

Characterization of a Perfluorinated Ketone for LIF Applications

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A perfluorinated ketone, 2-trifluoromethyl-1,1,1,2,4,4,5,5,5-nonafluoro-3-pentanone, has been investigated to determine several physical and spectroscopic properties. It was found to exhibit fluorescence similar to that of acetone, emitting over the 360-550 nm range with a peak near 420 nm when excited at 355 nm. This compound's emission is nearly unaffected over a wide range of temperature and pressure in an argon bath gas. Its fluorescence efficiency was found to be three times higher than that of acetone. Combined with low reactivity and thermal stability up to 500°C, this makes the material an excellent tracer for flow applications near critical conditions.

Nomenclature

P	=	pressure
P_c	=	critical pressure
P_R	=	reduced pressure, P/P_c
T	=	temperature
T_c	=	critical temperature
T_R	=	reduced pressure, T/T_c
V	=	molar volume
λ	=	wavelength
μ	=	dynamic viscosity
ν	=	kinematic viscosity
ρ	=	density

I. Introduction

THE molecular structure of the perfluorinated ketone discussed in the present paper, 2-trifluoromethyl-1,1,1,2,4,4,5,5,5-nonafluoro-3-pentanone, also known as FK-5-1-12, and referred to as "fluoroketone" for brevity herein, is shown in Figure 1.

This fluoroketone has several interesting features that make it an important material for research:

- ◆ High vapor pressure at ambient pressure – making the fluoroketone a good model for studies of the break-up and mixing of volatile fuels and enabling high seeding densities.
- ◆ Low critical pressure and temperature – facilitating the study of trans- and supercritical phenomena.
- ◆ Liquid fluoroketone low dynamic viscosity and high density – resulting in very low kinematic viscosity, making high-Re testing possible at modest flow speeds.
- ◆ Strong fluorescence with broadband excitation – making flow tracing using common high-power lasers, such as the 3rd and 4th order harmonics of a Nd:YAG laser, possible.

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- ◆ Low toxicity – thoroughly tested for use as a fire-suppressant.¹
- ◆ Inert – compatible with most common construction materials and does not exhibit thermal decomposition below 500°C in air.²
- ◆ Nonflammable – safe for use in large quantities.
- ◆ Environmentally acceptable – UV absorption promotes decay when exposed to sunlight, producing negligible ozone depletion and global warming potential.^{2,3,4}
- ◆ Commercially available in bulk quantities – sold as Novec 649 by 3M (Novec 1230 for fire suppression applications).

For experiments at high temperatures and pressures, e. g. the study of supercritical mixing, the fluoroketone offers a safer alternative to acetone. Fluoroketone could complement acetone as tracer and differences in their physical or fluorescence properties would measure another physical parameter in addition to density. This would require a wide range of data on the temperature and pressure dependency of the fluorescence spectra as well as third-party quenching behavior of the two species. Further, an additional benefit of having an additional tracer species makes it easier to match the absorption cross-section to the length scale and tracer density; it also ensures acceptable beam attenuation and fluorescence signal strength. This study represents an initial investigation of the relevant fluoroketone properties for LIF applications.

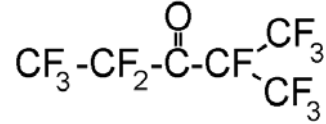


Figure 1. The molecular structure of the fluoroketone 2-trifluoromethyl-1,1,1,2,4,4,5,5,5-nonafluoro-3-pentanone investigated in this paper.

II. Physical properties

A. Density

The fluoroketone is a dense, colorless liquid at ambient conditions with a density of 1600 kg/m³. Figure 2 shows how the liquid density varies with temperature at ambient pressure. The least-squares fit shown suggests $\rho=1722(T-273.15)^{0.0222}$ kg/m³ over 283<T<318 K. Owens³ has suggested that the Peng-Robinson-Stryjek-Vera equation of state,⁵ Eq. (1), works well for the fluoroketone

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2} \quad (1)$$

with the critical conditions $P_c=1.8646$ MPa, $T_c=441.81$ K and the parameter values

$$\omega=0.471$$

$$\kappa_1=0.052$$

$$a = (0.457235 \frac{R^2 T_c^2}{P_c}) \alpha$$

$$b = 0.077796 \frac{RT_c}{P_c}$$

$$\alpha = (1 + \kappa(1 - \sqrt{T_R}))^2$$

$$\kappa = \kappa_0 + \kappa_1(1 + \sqrt{T_R})(0.7 - T_R)$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3$$

$T_R=T/T_c$ is the reduced temperature. The isobars produced when applying this model to the fluoroketone are shown in Figure 3.

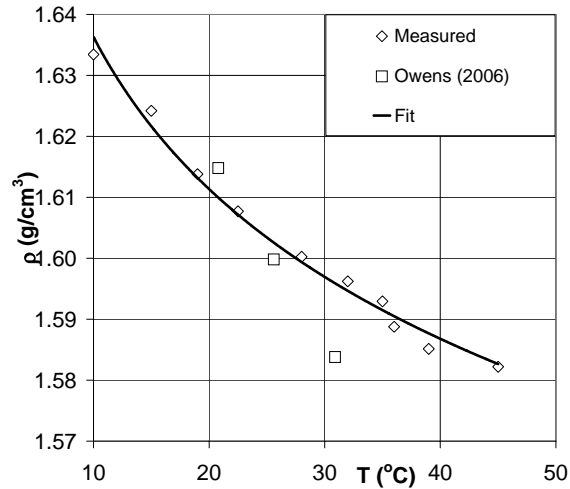


Figure 2. Density of liquid fluoroketone at 1 atm as a function of temperature. Points: measured data in current test and by Owens,⁶ Curve: least-squares fit to current data.

The vapor pressure of the fluoroketone may be approximated by the Antoine equation,

$$\log_{10} P = 10.205 - \frac{1861.01}{T + 34.883} \quad (2)$$

with P in Pa and T in K. At 298K, the vapor pressure is 40.4 kPa which can be compared to 31kPa of acetone. For certain applications, e. g. cavitation, it is also worth noting the unusually small liquid to vapor density ratio of $1600/5.56=287$ under 1 atm, 298K conditions.

B. Viscosity

Liquid fluoroketone has significantly lower dynamic viscosity than water at ambient conditions. Combined with the high density of the material, the kinematic viscosity is a factor 3 lower than water. The liquid dynamic viscosity shows a slight decrease with increasing temperature as shown in Figure 3 along with data from Owens⁶ and a least-squares fit to the present data giving $\mu=2634.23-6.7349T$ μ Pas over the range $288<T<318$ K.

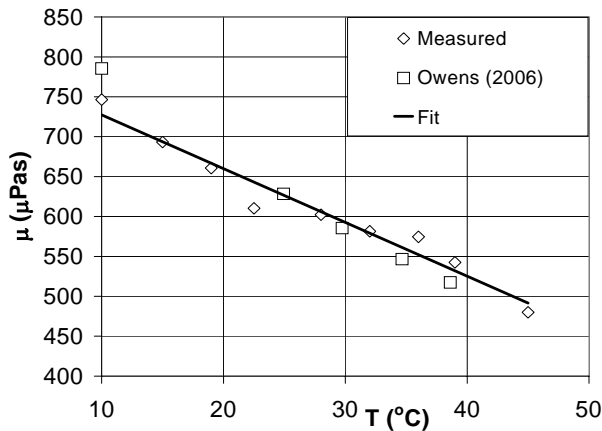


Figure 3. Dynamic viscosity of liquid fluoroketone at 1 atm as a function of temperature. Points: measured data in current study and by Owens,⁶ Line: least-squares fit to current data.

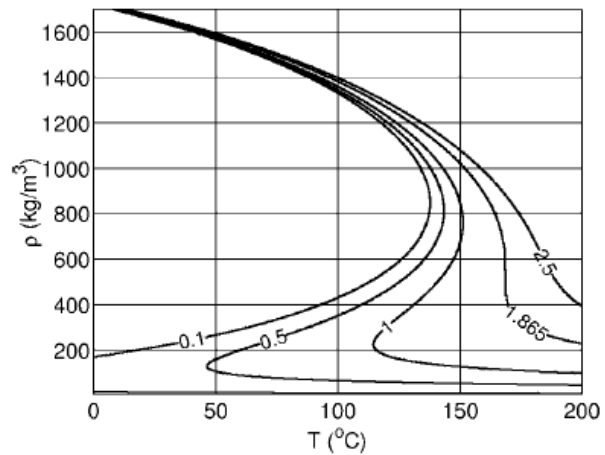


Figure 4. Isobars (MPa indicated) based on the PRSV equation of state. 1.865 MPa is the critical pressure.

III. Spectroscopy

The fluorescence spectroscopy of this material was investigated in two different setups - one for studying the absorption at 266 and 355 nm and the other to study emission at 355 nm under varying pressures and temperatures.

C. Absorption

The 3rd and 4th harmonics of the output of a Quantaray GCR-150 Nd:YAG laser were passed through a 4 cm pathlength fused silica cuvette which was partially filled alternatively with acetone or fluoroketone. A camera was used to observe the broadband emission in the blue range of the visible spectrum at 90° angle from the beam direction, producing results after corrections similar to that shown in Figure 5. The results obtained from this setup are summarized and compared to literature values from Taniguchi et al¹⁰ and Lozano et al⁷ in Table 1. In addition to cross-section measurements, this setup allowed the fluorescence efficiency of the two species to be compared using the corrected intensity, calculated cross-section and saturated vapor number density. After using the convolution of the camera sensitivity curve and the emission spectra for the two

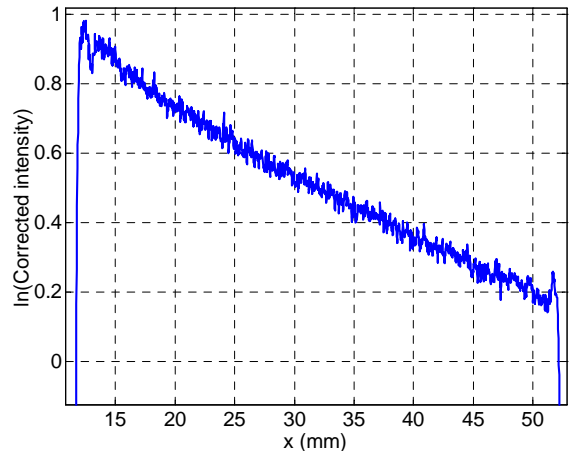


Figure 5. Spatial decay of fluorescence produced by a 266 nm laser beam passing through saturated fluoroketone vapor in air at 23.5°C from left to right.

Table 1. Comparison of absorption properties of fluoroketone and acetone in ambient air. Note that the small cross-sections of acetone and fluoroketone at 355 nm were measured in the liquid phase in the present study.

	Fluoroketone Taniguchi et al ¹⁰		Fluoroketone Current study		Acetone Lozano et al ⁷	Acetone Current study		
	355 nm	266 nm	355 nm	266 nm	266 nm	355 nm	266 nm	
Absorption cross section	0.11	1.78	0.23	2.40	4.33	0.0008	4.60	$\times 10^{-20}$ cm ² /molec
Optical depth, sat liq 298K	0.30	0.018	0.15	0.014	0.003	14.9	0.003	cm
Optical depth, sat vap 298K	93	5.72	45	4.24	3.07	16244	2.89	cm

species, utilizing the acetone spectrum given by Lozano et al,⁷ it was found that the fluoroketone fluorescence efficiency is three times higher than that of acetone.

D. Emission

1. Setup

For the emission measurements, the fluoroketone was excited at 355 nm using the third harmonic of a Continuum SL-II Nd:YAG laser with three 355 nm dielectric mirrors and a 355 nm dichroic beamsplitter used to eliminate the 532 nm residual. A schematic of the setup can be found in Figure 6. The testcell consisted of a carbon steel high-pressure cell from LJ Star fitted with fused silica windows for laser beam propagation and a 1" NPT Metaglas borofloat window for emission detection. The testcell was fitted with an Omega PR-11 RTD temperature probe and a 210 W tape heater for temperature control carried out by an Omega CN132 controller. An argon cylinder was used for injection of liquid fluoroketone and pressurization of the testcell up to 24 bar. Each test was started with purging the cell with argon and then addition of liquid fluoroketone until it was visible in the side windows of the testcell. The exhaust valve was then closed and the desired operating conditions were established through adjusting the argon pressure prior to closing the gas valve and through heating of the cell. To establish stable conditions in the thick-walled cell and make sure that the vapor had reached equilibrium conditions, this process took on the order of one hour. The cell was sealed off and maintained at constant temperature within 3K during the tests. The presence of a large free surface of liquid fluoroketone in the chamber replenishes the vapor to compensate for fluoroketone photolysis. The collection optics consisted of a Hoya L38 380 nm longpass filter, two $f=+50$ mm fused silica lenses feeding a 3 m long fused silica optical fiber with 200 μ m core diameter connected to a PI Acton HRE250 echelle spectrometer with a PIMAX2 512 \times 512 HB ICCD.

2. Results

Runs were carried out for 11 different P,T-conditions and the spectra taken. Three of these spectra are shown in Figure 7. Relatively minor variations in the acquired spectra were noted as the temperature and pressure were varied. In order to quantify these shifts, the L/R ratio, referring to the integrated intensities over the ranges L: 370-410 nm (left flank) and R: 460-500 nm (right flank), is used. Figure 8 shows how this quantity varies for the 11 runs. The L/R ratio increases at the saturation line near 90°C due to that the right flank from 440 nm and up growing weaker, making the emission spectrum approach that of hexafluoroacetone.⁸ When comparing the emission spectrum to that of acetone using 266 nm data from Tran et al,⁹ fluoroketone has an almost identical emission peak near 420 nm, and

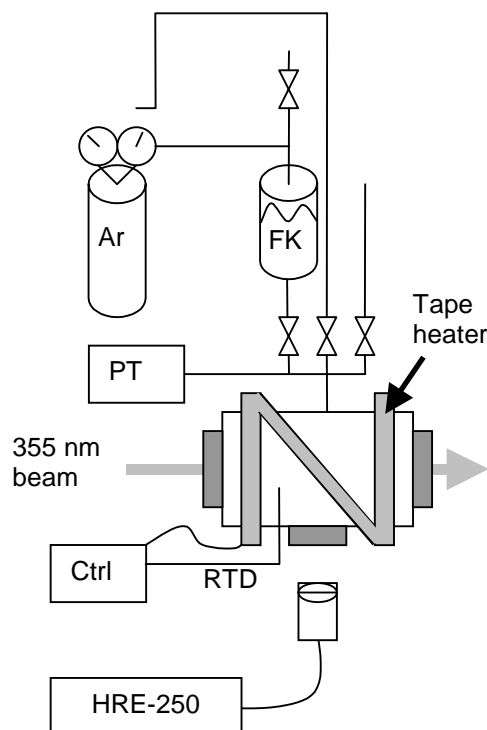


Figure 6. Schematic of the experimental setup used to determine the fluoroketone emission spectra. Ar: Argon cylinder, PT: Pressure transducer, Ctrl: Temperature controller, FK: Liquid fluoroketone supply, HRE-250: Echelle spectrometer, RTD: Temperature probe.

similar width FWHM 105 nm compared to 109 nm of acetone in ambient air. When phosphorescence is of importance, i. e. in the absence of oxygen, the emission spectrum of acetone will be broadened and red-shifted. Extrapolating from the 266 and 285 nm excitation results of Tran et al,⁹ using 355 nm rather than 266 nm excitation will lead to red-shift of the fluorescence signal and increased importance of the phosphorescence signal. While no data on acetone emission for 355 nm excitation was found in literature by the present author, the emission spectrum given for 308 nm excitation by Lozano et al⁷ is substantially red-shifted, exhibiting double peaks at 445 and 480 nm and having a FWHM of 153 nm.

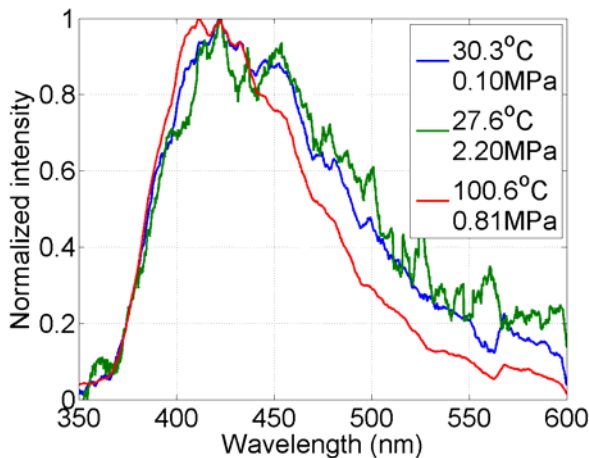


Figure 7. Fluoroketone emission spectra at various conditions.

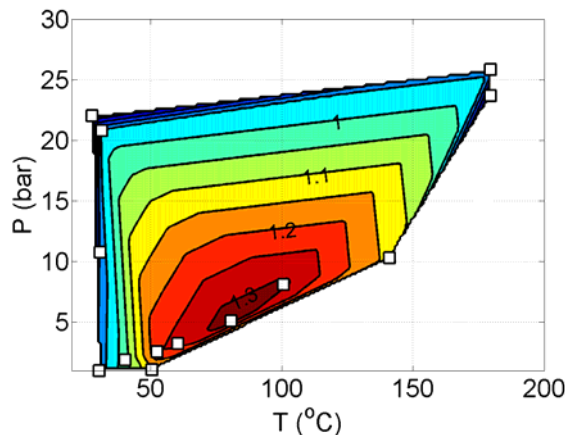


Figure 8. Shift in the fluoroketone emission spectrum as a function of pressure and temperature. Squares: Run conditions, Contours: Constant L/R ratios (indicated).

E. Photolysis

As has been discussed previously, UV light will lead to photolysis of the fluoroketone, creating its limited atmospheric lifetime. Taniguchi et al have studied the photolysis mechanism in air in great detail.¹⁰ The primary products were found to be COF_2 and $\text{CF}_3\text{C}(\text{O})\text{F}$ with minor amounts of CF_3OH and $\text{CF}_3\text{O}_3\text{CF}_3$ also identified. From a practical experimental standpoint, the formation of CF_3OH in the presence of water vapor is of particular concern, since this species will spontaneously decompose into COF_2 and HF . The highly corrosive hydrofluoric acid may then attack elastomers, glass windows etc. Taniguchi et al report a halflife of 4-5h for CF_3OH in their fog chamber, suggesting that removal of irradiated material from a test chamber may be prudent. We have also observed quartz window etching when irradiated liquid fluoroketone was left in the test chamber overnight. A second concern is the potential for fluorescence of decomposition products, analogous to that of biacetyl formed from photolysis of acetone. To quantify the decay of fluoroketone and the impact of decomposition products on the measured fluorescence spectra, a setup where fluoroketone vapor/bath gas mixtures of known concentration can be continuously passed through a test chamber has been developed. A sketch of this setup is shown in Figure 9.

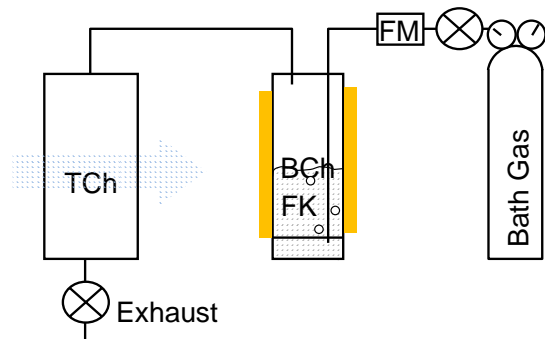


Figure 9. Fluoroketone spectroscopy setup for continuous feed. TCh: Test chamber, BCh: Bubble chamber with liquid fluoroketone and heaters, FM: Flowmeter.

IV. Conclusions

The density and dynamic viscosity of a perfluorinated ketone were investigated along with its fluorescence spectrum with 355 nm excitation. These were the key findings:

- ◆ The emission spectrum exhibits minor variation with pressure and temperature within the range of conditions tested, $1 < P < 23.6$ bar, $22.5 < T < 179.6$ °C in argon bath gas.
- ◆ The spectrum is qualitatively similar to the emission spectra of acetone and hexafluoroacetone with peak emission at 420 nm and a 50% of peak range of 386-490 nm.

- ◆ The fluorescence efficiency after excitation at 266 nm of saturated vapor in ambient air is approximately three times higher than that of acetone.

Acknowledgments

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