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Enthalpies and Activation Energies of Several Gas Reactions by Intrinsic Reaction Coordinate (IRC) Calculations

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Abstract: In the present study, we have theoretically obtained the enthalpies and activation energies of several gas reactions by Intrinsic Reaction Coordinate (IRC) calculations. Being a first time, the approximate transition states used in the IRC calculations were obtained from the saddle points on the two dimensional Potential Energy Surface (PES) scans trucking the pathway of the reactions. In all the calculations, the Density Functional Theory (DFT/B3LYP) with 6-31 G (d, p) level was used. The saddle points on the PES graphs of the reactions were used one by one as an approximate transition state (TS) in the IRC calculations until the appropriate reaction path was obtained. The obtained TS's from the IRC calculations were tested for having only one imaginary frequency. The energy diagram schemes showing the reactants, products, and transition states of all the reactions were drawn, and their enthalpies and activation energies were determined. From the enthalpy values it was decided whether the reactions are endothermic or exothermic. The calculated activation energies were compared with the ones in the literature.

Key words: Gas reaction, Enthalpy, Activation energy, IRC, DFT.

Bazı Gaz Reaksiyonlarının İçsel Reaksiyon Koordinat (IRC) Hesaplamaları ile Entalpileri ve Aktivasyon Enerjileri

Öz: Bu çalışmada bazı gaz reaksiyonlarının İçsel Reaksiyon Koordinat (IRC) hesaplamaları ile entalpileri ve aktivasyon enerjileri teorik olarak elde edildi. İlk kez olarak IRC hesaplamalarında kullanılan yaklaşık geçiş halleri, reaksiyon aşamalarını takip eden iki boyutlu Potansiyel Enerji Yüzey (PES) taramalarındaki merdiven noktalar olarak kullanıldı. Bütün hesaplamalarda**,** 6-31 G(d,p) seviyede Yoğunluk Fonksiyonel Teori (DFT/B3LYP) kullanıldı. Reaksiyonların PES grafiklerindeki merdiven noktalar, IRC hesaplamalarında uygun reaksiyon eğrisi bulununcaya kadar birer birer yaklaşık Geçiş Hali (TS) olarak alındı. IRC hesaplamaları ile elde edilen TS'ler tek bir negatif (sanal) frekans için test edildi. Bütün reaksiyonların, reaktant, ürün ve geçiş hallerini gösteren enerji diyagram şemaları çizildi ve onların entalpileri ve aktivasyon enerjileri elde edildi. Entalpi değerlerinden reaksiyonların, endotermik veya ekzotermik olduğu tespit edildi. Hesaplanan aktivasyon enerjileri literatürdeki değerlerle karşılaştırıldı.

Anahtar kelimeler: Gaz reaksiyonu, Entalpi, Aktivasyon enerjisi, IRC, DFT

1. Introduction

The transformation of one or more chemical substance to another is known as chemical reaction. While a chemical reaction is occurring, the more attention is often paid to the reactants and products. This is because the intermediates form rapidly in the reaction and disappear at the same

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rate, so they can hardly be measured, and often not. But, the intermediates can theoretically be obtained. Therefore, the chemical reactions have been subject of many theoretical studies to track the step wise sequences of the reaction mechanism. This track represents a significant challenge for theoretical chemists since it is possible to divide the reaction into a reacting subsystem which can be treated as quantum mechanically. Namely, the reaction paths and transition states can theoretically be obtained by using quantum methods. Some authors have calculated the structural and energy characteristics of the reagent molecules and reaction products [1]. The transition states, vibrational frequencies and reaction paths of the reaction $CO+NO_2 \leftrightarrow CO_2+NO$ were calculated by some authors [2]. In another study ab initio calculations have been applied on some reactions in which mono-nitrogen oxides react with ozone to generate higher oxidation states culminating in N_2O5 [3].

In the present study, we have calculated the enthalpies and activation energies of several gas phase reactions by the IRC calculations. The transition states of the reactions used in the IRC calculations were obtained from the saddle points on the two dimensional PES graph trucking the pathway of the reactions for the first time.

2. Calculation Details

Quantum chemical calculations were done by using Gaussian 0.9 software package [4] and Gauss View 5.0 program was used to *visualize* the calculated results [5]. The Density Functional Theory (DFT) are widely used in modeling chemical interaction of atom and molecules in both the gas phase [6] and catalytic surfaces [7], taking into account their internal structure. Therefore, Schrodinger equations were solved by the DFT method [8, 9] with the Becke hybrid three-parameter Exchange functional [10], supplemented by electronic correlation of Lee, Yang, and Par (B3LYP) [11] at 6-31 G (d, p) level of theory.

Firstly, the reaction products were optimized at the DFT (B3LYP)/6-31 G (d, p) level by taking a long distance (around 3 Å) between them. Then, to obtain the two dimensional Potential Energy Surface (PES) scans which describes the interaction of reacting particles the distances of the single O atom which completes the reactions as the products or reactants are systematically varied in the increments of 0.1 Å. In the Intrinsic Reaction Coordinate (IRC) calculations the step wise sequences on the saddle paths of the PES graphs of the reactions were used as the approximate transition states. They were used as one by one until the appropriate reaction path was reached. The IRC calculations were done by using Gaussian 0.3 [12] at the same level since it easily causes appropriate reaction path. In these calculations the charge was taken as 1. Since transition state (TS) is known as a configuration that has only one imaginary frequency among its vibrational frequencies, the obtained TS's from the IRC calculations were tested for one negative frequency. This test confirms that the transition state of the process under consideration is valid. For the study the selected gas phase reactions are as follows:

$$NO_2 + CO \longrightarrow NO + CO_2 \tag{1a}$$

$$NO + O_3 \longrightarrow NO_2 + O_2. \tag{1b}$$

$$O_3 + O \longrightarrow O_2 + O_2 \tag{1c}$$

$$O_3 + Cl \longrightarrow O_2 + ClO . \tag{1d}$$

2. Results and Discussions

A chemical reaction can be described as the formations of reactant, product and transition state since it can involve either combination of chemical substance or decomposition. The activation energy of a reaction (E_a) is the energy difference between the reactants and the activated molecule, also known as transition state (TS). TS is defined as the highest-energy state of the reaction process. The higher the activation energy is the harder a reaction occurs or vice versa.

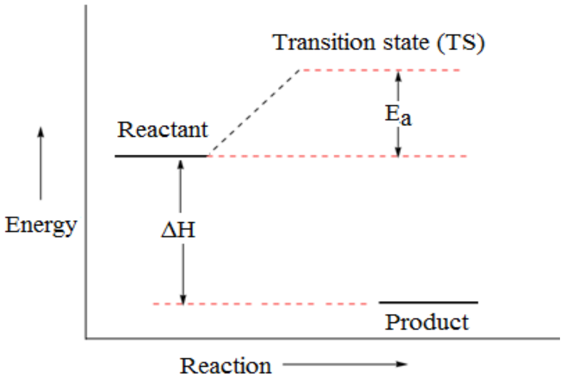


Figure 1. Reaction process in an exothermic reaction.

The change in the energy during the reaction is known as heat of reaction (ΔH) or enthalpy. The chemical reaction which proceeds through the absorption of energy is known as endothermic while the reaction in which some amount of energy released during reaction is called as exothermic. In an exothermic reaction, the products have lower energy than the reactants, hence the ΔH is negative and, is given as $\Delta H = H_{product} - H_{reactant}$ (See Figure 1). Similarly, for endothermic reaction the ΔH is positive since a heat energy is absorbed by the system, hence $H_{product} > H_{reactant}$.

The synchronous transit-guided quasi-Newton (STQN) method was generally used in order to obtain TS states of reactions [13]. In this study the step wise sequences on the saddle paths of the PES graphs of the reactions were taken as an approximate transition state. For all the selected gas reactions the PES scans calculated at the DFT (B3LYP)/6-31G (d, p) level are given in Figures 2-5. In the PES calculations the distances of the single O atom which completes reactions for the products and reactants are chosen as SC1 and SC2, respectively and, varied in the increments of 0.1 Å. The IRC results of all the reactions were also given in these figures. As we said before, the saddle points on the PES graphs of all the reactions were used as an approximate TS as one by one in the IRC calculations.

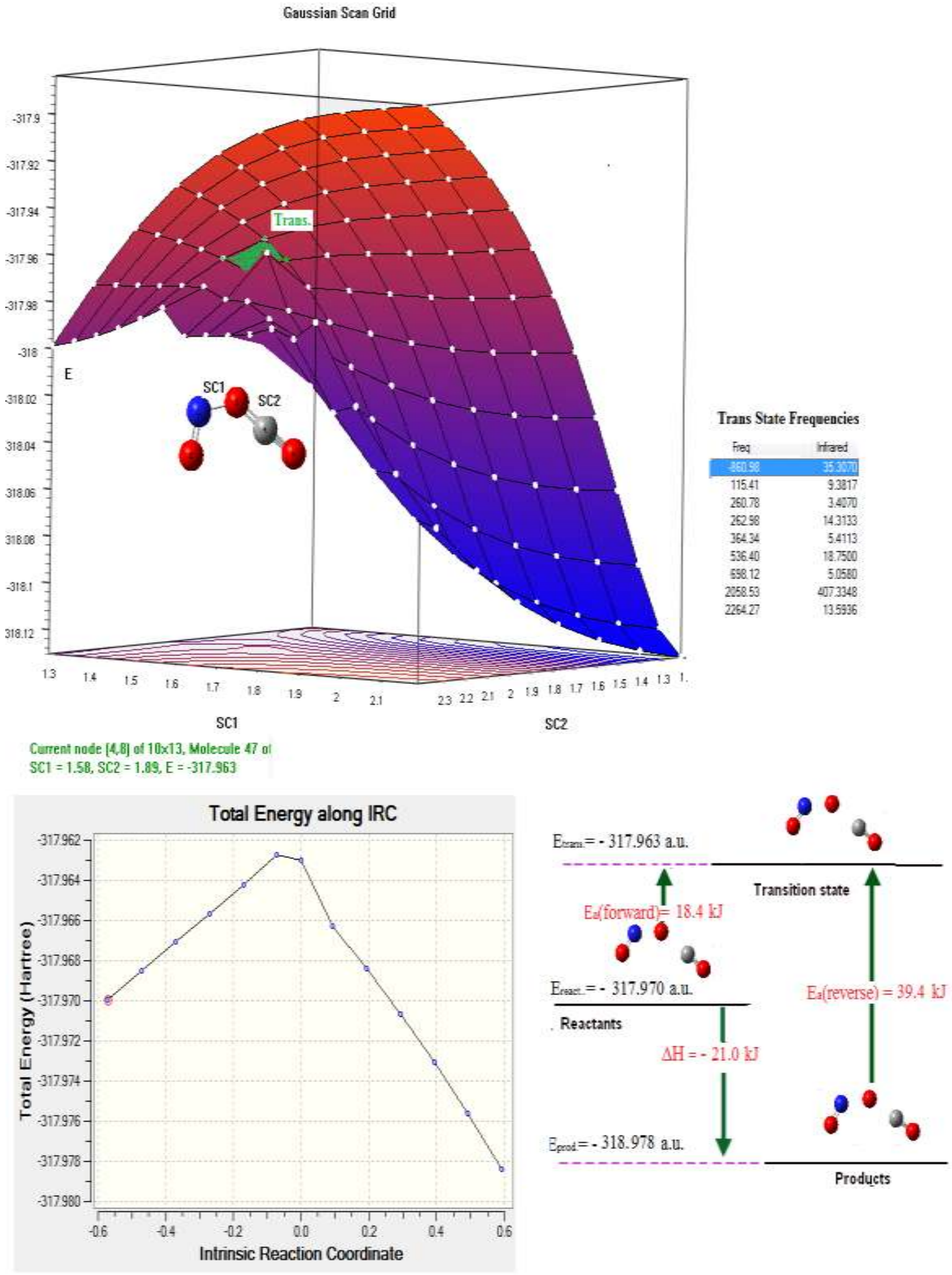
These calculations were continued until an appropriate reaction path was obtained. To confirm that the found TS by the IRC calculations is valid, it was tested for one negative frequency. The calculated frequencies of the TS's at the same levels are also given in these figures. So, a TS region were described on the PES graphs of the reactions as green color. The reactants, products and transition states of the reactions were assigned by the IRC calculations and their energy diagram schemes were drawn in these figures. From the energy diagrams, we can say that all the reactions are exothermic since the ΔH values (or enthalpies) of all the reactions are negative. Therefore, our selected reactions released energy during the reaction. The released reaction energies and activation energies can also be seen in the following details;

$$NO_2 + CO \longrightarrow NO + CO_2 \quad \Delta H = -21.0 \text{ kJ}; \quad E_a = 18.4 \text{ kJ} \qquad (2)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad \Delta H = -26.2 \text{ kJ}; \quad E_a = 7.9 \text{ kJ} \qquad (3)$$

$$O_3 + O \longrightarrow O_2 + O_2 \quad \Delta H = -39.4 \text{ kJ}; \quad E_a = 57.8 \text{ kJ}. \qquad (4)$$

$$O_3 + Cl \longrightarrow O_2 + ClO \quad \Delta H = -13.1 \text{ kJ}; \quad E_a = 31.5 \text{ kJ} \qquad (5)$$



Trans State Frequencies

Freq	Infrared
-860.98	35.3070
115.41	9.3817
260.78	3.4070
262.98	14.3133
364.34	5.4113
536.40	18.7500
698.12	5.0580
2058.53	407.3348
2264.27	13.5936

Current node [4,8] of 10x13, Molecule 47 of

SC1 = 1.58, SC2 = 1.89, E = -317.963

E_{trans} = - 317.963 a.u.

E_a(forward) = 18.4 kJ

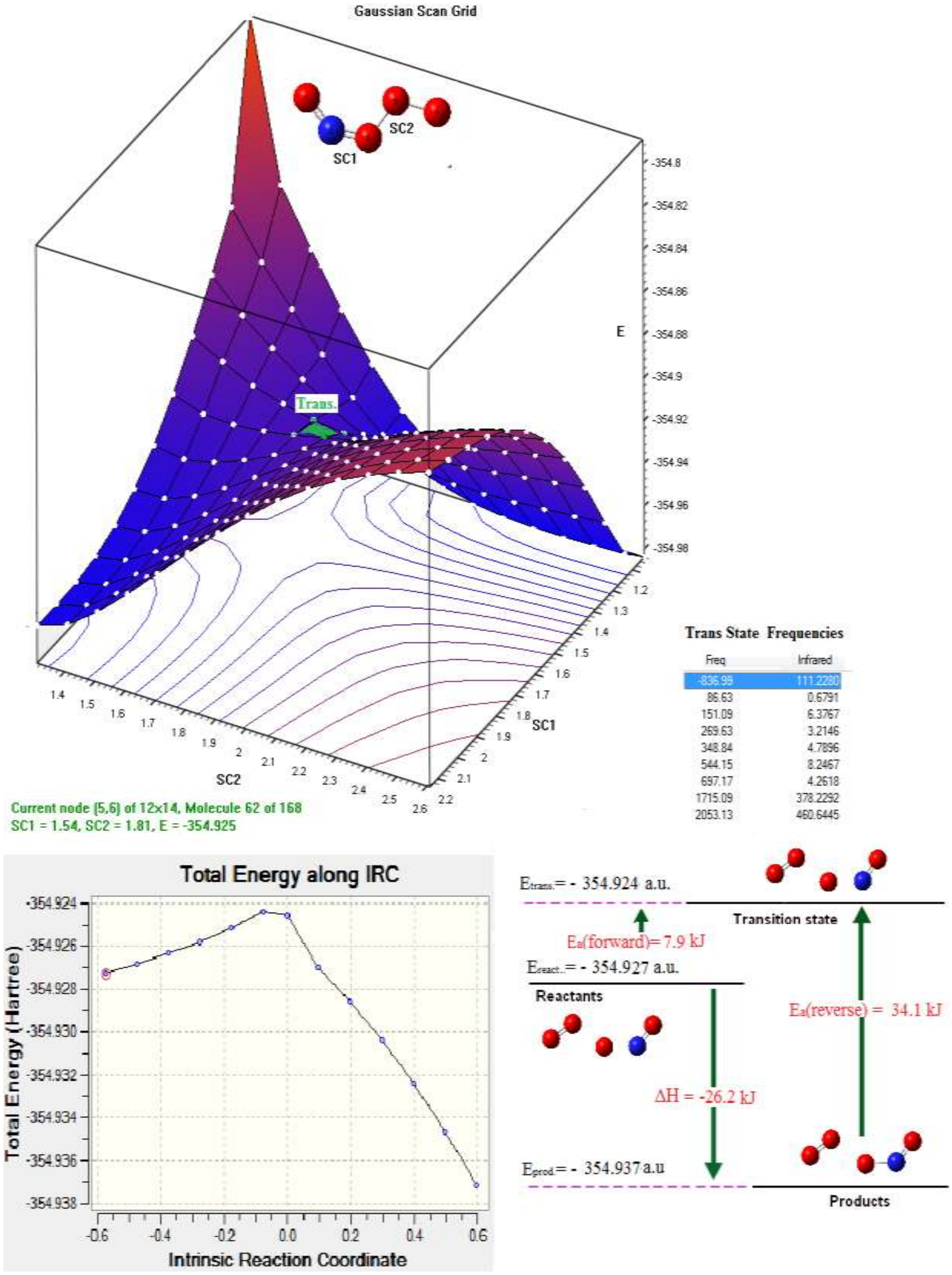
$E_{react.}$ = - 317.970 a.u.

ΔH = - 21.0 kJ

E_a(reverse) = 39.4 kJ

E_{prod} = - 318.978 a.u.

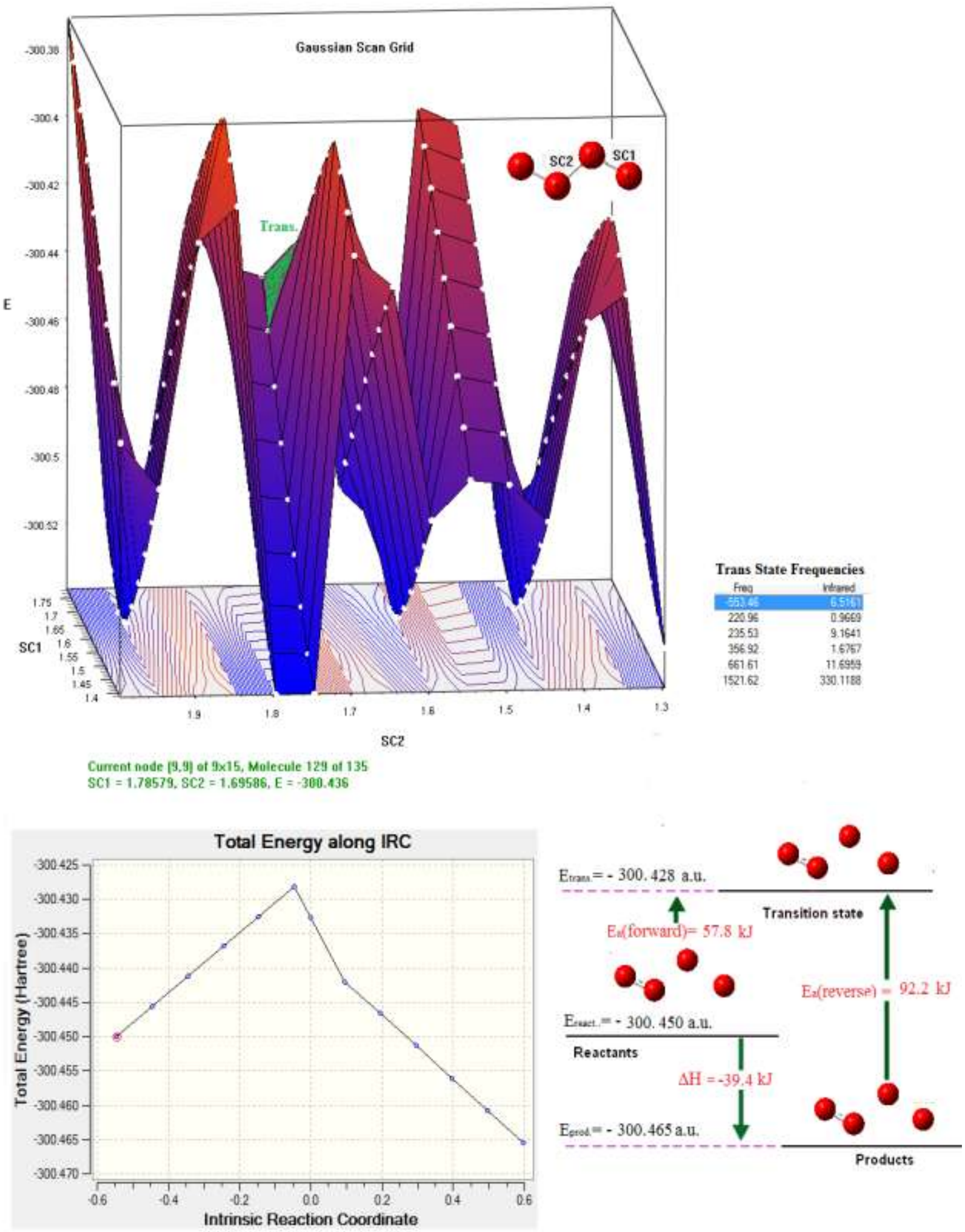
Figure 2. Two dimensional PES graph of the process of the reaction of $NO_2 + CO \longrightarrow NO + CO_2$. IRC reaction path and TS frequencies.



Trans State Frequencies

Freq	Infrared
-836.99	111.2280
86.63	0.6791
151.09	6.3767
269.63	3.2146
348.84	4.7896
544.15	8.2467
697.17	4.2618
1715.09	378.2292
2053.13	460.6445

Figure 3. Two dimensional PES graph of the process of the reaction of $NO + O_3 \longrightarrow NO_2 + O_2$. IRC reaction path and TS frequencies.

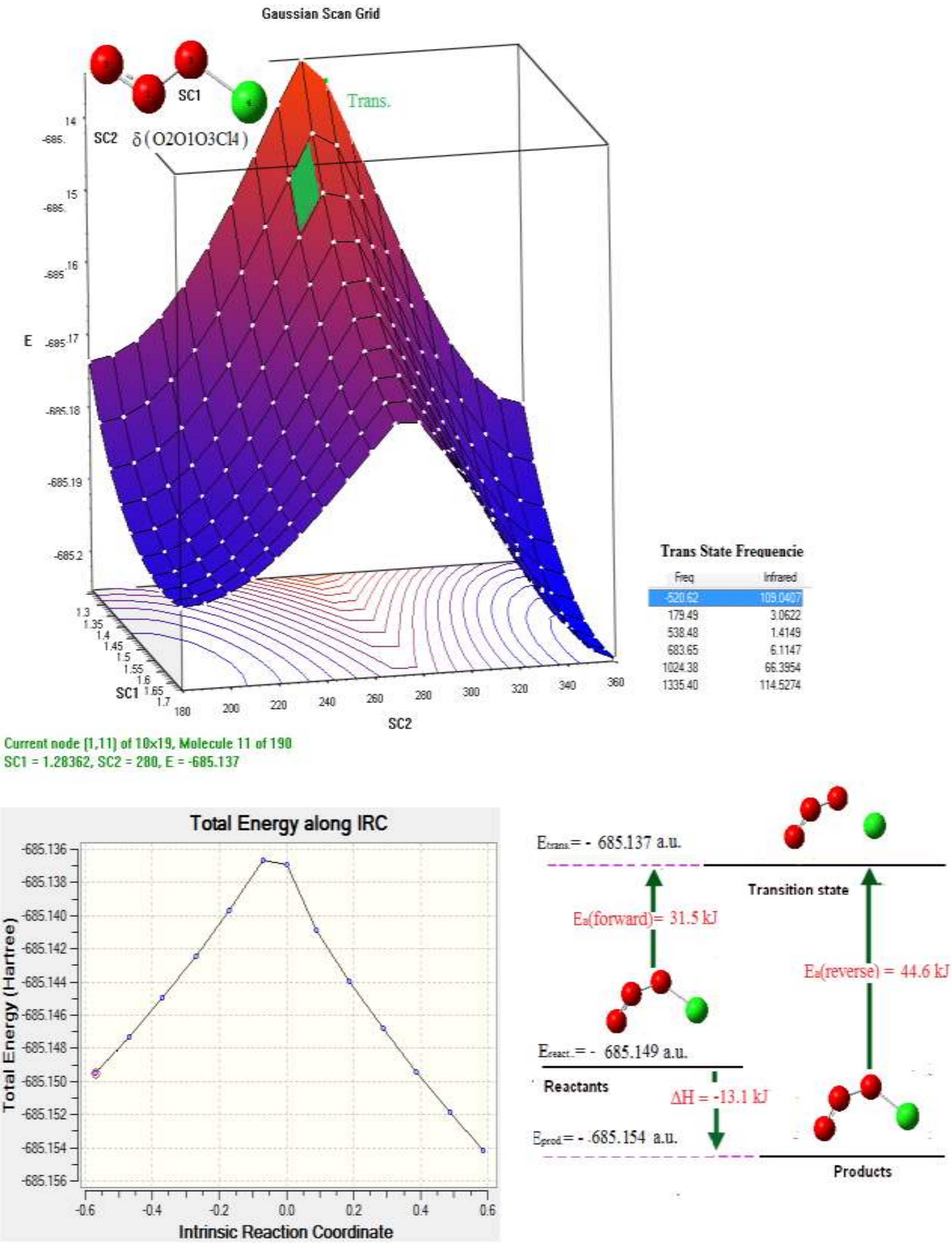


Current node [9,9] of 9x15, Molecule 129 of 135
SC1 = 1.78579, SC2 = 1.69586, E = -300.436

Trans State Frequencies

Freq	Infrared
-553.46	6.5161
220.96	0.9669
235.53	9.1641
356.92	1.6767
661.61	11.6959
1521.62	330.1188

Figure 4. Two dimensional PES graph of the process of the reaction of $O_3 + O \longrightarrow O_2 + O_2$. IRC reaction path and TS frequencies.



Trans State Frequencie

Freq	Infrared
-520.62	109.0407
179.49	3.0622
538.48	1.4149
683.65	6.1147
1024.38	66.3954
1335.40	114.5274

Current node (1,11) of 10x19, Molecule 11 of 190
SC1 = 1.28362, SC2 = 280, E = -685.137

Figure 5. Two dimensional PES graph of the process of the reaction of $O_3 + Cl \longrightarrow O_2 + ClO$. IRC reaction path and TS frequencies.

For the reaction (4) the activation energy is the highest while for the reaction (3) it is the lowest, and for the reaction (4) the released energy is the highest while for the reaction (3) it is the lowest. The experimental Arrhenius activation energy for the reaction (3) obtained using the data of the reference [14] is 1.2 kcal/mol, and it was calculated as 1.1 kcal/mol for the 6-

311 G(d,p) basis set , 1.3 kcal/mol for the ccpVDZ basis set and 2.2 kcal/mol for the aug-cc-pVDZ basis set levels [3]. As seen these values are very close to our activation energy 7.9 kJ (1.9 kcal) for the same reaction. All these results will be useful for experimental chemists.

4 Conclusions

In this study, the enthalpies and activation energies of several gas reactions were calculated by the IRC calculations using one by one the saddle points on the PES graphs of the reactions as an approximate TS for the first time. So the valid TS's of the reactions were found by the IRC calculations. They were tested for one imaginary frequency. The reactants, products and transition states of the reactions were assigned and their energy diagram schemes were drawn. So, the enthalpies and activation energies of the reactions were determined. From the enthalpy values it was stated all the reactions are exothermic, and the obtained activation energies were compared with each other and with the ones in the literature.

Contributions of the Authors

FU and NA wrote the article. The authors have read and approved the final version of the article.

Conflict of Interest

The authors declare that there is no conflict of interest.

References

[1]. Lefebvre A. H., Ballal D. R., "Gas Turbine Combustion: Alternative Fuels and Emissions (third ed.)", CRC Press, Boca Raton, (2010).

[2]. Kroupnov A. A., Pogosbekian M. Ju., "DFT calculation-based study of the mechanism for CO_2 formation in the interaction of CO and NO_2 molecules", Chem. Phys. Lett., 2018, 710, 90-95.

[3]. Jaroszynska-Wolinska J., "The reaction mechanism of ozone with the NO and NO2 oxides", J. Mol. Struct.Theochem, 2010, 952, 74-83.

[4]. Frisch M.J., et. al., Gaussian 09 Revision D.01, Gaussian Inc, Pittsburgh PA, (2009).

[5]. Frisch A., Nielsen A.B., Holder A.J., Gauss View User Manual, Gaussian Inc., Pittsburg PA, (2001).

[6]. Wang Y., Fu G., Zhang Y., Xu X., Wan H., "O-atom transfer reaction from N_2O to CO: A theoretical investigation",Chem. Phys. Lett., 2009, 475, 202-207.

[7]. Tiana D., Zenga C., Wanga H., Chenga X., Zhenga Y., Xiangd C., Lia K., Zhu X., "Effect of transition metal Fe adsorption on CeO2(110) surface in themethane activation and oxygen vacancy formation: a densityfunctional theory study", Appl. Surf. Sci., 2017, 416, 547-564.

[8]. Hohenberg P., Kohn W., "Inhomogeneous electron gas", Phys. Rev., 1964, 136, b864-b871.

[9]. Kohn W., Sham L.J., "Self-consistent equations including exchange and correlation Effects", Phys. Rev., 1965, 140, a1133–a1138.

[10]. Becke A.D., "Density-functional exchange-energy approximation with correct asymptotic behavior", Phys. Rev. A.,1988, 38, 3098-3100.

[11]. Lee C., Yang W., Parr R.G., "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", Phys. Rev. B.,1988, 37, 785-789.

[12]. Frisch M.J., et. al., Gaussian 03 Revision A.1, Gaussian Inc, Pittsburgh PA, (2003).

[13]. Peng C., Schlegel H. B., "Combining synchronous transit and Quasi-Newton methods for finding transition states", Israel J. Chem.,1993, 33, 449-454.

[14]. Baulch D., et al.,"Evaluated kinetic and photochemical data for atmospheric chemistry: supplement I CODATA task group on chemical kinetics", Suppl. Int. J. Phys. Chem. Ref. Data,1982, 11, 327-496.