

Photodissociation Cross Sections of N₂O₃ Adsorbed on Au(111)Shinri Sato,^{*,†} Dai Yamaguchi, Takehito Senga, and Masahiro Kawasaki

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The photochemistry of N₂O₃ adsorbed on a Au(111) surface has been studied at <100 K. N₂O₃ is prepared by a reaction of NO₂ chemisorbed on a Au surface with gas-phase NO. The adsorption states of N₂O₃ are characterized by IR reflection–absorption spectroscopy. Adsorbed N₂O₃ is found to undergo rapid photodissociation to form chemisorbed NO₂ and gas-phase NO under UV and visible illumination. The photodissociation cross section is determined to be $(3.0 \pm 1.8) \times 10^{-17}$ cm² at 350 nm, which is much greater than the maximum absorption cross section of gas-phase N₂O₃ and one of the highest values ever observed for photochemical reactions on a metal surface. The spectral profile of the NO yield is significantly shifted to longer wavelengths as compared to the absorption spectrum of gas-phase N₂O₃. The significant red shift of N₂O₃ absorption in aromatic solvents suggests that electron transfer from the surface to N₂O₃ enhances the absorption cross section of adsorbed N₂O₃ at longer wavelengths.

1. Introduction

A photochemical reaction of molecules adsorbed on a solid surface is often different in kinetics and dynamics from its gas-phase counterpart, depending on chemical and physical properties of the surface.^{1–3} In general, a photoexcited state on a metal surface undergoes rapid quenching due to the coupling of photoexcited states to the electron bath in the substrate, even when reactants are not bonded chemically to the surface. In some cases, however, a cross section of adsorbed molecule is comparable to or greater than that of the gas-phase counterpart. Metal substrate excitation, which involves photoelectron emission and photoinduced electron transfer from a metal surface to adsorbates, is thought to be responsible for such a large cross section.^{3–6} In our recent study,⁷ we found that a photodissociation cross section of N₂O₄ adsorbed on a NO₂-covered Au(111) surface is as large as those in the gas and condensed phase.⁷ Since the yield of the N₂O₄ photodissociation was significantly reduced when the surface was covered with a thin water-ice film, we concluded that the N₂O₄ photolysis is enhanced by photoexcitation of the surface. The spectral profile of the photodissociation cross sections is, however, not similar to the absorption spectrum of the Au surface but rather resembles the absorption spectrum of N₂O₄ adsorbed on LiF.⁷ On the basis of these results, we have proposed enhancement in the absorption cross section of adsorbed N₂O₄ due to electron transfer from Au surface to adsorbed N₂O₄.⁷

In the present paper, we report remarkably rapid photodissociation of N₂O₃ adsorbed on a Au surface, which was formed by a reaction of chemisorbed NO₂ with gas-phase NO at <130 K.^{8,9} The photodissociation cross section was determined to be $(3.0 \pm 1.8) \times 10^{-17}$ cm² at 350 nm, one of the highest values ever observed for photochemical reactions on metal surfaces,³ while the absorption cross section of gas-phase N₂O₃ is nearly zero at 350 nm. The large cross section of N₂O₃ photodisso-

ciation is attributable to enhancement in the absorption cross section of adsorbed N₂O₃ due to electron transfer from the surface.

2. Experimental Section

All measurements were carried out in an ultrahigh vacuum system that has been described in detail previously.⁷ An Au(111) single crystal (12 mm in diameter, 1.5 mm thick, 99.999% purity) used as a substrate was cleaned by repeating Ar-ion sputtering at 800 K and annealing at 900 K. Ozone was sometimes used for surface cleaning. Gases were analyzed with a mass spectrometer (ANELVA AQA-200). For IR reflection–absorption spectroscopy (IRAS) measurements, an IR beam from FTIR (BIO-RAD FTS-155) was p-polarized by a wire grid polarizer and then focused by a BaF₂ lens onto the sample through a BaF₂ window, the cutoff wavelength of which is around 900 cm⁻¹. The diameter of the IR beam at the sample position was ca. 8 mm. The incident angle of the IR beam was ~85°. The paths of the IR beam were purged with dry air to reduce the effects of moisture. IR 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 whole sample area through an MgF₂ window. The photon flux of monochromatized light was measured after the quartz lens with chemical actinometry using ferrioxalate.¹⁰ Substrate temperature was virtually unchanged under irradiation with monochromatized light. To reduce light intensity neutral density filters (Toshiba) were used.

NO₂ was stored in a glass reservoir in the presence of an excess of O₂ to prevent its decomposition to NO and O₂ during storage. The gas mixture was frozen at 77 K, and O₂ was pumped away before use. NO was used after adsorption on well-outgassed molecular sieve 13X at 77 K. Gases were introduced into the chamber through a long nozzle, the end of which was

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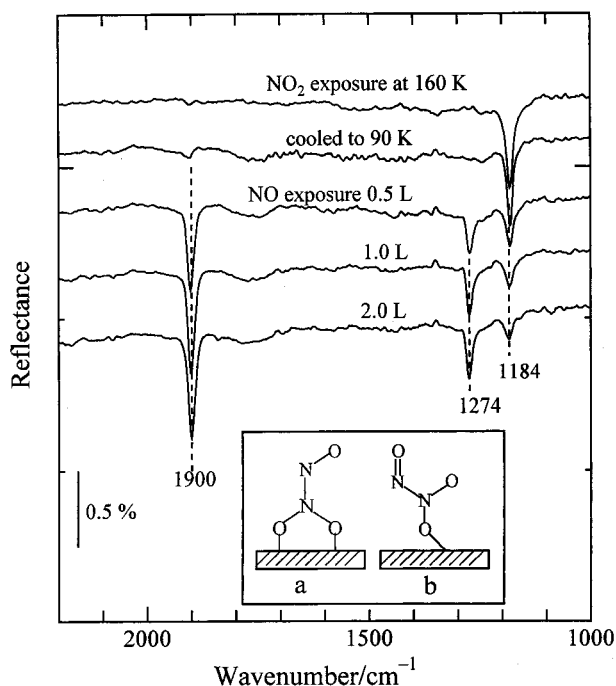


Figure 1. IRA spectra of adsorbed N_2O_3 formed by the reaction of NO_2 chemisorbed on Au(111) with gas-phase NO at 90 K. The inset shows the adsorption states of N_2O_3 (see text).

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. Since NO_2 adsorbed on Au surfaces at >150 K undergoes thermal decomposition upon desorption at around 210 K,⁷ we refer to this species as chemisorbed NO_2 . In the present study, N_2O_3 was prepared on the Au(111) surface at <100 K by the reaction of gas-phase NO with chemisorbed NO_2 .⁷⁻⁹ Figure 1 shows IRA spectra of chemisorbed NO_2 and N_2O_3 . The band at 1184 cm^{-1} is assigned to the NO_2 symmetric stretching of chemisorbed NO_2 . The NO_2 asymmetric stretching of chemisorbed NO_2 cannot be observed by IRAS because IRAS is sensitive only to vibrational modes perpendicular to the surface (surface selection rule).^{11,12} The chemisorbed NO_2 band decreased in intensity upon NO exposure with growth of the new bands at 1274 and 1900 cm^{-1} and remains even after the new bands are saturated after 2 langmuir exposure of NO. These new bands are assigned to NO stretching and NO_2 asymmetric stretching of N_2O_3 , respectively. The intensities of these bands at saturation were found to depend on the initial coverage of chemisorbed NO_2 . Figure 2 shows a relation between the relative coverages of chemisorbed NO_2 and adsorbed N_2O_3 . N_2O_3 coverage decreases with decreasing NO_2 coverage and drops to zero before NO_2 coverage becomes zero, indicating that part of chemisorbed NO_2 does not react with NO. The 1184 cm^{-1} band remained after saturation of the N_2O_3 bands is, therefore, attributable to chemisorbed NO_2 remaining unreacted. Thus, the asymmetric NO_2 stretching band of adsorbed N_2O_3 is not observed by IRAS due to the surface selection rule,^{11,12} similarly to the chemisorbed NO_2 case. In addition, the total intensity of the 1184 and 1274 cm^{-1} bands of adsorbed N_2O_3 does not change with NO exposure, suggesting that the former band converts into the latter band.

Koel and co-workers^{8,9} studied the adsorption states of chemisorbed NO_2 and adsorbed N_2O_3 on the Au(111) surface

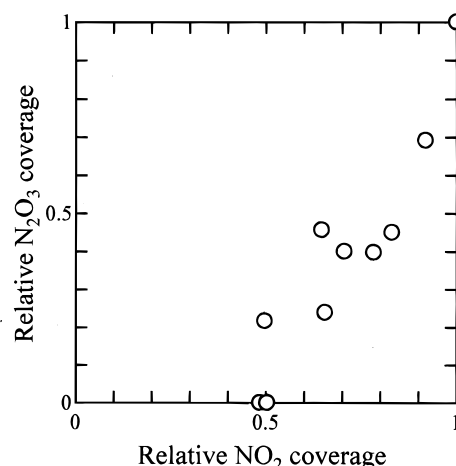


Figure 2. Relation between the relative coverages of chemisorbed NO_2 and adsorbed N_2O_3 . Relative coverage is defined as the intensity ratio of the IRAS band to the saturation intensity.

TABLE 1: Vibrational Frequencies (cm^{-1}) of N_2O_3 Adsorbed on Au(111) and N_2O_3 in CH_2Cl_2 ^a

mode	N_2O_3 in CH_2Cl_2		$\text{N}_2\text{O}_3/\text{Au}(111)$	
	IR (transmission) ^b	HREELS ^b	IRAS ^c	IRAS ^d
$\nu(\text{O}_2\text{N}-\text{NO})$	253	250		n.d.
$\rho(\text{O}_2\text{NNO})$	614	450–650		n.d.
$\delta(\text{NO}_2)$	772	800	806	n.d.
$\nu_s(\text{NO}_2)$	1291	1180	1182	1274
$\nu_a(\text{NO}_2)$	1600	1270	1272	(IRAS inactive)
$\nu(\text{NO})$	1849	1890	1897	1900

^a ν , stretching; ρ , rocking; δ , bending; n.d., no data due to the cutoff of the BaF_2 windows. ^b Reference 8. ^c Reference 9. ^d This work.

by HREELS and IRAS. They assigned the HREELS and IRAS bands of adsorbed N_2O_3 with reference to the IR transmission spectrum of N_2O_3 in CH_2Cl_2 . Their assignments are listed in Table 1 together with our IRAS results. Their assignments are in good agreement with the IR transmission spectrum of N_2O_3 in CH_2Cl_2 except for the 1180 and 1274 cm^{-1} bands, which were assigned to the symmetric and asymmetric stretching of chemisorbed NO_2 , respectively. Since our result indicates that part of chemisorbed NO_2 remains unreacted with gas-phase NO, it is reasonable to assign the 1180 cm^{-1} band to the NO_2 symmetric stretching of chemisorbed NO_2 and the 1274 cm^{-1} band to the NO_2 symmetric stretching of adsorbed N_2O_3 . For adsorbed N_2O_3 , Koel and co-workers⁸ had originally proposed the adsorption state (a) in the inset of Figure 1. Recently, they revised it to the adsorption state (b), since the symmetric and asymmetric NO_2 stretching bands have comparable intensity and the NO stretching band is stronger in intensity than the NO_2 stretching bands.⁹ Their recent revision is, however, inadequate, since the absence of asymmetric NO_2 stretching band indicates that this vibrational mode is parallel to the surface as in the case of chemisorbed NO_2 , which has the structure of chelating NO_2 . In addition, the strong NO stretching band of adsorbed N_2O_3 could arise from charge transfer from the Au surface to NO. Therefore, the adsorption state (a) is much more likely than the adsorption state (b).

When the substrate is heated, adsorbed N_2O_3 undergoes thermal decomposition at >110 K, as shown in Figure 3. The decomposition is completed at <160 K with the complete recovery of chemisorbed NO_2 . In agreement with these results, NO desorption occurred without NO_2 desorption during temperature-programmed desorption (TPD). Although the N–N bond breaking of adsorbed N_2O_3 thus occurs at temperatures

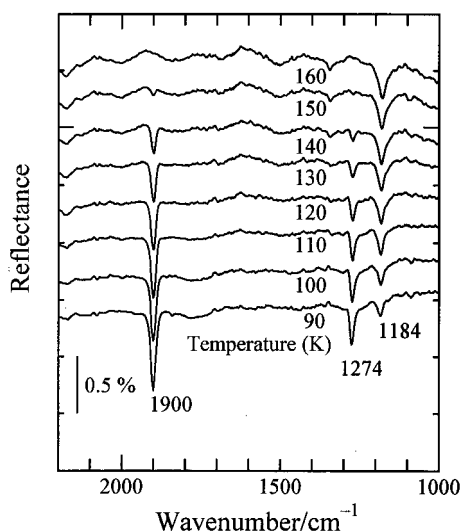


Figure 3. Change in the IRA spectrum of adsorbed N₂O₃ as a function of temperature.

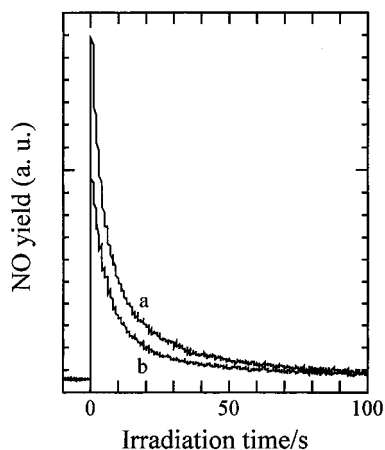


Figure 4. Temporal profile of NO yield during the 350 nm photolysis of adsorbed N₂O₃ at 93 K: (a) no filter; (b) 70% neutral density filter.

as low as 160 K, its N–N bond energy could be close to that of N₂O₃ in CH₂Cl₂ (9.7 kcal/mol), since the N–N stretching frequencies of both N₂O₃ molecules are very close to each other, as shown in Table 1. Bartram and Koel⁸ estimated the N–N bond energy of adsorbed N₂O₃ to be 10 kcal/mol from the maximum temperature of NO desorption.

3.2. Photodissociation of Adsorbed N₂O₃. Photodissociation of adsorbed N₂O₃ at 350 nm was so efficient that NO photodesorption was almost completed within 30 s, as shown in Figure 4. The initial rise of NO yield was almost proportional to light intensity. For IRAS measurements, light intensity was reduced by the use of a 5% neutral density filter to obtain a moderate photolysis rate. IRA spectra of adsorbed N₂O₃ during photolysis are shown in Figure 5. The bands at 1900 and 1274 cm^{−1} assigned to adsorbed N₂O₃ decreased with irradiation time, while the band at 1184 cm^{−1} assigned to chemisorbed NO₂ increased due to the conversion of adsorbed N₂O₃ into chemisorbed NO₂ and NO. No other bands were detected during irradiation. The residual amount of N₂O₃, N , is given as³

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

where N_0 is the initial amount of N₂O₃, σ is the photodissociation cross section, and n_{hv} the number of photons irradiated. The semilogarithmic plots of the absorbance of the 1900 cm^{−1} band are shown in the inset of Figure 5. The plots are not exactly

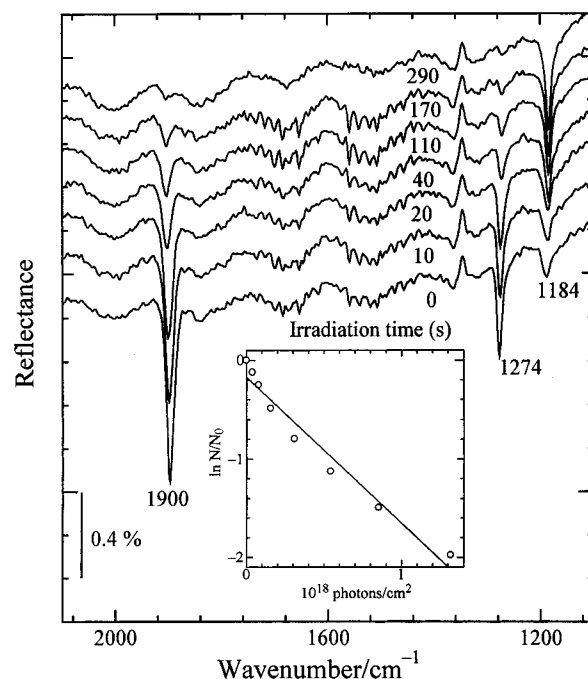


Figure 5. IRAS change during the 350 nm photolysis of adsorbed N₂O₃ at 93 K. A 5% neutral density filter was used to reduce light intensity. The inset shows semilogarithmic plots for the amounts of residual N₂O₃ during the photolysis.

linear with irradiation time; the cross section seems to decrease with a decrease in N₂O₃ coverage. In fact, the cross section becomes small when the initial coverage of N₂O₃ was reduced. The reason for this is, however, not clear at present. It should be noted that the nonlinearity of the plots is not due to a nonlinear relation between N₂O₃ coverage and IR band intensity, since the desorption amount of NO during TPD was proportional to the IRAS absorbance of adsorbed N₂O₃. The cross section is determined by least-squares fitting to be $(3.0 \pm 1.8) \times 10^{-17}$ cm². This value is one of the highest cross sections ever reported for surface photochemical reactions on metal substrates.¹

The wavelength dependence of the NO yield is shown in Figure 6. The yield is normalized by photon flux at each wavelength. The photodesorption of NO occurred to some extent even at 700 nm probably due to an $n \rightarrow \pi^*$ transition.¹³ The inset of Figure 6 shows the UV-region absorption spectra of N₂O₃ in the gas phase, an aqueous solution, and an *n*-hexane solution.¹³ The absorption maximized at around 250 nm is attributed to a $\pi \rightarrow \pi^*$ transition.¹³ The absorption of N₂O₃ increases upon dissolution in a solvent, and its peak shifts to longer wavelengths. A maximum cross section increases from 9.6×10^{-18} cm² at 225 nm for gas-phase N₂O₃ to 1.6×10^{-17} cm² at 240 nm for N₂O₃ in an aqueous solution. The maximum cross section observed for the photodissociation of adsorbed N₂O₃ is, however, much larger than the absorption cross sections of N₂O₃ in the gas-phase and the solutions. Furthermore, the absorption for the latter declines sharply toward longer wavelengths and becomes nearly zero at 350–400 nm. The large cross section of adsorbed N₂O₃, therefore, may be ascribed to substrate photoexcitation. Although photoelectron emission from the Au surface does not occur under irradiation at <234 nm due to its large work function (5.3 eV), photoinduced electron transfer from the surface to adsorbates can occur by tunneling through the metal/adsorbate barrier. 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

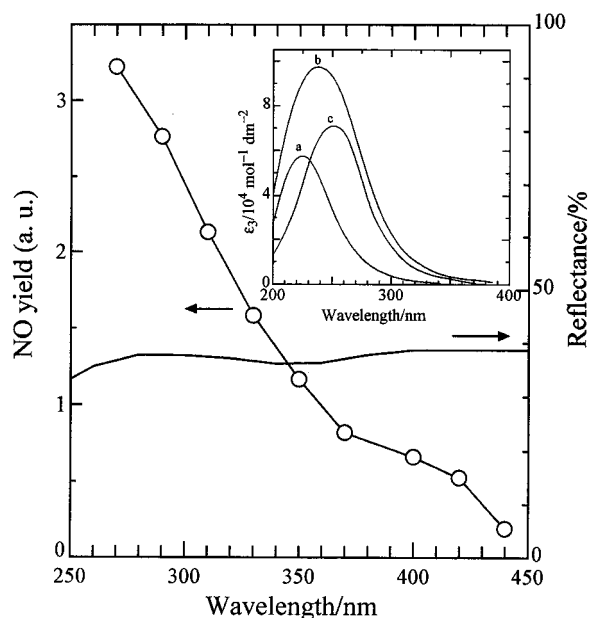


Figure 6. Wavelength dependence of initial NO yield in the photolysis of adsorbed N_2O_3 at 93 K and the reflectivity of an evaporated Au film.¹⁶ The inset is the absorption spectra of N_2O_3 in the gas phase (a), an aqueous solution (b), and an *n*-hexane solution (c).¹³

of the incident angle of light.³ Hasselbrink et al.¹⁴ applied this method to the photodissociation of N_2O_4 adsorbed on a NO-saturated Pd(111) surface at 193 and 248 nm and concluded that the photoabsorption by the metal is the dominant primary step in the photodissociation. Because photoelectron emission from a Pd surface does not occur at >220 nm due to its work function (5.6 eV), they attributed the photodissociation to electron transfer from the surface to the adsorbate. We have found a large cross section in the photodissociation of N_2O_4 adsorbed on a NO_2 -covered Au(111) surface.⁷ The yield of the N_2O_4 photodissociation was significantly reduced when the surface was covered with a thin water-ice film so that we concluded enhanced photolysis due to electron transfer from the surface to adsorbed N_2O_4 .⁷ Since photoinduced electron transfer from a metal surface to adsorbates has been reported for NO adsorbed on Cu(111) using the two-photon photoemission spectroscopy,¹⁵ similar photoinduced electron transfer may be responsible for the enhanced photodissociation of N_2O_4 over the Au surface.

The absorption spectra of Pd and Au, however, cannot explain the wavelength dependence of the N_2O_4 photodissociation yields, as discussed in our previous paper.⁷ The same is true for the present $\text{N}_2\text{O}_3/\text{Au}(111)$ system. As shown in Figure 6, the reflectivity of an evaporated Au film¹⁶ varies to a small extent in the wavelength range observed, while the N_2O_3 photodissociation yield changes drastically. Therefore, a simple mechanism involving electron attachment would be ruled out,⁷ and we

propose a mechanism involving enhancement in the direct absorption of adsorbed N_2O_3 by electron transfer from the surface. Shaw and Vosper¹³ observed that the visible absorption of N_2O_3 in organic solvents increases with a decrease in the ionization potential of the solvent. For instance, the absorption maximum of N_2O_3 was $97 \text{ mol}^{-1} \text{ dm}^2$ at 730 nm in carbon tetrachloride, while it was $275 \text{ mol}^{-1} \text{ dm}^2$ at 690 nm in *m*-dimethoxybenzene. Their results indicate that electron donation from the solvent to N_2O_3 enhances the absorption of N_2O_3 . Although the absorption maximum in the UV region could not be measured due to strong absorption of the solvents, it is sure that the UV absorption also increases with an increase in the donor ability of the solvent, judging from the significant increase in the tail of the $\pi \rightarrow \pi^*$ transition in the visible region.¹³ For NO_2/Au and $\text{N}_2\text{O}_3/\text{Au}$, Bartram and Koel⁸ observed a large increase in work function (1.6 eV) upon NO_2 adsorption on the Au(111) surface and the lowering of the work function (-0.8 eV) upon formation of adsorbed N_2O_3 . The increase in work function indicates electron transfer from the Au surface to chemisorbed NO_2 , and the decrease in work function after N_2O_3 formation would arise from electron transfer from NO_2 to NO in adsorbed N_2O_3 , which can reduce the shielding effect of NO_2 . The strong NO stretching of adsorbed N_2O_3 may indicate this electron transfer toward NO. It is therefore reasonably assumed that electron transfer from the Au surface to adsorbed N_2O_3 greatly enhances its absorption in the UV region as well as in the visible region. Thus, the wavelength dependence of the photodissociation of N_2O_3 adsorbed on the Au(111) surface is similar in shape to the absorption spectrum of N_2O_3 in the gas phase or in a solvent, as observed in the present study.

References and Notes

- (1) Chuang, T. J.; Seki, H.; Hussla, I. *Surf. Sci.* **1985**, *158*, 525.
- (2) King, D. S.; Cavanagh, R. R. *Adv. Chem. Phys.* **1989**, *76*, 45.
- (3) Zhou, X.-L.; Zhu, X.-Y.; White, J. M. *Surf. Sci. Rep.* **1991**, *13*, 73.
- (4) Gadzuk, J. W.; Richter, L. J.; Buntin, S. A.; Kingand, D. S.; Cavanagh, R. R. *Surf. Sci.* **1990**, *235*, 317.
- (5) Antoniewicz, P. R. *Phys. Rev. B* **1980**, *21*, 3811.
- (6) Miesewich, J. A.; Heinz, T. F.; Newns, D. M. *Phys. Rev. Lett.* **1992**, *68*, 3737.
- (7) Sato, S.; Senga, T.; Kawasaki, M. *J. Phys. Chem. B* **1999**, *103*, 5063.
- (8) Bartram, M. E.; Koel, B. E. *Surf. Sci.* **1989**, *213*, 137.
- (9) Wang, J.; Koel, B. E. *J. Phys. Chem. A* **1998**, *102*, 8573.
- (10) Gordon, A. J.; Ford, R. A. *The Chemist's Companion A Handbook of Practical Data, Techniques, and References*; John Wiley & Sons: New York, 1972; p 362.
- (11) Greenler, R. G.; Rahn, R. R.; Schwartz, J. P. *J. Catal.* **1971**, *23*, 42.
- (12) Suetaka, W. *Surface Infrared and Raman Spectroscopy*; Plenum Press: New York and London, 1995; p 13.
- (13) Shaw, A. W.; Vosper, A. J. *J. Chem. Soc., Dalton Trans.* **1972**, 961.
- (14) Hasselbrink, E.; Jakubith, S.; Nettesheim, S.; Wolf, M.; Cassuto, A.; Ertle, G. *J. Chem. Phys.* **1990**, *92*, 3154.
- (15) Kinoshita, I.; Misu, A.; Munakata, T. *J. Phys. Chem.* **1995**, *102*, 2970.
- (16) *Chronological Scientific Tables*; National Astronomical Observatory: Maruzen, Tokyo, 1997; p 521.