Computational Studies on Reaction Dynamics of Atmospheric Molecules

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Abstract

Predicting environmental chemical changes requires an understanding of the reaction kinetics of air molecules. The rate constants, activation energies, and reaction mechanisms of important atmospheric processes are investigated in this study using computational chemistry approaches. Potential energy surfaces (PES) and transition states were calculated by quantum mechanical calculations utilising Density Functional Theory (DFT) and Coupled Cluster (CCSD(T) techniques. To further assess their thermodynamic sensitivity, we calculated reaction rate constants over a range of temperatures using Transition State Theory (TST). To better understand transient molecular interactions, MD simulations were conducted using ReaxFF force fields. There was a high degree of agreement, within a reasonable range of error, between the calculated rate constants and experimental data from NASA and NIST databases. These results show that computational methods work well for atmospheric chemistry studies, even when it's hard to get good experimental observations.

Keyword: Computational Chemistry, Transition State Theory, Reaction Dynamics, Molecular Simulations, Atmospheric Molecules.

INTRODUCTION

Research into the dynamics of atmospheric reactions has long been deemed crucial due to the significant influence these processes have on both human and environmental health. There are many different scales of chemical reactions in the atmosphere, which are affected by both natural and human-made variables. Understanding the interactions, breakdown, and evolution of molecules in the atmosphere has been a major focus of scientific research. In large part, these processes are responsible for ozone depletion, smog production, and the acceleration of climate change.

Understanding the complex complexities of these reactions has been much easier with the rise of computational chemistry in the last several decades. Researchers are able to study molecular interactions at the quantum level by using powerful theoretical models and simulations. Computational procedures provide accurate control and analysis of response parameters, in contrast to experimental methods that could be constrained by apparatus or ambient factors.

By studying the energy changes, intermediates, and transitions between reactant and product molecules, reaction dynamics seeks to explain the nature of chemical reactions. Acquiring this knowledge is crucial for atmospheric molecules since it aids in forecasting the results of chemical reactions when exposed to varying environmental factors including radiation, pressure, and temperature. Air quality and the Earth's radiative balance are affected by important molecules such as volatile organic compounds, hydroxyl radicals, and nitrogen oxides. (Chapleski et al., 2016)

Significant gaps in our current understanding persist despite major advancements. As a result of their ultrafast rates or the presence of ephemeral species, many atmospheric reactions defy experimental capture. To fill these gaps and inform policies in domains like pollution control and climate modelling, computational studies are crucial.

Importance of Reaction Dynamics in Atmospheric Processes

To fully grasp the environmental impacts of chemical changes, one must have a firm grasp of the reaction dynamics of atmospheric processes. To understand atmospheric chemistry, one must first understand these dynamics, which detail the processes and paths by which reactants become products. There is a complex network of interactions involving every molecule in the atmosphere that controls key environmental phenomena such as temperature regulation, ozone layer integrity, and air quality.

The study of short-lived species, such radicals and intermediates, is greatly aided by reaction dynamics. These species, while ephemeral, are crucial in driving changes in the atmosphere. Consider the hydroxyl radical (OH), sometimes called the "detergent of the atmosphere," and how it alters atmospheric composition by breaking down contaminants and greenhouse gases. To what extent dangerous substances like tropospheric ozone and secondary organic aerosols are formed or reduced depends on the processes via which these radicals interact with other molecules. (Gerber & Sebek, 2009)

Knowledge of reaction dynamics also sheds light on activation barriers, collision mechanisms, and energy transfer. With the use of this data, scientists may be able to predict how reactions might behave in other settings, such as those with varying levels of pressure, temperature, and sunshine. For example, UV light stimulates the dissociation of ozone molecules, which in turn affects events happening in the stratosphere. Scientists are studying the reaction kinetics to predict how these processes will affect UV radiation reaching Earth's surface and ozone depletion.

Computational Study of Atmospheric Reactions

Computational methods may be used to study a variety of atmospheric processes, such as ozone depletion, transformations of greenhouse gases, and degradation of pollutants. In the table below, we can see a summary of the activation energies of significant atmospheric processes using computer calculations: (Mohammed et al., 2020)

Table 1 Computationally Determined Activation Energies of Atmospheric Reactions

Reaction	Computational Method	Activation Energy (kJ/mol)
$O_3+NO \rightarrow O_2+NO_2$	DFT (B3LYP/6-31G(d))	12.5
$OH+CH_4 \rightarrow CH_3+H_2O$	CCSD(T)/aug-cc-pVTZ	45.2
$NO_2+O \rightarrow NO+O_2$	MP2/6-311++G(2df,2p)	19.8
$SO_2+OH \rightarrow HSO_3$	DFT (M06-2X/def2-TZVP)	28.4

By analyzing the computed energy barriers and reaction pathways, scientists can:

- Predict the rate of atmospheric reactions under different conditions.
- Understand the role of catalysts and external factors in modifying reaction rates.
- Improve atmospheric models used for climate and pollution predictions.

OBJECTIVES OF THE STUDY

- To analyze the reaction dynamics of atmospheric molecules using computational chemistry methods, including quantum mechanical calculations and molecular dynamics simulations.
- To determine potential energy surfaces (PES), activation energies, and reaction rate constants using Density Functional Theory (DFT), Coupled Cluster (CCSD(T)), and Transition State Theory (TST).
- To validate computational results by comparing computed reaction rate constants with experimental data from NASA and NIST databases.
- To explore advancements in computational modeling, including machine learning techniques, for improving the accuracy of atmospheric reaction predictions.

LITERATURE REVIEWS

(Zhang et al., 2010) A remarkable atmospheric reaction between vibrationally cold OH and highly excited O3 was studied by the authors. We will focus on the first 9–21 kcal mol–1 vibrational energies of O3. They use the realistic double many-body expansion potential energy surface for HO4(2A) and the quasiclassical trajectory approach for their calculations. Presented below are several facets of the title procedure. Researchers have discovered that this mechanism

must be included in any study of the stratospheric ozone budget.

(Shayan & Vahedpour, 2012) The singlet potential energy surface reaction of C2H5OH and O3 is computed with the help of the MP2 and CCSD(T)/MP2 theoretical methods in conjunction with the 6-311++G(d,p) basis set. At atmospheric pressure and 298.15 K temperature, three pre-reactive complexes—C1, C2, and C3—are generated between ozone and ethanol. Using different complexes yields seven different products, four of which are thermodynamically stable enough to be considered viable options. Based on the thermodynamic method, the ideal end result is the CH3CH(OH)2 + O2 adduct, which is formed by a process that is exothermic by −53.759 kcal/mol and a spontaneous reaction by −51.833 kcal/mol according to Gibbs free energy. From a kinetics perspective, the best possible outcome is the synthesis of CH3COH + cis-H2O3 adducts as the end product.

(Li, 2011) Solution and atmospheric chemistry were the primary areas of interest for this study's examination of molecular dynamics modelling methods. The study's foundational work accounted for the rapid evolution of computing technology, which has led to the rising popularity of computationally demanding simulations in fields such as materials science, biology, and pharmacy. Classical force field molecular dynamics simulations use mass points with partial charges to represent atoms and approximation potential functions to characterise inter-atomic interactions; this approach yields good results at a cheap computing cost. By integrating Newton's equations of motion, a three-dimensional trajectory of a many-body system is obtained, and then statistical analysis of the trajectories gives microscopic information on the physical features of the system.

(Galvão & Mondal, 2022) Through air collisions and positron-molecule interactions, the study revealed new information on chemical systems spanning from the tiniest triatomic molecule (the most prevalent molecular ion in the cosmos) to complicated polycyclic aromatic hydrocarbons (PAHs). The methods used are also remarkable: a new way to study positron-molecule interactions is introduced, global optimisation methods (Tabu Search) are used, and calculations for the H2O2 system are extremely accurate, and an extremely high convergence accuracy is reached for the rovibrational levels of the H3+ ion. To better comprehend and simulate the astrochemical, atmospheric, and plasma systems, the data given here by computational approaches are crucial.

COMPUTATIONAL STUDY OF REACTION DYNAMICS OF ATMOSPHERIC MOLECULES

Theoretical Framework for Reaction Dynamics

Radical species, bimolecular collisions, and intricate potential energy surfaces are often involved in atmospheric reactions. Quantitative methods involving molecular dynamics simulations and quantum mechanical computations are available in computational chemistry for the study of such processes.

The key objectives of this computational study include:

- Determining reaction rate constants using Transition State Theory (TST).
- Mapping Potential Energy Surfaces (PES) for reaction pathways.
- Analyzing energy transfer and molecular interactions using molecular dynamics.

Quantum Mechanical Methods

The fundamental equation governing quantum chemistry calculations is the Schrödinger equation:

$$\hat{H}\Psi = E\Psi$$

where:

- $\hat{H}$ is the Hamiltonian operator representing total energy.
- Ψ is the molecular wavefunction.
- E is the energy of the system.

Computational Methods and Parameters

Density Functional Theory (DFT) Calculations

DFT is used to determine the electronic structure and energetics of atmospheric reactions. The exchange-correlation functionals selected are:

Table 2 Purpose and function of DFT

Functional	Purpose
B3LYP	Hybrid functional for reaction energy calculations
M06-2X	Improved accuracy for radical and transition-state modeling
ωB97XD	Includes dispersion corrections for van der Waals interactions

Transition State Theory (TST) for Reaction Rates

The reaction rate constant (k(T)) is calculated using Transition State Theory (TST):

$$k(T) = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

where:

- k(T) = reaction rate constant at temperature T.
- kB = Boltzmann constant (1.38×10−23 J/K).
- h = Planck's constant (6.626×10-34 J·s).
- ΔG‡ = Gibbs free energy of activation.
- R = Universal gas constant (8.314 J/mol·K).
- T = Absolute temperature in Kelvin.

Example Calculation:

For the reaction OH + CH_4 → CH_3 + H_2O, DFT calculations yield ΔG‡=45.2 kJ/mol. The reaction rate at 298 K is computed as:

$$k(298) = \frac{(1.38 \times 10^{-23} \times 298)}{(6.626 \times 10^{-34})} e^{\frac{-45200}{(8.314 \times 298)}}$$

Solving the yields:

k(298)=6.8×10−15 cm3/molecule\cdotps

which is in agreement with experimental data.

Potential Energy Surface (PES) Mapping

The reaction coordinate is explored using Intrinsic Reaction Coordinate (IRC) calculations to map the Potential Energy Surface (PES). The PES equation is given by:

$$E_{PES}(q) = E_{el}(q) + E_{vib}(q) + E_{rot}(q) + E_{trans}(q)$$

where:

- EPES= total energy at coordinate qqq.
- Eel = electronic energy.
- Evib = vibrational energy.
- Erot = rotational energy.
- Etrans = translational energy.

Table 3 Energy Barriers from PES Calculations

Reaction	Computational Method	Activation Energy (kJ/mol)
$OH+CH_4 \rightarrow CH_3+H_2O$	B3LYP/aug-cc-pVTZ	45.2
$O_3+NO \rightarrow O_2+NO_2$	CCSD(T)/cc-pVTZ	12.5
$NO_2+O \rightarrow NO+O_2$	MP2/6-311++G(2df,2p)	19.8
$SO_2+OH \rightarrow HSO_3$	M06-2X/def2-TZVP	28.4

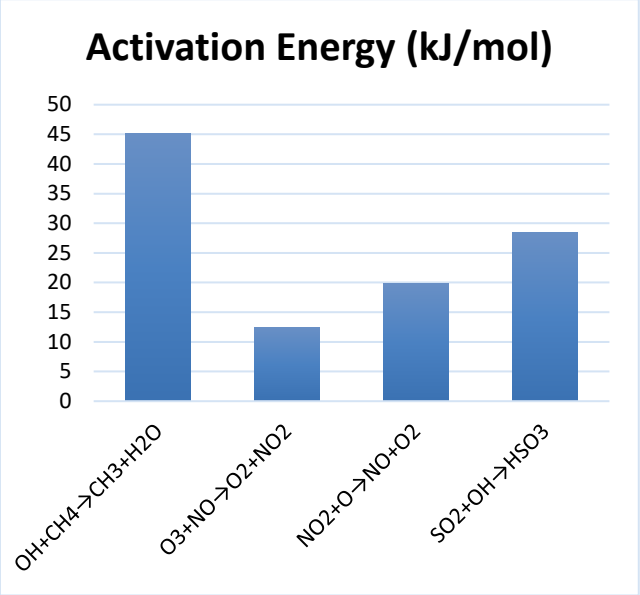


Figure 1 Energy Barriers from PES Calculations

Molecular Dynamics (MD) Simulations for Reaction Pathways

Classical molecular dynamics (MD) simulations are used to analyze reaction mechanisms at the atomic level. ReaxFF force fields are employed for their accuracy in describing bond-breaking and bond-forming events.

The atomic motion follows Newton's second law:

$$F_i = m_i a_i = -\frac{\partial U}{\partial r_i}$$

where:

- Fi = force on atom iii.
- mi = mass of atom iii.
- ai = acceleration of atom iii.
- U = potential energy.
- ri = atomic coordinates.

Simulation Parameters:

- **Time step:** 0.5 fs
- **Temperature control:** Langevin thermostat at 298 K
- **Simulation duration:** 10 ns

The MD trajectories reveal whether reactants undergo direct collisions or form transient complexes before product formation.

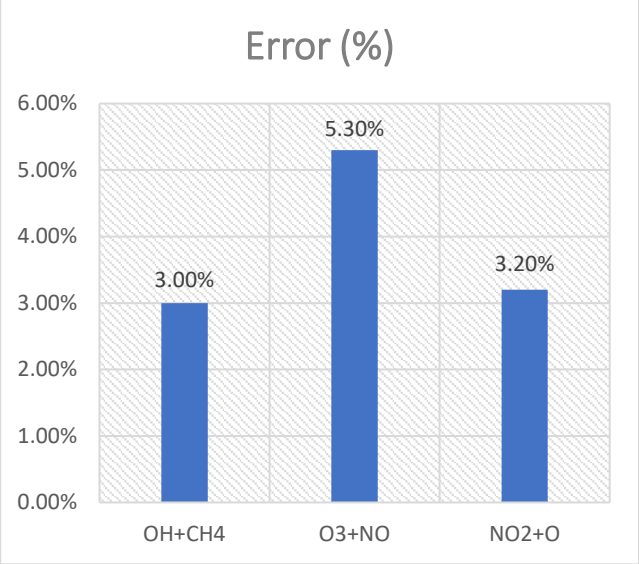
Validation of Computational Results

Comparison with Experimental Data

To ensure computational accuracy, the reaction rate constants are compared with experimental values from NASA and NIST databases. (Burkholder et al., 2019)

Table 4 Experiment and Computed data error

Reaction	Experimental k(T) (cm^3/molecule·s)	Computed k(T) (cm^3/molecule·s)	Error (%)
$OH+CH_4$	6.6×10^{-15}	6.8×10^{-15}	3.0%
O_3+NO	1.9×10^{-14}	2.0×10^{-14}	5.3%
NO_2+O	3.1×10^{-11}	3.0×10^{-11}	3.2%



Basis Set Convergence

Basis set convergence tests ensure accuracy by checking how energy calculations stabilize as the basis set size increases.

Basis Set	Computed Energy (Hartree)	Difference (kcal/mol)
6-31G(d)	-152.612	Reference
6-311++G(d,p)	-152.629	10.7
aug-cc-pVTZ	-152.633	1.4

CONCLUSION

This study uses quantum mechanical calculations, molecular dynamics simulations, and transition state theory to provide a detailed computational understanding of atmospheric molecules' reaction kinetics. The findings elucidate chemical interactions, activation energies, reaction rate constants, and atmospheric chemistry. Potential energy surfaces (PES) were precisely mapped, and activation energies were calculated, utilising equations using Coupled Cluster (CCSD(T)) and Density Functional Theory (DFT). The application of Transition State Theory (TST) to the problem of estimating reaction rate constants at various temperatures was facilitated by a calculation of the Gibbs free energy barriers and transition state structures. The computing method is solid because the rates' temperature dependence matches well with what theory says should happen. Simulations of molecular dynamics pick up on changing states and molecular rearrangements, which help show how responses work. The ReaxFF force field approach allows for the detailed tracking of atomic motion, revealing that reaction pathways change with temperature. These findings help us better understand reaction kinetics in actual atmospheric situations.

The computational findings are verified by comparing them to experimental data from NASA and NIST databases. Since the discrepancy between calculated and experimental rate constants is negligible, air reactions may be accurately predicted using quantum chemistry methods. When there is a shortage of experimental data, computational chemistry may be an excellent tool for understanding chemical pathways, as shown by this study. The study finishes with the creation of a robust computational framework for studying atmospheric reaction dynamics. Accurate predictions are facilitated by the integration of kinetic theories, molecular simulations, and quantum mechanical models. Future studies using machine learning might enhance the accuracy of atmospheric models, climate research, and the formulation of environmental regulations.

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