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Detection of paramagnetic particles in a flame using terahertz radiation

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The possibility of detection of paramagnetic particles (NO, OH radical) in a flame by using terahertz radiation was shown.

The application of terahertz radiation (1–10 THz or 30–300 μm) to flame diagnostics is promising for the following reason: this radiation range contains the lines of rotational transitions of many free radicals, which play a significant role in combustion processes. These include OH, CN, CH, CH_2 and other radicals.[1] Another attractive feature is a low scattering of long-wave radiation by micron-size particles. Unlike the existing optical techniques of radical detection that use visible-light and UV lasers, terahertz radiation can be suitable for studying strongly scattering mediums, which are opaque for visible light. Examples of such objects are heavily sooting flames.

Cheville and Grischkowsky[2] were the first to measure absorption spectra of a flame at atmospheric pressure in the terahertz range using time domain terahertz spectroscopy. In a premixed propane–air flame, many absorption lines within 0.2–2.65 THz frequency range were observed. Most of these lines were related to water vapour, but some of them were assigned to CH radical absorption lines.

In the further works,[3,4] the absorption lines of hot water vapour in flame were considered. Agreement between relative intensity of observed lines and those calculated on the basis of known intensities at room temperature was examined.[3] Absorption lines of water molecules in ground vibrational state and vibrationally excited state $v_2 = 1$ were observed. Significant reduction of intensities of lines in rotational spectrum of water with growth of temperature was noticed. Collisional broadening of rotational lines of hot water vapours was studied elsewhere.[4] Peculiarities of absorption of hot water vapour were studied also by Stringer and coworkers.[5]

Thus, the available works on spectroscopy of flames in terahertz frequency range are dedicated to the absorption spectra of stable combustion products, usually of water.

The present work aims to study the use of terahertz radiation for the detection of paramagnetic particles in a flame. On frequencies coincident to absorption lines of paramagnetic particles, the Faraday effect (rotation of polarization plane in magnetic field) should be observed.[6] This effect is due to a difference in refraction indexes of medium for clockwise- and counterclockwise polarized waves. As a result of abnormal dispersion of medium refraction index for radiation with a frequency close to absorption line of the paramagnetic particle, magnitude of polarization rotation considerably increases with getting closer to resonance. High sensitivity of the Faraday method is provided by possibility of measurements of small angles of polarization rotation.

A Novosibirsk Terahertz FEL free-electron laser[7] was used as a source of radiation. The parameters of radiation were the following: tuning range, 1.3–2.5 THz; relative linewidth, 0.005; repetition rate, 5.6 MHz; pulse length, 0.12 ns; average power, 10–50 W.

The most convenient object for registration of Faraday rotation in flame is the OH radical due to its high concentration in flame and intense absorption lines in the terahertz region. Two absorption lines of the OH radical are within the tuning range of FEL: 1835 and 2512 GHz. These lines correspond to transitions from lower rotational states $^2\Pi_{1/2}$ ($^1/_2 \rightarrow 1^1/_2$) and $^2\Pi_{3/2}$ ($1^1/_2 \rightarrow 2^1/_2$). Both of the lines are in the atmospheric transparency microwindows. The distances to the closest intense absorption lines of water vapour are 33 and 20 GHz, respectively.[1]

The experimental setup consists of an electromagnet with a burner between its poles, an input polarizer, an output polarizer (analyzer), a pyroelectric radiation detector and required optical elements. FEL radiation was directed along the magnetic field through the holes in magnet poles. Combination of convex and concave mirrors has been used for radiation focusing. In the burner area, laser beam was approximately 1 mm in diameter. Radiation was modulated at a frequency of about 300 Hz by rotating disc with holes. Alternating signal from the radiation receiver was detected with a phase-lock amplifier and entered into a computer.

A premixed flame of $H_2/O_2/N_2$ (16.6%/7.4%/76.0%) was stabilized on the flat burner at 1 atm. The volumetric flow rate of the unburned mixture was 84 $cm^3\ s^{-1}$ under normal conditions. The burner consisted of a tube with an attached copper disk 16 mm in diameter and 3 mm thick with 0.5 mm diameter orifices spaced 0.7 mm apart. The burner temperature was kept constant at 35 °C with a thermostat.

FEL radiation is linearly polarized with the degree of polarization of 99.5%. To enhance the degree of polarization, an additional polarizer was installed in front of electromagnet entrance. The broadband polarizer (Tydex, St. Petersburg) used as an analyzer ensured the suppression of undesirable polarization down to 10^{-3} in the range of wavelengths of 120–180 μm. Axis direction of output polarizer was chosen either perpendicular to the direction of polarization or it was turned by a small angle φ_0.

To measure a spectrum of laser radiation, a Bruker IFS-66V Fourier spectrometer was used. FEL radiation frequency was tuned to absorption line before the experiment. The measurements consisted in comparison of intensity of radiation, which passed through the output polarizer, with and without magnetic field. If polarization plane rotates by angle $\Delta\varphi_0$ with turning on the magnetic field, the radiation intensity at the receiver should be the following:

$$I = I_0\sin^2(\varphi_0 + \Delta\varphi) \approx I_0(\varphi_0^2 + 2\varphi_0\Delta\varphi + \Delta\varphi^2). \quad (1)$$

The intensity change due to magnetic field switch is:

$$\Delta I = 2I_0\varphi_0\Delta\varphi + I_0(\Delta\varphi)^2. \quad (2)$$

Expression (2) has two terms: linear and quadratic on $\Delta\varphi$.

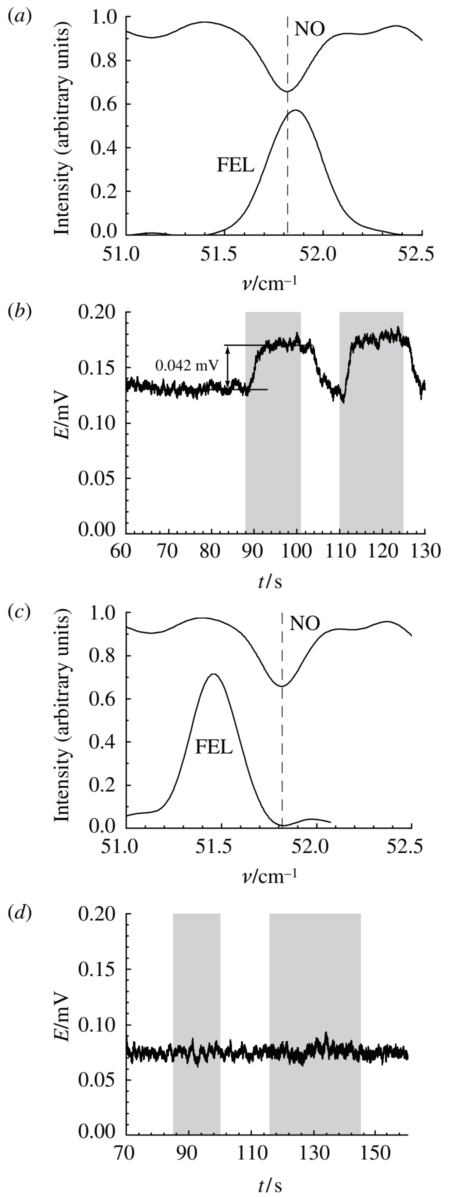

Figure 1 Observation of Faraday effect in rotational spectrum of NO. (*a*), (*c*) FEL radiation spectra. Vertical line marks the position of NO absorption line $^2\Pi_{3/2}$ (15.5) → $^2\Pi_{3/2}$ (16.5). (*b*), (*d*) Alteration of radiation due to turning on the magnetic field of 8 kGs (gray areas).

For relatively big rotation ($\Delta\varphi > 10^{-2}$) effect due to the quadratic term could be observed. For small rotation the contribution of the quadratic term is negligible, and the linear term should be used. To work in this regime, we have to set nonzero φ_0 for the output polarizer. The value of the φ_0 was chosen to make better signal to noise ratio. Typically, $\varphi_0 \sim (3–12)\times10^{-2}$ rad.

Before working with the flame, operation of the setup was tested with NO absorption lines. Instead of burner, optical cell with polyethylene windows and filled with NO was placed. NO molecules have permanent magnetic moment, and the Faraday effect should be observed on the absorption lines of NO (similarly to those of free radicals).

In Figure 1, the results of experiments with NO are shown. The relatively big rotation of the polarization of terahertz FEL radiation induced by magnetic field was observed and measured for $\varphi_0 = 0$. The effect appeared when laser radiation was tuned to NO absorption line [Figure 1(*a*),(*b*)]. When the magnetic field was turned on (the moment of switch is marked with vertical line), polarization plane rotated, resulting in the change of radiation intensity, which restored when the magnetic field was turned off. A certain delay is associated with a high inductance of electromagnet winding, which results in low rate of field growth. If the laser is tuned sideways from the NO absorption line, as shown in Figure 1(*c*),(*d*), then the magnetic field had no effect on terahertz radiation polarization.

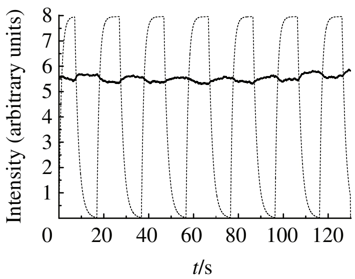

Figure 2 Alteration of laser radiation due to switching off the magnetic field on the line of OH radical 2512 GHz. Dashed line shows the dependence of the magnetic field on time.

The results of experiments on polarization rotation on radical OH $^2\Pi_{3/2}$ ($1^1/_2 \rightarrow 2^1/_2$) line are depicted in Figure 2. The burner described above was placed between the magnet poles. FEL was tuned to the frequency of 2512 GHz and the line width of FEL was 18 GHz. Signal was detected when output polarizer was turned by an angle $\varphi_0 = 0.05$ rad. The angle of plane polarization rotation calculated using formulas (1) and (2) was 1×10^{-3} rad.

Thus, the magnitude of Faraday polarization rotation for terahertz radiation tuned to the lines of OH radical absorption in atmospheric flame is available for measurement (~10^{-3} rad). On the basis of this effect, a sensitive method of detection of free radicals in a flame in the terahertz region can be developed. This result opens a prospect for developing a technique for detection and measurement of concentration of such compounds, which are important for combustion chemistry, as OH, CN, CH, CH_2 and NO in sooty and dusty flames.

Note that standard terahertz absorption spectroscopy based on commercial instruments cannot be used for studying such flames. The radiation of these nontransparent flames is stronger than the one of the hot surface, which is used as a radiation source in the standard spectrometers. The spectral power density of FEL radiation is 10^7 higher[7] than spectral density of radiation source in the standard spectrometers. Therefore, the contribution of flame radiation in our experiments was negligible.

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