

IR Absorption Spectra of Electrochromic WO₃ Films

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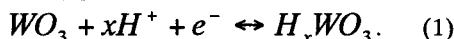
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WO₃ films were prepared by thermal evaporation. The IR absorption spectra of the films were measured for various amount of injected protons. Three peaks of ν (OH), ν (W=O) and ν (O—W—O) vibrations were observed. With increasing injected protons, the intensity of peak of ν (OH) increased and its position shifted hugely from 3200 to 2400 cm⁻¹. We calculated various bond-patterns of OH vibrations. Then OH vibrations accompanied with hydrogen bonds were plausible for observed OH peaks. On the other hand, with increasing injected protons the intensity of peak of ν (W=O) bond also increased, but its position shifted a little. It is considered that parts of W—O—W—O—W bonds were broken by injected protons and then W=O bonds were brought about.

Key words: electrochromism, WO₃ film, evaporated film, IR absorption

1. INTRODUCTION

Hydroxyl group and water molecules have been pointed out to play a considerable role in electrochromic (EC) phenomenon [1]. Different EC reactions in WO₃ films have been proposed. The most typical reaction is as follows [2]:



Here, coloring/bleaching mechanism of WO₃ is considered to be simultaneous injection/extraction of protons and electrons, and the coloration is caused by the intervalence transfer [2,3].

From IR measurements of WO₃ films prepared by thermal evaporation, the peaks of stretching vibrations of ν (OH) bond and ν (W=O) bond were found to shift to lower wave number with increasing injected protons. The origin of peak shift is supposed to be that injected protons produce bond switching, OH radicals and/or hydrogen bonds. Then we calculated various bond-patterns of OH vibrations by using an application software of molecular orbital theory, and the results were compared with IR absorption spectra.

2. EXPERIMENTAL

The measurement cells were configured to substrate/Au(electrode)/WO₃. The IR absorption spectra of WO₃ films were measured in the reflection mode [4]. The Au film was used as reflector and electrode. The Au film (~100 nm thickness) was deposited on glass substrate by DC sputtering. The WO₃ film (~1.2 μ m film thickness) was prepared onto Au film by thermal evaporation under atmosphere of 5.3×10^{-3} Pa. Both films were deposited on unheated substrate. An electrolyte of 1N-H₂SO₄ ethanol solution was used to inject protons into WO₃ films with applying the voltage of 1.5 V between the Au film and the counter

electrode of Pt wire. The amount of injected protons were measured by a Coulomb meter. The IR absorption spectra were measured by FTIR equipment (JIR-WINSPEC) for various amount of injected protons at wave numbers ranging from 4000 to 200 cm⁻¹ in reflection mode. Optical density (OD) was estimated from transmittance date,

$$OD = \frac{1}{2} \log \left(\frac{I_0}{I_1} \right), \quad (2)$$

where I_0 is the incident light intensity and I_1 the reflected one [4]. The effect of forming OH radicals and hydrogen bonds on OH vibrations was investigated. The calculation of various models for bond-patterns of OH vibrations was carried out using the application software of GAUSSIAN98. The calculation was performed in the Hartree-Fock approximation with the LANL2DZ basis set.

3. RESULT AND DISCUSSION

3.1 IR Absorption Spectra

Fig.1 shows the IR absorption spectra of a WO₃ film

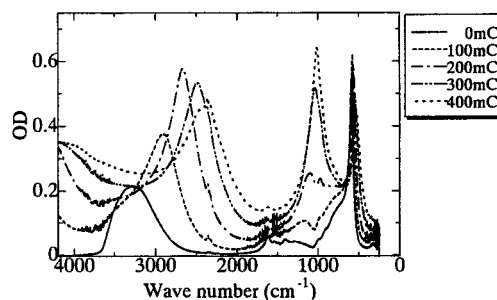


Fig.1 IR absorption spectra of WO₃ film for various amount of injected protons.

for various amount of injected protons. The WO_3 film had been completely bleached before IR spectra measurement. The ordinate denotes OD. In case of the film without injected protons, there are three large peaks at about 3300, 1000 and 600 cm^{-1} , which correspond to $\nu(\text{OH})$, $\nu(\text{W}=\text{O})$ and $\nu(\text{O}-\text{W}-\text{O})$, respectively [5]. When an amount of protons were injected, OD in the region of higher wave number increase due to absorption tail of EC band at colored state. The position of peaks of $\nu(\text{OH})$ and $\nu(\text{W}=\text{O})$ shifted to the lower wave number with increase of injected protons. The dependence of their positions on amount of injected protons is shown in Fig.2. The peak position of $\nu(\text{OH})$ shifted enormously from 3200 to 2400 cm^{-1} and that of $\nu(\text{W}=\text{O})$ shifted from 1300 to 1000 cm^{-1} . Since these peak-positions decreased monotonously with increasing amount of injected protons, new absorption peaks are not considered to arise. The ordinary stretching vibrations will not probably produce the huge shift of the peak to lower wave number. As the intensity of $\nu(\text{OH})$ and $\nu(\text{W}=\text{O})$ increased with increasing amount of injected protons, it is considered that OH and W=O bonds were formed at colored state (i.e. by injection of protons). The peak position and intensity of $\nu(\text{O}-\text{W}-\text{O})$ were independent of amount of injected protons.

We examine the origin of the shift for $\nu(\text{OH})$ with amount of injected protons. First, we assume that the peak shift of $\nu(\text{OH})$ is brought about by the bond switch, which is considered to occur between OH and W=O bonds. If the huge peak-shift arises from the bond switch within H_xWO_3 , the force constant of OH vibration should theoretically become half. As this is improbable in actuality, the huge shift of $\nu(\text{OH})$ is not explained by the bond switch. Second, we assume that OH radicals are incorporated in WO_3 matrix. It was

pointed out [6] that the absorption of OH radicals appears at near 2400 cm^{-1} in the colored state. From the results of molecular orbital calculation using hybrid density functional theory B3LYP with the cc-pVTZ basis set, OH, OH^- and OH^+ species were found to give absorption lines at 3695, 3590 and 3041 cm^{-1} , respectively. Accordingly, the peak shift of $\nu(\text{OH})$ is not considered to be produced due to OH radicals. Third, formation of dimer may make the huge shift of the peaks. The monomer of carboxylic acid give a absorption peak of $\nu(\text{OH})$ at 3550 cm^{-1} . When carboxylic acids formed dimer, it is known that the dimer gives a wide and strong absorption band of $\nu(\text{OH})$ from 3050 to 2400 cm^{-1} . In WO_3 films, it can be considered that when parts of $\text{W}-\text{O}-\text{W}-\text{O}-\text{W}$ bonds are broken by injected protons, W=O bonds are replaced with O-W bonds, and also OH bonds are made at colored state. Then hydrogen bonds ($\text{W}=\text{O} \cdots \text{H}-\text{O}$) may be made between a pair of H_xWO_3 . If the dimer of H_xWO_3 is brought about, the absorption peaks may shift hugely. In order to examine this, we calculated the various vibrations within the dimer.

3.2 Calculation

The crystal WO_3 is constituted by the octahedron that has a tungsten atom at the center and six oxygen atoms at the corner. The octahedron was modeled by clusters and calculations were carried out for these clusters.

First, the smallest model, WO_6H_6 , in which each oxygen atom is terminated with a hydrogen atom, was calculated and the theoretical IR spectrum was obtained. The result is shown in Fig.3. The lines appeared at about 4300 and 700 cm^{-1} were originated from $\nu(\text{OH})$ and bending vibration of $\delta(\text{OH})$, respectively. The

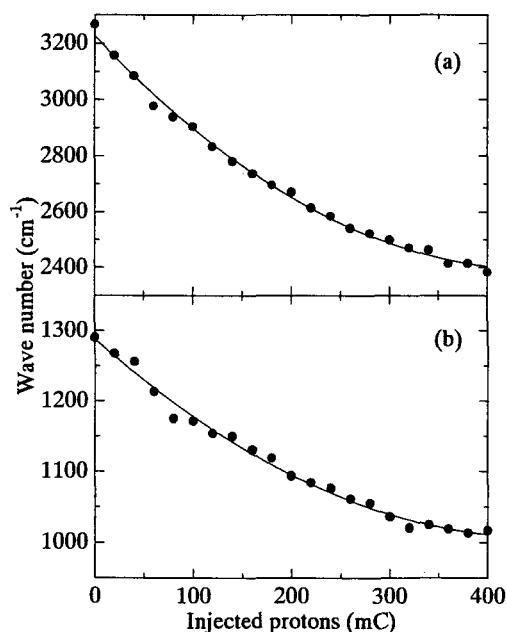


Fig.2 The dependences of the peak positions of (a) $\nu(\text{OH})$ and (b) $\nu(\text{W}=\text{O})$ on amount of injected protons.

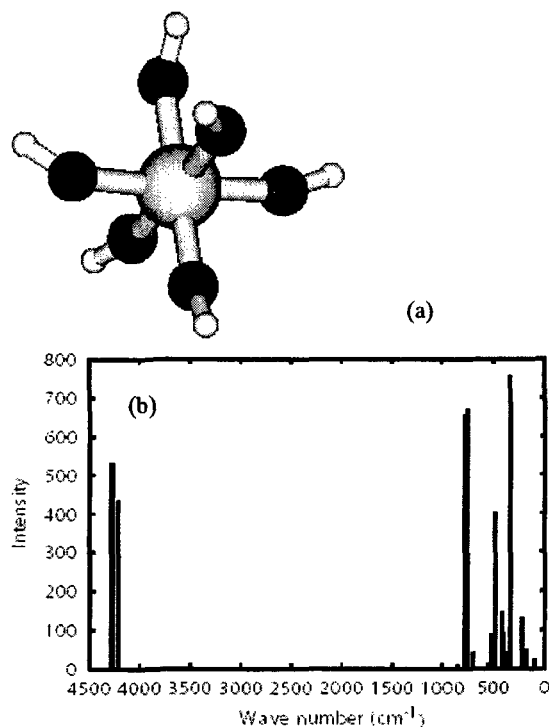
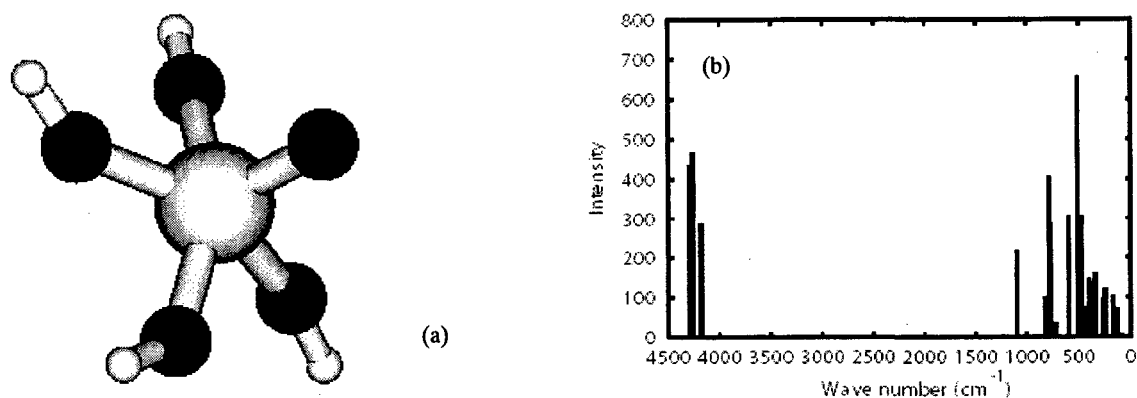
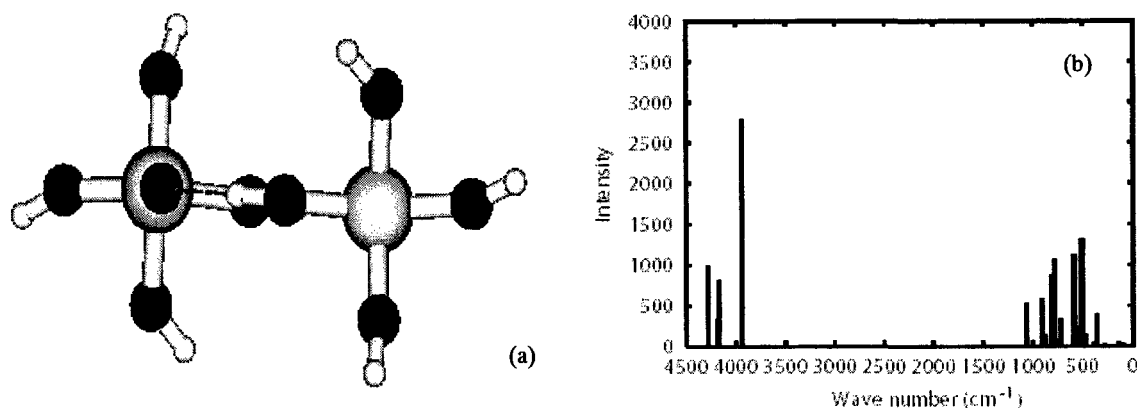


Fig.3 The geometry (a) and calculation result (b) of WO_6H_6 model.

Fig.4 The geometry (a) and calculation result (b) of WO_5H_4 model.Fig.5 The geometry (a) and calculation result (b) of $\text{W}_2\text{O}_{10}\text{H}_8$ model.

lines appeared below 700 cm^{-1} were basically originated from libration of framework.

The growing peak near 1000 cm^{-1} in Fig.1 was assigned to the shortened W–O bonds, which has the double bond character partly [5]. Thus, the IR spectrum of WO_5H_4 , which models double bond formation, was calculated. The result is shown in Fig.4. The line originated from $\nu(\text{W}=\text{O})$ appeared at about 1000 cm^{-1} , which is confirmed by the previous assignment.

As described above, a dimer may form in the colored state. The dimer model, $\text{W}_2\text{O}_{10}\text{H}_8$, which is formed by two WO_5H_4 with two pairs of hydrogen bonds $\text{O}=\text{H}\cdots\text{O}$, was calculated. The result is shown in Fig.5. The strong absorption line appeared at about 4000 cm^{-1} was originated from $\nu(\text{OH})$ accompanied with hydrogen bond. This line appeared at a lower wave number than the line originated from a stretching vibration of OH bond unaccompanied with hydrogen bond in Figs. 3 and 4. We call the latter a free $\nu(\text{OH})$. However, the magnitude of displacement was not so huge. Therefore, forming the dimer is not a direct origin of observed peak

shift. The line originated from $\nu(\text{W}=\text{O})$ accompanied with hydrogen bond appeared at slightly lower wave number than the free $\nu(\text{W}=\text{O})$.

As described above, the line of OH^+ appeared at the lowest wave number of all OH species. Thus, the $\text{W}_2\text{O}_{10}\text{H}_8^+$ model was calculated to evaluate the effect of positive charge. The result is shown in Fig.6. It is remarkable that the line originated from $\nu(\text{OH})$ accompanied with hydrogen bond appeared at much lower wave number than the neutral one. The lines originated from $\nu(\text{W}=\text{O})$ accompanied with the hydrogen bond hardly displaced.

Finally, Fig.7 shows calculation result of the $\text{W}_2\text{O}_{10}\text{H}_8^{2+}$ model to examine the effect further. In this model, the IR intensity was strong although $\nu(\text{OH})$ accompanied with hydrogen bond did not appear at a lower wave number. The line appeared at 990 cm^{-1} was originated from $\nu(\text{W}=\text{O})$ accompanied with the hydrogen bonds and the intensity was smaller than that of a free one.

From these figures, the lines originated from $\nu(\text{OH})$ and $\nu(\text{W}=\text{O})$ accompanied with the hydrogen bonds

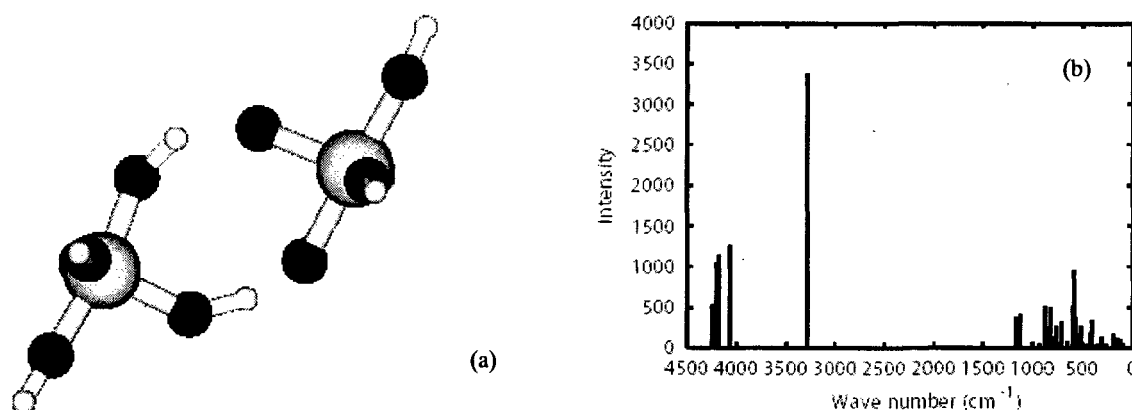


Fig.6 The geometry (a) and calculation result (b) of $\text{W}_2\text{O}_{10}\text{H}_8^+$ model.

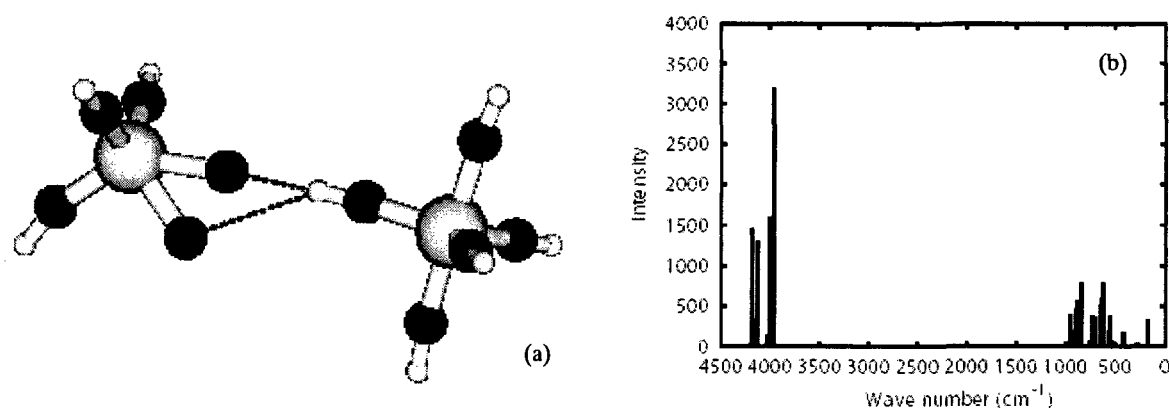


Fig.7 The geometry (a) and calculation result (b) of $\text{W}_2\text{O}_{10}\text{H}_8^{2+}$ model.

were appeared at lower wave number than the free ν (OH) and ν (W=O). The comparison of the observed IR absorption spectra with theoretical IR spectra for several models leads to the conclusion that the hydrogen bonds are formed when protons were injected and that the peak shift may be brought about due to positive charge of H^+ .

4. CONCLUSION

WO_3 films were prepared by thermal evaporation. IR absorption spectra of films were measured for various amount of injected protons. The peak originated from ν (OH) and ν (W=O) shifted to lower wave number, and their intensity increased with increase of injected protons. The calculation of various bond-patterns of OH vibrations was performed. The lines originated from ν (OH) and ν (W=O) accompanied with hydrogen bond appeared at lower wave number, and intensity of the former increases. Like this, there were some qualitative agreement between the IR absorption spectra of films and the calculation results for various

bond-patterns of OH vibrations. Thus it is considered that hydrogen bonds are formed at colored state.

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