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Radiative lifetimes of the FeO orange system

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Abstract

The ground-state FeO molecules are generated from photolysis of $Fe(CO)_5$ in a $Fe(CO)_5/M(O_2$ or $N_2O)/Rg$(He or Ar) mixture using an unfocused weak UV laser beam. The formation of ground-state FeO molecules is identified by a laser-induced fluorescence (LIF) method. The LIF signal from FeO molecules is stronger in O_2 than in N_2O at the same partial pressures. The radiative lifetimes for seven bands in the FeO orange system are measured. They are substantially different depending on the excited band ranging from 260 ± 30 ns to 590 ± 50 ns. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

There have been substantial interests in the FeO molecule because of its complicated electronic states with six d electrons and its potential astrophysical importance of this molecule [1]. Various experimental techniques have been employed to generate FeO molecules in the gas phase; they involve reactions of O_2 with Fe atoms generated from various sources, such as arc discharge of an iron electrode [2], a high-temperature oven containing metallic iron [3,4], hallow cathode discharge [5], burning ferrocene, $Fe(C_5H_5)_2$, in a 2450-MHz microwave discharge [6,7], and laser ablation method [8,9]. Most of the previous works have been focused on the spectroscopic characterization of the ground-state FeO molecule and the FeO orange system. However, radiative lifetimes of the FeO orange system have been rarely studied [4].

In this Letter, we like to report a simple method of generating the ground-state FeO molecules and the results of radiative lifetime measurements for the FeO orange system. We have previously reported that a state-selected excited state of Fe atoms can be generated by multiphoton dissociation (MPD) of $Fe(CO)_5$ vapor at Fe atomic transition frequencies using an unfocused weak UV laser pulse [10,11]. As a continuing research, we attempted to investigate the reaction of a state-selected excited-state Fe atoms, $Fe(z^3D_3)$ for an example, with O_2 and N_2O by photolyzing $Fe(CO)_5$ molecules in a $Fe(CO)_5/M(O_2$ or $N_2O)/Rg$(He or Ar) mixture at 319.16 nm. Strong atomic emissions originated from $Fe(z^3D_3)$ state were easily observed, but no chemiluminescence from FeO^* was detected. We pursued two-color photolysis-probe experiments to look for the formation of the ground-state FeO molecules under our experimental conditions. When a visible probe laser was tuned to excite the FeO molecules following the irradiation of a $Fe(CO)_5/M(O_2$ or $N_2O)/He$ mixture with an unfocused weak UV laser pulse, rela-

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tively strong laser-induced fluorescence (LIF) signals from the FeO orange system were observed. This finding of an easy way to generate ground-state FeO molecules in the gas phase enabled us to study the radiative lifetimes and quenching rate constants for seven bands of the FeO orange system.

2. Experimental method

An experimental setup used for this work is basically the same as that reported previously [10]. The reaction cell was made of a 1-liter pyrex bulb and two pairs of 2.5 cm pyrex O-ring joints were attached to the bulb for the laser beam path and for the connection to a gas handling vacuum rack. A premixture of 0.75% $Fe(CO)_5$ in He or Ar was slowly flowed through the cell. When the flow was stabilized at a certain pressure, the other reactant gas (pure O_2 or N_2O) was introduced directly to the cell through a needle valve installed on a separated line. A typical flow rate of gases in the reaction cell was ~ 0.2 mmol min^{-1}. The total pressure as well as the partial pressures of the gases in the cell was controlled by adjusting the openings of inlet needle valves and an exit teflon valve. When the pressure in the cell was stabilized again, unfocused UV laser pulses in the 298–320 nm region were directed to the cell. The pulse energy of the photolysis laser (Quantel YG681-TDL50 with NBP) was $0.5 \sim 1.0$ mJ/pulse and the beam diameter was ~ 7 mm.

The ground-state $FeO(X^5\Delta_4)$ molecules were probed by LIF signals from the FeO orange system. The probe laser (Quantel YG581-TDL60 with NBP and DGO) was scanned in the 555–615 nm region and fluorescence from the FeO orange system was monitored at longer wavelengths shifted about 880 cm^{-1} from the excitation frequencies. The monitoring wavelengths correspond to the FeO^*(orange system) $\rightarrow FeO(X^5\Delta_4,\ v''=1)$ transitions [6,7]. A typical delay time between the photolysis and probe was set at ~ 20 μs to avoid interference from the Fe atomic fluorescence caused by the photolysis laser pulse. The pulse energy and linewidth of the probe laser was ~ 0.3 mJ/pulse and ~ 0.05 cm^{-1}, respectively. Fluorescence from the excited FeO molecules was monitored at the right angle with respect to the laser beam direction by using a 50 cm monochromator (Spex 1870C) equipped with a holographic grating and a Hammamatsu R928 photomultiplier (PM) tube. The signal from the PM tube was digitized with a transient digitizer (Tektronix 7912HB) and transferred to a laboratory computer for signal averaging and storage.

3. Results

3.1. Excitation and emission spectra

Fig. 1a shows a low resolution excitation spectrum of FeO molecules in the 555–615 nm region, which corresponds to the FeO^*(orange system) $\leftarrow FeO(X^5\Delta_4)$ transitions [6,7]. The photolysis wavelength was 319.16 nm, which corresponds to the

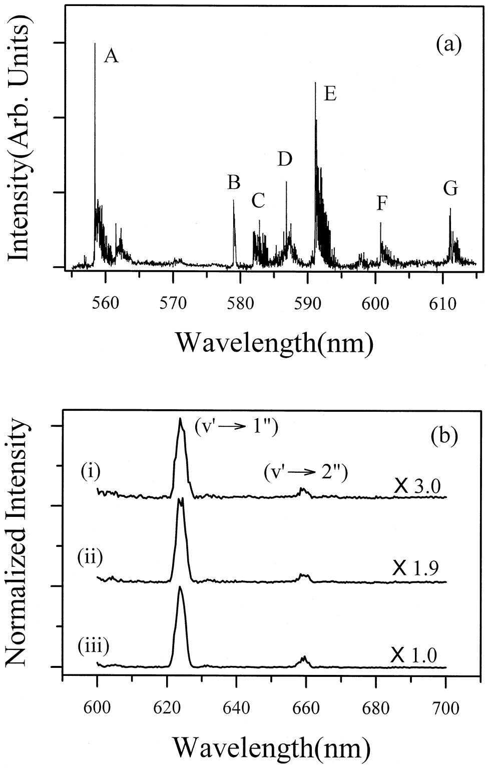

Fig. 1. (a) A low-resolution excitation spectrum of FeO generated from photolysis of a 0.75% $Fe(CO)_5$, 25% O_2 and $\sim 74\%$ He mixture. Total pressure was 0.4 Torr. (A) 558.3, (B) 579.0, (C) 582.0, (D) 586.8, (E) 591.9, (F) 600.5, and (G) 611.0 nm band. (b) Typical time resolved fluorescence spectra of FeO^* observed from 591.1 nm band excitation: (i) 30–130, (ii) 130–230, and (iii) 230–330 ns period. The composition of the gas mixture and total pressure are the same as those in (a). The intensities of the $v' \rightarrow 1''$ peak are normalized and the normalization factors are shown.

$z^3D_3 \leftarrow a^5D_4$ transition of the Fe atom. While scanning the probe laser in the 555–615 nm region, the fluorescence from the excited states was monitored at (A) 587.2, (B) 610.2, (C) 613.6, (D) 618.5, (E) 623.6, (F) 634.1, and (G) 645.8 nm, respectively. The total pressure was 0.4 Torr and the gas mixture was composed of 0.75% $Fe(CO)_5$, 25% O_2 and about 74% He or Ar. The excitation spectrum clearly shows characteristic features of FeO orange system indicating the formation of the ground-state FeO molecules in the reaction cell. When only one laser was employed, no fluorescence from the FeO orange system was detected, ensuring that FeO molecules in the orange system were not formed directly by side reactions. Small changes in the photolysis wavelength from the Fe atomic transition frequency induced no significant changes in the shape and relative intensities of the excitation spectra, suggesting that contributions from the excited state Fe atoms generated by the photolysis laser seemed not important. However, the LIF intensities from the FeO orange system became much stronger when the photolysis wavelength was moved to shorter wavelength.

Fig. 1b shows time resolved fluorescence spectra obtained from excitation of the 591.1 nm band head of the ${}^5\Delta_4(v') \rightarrow X^5\Delta_4(v''=0)$ transition. The pressure and compositions of the gas mixture were identical to those of Fig. 1a. The fluorescence signal was collected after 30 ns from the probe laser pulse to avoid the effect of the scattered laser light. The time intervals were arbitrarily chosen to examine the variation of relative emission intensities of the two peaks in different time domains. The relative emission intensities of the two peaks in Fig. 1b remain constant in different time periods, suggesting that they come from the common upper state. The energy spacing between the excitation frequency and the first strong emission peak is $882 \pm 10\ \text{cm}^{-1}$, and that between the two successive emission peaks is $866 \pm 9\ \text{cm}^{-1}$. These energy spacings match well with those of the ground-state vibrational levels reported by Merer and coworkers [6,7], where the two emission peaks are assigned for $(0', 1'')$ and $(0', 2'')$ bands, respectively.

3.2. Radiative lifetimes of the FeO orange system

Typical time profiles observed from the FeO orange system at 0.4 Torr of a $Fe(CO)_5/M(O_2$ or $N_2O)/He$ mixture are shown in Fig. 2a. The excitation wavelength was 591.1 nm, and the fluorescence was observed at 623.6 nm. Both time profiles clearly show single exponential decay. Since the partial pressure of $Fe(CO)_5$ (~ 2 mTorr) is much lower than those of other gases, the decay rate of the 623.6 nm emission can be written as

$$1/\tau = 1/\tau_0 + k_q[M] + k'_q[He]. \qquad (1)$$

M represents O_2 or N_2O, τ_0 is the radiative lifetime, k_q and k'_q are the quenching rate constants. Both k_q and k'_q were determined by varying the pressure of one component while keeping other component constant. In order to determine k_q for O_2 or N_2O, the pressure of a 0.75% $Fe(CO)_5$ in He mixture was kept constant at 0.3 Torr. To determine k'_q for He or Ar, the pressure of O_2 was kept constant at 0.1 Torr and the pressure of the rare gases containing 0.75%

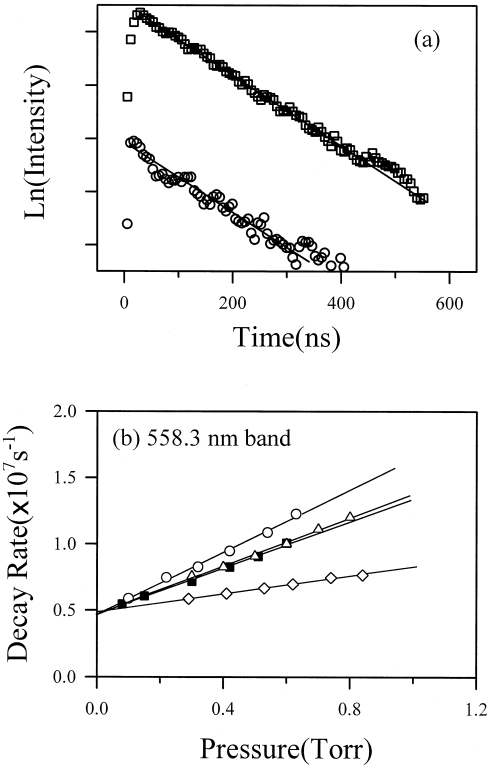

Fig. 2. (a) Typical time profile of FeO* observed at 587.3 nm following 558.3 nm excitation in O_2 (□) and N_2O (○). The total pressure was 0.4 Torr. (b) Pressure dependence of decay frequencies for the emission observed at 587.3 nm; He (◇), Ar (△), O_2 (■), and N_2O (○).

$Fe(CO)_5$ was varied in the 0.2–1.1 Torr range. Since the concentration of $Fe(CO)_5$ was very low, contribution of $Fe(CO)_5$ to the quenching rate constants for He or Ar was neglegible. The pressure dependence of the decay rates obtained in this way for the 558.3 nm band is plotted in Fig. 2b, and those for other bands are shown in Fig. 3. Since the zero-pressure intercepts in Fig. 2b and Fig. 3 contain the quenching rate from the fixed component, the radiative lifetimes are obtained by substracting the calculated quenching rate of the fixed component from the zero-pressure intercept. The radiative lifetimes and quenching rate constants by O_2, N_2O, He and Ar for seven bands of the FeO orange system are shown in Table 1. The radiative lifetimes and apparent quenching rate constants measured for the 558.3 and 586.8 nm bands are virtually the same, because the upper level for these two bands is known to be the same one [7]. In general, the magnitude of the apparent quenching rate constants by Ar and O_2 is very similar, but that by N_2O is about 25% larger than that by O_2.

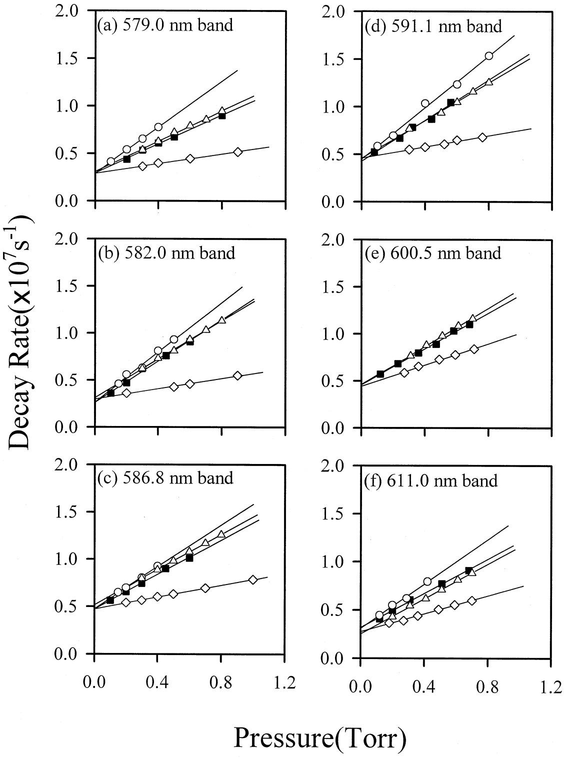

Fig. 3. Pressure dependence of decay frequencies for the emissions from (a) 579.0, (b) 582.0, (c) 586.8, (d) 591.1, (e) 600.5, and (f) 611.0 nm band excitation. The emissions were observed at (a) 610.2, (b) 613.6, (c) 618.5, (d) 623.6, (e) 634.1, and (f) 645.8 nm, respectively; He (◇), Ar (△), O_2 (■), and N_2O (○). The pressure in the abscissa represents either the added pressures of O_2 or N_2O to the 0.3 Torr of 0.75% $Fe(CO)_5$ in He, or those of 0.75% $Fe(CO)_5$ in He or Ar to the 0.1 Torr of O_2.

Table 1
Radiative lifetimes and quenching rate constants for FeO orange system

FeO band	τ_o (ns)[a]	Quenching gas	k_q [b]
611.0 nm	590 ± 50	He	1.4 ± 0.1
		Ar	2.8 ± 0.2
		O_2	2.7 ± 0.2
		N_2O	3.6 ± 0.3
600.5 nm	360 ± 40	He	1.8 ± 0.1
		Ar	3.1 ± 0.3
		O_2	3.0 ± 0.3
591.1 nm	280 ± 30	He	0.90 ± 0.05
		Ar	3.1 ± 0.2
		O_2	3.3 ± 0.3
		N_2O	4.2 ± 0.2
586.8 nm	260 ± 30	He	0.95 ± 0.05
		Ar	2.9 ± 0.2
		O_2	2.8 ± 0.2
		N_2O	3.4 ± 0.2
582.0 nm	560 ± 50	He	0.84 ± 0.03
		Ar	3.1 ± 0.2
		O_2	3.4 ± 0.2
		N_2O	4.0 ± 0.2
579.0 nm	460 ± 50	He	0.79 ± 0.03
	(450 ± 100)[c]	Ar	2.5 ± 0.2 (0.034)[c]
		O_2	2.4 ± 0.2
		N_2O	3.7 ± 0.2
558.3 nm	260 ± 30	He	0.94 ± 0.04
	(~ 500)[c]	Ar	2.8 ± 0.2
		O_2	2.6 ± 0.2
		N_2O	3.6 ± 0.2

[a] The error limits are 2σ from the average values obtained from the intercepts in Fig. 2b and Fig. 3.

[b] Units: 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

[c] Ref. [4].

3.3. Power dependence and optical pumping

To look for the origin of the ground-state FeO molecules, we have investigated photolysis laser power dependence of LIF intensities from the FeO molecules as well as the Fe atoms under the same experimental conditions as the excitation spectra except the photolysis laser wavelength. Since the FeO LIF signal was much stronger at shorter photolysis laser wavelength, the sample gas mixture was photolyzed at 298.0 nm. For FeO molecules, the probe laser wavelength was at 558.3 nm and the LIF intensities were monitored at 587 nm. For Fe atoms, the probe laser was at $y^3D_3 \leftarrow a^3F_4$ (381.58 nm) and $y^5D_4 \leftarrow a^5F_5$ (382.04 nm) transition frequencies for the a^3F_4 and a^5F_5 states, respectively, and the LIF intensities were monitored at $y^3D_3 \rightarrow a^3F_3$ (390.2 nm) and $y^5D_4 \rightarrow a^5D_3$ (305.9 nm) transitions for the a^3F_4 and a^5F_5 states, respectively. Because of the fast disappearance of a^3F_4 and a^5F_5 states of Fe atoms, the atomic LIF signal was monitored after 10 μs from the photolysis pulse. The LIF intensities from the FeO orange bands were first-order as shown in Fig. 4a, whereas those from atomic species (Fe a^3F_4 and a^5F_5) showed second-order dependence as plotted in Fig. 4b and c. Thus, the ground-state FeO molecules generated in our experimental conditions seemed to be originated from the reaction of photofragments of $Fe(CO)_5$ and oxidant molecules.

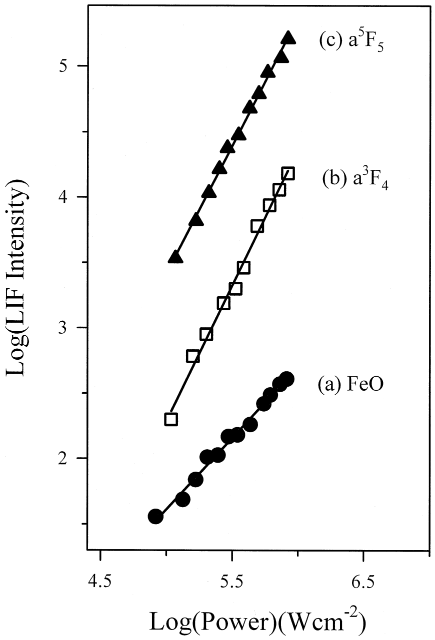

Fig. 4. Photolysis laser power dependence of (a) FeO, (b) $Fe(a^3F_4)$, and (c) $Fe(a^5F_5)$ LIF intensity. The magnitude of the slope is (a) 1.1 ± 0.1, (b) 2.0 ± 0.1 and (c) 2.0 ± 0.1, respectively. The gas mixture was composed of 0.3 Torr of 0.75% $Fe(CO)_5$ in He and 0.1 Torr of O_2.

We also employed an optical pumping method to examine changes in FeO LIF intensity with increase in concentration of the metastable Fe atomic species. When the gas mixture was photolyzed at the $Fe(y^5F_5 \leftarrow a^5D_4)$ atomic transition frequency (296.7 nm), the LIF intensity from $Fe(a^5F_5)$ state was three times stronger than that observed from photolyzing the gas mixture using a nearby off-resonance wavelength (296.6 nm) because of the optical pumping of the a^5D_4 state Fe atoms to the a^5F_5 state through the short lived y^5F_5 state ($\tau = 8.7$ ns). However, the LIF intensities from the FeO molecules remained constant within the experimental fluctuations when the photolysis laser wavelength was scanned in the 296.6–297 nm region. Optical pumping for other levels in the a^5F and a^3F terms also attempted, and similar results were obtained. Thus, these metastable states of Fe atoms do not contribute appreciably, if any, to the formation of FeO molecules observed in this work.

4. Discussion

The spectroscopic properties of the ground state and orange system of FeO have been established by Merer and coworkers [6,7,12]. They have shown that there are two excited electronic states ($D^5\Delta$ and $D'^5\Delta$) in this spectral region [12], and reassigned some of the vibrational assignments reported by West and Broida [4]. The LIF spectrum shown in Fig. 1a, which is consistent with those spectra from FeO reported by Merer and coworkers, manifest itself as the direct evidence of the formation of ground-state FeO molecules in the reaction cell. Also, the first-order dependence of the FeO LIF intensities on the photolysis laser power strongly suggests that FeO molecules are formed from the reaction of O_2 or N_2O with $Fe(CO)_x$ ($x = 1–4$) produced by the photolysis laser pulse. It is found that the radiative lifetimes of the FeO orange system are substantially different from band to band. The radiative lifetime for the 579.0 nm band measured in this work agrees well with the one reported by West and Broida [4], while that for the 558.3 nm band is quite different from the previous one.

The chemical reactivity of Fe atoms with various small molecules near room temperature has been studied by Mitchell and Hackett [13]. They observed that the removal rate of the ground-state Fe(a^5D_4) atoms did not increase significantly over the diffusion rate in the presence of O_2 or N_2O, thereby concluding that the ground-state Fe atoms were not reactive toward O_2 or N_2O. We checked for the depletion kinetics of the ground-state Fe atoms by using a photolysis-probe method and reached the same conclusion as Mitchell and Hackett [13]. In fact, the reaction of the ground-state Fe atoms with O_2 (Eq. (2)) is endothermic by 84–92 kJ mol^{-1} [3,13–15], so that the reaction in Eq. (2) is very unlikely to occur under our experimental conditions.

$$\mathrm{Fe}\left(a^5D_4, g\right) + O_2(g) \rightarrow \mathrm{FeO}(g) + O. \qquad (2)$$

On the other hand, the reaction of the ground-state Fe atoms with N_2O, Eq. (3), is highly exothermic by ~ 247 kJ mol^{-1} [13,14,16].

$$\mathrm{Fe}\left(a^5D_4, g\right) + N_2O(g) \rightarrow \mathrm{FeO}(g) + N_2(g). \qquad (3)$$

But it has been reported that the reaction in Eq. (3) does not proceed in an appreciable rate at low temperature [13,16]. The activation energy for the reaction in Eq. (3) has been reported to be 44.4 ± 1.0 and 45.1 ± 2.3 kJ mol^{-1} by Campbell and Metzger [16] and Zaslonko and Smirnov [17], respectively. Thus, the ground-state Fe atoms are not considered to be the source of ground-state FeO molecules observed in this work. Since the LIF signal from the FeO orange system is absent unless the photolysis laser pulse is preceded, the direct reaction of $Fe(CO)_5$ with O_2 or N_2O in the gas phase is also ruled out for the source of the ground-state FeO molecules. As the Fe(a^5F_J) state lies 6928–8154 cm^{-1} (~ 83–97 kJ mol^{-1}) above the ground state [18], it is nearly thermoneutral or slightly exothermic to form ground-state FeO molecules in reactions with O_2. The Fe(a^3F_J) atoms lying 11 976–12 969 cm^{-1} (~ 143–155 kJ mol^{-1}) above the ground state are also energetically viable for the formation of ground-state FeO molecules. Nevertheless, both metastable states of the Fe atoms are also ruled out as the source of the ground-state FeO, because the FeO LIF intensities remain unchanged in spite of increasing the concentrations of these states by optical pumping. Mitchell and Hackett have measured the bimolecular removal rate constants for a^5D_3, $a^5F_{5,4}$ and $a^3F_{4,3}$ states of Fe atoms by various small molecules [19]. They reported the depletion rate constants for Fe(a^5F_5) atoms by O_2 and N_2O to be 8.3×10^{-11} and 3.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. We also measured the depletion rate constants for the Fe(a^5F_5) atoms by O_2 and N_2O, and obtained $8.6 \pm 0.3 \times 10^{-11}$ and $3.0 \pm 0.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, which are in good agreement with Mitchell and Hackett. They assigned the depletion rate constants for the metastable Fe atoms to the collisional relaxation processes based on kinetic modeling studies, since they did not succeed to observe LIF signals from FeO at 578.9 nm. Our observation of the formation of the ground-state FeO in this work, however, does not change Mitchell and Hackett's assignment of large depletion rate constants for the collisional relaxation processes, because we observe almost no enhancement of FeO LIF intensity in spite of increasing the concentration of metastable Fe atoms by optical pumping.

Ryther and Weitz have studied reaction kinetics of unsaturated $Fe(CO)_x$ ($x = 1$–4) photo-fragments in the gas phase [20]. They have shown that the triplet state of $Fe(CO)_4$ reacts much faster with O_2 having triplet ground state than H_2 or CO having singlet ground state. Since the ground states of $Fe(CO)_x$ ($x = 1$–4) photofragments are triplet [21], the much stronger FeO LIF intensity observed in an O_2 mixture in comparision with that in a N_2O mixture seems consistent with the spin selection rule proposed by Weitz and coworkers [20]. It seems that reactions of $Fe(CO)_x$ ($x = 1$–4) photofragments, most likely those highly unsaturated $Fe(CO)_2$ or FeCO, with O_2 and N_2O are responsible for the production of FeO in this work.

Acknowledgements

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