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Sorption and desorption phenomena of D_2O on the surface of piping materials

Rumi Ohmori *, Toshiaki Yoneoka, Masaki Taniguchi, Satoru Tanaka

Department of Quantum Engineering and Systems Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

D_2O adsorption and desorption behavior on stainless steel, Cr_2O_3 and NiO have been studied with a Fourier transform infrared absorption spectrometer (FT-IR) and a quadrupole mass spectrometer (QMS). The O–D stretching vibration band was observed in the region of 2100–2700 cm^{-1}, which was considered to be from the physically adsorbed D_2O on the sample. Adsorption of D_2O was found to be heterogeneous on the surface. Desorption of D_2O with a higher O–D vibration frequency occurred more slowly. The light irradiation was found to enhance D_2O desorption. The 250 nm light stimulated D_2O desorption more strongly than the one of 400 or 600 nm. It seems that D_2O with a higher O–D wave number is more effective for light stimulated desorption. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Tritium contamination on many materials in a fusion reactor is a matter of concern from the viewpoints of safety and tritium accountancy. Among various materials, stainless steel is a common material often used in tubes and equipments. Surface of stainless steel is not clean from the sorption viewpoints but easily oxidized or contaminated with oil or chemical species in the atmosphere. Hence, a sorption mechanism and an effective desorption method on actual surface of stainless steel should be studied.

Ishihara et al. [1] studied the adsorption isotherm and the adsorption heat of a very small amount of H_2O on the surface of stainless steel under vacuum. The activation energy for desorption was 0.066 eV on Fe_2O_3 at H_2O partial pressure 5×10^{-4} Pa and 0.047 eV on Cr_2O_3 at 10^{-2} Pa H_2O. When the surface coverage of H_2O increased, the activation energy converged upon 0.1 eV on both of the materials. They also showed that adsorption and desorption of a very small amount of H_2O coincided with a simulation using the Freundlich adsorption isotherm. Recently, a decontamination technique combining ultraviolet radiation and ozone gas to remove tritium from the stainless steel surface has been reported. Hasegawa et al. [2] showed that the formation of UV-stimulated HTO in H_2 (HT)-O_2–O_3 was about 14 000 times greater than in H_2 (HT)-O_2 atmosphere. Krasznai and Mowat [3] showed that UV/ozone exposure of tritium-contaminated stainless steel was successful in removing 94% of the total tritium inventory.

While the study on the interaction of hydrogen isotopes with a metal surface has a broad data base, the study on the tritium sorption mechanism and active desorption method on actual surfaces is somewhat limited. In the present paper we observed adsorption and light stimulated desorption of D_2O on the surface of the oxides (Cr_2O_3, NiO) of the components of stainless steel and stainless steel itself mainly using a Fourier transform infrared absorption spectrometer (FT-IR) with a diffuse reflectance method.

2. Experimental

We observed the infrared absorption of the O–D stretching vibration on the specimen by a FT-IR with a diffuse reflectance method. This method can measure the infrared absorption of adsorbed species under controlled atmosphere at elevated temperature [4]. The temperature was controlled in a range of 300–673 K. The atmosphere was Ar gas with H_2O or D_2O vapor added and the

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* Corresponding author. Tel.: +81 3812 2111; fax: +81 3 3818 3455; e-mail: rumi@q.t.u.-tokyo.ac.jp.

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partial pressure was controlled from 0 to 400 Pa. Particle sizes of the samples, Cr_2O_3, NiO and SS316L, were in average 1, 1–20 and 8 μm, respectively. Before measurement, pre-treatment of the specimens was carried out over 720 min each at 303 or 673 K with flowing Ar gas to remove water from the specimen surfaces. Sanders et al. [5] suggested that molecular water is adsorbed at Ni^{2+} cation sites on thin film NiO/Ni(1 1 0). In order to recover all surface cation sites, the surface with adsorbed water must be annealed to temperatures in excess of 600 K. S. Andersson et al. [6] reported that hydroxyl species desorb from NiO surfaces at temperature above 500 K. Here, surface modification is anticipated by heating at 673 K.

In order to observe the effect of photon irradiation on adsorption and desorption behavior, the quantity of desorbed D_2O was measured using a quadrupole mass spectrometer (QMS). Each sample set in the sample holder was irradiated with a light through the quartz glass window of a small chamber under a flow of the sweep gas. The volume of this chamber was 200 ml and the inner surface was gold plated. Sweep gas was N_2 added with D_2O or H_2O vapor if necessary. Temperature of the sample was controlled in a range of 303–573 K. We also observed IR absorption under photon irradiation. Fig. 1 shows the experimental apparatus schematically. After passing through the monochromator, the light was transmitted to the sample set in the diffuse reflectance apparatus. In these light irradiation experiments, Hg–Xe lamp was used as a light source. The relative spectral intensities of the light after through the monochromator were 1 (250 nm):5 (400 nm):3.5 (600 nm). The transmission factor of KBr window (2 mm thick) for the diffuse reflectance method was about 72 (250 nm):89 (400 nm):92 (600 nm).

3. Results and discussion

3.1. Infrared absorption spectra of D_2O adsorbed on the sample

The absorption spectra for O–D stretching vibrations on Cr_2O_3, NiO and SS316L were observed at 303 K. Before measurement, pre-treatment was carried out for 900 min at 303 K for Cr_2O_3 and NiO, and at 673 K for SS316L. A broad IR peak was observed for each sample due to the adsorbed D_2O as shown in Fig. 2. The large peak in the range of 2250–2400 cm^{-1} is caused by CO_2 in the air. When the added vapor was switched from D_2O to H_2O, the broad peak disappeared in about 300 min on Cr_2O_3 and 100 min on NiO, and a new broad peak appeared in the range of 3000–3600 cm^{-1} corresponding to O–H stretching vibrations. Therefore, each broad peak was considered to originate from the physically adsorbed D_2O or H_2O on the sample.

The absorption spectra due to O–D stretching vibration was not observed for SS316L pre-treated at 303 K. Heat treatment at 673 K under Ar sweep gas was considered to have modified the surface of SS316L, presumably due to oxidation by low pressure H_2O vapor in the sweep gas. The surface modification of SS304L on heating at 673 K was also observed with an atomic force microscope.

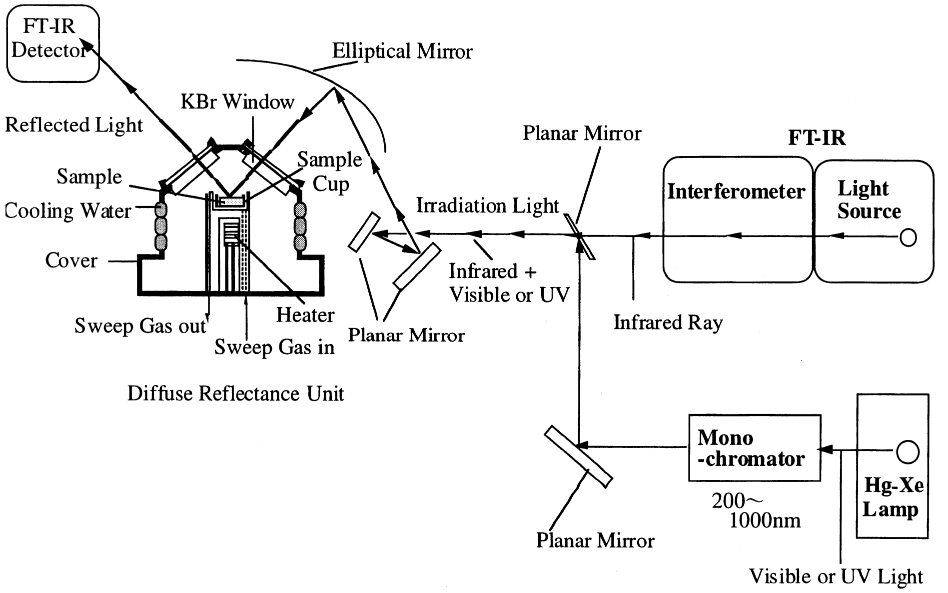

Fig. 1. A schematic diagram of FT-IR diffuse reflectance method with simultaneous photon injection.

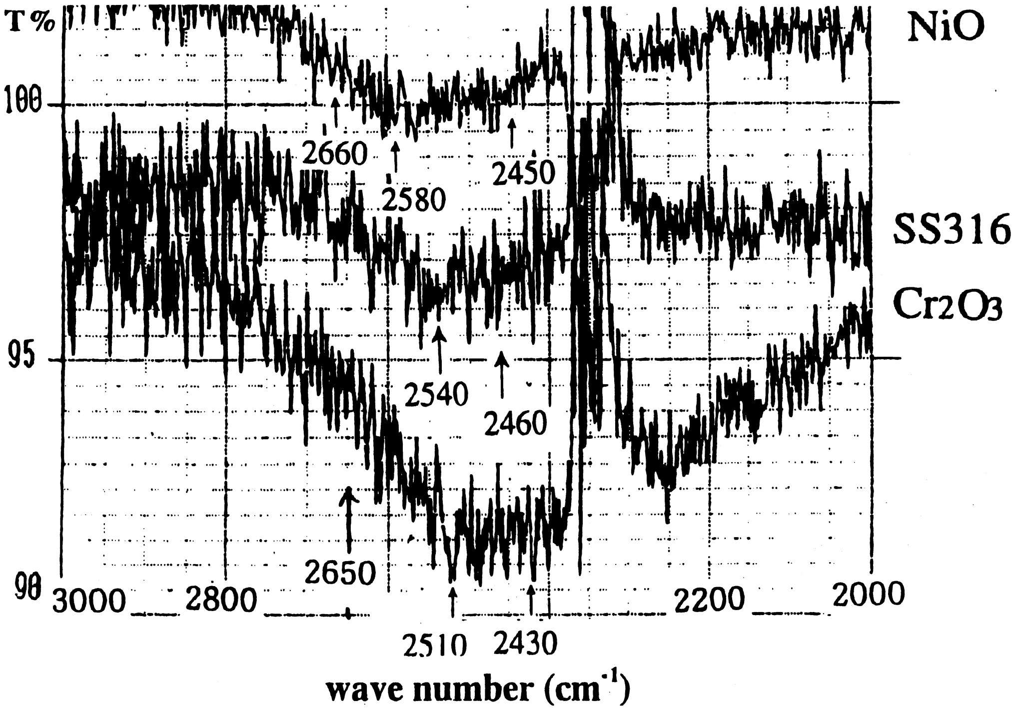

Fig. 2. Infrared absorption spectra by D_2O absorbed on Cr_2O_3, NiO and SS316L. Heat treatment temperature was 303 K for Cr_2O_3 and NiO, and 673 K for SS316L. D_2O absorption was carried out at 303 K for each sample.

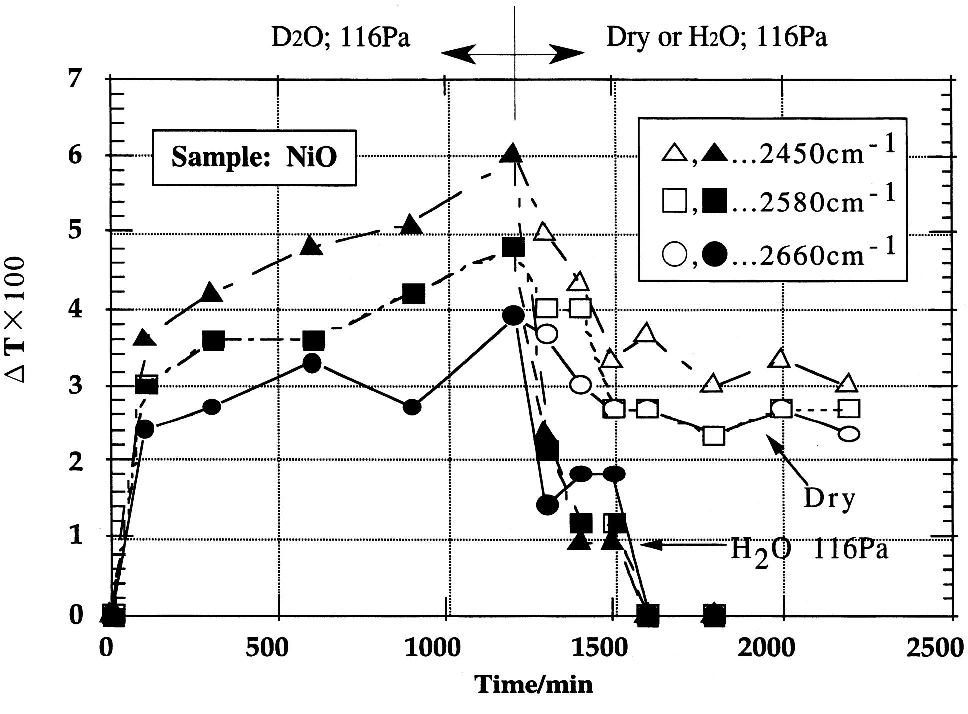

Fig. 3. Change of absorption spectra during adsorption (116 Pa) and desorption (drying or exchange with H_2O) for NiO at 303 K. T_t is an absorption factor, when time is t (min). $\Delta T = T_t - T_0$.

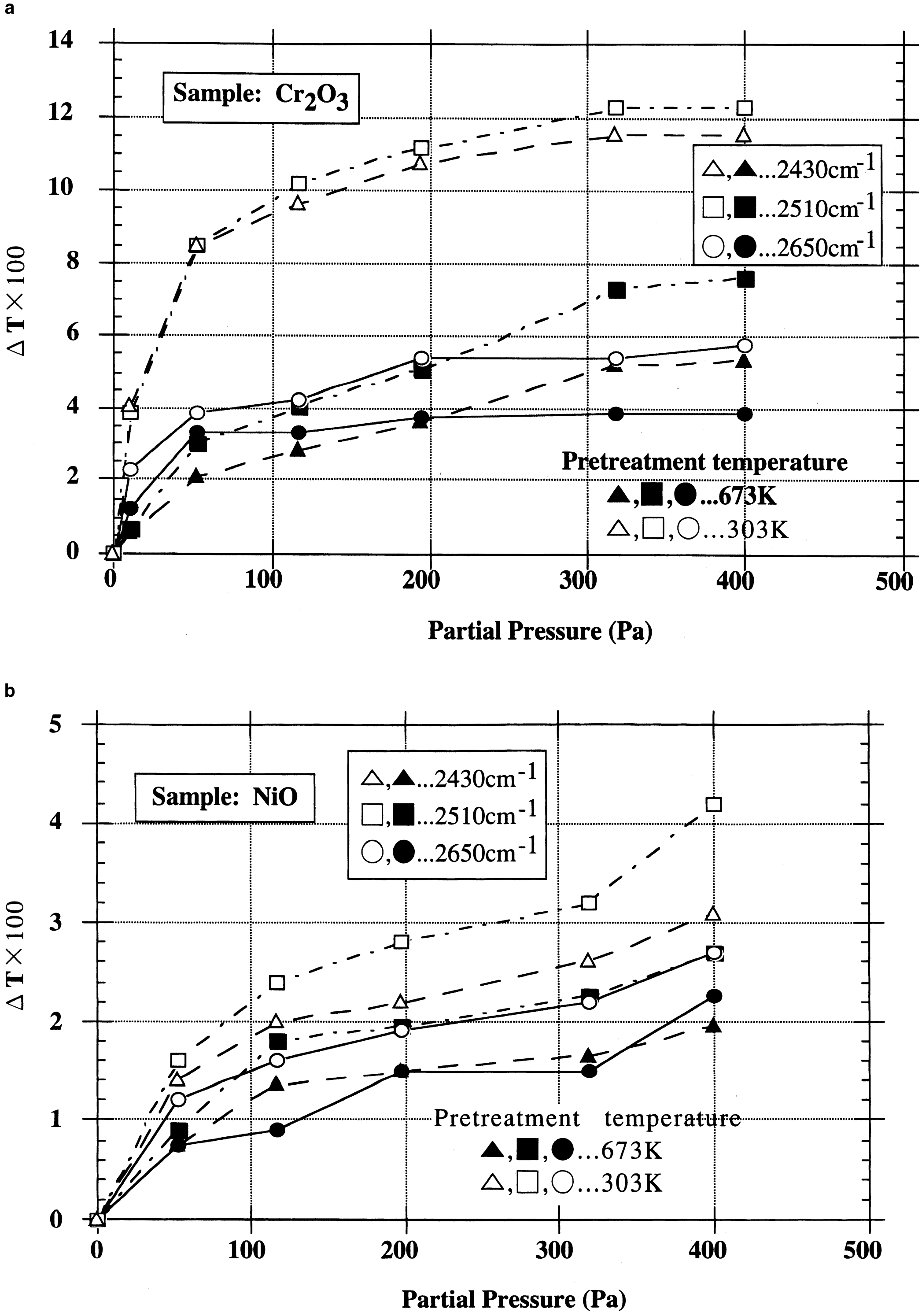

Fig. 4. Partial pressure dependencies of absorption intensities for (a) Cr_2O_3 and (b) NiO pre-dried at 303 and 673 K. T_t is an absorption factor, when time is t (min). $\Delta T = T_t - T_0$.

From the observed broad peak it is clear that adsorption of D_2O on the surface is not homogeneous. One reason for the broad peak is considered to be by various adsorption force of D_2O to the heterogeneous surface. The other is by hydrogen bond among adsorbed species. It is known that O–H bonding strength of the noted H_2O molecule becomes smaller by hydrogen bond with the surroundings H_2O. Thus, decrease of the bonding strength causes the decrease of vibration frequency of O–H. The observed broad peaks seemed to be composed of several peaks, while decomposing into contributing peaks was not easy. However, in order to study the wave number dependence on adsorption and desorption behavior, the following specific wave numbers were assumed to constitute the broad peaks respectively: 2430, 2510 and 2650 cm^{-1} for Cr_2O_3, 2450, 2580 and 2660 cm^{-1} for NiO, and 2460, 2540 and 2650 cm^{-1} for SS316L. These wave numbers were selected from careful observation of the spectrum. Although this selection is subjective, it has a coincidence with the peaks evaluated from the reported wave numbers for a small amount of H_2O on α-Cr_2O_3 surface [7]. In that report, several peaks appeared at 2430, 2520 and 2670 cm^{-1} at 398 and 498 K, as well as at 2630 and 2660 cm^{-1} after cooling of the specimen to room temperature from 498 K.

Fig. 3 shows the changes of the absorption peak intensities during adsorption and desorption of D_2O on NiO for the selected wave numbers mentioned above. The absorption peaks rapidly increased during the initial 100 min, then turned to a gradual growth. But they did not reach constant levels even after 1200 min. This behavior could be due to the large particle size (1–20 μm) and porous structure of NiO. In the case of Cr_2O_3, absorption intensities showed constant levels after rapid increase in the initial 100 min. During desorption of D_2O with Ar, the intensities of the absorption peaks did not return to zero in 1000 min. This indicates that D_2O cannot be desorbed fully only by drying with Ar. The fraction of the O–D removed by drying was found to be smaller for D_2O with a higher IR wave number, suggesting that the D_2O with a higher O–D frequency adsorbs more strongly on the samples (Cr_2O_3 and NiO). While, we observed D_2O desorption to occur from Cr_2O_3 during a temperature increase from 303 to 673 K under a constant D_2O vapor pressure of 116 Pa. In this case, the absorption intensities at 2430 and 2510 cm^{-1} decreased substantially by heating. However, the peak intensity at 2650 cm^{-1} decreased only a little, suggesting a stronger adsorption of the D_2O with this absorption frequency.

Fig. 4 shows D_2O pressure dependencies of the absorption peaks for (a) Cr_2O_3 and (b) NiO at room temperature. Before each run, the samples were dried at 303 or 673 K. A saturation of adsorption of D_2O with increase of D_2O pressure was observed for Cr_2O_3. In the case of NiO, Freundlich-like adsorption isotherm was observed. This also reflects the nature of the surface of these oxides. The absorption intensity was found to be smaller for a sample heat-treated at 673 K. The pretreatment at 673 K was considered to cause surface modification or stabilization by rearrangement of surface atoms. Zacchina et al. [8] have claimed that, upon prolonged thermal treatment at 473 and 673 K, surface stabilization of α-Cr_2O_3 took place due to the onset of mobility of surface OH^- and O^{2-} ligands. For η-Al_2O_3, effect of heat treatment at different temperatures (573, 695 and 873 K) was studied and it was reported that the amount of adsorbed D_2O on the surface decreased

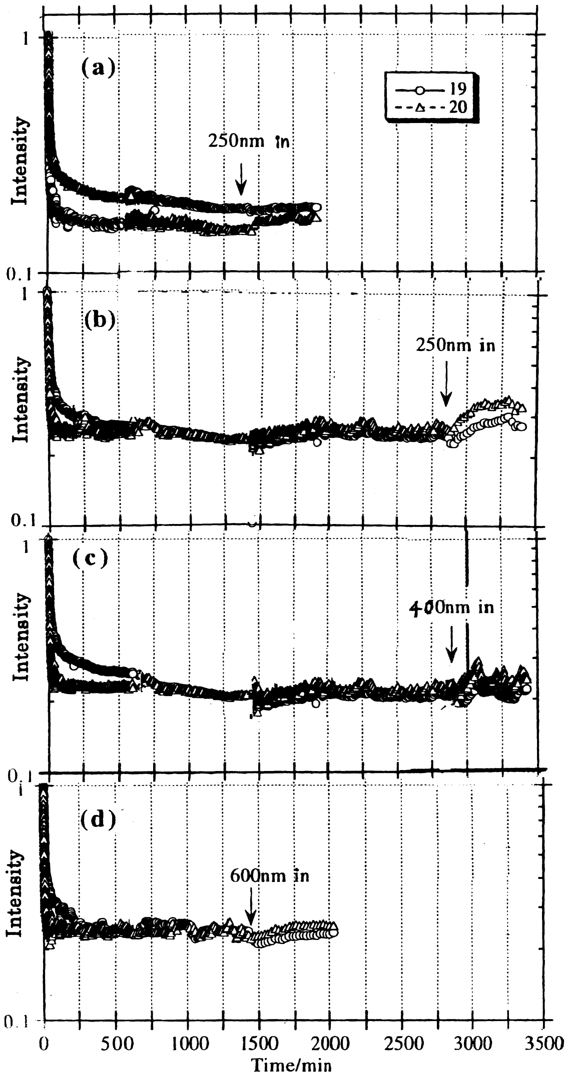

Fig. 5. Change of desorption intensities for the mass numbers 19 and 20 from Cr_2O_3 at 453 K. (a) Blank test without specimen, (b) 250 nm, (c) 400 nm, (d) 600 nm.

when heat treatment was carried out at higher temperature [9].

3.2. D_2O desorption by photon irradiation

Cr_2O_3 powder was contacted with N_2 + D_2O at 41.3 Pa for 900 min and then swept with N_2. After drying for a certain time (1400–3000 min), the light irradiation was started on the sample. The sweep gas containing desorbed species was led into a QMS in order to analyze the species with $m/e = 19$ (HDO) and 20 (D_2O). Temperature was controlled to 453 K at the surface of the sample in order to effectively study adsorption and desorption of D_2O with low adsorption coverage. A typical desorption curve is shown in Fig. 5. The light was injected after about 1400 min when no distinctive desorbed species were observed only by sweeping with N_2. The ordinate indicates the relative ion current intensity which was normalized to that of $m/e = 28$ (sweep gas: N_2). These figures show that the light of 250 nm stimulated desorption of D_2O from the sample surface to a larger degree than the light of either 400 nm or 600 nm.

We also conducted another experiment, where the light irradiation was started after drying time of 60 min. Ion current intensities for $m/e = 19$ and 20 by the light of 250 nm decreased slightly faster than by drying only or by the light irradiation with either 400 or 600 nm.

3.3. Observation of infrared absorption under photon irradiation

These experiments were conducted by using the experimental system shown in Fig. 1. Powder of Cr_2O_3 was contacted with Ar + D_2O at 43.7 Pa for about 900 min, then switched from Ar + D_2O to Ar for drying. After about 120 min, the light was injected to the sample. IR absorption was continuously measured during these processes. Fig. 6 shows that the 250 nm light irradiation enhanced desorption of D_2O with a high wave number (2650 cm^{-1}). In the case of the light irradiation of either 400 or 600 nm, no desorption enhancement was observed within experimental error. For D_2O with 2430 and 2510 cm^{-1}, no stimulated desorption was observed by the light irradiation.

From these experiments of the light stimulated desorption, it is summarized that: (i) 250 nm UV light irradiation was effective for desorption, but neither 400 nor 600 nm light. (ii) D_2O with a higher O–D vibration frequency was easily stimulated by the ultraviolet light irradiation.

This means that a photon with a higher frequency may be more effective for stimulating desorption. One possible explanation for the mechanism of the light stimulated desorption is light energy acceptance by the solid surface and following energy transfer from the surface to the adsorbed species or adsorbing bond.

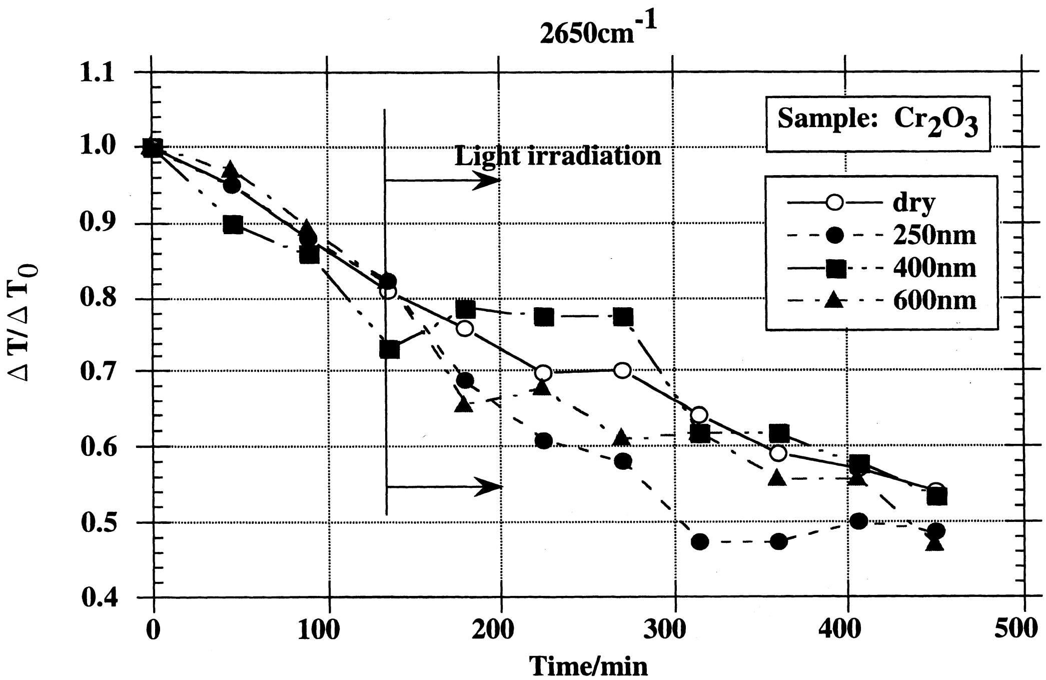

Fig. 6. Change of absorption spectra for Cr_2O_3 during D_2O desorption under photon irradiation at 453 K. ΔT is normalized by that $\Delta T_t = 0$.

These processes are considered to be effective for the adsorption system with low coverage which was the experimental condition in the present study. The experimental results seem to show that energy transfer for desorption is more effective for weakly bonded D_2O.

4. Conclusions

1. Adsorption of D_2O on the surface of NiO, Cr_2O_3, and SS316L was found to be heterogeneous.
2. Desorption by drying was slower for D_2O with a higher O–D vibration frequency.
3. UV irradiation was found to be effective for D_2O desorption.
4. It seems that D_2O with higher O–D frequency is more effective for photon stimulated desorption.

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