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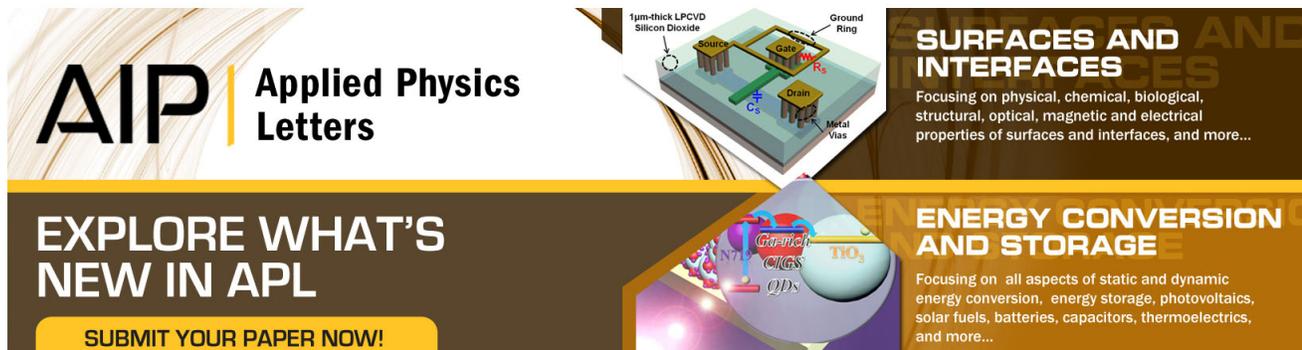
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## Direct observation of the terahertz optical free induction decay of molecular rotation absorption lines in the sub-nanosecond time scale

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Optical free induction decay (FID) in the region of 60–75 cm<sup>-1</sup> was detected using 120 ps pulses of free electron laser. Signals were detected in real time using ultra-fast Schottky diode detectors. The oscillations corresponding to the splitting of absorption lines in deuterated water vapor ( $\Delta f = 0.15$  cm<sup>-1</sup>) and hydrogen bromide ( $\Delta f = 0.02$  cm<sup>-1</sup>) were detected. At high optical density, we observed the oscillations arising from “top-hat” shape of absorption lines. Free induction decay signals could be detected in a single shot. This observation allowed obtaining a spectrum in one laser pulse, which facilitates studies of very fast processes. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4754826>]

Modern experimental methods in terahertz (THz) spectroscopy can be divided into two categories. The methods of the first category are based on generation of cw frequency tunable narrow bandwidth radiation. A substantial advantage of these methods is high spectral resolution. The resolution better than 30 kHz is reported.<sup>1</sup> Line positions in the rotation spectra of many simple molecules and radicals<sup>2</sup> of astrophysical importance have been determined using THz cw radiation sources with accuracy better than 0.1 MHz. In these experiments, the cw terahertz radiation was produced by generation of different frequency of two tunable CO<sub>2</sub>-lasers<sup>3</sup> or single frequency distributed feedback semiconductor lasers.<sup>4</sup> Also, a sideband generator based on optically pumped terahertz gas laser was used.<sup>5,6</sup> Recently, a high-resolution terahertz spectrometer based on a quantum cascade laser was described.<sup>7</sup> The drawback of most of the THz cw radiation sources is low output power of the THz radiation. Highly sensitive detectors and long integration times are required to record the spectra. This limits the application of THz cw radiation sources to spectroscopy under steady-state conditions only.

The methods of the second category consist of time-domain spectroscopy techniques applied to the THz spectral region.<sup>8</sup> In these methods, short pulses of broadband terahertz radiation are used and changes in the temporal structure of the individual THz pulse propagated through a test media are detected. These changes can be described in terms of free induction decay (FID) of the test media. Optical FID is a coherent radiation of a dipole moment of the media induced by a short light pulse. It was observed soon after the invention of CO<sub>2</sub> lasers in the infrared region.<sup>9,10</sup> Later, it was observed in different spectral regions.<sup>11–13</sup> Short pulses of free electron lasers have also been successfully applied to induce the FID<sup>14–16</sup> signals, and to perform photon echo experiments.<sup>17</sup>

The FID signal generated in absorbing media by a short optical pulse contains the complete information on absorption spectra within the frequency range of the input pulse.

These spectra can be reconstructed from the time dependence of the amplitude of the FID signal. The time dependence of the FID signal amplitude is obtained by scanning an optical delay for a gating optical pulse<sup>18</sup> or by using two lasers with small difference of the repetition rates.<sup>19</sup> Therefore, applications of the existing methods of time-domain spectroscopy are limited to steady-state spectroscopy or to time-resolved spectroscopy of repetitive processes, which can be synchronized with laser pulses. These methods are not suitable to study fast non-repetitive processes, in which spectra change on a time scale shorter than the time of the scan should be detected.

Many processes are inherently non-repetitive (e.g., irreversible chemical reactions such as explosion and various unstable phenomena). Therefore, the development of methods for real-time detection of the FID signals induced by a single laser pulse is necessary. In this paper, we report on the first direct real-time detection of the FID signal in the THz region using short optical pulses of a THz free electron laser. The signals were observed near absorption lines of the rotation spectra of bi- and mono-deuterated water D<sub>2</sub>O, HDO, and hydrogen bromide HBr molecules. A main application of the observed FID signals in our case will be ultrafast one-pulse time-domain spectroscopy. Investigation of a spectral dynamics is also possible by using the continuous train of Novosibirsk free electron laser (NovoFEL) pulses (maximal repetition frequency of the pulses is 22.5 MHz).

Tunable pulses of the terahertz radiation were generated by NovoFEL.<sup>20</sup> The laser emits a continuous sequence of pulses at repetition frequency of 5.6 MHz with the energy of 5–20  $\mu$ J and duration of 100–150 ps. The experimental set-up includes a self-made ultra-fast Schottky diode detectors,<sup>21</sup> 30 GHz LeCroy oscilloscope for direct measurements (a rise time of 15 ps), and gas cells. The resolution time of the detector was checked using the specific unstable regime of FEL when it emits several short independent sub-pulses within one 150 ps pulse.<sup>22</sup> The duration of individual sub-pulses was 25–30 ps; the detector was able to resolve these signals. For FID observation, we used the stable regime of the FEL in which it emits smooth Gaussian-like full coherent pulses.

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Before the entrance of the gas cell, the laser beam of Gaussian profile (FWHM = 20 mm) was split by a flat 30  $\mu\text{m}$  polypropylene film. One part of the beam was directed to the first detector, which was used to trigger the oscilloscope and to monitor the pulse intensity. Another part of the beam passed through the gas cell to the second detector. A grating monochromator with a pyroelectric detector with a spectral resolution of 0.1  $\text{cm}^{-1}$  was used to record the spectra after the gas cell. The gas cells were made of Pyrex glass and had a finger, which was cooled by liquid nitrogen. In a standard experiment, the signal was collected when the cell was filled; then the gas was frozen and thus the signal of the empty cell was observed. The triggering pulse for both experiments was the same; therefore, the delay of the signal in the gas could be measured accurately. Usually, we accumulated 200 or 400 pulses but the signal was large enough to get it in one shot. An example of the single shot signal is shown in Fig. 3.

Figure 1 demonstrates the laser pulses after passing through the empty cell and the cell with  $\text{D}_2\text{O} + \text{HDO}$  mixture vapor. This mixture was chosen to demonstrate the beats in FID signal originating from the excitation of two oscillators with slightly different frequencies. The rotation spectrum of HDO has a strong absorption line at 70.756  $\text{cm}^{-1}$  (transition  $7_{1,6} \leftarrow 7_{0,7}$ ), and  $\text{D}_2\text{O}$  has absorption lines at 70.883  $\text{cm}^{-1}$  ( $10_{2,8} \leftarrow 10_{1,9}$ ) and 70.900  $\text{cm}^{-1}$  ( $9_{3,7} \leftarrow 9_{2,8}$ ). By tuning the center of laser line to 70.82  $\text{cm}^{-1}$ , these absorption lines overlapped by laser as shown in the Figure 1. The concentrations of the  $\text{D}_2\text{O}$  and HDO in this mixture (39% and 47%, respectively) were chosen to make the total integrated intensity of two  $\text{D}_2\text{O}$  lines approximately equal to the intensity of HDO line.<sup>2</sup> Therefore, the beats in the FID signal are expected to correspond to the frequency difference between  $\text{D}_2\text{O}$  and HDO lines about 0.14  $\text{cm}^{-1} = 4.2$  GHz. Two absorption lines of  $\text{D}_2\text{O}$  appear as one line since the collision broadening<sup>23</sup> at 10 Torr ( $\approx 500$  MHz) is comparable with their frequency separation.

The experimentally observed FID signal contains several oscillations after the laser pulse. The period of these oscillations is around 220 ps, which roughly corresponds to the expected value. The FID signal has significant energy

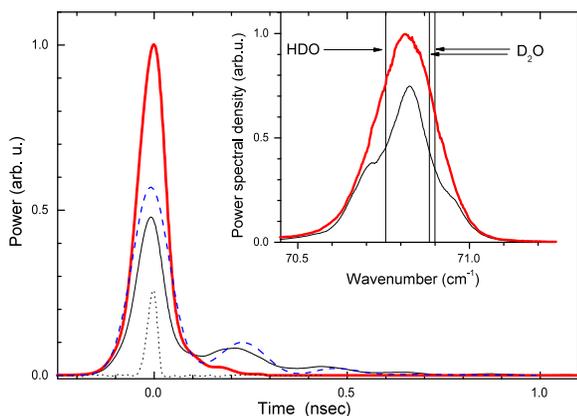


FIG. 1. The FID signal in  $\text{D}_2\text{O} + \text{HDO}$  mixture (200 pulses averaged): the bold red line is the laser pulse after empty cell, the thin black line is the pulse after the cell containing gas (10 Torr). The spectra of laser radiation recorded after the empty cell (thick red) and after the cell with gas (thin black) are shown in the inset. Dashed-blue lines show the calculated FID signal, and the dotted-black line is the instrument response function.

comparable with the energy of incident laser pulse. During the laser pulse, about 50% of the energy is absorbed by water vapor, and after the laser pulse about 20% of the energy is emitted as the FID signal. The total absorption of the energy is about 30%, which is in good agreement with 33% absorption obtained from the experimentally recorded spectra of the mixture.

The estimated Rabi frequency in our experiments is  $(\mathbf{d} \cdot \mathbf{E})/\hbar \approx (1 \dots 3) \cdot 10^9 \text{ s}^{-1}$ . The transition probability during the laser pulse is small, so we expect the observed signals having a linear origin. This was checked experimentally by attenuating the laser pulse with absorption filters. The observed signals do not depend on the laser energy.

The linearity of the signals significantly simplifies their theoretical description, since the well-known linear Lorentz model of dispersion in gas can be used. Doppler broadening in the presented experiments is two orders of magnitude smaller than the collision broadening. The complex index of refraction of the gas near Lorentz absorption lines can be calculated as

$$n(\omega) = n_r(\omega) - i n_i(\omega) = 1 + \sum_m A_m \frac{(\omega_m - \omega)\gamma_m - i\gamma_m^2}{(\omega_m - \omega)^2 + \gamma_m^2}, \quad (1)$$

where  $n_r(\omega)$  and  $n_i(\omega)$  are the real and imaginary parts of the refraction index,  $\omega_m$  is the frequency of the absorption line,  $\gamma_m$  is the half-width of the absorption line,  $A_m$  is a dimensionless coefficient proportional to the line intensity. The amplitude of the electromagnetic wave after passing through a sample of length  $L$  is

$$\begin{aligned} \tilde{E}(\omega) = E(\omega) \cdot \exp[n_i(\omega) \cdot \omega L/c] \\ \cdot \exp[i \cdot (n_r(\omega) - 1) \cdot \omega L/c]. \end{aligned} \quad (2)$$

Inverse Fourier transform of  $\tilde{E}(\omega)$  gives the complex amplitude of the electromagnetic wave after the sample  $\tilde{E}(t)$ , and  $|\tilde{E}(t)|^2$  is the shape of the light pulse after the sample.

Three absorption lines at 70.756, 70.883, and 70.900  $\text{cm}^{-1}$  were used in the calculation. The relative intensities of these lines (0.53:0.18:0.29) were taken from spectral line catalog.<sup>2</sup> We assumed that the widths of all absorption lines are equal; the width was adjusted to get the best fit to the experimental data. The most sensitive parameter to the line width is the rate of total decay of the signal: larger line width corresponds to faster signal decay. By fitting, we obtained  $2\gamma = 390$  MHz at 10 Torr. The literature data for collision line broadening in  $\text{H}_2\text{O}$  vary within the range of 34–43 MHz/Torr for different lines.<sup>23</sup> Therefore, our result is in reasonable agreement with these data.

The calculated signal is also presented in Fig. 1. The calculations describe the total decay of the observed signal and the period of oscillations correctly. The laser pulse in this calculation was approximated by Gaussian time profile, while the real laser pulse is not exactly Gaussian. This effect can explain the difference between the experimental and calculated signals.

Figure 1 shows the free induction signal when the laser spectrum overlaps two or more absorption lines and the total

absorption is relatively small ( $<30\%$ ). Alternatively, we made an experiment with the laser spectrum overlapping only one narrow absorption line. In this experiment, a free induction signal was observed, monotonically decreasing after the laser pulse, without significant oscillations. This experiment confirms the simple explanation of the nature of oscillation as interference between oscillators associated with absorption lines.

When the total absorption is high, the shape of the free induction signal becomes more complicated even for one absorption line. We observed such signals for different strong lines of  $D_2O$ . In these experiments, the medium was “optically thick,” and absorbing gas completely blocked the radiation in the spectral range inside the laser line. Under these conditions, the transmitted pulse is almost completely formed by the free induction signal.

The effects of “optically thick” media became more significant in the experiments with HBr, which has more narrow absorption lines due to smaller collisional self-broadening.<sup>24</sup> The line width of HBr rotation at the same pressure is 3–5 times smaller than water vapor lines. The smaller linewidth of HBr absorption lines leads to the longer expected FID signal. We used the absorption line near  $66.7\text{ cm}^{-1}$ , which corresponds to the  $(J=4) \leftarrow (J=3)$  transition in HBr molecules.<sup>17</sup> This line has an isotopic splitting of  $0.02\text{ cm}^{-1}$  due to  $^{79}\text{Br}$  and  $^{81}\text{Br}$  isotopes.<sup>25</sup>

Figure 2 shows the FID signal observed in HBr at a pressure of 21 Torr. At this pressure, two absorption lines were not resolved, as it is shown in the inset. Despite the fact that there is only one absorption line inside the laser spectra, the experimental signal has many oscillations. Calculations showed that such oscillations always occur in the case of optically thick media: the shape of absorption line becomes inverted top-hat with an abrupt slope (see inset). The period of oscillations approximately corresponds to the beating between the peaks in the spectrum after the cell.

The only parameter adjusted in the calculations was the collision line width. The calculated signal corresponds to HBr line width of 112 MHz. The calculations describe the experimental signal well, including almost all oscillations

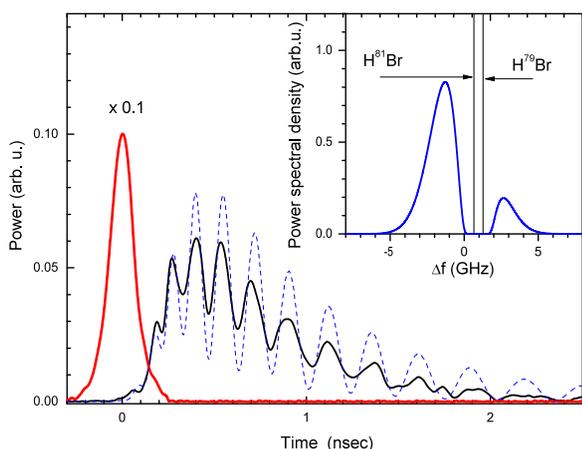


FIG. 2. FID signal observed in HBr at  $66.7\text{ cm}^{-1}$  (200 pulses averaged): initial (bold red line) and FID experimental (thin black line) signals; calculated signal (dashed-blue line). The cell was 20 cm long, pressure was 21 Torr. Inset shows the spectrum after the cell, which was used in the calculation of the FID signal.

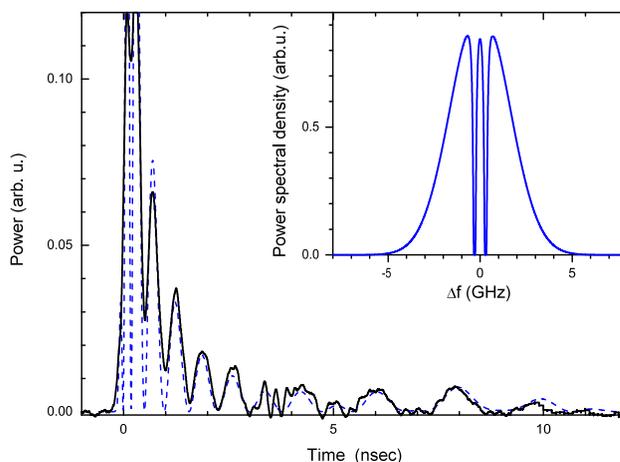


FIG. 3. The tail of FID signal in HBr at low pressure (one shot): experimental signal (black), calculated signal (dashed-blue). Inset shows calculated spectrum. Cell length was 60 cm, pressure of HBr vapor was 0.6 Torr.

(Fig. 2). The main difference is that the oscillations in the experimental signal are smoother than those in the calculated one. The nature of this difference is unclear. A possible explanation could be that a laser pulse does not ideal Gaussian shape. Besides, in this experiment, the center of laser spectrum was shifted by  $0.03\text{ cm}^{-1}$  from the absorption line. Without this shift, calculations predicted 100% oscillation, which was not observed under any conditions.

At low pressure, two absorption lines of HBr isotopomers could be resolved. Under these conditions, in the FID signal long-lived oscillations with  $\sim 2\text{ ns}$  period corresponding to  $0.02\text{ cm}^{-1}$  ( $0.6\text{ GHz}$ ) line splitting were observed. Figure 3 demonstrates the tail of this signal. In this region, the calculated curve describes the signal with good accuracy. This calculation did not require adjusting of parameters, the line width for low pressure ( $3.2\text{ MHz}$ ) was taken from the previous fitting at 21 Torr.

In this work, we demonstrated that FID in gases initiated by the terahertz pulse of the free electron laser could directly be detected using the ultra-fast Schottky diode detector. This observation can have different applications. The most interesting one is the possibility to get the spectrum in one laser pulse, which allows studying of very fast processes. The spectral resolution of this method is limited by the minimal repetition rate of the laser pulses, which is  $5.6\text{ MHz}$  in our case. Complete information about the FID signal vs. time, including intensity  $I(t)$  and phase  $\varphi(t)$ , is needed to obtain a correct spectrum. In the described experiments, only the signal intensity was measured. Obtaining information on  $\varphi(t)$  by combining various interferometric techniques with ultra-fast detection is the subject of our activity now.

Another interesting application is the detection of FID in a pump-prob experiment. Free electron laser already was used with pump-prob technique to study the time dynamics of quantum systems in semiconductors.<sup>26</sup> The FID signal in such experiments can provide information about temporal spectra of the system after pump pulse.

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