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Non-linear pressure dependence of A-state fluorescence lifetime of formaldehyde

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ABSTRACT Fluorescence lifetimes of formaldehyde excited at 352 nm ($\tilde{A}^1A_2 - \tilde{X}^1A_1 4_0^1$ band) were measured as a function of bath gas pressure. He, N_2, O_2, CO_2 and HCHO were investigated for the bath gas and the temperature dependence between 298 and 500 K for N_2 and O_2 bath gases was also examined. It was found that the non-linear pressure dependence of the lifetime τ is successfully reproduced by the model formula

$$\tau^{-1} = k_\mathrm{f} + (k_\mathrm{q} + k_\mathrm{a})[\mathrm{M}] - \frac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{b}[\mathrm{M}] + k_\mathrm{p}}[\mathrm{M}]^2,$$

where [M] is the concentration of a bath gas and k_f, k_q, k_a, k_b and k_p are the constants determined for each bath gas. This model assumes that the optically excited formaldehyde undergoes a reversible collision transfer to a state of higher spontaneous decay rate along with direct collisional and spontaneous deactivation pathways. It was confirmed that a lifetime in a bath gas mixture can be reproduced by this formula with the constants individually obtained as linear combinations of each bath gas contribution. The temperature dependence is expressed by assigning activation energies for the constants in the formula.

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1 Introduction

Formaldehyde (H_2CO) is a significant intermediate in hydrocarbon oxidation and one of a few polyatomic stable species detectable by laser-induced fluorescence (LIF). A number of measurements of formaldehyde in burners and internal combustion engines have been performed since the initial demonstration of Harrington and Smith [1–6]. The role of formaldehyde in the influence of the growth of a low-temperature chain reaction in compression ignition was reported recently [7]; thus, the demand to monitor this species quantitatively in a pressure-changing environment is increasing. Based on past studies, the most popular transitions for fluorescence observations are $\tilde{A}^1A_2 - \tilde{X}^1A_1 4_0^1$ around 352 nm and $2_0^1 4_0^1$ around 339 nm. Frequency-tripled Nd:YAG lasers (355 nm) were also used to excite a weak part of the 4_0^1 band because of the convenience of a non-tunable source.

The understanding of quenching behavior necessary to quantify the fluorescence signal has not been fully established. Very recently, Metz et al. [6] have reported pressure-dependent fluorescence lifetimes of formaldehyde in nitrogen bath gas up to 10 bar between 295 K and 770 K. They showed significantly curved Stern–Volmer plots at every temperature empirically fitted to the nth power of pressure, where n lies between 0.2 and 0.4. This anomalous behavior has already been reported for Ar, CO_2, CHF_3 and O_2 bath gases up to 1 bar in the measurements of Weisshaar et al. [8]. It is known that the lifetime of A-state formaldehyde depends significantly on vibrational and rotational states, with a general trend of decreasing lifetime with increasing energy level of the states, primarily because of an increasing predissociation rate [9, 10]. Collisional transfer between these states is suggested to be responsible for this pressure dependence; however, there seems to be no reported formulation that reflects the physical mechanism that will permit one to estimate the fluorescence quantum yield in a real gas of mixed composition.

In this communication, we provide data of formaldehyde fluorescence lifetimes as a function of bath gas pressure in N_2, O_2, CO_2 and CH_3OCH_3, and then propose a model formula successfully expressing the curved pressure dependence. The physical meaning of the fit parameters, low- and high-pressure limits, responsible quantum states and availability of the model in practical conditions are discussed.

2 Fluorescence-lifetime measurements

2.1 *Experimental*

The fluorescence lifetime of A-state formaldehyde was measured in a cell consisting of a 20 × 20-cm^2 stainless steel cross, quartz windows at the four ends, a gas supply and a vacuum pumping setup. Formaldehyde was synthesized from polyaldehyde, distilled in vacuo and stored in glass bulbs in a pure or diluted state at a partial pressure

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less than a few Torr. The center portion of the cell is electrically heated on necessity up to 700 K. The partial pressure of formaldehyde and the total pressure were set in a flowing or static state. Mass-flow controllers and capacitance manometers of different ranges were used to set the pressures.

The excitation light source is a pulsed dye laser (Lambda Physik, LPD 3002) pumped by an excimer laser (Lambda Physik, LPX 101i). Mixed solutions of *p*-terphenyl and DMQ dyes in dioxane solvent were used to generate tunable oscillations around 352 nm. The $^{R}R_3$ rotational band head in the 4_0^1 vibrational transition at 352.4 nm was mainly excited for the lifetime measurements in this work. Typical pulse energy after collimating to a 0.2-cm-diameter beam is 1.0 mJ. The pump beam was fed through an optical axis of the cell and the fluorescence was detected through another axis by a photomultiplier (Hamamatsu, R4220P) and stored in a digital oscilloscope with an input impedance of 50 Ω. A long-pass filter was placed in the detection path to cut out the stray signal of the pumping light. Usually, 10–30 signals were averaged to obtain a good-quality decay profile. A photodiode was also used to monitor the laser pulse incidence and trigger the oscilloscope so that jittering of the excimer laser oscillation did not influence the averaging.

3 Results

Figure 1 shows the observed fluorescence decay rate as a function of bath gas pressure up to 1000 Torr for bath gases of He, N_2, O_2, CO_2 and DME at 295 K. The partial pressure of formaldehyde was 30 mTorr. For all bath gases except O_2, the decay rate increases rapidly at lower pressures, and the slope levels at higher pressures toward a high-pressure limit. Similarly curved, non-Stern–Volmer behaviors have already been reported for bath gases of Ar, CO_2 and CHF_3 by Weisshaar et al. [8], and by Metz et al. [6] for N_2. The latter measurement was conducted over a wider range of pressures up to 10 bar with a better time resolution of a mode-locked YAG laser system in comparison to ours. Although Metz et al. excited formaldehyde at a slightly longer wavelength of 355 nm, their 295-K result is in good agreement with our current result for N_2 within our pressure range up to 1000 Torr. In the case of O_2, it is shown that the highest slope in the current investigation and the change of the slope are hardly recognized until the decay rate reaches 0.1 ns^{-1} at 700 Torr, which is the upper limit of our measurements. This is consistent with the study of Weisshaar et al., in which O_2 and NO are reported to be in the group of highest quenching rate.

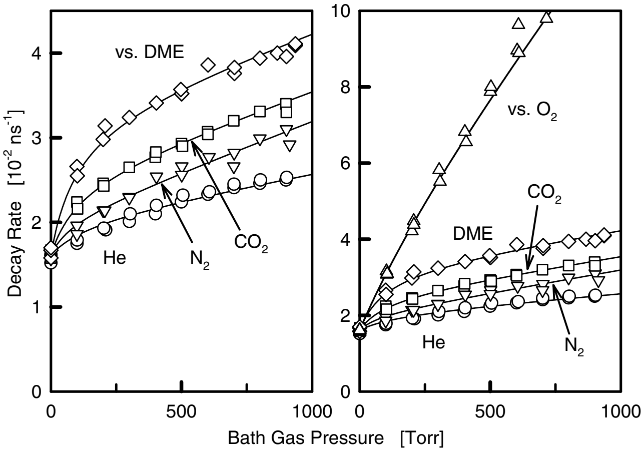

FIGURE 1 Fluorescence decay rates (inverse lifetimes) of formaldehyde as a function of bath gas pressure at room temperature (295 K). *Solid lines* are fitted by the current model. *Right* O_2 data with the same data as on the *left* in a different scale

4 Two-step quenching model

4.1 *Model description*

Metz et al. fitted their data of fluorescence decay rate as a function of pressure *p* empirically to a formula $\tau^{-1} = Ap^n$, where *A* and *n* are adjustable parameters [6]. The value *n* lies between 0.2 and 0.4 for N_2 bath gas depending on the temperature residing between 295 K and 770 K. However, this formula itself does not reflect the physical mechanism; hence, it does not assure the availability of extrapolation to higher pressure beyond the experimental range. Here we propose another expression derived by the following postulated mechanism.

A conceptual drawing of the mechanism is shown in Fig. 2. Let **A** be a quantum state of formaldehyde excited from the ground state **X** by the pumping laser. The **A** state may deactivate through a spontaneous process, i.e.

$$\mathrm{A} \rightarrow \mathrm{X}, \tag{1}$$

with a first-order rate constant k_f. This process includes fluorescence and nonradiative pathways such as predissociation and the product is not strictly limited to the ground state of the original molecule. In a finite-pressure environment, the **A** state may collisionally deactivate, i.e.

$$\mathrm{A} + \mathrm{M} \rightarrow \mathrm{X} + \mathrm{M}, \tag{2}$$

with a bimolecular rate constant k_q. The above two processes alone provide the regular decay behavior in which the rate is linear to pressure with the intercept k_q.

Here, we assume that the **A** state also undergoes a transfer to another state $\mathbf{A}^*$ collisionally, i.e.

$$\mathrm{A} + \mathrm{M} \leftrightarrow \mathrm{A}^* + \mathrm{M}, \tag{3}$$

with a bimolecular rate constant k_a. This is a reversible step with a backward bimolecular rate constant k_b. Finally, the $\mathbf{A}^*$ state deactivates spontaneously, i.e.

$$\mathrm{A}^* \rightarrow \mathrm{X}, \tag{4}$$

with a first-order rate constant k_p.

The combined rate of decay of **A** population according to the above sequence is

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_\mathrm{f}[\mathrm{A}] - k_\mathrm{q}[\mathrm{A}][\mathrm{M}] - k_\mathrm{a}[\mathrm{A}][\mathrm{M}] + k_\mathrm{b}[\mathrm{A}^*][\mathrm{M}], \tag{5}$$

and the rate expression of $\mathbf{A}^*$ is given by

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{A}][\mathrm{M}] - k_\mathrm{b}[\mathrm{A}^*][\mathrm{M}] - k_\mathrm{p}[\mathrm{A}^*]. \tag{6}$$

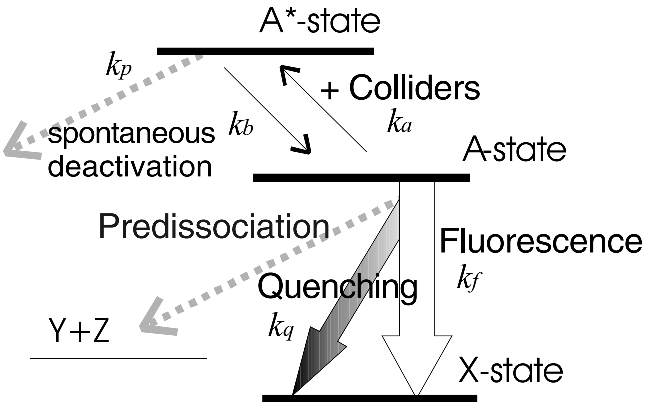

FIGURE 2 A conceptual scheme of the present model of pressure-dependent fluorescence lifetime

	Bath gas dependent bimolecular rate constants (s^{-1} $Torr^{-1}$)		
Bath gas	$k_a \times 10^{-5}$	$k_b \times 10^{-6}$	$k_q \times 10^{-4}$
He	2.12	2.12	0.57
N_2	2.98	3.00	1.18
CO_2	3.20	2.25	1.10
DME	5.25	2.25	0.55
O_2	2.42	0.80	8.90
Bath gas independent rate constants (s^{-1})			
k_p	35.0×10^7	k_f	1.42×10^7

TABLE 1 Fitted model parameters for the pressure-dependent fluorescence decay rate at room temperature (295 K)

Setting this equation to zero under the steady-state approximation gives the value of **A*** as

$$[A^*]_{SS} = \frac{k_a[A][M]}{k_b[M] + k_p}. \tag{7}$$

Substituting this value into Eq. (5) gives

$$\begin{aligned}\frac{d[A]}{dt} &= -k_f[A] - (k_q + k_a)[A][M] \\ &\quad + \frac{k_a k_b}{k_b[M] + k_p}[A][M]^2. \end{aligned} \tag{8}$$

One obtains the effective decay-rate constant with the definition $-d[A]/dt = k_{eff}[A]$ as

$$\begin{aligned}k_{eff} &= k_f + (k_q + k_a)[M] \\ &\quad - \frac{k_a k_b}{k_b[M] + k_p}[M]^2. \end{aligned} \tag{9}$$

A curve showing the features of this equation is illustrated in Fig. 1. It is apparent that the intercept of the curve at zero pressure is k_f and the slope in the low-pressure limit is $k_q + k_a$. A high pressure limit expression is

$$\begin{aligned}k_{eff}(\infty) &= \lim_{[M]\to\infty} \left\{ k_f + (k_q + k_a)[M] \right. \\ &\quad \left. - \frac{k_a}{1 + k_p/k_b[M]}[M] \right\} \\ &\cong k_f + (k_q + k_a)[M] \\ &\quad - k_a\left(1 - \frac{k_p}{k_b[M]}\right)[M] \\ &= k_f + \frac{k_a k_p}{k_b} + k_q[M]. \end{aligned} \tag{10}$$

Hence, the high-pressure asymptote has the slope k_q and the intercept is $k_f + k_a k_p/k_b$. By using fittings to these limiting slopes and intercepts, k_f, k_q, k_a and k_p/k_b can be uniquely determined. Assuming that k_f is independent of the bath gas species, k_f and k_b could be determined in the entire curve-fitting procedure.

4.2 *Fitting to room-temperature data*

Parameter fittings were conducted for the current experimental data. The results are listed in Table 1 and the calculated curves are drawn in Fig. 1. It is shown that not only high- and low-pressure asymptotic behaviors are well reproduced but also the transient rates for all investigated bath gases.

Figure 3 shows an example of the decay rates in mixtures of different bath gases. In this case CO_2 was added to a HCHO sample with 400 Torr N_2 bath gas. It is demonstrated that the simple sum of pure bath gas decay rates, i.e.

$$\tau_{mix}^{-1} = \sum_j \tau_j^{-1}(P_j), \tag{11}$$

overestimates the measured mixture decay rate. In contrast, linear combinations of each of the collision parameters in Eq. (9), i.e.

$$k_{i,mix} = \sum_j k_{i,j} x_j, \tag{12}$$

where k_i is any of k_q, k_a or k_b, and x_j is the mole fraction of the jth bath gas species, successfully represent the experimental observations.

4.3 *Fitting to higher-temperature data*

Higher-temperature decay rates for N_2 and O_2 bath gases are shown in Fig. 4. In these fittings, k_f and k_p are

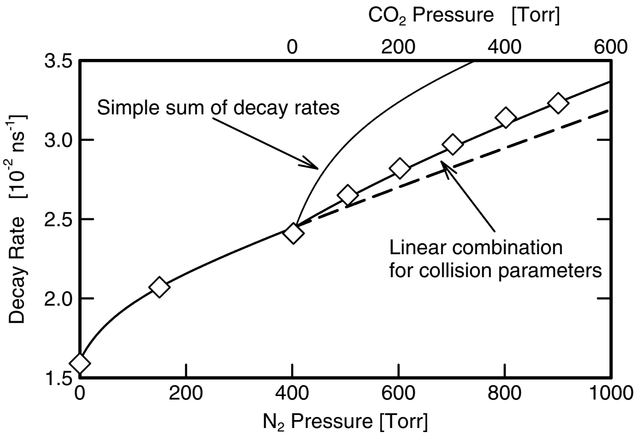

FIGURE 3 Decay-rate variation in bath gas mixing. Firstly, N_2 bath gas pressure was increased while the partial pressure of HCHO was constant, and then CO_2 was added to the sample of 400 Torr N_2 bath gas. *Symbols* are measured decay rates and the *thick solid curve* is calculated by the current model with the linear combination rule for individual collision parameters (see text). The *thin solid curve* overestimating the measurement is a simple sum of decay rates of pure bath gases at corresponding partial pressures

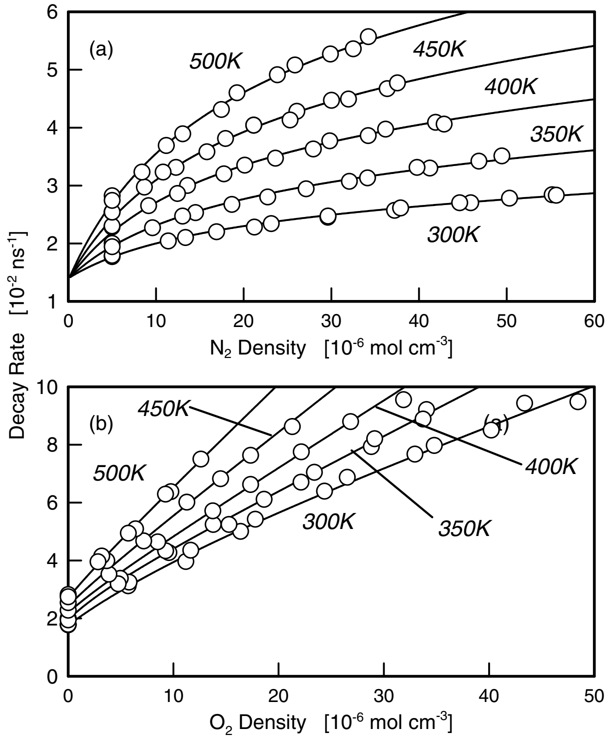

FIGURE 4 Pressure-dependent decay rates at various temperatures for N_2 (a) and O_2 (b) bath gases

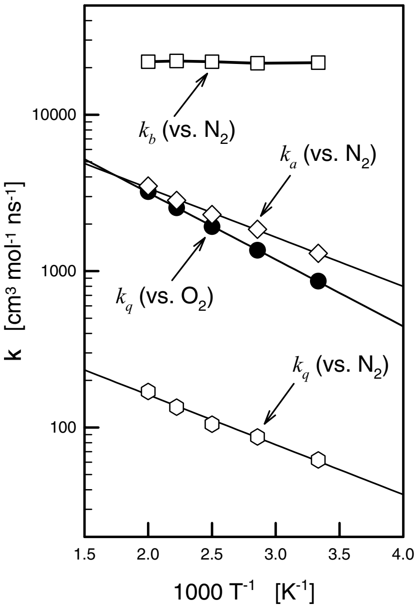

Figure 5 Arrhenius plot of the model parameters

given as constants independent of temperature. In the case of N_2 bath gas, all bimolecular constants (k_a, k_b and k_q) could be determined individually for each temperature. However, in the case of O_2 bath gas, only k_q could be determined since the linear trend is more significant at higher temperatures. The N_2 results are in good agreement with those of Metz et al. [6].

The temperature dependence of the fit parameters is shown in Fig. 5 in the form of an Arrhenius expression. It should be noted that the parameters for each temperature are individually determined; nevertheless, they are well within the straight lines drawn for the respective parameters, i.e. elementary steps corresponding to the parameters can be regarded as thermally activated processes having certain activation energies. k_a and k_q have similar activation energies of ~ 8.2 kJ/mol, whereas k_b is almost temperature independent. It seems reasonable that $\mathbf{A}^*$ is at a higher energy state than A so that the downward step corresponding to k_b has a lower activation energy than that of k_a.

5 Discussion

In the current model fitting procedure, the determination of parameters is empirical and the supposed lower and upper states (**A** and $\mathbf{A}^*$) are more or less imaginary, although the success of the fittings may suggest that the current formulation reflects the essential portion of the true physical mechanism forming the non-linear pressure dependence. It has been shown in past studies [9] that the rotationally resolved natural (collision-free) lifetime of the $\tilde{A}(S_1)$ state of formaldehyde varies non-systematically through different resonances to dissociative triplet $\tilde{a}(T_1)$ or high vibrational ground $\tilde{X}(S_0)$ states. The difference in lifetimes between rotational states is resolved within a few Torr of pressure owing to the fast rotational relaxation; hence, the 'zero-pressure' lifetime that we are observing in the current scale of pressure is the rotationally averaged lifetime. Higher vibrational states in $\tilde{A}$ tend to have shorter lifetimes; for example, the observed lifetime range of the 4^3 level is 14–52 ns, but unobserved lifetimes shorter than 10 ns were suggested [10]. The v_4 mode is the out-of-plane bending vibration having the smallest energy spacing of the six vibrational modes. The anharmonic energy levels of 4^1, 4^2 and 4^3 relative to 4^0 are 1.5, 6.5 and 11.3 kJ/mol, respectively, followed by the 2^1 state at 14.1 kJ/mol. Hence, it seems reasonable that the '**A** state' in the current model corresponds to the thermalized $\tilde{A}$ state, mainly distributed in 4^0 and 4^1 vibrations, rather than the laser-excited single 4^1 vibrational state. The '$\mathbf{A}^*$ state', for which about 10 kJ/mol of activation energy was obtained in the model fitting, may correspond to a number of higher vibrational states with a significant contribution in the 4^3 state.

The idea leading to the current formulation is similar to the Lindemann theory, which is the most basic form of the unimolecular reaction theory [11]. In the case of pressure dependence of rate constants for unimolecular reactions such as thermal dissociation, the simplest Lindemann formula is quantitatively incorrect in the fall-off pressure range, whereas high and low limit rates are well represented. A more advanced treatment like RRKM theory or an empirical correction with the 'fall-off factor' is required for a more precise expression. A similar improvement might be needed for the complete expression over a wider range of pressure and temperature for the present issue; however, the present fittings are sufficiently successful in representing the experimental lifetimes. This may be a result of the limited range of relevant energy levels compared to the case of general unimolecular reactions.

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