# 진동에너지에 의한 산화질소 분자(NO)의 음이온(NO⁻)으로의 환원반응에 관한 연구

**趙 鮮 郁**

신라대학교 화학과

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# A Study on the Reduction of Nitric Oxide Molecule (NO) to Nitroxyl Anion (NO⁻) by Vibrational Energy

**Seon-Woog Cho**

*Department of Chemistry, Silla University, Pusan 617-736, Korea*

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**요 약.** 산화질소 분자(NO)가 전자 한 개를 받아 산화질소 음이온(NO⁻)으로 환원되는 반응의 정도가 진동에너지에 따라 크게 달라질 수 있음을 제시하였다. NO와 NO⁻의 포텐샬에너지 표면은 진동에너지가 많아짐에 따라 NO 분자가 전자를 받아 NO⁻ 음이온으로 바뀔수 있는 에너지적 측면을 가짐을 보여준다. 또한, 진동 파동함수간의 Franck-Condon 인자를 계산하였다. 진동에너지가 많아지면 NO에서 NO⁻로 바뀔 경로가 더 많이 증가함을 보인다. 이 결과는 NO 분자에게 적절한 빛을 조사시킴으로 NO⁻ 이온으로의 환원반응속도를 조절할 수 있음을 의미한다.

**주제어:** NO, NO⁻, 전자전달, 산화환원

**ABSTRACT.** It is shown that one-electron reduction of nitric oxide (NO) to nitroxyl anion (NO⁻) can be accelerated by vibrational energy. Potential energy surfaces of NO and NO⁻ reveal that the vertical transition between them has favorable energetics for vibrationally excited molecule. Also, Franck-Condon factors between NO and NO⁻ vibrational wave functions are calculated. It shows that the number of open channels increases with increased vibrational energy. These results mean that we can control the rate of reduction of NO to NO⁻ by radiating an appropriate light.

**Keywords:** NO, NO⁻, electron transfer, oxidation-reduction

The Nobel Prize in Physiology or Medicine for 1998[1] was awarded to Robert F. Furchgott, Louis J. Ignarro, and Ferid Murad for their discoveries of nitric oxide (NO) as a signalling molecule in the cardiovascular system. It was a sensation that this simple, common air pollutant, which is formed when nitrogen burns, for instance in automobile exhaust fumes, could exert important functions in the organism. Further research results rapidly confirmed that NO is a signal molecule of key importance for the cardiovascular system and it was also found to exert a series of other functions. We know today that NO acts as a signal molecule in the nervous system, as a weapon against infections, as a regulator of blood pressure, and as a gatekeeper of blood flow to different organs. The medical applications of NO are best known; it acts to dilate blood vessels by relaxing smooth muscle, and so reduce

blood pressure. In turn, this makes it a useful therapy for impotence, and perhaps asthma, in addition to hypertension. Recently, an extremely successful medication, Viagra, made headlines worldwide.

NO is greatly increased when the body is invaded by bacteria. This increased NO is a defense mechanism. When NO is produced in white blood cells, huge quantities are achieved and become toxic to invading bacteria and parasites. However, if there is too much NO it may cause significant harm. When this process spirals out of control then septic shock develops. Septic shock is characterized by a loss of blood pressure and poor circulation to the vital organs. When blood flow to the brain is blocked, the symptoms of paralysis and loss of speech then result. This condition is typically known as a stroke. In this situation, NO plays a harmful role. White blood cells react to bacterial products by releasing enormous amounts of NO that dilate the blood vessels. The blood pressure drops and the patient may become unconscious. In this situation, inhibitors of NO synthesis may be useful in intensive care treatment.

NO molecule is paramagnetic because it has one unpaired electron. This extremely reactive free radical seeks to obtain another electron to fulfill the octet rule and become a lower energy species, nitroxyl anion (NO⁻). The chemical biology of NO⁻ is largely unknown. However, a recent study[2] shows that NO⁻ - unlike NO - reacts mainly with N-methyl-D-aspartate (NMDA) receptor to downregulate receptor activity and thus provide neuroprotection from excitotoxic insults. So they suggested a new therapeutic approach, using NO⁻ donors, to ameliorate NMDA receptor-mediated neuronal damage. They also verified that NO is ineffective for this reaction. Relating this approach with the excessive NO problem mentioned above, we may have an easy way of converting NO to NO⁻. This might be a more convenient method than inhibiting NO synthesis itself. Of course, human body is very complicated system. Our suggestion is not a conclusive method for treating the excessive NO problem. However, here we can have a method purely based on molecular dynamics. Anyway, the elec-

tron transfer reaction, or oxidation-reduction reaction, is one of the most interesting topics in chemistry. Theoretical explanation of this reducing method from NO to NO⁻ follows in the next two sections.

## POTENTIAL ENERGY SURFACES

We have reported[3] a Franck-Condon factor study for the vibrational relaxation of NO molecules colliding with a metal surface. This study was stimulated by the experimental results of Wodtke and his coworkers.[4] They observed an efficient multi-quantum vibrational relaxation of NO ($v$=15) molecules colliding with a gold surface in a single molecule-surface encounter. Underlying mechanism for this vibrational energy transfer is the electron-hole pair mechanism.[5,6] On the other hand, essentially no vibrational relaxation was observed on an insulating LiF surface even at all incident energies, indicating that vibration of molecule couples very weakly to electronic states of the insulating solid. Then, the vibrational relaxation of high efficiency should be applied only to metallic surface. Most remarkable thing we have learned from the series of experiments is that the survival probability for NO($v$) scattered on Au(111) surface varies dramatically depending on the vibrational quantum number $v$ of NO.

To understand how vibrational energy of a molecule can promote electron transfer from a metal surface to a molecule, let us see the potential energy surfaces (PES) of NO($X^2\Pi$) and NO⁻ ($X^3\Sigma^-$) (*Fig.* 1). These potential energy curves[7] for NO and NO⁻ were calculated at high levels, and the curves were fit with a modified Morse potential.[8] We use the following form:

$$U(r)=D_e[(1-e^{-\beta x})^2+c(\beta x)^3 e^{-2\beta x}(1+bx)] \qquad (1)$$

where $x=(r-r_e)$ and $r$ is the intramolecular bond distance. The parameters for the PES are listed in *Table* 1.

The vertical difference between NO potential energy curve and NO⁻ curve is the electron affinity as a function of intramolecular bond distance. The asymtotic electron affinity should be that of O atom, that is the difference between O and O⁻. It is known[9]

*Table* 1. Parameters for the potential energy surfaces of NO and NO⁻. These numbers are obtained by fitting the QCISD(T)/aug-cc-pVTZ results of Kelly Sullivan (Ref. 7)

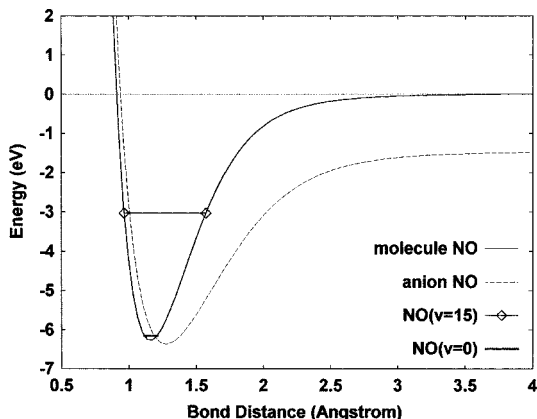|            | $D_e$ (eV) | $r_e$ (Å) | $\beta$(Å⁻¹) | $b$ (Å⁻¹) | $c$      |
|------------|------------|-----------|--------------|-----------|----------|
| NO molecule | 6.27       | 1.159     | 2.845        | 3.0       | 0.0125   |
| NO⁻ anion  | 4.90       | 1.273     | 2.159        | 72.5      | 0.004613 |



*Fig*. 1. The potential energy curves of NO and NO⁻. The energy difference between these curves at long bond distance reflects the known O atom electron affinity 1.461 eV. Also marked are the vibrational energy levels for $v$=0 and 15 of NO.

that the electron affinity of oxygen atom is $Ea=$ 11784.645±0.006 cm⁻¹=1.461122±0.000003 eV. If we set zero of energy as the limit of NO→N+O, $U(r)$ for NO must be subtracted by $D_e$ (or 6.27 eV). And $U(r)$ for NO⁻ must be subtracted by 1.461+4.90= 6.361 eV. This is well reflected on *Fig*. 1.

Near the potential minima, there is little energy difference between the neutral and anion curves, in agreement with a measured small electron affinity[10] (0.026 eV). Vibrationally cold NO ($v$=0) shows not much energy difference with NO⁻. However, for vibrationally excied state, the vertical difference between two curves changes dramatically. For NO $v$=15 vibrational state, the classical inner turning point is $r_-$=0.9652 Å and the outer turning point is $r_+$=1.5725 Å. The vertical difference, $U$(NO)-$U$(NO⁻), at the inner turning point is -1.562 eV. And, at the outer turning point, it is 2.186 eV. We see that vibrationally excited NO ($v$=15) shows about 3.75 eV difference as a function of intramolecular bond distance. This much energy is comparable with the work function of Ag or Au

(4.3 eV), so has increased tunneling probabilities from metal, if a metal is nearby. In human body, NO molecule can get an electron from any electron donor nearby. We note here that the electron transfer from electron donor to NO molecule brings a NO⁻ anion. Near the outer turning point of vibrating NO, the reduction of nitric oxide molecule (NO) to form nitroxyl anion (NO⁻) is an exothermic reaction. On the other hand, near the inner turning point, the reduction of NO to NO⁻ is an endothermic reaction. We pay special attention to the classical outer turning point, because at that point electron affinity is favorable for the transition. And also, at the outer turning point the vibrational wave function has high amplitude and higher probability for the vertical transition. Most notable key point here is that the electron transfer can be controlled as exothermic or endothermic by vibrational energy of the molecule NO. Of course, we can supply the vibrational energy to the molecule either thermally or optically. In summary, PES of NO and NO⁻ reveal that the vertical transition between them has favorable energetics for vibrationally excited molecule. In other words, a large-amplitude vibration causes a great electron affinity of NO, so it brings an enhanced probability for the reduction of NO to NO⁻. To see another effect of vibrational energy for the promotion of electron transfer, we calculate the Franck-Condon factors in the following section.

## FRANCK-CONDON FACTORS

The reduction reaction from NO molecule to NO⁻ (or the electronic reaction) will accompany a change in the nuclear (vibrational) wave functions of the molecule. Quantum mechanically, the transitions between two potential energy curves of NO and NO⁻ can be explained with the Golden Rule.[11] As Gadzuk and Metiu[12] pointed out in their theory, the

Franck-Condon (FC) overlap between them will be one of the major factors determining the Golden Rule transition rate. Because only those transitions of substantial FC overlap will contribute substantially to the rate. The transition probability amplitude from the state $|g>\|gb>>$ to $|\lambda>\|\lambda a>>$ is given as

$$T_{\lambda a \leftarrow gb} \simeq VS \qquad (2)$$

where

$$V = \int dr \phi_\lambda^*(r,R) H_{el}(r,R)\phi_g(r,R) \qquad (3)$$

$$S = \int dR \tau_{\lambda a}^*(R)\eta_{gb}(R) \qquad (4)$$

The first integral $V$ is electronic coupling matrix element, and the second integral $S$ is the FC overlap. The FC approximation should be reasonably good for this case. Within this approximation, the coupling matrix may be treated as an averaged quantity. We treat the coupling as a constant for simplicity in our model. So, the transition probability from the state $|g>\|gb>>$ to $|\lambda>\|\lambda a>>$ is given to be proportional to the FC factors.

To obtain the FC factors, we used the eigenvalue program LEVEL[13] which is using the Cooley-Numerov method[14,15] to solve the Schrödinger equation. We modified a part of the source program for our purpose, and supplied our own functional form of the potential energy curves. At first, we produced a nuclear wave function of NO($v$) molecule, and then calculated the FC overlap with nuclear wave functions of NO⁻ ($v'$). Two of the vibrational wave functions of NO molecule are shown in *Fig.* 2. The wave function for $v$=0 is localized around the equilibrium bond distance $r_e$ = 1.159 Å. For $v$=15, the wave function spans wide range of bond distance. The vibrationally excited state has high amplitude near the turning points, especially at the outer one, as it should be.

The FC factors between $v$ state of NO and $v'$ states of NO⁻ are calculated and presented in *Fig.* 3. These FC factors reflect the probabilities of finding in which final vibrational state of the anion NO⁻($v'$) when the molecule NO($v$) accepts one electron. The FC factors are calculated for three different initial states ($v$=0, 2, 15) to see the effect of vibrational
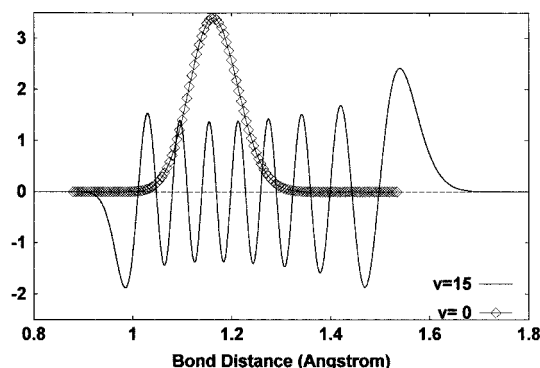


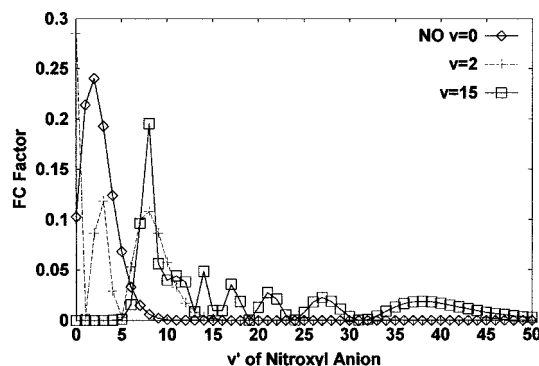*Fig.* 2. Vibrational wave functions ($v$=0 and 15) of NO molecule.



*Fig.* 3. Franck-Condon factors for the vertical transitions from NO($v$) to NO⁻ ($v'$). The FC factors are calculated for three different initial states, $v$=0, 2, and 15.

energy accompanying the electron transfer. For $v$=0, we see only one big hump which has the maximum at $v'$=2. We see also that higher $v'$ states (>10) are essentially closed for vibrationally cold molecule. For $v$=2, we see three maxima at $v'$=0, 3, 8. For this mildly excited state, the number of open channels for the vertical transition increased by about 5. As the vibrational energy increases, the FC factors reveal more dynamic features of the vertical transition. For highly excited state $v$=15, we see a strong peak at $v'$=8 and many small peaks which appear almost everywhere. This means that we have many open channels for the vertical transition in case of vibrationally highly excited state.

Our FC results show that we can have an increased number of open channels for the reduction of NO to NO⁻ just by supplying vibrational energy to NO

molecules. Comparing FC factors for $v$=2 and $v$=15, we see this tendency becomes more apparent with increased vibrational quanta. A conclusion obtained in this section is that the number of open channels increases with increased vibrational energy. In the following section, we imply a possible application of this result, and make conclusions of this work.

## SUMMARY

It is shown that one-electron reduction of nitric oxide (NO) to nitroxyl anion (NO⁻) can be accelerated by vibrational energy. On energetic grounds, PES of NO and NO⁻ reveal that the vertical transition between them has favorable energetics for vibrationally excited molecule. We see that vibrationally excited NO ($v$=15) shows about 3.75 eV difference as a function of intramolecular bond distance. Near the outer turning point of vibrating NO, the reduction of nitric oxide molecule NO to form nitroxyl anion NO⁻ is an exothermic reaction. On the other hand, near the inner turning point, the reduction of NO to NO⁻ is an endothermic reaction. We see that a large-amplitude vibration causes a great electron affinity of NO, so it brings an enhanced probability for the reduction of NO to NO⁻. Also, FC factors between NO and NO⁻ vibrational wave functions show that the number of open channels increases with increased vibrational energy. For vibrationally cold NO, we see that higher $v'$ states are essentially closed. For mildly excited state $v$=2, the number of open channels for the vertical transition increased modestly. For highly excited state $v$=15, we see a strong peak at $v'$=8 and many small peaks which appear almost everywhere. This result is interpreted as that we have many open channels for the vertical transition in case of vibrationally highly excited state. We conclude that both energetic effect and opening more channels are the main aspects for the vibrational promotion of the electron transfer reaction. These results mean that we can control the rate of reduction of NO to NO⁻ (or oxidation of NO⁻ to NO) by radiating an appropriate light or by selecting a good method of supplying vibrational energy to NO molecule.

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