

**CARBON NITRIDE MODIFIED HIGHLY REDUCED
GRAPHENE AS A POTENTIAL PHOTOCATALYST FOR
CO₂ REDUCTION: A FIRST-PRINCIPLE STUDY**

BY

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A Thesis Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

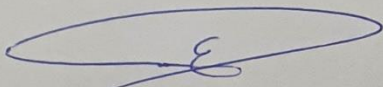
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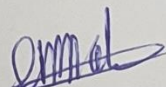
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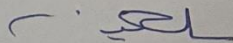
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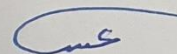
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|To almighty Allaah and my family|

ACKNOWLEDGMENT

All glory and adorations are given to the Almighty Allah for the successful completion of this project who gave me life to witness this and gave me knowledge, wisdom, and understanding to apply to every of my daily life activities, praise be to him. I would like to express my special appreciation to my parents and family who have been there for me in terms of prayer, I pray for you to witness and eat the fruits of your labor.

I want to sincerely thank King Fahd University of Petroleum and Minerals for supporting my thesis and providing the scholarship. My sincere gratitude goes to my supervisor, Professor Abdulaziz Al-Saadi who has contributed to the huge success of this thesis and who also gave me his precious time and professional counsel from the start to the completion of the thesis work. I am also indebted to Dr. Abduljabar Al-Sayoud for his consistent support, valuable comments, and suggestions. I would like to thank Dr. Saheed Ganiyu for his valuable comments and suggestions.

For he that forgets his source, then is ready to perish, is one of the Yoruba's adage. I used this opportunity to thank every lecturer in the Department of Chemistry who has impacted one or two things in me. Money can't buy what you have inculcated in me and I promise to be a good ambassador of the department, the school, and the society at large wherever I meet myself. My sincere appreciation also goes to Dr. Ismail Abdulazeez for his relentless effort, support, and contributions to my DFT knowledge.

Finally, my profound gratitude also goes to the Chairman of the Chemistry Department, Dr. Jameel Al-Thagfi, and my colleagues who in one way or the has impacted positively, I have learned human relations to an extent which is a whole course studied at the university.

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LIST OF ABBREVIATIONS

CO2RR: Carbon dioxide Reduction Reaction

DFT: Density Functional Theory

CN: graphitic Carbon Nitride (g-C₃N₅)

HRG: Highly Reduced Graphene

LDA: Local Density Approximation

GGA: General Gradient Approximation

PDOS: Partial Density of State

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

MEP: Molecular Electrostatic Potential

MD: Molecular Dynamics

FMO: Frontier Molecular Orbital

HER: Hydrogen Evolution Reaction

VR: Volmer Reaction

HR: Heyrovsky Reaction

TR: Tafel Reaction

SAS: Substituted Salicylideneaniline

ML: Machine Learning

NLO: Non-Linear Optics

ICT: Intramolecular Charge Transfer

D-A: Donor-Acceptor

E: Enol

K: Keto

TK: Trans-Keto

IEFPCM: Integral Equation Formalism Polarized Continuum Model

TD-DFT: Time-Dependent Density Functional Theory

MOT: Molecular Orbital Transition

MMOT: Multi-Molecular Orbital Transition

CF: Contribution Factor

OS: Oscillator Strength

KNN: K-Nearest Neighbour

SVM: Support Vector Machine

ANN: Artificial Neural Network

RMSE: Root Mean Square Error

MAE: Mean Absolute Error

TP: True Positive

TN: True Negative

I: Ionization Potential (ϕ)

A: Electron Affinity (χ)

ABSTRACT

Full Name: Abdulraheem Bello

Thesis Title: Carbon Nitride Modified Highly Reduced Graphene as A Potential Photocatalyst For CO₂ Reduction: A First-Principle Study.

Major Field: Physical Chemistry

Date of Degree: December, 2024

The level of carbon dioxide in the atmosphere continues to increase as a result of anthropogenic activities which impose greater threats in terms of global warming and climate change. Catalytic reduction reactions of CO₂ (CO₂RR) leading to useful products are considered an attractive means for carbon utilization and greenhouse gas mitigation. Graphitic carbon nitride photocatalysts have attracted a great deal of interest due to their low band gap energy and good absorption ability, due to the involvement of the lone pair on the N atom with the π -conjugated system of heptazine motifs and a longer conjugated network. However, such two-dimensional materials still need to be upgraded regarding the photo-generated carrier dynamics for more efficient photoactivity. In addition to facilitating the spatial separation of photoinduced charge carriers, Z-scheme heterojunctions made of two or more appropriate semiconductors can also maintain comparatively stronger oxidative and reductive capabilities. Herein, we have explored the catalytic activity of g-C₃N₅ (CN) nanosheets combined with highly reduced graphene (HRG) towards CO₂ reduction based on the density functional theory (DFT). To gain insights into the appropriateness and capability of such nanomaterials, key electronic and optical properties, such as band structures, work functions, frontier molecular orbitals, and UV-Vis absorption, were theoretically derived and thoroughly analyzed. The band gap is predicted to drop from 1.8 to less than 0.5 eV upon combining HRG with CN, showing the ease of separation of photogenerated electron/hole pairs as a heterojunction is formed. The magnitude of the work function of pristine g-C₃N₅ (5.4 eV)

decreases to 5.2 eV when HRG is incorporated, which is indicative of a higher tendency of the new material to have a better reduction capability. The simulated electronic spectra depict a shift of λ_{max} from 360 to 540 nm, before and after the heterojunction modification, respectively. The change in the absorption pattern is evidence of the increase in the photocatalytic performance of the nanocomposite materials. The CO₂RR via the two layers (CN and HRG adsorption sites) of CN-HRG-CO and CN-HRG-COOH configurations respectively, have been theoretically derived and presented. The limiting potentials are -0.87, -0.80, -0.16, and -0.08 V respectively. It is therefore evident that CN-HRG-COOH has better reduction capacity and selectivity for CO₂RR due to its low limiting potential. These results provide valuable insights for rationally designing effective photocatalysts for CO₂RR applications.

One of the competing side reactions for CO₂RR is the hydrogen evolution reaction (HER). Therefore, the designed materials were also used to explore the adsorption-desorption of hydrogen and possible mechanisms of HER. The computed free energy of hydrogen adsorption predicts that the g-C₃N₅/HRG 2D/2D combination performs better through the adsorption site of the graphitic carbon-nitride (CN) layer, especially when functionalized with carbonyl groups. The Volmer-Heyrovsky HER mechanism is predicted to be the leading pathway with an energy barrier as low as 0.5 eV using such a metal-free catalyst. It was observed that while the CN-HRG-COOH has better catalytic performance towards CO₂RR, the CN-HRG-CO has excellent catalytic behavior towards HER.

ملخص الرسالة

الاسم الكامل: عبد الرحيم بيلو
عنوان الرسالة: نيتريد الكربون المعدل الجرافين المختزل للغاية كمحفز ضوئي محتمل لتقليل CO₂: دراسة المبدأ الأول.
المجال الرئيسي: كيمياء فيزيائية
تاريخ الدرجة: ديسمبر، 2024

يستمر مستوى ثاني أكسيد الكربون في الغلاف الجوي في الزيادة نتيجة للأنشطة البشرية التي تفرض تهديدات أكبر من حيث الاحترار العالمي وتغير المناخ. تعتبر تفاعلات الاختزال التحفيزية لثاني أكسيد الكربون (CO₂RR) التي تؤدي إلى منتجات مفيدة وسيلة جذابة لاستخدام الكربون والتخفيف من غازات الاحتباس الحراري. جذبت المحفزات الضوئية لنيتريد الكربون الجرافيني قدرا كبيرا من الاهتمام بسبب طاقة فجوة النطاق المنخفضة وقدرتها الجيدة على الامتصاص، بسبب مشاركة الزوج الوحيد على ذرة N مع نظام مقترن π من زخارف السباعي وشبكة مترافقة أطول. ومع ذلك، لا تزال هذه المواد ثنائية الأبعاد بحاجة إلى ترقية فيما يتعلق بديناميكيات الناقل المولدة بالصور من أجل نشاط ضوئي أكثر كفاءة. بالإضافة إلى تسهيل الفصل المكاني لحاملات الشحنة المستحثة ضوئيا، يمكن للوصلات غير المتجانسة ذات المخطط Z المصنوعة من اثنين أو أكثر من أشباه الموصلات المناسبة أن تحافظ أيضا على قدرات مؤكسدة واختزالية أقوى نسبيا. هنا، استكشفنا النشاط التحفيزي للصفائح النانوية (CN) g-C₃N₅ جنباً إلى جنب مع الجرافين المختزل للغاية (HRG) نحو تقليل CO₂ بناء على نظرية الكثافة الوظيفية (DFT). ولاكتساب نظرة ثاقبة حول مدى ملائمة وقدرة هذه المواد النانوية، تم نظريا اشتقاق وتحليل الخصائص الإلكترونية والبصرية الرئيسية، مثل هياكل النطاق، ووظائف العمل، والمدارات الجزيئية الحدودية، وامتصاص الأشعة المرئية وفوق البنفسجية، وتحليلها بدقة. من المتوقع أن تنخفض فجوة النطاق من 1.8 إلى أقل من 0.5 فولت عند الجمع بين HRG وCN، مما يدل على سهولة فصل أزواج الإلكترونات / الثقوب المولدة ضوئيا عند تكوين تقاطع غير متجانس. ينخفض حجم دالة العمل لـ g-C₃N₅ البكر (eV 5.4) إلى eV 5.2 عند دمج HRG، مما يدل على ميل أعلى للمادة الجديدة للحصول على قدرة اختزال أفضل. تصور الأطياف الإلكترونية المحاكاة تحولا لمبدأ أقصى من 360 إلى 540 نانومتر، قبل وبعد تعديل الوصلة غير المتجانسة، على التوالي. التعبير في نمط الامتصاص هو دليل على الزيادة في أداء التحفيز الضوئي للمواد المركبة النانوية. تم اشتقاق CO₂RR عبر طبقتين (مواقع امتصاص CN وHRG) لتكوينات CN-HRG-CO وHRG-COOH-CN على التوالي، نظريا وتقديما. الإمكانات المحددة هي -0.87 و -0.80 و -0.16 و -0.08 فولت على التوالي. لذلك من الواضح أن CN-HRG-COOH لديها قدرة تخفيض وانتقائية أفضل لـ CO₂RR بسبب إمكاناتها المنخفضة الحد. توفر هذه النتائج رؤى قيمة لتصميم محفزات ضوئية فعالة بشكل عقلائي لتطبيقات CO₂RR.

أحد التفاعلات الجانبية المتنافسة لـ CO₂RR هو تفاعل تطور الهيدروجين (HER). لذلك، تم استخدام المواد المصممة أيضا لاستكشاف امتصاص وامتصاص الهيدروجين والآليات الممكنة لـ HER. تتنبأ الطاقة الحرة المحسوبة لامتصاص الهيدروجين بأن تركيبة g-C₃N₅ / 2D / 2D HRG تعمل بشكل أفضل من خلال موقع الامتزاز لطبقة نيتريد الكربون الجرافيتية (CN)، خاصة عند تشغيلها باستخدام مجموعات الكربونيل. من المتوقع أن تكون آلية Volmer-Heyrovsky HER هي المسار الرائد مع حاجز طاقة منخفض يصل إلى 0.5 فولت باستخدام مثل هذا المحفز الخالي من المعادن. لوحظ أنه في حين أن CN-HRG-COOH يتمتع بأداء تحفيزي أفضل تجاه RRCO₂، فإن CN-HRG-CO لديه سلوك تحفيزي ممتاز تجاه HER.

CHAPTER 1

INTRODUCTION

Global warming and climate change are caused by human actions such as the burning of fossil fuels, which continuously raise the amount of carbon dioxide in the atmosphere. One cost-effective and plentiful carbon source is CO₂, which has the potential to be a valuable feedstock for the synthesis of polymers, industrial chemicals, and fuel for transportation. The CO₂ molecule is inert and thermodynamically stable, therefore to convert it into usable clean fuels, a very high dissociation energy is needed, which begs the application of a unique catalytic system. Products of CO₂ reduction, for instance, methane, methanol, ethanol, and so on, are widely desired due to their economic values and high energy densities.

Semi-conductor-based photocatalytic CO₂ reduction has gained popularity recently since photocatalysts operate in milder environments with less energy contribution, particularly when the reaction is triggered by solar power or other readily available light supplies.

Due to its remarkable optical, electronic, and physiochemical properties, g-C₃N₄ has been widely explored for photocatalytic CO₂ reduction. However, due to its approximately 2.7 eV band gap, its performance and applicability are severely limited by the high level of recombination of photoinduced charge transporters. Due to its more extended conjugated system and the engagement of the non-bonding pair on the nitrogen atom with the π conjugated system of heptazine motif, g-C₃N₅, an analogue of g-C₃N₄, has garnered a lot of attention because of its low bandgap energy (~ 2 eV) and strong absorption capacity. Unfortunately, carbon nitrides with narrow band gap values, like all semiconductors used in photocatalysis, are vulnerable to strong

carrier recombination. This prevents photoelectrons from migrating to the semiconductor layer and contacting the target, which has a substantial negative impact on the photochemical process.

Thus, creating a heterojunction with C_3N_5 shall aid in lessening this disadvantage by possibly directing charge transit in composites at component interfaces. In this piece of research, a novel C_3N_5 /highly reduced graphene (g- C_3N_5 /HRG) is proposed for the conversion of CO_2 to several value-added products, for example, CH_3OH , $HCHO$, and CH_4 , with selectivity for the best adsorbing species via density functional theory study.

A major competing side reaction with CO_2RR is the hydrogen evolution reaction (HER). Therefore, the study shall investigate HER mechanism to explore its impact on CO_2RR . Two potential mechanisms for HER to reduce protons to hydrogen in acidic conditions have been postulated: the Volmer-Heyrovsky pathway and the Volmer-Tafel process (Scheme 3). The first proton adsorption from the acid solution to generate adsorbed H ($H^+ + e^- \rightarrow H_{ad}$) is known as the Volmer reaction, and it is typically thought to occur quickly. Whereas two adsorbed surface hydrogens close to each other react to generate an H_2 molecule ($H_{ad} + H_{ad} \rightarrow H_2$) in the Volmer-Tafel mechanism, a solvated proton from the water layer combines with one adsorbed surface hydrogen to form H_2 ($H_{ad} + H^+ + e^- \rightarrow H_2$) [56].

This research aims to address the following by using the DFT approach:

1. To assess the photocatalytic efficiency of a single semiconductor (C_3N_5) upon introducing a well-known HRG.
2. To explore the combined 2D nanosheets for CO_2RR and predict the possible products of the reduction reaction, especially C1 products (CH_3OH and CH_4).

3. To compute the adsorption energies of viable products on each of the adsorption sites, the bandgaps, partial density of state (PDOS), HOMO-LUMO energies, and optical properties like UV-Vis.
4. To calculate the pathway of a possible side reaction, mainly the hydrogen evolution reaction (HER) including its mechanisms.

CHAPTER 2

LITERATURE REVIEW

2.1 DENSITY FUNCTIONAL THEORY

Density Functional theory (DFT) is a theory that is based on finding the energy of a system in terms of the electronic structure of atoms, solids, and molecules. The primary objective of DFT is to understand the processes of materials from quantum mechanics. Traditional methods of finding solutions to electronic properties of materials use the Schrodinger equation. However, there are limitations, one of which is the limited to small electronic problems and its result in complicated wavefunctions. DFT took a different approach by treating many electron problems as electron density (one-density problem) in three different directions. Subsequently, this makes it feasible for large and complicated systems [1]. Having been used by physicists for over three decades for solving electronic systems, it has become more famous amongst theoretical and computational chemists [2]. To put this theory to practical use, an approximation is needed, and the simplest approximation that has been the basis of DFT is the local density approximation (LDA). However, for some underlying reasons, it gives results to physical and chemical systems that are not satisfying. The GGA is the preferred method for many first principles studies of materials, and it has been used to calculate a wide range of materials. Due to the numerous comparison studies that have been conducted, the behavior of the GGA in relation to the LDA is well understood.

The following deductions may be made based on these outcomes: (1) The ground state characteristics of light atoms, molecules, clusters, and solids made of them are greatly enhanced by GGAs; (2) Although GGAs occasionally cause the LDA errors in lattice parameters to be

overcorrected, structural characteristics are typically enhanced. (3) The magnetic energy for certain 3D transition metals may be overstated because GGA functionals typically favor magnetism more than the LSDA; (4) Similar to the undoped phases of high-T_c cuprates, the description of Mott-Hubbard insulators is not appreciably better than the LSDA; and (5) The properties of 3D transition metals exhibit significant enhancements; for instance, in contrast to the LSDA, the accurate bcc ground state of Fe is achieved. These deteriorate in accordance with the experiment in comparison to the LDA in certain materials that contain heavy elements, such as 5D compounds. However, it should be noted that efforts are still being made to create even better GGA functionals, and a better version that addresses the aforementioned shortcomings might be discovered.

2.2 DFT METHODS AND PHOTOCATALYSTS

Table 1. The overview of the theoretical studies of photocatalysts [3].

catalyst	method	excited states	investigated	proposed reaction mechanism
GaP(100)/TiO ₂ (001)	PBE-GGA	pseudo (emulated with increased H* coverage)	reaction pathway	CO ₂ → HCOOH → H ₂ CO → CH ₃ OH
anatase TiO ₂ (101)	PBE-GGA+U/HSE	not explicitly	reaction pathway	CO ₂ → HCOOH, CO → CH ₂ O → CH ₃ OH → CH ₃ OH → CH ₃
oxygen vacant anatase TiO ₂ (101)	DFT+U	not explicitly	reaction pathway	CO ₂ → CO → CH ₂ O → CH ₃ O → CH ₃ → CH ₃ OH CO ₂ → CO → CHO → CHOH → CH ₂ OH → CH ₃ OH/ CH ₄ CO ₂ → CO → CHO → CH ₂ O → CH ₃ OH → CH ₃ OH/ CH ₄
Pd/g-C ₃ N ₄	PBE-GGA	not explicitly	reaction pathway	CO ₂ → HCOOH → HCHO → CH ₃ OH → CH ₄
Pd/g- C ₃ N ₄	PBE-GGA+ Grimme D3	not explicitly	reaction pathway	CO ₂ → HCOO → HCOOH → HCO → CH ₂ O → CH ₂ OH → CH ₃ OH
Pt/g- C ₃ N ₄				CO ₂ → HCOO → HCOOH → HCO → CH ₂ O → CH ₂ OH → CH ₂ → CH ₃ → CH ₄
g- C ₃ N ₄				
g- C ₃ N ₄	PBE-GGA	no	reaction pathway	CO ₂ → HCO ₃ , HCOOH, CO CO → C → CH → CH ₂ → CH ₃ → CH ₄
1%KBH- C ₃ N ₄				
2%KBH- C ₃ N ₄				
3%KBH- C ₃ N ₄				
5%KBH- C ₃ N ₄				
Ag ₃ PO ₄ (111)/g- C ₃ N ₄	PBE-GGA +Grimme D3	not explicitly	reaction pathway	CO ₂ → HCOO → t,c-COOH → HCOOH → HCO → t, c-HCOH → CH ₂ O → CH ₂ OH → CH ₂ → CH ₃ → CH ₄ CO ₂ → t,c-COOH → tt-HOCOH → COH → t-HCOH → CH ₂ O → CH ₂ → CH ₃ → CH ₄
g- C ₃ N ₄	PBE-GGA+ GrimmeD3	not explicitly	reaction pathway	CO ₂ → HCOO → HCOOH
Fe/g- C ₃ N ₄				
Co/g- C ₃ N ₄				
Cu/g- C ₃ N ₄				
Ni/g- C ₃ N ₄				
g- C ₃ N ₄	PBE-GGA+ GrimmeD3	not explicitly	reaction pathway	CO ₂ → HOCO → CO → HCO → H ₂ CO → CH ₃ O → CH ₃ OH
B ₄ C ₃	PBE-GGA + Grimme correction	not explicitly	reaction pathway	CO ₂ → HCOO → HCO → CHOH → CH ₂ OH → CH ₂ → CH ₃ → CH ₄
B ₈₀ fullerene	PBE-GGA + Grimme D2	no	reaction pathway	CO ₂ → HOCO → HCOOH
ZnO NSs	PBE-GGA + GrimmeD2	not explicitly	reaction pathway	CO ₂ → H ₂ COOH → H ₂ CO → H ₃ COH → H ₄ COH → CH ₄
Au/ZnO NSs				
Ag/ZnO NSs				
Pd/ZnO NSs				
In ₂ O ₃	B3LYP	LR-TDDFT	absorption spectra	CO ₂ +H ₂ → CO+ H ₂ O
In ₂ O _{3-x}				
In ₂ O ₃ (OH) _y				
In ₂ O _{3-x} (OH) _y				

Several carbon-containing molecules, including CO, HCOOH, CH₃OH, and CH₄, can be produced by reducing CO₂. From a thermodynamic perspective, it is easier to create multielectron-reduced species than CO₂⁻, which is used in electrocatalysis. The procedure is very complicated and

comprises a number of basic components. The selection of the reducing agent is a crucial component of the reaction mechanism. H_2O and H_2 are the most often utilized, however, CH_4 and CH_3OH are occasionally used as well.

H_2O has the obvious advantage of being abundant and inexpensive, making it frequently used. However, it has a few drawbacks, including competing reactions (water splitting) caused by its high adsorption affinity, which covers numerous active sites and impedes CO_2 reduction. The oxygen produced by the oxidation of water can also reduce its photocatalytic effectiveness and potentially assist generate CO_2 . Using H_2 , which, depending on the reaction system, creates identical compounds via a different mechanism, is one alternate solution. The H_2 method enables higher yields because no oxygen is produced.

Each system under study has its unique reaction mechanism, route, kinetics, and products. The most widely used photocatalysts for reducing CO_2 with H_2 or H_2O , together with various functionals and the resulting products, are listed in Table 1. Postulating a single reaction mechanism to explain the photocatalytic reduction of CO_2 is still difficult, though. The majority of research is mostly concerned with determining catalyst yields and properties experimentally [56].

Furthermore, molecular simulation tools have been intensively used to build a fundamental understanding of electro- and photocatalytic H_2 production routes at the atomistic level. These tools not only offer deeper insights into the mechanistic features of HER pathways but also help experimentalists design new and efficient catalysts at much lower cost. An inherent bandgap is typically required for photocatalytic HERs. Photocatalysts would absorb specific wavelengths of light depending on their bandgaps when exposed to sunlight. The most effective hydrogen evolution reaction (HER) catalysts at the moment are noble metals, like platinum and its alloys,

which have been characterized by their powerful catalytic performance at low overpotential and closely zero Gibbs free energy of hydrogen adsorption on the catalyst surface [69, 70]. Unfortunately, their high price and scarcity make them very challenging to employ broadly. Therefore, it has become essential to explore earth-available, stable, reasonably priced, and potentially active alternative catalysts suitable for hydrogen evolution reactions.

CHAPTER 3

DENSITY FUNCTIONAL THEORY ASSESSMENT OF CO₂ REDUCTION REACTION USING CARBON NITRIDE MODIFIED HIGHLY REDUCED GRAPHENE

3.1 INTRODUCTION

Due to the connection to climate change, growing CO₂ emissions have become a major environmental issue since industrialization and the transition to a carbon-based civilization. Therefore, the conversion of carbon dioxide (CO₂) to liquid fuels (such as methane and alcohol) by photocatalysis, electrocatalysis, or photo-electrochemical processes employing energy from renewable sources is pertinent [4, 5]. For greenhouse gas mitigation and carbon utilization, photocatalytic conversion of CO₂ to valuable fuels and chemical feedstocks is seen to be an appealing option among all of the potential technologies to address these significant concerns [6, 7]. Furthermore, CO₂ reduction by photocatalytic processes differs from other commercial conversion techniques in that it typically does not require harsh reaction conditions, such as high temperature and/or high pressure, making it an environmentally acceptable process [8-10].

The following sums up the photocatalysis mechanism: Under light irradiation, (1) electrons move from the valence band (VB) to the conduction band (CB), (2) electron-hole pairs (e^-/h^+) are created, and (3) electron-hole pairs can reduce CO₂ into a variety of reducing chemicals [11-13]. Additionally, the characteristics of catalysts and the circumstances of the reaction usually determine the products for CO₂ reduction [14-16]. The reduction of CO₂ to C1 products, for instance, formaldehyde (HCHO), methanol (CH₃OH), formic acid (HCOOH), and methane (CH₄)

by using semiconductive materials WO_3 [17], TiO_2 [16], GaN [18], ZnO [19], Fe_2O_3 [20], and $\text{g-C}_3\text{N}_4$ [21-24] has been reported and extensively investigated by first-principle calculations.

In comparison to conventional $\text{g-C}_3\text{N}_4$, the polymeric carbon nitride of C_3N_5 is developing to fulfill a historic destiny because of its superior visible-light response, greater strength of the conductive band (CB), and greater N ratio for efficient binding capability and enhanced transport of electrons [25-29]. Additionally, it has been suggested that it may find use in the reduction of water, oxygen, nitrogen fixation, CO_2 emissions, and the detoxification of air and water. Nonetheless, for effective photoactivity, bulk $\text{g-C}_3\text{N}_5$ still needs to be improved in the photogenerated transport dynamics. In contrast, methods such as heterostructure construction have been adopted [30-33]. Z-scheme combinations made of two or more appropriate electronic semiconductors can, in comparison to a single-component photocatalyst, not only encourage the spatial dispersion of photoinduced charge carriers but also maintain comparatively better oxidative and reductive activity [34-37]. Z-scheme catalysts also aid in overcoming significant overpotentials, which boosts their photocatalytic efficiency [38, 39]. Nevertheless, there is little computational simulation, and most study is concentrated on synthesis as well, characterization, and laboratory efficacy.

However, highly reduced graphene (HRG) has been identified as a capable support system or electron-transport mediator [40] due to its π -conjugated framework. As a result, HRG nanolayers would be a better solid-state electron intermediary for coupling with the aforementioned π -conjugated carbon nitrides, and they would then perfectly facilitate the redox reactions due to the efficient separation of charges at the interface [41, 42].

Recently, a 2D/2D Nanosheet heterostructure, named g-C₃N₅/highly reduced graphene (g-C₃N₅/HRG) has been reported by Linzhen et.al. The carefully constructed 2D/2D nanosheet heterojunction was shown to improve the migration efficacy, significantly decrease the subsequent recombination of electrons/holes created by illumination, and boost the photophysical procedure, all of which increased the unsteady carrier concentration [42].

Sequel to the literature findings, these two 2D sheets, namely: g-C₃N₅/HRG were combined for CO₂RR. This was meted out to enhance the photocatalytic activity and also to prevent possible recombination which can impede redox reactions. Out of the inquisitiveness, the scope of the research was expanded by screening four different materials, of which the best two were selected, which are promising in terms of their electronic and optical properties. These four materials include the pristine g-C₃N₅ (CN), g-C₃N₅-Graphene (CN-G), g-C₃N₅-HRG-CO (CN-HRG-CO) and g-C₃N₅-HRG-COOH (CN-HRG-COOH). The electronic and optical properties simulation showed that CN-HRG-CO and CN-HRG-COOH are the best composites out of all the materials, therefore we studied the possible mechanistic pathway for CO₂RR on their surfaces. All the studies were carried out by density functional theory (DFT) using Material Studio. With the CN-HRG-CO, a maximum limiting potential of 0.87 V was recorded, while with the other CN-HRG-COOH, a maximum limiting potential of 0.16 eV was achieved. This shows that CN-HRG-COOH has an excellent performance towards CO₂RR.

3.2 COMPUTATIONAL DETAILS

Dmol3 module embedded in the Materials Studio software was employed for the whole system [43]. Generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE)

type with Van der Waals correction was used to optimize their geometric structures. Valence electrons were treated with the DNP basis set. The cutoff energy quality was set to fine and the $4 \times 4 \times 1$ of Monkhorst–Pack k-mesh was adopted for all systems. Additionally, the spin polarization scheme was employed for all calculations [44]. To prevent interaction between opposite structures and neighboring atoms, a vacuum layer with a thickness of around 25 Å was adopted along the z-axis. Grimme’s method was adopted for the surface adsorption calculations [45]. The convergence criteria for structure optimization were set to a maximum force tolerance of 0.002 Ha/Å, energy tolerance of 1.0×10^{-5} Ha, and maximum displacement tolerance of 0.05 Å. The change in ΔG [46, 47] was defined as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U \quad (1)$$

where ΔE is the change of reaction energy, ΔE_{ZPE} is known as the change of zero-point energy and obtained from the output file of the calculations, T is the temperature and was set to (298.15 K), and ΔS is the entropy change of the system. $\Delta G_U = -neU$, where n is the number of transferred electrons and U is the electrode potential. ΔG_{pH} is the correction of the H^+ free energy by the concentration, ΔG_{pH} is given as $k_B T \times \ln 10 \times pH$, where k_B is the Boltzmann constant, and the value of zero pH was set for acidic conditions. Additionally, entropies and zero-point energies of the CO₂RR intermediates were computed from the vibrational frequencies. The band structure, projected density of states (PDOS), work functions, and HOMO-LUMO iso-surfaces were simulated using the GGA-PBE functionals embedded in the Dmol³ code library, while the absorption spectra were simulated using the Vamp code library situated in the material studio.

Accordingly, the adsorption energies (E_{ads}) were calculated by the following equation [47, 48]:

$$E_{ads} = E_{ad/sub} - E_{ad} - E_{sub} \quad (2)$$

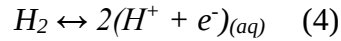
where $E_{ad/sub}$, E_{ad} , and E_{sub} are the energies of the optimized adsorbate/substrate system and the adsorbate in the structure and the substrate, respectively.

Limiting potential, U_L for the entire reduction process is established by the potential-limiting step with the highest positive ΔG (ΔG_{max}), calculated by:

$$U_L = -\Delta G_{max}/e \quad (3)$$

Work function was calculated from electronic result output by using the equation $\Phi = E_{vac} - E_{fermi}$, where E_{vac} and E_{fermi} refer to the vacuum and fermi levels, respectively [49].

In addition, Nørskov et al. [50] describe how the computational hydrogen electrode (CHE), which measures the energy of a proton-electron pair ($H^+ + e^-$) in an aqueous solution, was utilized for the reduction processes by assuming:



and that the free energy change of $*A + H^+ + e^- \rightarrow *AH$ is equivalent to $*A + 1/2H_2(g) \rightarrow *AH$ [51].

3.3 RESULTS AND DISCUSSION

3.3.1 Geometry optimization and Molecular dynamics

To start with, the geometric structure of g-C₃N₅ in a hexagonal unit as shown in Fig. 1a was optimized. The structure consists of 32 atoms, which are 12 carbon atoms and 20 nitrogen atoms per cell, and belongs to the space group P6/m. The lattice parameters after optimization are $a = b = 15.128 \text{ \AA}$, $c = 25 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ [52]. Vacuum layers of thickness of $25 \text{ \AA}$ were added to the z-axis direction to avoid the interaction of neighboring atoms. Followed by the introduction of the graphene (G), HRG-CO, and HRG-COOH on the surface of the g-C₃N₅ (CN)

sheet which was at a distance of 3.545, 3.618, and 3.225 Å respectively after being subjected to further optimization. We observed that all the g-C₃N₅ (CN) in these composites (CN-G and CN-HRG-CO) were planar except for the CN-HRG-COOH which the configuration turns out to be corrugated (see Figure 1c). Interestingly, Azofra [53] and Wang [48] have respectively reported the corrugated structure of g-C₃N₄ and g-C₃N₅ to be more stable than their respective planar structure. This has been proven by their electron localization function (ELF) and molecular electrostatic potential (MEP) [53].

One of the DFT parameters that can be used to assess the stability of a structure is performing the ab initio molecular dynamics. To ascertain the stability of the pristine material as well as the composites, the ab initio molecular dynamics was performed for 2.5 ps with a step size of 0.5 fs between 200-1600 K. The output structure of the ab initio MD simulations shows that the materials are relatively stable with very little configurational change when the highly reduced graphene (HRG) is introduced (figure 2).

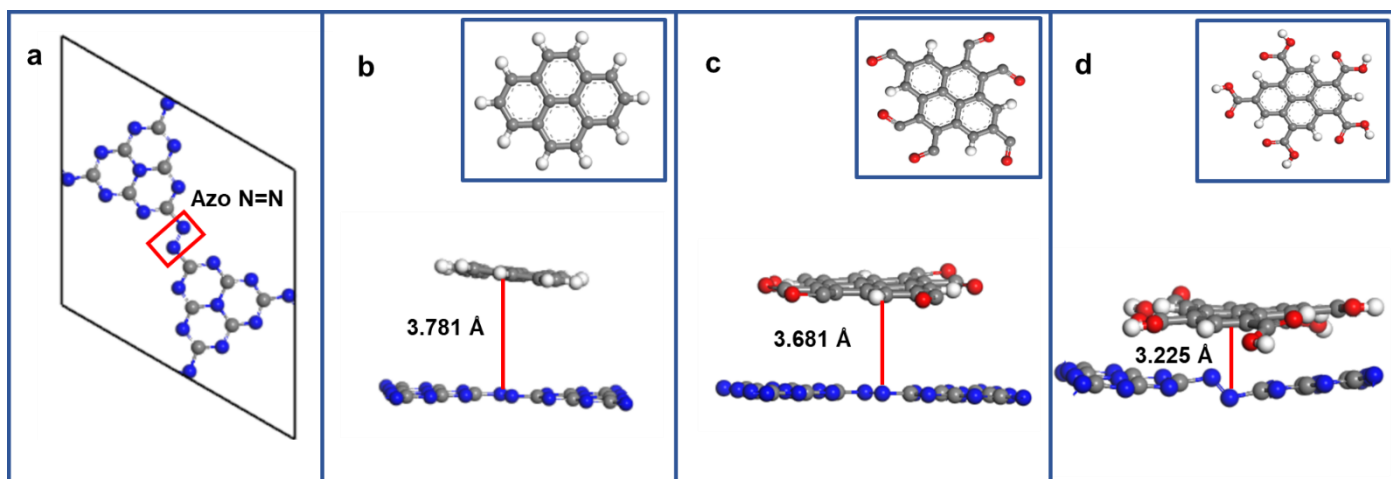


Figure 1. Optimized structure of (a) g-C₃N₅ (CN) (b) CN-G (G-Graphene) (c) CN-HRG-CO and, (d) CN-HRG-COOH.

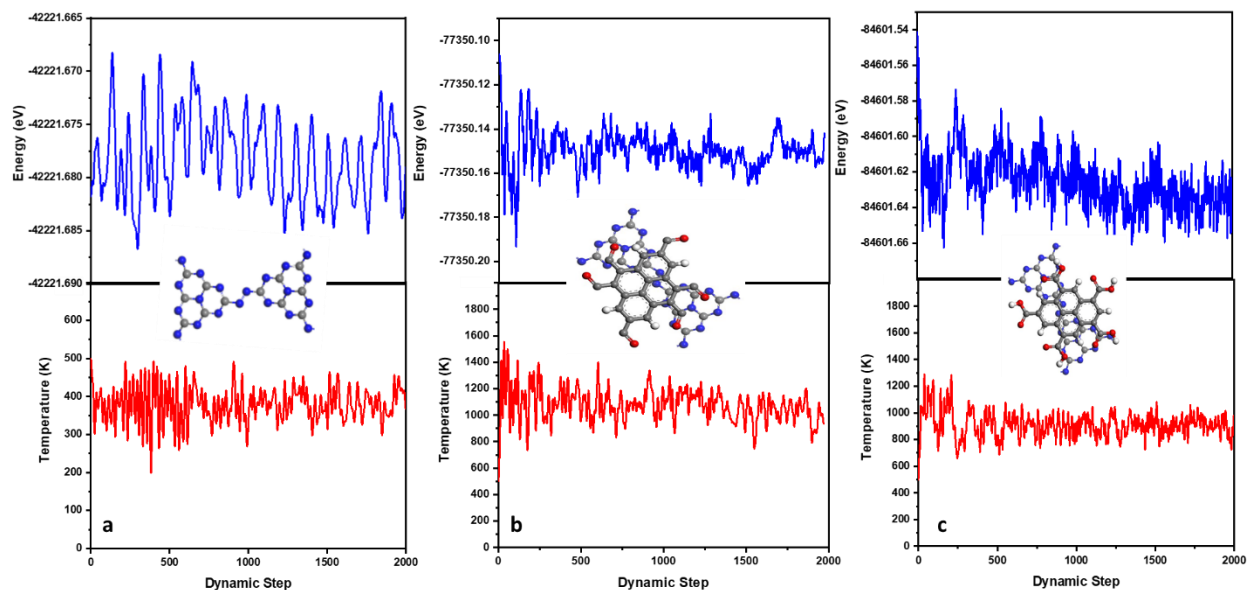


Figure 2. Variations of temperature and energy against time for MD simulations of (a) g-C₃N₅ (CN) (b) CN-HRG-CO (c) CN-HRG-COOH, and the insets show the top view of the snapshot of atomic configuration. The simulation is performed at 200-1600 K for 1 ps with a time step of 0.5 fs.

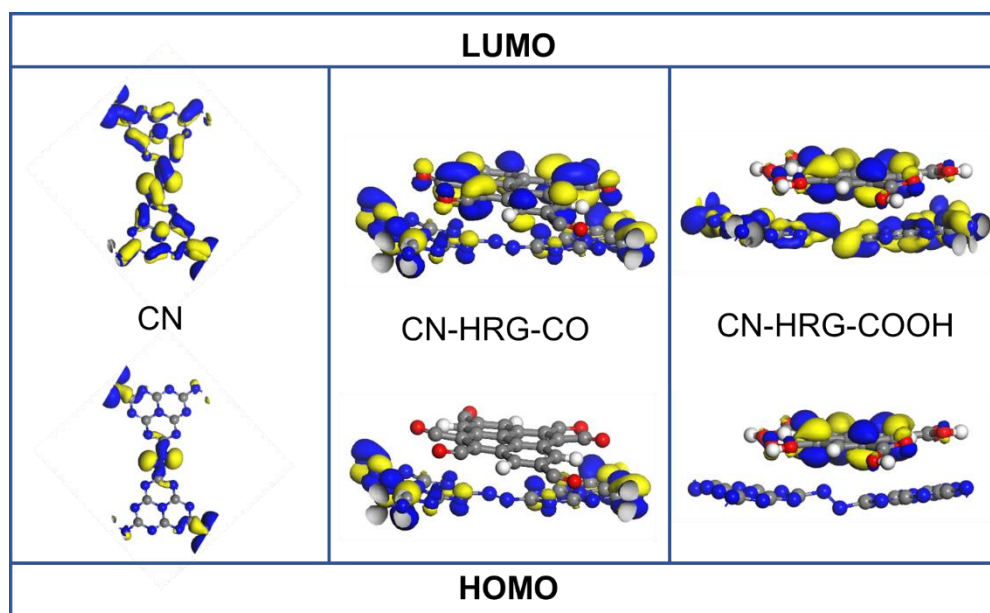


Figure 3. Frontier Molecular Orbital (FMO) of pristine CN (g-C₃N₅) and its respective composites.

3.3.2 Electronic and Optical Properties

Key electronic properties such as bandgap, partial density of state (PDOS), work function, and frontier molecular orbital were all calculated. All these parameters serve as a bedrock for assessing the feasibility of the materials for CO₂RR. The band structure gives an insight into the bandgap inherent in a material, therefore it was observed from the band structure that g-C₃N₅ (CN) has a bandgap of approximately 1.84 eV which is relatively closer to the experimental determination of around 1.76 eV. Other materials exhibited a reduction in bandgap from 1.45 eV for (CN-G), 0.28 eV for (CN-HRG-CO) to 0.54 eV (CN-HRG-COOH) (figure 4). The reduction in bandgap has been associated with ease of separation of photogenerated electron (e^-)/hole (h^+) pairs, and subsequently high reduction potential. PDOS distributions indicate that the CB of g-C₃N₅ and other composites are dominated by C (2p) and N (2p) orbitals (Fig. 11). Additionally, the PDOS also shows that the introduction of HRG leads to a reduction in energy gap, therefore this has been extensively used to wrap semi-conductors leading to an enhancement of the photoinduced carrier separation. Work function (Φ) is the minimum energy needed to eject an electron at the fermi level to the vacuum. To calculate the work function of a system, the equation $\Phi = E_{vac} - E_{fermi}$ was employed, where E_{vac} and E_{fermi} refer to the vacuum and fermi level energy, respectively [49]. The work function is known to give information about the reduction capability of a material. The lower the value of the work function the better electron transport ability to the surface and the better the reduction capability [49]. It was found that the value of the work function reduces from 5.44 eV for CN, 5.33 eV for CN-HRG-CO, and 5.22 eV for CN-HRG-COOH to about 5.01 eV for CN-G (Figure 4). This reveals the potential of these composites for better reduction capacity. However, it is pertinent to mention here that the lowest value of work function observed for the CN-G does not mean it is performing better compared to other composites, the overall properties of all the composites will speak in favor of the best-performing composites.

To examine and understand the effect of HRG on the g-C₃N₅ through electron distribution, the Mulliken population analysis of CN, CN-HRG-CO, and CN-HRG-COOH were all calculated. Mulliken electron distribution also known as the Mulliken atomic charges can be calculated from the population analysis. From the Mulliken atomic charge analysis in Tables 5-7, it was observed that the introduction of the HRG led to a drift in the electronic structure of CN. The azo link nitrogen has a less negative charge (-0.0677) in the pristine CN, this has increased to a more negative charge (-0.08463) upon combination with HRG. Additionally, it was also observed that an increase in the charges of all the atoms of CN after HRG had been incorporated. Therefore, the shift in surface charge distribution is an important parameter to improve the CO₂RR of these composites. Also, an increase in charge implies a large charge transfer between the surfaces and the respective intermediates, which is an indication of good adsorption energies. It is important to mention here that having a moderate charge distribution within the surfaces is better because this will enhance the adsorption-desorption processes for the intermediates and products [49]. Figure 3 is a visualization of the frontier molecular orbital (FMO) of the materials under study. This also proves to us how the electron is being delocalized within the system from HOMO to LUMO level as the HRG is being incorporated.

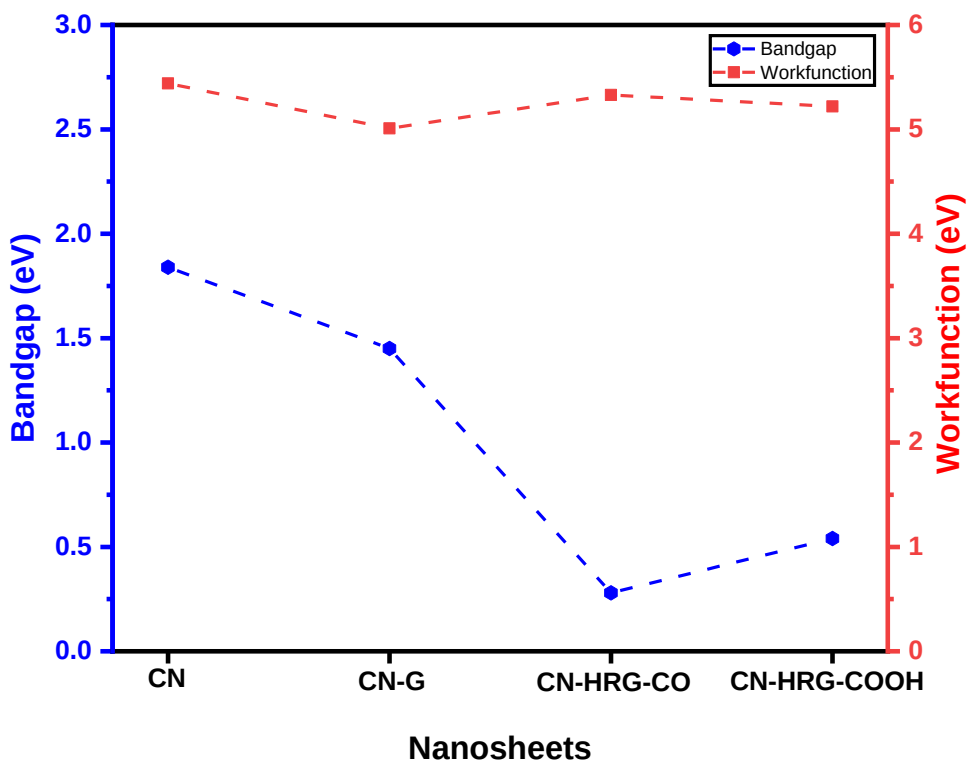


Figure 4. Comparison of the computed band gaps and work functions, both in eV unit, of the pristine $\text{g-C}_3\text{N}_5$ (CN) sheet and its respective heterostructure nanocomposites.

The optical property of photocatalytic material has been considered an important factor for semiconductors to utilize a broad light range within the UV-vis to produce more electron-hole pairs for subsequent reactions [54]. Concerning this, the optical properties of all the composite was calculated and visualized in Figure 5. It can be observed that the pristine CN absorbs light at approximately 356 nm with an absorption edge of 400 nm, this is not too far from the experimental observation of approximately 400 nm with an absorption edge of 560 nm [55]. Additionally, it is obvious that there was an improvement in the light absorption in the UV-vis range when HRG was incorporated. While the CN-G shows absorption at 393 nm, the CN-HRG-CO and CN-HRG-COOH show maximum absorption at 435 and 536 nm respectively. Although the CN-HRG-CO has a low oscillator strength compared to other composites, this has been shown in the inset of Figure 4 separately. The result of our findings revealed that the incorporation of HRG into the

existing CN improves light absorption, which will ultimately provide more photoinduced charge carriers for CO₂RR.

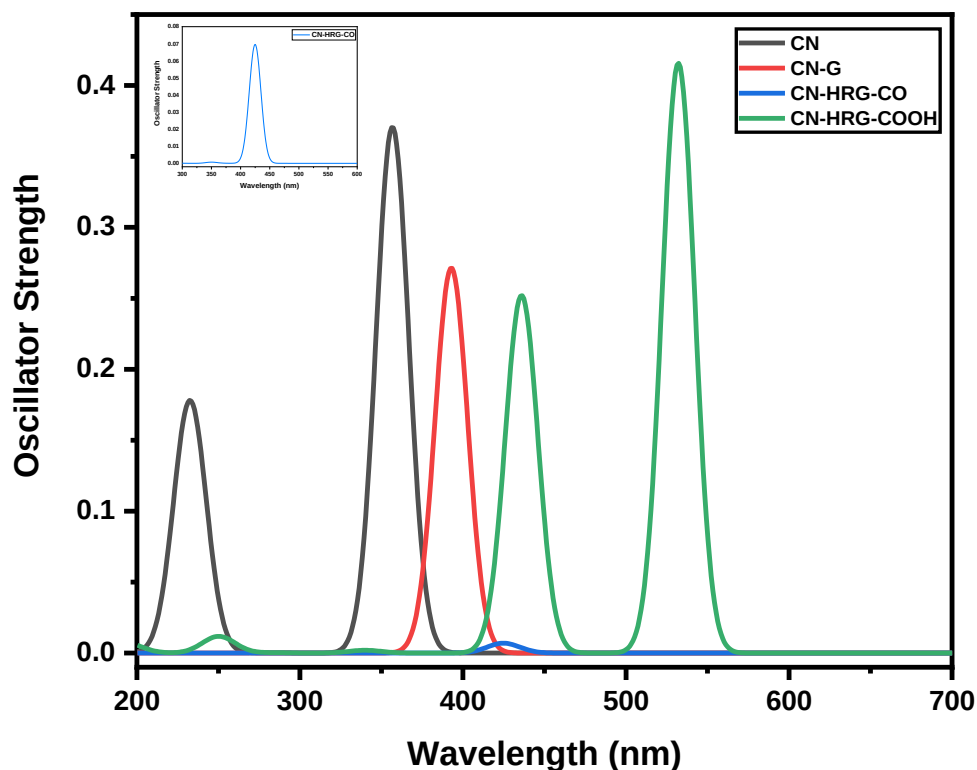


Figure 5. Comparison of the computed UV-Vis absorption spectra, in *nm* unit, of the pristine g-C₃N₅ (CN) sheet and its respective heterostructure nanocomposites. The inset is the absorption spectra of CN-HRG-CO for better visualization.

3.3.3 Adsorption studies

Just as it has been stated in section 3.2 above, all the materials in terms of their electronic and optical properties were screened, and the two most promising composites were selected; these are the CN-HRG-CO and CN-HRG-COOH. One of the important factors in studying the mechanism of reactions over a catalyst is to choose the right adsorption positions. It can be seen from Figure 1 that there are two layers to be explored for the adsorption studies. As for the CN layer, Wang et al. [48], have reported that out of all the possible chemical environments present in the g-C₃N₅, the active site for the CO₂RR pathway is the N₃ atom in —N=N— linkage. Whereas

it was observed that the HRG terminated with CO and COOH all have similar chemical environments. Therefore, the adsorption studies on the surfaces of these two layers were based on them. It is important to also mention that while it was easy for the CN layer to be chemisorbed on the intermediate species, the HRG layer prefer the physisorption mode of interaction with the intermediates. This was ascertained while we intended to make the intermediate species form a chemical bond with the HRG layer which leads to structural deformation of the whole composites. In summary, two prominent adsorption layers were identified for the intermediate species, which are the azo linkage of the CN layer as well the surface of the HRG layer at an optimum distance (figure 1).

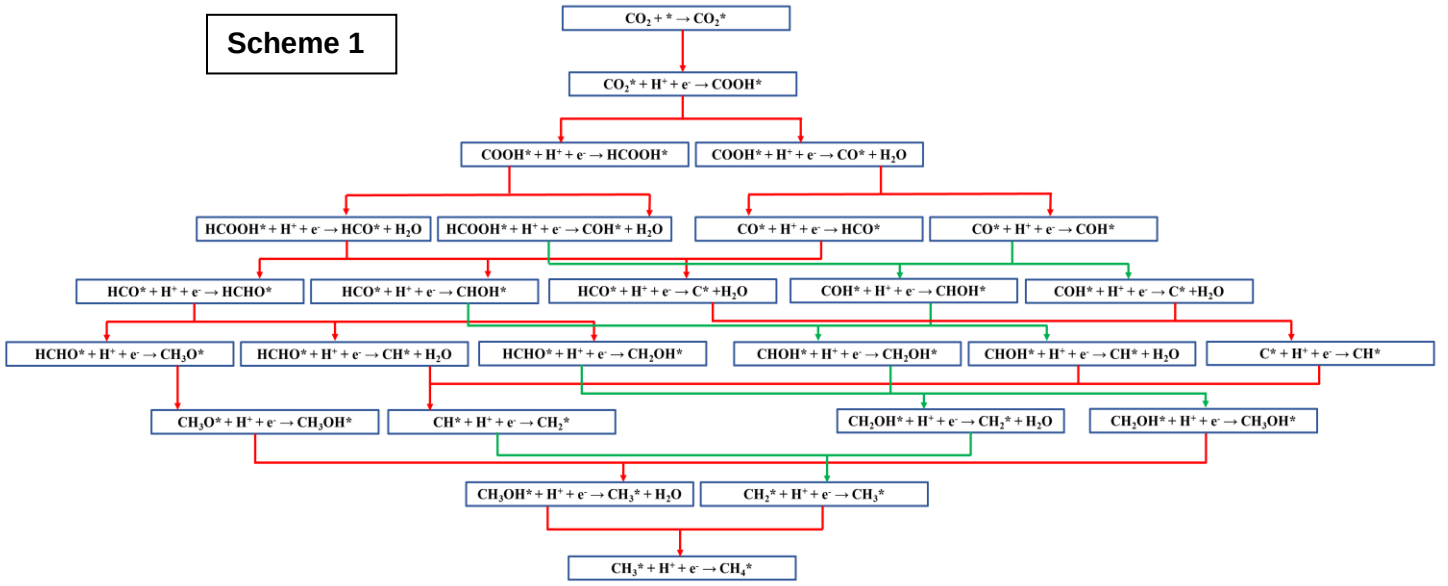
3.3.4 Mechanism of CO₂ Reduction Reaction to C1 product

The possible reaction path that has been followed to study CO₂RR, forming methane and methanol on the surfaces of the two layers of CN-HRG-CO and CN-HRG-COOH is presented in Scheme 1 and 2. The first step has to do with the adsorption of CO₂ on these surfaces in the presence of a reducing agent, for instance, hydrogen. Water was not considered for the reduction process because of the high adsorption affinity of water towards most surfaces as well as the production of oxygen from water which can also be a competitor for the CO₂RR on the surfaces of these layers [56]. Therefore, only hydrogen was utilized as the reducing agent to mimic the experimental approach where hydrogen gas can be employed for the reduction processes. It is very germane to mention here that reduction processes have been carried out using the computational hydrogen electrode (CHE) where proton-coupled electron transfer is accounted for by DFT simulation [50, 51]. The possible intermediate products after the first reduction process could be COOH or HCOO. The subsequent step shall take place by further reduction of the previous intermediate products. These reduction processes could produce either the CO and H₂O or

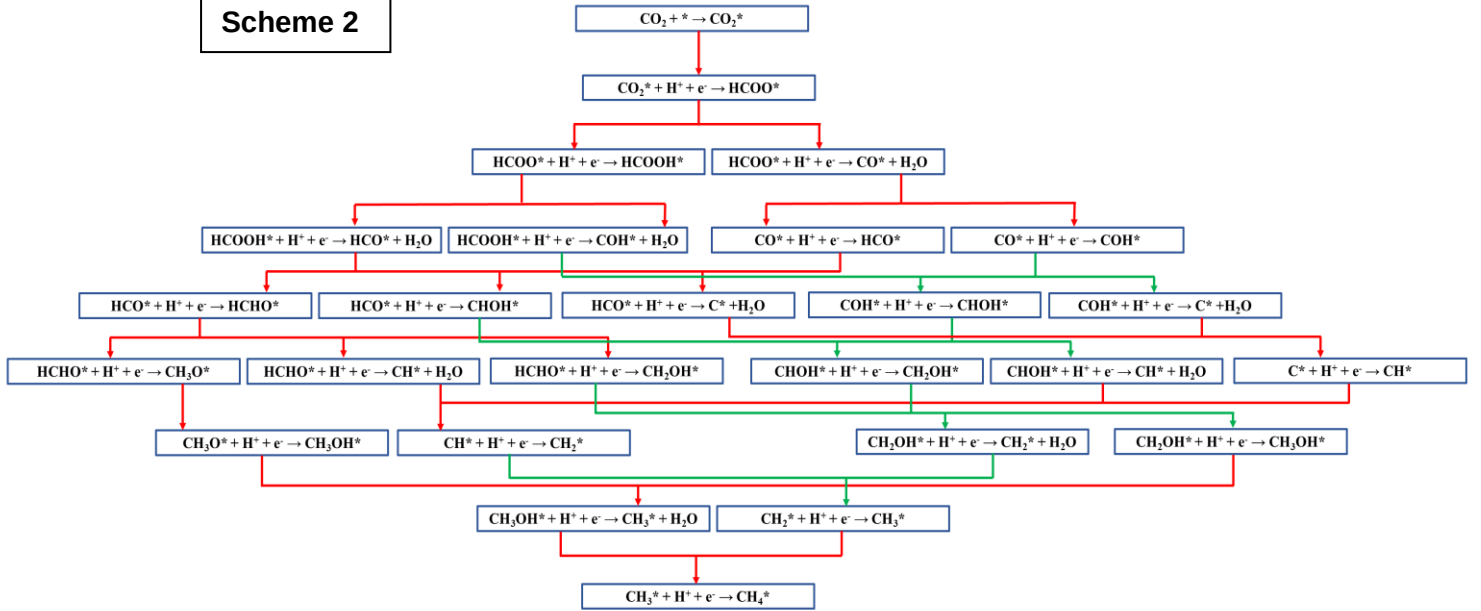
HCOOH. The third step of this reduction process produces two possible intermediates which are HCO and COH. These two intermediate products require either C-H or O-H bond formation. The feasibility of these two bond formations would be clarified by the free energy value. The fourth step of the reduction process requires studying about five reaction paths to produce three intermediates which are CHOH, HCHO, and C(H₂O). While CHOH and C(H₂O) can be obtained from COH after reduction, HCHO can only be obtained from HCO intermediate. The fifth step requires six reaction pathways. With this, three intermediate products could be obtained. These are CH₂OH, CH (H₂O) and CH₃O. It was studied that only the HCHO intermediate can produce the CH₃O, whereas CH₂OH and CH (H₂O) were obtained from the other two intermediates from step four above. The subsequent step, step six, is one of the most crucial steps in these reduction processes because one of the main products could be obtained from it. So, it is possible to have one intermediate product and one main product which are CH₂ and CH₃OH. CH₃OH can trace itself back to CH₂OH and CH₃O, which could be formed by either the C-H or O-H bond, before emerging as one of the possible major products. The seventh and eighth steps only require concurrent reduction of the products of step six to form CH₄ as the final possible product.

In summary, the study on CO₂RR requires about six-eight mechanistic steps with approximately 23 and 28 mechanistic reaction pathways to follow in order to selectively obtain CH₃OH and CH₄ as major products, respectively on each of the studied layers of CN-HRG-CO and CN-HRG-COOH.

Scheme 1



Scheme 2



Scheme 1 & 2: Proposed reaction paths for CO₂ reduction over CN-HRG-CO and CN-HRG-COOH, producing, methanol (CH₃OH) and methane (CH₄).

3.3.5 Catalytic Performance for the CO₂RR on g-C₃N₅ (CN) and Adsorption studies

Wang et al. have studied the catalytic performance of CO₂RR on the g-C₃N₅ to catalyze through the following optimum pathway to C1 products to be: CO₂ → COOH* → CO* → COH* → CHOH* → CH* → CH₂* → CH₃* → CH₄. Whereas the optimum reaction path for the C2 product pathway have been reported as: CO₂ → COOH* → CO* → COH* → CHOH* → CH* → CH₂* → CH₂CO* → CH₂COH* → CH₃COH* → CH₃CHOH* → CH₃CH₂OH. The reduction potentials have been theoretically calculated as -0.54 and -0.61 V respectively [48]. It has also been reported that a complete study and C1 reduction pathway produces CH₃OH and CH₄ as the main products. These invariably depend on the material used for the reduction process [48, 57]. Herein, we studied the adsorption of these viable products on the CN-HRG-CO and CN-HRG-COOH photocatalytic materials. As mentioned above, these two composites are the best-performing photocatalytic materials out of all the studied composites. For the adsorption studies, the azo link nitrogen of the CN has been considered as well as the surface of the HRG at the shortest possible distance to the surface of the CN-HRG-CO and CN-HRG-COOH composites. Therefore, a total of four adsorption studies have been investigated on the surfaces of these two configurations. It has been mentioned that negative adsorption energy indicates that the process is exothermic. Also, the adsorption energy of adsorbates greater than 1 means the adsorbate is chemisorbed on the surface of the catalyst [58, 59]. Table 1 shows the calculated adsorption energy of the reactant and important products for all the catalysts. The adsorption energy of CO₂, CH₃OH, and CH₄ are -0.198/-0.158, -0.745/-0.372, and -0.381/-0.220 eV respectively on the surfaces of CN and HRG layer of the CN-HRG-CO composite. Similarly, the adsorption energy of CO₂, CH₃OH, and CH₄ are -0.218/-0.455, -1.07/-0.727, and -0.608/-0.511 eV respectively on the surfaces of CN and HRG layer of the CN-HRG-COOH composite. These values indicate the adsorption is between weak chemisorption and strong physisorption, except for the adsorption of the CH₃OH on the CN

layer of the CN-HRG-COOH composite, which shows a strong chemisorption. Additionally, the adsorption values of CO₂ on all the adsorption sites show a moderate to weak physisorption, indicating the ease of conversion to other possible intermediates before the eventual products. The large negative value of CH₄ adsorption on the CN layer of the CN-HRG-CO and CN-HRG-COOH indicates that it is likely that the mechanistic reduction studies favor its formation, rather than the HRG layer. Conversely, the lower adsorption energy of the CH₃OH on the HRG layer of CN-HRG-CO and CN-HRG-COOH indicates the ease of desorption of this product when compared to its CN layer counterpart of the two composites. That is because a good catalyst surface has been proven to be the one that has moderate adsorption-desorption energetics.

Table 2. Comparison of the adsorption energy (in eV) of the reactant and products on the surfaces of the modified photocatalytic materials.

CN-HRG-CO			CN-HRG-COOH	
Molecules	Adsorption sites			
	$\Delta E_{ads}CN$	$\Delta E_{ads}HRG$	$\Delta E_{ads}CN$	$\Delta E_{ads}HRG$
CO ₂	-0.198	-0.158	-0.218	-0.455
CH ₃ OH	-0.745	-0.372	-1.07	-0.727
CH ₄	-0.381	-0.22	-0.608	-0.511

3.3.6 The Mechanism of CO₂RR over CN-HRG-CO

As it has been mentioned above, heterojunctions consist of at least two layers, as for the studied system, there are two layers, the CN and HRG layers which are both sandwiched as CN-HRG-CO. Likewise, based on our findings of the adsorption studies for these two layers. Therefore, all possible pathways for the reduction processes were studied. As for the CN layer (Fig. 6a and b), Table 3 shows the ΔG value for each reduction step. For the first step, the ΔG value for CO₂* $\rightarrow$ COOH* is -0.58 eV, while the ΔG value for the CO₂* $\rightarrow$ HCOO* is -1.60 eV.

The ΔG for the latter is too large, therefore it is too adsorbing, and it can affect its reduction process to the next intermediate. Thus, it is not considered. The second step is the reduction of the COOH^* to CO producing H_2O as a by-product. The ΔG is calculated as -0.92 eV which is more adsorbing than the initial step. The following step has to deal with the $\text{H}^+ + \text{e}^-$ attacking either the C or the O of the CO to form HCO or COH. However, the $\Delta G = -0.35 \text{ eV}$ for HCO is more feasible and stable when compared to the ΔG value of formation of COH, 0.60 eV . This intermediate can further be attacked by the pair of $\text{H}^+ + \text{e}^-$ to form either CHOH^* or H_2CO^* . We observed that the ΔG of -1.21 eV for the H_2CO is more feasible when compared to the large formation energy barrier of the CHOH . The next step supplies hydrogen-coupled electrons to H_2CO^* to form either CH_3O^* or CH^* . Similarly, the formation energy (-1.19 eV) of CH^* is quite reasonable than its counterpart with a large negative formation energy. The subsequent reduction reactions feature the three-step reduction with hydrogen to form CH_2^* , CH_3^* , and CH_4 with ΔG values of -1.92 , -1.87 , and -2.35 eV , respectively. Thus, the optimum reaction pathway on the surface of the CN layer is $\text{CO}_2 \rightarrow \text{COOH}^* \rightarrow \text{CO}^* \rightarrow \text{HCO}^* \rightarrow \text{H}_2\text{CO}^* \rightarrow \text{CH}^* \rightarrow \text{CH}_2^* \rightarrow \text{CH}_3^* \rightarrow \text{CH}_4$. The rate-determining step for this reduction process is $\text{HCO}^* \rightarrow \text{H}_2\text{CO}^*$ with a maximum ΔG of 0.87 eV . In addition, the limiting potential is calculated as -0.87 V . Overall reaction for all the reduction steps is given below:



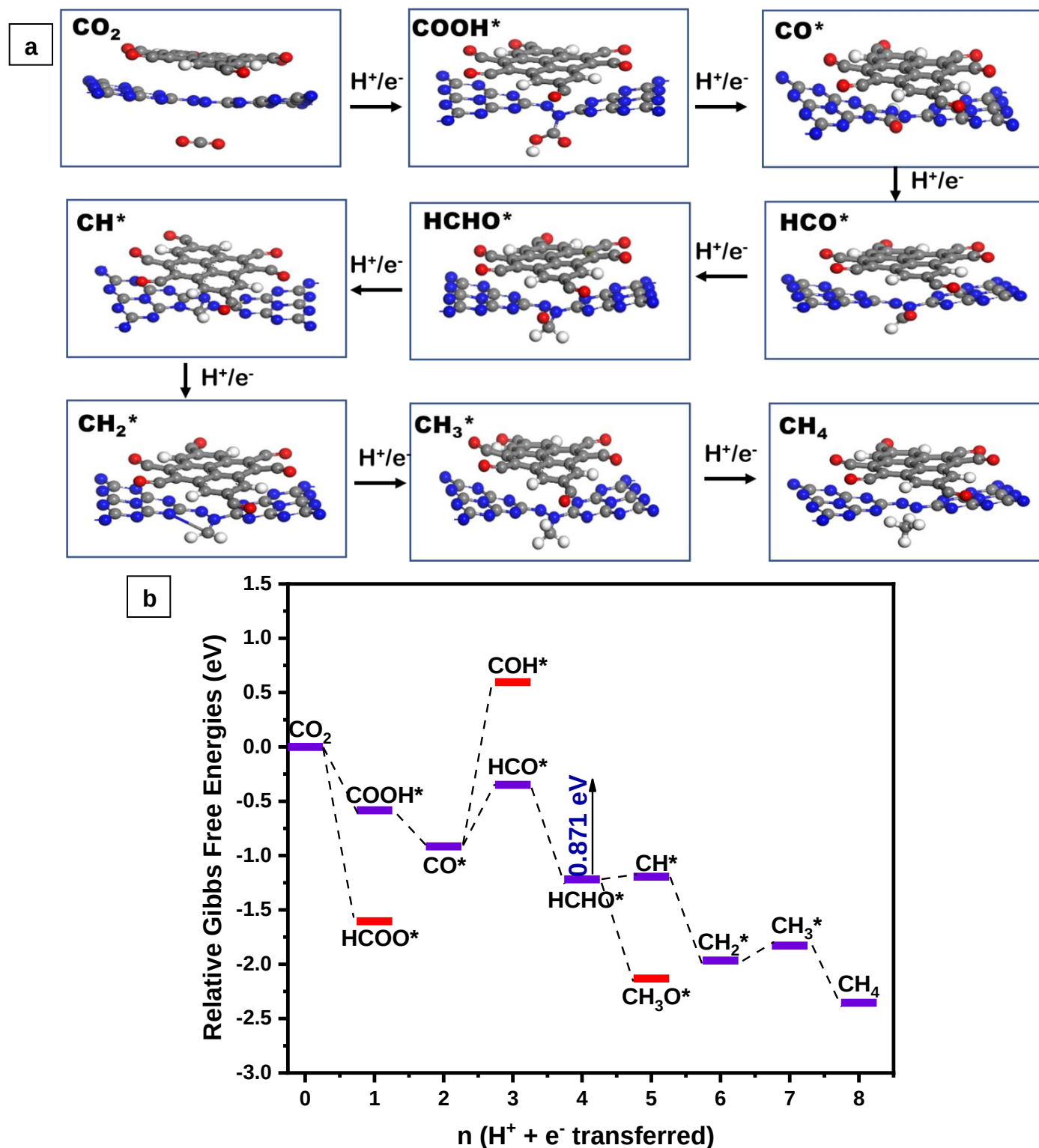


Figure 6. (a) Optimized structures corresponding to the optimal reaction path followed by the CO₂RR on the (CN) adsorption site of CN-HRG-CO (b) Free energy diagram corresponding to the reaction pathway followed by the CO₂RR to CH₄.

As for the HRG layer, it shows a different reduction pathway. While the former features 8 mechanistic pathways, the latter shall enunciate 6 mechanistic reduction steps with different product selectivity (Fig. 7a and b). As shown in Table 3, the first step shows a reduction to two different intermediates as mentioned earlier, these are COOH* and HCOO*. The ΔG value for CO₂* → COOH* is 0.89 eV, while the ΔG value for the CO₂* → HCOO* is 0.26 eV. The ΔG of the former is too large, therefore it is not stable and weakly adsorbing, and this can affect the reduction process of the next intermediate. Thus, it is not considered. The next reduction step produces HCOOH* with a formation energy of 0.30 eV. Although, this is a product the ΔG value shows that it is not stable, therefore, we proceed to the next reduction step. In the third step, H⁺ + e⁻ was used to further reduce HCOOH* to HCO* ($\Delta G = 0.47$ eV) against its possible competitor, COH* ($\Delta G = 1.78$ eV). Furthermore, HCO* was further attacked with H⁺ + e⁻ to produce H₂CO* ($\Delta G = -0.1$ eV) or CHOH* ($\Delta G = 1.37$ eV). It can be seen that H₂CO* formation is more feasible in terms of stability and adsorption than CHOH*. The subsequent steps feature further reduction with proton-coupled electrons to form CH₃O* and CH₃OH with -0.90 and -0.32 eV respectively. Therefore, the optimum reaction pathway on the surface of the HRG layer is CO₂ → HCOO* → HCOOH* → HCO* → H₂CO* → CH₃O* → CH₃OH*. The rate-determining step for this reduction process is H₂CO* → CH₃O* with a maximum ΔG of 0.80 eV. In addition, the limiting potential is calculated as -0.80 V.

In summary, the reduction process on the CN layer follows 8 steps with selectivity towards CH₄, whereas on the HRG layer, it follows 6 steps with selectivity towards CH₃OH. The results of this reduction process agree with our initial calculation of adsorption energies on the surfaces of these layers.



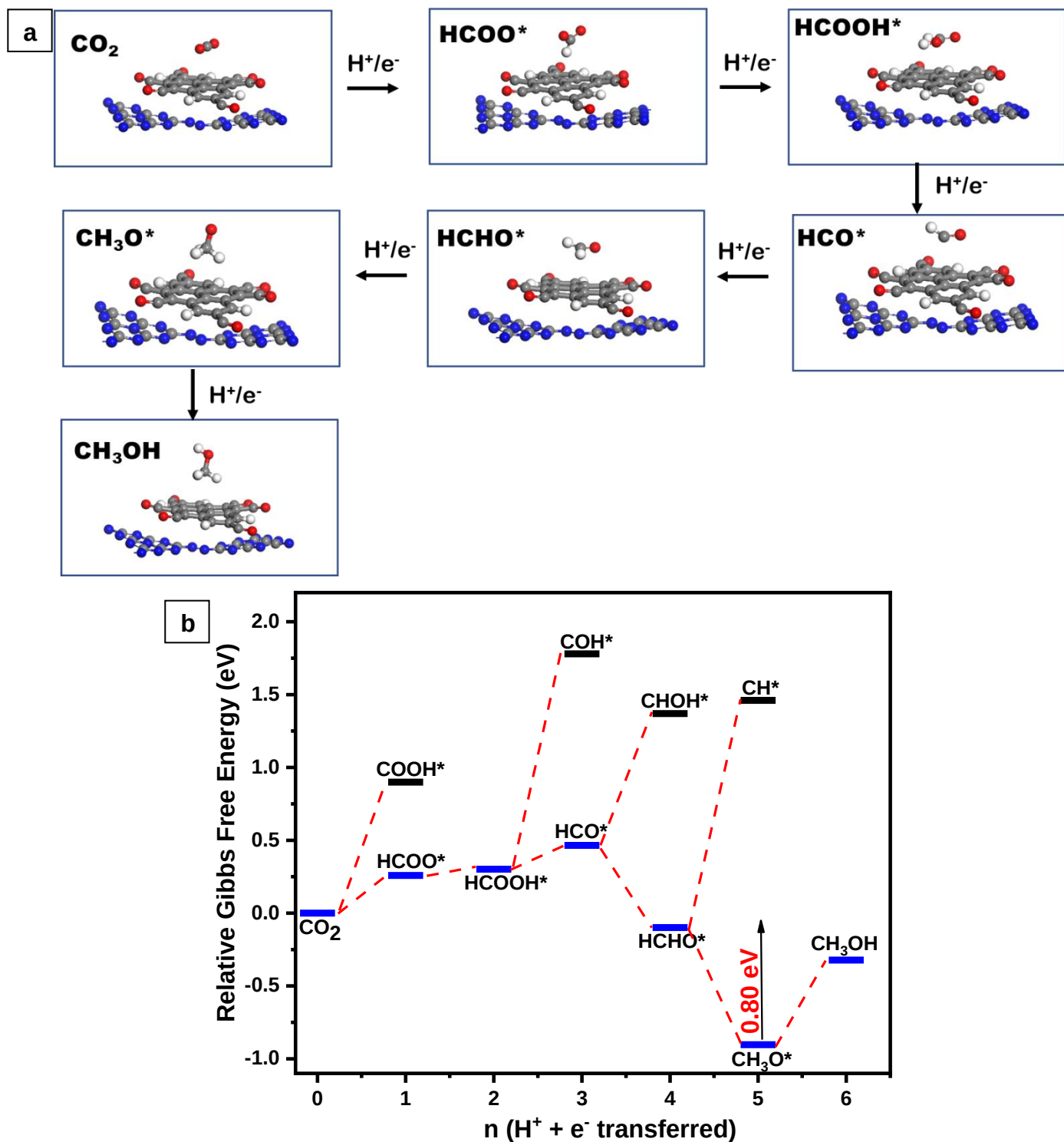


Figure 7. (a) Optimized structures corresponding to the optimal reaction path followed by the CO₂RR on the (HRG) adsorption site of CN-HRG-CO (b) Free energy diagram corresponding to the reaction pathway followed by the CO₂RR to CH₃OH.

3.3.7 The Mechanism of CO₂RR over CN-HRG-COOH

Similar to CN-HRG-CO, the CN-HRG-COOH consists of two layers, these are the CN and HRG layers as well. The surfaces of these two layers were explored based on our prediction in section 3.5, Table 1. Starting with the lower layer, CN (Fig 8a and b), Table 4 shows the computed energy values for this reduction process. The first step reduces CO₂ to two intermediates either by forming the O-H or C-H bond to produce COOH and HCOO respectively. The ΔG value for CO₂* $\rightarrow$ COOH* is 0.074 eV, while the ΔG value for the CO₂* $\rightarrow$ HCOO* is -0.091 eV. This formation energy value shows that HCOO formation is more feasible than COOH. Therefore, we consider this intermediate and move on to the next reduction phase. The HCOO intermediate produced from the previous step is further attacked by $H^+ + e^-$ to produce CO and water as a by-product. It is also possible to form HCOOH, but this is not feasible because of the large value of ΔG compared to the former intermediate. The third reduction step also features C-H and O-H bond formation to produce HCO and COH. However, the COH is not considered because of its weak adsorption on the surface of the catalyst. The intermediate HCO was further attacked by the proton-coupled electrons to produce H₂CO ($\Delta G = 0.064$ eV) and CHOH ($\Delta G = 0.120$ eV). From this, it is obvious that the C-H bond formation is more feasible than its counterpart. The fifth reduction step produces CH₃O and CH (H₂O) with ΔG values of -0.035 and -0.057 eV respectively. Thus, the CH pathway was considered as the feasible intermediate. The subsequent steps (6-8) feature successive reduction with hydrogen to produce CH₂, CH₃, and CH₄ with 0.027, -0.020, and -0.076 eV respectively. Therefore, it can be concluded that the feasible pathway for CO₂RR on the CN layer of this composite is CO₂ $\rightarrow$ HCOO* $\rightarrow$ CO* $\rightarrow$ HCO* $\rightarrow$ H₂CO* $\rightarrow$ CH* $\rightarrow$ CH₂* $\rightarrow$ CH₃* $\rightarrow$ CH₄. The rate-determining step for this reduction process is HCOO* $\rightarrow$ CO* with a maximum ΔG of 0.16 eV. In addition, the limiting potential is calculated as -0.16 V. This is very close to the experimental reduction potential of CO₂ reduction to CH₄ with a potential of -0.25 V [53].

Furthermore, the pathway that could be followed on the topmost layer of this composite was also studied. As shown in Table 4, and Fig. 9a and b, similar to the CN-HRG-CO composite, the first reduction step leads to two different intermediates as mentioned earlier, COOH* and HCOO*. The ΔG value for $\text{CO}_2^* \rightarrow \text{COOH}^*$ is 0.057 eV, while the ΔG value for the $\text{CO}_2^* \rightarrow \text{HCOO}^*$ is -0.053 eV. The ΔG of the former shows that it is quite weakly adsorbing on the surface of the catalyst. Thus, it is not considered. The next reduction step produces HCOOH* and CO (H₂O as a by-product) with formation energies of 0.050 and 0.023 eV respectively. Since CO formation energy seems more feasible than its co-intermediate, then it was preferentially chosen for the next reduction process. In the third step, $\text{H}^+ + \text{e}^-$ was used to further reduce CO* to HCO* ($\Delta G = 0.03$ eV) against its possible competitor, COH* ($\Delta G = -0.1$ eV). Although COH* looks more feasible than HCO*, the energy barrier is quite high, thus we did not consider it as being the potential pathway.

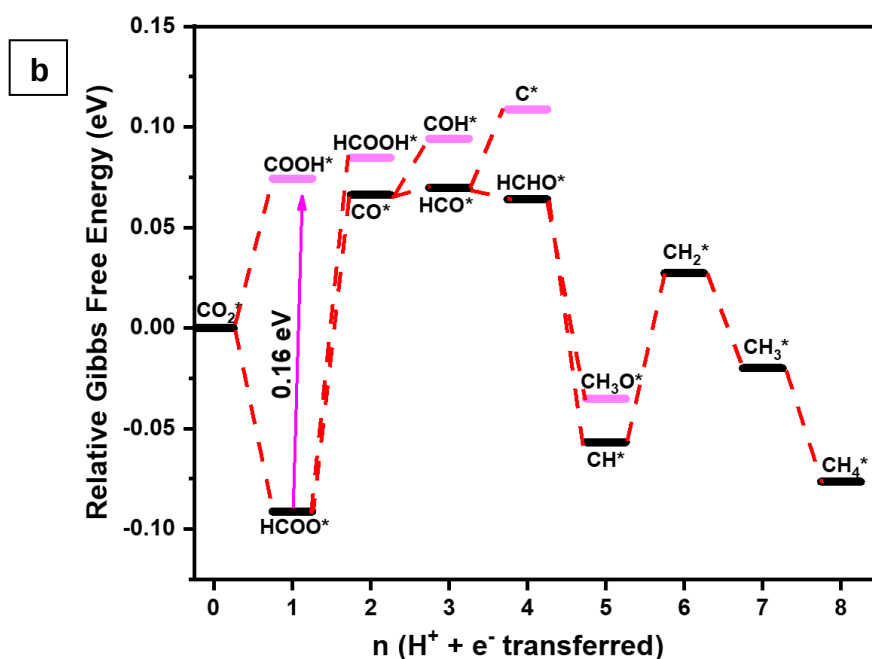
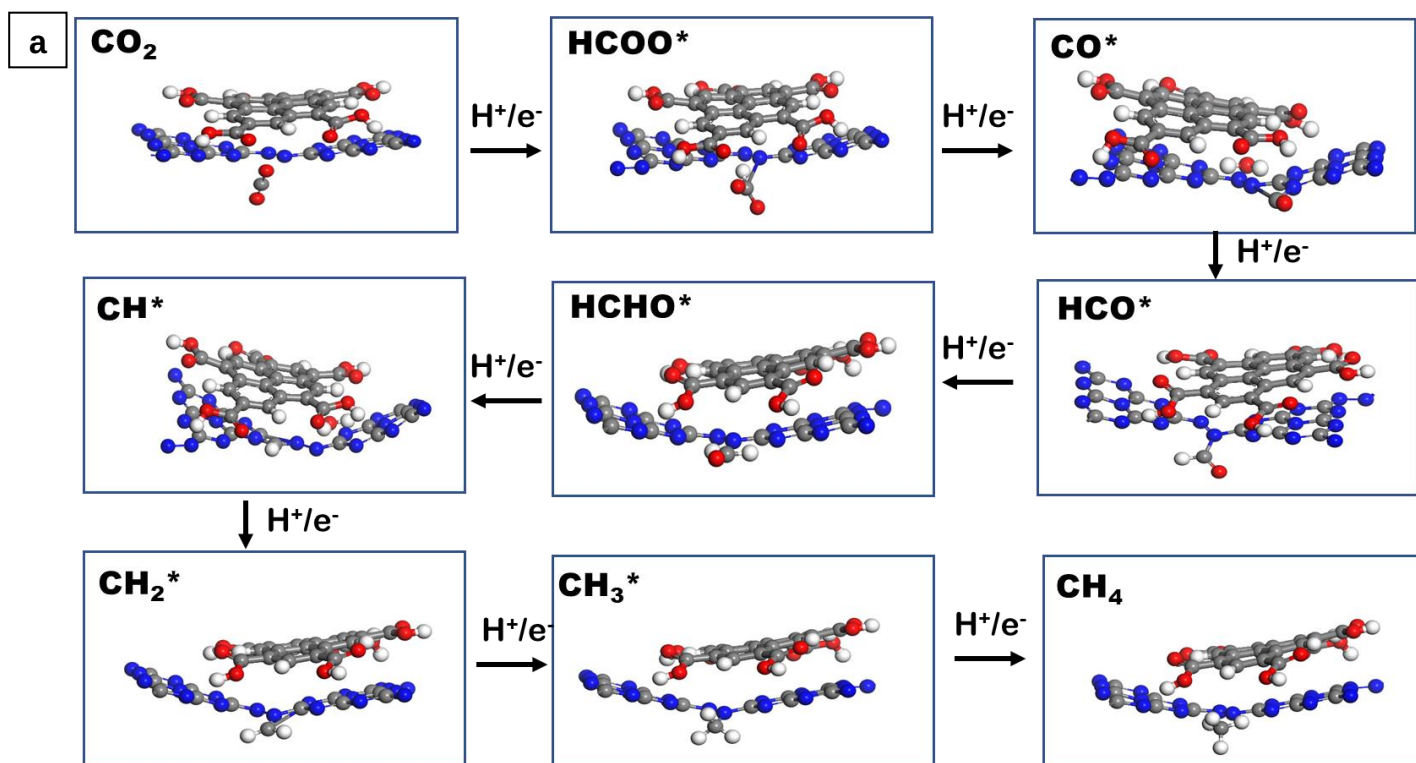
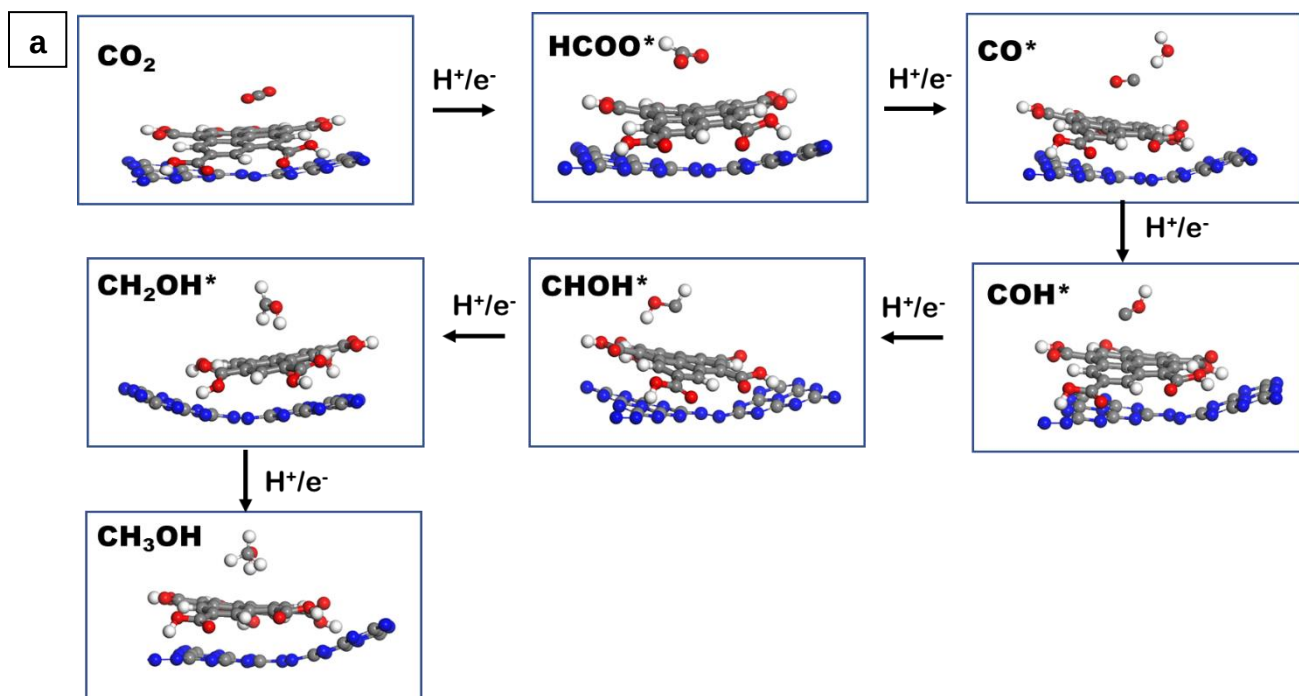


Figure 8. (a) Optimized structures corresponding to the optimal reaction path followed by the CO₂RR on the (CN) adsorption site of CN-HRG-COOH (b) Free energy diagram corresponding to the reaction pathway followed by the CO₂RR to CH₄.

Furthermore, HCO^* was further attacked with $\text{H}^+ + \text{e}^-$ to produce H_2CO^* ($\Delta G = 0.150 \text{ eV}$) or CHOH^* ($\Delta G = 0.055 \text{ eV}$). It can be seen that CHOH^* formation is more feasible in terms of stability and adsorption than H_2CO^* . The subsequent steps feature further reduction with proton-coupled electrons to form CH_2OH^* and CH_3OH with 0.003 and 0.011 eV respectively. Therefore, the optimum reaction pathway on the surface of the HRG layer is $\text{CO}_2 \rightarrow \text{HCOO}^* \rightarrow \text{CO}^* \rightarrow \text{HCO}^* \rightarrow \text{CHOH}^* \rightarrow \text{CH}_2\text{OH}^* \rightarrow \text{CH}_3\text{OH}$. The rate-determining step for this reduction process is similar to the CN layer, $\text{HCOO}^* \rightarrow \text{CO}^*$ with a maximum ΔG of 0.08 eV . In addition, the limiting potential is calculated as -0.08 V. This is quite much lower than the reported experimental value for the reduction of CO_2 to CH_3OH with a potential value of -0.40 V [56].



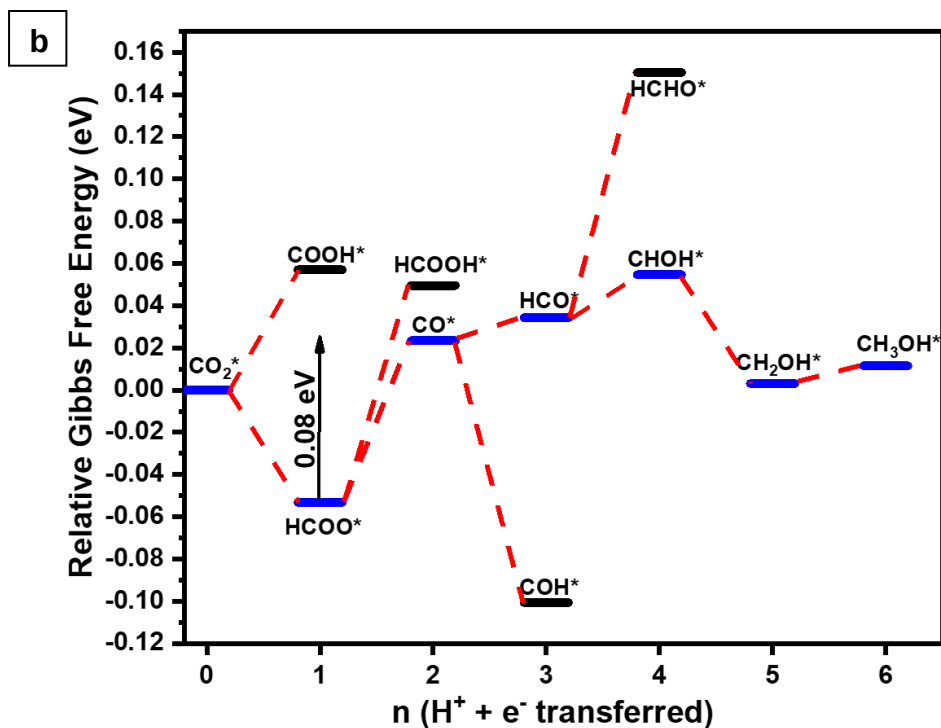


Figure 9. (a) Optimized structures corresponding to the optimal reaction path followed by the CO2RR on the (HRG) adsorption site of CN-HRG-COOH (b) Free energy diagram corresponding to the reaction pathway followed by the CO2RR to CH₃OH.

In general, the photocatalytic reduction of CO₂ has been explored using the two different configurations and on the surfaces of their four layers. While the CN layer of these configurations is going through a longer reduction process with eight mechanistic steps with product selectivity towards CH₄, the upper layer, HRG features six mechanistic steps with product selectivity towards CH₃OH. It can also be observed that the limiting potential is between -0.80 to -0.87 V on the CN-HRG-COOH, whereas the limiting potential window on the CN-HRG-COOH is between -0.08 to -0.16 V. The result of these findings shows that CN-HRG-COOH performs better as a photocatalyst compared to its counterpart. This also corroborates our findings on the electronic and optical properties. Interestingly, the CN and HRG layers in both configurations are selective towards CH₄ and CH₃OH respectively, although through different reduction pathways.

3.3.8 Side reaction - HER

One of the major competing side reactions with CO₂RR is the hydrogen evolution reaction (HER) [60], therefore, the mechanism of HER was investigated to explore its impact on CO₂RR. In one of our submitted papers for HER on these composites, we found out that the minimum ΔG_H^* for HER on CN-HRG-CO and CN-HRG-COOH are 0.16 and 0.39 eV respectively. It can be observed that while ΔG_H^* of CN-HRG-CO is lower than the rate-limiting step for the CO₂RR, ($\Delta G_H^* = 0.39$ eV) of CN-HRG-COOH is larger than the rate-determining step for CO₂RR ($\Delta G = 0.08$ and 0.16 eV). This means that the CN-HRG-COOH has a significant suppressing effect on the HER compared to the CN-HRG-CO, where HER is very easy. Therefore, CN-HRG-CO might not be an efficient photocatalyst for CO₂RR due to the ease of HER. In addition, the difference between the limiting potential of CO₂ (U_L (CO₂)) and H₂ (U_L (H₂)) should determine which configuration is selective towards CO₂RR [61, 62]. As it has been depicted and visualized in Figure 10, the U_L (CO₂ – H₂) on the CN-HRG-COOH is positive, while that of CN-HRG-CO is negative. These findings prove that the CN-HRG-COOH is more selective towards CO₂RR than its counterpart.

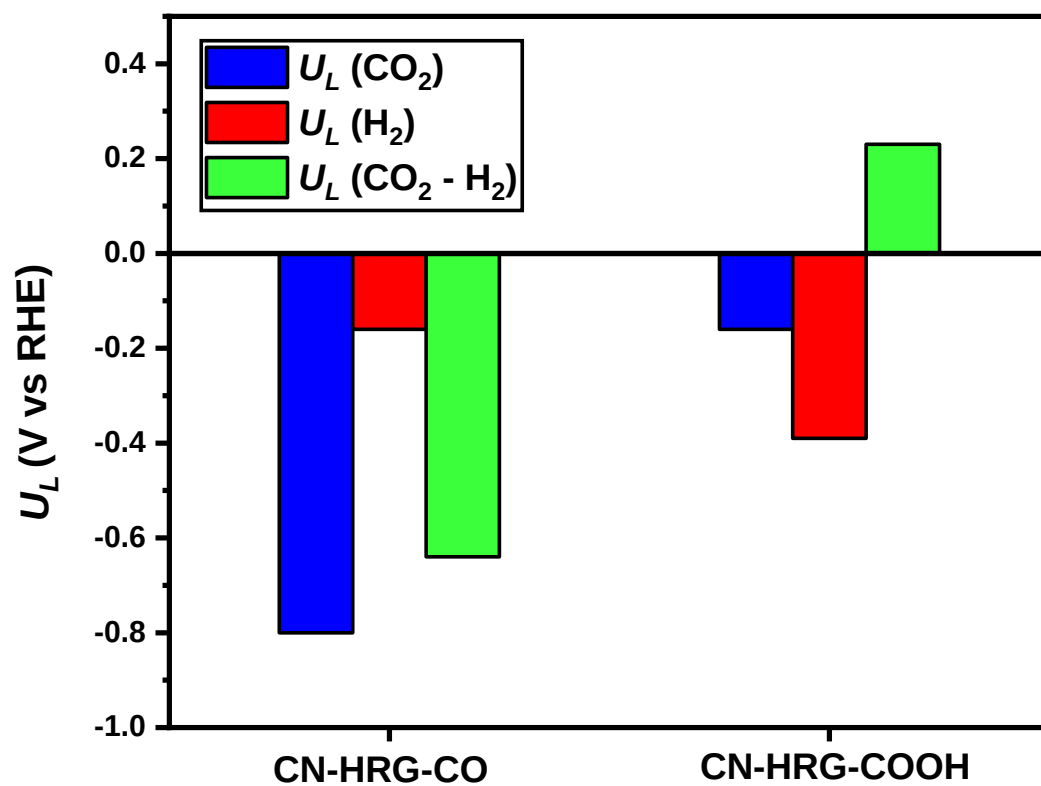


Figure 10. Calculated limiting potential difference for CO₂RR and HER over CN-HRG-CO and CN-HRG-COOH

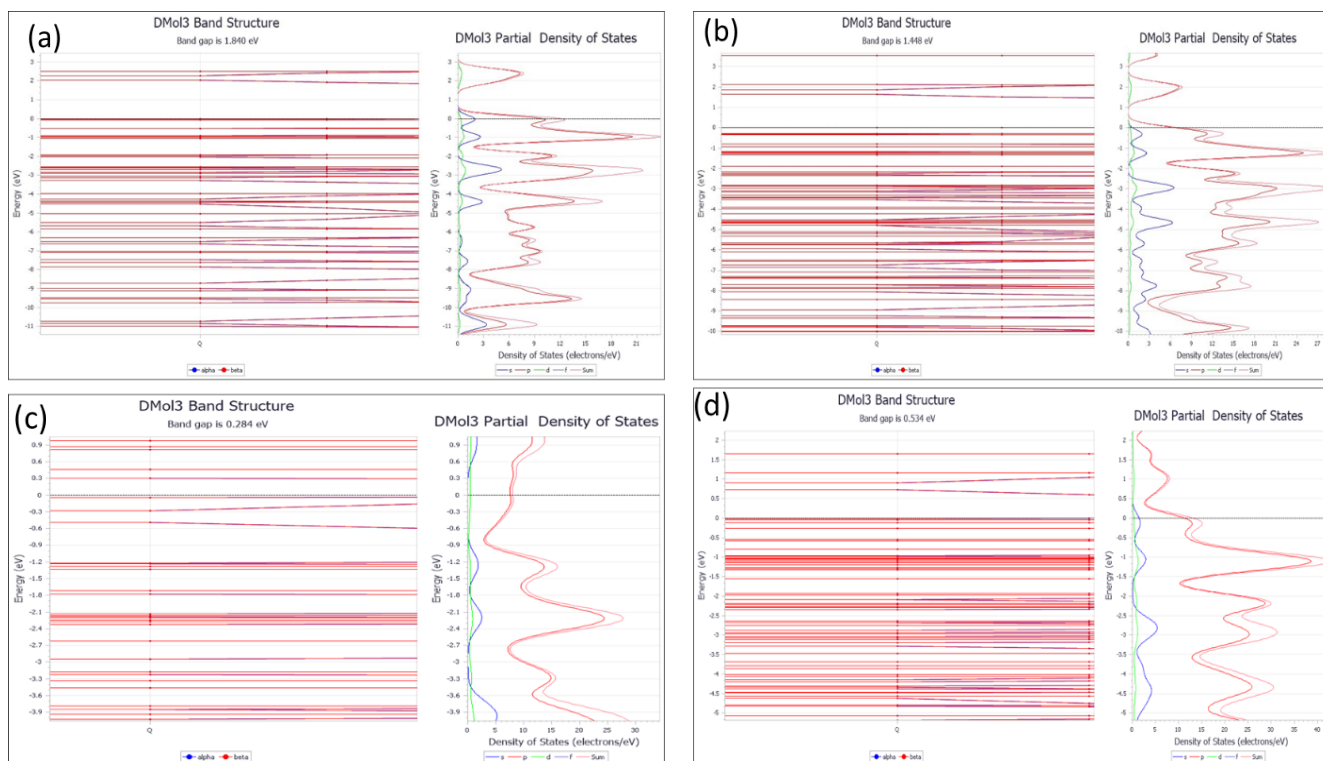


Figure 11: The bandgap and PDOS of (a) CN (b) CN-G (c) CN-HRG-CO (d) CN-HRG-COOH

Table 3. Calculated Gibbs free energy (in eV) of the reaction path followed by CO₂RR to various intermediate products on CN and HRG of the CN-HRG-CO

Pathways		CN	HRG
		ΔG (eV)	ΔG (eV)
1 e-	$\text{CO}_2 + \text{e}^- + \text{H}^+ + * \rightarrow \text{COOH}^*$	-0.58	0.89
	$\text{CO}_2 + \text{e}^- + \text{H}^+ + * \rightarrow \text{HCOO}^*$	-1.60	0.26
2 e-	$\text{COOH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CO}^* + \text{H}_2\text{O}$	-0.92	---
	$\text{HCOO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCOOH} + *$	---	0.30
3 e-	$\text{CO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCO}^*$	-0.35	---
	$\text{CO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{COH}^*$	0.60	---
	$\text{HCOOH} + * + \text{e}^- + \text{H}^+ \rightarrow \text{HCO}^* + \text{H}_2\text{O}$	---	0.47
	$\text{HCOOH} + * + \text{e}^- + \text{H}^+ \rightarrow \text{COH}^* + \text{H}_2\text{O}$	---	1.78
4 e-	$\text{HCO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCHO} + *$	-1.22	-0.10
	$\text{HCO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CHOH}^*$	---	1.37
5 e-	$\text{HCHO} + * + \text{e}^- + \text{H}^+ + * \rightarrow \text{CH}_3\text{O}^*$	2.13	-0.90
	$\text{HCHO} + * + \text{e}^- + \text{H}^+ + * \rightarrow \text{CH}^* + \text{H}_2\text{O}$	-1.19	1.46
6 e-	$\text{CH}_3\text{O}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3\text{OH}$	---	-0.32
	$\text{CH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_2^*$	-1.97	---
7 e-	$\text{CH}_2^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3^*$	-1.83	---
8 e-	$\text{CH}_3^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_4$	-2.35	---

Table 4. Calculated Gibbs free energy (in eV) of the reaction path followed by CO₂RR to various intermediate products on CN and HRG of the CN-HRG-COOH

	Pathways	CN	HRG
		ΔG (eV)	ΔG (eV)
1 e⁻	$\text{CO}_2 + \text{e}^- + \text{H}^+ + * \rightarrow \text{COOH}^*$	0.074	0.057
	$\text{CO}_2 + \text{e}^- + \text{H}^+ + * \rightarrow \text{HCOO}^*$	-0.091	-0.053
2 e⁻	$\text{HCOO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CO}^* + \text{H}_2\text{O}$	0.066	0.023
	$\text{HCOO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCOOH} + *$	0.085	0.050
3 e⁻	$\text{CO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCO}^*$	0.069	0.030
	$\text{CO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{COH}^*$	0.094	-0.100
4 e⁻	$\text{HCO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCHO} + *$	0.064	0.150
	$\text{HCO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CHOH}^*$	0.120	0.055
5 e⁻	$\text{HCHO} + * + \text{e}^- + \text{H}^+ + * \rightarrow \text{CH}_3\text{O}^*$	-0.035	---
	$\text{HCHO} + * + \text{e}^- + \text{H}^+ + * \rightarrow \text{CH}^* + \text{H}_2\text{O}$	-0.057	---
	$\text{CHOH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_2\text{OH}^*$	---	0.003
6 e⁻	$\text{CH}_2\text{OH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3\text{OH}$	---	0.011
	$\text{CH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_2^*$	0.027	---
7 e⁻	$\text{CH}_2^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3^*$	-0.020	---
8 e⁻	$\text{CH}_3^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_4$	-0.076	---

Table 5: Mulliken Atomic charge for g-C₃N₅ (CN)

S/N	Atom	Charge
1)	C	0.197919
2)	C	0.312262
3)	N	-0.16992
4)	N	-0.17341
5)	N	-0.0677
6)	C	0.197919
7)	C	0.312262
8)	N	-0.16992
9)	N	-0.17341
10)	N	-0.0677
11)	C	0.197919
12)	C	0.312262
13)	N	-0.16992
14)	N	-0.17341
15)	N	-0.0677
16)	C	0.197919
17)	C	0.312262
18)	N	-0.16992
19)	N	-0.17341
20)	N	-0.0677
21)	C	0.197919
22)	C	0.312262
23)	N	-0.16992
24)	N	-0.17341
25)	N	-0.0677
26)	C	0.197919
27)	C	0.312262
28)	N	-0.16992

29)	N	-0.17341
30)	N	-0.0677
31)	N	-0.29748
32)	N	-0.29748

Table 6. Mulliken Atomic charge for CN-HRG-CO

S/N	Atom	Charge
1)	C	0.223024
2)	C	0.300107
3)	N	-0.17
4)	N	-0.16703
5)	N	-0.07762
6)	C	0.20537
7)	C	0.280945
8)	N	-0.1774
9)	N	-0.17333
10)	N	-0.06928
11)	C	0.220479
12)	C	0.284695
13)	N	-0.15386
14)	N	-0.18019
15)	N	-0.08463
16)	C	0.219915
17)	C	0.29548
18)	N	-0.16561
19)	N	-0.16364
20)	N	-0.07052
21)	C	0.206083
22)	C	0.280591
23)	N	-0.17798

24)	N	-0.16949
25)	N	-0.06974
26)	C	0.219203
27)	C	0.277324
28)	N	-0.15671
29)	N	-0.18912
30)	N	-0.08747
31)	N	-0.29825
32)	N	-0.29764
33)	C	0.091336
34)	C	0.014884
35)	C	0.020948
36)	C	0.059153
37)	C	-0.00856
38)	C	0.027588
39)	C	0.090172
40)	C	0.045081
41)	C	-0.00549
42)	C	0.050458
43)	C	-0.13648
44)	C	0.085734
45)	C	-0.12044
46)	C	-0.12572
47)	C	0.089899
48)	C	-0.13238
49)	C	0.115055
50)	C	0.128725
51)	H	0.151662
52)	H	0.11197
53)	C	0.158309
54)	O	-0.24753

55)	O	-0.19981
56)	C	0.136522
57)	C	0.128996
58)	C	0.156175
59)	H	0.12102
60)	H	0.134959
61)	O	-0.18297
62)	O	-0.23254
63)	O	-0.2258
64)	O	-0.21465

Table 7. Mulliken Atomic charge for CN-HRG-COOH

S/N	Atom	Charge
1)	C	0.221355
2)	C	0.3184
3)	N	-0.19187
4)	N	-0.18772
5)	N	-0.06426
6)	C	0.209268
7)	C	0.319831
8)	N	-0.20028
9)	N	-0.1966
10)	N	-0.05648
11)	C	0.217794
12)	C	0.321228
13)	N	-0.20555
14)	N	-0.19478
15)	N	-0.04177
16)	C	0.237118
17)	C	0.348062

18)	N	-0.20936
19)	N	-0.24836
20)	N	-0.03919
21)	C	0.212889
22)	C	0.333042
23)	N	-0.20141
24)	N	-0.20516
25)	N	-0.05319
26)	C	0.214857
27)	C	0.344792
28)	N	-0.20837
29)	N	-0.21482
30)	N	-0.04542
31)	N	-0.29629
32)	N	-0.29825
33)	C	0.035497
34)	C	0.026273
35)	C	0.022311
36)	C	0.065325
37)	C	-0.13493
38)	C	-0.02864
39)	C	0.0507
40)	C	-0.15242
41)	C	0.021979
42)	C	0.074785
43)	C	0.003871
44)	C	-0.08751
45)	C	-0.00477
46)	C	-0.16839
47)	C	0.032047
48)	C	-0.10906

49)	H	0.193736
50)	H	0.168341
51)	H	0.157175
52)	H	0.169086
53)	H	0.158012
54)	C	0.472323
55)	O	-0.42138
56)	O	-0.41888
57)	H	0.29372
58)	C	0.490677
59)	O	-0.46544
60)	O	-0.41624
61)	H	0.289676
62)	C	0.492279
63)	O	-0.41074
64)	O	-0.44592
65)	H	0.28939
66)	C	0.464722
67)	O	-0.4232
68)	O	-0.42747
69)	H	0.28731
70)	C	0.48093
71)	O	-0.40891
72)	O	-0.43698
73)	H	0.2812

CHAPTER 4

THE FIRST PRINCIPLE STUDY TO INVESTIGATE THE POTENTIAL OF CARBON NITRIDE-MODIFIED HIGHLY REDUCED GRAPHENE FOR HYDROGEN EVOLUTION REACTION (HER)

4.1 INTRODUCTION

The emerging industrial activities have brought to attention the challenges associated with acute energy shortage and environmental degradation procedures, making the establishment of sustainable and clean energy protocols on a worldwide scale imperative. [63-66]. From this angle, hydrogen energy is considered an ultraclean and potent substitute to address future fuel needs because it contributes hugely to the gravimetric energy density compared to other chemical fuels [67, 68]. The most effective hydrogen evolution reaction (HER) catalysts at the moment are noble metals, like platinum and its alloys, which have been characterized by their powerful catalytic performance at low overpotential and closely zero Gibbs free energy of hydrogen adsorption on the catalyst surface [69, 70]. Unfortunately, their high price and scarcity make them very challenging to employ broadly. Therefore, it has become essential to explore earth-available, stable, reasonably priced, and potentially active alternative catalysts suitable for hydrogen evolution reactions. Myriads of interesting HER non-Pt electrocatalysts have been developed and assessed [71, 72]. Examples include nitrides [73, 74], non-noble transition metals (Fe, Co, Ni) [75, 76], metal-free catalysts including boron-doped graphene [77] or nitrogen-doped graphene [78], fullerenol [79], carbon nanotubes [80], g-C₃N₄ [81], in addition to transition-metal phosphides, e.g. CoP [82] and Ni₂P [83], Mo₂C carbide [84], and pyrite-type cobalt phosphosulfide, which is

presently considered among the best performing non-platinum catalysts [85]. Moreover, molecular simulation tools have been intensively used to build fundamental understanding of electro- and photocatalytic H₂ production routes at the atomistic level. These tools not only offer deeper insights into the mechanistic features of HER pathways, but also help experimentalists to design new and efficient catalysts with much less cost. An inherent bandgap is typically required for photocatalytic HERs. Photocatalysts would absorb specific wavelengths of light depending on their bandgaps when exposed to sunlight. A minimum photon energy can excite electrons from the valence band maximum and cause them to jump into the conduction band minimum when the excitation energy is higher than or at least matching the bandgap associated with the photocatalyst. Consequently, the valence band retains the photogenerated holes (h^+) while the conduction band introduces photogenerated electrons (e^-). Photogenerated holes and electrons can oxidize and reduce, respectively, a molecule depending on what is required by the analyte [86].

In recent years, a growing interest has been shown in metal-free catalysts, especially graphitic carbon nitride polymeric materials. In comparison to the conventional g-C₃N₄ carbon nitride family, the g-C₃N₅ based nanostructured sheets are considered emerging and attractive due to their superior conductivity, visible-light response, and the higher N/C ratio for a possibly optimal adsorption capability and improved electron transport [87-91]. In terms of photoactivity, bulk g-C₃N₅ needs to be improved in regard to the photogenerated carrier dynamics. Therefore, methods, such as element and ion doping [96-99] and heterostructure engineering [92-95], have been implemented. Also, Z-scheme heterojunction catalysts were found to be very useful not only because they help beat large overpotentials but also due to their increasing photocatalytic performance [100, 101]. It should be mentioned that theoretical studies aiming to develop feasible manners that can improve the photoactivity of g-C₃N₅ as an HER based catalyst are still limited.

Recently, a promising 2D sandwich-like nanosheet heterostructure, referred to as g-C₃N₅/highly reduced graphene (C₃N₅/HRG), has been reported by Linzhen et al. The well-designed 2D/2D nanosheet heterojunction was shown to have an outstanding migration efficiency, to significantly reduce the recombination of electrons/holes produced by the light stimulation, and to boost the photophysical process, leading to an increase in the non-equilibrium carrier concentration [102]. Herein, in this study and using the density functional theory (DFT), the g-C₃N₅ modified highly reduced graphene (CN-HRG) has been evaluated as an active nanolayered surface for HERs. Fundamental electronic properties, including the bandgaps, densities of states, and work functions, have been used as screening criteria for the catalytic activity of these non-metal materials. The Gibbs free energy of hydrogen adsorption-desorption steps can be assessed by applying either carboxylic acid or carbonyl functionalities on the graphene sheet. The Volmer-Heyrovsky and Volmer-Tafel HER mechanisms in the acidic medium have been studied by evaluating the accessible energy paths.

4.2 Computational Details

All simulation studies were conducted using DMol³ embedded within the Materials Studio software [103]. To optimize the geometric structures including the Van der Waals correction, the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) was adopted (Figure 1). The double numerical plus polarization (DNP) basis set was employed for treating the valence electrons. We set the cutoff energy quality to fine, and adopted the 4×4×1 Monkhorst–Pack k-mesh for all systems. In addition, the spin polarization scheme was used [104]. The vacuum layer with a thickness of around 20 Å was set along the c direction to prevent any interaction between adjacent structures. In order to better determine and understand the interaction between intermediates and g-C₃N₅, the Grimme’s method (DFT-D3) was adopted for all surface

interaction calculations [105]. An energy tolerance of 1.0×10^{-5} Ha, a maximum force tolerance of 0.002 Ha/Å, and a maximum displacement tolerance of 0.05 Å were set for the convergence criteria for the structural optimization. In tandem with the computational hydrogen electrode method and HER reaction pathways, the change in Gibbs free energy of H adsorption (ΔG_{H^*}) can be calculated (Tables 8 and 9) using the thermodynamic process of the H intermediate as:

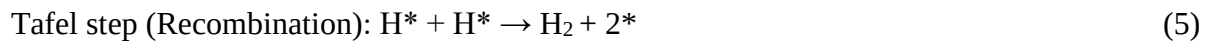
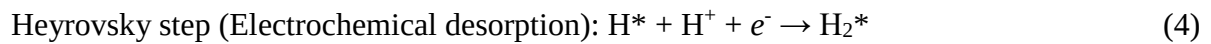
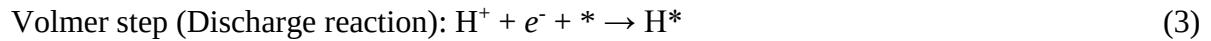
$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U \quad (1)$$

where ΔE_{H^*} is the energy change of adsorption of an H intermediate, and ΔE_{H^*} is given by $E_{H^*} - E^* - E_{1/2H_2}$, ΔE_{ZPE} is the change in zero-point energy, T is the absolute temperature (set at 298.15 K), and ΔS is the entropy change of the system. The effect of the applied electrode potential, U , is catered for by G_U , which is set to $-eU$. The effect of the pH is accounted for by the G_{pH} term which is calculated by the H^+ concentration dependence given by $-kT\ln[H^+]$ [106]. Since the contribution of ΔG_{pH} is quite negligible, therefore, we disregarded it in all calculations. The energy of adsorption (E_{ads}) of the adsorption processes was calculated by [107]:

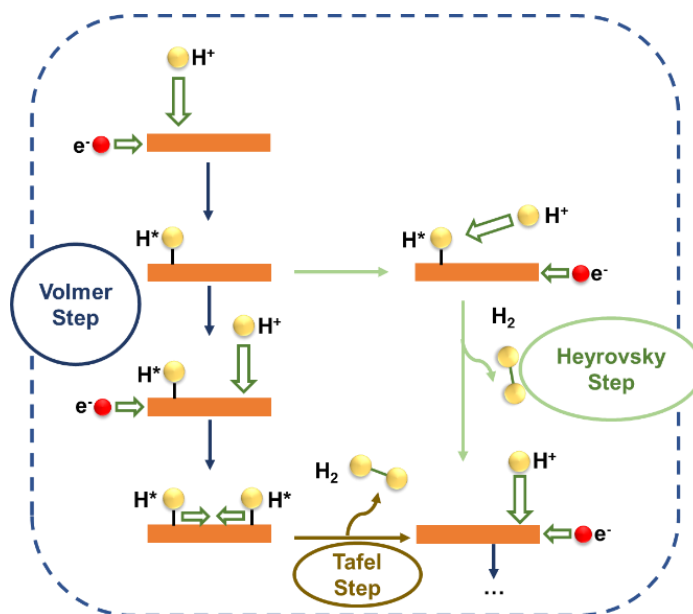
$$E_{ads} = E_{ad/sub} - E_{ad} - E_{sub} \quad (2)$$

where $E_{ad/sub}$ is the energy of the optimized adsorbate substrate system, E_{ad} is the energy of the adsorbate in the structure, and E_{sub} is the energy of the optimized nano-substrate.

Furthermore, the chemical equations below represent the possible HER pathway (Scheme 3) revealed from the reaction kinetics, and calculated as follows in the acidic medium:



The selection of the acidic medium has been made in this study as the alkaline medium lacks a supply of H^+ ions at the initial step, which is needed for the HER to emanate. Thus, a great amount of energy is required for the process to occur, which invariably shows inferior catalytic performance in the alkaline medium [116].



Scheme 3. A schematic pathway for the hydrogen evolution reaction (HER) under acidic conditions.

4.3 Results and Discussion:

4.3.1 Electronic properties

The electronic properties of four models of nanomaterials were investigated and compared. The band structure and work function of pristine $g-C_3N_5$ (CN) were computed and compared with those for the heterostructures of $g-C_3N_5$ /graphene (CN-G), $g-C_3N_5$ /highly reduced graphene functionalized with carbonyl groups (CN-HRG-CO), and $g-C_3N_5$ /highly reduced graphene functionalized with carboxylic acid groups (CN-HRG-COOH). The band structures (Figure 11) provide the details of the bandgaps, which were calculated for the four catalytic materials to be

1.84, 1.45, 0.28, and 0.53 eV, respectively (Figure 12). As the modified material is incorporated, the significant decrease in the bandgap values suggests the ease of separating photogenerated electron (e^-)/hole (h^+) pairs, which is required to drive reduction and adsorption reactions of interest. It can be also noticed that the functionalized graphene layers have more impact on the band gap size compared to the non-functionalized analogue. As reported by Sue-Faye *et al.*, the work function (Φ) has been defined as the minimum energy required for an electron to jump from the Fermi level into the vacuum. Therefore, the equation $\Phi = E_{\text{vac}} - E_{\text{fermi}}$ has been deployed to calculate the work function, where E_{vac} and E_{fermi} refer to the vacuum and fermi level energies, respectively [108]. As depicted in Figure 12, it can be observed that the incorporation of a highly reduced graphene (HRG) sheet leads to a slight decrease in the value of the work function, indicating the improvement in the ability of the electron flow to the surface of the catalyst to partake in the catalytic reduction process [108]. Hence, the combined effect of both the band structure and work function properties indicate the potential of CN-HRG-CO and CN-HRG-COOH heterostructures as promising candidates for the catalytic HER process.

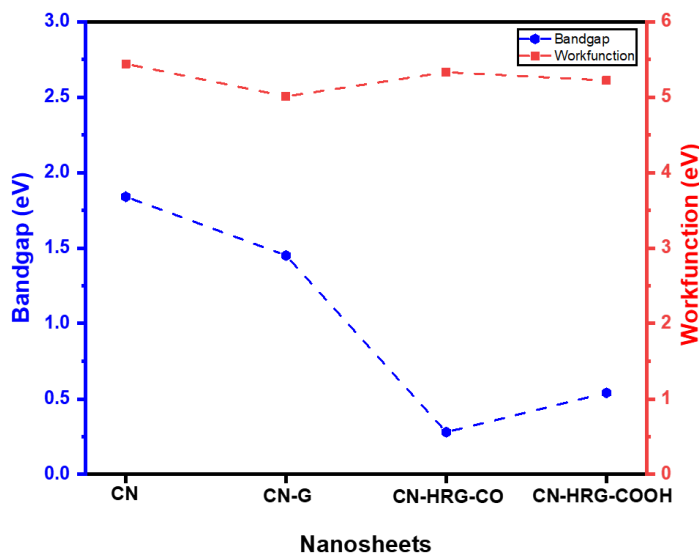


Figure 12. Comparison of the computed band gaps and work functions, both in eV unit, of the pristine $\text{g-C}_3\text{N}_5$ (CN) sheet and its respective heterostructure nanocomposites.

4.3.2. Energy profiles of HER over CN-HRG-CO and CN-HRG-COOH

The change in Gibbs free energy of H adsorption (ΔG_{H^*}) is considered an essential parameter to assess the HER activity towards electro- and photocatalysts either in acidic or basic media. To the best of knowledge, HER mechanisms associated with carbon-modified highly reduced graphenes have not been explored yet [109]. To pursue this direction, this study was designed to gain insights into the HER activity by employing CN-HRG-CO and CN-HRG-CO 2D/2D catalysts and simulating possible sites feasible for the adsorption process. As depicted in Figure 13, both sides can be explored for their catalytic activity; the g-C₃N₅ layer and the HRG-CO or HRG-COOH layers. Recently, Wang et al. reported that the azo-link nitrogen (N=N) of the g-C₃N₅ has a higher reduction capability than any other site in the moiety. This is attributed to the participation of the nitrogen lone pairs with the extended conjugated networks of the heptazine motifs in the system. In general, hydrogen adsorptions on both layers through the N=N and carbon adsorption sites have been explored either at a distance or chemically bonded to the identified adsorption site. A key indicator of HER activity is the free energy change of the atomic hydrogen adsorbed on a catalyst surface; denoted as ΔG_H [110]. When ΔG_H is close to zero, an ideal HER activity can be accomplished, indicating that the free energy of adsorbed H is nearly equal to that of the reactant or product. When ΔG_H is high, on the other hand, it will cause the protons to bond too weakly to the surface of the catalyst, invariably slowing down the HER kinetics. Also, low ΔG_H value reflects a strong adsorption taking place leading to a very stable bonding of the adsorbed hydrogen atom.

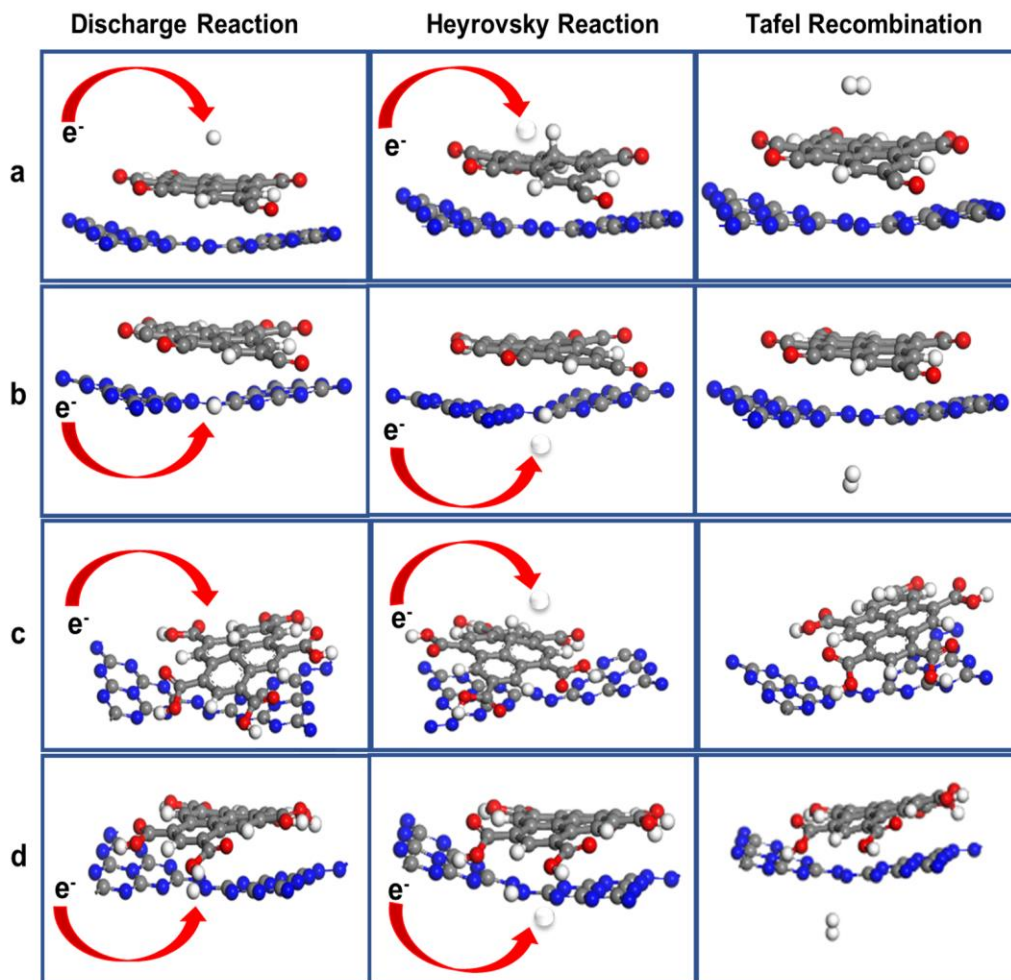


Figure 13. Optimized geometries of the adsorption steps of hydrogen on the (a) HRG and (b) CN layers of the CN-HRG-CO nanocatalyst; and on the (c) HRG and (d) CN layers of the CN-HRG-COOH nanocatalyst for HER.

The free energy diagram of the hydrogen adsorption on CN-HRG-CO is depicted in Figure 14a. It shows that ΔG_H using HRG-CO was calculated to be 1.36 eV when hydrogen is weakly interacting with the HRG layer (denoted as HRG-D) and 0.53 eV when the hydrogen is chemically bonded to the nanolayer (denoted as HRG-A). The latter value predicts more feasibility of reduction when chemical bonding takes place, unlike the case of weak interaction between hydrogen atom and the carbonyl-functionalized HRG. Moreover, the free energy changes of the hydrogen adsorbed on the CN side were calculated to be -0.16 and -0.17 eV for CN-D and CN-A

possibilities. These values show a stronger affinity towards the graphitic carbon nitride for HER rather than HRG-CO. In addition to the extended π -conjugation across the CN skeleton, it could be due to the lone pair of electrons on the nitrogen, facilitating a more meaningful interaction with the incoming proton. That should mediate a good electron transfer to hydrogen resulting in a better adsorption. As for the CN-HRG-COOH, similar adsorption fashions were computed (Figure 14b). The simulated ΔG_H for HRG-D, HRG-A, CN-D, and CN-A were predicted to be 0.41, 0.39, -0.46 and -0.48 eV, respectively. These results show that each site is closely related to the corresponding free energy of adsorption values. The values of the HRG and CN adsorption sites are noticed to be far from each other in terms of positive to negative free energy. In the HRG context, it may be due to the lower reduction capability of the HRG-COOH site, as the carboxylic groups compete for electrons with the hydrogen. Also, for the CN layer, the results predict a little charge transfer between the two nanolayers. Therefore, it is rich in electrons, giving it a stronger adsorption capability towards hydrogen atoms. Overall, it can be concluded that out of CN-HRG-CO and CN-HRG-COOH configurations, the carbonyl functionalized graphene double-layered with g-C₃N₅ represents more potential HER performance over its counterpart.

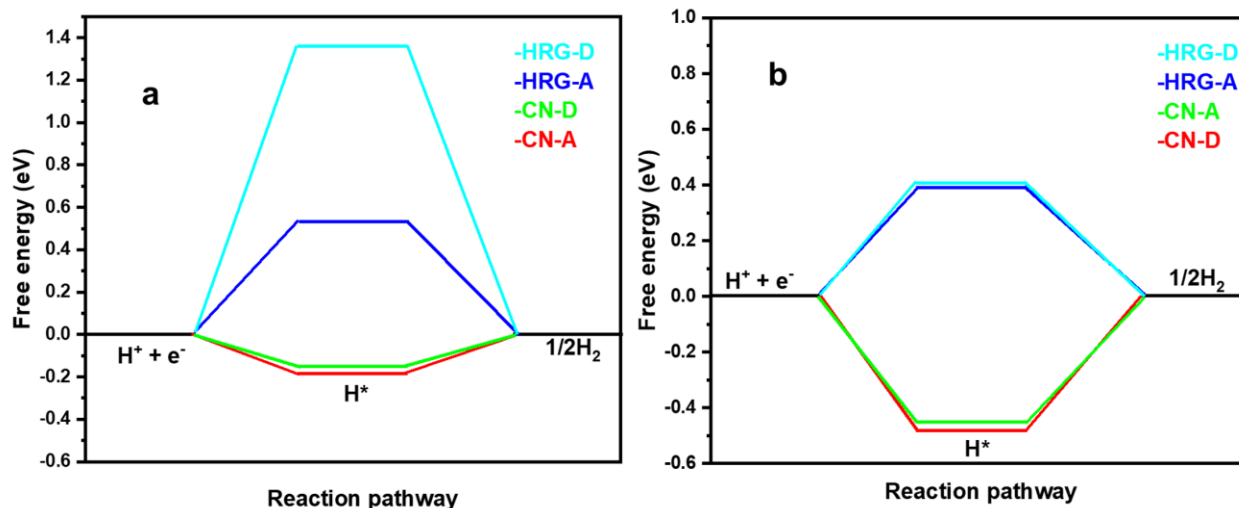


Figure 14. The calculated free energy diagrams for the possible hydrogen evolution pathways using (a) CN-HRG-CO and (b) CN-HRG-COOH. The letters D and A denote a long-distance interaction and a chemical bonding formation, respectively, between hydrogen and the nanolayers.

4.3.3 Volmer/Heyrovsky/Tafel Mechanisms of HER

Commonly, two mechanistic pathways have been identified and accepted for the HER process whether in acidic or basic aqueous media. These are Volmer-Heyrovsky and Volmer-Tafel mechanisms [111]. The first step is the discharge reaction, also known as the Volmer reaction, which involves the creation of H^* by transferring an electron to the proton in an active site on a surface [$H^+ + e^- \rightarrow H^*$]. Either the electrochemical desorption step, known as the Heyrovsky reaction [$H^* + H^+ + e^- \rightarrow H_2(g)$], or the chemical desorption step, known as the Tafel reaction [$H^* + H^* \rightarrow H_2(g)$], deals with the proton recombination (Scheme 3). In the second step, the Heyrovsky and Tafel reactions can co-occur, and the Tafel slope is the major experimental characteristic for determining the rate-limiting step for the specified system [112]. Furthermore, the Tafel mechanism of hydrogen evolution is the leading mechanism in the HER reaction since the associated ΔG_{H^*} approaches zero [109]. Hence, we have thoroughly investigated the Heyrovsky and Tafel mechanism for the possible HER reactivity from the first principle study on the non-metal CN-HRG-CO and CN-HRG-COOH catalysts. As for the CN-HRG-CO catalyst, the Volmer-Heyrovsky energy barriers have been predicted to be 2.6, 0.95, -0.48 and -0.47 eV (Figure 15a) for HRG-D, HRG-A, CN-D and CN-A adsorptions, respectively, while the Volmer-Tafel barriers have been calculated to be 3.9, 1.5, -0.64 and -0.65 eV (Figure 15b) for HRG-D, HRG-A, CN-D and CN-A adsorptions, respectively. These DFT findings predict that the Volmer-Heyrovsky pathway for hydrogen desorption over the CN-HRG-CO catalyst is thermodynamically more feasible due to the lower energy barrier associated with the hydrogen evolution. When the CN-HRG-COOH catalyst is considered, the Volmer-Heyrovsky barriers were computed as 0.95, 1.0, -

0.77, and -0.87 eV (Figure 15c) for HRG-D, HRG-A, CN-D and CN-A adsorptions, respectively, while those produced based on the Volmer-Tafel pathway were 1.3, 1.4, -1.2 and -1.3 eV (Figure 15d) for HRG-D, HRG-A, CN-D and CN-A, respectively, suggesting that the Volmer-Heyrovsky reaction pathway is more feasible than its counterpart for the CN-HRG-CO nanocatalyst as well. It is imperative to mention that CN-HRG-CO with the chemisorption on the g-C₃N₅ layer led to the lowest energy pathway of all configurations and adsorption studies, while the weak adsorption with the same catalyst but from the HRG side presented the highest energy barrier. Also, all the CN-HRG-COOH adsorption studies reflected moderate energy barriers for HER. More interestingly and comparing with the activation barrier of 0.85 eV for the Tafel step on the Pt(111) surface [112], the outstanding activity of the two configurations through the CN adsorption site for HER can be demonstrated.

Remarkably, the Gibbs free energy of hydrogen adsorption on CN-D (-0.16 eV) through (CN-HRG-CO) can be compared to the reference Pt/C catalyst (-0.085 eV), which can also be evidence due to its laudable performance as a metal-free HER catalyst when compared to other semi-conductive catalysts, such as boron nitride (2.66 eV) [113], graphene oxide (1.13 eV) [114] and pristine carbon nitride (1.18 eV) [115]. In addition, the CN-HRG-CO and CN-HRG-COOH photocatalytic performance through the CN adsorption site display a better activity in acidic media through the Volmer-Heyrovsky pathway with a rate-determining step (RDS) of 0.47, 0.48, 0.77, and 0.87 eV, respectively, when compared to the benchmark Pt one (0.85 eV) and other previously reported catalysts, such as NbC (0.89 eV) [109] and TaC (1.23 eV) [109].

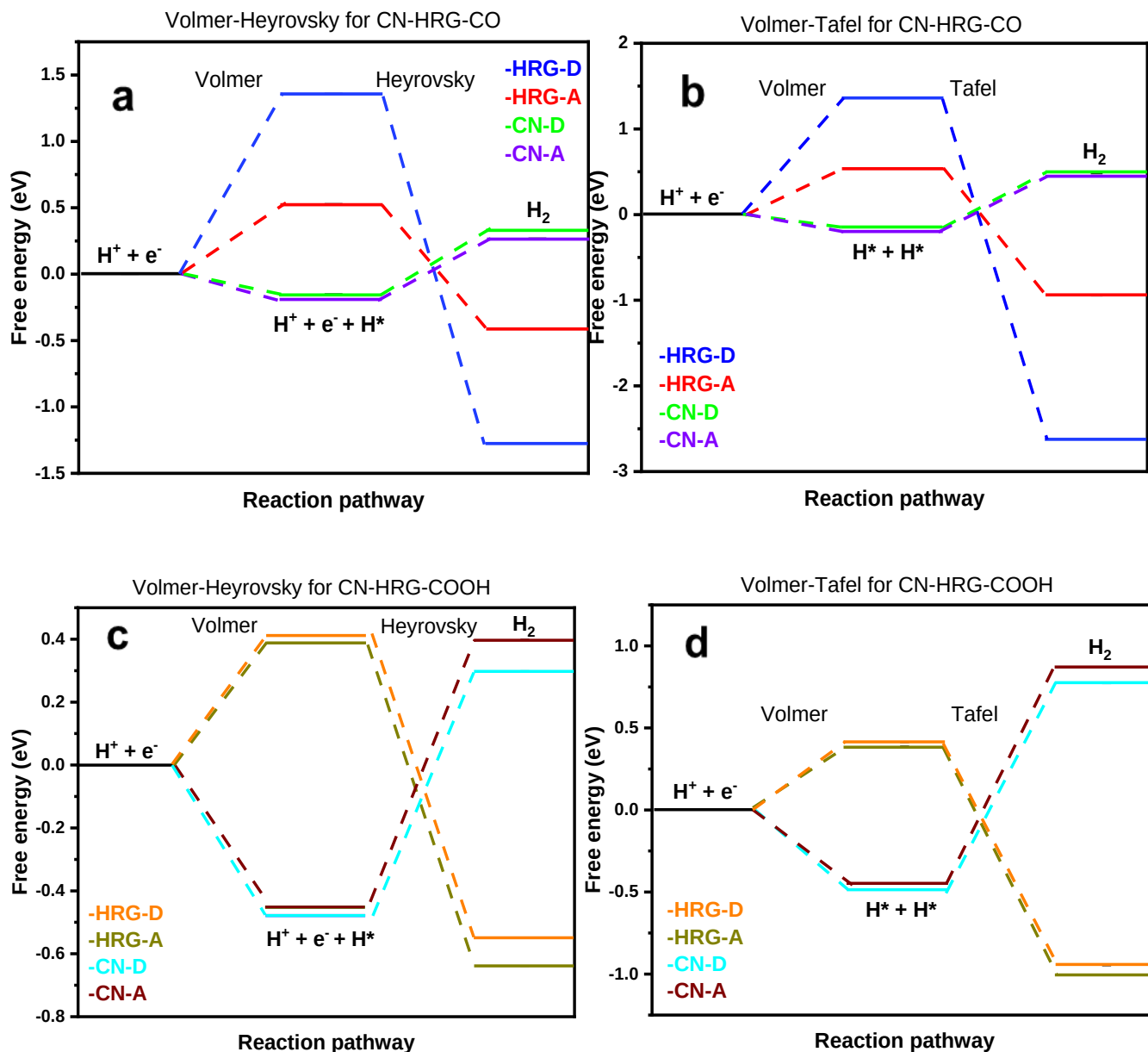


Figure 15. Calculated free energy diagrams of (a) Volmer-Heyrovsky, (b) Volmer-Tafel (both on the CN-HRG-CO catalyst), (c) Volmer-Heyrovsky and (d) Volmer-Tafel (both on the CN-HRG-COOH catalyst) for HER.

Table 8. Gibbs free energies at 298.15 K in eV of H adsorption on the CN-HRG-CO at various adsorption sites.

Adsorption site	ΔE_{ads}	ΔE_{ZPE}	ΔS	$T\Delta S$	ΔG_{H^*}
HRG-D	1.333035	-0.10982	-0.00047	-0.13929	1.362507
CN-D	-0.56318	0.179611	-0.00073	-0.21619	-0.16737
HRG-A	0.371204	0.087505	-0.00025	-0.07426	0.532965
CN-A	-0.56487	0.179826	-0.0007	-0.20747	-0.17757

Table 9. Gibbs free energies at 298.15 K in eV of H adsorption on the CN-HRG-COOH at various adsorption sites.

Adsorption site	ΔE_{ads}	ΔE_{ZPE}	ΔS	$T\Delta S$	ΔG_{H^*}
HRG-D	0.109891	0.100706	-0.00065	-0.19376	0.404352
CN-D	-0.82884	0.165034	-0.00064	-0.18941	-0.4744
HRG-A	0.110119	0.100749	-0.00064	-0.19167	0.402534
CN-A	-0.83341	0.160304	-0.00069	-0.20617	-0.46694

Table 10. Gibbs free energies and relative energy barriers at 298.15 K in eV of HER mechanisms on the CN-HRG-CO at various adsorption sites.

Adsorption sites	ΔE	ΔE_{ZPE}	ΔS	$T\Delta S$	ΔG	Energy Barrier
HRG-D						
DR	1.33303478	-0.10982	-0.00047	-0.13929	1.362507	
TR	-2.8530309	0.239252	6.69E-05	0.019949	-2.63373	3.996235
HR	-1.5199962	0.12943	-0.0004	-0.11935	-1.27122	2.633728
CN-D						
DR	-0.5631753	0.179611	-0.00073	-0.21619	-0.16737	
TR	0.93873343	-0.33097	0.000435	0.129769	0.477994	-0.64537
HR	0.37555814	-0.15136	-0.00029	-0.08642	0.310621	-0.47799
HRG-A						
DR	0.37120431	0.087505	-0.00025	-0.07426	0.532965	
TR	-0.928687	-0.17183	-0.00052	-0.1549	-0.94562	1.478584
HR	-0.5574827	-0.08432	-0.00077	-0.22915	-0.41265	0.945618
CN-A						
DR	-0.5648678	0.179826	-0.0007	-0.20747	-0.17757	
TR	0.92599578	-0.32439	0.000429	0.127961	0.473643	-0.65121
HR	0.36112793	-0.14457	-0.00027	-0.07951	0.296074	-0.47364

DR denotes Discharge reaction (Volmer reaction), TR denotes Tafel Reaction and HR denotes Heyrovsky reaction.

Table 11. Gibbs free energies and relative energy barriers at 298.15 K in eV of HER mechanisms on the CN-HRG-COOH at various adsorption sites.

Adsorption sites	ΔE	ΔE_{ZPE}	ΔS	$T\Delta S$	ΔG	Energy Barrier
HRG-D						
DR	0.109891	0.100706	-0.00065	-0.19376	0.404352	
TR	-0.68848	-0.20249	0.000207	0.06173	-0.95269	1.357045
HR	-0.57859	-0.10178	-0.00044	-0.13202	-0.54834	0.952693
CN-D						
DR	-0.82884	0.165034	-0.00064	-0.18941	-0.4744	
TR	1.190847	-0.31635	0.000339	0.101102	0.773394	-1.24779
HR	0.362007	-0.15132	-0.0003	-0.08831	0.298997	-0.77339
HRG-A						
DR	0.110119	0.100749	-0.00064	-0.19167	0.402534	
TR	-0.69105	-0.21457	0.000446	0.132974	-1.03859	1.441127
HR	-0.58093	-0.11382	-0.0002	-0.05869	-0.63606	1.038594
CN-A						
DR	-0.83341	0.160304	-0.00069	-0.20617	-0.46694	
TR	1.206368	-0.32074	6.49E-05	0.019346	0.866285	-1.33322
HR	0.372959	-0.16043	-0.00063	-0.18682	0.399346	-0.86629

DR denotes Discharge reaction (Volmer reaction), TR denotes Tafel Reaction and HR denotes Heyrovsky reaction.

CHAPTER 5

COMBINED DFT-ML APPROACH TOWARD THE PREDICTION OF PHOTOCHROMIC CHARACTERISTICS OF SUBSTITUTED SALICYLIDENEANILINE (SAS)

5.1 INTRODUCTION

The behavior of light in nonlinear media and materials is described by nonlinear optics.

[117-120]. In organic chemistry and materials science, where new compounds and materials with desirable features for engineering applications are sought, nonlinear optical (NLO) properties of molecules and polymers are of special interest [121-127]. In addition to its use in information technology and data storage, NLO materials are also used in optical computing, optical communication, dynamic holography, optical switching, harmonic generating, and frequency mapping [128-135]. Over the years, extensive research has been carried out on a number of materials that exhibited excellent NLO responses. These include but are not limited to organometallics [136] inorganic [137], organic-inorganic composites [137, 138], and organic materials [139, 140].

Salicylideneaniline (SA) derivatives (N-(3,5-Di-tert-butylsalicylidene)-4-X-benzene), also known as anils or Schiff bases [141] have been reported and synthesized according to the procedure described by Senir et al. [142]. To summarize, the synthesis involves the condensation of salicylaldehydes and anilines [143, 144]. Furthermore, the family of SA derivatives has been reported to be photochromic and thermochromic in nature. Upon UV-Vis light irradiation, the compounds change from yellow to red and vice versa depending on the specific irradiation energy [144]. These Schiff bases are very interesting to study since the presence or absence of distortion

between the two phenyl rings can lead to photochromism or thermochromism respectively. It was becoming apparent that crystals or compounds with non-planar conformation would exhibit photochromic properties, while compounds with planar conformation would exhibit thermochromic behavior [145]. Furthermore, however, it has been revealed that, due to the tautomerization between the enol and cis-keto forms of these SA compounds, it is likely that most of them have thermochromic properties, irrespective of their photochromic properties [146, 147]. In addition, SA derivatives have demonstrated excellent fatigue resistance, especially during photoswitching, which is of utmost importance for non-linear optical (NLO) properties [148, 149].

Moving on, strategies such as substituting the end groups of these compounds have improved their NLO response. Therefore, Donor-Acceptor (D–A) π -conjugated systems, also known as push-pull molecules, are created by adding an electron-donating group at one end of a π -conjugated chain and an electron-withdrawing one at the other end. For these molecules, the length of the conjugated backbone—that is, the distance between the donor and the acceptor—increases superlinearly with the amount of NLO characteristics. These systems have garnered a lot of attention due to their strong nonlinear response qualities and applicability in three-dimensional optical data storage, whether they are symmetrical D– π –A– π –D or A– π –D– π –A [150–156]. These compounds' NLO characteristics are influenced by intramolecular charge transfer (ICT), conjugation length, donor-acceptor strength, and molecular structure. By altering the donor and acceptor moieties, it is simple to adjust the response of these molecules. Sequel to these findings, strong donors such as NMe₂, strong acceptors such as NO₂, and intermediate donors such as CH₃ have been considered for the NLO activity.

The solvent effect can significantly affect the linear and non-linear optical behavior of compounds compared to the gas phase. This usually results in changes in the position, intensity, absorption,

and emission lines of optically active compounds. It is very important in understanding the energy changes in electronic transitions and gives insights into molecular interactions. It has also been reported that the NLO activity of compounds increases with solvents especially, with polar solvents. That is the polarizability (α), first hyperpolarizability (β) also known as the second harmonic generation (SHG), and second hyperpolarizability (γ) [157].

To the best of these research findings and investigations, only halogenated derivatives of the SA have been explored, while the main substituted SA derivatives (SAS), that is, D-A leading to the push-pull effect of the SAS are scarce and are yet to be explored computationally. These studies considered strong donors, strong acceptors, and intermediate acceptors which are NMe₂, NO₂, and CH₃ respectively. Sixteen (16) SAS compounds have been studied by changing the end group with the D and A, and also based on the enol-keto tautomerization. Based on research, since NLO response increases with solvent and specifically solvent polarity. Therefore, a range of non-polar to polar solvents that are related to optical properties has been considered with increasing dielectric constant. These include toluene, methanol, and water respectively. It is important to mention that a total of 24 SAS were initially studied, and then 8 were screened out, which were the trans-keto forms of these compounds due to their lower stability and lack of intramolecular hydrogen bonding. For the NLO activity, the studies focus on the polarizability, second-order nonlinear hyperpolarizability, UV-Vis absorption spectra, electronic transitions, optimized dihedral angles, and HOMO-LUMO energy gap which are capable of explaining the photoswitching phenomenon of SAS.

5.2 COMPUTATIONAL DETAILS

The Gaussian 16 [158] program package was used to carry out the density functional theory (DFT) calculations, and Gauss View 6 [159] software was used for result visualization. The studied SAS compounds were optimized and their frequencies were calculated at the DFT-B3LYP level of theory with the 6-311++G(d,p) basis set. B3LYP functional was used since it employs 20% Hartree–Fock (HF) exchange and is a flexible functional for modeling small and medium-sized organic compounds, it was therefore selected [160]. Based on the optimized geometries, the frontier molecular orbital (FMO) of the first excited state, HOMO-LUMO energy gap, and electronegativity properties were calculated at the same level with optimization. The FMO was visualized using Gauss View 6 and Vesta software. The first hyperpolarizability (β_{tot}) is an important parameter for nonlinear optical (NLO) properties of a material. Additionally, to consider the effect of solvents, the integral equation formalism polarized continuum model (IEFPCM) [161] was employed. The total polarizabilities (α_{tot}) [162, 163] and first hyperpolarizabilities (β_{tot}) [164] of the current system can be mathematically stated as:

$$\alpha_{tot} = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

where α_{xx} , α_{yy} , and α_{zz} are the components of the first-order polarizability tensor along the x, y, and z axes, respectively.

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

where β_x , β_y , and β_z are the components of the second-order polarizability tensor along the x, y, and z axes, respectively, and where β_i is defined as:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jji} + \beta_{jji}) \quad (3)$$

The complete equation to calculate the magnitude of the total first hyperpolarizability tensor can be expressed as:

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (4)$$

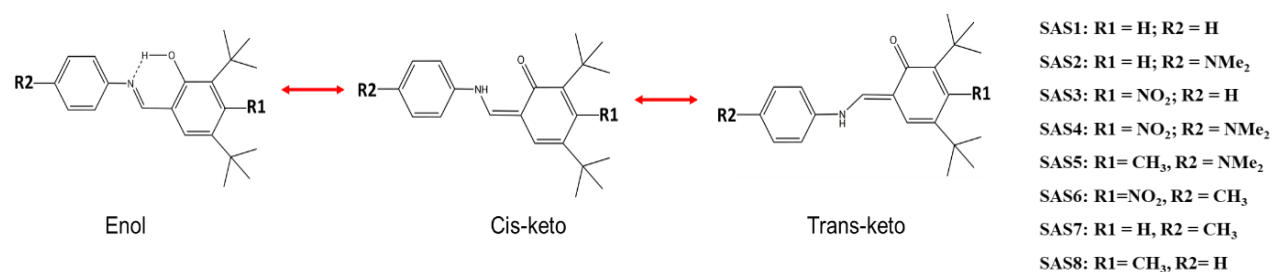
In order to further strengthen the findings of the polarizability and hyperpolarizability, the time-dependent density functional theory (TD-DFT) has been simulated to verify the NLO properties of these photochromic compounds.

5.3 RESULTS AND DISCUSSION

5.3.1 Geometry Optimization and Structural Stability

The possible conformations of N-3,5-di-tertiarybutyl-salicylidene-4-R-aniline (SA) and substituted SA derivatives (SAS) have been optimized and juxtaposed. There are three possible conformations of the SA, the enol, cis-keto, and trans-keto forms, which were a result of tautomerization. In other words, as Scheme 4 illustrates, a proton is transferred from the phenolic OH group of the enol form to the N atom of the imine group, creating the cis-keto form, which is then transformed into the trans-keto form. As displayed in Table 12, eight SAS compounds were optimized concerning the conformations earlier mentioned, giving a total of twenty-four compounds. For simplicity, they have been giving the codes from SAS1 to SAS8, while the enol, cis-keto, and trans-keto forms have been denoted as E, K, and TK respectively. The optimized relative energies show that the SAS compounds show relative stability in the order: Enol > Cis-keto > Trans-keto, with the enol forms being the most stable. The preferential stability of the enol forms has been attributed to the intramolecular hydrogen bonding between the hydrogen of the phenolic OH and the N of the imine group. There is a comparative stability of the cis-keto forms

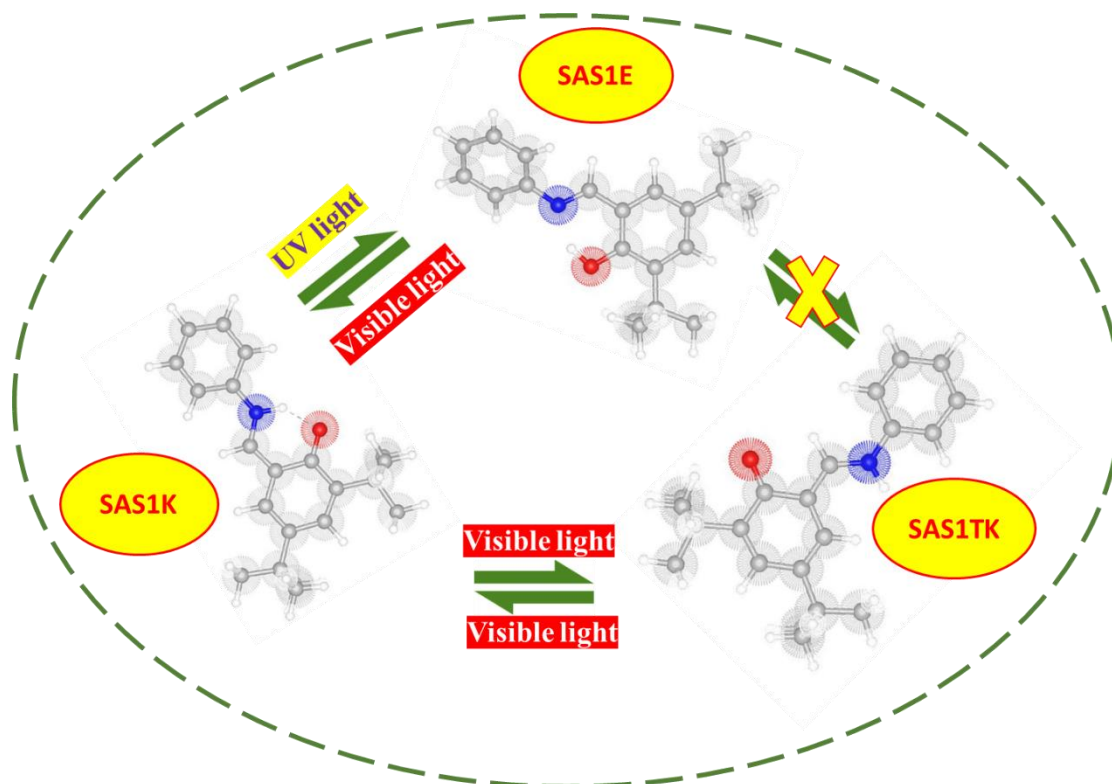
to the enol forms of SAS. This ranges between 2.21 – 3.05 kcal/mol. This comparable relative stability has been accredited to the partial intramolecular hydrogen bonding experienced between the hydrogen attached to the N of the imine group and the oxygen of the phenyl group. As for the trans-keto forms, they are about 3.9-5.3 times less stable compared to the cis-keto and more than 10 times less stable than their enol counterparts. This was due to a lack of intramolecular hydrogen bonding within these structures. Sequel to these findings, the scope of the research was narrowed towards the enol and cis-keto forms of the eight SAS compounds, giving room to sixteen SAS compounds being studied.



Scheme 4. Conformations of the SAS compounds are displayed on the left, while different substitutions on the SA ranging from strong D to A are displayed on the right.

Table 12. Calculated total electronic energies (in Hartree) and relative stabilities (in kcal/mol) for the substituted salicylideneaniline (SAS) derivatives, calculated at the B3LYP/6-311++G(d,p) level of theory.

Derivatives (SAS)		Total Energy (Hartree)	Relative Energies (kcal/mol)
SAS1	Enol	-946.365	0.00
	Cis-Keto	-946.361	2.56
	Trans-Keto	-946.348	10.55
SAS2	Enol	-1080.302	0.00
	Cis-Keto	-1080.297	2.82
	Trans-Keto	-1080.282	12.03
SAS3	Enol	-1150.931	0.00
	Cis-Keto	-1150.926	3.05
	Trans-Keto	-1150.912	11.76
SAS4	Enol	-1284.834	0.00
	Cis-Keto	-1284.830	2.21
	Trans-Keto	-1284.816	11.77
SAS5	Enol	-1119.566	0.00
	Cis-Keto	-1119.562	2.58
	Trans-Keto	-1119.547	11.70
SAS6	Enol	-1190.201	0.00
	Cis-Keto	-1190.197	2.42
	Trans-Keto	-1190.183	11.62
SAS7	Enol	-985.669	0.00
	Cis-Keto	-985.664	2.66
	Trans-Keto	-985.650	11.58
SAS8	Enol	-985.629	0.00
	Cis-Keto	-985.625	2.68
	Trans-Keto	-985.611	11.07



Scheme 5. Schematic flow showing the photochromism process between the different conformations of SAS.

5.3.2 Electronic features of SAS compounds

Compounds with planar configurations are expected to show thermochromic properties, while those with slight or moderate distortion (non-planar) are expected to exhibit photochromic properties, a dual behavior necessary for NLO responses of materials [145]. To gain insight into this assertion, the dihedral angles in a compound are directly proportional to understanding the planarity of such compounds. Therefore, attention has been directed to all possible dihedral angles present in the SAS compounds. As presented in Table 13, there are only five possible dihedral angles in these compounds, these include, C9-N10-C12-C14, C2-C3-C9-N10, C4-C3-C9-N10, C3-C9-N10-C12, C9-N10-C12-C13. Interestingly, C9-N10-C12-C14 is directly related to what has been reported and asserted by Johmoto et al [144]. That is, compounds with a dihedral angle less than 20° are non-photochromic, while those with a dihedral angle above 30° are photochromic. The compounds with dihedral angles between $20\text{-}30^\circ$ are either photochromic or thermochromic.

It can be seen that all the enol conformations have dihedral angles above 30°, except for SAS2E, SAS4E, and SAS5E, which are very close to 30°. This might mean that the enol of SAS compounds is photochromic. Conversely, the keto forms exhibited dihedral angles below 20°, which is likely that they are thermochromic.

Table 13. Optimized dihedral angles of enol and keto conformations of SAS compounds at B3LYP/6-311++G(d,p) level of theory.

SAS Derivatives		Dihedral Angles			
Compounds	C9-N10-C12-C14	C2-C3-C9-N10	C4-C3-C9-N10	C3-C9-N10-C12	C9-N10-C12-C13
SAS1E	-38.1	179.2	0.73	177.2	144.3
SAS1K	9.9	-179.7	0.02	-179.1	-170.7
SAS2E	29.5	-179.5	0.47	-177.3	-153
SAS2K	15.7	-179.8	-0.09	-178.5	-165.5
SAS3E	39.2	-179	0.93	-176.8	-143.5
SAS3K	-0.01	180	0.00	180	180
SAS4E	-26.6	178.9	-1.2	177.4	155.7
SAS4K	-16.6	178.9	-0.68	177.9	164.5
SAS5E	-29.4	177.8	-3.1	177	152.3
SAS5K	-15.3	177.2	-2.5	177.1	164.9
SAS6E	35.7	-179.9	-0.13	-177.4	-146.8
SAS6K	-14.1	178.9	-0.72	178.4	166.3
SAS7E	36.6	-179.3	0.69	-177.1	-145.5
SAS7K	11.4	-179.8	-0.02	-179.1	-169.4
SAS8E	37.8	-177.5	3.3	-177	-144.5
SAS8K	-11.4	177.1	-2.6	177.7	169.1

E and K denote enol and cis-keto respectively.

HOMO-LUMO energy gap (E_{gap}) is another key factor that is used in describing the NLO response of materials. It is germane to state that a reduced E_{gap} magnitude is crucial as it facilitates easier electronic transitions when subjected to an external electric field, a key factor in enhancing nonlinear optic (NLO) properties. As presented in Table 17 and visualized in Figures 16 and 17, the E_{gap} reduces from approximately 4.01 eV (SAS1E) to 2.60 eV (SAS3K). The reduction in E_{gap} shows that the substitution of D-A to the SA derivatives has a significant effect on them. It was also observed that keto forms have lower E_{gap} than their enol counterpart. This might be a result

of stabilization enjoyed by the enol conformations, owing to the intramolecular hydrogen bonding within the compounds. This also predicts that the keto forms might give a large NLO response compared to the enol forms. In addition, the trend of the effect of the D-A system on the E_{gap} of SAS is observed as $\text{NO}_2 > \text{NMe}_2 > \text{CH}_3 > \text{H}$. Consequently, E_{gap} of the enol and keto forms of the SAS compounds follow this outlined order respectively: $\text{SAS3} \rightarrow \text{SAS4} \rightarrow \text{SAS2} \rightarrow \text{SAS5} \rightarrow \text{SAS6} \rightarrow \text{SAS8} \rightarrow \text{SAS7} \rightarrow \text{SAS1}$.

Electronegativity is another key factor important to understanding the model behavior in the presence of electron-withdrawing and donating groups. Similar to the trend observed for the E_{gap} of enol and keto forms, it was noticed that the enols are more electronegative than their keto counterparts (Table 17 and Figure 17). The electronegativity character of the SAS compounds reduces from 4.68 eV (SAS3) to 3.43 eV (SAS5) in the following order: $\text{SAS3} \rightarrow \text{SAS6} \rightarrow \text{SAS1} \rightarrow \text{SAS4} \rightarrow \text{SAS8} \rightarrow \text{SAS7} \rightarrow \text{SAS2} \rightarrow \text{SAS5}$. Furthermore, compounds with the strongest electron-withdrawing group (NO_2) had the highest electronegativities, while compounds with the strongest electron-donating groups (NMe_2 , CH_3) had the lowest electronegativities values. This also proves the compounds with acceptor group (A) propensity to show a stronger NLO response than compounds with or without the D-A group. This further strengthens the observation than with the reduced E_{gap} .

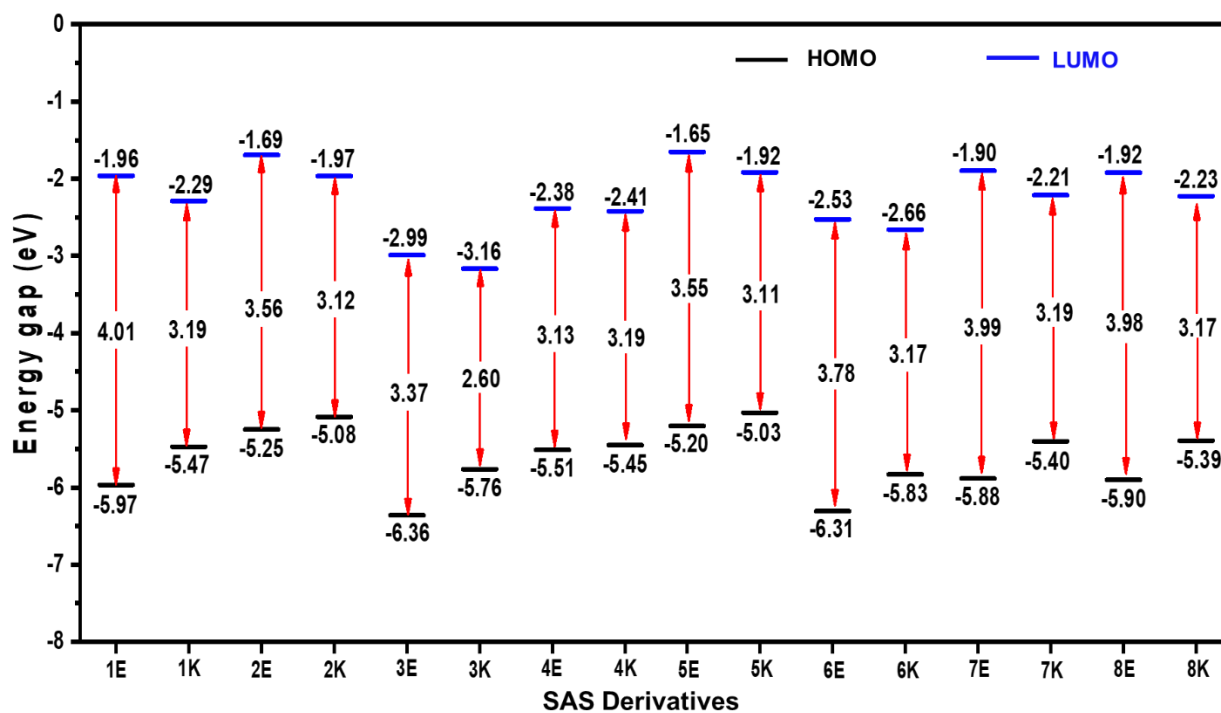


Figure 16. HOMO-LUMO and energy gap of the enol-keto conformations of the SAS compounds at B3LYP/6-311++G(d,p) level in the gas phase. *E* and *K* denote enol and cis-keto respectively.

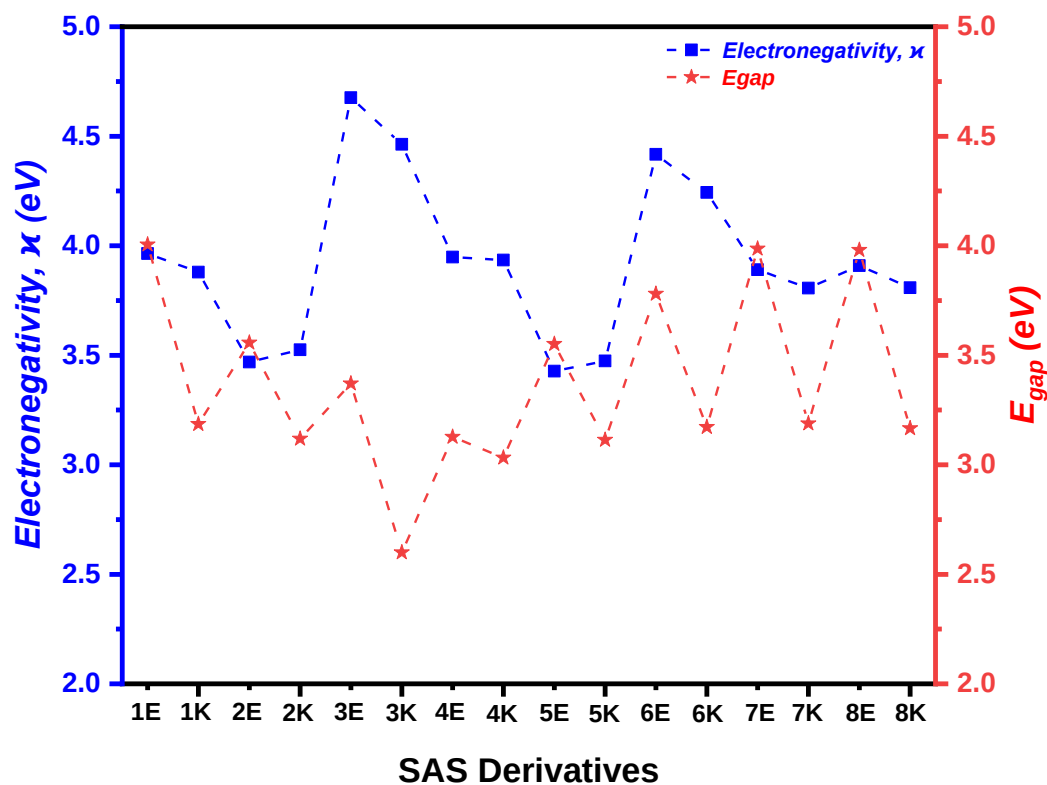


Figure 17. Relationship between the SAS compounds' electronegativity and HOMO-LUMO energy gap (E_{gap}). *E* and *K* denote enol and cis-keto respectively.

5.3.3 Non-linear optical (NLO) response of SAS compounds

Among the parameters that could be used to assess the NLO response of materials is first polarizability (α_{tot}), and first hyperpolarizability (β_{tot}). While the former is directly related to the first-order NLO property of a material, the latter is directly related to the second-order NLO property. Therefore, the magnitude of the NLO response of a material is greatly influenced by α_{tot} and β_{tot} , which are inverse to the E_{gap} but strongly depend on the electronegativity of such materials [163]. NLO response of a material is also greatly improved in the presence of a solvent, this was considered in the study.

Table 21-24 shows the values of the α_{tot} with the major contributing tensor being the α_{zz} , which shows that most of the SAS compounds lie in this direction. A similar trend was also observed in other solvents (toluene, methanol, and water) used. To visually compare this trend in the gas and solvent phases, visualization of the α_{tot} both in the vacuum and water is displayed in Figure 18a. Similar to the previous observation, the α_{tot} of the enol forms of the SAS compound are smaller compared to the keto forms. The α_{tot} has decreased from $6.34 \times 10^{-39} \text{ C}^2\text{m}^2\text{J}^{-1}$ for SAS4K (with the push-pull effects) to $4.79 \times 10^{-39} \text{ C}^2\text{m}^2\text{J}^{-1}$ for SAS1E (without the push-pull effects) in the vacuum and from $8.84 \times 10^{-39} \text{ C}^2\text{m}^2\text{J}^{-1}$ for SAS4K to $6.48 \times 10^{-39} \text{ C}^2\text{m}^2\text{J}^{-1}$ for SAS1E in the water. The order of the NLO response for the α_{tot} of the SAS compounds is summarized as SAS4 $\rightarrow$ SAS5 $\rightarrow$ SAS3 $\rightarrow$ SAS2 $\rightarrow$ SAS6 $\rightarrow$ SAS7 $\rightarrow$ SAS8 $\rightarrow$ SAS1 in the gas and solvents phases respectively. It is important to mention that the NLO response of these compounds increases from gas to solvent phases, especially with increasing dielectric constants. These findings further strengthen the observation of E_{gap} and electronegativity data.

Table 14. The first total polarizability (in $\text{C}^2\text{m}^2\text{J}^{-1}$) and total hyperpolarizabilities (in $\text{C}^3\text{m}^3\text{J}^{-2}$) of the studied photochromic compounds as calculated at the B3LYP/6-311++G(d, p) level of theory.

SAS Derivatives	α_{tot}^a ($10^{-41} \text{C}^2\text{m}^2\text{J}^{-1}$)	α_{tot}^b ($10^{-41} \text{C}^2\text{m}^2\text{J}^{-1}$)	β_{tot}^a ($10^{-52} \text{C}^3\text{m}^3\text{J}^{-2}$)	β_{tot}^b ($10^{-52} \text{C}^3\text{m}^3\text{J}^{-2}$)
SAS1E	479	648	208	423
SAS1K	502	686	168	566
SAS2E	580	786	2180	5910
SAS2K	601	826	2650	8590
SAS3E	533	730	2160	6470
SAS3K	570	801	3510	12000
SAS4E	614	843	3130	10300
SAS4K	634	884	3370	12500
SAS5E	606	824	2130	5590
SAS5K	627	864	2690	8510
SAS6E	535	721	320	1200
SAS6K	559	763	442	2150
SAS7E	509	683	230	570
SAS7K	533	723	377	1410
SAS8E	505	688	299	715
SAS8K	527	725	129	381

E and K denote enol and cis-keto respectively, while a and b represent vacuum and water respectively.

The first hyperpolarizability (β_{tot}) values are highlighted in Table 25-28. The major contributing tensor is the β_z , which is similar to what was observed for the first polarizability data. Likewise, a similar trend of solvent simulation conducted on the α_{tot} was used and a partial similar trend was observed. To visually compare this trend, Figure 18b shows the second-order NLO response of the SAS compounds. The β_{tot} has decreased from $35.1 \times 10^{-50} \text{C}^3\text{m}^3\text{J}^{-2}$ for SAS3K (with the pull effect) to $1.29 \times 10^{-50} \text{C}^3\text{m}^3\text{J}^{-2}$ for SAS8K (with the push effect) in the vacuum and from $125 \times 10^{-50} \text{C}^3\text{m}^3\text{J}^{-2}$ for SAS4K to $3.81 \times 10^{-50} \text{C}^3\text{m}^3\text{J}^{-2}$ for SAS1E in the water. The order of the NLO response for the β_{tot} of the SAS compounds is summarized as SAS3 $\rightarrow$ SAS4 $\rightarrow$ SAS5 $\rightarrow$ SAS2 $\rightarrow$ SAS6 $\rightarrow$ SAS7 $\rightarrow$ SAS1 $\rightarrow$ SAS8 in the gas and SAS4 $\rightarrow$ SAS3 $\rightarrow$ SAS2 $\rightarrow$ SAS5 $\rightarrow$ SAS6 $\rightarrow$ SAS7 $\rightarrow$

SAS1 $\rightarrow$ SAS8 in the solvent's phases respectively. This slightly dissimilar trend shows the effect of solvent in modulating the push-pull effect present in the studied compounds. The effect of solvents tends to improve the NLO response with approximately 1.9-3.6 times (toluene $\rightarrow$ methanol $\rightarrow$ water) the response in the gas phase. The magnitude of the NLO response is about 16 times above the original SA compound in the gas phase, whereas it is approximately 29 times the original compound in the solvent phase (water). These observations further corroborate the analysis of the E_{gap} and electronegativity data. Furthermore, a comparative study was carried out amongst the SAS compounds and urea molecule ($\beta_{tot} = 1.380 \times 10^{-51} \text{ C}^3\text{m}^3\text{J}^{-2}$) which is used as a standard compound to examine the NLO response of photonic materials [165]. To the best of this research outcome, all the studied compounds exhibit excellent NLO responses compared to the benchmark material. In fact, SAS3K and SAS4K were approximately 254 and 906 times more NLO responsive in the vacuum and water phases respectively, compared to the benchmark urea material.

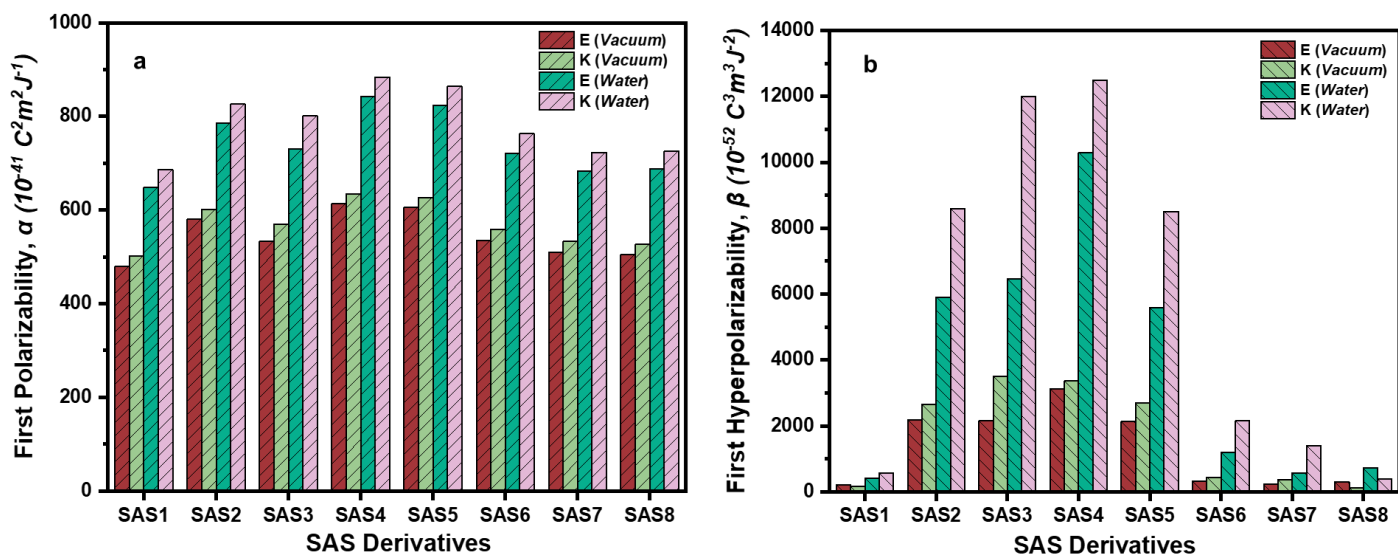


Figure 18. Comparative values of the (a) first polarizability and (b) first hyperpolarizability of SAS compounds, simulated using the B3LYP/6-311G++(d,p) level of theory in the vacuum and water. *E* and *K* denote enol and *cis*-keto respectively.

5.3.4 UV-Vis absorption studies of SAS

UV-visible absorption spectra and electronic transition are other interesting metrics for understanding the photochromic and thermochromic properties of compounds, which are directly related to the first and second-order NLO properties of materials. Sequel to this understanding, the time-dependent density functional theory (TD-DFT) was used to simulate the UV-Vis absorption spectra and electronic transitions of SAS compounds at the first excited state ($S_0 \rightarrow S_1$). This aspect of the study is made available in Gaussian, while visualization was done with Gauss view, Vesta, and origin software.

Furthermore, according to Spangenberg *et al.* [166], the family of SA derivatives can be photo-activated using UV or visible light sources. For instance, a system is said to be turned on by a UV light [200-400 nm] if it absorbs light within the UV region, likewise is said for visible light [400-800 nm] induced systems. Such a class of organic systems can either be turned off in the dark or when irradiated with lights not specific to their absorption energy. This implied that compounds with an absorption energy within the UV region are said to be photochromic, while those within the visible region are regarded as thermochromic (non-photochromic).

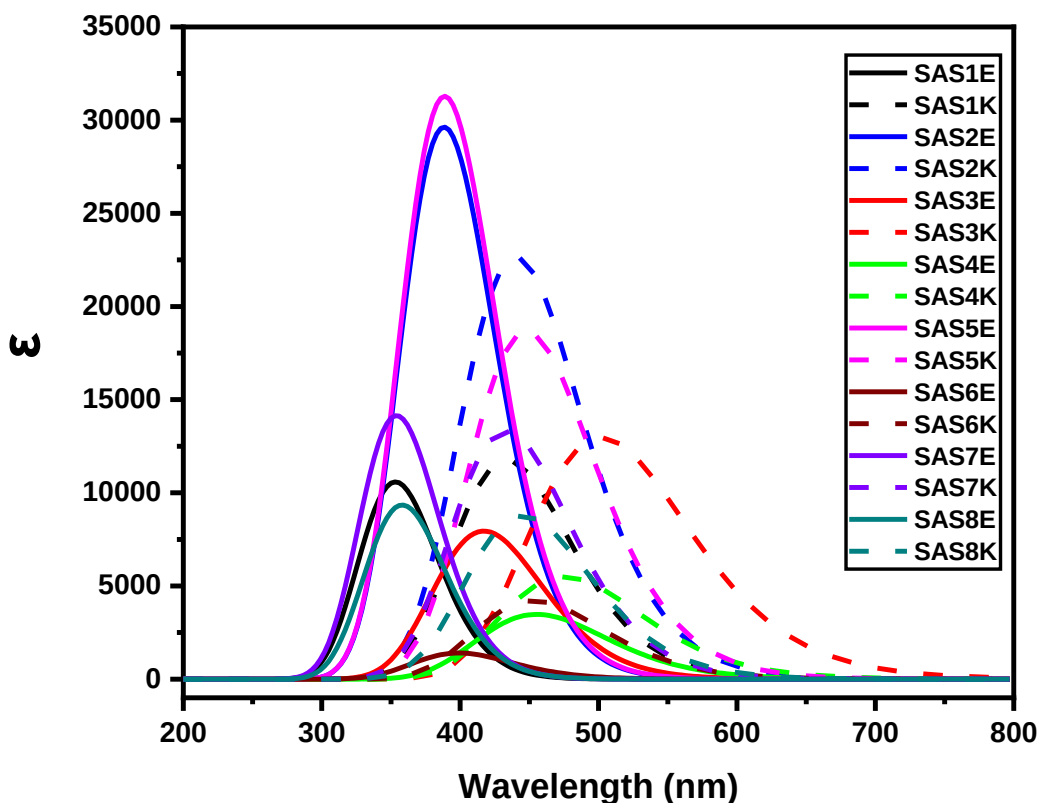


Figure 19. UV–vis spectra of all the studied SAS compounds as computed at the B3LYP/6-311++G(d,p) level of theory in the vacuum. *E* and *K* denote *enol* and *cis-keto* respectively.

The absorption wavelength of the SAS compounds in the gas phase are presented in Table 15, and visualized in Figure 19. It was observed that all the enol forms of the SAS compounds have an absorption wavelength between 200 - 400 nm, except SAS3E (A) and SAS4E (D-A) with a wavelength above 400 nm. Subsequently, SAS6E (D-A) shows the highest absorption wavelength in the enol series. The keto forms of the studied SAS compounds absorb above 400 nm with SAS3K (A) having the highest wavelength of absorption in the keto series. It should be noted that all the SAS compounds with donor (D) or acceptor (A) and/or a combination of both (D/A) show excellent absorption wavelength, which also aligns with the properties earlier mentioned for the SAS compounds.

Other important parameters that can be obtained from the electronic transition are the excitation energy, oscillator strength (f_{os}), contribution factor (CF) of the HOMO-LUMO excitation to the

molecular orbital transition (MOT) and multi-molecular orbital transition (MMOT). As shown in Table 3, these parameters are related to one another. It can be seen that the higher the excitation energy, the higher the oscillator strength, and the lower the wavelength of absorption; and vice versa.

Table 15. Maximum simulated wavelengths (λ , nm), excited-state transition energies (ΔE , eV), oscillator strengths (f_{os}), significant molecular orbital contributions, and transitions of the studied SAS compounds calculated at the B3LYP/6–311++G(d, p) level in the gas phase. *E* and *K* denote *enol* and *cis-keto* respectively.

SAS Derivatives	State	ΔE (eV)	λ (nm)	f_{os}	Contribution	Main Transition	% Contribution
SAS1E	1	3.5103	353.2	0.2614	0.69188	H→L	95.7
SAS1K	1	2.8586	433.7	0.29	0.70107	H→L	98.3
SAS2E	1	3.1924	388.4	0.7315	0.7002	H→L	98.1
SAS2K	1	2.8155	440.4	0.5594	0.70286	H→L	98.8
SAS3E	1	2.9721	417.2	0.1962	0.70134	H→L	98.4
SAS3K	1	2.4693	502.1	0.3196	0.7035	H→L	99.0
SAS4E	1	2.7232	455.3	0.0858	0.67866	H→L	92.1
					0.13269	H-1→L	3.5
SAS4K	1	2.6088	475.26	0.1356	0.53514	H→L	57.3
					0.42233	H→L+1	35.7
					0.15187	H-1→L+1	4.6
					0.10646	H-1→L	2.3
SAS5E	1	3.1888	388.8	0.7724	0.69824	H→L	97.5
SAS5K	1	2.7683	447.9	0.4601	0.69393	H→L	96.3
					0.10495	H-1→L	2.2
SAS6E	1	3.1068	399.1	0.0346	0.65543	H→L	85.9
					0.16534	H→L+1	5.5
					0.12975	H-1→L	3.4
SAS6K	1	2.7366	453.1	0.1041	0.53069	H→L	56.3
					0.4573	H→L+1	41.8
SAS7E	1	3.5021	354	0.3494	0.69165	H→L	95.7
SAS7K	1	2.8622	433.2	0.3291	0.70142	H→L	98.4
SAS8E	1	3.4616	358.2	0.2307	0.67871	H→L	92.1
					0.16138	H-1→L	5.2
SAS8K	1	2.7837	445.4	0.2168	0.69285	H→L	96.0
					0.12902	H-1→L	3.3

Therefore, the enol forms of the SAS compounds follow this assertion, while the reverse is adopted by the keto forms. This might be due to the stabilization energy enjoyed by the enol compounds. As for the CF and MOT, it was clear that the enol forms of the SAS compounds have a lower percentage contribution factor compared to their keto counterparts. Likewise, the keto forms exhibited several multi-molecular orbital transitions. This may be ascribed to their lower stability and probably, the degree of freedom they possessed, which ease their transitions within the orbitals. The FMO of the MOT and MMOT are displayed in Figure 20 for better visibility.

Finally, the results obtained are similar to the findings highlighted for the dihedral angle, E_{gap} , electronegativity, and most importantly the NLO responses of these compounds. Meticulously, it became evident that SAS2E and SAS5E are the most photochromic followed by SAS6E, SAS8E, SAS7E, and SAS1E. Whereas SAS3E and SAS4E are likely to be photochromic or thermochromic. Also, without mincing words together, all the keto forms of the studied SAS compounds are thermochromic based on the result obtained. Consequently, SAS3K and SAS4K emerged as the most thermochromic compounds, followed by SAS2K, SAS5K, SAS6K, SAS8K, SAS7K, and SAS1K.

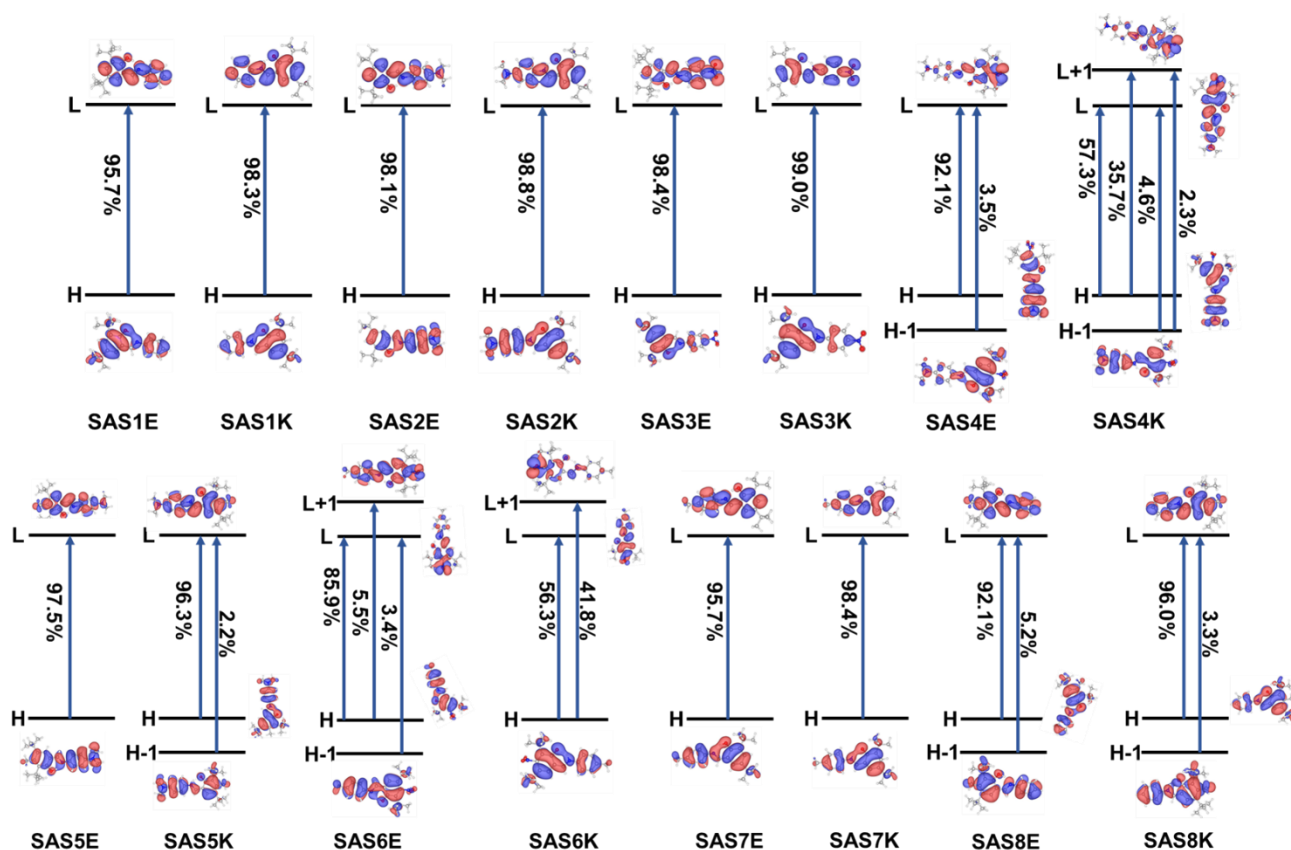


Figure 20. The molecular and multi-molecular orbital transition of the studied SAS compounds at the first excited state. *E* and *K* denote *enol* and *cis-keto* respectively.

5.3.5 Solvent Effects on SAS Compounds

Different solvents have been employed to predict the NLO features of materials experimentally and computationally. The decision on the solvent to be employed depends on the solubility of the materials in specific solvents. It also depends on the solvents that can play a significant role in enunciating the NLO properties of photonic materials. For the purpose of this study, three solvents have been explored based on their polarity and dielectric constants. These are toluene, methanol, and water, with increasing polarity and dielectric constants respectively.

As for the E_{gap} and electronegativity values presented in Table 17-20, it was observed that solvents have a significant impact on the SAS compounds compared to the gas phase. It was also observed that the influence of the solvents on the electronic properties of SAS compounds follows this order:

toluene < methanol < water. For instance, the higher the dielectric constant, the higher the electronegativity, and the lower the E_{gap} of the SAS compounds. It should be noted that the E_{gap} is minimized in the vacuum phase compared to the solvent phases, while electronegativity is maximized in the case of water.

With respect to the NLO responses of the SAS compounds, a similar trend was also observed for the solvent effects. That is, toluene < methanol < water. Interestingly, similar trends were observed for both polarizability and hyperpolarizability values (Table 21-28). Furthermore, all the SAS compounds show excellent NLO response in the solvent phases compared to the vacuum phase. It can be concluded that the higher the solvent polarity, the higher the NLO responses of the SAS compounds.

Finally, the UV-vis absorption spectra are presented in Figure 26-28, while the electronic transition features are presented in Table 29-31. It can be observed that all the solvents have a great impact on the UV-Vis spectra and the electronic transition features of SAS compounds compared to the gas phase. The influence of the solvents can be summarized as toluene < methanol < water. It is important to note that MMOT is minimized in the case of the solvent phases, especially for water and methanol. This can be due to the lower degree of freedom they have in the solvents compared to the vacuum.

5.4 MACHINE LEARNING PREDICTION OF PHOTOCHROMIC SAS

A machine learning (ML) algorithm was introduced to strengthen the predictions of the DFT calculations on the sixteen studied SAS compounds and to further establish a strong correlation between the parameters used in judging the fate of the compounds and the actual predictions. Figure 21 shows the schematic representation of the machine learning processes as applicable to this study. For a rapid and efficient ML model that predicts the photochromic properties of

compounds, feature selection is a key parameter to consider. Therefore, eleven (11) features/attributes were found to be directly related to the photochromic nature of compounds. Technically, the prediction of these compounds is within the binary classification, which is at the junction of statistics and artificial intelligence. Binary classification is based on two types, which are the predictive (supervised) (e.g. KNN- K nearest neighbor), in which the class of each instance is known, and exploratory (unsupervised) [167, 168]. Furthermore, supervised learning consists of two major approaches: training and testing the model [169].

Several data mining techniques such as Support Vector Machine (SVM), Artificial Neural Network (ANN) [170], Ensemble classifier, k-nearest Neighbor (KNN) [171, 172], and Bayesian classifier have been adopted by different researchers. However, the KNN algorithm has distinct features which include but are not limited to simplicity, multi-class accuracy, descriptiveness, lower noisy pattern, fastness, and generalization to solving real-life classification problems [173-175]. Therefore, this study is based on the KNN ML model.

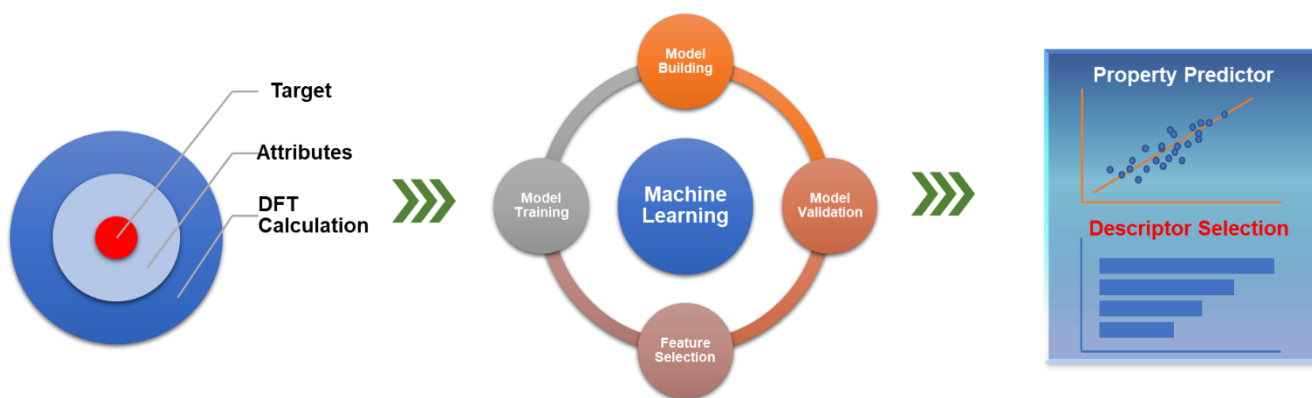


Figure 21. Schematic representation describing the process of the machine learning model used for the studied SAS compounds. Starting from data acquisition, followed by feature selections, building an ML model, and predicting the property.

The computational strategy and implementation were conducted using a codeless ML tool environment, known as WEKA [176, 177]. To achieve a higher predictive accuracy of the KNN algorithm, different optimization metrics were considered. This is known as hyperparameter optimization. As shown in Figures 22a and b, the k value was optimized from 1 to 7 for two different types of data split methods: cross-validation and percentage split. Since the KNN algorithm is based on a voting technique, an odd number of k was chosen to avoid a tie. Another optimization technique is the distance measure within the KNN algorithm, for the model building and testing, Euclidean and Manhattan distance measures were considered using different k values. A 10-fold cross-validation data split and a 70/30% training/testing data split were used for the whole analysis.

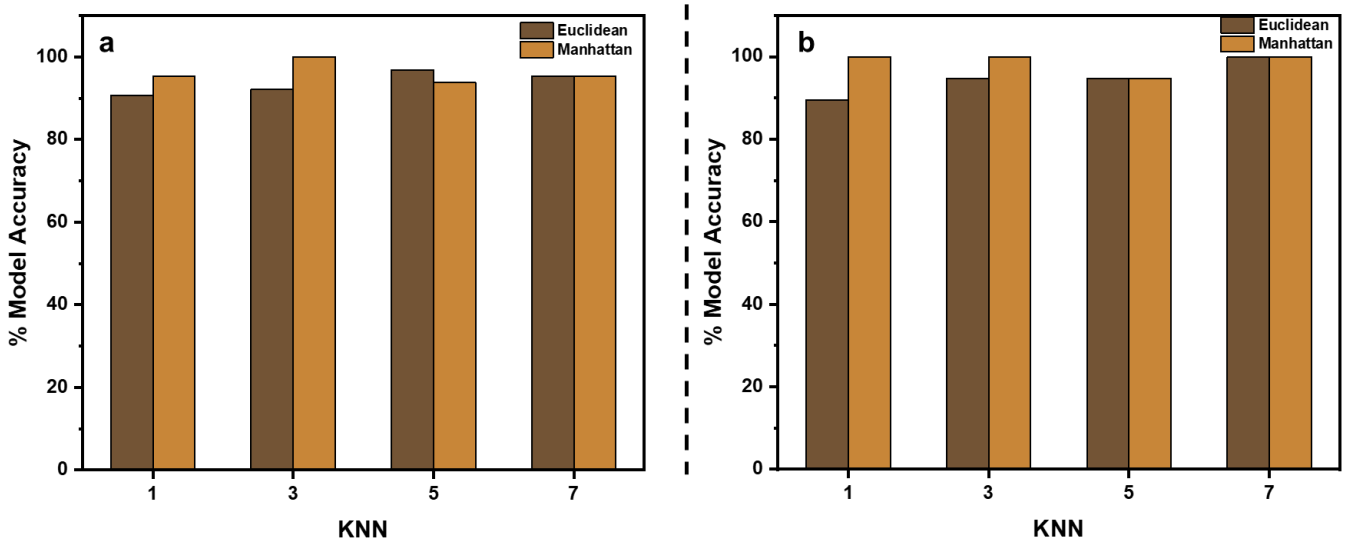


Figure 22. Percentage model accuracy of the testing set against different k values using Euclidean and Manhattan distance measures for (a) Cross-Validation and, (b) Percentage split (70/30%).

Among the figure of merits that could be considered to ascertain if a KNN machine learning model is performing better are the Kappa statistic, root mean square error (RMSE), model accuracy (% of correct classification), and confusion matrix. Therefore, Figure 22 shows the percentage model accuracy against the k values using Euclidean and Manhattan distance measures for the ten-fold cross-validation data split. All the models achieved accuracy above 90%. As the k-values increase

from 1 to 3, the percentage performance increases in both distance measures, after this the model accuracy decreases. An optimum accuracy of 100% was achieved with a k value of 3 using the Manhattan distance measure. Additionally, there is a better performance of the Manhattan distance measure over the Euclidean. As for the percentage split, the data was divided into 70 and 30 % for the training and testing sets respectively. Similarly, the model performance increases from 89% (k = 1) to 100% (k = 7) using the Euclidean distance measure, while 100% accuracy was obtained for all the k values of Manhattan distance measures, except when k = 5 (95%). In all cases, Manhattan shows exceptional performance over the Euclidean. In addition, the model with the k = 1, data split of 70/30% (training/testing) and Manhattan distance has exceptional performance over all other models, due to the model accuracy of 100%, RMSE, and MAE of 0.0213 of the testing set after training the model (Figure 23, Table 34).

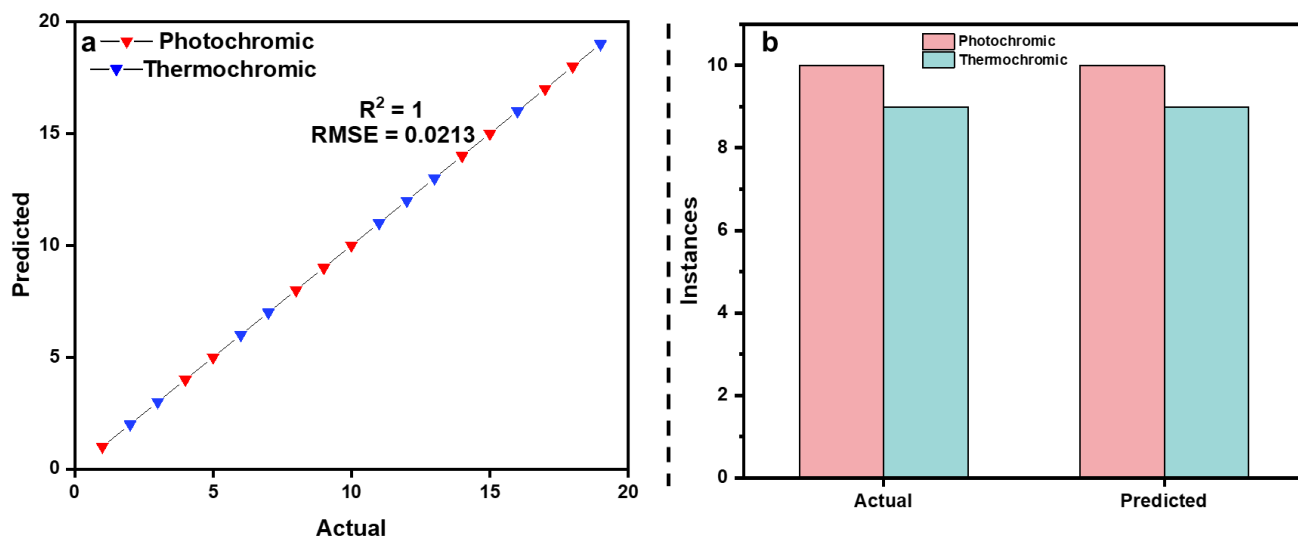


Figure 23. (a) The predicted versus actual classes of the testing set of SAS compounds using k=1 and Manhattan distance measure. (b) A plot of the number of instances against the actual and predicted classes of SAS compounds.

The predicted and actual classes of the SAS compounds are displayed in Figure 8a, with a correlation coefficient of 1. Figure 23b is a graphical representation of the actual and predicted properties of SAS compounds. The confusion matrix of the actual and predicted outcome of the ML model is presented in Table 16. The confusion matrix remains the ultimate criterion for judging this kind of classifier algorithm. In summary, 64 data sets (Table 32) were used and 30% of the data set is 19, and the model predicted 10 SAS compounds to be photochromic which is equivalent to the actual class input in the model, also known as true positive (TP) class, whereas it predicted 9 SAS compounds to be thermochromic which is also equal to the actual class given to the model, also known as true negative (TN) class.

Overall, all the features selected for the prediction of the photochromic behavior of SAS compounds are crucial. This is proven by the high model accuracy of 89-100% for all the optimizations employed. The DFT-ML used in this study will enable industries to screen the eventual materials with the salient features before producing such materials on a large scale. This can also be of potential application to photonic technologies and industries.

Table 16. Confusion matrix showing the actual and predicted SAS compounds based on 30% testing set and their properties.

Actual Predicted	Photochromic	Thermochromic
Photochromic	10	0
Thermochromic	0	9

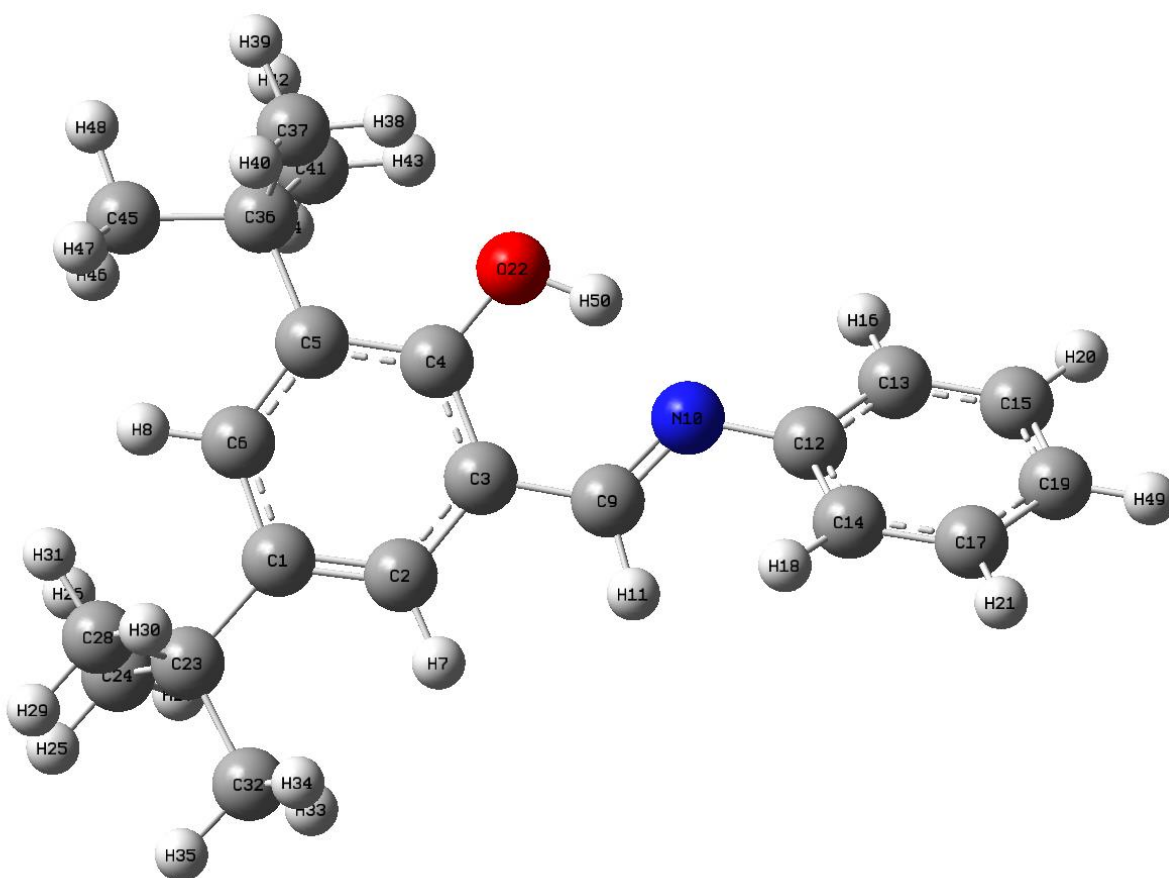
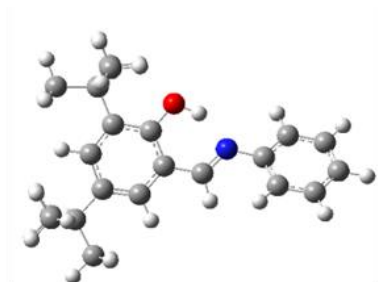
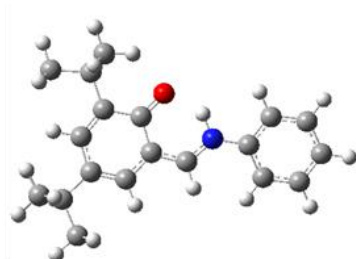


Figure 24. Optimized representative SAS compound showing the atomic numbering and labeling for better visualization of the dihedral angles.

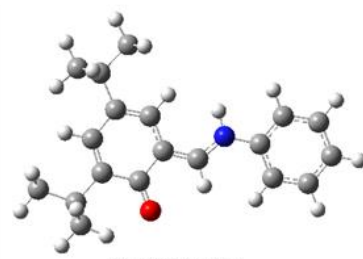
NOTE: Throughout this document, *E*, *K* and *TK* have been used to denote *enol*, *cis-keto* and *trans-keto* of the studied compounds.



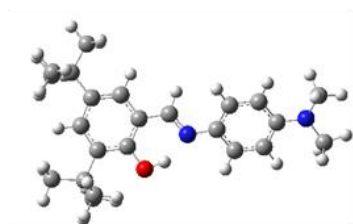
SAS1E



SAS1K



SAS1TK



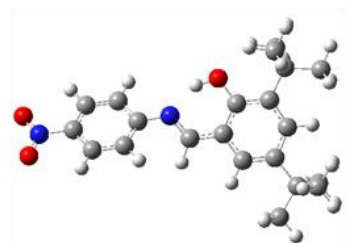
SAS2E



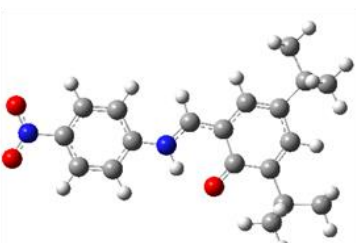
SAS2K



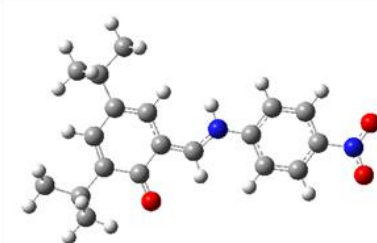
SAS2TK



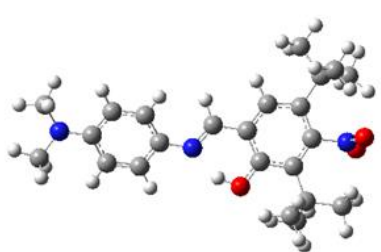
SAS3E



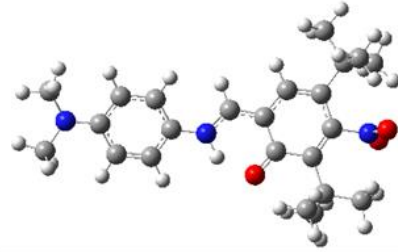
SAS3K



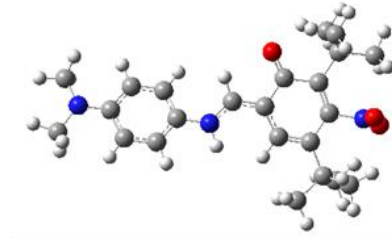
SAS3TK



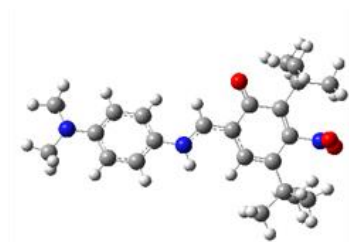
SAS4E



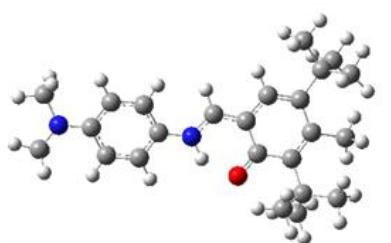
SAS4K



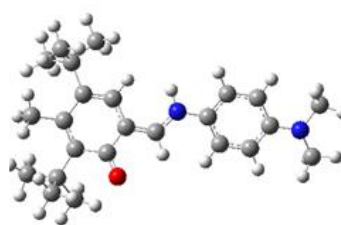
SAS4TK



SAS5E



SAS5K



SAS5TK



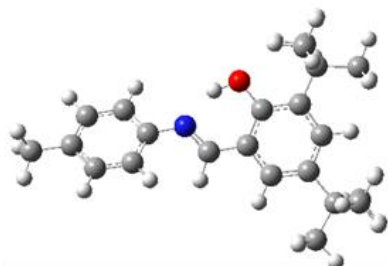
SAS6E



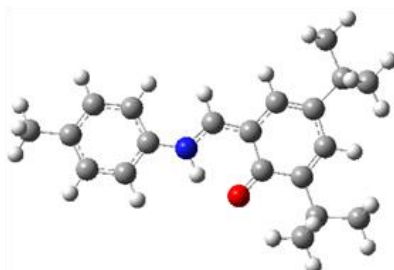
SAS6K



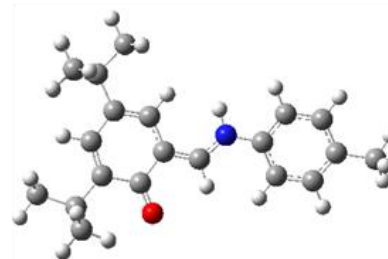
SAS6TK



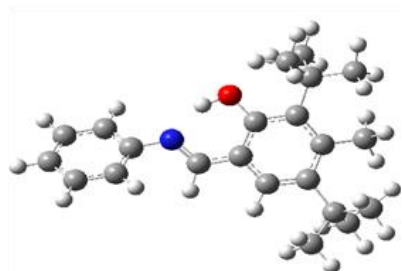
SAS7E



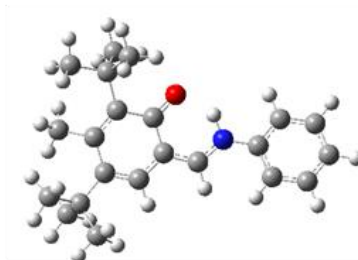
SAS7K



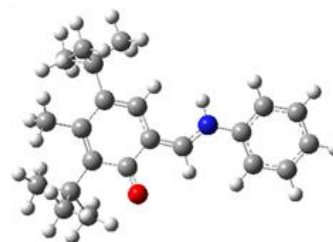
SAS7TK



SAS8E



SAS8K



SAS8TK

Figure 25. Optimized geometries of the 24 SAS compounds at B3LYP/6-311G++(d,p) level of theory.

Table 17. HOMO, LUMO, Energy gap (E_{gap}), ionization potential (I), electron affinity (A), and electronegativity in eV of the simulated SAS compounds in the **vacuum (gas) phase**.

SAS Derivatives	HOMO	LUMO	HOMO (eV)	LUMO (eV)	E_{gap} (eV)	I	A	Electronegativity (eV)
SAS1E	-0.21929	-0.0721	-5.97	-1.96	4.01	1.96194	5.967188	3.96
SAS1K	-0.2011	-0.08403	-5.47	-2.29	3.19	2.28657	5.472213	3.88
SAS2E	-0.19284	-0.06212	-5.25	-1.69	3.56	1.69037	5.247446	3.47
SAS2K	-0.18684	-0.07223	-5.08	-1.97	3.12	1.96548	5.084178	3.52
SAS3E	-0.23379	-0.10991	-6.36	-2.99	3.37	2.9908	6.361753	4.68
SAS3K	-0.21179	-0.11626	-5.76	-3.16	2.60	3.1636	5.763102	4.46
SAS4E	-0.20256	-0.08763	-5.51	-2.38	3.13	2.38453	5.511941	3.95
SAS4K	-0.20032	-0.08889	-5.45	-2.42	3.03	2.41882	5.450988	3.93
SAS5E	-0.19121	-0.06071	-5.20	-1.65	3.55	1.652	5.203092	3.43
SAS5K	-0.18488	-0.07046	-5.03	-1.92	3.11	1.91732	5.030844	3.47
SAS6E	-0.2318	-0.09287	-6.31	-2.53	3.78	2.52712	6.307603	4.42
SAS6K	-0.21423	-0.09765	-5.83	-2.66	3.17	2.65719	5.829498	4.24
SAS7E	-0.21624	-0.06973	-5.88	-1.90	3.99	1.89745	5.884193	3.89
SAS7K	-0.19846	-0.08129	-5.40	-2.21	3.19	2.21201	5.400374	3.81
SAS8E	-0.2168	-0.07051	-5.90	-1.92	3.98	1.91868	5.899432	3.91
SAS8K	-0.19813	-0.08176	-5.39	-2.22	3.17	2.2248	5.391395	3.81

Table 18. HOMO, LUMO, Energy gap (E_{gap}), ionization potential (I), electron affinity (A), and electronegativity in eV of the simulated SAS compounds in the **Toluene**.

SAS Derivatives	HOMO	LUMO	HOMO (eV)	LUMO (eV)	E_{gap} (eV)	I	A	Electronegativity (eV)
SAS1E	-0.22041	-0.07239	-6.00	-1.97	4.03	1.969833	5.997665	3.98
SAS1K	-0.20237	-0.08403	-5.51	-2.29	3.22	2.286574	5.506771	3.90
SAS2E	-0.19303	-0.0643	-5.25	-1.75	3.50	1.749693	5.252617	3.50
SAS2K	-0.1884	-0.07425	-5.13	-2.02	3.11	2.020446	5.126628	3.57
SAS3E	-0.23058	-0.11135	-6.27	-3.03	3.24	3.029989	6.274405	4.65
SAS3K	-0.21454	-0.11564	-5.84	-3.15	2.69	3.146726	5.837934	4.49
SAS4E	-0.19971	-0.09479	-5.43	-2.58	2.86	2.579369	5.434389	4.01
SAS4K	-0.19868	-0.09249	-5.41	-2.52	2.89	2.516782	5.406361	3.96
SAS5E	-0.19161	-0.06288	-5.21	-1.71	3.50	1.711053	5.213976	3.46
SAS5K	-0.18675	-0.07251	-5.08	-1.97	3.11	1.973099	5.081729	3.53
SAS6E	-0.23098	-0.0978	-6.29	-2.66	3.62	2.661275	6.285289	4.47
SAS6K	-0.21415	-0.09773	-5.83	-2.66	3.17	2.65937	5.827321	4.24
SAS7E	-0.21766	-0.07041	-5.92	-1.92	4.01	1.915955	5.922833	3.92

SAS7K	-0.20015	-0.08171	-5.45	-2.22	3.22	2.223443	5.446362	3.83
SAS8E	-0.21793	-0.07092	-5.93	-1.93	4.00	1.929832	5.93018	3.93
SAS8K	-0.19963	-0.08193	-5.43	-2.23	3.20	2.22943	5.432212	3.83

Table 19. HOMO, LUMO, Energy gap (E_{gap}), ionization potential (I), electron affinity (A), and electronegativity in eV of the simulated SAS compounds in the **Methanol**.

SAS	HOMO		LUMO	Electronegativity				
Derivatives	HOMO	LUMO	(eV)	(eV)	E_{gap} (eV)	I	A	(eV)
SAS1E	-0.22313	-0.07404	-6.07	-2.01	4.06	2.014732	6.07168	4.04
SAS1K	-0.20539	-0.08553	-5.59	-2.33	3.26	2.327391	5.588949	3.96
SAS2E	-0.19496	-0.06816	-5.31	-1.85	3.45	1.854729	5.305135	3.58
SAS2K	-0.19119	-0.07796	-5.20	-2.12	3.08	2.121401	5.202548	3.66
SAS3E	-0.22896	-0.11402	-6.23	-3.10	3.13	3.102644	6.230322	4.67
SAS3K	-0.21292	-0.11672	-5.79	-3.18	2.62	3.176115	5.793851	4.48
SAS4E	-0.19842	-0.10351	-5.40	-2.82	2.58	2.816652	5.399286	4.11
SAS4K	-0.1975	-0.10143	-5.37	-2.76	2.61	2.760052	5.374252	4.07
SAS5E	-0.19386	-0.06685	-5.28	-1.82	3.46	1.819082	5.275202	3.55
SAS5K	-0.1899	-0.07629	-5.17	-2.08	3.09	2.075958	5.167445	3.62
SAS6E	-0.23106	-0.10473	-6.29	-2.85	3.44	2.84985	6.287466	4.57
SAS6K	-0.21497	-0.10317	-5.85	-2.81	3.04	2.8074	5.849635	4.33
SAS7E	-0.2207	-0.07253	-6.01	-1.97	4.03	1.973643	6.005556	3.99
SAS7K	-0.20365	-0.08317	-5.54	-2.26	3.28	2.263172	5.541602	3.90
SAS8E	-0.22075	-0.07276	-6.01	-1.98	4.03	1.979901	6.006917	3.99
SAS8K	-0.20281	-0.08352	-5.52	-2.27	3.25	2.272696	5.518744	3.90

Table 20. HOMO, LUMO, Energy gap (E_{gap}), ionization potential (I), electron affinity (A), and electronegativity in eV of the simulated SAS compounds in the **Water**.

SAS	HOMO		LUMO	Electronegativity				
Derivatives	HOMO	LUMO	(eV)	(eV)	E_{gap} (eV)	I	A	(eV)
SAS1E	-0.22335	-0.07419	-6.08	-2.02	4.06	2.018814	6.077666	4.05
SAS1K	-0.20563	-0.08567	-5.60	-2.33	3.26	2.331201	5.59548	3.96
SAS2E	-0.19514	-0.06844	-5.31	-1.86	3.45	1.862348	5.310033	3.59
SAS2K	-0.19141	-0.07824	-5.21	-2.13	3.08	2.12902	5.208534	3.67
SAS3E	-0.22891	-0.11419	-6.23	-3.11	3.12	3.10727	6.228962	4.67
SAS3K	-0.21288	-0.11681	-5.79	-3.18	2.61	3.178564	5.792763	4.49
SAS4E	-0.1984	-0.10406	-5.40	-2.83	2.57	2.831618	5.398742	4.12
SAS4K	-0.19747	-0.10204	-5.37	-2.78	2.60	2.776651	5.373435	4.08

SAS5E	-0.19406	-0.06715	-5.28	-1.83	3.45	1.827246	5.280644	3.55
SAS5K	-0.19013	-0.07658	-5.17	-2.08	3.09	2.083849	5.173703	3.63
SAS6E	-0.23109	-0.10517	-6.29	-2.86	3.43	2.861823	6.288282	4.58
SAS6K	-0.21505	-0.10365	-5.85	-2.82	3.03	2.820462	5.851812	4.34
SAS7E	-0.22094	-0.0727	-6.01	-1.98	4.03	1.978269	6.012087	4.00
SAS7K	-0.20392	-0.08389	-5.55	-2.28	3.27	2.282764	5.548949	3.92
SAS8E	-0.22097	-0.07292	-6.01	-1.98	4.03	1.984255	6.012903	4.00
SAS8K	-0.20307	-0.08367	-5.53	-2.28	3.25	2.276778	5.525819	3.90

Table 21. First polarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **vacuum (gas) phase**.

SAS Derivatives	α_x	α_y	α_z	α_{tot} (a.u)	α_{tot} (C ² m ² J ⁻¹)
SAS1E	413.273	185.402	274.004	290.893	4.79E-39
SAS1K	338.87	236.967	338.426	304.7543	5.02E-39
SAS2E	266.758	317.201	472.189	352.0493	5.80E-39
SAS2K	232.275	339.309	523.048	364.8773	6.01E-39
SAS3E	205.003	283.467	481.28	323.25	5.33E-39
SAS3K	202.682	318.536	516.462	345.8933	5.70E-39
SAS4E	237.806	324.713	555.782	372.767	6.14E-39
SAS4K	231.984	332.353	589.968	384.7683	6.34E-39
SAS5E	298.607	341.962	463.253	367.9407	6.06E-39
SAS5K	268.18	344.698	528.012	380.2967	6.27E-39
SAS6E	228.334	310.026	435.683	324.681	5.35E-39
SAS6K	228.029	307.076	483.036	339.3803	5.59E-39
SAS7E	409.68	216.291	301.154	309.0417	5.09E-39
SAS7K	299.835	281.836	388.492	323.3877	5.33E-39
SAS8E	424.872	204.174	291.064	306.7033	5.05E-39
SAS8K	402.158	224.197	332.993	319.7827	5.27E-39

Table 22. First polarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **Toluene**.

SAS Derivatives	α_x	α_y	α_z	α_{tot} (a.u)	α_{tot} (C ² m ² J ⁻¹)
SAS1E	471.01	212.764	316.455	333.4097	5.49E-39
SAS1K	398.859	267.392	388.697	351.6493	5.80E-39
SAS2E	317.59	362.711	532.404	404.235	6.66E-39
SAS2K	270.462	393.981	601.871	422.1047	6.96E-39
SAS3E	237.396	327.049	555.392	373.279	6.15E-39
SAS3K	238.049	374.176	602.022	404.749	6.67E-39
SAS4E	276.79	375.278	640.989	431.019	7.10E-39
SAS4K	269.162	385.482	690.799	448.481	7.39E-39
SAS5E	358.745	391.753	519.809	423.4357	6.98E-39
SAS5K	317.847	398.027	606.803	440.8923	7.27E-39
SAS6E	264.534	358.653	492.055	371.7473	6.13E-39
SAS6K	265.348	354.169	554.69	391.4023	6.45E-39
SAS7E	478.8	239.31	340.841	352.9837	5.82E-39

SAS7K	353.382	319.468	442.473	371.7743	6.13E-39
SAS8E	480.876	238.625	339.136	352.879	5.82E-39
SAS8K	477.068	251.549	382.332	370.3163	6.10E-39

Table 23. First polarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **Methanol**.

SAS Derivatives	α_x	α_y	α_z	α_{tot} (a.u)	α_{tot} (C ² m ² J ⁻¹)
SAS1E	530.438	263.672	373.185	389.0983	6.41E-39
SAS1K	485.563	307.451	443.244	412.086	6.79E-39
SAS2E	405.812	421.441	588.852	472.035	7.78E-39
SAS2K	340.318	466.857	681.558	496.2443	8.18E-39
SAS3E	294.369	384.276	636.591	438.412	7.23E-39
SAS3K	301.059	447.66	693.189	480.636	7.92E-39
SAS4E	347.335	442.158	729.343	506.2787	8.34E-39
SAS4K	337.42	455.727	799.489	530.8787	8.75E-39
SAS5E	461.643	452.977	571	495.2067	8.16E-39
SAS5K	404.171	468.3	684.322	518.931	8.55E-39
SAS6E	327.293	422.557	549.437	433.0957	7.14E-39
SAS6K	331.018	415.135	628.629	458.2607	7.55E-39
SAS7E	559.644	280.501	391.654	410.5997	6.77E-39
SAS7K	438.622	366.275	497.544	434.147	7.15E-39
SAS8E	539.808	297.315	401.974	413.0323	6.81E-39
SAS8K	574.485	292.732	438.151	435.1227	7.17E-39

Table 24. First polarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **Water**.

SAS Derivatives	α_x	α_y	α_z	α_{tot} (a.u)	α_{tot} (C ² m ² J ⁻¹)
SAS1E	533.955	268.071	377.085	393.037	6.48E-39
SAS1K	491.637	310.655	446.632	416.308	6.86E-39
SAS2E	412.837	425.654	592.026	476.839	7.86E-39
SAS2K	346.186	471.988	686.223	501.4657	8.26E-39
SAS3E	299.14	388.205	641.552	442.9657	7.30E-39
SAS3K	306.281	452.707	698.568	485.852	8.01E-39
SAS4E	353.357	446.818	734.545	511.5733	8.43E-39
SAS4K	343.3	460.598	806.03	536.6427	8.84E-39
SAS5E	469.676	457.311	573.867	500.2847	8.24E-39

SAS5K	411.087	473.354	688.766	524.4023	8.64E-39
SAS6E	332.528	427.015	552.815	437.4527	7.21E-39
SAS6K	336.482	419.352	632.989	462.941	7.63E-39
SAS7E	564.59	284.316	395.206	414.704	6.83E-39
SAS7K	444.971	369.746	500.87	438.529	7.23E-39
SAS8E	543.453	302.135	406.203	417.2637	6.88E-39
SAS8K	580.844	296.323	441.717	439.628	7.25E-39

Table 25. First hyperpolarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **vacuum (gas) phase**.

SAS Derivatives	β_x	β_y	β_z	β_{tot} (a.u)	β_{tot} ($C^3 m^3 J^{-2}$)
SAS1E	349.511	-48.617	545.718	649.869	2.08E-50
SAS1K	-271.379	-183.45	407.689	522.9826	1.68E-50
SAS2E	-2346.44	3042.107	-5607.3	6797.205	2.18E-49
SAS2K	1583.667	3856.676	-7145.59	8272.93	2.65E-49
SAS3E	-316.723	-2298.45	-6337.84	6749.174	2.16E-49
SAS3K	-2008.42	4621.174	-9724.45	10952.34	3.51E-49
SAS4E	1575.588	2647.454	-9260.09	9759.133	3.13E-49
SAS4K	1657.635	2886.084	-9976.8	10517.31	3.37E-49
SAS5E	3394.343	-3156.85	-4766.93	6649.126	2.13E-49
SAS5K	2090.726	4208.927	-6962.23	8399.929	2.69E-49
SAS6E	522.265	619.671	-582.618	998.0965	3.20E-50
SAS6K	459.904	764.139	-1052.04	1379.206	4.42E-50
SAS7E	582.293	-282.135	307.823	716.5335	2.30E-50
SAS7K	848.343	735.596	-350.905	1176.402	3.77E-50
SAS8E	-854.399	-139.599	350.457	933.973	2.99E-50
SAS8K	-158.356	57.664	365.078	402.0991	1.29E-50

Table 26. First hyperpolarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **Toluene**.

SAS Derivatives	β_x	β_y	β_z	β_{tot} (a.u)	β_{tot} ($C^3 m^3 J^{-2}$)
SAS1E	514.62	-98.776	751.953	916.5281	2.94E-50
SAS1K	-685.875	-419.814	408.373	901.9073	2.89E-50
SAS2E	-4223.11	5292.695	-9262.56	11473.55	3.68E-49
SAS2K	3336.857	7100.838	-13085.4	15257.28	4.89E-49
SAS3E	-692.609	-4096.59	-11198.5	11944.36	3.83E-49
SAS3K	-4215.25	8967.015	-17991.1	20539.08	6.58E-49
SAS4E	2929.387	5065.165	-17191.3	18159.76	5.82E-49
SAS4K	3168.448	5820.014	-19711	20795.06	6.67E-49
SAS5E	5922.47	-5286.61	-7737.19	11085.49	3.55E-49
SAS5K	4285.873	7615.835	-12640.3	15367.09	4.93E-49
SAS6E	944.731	1139.469	-1467.72	2084.494	6.68E-50
SAS6K	978.12	1629.166	-2797.17	3381.577	1.08E-49
SAS7E	981.612	-399.351	431.806	1144.334	3.67E-50

SAS7K	1678.637	1403.318	-938.821	2380.863	7.63E-50
SAS8E	-1337.62	-282.447	424.401	1431.477	4.59E-50
SAS8K	-478.6	-0.645	402.098	625.0929	2.00E-50

Table 27. First hyperpolarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **Methanol**.

SAS Derivatives	β_x	β_y	β_z	$\beta_{tot} \text{ (a.u)}$	$\beta_{tot} \text{ (C}^3 \text{ m}^3 \text{ J}^{-2}\text{)}$
SAS1E	743.871	-209.858	1037.852	1294.033	4.15E-50
SAS1K	-1451.589	-764.6	454.227	1702.365	5.46E-50
SAS2E	-7804.45	8528.22	-13737.7	17954.49	5.76E-49
SAS2K	6900.574	12649.82	-21662.5	26017.26	8.34E-49
SAS3E	-1542.783	-7168.49	-18222.9	19642.83	6.30E-49
SAS3K	-8869.328	16793.51	-30780.9	36168.37	1.16E-48
SAS4E	5637.169	9262.357	-29262.8	31207.09	1.00E-48
SAS4K	6289.395	11186.15	-35426.5	37679.25	1.21E-48
SAS5E	10312.15	-7978.28	-10890.5	16988.11	5.45E-49
SAS5K	8716.432	13115.33	-20425.4	25791.16	8.27E-49
SAS6E	1623.51	1909.989	-2628.52	3632.214	1.16E-49
SAS6K	1932.854	3063.614	-5373.67	6480.586	2.08E-49
SAS7E	1499.042	-476.769	735.036	1736.293	5.57E-50
SAS7K	3144.123	2356.087	-1621.96	4250.578	1.36E-49
SAS8E	-2054.919	-530.909	488.41	2177.866	6.98E-50
SAS8K	-1019.512	-20.004	523.874	1146.407	3.68E-50

Table 28. First hyperpolarizability values of the SAS compounds simulated at B3LYP/6-311++G(d,p) level of theory in the **Water**.

SAS Derivatives	β_x	β_y	β_z	$\beta_{tot} \text{ (a.u)}$	$\beta_{tot} \text{ (C}^3 \text{ m}^3 \text{ J}^{-2}\text{)}$
SAS1E	758.918	-219.627	1058.258	1320.645	4.23E-50
SAS1K	-1512.49	-787.876	461.412	1766.713	5.66E-50
SAS2E	-8098.37	8820.06	-14013.5	18432.48	5.91E-49
SAS2K	7202.801	13076.33	-22255.1	26798.53	8.59E-49
SAS3E	-20043	-2244.9	-188.41	20169.22	6.47E-49
SAS3K	-9258.89	17387.77	-31656.7	37285.53	1.20E-48
SAS4E	5867.885	9585.757	-30121.6	32150.09	1.03E-48
SAS4K	6558.691	11612.52	-36583.3	38938.46	1.25E-48

SAS5E	10652	-8264.36	-11060	17438.12	5.59E-49
SAS5K	9088.074	13521.35	-20942.9	26533.44	8.51E-49
SAS6E	1673.973	1963.399	-2700.92	3735.252	1.20E-49
SAS6K	2008.805	3169.798	-5547.76	6697.804	2.15E-49
SAS7E	1532.069	-479.804	761.671	1776.961	5.70E-50
SAS7K	3258.243	2420.476	-1659.72	4385.147	1.41E-49
SAS8E	-2106.47	548.58	492.317	2231.709	7.15E-50
SAS8K	-1059.6	-15.715	537.503	1188.237	3.81E-50

Table 29. Maximum simulated wavelengths (λ , nm), excited-state transition energies (ΔE , eV), oscillator strengths (f_{os}), significant molecular orbital contributions, and transitions of the studied SAS compounds calculated at the B3LYP/6–311++G(d, p) level in the **Toluene**.

SAS Derivatives	State	$\Delta E(\text{eV})$	λ (nm)	f_{os}	Contribution Factor	Main Transition	% Contribution
SAS1E	1	3.4786	356.4	0.3792	0.69809	H→L	97.46593
SAS1K	1	2.8132	440.7	0.3933	0.70456	H→L	99.28096
SAS2E	1	3.0613	405	0.8573	0.70217	H→L	98.60854
SAS2K	1	2.7142	456.8	0.7535	0.70535	H→L	99.50372
SAS3E	1	2.8343	437.4	0.2551	0.70291	H→L	98.81649
SAS3K	1	2.3459	528.5	0.4145	0.70577	H→L	99.62226
SAS4E	1	2.4661	502.8	0.0806	0.69154	H→L	95.64551
					0.11118	H-1→L	2.472198
SAS4K	1	2.3841	520	0.0968	0.64441	H→L	83.05285
					0.19485	H→L+1	7.593305
					0.18681	H-1→L	6.979595
					0.10543	H-1→L+1	2.223097
SAS5E	1	3.0633	404.7	0.9138	0.70143	H→L	98.40081
SAS5K	1	2.6899	460.9	0.6843	0.7014	H→L	98.39239
SAS6E	1	2.9524	420	0.0355	0.66734	H→L	89.06854
					0.17776	H-1→L	6.319724
					0.10013	H-3→L	2.005203
SAS6K	1	2.5674	482.9	0.0521	0.57495	H→L	66.1135
					0.39981	H→L+1	31.96961
SAS7E	1	3.4623	358.4	0.4991	0.69819	H→L	97.49386
SAS7K	1	2.816	440.3	0.4433	0.70472	H→L	99.32606
SAS8E	1	3.4339	361.1	0.3574	0.69103	H→L	95.50449
SAS8K					0.10334	H-1→L	2.135831
	1	2.7527	450.4	0.3138	0.70024	H→L	98.06721

Table 30. Maximum simulated wavelengths (λ , nm), excited-state transition energies (ΔE , eV), oscillator strengths (f_{os}), significant molecular orbital contributions, and transitions of the studied SAS compounds calculated at the B3LYP/6–311++G(d, p) level in the **Methanol**.

SAS Derivatives	State	$\Delta E(\text{eV})$	λ (nm)	f_{os}	Contribution Factor	Main Transition	% Contribution
SAS1E	1	3.52	352.3	0.3506	0.69642	H→L	97.00016
SAS1K	1	2.8669	432.5	0.3751	0.70378	H→L	99.06126
SAS2E	1	3.0446	407.2	0.8123	0.70246	H→L	98.69001
SAS2K	1	2.7213	455.6	0.7737	0.70489	H→L	99.37398
SAS3E	1	2.7426	452.1	0.211	0.70412	H→L	99.15699
SAS3K	1	2.2998	539.1	0.3729	0.70577	H→L	99.62226
SAS4E	1	2.2153	559.7	0.0471	0.6963	H→L	96.96674
SAS4K	1	2.1367	580.3	0.0376	0.66791	H→L	89.22075
					0.21468	H-1→L	9.2175
SAS5E	1	3.0516	406.3	0.8674	0.70201	H→L	98.56361
SAS5K	1	2.7074	458	0.7263	0.70018	H→L	98.05041
SAS6E	1	2.7838	445.4	0.0197	0.6609	H→L	87.35776
					0.21771	H-1→L	9.479529
SAS6K	1	2.3701	523.1	0.0163	0.68053	H→L	92.62422
					0.15925	H→L+1	5.072113
SAS7E	1	3.5025	354	0.4785	0.69658	H→L	97.04474
SAS7K	1	2.8695	432.1	0.43	0.70394	H→L	99.1063
SAS8E	1	3.4727	357	0.325	0.68649	H→L	94.2537
					0.12685	H-1→L	3.218185
SAS8K	1	2.8057	441.9	0.2978	0.699	H→L	97.7202

Table 31. Maximum simulated wavelengths (λ , nm), excited-state transition energies (ΔE , eV), oscillator strengths (f_{os}), significant molecular orbital contributions, and transitions of the studied SAS compounds calculated at the B3LYP/6–311++G(d, p) level in the **Water**.

SAS Derivatives	State	$\Delta E(\text{eV})$	λ (nm)	f_{os}	Contribution Factor	Main Transition	% Contribution
SAS1E	1	3.5214	352.1	0.3516	0.69643	H→L	97.00294898
SAS1K	1	2.8685	432.2	0.3579	0.70379	H→L	99.06407282
SAS2E	1	3.0417	407.6	0.8125	0.70249	H→L	98.69844002
SAS2K	1	2.7193	456	0.77	0.70488	H→L	99.37116288
SAS3E	1	2.7374	452.9	0.2106	0.70416	H→L	99.16826112
SAS3K	1	2.2961	540	0.3728	0.70579	H→L	99.62790482
SAS4E	1	2.2007	563.4	0.0464	0.69653	H→L	97.03080818

SAS4K	1	2.1213	584.5	0.0366	0.66857	H→L	89.39716898
					0.21425	H-1→L	9.1806125
SAS5E	1	3.049	406.6	0.8677	0.70206	H→L	98.57764872
SAS5K	1	2.7061	458.2	0.7315	0.70021	H→L	98.05880882
SAS6E	1	2.7734	447.1	0.0194	0.66048	H→L	87.24676608
					0.21965	H-1→L	9.6492245
SAS6K	1	2.3577	525.9	0.0157	0.68269	H→L	93.21312722
					0.14935	H→L+1	4.4610845
SAS7E	1	3.5037	353.9	0.4803	0.6966	H→L	97.050312
SAS7K	1	2.871	431.9	0.4314	0.70395	H→L	99.1091205
SAS8E	1	3.4741	356.9	0.3262	0.68647	H→L	94.24821218
					0.12688	H-1→L	3.21970688
SAS8K	1	2.8076	441.6	0.2989	0.69904	H→L	97.73138432

Figure 26. UV–vis spectra of all the studied SAS compounds as computed at the B3LYP/6-311++G(d,p) level of theory in **Toluene**.

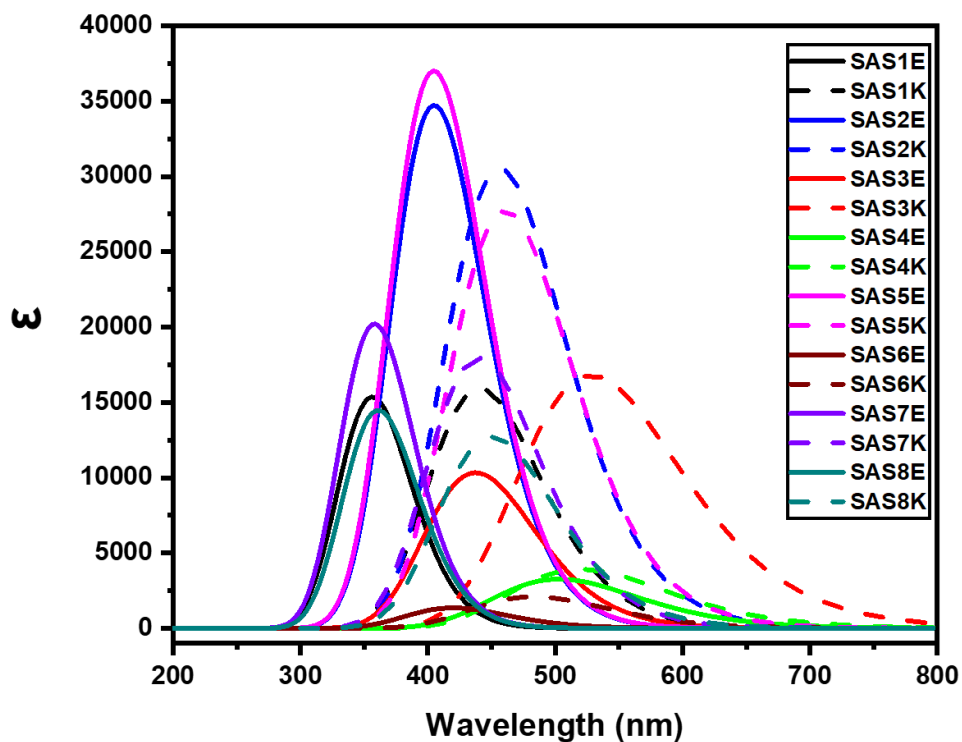


Figure 27. UV–vis spectra of all the studied SAS compounds as computed at the B3LYP/6-311++G(d,p) level of theory in **Methanol**.

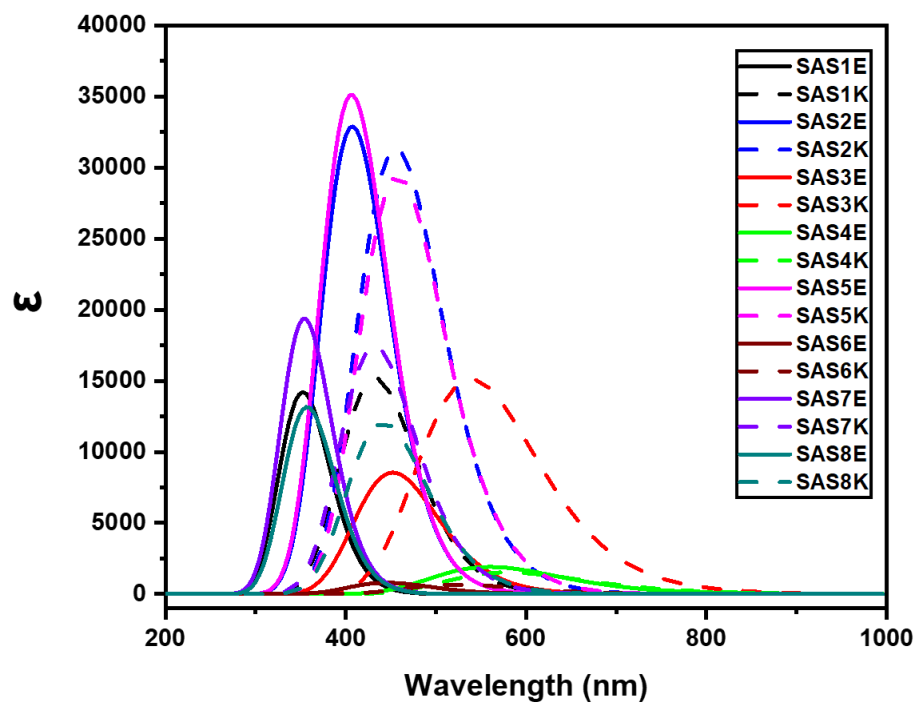


Figure 28. UV–vis spectra of all the studied SAS compounds as computed at the B3LYP/6-311++G(d,p) level of theory in **Water**.

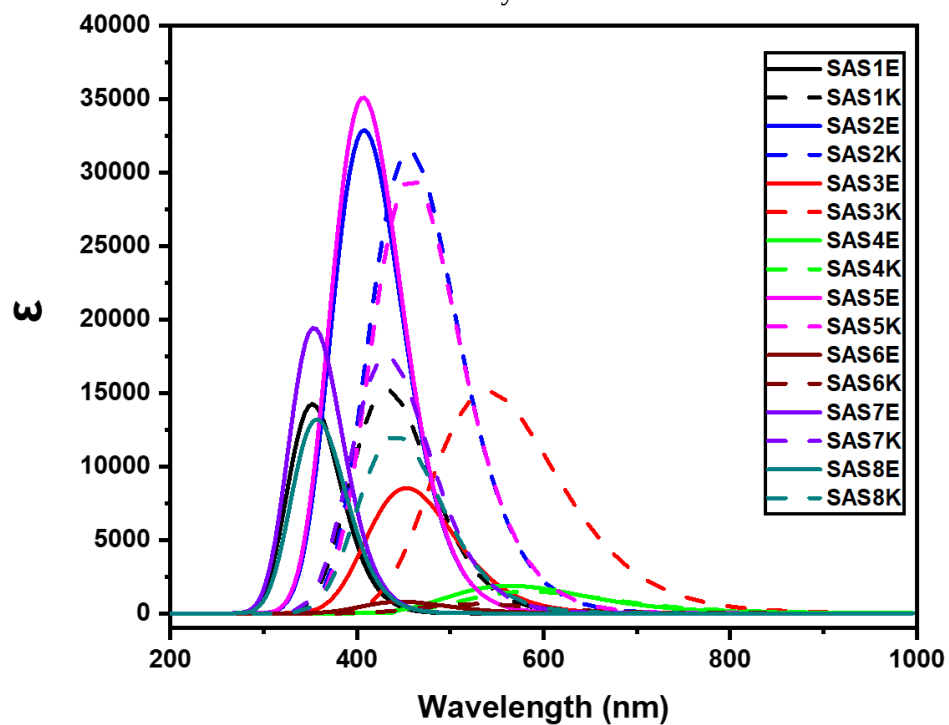


Table 32. Input selected features for training and testing the ML model

Compound	Conformations	Phase	Energy				Excitation		Oscillator		Class
			Electronegativity	gap	Polarizability	Hyperpolarizability	energy	Wavelength	strength	MOT	
SAS1E	enol	vacuum	3.96	4.01	290.893	649.869	3.5103	353.2	0.2614	1	photochromic
SAS1K	keto	vacuum	3.88	3.19	304.7543	522.9826	2.8586	433.7	0.29	1	thermochromic
SAS2E	enol	vacuum	3.47	3.56	352.0493	6797.205	3.1924	388.4	0.7315	1	photochromic
SAS2K	keto	vacuum	3.52	3.12	364.8773	8272.93	2.8155	440.4	0.5594	1	thermochromic
SAS3E	enol	vacuum	4.68	3.37	323.25	6749.174	2.9721	417.2	0.1962	1	thermochromic
SAS3K	keto	vacuum	4.46	2.6	345.8933	10952.34	2.4693	502.1	0.3196	1	thermochromic
SAS4E	enol	vacuum	3.95	3.13	372.767	9759.133	2.7232	455.3	0.0858	2	thermochromic
SAS4K	keto	vacuum	3.93	3.03	384.7683	10517.31	2.6088	475.26	0.1356	4	thermochromic
SAS5E	enol	vacuum	3.43	3.55	367.9407	6649.126	3.1888	388.8	0.7724	1	photochromic
SAS5K	keto	vacuum	3.47	3.11	380.2967	8399.929	2.7683	447.9	0.4601	2	thermochromic
SAS6E	enol	vacuum	4.42	3.78	324.681	998.0965	3.1068	399.1	0.0346	3	photochromic
SAS6K	keto	vacuum	4.24	3.17	339.3803	1379.206	2.7366	453.1	0.1041	2	thermochromic
SAS7E	enol	vacuum	3.89	3.99	309.0417	716.5335	3.5021	354	0.3494	1	photochromic
SAS7K	keto	vacuum	3.81	3.19	323.3877	1176.402	2.8622	433.2	0.3291	1	thermochromic
SAS8E	enol	vacuum	3.91	3.98	306.7033	933.973	3.4616	358.2	0.2307	2	photochromic
SAS8K	keto	vacuum	3.81	3.17	319.7827	402.0991	2.7837	445.4	0.2168	2	thermochromic
SAS1E	enol	toluene	3.98	4.03	333.4097	916.5281	3.4786	356.4	0.3792	1	photochromic
SAS1K	keto	toluene	3.9	3.22	351.6493	901.9073	2.8132	440.7	0.3933	1	thermochromic
SAS2E	enol	toluene	3.5	3.5	404.235	11473.55	3.0613	405	0.8573	1	photochromic
SAS2K	keto	toluene	3.57	3.11	422.1047	15257.28	2.7142	456.8	0.7535	1	thermochromic
SAS3E	enol	toluene	4.65	3.24	373.279	11944.36	2.8343	437.4	0.2551	1	thermochromic
SAS3K	keto	toluene	4.49	2.69	404.749	20539.08	2.3459	528.5	0.4145	1	thermochromic
SAS4E	enol	toluene	4.01	2.86	431.019	18159.76	2.4661	502.8	0.0806	2	thermochromic
SAS4K	keto	toluene	3.96	2.89	448.481	20795.06	2.3841	520	0.0968	4	thermochromic
SAS5E	enol	toluene	3.46	3.5	423.4357	11085.49	3.0633	404.7	0.9138	1	photochromic
SAS5K	keto	toluene	3.53	3.11	440.8923	15367.09	2.6899	460.9	0.6843	1	thermochromic
SAS6E	enol	toluene	4.47	3.62	371.7473	2084.494	2.9524	420	0.0355	3	photochromic
SAS6K	keto	toluene	4.24	3.17	391.4023	3381.577	2.5674	482.9	0.0521	2	thermochromic
SAS7E	enol	toluene	3.92	4.01	352.9837	1144.334	3.4623	358.4	0.4991	1	photochromic
SAS7K	keto	toluene	3.83	3.22	371.7743	2380.863	2.816	440.3	0.4433	1	thermochromic
SAS8E	enol	toluene	3.93	4	352.879	1431.477	3.4339	361.1	0.3574	2	photochromic
SAS8K	keto	toluene	3.83	3.2	370.3163	625.0929	2.7527	450.4	0.3138	1	thermochromic
SAS1E	enol	methanol	4.04	4.06	389.0983	1294.033	3.52	352.3	0.3506	1	photochromic
SAS1K	keto	methanol	3.96	3.26	412.086	1702.365	2.8669	432.5	0.3751	1	thermochromic
SAS2E	enol	methanol	3.58	3.45	472.035	17954.49	3.0446	407.2	0.8123	1	photochromic
SAS2K	keto	methanol	3.66	3.08	496.2443	26017.26	2.7213	455.6	0.7737	1	thermochromic
SAS3E	enol	methanol	4.67	3.13	438.412	19642.83	2.7426	452.1	0.211	1	thermochromic
SAS3K	keto	methanol	4.48	2.62	480.636	36168.37	2.2998	539.1	0.3729	1	thermochromic
SAS4E	enol	methanol	4.11	2.58	506.2787	31207.09	2.2153	559.7	0.0471	1	thermochromic
SAS4K	keto	methanol	4.07	2.61	530.8787	37679.25	2.1367	580.3	0.0376	2	thermochromic
SAS5E	enol	methanol	3.55	3.46	495.2067	16988.11	3.0516	406.3	0.8674	1	photochromic
SAS5K	keto	methanol	3.62	3.09	518.931	25791.16	2.7074	458	0.7263	1	thermochromic
SAS6E	enol	methanol	4.57	3.44	433.0957	3632.214	2.7838	445.4	0.0197	2	photochromic
SAS6K	keto	methanol	4.33	3.04	458.2607	6480.586	2.3701	523.1	0.0163	2	thermochromic
SAS7E	enol	methanol	3.99	4.03	410.5997	1736.293	3.5025	354	0.4785	1	photochromic
SAS7K	keto	methanol	3.9	3.28	434.147	4250.578	2.8695	432.1	0.43	1	thermochromic
SAS8E	enol	methanol	3.99	4.03	413.0323	2177.866	3.4727	357	0.325	2	photochromic
SAS8K	keto	methanol	3.9	3.25	435.1227	1146.407	2.8057	441.9	0.2978	1	thermochromic
SAS1E	enol	water	4.05	4.06	393.037	1320.645	3.5214	352.1	0.3516	1	photochromic
SAS1K	keto	water	3.96	3.26	416.308	1766.713	2.8685	432.2	0.3579	1	thermochromic
SAS2E	enol	water	3.59	3.45	476.839	18432.48	3.0417	407.6	0.8125	1	photochromic
SAS2K	keto	water	3.67	3.08	501.4657	26798.53	2.7193	456	0.77	1	thermochromic
SAS3E	enol	water	4.67	3.12	442.9657	20169.22	2.7374	452.9	0.2106	1	thermochromic
SAS3K	keto	water	4.49	2.61	485.852	37285.53	2.2961	540	0.3728	1	thermochromic
SAS4E	enol	water	4.12	2.57	511.5733	32150.09	2.2007	563.4	0.0464	1	thermochromic
SAS4K	keto	water	4.08	2.6	536.6427	38938.46	2.1213	584.5	0.0366	2	thermochromic
SAS5E	enol	water	3.55	3.45	500.2847	17438.12	3.049	406.6	0.8677	1	photochromic

SAS5K	keto	water	3.63	3.09	524.4023	26533.44	2.7061	458.2	0.7315	1	thermochromic
SAS6E	enol	water	4.58	3.43	437.4527	3735.252	2.7734	447.1	0.0194	2	photochromic
SAS6K	keto	water	4.34	3.03	462.941	6697.804	2.3577	525.9	0.0157	2	thermochromic
SAS7E	enol	water	4	4.03	414.704	1776.961	3.5037	353.9	0.4803	1	photochromic
SAS7K	keto	water	3.92	3.27	438.529	4385.147	2.871	431.9	0.4314	1	thermochromic
SAS8E	enol	water	4	4.03	417.2637	2231.709	3.4741	356.9	0.3262	2	photochromic
SAS8K	keto	water	3.9	3.25	439.628	1188.237	2.8076	441.6	0.2989	1	thermochromic

Table 33. The performance measure for the KNN ML model using the cross-validation data split. *MAE and RMSE denote mean absolute error and root mean square error respectively.*

Distance Measure	Euclidean					Manhattan			
	K	RMSE	MAE	% Model Accuracy	Kappa Statistic	RMSE	MAE	% Model Accuracy	Kappa Statistic
1	0.302	0.107	90.6	0.800	0.214	0.062	95.3	0.899	
3	0.208	0.083	92.2	0.835	0.119	0.047	100	1.000	
5	0.166	0.072	96.9	0.934	0.166	0.059	93.8	0.867	
7	0.191	0.087	95.3	0.902	0.199	0.089	95.3	0.899	

Table 34. The performance measure for the KNN ML model using the percentage data split. *MAE and RMSE denote mean absolute error and root mean square error respectively.*

Distance Measure	Euclidean					Manhattan			
	K	RMSE	MAE	% Model Accuracy	Kappa Statistic	RMSE	MAE	% Model Accuracy	Kappa Statistic
1	0.318	0.122	89.5	0.789	0.0213	0.0213	100	1.000	
3	0.203	0.094	94.7	0.895	0.109	0.042	100	1.000	
5	0.221	0.119	94.7	0.895	0.200	0.098	94.7	0.895	
7	0.213	0.153	100	1.000	0.193	0.115	100	1.000	

CHAPTER 6

CONCLUSION

The study presents the photocatalytic activity of metal-free graphitic-carbon nitride and carbon nitride-modified highly reduced graphene, and the mechanism of CO₂RR on the surfaces of CN-HRG-CO and CN-HRG-COOH using the DFT approach. Initially, the optical and electronic properties of CN, CN-G, CN-HRG-CO, and CN-HRG-COOH were investigated to ascertain the best-performing photocatalytic materials. It was observed that the introduction of HRG on the surface of the pristine CN improved its catalytic efficiency. Sequel to our findings, CN-HRG-CO and CN-HRG-COOH are the most promising photocatalytic materials due to their exhibited exceptional properties. We have presented the CO₂RR via the CN and HRG adsorption sites of CN-HRG-CO and CN-HRG-COOH configurations. The limiting potentials are -0.87, -0.80, -0.16, and -0.08 V respectively. It is therefore evident that CN-HRG-COOH has better reduction capacity and selectivity for CO₂RR due to its low limiting potential. This is also supported by the result obtained for HER on this configuration. Interestingly, while the CN-HRG-CO has better performance towards HER, CN-HRG-COOH catalytic performance towards HER is poor. Additionally, while CN-HRG-CO has poor performance towards CO₂RR, CN-HRG-COOH shows fantastic performance towards CO₂RR. Because the experimental CO₂RR on a Z-scheme photocatalyst is scarce, we hope that the outcome of this research will open a fundamental avenue for catalysis on CO₂RR from the experimental point of view, which can subsequently be applied on a large scale.

Furthermore, the free energy of hydrogen adsorption shows that CN-HRG-CO has a better performance through the CN (-0.16 eV) adsorption site, which is relatively close to the benchmark

catalyst (Pt/C = -0.085 eV). The mechanism of HER shows that Volmer-Heyrovsky is the leading pathway for hydrogen desorption on both studied configurations, with an energy barrier of 0.47 and 0.77 respectively. This also shows its excellent performance when compared with the benchmark Pt (0.85 eV) and other kinds of catalysts as reported in the literature. We hope the result of our DFT finding will open a new pathway for the experimentalist to consider these photocatalytic materials for renewable energy and as well replace the most expensive and scarce Pt catalyst.

As for the photochromic SAS compounds, the research presents the study on the conformational interchange, intramolecular hydrogen bonding, and photochromic behavior of substituted salicylideneaniline (SAS) with electron-withdrawing and electron-donating groups. The following models were used for the study: **SAS1: R1 = H; R2 = H**, **SAS2: R1 = H; R2 = NMe₂**, **SAS3: R1 = NO₂; R2 = H**, **SAS4: R1 = NO₂; R2 = NMe₂**, **SAS5: R1= CH₃, R2 = NMe₂**, **SAS6: R1=NO₂, R2 = CH₃**, **SAS7: R1 = H, R2 = CH₃**, **SAS8: R1= CH₃, R2= H**. The study features the enol and cis-keto conformations of the SAS compounds giving a total of 16 SAS compounds studied due to their preferential stability over the trans-keto forms. The increase in electronegativity values and decrease in the E_{gap} show that there is an ease of electron transition within the compounds, which is paramount for light absorption within the UV-visible region. The studied SAS compounds show excellent NLO responses both in the vacuum and solvents, which are comparable and far more responsive than the benchmark, urea compound. The dihedral angles, UV-visible, first polarizability, and hyperpolarizability prove that the enol forms of SAS compounds are photochromic in nature, except SAS3E and SAS4E which may be between photochromic and non-photochromic. Consequently, the keto forms of SAS compounds are thermochromic in nature. This implied that these compounds can undergo photoswitching between one another. In addition,

a machine learning (ML) algorithm was used to predict and validate the DFT findings. With the KNN (K-nearest neighbor) ML model, 100% model prediction accuracy was achieved with a kappa statistic of 1 and a root mean square error (RMSE) of 0.0213. These can be generalized to predict subsequent compounds which can either be photochromic or non-photochromic. Finally, these properties are of prior importance in photo storage and information technologies. Therefore, they can be applicable in photonic technologies and engineering.

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Publications:

RESEARCH OUTCOMES

1. **Abdulraheem K. Bello**, Mohammed T. Abdullahi, Muhammad N. Tahir, Abdulaziz A. Al-Saadi. SERS Activity of Silver Nanoparticles and Silver-modified 2D Graphitic Carbon Nitride towards Ciprofloxacin Drug. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2024), doi: <https://doi.org/10.1016/j.saa.2024.125237>.
2. Nur Allif Fathurrahman, Maria A. Alhaboudal , Shehu Mohammed, **Abdulraheem K. Bello**, Abdulaziz A. Al-Saadi. The role of hydrogen bonding in the conformational stability of 2-methoxy resorcinol: Insights from theoretical calculations, SERS spectroscopy, and solvent effect. *Journal of Molecular Liquids* (2024), <https://doi.org/10.1016/j.molliq.2024.126201>.
3. **Abdulraheem K. Bello**, Nur Allif Fathurrahman, Abdulmalik P. Peedikakkal, Abdulaziz A. Al-Saadi. Photochromic characteristics of N-(3,5-di-tert-butylsalicylidene)-4-X-benzenes

(X = H, F, Cl, Br or I): The impact of conformational interchange, intramolecular hydrogen bonding, and second-order NLO response. **(Submitted and Under Review)**

4. **Abdulraheem K. Bello**, Abdulaziz A. Al-Saadi. Unveiling the potential of metal-free, g-C₃N₅ modified-highly reduced graphene catalysts for hydrogen evolution: A DFT study. **(Submitted and Under Review)**
5. **Abdulraheem K. Bello**, Abdulaziz A. Al-Saadi. Carbon Nitride Modified Highly Reduced Graphene as a Potential Photocatalyst for CO₂ Reduction: A First-Principle Study. **(To be Submitted)**
6. **Abdulraheem K. Bello**, Abdulaziz A. Al-Saadi. Machine Learning-based Predictions of Photochromic Characteristics of Substituted Salicylideneaniline (SAS): A Combined DFT-ML Approach. **(To be Submitted)**