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DETERMINATION OF ABSOLUTE OH AND CH CONCENTRATIONS IN A LOW PRESSURE FLAME BY LASER-INDUCED SATURATED FLUORESCENCE

K. KOHSE-HÖINGHAUS, R. HEIDENREICH,* TH. JUST
Institut für Physikalische Chemie der Verbrennung, DFVLR
Pfaffenwaldring 38, 7000 Stuttgart 80, West Germany

The method of species concentration measurements by laser-induced fluorescence (LIF) in flames was further developed. The applicability of the two-level rate-equation model was examined for the experimental conditions. Inhomogeneous saturation due to the spatial intensity distribution of the laser light was corrected for using a field of local laser intensities obtained experimentally. Among other things, the accuracy of the calibration of the optical detection system was crosschecked by two methods. Absolute number densities of CH and OH could be determined in a 13 mbar C_2H_2—O_2 flame from measurements of the average saturation degree as a function of laser intensity. From these saturation curves approximate oscillator strengths could be obtained which provided a check of the evaluated number densities. Temperatures were determined from rotational spectra of the excited molecules. For the extension of the method to higher pressure, preliminary results obtained with a multilevel relaxation model are presented.

Introduction

Since the saturated LIF method was proposed,[1,2] several quantitative saturated fluorescence experiments on flame radicals such as C_2,[3,4] CH,[4–6] CN,[5,6] OH,[7] and NH[8] have been reported. For the investigation of flames at atmospheric pressure, discrepancies with factors of two to five[5,6] from absorption measurements were found, showing that large errors can be introduced by inappropriate assumptions, as, for example, by neglecting collisional relaxation.

At low pressures, the influence of collision processes is reduced and can be accounted for. Thus, the most reliable concentration measurements have been obtained in low-pressure flames with single-line excitation and time-resolved fluorescence detection.[7,8] However, even for these conditions, the interpretation of the fluorescence data may be complicated by non-uniform saturation depending on the spatial intensity distribution across the laser beam.[9] Spatial laser beam profiles have been described as Gaussian[10,11] or truncated Gaussian.[12] These assumptions need not be valid for the multimode lasers commonly used. Also, pulse-to-pulse variations of the spatial, temporal, and spectral laser intensity distributions may influence the saturated fluorescence signal. Accurate number densities of radicals in flames can only be obtained, if these effects are considered correctly. In this work, an improvement to the saturated LIF method has been attempted.

Experiment

Details of the experimental arrangement can be found in Ref. 13. Most of the experiments have been performed in a 13 mbar premixed C_2H_2—O_2 flame with an equivalence ratio of $\phi = 1.2$ and a total flow rate of 650 cm^3 NTP/min. The height of the porous disk burner with a diameter of 20 mm could be adjusted.

The molecular species in the flame were excited by a Nd: YAG laser-pumped dye laser (Quanta Ray). For CH excitation in the ($A^2\Delta - X^2\Pi$, 0—0) band near 431 nm, the dye laser was operated with stilbene 3. The frequency-doubled laser light of a mixture of cresyl violet and rhodamine 640 was used to excite OH in the ($A^2\Sigma^+ - X^2\Pi$, 0—0) band near 315 nm.

The laser intensity was monitored with a calibrated photodiode. The energy of a laser pulse of about 5 ns halfwidth amounted to up to 0.25 mJ for the excitation of CH and to up to 1 mJ for OH excitation. Pulse-to-pulse fluctuations in laser energy were less than 15%. The laser bandwidth was about 0.6 cm^{-1} in the CH and 1.5 cm^{-1} in the OH experiments.

Fluorescence was detected at right angles to the laser beam axis by a photomultiplier (RCA 1P28 or

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*Present address: BAYER AG, 5090 Leverkusen.

Hamamatsu R 928) after being spectrally dispersed by a 0.6 m monochromator (Jobin Yvon). In our optical configuration, the length of the collection volume parallel to the laser beam axis was given by the slit height, the collection volume diameter normal to it was determined by the slit width.

Fluorescence signals were recorded with a fast transient digitizer (Tektronix R 7912, minimal time resolution ≤1 ns) or a boxcar integrator. Data could be stored and processed in a PDP 11/05 laboratory computer or transferred to a PDP 11/44 computer for further evaluation.

Results and Discussion

For simplicity, a strict two-level system connecting two rovibronic states of a molecule is the basis of the following equations. This idealized model is a reasonable approximation for slow energy transfer as found in our low-pressure flame (see below). The time-dependent population of the upper level given by the widely accepted rate equation approach is:

$$\frac{dN_2}{dt} = N_1 u_\nu B_{12} - N_2(u_\nu B_{21} + A_{21} + Q_{21}). \quad (1)$$

N_1 is the number density of molecules in the ground state, N_2 the number density of the excited species. B_{12}, B_{21}, and A_{21} are the Einstein coefficients for absorption, stimulated, and spontaneous emission, respectively, and Q_{21} is the quenching rate constant.

Fluorescence experiments are often performed with high power multi-mode laser pulses whose intensity, phase, and mode distribution undergo fluctuations. Therefore, on general grounds, the population of the excited state of a quasi two-level molecule should be described by stochastic differential equations (master equations) rather than by the rate equation (1).

In the simplest approach, we have compared the phase diffusion model[14] and the rate equation for the case when the laser bandwidth is larger than the molecular linewidth. For the laser intensity range of our experiment, the results from both models were the same in this case. Thus, if our measured average laser bandwidth could be approximated by a broad "single" mode, the rate equation might safely be applied. In the extreme case of a much smaller bandwidth of the laser line relative to the absorbing line, in contrast to the rate equation the phase diffusion model exhibits, as expected, oscillations in the time-dependent populations occuring even at moderate laser intensities. Further calculations modeling a multi-mode laser pulse should show the limits of the applicability of the rate equation for experimental conditions. Probably, when the number of oscillating modes in the Nd-YAG/dye system is high as observed experimentally,[15] the rate equation might give a reasonable approximation.[16]

Therefore, in this paper, further evaluations will be based upon the rate equation (1). For a constant population within the two-level model

$$N_0 = N_1 + N_2, \quad (2)$$

Eq. (1) was integrated using an averaged experimental time-dependent laser pulse, as well as a simplified rectangular "equivalent pulse" of width τ_L, whose height and area were assumed to be equal to those of the experimental pulse. As the computational results did not differ markedly, further evaluations were performed with the solution of Eq. (1) for the rectangular "equivalent pulse" at $t = \tau_L$:

$$N_2 = \frac{N_0 \cdot (g_2/g_1) \cdot \hat{u}}{[1 + (g_2/g_1)] \cdot \hat{u} + \alpha} \cdot \{1 - \exp - \langle([1 + (g_2/g_1)] \cdot \hat{u} + \alpha) \cdot \tau_L\rangle\}. \quad (3)$$

Here, $\hat{u} = u_\upsilon \cdot B_{21}$ and $\alpha = A_{21} + Q_{21}$.

For complete saturation at $t = \tau_L$, Eq. (3) reduces to

$$N_{2,s} = \frac{N_0}{1 + (g_1/g_2)} \quad (4)$$

with $\alpha << \hat{u}$, giving the highest possible population in the excited level independent of laser intensity and collision processes.

As the spatial laser intensity distribution is not homogeneous, different degrees of saturation in the collection volume have to be considered. With

$$V \equiv \int \frac{N_2(x,y,z)}{N_0} dxdydz, \quad (5)$$

integration over the beam diameter gives

$$V = z \int \frac{(g_2/g_1) \cdot \hat{u} \cdot f(x,y)}{[1 + (g_2/g_1)] \cdot \hat{u} \cdot f(x,y) + \alpha} \cdot \left\{1 - \exp - \langle([1 + (g_2/g_1)] \cdot \hat{u} \cdot f(x,y) + \alpha) \cdot \tau_L\rangle\right. \cdot \frac{\Omega(x,y)}{\Omega_o} dxdy; \quad (6)$$

where z is the observed length of the collection volume in the axis of the laser beam; $f(x,y)$ is a local intensity factor which has to be determined experimentally, and $\Omega(x,y)$ is a local imaging factor. With V evaluated from Eq. (6) and the experimentally obtained absolute fluorescence intensity I_{Fl}, the number density N_0 is calculated from

$$I_{Fl} = A_{21}\cdot h\cdot\nu\cdot\frac{\Omega_o}{4\pi}\cdot V\cdot N_0; \qquad (7)$$

where ν is the fluorescence frequency and Ω_o the collection angle. If the ground state population is thermal, and if the local temperature is known, the total species number density N_T can be evaluated using the Boltzmann factor f_T

$$N_T \simeq N_0/f_T,\ f_T = \frac{g_1}{Q}\cdot\exp-(E_1/kT). \qquad (8)$$

The integral V (Eq. 6) was calculated for typical values of $\hat{u}$ considering a two-dimensional field of at least 30 × 30 average local intensity factors $f(x,y)$, which were measured by translating a pin-hole across the laser beam. $f(x,y)$ displays a slightly asymmetric distribution with Voigt profile characteristics. In our calculations we applied

$$\hat{u} \equiv u = u_{\nu,\max}\cdot B_{21}. \qquad (9)$$

This is permissible in our case, because the laser bandwidth is much larger than the molecular bandwidth.

The laser intensity is given by the following equation:

$$I_L = c\cdot u_{\nu,\max}\cdot\int f(x,y)dxdy\cdot\int f(\nu)d\nu. \qquad (10)$$

where $f(x,y)$ is the spatial laser intensity distribution as above, and $f(\nu)$ is the spectral profile of the laser, both normalized so that the maxima of the distributions are 1. In Fig. 1, the dependence of the integral V on u is shown schematically for a two-level system. For low laser intensities, V increases linearly with increasing u. For very high values of u, V approaches a saturation limit. In Fig. 1, the saturation degree S is obtained, for example, for a filter of 50% transmission in the laser beam. In this case S is given by

$$S = \frac{V(0.5u)}{V(u)} \qquad (11)$$

as indicated by the squares in Fig. 1. For linear conditions, S starts at 50%; for complete saturation, S approaches 100%.

The circles in Fig. 1 show for one example that for each measured saturation degree S_{exp}, corresponding values of V_{exp} and u_{exp} are obtained, using the theoretically constructed curve for S. The number density N_0 can be calculated from Eq. (7), if the absolute fluorescence intensity is known. [In modification of the strict two-level system for this calculation, the overall decay rate α in Eq. (6) includes allowed spontaneous emission and quenching to a set of lower levels as well as contributions of rotational energy transfer.] α was obtained experimentally from the time-resolved fluorescence decay. Comparison of the two-level model, using an empirical α, with a multi-level model, including rotational relaxation, showed that deviations from $N_0 = N_1 + N_2$ were less than 10% under our experimental conditions (see also Lucht[17]).

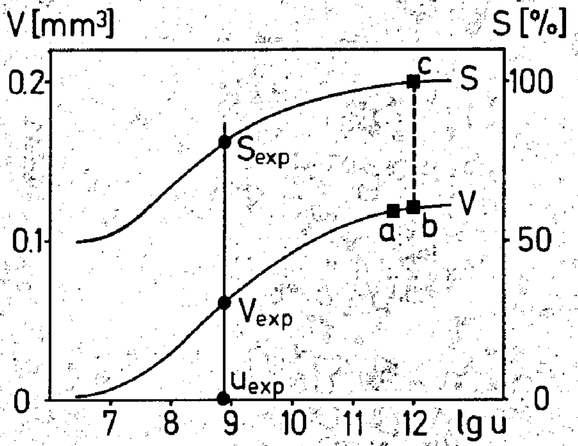

FIG. 1. Schematic diagram of integral V (Eq. 6) and saturation degree S vs. laser intensity u for a two-level model. *Squares:* example for the construction of the curve S from V (see Eq. 11); a: V(0.5 u), b: V(u), c: resulting S. *Circles:* S_{exp}: measured saturation degree; V_{exp}: corresponding integral V from which the number density is calculated; u_{exp}: corresponding laser intensity u from which the approximate oscillator strength is determined.

To determine the absolute fluorescence intensities, two independent calibration procedures were used. The first method was applied for the CH as well as for the OH experiments. The overall efficiency factor for the entire optical detection system, including the imaging lens and mirrors, the monochromator, and the photomultiplier was obtained in two steps. First, the transmission of the monochromator and the efficiency and gain of the photomultiplier were measured using a calibration pulse. For this the laser was tuned to the fluorescence wavelength and scattered at the surface of a grounded quartz disk which was mounted on the top of the burner head. The quartz plate was adjusted so that the scattered light filled the fluorescence collection angle Ω_o; the imaging geometry was the same as in the fluorescence experiment. Residual polarization of the scattered light was negligible. For different incident laser intensities, the absolute intensity of the scattered light was measured with the calibrated photodiode directly behind the entrance slit of the monochromator. This was related to the signal obtained by the photomultiplier at the exit slit corresponding to the same scattered light intensity. Additionally, the losses of the imaging lens and mirrors were measured using the attenuated and enlargened laser beam as light source and the photodiode as detector.

An alternative calibration was performed for the OH experiments. A common method uses Rayleigh scattering to evaluate the efficiency of the optical detection system.[5,18,19] This has the disadvantage of producing the scattered light at the laser wavelength, so that a careful discrimination against stray light is necessary. As in Ref. 20, we deduced the detection efficiency from a Raman experiment. The scattered light produced by N_2 from ambient air in the Q-branch at $\tilde{\nu}_0 + 2331\ \mathrm{cm}^{-1}$ was monitored for different known laser intensities. The absolute differential cross section of the N_2 Q-branch has a well established value of $(5.05 \pm 0.1) \cdot 10^{-48} (\tilde{\nu}_0 - \tilde{\nu}_{N_2})^4$ $\mathrm{cm}^6/\mathrm{sr}$.[21] The different efficiencies of the photomultiplier and the monochromator at the slightly displaced Raman wavelength have been taken into account. The detection efficiency of the entire optical system obtained from the Raman method differed for all applied laser intensities by less than 20% from that measured by the first calibration procedure, thus showing satisfactory agreement if the experimental difficulties are considered. With V_{exp} corresponding to the experimentally observed average saturation degree S_{exp} and with the absolute fluorescence intensity I_{Fl}, we can finally calculate N_0 from Eq. (7) and N_T from Eq. (8).

Fig. 1 provides additional information on the reliability of our determination of absolute radical concentrations. From the intercept u_{exp} corresponding to a particular experimental value of S_{exp}, an approximate oscillator strength f_{12} can be calculated:

$$f_{12} = \frac{4 \cdot m_e \cdot h \cdot \epsilon_0 \cdot \nu}{e^2} \cdot \frac{g_2}{g_1} \cdot B_{21}. \qquad (12)$$

where B_{21} is obtained from Eq. (9) with $u = u_{\mathrm{exp}}$, $u_{\nu,\mathrm{max}}$ is expressed by experimental parameters (Eq. (10)). Oscillator strengths for the CH[22] and OH[23,24] bands considered in the experiments are well known. One of the advantages of our method therefore is, that we have the possibility to check the validity of the assumption used for the calculation of absolute number densities.

The LIF determination of the local temperatures necessary for the evaluation of the total species number density N_T (Eq. (8)) can lead to considerable errors, if non-thermal populations are probed.[23a,25] In this work, CH and OH rotational temperatures of the excited molecules were determined after a sufficient time delay with respect to the laser pulse, so that the population had thermalized. This delay was determined to be of the order of 150–250 ns by recording the ratios of the fluorescence intensities of different line pairs as a function of delay time until these ratios remained constant, within experimental error. The temperatures obtained seem reasonable for a low-pressure flame with large heat conduction to the burner plate. Comparison with measurements by a radiation-loss corrected[26] thermocouple gave good agreement with the rotational temperatures.

Figures 2 and 3 and Table I display the experimental results. Fig. 2 shows approximately 70 values of S_{exp} for CH, measured with a filter with 50% transmission. The laser intensity was varied by 3-1/2 orders of magnitude by inserting more and more filters into the laser beam. In this case, a four-level model had to be used, because $Q^{0,0}$ (7) and $Q^{1,1}$ (7) were excited within the laser bandwidth. Because of the laser being centered on the (0,0) transition and detuned from the (1,1) Q (7) line, the latter was saturated at higher laser intensities than the (0,0), Q (7) line, resulting in a distortion of the

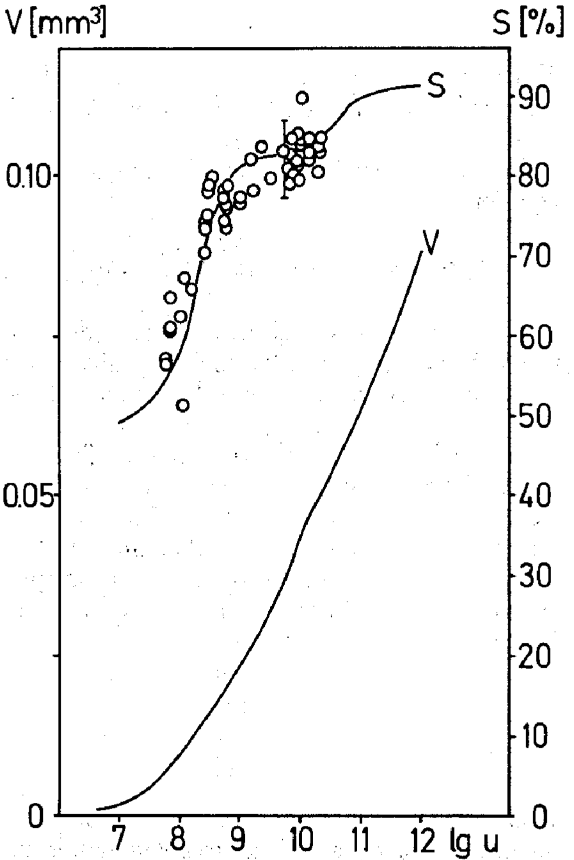

FIG. 2. Integral V and saturation degree S vs. laser intensity u. $CH(A^2\Delta - X^2\Pi)$ $Q^{0,0}$ (7) and $Q^{1,1}$ (7) were excited, $R^{0,0}$ (6) and $R^{1,1}$ (6) were monitored at h = 2.6 mm above the burner surface in a 13 mbar, ϕ = 1.2 C_2H_2—O_2 flame with a local temperature of 1750 K in the collection volume.

TABLE 1

CH and OH number densities determined by saturated fluorescence for a 13 mbar, $\phi = 1.2$ C_2H_2—O_2 flame

Molecule	CH	CH	OH
spectral band system	$A^2\Delta - X^2\Pi$	$A^2\Delta - X^2\Pi$; 0—0	$A^2\Sigma^+ - X^2\Pi$, 0—0
excitation	$Q^{0,0}$ (7), $Q^{1,1}$ (7)	P (7)	$Q_2(16.5)$, $^QR_{12}(16.5)$
observation	$R^{0,0}$ (6), $R^{1,1}$ (6)	R (5)	$P_2(17.5)$, $^PQ_{12}(17.5)$
height above burner surface	2.6 mm	2.6 mm	7.5 mm
temperature	(1750 ± 80) K	(1750 ± 80) K	(2000 ± 100) K
number density	$1.1 \cdot 10^{13}/cm^3$ (±25%)	$1.1 \cdot 10^{13}/cm^3$ (±20%)	$8.9 \cdot 10^{14}/cm^3$ (±15%)
mole fraction	200 ppm	200 ppm	18 500 ppm
oscillator strength			
experiment	$(2.5 - 10) \cdot 10^{-3}$	$(2.5 - 10) \cdot 10^{-3}$	$(0.4 - 3.3) \cdot 10^{-3}$
literature	$5.2 \cdot 10^{-3}$ [22]	$5.2 \cdot 10^{-3}$ [22]	$1.1 \cdot 10^{-3}$ [23,24]

V curve and a plateau in the S curve (Fig. 2).

Table I shows the calculated number densities for this experiment in the first column. For the four-level system indicated in the first line, 200 ppm of CH were measured with a statistical deviation of ±25%. This number density corresponds to a height *h* of 2.6 mm above the surface of the burner, where the CH maximum was found, and a measured local temperature of (1750 ± 80) K. As shown in the second column of Table I, an equivalent experiment for a two-level system resulted in a very good agreement for the CH concentration. The approximate oscillator strengths determined from both experiments were equal to the value of Ref. 22 within a factor of two, corresponding to the accuracy which may be expected for the simultaneous action of different error sources, which of course, have different degrees of influence at different laser intensities.

Fig. 3 shows 48 values of S_{exp} for OH measured by inserting a filter of 30% transmission into the laser beam. The laser was tuned to the Q_2 (16.5) transition, but within the laser bandwidth, $^QR_{12}$ (16.5) was also excited, although the radiation density for this transition was much weaker due to the detuning and the lower Franck-Condon factor. As in Fig. 2, a bend in the saturation curve S is observed for this reason.

As considerable polarization effects have recently been found in OH fluorescence experiments,[27,28] we examined this for our experimental conditions. For different incident laser polarizations, only minor differences in the fluorescence signal could be

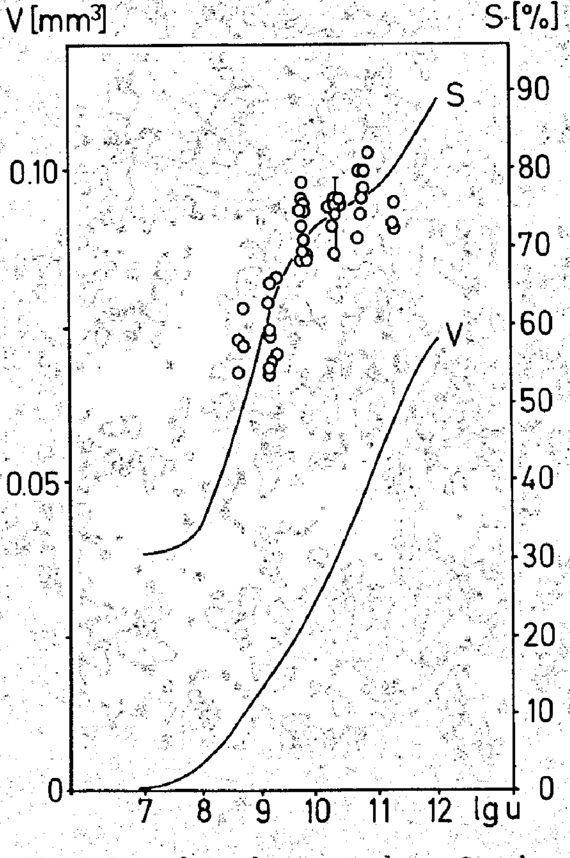

FIG. 3. Integral V and saturation degree S vs. laser intensity *u*. OH($A^2\Sigma^+ - X^2\Pi$, 0—0)$Q_2(16.5)$ and $^QR_{12}(16.5)$ were excited, $P_2(17.5)$ and $^PQ_{12}(17.5)$ were monitored at $h = 7.5$ mm above the burner surface in a 13 mbar, $\phi = 1.2$ C_2H_2—O_2 flame with a local temperature of 2000 K in the collection volume.

observed which did not need to be corrected.

The absolute number density calculated from the OH experiment is given in the third column of Table I; 18500 ppm of OH were measured with a statistical deviation of ±15%, corresponding to a height of 7.5 mm above the burner surface, where the OH maximum was observed, and the measured local temperature was 2000 ± 100 K. The statistical deviation of ±15% is not evident from Fig. 3. The measured fluorescence intensities I_{Fl} are shown in Fig. 4 as a function of laser intensity *u*. The ratio I_{Fl}/V_{exp} is also displayed and is proportional to N_0 (Eq. (7)); V was taken from Fig. 3. The ±15% interval given by the standard deviation which is indicated by horizontal lines in Fig. 4 encloses 41 of the 48 values of I_{Fl}/V_{exp}.

The mole fraction of 18500 ppm is in good agreement with the results of preliminary OH experiments,[13] where both the saturated fluorescence and the linear fluorescence method following Ref. 29 were used. Furthermore, very similar OH number densities have been found in hydrogen[7] and propane[29] low-pressure flames. The approximate oscillator strengths determined from the intercepts in Fig. 3 were equal to the literature value[23,24] within a factor of 3.

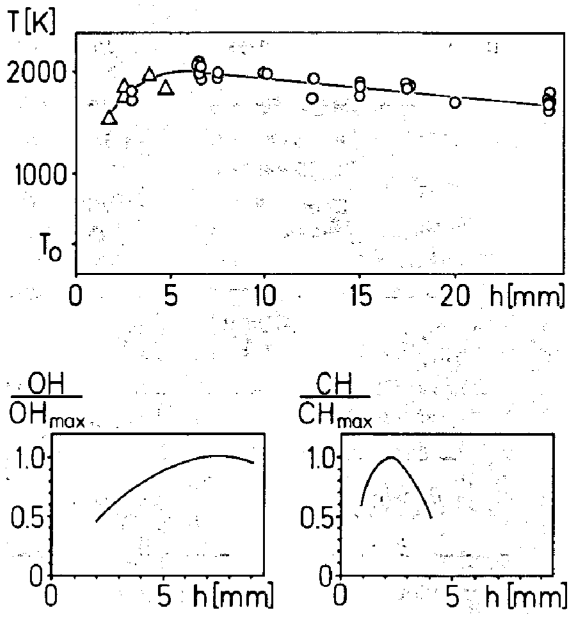

FIG. 5. a) Temperature T vs. height *h* above the burner surface; O: OH rotational temperatures; Δ: CH rotational temperatures; b) CH concentration profile, CH_{max} see Table I; c) OH concentration profile, OH_{max} see Table I.

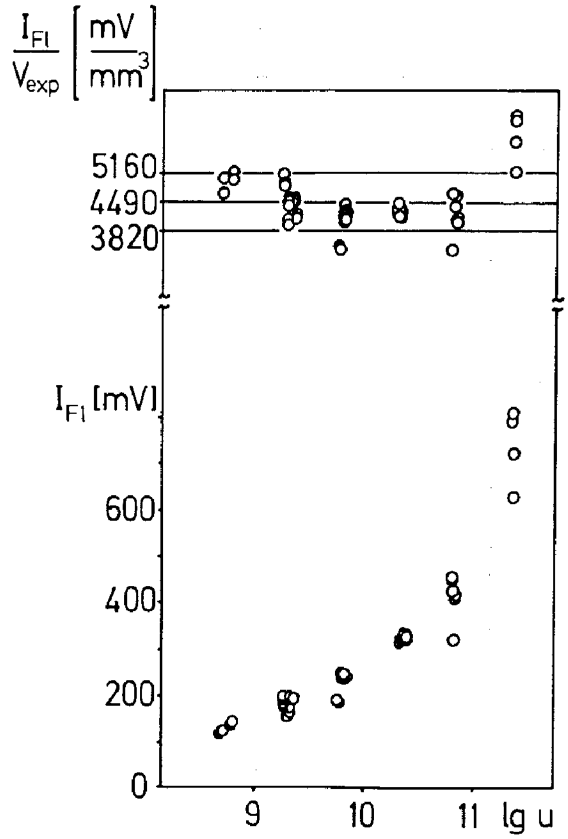

FIG. 4. Fluorescence intensity I_{Fl} and I_{Fl}/V_{exp} vs. laser intensity *u* for the experiment shown in Fig. 3. The average value of I_{Fl}/V_{exp} and the error limits of ±15% given by the standard deviation are indicated by horizontal lines.

The measured rotational temperatures and the concentration profiles of CH and OH as a function of the height above the burner surface are shown in Fig. 5. We did not perform a chemical-kinetic analysis of our profiles. It is doubtful whether a one-dimensional flame program, which is available to us,[30] can adequately predict the radical profiles obtained with our small burner. We suspect that there may be a non-negligible amount of radial diffusion. It was not the primary intention of this work to produce data which can be safely evaluated kinetically by comparing them with a one-dimensional flame program. For this purpose, a burner with a larger diameter should be used.

The determination of accurate absolute number densities in flames at atmospheric and higher pressures will require a proper description of the relaxation processes. Several attempts have been made[17,31–36] to model the energy transfer. The basic idea of our multi-level relaxation model is to describe state-to-state transfer probabilities according to a combined exponential/power law. Preliminary results of the model are shown in Fig. 6. Details of the calculations will be presented in a separate publication.

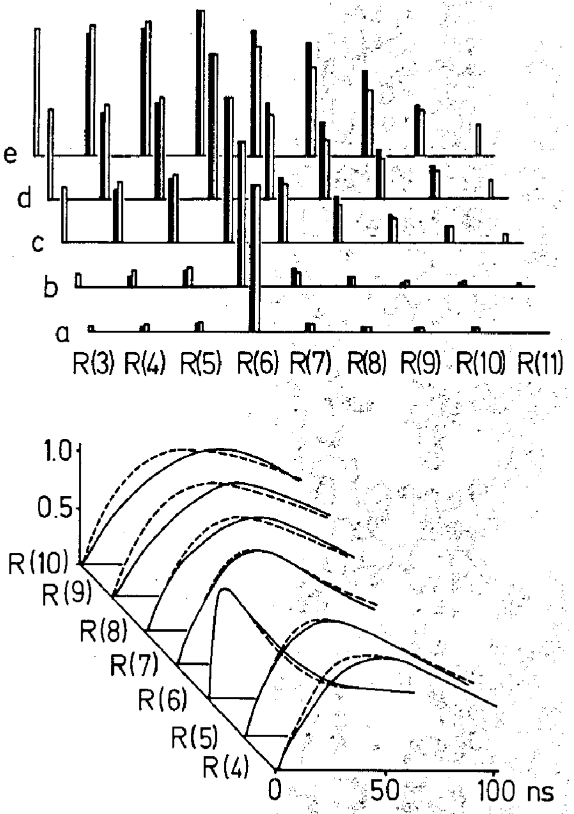

FIG. 6. Schematically displayed CH spectra (top) and their time development (bottom) in a 13 mbar C_2H_2—O_2-flame. ——, ■ experiment; - - -, □ relaxation model; a: t = 10 ns, b: 20 ns, c: 50 ns, d: 70 ns, e: 100 ns. The probabilities R_{ji} of downward state-to-state rotational energy transfer were modeled by $R_{ji} = R_o \cdot \exp[-(\Delta E/\alpha_R)^d]$. The parameters R_o and d or R_o and α_R were optimized by comparison of experiment and computer model. For the CH experiments we obtained either: $R_o = 2.3 \cdot 10^8$ s^{-1}, $\alpha_R = 1$ cm^{-1}, $d = 0.23$; or $R_o = 4.0 \cdot 10^7$ s^{-1}, $\alpha_R = 400$ cm^{-1}, $d = 1$. The first set of coefficients with variation in R_o and d seem to predict our data slightly better than the second set where d was set equal to 1.

Conclusions

An attempt has been made to demonstrate that the method of laser-induced saturated fluorescence can be applied for the accurate determination of radical concentrations in low-pressure flames, provided that the validity of some assumptions which have been discussed in the text can be verified. The extension of the method to higher pressures implies the knowledge of state-to-state energy transfer constants for the appropriate flame conditions or the description of such collision processes by adequate modeling.

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COMMENTS

S. S. Penner, University of California, San Diego, USA. How accurately did the absolute intensities (oscillator strengths) obtained for OH and CH agree with other measurements of these parameters?

Authors' Reply. As displayed in Table I, the extrapolated oscillator strengths typically deviate from the literature values of Ref. 22 (CH) and Ref. 23, 24 (OH) by factors of 2 to 3, which may be expected for the extrapolation in a logarithmic scale. Therefore, we do not recommend this as a method for the determination of oscillator strengths with high accuracy, but rather as a control for the reliability of the evaluated number densities.

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R. A. Copeland, SRI International, USA. Quenching rates for OH are found to decrease as the rotational energy increases in a low pressure flow cell.[1] Is there any evidence of this effect in your experiments and would your experiment be sensitive to such a variation?

REFERENCE

1. R. A. Copeland and D. R. Crosley, Chem. Phys. Lett *107,* 295 (1984).

Authors' Reply. The experiments for the determination of OH and CH concentrations have been performed using selected line pairs for excitation and fluorescence. Overall decay rates including spontaneous and stimulated emission, quenching, and relaxation for particular excited levels have been measured under different flame conditions; only this overall decay rate is needed for our calculations. We did not perform a study of quenching rate dependence on rotational level for our flame up to now. The time resolution of our experiment is sufficient to give differences in overall decay rate on the order of a nanosecond, but the amount of quenching within the overall decay rate cannot be obtained directly from the measured time-dependence of the fluorescence signal.

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D. R. Crosley, SRI International, USA. You mentioned determining temperature from the rotational distribution in the excited state, after a time delay. How long did you need to wait for thermalization to occur? Were there differences for different initially excited rotational levels, or between OH and CH? did you make comparison with ground state temperatures from excitation scans?

Authors' Reply. The delay times were on the order of 150 to 250 ns for the 13 mbar flame and 100 ns for the 40 mbar flame, where the thermalization occurred slightly faster for CH than for OH. Most of the temperature measurements were performed exciting one strong rotational transition for each radical; test measurements with different excited lines did not result in different temperatures within our experimental error of ±3% to ±5%. We did not take excitation spectra for comparison, considering the agreement between both CH and OH temperatures for all the flame conditions investigated.