

Depletion Kinetics of the Ground State CrO Generated from the Reaction of Unsaturated Cr(CO)_x with O₂ and N₂O

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Unsaturated Cr(CO)_x ($1 \leq x \leq 5$) molecules were generated in the gas phase from photolysis of Cr(CO)₆ vapor in He using an unfocussed weak UV laser pulse and their reactions with O₂ and N₂O have been studied. The formation and disappearance of the ground state CrO molecules were identified by monitoring laser-induced fluorescence (LIF) intensities vs delay time between the photolysis and probe pulses. The photolysis laser power dependence as well as the delay time dependence of LIF intensities from the CrO orange system showed different behavior as those from ground state Cr atoms, suggesting that the ground state CrO molecules were generated from the reaction between O₂/N₂O and photo-fragments of Cr(CO)₆ by one photon absorption. The depletion rate constants for the ground state CrO by O₂ and N₂O are $5.4 \pm 0.2 \times 10^{-11}$ and $6.5 \pm 0.4 \times 10^{-12}$ cm³molecule⁻¹s⁻¹, respectively.

Keywords : Depletion kinetics, CrO, Photolysis, Cr(CO)_x.

Introduction

The diatomic oxides of 3d transition metals have drawn substantial interest because of their importance in astrophysics and in high temperature chemistry.¹⁻⁴ Also, there have been considerable efforts to understand the nature of the bonding with oxygen and 3d transition metals.^{5,6}

The CrO molecule is one of many diatomic oxides of 3d transition metals that contribute to the spectra of cool red giant stars. It was first identified in the spectrum of β -Pegasi in 1947.⁷ Since the pioneering work of Ninomiya,⁸ who analyzed a partially resolved rotational spectrum of the 600 nm band system of CrO, Merer and coworkers generated CrO molecules in the gas phase using a microwave discharge in flowing CrO₂Cl₂ and He or using a microwave discharge through argon over solid CrO₃, and analyzed rotational structures of the B⁵ Π -X⁵ Π , A⁵ Σ -X⁵ Π , and A⁵ Δ -X⁵ Π transition bands.⁹⁻¹¹ Debre and Gole generated excited state CrO from the reaction of hot Cr atoms with O₃ and N₂O, and assigned vibrational band structures of electronic transitions observed in their chemiluminescence spectra.¹²

In our previous work, we have reported that the ground state FeO molecules can be easily generated in the gas phase by photolyzing a Fe(CO)₅/O₂ or N₂O/He mixture using unfocussed weak UV laser pulses at room temperature and highly unsaturated iron carbonyls are responsible for the formation of ground state FeO molecules.¹³ In this work, we report that the ground state CrO molecules also can be easily produced by photolyzing a Cr(CO)₆/O₂ or N₂O/He mixture using unfocussed weak UV laser pulses. This finding of an easy method for producing ground state CrO molecules in the gas phase enabled us to study the depletion kinetics of CrO molecules by He, Ar, O₂ and N₂O molecules at room temperature.

Experimental Method

An experimental setup used for this work is basically the same as that reported previously.¹⁴ 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 the bulb for the laser beam path and for the connection to a gas handling vacuum rack. A premixture of 10% O₂/N₂O in He was slowly flowed through over Cr(CO)₆ powder at 273 K to entrap Cr(CO)₆ vapor in the gas phase and the resulting gas mixture was introduced to the photolysis/LIF cell. A typical flow rate of the gas in the reaction cell was 0.2 mmol min⁻¹. The actual Cr(CO)₆ vapor pressure in the flowing cell was estimated to be about 2.5 mTorr under our experimental conditions by comparing the LIF intensities of the ground state Cr atoms with those from premixtures of known compositions. The total pressure in the cell was controlled by adjusting the openings of an inlet needle valve and an exit teflon valve. When the pressure in the cell was stabilized, unfocussed UV laser pulses in the 290-300 nm region were directed to the cell. The pulse energy of the photolysis laser (Quantel YG681-TDL50 with NBP) was 0.7-1.0 mJ/pulse and the beam diameter was 7 mm.

The ground state CrO (X⁵ Π_0) molecules were probed by LIF signals from the CrO orange system. The probe laser (Quantel YG581-TDL60 with NBP and DGO) was scanned in the 605-611 nm region and fluorescence from the CrO (B⁵ Π , $v=0$) \rightarrow CrO (X⁵ Π , $v'=1$) was monitored at 640 nm.⁹ A typical delay time between the photolysis and probe pulses was set at 2 μ s to avoid interference from the Cr atomic fluorescence caused by the photolysis laser pulse.^{15,16} The pulse energy and linewidth of the probe laser was \sim 0.2 mJ/pulse and 0.05 cm⁻¹, respectively. Fluorescence from the excited CrO 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 Hamamatsu 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

A. Laser-induced fluorescence spectra from CrO. The strong $B^5\Pi_{g^-}X^5\Pi_{g^-}$ absorption/emission bands of CrO molecules lie in the 550-750 nm region.^{1,9,12} Figure 1 shows a typical low resolution excitation spectrum of CrO ($B^5\Pi_{g^-}, v' = 0 \leftarrow X^5\Pi_{g^-}, v'' = 0$) molecules generated from photolysis of a $\text{Cr}(\text{CO})_6/\text{N}_2\text{O}/\text{He}$ mixture in this work. The wavelength of the photolysis laser was 295.25 nm, which is slightly off-resonance frequency of the $\text{Cr}(z^3D_4 \leftarrow a^7S_3)$ transition. The probe laser was scanned in the 605-611 nm region while the fluorescence from the $\text{CrO}(B^5\Pi_{g^-}, v' = 0 \rightarrow X^5\Pi_{g^-}, v'' = 1)$ transition was monitored at 640 nm. The total pressure was 0.5 Torr, and $\text{Cr}(\text{CO})_6$ vapor was entrapped by a slowly flowing premixture of 10% N_2O in He. The delay time between the photolysis and probe pulses was 6 μs to avoid interference from the emissions caused by the photolysis laser. When a premixture of 10% O_2 in He was used to entrap $\text{Cr}(\text{CO})_6$ vapor, the LIF intensity from CrO became much stronger under the same experimental conditions. The excitation spectrum clearly shows characteristic features of $\text{CrO}(B^5\Pi_{g^-} \leftarrow X^5\Pi_{g^-})$ transition which was partially analyzed by Hocking *et al.*⁹ We have also investigated the effect of photolysis laser wavelength on the excitation spectrum of the CrO molecules. For this purpose, we have set the photolysis laser wavelength at 295.72 nm, which corresponds exactly to the $\text{Cr}(z^3D_4 \leftarrow a^7S_3)$ atomic transition frequency. The shape and relative intensities of the excitation spectrum

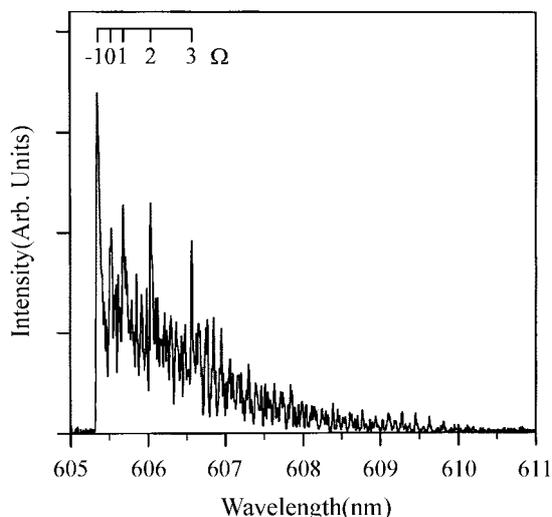


Figure 1. A typical low-resolution excitation spectrum of CrO generated from photolysis of a $\text{Cr}(\text{CO})_6/\text{N}_2\text{O}/\text{He}$ mixture. The $\text{Cr}(\text{CO})_6$ vapor was entrapped with 10% N_2O in He mixture at 273 K and total pressure was 0.5 Torr.

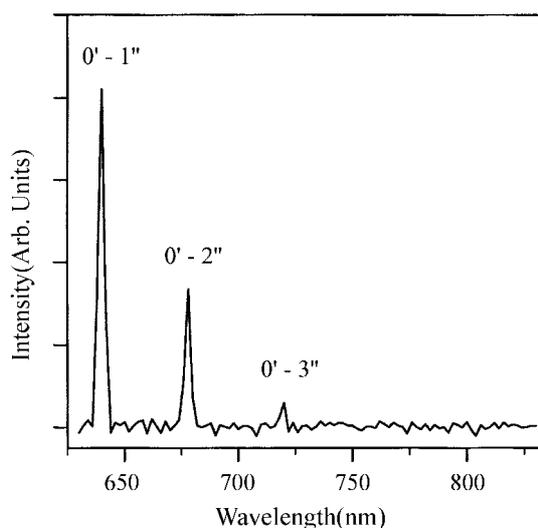


Figure 2. A typical fluorescence spectrum from $\text{CrO}(B^5\Pi_{1-1})$ excitation at 605.35 nm.

did not vary by changing the photolysis laser wavelength whether it matches the atomic transition frequency of the Cr atom or not.

A typical fluorescence spectrum observed from excitation at 605.35 nm is shown in Figure 2. The excitation wavelength corresponds to the $X^5\Pi_{1-1}(v''=0) \rightarrow B^5\Pi_{1-1}(v'=0)$ transition.^{9,12} The pressure and compositions of the gas mixture were the same as those of Figure 1. The fluorescence signal was collected after 30 ns from the probe laser pulse to avoid the effect of the scattered laser light. The energy spacing between the laser frequency and the first strong emission peak is $(885 \pm 40) \text{ cm}^{-1}$, and those between the successive emission peaks are (872 ± 40) and $(860 \pm 40) \text{ cm}^{-1}$, respectively. These energy spacings match well with those of ground state vibrational levels reported previously,^{9,12} when the emission peaks are assigned for the $(0,1'')$, $(0,2'')$ and $(0,3'')$ bands, respectively.

B. Radiative lifetimes of the $\text{CrO}(B^5\Pi_{g^-})$ state. A typical time profile observed from 0.5 Torr of a $\text{Cr}(\text{CO})_6/\text{N}_2\text{O}/\text{He}$ mixture is shown in Figure 3a. The excitation wavelength was 605.67 nm, which corresponds to $\text{CrO}(B^5\Pi_{1-1}, v'=0 \leftarrow X^5\Pi_{1-1}, v''=0)$ transition, and the fluorescence was observed at 640 nm. The time profile clearly shows single exponential decay. Since the partial pressure of $\text{Cr}(\text{CO})_6$ (~ 2.5 mTorr) is much lower than those of other gases, the decay rate of the 640 nm emission can be written as the following Eq. (1),

$$1/\tau = 1/\tau_0 + k_q[\text{N}_2\text{O}] + k'_q[\text{M}] \quad (1)$$

where M represents O_2 , He or Ar, τ_0 is the radiative lifetime, k_q and k'_q are the quenching rate constants by N_2O and M, respectively. In order to determine k_q and k'_q for N_2O , O_2 , Ar, and He, the pressure of $\text{Cr}(\text{CO})_6$ entrapped with 10% N_2O in He was kept constant at 0.5 Torr, and an appropriate amount of the quenching gas was added to the LIF cell. When a time profile was obtained at one pressure, the cell was evacuated and a new gas mixture was prepared to collect another time profile. The pressure dependence of the decay rates obtained

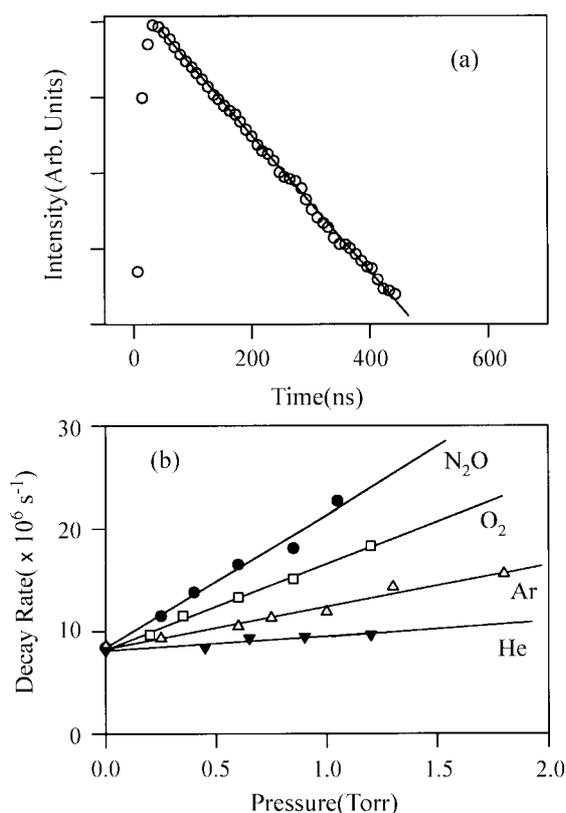


Figure 3. (a) A typical LIF time profile from CrO* observed at 640.0 nm following 605.67 nm excitation, and (b) pressure dependence of decay frequencies; N₂O(●), O₂(□), Ar(△), and He(▼).

from analyzing the time profiles are plotted in Figure 3b. Since the intercept in Figure 3b contains the quenching rates due to the fixed components (e.g. 0.05 Torr N₂O and 0.45 Torr He), the radiative lifetime is obtained by subtracting the calculated quenching rates of the fixed components from the decay rates at the intercept. We also investigated the fluorescence decay rate of CrO* by exciting at 605.35 nm ($B^5\Pi_{-1}, v'=0 \leftarrow X^5\Pi_{-1}, v''=0$ transition), and similar results were obtained as shown in Table 1.

C. Photolysis laser power dependence of CrO LIF

Table 1. Radiative lifetimes and quenching rate constants for CrO($B^5\Pi_{\Omega}$)

State	Quenching Gas	Quenching rate constant ^a	τ_0 (ns) This work	Others ^b
$B^5\Pi_{-1}$	N ₂ O	3.4 ± 0.2	150 ± 20	118.4 ± 4.4
	O ₂	2.4 ± 0.2		
	Ar	1.1 ± 0.2		
	He	0.43 ± 0.03		
$B^5\Pi_1$	N ₂ O	3.9 ± 0.3	154 ± 20	134.9 ± 9.2
	O ₂	2.6 ± 0.2		
	Ar	1.3 ± 0.2		
	He	0.43 ± 0.03		
$B^5\Pi_0$			121.0 ± 8.0	

^aUnits: $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^bRef. 18.

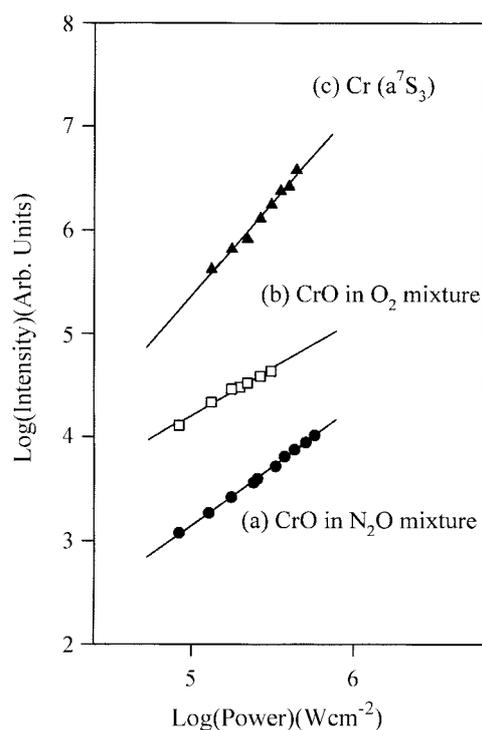


Figure 4. Photolysis laser power dependence of LIF intensity from (a) CrO($X^5\Pi_{-1}$) in N₂O, (b) CrO($X^5\Pi_{-1}$) in O₂, and (c) Cr(a^7S_3). The magnitude of the slope is (a) 1.1 ± 0.1 , (b) 0.9 ± 0.1 , and (c) 1.8 ± 0.2 , respectively.

intensities. To obtain information on the reactant species for the ground state CrO formation, we have investigated photolysis laser power dependence of LIF intensities from the CrO molecules as well as the Cr atoms under the same experimental conditions. The sample gas mixture, i.e. Cr(CO)₆ vapor entrapped 10% N₂O in He, was photolyzed at 295.3 nm. The probe laser wavelength for the ground state CrO molecules was set at 605.35 nm ($B^5\Pi_{-1}, v'=0 \leftarrow X^5\Pi_{-1}, v''=0$ transition), and the fluorescence was monitored at 640 nm ($B^5\Pi_{\Omega}, v'=0 \rightarrow X^5\Pi_{\Omega}, v''=1$ transition). To monitor LIF intensity from the ground state Cr atoms, the Cr($z^5P^o_3 \leftarrow a^7S_3$) transition frequency at 373.20 nm was chosen for the probe laser wavelength, and the fluorescence was observed from the Cr($z^5P^o_3 \rightarrow a^5S_2$) transition at 520.8 nm. The LIF intensity from the ground state CrO was first-order, while that from the Cr atoms showed second-order dependence as plotted in Figure 4. Thus, the ground state CrO molecules must be formed from the reaction of unsaturated Cr(CO)_x ($x=1-5$) generated from the Cr(CO)₆ vapor by one photon absorption with N₂O or O₂.

D. Depletion kinetics of the ground state CrO by O₂ and N₂O. Depletion kinetics of the ground state CrO molecules by O₂ and N₂O are studied by exciting CrO molecules at 605.35 nm ($X^5\Pi_{-1}, v''=0 \rightarrow B^5\Pi_{-1}, v'=0$) and monitoring the LIF intensities at 640 nm ($X^5\Pi_{\Omega}, v''=1 \leftarrow B^5\Pi_{-1}, v'=0$) as a function of the time delay between the photolysis and probe laser pulses. Figure 5 shows the temporal variation of time integrated CrO* emission intensities at various pressures of O₂ and N₂O. To avoid congestion, the rising part of the LIF

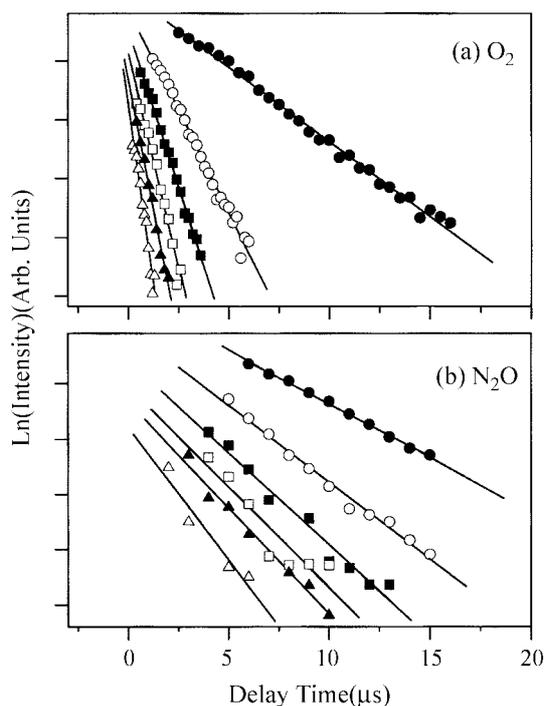


Figure 5. Variation of LIF intensities observed at 640.0 nm following 605.35 nm excitation vs delay time and O₂/N₂O pressure; (a) 0.05 (●), 0.25 (○), 0.45 (■), 0.65 (□), 0.95 (▲), and 1.25 (△) Torr of O₂, and (b) 0.25 (●), 0.65 (○), 0.85 (■), 1.05 (□), 1.30 (▲), and 1.55 (△) Torr of N₂O. As the pressure of O₂/N₂O increases, the ground state CrO formation rate also increases and LIF signals were monitored at shorter interpulse delay times.

intensities for the ground state CrO formation time period was not plotted. The partial pressure of the entrapped Cr(CO)₆ in 10% O₂/N₂O in He was kept constant at 0.5 Torr and that of the pure quenching gas (O₂ or N₂O) was varied, and the LIF intensities were monitored vs interpulse delay time to obtain depletion rate constants by O₂ and N₂O. To reduce the effect of high-lying excited state Cr atoms,

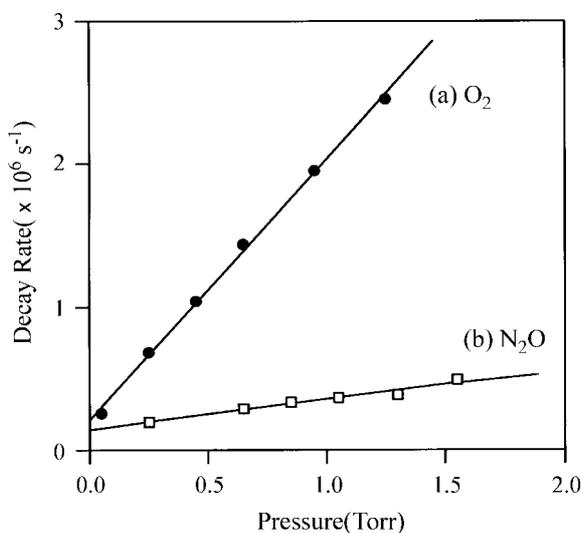


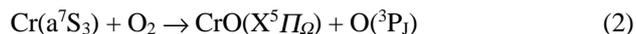
Figure 6. Pressure dependence of disappearance rate of the ground state CrO; (a) O₂ (●) and (b) N₂O (□).

Cr(CO)₆ was photolyzed at 295.3 nm, which is off resonant from the Cr atomic transition frequency (295.72 nm). As the partial pressure of the quenching gas increases, the CrO* 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 CrO* intensity and the increase in decay rates with increasing the pressure of the quenching gas are suggestive of the collisional depletion of the ground state CrO 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 $5.4 \pm 0.2 \times 10^{-11}$ and $6.5 \pm 0.4 \times 10^{-12}$ cm³molecule⁻¹s⁻¹ for O₂ and N₂O, respectively.

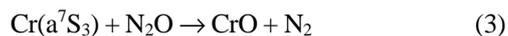
Discussion

The excitation and fluorescence spectra in Figures 1 and 2 clearly show that the ground state CrO molecules are formed in the reaction cell. Parnis and coworkers produced ground state Cr atoms by multiphoton dissociation (MPD) of Cr(CO)₆ using a visible laser wavelength in a static-pressure gas cell and investigated the reaction kinetics of Cr atoms with various small molecules including O₂ and N₂O.¹⁷ They obtained large pseudo-second-order rate constants for the reaction of Cr with O₂, however, small bimolecular rate constant was observed for the reaction of Cr with N₂O. They attributed the large rate constant for the reaction of Cr with O₂ to the CrO₂ formation by a termolecular association reaction, because they did not succeed in observing LIF signal from ground state CrO. NO detection of LIF signal from Parnis *et al.*'s work could be due to the use of focussed laser pulse for MPD of Cr(CO)₆. If the Cr(CO)₆ vapors were completely dissociated into Cr and CO by the intense focussed laser beam in their small observation volume ($1.3\text{--}5 \times 10^{-6}$ cm³), CrO molecules would not be produced under their experimental conditions as discussed below.

The photolysis laser power dependence of CrO LIF intensities provides a clear evidence that the ground state CrO molecules are generated from the reaction of Cr(CO)_x ($x=1\text{--}5$), produced by one photon absorption of Cr(CO)₆, with N₂O or O₂, and not from the reaction of Cr atoms with N₂O or O₂. Recently, Hedgecock and coworkers have reported that the Cr atom reaction with O₂, Eq. (2), is 0.38 ± 0.09 eV endoergic from the crossed molecular beam studies.¹⁸



If the Cr atoms produced by two-photon absorption of Cr(CO)₆ in an unfocused weak UV laser pulse have enough translational energy to surmount the endoergicity of Eq. (2), then the power dependence might show second-order dependence at higher photolysis laser power. Futerko and Fontijn have reported that the activation barrier for the Cr atom reaction with N₂O, Eq. (3), is 0.23 eV, and the reaction does not occur efficiently at room temperature.^{19,20}



Thus, the first-order dependence of the CrO LIF intensities on the photolysis laser power also implies that the Cr atoms generated by two-photon absorption do not have enough translational energy for reactions (2) and (3).

The radiative lifetimes as well as the quenching rate constants obtained in this work for the CrO($B^5\Pi_{g^-}$) state by N₂O, O₂, Ar and He are basically the same for $\Omega = -1$ and 1 as shown in Table 1. However, they are somewhat longer than those from recently reported by Hedgecock *et al.*²¹ Hedgecock and coworkers obtained the radiative lifetimes under collisionless condition, whereas our values are obtained under multiple collision conditions. Because of the small energy difference (~ 55 cm⁻¹) among the substates of CrO($B^5\Pi_{g^-}$),⁹ the longer lifetimes in this work might be ascribed to the efficient collisional mixing among the different substates of CrO ($B^5\Pi_{g^-}$).²²

The magnitude of the ground state CrO depletion rate by O₂ is much larger than that by N₂O. The present results show a striking contrast to the previous results of FeO depletion rate constants by O₂ and N₂O.¹⁴ For the ground state FeO molecules, N₂O was 2.5 times more efficient than O₂. The depletion rate constants of N₂O for both FeO and CrO are not much different. However the depletion rate constant of O₂ for CrO is about 30 times larger than that for FeO. This big difference in depletion kinetics could be ascribed to the different electronic states of the FeO($X^5\Delta_{g^-}$) and CrO($X^5\Pi_{g^-}$) ground states.

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