PHOTOCHEMISTRY OF NO_2 ADSORBED ON AU(111) AND WATER ICE SURFACES

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The photochemistry of NO_2 adsorbed on Au(111) and water ice surfaces 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 on Au(111) leads to formation of chemisorbed NO_2, chemisorbed N_2O_4 (D_{2h} symmetry), and well-ordered N_2O_4 (D_{2h} symmetry) physisorbed on these species with its N-N bond axis perpendicular to the surface, while N_2O_4 (D_{2h} symmetry) alone is formed on ice surfaces. No unstable N_2O_4 isomers such as D isomers were detected by IRAS on both the surfaces.

The chemisorbed species on an Au surface undergo neither photodissociation nor photodesorption, and N_2O_4 physisorbed on both the surfaces is dissociated to NO_2, NO, and adsorbed atomic oxygen under irradiation at λ < 430 nm. The photodesorption yields of NO_2 and NO increase with increasing temperature from 100 K to 120 K, indicating that some thermal processes reduce the photodesorption yields. 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 N_2O_4 physisorbed on an Au surface at 350 nm was measured from the N_2O_4 band intensity in IRAS to be 5.6×10^{-19} cm^2, which is close to the absorption cross section of gas-phase N_2O_4. The cross section was linear on incident light intensity. Wavelength dependence of the cross section is not similar to the absorption spectrum of gas-phase N_2O_4[1] but resembles to that of N_2O_4 adsorbed on LiF at 68 K[2] as shown in Fig. 1. Physisorbed N_2O_4 photolysis over an Au surface was inhibited significantly when the Au surface was covered with a thin water ice film (~5 ML). This result suggests that the photolysis is enhanced by

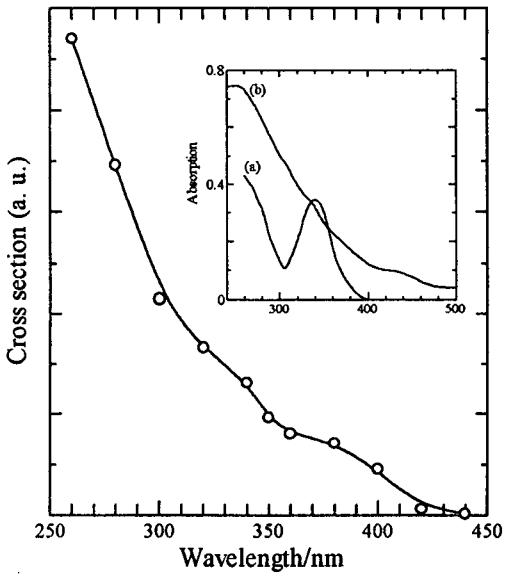

Fig. 1 Wavelength dependence of the photodissociation cross section of physisorbed N_2O_4 on Au(111) at 93 K. The total coverage of adsorbed NO_2 was 3 ML. The inset shows the absorption spectra of (a) gas-phase N_2O_4[1] and (b) N_2O_4 adsorbed on LiF at 68 K[2].