Far-infrared terahertz time-domain spectroscopy of flames

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We present what is to our knowledge the first comprehensive far-infrared absorption measurement of flames. These measurements, covering the region of 7–88 wave numbers (0.2–2.65 THz) are only now made possible by the technique of terahertz time-domain spectroscopy. We observe a large number of absorption lines— including those of water, CH, and NH_3—in a stationary, premixed, propane–air flame. The absorption strength permits the determination of species concentration along the beam path. The flame temperature is determined by comparison of the relative strengths of the water vapor lines. © 1995 Optical Society of America

For commercial as well as scientific reasons, combustion processes have been the subject of intensive investigation. Important questions for understanding and accurately modeling combustion are the species present in the flame and the spatial distribution and temperature of these species. A wide variety of laser-based techniques, such as laser-induced fluorescence, four-wave mixing, and various Raman processes, have been used to measure one or more of these parameters.[1] Nonlinear techniques offer excellent spatial resolution but provide data that can be difficult to interpret, and the high intensities required may perturb the flame. Fluorescence methods have excellent sensitivity but are often affected by quenching and broadband emission from soot. Since no method is capable of providing a complete characterization of flames, alternative techniques are often used in conjunction.

Here we report what is to our knowledge the first panoramic far-infrared [terahertz (THz)] absorption measurement of combustion products in a premixed laminar hydrocarbon–air flame. The comprehensive spectra that we obtain provide a survey of the relative abundance of the constituents of the flame. Such overview data are also valuable in guiding higher-resolution methods to spectral regions of interest and in determining absolute concentrations of important constituents for application of other techniques having better spatial and temporal resolution. We also determine the flame temperature by comparing relative populations of rotational states of water vapor. Previous studies that used diode lasers to monitor vibrational–rotational transitions[2] and coherent anti-Stokes Raman spectroscopy of the ν_1 band[3] have demonstrated the importance and accuracy of water vapor thermometry.

Before the research described in this Letter, comprehensive far-infrared (THz) absorption spectroscopy of flames had not been possible. This situation is due mainly to the fact that alternative methods such as Fourier-transform spectroscopy use incoherent bolometric (liquid-helium-cooled) detection, which is overwhelmed by the copious amounts of far-infrared radiation emitted by flames. In contrast, our newly developed THz time-domain spectroscopy (THz-TDS) technique[4] uses a time-gated coherent receiver, which is immune to the THz radiation emitted by the flame.

At the same time the coherent detection is 1000 times more sensitive to THz radiation than a helium-cooled bolometer. Another important advantage is that the THz source generates a well-collimated, low-divergence beam for which the receiver has a corresponding small acceptance angle. Amplitude signal-to-noise ratios in THz-TDS can exceed $10^4{:}1$ ($10^8{:}1$ in power). Finally, the bandwidth of THz-TDS can extend continuously over a wide spectral range, from 0.1 to greater than 6 THz, permitting the simultaneous detection of many species.

The THz-TDS setup shown in Fig. 1(a) was described previously.[4] As depicted in Fig. 1(a), the collimated 1-cm-diameter THz beam passed through a premixed laminar flame. The atmospheric pressure flame was stabilized on a water-cooled porous sintered bronze burner,[5] 2.5 cm wide by 12.5 cm long. Such flames are stationary—the spatial geometry and composition remain constant in time. Our flame was stable over the duration of the experiment. Propane and dry air in a near-stoichiometric 1:22 ratio were supplied to the burner at a 20-L/min total flow rate. The entire apparatus was contained in an airtight box purged with dry air to eliminate the effects of ambient water vapor.[6] The burner was isolated in a metal chimney separate from the airtight box and vented to air through a metal baffle to prevent contamination of the dry air by combustion products. The windows separating the flame from the enclosure were thin quartz plates (~ 0.16 mm thick) fused onto quartz tubes that extended the windows into the flame.

A measured THz pulse envelope for this system with 12.5 cm of laboratory air (15% relative humidity) between the windows is partially shown in Fig. 1(b). The complete measurement extended to 290 ps. Shorter scans provide less spectral resolution but a better signal-to-noise ratio. All the structure following the excitation pulse is signal from water vapor. The noise level on this scan is <0.1 pA, resulting in a signal-to-noise ratio of more than 10,000:1. To obtain a better numerical spectral resolution, we extended the full 290-ps time-domain data with zeros[7]—increasing the length by a factor of 16 before taking the Fourier transform shown in Fig. 1(c). The n-fold extension of a data set by zeros at equally
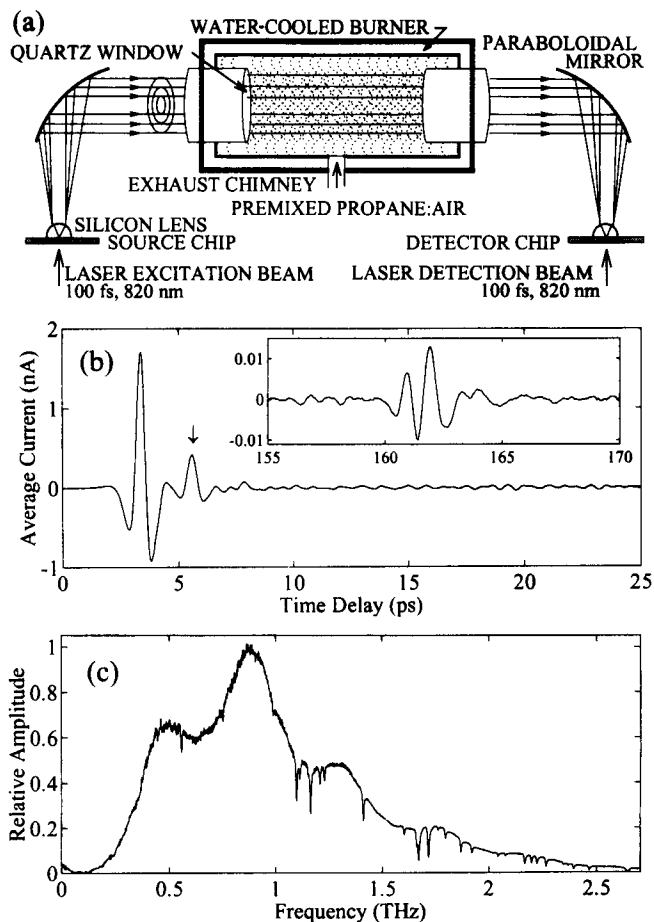
Fig. 1. (a) THz-TDS system. (b) Measured THz pulse after propagating through 12.5 cm of laboratory air. The reflected pulse from the quartz window is identified by the arrow. The inset shows reflections from the end of the transmission line. (c) Fourier transform of the THz pulse in (b).

spaced time intervals is mathematically equivalent to an n-fold interpolation of the Fourier spectrum. A similar procedure is well known in Fourier-transform spectroscopy.[7] The sharp absorption lines are due to water vapor at 2.7-Torr partial pressure (15% relative

humidity). The secondary pulses (indicated by the arrow) delayed 1.71 ps from the main pulse in Fig. 1(b) are window reflections and are responsible for the slow, 0.6-THz sinusoidal oscillation imposed on the spectrum shown in Fig. 1(c). These slow oscillations do not interfere with accurate measurement of sharp absorption lines. In addition to the sample response, we detected pulses reflected from the ends of the coplanar strip lines ~1 cm from the dipole antenna [inset of Fig. 1(b)]. These reflections are responsible for the very rapid oscillations appearing as noise on the spectral data presented in Figs. 1(c) and 2.

Absorption spectra of the laboratory air data [Fig. 1(c)] and a propane–air flame are presented in Figs. 2(a) and 2(b), respectively, for a 12.5-cm path length. To obtain these quantitative measures of absorption, we measured the transmission of the THz beam through dry air (<1% relative humidity) before and after the flame data scan to provide reference spectra. The laboratory air spectrum agrees well with previous measurements.[6] The laboratory air data of Fig. 2(a) are from a single 20-min scan,whereas the flame spectrum is an average of nine such scans.

In comparing the spectra of Figs. 2(a) and 2(b) we first note that all the absorption lines in laboratory air are due to water vapor. Also, since the main combustion products of propane are carbon dioxide (with no permanent dipole moment) and water, most of the absorption lines of the flame are due to the generated water vapor. All the lines of Fig. 2(a) appear in the flame spectrum but with several differences: the relative heights have changed, the lines have narrowed, several new lines have appeared, and the total absorbance has dropped. Most of these changes are directly attributable to thermal effects within the flame; for example, the new W lines in Fig. 2(b) are from high-energy rotational states of water.[8,9]

Several of the new absorption lines are tentatively identified with the species CH and NH_3 by a comparison with tabulated line strength data[9] at the measured temperature of 1150 K. For both CH and NH_3 the calculated relative magnitude of the absorption between peaks is in reasonable agreement
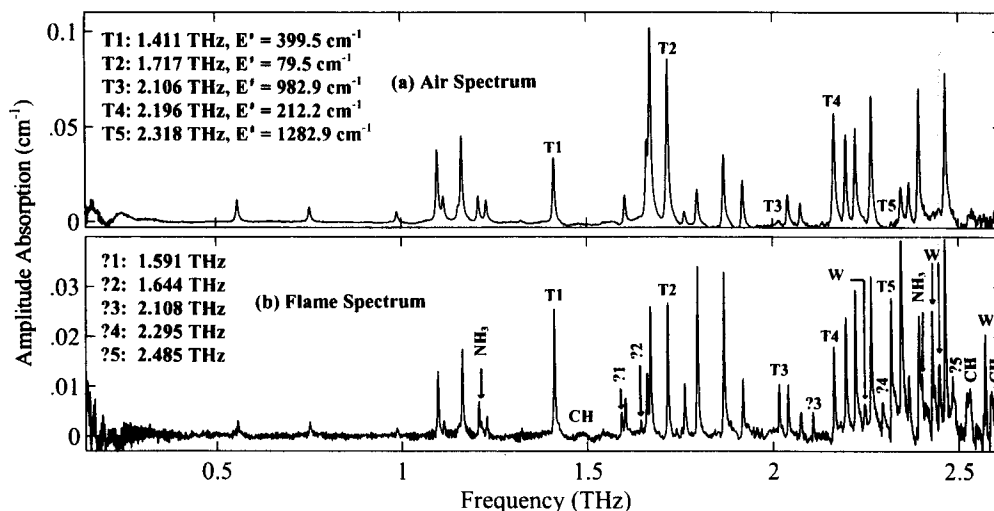

Fig. 2. Amplitude transmission spectra of (a) room-temperature air and (b) a propane–air flame. E' designates the energy of the lower level of the indicated transition.
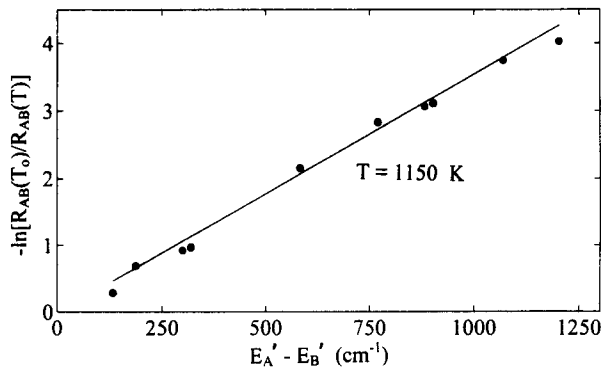
Fig. 3. Ratio of absorption change of the water lines T1–T5 between room air and a propane–air flame plotted against the difference in lower-state energies.

with that observed. Furthermore, all the calculated lines appear in the measured spectrum, although some lines are masked by water vapor absorption. Given the relative absorptions of H_2O, CH, and NH_3, a flame temperature of 1150 K, and a 1.2-GHz linewidth,[10] we estimate that at the sampled position the flame contains 3.3% water, 0.4% CH, and 0.8% NH_3. Five unidentified absorption lines (?1–?5) are visible as well. These lines are not observed in the unburned propane gas. We suspect that some of these lines may be due to methylene CH_2 free radicals, but we have not been able to verify this because of an absence in the literature of their comprehensive far-infrared spectra. This situation illustrates the potential importance of THz-TDS for transient species. We do not detect OH rotational transitions, despite a dipole moment of 1.67 D (Ref. 9) and the observed high concentration in hydrocarbon flames.[11]

The observed rotational transitions in water vapor have lower-state energies ranging from 0 to approximately 1280 cm^{-1}, or six times kT at room temperature. As shown in Fig. 2, transitions with large lower-state energies that have negligible population at room temperature may have significant population at higher temperatures and thereby dramatically increase in absorption strength. Given that the relative populations of the rotational states are determined by Boltzmann statics, the temperature of the flame may be obtained from the relative change between absorption lines of known energy.

Following the procedure of Ref. 2 and taking the ratio of two absorption lines, $R_{AB}(T) = \alpha_A/\alpha_B$, at an unknown temperature T and the same ratio $R_{AB}(T_0)$ at a known temperature T_0 we find that the ratio $R_{AB}(T)/R_{AB}(T_0)$ is a function only of the lower-state energies of the transitions A and B (E_A', E_B') and temperatures T and T_0. Expanding the exponential terms as a series and taking only the first-order terms, we have

$$\frac{R_{AB}(T_0)}{R_{AB}(T)} = \exp\left[\frac{(E_B' - E_A')}{k}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\left(\frac{T_0}{T}\right)^{\Delta n}.$$

(1)

The term $(T_0/T)^{\Delta n}$ describes the variation of the linewidth γ with temperature,[10] given by

$\gamma(T) = \gamma(T_0)(T_0/T)^n$. The exponent n varies with species and rotational quantum number; $n \cong 0.7$ for N_2-broadened low-J water vapor. This dependence leads to the observed absorption line narrowing within the flame. In Eq. (1), $\Delta n = (n_A - n_B)$ is the difference in the γ temperature exponent of lines A and B.

To determine temperature we logarithmically plot the measured values $R_{AB}(T_0)/R_{AB}(T)$ versus $E_B' - E_A'$ in Fig. 3, for the 10 possible ratios of the five lines labeled T1–T5 in Fig. 2. We obtained these data by extending the windows further into the flame for a path length of 11.5 cm. All these lines are predicted to have a similar linewidth dependence on temperature ($\Delta n < 0.05$) (Ref. 10); thus the $(T_0/T)^{\Delta n}$ term was ignored in the calculation. It was assumed that N_2 broadening of H_2O was the dominant collisional process. These five lines do not have other strong lines close in frequency that might interfere with measurement of peak absorption. Since the peak absorption of lines T3 and T5 at room temperature lies near our noise limit, calculated peak absorptions[9] were used for $R_{AB}(T_0 = 300$ K). The temperature $T = 1150 \pm 80$ K is determined by the slope of the fit. The accuracy of the temperature depends on the precision to which the peak absorption of lines T1–T5 can be determined—in this case $\pm 7\%$. The fit accuracy is further dependent on E', with larger values of E' giving a more accurate indication of the line slope. The measured value is in excellent agreement with the temperature $T = 1150 \pm 40$ K measured by a thermocouple under identical propane–air mixtures 1 cm above the burner surface.

References

1. For a review see A. C. Eckbreth, *Laser Diagnositcs for Combustion Temperature and Species* (Abacus, Kent, UK, 1988).
2. M. P. Arroyo and R. K. Hanson, Appl. Opt. **32**, 6104 (1993).
3. F. M. Porter and D. R. Williams, Appl. Phys. B **54**, 103 (1992).
4. D. Grischkowsky, S. R. Keiding, M. Van Exter, and Ch. Fattinger, J. Opt. Soc. Am. B **7**, 2006 (1990).
5. J. P. Botha and D. B. Spalding, Proc. R. Soc. London Ser. A **225**, 71 (1954).
6. M. Van Exter, Ch. Fattinger, and D. Grischkowsky, Opt. Lett. **14**, 1128 (1989).
7. P. R. Griffiths, Appl. Spectrosc. **29**, 11 (1975).
8. J. M. Flaud, C. Camy-Peyret, and R. A. Toth, *Water Vapour Line Parameters from Microwave to Medium Infrared* (Pergamon, Oxford, 1981).
9. H. M. Pickett, R. L. Poynter, and E. A. Cohen, *Submillimeter, Millimeter, and Microwave Spectral Line Catalog*, accessed via World Wide Web (http://spec.jpl.nasa.gov) from the Jet Propulsion Laboratory, Pasadena, California.
10. C. Delaye, J.-H. Hartmann, and J. Taine, Appl. Opt. **28**, 5080 (1989).
11. J. S. Bernstein, A. Fein, B. Choi, T. A. Cool, R. C. Sausa, S. L. Howard, R. J. Locke, and A. W. Misiolek, Combust. Flame **92**, 85 (1993).