

Terahertz Free-Electron Laser Radiation to Determine Water Concentration in Flames

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Abstract: The possibility of measuring the concentration of H₂O molecules in flames based on the absorption of terahertz free-electron laser radiation was studied. These measurements were performed using the 177.32 cm⁻¹ absorption line in the rotational spectrum of H₂O. This line has a low intensity at room temperature, and at about 1000 K, its intensity is comparable to that of the strongest lines. The temperature dependence of the radiation absorption coefficient at a frequency of 77.32 cm⁻¹ was studied theoretically and experimentally. It is shown that the method can be used for measurements in a sooty C₂H₄/O₂/Ar flame, which strongly scatters visible and UV radiation.

Keywords: free electron laser, terahertz radiation, flame.

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INTRODUCTION

Interest in the use of terahertz radiation (1–10 THz or 30–300 μm) for flame measurements is due to the fact that this range contains the rotational transition lines of many free radicals that play an important role in combustion processes. The absorption spectra of atmospheric-pressure flames in the terahertz range have been studied [1–4] by time domain terahertz spectroscopy using femtosecond lasers to generate short pulses of terahertz radiation. It has been found that most of the absorption lines of the flames are due to the rotational transitions of water molecules in the ground and vibrationally excited states [2]. The absorption lines of free radicals whose concentration is much lower than the concentration of water have low intensity. Detection of free radicals in the terahertz range requires special techniques to improve sensitivity. In [5, 6], OH

radicals were detected using a technique based on the rotation of the plane of polarization in a magnetic field.

The free electron laser (FEL) currently operated in Novosibirsk is a powerful source of laser radiation tunable in the terahertz range [7]. A technique is being developed to produce two-dimensional images in the terahertz range [8]. Of great interest is the application of this technique to producing flame images with the use of laser radiation tuned to the absorption lines of combustion products. The long-wave FEL radiation is weakly scattered by micron-size particles, which makes this technique a promising tool for studies of strongly scattering media which are nontransparent in the visible range, such as sooty flames (with a large equivalence ratio) and coal dust flames.

This paper describes a technique of noncontact measurement of water vapor concentration from absorption in the terahertz range, and demonstrates the possibility of using this method to measure water vapor concentration in sooty flames.

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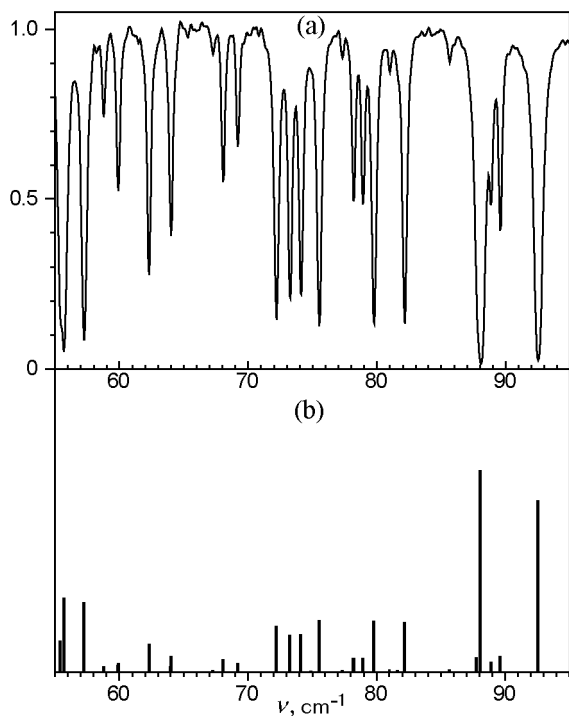


Fig. 1. Region the spectrum of atmospheric air containing water vapor (a) and the position and relative intensities of the absorption lines of water vapor from the database of [9] (b).

SELECTION OF THE ABSORPTION LINE FOR MEASUREMENTS

At room temperature, the water vapor contained in the atmosphere has intense absorption lines in the terahertz range. Figure 1a shows the absorption spectrum of atmospheric air in the tuning region of the free electron laser. The spectrum was recorded by a Bruker IFS-66 spectrometer with a resolution of 0.12 cm^{-1} for an optical path length of 18 cm, a temperature of 25°C , and a relative humidity of $\approx 40\%$. Figure 1b, plotted using the database of [9] shows the position and relative intensities of the lines in the rotational spectrum of water at 300 K. All the observed absorption lines of atmospheric air coincide with the known absorption lines of water vapor. The absorption coefficient of atmospheric air at the strong lines is large enough: more than 98% of the radiation is absorbed at a frequency of $\nu = 88 \text{ cm}^{-1}$ and a length of 18 cm.

In a typical experiment, the length of the supply optical paths is usually significantly greater than the optical path length in the flame. Therefore, it is required to decrease the absorption in the supply paths in the region adjacent to the flame by purging with a dry inert gas. The problem of radiation absorption in

the paths is exacerbated by the fact that the width of the laser emission spectrum is greater than the width of the absorption line. Therefore, the spectrum of the FEL radiation that reaches the flame may be very different from the original one. In fact, in a situation where the free-electron laser is tuned to a strong absorption line of water vapor, even when purging the paths, one cannot be sure that the radiation spectrum on the sample is not distorted. A situation easily arises where the spectral radiation components coincident with the absorption line have already been absorbed in the paths, and the radiation incident on the sample does not coincide with the absorption line.

Another factor that complicates the measurement of the absorption of terahertz radiation in the flame is a sharp decrease in the intensity of most of the absorption lines of water vapor with increasing temperature. This is due to a change in the distribution of water vapor molecules over the rotational levels, resulting in a decrease in the population difference between the rotational levels. For strong absorption lines of water vapor, the intensity decreases with increasing temperature as $\approx Z_{\text{rot}}^{-1}T^{-1} \approx T^{-5/2}$ [6], where Z_{rot} is the rotational partition function.

These problems can be overcome by a special choice of the absorption line for measurements. Due to high absorption in the atmosphere, one should not use the strongest lines. An important factor is the energy of the rotational state of the radiation-absorbing molecules. If the absorption line corresponds to the transition from a high rotational level of H_2O molecules, which is sparsely populated at room temperature, the absorption coefficient at room temperature will be small, and at higher temperatures it should increase.

For the measurements we chose the absorption line at a frequency of 77.32 cm^{-1} . This line corresponds to the $9_{3,6} \rightarrow 9_{4,5}$ rotational transition (the standard notation of the rotational states of water molecules J_{K_a, K_c} is used). According to information from [9], the energy of the lower state is $E(9_{3,6}) = 1283 \text{ cm}^{-1}$, which is about $6kT$ (k is Boltzmann's constant) at room temperature. For this reason, the absorption coefficient of this line at room temperature is small (see Fig. 1). With increasing temperature, the population of the lower state increases, which leads to an increase in the absorption coefficient.

Figure 2 shows how the redistribution of the population of rotational levels on heating changes the relative intensity of four absorption lines of water vapor in the range of $77\text{--}80 \text{ cm}^{-1}$. For the most intense line at a frequency of 79.77 cm^{-1} , the energy of the lowest rotational state is $E_4 = 142 \text{ cm}^{-1}$. The intensity of this line decreases rapidly on heating. This temperature depen-

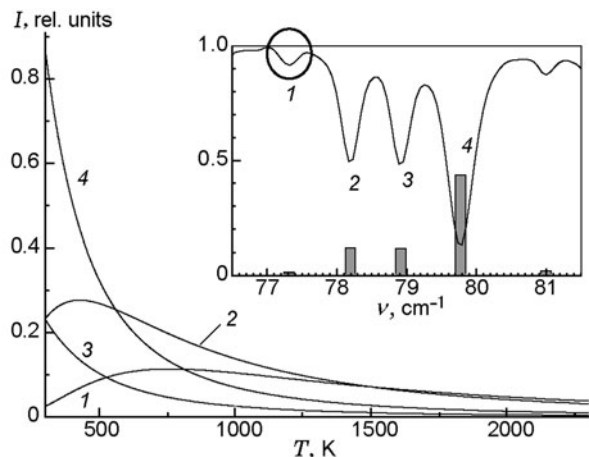


Fig. 2. Variation in the relative intensity of four absorption lines of water vapor in the range of $77\text{--}80\text{ cm}^{-1}$: the corresponding portion of the spectrum at room temperature is shown in the inset; the line chosen for the measurements is enclosed in a circle.

dence of the absorption coefficient is typical of strong lines with a low-lying lower state. The 78.92 cm^{-1} line, for which the energy of the lower state is $E_3 = 206\text{ cm}^{-1}$, shows a similar temperature dependence.

A different behavior is observed for the lines at frequencies of 77.32 and 78.20 cm^{-1} , for which the energy of the lower rotational state is 1283 and 704 cm^{-1} , respectively. The intensities of these lines increase with increasing temperature. The most suitable line for the measurements in the flame is the one at a frequency of 77.32 cm^{-1} , which has a small absorption coefficient at room temperature and a relatively weak temperature dependence at $\approx 1000\text{ K}$.

EXPERIMENTAL METHOD

The experiments were performed using a NovoFEL free-electron laser [7]. The laser wavelength can be tuned in the range of $118\text{--}230\text{ }\mu\text{m}$ ($2.5\text{--}1.3\text{ THz}$) with a power of up to 100 W . The FEL radiation spectrum is controlled by a Bruker IFS-66 infrared spectrometer.

For this work, an important component of the experimental setup was a system of beam distribution over the workstations. The FEL is located in a radiation-hazardous area in which the location of personnel and experimental equipment of users is not allowed. A sealed system containing rotating mirrors and transport metal tubes serves to couple out the radiation. The system is filled with continuously circulating dry nitrogen. At the workstation, radiation exits from the distribution system through a window with

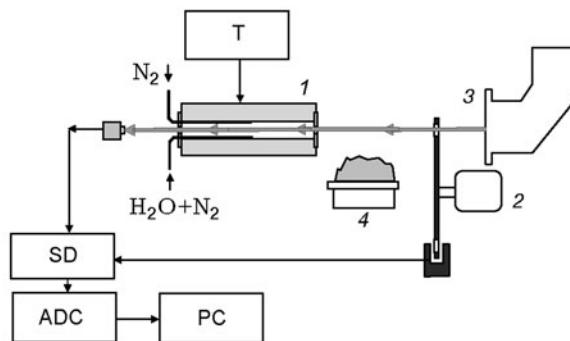


Fig. 3. Experimental setup: (1) tube furnace; (2) laser beam chopper; (3) exit of the laser beam distribution system; (4) burner; T is a temperature control unit, SD is a synchronous detector, and ADC is an analog-to-digital converter PC is a computer.

a polypropylene film 0.3 mm thick. The length of the optical path to the workstations is about 50 m . The water vapor content in the system is reduced to $10^{-3}\text{--}10^{-4}$ of the saturated vapor pressure. However, due to the large path length in the distribution system, the radiation that coincides with the strong absorption lines of water vapor is attenuated by several times. Therefore, using the FEL radiation tuned to these frequencies is impossible in practice.

A tube furnace 50 cm long and 5 cm in inner diameter (Fig. 3) was produced to measure the temperature dependence of the absorption coefficient of FEL. The furnace temperature was measured with a thermocouple and stabilized by an electronic regulator. Inside the furnace there were quartz tubes for supplying dry nitrogen for purging or nitrogen containing water vapor to the central region. The water vapor concentration in nitrogen was varied by changing the temperature of the device for saturation (bubbler). To slow the escape of water vapor from the furnace due to convection, the ends of the furnace were closed by diaphragms with 1 cm diameter holes. This kept the water vapor inside the furnace for more than 1 min .

The FEL radiation was interrupted at a frequency of $\approx 300\text{ Hz}$ by a rotating disk with holes. The disc is equipped with an optical sensor which produces the reference signal for the synchronous detector. After passing through the furnace, the laser beam was incident on an MG-33 pyroelectric receiver, whose signal was sent to the synchronous detector. The detected signal was fed to an ADC (16 bits ; sampling step of $4\text{ }\mu\text{s}$) and then to a PC.

For flame measurements, a burner was placed ahead of the furnace. The internal cavity of the furnace was previously purged with dry nitrogen. The flame was stabilized on a flat burner of rectangular cross sec-

tion (17.5×86.5 mm), and the burner temperature was maintained by a thermostat at 35°C . The composition of the premixed fuel–air mixture was $\text{C}_2\text{H}_4/\text{O}_2/\text{Ar} = 16/18/66\%$ (equivalence ratio $\phi = 2.67$). The burner was made of a sintered brass powder. The speed of the combustible mixture at the exit from the burner was 16 cm/s (at 20°C). The flame temperature was measured with a Pt–Pt/10%Rh thermocouple with a wire diameter of 0.05 mm coated with a SiO_2 layer. The thermocouple placed in this flame was quickly covered with soot, so that it was regularly annealed in the flame of a spirit lamp. The H_2O concentration in the sooty flame was measured in the postflame zone at a distance of 15 – 30 mm from the burner surface.

CALCULATION OF THE ABSORPTION COEFFICIENT OF THE FEL RADIATION

Information on the integral intensity of each of the lines in the rotational spectrum of water at 300 K is contained in the database of [9]. The integral intensity for an arbitrary temperature $A(T)$ can be calculated by the formula [6]

$$\frac{A(T)}{A_{300}} = \frac{\exp(-E_1/kT) - \exp(-E_2/kT)}{\exp(-E_1/300kT) - \exp(-E_2/300kT)} \left(\frac{300}{T}\right)^{3/2}, \quad (1)$$

where $A(T)$ is the integral intensity at temperature T , A_{300} is the integral intensity at 300 K, and E_1 and E_2 are the energies of the upper and lower rotational levels, respectively. Equation (1) takes into account the fact that with temperature variation, the value of $A(T)$ varies only due to changes in the populations of the rotational levels.

To calculate the absorption coefficient of the laser radiation, we introduce a function $f_l(\nu)$ that describes the shape of the laser radiation spectrum and a function $f_A(\nu)$ that describes the shape of the absorption lines. We assume that $f_l(\nu)$ and $f_A(\nu)$ are normalized, i.e.,

$$\int f_A(\nu) d\nu = \int f_l(\nu) d\nu = 1.$$

The absorption cross section of monochromatic radiation of frequency ν is given by the formula

$$\sigma(\nu) = A f_A(\nu),$$

where A is the integral intensity. The laser radiation absorption is described by the cross section averaged over the spectrum $f_l(\nu)$:

$$\langle \sigma \rangle = \int \sigma(\nu) f_l(\nu) d\nu = A \int f_A(\nu) f_l(\nu) d\nu.$$

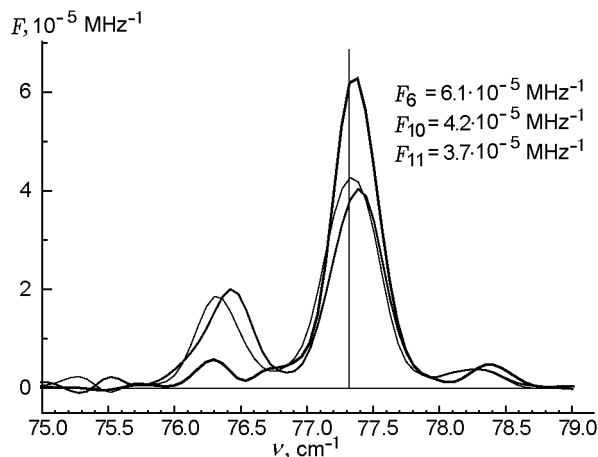


Fig. 4. Examples of normalized spectra of the FEL: the three spectra shown here correspond to three slightly different regimes of laser operation; the vertical line is the center of the absorption line.

From this formula, it follows that the absorption cross section of the laser radiation is equal to the product of the integral intensity of the line A by the form factor:

$$F = \int f_A(\nu) f_l(\nu) d\nu. \quad (2)$$

If the frequency of ν is measured in megahertz, the form factor F has the dimension MHz^{-1} . The calculation of the form factor is simplified if the absorption linewidth is considerably smaller than the width of the laser radiation spectrum. In this case, formula (2) is transformed to

$$F = f_l(\nu_0), \quad (3)$$

where ν_0 is the central frequency of the absorption line.

In experiments with flames, instead of absorption cross section it is more convenient to use the absorption coefficient α per unit pressure, determined from the condition

$$I/I_0 = \exp(-\alpha p \chi l), \quad (4)$$

where p is the pressure, χ is the mole fraction of the absorbing component, and l is the path length. The absorption coefficient α [$\text{cm}^{-1} \cdot \text{bar}^{-1}$] is expressed in terms of the absorption cross section as

$$\alpha = \frac{\langle \sigma \rangle}{kT} = \frac{AF}{kT} = \frac{AF \cdot 10^8}{1.38T}, \quad (5)$$

where A is in $\text{nm}^2 \cdot \text{MHz}$ and F is in MHz^{-1} .

MEASUREMENT RESULTS

Prior to the measurements, the FEL radiation frequency was tuned to 77.32 cm^{-1} . Figure 4 gives examples of the FEL radiation spectra recorded during

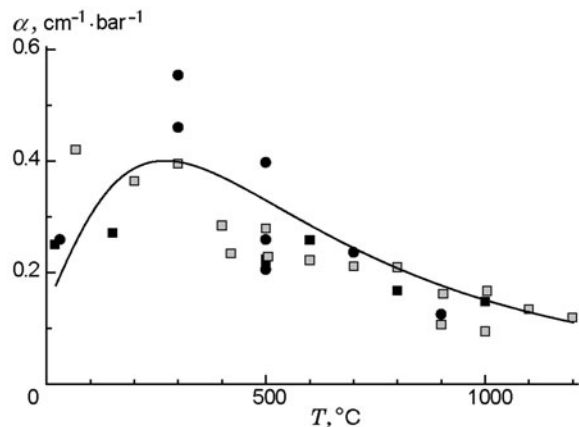


Fig. 5. Measured absorption coefficients of the FEL radiation by water vapor at different temperatures: FEL was tuned to the absorption line at 77.3 cm^{-1} ; the curve was calculated by formulas (1) and (5).

one day. The spectrum contained a base peak about 0.6 cm^{-1} (FWHM) wide and additional peaks. The intensity distribution between them depended on the FEL tuning. Figure 5 shows the results of measurements of the absorption coefficient of water vapor at the 77.32 cm^{-1} line at different temperatures. In the calculations, the form factor was chosen so as to obtain the best agreement with the experiment. The curve shown in the figure corresponds to $F = 3.1 \cdot 10^{-5} \text{ MHz}^{-1}$.

As can be seen from Fig. 5, despite the large scatter of the experimental points, the calculation correctly reproduces the temperature dependence of the absorption coefficient. The scatter of the measured values of the absorption coefficient is about $\pm 30\%$. This scatter limits the accuracy of the concentration measurements from the FEL radiation absorption. The cause of the scatter is the instability of the FEL radiation spectrum and, hence, the variation of the form factor F . Unfortunately, we were not able to control the FEL spectrum in each experiment and to calculate the value of the form factor for each measurement. Currently, work is underway to design a system of operational monitoring of the FEL spectrum. It is hoped that the advent of this system will improve the measurement accuracy.

The obtained FEL radiation absorption coefficient can be used to measure the water vapor concentration in flames. Since the absorption coefficient depends on temperature, independent temperature measurements are needed.

Figure 6 shows a photograph of a $\text{C}_2\text{H}_4/\text{O}_2/\text{Ar}$ flame. The flame has a characteristic bright yellow luminous zone associated with the formation of soot particles. According to visual observations, the soot formation zone is at a distance of about 10 mm from the

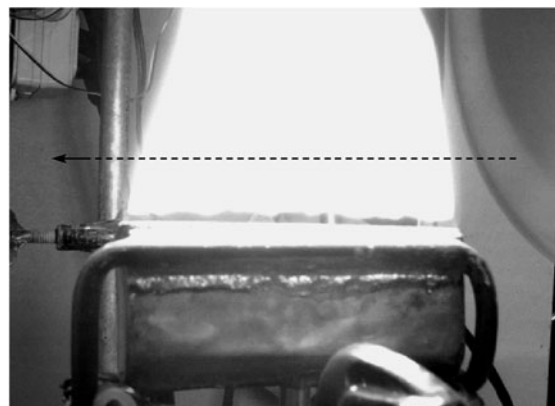


Fig. 6. Photograph of a rich sooty $\text{C}_2\text{H}_4/\text{O}_2/\text{Ar}$ ($\varphi = 2.67$) flame stabilized on a cooled rectangular porous burner: the dashed arrow is the terahertz laser beam passing from right to left parallel to the burner surface at a distance of 20 mm from it.

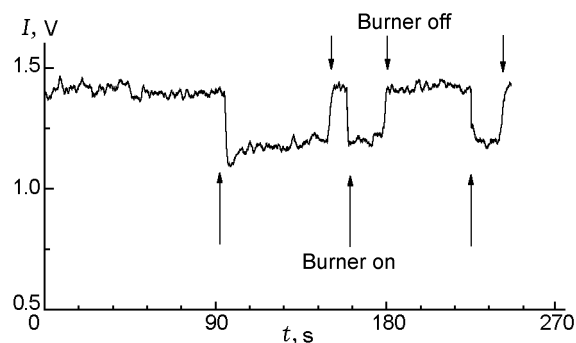


Fig. 7. Example of a record of the FEL beam intensity with the turning-on and turning-off of the burner: the beam passes at a distance of 20 mm from the burner surface.

burner surface. The transmission of the flame in the visible range was measured. Radiation with a 532 nm wavelength (semiconductor laser) was attenuated by 30% by soot particles. The optical path length was 86 mm, and the beam passed at a height of ≈ 20 mm parallel to the burner surface, i.e., in approximately the same flame region in which the water vapor concentration was measured from the FEL radiation absorption.

Measurements of the FEL radiation absorption in the flame were carried out by turning the burner on and off. Figure 7 shows how the FEL beam intensity changed therewith. The water concentration can be determined from these data, using values of the absorption coefficient of water vapor and the measured temperature at this point. Results of measurements of the water vapor concentrations at a distance of 15–30 mm from the burner surface are shown in Fig. 8 together with

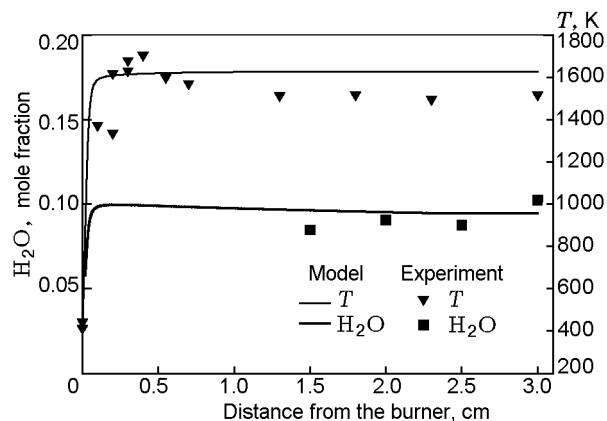


Fig. 8. H₂O concentration profile in a rich sooty C₂H₄/O₂/Ar flame ($\varphi = 2.67$).

measured temperatures. The same figure presents data of numerical simulation performed with the CHEMKIN and PREMIX software using the GRI-Mech 3.0 detailed mechanism of chemical oxidation of hydrocarbons. It is seen that at a distance of 20 mm from the burner surface, the experimentally measured molar concentration of water vapor is 0.088 ± 0.010 , which is slightly lower than the calculated water vapor concentration of 0.095. The reason for this difference may be due to the fact that in the numerical simulation, a one-dimensional flame model is considered (all parameters of the flame are only functions of the distance from the burner surface) and radiative heat loss from the flame to the environment is ignored.

CONCLUSIONS

Comparison of the results of experiments and calculations for the flame model showed that the H₂O vapor concentrations measured from the FEL radiation absorption (0.088 ± 0.010) are in good agreement with the calculations (0.095). Thus, terahertz rotational spectroscopy provide sufficiently accurate measurements of water vapor concentrations in sooty flames and in flames of two-phase flows in which such traditional optical methods are difficult to apply.

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