Absorption dynamics of nitric oxide in gas mixtures
excited by pulsed e-beam sustained discharge

S.P. Derevyashkin[1,2], A.A. Ionin[1], Yu.M. Klimachev[1], I.O. Kinyaevskiy[1],

A.A. Kotkov[1], A.Yu. Kozlov[1], A.K. Kurnosov[3]

[1] *P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, Russia*

[2] *National Nuclear Research University «MEPHI», Moscow, Russia*

[3] *Troitsk Institute for Innovation and Fusion Research, Moscow, Russia*

Vibrational relaxation of NO molecules excited by a pulsed e-beam sustained discharge (EBSD) was studied with the usage of CO laser probing. We developed numerical model of vibrational kinetics in ensemble of NO molecules and compared the experimental and calculated data on absorption dynamics of vibrational excited NO molecules.

Relaxation properties of NO molecules were investigated mainly on lower vibrational levels ($v = 1 \div 3$) [1-5]. Analysis of experimental data showed that the vibrational relaxation of NO molecules is a very fast process [2, 3, 6] in comparison with the vibrational relaxation of CO molecules. Vibrational relaxation is a complex process that includes vibration-to-translation (VT) relaxation and vibration-to-vibration (VV) exchange. To explain fast vibrational relaxation of NO molecules, it was assumed that the rate of VT relaxation of NO molecules is five orders of magnitude higher than the rate of VT relaxation of CO molecules [3]. Although it was believed that the rate of VV exchange of NO molecules is close to the rate of VV exchange of CO molecules [2-6].

We suggest a different explanation for the fast vibrational relaxation of NO molecules. We assume that the rate of VV exchange of NO molecules is much greater than the rate of VV exchange of CO molecules. It is possible, considering that the NO molecule is a doublet $^2\Pi$ in the ground electronic state, and has two systems of rotational-vibrational (briefly ro-vibrational) levels separated by the energetic gap of 120 cm^{-1}. In our numerical model of vibrational kinetics of NO molecules we proceeded following this assumption. The purpose of this paper is to study in detail the vibrational relaxation of NO molecules. In our experiments, we applied a powerful-pulsed pump of lower vibrational levels of NO molecules and a CO laser probing population dynamics on higher vibrational levels.

THEORY

The theoretical model of vibrational kinetics in an ensemble of NO molecules and buffer gases was developed by comparing the experimental and calculated data on absorption dynamics of vibrational excited NO molecules. The theoretical model includes a self-consistent numerical solution of the equations of vibrational kinetics in mixtures of NO:He,

NO:Ar и NO:N$_2$ and Boltzmann equation for the distribution function of electron energy of pulsed EBSD. The rate constants for N$_2$-N$_2$ VV-exchange processes were taken from the work [7]. As to processes NO(u)+NO(v)→NO(u+1)+NO(v-1), the corresponding rate coefficients were calculated with an approximate analytical expression taking into account the dominant role of dipole-dipole interaction between NO molecules:

$$K_{v,v-1}^{u,u+1} = b \cdot \frac{Z}{T} \cdot \frac{v}{(1-v \cdot \delta)} \cdot \frac{(u+1)}{(1-(u+1) \cdot \delta)} \cdot \exp\left(\frac{\Delta E}{2 \cdot T}\right) \cdot \exp\left(-\frac{\Delta E^2}{C \cdot T}\right). \qquad (1)$$

The structure of this formula is the same as was proposed in [8]. Here ω_e is the fundamental frequency, $x_e\omega_e$ is an anharmonicity constant, $\delta = x_e\omega_e / \omega_e$, Z=$\pi\sigma^2$ V$_M$, V$_M$ is the average relative translational velocity, $\pi\sigma^2$ is the gas kinetic collision cross-section in the hard spheres model [9]; ΔE is energy mismatch of VV process in K, b and C are the semi-empirical parameters found in comparison between the theory and experiment. For gas temperature T=300 K the expression (1) with coefficients b=1.92 K and C=31.46 K enables a good agreement with experimentally measured VV rate constant [4] for process: NO(1)+NO(1)→NO(2)+ NO(0).

The VV′ processes between NO and N$_2$ molecules are nowadays also poorly known. On the first step of our study we have calculated the rate constants for these processes with analytic expression used early for calculations of rate constants for VV′ processes between N$_2$ and CO molecules [7]. Such approach is based on the qualitative similarity of the intermolecular potentials for two pairs of molecules: CO-N$_2$ and NO-N$_2$. Thus the rate constants for VV′ processes NO(v)+N$_2$(u)→NO(v-1)+N$_2$(u+1) were determined with an analytic expression:

$$K_{v,v-1}^{u,u+1} = a \cdot Z \cdot T \cdot \frac{v}{(1-v \cdot \delta)} \cdot \frac{(u+1)}{(1-(u+1) \cdot \delta)} \cdot \exp\left(\frac{\Delta E}{2 \cdot T}\right) \cdot f(y) \cdot F +$$
$$+ b \cdot \frac{Z}{T} \cdot \frac{v}{(1-v \cdot \delta)} \cdot (u+1) \cdot \exp\left(\frac{\Delta E}{2 \cdot T}\right) \cdot \exp\left(-\frac{\Delta E^2}{C \cdot T}\right). \qquad (2)$$

The first additive term in expression (2) corresponds to the joint action of the short range repulsion and van der Waals attraction, the second term corresponds to dipole-quadrupole interaction. Here $f(y)$ is the adiabatic function calculated in accordance with [8], $y = l_{ST} \cdot |\Delta E| \cdot \pi^2 \cdot \sqrt{\frac{2 \cdot \mu \cdot k}{h^2 \cdot T}}$, l_{ST} - is the semi-empirical parameter introduced in Schwartz-Slawsky-Herzfeld (SSH) theory for the case of 1D model and characterizing the specific size of the short-range repulsion, μ is the reduced mass of the colliding molecules, while h and k

are the Planck and Boltzmann constants respectively, F is the Shin's factor for approximate description of van der Waals attraction [8]. The values of the semi-empiric parameters a, b, C and l_{ST} were taken the same as for N_2-CO VV′ rate constants [7]. Data on the rate constants for the VT relaxation of $NO(1) + NO(0) \rightarrow NO(0) + NO(0)$ were taken from paper [10]. The calculations of rate constant for the VT relaxation of molecules for higher vibrational levels v were made with the use of the SSH theory [8].

<div align="center">EXPERIMENT</div>

In our experiments, the NO molecules excited in mixtures $NO:Ar$ and $NO:N_2$ by the pulsed EBSD with duration up to ~100 μs. The experiments were performed on a pulsed EBSD laser system with active medium length $L = 1.4$ m, described in detail in [11], with the possibility to excite a large volume (up to 2.4 liters) of gas mixtures. For probing the dynamics of vibrational excited states of NO molecules the radiation of frequency-selective cryogenic low pressure CO laser [12] was used. This probe CO laser operated in a band of fundamental vibrational transitions on more than 200 spectral lines.

The optical scheme of experiments and methodic of measuring of the temporal dynamics of absorption of NO molecules is described in detail in [13].
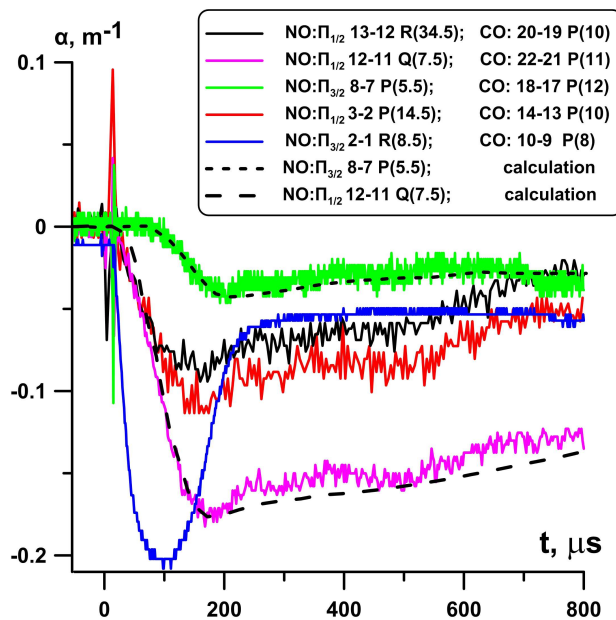

Fig 1. Temporal behavior of absorption coefficients in gas mixture NO:Ar=1:5, pressure 0.24 atm, T=293 K. Inset shows NO transitions and CO laser lines.

An absorption dynamics for different probe CO laser lines in the mixture NO:Ar=1:5 at specific input energy (SIE) Q_{in}=50 J/(l atm) is presented in Fig. 1. In all gas mixtures at initial gas temperature T=293 K the absorption at the lowest NO transition $\Pi_{1/2}$ 2-1 R(8.5) appears almost immediately with the start of the EBSD (t=0). We observed well-defined maximum of absorption at t=100 μs for the NO transition $\Pi_{1/2}$ 2-1 R(8.5) with time duration ~180 μs on the level 0.5 and then slowly falling tail up to 3 ms. The maximum absorption coefficient at the NO transition $\Pi_{1/2}$ 2-1 R(8.5) was 5 times higher in the nitrogen-reach gas mixture at SIE 250 J/(l atm) than in the argon-reach mixture at SIE 50 J/(l atm). As it is presented in Fig. 1

absorption at higher vibrational transitions of NO from 3-2 to 13-12 band peaked almost simultaneously at t=160-200 µs. Then absorption at these transitions decreased slowly during a few milliseconds.

We calculated rate constants for VV exchange between NO molecules and VV′ exchange between N_2 and NO for our experimental conditions. The calculated temporal behavior of the absorption coefficients on NO transitions $\Pi_{1/2}$ 12-11 Q(7.5) and $\Pi_{3/2}$ 8-7 P(5.5) is also presented in Fig. 1 and is in good agreement with the measured absorption.

Another behavior was observed at probing the absorption in gas mixtures NO:Ar = 1:6 and NO:N_2=1:20 cooled down to T=122±2 K (see Fig 2). Dynamics of absorption slowed down with decreasing gas temperature. Absorption on NO transition $\Pi_{1/2}$ 2-1 R(8.5) and higher transitions was observed for about 3 s at the level 0.1 of maximum.

This fact suggests that under these conditions the gas mixture accumulates a sufficiently large amount of vibrational energy and the energy relaxes very slowly to heat due to VV′ exchange between nitrogen and NO molecules and VT-relaxation of the NO molecules.

Fig 2. Temporal behavior of absorption coefficients in gas mixture NO:N_2=1:20, at T=122±2 K. Inset shows NO transitions and CO laser lines. Q_{in}=180 J/(l*Amagat).

REFERENCES

[1] Y. Nachshon, P.D. Coleman, J. Chem. Phys. 61 (1974) 2520-2524.

[2] J.C. Stephenson, J. Chem. Phys. 59 (1973) 1523-1527.

[3] J.C. Stephenson, J. Chem. Phys. 60 (1974) 4289-4294.

[4] I.J. Wysong, J. Chem. Phys. 101 (1994) 2800-2810.

[5] I.J. Wysong, Chem. Phys. Lett. 227 (1994) 69-73.

[6] H. Horiguchi, S. Tsuchiya, Japanese J. of Appl. Phys. 18 (1974) 1207-1212.

[7] A.K. Kurnosov, A.P. Napartovich, S.L. Shnyrev and M. Cacciatore, Plasma Sources Sci. Technol. 19 (2010) 045015-1-045015-13.

[8] N.S. Smith, H.A. Hassan, AIAA Journal, 14 (1976) 374-381.

[9] J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird. Molecular theory of gases and liquids. John Wiley & Sons, Inc., New York (1967).

[10] L. Doyennette, M. Margottin-Maclow, J. Chem. Phys. 84 (1986) 6668–6678.

[11] A.A. Ionin, Yu.M. Klimachev, Yu.B. Konev, et al. Quantum Electronics, 30 (2000) 573–579.

[12] S. Vetoshkin, A. Ionin, Yu. Klimachev, et al. J. of Russian Laser Research, 27 (2006) 33-69.

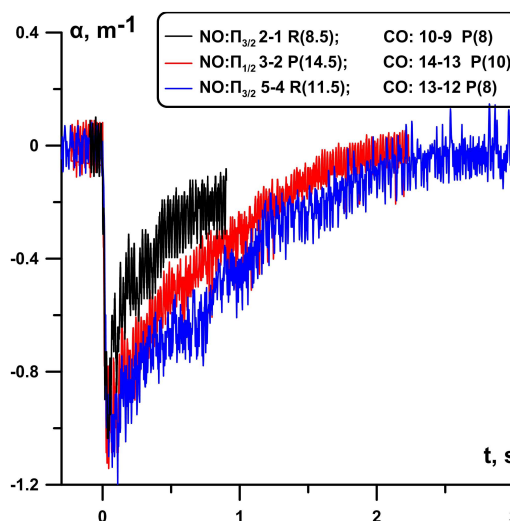[13] S.P. Derevyashkin, A.A. Ionin, I.O. Kinyaevskiy, et al. Physics Procedia (2015) (in print).