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Cavity ring-down spectroscopy of OH radicals in low pressure flame

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Abstract. Cavity ring-down laser spectroscopy (CRDS) is used to measure the OH concentration profile and the rotational temperature profile in low-pressure (30 torr) methane/air flames. Very high sensitivity (2×10^{10} molecules/cm^3) and large dynamic range (more than 20 000) are demonstrated. CRDS also provides accurate temperature measurements, with statistical errors less than 2%. Measured concentration profiles are in reasonable agreement with calculated values. It is observed that in the preflame zone (where the temperature is about 1000 K), the OH concentration at the first vibrational excited state is about seven times larger than the equilibrium OH($v'' = 1$) concentration at this temperature.

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One of the most widespread experimental approaches to combustion chemistry is through measurements of spatial concentration profiles of the intermediate products of combustion in quasi one-dimensional continuous flames (e.g. in laminar premixed flat flames). The results of these measurements are then compared with model calculations [1].

Laser induced fluorescence (LIF) is usually the method of choice for nonintrusive concentration and temperature measurements. Important progress in this direction has been achieved recently, particularly in studies of low-pressure premixed flat flames (see for example [2, 3]). However, LIF has only a limited ability for absolute concentration measurements because of the uncertainties in the determination of the fluorescence quantum yield. Even rotational temperature measurements must be made with extreme care to avoid systematic errors [4].

In contrast, absorption spectroscopy provides much more direct and accurate access to absolute concentration and temperature measurements. We have used intra-cavity laser absorption spectroscopy (ICLAS) for detection of HCO and singlet CH_2 radicals in low and atmospheric pressure flames [5–7]. However, at the moment ICLAS does not allow monitoring of absorption in the UV range, where the spectra of many radicals are located, and this is due to the lack of homogeneously broadened broadband amplifying laser media in the range. In this work we have thus used another absorption spectroscopy technique, cavity ring-down spectroscopy (CRDS), to monitor the OH radical spectrum in the range 307–312 nm.

CRDS is a highly sensitive absorption method based on the measurement of the intensity decay rate of a laser pulse injected into an optical cavity built with highly reflective mirrors. CRDS may be considered as a multipass absorption technique, with an equivalent absorption path length given by the number of passages inside the cavity before the injected intensity decays by 1/ e. This path length may be of the order of tens of km in the visible range, where the best mirrors are available. In contrast to standard multipass absorption methods, in CRDS the probe volume is confined within the fundamental cavity mode. This provides a spatial resolution of a fraction of a millimeter, sufficient for measurements in low-pressure flat flames. Since the first demonstration by O'-Keefe and Deacon [8], this method has been used in many different applications (see, for example, the review conducted by Scherer et al. [9] and references therein), including measurements in flames [10–12]. Recently, CRDS was extended to cw dye and diode laser sources, which opens up even more interesting possibilities [13, 14].

In this work, we intend to demonstrate that CRDS is a very convenient technique that can provide accurate concentration and temperature profiles in flat flames using direct absolute measurements of the absorption rather than of the fluorescence. The spectrum of the OH radical is a very useful thermometer in flames, because there exists an appreciable concentration of this radical in all parts of the flame. The accuracy of temperature measurements depends greatly on the dynamic range and linearity of the absorption signal provided by the method; in this work, we measured OH absorption lines in a dynamic range of more than 20 000, which allowed very accurate temperature determination.

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1 Experimental

The essential feature required of any spectroscopic method for measurement of concentration profiles in flat flames is a good spatial resolution. As an example, the width of HCO concentration profile in a 30-torr methane/air flame is about 3 mm, but this will reduce to a fraction of a millimeter at atmospheric pressure.

The best spatial resolution can be obtained with a collimated Gaussian beam. The minimum average beam size for a laser wavelength λ can be reached when the confocal parameter of the Gaussian beam $2\pi\omega_0^2/\lambda$ is equal to the diameter D of the burner. In that condition, the minimum average beam size across the burner can be provided. The Gaussian beam diameter at the center of the burner can then be found from the equation $2\omega_0 = \sqrt{2\lambda D/\pi}$. The beam diameter will be $\sqrt{2}$ times larger on the burner edge. For a McKenna burner with 6 cm diameter, we obtain the maximum possible spatial resolution of about 0.15 mm at a wavelength of 308 nm. To achieve this spatial resolution, it is necessary to mode match the excitation laser beam to the cavity, so that the light injected into the cavity belongs mostly to the lowest order TEM_{00} mode.

Linear response over a large dynamic range of the absorption measurements is another important feature. In fact, we want to be able to determine the temperature in different parts of the flame, where the concentration of the species (OH in this work) can vary by orders of magnitude. Moreover, the accuracy of the temperature measurements depends on the ability to observe simultaneously spectral lines with very different intensities. The absorption signal in CRDS is given by the inverse decay time

$$\frac{1}{\tau} = \frac{(T + \Lambda + \sigma(\lambda) n l) c}{L} \quad , \tag{1}$$

where $T + \Lambda$ are cavity losses due to the mirror transmission (T), absorption and scattering (Λ); $\sigma(\lambda)$ is the absorption cross-section of the sample placed inside the cavity; the sample has concentration n and length l (equal in our case to the burner diameter D); c is the velocity of light; and L is the cavity length.

The dynamic range is determined by the accuracy of the measurement of the decay time $\delta\tau$, which gives the minimum measurable absorption, and by the minimum measurable decay time $\tau_{\min}$, which gives the maximum measurable absorption. The sensitivity limits of CRDS, its dynamic range and noise level are discussed by Romanini and Lehmann [15], so we will not go very much into the details here. In practice, values of $\delta\tau/\tau$ from 1% to 0.1% can be achieved. Thus, the minimum concentration $n_{\min}$ that can be measured by CRDS can be evaluated from the condition (see (1)):

$$\frac{\sigma(\lambda) n_{\min} l}{T + \Lambda} = \frac{\delta\tau}{\tau_0} \quad , \tag{2}$$

where $\tau_0 \equiv L/c(T + \Lambda)$ is the decay time without sample in the cavity. Therefore

$$n_{\min} = \frac{T + \Lambda}{l\sigma(\lambda)} \frac{\delta\tau}{\tau_0} \tag{3}$$

which does not depend on cavity length, L, for a fixed sample length l and a given relative accuracy of the decay time measurement, $\delta\tau/\tau$.

The maximum measurable concentration is limited by the difficulties in the measurement of decay times smaller than 10–20 ns. As a consequence of this, longer cavities should be used in order to extend the dynamic range with a given mirror set. Indeed, for a fixed sample size, such as in the case of a flame, the measurement sensitivity is not affected by the cavity length L (see (1, 3)). On the other hand, a longer cavity provides a longer decay time at the same losses, and therefore a higher maximum measurable absorption level.

We implemented these recommendations in the experimental setup whose diagram is shown in Fig. 1. The flame burner and low-pressure chamber were similar to those used in the experiments where ICLAS was used for monitoring the HCO radical [6]. Two long arms were connected to the low-pressure chamber by stainless steel bellows. These arms were closed by two concave mirrors (radii of curvatures were 0.5 m) forming the ring-down cavity. Both mirrors were by Virgo Optics Corp. and had a specified reflectivity $R > 99.9\%$. The observed ring-down time in the empty cavity was about 0.8 μs, corresponding to a reflection $R \approx 99.75\%$. Slow flows of nitrogen were added through the thin tubes near the mirrors in order to decrease contamination of the mirrors by combustion products. The length of the ring-down cavity was 0.75 m.

The laser beam from the second harmonic of a dye laser (Continuum Corp. Nd-60) was injected into the cavity through one of the mirrors. The laser linewidth was rather narrow, 0.08 cm^{-1} as measured by a Burleigh WA-4500 wavemeter. Two lenses and a pinhole (50 microns in diameter) were used to match the laser beam to the TEM_{00} modes of the cavity. We observed the ring-down signal through the second mirror using a solar blind photomultiplier (Hamamatsu R-166). The signal was digitized by a LeCroy 9310 oscilloscope and was transferred after each laser pulse to a personal computer (PC) for processing. The ring-down decay rate was determined for each curve and the values obtained were averaged through 40–50 consecutive laser pulses.

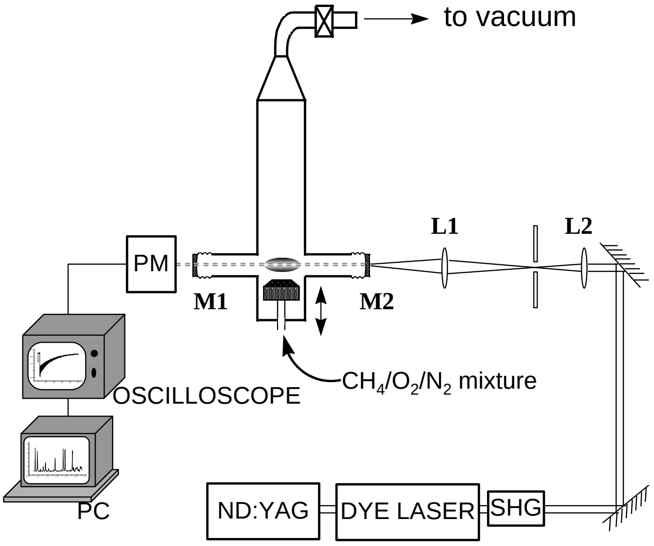

Fig. 1. A schematic diagram of the experimental apparatus. The cavity of the CRDS is formed by mirrors M1 and M2. The pinhole and the lenses L1 and L2 are set to mode match the laser beam with the cavity. SHG is a KDP crystal used for doubling the output of the Nd:YAG pumped dye laser

Special software was written to provide real-time processing and averaging of the signal.

2 Results and discussions

Figure 2 shows a part of the OH ($A^2\Sigma^+ \leftarrow X^2\Pi_i$) spectra in the region that has often been used for temperature measurements in flame by the LIF technique [4, 16]. The spectrum is practically noise-free, displaying the high dynamic range of the signal. Linearity of the method and the absence from saturation were checked by comparing the experimental ratios of the intensity of main and satellite lines (2 and 2′, 3 and 3′, 4 and 4′) with those tabulated by Dieke and Crosswhite [17]. It is interesting to note that we did not observe saturation even up to the very strong absorption level that corresponds to a ring-down decay rate of $50 \times 10^6\,\mathrm{s}^{-1}$. Good linearity of the absorption signal can be seen also from the linearity of the Boltzmann plot shown in Fig. 3.

The observed individual linewidths varied from 0.17 to $0.25\,\mathrm{cm}^{-1}$, which is close to the Doppler width ($0.18\,\mathrm{cm}^{-1}$ at 1000 K). We could also observe the increase of the linewidths with temperature. However, the linewidth of our laser was not sufficiently narrow to determine accurately the temperature just from the Doppler width of the individual lines. On the other hand, the laser linewidth is narrower than the OH linewidth, which is a necessary condition to fit the ring-down decays by a single exponential function. This point has been discussed in detail in several publications [9, 18, 19]. The sensitivity of the OH detection can be estimated based on the measured baseline noise value of about $2.5 \times 10^3\,\mathrm{s}^{-1}$(rms). It leads to a minimum detectable absorption coefficient of about $1 \times 10^{-6}\,\mathrm{cm}^{-1}$ in the flame. This corresponds to an OH radical concentration of about 1.2×10^{10} radical/cm^3 at a temperature of about 1500 K if the most intensive line is used in the measurements [20]. The sensitivity at room temperature can be estimated as $2.4 \times 10^9\,\mathrm{cm}^{-3}$.

These values are more than an order of magnitude better than the estimate of $10^{11}\,\mathrm{cm}^{-3}$ by Meijer et al. [10], and suffice for most combustion experiments involving the OH radical. Better sensitivity obtained in this work has resulted from higher reflectivity in the mirrors used by us and a longer cavity length that provides longer ring-down time in the empty cavity ($> 0.8\,\mu\mathrm{s}$ in this work, in comparison with about 100 ns in the Meijer et al. work). More accurate measurement of the ring-down time (with an error variance of about 0.2%) was also available since TEM_{00} was mainly excited in the ring-down cavity, and this provides an additional sensitivity improvement. However, in order to detect other species that are present in the flame at lower concentra-

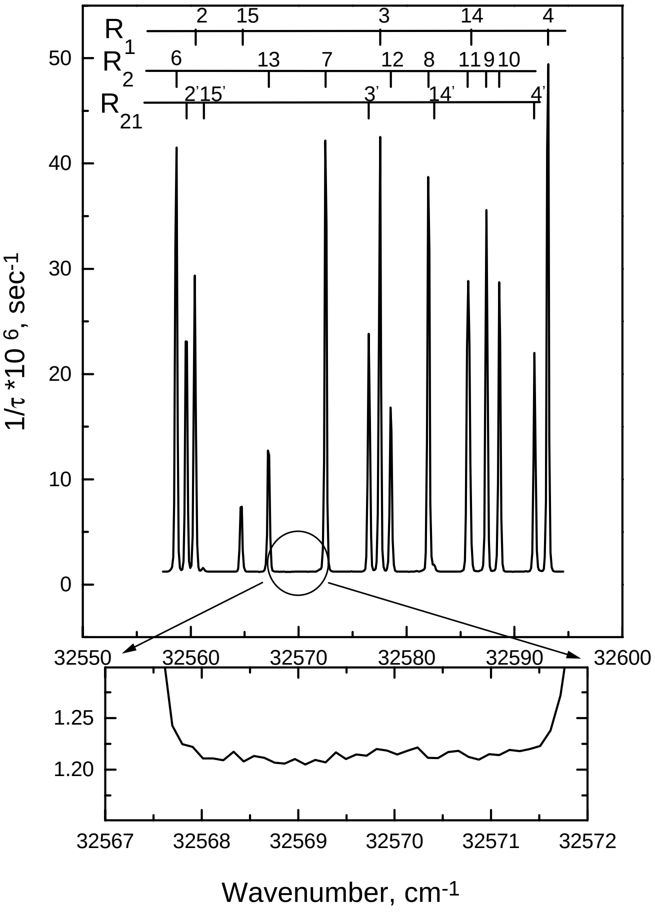

Fig. 2. CRDS spectrum of a part of the OH ($A^2\Sigma^+ \leftarrow X^2\Pi_i$) spectrum in a stoichiometric ($\phi = 1.0$) $CH_4/N_2/O_2$ flame. Oxygen/(Oxygen+Nitrogen) ratio is 0.23. Total pressure is 30 torr. Laser beam is located 0.86 cm above the burner. Note that the $10^6\,\mathrm{s}^{-1}$ ring-down decay rate corresponds to the absorbance of 4.2×10^{-4} /cm or 2500 ppm per pass under our conditions

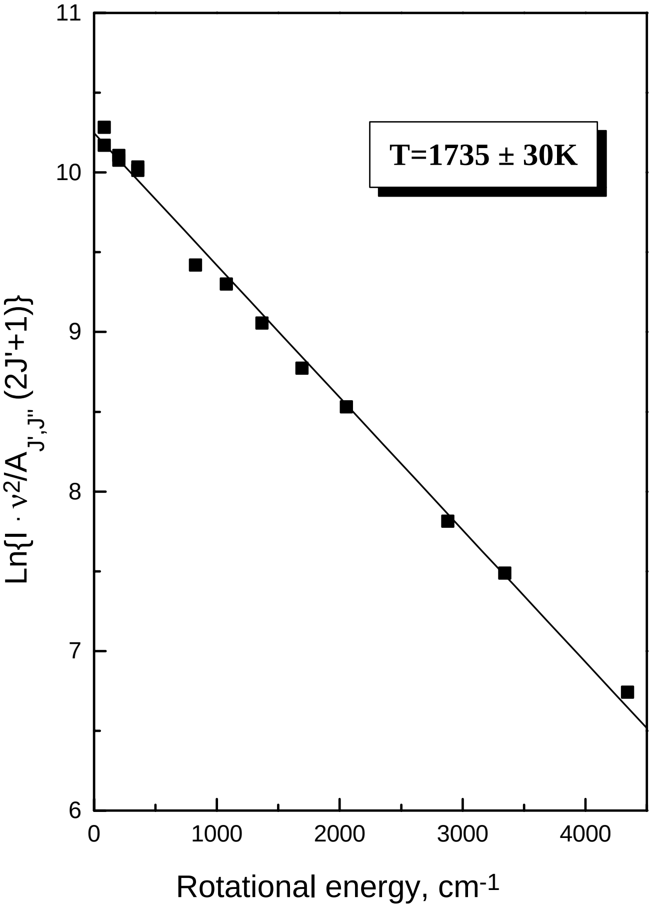

Fig. 3. A Boltzmann plot obtained for the experimental spectrum shown in Fig. 2. The experimental error was estimated from the scattering of the individual points

tions and/or have a lower absorption cross section than the OH radical, an additional sensitivity improvement might be needed. This could be achieved by using mirrors with higher reflectivity and by increasing the repetition rate of the laser, which would allow better averaging.

Figure 3 shows a Boltzmann plot of the OH line intensity divided by an appropriate factor $A_{J',J''}(2J'+1)/\nu^2$, where $A_{J',J''}$ is the Einstein coefficient for an individual line [20], ν is the frequency of the transition, and J‘ is the OH rotational quantum number in the upper $A^2\Sigma^+(0)$ state. The quality of the fit shown in the plot in Fig. 3 also demonstrates the absence of saturation effects. The statistical error of fitting is usually about 2%, or about 30 K at a temperature of 1500 K. This value is similar to that obtained by LIF, but CRDS is free from the many possible systematic errors of LIF [2, 4]. Absorption spectroscopy temperature measurement can include additional errors, reflecting averaging of the spectral line intensity over the diameter of the flame [4]. However, this error will be less if the lines with high rotational numbers are used for temperature evaluation. The populations of those lines are negligible in the “cool” perimeter zone. Therefore, good linearity of the Boltzmann plot demonstrates that the cool edge does not essentially affect the determination of the temperature.

The temperature profile measured in stoichiometric methane/air flame is shown in Fig. 4, along with calculated and measured profiles of OH and HCO. The experimental OH profile was calculated using averaging of concentration values obtained for each spectral line shown in Fig. 2. The theoretical dependence of Doppler width on temperature was taken into account for concentration evaluation. The statistical error in the concentration measurements, which also involves the error in the temperature determination, was about 20–30% (the uncertainty in the literature data of the OH absorption cross-section has a similar value). The HCO profile was measured by intracavity laser absorption spectroscopy (ICLAS) as was reported elsewhere [6]. Note that the temperature profile measured in this work allows us more accurate evaluation of HCO concentrations from ICLAS spectra than was obtained previously using a temperature profile determined from HCO spectra with accuracy of about 200 K [6]. In all measurements, the optical path length through the flame was assumed to be equal of the flame burner diameter, 6 cm. The error caused by the deviation of real flame size from this value is less than the other errors caused, for example, by the uncertainties in the radical absorption cross sections.

Calculations were made using Sandia PREMIX code [21] and the GRI 2.11 mechanism [22]. A more detailed comparison of measured and calculated profiles, including other species, will be published in the near future [23]. Here we would like to note that the experimental concentration profiles are absolute concentration profiles that have been evaluated using the cross-section values in the literature [6, 20]. The plot in Fig. 4 shows that both relative position and absolute concentration values of the experimental HCO profile are in excellent agreement with the calculated values. The experimental OH profile is somewhat lower than the calculated profile at distance > 0.4 cm; a more detailed investigation is needed to clarify this difference.

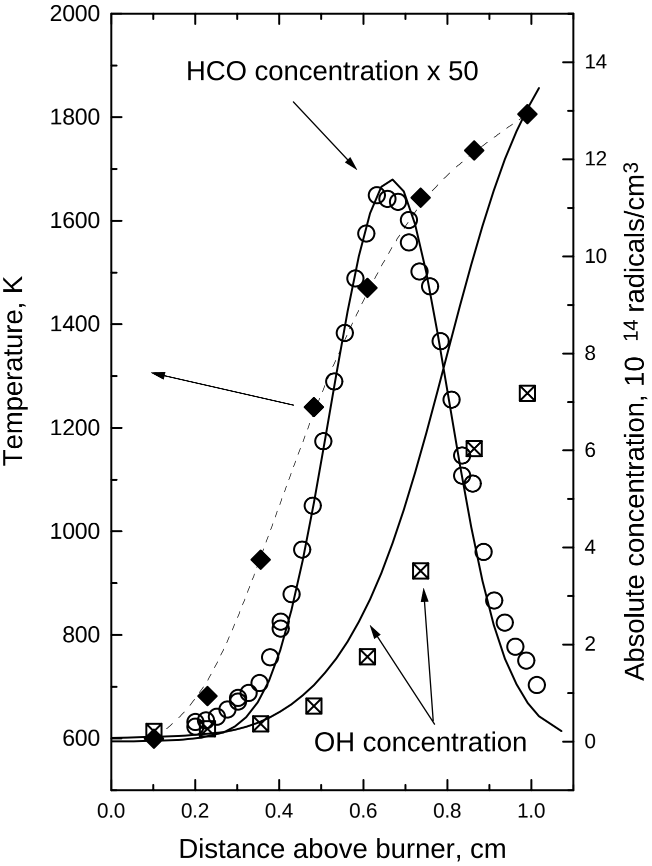

Fig. 4. Temperature profile (measured by CRDS, represented by solid diamonds), and calculated and measured OH and HCO profiles for a stoichiometric $CH_4/N_2/O_2$ flame. All conditions are as in Fig. 2. Squares represent the OH concentration measured by (CRDS); circles represent the HCO concentration measured by ICLAS using the same procedure as in [6]. Solid lines are from the model calculations using experimental temperature profile

We also observed a strong deviation from Boltzmann equilibrium for vibrationally excited OH radicals ($v = 1$) in the preflame zone at distances 1–3 mm and temperature 600–1000 K. We measured the absolute concentration of OH at $v'' = 1$ level using part of the spectrum in the region of the R_1 branch of the (1, 1) transition ($\nu = 32\,000$–$32\,025\ \mathrm{cm}^{-1}$). The results are presented in Table 1 for two different flame locations.

Table 1. Absolute concentration of OH at two different locations in flame

Distance above burner mm	Temperature K	OH ($v=0$) cm^{-3}	OH ($v=1$)[1] measured cm^{-3}	OH ($v=1$) equilibrium cm^{-3}	OH ($v=1$) measured /equilibrium
3.6	945	3.3×10^{13}	1.0×10^{12}	1.5×10^{11}	6.8
7.4	1645	3.1×10^{14}	1.3×10^{13}	1.4×10^{13}	0.9

[1] Measured using $R_1(7)$ of (1, 1) transition ($\nu = 32\,023.93\ \mathrm{cm}^{-1}$)

The error in the concentration determination of the OH ($v''=1$) was much higher than that for the ground state because of less reflectivity of our mirrors at the wavelengths corresponding to the $v''=1$ transitions ($\nu \approx 312\,\mathrm{nm}$). However, this error (about 70%) was much less than the observed deviation from the equilibrium value. Note that in spite of the population of OH radicals ($v''=1$) exceeding the equilibrium value by a factor of nearly seven, the OH ($v''=1$) concentration is only about 3% more than for OH ($v''=0$). A detailed investigation of the observed deviation from the vibrational equilibrium in a flame is currently in progress.

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