Depletion Kinetics of Ground State FeO Molecules by O_2, N_2O, and N_2

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Depletion kinetics of ground state FeO molecules by O_2, N_2O and N_2 has been studied at room temperature. The ground state FeO molecules were generated by photolysis of a $Fe(CO)_5/M(O_2, N_2O)/He$ mixture using an unfocused weak UV laser beam. The formation of ground state FeO molecules was identified by a laser-induced fluorescence (LIF) method. The intensity distribution of those undisturbed rotational lines suggests that the rotational temperature of the ground state FeO molecules is lower than room temperature. The LIF intensities of FeO molecules at different partial pressures of O_2, N_2O and N_2 were monitored as a function of the time delay between the photolysis and probe laser pulses to obtain the depletion rate constants for the ground state FeO. They were $1.7 \pm 0.2 \times 10^{-12}$, $4.8 = 0.4 \times 10^{-12}$, and $1.4 \pm 0.2 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$ by O_2, N_2O, and N_2, respectively.

Introduction

The FeO molecule in the gas phase is a transient molecular species which has drawn substantial interest because of its complicated spectroscopic properties with high multiplicity as well as its potential importance in astrophysics.[1] Various experimental techniques have been employed to generate FeO in the gas phase. They involve reactions of O_2 with Fe atoms evaporated from arc discharge of an iron electrode,[2] hallow cathode discharge,[3] a high temperature oven containing metallic iron,[4,5] burning ferrocene in a 2450-MHz microwave discharge,[6-8] and laser ablation.[9] However, most of these experimental methods generate excited state FeO molecules having substantial thermal energies due to the high temperature conditions.[4-8] Thus, Merer and coworkers used pulsed laser ablation/molecular beam apparatus to generate ground state FeO molecules having low rotational temperature.[9] Recently, we have reported that ground state FeO molecules in the gas phase can be easily prepared at room temperature by photolyzing a $Fe(CO)_5/O_2/He$ mixture using an unfocused weak UV laser pulse and the results of radiative lifetime measurement for the FeO orange system.[10]

The reaction of atomic Fe with O_3 and O_2 in the upper atmosphere has drawn substantial interest since the first observation of thin atomic iron layer in the mesosphere.[11] Recently, Helmer and Plane have studied the following reactions to understand kinetic behavior of the atomic iron layer in the mesosphere.[12]

$$Fe + O_3 \xrightarrow{k_1} FeO + O_2 \qquad (1)$$

$$Fe + O_2 + N_2 \xrightarrow{k_2} FeO_2 + N_2 \qquad (2)$$
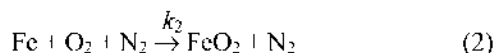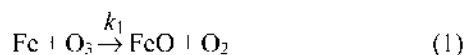
They observed that the reactions (1) and (2) proceeded very efficiently with $k_1 = 1.85-2.0 \times 10^{-10}$ $cm^3molecule^{-1}s^{-1}$ and $k_2 = 4.87 \times 10^{-33}$ $cm^6molecule^{-2}s^{-1}$ at 300 K. Since the reaction in Eq. (1) occurs very efficiently, the kinetic behavior of FeO in O_2 and N_2 will be important for understanding atmospheric chemistry at high altitude.

In this work, we have generated the ground state FeO molecules from photolysis of a $Fe(CO)_5/O_2$ or N_2O/He mixture at room temperature, and investigated the depletion kinetics of the transient FeO molecule in the gas phase. Monitoring the variation of LIF intensities of the FeO molecules with respect to the delay time between the photolysis and probe pulses enabled us to obtain the depletion rate constants for the transient FeO molecules by O_2, N_2O and N_2 at relatively low temperature conditions.

Experimental Method

A schematic diagram of the experimental setup is shown in Figure 1. The reaction cell was made of a 1 l pyrex bulb and two-pairs of 2.5 cm pyrex O-ring joints were attached to allow laser beam to pass and to connect to a gas handling vacuum rack. The sample gas for Fe atom source was a premixture of 0.7% $Fe(CO)_5$ in He or in N_2 and slowly flowed through the cell. When the pressure of the $Fe(CO)_5$ in He or in N_2 flowing through the cell was stabilized at a certain pressure, the other reactant gas, pure O_2 or N_2O, was introduced directly to the cell opening a needle valve installed on
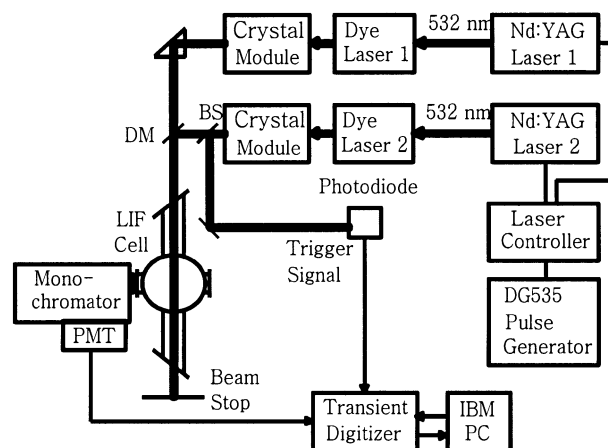

Figure 1. A schematic diagram of the experimental setup.

a separated line. The flow rate of the gases in the reaction cell was ~0.2 mmol min^{-1} and the total pressure as well as the partial pressures of the gases in the cell was controlled by adjusting the openings of the inlet needle valves and the exit Teflon valve. When the pressure in the cell was stabilized again, unfocussed UV laser pulses were sent to the cell to photolyze $Fe(CO)_5$. The pulse energy of the photolysis laser (Quantel YG681-TD1.50 with NBP) was ~1.0 mJ/pulse and the beam diameter was 7 mm.

A second laser (Quantel YG581-TD1.60 with NBP and DGO) was used to probe the ground state $FeO(X^5\Delta_i)$ molecules. The delay time between the photolysis and probe was set at 5-20 μs to avoid the interference from any fluorescence due to the photolysis laser pulse. The pulse energy of the probe laser was ~0.3 mJ/pulse. The linewidth of the probe laser was narrow (~0.05 cm^{-1}) enough to excite a few rovibronic levels. The laser was scanned in the 557-612 nm region to excite $FeO(X^5\Delta_i)$ to orange system.[7-9] Fluorescence from the excited FeO molecules was monitored at 90° with respect to the laser beam direction 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.

Results

Absorption and emission spectra and rotational temperature. The strong absorption bands in the orange system of FeO molecules lie in the 557-615 nm region.[8] Figure 2 shows a portion of a low resolution excitation spectrum of FeO molecules generated in the reaction cell. The wavelength of the photolysis laser was 319.2 nm, which is slightly off-resonance frequency of the $Fe(z^5D_3 \leftarrow a^5D_4)$ transition.
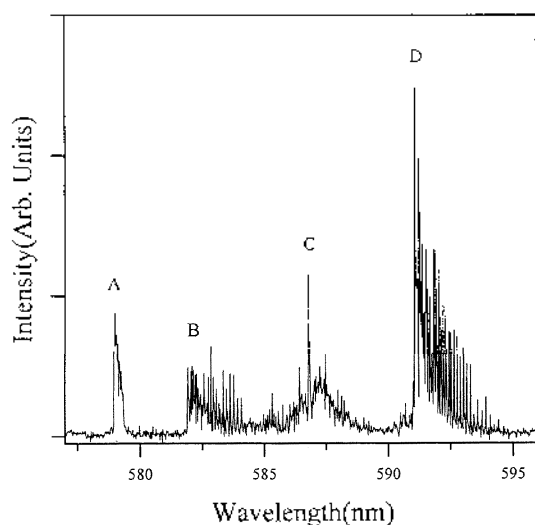
The probe laser was scanned in the 577.0-584.0, 584.0-590.0, and 590.0-596.5 nm regions while the fluorescence from the excited states was monitored at 613.6, 618.5 and 623.6 nm, respectively. The total pressure was 0.4 Torr of a gas mixture composed of 0.7% $Fe(CO)_5$, 25% O_2 and about 74% He. The delay time between the photolysis and probe pulses was 20 μs to avoid interference from the emissions caused by the photolysis laser. The excitation spectrum clearly shows characteristic features of FeO orange system which was partially analyzed by Merer and coworkers.[8,9] We also investigated excitation spectra for FeO molecules using different photolysis laser wavelength which corresponds exactly to the Fe atomic transition frequency. The shape and relative intensities of the excitation spectra did not change by changing the photolysis laser wavelength whether it matches the atomic transition frequency of the Fe atom or not.

A typical time resolved fluorescence spectra observed from excitation of 591.1 nm band head is shown in Figure 3. This band has been assigned for the $X^5\Delta_4$ ($v'' = 0$) → $^5\Delta_4(v' = 0)$ transition by Merer and coworkers.[8] The pressure and compositions of the gas mixture were the same as those of Figure 2. 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 are arbitrarily chosen to examine any change of the relative emission intensities of the two peaks in different time domains. It is clearly seen that the relative emission intensities of the two peaks in Figure 3 are the same in different time periods, suggesting that they come from the same upper state. The energy spacing between the laser frequency and the first strong emission peak is 882 ±
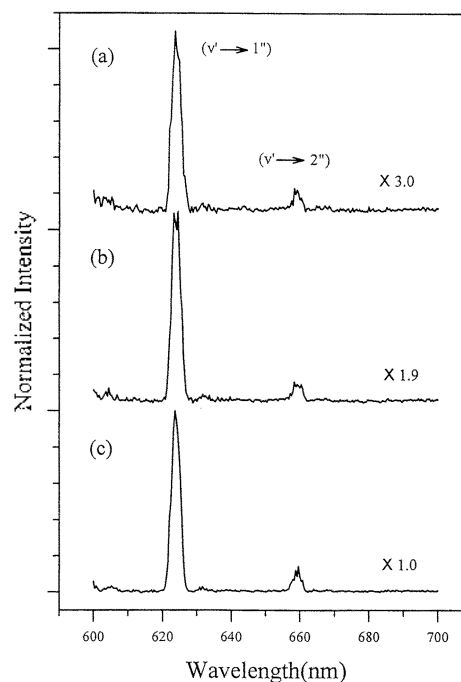

Figure 2. A portion of a low resolution excitation spectrum of FeO generated from photolysis of a 0.7% $Fe(CO)_5$, 25% O_2 and ~74% He mixture. Total pressure was 0.4 Torr. A: 579.0 nm band. B: 581.9 nm band. C: 587.0 nm band. and D: 591.1 nm band.

Figure 3. Typical time resolved fluorescence spectra of FeO observed from 591.1 nm band excitation at 591.1 nm: (a) 30-130 ns. (b) 130-230 ns. and (c) 230-330 ns period.
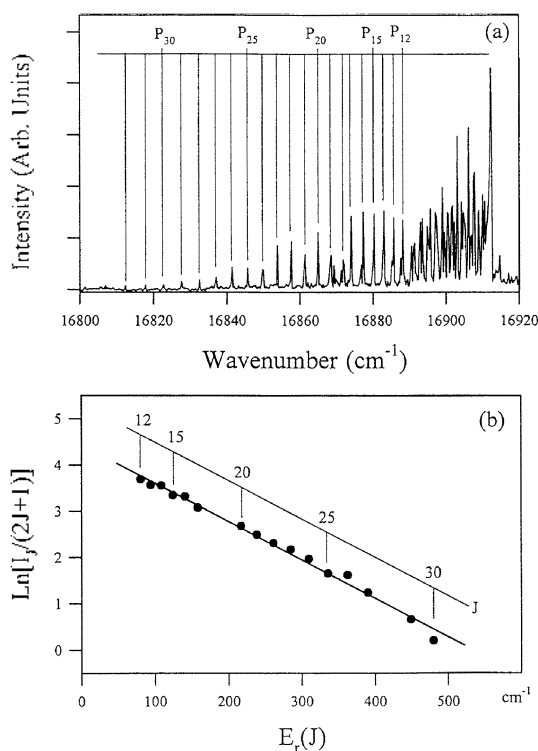
Figure 4. (a) Partially resolved rotational excitation spectrum, and (b) intensity distribution of those P-branch rotational lines of the FeO molecule. The laser was scanned in the 16920 (591.0 nm)-16800 (595.2 nm) cm⁻¹ region, and fluorescence was monitored at 623.6 nm.

10 cm⁻¹, and that between the two emission peaks is 866 ± 9 cm⁻¹. These energy spacings match well with those of ground state vibrational levels reported previously,[5,7,13] when the emission peaks are assigned for (0',1") and (0',2") bands, respectively.

Figure 4(a) shows a partially resolved rotational excitation spectrum of the FeO molecule. The laser was scanned in the 16920 (591.0 nm)-16800 (595.2 nm) cm⁻¹ region, and fluorescence was monitored at 623.6 nm. Because of the smaller rotational constant of the upper level (0.449 cm⁻¹) compared to that of the ground state (0.5168 cm⁻¹), the spectrum shows a red degraded shape.[7,8] Although the rotational lines appearing above 16890 cm⁻¹ are severely conjested, a portion of the P-branch rotational lines are well resolved and these lines are assigned from Merer and coworkers.[8] It is seen that the rotational line intensities are not regular shape due to extensive rotational perturbations. Nevertheless, we can deduce an approximate rotational temperature based on the intensities of those less disturbed rotational lines. When the intensity distributions of the less disturbed P-branch rotational lines are considered, a value of 174 ± 10 K is obtained from the slope of $ln[I(J)/2J + 1]$ with respect to $E_r(J)$ as shown in Figure 4(b).

Depletion kinetics of the ground state FeO by O_2, N_2O and N_2. Depletion kinetics of the ground state FeO molecules by O_2, N_2O and N_2 was studied by exciting FeO molecules at 591.1 nm and monitoring the LIF intensities at 623.6 nm as a function of the time delay between the photolysis
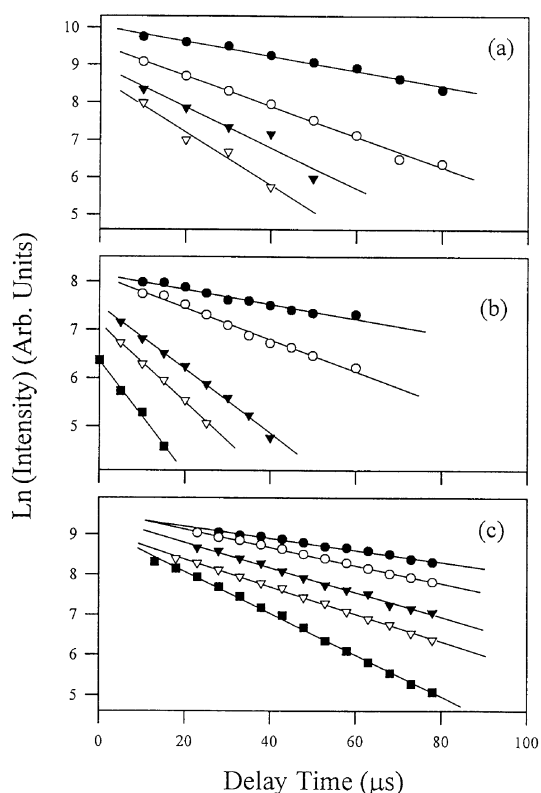

Figure 5. Variation of LIF intensities observed at 623.6 nm following 591.1 nm excitation vs delay time and O_2/N_2O pressures: (a) 0.4(●), 0.8(○), 1.0(▼), and 1.2(▽) Torr of O_2, (b) 0.1(●), 0.2(○), 0.35(▼), 0.5(▽), and 0.7(■) Torr of N_2O, and (c) 0.3(●), 0.5(○), 0.6(▼), 0.7(▽) and 1.05(■) Torr of N_2.

and probe laser pulses. Figure 5 shows the temporal variation of time integrated FeO* emission intensities at 623.6 nm at various pressures of O_2, N_2O, and N_2. The partial pressure of 0.7% Fe(CO)₅ in He was kept constant at 0.3 Torr and that of the pure quenching gas (O_2 or N_2O) was varied to measure depletion rate constants by O_2 and N_2O. On the other
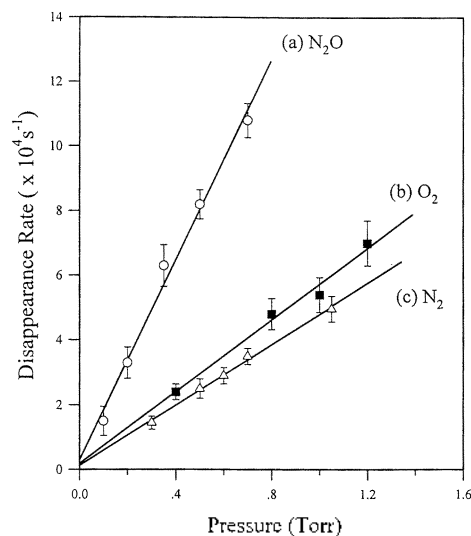

Figure 6. Pressure dependence of disappearance rate of the ground state FeO: (a) N_2O (○), (b) O_2 (■) and (c) N_2 (△).

hand, the partial pressure of O_2 was kept constant at 0.1 Torr and the partial pressures of 0.7% $Fe(CO)_5$ in N_2 were changed to investigate depletion rate constant by N_2. To avoid the effect of high-lying excited state Fe atoms, $Fe(CO)_5$ was photolyzed at 298.0 nm, which is off resonant from the Fe atomic transition frequency (298.4 nm). As the partial pressure of the quenching gas increases, the FeO* emission intensity decreases but its decay rate increases. Since the diffusional loss from the observation volume becomes smaller at higher pressures, both the systematic decrease of FeO* intensity and the increase in decay rate with increasing pressures of the quenching gas are suggestive of the collisional depletion of the ground state FeO molecules by these quenching gases. The magnitudes of the depletion rate constants are determined from the slopes of Stern-Volmer plots shown in Figure 6. They are $1.7 \pm 0.2 \times 10^{-12}$, $4.8 \pm 0.4 \times 10^{-12}$, and $1.4 \pm 0.2 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ for O_2, N_2O, and N_2, respectively.
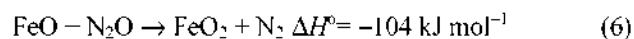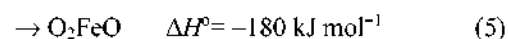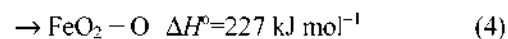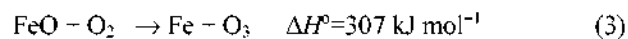
Discussion

The strong bands in the absorption spectrum shown in Figure 1 correspond to the $\Omega''(\Omega')$=4 transitions.[8] and the intensities for the Ω''=3 (600.5 nm) and Ω''=2 (561.9 nm, not shown)[10] transitions appear much weaker than those of Ω''= 4. Since the spin-orbit splittings in the ground state of FeO are 185-193 cm^{-1}, the intensities of the absorption spectrum suggest that the reaction temperature for the FeO formation is not high. Indeed, this is consistent with the low rotational temperature obtained from the qualitative analysis of the rotational line intensity distributions.

Downs and coworkers have studied photooxidation of matrix-isolated $Fe(CO)_5$.[14,15] They photolyzed $Fe(CO)_5$ molecules in an O_2-doped Ar matrix, and they identified five intermediates $[(\eta^2-O_2)Fe(CO)_4$, $(\eta^1-O)_2Fe(CO)_3$, $(\eta^1-O)_2$-FeCO, $(\eta^1-O)_2(\eta^2-O_2)FeCO$, and $(\eta^1-O)FeCO]$ and two end products, i.e., peroxoiron $[(\eta^2-O_2)Fe]$ and iron trioxide $[(\eta^1-O)_3Fe]$. Thus, the results from photooxidation reaction in the matrix-isolated medium cannot explain the formation of transient FeO molecules observed in this work.

Mitchell and Hackett have studied reactions of Fe atoms with small molecules, including O_2 and N_2O, in the gas phase.[16] They used a focussed visible laser pulse to generate Fe atoms from MPD of $Fe(CO)_5$ or ferrocene contained in the gas mixture, and measured removal rates of Fe atoms. They reported that the ground and meta stable states Fe atoms were unreactive with O_2 or N_2O at room temperature, because they could not observe any LIF signal from FeO molecules. We also investigated the reaction of Fe atoms with O_2 and N_2O and reached the same conclusion with Mitchell and Hackett based on the laser power dependence of LIF intensities of FeO molecules and Fe atoms.[10] Nevertheless, the MPD of $Fe(CO)_5$ in the presence of O_2 or N_2O by Mitchell and Hackett is basically the same photooxidation reaction in this work, although they used a focussed laser beam. However, it would be very difficult for them to observe LIF from FeO molecules under their high pressure conditions, consid-

ering the relatively large depletion rate constants of the ground state FeO molecules with respect to O_2 and N_2O.

It was not possible to identify the quenching products in this work. However, there are a few plausible bimolecular reactions for the depletion of the ground state FeO by O_2 and N_2O.

$$FeO - O_2 \rightarrow Fe - O_3 \quad \Delta H^o\!=\!307 \text{ kJ mol}^{-1} \tag{3}$$

$$\rightarrow FeO_2 - O \quad \Delta H^o\!=\!227 \text{ kJ mol}^{-1} \tag{4}$$

$$\rightarrow O_2FeO \quad \Delta H^o\!=\!-180 \text{ kJ mol}^{-1} \tag{5}$$

$$FeO - N_2O \rightarrow FeO_2 + N_2 \; \Delta H^o\!=\!-104 \text{ kJ mol}^{-1} \tag{6}$$

The reaction enthalpies were taken from Helmer and Plane[12] and Ref. 17. Since the reactions (3) and (4) are highly endothermic, these reactions are unlikely to occur at low temperature. On the other hand, reactions (5) and (6) are sufficiently exothermic, the ground state FeO molecules seem to be readily depleted by these reactions. Because the wavelength ($\lambda > 290$ nm) of the photolysis laser is too long to dissociate O_2, the depletion of FeO molecules by atomic oxygen is not considered in this work.

The magnitude of the ground state FeO depletion rate constant by N_2 is similar to that of O_2. Andrews and coworkers[18] have studied reaction of laser-ablated Fe atoms with N_2O, NO, and O_2 in condensing nitrogen, and they have identified various ternary iron nitride oxide molecules such as NFeO, $NFeO_2$, N_2FeO etc. Even though it was not possible to identify the N_2 quenching product in this work, one of the primary exit channel might be the formation of N_2FeO, since it is also expected highly exothermic considering the large exothermicity of Eq. (5).

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