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Measurements of picosecond laser induced fluorescence from gas phase 3-pentanone and acetone: Implications to combustion diagnostics

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Abstract. The effective lifetimes of the first excited electronic state of 3-pentanone and acetone have been measured at temperatures between 323 K and 723 K at pressures of nitrogen and air between 0.001 MPa and 1.0 MPa. The ketone molecules were excited in a cell with picosecond laser radiation at a wavelength of 266 nm and the relaxation of the radiative emission was measured temporally resolved with a streak camera. Changes in the effective lifetime of the emission were observed with pressure and temperature. The effective lifetime increased or reached a maximum with increasing pressure of nitrogen. Temperature was found to have a quenching effect on the emission. In the full range of temperature at pressures between 0.1 MPa and 1.0 MPa, acetone showed a larger sensitivity to both temperature and pressure compared to 3-pentanone. Mixtures of 3-pentanone and air did not react at temperatures lower than 548 K when the concentration of 3-pentanone was kept low. The effective lifetime varied less than ±20% between 323 K and 473 K at pressures of air or nitrogen between 0.1 MPa and 1.0 MPa.

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Laser-induced fluorescence (LIF) techniques have become quite important in the characterization of different combustion phenomena, see e.g. [1]. The lasers used generally operate in the UV-spectral region, which allows the detection of a variety of organic species formed during combustion such as PAH. In combustion engine experiments isooctane (IO) is often used as a standard liquid fuel. The studies are frequently focused on mixing and evaporation processes in the engine prior to ignition. Spectroscopic grade isooctane is not supposed to fluoresce in the UV-spectral region but the addition of some fluorescing species (dopants) allows in principle the application of LIF. Fluorescence from impurities in isooctane will then be of no importance if it is much weaker.

The final aim in an experiment is generally to map the spatial distribution of the fuel inside the engine. The distribution of the dopant and its fluorescence-emission intensity, which is the quantity which is truly monitored, should then preferably be proportional to the fuel distribution. However, this cannot be expected to be the case if the fluorescent abilities of the dopant molecules, i.e. the fluorescence yield, may change with parameters such as the temperature and the pressure of nitrogen and oxygen. Therefore it is necessary to do an investigation of the sensitivity of the fluorescence emission properties to the parameters that are expected to change inside the engine. When such an investigation has been made it would in practice be possible to compensate for these variations once the local variations of the temperature and the pressure are known. If the effective lifetime of the fluorescence is measured it may be used as a calibration factor as it proportional, within a degree of uncertainty, to the fluorescence yield. The most common flowfield tracers that have been used as dopants are: acetaldehyde [2, 3], acetone [4], biacetyl [5, 6] and TMPD [7, 8].

Acetaldehyde has a quantum yield which is rather typical for substances containing a keto-group, i.e. on the order of 0.001. The evaporation characteristics are not comparable with those of isooctane and therefore it is not suggested to engine applications. Acetone has a fluorescence spectrum not much different from that of acetaldehyde also its quantum yield is of the same order. The evaporation characteristics are still too dissimilar with those of IO. Biacetyl has evaporation characteristics that are more similar to IO but they deviate considerably at temperatures higher than 350 K. UV-absorption results in a very low fluorescence quantum efficiency and all the emission is through phosphorescence, which is sensitive to the presence of oxygen. TMPD emits fluorescence which is strongly quenched by oxygen and therefore it is very difficult to discriminate between a loss of fluorescence and a lower degree of evaporation in imaging experiment.

During the last years there have been applications using 3-pentanone (3P) also known as diethyl ketone as a dopant [9–11]. The main reason is the very good agreement with the evaporation characteristics of IO (up to 410 K). The fluorescence quantum yield is similar to that of acetone. 3P solved in IO has a higher vapor pressure than IO, which can be explained as due to the repulsion that the majority species exerts on the minority species in the solution and considering this effect 2-hexanone seems to be a better choice than

3P [12]. 2-hexanone is known to be toxic whereas the toxicity of 3P is not specified.

The fluorescence yield is given by k_r/k where k_r is the radiative decay rate and k is the total decay rate, which is composed of contributions from stimulated emission, spontaneous emission, ionization, internal conversion, dissociation and collisional quenching. For larger molecules the separation between energy levels tends to decrease as the number of atoms increases. In this case internal vibrational relaxation (IVR) becomes important and also processes such as intersystem crossing and internal conversion contribute to an increasing complexity of the relaxation dynamics. The result is that fluorescence emission can be observed from several states simultaneously in an ensemble of molecules. The temporal evolution of the fluorescence emission does no longer obey a simple one-exponential decay, but a decay that in the simplest cases can be described as a sum of one-exponential functions, see e.g. [13]. Molecules such as 3-pentanone and acetone are in the intermediate region but behave as large molecules when they are excited to high vibrational energies where the energy separation is small. Thus due to IVR, an ensemble of molecules with different content of vibrational energy can coexist. Further relaxation may be obtained by introducing a buffer gas such as nitrogen so that its molecules can absorb the excess of vibrational energy. It is therefore plausible that the effective lifetime of fluorescence emission may change with temperature and pressure of nitrogen or oxygen.

In this paper we have studied time resolved laser-induced fluorescence emission from 3-pentanone and acetone after ps-laser excitation at a wavelength of 266 nm, under various conditions of temperature and of pressure of nitrogen and air. These LIF measurements can be considered not only a complement to the measurements made by Grossman et al. [14] at excitation wavelengths of 248 nm, 277 nm and 312 nm, but also an extension of the study of relaxation in the temporal and spectral domains. The attention in these measurements has been focused on 3-pentanone where also a spectral investigation was made. The results have been concentrated on the determination of the effective lifetime of the fluorescence emission at various temperatures and pressures of nitrogen and air. We try to expose the main features of these dependencies with experimental results, some brief theoretical considerations and calculations and discussions considering the validity of the results. The objective of the paper is to give indications on the reliability of applying 2D-imaging of the dopant 3P to achieve quantitative information in engine applications, and give the possibility to compensate for varying fluorescence yields.

1 Experimental Setup

A setup of the experiment is shown in Fig. 1. Laser pulses from a 10 Hz mode-locked Nd:YAG laser (Quantel YG572-C) (1) with 35 ps duration at a wavelength of 1064 nm was frequency doubled in a KDP crystal (2) to 532 nm and subsequently quadrupled (3) to 266 nm. The horizontally polarized laser pulse was spectrally isolated from residual 532 nm radiation with a dichroic mirror (4) and was then sent to a delay line ≈ 50 ns by dielectric mirrors (5). The delay was used to match the electronic delay times of the receiving electronics and contained a contracting telescope to reduce the extension of the transversal spatial mode. A rotating prism arrangement (6) was used to obtain a rotation of 90° of the direction of polarization and to send the pulse through an aperture (7) onto a dielectric mirror placed under the measurement cell. The laser pulse was then focused with a $f = 100$ mm quartz lens into the cell (8), which was connected to the evaporation chamber (9) through a valve. The laser radiation in the focus was polarized in the horizontal plane in the direction orthogonal to the axis of collection of the fluorescence emission. Fluorescence was collected with a $f/2$, $f = 100$ mm achromatic UV lens (10) onto the slit (slit width 100 μm) in front of the photocathode of the streak camera (Delli Delti Dellistrique III) (11) or by an aluminium-mirror (12) onto the slit (slit width 200 μm) of a spectrometer (Jarrell-Ash, 150 l/mm blazed at 450 nm) with a dispersion of 24 nm/mm (13). Appropriate filters were placed in front of the slit of the streak camera or the spectrometer. The streak camera was triggered by an electronic pulse from a diode (14), which was exposed by a reflection from the 1064 nm laser pulse inside the laser. The image on the output phosphor of the streak camera was captured with a CCD camera (EG&G PARC 1430-P, 576×384 pixels) (15). The camera was connected to a control unit (16) and personal computer (17) for data storage and further evaluation. The CCD camera was run with accumulations of 50 or 100 exposures and with a gate of 100 ms. In every fluorescence measurement a background accumulation was recorded and subtracted from the signal accumulation. The spectrometer was not used simultaneously with the streak camera due to the mirror arrangement. The signal from the spectrometer was recorded with a diode array detector (EG&G PARC 1420 UV solid state) (18), connected to an optical multichannel analyzer (PARC OMA model 1461) (19) followed by a personal computer (20). The detector was operating in the free running mode with a continuous gate and a sampling frequency of 10 Hz and with a measurement time corresponding to 100 laser shots.

The cell had a dual inlet/outlet port which was connected to the buffer gas bottles containing air (21) and nitrogen (22) and to the vacuum pump (23). Diethyl ketone (3-pentanone, 3P) (Merck, purity $\geq 99\%$) and acetone (Ac) (Merck, Pro Analysi) were used. The cell was made of stainless steel and was operative in a temperature range of 323 K to 723 K and in range of gas pressures up to 1.0 MPa. The cell could be evacuated through the dual inlet/outlet port and the lowest pressure of the experiment was determined by the resolution of the piezo-resistive transducer (Special Instruments PA-13/04) to 0.001 MPa. The temperature of the cell was controlled by changing the current through the heating wires around the cell and it was measured with a Chromel-Alumel thermocouple (Thermocoax FK 10/25) situated 5 mm from the measurement site (the laser focus).

The ketone gas was introduced into the measurement chamber of the cell through an inlet port connected to the reservoir containing the ketone in both gas phase and liquid phase. The gas phase of the ketone was held at equilibrium with its liquid phase and the state of the equilibrium could be varied by changing the temperature of the reservoir with heating wires. An amount of ketone up to a desired pressure between 0.001 and 0.02 MPa was injected between the time of the opening and the closing of the port. The concentration was then easily obtained from the perfect gas equation as the

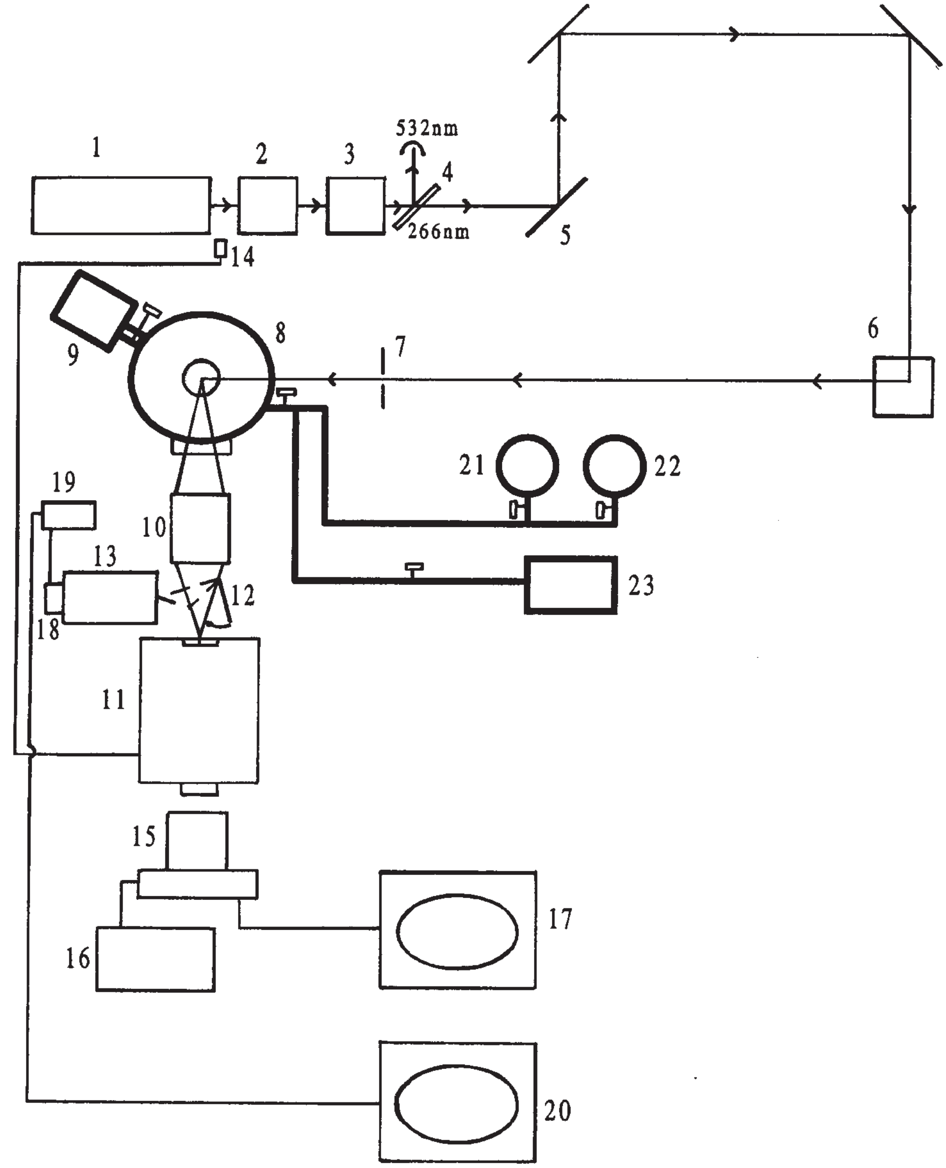

Fig. 1. The experimental setup. 1 – 10 Hz mode-locked Nd:YAG laser; 2 – KDP crystal; 3 – quadrupled; 4 – dichroic mirror; 5 – dielectric mirrors; 6 – rotating prism arrangement; 7 – aperture; 8 – cell; 9 – evaporation chamber; 10 – UV lens; 11 – streak camera; 12 – aluminium mirror; 13 – dispersion of 24 nm/mm; 14 – diode; 15 – CCD camera; 16 – control unit; 17 – personal computer; 18 – diode array detector; 19 – optical multichannel analyzer; 20 – personal computer; 21 – gas bottles containing air; 22 – gas bottles containig nitrogen; 23 – vacuum pump

temperature was measured. After the closing of the inlet, air or nitrogen could be added from the dual inlet/outlet port to the desired pressure measured with the transducer.

2 Experimental

2.1 Spectral investigation

The conditions of the experiments were to as a large degree as possible maintained such that they would be of relevance for engine experiments. In particular, it was decided to operate at relatively low concentrations of 3P in the cell. The greatest difference with respect to ordinary engine conditions was that pressure and thermally dynamic processes could not be studied as the cell was operated under static conditions. The shortest time from the start of a measurement after the introduction of the ketone and buffer gas was about one minute.

The lowest possible resolvable concentration was about $0.4\,\mathrm{mol/m^3}$ at 323 K corresponding to the resolution of the transducer (0.001 MPa) given above. The signal from the fluorescence was low and in order to obtain enough signal with sufficient signal to noise ratio (S/N) it was decided to carry out the experiments with as high pulse energy as possible without introducing anomalies in the measured spectral profiles.

The first measurements were therefore set to investigate possible dependencies of the spectral emission from 3P on laser power, residence time in the cell and exposure to laser radiation at different temperatures and pressures of nitrogen and air.

The laser intensity used in the experiments was $200\,\mathrm{GW/cm^2}$ or lower. No significant changes of the spectral profiles, i.e. the spectrally resolved signal counts divided by the maximum value of the same spectrum, were found when the laser pulse energy was changed with one order of magnitude. The spectral profiles were also insensitive to changes of the concentration. The intensity of the total fluorescence emission (IFE) was proportional to the concentration of 3P while it showed a weaker dependence with respect to laser power when the focusing lens was used, probably due to saturation effects.

The pure substance of 3-pentanone and mixtures with nitrogen showed good stability both to radiation and residence time up to 30 min or more for temperatures of 473 K or lower. The IFE for the pure substance would first decrease soon after the inlet, but was then stabilized after ≈ 2 min. Mixtures with nitrogen or air showed an increase of the IFE which would reach a maximum and then stop to increase after 2–5 min, depending on pressure and temperature.

In Fig. 2 are shown some uncorrected spectral profiles recorded for different $3P/N_2$ mixtures and for pure 3P at 333 K where the concentration of 3P was held at $1.4\,\mathrm{mol/m^3}$ (0.004 MPa). The first and second order scattering peaks observed at 266 nm and 532 nm were due to partial transmission of the WG 280 filter at 266 nm. The spectral profiles peaked at about 420 nm and the 5% of peak-intensity values are at 330 nm and 580 nm for the pure substance. A slight narrowing of the full width at half maximum (FWHM) was observed as the pressure of the nitrogen was increased. Measurements on acetone and on its mixtures with air or nitrogen yielded similar results. The differences were mainly observed in that the bandwidth of the acetone spectrum was slightly larger ≈ 10 nm (FWHM). Due to the similarity of the results between Ac and 3P most of the measurements were made only on 3P. The results of these measurements are reported below.

Mixtures 0.004 MPa 3P/0.05 MPa air showed the same behaviour as the 0.004 MPa 3P/0.05–0.5 MPa N_2-mixtures. The ratio of the IFE between 0.003 MPa 3P/1.0 MPa N_2 and pure 0.003 MPa 3P was 2 at 473 K. Air mixtures showed lower values than the corresponding nitrogen mixtures at higher pressures. In Fig. 3 are shown profiles for pure $1.4\,\mathrm{mol/m^3}$ 3P at three different temperatures. More distinct changes in the spectral profiles were observed for the highest temperature with increasing pressure of the gas mixtures, air mixtures in particular. In Fig. 4 are reported the spectral profiles for different mixtures of $3P/N_2$ at 723 K. A shift towards shorter wavelengths was observed as the N_2 pressure was increased. The corresponding results for 3P/air are reported in Fig. 5. The profiles showed much larger changes with increasing pressure with prominent blue shifts of the entire spectra, probably due to changes preceding chemical reactions between 3P and oxygen. The spectral profiles collapsed at air pressures of 0.5 MPa and higher and only strong scattering peaks were present in the profiles, which indicated that either particulate or larger, non-fluorescent molecules were formed.

Changes in the spectrum were sometimes probably caused by photoinduced reactions of 3P with air, since they appeared in combination with a light pulse emitted from the cell when the laser radiation was initiated. These pulses, which were easily observed with the naked eye, appeared in a narrow range of temperatures between 433 K and 463 K and 3P/air combinations about 0.02 MPa/0.5 MPa and were presumably caused by chemiluminescence. In Fig. 6 are reported typical spectra for this event before the fluorescence signal disappeared and only elastic scattering was observed. The shown spectra were composed from two separate recordings in different wavelength regions. There were differences, not only compared to the ordinary spectra from 3P, but also with respect to the ones when spontaneous reactions were observed.

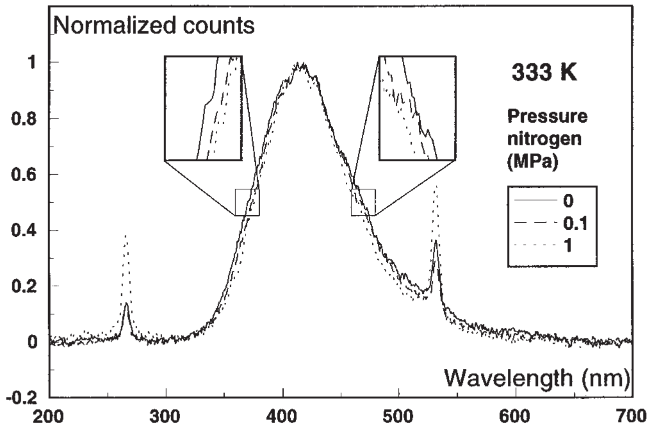

Fig. 2. Spectral profiles (normalized counts) of the laser induced signal from 3-pentanone at 333 K at various pressures of nitrogen. The profiles have not been corrected for the spectral response of the spectrograph/OMA-system. A SCHOTT WG 280 filter was used in front of the entrance slit of the spectrometer

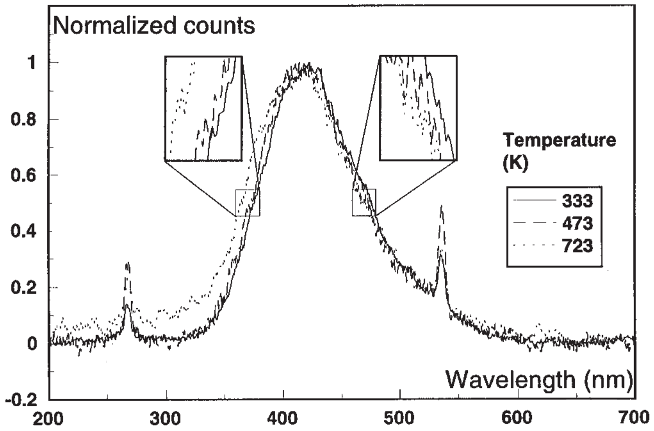

Fig. 3. Spectral profiles (normalized counts) of the laser induced signal from pure 3-pentanone at various temperatures. The profiles have not been corrected for the spectral response of the spectrograph/OMA-system. A SCHOTT WG 280 filter was used in front of the entrance slit of the spectrometer

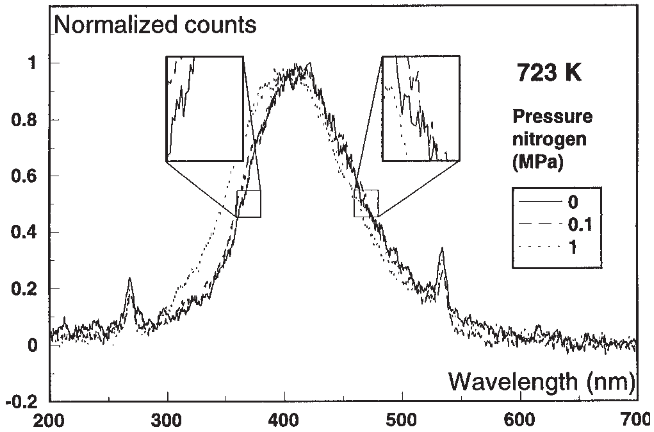

Fig. 4. Spectral profiles (normalized counts) of the laser induced signal from 3-pentanone at 723 K at various pressures of nitrogen. The profiles have not been corrected for the spectral response of the spectrograph/OMA-system. A SCHOTT WG 280 filter was used in front of the entrance slit of the spectrometer

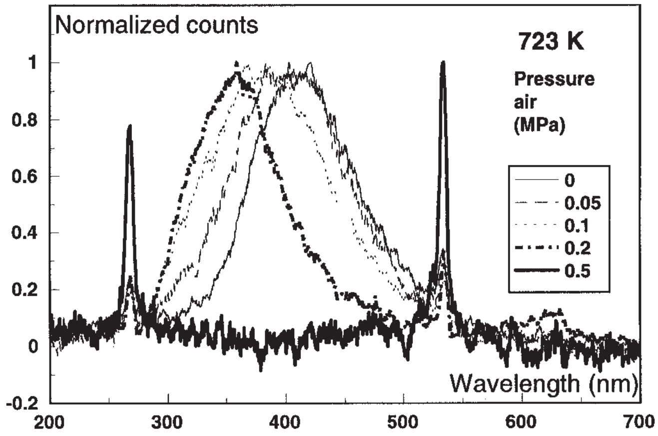

Fig. 5. Spectral profiles (normalized counts) of the laser induced signal from 3-pentanone at 723 K at various pressures of air. The profiles have not been corrected for the spectral response of the spectrograph/OMA-system. A SCHOTT WG 280 filter was used in front of the entrance slit of the spectrometer

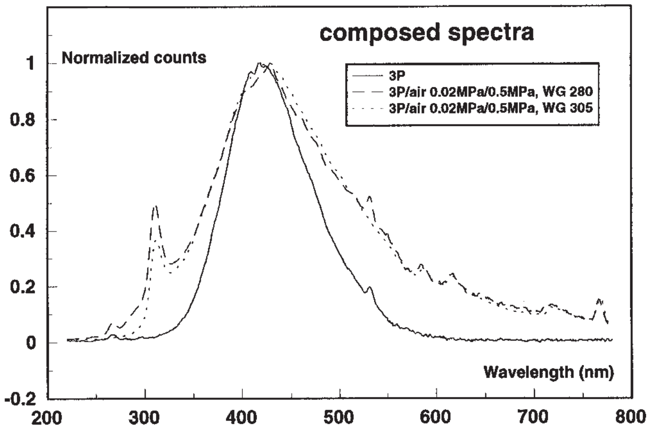

Fig. 6. Spectral profiles (normalized counts) of the laser induced signal from pure 3-pentanone and mixtures with air ($P_{3P}/P_{air} = 0.02\,\mathrm{MPa}/0.5\,\mathrm{MPa}$) at temperatures between 433 and 463 K. The profiles are composed from measurements in two different spectral regions and have not been corrected for the spectral response of the spectrograph/OMA-system

The resolution did not permit the identification of any radical elements, however, the OH radical was most certainly responsible for the peak observed at about 308 nm. In order to avoid photoinduced reactions, most of the measurements reported below were performed with much lower concentrations of 3P (0.002–0.005 MPa, depending on temperature).

Absorption measurements were made on 3P vs. concentration at different temperatures. The absorption was observed to follow a Lambert-Beer's relation. The measured decadic absorption coefficients were: $19\,\mathrm{cm^{-1}mol^{-1}m^{3}}$ at 323 K, $18\,\mathrm{cm^{-1}mol^{-1}m^{3}}$ at 473 K and $15\,\mathrm{cm^{-1}mol^{-1}m^{3}}$ at 723 K.

2.2 Time resolved studies

The time resolved measurements were made with the streak camera operating at a streak speed of 0.89 ns/mm corresponding to 0.020 ns/channel on the CCD chip.

The effective lifetimes of 3P could not be measured with the same resolution as that determined by the CCD, since the apparatus function was of the same order of the shortest lifetimes measured. A deconvolution scheme [15] was therefore used for the lifetime measurements on 3P in order to partly restore the resolution.

The apparatus function was defined by measuring the elastic scattering from 1.0 MPa nitrogen, at the same site of the fluorescence measurements without any optical filter in front of the slit of the streak camera. A typical profile for the apparatus function is shown in Fig. 7. The profile recorded using 3P without any filter compared to the one recorded with a SCHOTT WG 305, also shown in Fig. 7 demonstrate that elastic scattering had a strong influence on the time resolved emission. The SCHOTT WG 305 was therefore regarded as the optimal choice of filter in the fluorescence signal and at the same time reduced the elastic scattering contribution to a level below noise.

The fluorescence quantum yield can be defined, with a rate analysis, as τ_{eff}/τ_{rad}, where τ_{eff} is the effective lifetime and τ_{rad} is the radiative lifetime. τ_{rad} is insensitive to vibrational excitation, see e. g. [16]. Therefore the determination of τ_{eff} in an experiment could easily be translated in terms of the quantum yield and relative changes in the τ_{eff} and in the fluorescence quantum yield would be the same.

The determination of τ_{eff} of the fluorescence emission was the main concern of the measurements below. The effective lifetime was obtained from the best fit of the experimental curve with the convolution of the apparatus function and an exponential function. The decay constant of this function would correspond to the total decay rate k or the inverse of τ_{eff}. The results were generally improved when the exponential function was substituted with a sum of two exponential functions $I_1 \cdot e^{-t/\tau_1} + I_2 \cdot e^{-t/\tau_2}$. The effective lifetime was then defined by $\tau_{eff} = (I_1\tau_1 + I_2\tau_2)/(I_1 + I_2)$. Typical values of τ_1 and τ_2 were 0.2–0.8 ns and 1.5–4 ns, respectively. The relative amplitudes (I_1/I_2) were for the pure substance ≈ 0.2 at 323 K, 1 at 473 K and 8 at 723 K. Mixtures of 3P with air or nitrogen yielded a smaller contribution of the fast decay-

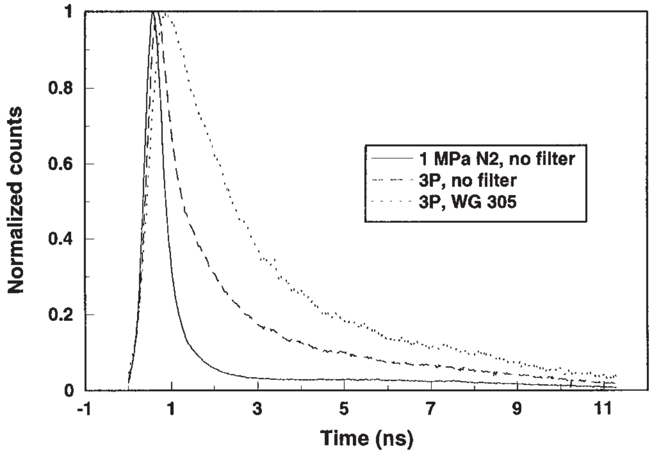

Fig. 7. Temporal profiles (normalized counts) of the laser induced signal during the first 10 nanoseconds from pure 3-pentanone at various temperatures. The profiles have not been corrected for the spectral response of the spectrograph/OMA-system. A SCHOTT WG 305 filter was used in front of the entrance slit of the streak camera in order to obtain maximum fluorescence intensity and at the same time obtain discrimination from elastic scattering

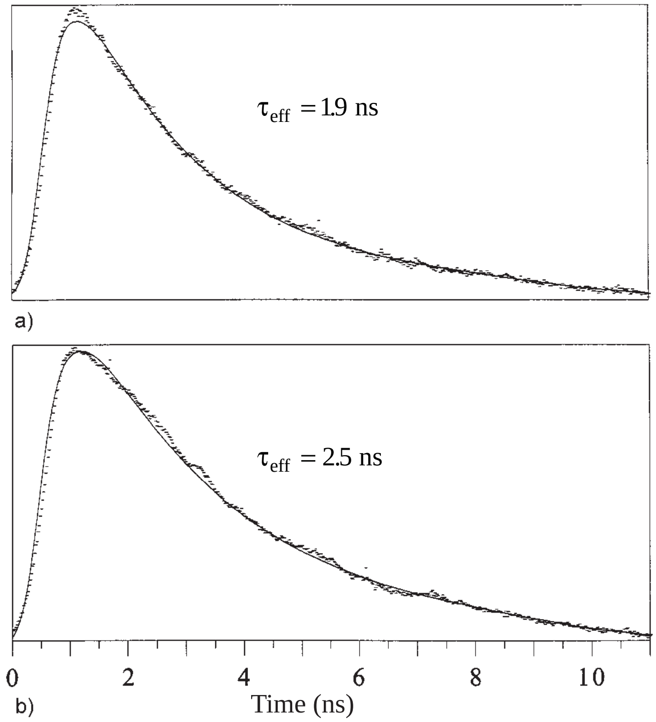

Fig. 8a,b. Time resolved signals of the fluorescence from pure 3-pentanone and a mixture with 0.5 MPa nitrogen at 323 K together with best fit convolutions: **a** pure 3-pentanone with a convolution including a sum of two single exponential functions and (**b**) 0.5 MPa nitrogen mixture with a convolution including a single exponential fuction

component which disappeared at the combination of low temperature and high pressures. In Fig. 8 are shown two typical temporal profiles of the fluorescence emission at 323 K with the corresponding best fits for (a) pure 3P (0.7 mol/m^3 or 0.002 MPa) and (b) for 0.002 MPa/0.5 MPa N_2. The evaluated lifetimes were 1.90 ns (±0.4 ns) and 2.50 ns (±0.4 ns) for the pure substance and the mixture, respectively. The evaluations were made with a sum of two exponential functions for the pure substance and with a single exponential function for the mixture.

The time resolved measurements showed that the temporal profiles were not sensitive to the laser pulse energy. In order to expand the range of laser intensity, measurements were also made with unfocused laser radiation corresponding to a laser intensity of 30 MW/cm^2 i. e. four orders of magnitude lower than for the laser radiation focused with the 100 mm focal length lens. In this low intensity region the IFE showed a linear relationship with the pulse energy. The comparisons were made at 473 K and at different pressures of nitrogen and the difference between lifetimes in the two type of measurements were within the error of the measurements. The relative changes of τ_{eff} and IFE with pressure of nitrogen or air were found to be the same in the two cases. The following experiments were made with the focused laser radiation since it was possible to use lower concentrations of 3P for a given S/N, further the width of the apparatus function was smaller, which in principle allowed a better resolution for the determination of the lifetime.

A check was made to see how the change in lifetime corresponded to the change in IFE with temperature for the pure substance. The decrease of IFE between 323 K and 723 K, when the changes in the extinction also were taken into account, was 17% lower than that of the effective lifetime.

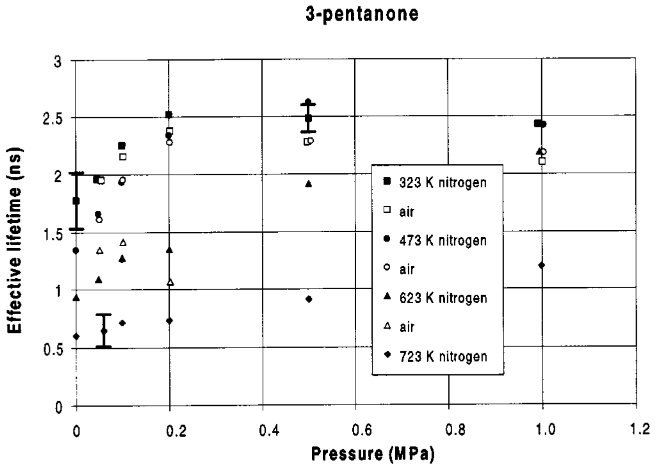

Fig. 9. Evaluated effective lifetimes of 3-pentanone-fluorescence measured at different pressures of nitrogen and air at different temperatures. The error bars indicate the estimated precision in one series of experiments and are exemplified in different domains of the effective lifetime. The effective lifetimes relative to that of the pure substance can be easily obtained by dividing corresponding mean values in the graph. The precision of the calculated relative values was estimated ±15%

The temporal evolution of the fluorescence emission from 3P was measured at different temperatures and pressures of nitrogen and air. The evaluated lifetimes are reported in Fig. 9. The lifetime increased with increasing pressure of nitrogen in most of the pressure range studied. For the lower temperatures the strongest changes were observed in the low pressure region. This region extended to higher pressures as the temperature was increased. For instance at 323 K the lifetime seemed to reach a maximum or an asymptotic value at the pressure of 0.2 MPa, whereas for 623 K and higher temperature no evidence of an asymptotic value was observed. Lifetimes were longer at low temperatures than at high temperatures. This effect was most evident at lower pressures, however in the high pressure range this effect was almost absent at temperatures of 473 K and lower.

Air mixtures behaved as nitrogen mixtures in the low pressure region (≤ 0.1 MPa). In the high pressure region at lower temperatures the lifetimes did not reach an asymptotic value, instead a decrease of the lifetimes with increasing pressure was observed at pressures above 0.2 MPa. Larger differences were observed in the high temperature region, e. g. at 623 K the lifetimes for air mixtures were higher than for the nitrogen mixtures of the same pressure. Above 0.2 MPa the fluorescence signal disappeared. Reactions, for 0.7 mol/m^3 3-pentanone mixtures, started to appear at temperatures between 548 K and 588 K.

The presence of two lifetime-components in the evaluated fluorescence decay imposed the question whether they belonged to different spectral emissions or not. In Fig. 10a are shown spectral components that were measured for pure 3P with different SCHOTT filters. Filter (1) yielded entire emission spectrum while filter combination (2) transmitted only the short wavelength region of the emission and filters (3) and (4) were used for the long wavelength-emission region. The corresponding evaluated lifetimes are reported in Fig. 10b. No significant differences could be observed in the effective life-

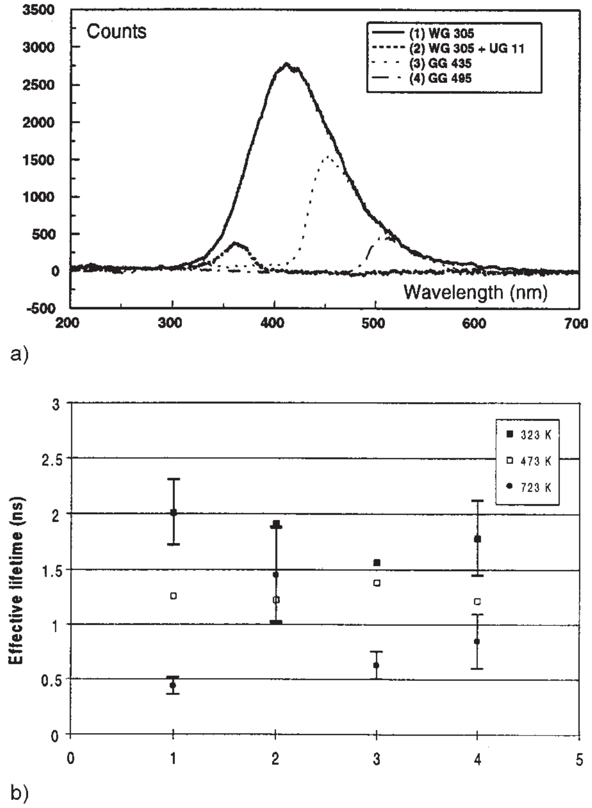

Fig. 10. **a** The spectral components that were measured with different SCHOTT filters. The spectral curves were not corrected for the spectral response of the spectrograph/OMA-system. **b** Evaluated effective lifetimes of fluorescence from pure 3-pentanone, measured with different SCHOTT filters at different temperatures. (1) WG 305, (2) WG 305+UG 11, (3) GG 435 and (4) GG 495. The error bars indicate the estimated precision

times except possibly for the highest temperature. At 723 K the signals and the S/N were lower, which increased the uncertainty of the evaluation. Therefore the high value given for the effective lifetime with filter combination (2) contains a great deal of uncertainty, which may effect the significance.

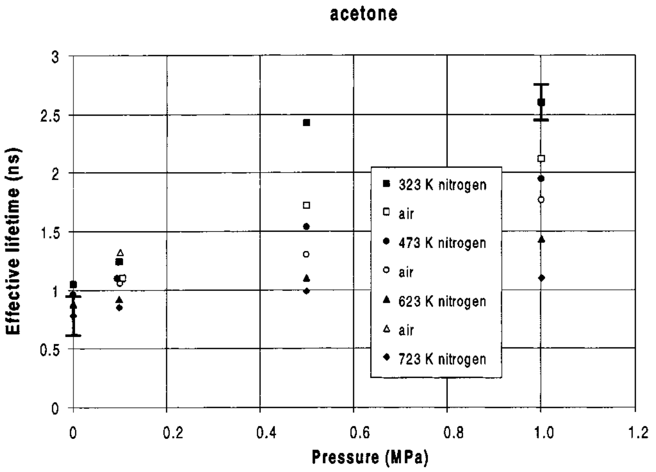

Fig. 11. Evaluated effective lifetimes of acetone-fluorescence measuered at different pressures of nitrogen and air for different temperatures. The error bars indicate the estimated precision in one series of experiments and are exemplified in different domains of the effective lifetime

Temporally resolved measurements were also made on acetone, however, the number of measurements and the number of different pressure conditions studied were less than for 3P. The concentration used was the same as with 3P. The evaluated mean lifetimes are reported in Fig. 11 for different temperatures and pressures. The filter used in these corresponding measurements was WG 305 as for 3P.

The lifetimes seemed to be lower than for 3P at all temperatures except for 723 K and in the high pressure region at 323 K. No tendency of the lifetimes to reach an asymptotic value with increasing pressure was observed. Measurements with different filters were made at 323 K and 623 K. No substantial differences between the evaluated lifetimes were observed at the respective temperatures.

3 Discussion

3.1 Error analysis

In order to obtain an indication of the uncertainty of the lifetime measurements several aspects of the measurements were considered. The streak speed had been calibrated before with a train of laser pulses, obtained from an etalon with a separation between its semi-transparent mirrors that could be determined with an accuracy of $1/10$ of a mm. After this calibration lifetimes of the fluorescence from three dyes were measured and compared with the ones measured with a photon counting technique, which has an accuracy of better than 1% [17]. The differences in the measured lifetimes using the two techniques were less than 10%.

The precision of the evaluations of the lifetimes in one series of experiments was estimated to be ±15% (one standard deviation, for the low-temperature values). The uncertainty of the ratio between the effective lifetime for $3P/N_2$ or $3P/air$ mixtures and pure 3P was estimated to be ±15% based on the precision of the corresponding ratio of the IFE at 473 K. The accuracy of the evaluations for the case when only one lifetime was present was estimated to be ±15%, but was lower, ±20%, at the presence of two exponential decays.

Comparisons were also made with previously reported lifetimes. The lifetimes at low-moderate temperatures and high nitrogen pressures measured in this way were ≈ 2.5 ns for 3P and Ac. Lifetimes given by Hansen & Lee [16] were 2.7 ns and 2.6 ns respectively for the pure substances in gas phase at room temperature (23 °C) and at low vibrational excitation at 320–330 nm wavelength. Also, the lifetimes for the pure substances, 1.8 ns and 1.0 ns at 323 K, in our case, were compared with interpolated and extrapolated values, 2.2 ns and 1.2 ns respectively, from the results by Hansen & Lee [16] and Breuer & Lee [18]. In these comparisons it was assumed that the lifetimes measured by Hansen & Lee [16] in the long wavelength region corresponded to states with low vibrational energies which should have been also the case in our measurements in the $3P/N_2$-mixtures at high pressures. The interpolated and extrapolated lifetimes on the other hand should have described states with higher vibrational energies. Under the assumptions made the differences between our results and those by Hansen & Lee [16] and Breuer & Lee [18] were 20% or less.

3.2 Analysis of the results

The behaviour of the fluorescence lifetime of 3-pentanone and acetone with respect to buffer gas pressure and temperature may seem puzzling, but there have been examples where similar behaviour has appeared.

Experimentally, the increase of the lifetime of the fluorescence emission with nitrogen pressure has been observed for polyaromatic hydrocarbons such as fluoranthene [19] and pyrene [20]. Stabilization of the fluorescence quantum yield by pressure has also been observed for carbonyl compounds, e.g. cyclobutanone [21] and formaldehyde [22]. Acetone has shown to have a fluorescence lifetime that decreases with the excess energy of the radiation [16], implying that collisional relaxation would result in an increase of the lifetime of the fluorescence. O'Neal and Larson found a temperature variation of the fluorescence at 314 nm which yielded an Arrhenius plot with a slightly negative activation energy, i.e. a positive exponent in the expression for decay rate [23]. Recently Grossmann et al. [14] obtained results from 3-pentanone that show that the fluorescence intensity is stabilized by nitrogen and that it is destabilized by an increase of temperature when the excitation occurs at 248 nm and 277 nm.

The Stern-Volmer relation applicable for atoms and small molecules is not a valid description in these cases. A complete physical description of the dynamics of the excitation and relaxation of the fluorescence emission would require a quantum mechanical treatment combined with density matrix calculations, which was beyond the scope of this work. Instead the analysis of the temporally resolved measurement results was directed towards the main features with the help of a simple rate analysis. Coherence effects in the emission, which require density matrix calculations, were therefore not considered.

In the process of excitation with a wavelength of 266 nm, high vibronic levels of the first excited electronic singlet state are accessed ($\approx 7000\,\mathrm{cm}^{-1}$ above the 0-0 band fore acetone at $30\,500\,\mathrm{cm}^{-1}$ [24]). The density of states in this region would be more than 100 per cm^{-1} [25], which should enable fast IVR. If one assumes that IVR to the lower vibronic states is very rapid, it would be plausible to expect molecules of an ensemble to be distributed among states with different vibrational energy. Since the lifetimes are known to decrease with increasing vibrational level, further relaxation due to collisions should result in an increase of the effective lifetime of the fluorescence. An increase of the temperature would instead yield a shortening of the lifetime.

In order to understand in a more detailed sense the effects of these conditions on the properties of the time resolved fluorescence emission with respect to buffer gas pressure and temperature, calculations were performed. The base point for the calculations was the work by Wilson, Noble and Lee [26], who demonstrated a simple principle to calculate the effects of the relaxation process on the fluorescence emission. Our description was based on two emitting states for simplification. The upper of these two states had a shorter lifetime than that of the corresponding lower one. The lower state could only be accessed from the upper state either spontaneously or by collisions with the buffer gas molecules. The total rate of transfer to the lower state was set to $k_0 + k_1 \cdot P \cdot \frac{323}{T}$, where P was the pressure of the buffer gas and T was the absolute Temperature and k_0 and k_1 were rates for the spontaneous and collisional relaxation. A modification was introduced for the interpretations of the air mixtures. The total depopulation rate losses were added with electronic quenching terms $0.2 \cdot 1/\tau_1 \cdot \frac{P}{T} \cdot \frac{323}{1.0}$ for the upper state and $0.2 \cdot 1/\tau_2 \cdot \frac{P}{T} \cdot \frac{323}{1.0}$ for the lower state, respectively, and the relaxation rate to the lower state was $k_0 + 0.8 \cdot k_1 \cdot P \cdot \frac{323}{T}$.

In order to describe the temperature dependence, the rate constants k_0 and k_1 were set to follow an expression proportional to $\mathrm{e}^{\Delta E/(k_\mathrm{B} \cdot T)}$, k_B being the Boltzmann constant. ΔE was set as an empirical parameter. The final expression for the relaxation rate (for nitrogen mixtures) was:

$$\left\langle k_0 + k_1 \cdot P \cdot \frac{323}{T} \right\rangle \cdot \left\langle \mathrm{e}^{(\Delta E - k_\mathrm{B} \cdot T)/(k_\mathrm{B} \cdot T)} \right\rangle .$$

In Fig. 12 are shown the effective lifetimes calculated for 3P for fixed τ_1 and τ_2 equal to 300 ps and 2.8 ns. In order to describe the experimental results qualitatively the values for k_0 and k_1 were set to $2 \times 10^8\,\mathrm{s}^{-1}$ and $5 \times 10^9\,\mathrm{s}^{-1}\mathrm{MPa}^{-1}$, respectively, and ΔE was set to $k_\mathrm{B} \cdot 1500$ J. In Fig. 13 are shown the calculated lifetimes for Ac using the same values of k_0 and k_1 and $\Delta E = k_\mathrm{B} \cdot 750$ J.

The values of ΔE should not be given any undue significance. It may be the case that the nature of the temperature dependence should be more connected to the distribution amongst the levels than to the "rate constants". It seems

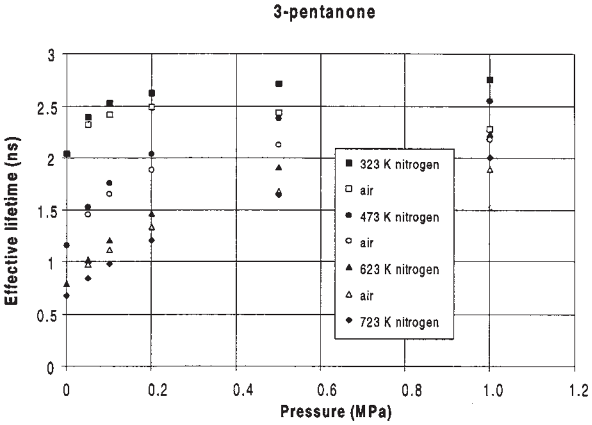

Fig. 12. Calculated effective lifetimes of 3-pentanone-fluorescence at different pressures of nitrogen and air for different temperatures

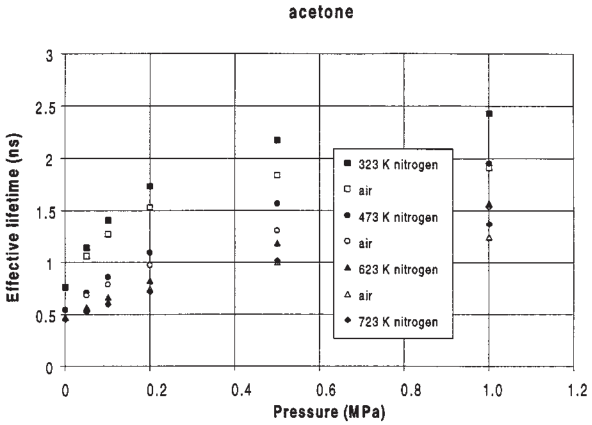

Fig. 13. Calculated effective lifetimes of acetone-fluorescence at different pressures of nitrogen and air for different temperatures

appropriate to assume that a “distorted” non-equilibrium Boltzmann distribution should be present in the significant part of the decay. The vibrational temperature at that moment would result higher than the equilibrium temperature. It is also possible that ΔE should include some effective threshold energy (a negative term included in ΔE) given by the Arrhenius law.

Even though the calculated lifetimes for pure Ac resulted lower than the measured values, the calculations showed a rather good agreement with the experiments in the trends of the behaviour of the fluorescence lifetime as a function of buffer gas pressure and temperature, despite the oversimplifications of the analysis.

Phosphorescence, $\tau_{\mathrm{eff}} \approx 0.20\,\mathrm{ms}$ [27] for acetone at the lowest level $27\,300\,\mathrm{cm}^{-1}$ [24], is expected to be heavily quenched by the presence of oxygen [16]. Following the analysis in [24], the long lifetime component of the emission could be attributed to phosphorescence from thermalized triplets. A contribution from phosphorescence would then be expected to red-shift the emission spectrum compared to that due to pure fluorescence. However, the spectral measurements of ours made with 100 ms gate time did not manifest any red shift with increasing pressure of nitrogen. The narrowing of the spectral profile observed with increasing pressure may have been due to the combined effects of relaxation in the singlet system and decreasing phosphorescence emission from the triplet system, if one assumes that intersystem crossing to the triplet manifold is inhibited by the relaxation.

In the lower temperature region where no spontaneous reactions were observed with air, the description of the dynamics above seemed reasonable. On the other hand, in the high temperature region, where reactions were observed for air mixtures, the description was probably not valid, since the spectral measurements showed a different behaviour with respect to pressure. For instance at 723 K a blue shift of the spectrum was observed with increasing pressure, the opposite to what would be expected from relaxation. No explanation to this discrepancy was found other than possibly it being caused by quantum mechanical effects accompanying the structural changes, which would appear in combination with the activation of the molecule before ensuing a chemical reaction. At high temperatures new substances are expected to be formed with air through thermolysis of 3P. Investigations on the decomposition of hydrocarbons and ketones in air have shown that peroxyacetic acid can be formed under atmospheric conditions [28]. In studies of 3P oxidation Barnard & Sheikh [29] obtained formaldehyde, methanol, ethylene and ethyl hydroperoxide at 523 K and formaldehyde, methanol, ethylene and methane at 723 K. Gas chromatographic measurements performed by Grossmann et al. in combination with their 3P/fluorescence investigation [14] revealed ethylene, butenes and small amounts of propionaldehyde after laser radiation.

The decomposition at moderate temperature does not seem to affect the spectral profiles in our measurement conditions. Thus formaldehyde, peroxyacetic acid and other products are probably not formed in such amounts to affect the spectral profiles. Formaldehyde should absorb in the UV-spectral region, but judging from the absorption profile [30] it is hard to say that it would explain our spectral results at high temperature. Methanol reveals continuous absorption only in the vacuum spectral region [31] and the same may be said for methane. The longest absorption band for ethylene between 260 nm and 340 nm is “extremely weak” according to Herzberg [31]. In addition propionaldehyde should have an emission spectrum not much different to that of acetaldehyde which has a spectrum [31] rather similar to that of 3P. Consequently these observations do not seem to explain the “UV-shift” with increasing air pressure found in our measurements.

Reactions which were believed to be photoinduced were found to appear for mixtures 0.02 MPa 3-pentanone/0.5 MPa air and in a narrow range of temperature. It is easily seen that the composition of the mixture yields approximately 1 carbon atom per oxygen molecule and that it is almost stoichiometric in the formation of H_2O and CO.

4 Conclusion

Effective lifetimes of the first excited electronic states of 3-pentanone and acetone have been measured at various temperatures between 323 K and 723 K and at pressures of nitrogen and air between 0.001 MPa and 1.0 MPa. The ketone molecules were excited with ps-laser radiation at a wavelength of 266 nm. The decay of the first excited electronic state was measured by monitoring the temporal evolution of the fluorescence emission with a streak camera. Changes of the decay time were observed with respect to temperature and pressure of nitrogen and air.

Nitrogen has been found to have a stabilizing effect on the fluorescence emission in that the effective lifetimes seem to reach an asymptotic value with increasing pressure. Air due to oxygen was instead found to have a destabilizing effect at higher pressures as the effective lifetime decreased with increasing pressure between 0.2 MPa and 1.0 MPa. A tendency to destabilization of the fluorescence with increasing pressure of nitrogen (at 323 K) could probably occur at the highest pressures, but the uncertainty of the experiment was too large to give any conclusive results. The temperature has a destabilizing effect on the fluorescence emission also in the regions where no reaction is observed for the 3-pentanone/air mixtures. The results obtained are concordant with those by Grossmann et al. [14], in that the trends of the effective lifetime with respect to temperature and pressure of nitrogen follows their results of the dependencies of the fluorescence emission intensity.

Reactions were avoided at temperatures lower than 548 K when the concentration of 3-pentanone was kept low ($\approx 0.7\,\mathrm{mol/m^3}$). The effective lifetimes changed less than $\pm 20\%$ for temperatures between 323 K and 473 K and pressures of air or nitrogen between 0.1 MPa and 1.0 MPa.

In the non-reactive temperature region, it was possible to obtain a qualitative picture of the temporally resolved measurements with a simple rate analysis. At higher temperatures the analysis did not give satisfactory results when compared with the spectral measurements.

The measurements in these experiments were performed with residence times of the order of minutes while normal engine-residence times are of the order of milliseconds or lower. The instabilities in the fluorescence observed at high temperatures may not have the time to develop in an engine during a cycle. There mixing characteristics between the dopant and the nitrogen or air may be different in the two types of experiments. In particular inhomogeneous mixing has to be considered in engine applications, where local variations of the composition may be significant.

In conclusion to summarize the results which can be of interest for engine applied studies one finds that the lifetime or yield of the 3-pentanone fluorescence at 266 nm laser excitation is mildly sensitive to the pressure of nitrogen at pressures between 0.2 MPa and 1 MPa and temperatures between 323 K and 473 K when the concentration of 3-pentanone is low. Air mixtures show somewhat lower lifetimes but the differences remain within 20%. The conditions for quantitative measurements of concentrations from 2D-fluorescence measurements of 3-pentanone should be particularly good in this region of pressures and temperatures. Acetone fluorescence on the other hand shows considerable sensitivity to pressure of nitrogen and air at low–moderate temperatures which makes it less suited for measurements applied to engines.

High concentrations of 3-pentanone in combination with air should not be used as photoinduced reactions may occur already at moderate temperatures (lower than 473 K).

At temperatures higher than ≈ 523 K one can expect the profile of the spectral emission to become noticeably sensitive to pressure of the buffer gas, in particular with air. High temperatures should be avoided not only because reactions may occur but also because detectors generally show spectral sensitivity and the shift of the spectral profile may affect the quantification of the fluorescence emission intensity. Lenses transparent in the UV should be used.

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