

Temperature and pressure dependences of the laser-induced fluorescence of gas-phase acetone and 3-pentanone

F. Grossmann, P. B. Monkhouse, M. Ridder, V. Sick, J. Wolfrum

Physikalisch-Chemisches Institut, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany
(Fax: + 49-6221/56-4255)

Received: 27 December 1994/Accepted: 12 September 1995

Abstract Laser-Induced Fluorescence (LIF) from the S_1 state of acetone and 3-pentanone was studied as a function of temperature and pressure using excitation at 248 nm. Additionally, LIF of 3-pentanone was investigated using 277 and 312 nm excitation. Added gases were synthetic air, O_2 , and N_2 respectively, in the range 0–50 bar. At 383 K and for excitation at 248 nm, all the chosen collision partners gave an initial enhancement in fluorescence intensity with added gas pressure. Thereafter, the signal intensity remained constant for N_2 but decreased markedly for O_2 . For synthetic air, only a small decrease occurred beyond 25 bar. At longer excitation wavelengths (277 and 312 nm), the corresponding initial rise in signal with synthetic air pressure was less than that for 248 nm. The temperature dependence of the fluorescence intensity was determined in the range 383–640 K at a constant pressure of 1 bar synthetic air. For 248 nm excitation, a marked fall in the fluorescence signal was observed, whereas for 277 nm excitation the corresponding decrease was only half as strong. By contrast, exciting 3-pentanone at 312 nm, the signal intensity increased markedly in the same temperature range. These results are consistent with the observation of a red shift of the absorption spectra (≈ 9 nm) over this temperature range. Essentially, the same temperature dependence was obtained at 10 and 20 bar pressure of synthetic air. It is demonstrated that temperatures can be determined from the relative fluorescence intensities following excitation of 3-pentanone at 248 and 312 nm, respectively. This new approach could be of interest as a non-intrusive thermometry method, e.g., for the compression phase in combustion engines.

PACS: 33.50; 33.20; 34.90

characterization of the fluorescence of acetone and 3-pentanone for this particular application was the motivation for this study. Second, carbonyls are involved in the combustion of hydrocarbons; their thermal decomposition leads largely to free radicals, which serve as chain starters for chemical reactions. Third, the production of free radicals by photodecomposition of carbonyl compounds is of considerable atmospheric importance for the same reason.

The absorption spectrum of acetone and 3-pentanone in the near UV is due to the excitation of the C=O group, whereby a non-bonding electron of oxygen is raised into the antibonding π_{CO}^* molecular orbital. The transition from the ground (S_0, n) state to the first excited (S_1, π^*) state is thus spin-allowed but orbital-forbidden, so that the absorption is relatively weak ($\approx 10^{-20}$ cm²). Absorption occurs from 220 to 330 nm with a maximum near 280 nm, fluorescence from 300 to 550 nm with broad maximum at about 400 nm.

The absorption and emission behaviour of a number of ketones have been studied both in the bulk gas [4] and isolated molecule regimes [5, 6]. The radiative lifetime for the first singlet state of acetone (isolated molecule regime) is around 2 ms. Many investigations, particularly the earlier ones, were made at total pressures of several torr and above, i.e., in the bulk gas. In this regime, effective lifetimes were found to increase with excitation wavelength, varying from 1.7 ns at 280 nm to 2.7 ns at 315 nm [4]; the corresponding quantum yields increase from 1×10^{-3} to 2×10^{-3} . For 3-pentanone, the variation in lifetime given in [4] is smaller, i.e., from 2.1 ns at 250 nm to 2.6 ns at 325 nm and the quantum yield is nearly constant in this wavelength range at 2.2×10^{-3} . In both cases, the S_1 state decays almost entirely (99%) by intersystem crossing to the triplet state.

In this work, we present results of fluorescence intensity measurements of gas-phase acetone and 3-pentanone for pressures up to 50 bar and in the temperature range 383–650 K. The excitation wavelengths selected were 248, 277 and 312 nm, which are on the left, near the centre and on the right of the absorption maximum, respectively.

There has been interest in the photophysics of carbonyl compounds for many years for several reasons. First, the use of carbonyls as fluorescent dopants was recently proposed for marking fuels in engine combustion [1–3]; the

1 Experimental

Time-integrated (relative intensity) measurements (Fig. 1a) were made in the gas phase on acetone and 3-pentanone in a heatable, high-pressure cell, which could be operated safely up to 650 K and 50 bar. Because the boiling point of 3-pentanone is 375 K, the cell was operated at a minimum temperature of 383 K. The cell was quadratic in outer form and had a cylindrical probe volume of about 320 cm³. The geometry and dimensions were selected so as to ensure instantaneous mixing of gases (Fig. 1b). The ketone of interest was injected through

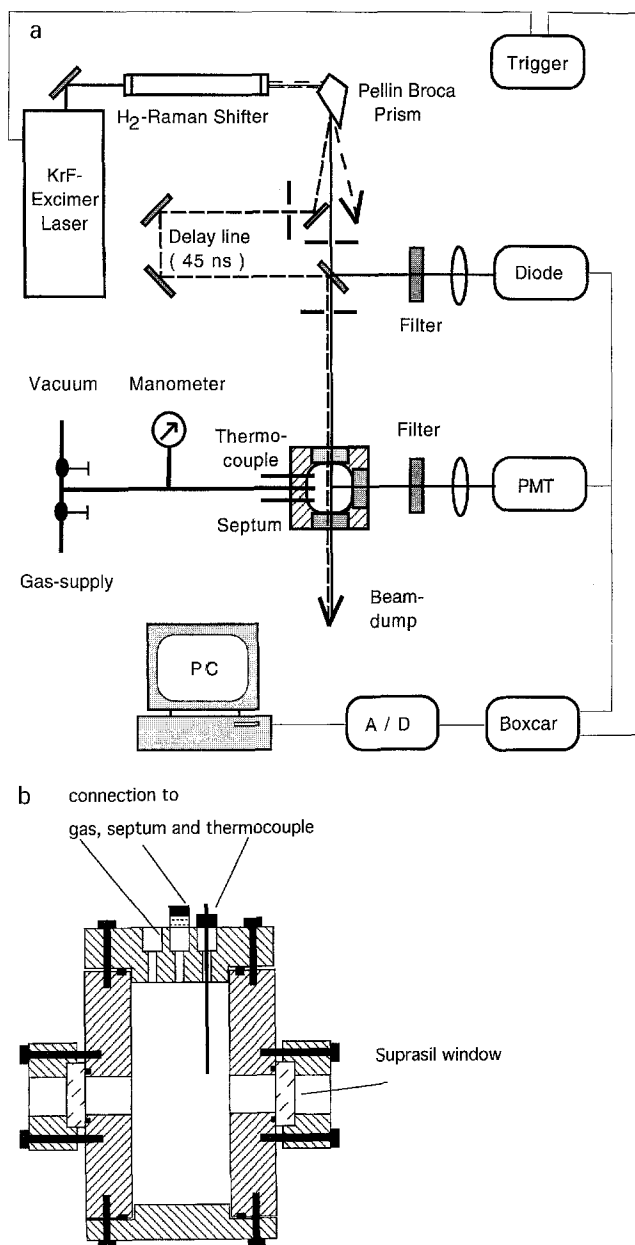


Fig. 1. **a** Experimental setup for LIF of acetone and 3-pentanone as a function of pressure and temperature. The *dashed lines* depict the setup used for temperature measurements. **b** Schematic drawing of the heatable high-pressure cell

a septum into the cell and nitrogen, oxygen or synthetic air was added.

For most measurements, a broadband KrF-excimer laser at 248 nm (Lambda Physik, EMG120ii) was used for excitation and a photomultiplier/boxcar system for detection (Thorn EMI 9783B, Stanford Research Systems 250). Additionally, some measurements were made using 277 and 312 nm radiation, obtained by Raman shifting the KrF-excimer wavelength (first and second Stokes lines of H₂, respectively). Laser intensities of < 1 mJ/cm² at a repetition rate of 10 Hz were used. It was verified that the fluorescence was in the linear regime; neutral density filters were used as required to avoid saturation of the photomultiplier. Approximately 10 laser shots were averaged for each measurement point and the cell was then refilled for the next measurement.

For the temperature measurements by two-line-excitation fluorescence, a slightly modified experimental setup was used. The fluorescence intensity was measured following excitation by two beams (248 and 312 nm) originating from the same laser pulse: As depicted in Fig. 1a, a Pellin-Broca prism separated the different wavelengths spatially. The 312 nm beam was focused directly into the cell, whereas the remaining laser light at 248 nm was sent through a delay line of approximately 14 m. The fluorescence signals from the two excitations were recorded with the photomultiplier tube (rise time < 3 ns) and two gated boxcar-integrators (gate width 15 ns).

Recorded emission spectra showed no indication of fragments produced by laser photolysis even at higher intensities. To check for thermal and photolytic decomposition of the investigated ketones, capillary gas chromatography [WCOT-quartz capillary (51 m*0.32 mm)] was performed with an iso-thermal programme using a Flame Ionisation Detector (FID). Absorption spectra of the ketones were recorded as a function of temperature using a modified Perkin Elmer, Lambda 7 UV-spectrometer.

2 Results and discussion

2.1 Pressure dependence

All measurements were made using a constant number of molecules ($2.8 \times 10^{17} \text{ cm}^{-3}$ for acetone, $2.6 \times 10^{17} \text{ cm}^{-3}$ for 3-pentanone). With an excitation wavelength of 248 nm, a series of fluorescence intensity measurements was made at a constant cell temperature of 383 K, adding nitrogen, oxygen or synthetic air up to total pressures of 30–50 bar. Very similar effects were observed for both acetone and 3-pentanone. As Figs. 2a and b show, the fluorescence intensity rises initially. In the case of N₂ (not shown here), the signal levels off when relaxation is complete. This occurred at 5 bar for 3-pentanone and 8 bar for acetone. For O₂, after the initial increase, a decrease in signal of 17% per 10 bar was measured. For synthetic air, on increasing the pressure beyond 25 bar, the signal intensity decreased about 10% per 10 bar.

The first increase of the signal intensity may be attributed to vibrational relaxation to levels with higher

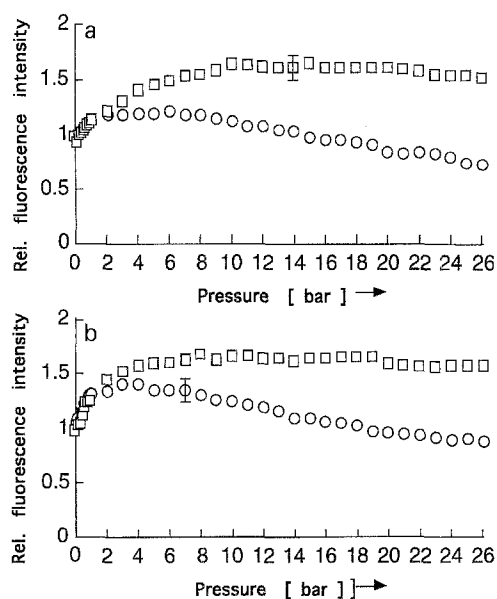


Fig. 2a,b. Pressure dependence of the relative LIF signal for excitation at 248 nm; cell temperature 383 K: **a** acetone, **b** 3-pentanone; (○) oxygen, (□) synthetic air

fluorescence quantum yields. However, quenching of the S_1 state by O_2 is able to compete effectively with this vibrational relaxation. Quenching of excited organic molecules by ground-state (triplet) oxygen is well known [7,8] and in this case may be due to the formation of a charge-transfer complex with the ketone, involving the electronegative oxygen atom of the excited carbonyl bond and electrons of the double bond. From this model one expects no change in the lifetime of the S_1 state in the presence of air or oxygen as opposed to nitrogen, as confirmed by Ossler and Alden [9], who obtained the same lifetime (2.6 ± 0.25 ns) for 3-pentanone in 9.2 bar nitrogen and air at 523 K. A similar result was obtained with aldehydes [10].

Two further series of experiments were conducted for excitation of 3-pentanone at 277 and 312 nm. At 277 nm, the fluorescence intensity increased slightly with synthetic air pressure up to 2 bar and then decreased approximately 40% at 50 bar. For 312 nm excitation, almost no initial increase in signal intensity is measured. Similar results were obtained at 473 and 533 K. Figure 3 shows the difference of the relative fluorescence intensity at 473 K using excitation at 248 and 312 nm. The longer wavelength at 312 nm is very close to the lowest vibrational level of the S_1 state of the ketone. Then, no or little vibrational relaxation takes place and, therefore, the quenching effect is observable at much lower pressures.

Because of the interest in ketones for engine diagnostics, the pressure dependence of 3-pentanone fluorescence on synthetic air pressure was also investigated using a mixture of *iso*-octane and 3-pentanone (80:20%) and 248 nm excitation. Again, an initial increase in signal intensity was observed up to 5 bar, followed by an almost constant intensity up to 25 bar.

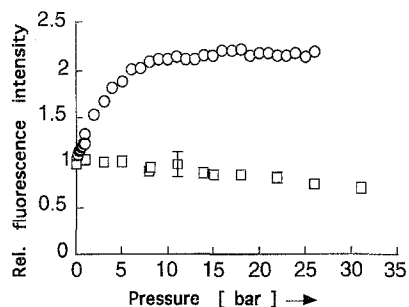


Fig. 3. Pressure dependence of the relative LIF signal of 3-pentanone. λ_{ex} : 248 nm (○) and 312 nm (□) at 473 K

2.2 Temperature dependence

Relative intensity measurements were made for both acetone and 3-pentanone at a constant pressure of 1 bar synthetic air in the temperature range 383–573 K. Using 248 nm as the excitation wavelength, the signal decreased as shown in Fig. 4 (approximately 35% per 100 K). To establish whether this effect was due to the decomposition of the fluorescing molecule, gas chromatographic measurements were made by sampling from the cell via a septum. Both the ketone and its decomposition products (ethylene, butenes and a small amount of propionaldehyde) were monitored. The results showed that even after 10 min residence time in the cell at 575 K, only 10% of the injected compound had dissociated. Thus, the observed fall in fluorescence intensity (measured immediately after injection) cannot be due to decomposition.

For further clarification, absorption spectra of acetone and 3-pentanone were recorded as a function of temperature in the range 298–573 K; Fig. 5 shows the results for 3-pentanone. The absorption peak at 275 nm shifts to longer wavelengths with increasing temperature, while the halfwidth remains almost constant (approximately 30 nm). This means that the absorption strength will decrease at 248 nm (on the left of the absorption maximum) and a decrease in fluorescence signal intensity is to be expected using this excitation wavelength, as observed. A smaller temperature dependence at 277 nm is expected since this wavelength is close to the absorption maximum. Accordingly, if this ketone is excited on the right-hand side of the absorption maximum, a positive temperature dependence should be measured, as observed by Greenhalgh and Tait [11] for 308 nm.

The temperature dependence of 3-pentanone was also determined using 277 and 312 nm excitation (Fig. 4). In the temperature range 383–573 K, the fluorescence intensity decreased by 15% per 100 K for 277 nm excitation, but increased about 80% for 312 nm excitation. For 277 nm excitation the same measurements were performed at 1, 10 and 20 bar (synthetic air), the observed temperature dependence was essentially the same at all three pressures (Fig. 6). Tait and Greenhalgh [11] investigated the temperature dependence of several carbonyl compounds at atmospheric pressure in a flow system. The

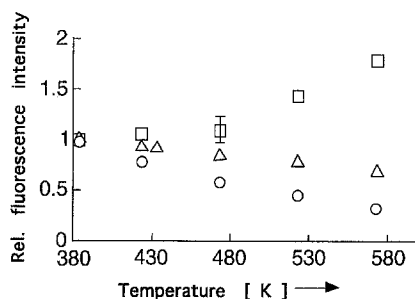


Fig. 4. Temperature dependence of the relative LIF signal for 3-pentanone for excitation at 248 nm (○), 277 nm (△) and 312 nm (□). All data are normalized with respect to the signal intensities at 383 K

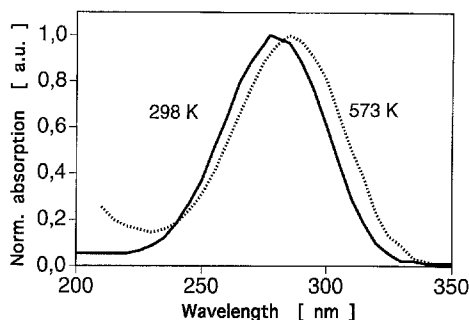


Fig. 5. Absorption spectrum of 3-pentanone at different temperatures and atmospheric pressure. 298 K (full line) and 573 K (dotted line)

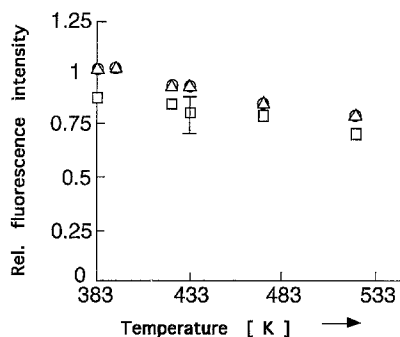


Fig. 6. Temperature dependence of the relative LIF signal for 3-pentanone. $\lambda_{\text{ex}} = 277$ nm, at 1 bar (○), 10 bar (△) and 20 bar (□) synthetic air pressure

excitation wavelength there was 308 nm (XeCl-excimer) and the temperature range studied was 300–800 K. For acetone and 3-pentanone, a steady increase in signal of 16% per 100 K was observed.

2.3 Temperature measurement using two-line-excitation technique of 3-pentanone

The temperature dependence of the absorption strength – and hence the fluorescence intensity – of ketones offers the possibility to determine the temperature. To

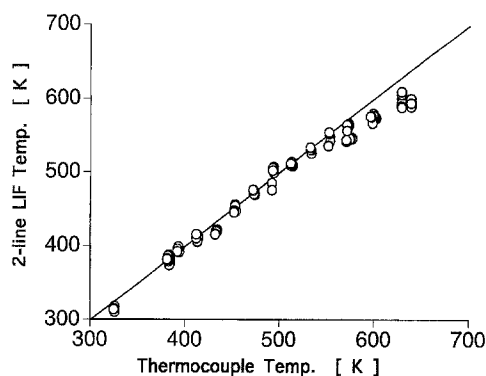


Fig. 7. Temperature measurement using two-line fluorescence of 3-pentanone. The calculated temperature from these measurements is shown as a function of the corresponding thermocouple readings

demonstrate the possibilities of this new approach, we measured the ratio of the fluorescence intensity following 248 and 312 nm excitations.

Measurements were performed at atmospheric pressure (synthetic air) in the temperature range 350–640 K. Again, the fluorescence intensities were measured as a function of temperature and all data were normalized with respect to the signal strengths at 383 K. For each pair of excitation pulses the ratio $I_{312 \text{ nm}}(T) / I_{248 \text{ nm}}(T)$ was then calculated. From the results of the measurements mentioned before (Fig. 4), we determined the relative fluorescence intensity as a function of temperature and used this calibration curve to calculate temperature from the measured ratio. Figure 7 shows the comparison of the calculated temperature and the thermocouple readings. Each measurement point corresponds to the mean value of 15 successive laser pulses. Within the whole temperature range investigated here, there is good agreement between the calculated and the measured temperatures. However, at the highest temperatures, the calculated values tend to underestimate the thermocouple readings by 40–50 K. The mean scatter within a series for a given temperature was ± 21 K.

3 Conclusions

Over a wide pressure range (ca. 5–25 bar), the fluorescence intensity of both acetone and 3-pentanone are constant. The temperature dependence of the fluorescence is dependent on the excitation wavelength and can be minimized near the absorption maximum. These results show that these ketones will be suitable fluorescent dopants for marking fuel distributions in combustors and fast-flow devices. 3-pentanone can be used with common model fuels, such as *iso*-octane [2, 3], because of similar boiling points and mass diffusion coefficients. These ketones are chemically relatively stable and only dissociate at higher temperatures (i.e., in the flame front).

It is demonstrated that two-line fluorescence of 3-pentanone is a new optical technique for non-intrusive thermometry. Since there is only little influence of pressure on

the ratio of the fluorescence intensities of two different excitation wavelengths, this new approach could be of special interest to applications operating at elevated pressures, e.g., in the compression stroke of Diesel engines. To improve the signal-to-noise ratio, i.e., to compensate for laser fluctuations or any other temporal drift effects, the laser power should be measured online before as well after the pressure vessel. Whereas the precision of this approach is quite satisfactory up to 550 K, the deviation at higher temperatures may be due to uncertainties of the calibration curve above 600 K; this will be investigated in further work.

Acknowledgements. This work was supported by the Bundesministerium für Forschung und Technologie (Arbeitsgemeinschaft TEC-FLAM) and the Commission of the European Union (Project MID-COM II)

References

1. A. Arnold, H. Becker, R. Sultz, P. Monkhouse, J. Wolfrum, R. Maly, W. Pfister: *Opt. Lett.* **15**, 831 (1989)
2. A. Arnold, A. Buschmann, B. Cousyn, M. Decker, F. Vannobel, V. Sick, J. Wolfrum: SAE Paper **932696** (1993)
3. H. Neij, M. Aldén: *Combust. Flame* **99**, 449 (1994)
4. D.A. Hansen, E.K.C. Lee: *J. Chem. Phys.* **62**, 183 (1975)
5. A. Lozano, B. Yip, R.K. Hanson: *Exp. Fluids* **13**, 369 (1992)
6. Y. Haas: *Spectrochim. Acta A* **46**, 541 (1990)
7. O.L. Gijzmann: *Faraday Trans. II* **70**, 708 (1973)
8. P.B. Merkel, D.J. Kearns: *J. Chem. Phys.* **58**, 398 (1973)
9. F. Ossler, M. Aldén: *Appl. Spectrosc.* (1996) (submitted)
10. A. Arnold, A. Bräumer, F. Dinkelacker, P. Monkhouse, K. Witte, M. Schäfer, M. Köllner, W. Ketterle, J. Wolfrum: Final Report, CEC-Project JOULE0021-UK/JC, European Commission (1992)
11. R. Tait, D. Greenhalgh: *Ber Bunsenges. Phys. Chem.* **97**, 1619 (1993)