

Observation of pure rotational absorption spectra in the ν_2 band of hot H₂O in flames

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We present measurements of absorption spectra of hot-water vapor generated in a propane–air flame in the far-infrared region of the spectrum from 0.1 to 3.5 THz (3.3 to 117 cm⁻¹). Transitions within the rotational manifold of both the ground and the $\nu_2 = 1$ vibrational levels were observed. The measurements are in good agreement with calculations of the predicted absorption spectra at 1300 K based on tabulated line intensities, whereas predicted theoretical line widths were found to be approximately one third too narrow. © 1998 Optical Society of America

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One of the more challenging problems in spectroscopy is the assignment of features in the spectrum of hot water.¹ The assignment of the lines of hot water has importance in astronomy since these lines were recently observed in the emission spectra of sunspots and other cool stars.² There have been numerous studies of water-vapor absorption under terrestrial conditions across the entire spectral region from the microwave to the UV owing to the effect of water vapor on atmospheric propagation. A detailed compilation of absorption lines has arisen from these studies.³ However, data on water at high temperatures are more limited. Experimentally, early studies^{4,5} looked at emission from hydrogen–oxygen flames in the spectral region from 2850 to 6200 cm⁻¹ with temperatures as high as 2900 K. More-recent investigations have measured emission from methane–air flames⁶ from 800 to 1300 cm⁻¹ at 2000 K and water vapor in a furnace¹ from 370 to 930 cm⁻¹ at 1550 °C. Congruent theoretical studies^{7,8} have provided assignments for many of the observed lines.

Here we report on direct absorption measurement of hot-water vapor generated in hydrocarbon flames in the far-IR region of the spectrum by laser-generated pulses of terahertz (THz) radiation. The spectrum of these subpicosecond pulses of THz radiation overlaps the pure rotational spectra of hot water. Except for one unidentified line at 2.864 THz, all the observed absorption lines in the flame are due to hot-water vapor. This technique permitted what we believe was the first direct observation of pure rotational absorption lines from the ground (000) and the ν_2 (010) vibrational states of hot-water vapor from 3.3 to 117 cm⁻¹. In conjunction with previous measurements that identified ground vibrational state absorption,⁹ these are to our knowledge the first far-IR absorption measurements and identification of pure rotational transitions in the ν_2 band of hot-water vapor in the spectral region below 150 cm⁻¹. In previous measurements at higher frequencies pure rotational transitions in the ν_2 state were observed via long-path-length absorption^{10,11} and in hot water by emission.^{1,5}

There are two characteristics of our coherent optoelectronic system that permit these measurements. First, the detector is blind to the incoherent thermal radiation emitted by the flame; second, the source generates a well-collimated beam, permitting measurements over long path lengths. This unique capability shows the potential of THz time-domain spectroscopy (THz-TDS) for measuring far-infrared properties of hot samples in the far-infrared region of the spectrum.

The experimental configuration used in this investigation is shown in Fig. 1. Compared with measurements obtained earlier,⁹ the bandwidth of the system was increased from 2.5 to 3.5 THz and the path length through the flame was increased from 12.5 to 20.7 cm. The time-resolved electric field of the THz pulse was measured with a 5000:1 signal-to-noise ratio. The premixed flame is supported on a 24.8 cm × 17.8 cm sintered bronze water-cooled burner. The burner assembly is enclosed to prevent contamination from room air, and the combustion gas (propane–air) ratio is measured to ±2% accuracy. The THz source and the detector are enclosed in separate chambers isolated from the burner. The THz beam is coupled into the burner enclosure through 100-μm-thick quartz windows fused to 5-cm-diameter quartz tubes, permitting the windows to be inserted directly into the flame.

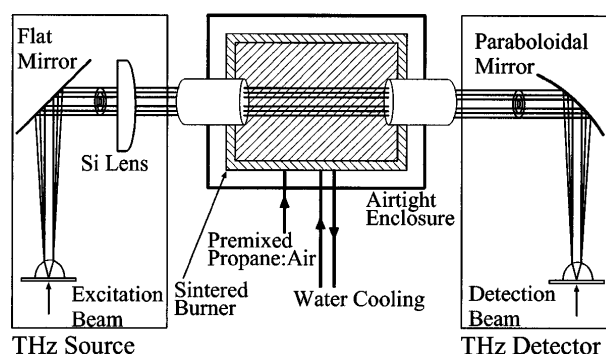


Fig. 1. Experimental schematic of THz time-domain spectroscopy (THz-TDS) setup and flat flame burner.

We obtained individual data sets by taking 2560 data points over a 154-ps time window. The 512 data points spanning the initial THz pulse had a time separation of 33.363 fs. To minimize signal drift, the remaining 2048 points had a separation of 66.727 fs numerically interpolated by a factor of 2 to provide uniform temporal spacing. A representative measurement with the flame on is shown in Fig. 2(a); the inset shows the main THz pulse in detail. As illustrated in Fig. 2(b), there is no increase in background noise with the flame on. Despite the high temperature within the flame, the gated coherent detection and the small acceptance angle of the THz optics are effective in blocking the incoherent THz radiation that is incident upon the detector.

The time-domain data were padded with zeros to 2^{15} points (1.1 ns) before the fast Fourier transform was taken to interpolate the results in the frequency domain. The normalized amplitude spectrum of the pulse in Fig. 2(a) is shown in Fig. 2(c). The spectrum covers the region from 0.1 to 3.5 THz. The 0.75-THz oscillatory structure in the spectrum is due to etalon effects of the 100- μm -thick quartz windows. The power absorption spectrum, which we measured¹² by taking the ratio of an average of three scans with the 1:30 propane–air flame on to that with the flame off and the burner enclosure purged with dry air, is shown as the individual points in Fig. 3.

The absorption spectra are fitted to a numerical model by use of integrated line intensities from the Molecular Spectroscopy Database.¹³ To convert the data from the database value at $T = 300$ K to an arbitrary temperature, the procedure outlined in Ref. 13 was used. Conversion of the tabulated integrated intensity to a frequency- and temperature-dependent absorption profile is essential because lines with high, lower-state energy that are unobservable at 300 K become comparatively strong at high temperatures.

In air (78% N_2 :21% O_2), if the propane–air (at a ratio of 1: N) combustion reaction $5 \text{O}_2 + \text{C}_3\text{H}_8 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}$ is limited by the amount of propane present, the combustion products are $(0.78N) \text{N}_2 + (0.21N - 5) \text{O}_2 + 4 \text{H}_2\text{O} + 3 \text{CO}_2$ and the percentage of water vapor is $4/(N + 2)$. Assuming that the combustion reaction is complete within several millimeters from the burner surface at 1-atm pressure,¹⁴ the hot gases within the THz beam path are primarily N_2 , O_2 , CO_2 , and H_2O , of which only H_2O absorbs THz radiation. Hence the measured linewidth is determined by the H_2O – N_2 , H_2O – CO_2 , H_2O – O_2 , and H_2O – H_2O collisions. Besides their dependence on collisional partners, linewidths typically have a temperature dependence¹⁵ of the form $\Delta\nu(T) = \Delta\nu(T_0)(T_0/T)^n$. Although the exponent n is strongly dependent on the J, K rotational state of the molecule, it can be approximated by a constant for each collisional species at high temperatures.¹⁶ The total FWHM linewidth, $\Delta\nu = 1/\pi\tau$, is dependent on the average time, τ , between intermolecular collisions weighted by the estimated percentage composition of each collision partner and is calculated to be 2.26 GHz. Because the broadening of the ν_2 state is found to be nearly identical with that of the ground vibrational state,¹⁷

with an average linewidth difference of less than 1%, we assume the same linewidth in calculating the ν_2 line profiles. In fitting the data we accounted for the 150-ps truncation that was due to the experimental data window by converting the calculated absorption spectra to the time domain¹² and then truncating the result to the same number of sample points as the data and zero padding. With the effects of data truncation incorporated, the calculated line shape is approximately one third less than that needed to fit our data.

The measured power absorption coefficient of the 1:30 propane–air flame shown in Fig. 3 is fitted to a calculated absorption coefficient at 1300 K, 12.5% water vapor, and $\Delta\nu = 3.3$ GHz. Two separate calculations are performed, one for the vibrational ground state (solid curves overlapping the data points in Fig. 3) and one for the $\nu_2 = 1$ vibrational state (solid curves offset by -0.01). The high temperature in the

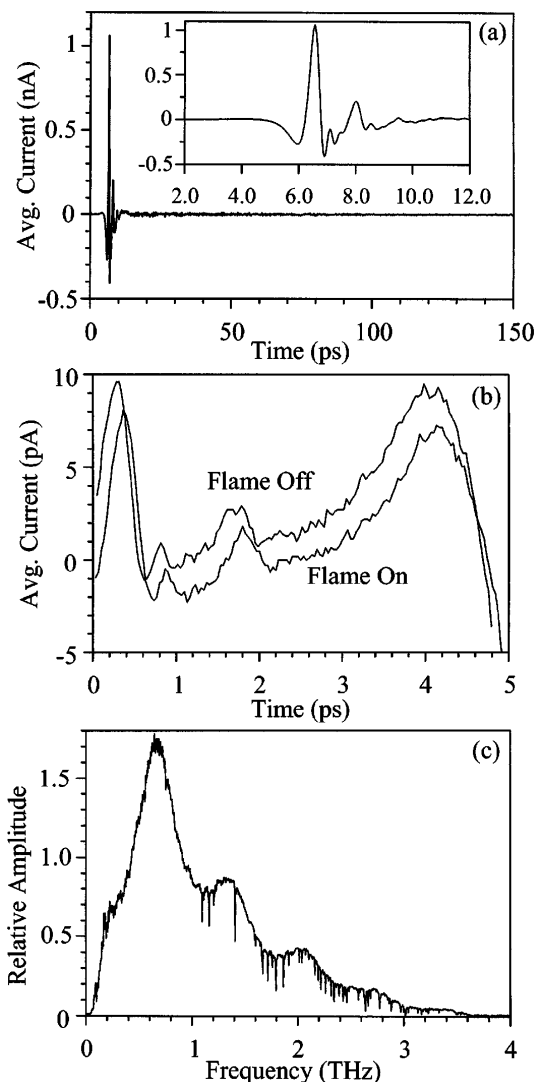


Fig. 2. (a) Time-domain scan with a 1:30 propane–air flame. The definition of zero time is arbitrary. The inset shows the main THz pulse in detail. (b) Closeup of the region before the arrival of the THz pulse both with and without the flame. (c) Amplitude spectrum of pulse in (a).

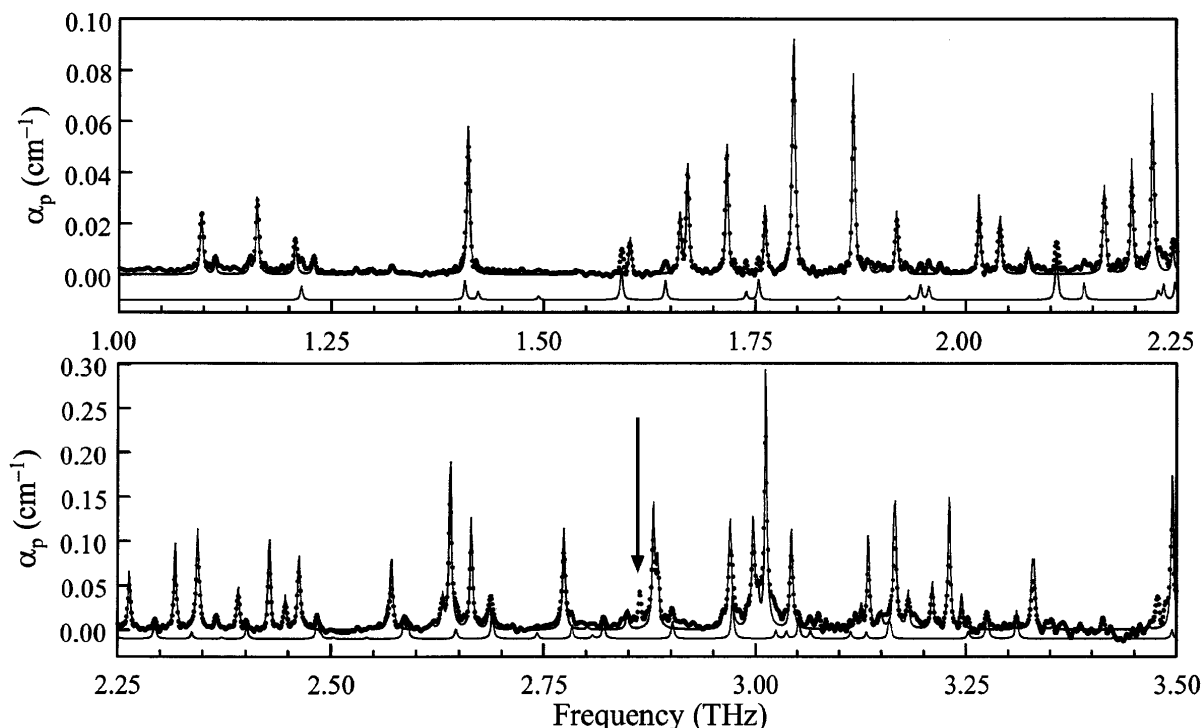


Fig. 3. Measured (filled circles) power absorption coefficient compared with that calculated for the vibrational ground state (solid curves) and the first ν_2 vibrational state (solid curves offset by -0.01) of hot-water vapor. The single unidentified line is indicated by the arrow.

flame leads to a Boltzmann distribution over a large range of rotational state energies. We observe transitions at $J, K_a, K_c = 1, 1, 1 \rightarrow 0, 0, 0$ (1.113 THz) up to the ν_2 transition $9, 4, 5 \rightarrow 9, 3, 6$ (2.82 THz), which cover a lower-state energy range of 0 to 2904.7 cm^{-1} , respectively (2904 cm^{-1} corresponds to $T \cong 4200$ K; $kT = 207$ cm^{-1} at 300 K). The measurements fit the calculated line positions to an accuracy of 1 GHz. We observed 22 rotational absorption lines from the ν_2 band; the measured strengths and linewidths agree reasonably well with calculations. However, an observable discrepancy between the measurement and calculated absorption becomes larger at higher frequencies, with the calculated absorption being greater than that measured. This result may be due to state-dependent variations of the linewidth. Higher-resolution measurements will help to resolve these issues.

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