TRANSIENT ABSORPTION SPECTRA OF VIBRATIONALLY EXCITED WATER MOLECULE ON ZEOLITE SURFACE

TATSUYA FUJINO^a, AKIHIDE WADA^a, SATORU S. KANO^b,
KAZUNARI DOMEN^a and CHIAKI HIROSE^{a,*}

^a *Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan;*

^b *College of Engineering, Hosei University, Koganei, Tokyo 184, Japan*

(Received 7 April 1997)

By means of infrared pump-probe technique, spectroscopic feature of vibrationally excited water molecule (D₂O) on mordenite zeolite (OD) has been investigated. Populational lifetime of the OD stretching band (ν_3 : 2730 cm⁻¹) was determined to be 43 ± 5 ps at 123 K by the time evolution of hot band. The transient bleachings and absorptions appeared when the D₂O molecule was promoted to the vibrationally excited level of the OD stretching modes. Especially, the transient absorption at 2680 cm⁻¹ has rapid decay time (≈ 15 ps) and it was assigned as the overtone between ν_3 mode and vibrationally excited ν_1 mode (2620 cm⁻¹).

Keywords: Vibrational relaxation; zeolite; water adsorption; pump-probe

INTRODUCTION

Vibrational energy transfer between an adsorbate and a substrate is the key factor in the activity and selectivity of surface reactions. The use of frequency tunable infrared laser pulses in surface vibrational spectroscopy is providing us rich information on the structure and dynamics of adsorbed molecules. Typically, the techniques of infrared–infrared pump-probe spectroscopy have been so successful in revealing the dynamics of molecules adsorbed on solid surfaces

* Corresponding author.

[1–4]. Zeolites are crystalline aluminosilicates with large internal surfaces due to the microscopic pores and have been widely investigated because of their catalytic activity. The hydroxyl group located between a silicon and the adjacent aluminum atoms is strongly Brønsted acidic and is responsible for many catalytic reactions. In this report, transient absorption spectra of the system having vibrationally excited OD group of water molecule (D_2O) adsorbed on the deuterated zeolitic hydroxyl group (OD) have been measured by the two-color pump-probe technique and possible origin of the signals is discussed.

EXPERIMENTAL

Infrared pump and probe pulses were generated from the fundamental output of a mode-locked Nd:YAG laser by optical parametric generation/amplification (OPO/OPA) in $LiNbO_3$ crystals. Pretreatment of the sample zeolite was the same as described in Ref. [5]. Self-supporting disk of zeolite, DM-20 (deuterated H-mordenite zeolite), was exposed to water vapor (D_2O) in such a way that one or less water molecule was hydrogen-bonded to a zeolitic OD group.

RESULTS AND DISCUSSION

Figure 1 is the spectrum observed for the D_2O -adsorbed sample at 123 K. The band at 2730 cm^{-1} has been assigned to the stretching mode, ν_3 , of the OD group of adsorbed water sticking away from the surface (see the inset of Fig. 1). The broad band at 2620 cm^{-1} is assigned to the OD stretching mode, ν_1 , of water molecule which is strongly hydrogen bonded to the zeolite surface [6]. The ν_1 and ν_3 here are used simply to make correspondence to the symmetric and antisymmetric OD stretching modes of D_2O in chloroform solution [7]. We denote by ν_2 the DOD deformation mode of the D_2O moiety. The irradiation by a pump beam tuned at the frequency (Fig. 1, 2730 cm^{-1}) of OD group of adsorbed water that is free from the hydrogen bonding gave the bleaching effect and Figure 2 is the transient difference spectrum $A_p - A_0$ obtained by scanning the frequency of probe beam. The transient absorption peak at

FIGURE 1 Linear absorption spectrum in the OD stretching region of D_2O -adsorbed DM-20 (deuterated H-mordenite zeolite; Si/Al = 10.0) at 123 K. The intense peak at 2730 cm^{-1} is the OD stretching band of water molecule sticking away from the zeolite surface. The broad peak at 2620 cm^{-1} is the stretching mode of the OD group water which is under strong hydrogen bonding.

FIGURE 2 Transient ratio spectrum of D_2O -adsorbed DM-20 at 123 K. The ratio spectrum was obtained by subtracting from the spectrum A_p , which was obtained under the irradiation of pump beam tuned at 2730 cm^{-1} , the spectrum A_0 , obtained without the irradiation by pump beam. The solid line represents the result of fitting using four Gaussian profiles.

2650 cm^{-1} had the decay time of $43 \pm 5\text{ ps}$ at 123 K . The time evolution of this band was very close to the temporal recovery of bleaching signal at 2730 cm^{-1} . This feature and the downshift by 80 cm^{-1} from the bleaching signal suggested that this transient absorption at 2650 cm^{-1} is the hot band transition ($\nu_3 = 2 \leftarrow 1$). Transmission of probe beam increased at around 2620 cm^{-1} . This band was assigned to the bleaching of the OD groups of water molecule hydrogen-bonded to the zeolitic hydroxyl group. This bleaching effect implies the occurrence of direct vibrational energy transfer between the two OD stretching modes of adsorbed water. The transient absorption at 2680 cm^{-1} had rapid decay time ($\approx 15\text{ ps}$) and was assigned to the ($\nu_1 = 1, \nu_3 = 1$) $\leftarrow$ ($\nu_1 = 1, \nu_3 = 0$).

References

- [1] Fujino, T., Furuki, M., Kashitani, M., Onda, K., Kubota, J., Kondo, J. N., Wada, A., Domen, K., Hirose, C., Wakabayashi, F., Ishida, M., Goto, F. and Kano, S. S. (1996). *J. Chem. Phys.*, **105**, 279.
- [2] Kashitani, M., Fujino, T., Fukuyama, K., Kubota, J., Kondo, J. N., Wada, A., Domen, K., Hirose, C., Wakabayashi, F., Ishida, M., Goto, F. and Kano, S. S. (1996). *J. Chem. Phys.*, **105**, 6665.
- [3] Bonn, M., Brugmans, M. J. P., Kleyn, A. W. and van Santen, R. A. (1995). *Chem. Phys. Lett.*, **233**, 309.
- [4] Bonn, M., Brugmans, M. J. P., Kleyn, A. W. and van Santen, R. A. (1995). *J. Chem. Phys.*, **102**, 2181.
- [5] Wakabayashi, F., Kondo, J. N., Domen, K. and Hirose, C. (1995). *J. Phys. Chem.*, **99**, 10573.
- [6] Pelmenchikov, A. G. and van Santen, R. A. (1993). *J. Phys. Chem.*, **97**, 10678.
- [7] Graener, H. and Seifert, G. (1993). *J. Chem. Phys.*, **98**, 36.