Adsorption States and Photochemistry of NO_2 Adsorbed on Au(111)

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The photochemistry of NO_2 adsorbed on an Au(111) surface has been investigated at <120 K in an ultrahigh vacuum system. The adsorption states of adsorbates were characterized by thermal desorption spectroscopy and IR reflection absorption spectroscopy (IRAS). The adsorption of NO_2 leads to formation of chemisorbed NO_2, N_2O_4 (D_{2h} symmetry) in direct contact to the surface, and well-ordered N_2O_4 (D_{2h} symmetry) physisorbed on these species without formation of other unstable N_2O_4 isomers. While the former two species undergo neither photodissociation nor photodesorption, physisorbed N_2O_4 is dissociated to NO_2, NO, and adsorbed atomic oxygen under irradiation at λ <430 nm. IRAS showed that no intermediate species such as adsorbed NO_2 or NO_3 were formed during N_2O_4 photolysis. The photodissociation cross section of physisorbed N_2O_4 at 350 nm was found to be 5.6×10^{-19} cm^2, which is close to the absorption cross section of gas-phase N_2O_4. Wavelength dependence of the cross section is very similar to the absorption spectrum of N_2O_4 adsorbed on LiF at 68 K. Physisorbed N_2O_4 photolysis is inhibited significantly when the Au surface is covered with a thin water ice film, suggesting that the photolysis is enhanced by metal substrate photoexcitation or electron transfer from the substrate to the adsorbates.

1. Introduction

The photochemistry of molecules adsorbed on a solid surface has received increasing attention in recent decades since it provides information for adsorbate−surface interactions, including energy and charge transfer, dynamics, and kinetics.[1] For the surface photochemistry of NO_2, Hasselbrink et al.[2] studied the UV laser-induced desorption of NO from submonolayer NO_2 (actually present as N_2O_4) adsorbed on top of a NO saturated Pd(111) surface. They found two different desorption channels using laser-induced fluorescence, one characterized by nonthermal state populations, and one showing accommodation to the surface. They also carried out polarization experiments, concluding that the photodissociation is initiated by excitation of metal electrons rather than direct photoabsorption by the adsorbate. Dixon-Warren et al.[3] investigated, on the other hand, the photodissociation of NO_2 (N_2O_4) adsorbed on LiF(001), which leads to desorption of NO and NO_2. They found two different translational energy distributions for NO, and NO_2-coverage-dependent translational energy for NO_2. Although they characterized reaction intermediates using IR transmission spectroscopy, its sensitivity was low, and the spectral region was limited to >1500 cm^{-1} due to cutoff of the LiF substrate.

While the motivation of these studies stems from the dynamics of a surface photochemical reaction, the heterogeneous reactions of NO_x species on water ice surfaces have attracted attention in recent years from an environmental chemistry point of view, since the surfaces of polar stratospheric clouds, which mainly consist of water ice, have been implicated as playing a central role in the photochemical mechanism responsible for the yearly occurrence of the ozone hole.[4−6] Rieley et al.[7] investigated the photochemistry of N_2O_4 adsorbed on ice films formed on a Cu foil using IR reflection absorption spectroscopy (IRAS) for characterization of the adsorption states. They observed the photodesorption of NO_2 under near-UV irradiation. Since the wavelength dependence of the NO_2 yield was comparable to the gas-phase absorption cross section for N_2O_4, they concluded that the photochemistry of N_2O_4 on ice is not significantly different to that of gas-phase N_2O_4. They also studied photodesorption dynamics of NO_2 from N_2O_4 adsorbed on ice surfaces.[8]

Since the photochemical properties of adsorbates are significantly affected by their adsorption states including orientations, in situ characterization of adsorbates by surface spectroscopy is essential to deeper insight into a mechanism of surface photochemistry. We have used IRAS for in situ observation of surface species before and during surface photoreactions.[9] Although a substrate for IRAS study is usually a smooth metal with a high reflection coefficient, various thin films coated on such a metal can also be used. A metal substrate used for surface photochemistry is required to be as inert as possible in order to minimize a change in electronic states due to adsorbates−surface interactions. We have used an Au single crystal as a substrate, since Au is known to be most inactive among transition metals.[9] In the present paper we report the photochemistry of NO_2 adsorbed on an Au(111) surface. The adsorption states of NO_2 on a clean Au(111) surface were already investigated by Koel and co-workers[10,11] using HREELS, IRAS, and TPD. They found that NO_2 is adsorbed molecularly on the surface to form a surface chelate at <170 K (we refer to this species as chemisorbed NO_2), and over the chemisorbed NO_2 layer, NO_2 is physisorbed as N_2O_4. They also found that the chemisorbed NO_2 reacts readily with gas-phase NO to form N_2O_3 on the surface. We report in the present paper the photochemistry of NO_x species on an Au(111) surface with the detailed characterization of adsorbates by IRAS and TPD.

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2. Experimental Section

The experimental apparatus used was similar to that described previously.[9] An Au(111) single crystal (12 mm in diameter, 1.5 mm thick, 99.999% purity) was purchased from Mateck. The sample was cleaned by repeating Ar ion sputtering and annealing at 800 K. Ozone was sometimes used for surface cleaning.

Thermal desorption spectra (TDS) of adsorbates were obtained using a quadrupole mass spectrometer (ANELVA AQA-200), which is located at ca. 35° with respect to the substrate surface normal. Since NO_2 undergoes fragmentation during ionization to produce NO^+, the mass analysis of a mixture of NO and NO_2 needs correction for the contribution of NO^+ from NO_2. The pattern coefficients of NO_2 were determined using the TDS of NO_2 from adsorbed N_2O_4. For IRAS measurements, the IR beam from FTIR (BIO-RAD FTS-155) was introduced into the chamber through a BaF_2 window, the cutoff wavelength of which is around 900 cm^{-1}. The incident angle of the IR beam was ~85°, and a wire grid polarizer was used to select p-polarized light, since only p-polarized light is effective for IRAS.[11,12] The paths of the IR beam were purged with dry air to reduce the effects of moisture. IRA spectra were recorded with 4 cm^{-1} resolution and 200 scans.

The light source was a paraboloidal-reflector Xe lamp (ILC LX300UV, 300 W), which was monochromatized by a grating monochromator (RITSU MC-20L) and focused by a quartz lens onto the sample through an MgF_2 window. A water filter (20 cm long) was placed in front of the lamp to remove radiative heat. Incident photon flux into the chamber was measured using chemical actinometry. When intense irradiation was necessary, a band-pass filter (230−400 nm, Toshiba UV-D33S) was used instead of the monochromator. The substrate temperature was initially elevated at ca. 1 K/min and leveled off at ca. 100 K in this case. To reduce light intensity, neutral-density filters (Toshiba) were used.

NO_2 was stored in a glass reservoir in the presence of an excess of O_2 to prevent its decomposition to NO and O_2 during storage. The gas mixture was frozen at 77 K and O_2 was pumped away before use. Since NO_2 was decomposed to some extent in the gas handling system, the inner wall of the stainless steel pipe was passivated by exposing a relatively high pressure of NO_2 or O_3 for a prolonged time. Gases were introduced into the chamber through a nozzle, the end of which was ca. 1 cm away from the substrate. A pulsed valve (General Valve) was used to control exposures of gases to the surface.

3. Results and Discussion

3.1. Characterization of Adsorption States. 3.1.1. TPD Experiments. Figure 1 shows thermal desorption spectra from NO_2 adsorbed on the Au(111) surface at 92 K. The desorption peak centered at 206 K (γ peak) is attributed to the desorption of NO_2 chemisorbed on the surface and the one at 132 K (α peak) to NO_2 physisorbed on chemisorbed NO_2. A small peak centered at 152 K (β peak) was also observed by Bartram and Koel,[10] but not characterized. We attribute this peak to N_2O_4 adsorbed on the vacant Au surface remained after NO_2 chemisorption based on our IRAS results. The fact that the β peak mainly comprises NO indicates that this N_2O_4 species undergoes thermal decomposition during TPD. Bartram and Koel[10] reported that the exposure necessary for the saturation coverage of chemisorbed NO_2 was ca. 2.0 langmuirs (1 langmuir = 10^{-6} Torr·s), and the sticking probability was close to unity for both chemisorbed NO_2 and physisorbed N_2O_4. On the basis of their results, we take a saturation coverage as 1 monolayer (ML). As seen in Figure 1, the NO_2^+/NO^+ ratio for the γ peak is

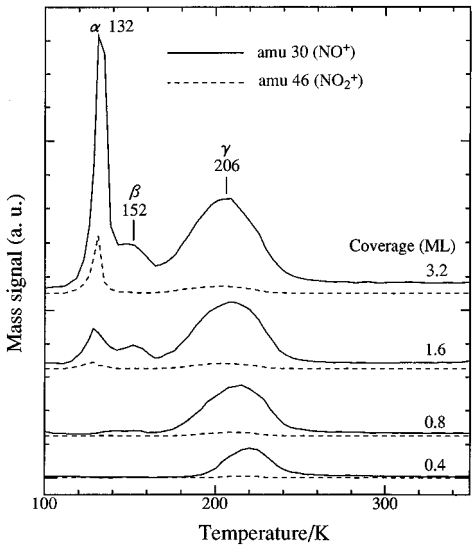

Figure 1. Thermal desorption spectra (TDS) from NO_2 adsorbed on an Au(111) surface as a function of coverage. The temperature ramp was 4 K/s.

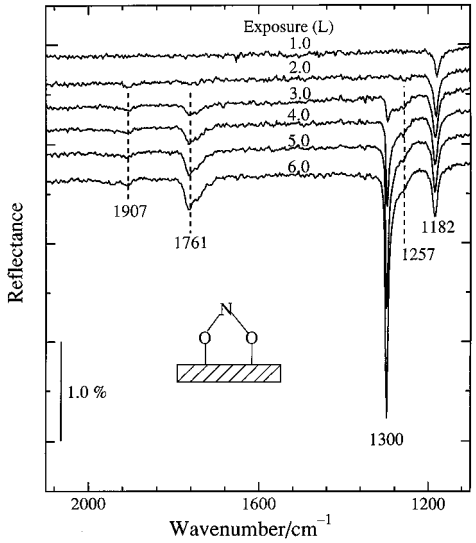

Figure 2. IRA spectra of NO_2 adsorbed on an Au(111) surface at 93 K as a function of exposure. The inset illustrates the adsorption state of chemisorbed NO_2.

smaller than that for the α peak, indicating that not only NO_2 but also NO was desorbed from chemisorbed NO_2. Corrected with the sensitivity ratio of NO to NO_2 in the mass analysis (ca. 32 in our case), the γ peak was found to involve 26% of NO in case of Figure 1 (temperature ramp of 4 K/s). The NO ratio in γ peak increased with decrease in the temperature ramp of TPD. For the heating rate of 1 K/s, 52% of the desorbed gases were NO. These results show that the desorption of NO_2 competes with decomposition to NO and adsorbed atomic oxygen. The destination of adsorbed oxygen will be discussed later.

3.1.2. IRAS Measurements. Figure 2 shows IRA spectra of NO_2 adsorbed on the Au(111) surface at 92 K as a function of exposure. Band assignments of adsorbed NO_2 and N_2O_4 are given in Table 1 together with those by Koel and co-workers[10,11] and Koch et al.[12] Because IRAS is insensitive to the vibrational modes parallel to the surface (surface selection rule),[13,14] the asymmetric stretching of chemisorbed NO_2, which is parallel to the surface, cannot be detected by IRAS. A similar surface selection rule has also been reported for HREELS.[15] The

TABLE 1: Vibrational Frequencies (cm^{-1}) and Assignments of Adsorbed NO_2 and N_2O_4 on Au Surfaces[a]

	chemisorbed NO_2			adsorbed N_2O_4			
mode	HREELS[b]	IRAS[c]	IRAS[d]	HREELS[b]	IRAS[c]	IRAS[e]	IRAS[d]
$\delta(NO_2)$	800	805	n.d.	770	783	785	n.d.
$\nu_s(NO_2)$	1180	1178	1182	1280	1298	1301	1257 (first layer) 1300 (multilayer)
$\nu_a(NO_2)$	1180		(IRAS inactive)	1755	1735 1760	1750	1761

[a] δ, bending; ν, stretching. n.d., no data due to the cutoff of the CaF_2 windows. [b] Reference 10. [c] Reference 11. [d] This work. [e] Reference 12; this N_2O_4 species was formed on an uncleaned Au surface, on which chemisorbed NO_2 is not produced.

complete absence of the strong asymmetric stretching band of NO_2 around 1600 cm^{-1} indicates the absence of other NO_2 species on the surface. The weak band at 1907 cm^{-1} is attributable to the N−O stretching of N_2O_3 formed by a reaction of chemisorbed NO_2 with gas-phase NO,[10,11] since a trace amount of NO was produced by decomposition of NO_2 during injection. Adsorbed N_2O_3 also exhibits a NO_2 symmetric stretching band at 1274 cm^{-1}. The bands at 1257, 1300, and 1761 cm^{-1} are attributed to condensed N_2O_4 with D_{2h} symmetry as assigned previously.[12,16,17] It is known that some unstable isomers of N_2O_4 are formed in a low-temperature inert matrix and in a condensed phase of NO_2.[18−24] Among such isomers, D-isomers, O═N−O−NO_2, may play an important role in the photochemistry of condensed N_2O_4, because D-isomers can be thermally converted into nitrosonium nitrate, $NO^+NO_3^-$,[21−24] and undergo more rapid photolysis than $N_2O_4(D_{2h})$ in an Ar matrix.[25] D-isomers exhibit IR bands at 1290−1310 cm^{-1} (NO_2 symmetric stretching), 1630−1645 cm^{-1} (NO_2 asymmetric stretching), and 1820−1830 cm^{-1} (N═O stretching) in IRAS as well as in transmission IR.[18−24] Although the band at 1300 cm^{-1} in Figure 2 is very close to the NO_2 symmetric stretching of D-isomers, any other bands attributable to D-isomers were not observed in our experiments. No change was observed in IRAS after adsorbed N_2O_4 was annealed at 110 K. These results indicate that the 1300 cm^{-1} band is not due to D-isomers.

In our IRAS measurements, the 1257 cm^{-1} band grew only at low coverages (<2 ML), and therefore, this band could be assigned to N_2O_4 adsorbed directly on Au surface (we refer to this species as first-layer N_2O_4). When the substrate temperature was elevated after NO_2 adsorption, the 1257 cm^{-1} band remained even after disappearance of the 1300 cm^{-1} band and finally disappeared at around 160 K. Therefore, the β peak in TDS is attributable to first-layer N_2O_4. The IRA spectrum of first-layer N_2O_4 resembles the IR transmission spectrum of gas-phase N_2O_4, in which the band intensities of symmetric and asymmetric NO_2 stretching are comparable, indicating random configuration of first-layer N_2O_4. NO_2 is physisorbed (condensed) on both chemisorbed NO_2 and first-layer N_2O_4 to form multilayer N_2O_4. For multilayer N_2O_4, the O−N−O symmetric stretching band, the vibrational mode of which is parallel to the C_2 axis (N−N bond axis), grows solely with increasing coverage as shown in Figure 2. Similar results have been obtained for the Au foil[16] and the water ice[7] surfaces as well as for the chemisorbed NO_2/Au(111) system.[11] Based on the surface selection rule of IRAS,[13,14] we can conclude that multilayer N_2O_4 is aligned preferentially with the C_2 axis perpendicular to the surface.

The sticking probability of NO_2 to form multilayer N_2O_4 was significantly attenuated at >110 K, although those for chemisorbed NO_2 and first-layer N_2O_4 were still close to unity. At 120 K the sticking probability to form multilayer N_2O_4 was about one-tenth of that observed at 90 K.

3.2. Photochemistry of NO_x Species. 3.2.1. Photodissociation Products. UV irradiation (230−400 nm) of chemisorbed NO_2, which was formed by NO_2 adsorption at 160 K, led to no evolution of gases. IRAS showed no change in the 1184 cm^{-1} band intensity even after prolonged irradiation. Thus, electric quenching is very rapid in the photodissociation of chemisorbed NO_2 due to bonding formation of the two oxygen atoms with the Au surface.[10]

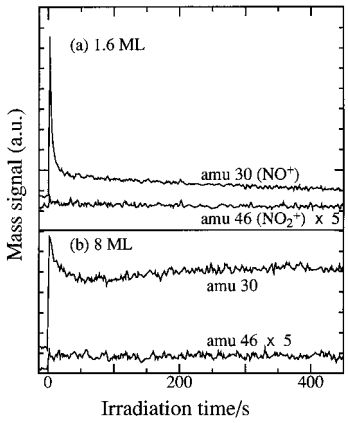

Figure 3. Photodesorption of NO_2 and NO from NO_2 adsorbed on an Au(111) surface at 92 K. A band-pass filter (UV-D33S, 230−400 nm) was used for irradiation.

UV irradiation of multilayer N_2O_4 led to desorption of NO and NO_2 without formation of any other species. Figure 3 shows time-dependent gas evolution during irradiation at 92 K. At low coverages, a sharp spike of NO desorption was observed at the beginning of illumination. This spike was found to arise from rapid photodissociation of adsorbed N_2O_3 in a separate experiment, in which adsorbed N_2O_3 alone was illuminated. The details of N_2O_3 photodissociation will be reported elsewhere. At higher coverages, the initial rapid desorption of NO was significantly suppressed. After complete decomposition of N_2O_3, the photodesorption of NO and NO_2 almost leveled off. A slight increase in NO yield after 1 min irradiation may be due to destruction of the ordered N_2O_4 layer, since the photodissociation of ordered N_2O_4 would undergo more rapid quenching than that of disordered one. The photodesorption yields of NO_2 and NO from multilayer N_2O_4 were determined as a function of coverage after the decomposition of N_2O_3 was completed (Figure 4). The NO_2/NO ratio was nearly unity at low coverages and increased with increasing coverage. The NO_2/NO ratio in the present system is greater than that reported for the N_2O_4/NO/Pd(111) system,[2] where at least 90% of the desorbed molecules were NO under 193-nm radiation. The NO_2/NO ratio in adsorbed N_2O_4 photolysis was found to be sensitive to surface species preadsorbed on the substrate. For instance, when the Au surface was covered with *n*-decane (∼1 ML), the photodesorbed molecules from the physisorbed N_2O_4 layer (1 ML) were predominantly NO at 350 nm.[26] The NO_2/NO ratio in the present system also depended upon substrate temperature as shown in Figure 5. In this experiment NO_2 was adsorbed at <96 K, and then the substrate was heated to each temperature, followed by

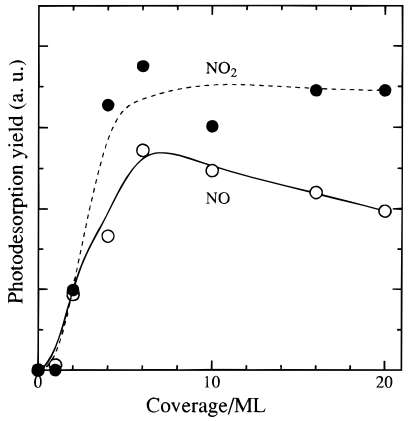

Figure 4. Photodesorption yields of NO_2 and NO as a function of coverage at 93 K. A band-pass filter (UV-D33S, 230−400 nm) was used for irradiation.

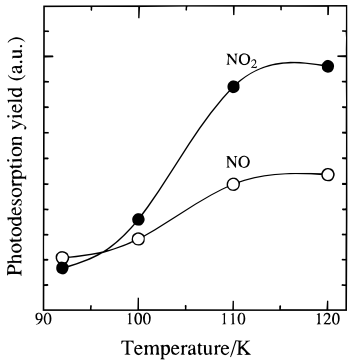

Figure 5. Temperature dependence of the photodesorption yields of NO_2 and NO. The total coverage of adsorbed NO_2 was 3.6 ML. A band-pass filter (UV-D33S, 230−400 nm) was used for irradiation.

measurement of photodesorbing species. N_2O_4 was not desorbed at any temperature. The temperature dependence for NO_2 photodesorption was more remarkable than for NO desorption; NO_2 yield at >110 K was more than 4 times greater than that at 95 K, while the increase in NO yield was about 2-fold. Because the photochemical yield is independent of temperature, this result indicates that some thermal processes significantly reduce the photodesorption yield at <110 K. NO_2 yield could be suppressed by the back reaction, $2NO_2(ad) \rightarrow N_2O_4(ad)$, while NO yield could be suppressed by a reaction such as $NO + O(a) \rightarrow NO_2(a)$.

Neither atomic nor molecular oxygen was detected in the gas phase during multilayer N_2O_4 photolysis, indicating that adsorbed atomic oxygen or oxygen-containing species must be formed on the surface. Careful examination of IRA spectra after prolonged irradiation led us to conclude that any new NO_x species such as NO_3 or N_2O_5 were not produced by the photolysis. We have recently investigated the reactivities of ozone and atomic oxygen adsorbed on Au(111) surface, which was produced from adsorbed ozone, and found that adsorbed N_2O_4 does not react with O or O_3 adsorbed on Au surface at <100 K while NO reacts with O to form $NO_2(a)$ and N_2O_4-(a).[26] For the NO-covered Pd(111) surface, Hasselbrink et al.[2] reported no formation of adsorbed oxygen after irradiation and ascribed this result to a reaction of adsorbed atomic oxygen with preadsorbed NO. They found, however, adsorbed atomic oxygen when N_2O_4 was directly adsorbed on a clean Pd(111) surface.[2]

To detect adsorbed oxygen in our system, TPD was carried out after the photodissociation of multilayer N_2O_4. As shown in Figure 6, O_2 desorption was observed at around 507 K in

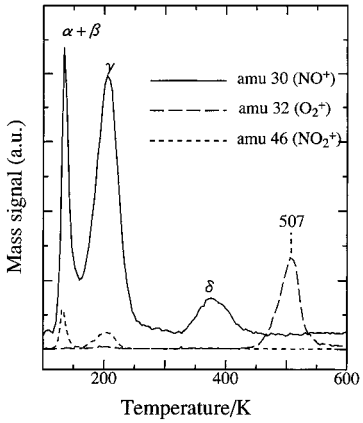

Figure 6. TDS after 8 min photolysis of NO_2 (2 ML) adsorbed on an Au(111) surface at 93 K. A band-pass filter (UV-D33S, 230−400 nm) was used for irradiation. The origin of the δ peak is not clear, but IRAS showed that the species giving the δ peak is not present on the front surface of the substrate.

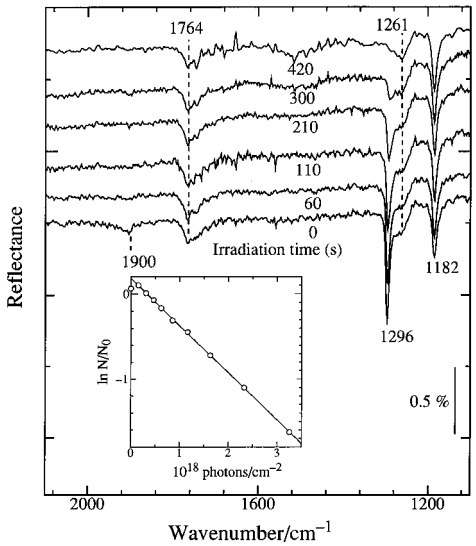

Figure 7. Change in IRA spectrum during the photolysis at 350 nm. The initial coverage of adsorbed NO_2 was 2.5 ML. The inset is the semilogarithmic plots of the residual amount of multilayer N_2O_4 for determination of a cross section (see text).

TDS, indicating the formation of adsorbed atomic oxygen during the photolysis. While it is widely known that Au surface is unable to adsorb O_2, Canning et al.[27] reported that atomic oxygen produced by a hot Pt filament is promptly adsorbed on Au surfaces at room temperature to form oxide layer, from which O_2 is desorbed at >500 K. It is therefore reasonably concluded that atomic oxygen produced by the photodissociation of multilayer N_2O_4 remains on the Au surface without reacting with the NO_x species. In passing, Figure 1 shows that chemisorbed NO_2 is partly decomposed to NO without O_2 evolution during TPD, but O_2 desorption was observed at 507 K, when the adsorption−desorption cycle of chemisorbed NO_2 was repeated a few times at <400 K to accumulate atomic oxygen on the surface.

3.2.2. Photodissociation Cross Sections. Figure 7 shows changes in the IRAS bands of chemisorbed NO_2, N_2O_3, and first-layer and multilayer N_2O_4 (2.5 ML total coverage) during irradiation at 350 nm. Within the first 1 min of illumination, the 1900 cm^{-1} band assigned to adsorbed N_2O_3 disappears due to its rapid photodecomposition, while the 1182 cm^{-1} band (chemisorbed NO_2) increases slightly corresponding to the conversion of N_2O_3 into chemisorbed NO_2. The 1296 cm^{-1} band

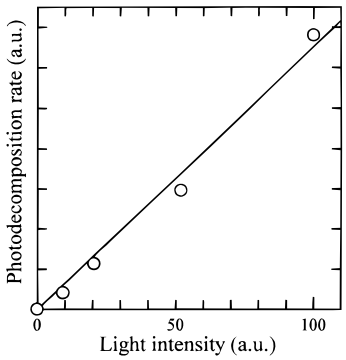

Figure 8. Light intensity dependence of the decreasing rate of multilayer N_2O_4 under irradiation at 350 nm. Neutral-density filters were used to control light intensity. The initial coverage of adsorbed NO_2 was 2.5 ML, and the substrate temperature 92 K.

(multilayer N_2O_4) also increased slightly upon illumination, but the reason for this is obscure at the present. The 1261 and 1182 cm^{-1} bands (first-layer N_2O_4 and chemisorbed NO_2) remain unchanged even under prolonged irradiation. This result indicates that the quenching of photoexcited states is significant for these species due to its direct contact with the surface. The decay of the 1296 cm^{-1} band absorbance assigned to the NO_2 symmetric stretching of multilayer N_2O_4 follows a simple exponential law. This indicates that the amount of residual multilayer N_2O_4, N, is given as[1]

$$N = N_0 \exp(-\sigma n_{h\nu}) \quad (1)$$

where N_0 is the initial amount of multilayer N_2O_4, σ the cross section, and $n_{h\nu}$ the number of photons irradiated. From the absorbance of the NO_2 symmetric stretching at 1296 cm^{-1}, N/N_0 was determined. The inset of Figure 7 shows the plots of ln N/N_0 versus $n_{h\nu}$. The cross section is determined from the slope to be 5.6×10^{-19} cm^2. This value is larger than the cross section, 1.3×10^{-19} cm^2, determined for the N_2O_4/NO/Pd(111) system[2] at 351 nm, but close to the absorption cross section, 5.7×10^{-19} cm^2, of gas-phase N_2O_4 at 350 nm.[28,29] Thus, the quantum yield of the present system is found to be remarkably high. Light intensity dependence of the photodissociation cross section of multilayer N_2O_4 was measured at 350 nm with neutral-density filters. The decreasing rate of the 1296 cm^{-1} band absorbance was virtually proportional to light intensity as shown in Figure 8. Wavelength dependence of the photodissociation cross section is shown in Figure 9. Similar wavelength dependence of the photodissociation cross section was reported for the N_2O_4/NO/Pd(111) system using 248, 308, and 351-nm lasers.[2] The inset of the figure shows the absorption spectra of gas-phase N_2O_4[28] and NO_2 (N_2O_4) adsorbed on LiF at 68 K.[30] The observed wavelength dependence of the cross section is very similar to the absorption spectrum of N_2O_4 adsorbed on LiF, except for the absorption edge. Although this similarity seems to imply direct photoabsorption by multilayer N_2O_4, there exists a possibility of photoexcitation of the Au surface.

To examine substrate photoexcitation, the photodissociation of adsorbed N_2O_4 was carried out on a thin film of water ice (~5 ML) formed on the Au surface. Gas-phase water was adsorbed at 130 K in order to minimize surface roughness and grain boundaries. Although photoinduced electrons were found to pass through water layers formed on a Ni(111) surface at 50 K, 5 ML water layers were enough to prevent electron transmission.[31] IRAS showed that NO_2 is adsorbed on the ice film as N_2O_4, which is very similar to multilayer N_2O_4 on the Au surface. Figure 10 shows the time-dependent mass signals

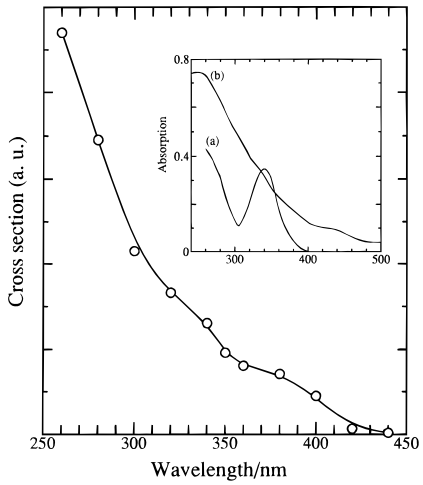

Figure 9. Wavelength dependence of the photodissociation cross section of multilayer N_2O_4 at 93 K. The total coverage of adsorbed NO_2 was 3 ML. The inset shows the absorption spectra of (a) gas-phase N_2O_4[27] and (b) N_2O_4 adsorbed on LiF at 68 K.[28]

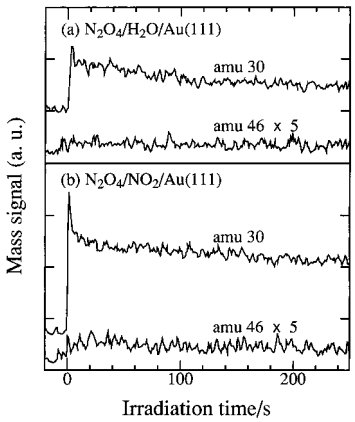

Figure 10. Effect of a thin ice film (~5 ML) covering the Au(111) surface on the photodesorption of NO_2 and NO from adsorbed NO_2 (2.5 ML) at 93 K under irradiation at 350 nm: (a) on the ice film and (b) on the bare Au surface.

of photodesorbing gases from N_2O_4 adsorbed on the ice surface at 92 K together with the corresponding profile for the N_2O_4/NO_2/Au(111) system. For Figure 10b the initial sharp peak of NO desorption is due to the rapid photodecomposition of N_2O_3 adsorbed on Au(111) surface. From comparison of the two photodesorption profiles, we are confident that the photodesorption yields of NO and NO_2 from multilayer N_2O_4 on the Au(111) surface are greater than those from N_2O_4 adsorbed on the ice surface. IRAS observation also confirmed greater photolysis rate of N_2O_4 on the Au surface than on the ice surface. Since the surface of an insulator such as water ice is thought to have little effect on the yield of a surface photoreaction, this result suggests the enhancement of N_2O_4 photodissociation by effects of the Au surface.

3.2.3. Mechanism of Multilayer N_2O_4 Photodissociation. Whether or not a surface photoreaction on a metal surface occurs by substrate photoexcitation can be determined by a polarization probe method, in which the polarization-dependent yield is measured as a function of the incident angle of light.[1] Hasselbrink et al.[2] applied this method to the N_2O_4/NO/Pd(111) system at 193 and 248 nm and concluded that the photoabsorption by the metal is the dominant primary step in the photodissociation. The enhancement of photoreactions on metal surfaces is usually ascribed to photoelectron capture by adsorbed molecules. Photoelectron emission from Pd, however, could not occur at

>220 nm, since the work function of clean Pd is 5.6 eV. Hasselbrink et al.,[2] therefore, assumed that electrons created by light energies less than the work function penetrate the potential barrier at the metal/adsorbate interface through tunneling and induce the photolysis. The optical absorption coefficient of Pd changes, however, only by a factor of 1.5 in the wavelength region from 351 to 193 nm. This change, therefore, cannot explain the observed pronounced increase (more than 10-fold) of the cross section with increase in photon energy. Weik et al.[32] have proposed the hot electron cascade mechanism to explain the wavelength dependence of the O_2 photodesorption from O_2 adsorbed on Pd(111) surface.

Photoabsorption by an evaporated Au film has been reported to be 64% at 360 nm and at normal incidence.[33] Although the absorption of Au(111) surface in the UV region is not available, it would be close to the evaporated-film value. Similar to Pd surfaces, photoelectron emission from an Au surface could not occur in the wavelength region of our present experiments, since the work function of Au is 5.3 eV, which corresponds to a photon wavelength of 234 nm. In addition, the formation of chemisorbed NO_2 results in an work function increase of 1.6 eV.[10] The photoelectron tunneling from the Au surface to multilayer N_2O_4 may be responsible for the large cross section of multilayer N_2O_4 photodissociation. A change in the absorption by an evaporated Au film in the wavelength region from 250 to 400 nm is, however, so small (only a 9% increase[33]) that the observed wavelength dependence of the cross section cannot be explained in terms of a simple photoelectron tunneling mechanism. Although the wavelength dependence could be ascribed to the hot electron cascade mechanism proposed by Weik et al.,[32] as an alternative mechanism, we propose enhancement in the photoabsorption cross section of multilayer N_2O_4 by electron transfer from the substrate. A large increase in the work function upon NO_2 adsorption on Au(111) surface[10] implies significant electron transfer from the substrate to chemisorbed NO_2. When NO_2 is adsorbed on chemisorbed NO_2, electron transfer would occur from chemisorbed NO_2 to multilayer N_2O_4. Such electron transfer could increase the photoabsorption cross section of multilayer N_2O_4. To determine whether direct absorption occurs or not, the polarization probe experiment is under preparation.

Sisk et al.[34] studied the dynamics of gas-phase N_2O_4 photolysis by a laser-induced fluorescence method and concluded that NO is not a primary photoproduct from the photodissociation channels of N_2O_4 at >300 nm. If the photodissociation process of multilayer N_2O_4 is similar to that of N_2O_4(g), then NO would not be a primary product but produced by the photodissociation of intermediate NO_2(ad). This mechanism is implausible for the NO photodesorption from multilayer N_2O_4. First, photodesorption of NO by this mechanism would depend quadratically on light intensity, if the cross section of NO_2(ad) is not so different from that of NO_2(g). Second, IRAS shows no formation of NO_2(ad) during the photolysis, because the stretching bands of NO_2 are strong enough to be detected even at coverages as low as 0.1 ML. Third, the electronic states of multilayer N_2O_4 are different from those of N_2O_4(g), as evidenced by the fact that the absorption spectrum of N_2O_4 adsorbed on LiF is quite different from that of N_2O_4(g). We assume, therefore, that N−O bond breaking occurs first in multilayer N_2O_4 photolysis to form N_2O_3, which undergoes spontaneous photodissociation to produce NO_2 and NO. Since the photodissociation cross section of adsorbed N_2O_3 is 1 order of magnitude greater than that of multilayer N_2O_4, the light intensity dependence is virtually linear in this case, and the population of N_2O_3 during photolysis becomes too small to detect by IRAS.

Hasselbrink et al.[2] found that the NO yield is linear on laser fluence and the mean translational energy of the desorbing NO is independent of laser energy at 193, 248, 308, and 351 nm in the N_2O_4/NO/Pd(111) system. On the basis of these results, they speculated the formation of nitrosonium nitrate, $NO^+NO_3^-$, in the dark, because this ionic form has often been observed in condensed N_2O_4 layers.[20−23] If $NO^+NO_3^-$ is present in adsorbed N_2O_4, neutralization of NO^+ by electron capture would result in NO desorption with simultaneous tunnel back of an electron from NO_3^- to the metal surface resulting in formation of NO_2. Givan and Lowenschuss[22] reported that $NO^+NO_3^-$ is produced upon temperature cycling only from less-ordered N_2O_4 layers, in which D-isomers are involved, but not from well-ordered $N_2O_4(D_{2h})$ layers. For our N_2O_4/NO_2/Au(111) system, IRAS showed clearly that multilayer N_2O_4 is dominantly ordered with the C_2 axis perpendicular to the surface. Furthermore, neither $NO^+NO_3^-$ nor NO_3^- was detected by IRAS before and during the photolysis. Failure in detecting $NO^+NO_3^-$ due to insufficient sensitivity of IRAS can be ruled out, since $NO^+NO_3^-$ has been detected by IRAS previously.[20−23] Therefore, the concentration of $NO^+NO_3^-$, if present, would be so small that it plays no important role in our system. It was also reported that matrix-isolated D-isomers are mainly converted into $N_2O_4(D_{2h})$ under illumination, but not to $NO^+NO_3^-$. [25]

In summary, multilayer N_2O_4 is photodecomposed to NO_2 and NO at <430 nm without formation of stable intermediates, while chemisorbed NO_2 and first-layer N_2O_4 undergo neither photodissociation nor photodesorption. The photodissociation cross section of multilayer N_2O_4 at 350 nm was determined to be 5.6×10^{-19} cm^2, which is close to the absorption cross section of gas-phase N_2O_4. The photodissociation on a water ice film was slower than that on the Au surface, suggesting that the photodissociation is enhanced by substrate excitation or by electron transfer from the surface to the adsorbates. The wavelength dependence of the cross section is very similar to the absorption spectrum of N_2O_4 adsorbed on LiF at 68 K. On the basis of these results, enhancement in the photoabsorption cross section of multilayer N_2O_4 by electron transfer from the substrate was proposed.

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