

## 論文の内容の要旨

論文題目      Photon stimulated desorption of and nuclear resonant scattering by noble  
gas atoms at solid surfaces  
(表面吸着した希ガス原子からの光刺激脱離と核共鳴散乱)

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### 1. Introduction

In this thesis, two experimental setups are presented which I developed. One is a time-of-flight measurement system following laser induced desorption of noble gas atoms from metal surfaces. The other is an ultra-high vacuum chamber installed in a synchrotron radiation facility (SPring-8 BL09XU, Japan) for measuring nuclear resonant scattering of synchrotron radiation by Kr multi- and monolayer physisorbed on a solid surface. I used the former instrument to investigate the photon stimulated desorption of Xe atoms from a Au(001) surface. The latter is used to investigate the local electronic structure of Kr at a TiO<sub>2</sub>(110) surface using nuclear energy levels of <sup>83</sup>Kr as a probe.

### 2. Photon stimulated desorption of Xe

The laser induced system consists of pulse laser sources, sample specimen and quadrupole mass spectrometer as a detector, the latter two of which are enclosed in a ultra-high vacuum chamber. The sample specimen is a clean Au(001) surface cooled at 20 K, on top of which physisorbed Xe layers are prepared by backfilling the chamber. The quadrupole mass spectrometer is tuned to acquire a high sensitivity to Xe atoms and is synchronized with the laser pulse source. The desorption signals of Xe following pulse laser irradiations are recorded with a digital oscilloscope.

#### 2.1. Thermal and non-thermal desorption of Xe

I experimentally obtained a series of time-of-flight spectra of Xe atoms following the pulse laser irradiations at 2.3 and 6.4 eV and at various laser fluence. The time-of-flight spectra are well analyzed with a sum of two Maxwell-Boltzmann distributions. The minor component is much smaller than the other and its origin is still unclear. Thus, we discuss only the major component. With this analysis, I obtained the desorption yield and translational temperature of desorbing Xe as a function of a wide range of the laser fluence.

The representative results are that at a large photon fluence the desorption of Xe is induced both at 2.3 and 6.4 eV photons indicating a desorption process independent of photon energy, whereas at a small photon fluence region the desorption of Xe is detected only at 6.4 eV indicating a desorption process dependent of photon energy. To further clarify the desorption process, I carried out numerical calculations of the time evolution of the surface temperature rise and desorption flux following the pulse laser irradiations. The calculated desorption yield and translational temperature both well reproduced the

experimentally observed values at large laser fluence, indicating that laser induced thermal desorption of Xe is a dominant desorption process at this laser fluence. At the same time, the analysis highlights that the laser induced thermal desorption is inconsistent with the desorption process observed at a small laser fluence where translational temperature of Xe is much higher than the surface temperature and that the desorption yield linearly depend on the photon fluence. The desorption process at a small laser fluence region is, thus, concluded to be a non-thermal process.

I speculate that the non-thermal desorption of Xe observed only at 6.4 eV involves a transient Xe<sup>-</sup> formation on Au. The non-thermal process should involve an electronic excitation process which is reachable with 6.4 eV and not with 2.3 eV photons. The possibilities of direct excitations, ionization of Xe and other elemental excitations are safely excluded, for they do not explain the observed photon energy dependence. The desorption dynamics following electronic excitation is assumed to be the Antoniewicz model. In order to clarify the validity of the model, I carried out numerical calculations to obtain the time-of-flight spectra and desorption probability based on a classical dynamics of Xe atoms on an adiabatic potential. The calculated results of the time-of-flight and desorption cross sections well reproduces when the lifetime of Xe<sup>-</sup> state on Au is assumed to be about ~15 fs.

## 2.2. Post-desorption collision effect

Another experiment using the laser desorption system concerns the post-desorption collision effects on the time-of-flight spectra. In the experiment, I fixed the laser fluence at the large laser fluence region in order to intentionally induce the thermal desorption of Xe. On the other hand, the initially prepared Xe coverage is varied from 0.3 monolayer to 10 monolayers, which is effectively a variation of desorption flux.

I obtained a series of time-of-flight spectra as a function of the initial Xe coverage. The spectrum close to 0 is well analyzed with a Maxwell-Boltzmann distribution with a translational temperature close to the surface temperature. On the other hand, with increasing the initial Xe coverage, the peak position of time-of-flight spectra shifts to the smaller time-of-flight regions. Furthermore, the time-of-flight spectrum become unable to be analyzed with a Maxwell-Boltzmann velocity distributions with increasing initial Xe coverage, whereas they become able to be analyzed with a shifted Maxwell-Boltzmann velocity distributions which is characterized with a stream velocity.

Analyzing the obtained time-of-flight spectra with the shifted Maxwell-Boltzmann velocity distribution, we deduced the translational temperatures and the stream velocities as a function of the initial Xe coverage. The translational temperature is at 300 K at the initial Xe coverage close to 0. It decreased with increasing initial Xe coverage and become constant at about 190 K with the initial Xe coverage above 3 ML. The stream velocity is close to 0 at the initial Xe coverage close to 0. It increases from 0 to 140 m/s with increasing initial Xe coverage and become constant about 140 m/s.

The time-of-flight spectra at the initial Xe coverage close to 0 is well explained by a

normal laser induced thermal desorption, whereas those at the large initial Xe coverage is inconsistent with the thermal desorption. The observed modification of the time-of-flight spectra increases with increasing initial Xe coverage which is assumed to be proportional to the desorption flux. Hence, I assumed that the modifications of the time-of-flight spectra are due to the post-desorption effects, which is in good agreement with the previous reports.

The observed phenomena that the translational temperature and the stream velocity become constant at the large initial Xe coverage are not explained by the post-desorption collision effects. I speculated that at a large desorption flux the desorption flow become well described by a rarefied gas dynamics in which an appreciable atomic collisions occur leading to the thermal equilibration of inside the desorption gas flow. Knudsen layer formation theory is such a theory which describes the dynamics of the desorption flow from the surface in the strong evaporations. The theory predicts the if the Knudsen layer is formed the temperature and the velocity become constant at a characteristics values.

I compared the experimental values of translational temperature and the stream velocity with the prediction based the Knudsen layer formation theory. The comparison shows a very good agreement of experimental values with the theoretical values. Hence, it is conclude that the observed behavior of the translational temperature and the stream velocity at a large desorption flux is understood as a manifestation of the formation of the Knudsen layer above the surface.

### 3. Nuclear resonant scattering by $^{83}\text{Kr}$ at $\text{TiO}_2(110)$

In the Mössbauer spectroscopy, resonant absorption of the nuclear energy levels are measured and one obtain the hyperfine splitting of its levels due to the local magnetic field or electric field gradient. The magnetic field or the electric field gradient is caused by the local magnetic state or electronic configurations of the atom. Thus, the method is of some significance when one is interested in local magnetic or electronic structures.

The local electronic structure of noble gas atoms at the surfaces is of some interest in view of the mechanism of the work function reduction after their adsorption. There were, however, several drawbacks for its application to studies on the physisorption systems. The method is not sensitive to the surface. The convenient radio-isotope source is not available for the noble gas atoms.

Recently, the use of the synchrotron radiation as a photon source for the Mössbauer spectroscopy has been developed which is called the nuclear resonant scattering of synchrotron radiation. This method has several advantages for the surface science. The wavelength is selective. Thus, the noble gas atoms like Kr are excitable. The synchrotron light is highly directive which is favorable as to the surface sensitivity, for it can be used with the glancing angle regime.

All the experiments were carried out in the SPring-8 BL09XU, where I installed an

ultra-high vacuum chamber. The chamber is precisely positioned for the synchrotron light on a mobile table. The sample was a clean  $\text{TiO}_2(110)$  cooled at 20 K suspended on a manipulator which is precisely rotated at the angle with the synchrotron light. The ground state of  $^{83}\text{Kr}$  possess  $I = 9/2$  with parity +. The first excited state is located at 9.4 keV above the ground state which possess  $I = 7/2$  with parity unchanged. It is the M1 transition.

The time spectra of the nuclear resonant scattering of synchrotron radiations by  $^{83}\text{Kr}$  mono- and multi-layers are obtained. The time spectrum at 5 monolayers shows a single exponential decay indicating the degenerate single peak in energy range. The time spectrum at monolayer shows, on the other hand, that the spectrum is well reproduced with a single exponential decay and a periodic function. The monolayer Kr is assumed to have a strong interaction with the substrate, which leads to the electronic modification of Kr.

The oscillation of the time spectrum observed at monolayer regime is analyzed assuming that it is a quantum beat originated from the quadrupole splitting of the nuclear energy levels due to the electric field gradient on the surface. By using the quadrupole moment in the previous reports and the quadruple splitting obtained in the present experiment, I deduced the electric field gradient applied to the Kr nuclei to be in the order of  $10^{21}$  V/m<sup>2</sup>.