Available online at www.sciencedirect.com
ScienceDirect
Surface Science 601 (2007) 1054–1063
SURFACE SCIENCE
www.elsevier.com/locate/susc

Infrared reflection absorption spectroscopic study of the adsorption structures of dimethyl ether and methyl ethyl ether on Cu(1 1 1) and Ag(1 1 1)

Takahiro Kasahara, Koichi Itoh *

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

Received 9 March 2006; accepted for publication 27 November 2006
Available online 3 January 2007

Abstract

Infrared reflection absorption (IRA) spectra measured for dimethyl ether (DME) adsorbed at 80 K on Cu(1 1 1) and Ag(1 1 1) give IR bands belonging only to the A_1 and B_2 species, indicating that the adsorbate takes on an orientation in which the C_2 axis bisecting the COC bond angle tilts away from the surface normal within the plane perpendicular to the substrates. The DFT method was applied to simulate the IRA spectra, indicating that the tilt angles of DME on Cu(1 1 1) and Ag(1 1 1) are about 50° and 55°, respectively, at submonolayer coverages. The results are in contrast to the case of DME on Cu(1 1 0) and Ag(1 1 0), where the C_2 axis is perpendicular to the substrates [T. Kiyohara et al., J. Phys. Chem. A 106 (2002) 3469]. Methyl ethyl ether (MEE) adsorbed at 80 K on Cu(1 1 1) gives IRA bands mainly ascribable to the *gauche* (*G*) form, whereas the IRA spectra measured for MEE on Ag(1 1 1) are characterized by the *trans* (*T*) form. The rotational isomers are identical with those on Cu(1 1 0) and Ag(1 1 0); i.e., MEE on Cu(1 1 0) takes the *G* form and the adsorbate on Ag(1 1 0) the *T* form [T. Kiyohara et al., J. Phys. Chem. B 107 (2003) 5008]. The simulation of the IRA spectra indicated that (i) the *G* form adsorbate on Cu(1 1 1) takes an orientation, in which the axis bisecting the COC bond angle tilts away from the surface normal by ca. 30° within the plane perpendicular to the surface to make the CH_3–CH_2 bond almost parallel to the surface, and (ii) the *T* form adsorbate on Ag(1 1 1) takes an orientation, in which the bisecting axis tilts away by ca. 60° from the surface normal within the perpendicular plane. Comparison of these adsorption structures of MEE on the (1 1 1) substrates with those of MEE on Cu(1 1 0) and Ag(1 1 0) indicates that the structures are mainly determined by a coordination interaction of the oxygen atom to the surface metals and an attractive van der Waals interaction between the ethyl group of MEE and the substrate surfaces. The coordination interaction plays an important role on Cu(1 1 1) and Cu(1 1 0), which makes the adsorbate on the Cu substrates to take the orientations with the bisecting axis near parallel to the surface normal and to assume the *G* form in order to make the ethyl group parallel to the surface, which is favorable for the van der Waals interaction. In the case of MEE on the Ag substrates the attractive van der Waals interaction plays a dominant role, resulting in the *T* form which is more favorable for the interaction than the *G* form.

Keywords: Infrared reflection absorption spectroscopy; Dimethyl ethers; Methyl ethyl ethers; Adsorption structure; Cu(1 1 1); Ag(1 1 1)

1. Introduction

In the previous papers we have studied the adsorption structures and rotational isomerism of dimethyl ether (DME) [1], dimethyl sulfide (DMS) [2], methyl ethyl ether (MEE) [3], methyl ethyl sulfide (MES) [2] and methyl propyl ether (MPE) [4] adsorbed on Cu(1 1 0) and Ag(1 1 0). If lateral interactions between the adsorbates can be neglected, the adsorption structures are determined mainly by the following factors: (i) coordination interaction of the oxygen and sulfur atoms with the surface atoms; (ii) the repulsive and attractive interaction between the alkyl groups and the substrate surfaces; and (iii) enthalpy

---

* Corresponding author. Tel.: +81 3 5286 3243; fax: +81 3 5273 2606.
E-mail address: itohk@waseda.jp (K. Itoh).

doi:10.1016/j.susc.2006.11.049

difference between rotational isomers. The results of the previous papers gave some insights into how three factors interplay to determine the adsorption structures. That is, all the adsorbates interact with the substrate surfaces through a weak coordination of the oxygen and sulfur atoms to the substrate metals. DME adsorbs on Cu(1 1 0) and Ag(1 1 0) with the C_2 axis perpendicular to the substrate surfaces at submonolayer coverage states, suggesting that the adsorbate tends to coordinate to the Cu and Ag atoms through the 2p lone pairs of the neighboring metal atoms (bridging coordination). MEE on Cu(1 1 0) take on the *gauche* (*G*) form with the COC plane almost perpendicular to the substrate surface, while MEE on Ag(1 1 0) take the *trans* (*T*) form with the molecular planes appreciably tilted away from the surface normal, the tilt angle being ca. 45°. One of the characteristic features of the adsorption structures of MEE on both substrates is that the ethyl group keeps an almost parallel orientation to the substrate surfaces with the distance between the group and the surface as small as possible. Thus, in addition to the coordination interactions an attractive interaction between the ethyl group and surfaces also play an important role in determining the adsorption structures. Presumably, an intrinsically stronger coordination interaction between the oxygen atom and the Cu atom on Cu(1 1 0) results in the perpendicular orientation of the COC plane relative to the substrate surface. In this orientation the ethyl group tends to take the gauche form in order to put the ethyl group in an orientation favorable for the attractive interaction, even if the enthalpy of the *G* form of MEE is higher than that of the *T* form by 5.65 kJ/mol.

In the present paper we extended the IRA studies to the case of DME and MEE adsorbed on Cu(1 1 1) and Ag(1 1 1) in order to clarify how the difference in the surface structures affects the adsorption structures. Comparison between the adsorption structures of DME and MEE on the (1 1 1) surfaces with those on the (1 1 0) surfaces will give more detailed insights to the interplay of the structure-determining factors.

2. Experimental

2.1. Materials

DME and MEE were purchased from Tokyo Kasei Kogyo Co., Ltd. and distilled prior to IR measurements.

2.2. Substrates

Cu(1 1 1) and Ag(1 1 1) single crystals (99.999%, 15 mm (∅) × 1 mm) were purchased from Techno Chemics, Inc. The surfaces of the crystals were cleaned by Ar^+ ion sputtering (0.7 μA cm^{-2}, 700 eV, 15 min at 700 K) and annealing at the same temperature, as already described in detail [1,5]. The surfaces were confirmed by observing the anticipated LEED patterns.

2.3. Measurement of IR spectra

The IR spectra were recorded by using the apparatus already explained [1,5]. Briefly, the apparatus consists of a load-lock chamber and two ultrahigh vacuum chambers; one of the UHV chambers containing a four-grid retarding field AES/LEED optics, a quadrupole mass spectrometer and an Ar^+ ion sputtering unit was used for preparing the clean surfaces and the other UHV chamber containing a Fourier transform IR spectrometer (Brucker model 66v/S) was used for IRA spectral measurements. The IR spectra were recorded at an incident angle of 80° with a liquid nitrogen cooled MCT detector. The base pressure of the two chambers was below 1×10^{-10} Torr. The temperature of the substrates was cooled to 80 K by liquid nitrogen. DME and MEE were exposed to the substrates precooled at 80 K through a 1/8 in. stainless tube by using a variable leak valve after several freeze–thaw cycles. Exact surface coverages could not be determined, but since the formation of multilayers of the adsorbates was easily detected by observing IR bands ascribable to a bulk (or multilayered) crystalline state, it was assumed that a saturation coverage is formed just before the appearance of the bulk bands. All the spectra were given by $-\log(R/R_0)$ as a function of wavenumber in the 4000–750 cm^{-1} region, where R and R_0 indicate measured reflection intensities with and without an adsorbate, respectively. Reflection intensities were recorded by adding 3000 scans at the resolution of 4 cm^{-1}.

3. Computation procedure

3.1. Normal frequency calculation

Ab initio quantum mechanical calculations were performed using GAUSSIAN 98 [6] and a DFT method at the B3LYP level with the 6-311++G** basis set. The normal frequencies were calculated for the optimized structures of DME and MEE with the *T* and *G* forms and corrected by multiplying the scale factor, which was obtained by the following equation proposed by Matsuura and Yoshida [7].

$$\frac{\nu_{\text{obs}}}{\nu_{\text{calc}}} = 1.0087 - 0.0000163\nu_{\text{calc}} \qquad (1)$$

3.2. Simulation of IRA spectra of DME and MEE

The simulation of the IRA spectra were carried out for DME and MEE in the *T* and *G* forms with various orientation on a metal surface by assuming as follows; (i) the transition dipole moment calculated for each normal mode of the free DME molecule and the free MEE molecules in the *T* and *G* forms can be used to estimate the intensity of the corresponding IRA band; (ii) the intensity of the IRA band is proportional to the square of the projection of the transition dipole moment to the surface normal; and