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Gas Phase Oxygen Quenching Studies of Ketone Tracers for Laser-Induced Fluorescence Applications in Nitrogen Bath Gas

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ABSTRACT In this paper we report the quantitative oxygen quenching effect on laser-induced fluorescence of acetone, methyl ethyl ketone, and 3-pentanone at low pressures (∼700 torr) with oxygen partial pressures up to 450 torr. Nitrogen was used as a bath gas in which these molecular tracers were added in different quantities according to their vapor pressure at room temperature. These tracers were excited by using a frequency-quadrupled, Q-switched, Nd:YAG laser (266 nm). Stern–Volmer plots were found to be linear for all the tracers, suggesting that quenching is collisional in nature. Stern–Volmer coefficients (k_{sv}) and quenching rate constants (k_q) were calculated from Stern–Volmer plots. The effects of oxygen on the laser-induced fluorescence of acetone, methyl ethyl ketone, and 3-pentanone were compared with each other. Further, the Smoluchowski theory was used to calculate the quenching parameters and compared with the experimental results.

KEYWORDS diffusion coefficient, fluorescence quenching, ketones, LIF, oxygen

INTRODUCTION

Laser-induced fluorescence (LIF) and planar laser-induced fluorescence (PLIF) techniques find vast applications in engineering[1] and biomedical imaging.[2,3] LIF and PLIF in gas phase are frequently used in fluid dynamics and combustion diagnostics. LIF intensity from the molecular tracer depends on the flow parameters such as pressure, velocity, temperature, and gas composition.[1,4,5] Ketones are the most frequently used organic carbonyls as tracers for gas flow visualization. Among these, acetone is known to be a very popular tracer due to its high vapor pressure, low boiling point (56°C), and excellent fluorescent properties.[6,7] Methyl ethyl ketone (MEK) has similar photo physical properties (absorption and fluorescence spectrum) as that of acetone. The LIF of 3-pentanone was previously explored by several researchers in temperature and jet mole fraction

imaging. This tracer has slightly higher quantum yield compared to the other two ketones.[8,9] Fluorescence quenching in organic molecules by oxygen and other quenchers is well known in liquid and gas phase.[10,11] For a long time quantitative fluorescence quenching of ketones in gas phase by molecular oxygen was not studied; however, Nau and Scaiano[12] found a little effect of oxygen on the fluorescence of ketones. They have investigated quantitative oxygen quenching of fluorescence from some ketones and diketones in liquid phase. The oxygen quenching of LIF of toluene in gas phase at elevated temperatures (300–650 K) for 248-nm and 266-nm excitation wavelengths was carried out by Koban et al.[13] Based on the Stern–Volmer (SV) plots, Koban et al. found that there is a decrease in the effect of oxygen quenching with an increase in the temperature. Koban et al.[14] also studied the effect of oxygen in LIF of a 3-pentanone tracer in nitrogen and air in engine-related conditions and concluded that at 248-nm excitation the oxygen effect becomes predominant at higher pressures.

Recently we have been using the LIF technique in quantitative high-speed flow studies in which these ketones have been used as tracers. Due to the natural presence of oxygen in many gas flow problems, for example, air, understanding the quantitative effect of oxygen on LIF intensity is more significant. As per our knowledge oxygen quenching rate constants for ketones relevant to LIF applications in gas phase have not been quantified in the previous literature. In this paper, we present oxygen quenching of a LIF signal from acetone, methyl ethyl ketone (MEK), and 3-pentanone in nitrogen bath gas at low pressures (~700 torr). The objective of the present work is to quantify oxygen quenching in ketones relevant to LIF and compare the results with the well-established Smoluchowski theory. Results presented here are very useful in LIF studies of high-speed flows using ketones as tracers.

THEORY

For weak excitation (linear excitation regime) the fluorescence intensity F is directly proportional to number density of exciting species n_{abs}(m^{-3}), absorption coefficient σ_a, and fluorescence quantum yield Φ:

$$F \propto n_{abs}(P, T)\sigma_a(\lambda, T)\Phi(\lambda, T, n_i) \qquad (1)$$

where P and T are total pressure and temperature of the tracer, respectively, and λ is the excitation wavelength. The effect of oxygen quenching depends on the fluorescence quantum yield as shown in the following equation:

$$\Phi = \frac{kf}{k_{total} + k_q \times n_{o2}} \qquad (2)$$

where k_f (s^{-1}) is the rate of fluorescence intensity, k_{total} (s^{-1}) is the total rate of deactivation including nonradiative decay, k_q (m^{3}s^{-1}) is the bimolecular quenching rate constant, and n_{o2} is the number density of quencher.

$$\frac{\Phi_0}{\Phi} = \frac{F_0}{F} = \frac{k_f}{k_{total}}\frac{k_{total} + k_q \times n_{o2}}{k_f} = 1 + \frac{k_q}{k_{total}} \times n_{o2} \qquad (3)$$

where Φ_0 and Φ are quantum yields in the absence and in the presence of quencher given by the following relation:

$$\Phi_0 = \frac{kf}{k_{total}}$$

The effect of molecular quenching is expressed as a Stern–Volmer coefficient (k_{sv}), which is given by the ratio of the quenching rate coefficient to the total rate of deactivation:

$$k_{SV} = \frac{k_q}{k_{total}} = k_q\tau_{eff} \qquad (4)$$

where τ_{eff} is the effective lifetime of the excited state and the SV factor (k_{sv}) can be easily obtained from the slope of the SV plot by using the following equation:

$$\frac{F_0}{F} - 1 = k_{SV} \times n_{o2} \qquad (5)$$

where F and F_0 are the LIF intensity in the presence and in the absence of quencher, respectively.[13,15]

For diffusion-controlled quenching, the reaction rate of quenching (k_q) is equal to the diffusion rate constant (k_d) of the reaction. According to Smoluchowski's simplified theory, the diffusional rate constant is given by the following equation:

$$k_d = 4\pi N_A R_c D \qquad (6)$$

where N_A is Avogadro's number, and R_c is the closest distance between the molecules (Å), given by the sum of radii of the fluorescent tracer and the quencher. D is the mutual diffusion coefficient (m²/s) expressed by the following Stokes–Einstein relation:

$$D = \frac{kT}{f\pi\eta}\left(\frac{1}{R_t} + \frac{1}{R_q}\right) \qquad (7)$$

where R_t and R_q are the radii of tracer and quencher (Å), respectively; η is the viscosity of the medium; f is the coefficient equal to 4 for slip boundary conditions and 6 for stick or no-slip boundary conditions; T is the absolute temperature; and k is the Boltzmann's constant.[15] The radius of the tracer was calculated by adding atomic volumes as given by Edward[16] and that of quencher was taken from Kuznicki et al.[17] The Stokes–Einstein diffusion equation is frequently used for modeling of fluorescence quenching in fluid.[10,11,18,19] For relatively small molecules the above equation underestimates the diffusion coefficient.[11] This is due to the basic assumption of the Stokes–Einstein relation, which is applicable for large massive particles diffused in smaller particles, at infinite dilutions.[20] Thus, in the present study, we have used an alternate equation (Chapman and Enskog relation) based on thermodynamic and physical properties such as Lennard–Jones (L–J) parameters, temperature, and pressure. The Chapman–Enskog relation for mutual diffusion coefficient is given by the following relation:[21]

$$D = 0.001858T^{\frac{3}{2}}\sqrt{\frac{M_t + M_q}{M_tM_q}}\frac{f_D}{p\sigma_{tq}^2\Omega_D} \qquad (8)$$

where M_t and M_q are the molecular mass of the tracer and the quencher molecules, and f_D is the second-order correction factor, usually between 1 and 1.03. The value f_D is taken as 1 in the present calculations and p is the total pressure of the gas mixture in Pa. σ is the Lennard–Jones potential parameter. The Ω_D is the collisional integral given by the following equation:

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.1930}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)} \qquad (9)$$

where $T^* = kT/\varepsilon_{tq}$, $\sigma_{tq} = 1/2(\sigma_t + \sigma_q)$, $\varepsilon_{tq} = (\varepsilon_t\varepsilon_q)^{1/2}$; σ and ε are the L–J potential parameters. Subscripts t and q represent tracer and quencher, respectively. These values were taken from the previous literature.[21,22]

EXPERIMENTAL

Experiments were carried out in a zinc-coated mild steel chamber of length 30 cm and inner diameter 10 cm with quartz windows (2.5 cm) on four sides of the chamber as shown in Fig. 1. A frequency-quadrupled Q-switched Nd:YAG (LAB190) laser (Newport Corporation, Irvine, California, USA) with a pulse width of 8 ns at 266 nm was used as an excitation source. An Acton VM502 monochromator (Princeton Instruments, Trenton, New Jersey, USA) connected to PMT was used to record the fluorescence intensity. Nitrogen gas was bubbled through the bottle containing tracers to produce tracer-saturated gas. Bath gas pressure inside the cell was kept at 700 torr for all the tracers. Oxygen pressure inside the chamber was varied from 0 to 450 torr.

To ensure the linearity of LIF intensity with input laser energy, LIF intensity was plotted as a function of laser energy as shown in Fig. 2. The linear fluorescence regime was observed for all three tracers. Thus, laser energy was kept at 30 mJ for all the experiments. The fluorescence emission from acetone and MEK tracers was collected at 435 nm ($\lambda_{\max}$);[23] for 3-pentanone the monochromator was set to 420 nm ($\lambda_{\max}$).[25]
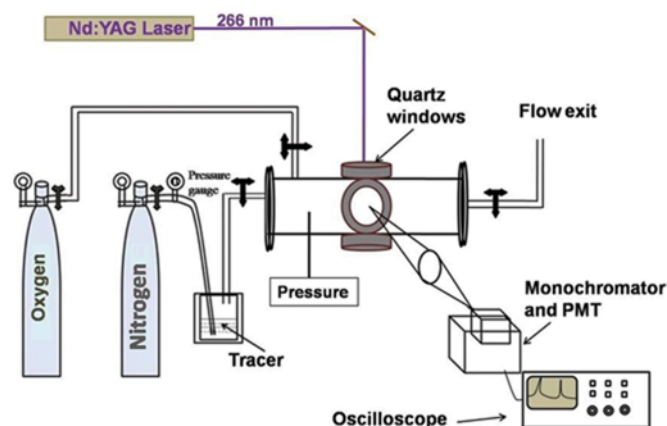

FIGURE 1 Experimental arrangement used for LIF studies. (Color figure available online).
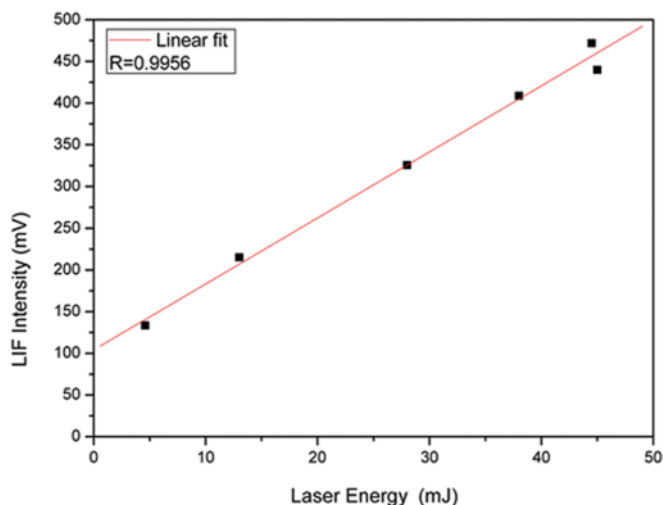
FIGURE 2 The laser energy dependence on the gas phase LIF of acetone for nitrogen gas pressure at one bar. (Color figure available online).

RESULTS AND DISCUSSION

Figures 3, 4, and 5 are the SV plots for acetone, MEK, and 3-pentanone in nitrogen bath gas, respectively. The linearity of the SV plot suggests that quenching is collisional in nature and any departure from the linearity is due to the contribution from the other processes like excimer or exciplex formation.[15] In the present study, oxygen quenching of the LIF signal shows the linear Stern–Volmer behavior for all the tracers. From SV plots SV coefficients k_{sv} and quenching rate constant k_q for tracers under study were calculated and are presented in Table 1.

FIGURE 4 Stern–Volmer plot for MEK LIF in nitrogen bath gas. Bath gas pressure was 700 torr and with 266-nm excitation. (Color figure available online).

To calculate the quenching rate constant the required lifetime of the excited state was taken from the previous literature.[12,24]

Molecular oxygen was found to be an efficient fluorescence quencher due to its ground triplet state ($^3\Sigma_g^-$), and there are two low-lying singlet states ($^1\Delta_g$ and $^1\Sigma_g^+$). Oxygen quenching of fluorescence from organic molecules is possible by electronic transition from the triplet ground state to either of these two low-lying singlet states of oxygen. Electronic energy transfer equations between the excited
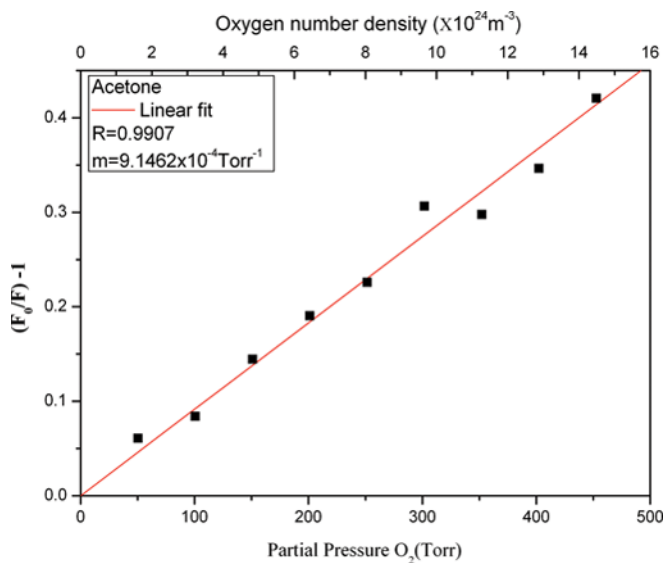

FIGURE 3 Stern–Volmer plot for acetone LIF in nitrogen bath gas. Bath gas pressure was 700 torr and with 266-nm excitation. (Color figure available online).

FIGURE 5 Stern–Volmer plot for 3-pentanone LIF in nitrogen bath gas. Bath gas pressure was 700 torr and with 266-nm excitation. (Color figure available online).
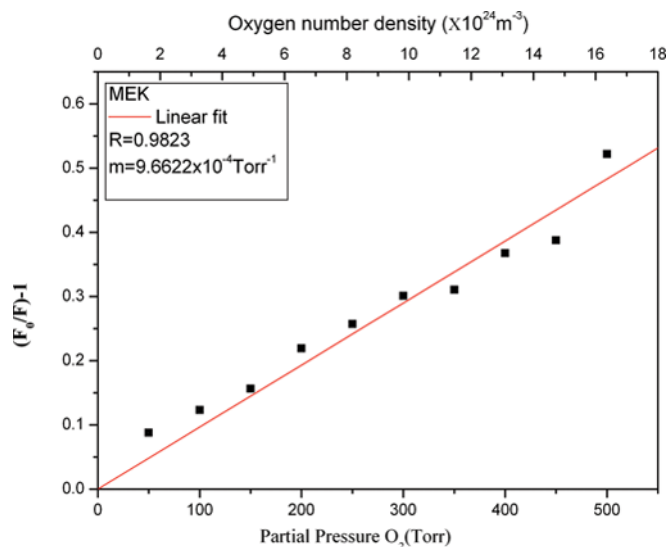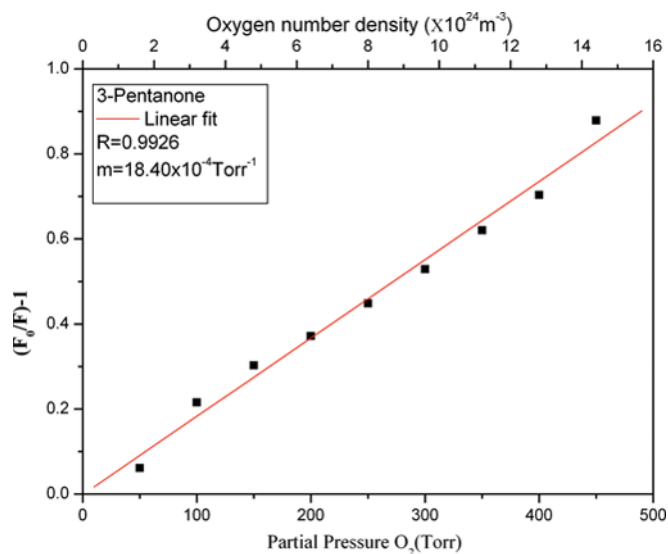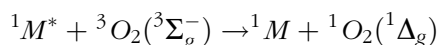
TABLE 1 SV Coefficients and Oxygen Quenching Rate Constants for the Ketones Under Study
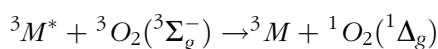
Tracers	Chemical formula	k_{sv} (10^{-4} Torr^{-1})	k_{sv} (Lmol^{-1})	τ(ns)	k_q (10^9 LM^{-1} s^{-1})
Acetone	CH_3-CO-CH_3	9.1462	17.104	1.95[a]	8.7711
MEK	CH_3-CO-C_2H_5	9.6622	18.069	2.9[b]	6.2306
3-Pentanone	C_2H_5-CO-C_2H_5	18.400	34.409	3.2[b]	10.753

[a]Reference 12.
[b]Reference 24.

molecule M* and the oxygen quencher can be written as:[1,15]

$$^1M^* + {}^3O_2(^3\Sigma_g^-) \rightarrow {}^1M + {}^1O_2(^1\Delta_g)$$

or

$$^3M^* + {}^3O_2(^3\Sigma_g^-) \rightarrow {}^3M + {}^1O_2(^1\Delta_g)$$

Excited state complex (exciplex, M*O$_2$) formation may also influence the quenching, but this requires an energy difference greater than 0.98 eV between the singlet and triplet state of the tracer, which is the first singlet excitation of oxygen. Hence, this process is less likely in the case of ketones, unlike quenching of fluorescence from aromatic molecules.[8] Thus, the influence of oxygen may be attributed to the collisional quenching. The k_q [O$_2$] is the measure of the oxygen quenching of LIF. Similar to the results observed in liquid phase by other researchers, we have found $k_q \sim 10^9$ Lmol^{-1} s^{-1}. Further, k_q values for acetone and MEK were found to be low and comparable, whereas for 3-pentanone they were slightly high. This may be attributed to the photo physical similarity of acetone and MEK compared to 3-pentanone. The long lifetime of the excited state may also contribute to more oxygen quenching sensitivity.[15] Thus, from the SV factors and quenching rate constants, the effect of oxygen

on the LIF of acetone and MEK is found to be relatively low.[13] This may be attributed to faster vibrational relaxation as compared to intersystem crossing.[6]

Oxygen quenching observed here is collisional in nature and hence diffusion controlled. For diffusion-controlled quenching, the theoretical approach explained in the theory was used to calculate the diffusion rate constant in the present work.

Experimental and calculated values of the S–V coefficient and quenching rate are tabulated in Table 2. The deviation is observed between the quenching rate calculated by using the Stokes–Einstein diffusion relation and experimentally determined values. This may be due to the underestimation of the diffusion coefficient for small molecules as observed by other researchers.[11] The k_q and k_{sv} calculated by using the mutual diffusion coefficient from the Chapman and Enskog relation are comparable with the experimentally estimated values. This may be due to the Chapman and Enskog relation taking into account physical properties such as total pressure of the gas mixture. Figure 6a and 6b shows the correlation between the experimental and theoretical estimates of k_{sv} and k_q by using the Chapman and Enskog relation. Relatively good correlation between experimental and theoretical values was observed for acetone and MEK, but not 3-pentanone. This deviation may be due to the longer fluorescence lifetime of 3-pentanone.

TABLE 2 Experimental and Calculated SV Coefficients and Oxygen Quenching Rate Constants

Tracers	Experimental			Calculated from the model		
	k_{sv} (Lmol^{-1})	k_q (10^9 LM^{-1} s^{-1})	k_{sv}[a] (Lmol^{-1})	k_q[a] (10^9 LM^{-1} s^{-1})	k_{sv}[b] (Lmol^{-1})	k_q[b] (10^9 LM^{-1} s^{-1})
Acetone	17.104	8.7711	1.1989	0.6148	14.939	7.6608
MEK	18.069	6.2306	1.8272	0.6300	21.743	7.4976
3-Pentanone	34.409	10.753	2.0606	0.6439	23.900	7.4800

[a]Stokes–Einstein relation (Eq. 7).
[b]Using Chapman and Enskog relation (Eq. 8).
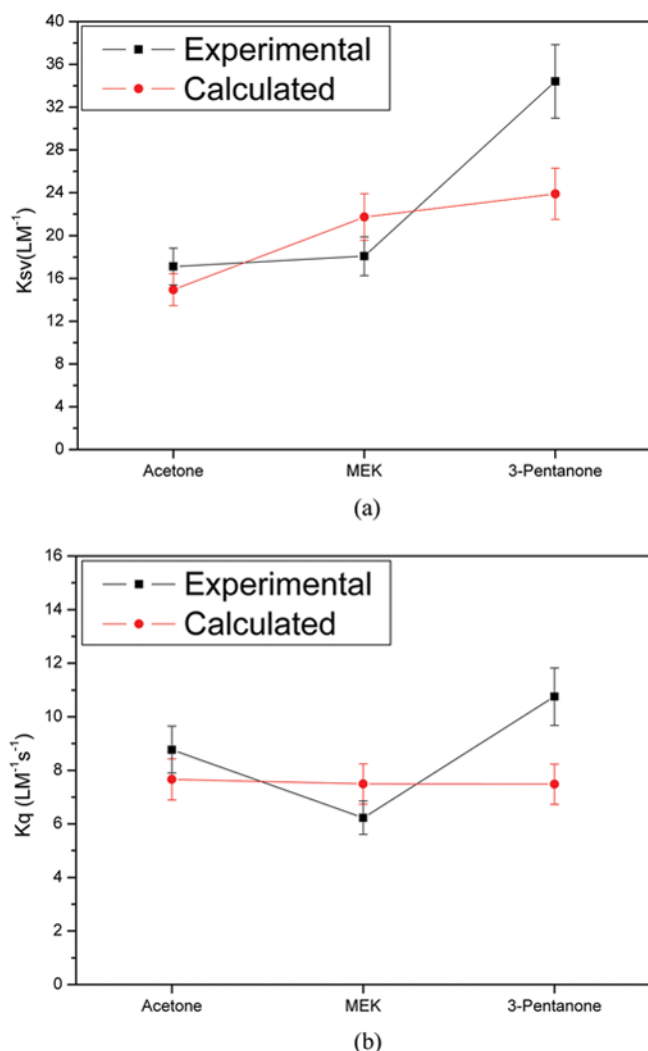
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FIGURE 6 Comparison of experimentally determined and calculated (by using Chapman and Enskog relation) values of (a) SV coefficient (k_{sv}) and (b) quenching rate (k_q) for all three tracers. (Color figure available online).

CONCLUSION

We have investigated the quenching of the LIF signal from the ketone tracers by molecular oxygen in nitrogen bath gas. Oxygen partial pressure was varied from 0 to 450 torr. From the SV coefficients and quenching rate constants, the effect of molecular oxygen was found to be relatively low in the case of acetone and MEK compared to 3-pentanone. This shows that, despite their low quantum yields compared to 3-pentanone, these tracers can be used for the gas flows that contain trace amounts of oxygen at atmospheric pressures. Further, the Smoluchowski theory was used to calculate the quenching rate and compared with the experimental results. It was found that the estimation of the quenching rate by

using the Stokes–Einstein diffusion relation deviates from the experimental result. This is due to the underestimation of the diffusion coefficient. The results obtained by using the diffusion coefficient from the Chapman and Enskog relation are comparable with the experimental quenching rates. The deviation in the case of 3-pentanone is attributed to its long fluorescence lifetime. The present study on the effect of oxygen quenching on LIF intensity in the presence of tracers is very useful in understanding the chemistry of high-speed flows generated in shock tunnels.

ACKNOWLEDGMENTS

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