Chemical Physics Letters 662 (2016) 62–66

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

The influence of magnetic field on the echo-like free induction decay in NO_2

E.N. Chesnokov [a,c,*], V.V. Kubarev [b,c], P.V. Koshlyakov [a], A.I. Chichinin [a,c], Y.V. Getmanov [b], O.A. Shevchenko [b,c]

[a] Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia
[b] Budker Institute of Nuclear Physics, Novosibirsk 630090, Russia
[c] Novosibirsk State University, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 29 June 2016
In final form 10 September 2016
Available online 12 September 2016

ABSTRACT

The effect of magnetic field on the free induction in NO_2 was studied. The experiments were performed using the Free Electron Laser in the terahertz frequency domain. A magnetic field affects the free induction decay in two ways. First, it reduces the integral intensity of the free induction radiation. Second, application of the magnetic field results in the rotation of the polarization of the free induction radiation. Both effects were observed experimentally as well as simulated numerically using a theoretical model. A large angle of the polarization plane rotation was observed upon application of magnetic field of 120 G.

1. Introduction

Free induction decay (FID) is one of the coherent transient effects which are observed when a short pulse of electromagnetic radiation creates a coherent superposition of two or several energy levels [1]. This non-stationary state emits radiation that continues as long as the phase coherence exists. If the pulse excites many absorption lines, FID exhibits various oscillations due to the beats of different lines [2]. In the case of rotational spectra of NO_2, the FID is quite unusual. It consists of short aperiodic echo-like bursts, which were called "commensurate echo" [3,4].

The NO_2 molecule has a magnetic moment, and its energy spectrum is sensitive to applied magnetic field. Therefore one should expect that application of magnetic field might have effect on the FID in NO_2. This effect might appear as a change of the FID shape due to Zeeman splitting and as a rotation of the plane of polarization of the FID radiation. The effect of rotation was observed recently in the experiments with NO [5]. It is similar to the rotation of the polarization of the photon echo that is called "non-Faraday" rotation [6].

The aim of this study was to investigate the effect of application of magnetic field on the echo-like FID in NO_2 The experiments were performed in the spectral region of the rotation spectrum of NO_2 using the radiation from the Terahertz Novosibirsk Free Electron Laser (NovoFEL [7]). The effect of deterioration of the FID signal in the magnetic field was observed. The integrated intensity of the FID signal decreases in the magnetic field, although the integrated intensity of the absorption spectrum remains constant. In addition, rotation of the polarization plane of the FID radiation upon application of magnetic field was observed.

2. Experimental

A detailed description of NovoFEL can be found in [7]. This laser is continuously tunable in the range 45–110 cm^{-1} with a spectral width of 0.2 cm^{-1}. It emits a sequence of pulses at the repetition frequency of 5.6 MHz with the energy of 5–20 μJ and duration of 100–150 ps. The laser radiation is linearly polarized. A home-made ultra-fast Schottky diode detector with the resolution <30 ps was used [8]. The signals were accumulated by a 30 GHz LeCroy digital oscilloscope. An additional Schottky diode detector was used to trigger the oscilloscope.

Two different solenoids and two different gas cells mounted inside the solenoids were used. The first solenoid is 35 cm long and provides magnetic field in the range 0–900 G. The second solenoid is 100 cm long and provides magnetic field in the range 0–120 G. The inhomogeneity of the magnetic field in the first solenoid was ±30%, and ±1.7% in the second one.

In order to measure the polarization rotation, the polarizer was placed after the cell. The polarizer completely blocks the FID signal in the absence of the magnetic field. In a magnetic field, the polarization of the FID radiation depends on time, and this radiation partially reaches the detector.

* Corresponding author at: Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia.
E-mail address: chesnok@kinetics.nsc.ru (E.N. Chesnokov).

http://dx.doi.org/10.1016/j.cplett.2016.09.029
0009-2614/

3. Numerical modeling of the effect of magnetic field on the FID

The modeling included several steps.

The first step: calculations of the rotational spectra for the right-hand and left-hand circular polarization in the magnetic field. The calculation details have been described in the laser magnetic resonance (LMR) study of NO_2 molecules [8] and are only briefly summarized here. Note that in the LMR study [8] we calculated Zeeman splittings and absorption cross sections for transitions between M_J-sublevels for all experimentally observed rotational lines of the ν_2 vibrational band. Therefore in the present analysis the same computational approach with minor modifications was used. These modifications take into account two differences between the previous LMR and the current FID experiments. First, in the LMR experiments the probe radiation frequency was fixed, and the magnetic field was varied, while in the FID experiments the probe radiation frequency is varied while magnetic field is kept constant. Second, in the LMR experiments ro-vibrational transitions were used, bur in the FID experiments purely rotational transitions are used.

In order to predict Zeeman splittings and the absorption cross sections in NO_2 molecule, we used the data from the GEISA-2009 database [9] as a starting point of our analysis. The database contains all the necessary information (i.e., energy levels, transition frequencies, intensities of lines, and self-broadening coefficients), except for the behavior of Zeeman sublevels. In the analysis, the spin-rotation energies $E(N_{Ka,Kc},J)$ were restored from the hyperfine structures as follows [12]:

$$E(N_{Ka,Kc},J) = \sum_{F=J-1}^{J+1} \frac{2F+1}{3(2J+1)} E(N_{Ka,Kc},J,F), \quad (1)$$

here we denote the energies of the rotational levels as $E(N_{Ka,Kc},J,F)$, and the energies without hyperfine interactions as $E(N_{Ka,Kc},J)$; $N_{Ka,Kc}$ is the rotational quantum number. Conventional notation for vectors are used: $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$ ($I = 3/2$) and $\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S}$, ($N = N_{Ka;Kc}$, $S = 1/2$) where $\boldsymbol{F}$, $\boldsymbol{I}$, $\boldsymbol{J}$, $\boldsymbol{N}$ and $\boldsymbol{S}$ are the total, nuclear, electron-rotational, rotational and spin moments, respectively. The following spin-rotation and Zeeman Hamiltonian was used:

$$H_{sr} + H_Z = \gamma(\mathbf{J}^2 - \mathbf{N}^2 - \mathbf{S}^2) + \sum_{i=a,b,c} g_{ii}(H_i S_i + S_i H_i)/2. \quad (2)$$

Here γ is the spin-rotational constant, H_i are the magnetic field components, g_{aa}, g_{bb}, and g_{cc} are coefficients, which are known from the literature [10]. For each $N_{Ka,Kc}$, the γ constants were calculated from the GEISA spin-rotational splittings using the relation [11]:

$$E(N_{K_a,K_c}, J = N + 1/2) - E(N_{K_a,K_c}, J = N - 1/2) = \gamma(N + 1/2). \quad (3)$$

Our approach is essentially the same as that in the study by Hougen [11], although the second term in Eq. (2) is different. This approach allows us to easily calculate the energies of M_J sublevels for a given rotational number N, because it neglects the interaction with neighbor rotational states. When $|M_J| < (N + 1/2)$, the Hamiltonian matrix for given $N_{Ka,Kc}$ and M_J rotational quantum numbers is a block diagonalized into 2×2 submatrices, and when $|M_J| = (N + 1/2)$, the matrix is replaced by a simple analytical expression. To calculate the intensities of the rotational lines, we used the approach of Devi et al. [13]. The matrix elements for Herman–Wallis factors were taken from Flaud and Camy-Peyret [14].

Fig. 1 shows the overall view of the $Q_{R(5)}$ branch of the rotational spectrum of NO_2. The Zeeman splitting of the absorption lines are shown in two small panels. Selection rules for these Zeeman components are $\Delta M_J = +1$ (right-hand circular polarization) and $\Delta M_J = -1$ (left-hand circular polarization). The plots clearly demonstrate the complex nature of the Zeeman splitting in NO_2. Even in a relatively small magnetic field of 400 G, the splitting is nonlinear – frequency shifts for the σ^+ and σ^- components are different. Different parts of the spectrum have different values of the frequency shifts. In the part, the of the spectrum shown in the left panel, the frequency of the σ^+ component is higher than the original line, while in the part the spectrum shown in the right panel the frequency is lower.

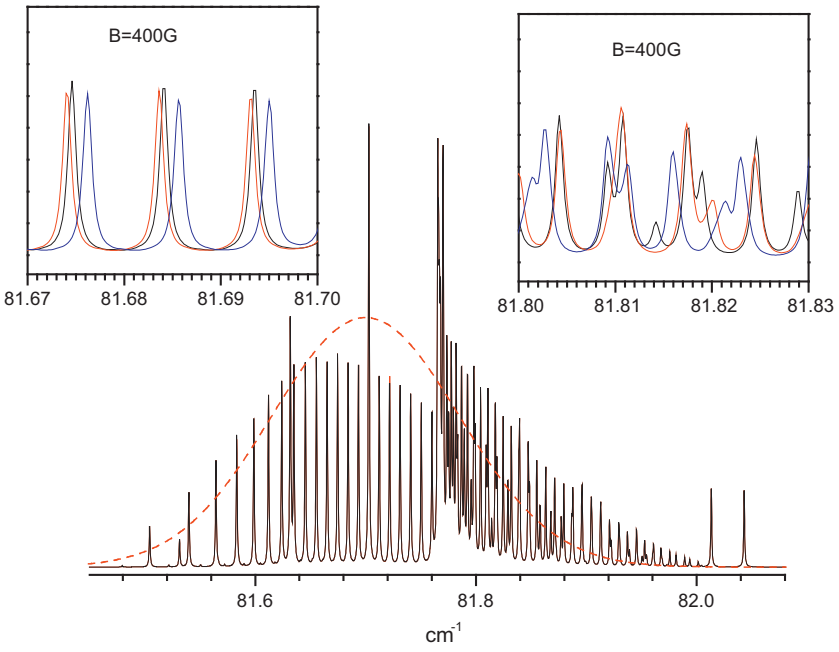

Fig. 1. A part of the rotational spectrum of NO_2 in 81.5–82.5 cm^{-1}. Red dash line shows the FEL spectrum in typical experiment. Two upper panels show Zeeman splitting in the longitudinal magnetic field 400 G. Red dash line – right-hand circular polarization, blue solid line – left circular polarization. Black solid line shows the spectrum in the zero magnetic field. The width of each line is 0.001 cm^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)