Nonlinear Zeeman Splitting of Nitric Oxide Rotational-Vibrational Spectral Lines in Strong Magnetic Field

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A dependence of Zeeman splitting of ro-vibrational lines of NO molecule on intensity of a strong magnetic field with magnetic induction up to 6 T was studied both experimentally and theoretically. The laser magnetic resonance (LMR) spectra were measured in pulsed magnetic field with continuous wave frequency-tunable CO laser operated in a single line mode.

Molecule of nitric oxide in the electronic ground state $^2\Pi$ stands out among other diatomic molecules by their chemical activity and paramagnetic properties, which are caused by the presence of the own magnetic moment. The presence of the own magnetic moment allows us to control the absorption spectrum of the molecule in the magnetic field due to the Zeeman splitting of the energy levels. On the other side, by using spectroscopic analysis of the Zeeman splitting of the ro-vibrational lines of NO molecules we can determine the value of the magnetic field.

In this paper experimental and theoretical study of the dependence of the Zeeman splitting of the ro-vibrational lines in the 0-1 band of the absorption spectrum of nitric oxide molecule on the magnetic field was carried out.

EXPERIMENT

Experiments were carried out in the Gas Lasers Laboratory at the Lebedev Physical Institute. The LMR spectrum was measured with the single-line cw liquid nitrogen cooled CO laser that could be tuned over ~200 ro-vibrational lines [1]. The optical scheme and the method of absorption coefficient measuring of NO molecules in the gas cell situated in the magnetic field were described in details in [2].

To investigate the temporal behavior of NO molecules absorption in a pulsed magnetic field a few CO laser lines was chosen, which are normally weakly ($<< 1$ m^{-1}) absorbed in nitric oxide. Measurements were carried out on four $^{12}C^{16}O$ molecular transitions indicated in Fig. 1. a-d. Absorption of radiation was measured at room temperature 296 K and pressure of NO 0.02 atm in gas cell. Magnetic induction in the solenoid with the gas cell was varieds with the period of damped oscillations $T = 3.5$ ms, and reached 6 T (Fig. 1. d).

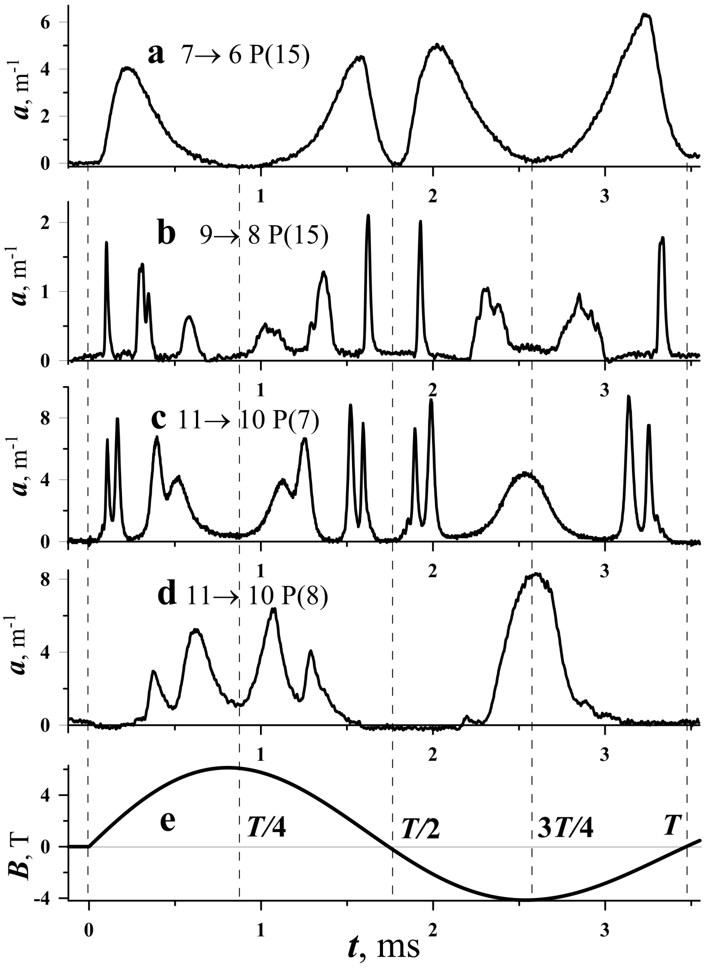

Fig. 1. The absorption coefficient *a(t)* of CO laser radiation on four lines (**a-d**) and the magnetic field *B(t)* (**e**).

Fig. 1. a-d shows the temporal behavior of the absorption coefficients in NO during one period of the magnetic field oscillation. Each quarter of the period of damped oscillations of the magnetic field is marked in Fig. 1 by vertical dotted line. The temporal behavior of the absorption coefficients in NO at the probe CO laser transitions 9→8 P(15) and 11→10 P(7) (Fig. 1, b-c) are the most informative and useful for comparison with theoretical calculation results, apparently, because of they have a narrow absorption peaks.

THEORY

The theory and numerical calculation of the Zeeman effect for diatomic paramagnetic molecules have been presented in numerous papers [3-7], where the linear dependence of Zeeman splitting is taken into account as a rule. This approximation corresponds to the consideration of the Zeeman operator as a first-order perturbation, and it is justified for weak magnetic fields.

To analyze experimental data in this paper we have used a very general approach, which was presented in papers [8-9]. The total effective Hamiltonian for a molecule in a magnetic field is written as [8] $\mathrm{H}_{\mathrm{eff}} = \mathrm{H}_0^{\mathrm{eff}} + \mathrm{H}_Z$, where $\mathrm{H}_0^{\mathrm{eff}}$ is the total effective Hamiltonian which describes the molecular motion in a zero magnetic field [8-11], and H_Z is the effective Zeeman Hamiltonian [9]. The energy levels of NO molecule in the presence of an arbitrary magnetic field have been obtained by means of numerical diagonalization of the total effective Hamiltonian matrix $\mathrm{H}_{\mathrm{eff}}$. As the first step, the diagonalization of the effective

Hamiltonian matrix H_0^{eff} written in the basis set of Hund's case (a) wave functions with well-defined parity was done. Thus, the energy levels and eigenvectors for NO molecule in the ground electronic state $X^2\Pi$ were determined. The splitting values of energy levels in magnetic field were calculated by diagonalizing the matrix of H_Z represented in the basis set of eigenfunctions of effective operator H_0^{eff}. It should be noted that the effective Hamiltonian matrix H_0^{eff} is diagonal in quantum numbers Λ, S, J and M, but non-diagonal in quantum numbers Σ and Ω, while the Zeeman interaction matrix is non-diagonal in quantum number *J* also. Thus only M remains as a good quantum number and the Zeeman operator matrix is constructed for each value of quantum number M. For the molecule in the presence of magnetic field the electric dipole selection rules allow the additional transitions with $\Delta M = 0, \pm 1$ - the transition between Zeeman components. The relative intensities of transitions between Zeeman components have been calculated using Honl-London factors [12-13] written as the product of a factor containing J and M and the usual Honl-London which is independent of magnetic quantum number:

$$S_{J,M,\Omega} = S_R(J\Omega, J'\Omega)\, S_M(J\, M, J'M').$$

COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL DATA

As an example, a comparison of the experimental and theoretical LMR spectrograms for the CO laser line 9→8 P(15) is presented in Fig. 2. The LMR spectrograms were normalized on the maximum of an absorption peak. This decreases the influence of factors such as the accuracy of the measurement of the absorption coefficients and the line widths of the probe radiation. Experimental and calculated LMR spectrograms are plotted up and down, respectively. As can be seen from the figure 2 that the calculated LMR spectrogram (figure 2b) reproduces peak locations of the experimental ones, which are due to transitions between the Zeeman components of two Q lines. The first «narrow peak» of absorption is formed by three transitions between Zeeman components of Q(1.5) line. The next peaks of absorption are formed by five transitions between Zeeman components of Q(2.5) line.

The comparison of calculated and experimental LMR spectrograms demonstrate that the numerical model adequately reproduces the location of absorption peaks for magnetic field up to ~4 T. But at the higher magnetic field (see Fig. 2. at 0.5-1.2 ms and 2.3-2.8 ms) locations of absorption peaks of calculated and experimental LMR spectrograms are different. To understand the reason of such difference, which can be connected with some anisotropy of absorption media in a strong magnetic field, further study is required.

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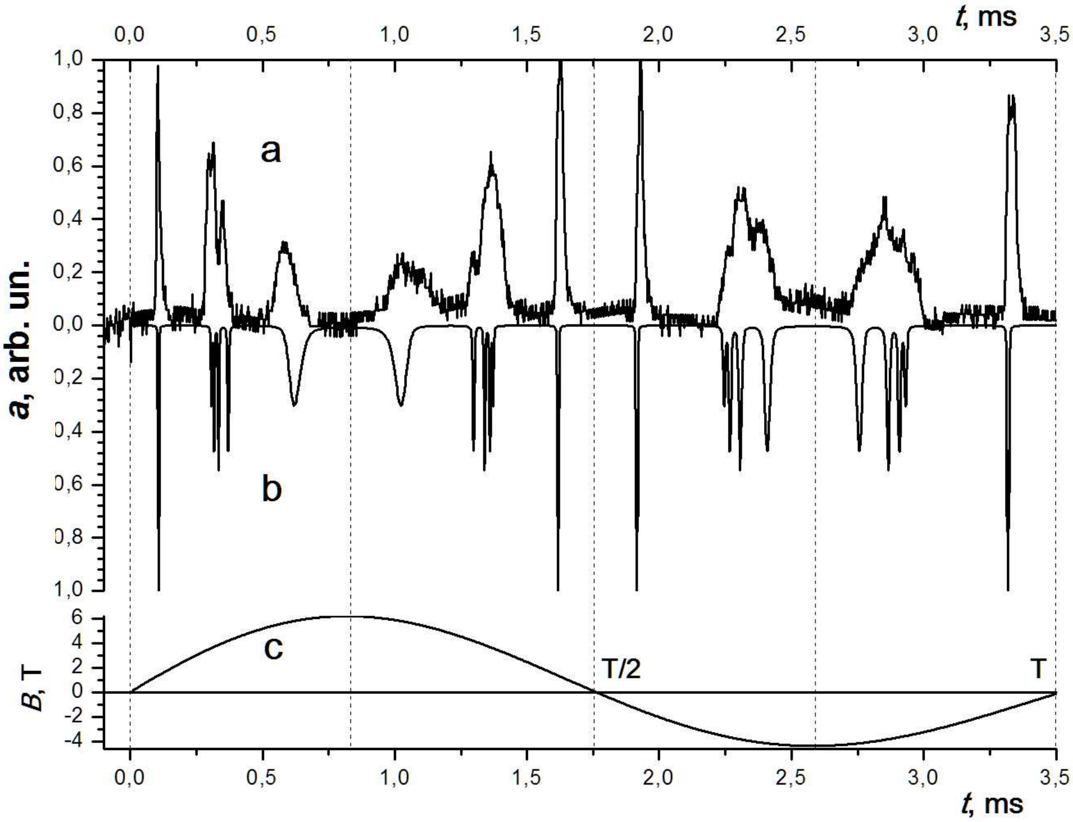

Fig. 2. Experimental (**a**) and calculated (**b**) LMR spectrograms for nitric oxide NO measured with the CO laser line 9→8 P(15) in a damped oscillating magnetic field $B(t)$ (**c**).

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