

NEGATIVE CORONA DISCHARGE IN FLOWING N₂O AND ITS MIXTURES WITH N₂ AND O₂

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The electrical properties of the negative corona discharge between coaxial cylindrical electrodes have been experimentally studied at an ambient temperature and atmospheric pressure in flowing pure O₂ and N₂O as well as in mixtures N₂ + N₂O and O₂ + N₂O. The discharge current was found to be slightly increasing within the flow rate range (100-500) cm³/min. At higher flow rates the effect of the flow rate was only marginal in all gases and mixtures tested in experiments. The calculated ion mobility in pure N₂O and its mixture with oxygen was found to be considerably below the value corresponding to expected ions O⁻, O₂⁻ or O₃⁻. The low values of the ion mobility can be contributed to the generation of O⁻·(N₂O)_n and NO⁻·(N₂O)_n clusters. The mobility of charged particles in drift region of the discharge, calculated by using Townsend formula from current-voltage data was almost increasing with increasing discharge current in all tested gases except of N₂ + N₂O mixture.

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1. Introduction

A detailed knowledge of the processes which determine the production of ozone in air fed ozonizer is important for an improvement of performance of such devices especially an increase of the ozone yield and the enhancement of energetic efficiency of ozone generation. It is well known that all nitrogen oxides compounds (NO)_x, which are generated in discharge, participate in processes limiting both of the mentioned parameters. The first channel through which the presence of (NO)_x can affects those parameters is the set of chemical reactions of nitrogen oxides or radicals produced in the discharge with ozone molecules formed also in the discharge gap. The second mechanism, which can be active, is the direct influence of nitrogen oxides on properties of the discharge used for ozone generation. This mechanism can be active via electron driven processes, namely ionisation, excitation and electron attachment. Especially the last process can considerably reduce the number of free electrons, which otherwise could be active in dissociation of oxygen molecules. The last process is the primary process in formation of ozone molecule; hence the decrease in the density of free electrons may lead to significant reduction in the ozone yield. The role of chemical compounds produced in discharge gap has been confirmed for example in the case of negative corona discharge [1].

The nitrous oxide N₂O is one of the final compounds produced in air fed electrical discharges at atmospheric pressure. Nitrous oxide is strongly electron attaching gas. Electron attachment is active via dissociative channel (DEA) in which O⁻ is formed. N₂O exhibits two maxima in the O⁻ yield with peak energies 0.55 and 2.4 eV [2] making DEA processes prevalent *throughout the discharge gap* and not just within the glow region. Moreover, the permanent dipole moment of nitrous oxide molecule can lead to the formation of ion clusters in the drift region. The conspicuous low mobility of negative ions calculated from current voltage data in negative corona

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discharge fed by pure N_2O and its mixtures with O_2 has been reported recently [3]. The formation of cluster ions $O^-(N_2O)_n$ and $NO^-(N_2O)_n$ has been deduced from the obtained data. The formation of such cluster was observed earlier by Gardiner and Craggs [4] at low pressure of 10 Torr in point-to-plane negative corona fed by pure nitrous oxide. However, in earlier studies mentioned in paper published by Moruzzi and Dakin [5] no cluster ions were observed at low pressures 0.1 Torr. Moruzzi and Dakin also experimentally confirm the generation of the cluster $O^-(N_2O)$ in drift tube experiment as one of ion product of electron attachment to N_2O .

In present experiments the effect of the flow rate of tested pure gases and gaseous mixtures on the discharge current of negative corona discharge has been studied in pure oxygen and nitrous oxide as well as in mixtures of $N_2 + N_2O$ and $O_2 + N_2O$. The average mobility of negative charge carriers in the drift region of corona has been calculated. The electron driven elementary processes and ion-molecule reactions, which might be contribute to the observed effects are analyzed.

2. Experimental apparatus

The experiments have been carried out at atmospheric pressure and ambient temperature by using the experimental apparatus shown in Fig. 1. A system of stainless steel coaxial electrodes was composed of an inner wire electrode (radius r_0 of 62.5 μm) and an outer cylinder (radius R of 7.5 mm). The active length of outer electrode d was 100 mm. The experiments were performed at selected flow rate within the range (100 – 2500) $cm^3/minute$. The flow rate interval corresponds to translation velocities of (1 -24) cm/sec and the gas residence time interval (10 – 0.4) sec. The pure O_2 and N_2O as well as mixtures 50:50% $N_2 + N_2O$ and $O_2 + N_2O$ were used in experiments. The gases of technical purity were used. The dependences of reduced discharge current I/d (I is the discharge current, d is the length of outer electrode collecting current) on the flow rate were measured. Ozone concentration was also measured at the outlet of the reactor by using FTIR spectrometer. The concentration 2 ppm of O_3 was a detectable limit of the used diagnostics.

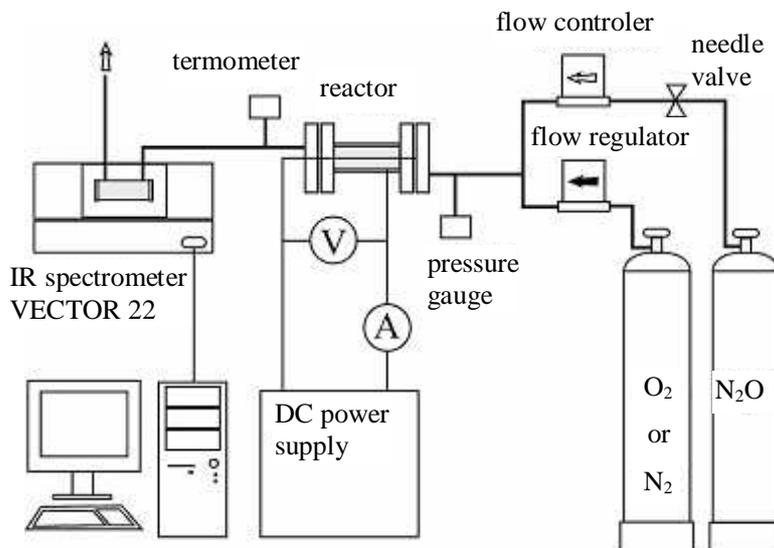


Fig. 1. Schema of used experimental apparatus.

3. Experimental results and discussion

The onset voltage U_0 of the negative corona discharge was practically not affected by the flow of the used gaseous mixture. This was remarkably higher in pure N_2O (5.2 kV) than in other gases (4.3-4.8) kV. The measured dependencies of discharge current on the flow rate are shown in Fig. 1-4 for different gases used in experiments and different voltages U applied on electrodes.

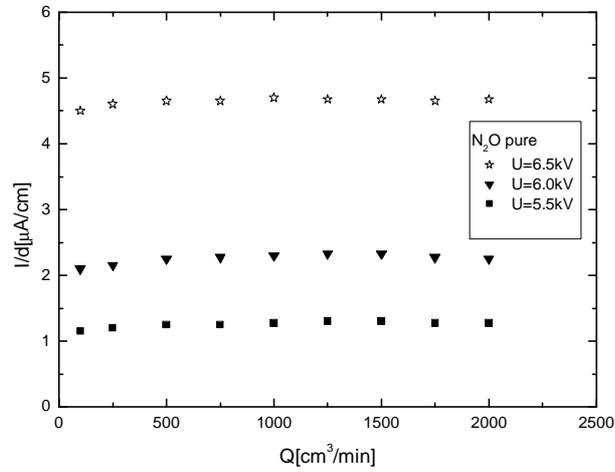


Fig. 2. The dependence of reduced discharge current I/d on the flow rate Q at three values of voltage U applied on electrodes in pure N_2O .

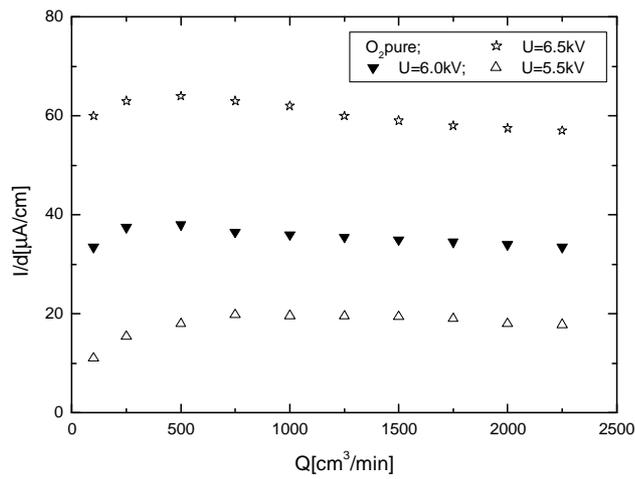


Fig. 3. The dependence of reduced discharge current I/d on the flow rate Q at three values of voltage U applied on electrodes in pure O_2 .

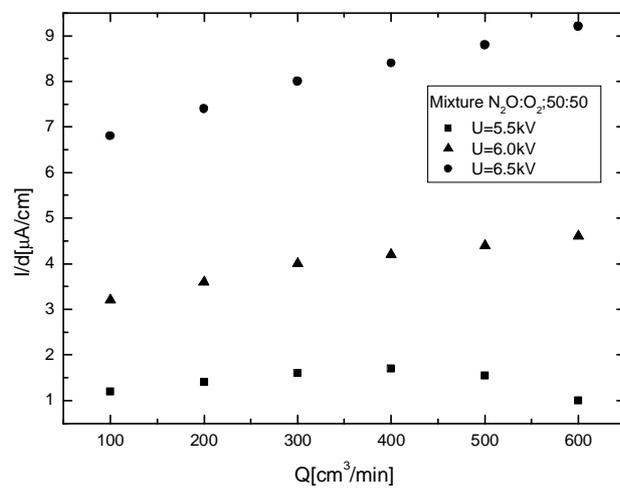


Fig. 4. The dependence of reduced discharge current I/d on the flow rate Q at three values of voltage U applied on electrodes in mixture $N_2O + O_2$.

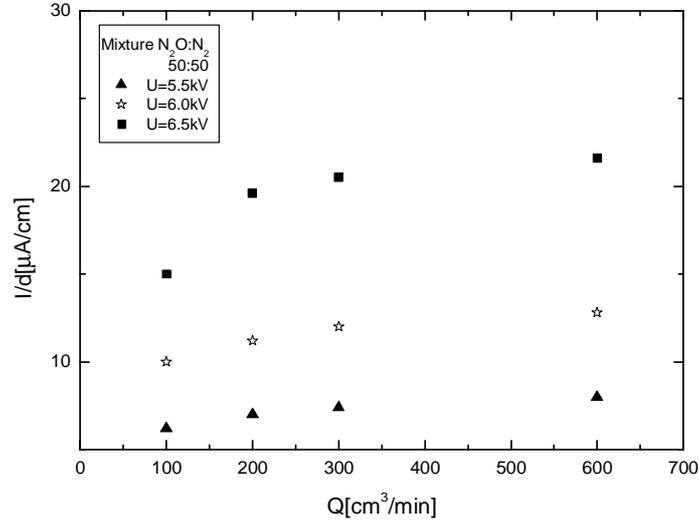


Fig. 5. The dependence of reduced discharge current I/d on the flow rate Q at three values of voltage U applied on electrodes in mixture $N_2O + N_2$.

Using the Townsend formula for current per unit length of outer electrode I/d

$$I/d = \frac{8\pi\epsilon_0\mu U(U - U_0)}{R^2 \ln R/r_0} \quad (1)$$

(ϵ_0 vacuum permittivity), the average mobility of ions μ in the drift region of the discharge gap was calculated from measured current-voltage characteristics (not shown here).

The calculated μ values at flow rate $Q > 500 \text{ cm}^3/\text{min}$ were practically not affected by the flow rate because only weak effect of the flow rate on discharge current was observed at such flow rates except of pure oxygen (see Fig. 1-4). In oxygen a flat maximum in $I/d = f(Q)$ exists at $Q \approx 250 \text{ cm}^3/\text{min}$. This is well pronounced at maximum of applied voltage. In contrast the different behaviour of calculated ion mobility was found in respect of increasing voltage U . The mobility value was increasing nearly linearly with the voltage in N_2O and its mixture with O_2 . In contrast in $N_2O + N_2$ mixture the μ value was practically constant. The increase of μ was more pronounced in pure O_2 . The data for average mobility obtained at $U = 6 \text{ kV}$ are summarised in Table 1.

Table 1. The averaged mobility of ions (averaged data calculated at different flow rates) at $U = 6 \text{ kV}$ in various gases.

Gas	$\mu [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$
O_2	5.9
N_2O	0.8
$N_2O + O_2$	1.6
$N_2O + N_2$	2.9

The calculated average mobility in pure nitrous oxide and mixture ($O_2 + N_2O$) is considerably less than the value expected if the O^- ions are only generated in the discharge gap. In pure nitrous oxide the primary O^- ions are formed via dissociative electron attachment [2]



If oxygen is present in mixture with N₂O also the dissociative electron attachment to oxygen can be partially effective in production of O⁻ ions



It must be noted however, that the rate constant for the process (2) is an order higher of that corresponding to process (3). Therefore contribution of process (3) is only marginal at concentration of N₂O (50%) in the mixture used in experiments.

The mobility of the O⁻ ions using the reduced electric field values in the discharge gap should be approximately 4.7 cm².V⁻¹.s⁻¹ at the boundary between the glow and drift region and 3.2 cm².V⁻¹.s⁻¹ at a surface of the outer cylindrical electrode [6] both of which are considerably higher than the measured value of 0.62 cm².V⁻¹.s⁻¹. Moreover process (2) is effective across the whole discharge gap because the maximum in the attachment cross section reaches maxima at 0.55 eV and 2.4 eV [2]. In pure nitrous oxide and its mixtures with oxygen the ions O⁻ undergo fast ion-molecule reactions producing either NO⁻ or NO₂⁻ ions



NO⁻ ion is not stable because of its extremely low electron affinity 0.024 eV. Therefore undergoes either fairly fast detachment process



Or may be converted via ion-molecule reaction to NO₂⁻ ion



The lifetime of NO⁻ ions at atmospheric pressure in N₂O is therefore of the order of 10 ns, hence NO₂⁻ ions should be the dominant ions in the drift region of the discharge at high pressures. At low pressures, close to 10 Torr, the reaction time of process (4) becomes comparable with the time required for the transport of O⁻ ions from the glow region to the outer electrode. Hence the O⁻ ion can be observed in mass spectra of negative ions extracted through the small orifice in the outer electrode. Gardiner and Craggs have experimentally reported this yield of O⁻ ions in pure nitrous oxide at a pressure of 1 Torr [4]. Surprisingly the yield of O⁻ ions was affected by the flow rate of gas through discharge gap. Gardiner and Craggs reported a O⁻ yield that was six times higher at high flow rate of N₂O gas through the discharge gap (undefined in paper) than the next most abundant negative ion signal which was attributed to either NO⁻ or O₂⁻ ions (the poor mass resolution of their mass spectrometer precluding these two ions from being distinguished). The existence of such a high yield of O₂⁻ can not, however, be explained by any known ion-molecule reaction, therefore we suggest that their signal was due to NO⁻ produced via the fast process (4). At extremely low flow rate of N₂O gas ensured by flow of gas through the extraction orifice the O⁻ signal was reduced and NO⁻ becomes the dominant anion [9]. The explanation made by authors, based on formation of molecular oxygen on the vessel walls, is problematic. If even some small amount of molecular oxygen is generated the rate constant for ion molecule process



is low. Hence the rate of process (5), which is active predominately in glow region of the discharge, is much higher than that of process (8) even at low concentration of N₂O. Hence the ions NO₂⁻ should be generated predominately in consecutive reactions (5) and (7).

Therefore the slight increase in the discharge current observed in our experiment within the flow rate interval (100 -2500) cm³/minute must be attributed to another mechanism. The current increase at increasing flow rate was even more pronounced in recently published data for the flow rate interval of (10 -100) cm³/minute [3].

The molecules NO₂ can be produced in discharge gap, especially in glow region, via the relatively fast process



if M is either O₂ or N₂. It can be presumed that for M = N₂O, the rate constant is close to the same high value. Moreover the ion molecule reaction competitive to process (4)



can efficiently contribute to generation of NO₂. The process is confined to glow region of the discharge where the ions O⁻ are formed. Some reactions of negative ions, which dominate in the glow region of negative corona discharge, with positive ions generated in this region via ionisation processes can also lead to formation of NO₂. Among them, the recombination of O⁻ and NO⁺ is very fast process



The ion NO⁺ is generated at nearly the same energy threshold as ion O⁺ via dissociative ionisation of N₂O molecules.

The origin of oxygen atoms, required for NO₂ formation via process (9), is the direct electron impact dissociation process,



which is very effective due to low dissociation energy of N₂O molecule (1.68 eV) [4]. Of course, there are more additional sources of oxygen atoms but of low importance.

The second constituent, NO, required for formation of NO₂ molecules via process (9) can be produced via many channels, however most likely the main source of such molecule is the electron impact dissociation of N₂O molecule competitive to (12)



The formation of NO₂ molecules was confirmed in our experiments by appearance of peak (wave number about 1600 cm⁻¹) in differential IR spectra of gaseous mixture at exhaust of the discharge tube when the N₂O gas and its mixtures with oxygen or nitrogen were treated by negative corona discharge. Contrary to this no traces of NO constituent were detected.

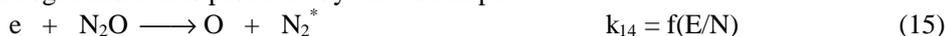
The formed electronegative NO₂ molecule undergoes very efficient third body electron attachment



The cited value of rate constant k₁₃ is valid for M = N₂ but one can guess that in the case of N₂O molecule this value is of the same order that means a very high rate of reaction (14) can be assumed. Therefore the origin of NO₂⁻ ions in N₂O fed negative corona discharge at atmospheric pressure can be ascribed to the three body process (14) and this process is beside the process (10) an additional sink of free electrons. It must be noted however that the ions NO₂⁻, which were appeared in mass spectra detected by Gardiner and Craggs [4] is in schema of subsequent reactions (2), (4), (5), and (7). Nevertheless, the increase in the flow of gas through the discharge gap led to evident slight decrease in the yield of such type of ions in their experiments. This could be an evidence that even at such low pressure (10 Torr) a small fraction of NO₂⁻ ions is also formed via process (14), because the mentioned schema of reactions (2), (4), (5), and (7) can not be affected by gas flow rate.

In our recently performed experiments the similar reduction of NO₂⁻ ionic yield was observed by IMS technique (Ion Mass Spectrometry) at atmospheric pressure at increasing gas flow rate of pure N₂O. The further experiments are in progress. The reason for decrease of ionic yield is the decrease in concentration of neutral NO₂ molecules, which are removed from discharge gap. Therefore the electron attachment process (14) becomes to be less effective and the density of free electron current is slightly increasing. This effect explains the considerable increase of the total discharge current described recently in [3] at low flow rate in N₂O as well as the slight increase in our experiments (Fig. 2). Of course not only the removal of neutral NO₂ molecules, but also NO molecules required for formation of NO₂ via process (9) contributes to observed phenomena.

In the mixture of N₂O with nitrogen the process of NO₂ formation is enhanced by active role of excited nitrogen molecules produced by electron impact



The most probable excited state of nitrogen is N₂(A³Σ_u⁺) [11]. Unfortunately there is little data on the process (15) [12] required for a quantitative analysis. The excited state of nitrogen N₂(A³Σ_u⁺) is producing NO molecule



required for generation of NO₂ via process (9). Therefore the current is more sensitive against changes in NO₂ concentration.

It is important, however, to notice that excited molecules of nitrogen N₂(A³Σ_u⁺) are active in detachment of electrons from O⁻ ions. Therefore the discharge current in mixtures N₂O + N₂ (Fig. 5) is considerably higher than in pure nitrous oxide (Fig. 2). The detached electrons at the boundary of glow and drift regions, where the process (2) is less effective, can easily form NO₂⁻ ions via process (14). This might be the second cause of relatively more pronounced increase in current with increasing gas flow rate found in mixture N₂ + N₂O than in pure N₂O.

The dependence of I/d = f(Q) measured in oxygen (Fig. 3) exhibits flat but well pronounced maximum, especially at highest voltage U applied on electrodes. In pure oxygen the primary ions O⁻ are formed by dissociative electron attachment (3). Process is confined to small volume of glow region because of existence of high electron energy threshold (approx. 4 eV) for that process. Therefore a small fraction of not attached free electrons can undergo in drift region three-body attachment



It is well known that in negative corona discharge fed by pure oxygen ozone molecules are formed efficiently. The value of around 1 % was found as a saturation value of the ozone concentration in our experiments at maximal values of average input energy density defined by formula

$$\eta = \frac{I \cdot U}{Q} \quad (18)$$

The concentration of ozone decreasing exponentially with decreasing η. In the presence of ozone in the discharge gap the charge transfer reactions

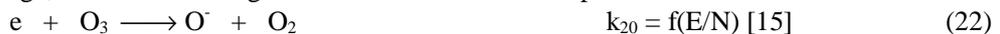


and ion conversion process



are active. The value of the rate constant k₁₉ is valid at gas temperature T = 300 K. The rate constant is inversely proportional to temperature T. Hence in the negative corona discharge fed by oxygen the ion O₃⁻ prevails among the ions produced in discharge as it follows from chemical and electrical modelling of negative DC corona in pure oxygen performed by Sorria et al. [13]. The IMS analysis of ions produced by negative corona discharge in pure oxygen between point-to-plane electrodes in our laboratory in present time confirmed that fact. [14].

Moreover, ozone is strongly attaching gas, depleting free electrons especially in drift region of the discharge, because of the high rate constant for dominant process



The rate constant reaches its flat maximum of order of 10⁻⁹ cm³/sec at electron energy of 1 eV, which is typical for drift region. Due to the presence of 1 % of ozone at minimal flow rate the total discharge current is at its minimum. With increasing flow rate Q the average energy density η is decreasing. Consequently ozone concentration is reduced exponentially with linear decrease in η and the role of the process (22) becomes to be marginal. This effect can explain an increase in discharge current observed at low flow rate Q (Fig. 3). Synchronously with depleting of ozone the process (17) starts to be dominant sink of free electrons in drift region. However the mobility of produced O₂⁻ ions is considerably below that of O₃⁻, hence the decrease in current was appeared. Effect of current reduction was however partially induced also by slight increase of pressure in the discharge tube at flow rate Q > 1500 cm³/min.

In mixture $O_2 + N_2O$ the ozone production is inhibited by more processes, especially by chemical reactions of ozone with NO and NO_2 oxides formed in consecutive reactions in the discharge gap. The primary process for formation of mentioned oxides is electron impact dissociation of N_2O . The ozone concentration in our experiments reached its maximum of approximately 250 ppm only at maximum of η . Because of low ozone concentration in tested mixture the increase in current observed experimentally (Fig. 4) can be most likely attributed to the removal of NO and NO_2 oxides from discharge gap. Due to this the role of electron attachment to NO_2 (14), becomes to be negligible and the component of free electron current in total discharge current is slightly increasing with increasing flow rate. However, the discharge current in such case is much smaller than that found in pure oxygen as well as in $N_2 + N_2O$ mixtures. This is due to dominant role of dissociative electron attachment (2) and formation of clusters $NO^{\cdot-}.N_2O$ and $O^{\cdot-}.N_2O$. Also the process (3) and process (17) contribute to reduction of free electron density. Moreover, there is no efficient detachment process of electrons from $O^{\cdot-}$ ion comparable with that one (15) active in $N_2 + N_2O$ mixture. The IMS measurements of ion spectra performed in mixtures of oxygen with nitrous oxide are required for better understanding of electron driven processes and ion molecule reactions in mentioned mixture.

4. Conclusions

The flow rate of pure N_2O and O_2 gases as well as the mixtures of $N_2O + O_2$ and $N_2O + N_2$ only slightly affects the discharge current of negative corona discharge fed by mentioned gases and/or gaseous mixtures. Almost slight increase in discharge current was observed except of pure oxygen in which slightly pronounced flat maximum was found. The discharge current is substantially reduced by addition of nitrous oxide into oxygen. Due to addition of nitrous oxide into nitrogen the stable negative corona discharge can be formed. The calculated average mobility of charged particles in drift region confirmed existence of ion clusters $NO^{\cdot-}.N_2O$ and $O^{\cdot-}.N_2O$. The preliminary IMS measurements of ion spectra have shown in pure nitrous oxide treated in negative corona between point and plane electrodes the existence of third cluster ion. The theoretical considerations led us to conclude that most likely the identity of newly observed ion is $NO_2^{\cdot-}.N_2O$. The further experiments aiming to confirm the theoretical hypothesis are in progress.

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