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Phase Control of Optical Free Induction of Paramagnetic Molecules in a Magnetic Field

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Abstract—We demonstrated the possibility of the phase switching of free optical induction (FID). This possibility arises in experiments with paramagnetic molecules (free radicals) in a magnetic field. Changing the direction of the magnetic field changes the direction of the free induction polarization plane rotation and inverts the phase of one of its components. This effect will be useful for heterodyne detection of free radicals in the terahertz frequency range.

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INTRODUCTION

The spectroscopy of free radicals in the terahertz range (approximately 1–10 THz or 30–300 μm) can be a useful tool for studying combustion processes. This region contains rotational transitions of many free radicals, such as OH, CN, CH, CH_2, etc. [1]. Several works [2–4] demonstrate the use of terahertz spectroscopy for kinetic studies.

The main feature of free radicals is the magnetic moment, which arises due to the presence of the unpaired electrons. An external magnetic field affects the energy levels of the radicals and hence the absorption and emission spectra of these radicals. Free radicals are usually present in low concentrations, so it is important to selectively detect free radicals against the background of stable molecules. The spectra of stable molecules are insensitive to a magnetic field, making possible to isolate the absorption of free radicals. The method of laser magnetic resonance uses the modulation of the absorption coefficient of radicals by a magnetic field [5]. It is more convenient to use the effect of a magnetic field on polarization than on absorption. This is realized in the method of Faraday rotation spectroscopy FRS [6, 7].

The modern trend in the development of spectroscopic methods is to move from measurements in the frequency domain to measurements in the time domain. In such experiments, a short radiation pulse creates a non-stationary state of the medium, which then emits a coherent response—a free induction radiation (Free Induction Decay—FID). For the methods of electron spin resonance (ESR) spectroscopy, such a transition has been completed quite a long time ago [8]. For terahertz spectroscopy, time domain methods and applications have been intensively developed in recent decades. The main advantage of the time domain approach is the ability to study short-term transient phenomena by obtaining spectroscopic information over a very short period [9–11].

For optical free induction of radicals in the terahertz range, various effects of the magnetic field were previously observed. The splitting of absorption lines due to the Zeeman effect leads to beats in the FID intensity [12]. The longitudinal magnetic field causes rotation of the FID polarization plane, at which the angle of rotation depends on the time after the excitation pulse [13, 14]. It should be noted that the angle of rotation of the polarization plane can be large, and this effect is very useful for isolating the signal of radicals against the background of stable molecules that do not have a magnetic moment.

In EPR spectroscopy, manipulation of the phases of excitation pulses is widely used [15]. Standard EPR spectrometers operate at a frequency of about 10 GHz, where the phase control of the microwave pulses is performed by standard electronic components. In the simplest case, alternating the phase of the excitation microwave pulses and measuring the difference between the corresponding FIDs makes it possible to eliminate all possible instabilities of the receiving system. All modern EPR spectrometers use this method. Also, in EPR spectroscopy, special techniques are used to excite a spin echo by a sequence of pulses with controlled phase shifts.

The terahertz region is not available for standard electronic devices, so phase control is much more difficult there. In this publication, we want to emphasize that for the FID of paramagnetic molecules in a mag-

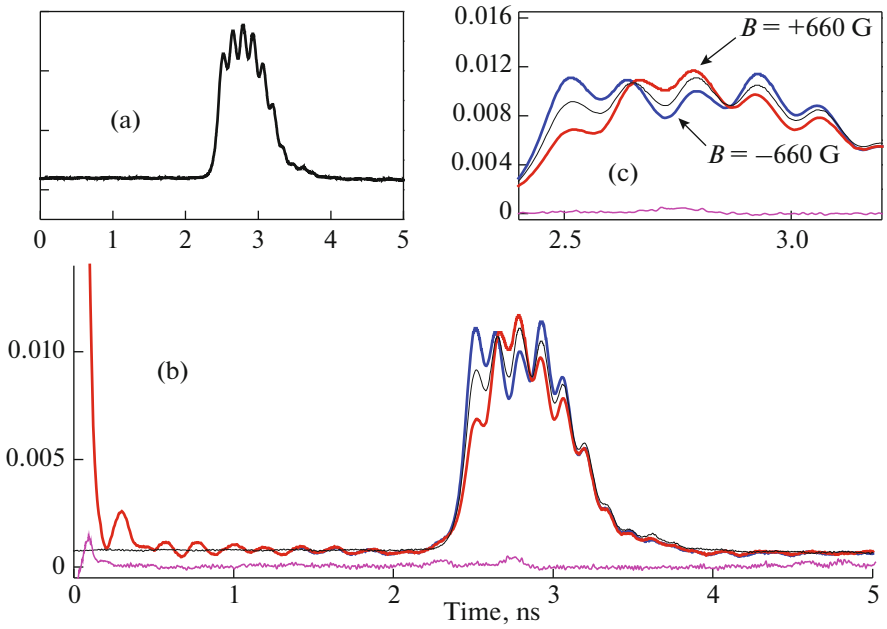

Fig. 1. Inversion of the FID phase. Experiments with the OH radical on the 83.8 cm^{-1} line. Magnetic field 660 G. (a) Reference signal formed from the FEL pulse. (b) Interference of a weak FID signal (pink) with the reference signal (black). When the direction of the magnetic field changes, the interference pattern is inverted (blue and red). (c) Stretched section of the reference signal.

netic field, there is a simple way to control the phase of an electromagnetic wave. We have demonstrated this method in experiments with the OH hydroxyl radical.

EXPERIMENTAL

The experiments were carried out at the Novosibirsk Free Electron Laser (NovoFEL) [17]. NovoFEL allows laser frequency tuning in the range of 86–340 μm (3.5–0.9 THz) with an average power in different parts of the tuning range from 20 to 300 W. The FEL radiation is a sequence of short pulses with duration of 70–140 ps and with a repetition rate of 5.6 MHz. The spectral linewidth of the NovoFEL laser is 0.2–0.5 cm^{-1} = 6–15 GHz.

The experimental setup is described in [13, 14] in detail. The method for obtaining the OH radical is also described in [18]. Hydroxyl radicals are formed because of the fast reaction of electronically excited oxygen atoms O(1D) with water molecules. Oxygen atoms O(1D) were generated by photolysis of ozone by radiation of the fourth harmonic of a Nd:YAG laser (266 nm). The UV laser pulses entered the cell with a gas mixture from one side, and NovoFEL terahertz radiation from the opposite side.

To register FID laser pulses, fast detectors of terahertz radiation based on Schottky diodes (rise time < 20 ps) were used [19, 20]. The signals were recorded in real time with a KeySight UXR0594 broadband oscilloscope (59 GHz).

The reactor was inside a 20 cm long solenoid. The magnetic field was varied in the range 0–825 G. All experiments were carried out at a low pressure of 7–11 Torr. The time delay between the generation of the $O(^1D)$ atom and the excitation of hydroxyl radicals by the THz pulse was 4 μs.

Without magnetic field, the FID radiation is linearly polarized in the same way as the therahertz excitation pulse (vertical polarization in our experiments). A horizontally mounted polarizer completely blocks the FID signal. When the longitudinal magnetic field was turned on a horizontally polarized component of the FID appeared.

The phase of the FID was determined relative to the reference optical signal generated from the NovoFEL excitation pulse. Approximately one third of the NovoFEL beam power was separated by a beam splitter. Then this radiation hit two Fabry-Perot interferometers, which increased the duration of the optical pulse to ~2.5 ns. The time-stretched reference pulse arrived at the detector with a delay of ~2.5 ns relative to the NovoFEL excitation pulse. Before entering the detector, the plane of polarization of the reference signal was rotated by 90° using a special system of mirrors. The reference signal and the FID signal were mixed in front of the detector using a second beam splitter. As a result, the horizontally polarized component of the FID signal interfered with the reference wave at the detector.

RESULTS AND DISCUSSION

The observed signals are shown in Fig. 1. The intensity of the horizontally polarized FID signal is shown in pink. In these experiments, the FID intensity was deliberately made low, and the FID signal was

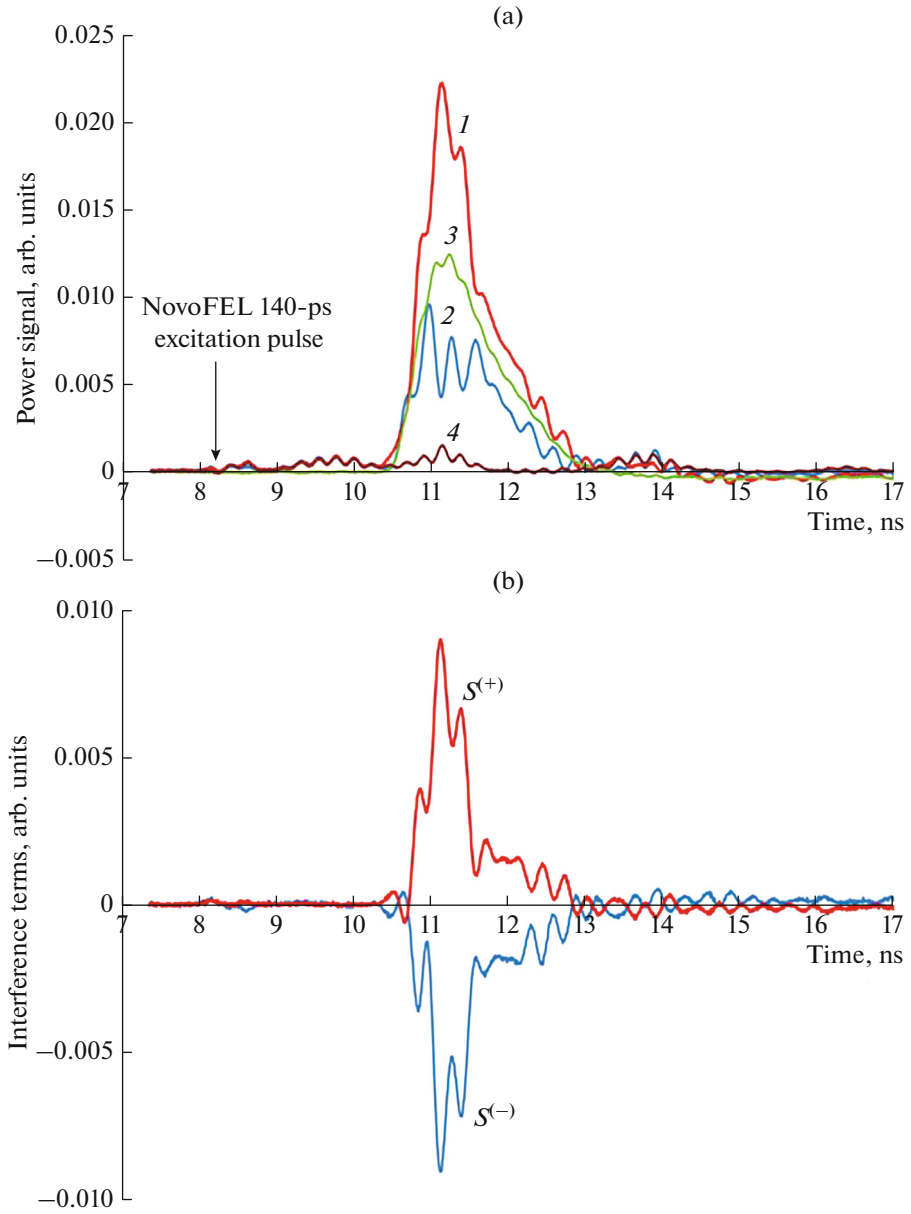

Fig. 2. Procedure for obtaining the electric field of the FID. (a) (*1*) $P_{\Sigma}^{(+)}$ (FID + Reference) $B = +550$ G, (*2*) $P_{\Sigma}^{(-)}$ (FID + Reference) B = –550 G, (*3*) P_{ref} (Reference), (*4*) P_{FID} (FID). (b) Interference terms $S^{(+)}$ and $S^{(-)}$. Designations in the text.

almost lost in the noise. When a reference signal was applied to the receiver along with a weak FID signal, the result of their interference was clearly observed. At some time, intervals, the intensity of the reference signal increased, at others it decreased. When the direction of the magnetic field was changed, the phase of the FID signal was reversed, and the interference pattern was inverted.

The origin of this effect is associated with a change in the direction of rotation of the FID polarization plane. The amplitudes of the vertical and horizontal components of the FID electric field are

$$E_x(t) = A(t)\cos(\varphi(t)), \quad E_y(t) = A(t)\sin(\varphi(t)), \quad (1)$$

where $\varphi(t)$ is the angle of rotation. Changing the direction of the magnetic field leads to $\varphi(t) \Rightarrow -\varphi(t)$ and $E_y(t) \Rightarrow -E_y(t)$.

The electric field of the FID can be determined from the experimental curves. The detector measures the signal power proportional to the square of the total field

$$P_{\Sigma}^{(+),(-)} = \left(E_{\text{ref}} + E_{\text{FID}}^{(+),(-)}\right)^2. \quad (2)$$

Signs (+) and (–) correspond to different directions of the magnetic field. Considering the ratios $P_{ref} \sim E_{ref}^2$ and $P_{FID} \sim E_{FID}^2$:

$$P_{\Sigma}^{(+),(-)} = P_{ref} + P_{FID} + 2E_{ref}E_{FID}^{(+),(-)} = P_{ref} + P_{FID} + S^{(+),(-)}, \quad (3)$$

and

$$S^{(+),(-)} = P_{\Sigma}^{(+),(-)} - P_{ref} - P_{FID}. \quad (4)$$

Two interference terms $S^{(+),\,(-)}$ are shown in Fig. 2b. They have approximately the same shape but different signs. Different signs $S^{(+),\,(-)}$ mean inverted phases $E_{FID}^{(+),(-)}$. A slight difference in the $S^{(+),\,(-)}$ signals is due to small temporal drifts of the four initial experimental signals, which were measured non-simultaneously.

This effect will be extremely useful for heterodyne measurement of FID signals. It is well known that methods of heterodyne detection of an electromagnetic wave are much more sensitive than detection by radiation intensity. This is shown in Fig. 1. A low intensity FID wave causes a large change in the intensity of the resulting signal because of interference with the reference wave. Using the phase change feature, it is very easy to determine the result of the interference as a difference between the signals for the opposite direction of the magnetic field. The direction of the magnetic field can be switched quickly enough. For example, in our experiments it was possible to change the direction of the field between UV pulses with a repetition rate of 8 Hz.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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