening for Thermochemical Ethanol Synthesis." National Renewable Energy Laboratory, [Online], [Dec. 1, 2019].
9. S. Bishnoi and G.T. Rochelle, "Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility", *Chemical Engineering Science*, vol. 55, no. 22, pp. 5531–5543, 2000.
10. R. Cadours, D. Roquet and G. Perdu, "Competitive Absorption-desorption of Acid Gas into Water-DEA Solutions", *Industrial and Engineering Chemistry Research*, vol. 46, no. 1, pp. 233–241, 2007.
11. E.F. da Silva and H.F. Svendsen, "Computational Chemistry Study of Reactions, Equilibrium and Kinetics of Chemical CO₂ Absorption", *International Journal of Greenhouse Gas Control*, vol. 1, no. 2, pp. 151–157, 2007.
12. F. Jensen, *Introduction to Computational Chemistry*. Wiley, 2016, pp. 664.
13. E.F. da Silva, "Computational Chemistry Study of Solvents for Carbon Dioxide Absorption." Ph.D. thesis, Fakultet for Naturvitenskap Og Teknologi, 2005.