Using Terahertz Radiation to Detect OH Radicals and NO Molecules in Flames

E. N. Chesnokov,[1] **O. S. Aseev,**[2]
O. P. Korobeinichev,[1] **S. A. Yakimov,**[1]
D. A. Knyaz'kov,[1] **and A. G. Shmakov**[1]

UDC 542.5

The possibility of detecting OH radicals and stable paramagnetic NO species in flames using the effect of rotation of the polarization plane of terahertz radiation (1–10 THz) in a magnetic field (Faraday effect) was experimentally demonstrated. Experimental data on detection of NO in a cell and OH radicals in an atmospheric–pressure $H_2/O_2/N_2$ flame using this method are given. The proposed method can be used to study highly scattering media which are opaque in the visible region, for example, dusty or sooty flames.

Key words: free electron laser, terahertz radiation, flame, paramagnetic species, Faraday effect, hydrogen combustion, OH detection.

INTRODUCTION

Using terahertz radiation (1–10 THz or 30–300 μm) for flame diagnostics seems to be promising for the following reasons. In this region there are bands of rotational transitions of many free radicals which play an important role in combustion processes: OH, CN, CH, CH_2 [1], etc. In addition, long-wave radiation is weakly scattered by micron-size particles. In contrast to existing optical methods of radical detection using visible and ultraviolet laser radiation, the method using terahertz radiation can be suitable for studying strongly scattering media which are opaque in the visible region. An example of such objects are flames with a high soot content.

Absorption spectra of atmospheric–pressure flames in the terahertz region were first studied by Cheville and Grischkowsky [2] using time domain terahertz spectroscopy based on using femtosecond lasers to generate short pulses of terahertz radiation. In a premixed propane–air flame, many absorption bands in the region

of 0.2–2.65 THz were recorded. Most of these bands belong to water vapor, but some of them were assigned by the authors to absorption bands of CH radicals.

Subsequent studies of the same authors [3, 4] have focused on studying the absorption bands of water vapor in flames. In [3], they verified the assignment of the relative intensities of the observed bands by a calculation based on known intensities at room temperature. Absorption bands of water molecules in the ground vibrational state and in the first vibrationally excited state were observed. A strong reduction in rotational band intensities of water with increasing temperature was noted. Collisional broadening of rotational bands of high-temperature water vapor was studied in [4]. Absorption spectra of hot water vapor were also studied in [5].

Thus, available papers on flame spectroscopy in the terahertz region deal with absorption spectra of stable combustion products, most often, water molecules. In [2], the assignment of some of the observed bands to CH radicals seems to be erroneous. This follows from the fact that, in the spectra given in [2] there are no absorption bands of OH radicals. Had the observed bands belonged to CH radicals, the spectrum should have contained strong bands of OH. The rotational absorption band intensities of OH radicals [1] exceed the rotational

[1]Institute of Chemical Kinetics and Combustion,
Siberian Division, Russian Academy of Sciences,
Novosibirsk 630090;
chesnok@kinetics.nsc.ru.
[2]Novosibirsk State University, Novosibirsk 630090.

band intensities of CH radical. In addition, it is well known that in a propane–air flame, the CH radical concentration is much lower than the OH concentration.

In the present work, we studied the possibility of using terahertz radiation to detect flame radicals.

ABSORPTION COEFFICIENTS ON THE BANDS OF OH RADICALS

The OH radical is the most convenient research subject because of its high concentration in flames and the presence of intense absorption bands in the terahertz regions. The Novosibirsk terahertz free electron laser (FEL) [6] was used as the radiation source. In this facility, the laser radiation frequency can be varied in a range of 118–230 μm (2.5–1.3 THz) at power of up to 50 W. The spectral width of the radiation is about 0.5 cm$^{-1} = 15$ GHz.

The FEL frequency range contains two absorption bands of OH radicals at frequencies of 1835 and 2512 GHz. These bands correspond to transitions from the lower rotational levels of the electronic states $^2\Pi_{1/2}\left(\frac{1}{2} \to 1\frac{1}{2}\right)$ and $^2\Pi_{3/2}\left(1\frac{1}{2} \to 2\frac{1}{2}\right)$. Both bands are in the atmospheric transmission microwindows. The distances to the nearest intense absorption bands of water vapor are 33 and 20 GHz, respectively [1].

Attempts were made to measure the absorption on both bands of OH radicals directly. We studied a 16.6/7.4/76.0 $H_2/O_2/N_2$ flame stabilized on a flat burner at a pressure of 1 atm. The volumetric flow rate of the gas mixture was 84 cm^3/sec (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 holes spaced uniformly 0.7 mm apart. The burner temperature was maintained at 35°C by a thermostat. The laser frequency was set at 1835 GHz or 2512 GHz.

In the experiments, we compared the powers of the radiation transmitted through the burner with the flame and without it. In some experiments, the burner operation modes and laser radiation wavelength were varied. In all cases, attenuation of the laser radiation by the flame was not observed (with an accuracy of 3%). Integrated intensities of various absorption bands of OH radicals at a temperature of 300 K are given in [1]. Using these data, the measured shape of the FEL radiation spectrum, the OH radical concentration known for this flame, and the collisional width of the absorption band, one can calculate the expected radiation absorption coefficient as follows.

The OH absorption cross section at a frequency of 1835 THz is estimated by the formula

$$\sigma(\nu) = \frac{2A}{\pi} \frac{w}{4(\nu - \nu_0)^2 + w^2}, \tag{1}$$

where A is the integrated band intensity, nm$^2 \cdot$ MHz, and w is the collisional bandwidth. For various temperatures, the integrated intensity can be found by calculating the change in the population of the rotational levels between which the transition occurs. The temperature dependence of the population densities of the lower and upper rotational levels is given by

$$n_0(T) = \frac{g_0}{Z_{\text{vib}}(T)Z_{\text{rot}}(T)} \exp\left(-\frac{E_0}{kT}\right), \tag{2}$$

$$n_1(T) = \frac{g_1}{Z_{\text{vib}}(T)Z_{\text{rot}}(T)} \exp\left(-\frac{E_0 + h\nu}{kT}\right),$$

where g_0 and g_1 are the degenerations of the rotational states, $Z_{\text{vib}}(T)$ and $Z_{\text{rot}}(T)$ are the vibrational and rotational statistical sums, respectively, h is Planck constant, and k is Boltzmann constant. The integrated intensity of a band is proportional to

$$n_0(T) - \frac{g_0}{g_1}n_1(T). \tag{3}$$

Thus, the temperature dependence of the integrated intensity is given by

$$A(T) = A(300)\frac{Z_{\text{vib}}(300)Z_{\text{rot}}(300)}{Z_{\text{vib}}(T)Z_{\text{rot}}(T)}$$

$$\times \exp\left(-\frac{E_0}{k}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$$

$$\times \left(\frac{1 - \exp(-h\nu/kT)}{1 - \exp(-h\nu/k \cdot 300)}\right). \tag{4}$$

A calculation for the bands at 1835 GHz shows that, as the temperature increases from 300 to 1450 K, the integrated intensity of the absorption band decreases by a factor of 24.3 times. This decrease is due to the redistribution of the population densities of the rotational levels: the difference in population density between the lower and upper rotational levels decreases sharply with increasing temperature.

The calculated absorption cross section of OH radicals averaged over the laser line spectral profile is $\sigma = 0.72 \cdot 10^{-19}$ cm^2. Under the conditions used in the experiments, the volumetric concentration of OH radicals in the flame is about 0.1%, i.e., $n = 4.8 \cdot 10^{15}$ cm^{-3} at a temperature of 1450 K. Under these conditions, the expected absorption at a length $l = 1$ cm is
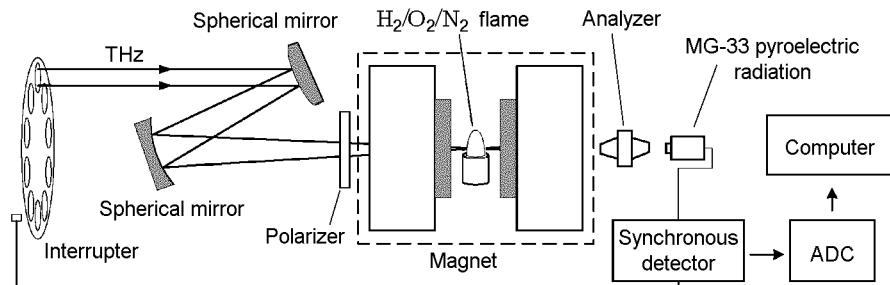
$$\Delta I/I = \sigma nl = 3.4 \cdot 10^{-4}.$$

Fig. 1. Diagram of the experimental setup.

Thus, the expected absorption coefficient of the FEL terahertz radiation at the bands of OH radicals is approximately two orders of magnitude smaller than that accessible to direct measurements (about 3%). This explains why absorption at the OH bands was not recorded in the experiment performed.

The small value of the absorption coefficient is partially due to the large spectral width of the FEL radiation. The width of the rotational bands of OH radicals in the flame is unknown. If the shock broadening of the OH bands is considered to be similar to that for water molecules [4], the width of the OH bands in the atmospheric–pressure flame should be ≈ 0.1 cm^{-1}, which is ≈ 5 times smaller than the FEL spectral width. Thus, if one uses a radiation source with a small spectral width, the absorption coefficient of the flame on the rotational lines of OH radicals cannot exceed $\approx 5 \cdot (3 \cdot 10^{-4}) \approx 1.5 \cdot 10^{-3}$ cm^{-1}.

The above estimates show that the value of the absorption coefficient on the rotational lines of OH radicals in the flame is insufficient for direct measurements of its concentration from a change in the radiation intensity. In addition, these estimates provide further evidence that in [2] the assignment of the observed lines to CH radicals is erroneous.

A METHOD USING ROTATION OF THE POLARIZATION PLANE IN A MAGNETIC FIELD

A more sensitive method of recording paramagnetic species is the one of recording the rotation of the polarization plane of radiation in a magnetic field (Faraday effect) [7]. Rotation of the polarization plane in a magnetic field is due to the difference in the refractive index of a medium for waves with right and left circular polarizations. Due to the abnormal dispersion of the refractive index of the medium for radiation frequency

close to the absorption band frequency of a paramagnetic species, the value of polarization plane rotation increases significantly upon reaching a resonance. The high sensitivity of the Faraday method is provided by the possibility of measuring small rotation angles of the radiation polarization plane.

Figure 1 shows a diagram of the experimental setup. The setup consists of an electromagnet, a burner placed between the electromagnet poles, an input polarizer, an analyzer (output polarizer), a radiation receiver, and necessary optical elements. The FEL radiation was directed along the magnetic field through holes drilled at the magnet poles. The radiation was focused by a combination of convex and concave spherical mirrors. The beam diameter in the region of the burner was 1 mm. The radiation intensity after the analyzer was recorded by a MG-33 pyroelectric radiation receiver. Because pyroreceivers are sensitive to a variable signal, the radiation was modulated by a rotating disk with holes at a frequency of ≈ 300 Hz. The variable signal from the radiation receiver was recorded by an USD-2 synchronous detector and sent to a computer.

The FEL radiation is linearly polarized but the degree of polarization was not high enough — 99.5%. To improve it, an additional polarizer was placed before the entrance of the electromagnet. The direction of the polarizer axis was aligned with the polarization direction of the laser radiation. The analyzer was a broadband Tydex polarizer (St. Petersburg). It provided suppression of undesired polarization up to 10^{-3} at wavelengths of 120–180 μm. The direction of the analyzer axis was rotated by an angle $\pi/2 + \varphi_0$ relative to the laser polarization direction, where φ_0 is a small deviation.

Before the measurements, the FEL radiation frequency was adjusted to the absorption band. The laser radiation spectrum was measured by a Bruker IFS-66V Fourier spectrometer. The measurements actually consisted of comparing the intensities of the radiation transmitted through the analyzer with the magnetic
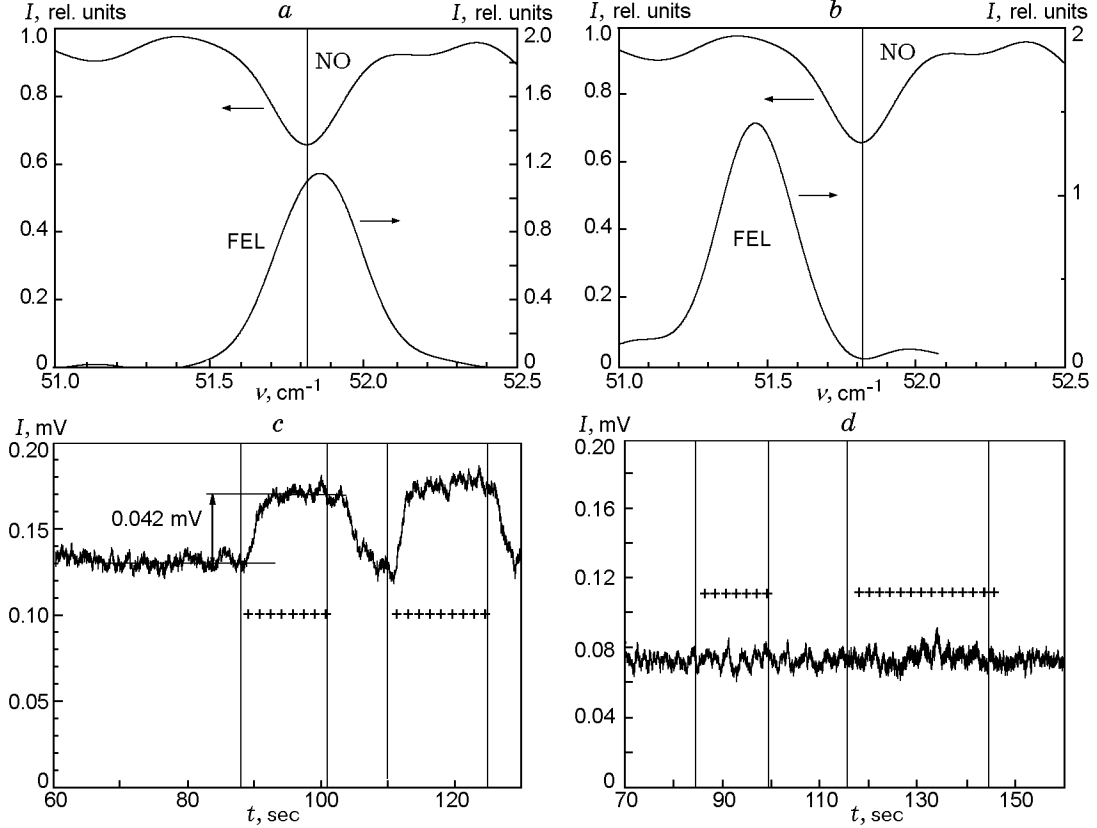
Fig. 2. Faraday effect in the rotational spectrum of NO: (a and b) FEL radiation spectrum, the vertical line shows the position of the $^2\Pi_{3/2}(16.5) \leftarrow\ ^2\Pi_{3/2}(15.5)$ NO absorption band; (c and d) change in the radiation intensity with a magnetic field of 8 kGs switched on (regions denoted by $+$) and switched off; the $^2\Pi_{3/2}(16.5) \leftarrow\ ^2\Pi_{3/2}(15.5)$ band.

field switched on and off. If polarization plane is rotated by an angle $\Delta\varphi$ as the magnetic field is switched on, the radiation intensity at the receiver is

$$I = I_0 \sin^2(\varphi_0 + \Delta\varphi) \approx I_0(\varphi_0^2 + 2\varphi_0\Delta\varphi + \Delta\varphi^2). \quad (5)$$

Accordingly, the change in the intensity due to switching on and off of the field is equal to

$$\Delta I \approx I_0(2\varphi_0\Delta\varphi + \Delta\varphi^2). \quad (6)$$

From formula (6), it is evident that the addition of the deviation φ_0 increases the value of ΔI and, hence, the sensitivity of the setup.

RESULTS

Before the experiment with the flame, we checked the operation of the setup at the NO absorption bands. In these experiments, the burner was replaced by an optical cell with polyethylene windows filled with NO. NO molecules have a constant magnetic moment, and the Faraday effect should be observed at the NO absorption bands as well as at the absorption bands of free radicals.

Figure 2 gives the results of experiments with NO. The magnetic field induced rotation of the polarization plane of the FEL terahertz radiation with the laser radiation adjusted to the absorption band of NO molecules. Figure 2a shows the FEL radiation spectrum and the absorption band in the rotational spectrum of NO, and Fig. 2c shows the intensity of the radiation transmitted through the cell with NO and the analyzer. When the magnetic field is switched on (the switching on and off times are denoted by vertical lines), the polarization plane is rotated, leading to a change in the intensity of the radiation transmitted through the analyzer. When the filed is switched off, the intensity is restored. Some delay is due to the fact that the magnetic field increases slowly due to a high inductance of the electromagnet winding. If the laser band is adjusted away from the NO absorption band (see Fig. 2b and d), the magnetic field does not influence the polarization of terahertz radiation.
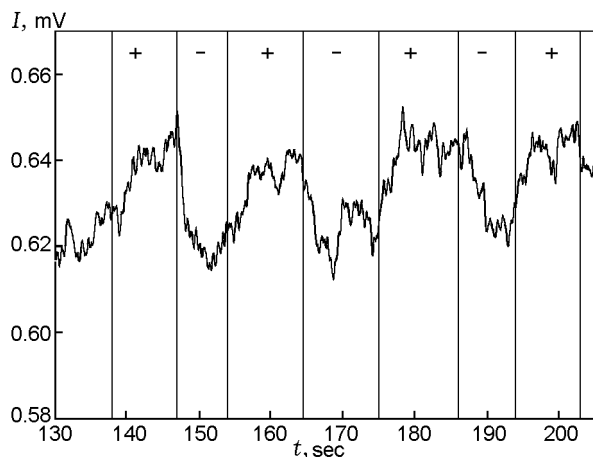
Fig. 3. Change in the intensity of the radiation transmitted through the polarizer with the magnetic field switched off $(-)$ and switched on $(+)$; laser frequency 1843 GHz; band $^2\Pi_{1/2}\left(\frac{1}{2} \to 1\frac{1}{2}\right)$ of OH radicals.

Figure 3 gives the experimental results on rotation of the polarization plane at the band $^2\Pi_{1/2}\left(\frac{1}{2} \to 1\frac{1}{2}\right)$ of OH radicals. The burner described above was placed between the magnet poles. The effect was detected when the FEL was adjusted to a frequency of 1843 GHz. The half-height width of the FEL band was 18 GHz. The rotation angle of the polarization plane of the laser radiation calculated by formula (2) was $(1.4 \pm 0.3) \cdot 10^{-3}$ rad.

Thus, for terahertz radiation adjusted to OH absorption band in an atmospheric–pressure flame, the value of the rotation of the polarization plane in the magnetic field is large enough ($\approx 10^{-3}$ rad) to be measured. This effect can be used to develop a method for detecting free radicals in flames in the terahertz region, which will require a detailed spectroscopic study of the effect.

CONCLUSIONS

The experimental results obtained in the work show the possibility of detecting OH radicals in flames and stable paramagnetic NO species by means of terahertz radiation. Because of low sensitivity, the method of direct measurement of radiation absorption cannot detect OH in flames. The sensitivity of the method can be increased by using the effect of rotation of the polarization plane of terahertz radiation in a magnetic field (Faraday effect). The proposed approach made it possible to detect OH radicals in $H_2/O_2/N_2$ flames at atmospheric pressure. The results open the way for the development of a method for detecting and measuring concentrations of chemically important species, such as OH, CN, CH, CH_2, NO, etc., in sooty and dusty flames.

REFERENCES

1. H. M. Pickett, R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, and H. S. P. Muller, "Submillimeter, millimeter, and microwave spectral line catalog," *J. Quant. Spectrosc. Rad. Transfer*, **60**, 883–890 (1998); http://spec.jpl.nasa.gov/home.html.
2. R. A. Cheville and D. Grischkowsky, "Far-infrared terahertz time-domain spectroscopy of flames," *Opt. Lett.*, **20**, 1646–1648 (1995).
3. R. A. Cheville and D. Grischkowsky, "Observation of pure rotational absorption spectra in the ν_2 band of hot H_2O in flames," *Opt. Lett.*, **23**, 531–533 (1998).
4. R. A. Cheville and D. Grischkowsky, "Far-infrared foreign and self-broadened rotational linewidths of high-temperature water vapor," *J. Opt. Soc. Amer. B.*, **16**, 317–322 (1999).
5. M. R. Stringer, J. Bassi, R. E. Miles, Y. Zhang, and K. Ozanyan, "THz spectroscopy through a high-pressure combustion system," in: *33rd Int. Conf. Infrared, Millimeter and Terahertz Waves* (IRMMW-THz 2008) (2008), pp. 1–2.
6. N. G. Gavrilov, B. A. Knyazev, E. I. Kolobanov, V. V. Kotenkov, V. V. Kubarev, G. N. Kulipanov, A. N. Matveenko, L. E. Medvedev, S. V. Miginsky, L. A. Mironenko, A. D. Oreshkov, V. K. Ovchar, V. M. Popik, T. V. Salikova, M. A. Scheglov, S. S. Serednyakov, O. A. Shevchenko, A. N. Skrinsky, V. G. Tcheskidov, and N. A. Vinokurov, "Status of the Novosibirsk high-power terahertz FEL," *Nucl. Instrum. Meth. Phys. Res. A*, **575**, 54–57 (2007).
7. A. Hinz, W. Pfeiffer, W. Bohle, and W. Urban, "Midinfrared laser magnetic resonance using the faraday and voigt effects for sensitive detection," *Molec. Phys.*, **45**, No. 6, 1131–1139 (1982).