Absorption dynamics of nitric oxide in gas mixtures excited by pulsed discharge

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Abstract

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

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Peer-review under responsibility of the National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)

Keywords: CO laser; laser probing; e-beam sustained discharge; nitric oxide, vibrational kinetics.

1. Introduction

Relaxation properties of NO molecules were investigated mainly on lower vibrational levels \(V = 1\pm3\) (see for example Nachshon and Coleman (1974), Stephenson (1973, 1974), Wysong (1994a), Wysong (1994b)). Analysis of experimental data showed that the vibrational relaxation of NO molecules is a very fast process [Stephenson (1973), Stephenson (1974), Horiguchi et al. (1974)] in comparison with the vibrational relaxation of CO molecules.

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Vibrational relaxation is a complex process that includes vibration-translational (VT) relaxation and vibrational-vibrational (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 [Stephenson (1974)]. However, it was assumed that the rate of VV exchange of NO molecules is close to the rate of VV exchange of CO molecules [Stephenson (1973), Stephenson (1974), Wysong (1994a), Wysong (1994b), Horiguchi and Tsuchiya (1974)].

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 2Π in the ground electronic state, and has two systems of 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 and CO laser probing of population dynamics on higher vibrational levels.

2. Theoretical model

The numerical 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 u NO:N₂ and Boltzmann equation for the distribution function of electron energy of pulsed EBSD. In our calculations, we used data from paper of Kurnosov et al. (2010) on rate constants of VV exchange between N₂ molecules. To calculate the rate constants of VV exchange between NO molecules in processes: \( NO(u) + NO(v) \rightarrow NO(u + 1) + NO(v - 1) \), we used an analytical expression that includes the role of long-range dipole-dipole interaction between NO molecules. The structure of this expression is similar to that proposed in paper of Smith and Hassan (1976) for the calculation of the rate constants of VV exchange between diatomic molecules with the dominance of long-range part of the interaction potential. Processes of VV' exchange between nitrogen molecules and nitric oxide molecules are also poorly understood. In the literature, there is no data on the rate constants of these processes. In the first stage the VV' exchange rate constants between NO and N₂ molecules was described by an analytical formula that was previously used to calculate the rate constants in the case of VV' exchange between N₂ and CO molecules taking into account the short-range repulsion, the dispersion attraction and dipole-quadrupole interaction. This approach is based on the similarity of interaction potentials for the two pairs of molecules. Data on the rate constants for the VT relaxation of \( NO(0) \rightarrow NO(1) \) were taken from paper of Doyennette and Margottin-Maclow (1986). The calculations of rate constant for the VT relaxation of NO molecules for higher vibrational levels \( V \) were made with the use of the Schwartz-Slawsky-Herzfeld theory (Smith and Hassan (1976)).

3. Results

In our experiments, the NO molecules excited in mixtures NO:Ar and NO:N₂ by the pulsed e-beam sustained discharge (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 paper of Ionin et al. (2000) 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 radiation of frequency-selective cryogenic low pressure CO laser was used. This probe CO laser operated in a band of fundamental vibrational transitions on more than 200 spectral lines (Vetoshkin et al. (2006)).

Analyses of the coincidence between the CO laser lines and the absorption lines of the vibrationally excited transitions of molecule NO was performed. Data on transitions of NO were obtained by the database system "HITRAN" [Rothman et al. (1998)], and the transitions of the CO molecules were calculated with Dunham coefficients obtained from paper of Guelachvili et al. (1983). From hundreds of NO transitions we selected several tens close in frequency (\( \Delta \nu < 0.1 \) cm⁻¹) with the CO laser lines. Laser probing was performed on the CO laser lines with the vibrational numbers \( V \) from 4 to 23.
The optical scheme of experiments to measure the temporal dynamics of absorption of NO molecules is shown in Fig. 1.

![Optical scheme of experiments](image)

Fig. 1. Optical scheme of experiments: 1 – active medium of probe CO laser; 2 – rear spherical mirror; 3 – rotary table; 4 – EBSD chamber; 5 – diffraction grating; 6 – spherical mirrors; 7 – semiconductor lasers $\lambda = 650$ nm; 8 – flat mirror; 9 – photodetectors; 10 – beam splitters; 11 – spectrometer; 12 – turning mirrors.

The active medium of the probe CO laser 1 was pumped by the DC discharge in cryogenically cooled gas mixture. The spherical mirror 2 (radius of curvature equals 10 m) was used as the rear mirror. The probe laser beam was directed into EBSD chamber 4 by the flat mirrors 12. Output windows of discharge chamber (CaF$_2$) were turned at an angle of ~5° to the laser beam in perpendicular planes to avoid parasitic reflection. Frequency selection of CO laser was carried out using the diffraction grating 5 (150 grooves/mm, blaze angle $\sim 26^\circ$), placed on the rotating table 3 with the flat mirror 8, so the angle of rotation didn’t affect the direction of the outgoing radiation. To control the alignment of CO laser cavity and rotation angle of the diffraction grating 5 we used a semiconductor lasers 7 with the wavelength $\lambda = 650$ nm. To control the spectral and temporal parameters of the probing radiation, the probe laser beam was split by CaF$_2$ beam splitters 10, and a part of the beam was directed into infrared spectrometer 11 and photodetector 9 (PEM L 3). The same photodetector 9 was used for detection of laser beam transmitted through EBSD chamber 4 after two passes. The laser beams were focused on photodetectors using spherical mirrors 6. The signals from photodetectors 9 were recorded by double-beam oscilloscope Tektronix TDS 1012. One characteristic oscillogram is shown in Fig 2.

Absorption coefficient was calculated with the formula:

$$\alpha = \frac{1}{L} \ln \left( \frac{I_2(t)}{I_1(t)} \right) \left( \frac{I_1(t)}{I_1(0)} \right)$$

where $I_1(t)$ is the intensity of the probe laser; $I_2(t)$ is the intensity of the laser beam transmitted through the discharge chamber; $L = 2.8$ m - absorption length. The moment $t = 0$ corresponds to the beginning of the EBSD pulse. The accuracy of calculating the value of the absorption coefficient according to the formula is characterized by an absolute error

$$\sigma(t) = |\Delta \alpha(t)|,$$

which in the case of a single measurement is proportional to the relative error of measurement signals $\Delta I = |I(t)/I_1(i)|$, with $i = 1, 2$.

$$\sigma = \frac{2(\Delta I_1 + \Delta I_2)}{L}.$$
σ(t) was calculated as the standard deviation from the average value \( \langle \alpha(t) \rangle \).

An absorption dynamics for different probe CO laser lines in the mixture NO:Ar = 1:5 at specific input energy (SIE) \( Q_{in}=50 \text{ J/(l-atm)} \) is presented in Fig. 3. In all gas mixtures at initial gas temperature \( T=293 \text{ K} \) the absorption at the lowest NO transition \( \Pi_{1/2} 2-1 \text{ R(8.5)} \) appears almost immediately with the start of the EBSD \((t=0)\). We observed well-defined maximum of absorption at \( t=100 \mu\text{s} \) for the NO transition \( \Pi_{1/2} 2-1 \text{ R(8.5)} \) with time duration \( \sim 180 \mu\text{s} \) on the level 0.5 and then slowly falling tail up to 3 ms. The maximum absorption coefficient at the NO transition \( \Pi_{1/2} 2-1 \text{ R(8.5)} \) 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. 3 absorption at higher vibrational transitions of NO from 3-2 to 13-12 band peaked almost simultaneously at \( t=160-200 \mu\text{s} \). Then absorption at these transitions decreased slowly during a few milliseconds.

We calculated rate constants for vibrational-vibrational exchange between NO molecules and between \( \text{N}_2 \) and NO for our experimental conditions. The calculated temporal behavior of the absorption coefficients on NO transitions \( \Pi_{1/2} \text{ 12-11 Q(7.5)} \) and \( \Pi_{3/2} \text{ 8-7 P(5.5)} \) is also presented in Fig. 3 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:\text{N}_2=1:20 cooled down to \( T=122 \pm 2 \text{ K} \) (see Fig. 4). Dynamics of absorption slowed down with decreasing gas temperature. Absorption on NO transition \( \Pi_{1/2} 2-1 \text{ R(8.5)} \) 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 slow to heat due to VV' exchange between nitrogen and NO molecules and VT-relaxation of the NO molecules.

**Fig 3.** Temporal behavior of absorption coefficients in gas mixture NO:Ar=1:5, pressure 0.24 atm, \( T=293 \text{ K} \). Inset shows NO transitions and CO laser lines.

**Fig 4.** Temporal behavior of absorption coefficients in gas mixture NO:N\(_2=1:20\), at \( T=122 \pm 2 \text{ K} \). Inset shows NO transitions and CO laser lines. \( Q_{in}=180 \text{ J/(l-Amagat)} \).

**Acknowledgements**

This research was supported by the Russian Foundation for Basic Research (Project 13-02-01135) and LPI Educational-Scientific Complex.
References


Wysong, I.J., 1994a, Vibrational energy transfer of NO (X 2Π, v = 2 and 1), Journal of Chemical Physics 101, 2800-2810.