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$N(^4S)$ Formation following the 193.3-nm ArF Laser Irradiation of NO and NO_2 and Its Application to Kinetic Studies of $N(^4S)$ Reactions with NO and NO_2

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Formation of the ground-state nitrogen atom, $N(^4S)$, following 193.3-nm ArF laser irradiation of NO and NO_2 was detected directly by a technique of laser-induced fluorescence (LIF) spectroscopy at 120.07 nm. Tunable vacuum ultraviolet (VUV) laser radiation around 120.07 nm was generated by two-photon resonance four-wave sum frequency mixing in Hg vapor. Photoexcitation processes of NO and NO_2 giving rise to the $N(^4S)$ formation are discussed on the basis of the Doppler profiles of the nascent $N(^4S)$ atoms produced from the photolysis of NO and NO_2 and the photolysis laser-power dependence of the $N(^4S)$ signal intensities. Using laser flash photolysis and vacuum ultraviolet laser-induced fluorescence detection, the kinetics of the reactions of $N(^4S)$ with NO and NO_2 have been investigated at 295 ± 2 K. The rate constants for the reactions of $N(^4S)$ with NO and NO_2 were determined to be $(3.8 \pm 0.2) \times 10^{-11}$ and $(7.3 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively, where the quoted uncertainties are 2σ statistical uncertainty including estimated systematic error.

1. Introduction

Photochemical processes involving the $N(^4S)$ atom and NO_x (NO and NO_2) molecules play a crucial rule in the terrestrial and planetary atmospheres.[1−4] For instance, the reaction of $N(^4S)$ with nitric oxide

$$N(^4S) + NO \rightarrow N_2 + O(^3P) \qquad (1)$$

has been thought to act as a sink of odd nitrogen in the middle and upper terrestrial atmosphere.[1,2] Possible significance of reaction 1 in the Martian and Venusian atmosphere has also been suggested.[2] The reaction of $N(^4S)$ with nitrogen dioxide

$$N(^4S) + NO_2 \rightarrow N_2O + O(^3P) \qquad (2)$$

plays a less significant role as a sink of odd nitrogen in the middle terrestrial atmosphere because of the small concentration of NO_2.[5] A small amount of N_2O may be formed by reaction 2 in the Martian atmosphere.[4] For the N + NO_2 reaction, other channels forming 2NO, $N_2 + O_2$, and $N_2 + O + O$ are energetically possible. However, those channels are suggested to be of minor importance as related to products.[5]

Although a number of kinetic studies of reactions 1 and 2 have been reported at room temperature, as listed in Table 1, agreement among them is relatively poor. In previous kinetic studies, several techniques such as microwave discharge of N_2,[5−14] vacuum ultraviolet (VUV) flash photolysis of N_2O,[10,15] and pulsed radiolysis of N_2[16] were employed to generate the $N(^4S)$ atoms. For $N(^4S)$ detection, mass spectrometry techniques were used in several studies.[6−9,13,14] With nitrogen atom lamps, resonance fluorescence detection[5,10−12,15] and resonance absorption detection[16] of $N(^4S)$ atoms were also used.

TABLE 1: Summary of the Present and Previous Studies on the Reaction Kinetics of $N(^4S)$ with NO and NO_2 at Room Temperature

reactant	rate coefficient[a]	method[e]	references
NO	1.7 ± 0.8[b]	DF/MS	Herron (1961) [6]
	2.2 ± 0.6	DF/MS	Philips and Schiff (1962) [7]
	2.2 ± 0.2	DF/MS	Clyne and McDermid (1975) [9]
	2.7 ± 0.4[c]	DF/RF	Lee et al. (1978) [10]
	4.0 ± 0.2[c]	FP/RF	Lee et al. (1978) [10]
	1.9 ± 0.2	PR/RA	Sugawara et al. (1980) [16]
	3.4 ± 0.3[c]	DF/RF	Cheah and Clyne (1980) [11]
	4.5 ± 0.2	FP/RF	Husain and Slater (1980) [15]
	2.77 ± 0.04[c]	DF/RF	Clyne and Ono (1982) [12]
	2.03 ± 0.17[c]	DF/MS	Brunning and Clyne (1984) [13]
	2.4 ± 0.2	DF/MS	Jeoung et al. (1991) [14]
	3.6 ± 0.4[d]	DF/RF	Wennberg et al. (1994) [5]
	3.0		NASA/JPL (2003) [30]
	3.8 ± 0.2[d]	LP/VUV-LIF	This work
NO_2	1.85 ± 0.22[c]	DF/MS	Philips and Schiff (1965) [8]
	0.14 ± 0.02	DF/MS	Clyne and McDermid (1975) [9]
	3.8 ± 0.1	FP/RF	Husain and Slater (1980) [15]
	0.301 ± 0.033[c]	DF/RF	Clyne and Ono (1982) [12]
	1.2 ± 0.1[d]	DF/RF	Wennberg et al. (1994) [5]
	1.2		NASA/JPL (2003) [30]
	0.73 ± 0.09 [d]	LP/VUV−LIF	This work

[a] In units of 10^{-11} cm^3 molecule^{-1} s^{-1}. [b] The error limits are estimates of 3σ. [c] The error limits are estimates of 1σ. [d] The error limits are estimates of 2σ. [e] Experimental techniques. DF: discharge flow, MS: mass spectrometry, KS: kinetic spectroscopy, RF: resonance fluorescence, FP: flash photolysis, PR: pulsed radiolysis, RA: resonance absorption, LP: laser photolysis, VUV-LIF: vacuum ultraviolet laser-induced fluorescence.

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Very recently, Nakayama et al.[17] reported a new detection technique for the N(^{4}S) atom using vacuum ultraviolet laser-induced fluorescence (VUV−LIF) spectroscopy at 120.07 nm, which is resonant to the N($2p^23s\,^4P_{1/2}-2p^3\,^4S_{3/2}$) transition. They photolyzed N_2O molecules at 193.3 nm, and the N(^{4}S) atoms produced were detected using the VUV−LIF technique. In the present study, we demonstrate that the laser flash photolysis/VUV−LIF detection technique is a powerful tool for the study of the kinetics of reactions 1 and 2, in which the N(^{4}S) formation following 193.3-nm laser irradiation of NO and NO_2 has been utilized as a photolytic source of N(^{4}S) atoms.

N(^{4}S) formation following 193.3-nm ArF laser irradiation of NO under shock-heated conditions (1400−3500 K) was reported by several groups,[18,19] in which the N(^{4}S) atoms were monitored by atomic resonance absorption spectroscopy at 119.9 nm.

$$\mathrm{NO} + h\nu(193.3\ \mathrm{nm}) \rightarrow \mathrm{N}(^4\mathrm{S}) + \mathrm{O}(^3\mathrm{P}) \qquad (3)$$

Three doublet states of NO—$A^2\Sigma^+(v' = 3)$, $B^2\Pi(v' = 7)$, and $C^2\Pi(v' = 3)$—lie near the dissociation limit of NO. They suggested that N atoms are produced by direct excitation of vibrationally excited states of NO($X^2\Pi$, $v \geq 1$) to the $D^2\Sigma^+$ state, following conversion from the $D^2\Sigma^+$ state to the predissociating $C^2\Pi$ state. In our present paper, we report the first observation of N(^{4}S) formation following 193.3-nm irradiation of NO at 295 K. Photoexcitation processes of NO giving rise to the N(^{4}S) atom formation at 295 K have been discussed.

Photoexcitation processes of NO_2 in the UV region have been thoroughly investigated at a number of wavelengths other than 193.3 nm.[20] At 193.3 nm, there are only a limited number of experimental studies on the photoexcitation processes. The following two channels are thought to be dominant as photodissociation pathways at 193.3 nm,

$$\mathrm{NO_2} + h\nu(193.3\ \mathrm{nm}) \rightarrow \mathrm{NO}(X^2\Pi) + \mathrm{O}(^3\mathrm{P}) \qquad (4a)$$

$$\rightarrow \mathrm{NO}(X^2\Pi) + \mathrm{O}(^1\mathrm{D}) \qquad (4b)$$

and the branching ratio for O(^{1}D) and O(^{3}P) productions was estimated to be $[\mathrm{O}(^1\mathrm{D})]/([\mathrm{O}(^1\mathrm{D})] + [\mathrm{O}(^3\mathrm{P})]) = 0.55 \pm 0.03$.[21] Gradd and Slanger[22] observed the vibrationally excited NO($X^2\Pi$, $v = 4-10$) in the photodissociation of NO_2 at 193.3 nm. Gong et al.[23] reported that the nascent vibrational state populations of NO($X^2\Pi$, $v = 1-7$) in the photodissociation of NO_2 at 193.3 nm have a maximum at $v = 5$. Tsuji et al.[24] studied the decomposition of NO_2 in N_2 atmosphere at 193.3 nm by ArF laser irradiation and observed a lower NO yield than that predicted from simple NO_2 photolysis (reactions 4a and 4b) at a low NO_2 concentration of 200 ppm. They suggested that the lower NO yield was attributable to the photolytic loss of vibrationally excited NO which was produced primarily from NO_2 photolysis at 193.3 nm. The N(^{4}S) and O_2 productions are energetically possible in the UV region below 272 nm:

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{N}(^4\mathrm{S}) + \mathrm{O_2} \qquad (4c)$$

Matsumi et al.[25] detected laser-induced fluorescence from the vibrationally excited O_2 molecules around 220−300 nm following the irradiation of focused visible laser light (470−580 nm) on NO_2 gas, and suggested that the vibrationally excited O_2 molecules were directly produced from a multiphoton absorption process of NO_2. However, further experimental studies revealed that the O_2 molecules were produced from the reaction of O* + NO_2 where O* was generated from the multiphoton dissociation of NO_2.[26,27] There has been no experimental observation of channel 4c with the irradiation of an ArF laser. In our present paper, we report a first experimental observation of N(^{4}S) production from NO_2 with high-power ArF laser irradiation at 193.3 nm. The photoexcitation processes of NO_2 giving rise to N(^{4}S) formation have been discussed.

2. Experiments

The experimental setup used in the present study is similar to that in our previous work using the VUV−LIF technique,[17] and therefore only a brief description related to this study is given here. Unpolarized output of an ArF excimer laser (Lambda Physik, COMPex 102) was employed for photoexcitation of NO and NO_2. Typical pulse energy of the 193.3-nm laser was 0.5−8 mJ. The N(^{4}S) atoms produced following 193.3-nm laser irradiation of NO and NO_2 were directly detected by the VUV−LIF technique at 120.07 nm, which corresponds to the N($2p^23s\,^4P_{1/2}-2p^3\,^4S_{3/2}$) transition. The tunable VUV laser around 120.07 nm was generated by four-wave sum frequency mixing ($\omega_{\mathrm{VUV}} = 2\omega_1 + \omega_2$) in Hg vapor,[28] in which Kr gas was added for phase matching. Two dye lasers were simultaneously pumped by a single XeCl excimer laser (Lambda Physik, COMPex 201, Scanmate2E and FL3002). One dye laser operating with Rhodamin 101 dye in CH_3OH solvent generated 4−5 mJ/pulse around 625 nm. The visible output was frequency-doubled in a KD*P crystal to obtain 312.76 nm (in air), which was two-photon resonant with the Hg electronic transition ($6s7s\ ^1S_0 \leftarrow 6s^2\ ^1S_0$). The other dye laser operating with Coumarin 307 dye in CH_3OH solvent produced 2−4 mJ/pulse around 517 nm. The two laser beams were carefully overlapped using a dichroic mirror and focused into the Hg vapor cell with a fused silica lens ($f = 250$ mm). Temperature in the Hg vapor cell was around 450−470 K, which corresponds to the equilibrium Hg vapor pressure of 8−14 Torr.[29] The VUV laser line width was estimated to be 0.40 cm^{-1} full-width-at-half-maximum (fwhm) with a Gaussian shape, which was estimated from the Doppler profile of thermalized N(^{4}S) atoms produced from 193.3-nm laser irradiation of NO_2 in the presence of 3.6 Torr of helium at a delay time of 5 μs between the photolysis and probe laser pulses. The repetition rate of the photolysis and probe laser pulses was 10 Hz. The delay time between the photolysis and probe laser pulses was controlled by a digital delay generator (Stanford Research Systems, DG535).

The photolysis and probe laser beams crossed at right angles in the reaction chamber. The VUV−LIF signal of N(^{4}S) atoms was detected using a solar-blind photomultiplier tube (EMR, 542J-09-17) mounted at right angles to the propagation directions of both the photolysis and probe laser beams. The PMT has an MgF_2 window and a KBr photocathode that is sensitive only between 115 and 165 nm. A band-pass filter was installed (Acton Research, model 122-VN, $\lambda = 122$ nm, $\Delta\lambda = 12$ nm). The output of the photomultiplier was preamplified and averaged over 10 laser pulses, using a gated integrator (Stanford Research, SR-250). The reaction chamber was continuously evacuated by a rotary pump (Alcatel, 300 L min^{-1}) through a liquid N_2 trap. The total gas pressure in the chamber was measured by a capacitance manometer (MKS Baratron, 122A). All experiments were performed at 295 ± 2 K.

NO gas (Nihon Sanso Co., >99%) purchased was used after purification by passing it through a cold trap that was immersed in a methanol/liquid N_2 slush bath at 175 K. Helium gas (Iwatani Gas Co., >99.99%) was used without further purification in the kinetic experiments. Much attention was paid to the handling of NO_2 gas reagent in this study, since purified NO_2 gas is easily degraded to NO mixture and the reaction rate constant of NO

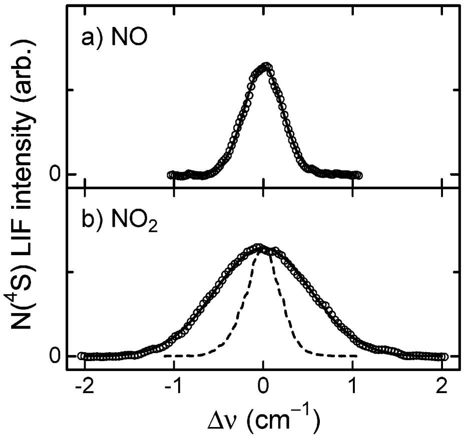

Figure 1. Fluorescence excitation spectra of N(^{4}S) produced from the 193.3-nm laser irradiation of (a) NO and (b) NO$_2$, respectively, which were recorded by scanning the probe laser wavelength across the resonance center of the $^4P_{1/2}-^4S_{3/2}$ transition for the N(^{4}S) atom at 120.07 nm. The solid curves indicate Gaussian shapes that fit the observed spectrum. Spectrum (a) was measured at an 80-ns delay time between the photolysis and probe laser pulses at the pressure of NO 145 mTorr. Spectrum (b) was measured at an 80-ns delay time at pressures of NO$_2$ 34 mTorr and O$_2$ 82 mTorr. The broken curve shows the fluorescence excitation spectrum of thermalized N(^{4}S), in which the N(^{4}S) atom was produced from 193.3-nm irradiation of NO$_2$ in the presence of 3.6 Torr of He. The delay time was 5 μs.

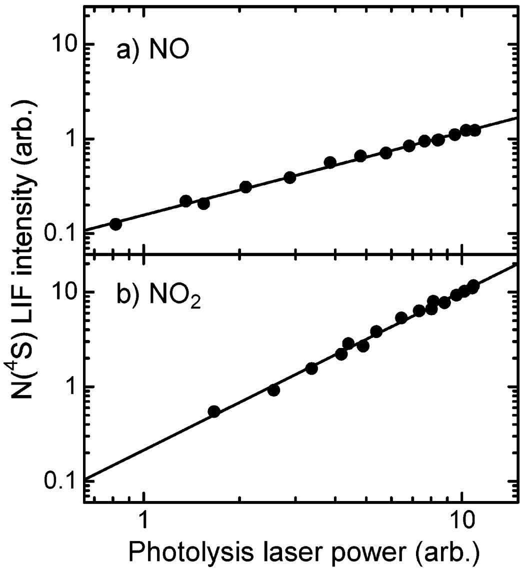

Figure 2. Plots of the photolysis laser power dependence of the LIF intensity of N(^{4}S) produced following 193.3-nm laser irradiation of (a) NO and (b) NO$_2$, respectively. The photolysis laser power was varied while monitoring the N(^{4}S) LIF signal at 120.07 nm. The probe laser power was kept constant during the measurements. Solid lines indicate the results of least-squares fit analysis in order to determine the order n of laser power dependence of the LIF signals. The values obtained for n are (a) 0.9 ± 0.1 and (b) 1.7 ± 0.2, respectively, which are described in the figure. The quoted uncertainties indicate the 2σ errors of the fit.

with N(^{4}S) has been reported to be about 5 times larger than that of NO$_2$ (Table 1). The NO$_2$ gas was synthesized by mixing the purified NO gas with excess O$_2$ (Nihon Sanso Co., >99.99%) in a glass vessel (2 L) and stored in the vessel for more than several days prior to use in the experiments. The total pressure of the NO$_2$/O$_2$ vessel was about 700 Torr with the mixing ratio $[NO_2]/[O_2] \approx 1:3$. For the NO$_2$ photolysis and kinetics experiments, the gas mixture of NO$_2$/O$_2$ was supplied to the reaction cell directly from the vessel through a mass flow controller. N$_2$O$_4$ equilibrates with NO$_2$ gas. The equilibrium between NO$_2$ and N$_2$O$_4$ in the reactant gas which was flowed into the reaction cell was estimated to be attained within 10^{-6} s[20] before the laser irradiation. When the partial pressure of NO$_2$ is 1×10^{16} molecule cm^{-3}, the partial pressure of N$_2$O$_4$ is about 1/400 of NO$_2$ at 298 K using the equilibrium constant presented by NASA/JPL.[30]

The concentration of NO$_2$ in the reaction chamber was determined directly by absorption measurements. The collimated output of a tungsten lamp was passed through the reaction chamber and focused onto the entrance slit of a spectrograph with a 2048-element diode array detector (Oceans Optics, HR2000, $f = 101$ mm). A 10-μm entrance slit was used for absorption measurements at a resolution of ~0.7 nm. The absorption features of the NO$_2$ spectrum recorded between 300 and 650 nm are in good agreement with previous measurements.[31−33] The wavelength of the spectrometer was calibrated at 404.66 and 435.84 nm using an Hg pen ray lamp. The concentration of NO$_2$ was determined by absorption measurements around 413.7 nm on the basis of the reported absorption cross-section.[31−33] The contribution of N$_2$O$_4$, if present, is minimized at this wavelength, as described by Gierczak et al.[33] The uncertainty associated with the measurements of NO$_2$ concentration was estimated to be ~10%.

3. Results and Discussion

3.1. N(^{4}S) Production following the 193.3-nm Laser Irradiation of NO. Figure 1a shows a typical fluorescence excitation spectrum of the nascent N(^{4}S) atoms produced following 193.3-nm laser irradiation of NO, which was obtained by scanning the probe laser wavelength across the $2p^23s\ ^4P_{1/2}-2p^3\ ^4S_{3/2}$ transition at 120.07 nm. The spectrum was taken at an 80-ns delay time with 145 mTorr of NO, and no buffer gas was added. It should be noted that the dissociation limit of rovibrationally cold NO giving rise to the N(^{4}S) + O(^{3}P) channel is 52397 ± 2 cm^{-1},[34] which is slightly larger than the photon energy of the 193.3-nm laser radiation of 51730 cm^{-1}. To reveal the photodissociation processes of NO producing the N(^{4}S) atom, photolysis laser power dependence of the LIF signal was measured. As shown in Figure 2a, we found that the LIF intensity was linearly dependent on the photolysis laser power. When we turned the ArF excimer laser off, no obvious LIF signal was observed. This indicates that N(^{4}S) production from the NO photodissociation at 120 nm was negligible under our experimental conditions. These results suggest that the N(^{4}S) formation observed in this study was attributable to the one-photon excitation process of NO:

$$NO + h\nu(193.3\ \text{nm}) \rightarrow N(^4S) + O(^3P) \qquad (3)$$

To check the interference in the measurements because of impurities, we recorded the fluorescence excitation spectra of the nascent N(^{4}S) atoms produced from purified and nonpurified NO. No significant change was observed in the signal intensities and spectral shapes of N(^{4}S).

Three doublet states of NO—A$^2\Sigma^+(v = 3)$, B$^2\Pi(v = 7)$, and C$^2\Pi(v = 3)$—lie near the dissociation limit of NO. Davidson and Hanson[18] and Koshi et al.[19] reported the N(^{4}S) formation following 193.3-nm laser irradiation of NO under shock-heated conditions. The N(^{4}S) atom formation was attributed to direct excitation of vibrationally excited states of NO X$^2\Pi(v \geq 1)$ to the D$^2\Sigma^+$ state.[18] In our experiments which were performed at room temperature, it is unlikely that the direct photoexcitation from the NO $X^2\Pi(v = 1)$ to the $D^2\Sigma^+(v = 0)$ state is significantly responsible for $N(^4S)$ formation, because the population of vibrationally excited NO $X^2\Pi(v = 1)$ is negligibly small at room temperature.

Shibuya and Stuhl[35−37] investigated the excited-states dynamics of NO through the measurements of emission spectra and fluorescence lifetimes following 193.3-nm laser irradiation. They observed the fluorescence from $B^2\Pi(v = 7)$, $C^2\Pi(v = 0)$, and $A^2\Sigma(v = 3)$ states. The 193.3-nm laser light can be resonant with the absorption of the NO $B^2\Pi(v = 7) \leftarrow X^2\Pi(v = 0)$ and $A^2\Sigma(v = 3) \leftarrow X^2\Pi(v = 0)$ transitions. From the available spectroscopic data,[38] NO $X^2\Pi$ $(v = 0)$ is expected to be excited to the $B^2\Pi(v = 7)$ state via the absorption lines $R_{11}(30.5-32.5)$, $P_{11}(27.5-29.5)$, $Q_{11}(28.5-31.5)$, $R_{22}(28.5-30.5)$, $P_{22}(25.5-27.5)$, and $Q_{22}(26.5-29.5)$. The $A^2\Sigma(v = 3)$ state can also be prepared via the absorption of $X^2\Pi(v = 0, J \sim 50.5)$. The Boltzmann population of the $X^2\Pi(v = 0, J \sim 50.5)$ state is much smaller than that of $X^2\Pi(v = 0, J \sim 28.5)$ at 295 K. Shibuya and Stuhl[35−37] suggested that the rotational levels of $J = 21.5-34.5$ for the F_1 component and $J = 20.5-33.5$ for the F_2 component of the $B^2\Pi(v = 7)$ state were prepared following 193.3-nm excitation at room temperature, and that the $C^2\Pi(v = 0)$ and $A^2\Sigma(v = 3)$ states were produced by the collisional relaxation from the $B^2\Pi(v = 7)$ state. They also indicated that the photoexcited levels of the $B^2\Pi(v = 7)$ state are predissociative and that the fluorescence quantum yield is about 0.15 and $<6 \times 10^{-3}$ for $J = 20.5-29.5$ and $J > 29.5$, respectively. Therefore, it is likely that the $N(^4S)$ atom formation observed in the 193.3-nm laser irradiation of NO in this study is due to the photoexcitation to the high rotational levels of the $B^2\Pi(v = 7)$ state, which is followed by the predissociation to $N(^4S) + O(^3P)$.

The Doppler profile of the nascent $N(^4S)$ atoms produced from the 193.3-nm irradiation of NO (Figure 1a) is slightly wider than that of the thermalized $N(^4S)$ atoms (broken curve in Figure 1b). The kinetic energy release in channel 3 is estimated to be ~1000 cm^{-1}, from the Doppler profile of the nascent $N(^4S)$ atoms. This is consistent with the fact that the high rotational levels (F_1 $J = 21.5-34.5$, F_2 $J = 20.5-33.5$) in the $B^2\Pi(v = 7)$ state lie above the dissociation limit by 500−1100 cm^{-1}.

3.2. $N(^4S)$ Production following the 193.3-nm Laser Irradiation of NO_2. Figure 1b shows a typical example of the fluorescence excitation spectrum of the nascent $N(^4S)$ atoms produced from the 193.3-nm laser irradiation of NO_2, in which gas pressure in the chamber was 34 mTorr and 82 mTorr for NO_2 and O_2, respectively, without buffer gas. The spectrum was taken at an 80-ns delay time. The fwhm of the spectrum was estimated to be 1.38 cm^{-1} with a Gaussian shape (Figure 1b). Assuming the Maxwell−Boltzmann velocity distribution, the average translational energy of the nascent $N(^4S)$ atoms in the laboratory frame was calculated to be ~7500 cm^{-1} (~21 kcal mol^{-1}).

Figure 2b shows a photolysis laser power dependence of the LIF signal intensity of $N(^4S)$ atoms produced from the 193.3-nm laser irradiation of NO_2. A quadratic photolysis laser power dependence of the $N(^4S)$ LIF signal intensity suggests that $N(^4S)$ formation is attributable to the sequential two-photon dissociation process or the simultaneous absorption of two photons by NO_2.

For the sequential two-photon dissociation process, it is likely that the vibrationally excited $NO(X^2\Pi, v)$ is produced from the photolysis of NO_2 at 193.3 nm, and then $NO(X^2\Pi, v)$ is photolyzed to produce the $N(^4S)$ atom.

$$NO_2 + h\nu(193.3\ nm) \rightarrow NO(X^2\Pi, v) + O \tag{4}$$

$$NO(X^2\Pi, v) + h\nu(193.3\ nm) \rightarrow N(^4S) + O \tag{5}$$

Gradd and Slanger[39] observed the vibrationally excited NO $X^2\Pi(v = 4-10)$ in the photodissociation of NO_2 at 193.3 nm. Gong et al.[23] reported that the nascent vibrational state populations of NO $X^2\Pi(v = 1-7)$ in the photodissociation of NO_2 at 193.3 nm have a maximum at $v = 5$. The average translational energy of $N(^4S)$ estimated in the present study (~21 kcal/mol in the laboratory frame) is consistent with the sequential two-photon dissociation process in which $NO(X^2\Pi, v = 7)$ is formed through channel 4.

For the simultaneous two-photon absorption mechanism, it involves the direct formation of $N(^4S)$ from an electronically excited state(s) of NO_2, where the following channels are available thermochemically:

$$NO_2 + 2h\nu(193.3\ nm) \rightarrow N(^4S) + 2O \tag{6}$$

$$NO_2 + 2h\nu(193.3\ nm) \rightarrow NO^* + O \rightarrow N(^4S) + O + O \tag{7}$$

$$NO_2 + 2h\nu(193.3\ nm) \rightarrow N(^4S) + O_2 \tag{8}$$

Haak and Stuhl[40] observed the NO emissions from its several excited states ($A^2\Sigma^+$, $D^2\Sigma^+$, and $E^2\Sigma^+$, and so on) following the multiphoton absorption of NO_2 at 193.3 nm. Further studies are required to elucidate the mechanism of $N(^4S)$ formation following 193.3-nm irradiation of NO_2.

3.3. Reaction Kinetics of $N(^4S)$ + NO and $N(^4S)$ + NO_2. The $N(^4S)$ formation following 193.3-nm irradiation of NO and NO_2 was applied to the kinetic studies of reactions 1 and 2. The pulsed ArF laser light was used to irradiate 150−570 mTorr of NO in the presence of 1.8 Torr of He diluent, and the chemical loss of $N(^4S)$ was measured to determine the rate coefficients for the $N(^4S)$ + NO reaction at 295 ± 2 K. Figure 3 shows a typical example of the temporal profile of the $N(^4S)$ LIF intensity following pulsed ArF laser irradiation of a mixture of 415 mTorr of NO and 1.8 Torr of He diluent, in which the VUV laser wavelength was fixed at the resonance center of the $N(2p^23s\,^4P_{1/2}-2p^3\ ^4S_{3/2})$ transition (120.07 nm). The time-resolved VUV−LIF signal of $N(^4S)$ atoms exhibits an initial jump due to photolytic formation of $N(^4S)$, followed by a slow decay due to its chemical removal in collisions with NO molecules. For the kinetic study of the $N(^4S) + NO_2$ reaction, the time profiles of the $N(^4S)$ LIF were measured under the conditions of NO_2 60−570 mTorr, O_2 200−1700 mTorr, and He 3.0 Torr. As described in the previous section, the translationally hot $N(^4S)$ atoms are produced following 193.3-nm irradiation of NO and NO_2. The translationally hot $N(^4S)$ atoms are thermalized within 2 μs under our experimental conditions in collisions with helium, which was confirmed by measuring the Doppler profiles of $N(^4S)$ atoms. The chemical loss of $N(^4S)$ by reaction with O_2 can safely be ignored under our experimental conditions ($[O_2]$ = 200−1700 mTorr, delay time 0−20 μs) because of its small rate constant of 8.5×10^{-17} cm^3 $molecule^{-1}$ s^{-1} at 298 K.[30] For both reaction systems 1 and 2, single-exponential decay was observed for temporal profiles of $N(^4S)$ as typically shown in Figure 3.

$$[N(^4S)]_t = [N(^4S)]_0 \times \exp(-k't) \tag{9}$$

The pseudo-first-order rate constant k' for a particular reactant pressure was derived by a nonlinear least-squares fit analysis.

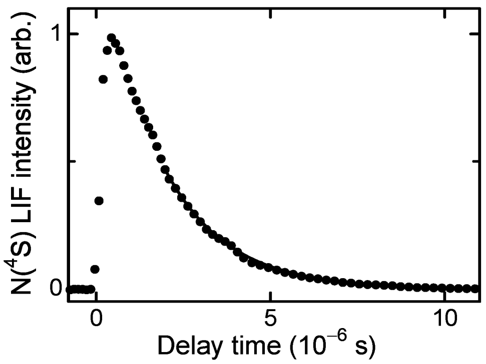

Figure 3. A typical example of the temporal decay curve of N(^{4}S) LIF intensity following the 193.3-nm pulsed laser irradiation of the gas mixture containing 415 mTorr of NO and 1.8 Torr of He diluent at 295 ± 2 K. The solid curve is a first-order decay fit to the data in the time domain after 2 μs.

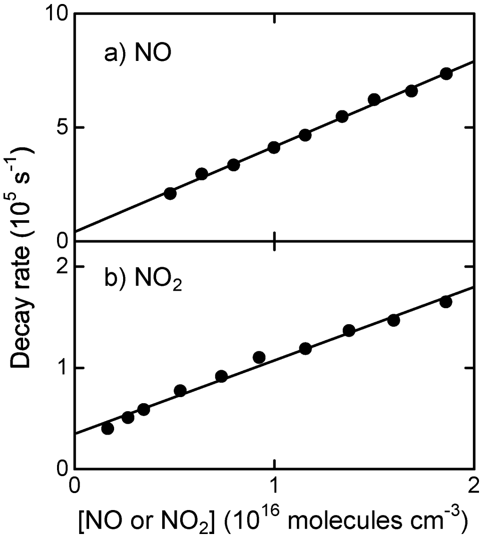

Figure 4. Plot of pseudo-first-order decay rates (k') versus the concentration of the reactants (a) NO and (b) NO$_2$. Results of the least-squares fit analysis of the data are drawn by straight lines, which yield the rate coefficients $(3.8 \pm 0.2) \times 10^{-11}$ and $(7.3 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 ± 2 K for N(^{4}S) reactions with NO and NO$_2$, respectively.

The resultant dependences of the k' values on the number densities of NO and NO$_2$ for the N(^{4}S) + NO and N(^{4}S) + NO$_2$ reactions, respectively, are shown in Figure 4. Linear least-squares fit analysis of the data in Figure 4 yielded the bimolecular rate constants of $k_{NO} = (3.8 \pm 0.2) \times 10^{-11}$ and $k_{NO_2} = (7.3 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 ± 2 K. The quoted uncertainties of the rate constants include 2σ statistical uncertainties and estimated systematic errors.

The rate constants for reactions 1 and 2 at 295 ± 2 K determined in the present study are listed in Table 1 with available literature data. The k_{NO} value determined in this study is in excellent agreement with the latest data reported by Wennberg et al.[5] within the quoted uncertainties. Our result is also in good agreement with that of Cheah and Clyne[11] and one of the values reported by Lee et al.[10] The latest NASA/JPL recommended k_{NO} value at 298 K[30] is smaller than both the values recently reported by Wennberg et al.[5] and obtained in the present study. For the reaction of N(^{4}S) + NO, the ground potential energy surface (PES) $^3A''$ and the first excited PES $^3A'$ were theoretically investigated by means of the CASPT2 method, and the variational transition state theory provided the temperature-dependent rate coefficients.[41] It was shown that the $^3A'$ PES was mainly responsible for the N(^{4}S) + NO reaction over the temperature range of 200−5000 K, and their k_{NO} value at 300 K was 4.68×10^{-11} cm^3 molecule^{-1} s^{-1}. The theoretical value is larger than our experimental and previous determinations.

The k_{NO_2} values reported previously range from 0.14 to 3.8 $\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} as listed in Table 1. The k_{NO_2} value determined in this study is larger than the result of Clyne and Ono,[12] and is smaller than that presented by Wennberg et al.[5] The experimental technique of laser flash photolysis combined with VUV laser-induced fluorescence detection has been utilized for the first time in this study, while Clyne and Ono[12] and Wennberg et al.[5] used the technique of discharge flow and resonance fluorescence detection with a nitrogen lamp. Clyne and McDermid[9] and Clyne and Ono[12] reported that the measured rate constant k_{NO_2} decreased as the ratio of [NO$_2$]/[N(^{4}S)]$_0$ increased at lower ratios of [NO$_2$]/[N(^{4}S)]$_0$ (<80). They argued that the change of the observed rate constant was due to catalytic interferences involving both H(^{2}S) + NO$_2$ and O(^{3}P) + NO$_2$ reactions, in which H(^{2}S) and O(^{3}P) atoms can be produced as impurities in the microwave discharge process and O(^{3}P) atoms can also be produced through reaction 2. In the present study, N(^{4}S) atoms were produced from the 193.3-nm pulsed laser irradiation of NO$_2$, and the ratio of [NO$_2$]/[N(^{4}S)]$_0$ was (5−20) $\times 10^5$ as estimated by considering the N(^{4}S) detection sensitivity reported in our recent paper by Nakayama et al.[17]

It should be noted that, in general, the literature data of the rate coefficients for N(^{4}S) reactions with simple molecules are more scattered than those of other atmospheric reactions involving atoms such as O(^{1}D) and Cl(^{2}P$_j$) atoms. This might be attributable to the relatively low reactivity of N(^{4}S) toward simple molecules and the lack of applicable experimental technique. The newly presented technique for investigation of N(^{4}S) reactions with NO and NO$_2$ will be applicable to examine some other N(^{4}S) reactions as a function of temperature and pressure. The pulsed laser photolysis/VUV−LIF technique has been utilized as a powerful tool to study the kinetics and dynamics of atmospheric reactions involving O(^{1}D) and Cl(^{2}P$_j$) atoms.[42,43]

4. Summary

In this work, the new technique of VUV−LIF spectroscopy was demonstrated as a powerful tool to study the photochemical processes of NO and NO$_2$ molecules at room temperature following 193.3-nm laser irradiation. Production of the N(^{4}S) atom from NO and NO$_2$ was directly detected at 120.07 nm which was resonant with the $2p^23s\ ^4P_{1/2}-2p^3\ ^4S_{3/2}$ transition. Doppler spectroscopy of the nascent N(^{4}S) atoms from NO molecules and the photolysis laser power dependence suggested that the N(^{4}S) formation process is attributed to the one-photon excitation of rotationally excited NO $X^2\Pi(v = 0, J \sim 28.5)$ to the rotationally excited levels of NO $B^2\Pi(v = 7)$ followed by decomposition into N(^{4}S) + O(^{3}P). N(^{4}S) formation from NO$_2$ following 193.3-nm laser irradiation was suggested to be due to the sequential or simultaneous two-photon dissociation process. N(^{4}S) formation following 193.3-nm pulsed laser irradiation of NO and NO$_2$ was utilized to kinetic studies of the N(^{4}S) reactions with NO and NO$_2$ at 295 ± 2 K. The experimental technique of laser flash photolysis combined with the VUV laser-induced fluorescence detection was applied for the first time to the kinetic studies of the reactions. The rate coefficients were determined to be $(3.8 \pm 0.2) \times 10^{-11}$ and $(7.3 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for NO and NO$_2$ reactions, respectively.

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References and Notes

(1) Siskind, D. E; Rusch, D. W. *J. Geophys. Res.* **1992**, *97*, 3209.

(2) Gerard, J.-C. *Planet. Space Sci.* **1992**, *40*, 337.

(3) Nelvison, C. D.; Solomon, S.; Garcia, R. R. *Geophys. Res. Lett.* **1997**, *24*, 803.

(4) Yung, Y. L; DeMore, W. B. *Photochemistry of Planetary Atmosphere*; Oxford University Press, New York, 1999.

(5) Wennberg, P. O.; Anderson, J. G.; Weisenstein, D. K. *J. Geophys. Res.* **1994**, *99*, 18839.

(6) Herron, J. T. *J. Chem. Phys.* **1961**, *35*, 1138.

(7) Philips, L. F.; Schiff, H. I. *J. Chem. Phys.* **1962**, *36*, 1509.

(8) Philips, L. F.; Schiff, H. I. *J. Chem. Phys.* **1965**, *42*, 3171.

(9) Clyne, M. A. A.; McDermid, I. S. *J. Chem. Faraday. Trans. 1* **1975**, *71*, 2189.

(10) Lee, J. H.; Michael, J. V.; Payne, W. A.; Steif, L. J. *J. Chem. Phys.* **1978**, *69*, 3069.

(11) Cheah, C. T.; Clyne, M. A. A. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1543.

(12) Clyne, M. A. A.; Ono, Y. *Chem. Phys.* **1982**, *69*, 381.

(13) Brunning, J.; Clyne, M. A. A. *J. Chem. Soc., Faraday. Trans. 2* **1984**, *80*, 1001.

(14) Jeoung, S. C.; Choo, K. Y.; Benson, S. W. *J. Phys. Chem.* **1991**, *95*, 7282.

(15) Husain, D.; Slater, N. K. H. *J. Chem. Soc., Faraday. Trans. 2* **1980**, *76*, 606.

(16) Sugawara, K.; Ishikawa, Y.; Sato, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3159.

(17) Nakayama, T.; Takahashi, K; Matsumi, Y.; Taniguchi, N.; Hayashida, S. *J. Geophys. Res.* **2003**, *108*, doi: 10.1029/2003JD003709.

(18) Davidson, D. F.; Hanson, R. K. *Int. J. Chem. Kinet.* **1990**, *22*, 843.

(19) Koshi, M.; Yoshimura, M.; Fukuda, K.; Matsui, H.; Saito, K.; Watanabe, M.; Imamura, A.; Chen, C. *J. Chem. Phys.* **1990**, *93*, 8703.

(20) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmos. Chem. Phys.* **2004**, *4*, 1461.

(21) Sun, F.; Glass, G. P.; Curl, R. F. *Chem. Phys. Lett.* **2001**, *337*, 72.

(22) Gradd, G. E.; Slanger, T. G. *J. Chem. Phys.* **1990**, *92*, 2194.

(23) Gong, V. C.; Chen, X. R.; Weiner, B. R. Fifth International Conference on Chemical Kinetics, National Institute of Standards and Technology, Gaithersburg, MD, 2001.

(24) Tsuji, M.; Noda, K.; Sato, H.; Hamagami, T.; Tsuji, T. *Chem. Lett.* **2005**, *34*, 496.

(25) Matsumi, Y.; Murasawa, Y.; Obi, K.; Tanaka, I. *Laser Chem.* **1983**, *1*, 113.

(26) Jusinski, L. E.; Sharpless, R. L.; Slanger, T. G. *J. Chem. Phys.* **1987**, *86*, 5509.

(27) Nagai, H.; Kusumoto, T.; Shibuya, K.; Obi, K.; Tanaka, I. *J. Phys. Chem.* **1988**, *92*, 5432.

(28) Hilbig, R.; Wallenstein, R. *IEEE J. Quantum Electron.* **1983**, *QE-19*, 1759.

(29) Smith, A. V.; Alford, W. J. *J. Opt. Soc. Am.* **1987**, *B4*, 1765.

(30) Sander, S. P.; Friedel, R. R.; Golden, D. M.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Moortgat, G. K.; Ravishankara, A. R.; Kolb, C. E.; Molina M. J.; Finlayson-Pitts, B. J. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*; Evaluation Number 14, JPL Publication 02-25, JPL, Pasadena, CA, 2003.

(31) Harder, J. W.; Brault, J. W.; Johnston, P. V.; Mount, G. H. *J. Geophys. Res.* **1997**, *102*, 3861.

(32) Vandaele, A. C.; Hermans, C.; Simon, P. C.; Carleer, M.; Colin, R.; Fally, S.; Merienne, M. F.; Jenouvrier, A.; Coquart, B. *J. Quant. Spectrosc. Radiat. Trans.* **1998**, *59*, 171.

(33) Gierczak, T.; Burkholder, J. B.; Ravishankara, A. R. *J. Phys. Chem.* **1999**, *A103*, 877.

(34) Rottke, H.; Zacharias, H. *J. Chem. Phys.* **1985**, *83*, 4831.

(35) Shibuya, K.; Stuhl, F. *J. Chem. Phys.* **1982**, *76*, 1184.

(36) Shibuya, K.; Stuhl, F. *Chem. Phys.* **1983**, *79*, 367.

(37) Shibuya, K.; Stuhl, F. *Chem. Phys.* **1985**, *94*, 167.

(38) Gilmore, F. R. *J. Quant. Spectrosc. Radiat. Transfer* **1965**, *5*, 369.

(39) Gradd, G. E.; Slanger, T. G. *J. Chem. Phys.* **1990**, *92*, 2194.

(40) Haak, H. K; Stuhl, F. *J. Photochem.* **1981**, *17*, 69.

(41) Gamallo, P.; Gonzalez, M.; Sayos, R. *J. Chem. Phys.* **2003**, *119*, 2545.

(42) Takahashi, K.; Takeuchi, Y.; Matsumi, Y. *Chem. Phys. Lett.* **2005**, *410*, 196., and references therein.

(43) Taketani, F.; Takahashi, K.; Matsumi, Y.; Wallington, T. J. *J. Phys. Chem. A* **2005**, *105*, 3935, and references therein.