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Journal of Science and Technology

E-ISSN 2146-7706

The Possible External Factor Effecting On NO_2 Molecule During Lightning Flash Under Corona Discharge

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ARTICLE INFO

Article history:
Received 26 October 2021
Received in revised form 03 November 2021
Accepted 01 December 2021

Keywords:
Corona discharge
Lightning Flash
Electric Field
NO2 molecule
Cloud

ABSTRACT

The focus in this study is on the formation of the NO_2 molecule on the O+NO system, which is the atom-diatom reaction that occurs the most according to the molecular concentrations formed as a result of lightning flashes. In this study, it was mentioned that another external effect that affects NO_2 molecule concentrations, other than temperature and visible electromagnetic radiation, is the electric field. This will suppress the formation of O_2 at high temperatures and the formation of NO concentration at low temperature, as it increases the barrier in the product channel on the reaction pathway and NO+O recombination in the reactant channel under favorable conditions. Under these two conditions, the NO_2 population might be supported by electric field

1. Introduction

Troposphere is an atmospheric layer in which the activity of anthropogenic and greenhouse gases is high (C, Cl, F etc.), and where water molecules are important for all living activity in the world. This layer has a height of approximately 18 km from the ground in the equator, but extends up to 5 km at the poles. Within this layer, many reactions can take place by means of reactive scattering, recombination, and photo-dissociation. Apart from human activity and sunlight, another reaction medium in this layer is the lightning flash, which provides rapid combustion and cooling environment. Lightning is a natural radioactive source with its fusion and fission reactions at high temperature (Levine, 1995). To nearly a height of clouds from the ground surface, the concentrations of O_2 and N_2 molecules are about 99% when compared to other molecules. For this reason, NO molecule shows the most formation with atomization of these molecules in the air environment as a result of electron discharge. Other molecules formed rather than this molecule are respectively, from large ones toward small ones according to their concentration density, listed as NO_2, HONO, N_2O, H_2O_2, HO_2, CO. The change in the number of NO molecules is proportional to the electron flux per lightning flash. Lightning is redirected to the earth from cloud, to cloud from the earth and cloud from cloud. However, this is not a factor affecting the formation of molecules. It only affects concentration. Another factor affecting the molecular density of NO is the electric field in the environment, also known as a parameter that initializes lightning. The electric field is predominantly vertical between the cloud and the earth's surface and is continually active before, after and during the flash. With flash, magnitude of the electric field changes in the degree of kV/m. It varies in the range of 25-100kV/m in size (Rakov and Uman, 2003). The minimum stretch of electric field to start lightning is around a few kV/m. In addition, width of the electric field can be up to range of several km [Jacobson and Streets, 2009; Coleman et al., 2003]. In the open and clean air, the electric field power is 20-30 V/m and in the lightning-free cloudy environments it is around 800 V/m (Larossi et al., 2011). Unlike the above mentioned electric fields, in positive and negative Corona discharge events, it can occur under high electric field, from 10^6 to 10^8 V/m (1 a.u. =5.14x10^{11} V/m) (Riba et al., 2018; Bazelyan et al., 2008;

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Kherbouche et al., 2016; MacGorman and Rust, 1998). If assuming that there are no greenhouse gases (H_2O, CO_2, O_3, N_2O, CH_4 and NO_2, formed as a result of combustion reaction and of human activity) in lightning flash, and that lightning occurs in dry weather (no rain), NO (nitrogen oxide) and NO_2 (nitrogen dioxide) are the most two concentrated gases in the environment (Salonen et al., 2019; Smirnov and Marapulets, 2012). In fact, when considering the concentrations of trace gases such as H_2O and CO_2 at the temperature considered, they have no effect on the formation of gases such as NO and NO_2. Typical hurricane produces 2-40x10^{25} molecules of NO per flash (Schumann and Huntrieser, 2007). NO is known as short-lived trace gases and can be converted to stable free radical NO_2 by NO + O reaction (Lagzi et al., 2013). Since the concentrations of greenhouse gases in the environment are relatively low, the effect of X-ray, Gamma rays and free electrons in the reaction medium known as the center of lightning, which can reach temperatures up to 40000 K, is more effective on the NO_2 molecule. NO_2 +hc/μ (μ <420 nm) can be re-separated into NO + O by depending on lifetime of the excited complex (Michalski et al., 2004; Grebenshchikov et al., 1999; Ivanov et al., 2007). In addition, under the influence of lightning in the environment, interaction of cold environment O_2 molecules with the dissociated hot O atoms can form O_3 and this molecule is a strong radical which is prone to reaction (Franzblau and Popp, 1989). The presence of trace gases in the environment, such as water vapor, makes the formation of nitrogen oxides HNO_2 (nitrous acid) and HNO_3 (nitric acid) more efficient (Tuck, 1976). Since a number of chain reactions caused by charge discharges in the air environment in the mixture of nitrogen and oxygen affect each other's intensities, they support different formations (Fedotov and EYa, 2015). Thus, the NO molecule decreases over time. Lightning system was tried to be done in the laboratory by Hill et al. (1980). The production of NO and NO_2 was attempted to be detected with mixed of heated air by lightning and surrounding air molecules (air cooling channel). Two important ions between 3000-10000 K are e- (electron) and NO^+. NO^+ e- → N + O reaction has reaction rate constant of 10^{-7} cm^3/s. Lightning is a heating system that can affect the area of 20 cm from the surface of the main electron flow line. At the same time, it emits heat in the shape of a shock wave. Therefore, if considered the ambient temperature to be 200-300 K and the ambient pressure below about 1 atm, an effective reaction medium is formed up to 9 cm from the main energy line. Temperature varies at every point in order of microseconds. In other words, the environment first goes into the process of heating and then cooling. Kunova and Nagnibeda (2017) showed that the rate constant of the NO + O →N + O_2 reaction is 1.56x10^9.T .exp (-19450 / T) in simulation of the gaseous molecular reaction. They also achieved experimentally the highest NO concentration at 4000 K and examined N_2+O→NO+N and O_2+N→NO +O reactions according to vibrational quantum numbers of product and reactant molecular. In the work is seen that the increased vibration energy of the reactant molecule causes the product molecule in high vibration quantum states. At the program designed under shock wave was used in non-equilibrium air environment. It has been observed that the shock has dropped from 12000K to 8000K temperature up to 0.5 cm from the center. It has also been observed that ambient temperature decreases linearly from 8000 to 6500K from 0.5 cm to 3.5 cm distance. This temperature change has also effected on the concentration of molecules and atoms in the environment. As seen in that work, while number of O and N atoms increase up to 0.5 cm, NO molecules increase at the same rate and at the same range. From 0.5 cm to 3.5 cm the increase rate in O and N atoms is less while NO and O_2 molecules start to decrease. NO formed in the range of 0-0.5 cm start to decrease by means of reacting with O atom in the range of 0.5 and 3.5 cm. Thus NO_2 which has the second highest concentration in the medium starts to form. Thus the current process constitutes the NO + O reaction from the reactant channel to the transition state region. In order to form the system as N + O_2, it needs to receive external energy. UV radiation generated by high electric current, which continues in milliseconds, can affect the molecular system created by the shock wave occurring in microseconds. Such a system takes place under appropriate temperature, electric field and ro-vibration energies.

The aim of this study is to investigate the NO_2 that occurs during lightning flashing under an electric field which is an effective factor in the corona discharge event. To do this, after optimizing the system in all minimum and transition state regions along the reaction path, it is necessary to re-optimize by applying electric fields in three dimension. In regions showing the most effective change, a new total electronic energy is determined. Thus, a new fit function that defines the energy difference in those regions is needed. When this is applied, the system acts as if it were under a constant electric field.

2. Computational Details and Approaches

The present calculations are performed on DFT-B3LYP function with aug-cc-pvTZ, basis set in doublet spin in Gaussian09 (Frisch et al., 2009). The potential energy surface (in Sayos et al. (2002)) used by modifying in this work is based on CASPT2 (17,12) G2/aug-cc-pvTZ. The Table 1 shows the equilibrium bond distances and total energies of the related region for both works. The molecular system is kept under an electric field of 10^8 V/m in these regions. This value of used electric field is the maximum electric field value observed between the clouds and the earth surface in the Corona discharge event. The transition state and minimum energy zones in the Table 1 have been recalculated under the electric field with the base function in present calculations. In the calculations, the effects of electric field in three dimensions are examined. As a result, under such a high electric field, the total energy has only changed in the TS-1 and Min-1 regions. The other regions are exposed 100 times more to electric field just to see how far it can go. But their total energies have no an effective change. The changes related to corona discharge are shown in detail in both Table 1 and the following reaction path graph (Figure 1).

There is no a serious inconsistency between the basis function used in Sayos et al. (2002) and basis function used to show the effect of electric field in the present work. The meaning of the most effective change mentioned in the title is to determine the maximum affected direction under the maximum electric field. That is, the maximum change in the electric field applied in Ts-1 is shown in the x-direction and one in Min-1 is achieved in the y-direction. Figure 1 shows the differences in total energy between ordinary lightning flash and corona discharge event. To apply the energy changes obtained by basing on another potential function to the potential energy surface in Sayos et al. (2002) causes a small amount of error. However, differences in these potential and distances among atoms are not very effective at the related areas. Other regions are not affected much in any way under the electric field although this is not mentioned in detail. Because the energy differences under the electric field in these regions are in the order of 10^{-4} eV. Therefore, it is not taken into account.

Figure 1. The reaction path of O+NO → N+O_2 Reaction. Reactant asymptote is referenced to 0 au. Note that the energy values in Table 1 are not referenced to zero.

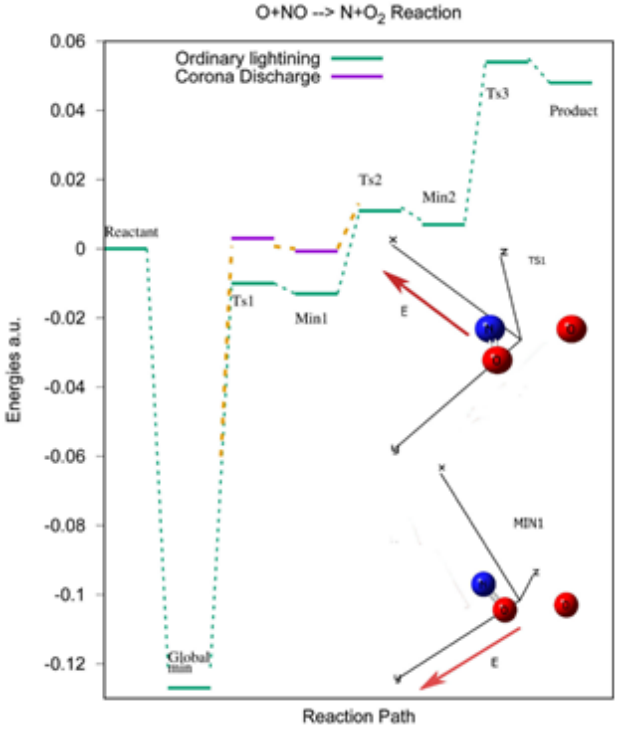

Table 1. Equilibrium bond distances and total energies belonging to transition state and minimum energy points on O+NO→ N+O_2 reaction system. The calculated values in Sayos et al. (2002) are indicated by the upper index "a". Energies are atomic units and distances are angstrom. O_2 is the coming atom, E.F is the case applied of electric field and E is total energy of system.

Regions	$R_e(NO_2)^a$	$R_e(NO_2)$	$R_e(O_1O_2)^a$	$R_e(O_1O_2)$	$<NO_2O_1^a$	$<NO_2O_1$	E^a	E
Global Min	1.218	1.191	-----	-----	-----	-----	-0.1731	-0.1760
Ts-1	1.151	1.125	2.007	2.293	88.4	89.76	-0.0545	-0.0586
TS-1-E.F	------	1.103	------	1.934	-------	87.32	-----	-0.0028
Min-1	1.168	1.125	1.966	2.186	116.98	118.11	-0.0599	-0.0613
Min-1-E.F	------	1.126	-------	2.188	------	118.02	-----	-0.0082
TS-2	1.202	1.132	1.475	1.557	125.81	131.78	-0.043	-0.037
Min-2	1.241	1.194	1.338	1.358	121.7	124.83	-0.0454	-0.0405
TS-3	1.901	1.864	1.233	1.220	109.06	114.18	0.0109	0.0061

Another neglected point is the reactant minimum. The reactant minimum could be optimized under the electric field applied in the direction of O----O-N atomic distribution. There was no effective change in such a situation. However, if an electric field is applied in a direction perpendicular to this direction, the reactant minimum cannot be optimized and tends to form a global minimum. That is, the electric field for the reactant minimum is parallel to the O---O-N distribution. This case is a limitation for the global approach. As a result, under an electric field of 10^8 V / m, Ts-1 shows the most effective change with an increase of 0.37 eV, and secondly by 0.33 eV, Min-1 changes. Others have been neglected with a change of 10^{-4} eV as mentioned above. The final shape of the potential energy surface was fit using the difference polynomial in the Mathematica 12.0 program (Wolfram Research, Inc., (2019)). This difference polynomial as a function of the distances between atoms is $\Delta V = 0.416678 - 0.0143469 * RO_2N - 0.13848 * RO_1O_2 - 0.0813487 * RO_1N$. Here distances between atoms are unit of Angstrom and are defined as $1.60 \leq RO_2N \leq 2.69$, $1.55 \leq RO_1O_2 \leq 2.15$ and $1.15 \leq RO_1N \leq 2.20$. These values start from a point that is close to the global minimum region and continue up to Ts-2. Energy changes in the global minimum and Ts-2 regions is considered as 0. They act as the node point for the exchange

polynomial. To take a picture of potential energy surface in 3 dimensions, it should be showed in the geometry that indicates the most effective change. This region is between Ts-1 and Min-1 as seen Figure1. The factor that facilitates to polynomial fit between these two regions is that the distance between O_1 and N changes effectively. As seen in Table 1, the distances between atoms do not change much, while the angle is more variable. This angle on the O_2 atom (the atom transferred from N atom to O_1 atom) in the system varies between 20-27 degrees. The change of 3-dimensional potential energy at approximately 25 degrees is seen in Figure 2.

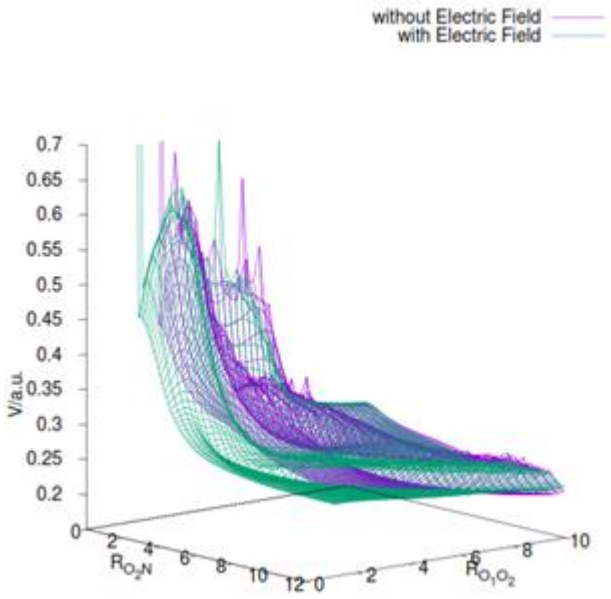

Figure 2. Potential energy surface at approximately 25 degrees in 3 dimensions with and without electric field. Here distances between atoms is unit of atomic.

The potential energy surface region that is fit is a very small surface once compared to the global surface. The fact that the atomic distance between Ts-1 and Min-1 does not change very effectively (except for the change of distance between O_1-N) made it easier to make fit. Another simplicity is that it does not require a very detailed convergence test in time propagation.

3. Conclusions

The focus was on the formation of the NO_2 molecule on the O+NO system, which is the atom-diatom reaction that occurs the most according to the molecular concentrations formed as a result of lightning flashes. In this study, it was mentioned that another external effect that affects NO_2 molecule concentrations, other than temperature and visible electromagnetic radiation, is the electric field. It was observed that the electric field in question affected only two transition regions (Ts-1 and Min-1) on the O+NO → N+O_2 reaction system. It also increased the barrier energy by increasing the total energy in these regions. In such increased barrier reactions, the reaction rate slows down. So, these situations suppress the formation of O_2 at high temperatures and the formation of NO concentration at low temperature, as it increases the barrier in the product channel on the reaction pathway and NO+O recombination in the reactant channel under favorable conditions. Under these two conditions, the NO_2 population might be supported by electric field. It is important to research the reactions belonging to O(^{3}P) (atom used in present study) with high concentration occurred in airglow events such as lightning flash. O_2 can be produced by the interaction of O(^{3}P) atoms to each other, which also causes the emergence of the O (^{1}S) atom (it interacts with excited oxygen molecules and disappears to form ozone) in the high temperature region. However, it is 10^6 times less than NO molecules in population. Moreover, in the low temperature region, these stimulated oxygen contributes very little to O_2 production. Another reaction that produces O_2 in atmospheric chemistry in the presence of NO and O_3 in high population is NO+O_3→ NO_2 +O_2. This reaction is defined below 500 K. However, this reaction does not show Arrhenius behaviour in the studied shock wave temperature range as can be seen from the change in concentrations in the study of Ripoll et al. (2014). To produce O_2 around 1000 K as in atmospheric and experimental, higher reactant vibrational energy must be obtained. High vibration energy is the reaction starter in reactions occurring under such shock waves.

Acknowledgements

The numerical calculations reported in this paper were partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources). That is why, the author is grateful to the Scientific and Technological Research Council of Turkey for TR-Grid facilities and to Bitlis Eren University for Gaussian09W and GaussView5.0 Program support.

References

Bazelyan EM, Raizer YP, Aleksandrov NL. 2008. Corona Initiated from Grounded Objects Under Thunderstorm Conditions and its Influence on Lightning Attachment, Plasma Sources Sci. Thechnol. 17: 024015. doi:10.1088/0963-0252/17/2/024015.

Coleman LM, Marshall TC, Stolzenburg M, Hamlin T, Krehbiel PR et al. 2003. Effects of Charge and Electrostatic Potential on Lightning Propagation. Journal of Geophysical Research 108 (D9): 4298. doi:10.1029/2002JD002718.

Fedotov VG, EYa F. 2015. The Chain Reaction of Atmospheric Nitrogen Oxidation, Initiated by an Electric Discharge in Air, J. Phys. Chem. Biophysics, 5: 195. doi:10.4172/2161-0398.1000195.

Franzblau E, Popp CJ. 1989. Nitrogen Oxides Produced from

Lightning, Journal of Geophysical Research, 94 (D8): 89-104. doi:10.1029/JD094iD08p11089.

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, et al. 2009. Gaussian 09, Revision A.1, Gaussian Inc., Wallingford CT.

Grebenshchikov SY, Beck C, Flöthmann H, Schinke R, Kato S. 1999. Unimolecular Dissociation of NO_2. I. Classical Trajectory and Statistical Calculations on a Global Potential Energy Surface, J. Chem. Phys. 111: 619. doi.org/10.1063/1.479342.

Hill RD, Rinker RG, Wilson HD. 1980. Atmospheric Nitrogen Fixation by Lightning, Journal of Atmos. Sci. 37: 179-192. doi.org/10.1175/1520-0469(1980)037<0179:ANFBL>2.0.CO;2.

Ivanov MV, Zhu H, Schinke R. 2007. Theoretical Investigation of Exchange and Recombination Reactions in $O(^3P)$ + NO ($^2\Pi$) Collisions, The Journal of Chemical Physics 126: 054304. doi.org/10.1063/1.2430715.

Jacobson MZ and Streets DG. 2009. Influence of Future Anthropogenic Emissions on Climate, Natural Emissions and Air Quality. Journal of Geophysical Research 114: D08118. doi:10.1029/2008JD011476.

Kherbouche F, Benmimoun Y, Tilmatine A, Zouaghi A, Zouzou N. 2016. Study of a New Electrostatic Precipitator with Asymnetrical Wire-to- Cylinder configuration for Cement Particles Collection, Journal of Electrostatics 83: 7-15. doi.org/10.1016/j.elstat.2016.07.001.

Kunova O, Nagnibeda E. 2017. On the Influence of State-Resolved Rates of Zeldovich Reactions on Shock Heated Air Flow Parameters, J. Phys., Conf. Ser. 815: 012009. pp. 1-8.

Lagzi I, Meszaros R, Gelybo G, Leelossy A. 2013. Atmospheric Chemistry, Eötvös Lorand University, Consortium Members: ELTE Faculties of Science Student Foundation, ITStudy Hungary Ltd.

Larossi S, Poscolieri M, Rafanelli C, Franceschinis D, Rondini A et al. 2011. The Measure of Atmospheric Electric Field.In G. Neri et al. (eds.), Sensors and Microsystems, Lecture Notes in Electrical Engineering 91, Springer Science+Business Media B.V, pp. 175-179.

Levine IN. 1995. Physical Chemistry. 4th Edition, McGraw-Hill, Inc., New York.

MacGorman DR, Rust WD. 1998. The Electrical Nature of Storms, Oxford University Press. Inc., 198 Madison Avenue, New York 10016.

Michalski G, Jost R, Sugny D, Joyeux M, Thiemens M. 2004. Dissociation Energies of Six NO_2 Isotopologues by Laser Induced Fluorescence Spectroscopy and Zero-Point Energy of Some Triatomic Molecules, J. Chem. Phys. 121: 7153. doi:10.1063/1.1792233

Rakov VA, Uman MA. 2003. Lightining Physics and Effects. Cambridge University Press, Cambridge, CB2 2RU, UK.

Riba JR, Morosini A, Capelli F. 2018. Comparative Study of AC and Positive and Negative DC Visual Corona for Sphere-Plane Gaps in Atmospheric Air, Energies, 11: 2671. doi.org/10.3390/en11102671.

Ripoll J-F, Zinn J, Jeffery CA, and Colestock PL. 2014. On the Dynamics of Hot Air Plasmas Related to Lightning Discharges: 1. Gas dynamics. J. Geophys. Res. Atmos., 119, 9196–9217.

Salonen H, Salthammer T, Morawska L. 2019. Human exposure to NO_2 in School and indoor environments, Environment International, 130: 104887. doi: 10.1016/j.envint.2019.05.081.

Sayos R, Oliva C, Gonzalez M. 2002. New Analytical ($^2A'$, $^4A'$) Surfaces and Theoretical Rate Constants for the $N(^4S)$ + O_2 Reaction, Journal of chemical Physics, 117 (2): 670-679. doi.org/10.1063/1.1483853.

Schumann U, Huntrieser H. 2007. The global Lightning-Induced Nitrogen Oxides Source, Atmos. Chem. Phys., 7: 3823-3907. doi.org/10.5194/acp-7-3823-2007.

Smirnov SE, Marapulets YV. 2012. Influence of a Single Lightning Discharge on the Intensity of an Air Electric Field and Acoustic Emission of Near-Surface Rocks, Soild Earth, 3: 307-311. doi.org/10.5194/se-3-307-2012.

Tuck AF.1976. Production of Nitrogen Oxides by Lightning Discharges, Quart. J. R. Met. Soc., 102: 749-755. doi.org/10.1002/qj.49710243404.

Wolfram Research, Inc., 2019. Mathematica, Version 12.0, Champaign, IL.