

# Infrared Reflection Absorption Spectroscopic Study on the Rotational Isomerism of Methyl Propyl Ether on Cu(110) and Ag(110)

Hironao Shinohara, Takahiro Kasahara, Kei Kadokura, Yoichi Uryu, and Koichi Itoh\*

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

Received: August 28, 2003; In Final Form: January 5, 2004

Infrared reflection absorption (IRA) spectra were measured for methyl propyl ether (MPE) adsorbed on Cu(110) and Ag(110) at 80 K. The IRA spectra of MPE on the substrates at sub-monolayer and full monolayer coverages exhibit simple spectral features, indicating that each adsorbate exists in a rotational isomeric form with a specific orientation relative to the substrate surface. Comparison of the IRA spectra of the adsorbates with those characteristic of MPE in bulk states taking known isomeric forms including TT, TG, GT, and GG forms (T and G are trans and gauche conformations, respectively, and the first symbol indicates the isomeric form around the O–CH<sub>2</sub> bond and the second the form around the CH<sub>2</sub>–CH<sub>2</sub> bond) and the simulation performed by using the density functional theory method for the IRA spectra of each isomer with varying orientations on a metal surface proved that MPE on Cu(110) takes on the GG form and MPE on Ag(110) the GT form. These forms are favorable for the coordination interaction of the oxygen atom to the metal surfaces. The spectral simulation indicated that the COC plane of the GG form tilts away from the substrate surface by about 30° to reduce the repulsion between the ethyl group and the Cu(110) surface, while the COC plane of the GT form tilts away from the surface by about 30° to a direction opposite of that of the GG form, resulting in the ethyl group with the C–C bond more or less parallel to the Ag(110) surface. From these results, it was concluded that the rotational isomerism and the orientation of the isomer on each surface are determined by the balance between the coordination interaction and an attractive (or van der Waals) interaction between the surface and the alkyl groups, the former interaction being more important on Cu(110) and vice versa on Ag(110).

## Introduction

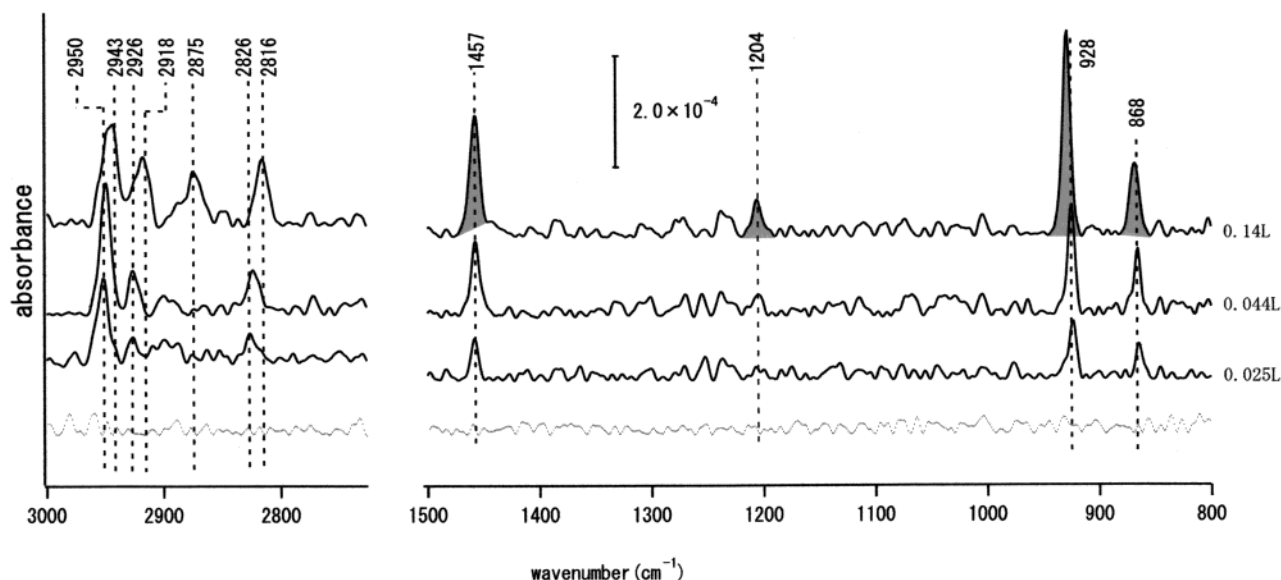
In previous papers,<sup>1,2</sup> we reported the infrared reflection absorption (IRA) spectroscopic study on dimethyl ether (DME) and methyl ethyl ether (MEE) adsorbed at Cu(110) and Ag(110). The analyses of the spectra indicated that (i) the ethers adsorb on the surfaces through a weak coordination of the oxygen to the substrate atoms, (ii) DME adsorbs on the substrates with the COC plane and the C<sub>2</sub> axis almost perpendicular to the surfaces at submonolayer coverages, (iii) MEE on Cu(110) takes a gauche (G) form (around the O–CH<sub>2</sub> bond) while MEE on Ag(110) takes a trans (T) form, and (iv) MEE in the G form adsorbs on Cu(110) with the COC plane almost perpendicular to the surface and with the O–CH<sub>2</sub> bond tilted away from the surface by about 22.5°, while MEE in the T form adsorbs on Ag(110) with the molecular plane tilted about 45° from the surface normal with the line connecting the C atom of the CH<sub>3</sub>–(CH<sub>2</sub>) group and the O atom more or less parallel to the surface. The detailed information about the rotational isomerism and the orientations of MEE on the substrates were obtained based on the simulation of the IRA spectra performed by the density functional theory (DFT) method at the B3LYP/6-311++G\*\* level.

In the present paper, we extend the above studies to the case of methyl propyl ether (MPE) on Cu(110) and Ag(110). The rotational isomerism of MPE in bulk states has been extensively studied by infrared (IR) and Raman spectroscopy and normal frequency calculations, indicating that MPE in the crystalline state takes on the TT form, MPE in the glassy state the TT and

TG forms, and MPE in the liquid and gaseous state the TT, TG, GT, and GG forms.<sup>3</sup> (The first symbol indicates the isomeric form around the O–CH<sub>2</sub> bond and the second symbol the form around the CH<sub>2</sub>–CH<sub>2</sub> bond. The GG' form, where the internal rotation angle around the O–CH<sub>2</sub> bond is about 120° and that around the CH<sub>2</sub>–CH<sub>2</sub> bond is about –120°, was excluded because of a large steric repulsion between the CH<sub>3</sub>(–O) and CH<sub>3</sub>(–CH<sub>2</sub>) groups.)<sup>3</sup> The vibrational frequencies characteristic of each isomer have also been established.<sup>3</sup> The observed IRA spectra of MPE adsorbed on Cu(110) and Ag(110) were analyzed on the basis of the characteristic IR frequencies of each isomer in the bulk states to determine the rotational isomers of the adsorbates, and the orientation of each adsorbate was determined by the spectral simulation performed by the DFT calculation. If lateral interactions between the adsorbates can be neglected, the adsorption structures on the surfaces are determined by the following factors: (i) enthalpy difference between rotational isomers, (ii) coordination interaction between the oxygen atom of MPE and the surface atoms, and (iii) the repulsive and attractive interaction between the alkyl groups and the substrate surfaces. The results of the present study combined with those of the previous papers<sup>1,2</sup> will give insight into the fundamental but less explored problem about how these factors interplay to determine the rotational isomerism and the orientation of the adsorbates.

## Experimental Section

**Materials.** MPE (99% purity) was purchased from Tokyo Kasei Kogyo Co., Ltd., and distilled prior to IR measurements.



**Figure 1.** IRA spectra of MPE adsorbed on Cu(110) measured at 80 K with an increasing amount of exposure. The number on the right-hand side of each spectrum indicates the amount of exposure in the Langmuir unit. The bottom dashed line shows a background spectrum. See text.

**Substrates.** Ag(110) and Cu(110) single crystals (99.999%, 15 mm( $\phi$ )  $\times$  1 mm) were purchased from Techno Chemicals, Inc. The surfaces of the crystals were cleaned by Ar<sup>+</sup> ion sputtering (0.7  $\mu$ A cm<sup>-2</sup>, 700 eV, 15 min at 600 K) and annealing at the same temperature, as already described in detail.<sup>2,4</sup> The formation of the reconstructed surfaces was confirmed by observing the anticipated low-energy electron diffraction (LEED) patterns.

**Measurement of IR Spectra.** The IR spectral measurements were performed by the apparatus already explained.<sup>2,4</sup> Briefly, the apparatus consists of a load-lock chamber and two ultrahigh vacuum (UHV) chambers (base pressure  $< 1 \times 10^{-10}$  Torr); one of the UHV chambers containing a four-grid retarding field Auger electron spectroscopy (AES)/LEED optics, a quadrupole mass spectrometer, and an Ar<sup>+</sup> ion-sputtering unit, and the other UHV chamber contains a Fourier transform IR spectrometer (Bruker model 66v/S) equipped with a liquid nitrogen cooled MCT detector. The IR spectra recorded at an incident angle of 80° were measured for MPE, which was exposed to the substrates precooled at 80 K through a 1/8-in. stainless tube by using a variable leak valve. Since exact surface coverages were not determined in the measurements, the amounts of exposure were shown in the Langmuir unit, i.e., 1 L =  $1 \times 10^{-6}$  Torr s. All the spectra were given by  $-\log(R/R_0)$  as a function of wavenumber in the 4000–750 cm<sup>-1</sup> 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<sup>-1</sup>.

### Computation Procedure

**Normal Frequency Calculation.** A DFT method at the B3LYP level with the 6-311++G\*\* basis set was applied to calculate the normal frequencies of the optimized structures of MPE with the GG, GT, TG, and TT forms. The Gaussian 98<sup>5</sup> program was used for the calculation. The calculated normal frequencies were corrected by multiplying the scale factor, which was obtained by the following equation proposed by Matsuura and Yoshida<sup>6</sup>

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

### Simulation of the IRA Spectra of MPE on the Substrates.

The simulation of the IRA spectra were carried out for MPE in each isomeric form with various orientations on a metal surface. The followings were assumed for the simulation: (i) the intensity of each IRA band is proportional to the square of the projection to the surface normal of the transition dipole moment of the corresponding normal mode; (ii) the transition dipole moment calculated for each normal mode of the free MPE molecule in each isomeric form can be used to estimate the intensity of the corresponding IRA band; and (iii) each IRA band with a calculated frequency,  $\nu_{\text{calc},i}$ , has a Lorentzian shape with the half-width at half-maximum ( $\sigma$ ) of 1 cm<sup>-1</sup>. Then, the calculated spectra are expressed by using the following formula

$$S(\nu) = \sum_{i=1}^N P_i \frac{\sigma}{\pi} \frac{1}{(\nu - \nu_{\text{calc},i})^2 + \sigma^2} \quad (2)$$

where  $N$  is the number of the normal modes and  $P_i$  is calculated by the formula

$$P_i = (\mu_{\perp})^2 \quad (3)$$

$\mu_{\perp}$  in eq 3 is the projection to the surface normal of the calculated transition-moment vector for the normal vibration with the frequency,  $\nu_{\text{calc},i}$ , of MPE in an assumed orientation on a metal surface.

### Results

**IRA Spectra of MPE on Cu(110).** Figure 1 exhibits the IRA spectra of MPE adsorbed on Cu(110) at ca. 80 K with increasing amount of exposure up to 0.14 L. The baseline spectrum is shown at the bottom in order to indicate the noise level of the measured spectra. The intensities of the IRA bands observed at 1457, 1204, 928, and 868 cm<sup>-1</sup> in the 1500–800 cm<sup>-1</sup> region increase with the amount of exposure, and on further increase of the exposure above 0.14 L, the intensities do not show any change, then the adsorbates at the exposure level of 0.14 L exist in a saturation (or full monolayer) coverage state. The spectral features are much simpler than the IR spectra of the bulk states (i.e., liquid, glass, and crystalline states) of MPE observed by Shimanouchi et al.,<sup>3</sup> indicating that MPE on Cu(110) exists in

**TABLE 1: Comparison between the Observed and Calculated Frequencies of IR Bands for MPE in Each Rotational Isomer and the Observed Frequencies of IRA Bands of MPE on Cu(110) and Ag(110)**

obsd freqs <sup>a</sup>		calcd freqs. <sup>b</sup>				obsd IRA freqs <sup>c</sup>		assignments <sup>d</sup>
liquid and glass	crystal	GG	GT	TG	TT	Cu(110)	Ag(110)	
1286(w)	1288(vw)	1301.2(7.5)		1296.1(3.6)	1302.4(0.2)			CH <sub>2</sub> twist
1268(vw)		1279.6(4.8)	1278.8(3.1)					CH <sub>2</sub> twist
1249(w)	1251(m)			1258.2(4.0)	1255.3(1.9)			CH <sub>2</sub> twist
	1214(vs)				1210.1(27.3)			CH <sub>3</sub> ip-rock
1205(s)		1208.2(17.3)	1213.5(10.8)	1208.2(21.5)		1204	1199	CH <sub>3</sub> ip-rock
1165(s)	1174(w)	1168.1(55.7)	1174.6(65.7)		1179.6(5.1)			CH <sub>2</sub> rock, CH <sub>3</sub> op-rock
1151(vw,sh)	1152(vw,sh)	1158(8.3)	1157.0(5.3)	1170(7.6)	1152.7(0.4)		1167	CH <sub>3</sub> op-rock
1144(vs)				1149.1(20.2)				CH <sub>3</sub> op-rock
1130(vs)	1132(vs)				1138.7(129.7)			CC str
1114(vs)		1112.5(34.6)	1115.1(26.7)	1129.1(138.4)				CH <sub>3</sub> ip-rock, CO str,
1100(vs)	1098(vs)	1087.2(44.5)	1100.8(75.1)		1110.9(44.2)			CC str, CO str
1077(vw)				1105.2(3.8)				CO str
1050(s)				1051.8(17.3)				CC str
1042(w)			1024.5(1.5)				1040	CC str
1042(w)	1042(m)				1040.1(2.9)			CC str
1026(w)		1024.8(15.7)						CO str
960(s)	960(vs)				959.0(27.2)			CO str
942(m)			942.2(34.1)				948	CO str
935(s)		934.5(21.9)		938.2(15.4)		928		CH <sub>3</sub> ip-rock, CO str,
912(s)				915.3(11.8)				CH <sub>2</sub> rock
905(m)	909(vw)	892.8(11.6)			902.2(6.0)	868		CC str, CH <sub>2</sub> rock,
897(w)	897(s)		889.4(0.6)		900.5(1.5)			CC str, CH <sub>3</sub> ip-rock,
879(m)			878.4(9.0)	876.1(2.7)			876	CC str
852(vw)		848.8(4.0)						CC str

<sup>a</sup> Frequencies of the IR bands observed for MPE in the liquid, glassy, and crystalline states are taken from ref 3. vw, w, m, vs, and s in the parentheses mean “very weak”, “weak”, “medium”, “very strong”, and “strong”, respectively, indicating the approximate observed intensity of each band. sh means “shoulder band”. <sup>b</sup> Frequencies and intensities were calculated for the optimized structure of MEE in the GG, GT, TG, and GG forms by using the B3LYP/6-311++G\*\* level calculation. (See text.) The calculated frequencies were corrected by using the formula proposed by Matsuura and Yoshida.<sup>6</sup> See text. <sup>c</sup> Frequencies observed for MPE at the saturation coverage on Cu(110) (GG) and Ag(110) (GT). See text. <sup>d</sup> Vibrational modes mainly associated with each normal vibration. Str, twist, and rock indicate stretching, twisting, and rocking vibrations, respectively, and ip and op mean in-plane and out-of-plane, respectively.

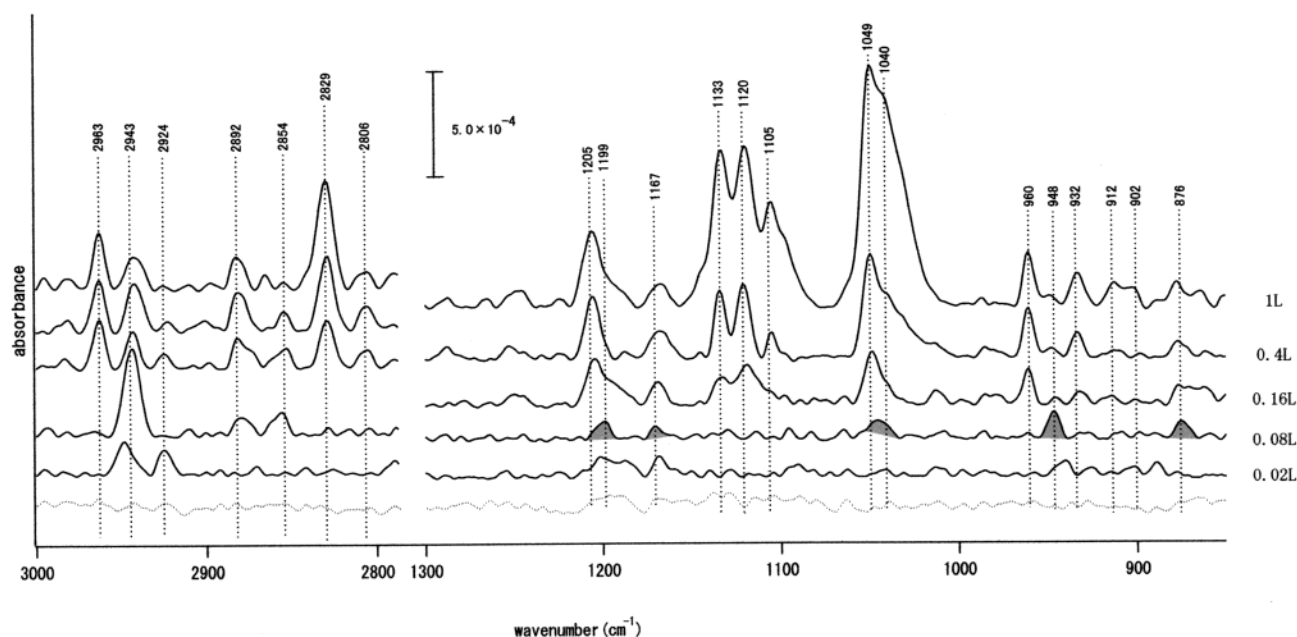
one of the rotational isomeric forms (TT, TG, GT, and GG) with a specific orientation on the surface. The spectral features do not change, except for slight intensity decrease, when the substrate temperature is increased to 150 K, at which point the adsorbate begins to desorb, and then cooled again to 80 K. This result indicates that the adsorption state giving the spectrum at 0.14 L can be ascribed to a thermodynamically stable state. As listed in Table 1, MPE in the crystalline state gives strong IR bands at 1390, 1214, 1132, 1098, 960, and 897 cm<sup>-1</sup>, which are assigned to the TT form.<sup>3</sup> All these bands are absent in the spectra in Figure 1. Thus, the TT form, which is the most stable form in the bulk states, can be ruled out as the possible isomer on Cu(110). The 1204-cm<sup>-1</sup> IRA band in Figure 1 corresponds to the IR band at 1205 cm<sup>-1</sup>, which has been assigned to the TG, GT, and GG forms of MPE in the liquid and glassy states,<sup>3</sup> the IRA band at 928 cm<sup>-1</sup> to the IR band at 935 cm<sup>-1</sup>, which have been assigned to the GG and TG forms,<sup>3</sup> and the IRA band at 869 cm<sup>-1</sup> either to the IR band at 879 cm<sup>-1</sup>, which has been assigned to the TG and GT form, or to the IR band at 905 cm<sup>-1</sup>, which has been assigned to the GG form<sup>3</sup> (see Table 1). Considering these results, we can conclude that MPE on Cu(110) takes on either the TG form or the GG form. According to Shimanouchi et al.,<sup>3</sup> the TG form exhibits a strong IR band at 1050 cm<sup>-1</sup> in the liquid and glassy states (Table 1), which is absent in the IRA spectra (Figure 1). Although the absence could be ascribed to the orientation effect of the adsorbate, the result suggests that the GG form is more favorable as the isomeric form on Cu(110) than the TG form, which is consistent with the result of spectral simulation explained below.

Figure 1 indicates that the IRA spectrum of MPE on Cu(110) at the exposure of 0.025 L gives the bands at 2950, 2926, and 2826 cm<sup>-1</sup>, which increases their intensities on increasing the exposure to 0.044 L. Upon further increase of the exposure to

0.14 L, the 2950, 2943, and 2826 cm<sup>-1</sup> bands shift to 2943, 2918, and 2816 cm<sup>-1</sup>, respectively. In addition, there appears a new band at 2875 cm<sup>-1</sup>. These spectral changes suggest the appearance of a new adsorption state at the coverage of 0.14 L, which cannot be detected by the IRA spectra in the 1500–800-cm<sup>-1</sup> region. In the previous paper,<sup>1</sup> we reported the IRA spectra of dimethyl ether (DME) adsorbed on Cu(110), Ag(110), and their atomic oxygen reconstructed surfaces. The spectral changes observed for DME with increasing exposure levels in the 3000–2800-cm<sup>-1</sup> region exhibit more complicated features compared to those in the 1500–800-cm<sup>-1</sup> region; this was interpreted as due to the Fermi resonance effect between the CH<sub>3</sub> stretching vibration and the overtone and/or combination bands of CH<sub>3</sub> deformation vibrations. Presumably, the formation of the saturation coverage state of MPE on Cu(110) results in slight frequency shifts of the CH<sub>3</sub> stretching and/or CH<sub>3</sub> deformation vibrations due to lateral interactions between the adsorbates. As in the case of DME on the substrates, these shifts are enhanced through the Fermi resonance to give the spectral changes observed for MPE on Cu(110) at the saturation coverage.

**IRA Spectra of MPE on Ag(110).** Figure 2 exhibits the IRA spectra of MPE adsorbed on Ag(110) at ca. 80 K with increasing amounts of exposure up to 1.0 L. The spectrum measured at the exposure level of 0.08 L gives the IRA bands at 1199, 1167, 1040, 948, and 879 cm<sup>-1</sup>; although these bands are not always observed clearly at the exposure of 0.02 L because of a low S/N ratio of the measurements (see the bottom line in Figure 2), they are observed reproducibly in repeated measurements. Upon an increase of the exposure to 0.16 L, the spectral features show explicit changes, giving new bands at 1205, 1133, 1120, 1105, 1049, 960, and 932 cm<sup>-1</sup> in addition to those observed at the exposure of 0.08 L. On further increase of the exposure,





**Figure 2.** IRA spectra of MPE adsorbed on Ag(110) measured at 80 K with an increasing amount of exposure. The number on the right-hand side of each spectrum indicates the amount of exposure in the Langmuir unit. The bottom dashed line shows a background spectrum. See text.

the new bands increase their intensity, while the 1199-, 1167-, 1040-, 948-, and 879- $\text{cm}^{-1}$  bands keep their intensity at the same level measured at 0.08 L. Presumably, the bands observed at the exposure of 0.08 L are ascribed to MPE forming a saturation coverage state and the bands observed at exposures above 0.16 L to the adsorbate in a multilayered state. Neither the 928- and 868- $\text{cm}^{-1}$  bands prominently observed for MPE on Cu(110) (see Figure 1) nor the 1214-, 1132-, 1098-, 960-, and 897- $\text{cm}^{-1}$  bands, which are characteristic of MPE in the TT form,<sup>3</sup> are present in the IRA spectrum measured at 0.08 L; then the TG, GG, and TT forms are ruled out as a possible rotational isomer for MPE forming the saturation coverage state on Ag(110). Actually, the 1199-, 1167-, 1040-, 948-, and 876- $\text{cm}^{-1}$  bands measured at the exposure level of 0.08 L correspond to the IR bands at 1205, 1151, 1042, 942, and 879  $\text{cm}^{-1}$ , which are observed for MPE in the liquid and glassy states and ascribed to the GT form.<sup>3</sup> (See Table 1.) Thus, MPE on Ag(110) at the saturation coverage takes on the GT form, contrasting the case of the adsorbate on Cu(110), where MPE exists in either the GG or the TG form. When the substrate temperature is increased after measuring the spectrum at the exposure of 1.0 L, the IR bands associated with the multilayered state begin to reduce their intensities around 110 K, leaving the spectral features due to the saturation coverage state, which finally disappears around 120 K. These results suggest that the GT form at the saturation coverage is in a thermodynamically stable state.

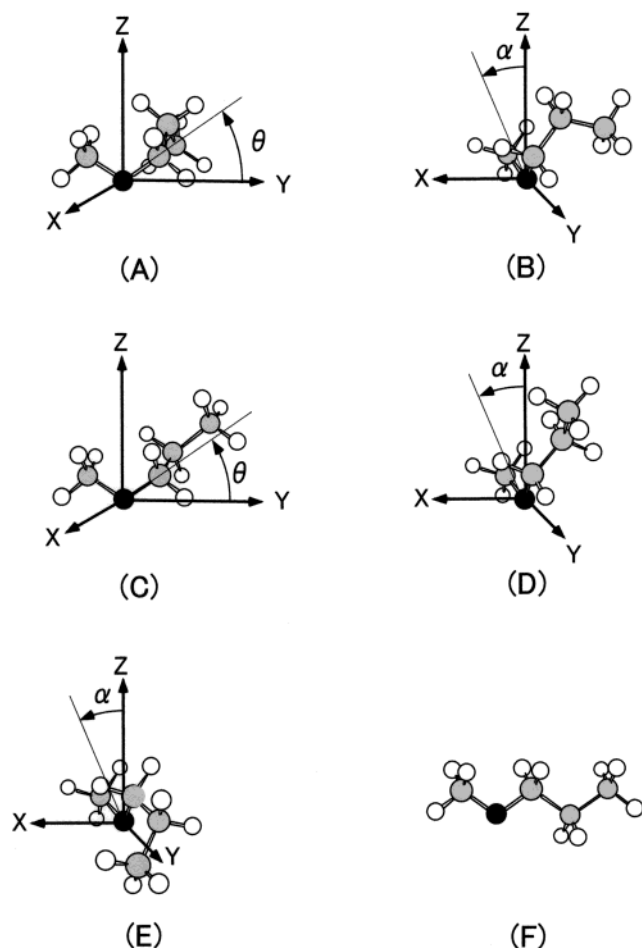
The IRA bands measured at exposure levels above 0.16 L are ascribable to the TG and TT forms; i.e., the IRA bands at 1205, 1120, 1049 and 932  $\text{cm}^{-1}$  correspond to the IR bands reported to be characteristic of the TG form<sup>3</sup> and the IRA bands at 1133 and 960  $\text{cm}^{-1}$  to the IR bands characteristic of the TT form.<sup>3</sup> The IRA spectrum measured at the exposure level of 1 L is similar to MPE in the glassy state, in which, according to Shimanouchi et al.,<sup>3</sup> the TT and TG forms coexist.

The IRA spectrum in the 3000–2800- $\text{cm}^{-1}$  region measured at 0.02 L gives the bands at 2943 and 2924  $\text{cm}^{-1}$ , and on increasing the exposure to 0.08 L (saturation coverage), the latter band decreases its intensity and new bands appear at 2892 and 2854  $\text{cm}^{-1}$ . Presumably, as in the case of MPE on Cu(110), lateral interactions between the adsorbates cause slight frequency

shifts in the  $\text{CH}_3$  symmetric stretching and/or the  $\text{CH}_3$  deformation vibrations, resulting in the spectral changes due to the Fermi resonance. The IRA spectra in the 3000–2800- $\text{cm}^{-1}$  region at the exposures above 0.16 L in Figure 2 gives the IRA bands at 2963, 2924, 2829, and 2806  $\text{cm}^{-1}$  in addition to those observed for the saturation state, which is due to the appearance of the TG and TT forms in the multilayered states.

**Comparison between the Observed and Calculated Frequencies for MPE in Various Isomeric Forms.** As mentioned above, the IRA spectra in the 1500–800- $\text{cm}^{-1}$  region indicate that MPE adsorbed on Cu(110) and that on Ag(110) at the saturation coverage state exist in either the GG or TG states and the GT state, respectively. To get more clear insights into the adsorption states, the DFT calculations were performed. The calculated frequencies and relative intensities in the 1300–800- $\text{cm}^{-1}$  region for MPE in the GG, GT, TG, and TT forms are listed in Table 1 together with the observed frequencies of IR bands of MPE in the crystalline state, where MPE takes on the TT form, and in the liquid and glassy states, where MPE takes the GG, GT, and TG forms.<sup>3</sup> From the table it is clear that the calculated frequencies and intensities reproduce the observed ones quite well. For example, the strongly observed IR bands at 1214, 1132, 1098, and 960  $\text{cm}^{-1}$  due to the TT form correspond to the calculated bands at 1210.1, 1138.7, 1110.9, and 959.0  $\text{cm}^{-1}$ , the calculated relative intensities of which give appreciably large values.

The frequencies of the IRA bands observed for MPE on Cu(110) and Ag(110) are compared with the calculated frequencies in Table 1. Each of the IRA bands observed for MPE on Cu(110) has the counterparts of the calculated bands both for the GG and TG forms; i.e., the 1204- $\text{cm}^{-1}$  band corresponds to the calculated frequencies at 1208.2  $\text{cm}^{-1}$  (GG and TG), the 928  $\text{cm}^{-1}$  band to those at 934.5 (GG) and 938.2  $\text{cm}^{-1}$  (TG), and the 868  $\text{cm}^{-1}$  band to those at 892.8 (GG) and 876.1  $\text{cm}^{-1}$  (TG). Thus, the normal frequency calculation cannot determine the rotational isomer of the adsorbate on Cu(110) either. On the other hand, the frequencies of the IRA bands observed for MPE at the saturation coverage state on Ag(110) correspond to the calculated frequencies for the GT form; i.e., the IRA frequencies at 1199, 1167, 1040, 948, and 876  $\text{cm}^{-1}$  correspond



**Figure 3.** Schematic representations of the GG (A,B), GT (C,D), TG (E), and TT (F) forms and the definition of the angles,  $\alpha$  and  $\theta$ , specifying the orientations. See text.

to the calculated ones for the GT form at 1213.5, 1157.0, 1024.5, 942.2, and 878.4  $\text{cm}^{-1}$ . Thus, the results of the DFT calculation confirms that the adsorbate on Ag(110) takes on the GT form at the saturation coverage.

**Simulation of the IRA Spectra of MPE on Cu(110) and Ag(110).** Figure 3 shows the schematic representations of the GG(A,B), GT(C,D), TG(E), and TT(F) forms. The orientation of each form on a metal surface can be expressed by angles,  $\theta$  and  $\alpha$ , successively, as shown for the cases of the GG and GT forms in Figure 3; the XYZ axes in the figure are defined with the XY plane parallel to the metal surface and the Z axis perpendicular to the surface. The initial orientation is defined so that the COC plane of each form is in the YZ plane with the O—CH<sub>2</sub> bond along the Y axis. The angle  $\theta$  is the rotation angle of the O—CH<sub>2</sub> bond away from the Y axis keeping the COC plane in the YZ plane, and the angle  $\alpha$  is defined by the angle between the COC plane and the YZ plane.

The simulation of the IRA spectra of the GG, TG, and GT forms on a metal surface was performed by changing the  $\theta$  angle from 0 to 90° and the  $\alpha$  angle from -60 to 60° at the interval of 30°; the regions of the  $\theta$  and  $\alpha$  values are chosen so that the oxygen atom of the adsorbate can interact with the surface metals through the coordination. The results of simulation for the  $\theta$  values except for  $\theta = 30^\circ$  with any values of  $\alpha$  cannot reproduce the IRA spectra in Figures 1 and 2. (The frequencies and relative intensities of the IRA bands marked by gray color in the IRA spectrum measured for MPE on Cu(110) at 0.14 L and the spectrum for MPE on Ag(110) at 0.08 L are compared the results of the simulation.) So, assuming the  $\theta$  value to be

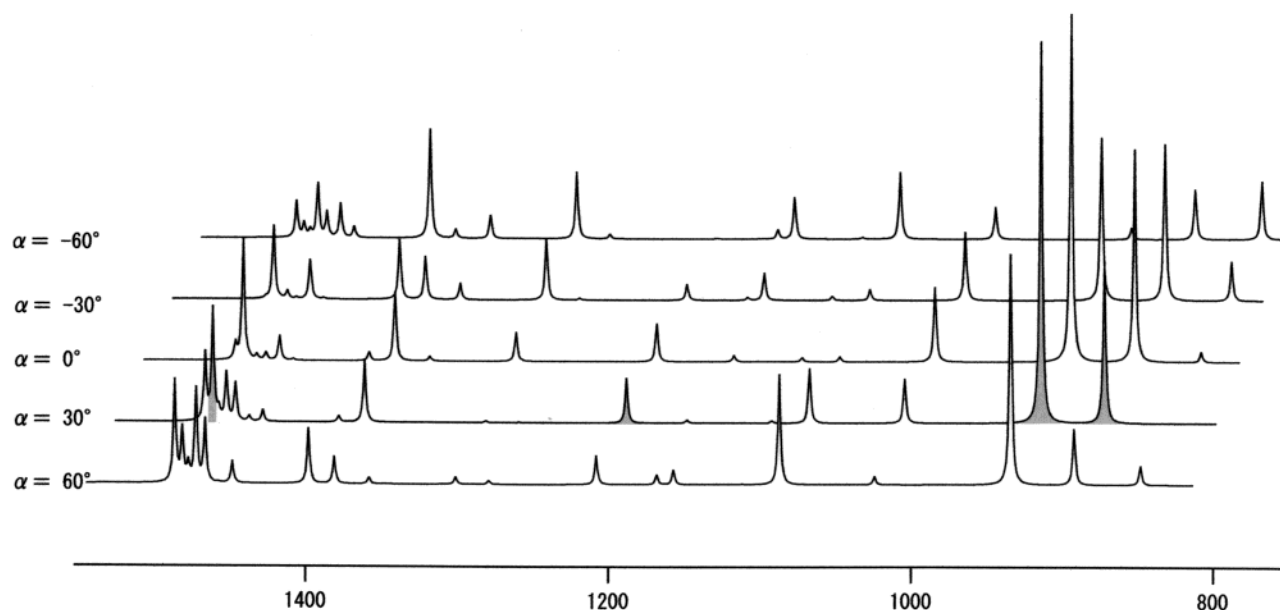
30°, the simulations were performed for the GG, TG, and GT forms, the results of which are shown in Figures 4, 5, and 6, respectively.

From Figure 4 it is clear that the simulated spectrum for MPE in the GG form with the orientation angle of  $\alpha = 30^\circ$  reproduces the observed IRA spectrum of MPE on Cu(110) at the saturation coverage much better than the simulated spectra for the adsorbate taking the other orientation angles. As can be seen from the calculated bands marked by gray color, the relative intensities of the calculated bands at 934.5 and 892.8  $\text{cm}^{-1}$  correspond to those of the observed bands at 928 and 868  $\text{cm}^{-1}$  and the intensities of the calculated bands at 1481.4 (not listed in Table 1) and 1208.2  $\text{cm}^{-1}$  correspond to the observed IRA bands at 1457 and 1204  $\text{cm}^{-1}$ . The calculated spectrum predicts the appearance of the bands at 1398.5 (not listed in Table 1), 1087.2, and 1024.8  $\text{cm}^{-1}$ , which are not clearly discernible in the IRA spectrum at 0.14 L in Figure 1. This may be due to the low S/N ratio of the measured spectrum. On the other hand, the results of simulation for the TG form in Figure 5 do not reproduce the observed spectra of MPE on Cu(110); e.g., the intensity ratios of the calculated bands at 938.2 and 876.1  $\text{cm}^{-1}$ , which are the counterparts of the observed IRA bands at 928 and 868  $\text{cm}^{-1}$ , do not correspond to the observed ratio, and the calculated bands at 1051.8 and 915.3  $\text{cm}^{-1}$  with appreciable intensities do not have any counterparts in the IRA spectrum. Thus, the spectral simulation indicates that MPE on Cu(110) at the saturation coverage state exists in the GG form taking the orientation with the orientation angles of  $\theta$  and  $\alpha$ , both of which are approximately equal to 30°.

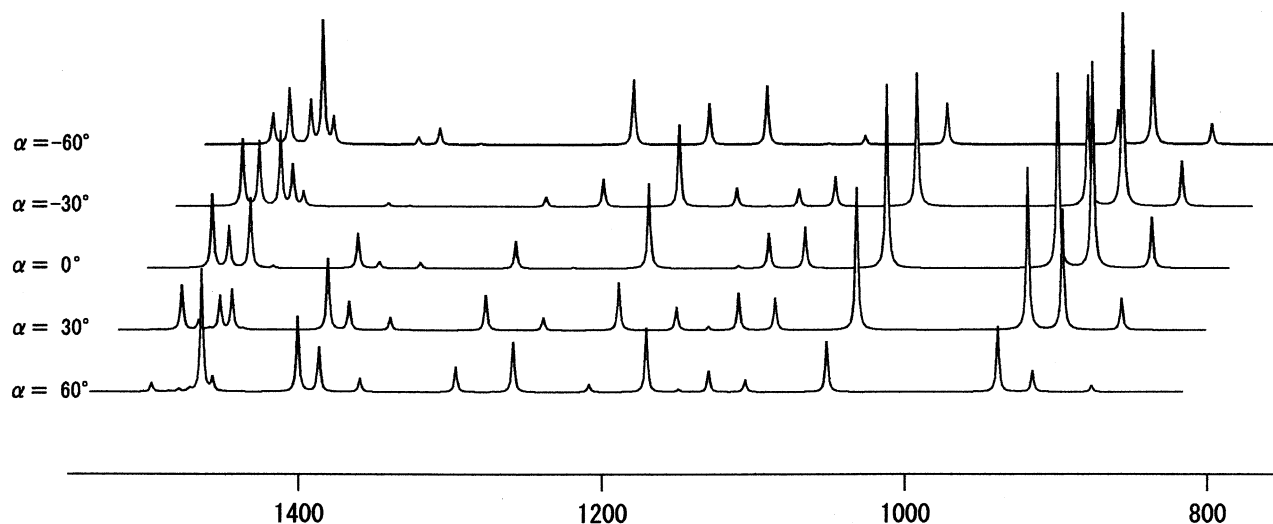
The results of the spectral simulation for MPE in the GT form in Figure 6 indicate that only the spectrum simulated for the orientation angle of  $\alpha = -30^\circ$  predicts all the observed bands in the 1200–850- $\text{cm}^{-1}$  region; i.e., the calculated bands at 1213.5, 1157.0, 1024.5, 942.2, and 878.4  $\text{cm}^{-1}$  (marked by gray color in Figure 6) correspond to the IRA bands at 1199, 1167, 1040, 948, and 876  $\text{cm}^{-1}$  in the IRA spectrum at 0.08 L in Figure 2. In the calculated spectra for other  $\alpha$  values, at least one of the calculated bands exhibit too little intensity to be compared with the result of observation; e.g., in the calculated spectrum for  $\alpha = -60^\circ$ , the band corresponding to the observed one at 1040  $\text{cm}^{-1}$  is missing and in each of the calculated spectra for  $\alpha = 0$ –60° the band corresponding to the observed one at 1167  $\text{cm}^{-1}$  predicts too little intensity. In addition, the calculated spectra for  $\alpha = 30$  and 60° predict the bands at 1100.8  $\text{cm}^{-1}$ , which are absent in the observed spectrum. The calculated spectrum for  $\alpha = -30^\circ$ , however, predicts the 942.2  $\text{cm}^{-1}$  band, the intensity of which is too large for the observed intensity. Despite this fact, which exhibits the inaccuracy at the present level of the DFT calculation, the results of the simulation indicate that MPE on Ag(110) exists in the GT form with  $\theta$  and  $\alpha$ , which are approximately equal to 30 and  $-30^\circ$ , respectively. The orientations of the adsorbates on Cu(110) and Ag(110) are schematically shown in Figure 7, parts C and D, respectively.

## Discussion

**The Spectral Simulation of the IRA Spectra and the Rotational Isomerism and Orientation of MPE on Ag(110) and Cu(110).** As can be seen from Table 1, most of the frequencies of the IRA bands ascribable to the GG and GT forms of MPE coincide well with those of the corresponding IR bands in the liquid or glassy states, indicating that the molecular force fields determining the vibrational frequencies of MPE in the GG and GT forms are not strongly perturbed by the adsorption



**Figure 4.** Calculated IRA spectra of MPE in the GG form with varying orientations as defined by the angle  $\alpha$  in the insert and  $\theta = 30^\circ$  on a metal surface. See text.

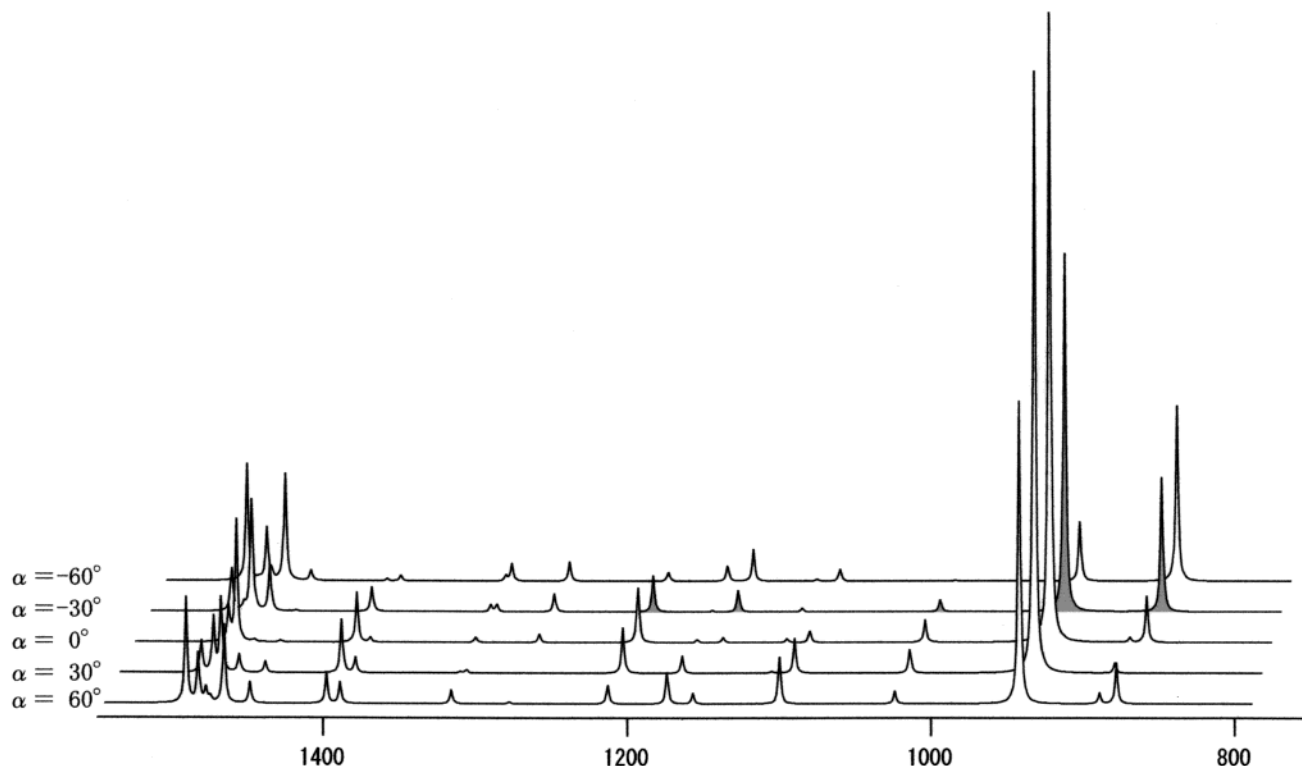


**Figure 5.** Simulated IRA spectra of MPE in the TG form with varying orientations as defined by the angle  $\alpha$  in the insert and  $\theta = 30^\circ$  on a metal surface. See text.

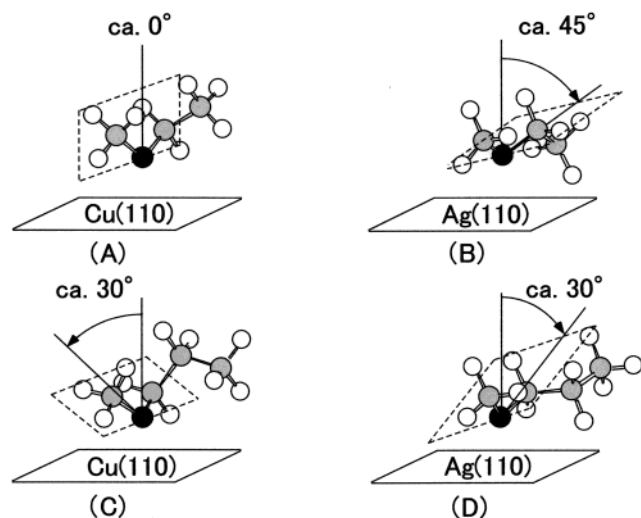
process. In this case, the frequencies and transition moments calculated by the DFT calculation analyses based on the B3LYP/6++31G\*\* level performed on MPE in the GG and GT forms are expected to give reliable information with regard to the frequencies as well as the intensities of the IRA bands. Actually the calculated frequencies of MPE in the GG and GT forms are in good agreement with the observed IRA frequencies of MPE on Cu(110) and Ag(110), respectively, and the calculated spectrum for the GG form with the orientation angles of  $\theta = 30^\circ$  and  $\alpha = 30^\circ$  and that for the GT form with the angles of  $\theta = 30^\circ$  and  $\alpha = -30^\circ$  reproduce the observed IRA spectra of the adsorbates on Cu(110) and Ag(110), respectively. Although the TG form is one of the possible isomers on Cu(110), the simulation for the isomer does not give any spectra corresponding to the observed IRA spectrum, which allows us to rule out the TG form as the isomer on the substrate. The simulated spectra, however, predict several bands with appreciable intensity, which are not discernible in the observed IRA spectra. This may be ascribable to the inaccuracy in the present level of the DFT calculation and/or to the low S/N ratio of the spectral

measurement to detect the corresponding IRA bands. So, the determined orientation angles for the adsorbates on Cu(110) and Ag(110) should be taken to be within the error of  $\pm 15^\circ$ . Despite these facts, the results of the present study and those of the previous ones<sup>1,2</sup> prove that the analyses of the IRA spectra based on the DFT calculation is one of the most efficient methods to elucidate the adsorption structures of organic molecules on metal surfaces, where adsorbate–substrate interactions are not so large to hamper the application of the calculated frequencies and transition moments of the molecules in isolated states to the spectral simulation.

**Factors Determining the Rotational Isomers and the Orientations of the Adsorbates.** Figure 7 exhibits schematically the rotational isomers and the orientations of MEE (A, B) and MPE (C, D) on Cu(110) and Ag(110). Although the lateral interactions between the adsorbates at the saturation coverage state cannot be neglected, as can be seen from the spectral changes in the  $3000\text{--}2800\text{-cm}^{-1}$  region, the orientations of MPE on the substrates remain virtually identical at sub-monolayer and saturation coverage states. Then, the rotational isomerism



**Figure 6.** Simulated IRA spectra of MPE in the GT form with varying orientations as defined by the angles, SD, in the insert on a metal surface. See text.



**Figure 7.** Schematic representations of the rotational isomers and the orientations of MEE and MPE on Cu(110) and Ag(110). (A) MEE in the G form on Cu(110), (B) MEE in the T form on Ag(110), (C) MPE in the GG form on Cu(110), and (D) MPE in the GT form on Ag(110).

and the orientation of the adsorbates are mainly determined by the following factors: (i) enthalpy difference between the isomeric forms; (ii) coordination interaction between the oxygen atom of the ethers and the surface metals; and (iii) repulsive and/or attractive interactions between atoms and/or groups within the adsorbates and metal surfaces. As for the factor (i), it has been known that the T form of MEE in the gaseous state is more stable than the G form with the enthalpy difference of 5.65 kJ/mol.<sup>8</sup> Although the enthalpy differences between the rotational isomers of MPE have not been determined yet, MPE in the crystalline state takes only the TT form, suggesting that the TT form is thermodynamically the most stable.<sup>3</sup> The DFT

calculation based on the 6-311++G\*\* level in the present study indicates that the order of the stability in terms of the total energy of each conformer is as follows; TT > TG (1.24 kJ/mol) > GT (7.52 kJ/mol) > GG (8.12 kJ/mol). (The numbers in the parentheses indicate the total energy relative to the energy of the TT form.) Thus, the DFT calculation also indicates that the TT form is the most stable, while the GG form is the most unstable, the energy difference between the two forms is about 8 kJ/mol. The TT form, however, does not exist at the submonolayer and saturation coverage states of MPE on Cu(110) and Ag(110), which means that the enthalpy factor i does not play important role in determining the rotational isomerism and orientation of MPE on the substrates. According to the IRA study on dimethyl ether (DME) and MEE adsorbed on Cu(110) and Ag(110),<sup>1,2</sup> the coordination interaction between the oxygen atom of the adsorbates and the surface metals is one of the stabilizing factors, the interaction on Cu(110) being stronger than that on Ag(110). As can be seen from Figure 7, parts A and C, the G form of MEE and the GG form of MPE is the most favorable for the coordination interaction, indicating that the factor ii plays an important role in determining the adsorption structures on Cu(110). The COC plane in the G form of MEE on Cu(110) is almost perpendicular to the surface, which has been explained due to the fact that the adsorbate forms a bridging coordination bond between the oxygen and the surface atoms,<sup>2</sup> as in the case of DME adsorbed on Cu(110) at submonolayer coverage states.<sup>1</sup> On the other hand, the COC plane of the MPE in the GG form on Cu(110) tilts away from the surface normal by about 30° in order to reduce the repulsive interaction between the CH<sub>3</sub>(-CH<sub>2</sub>) group and the substrate surface; i.e., if the GG form were in the perpendicular orientation, the distance between the CH<sub>3</sub> group and the surface would be too close to keep the orientation. To reduce the repulsive interaction, however, the GT form would be more favorable than the GG form. Presumably, there is an attractive



interaction between the CH<sub>3</sub> group and the substrate surface at a proper distance between them, resulting in the formation of the GG form. As the methyl (or alkyl groups in general) group approaches the surface at a certain distance, a correlation arises between the instantaneous dipole fluctuations present both in the metal and the methyl group, causing the attractive (or van der Waals) force. According to Wetterer et al.,<sup>9</sup> the adsorption energies of simple alkanes such as methane, ethane, and butane on Au(111) are 14.5, 24.1, and 40.5 kJ/mol, respectively. These values are large enough to compensate for the energy difference between the GG and GT forms. Thus, the orientation and the rotational isomerism of MPE on Cu(110) are determined mainly by the balance between the coordination interaction (factor ii) and the attractive interaction (factor iii), although the former is more important than the latter.

MEE on Ag(110) exists in the T form, indicating that factor i plays an important role in the rotational isomerism. As can be seen from Figure 7B, one of the lone pair electrons of the oxygen atom participates in the coordination interaction. The COC plane of MPE in the GT form on Ag(110) tilts away from the surface normal in the direction opposite to that of MPE on Cu(110), resulting in the orientation of the propyl group more or less parallel to the Ag(110) surface. (See Figure 7D). The orientation is more favorable for the attractive interaction between the alkyl group and the surface (factor iii) than the orientation of MPE in GG form on Cu(110). Then, in the case of MEE and MPE on Ag(110), where the coordination interaction is relatively weak, factor i (for MEE) and factor iii (for MPE) play more important roles than factor ii in determining the rotational isomerism and orientation of the adsorbates.

## Conclusion

Comparison between the IR spectra of MPE characteristic of the GG, GT, TG, and TT forms in the bulk states and the IRA spectra of MPE adsorbed on Cu(110) and Ag(110) at the saturation coverage suggests that MPE on Cu(110) takes either the GG form or the TG form on Cu(110) and that the adsorbate on Ag(110) the GT form. The result of the IRA spectral simulation performed by the B3LYP/6-311++G\*\* method, however, ruled out the TG form as the isomer on Cu(110). The

simulation indicated also that (1) MPE in the GG form on Cu(110) takes the orientation with the COC plane tilted about 30° from the surface normal (Figure 7C) and (2) MPE in the GT form on Ag(110) the orientation with the COC plane tilted by about 30° in the direction opposite to that of the GG form on Ag(110) (Figure 7D). The adsorption structures of MPE on Cu(110) and Ag(110) are mainly determined by the balance between the coordination interaction between the oxygen atom and surface atoms and the attractive interaction between the alkyl groups and the surfaces, the former being more important than the latter on Cu(110) and vice versa on Ag(110). The simulation of the IRA spectra based on the DFT calculation has proved to be one of the efficient methods to determine the adsorption states (rotational isomeric form and orientation) of simple organic molecules such as MPE and MEE on metal surfaces.

## References and Notes

- (1) Kiyohara, T.; Akita, M.; Ohe, C.; Itoh, K. *J. Phys. Chem. B* **2002**, *106*, 3469.
- (2) Kiyohara, T.; Shinohara, H.; Kasahara, T.; Okubo, R.; Itoh, K. *J. Phys. Chem. B* **2003**, *107*, 5008.
- (3) Shimanouchi, T.; Ogawa, Y.; Ohta, M.; Matsuura, H.; Harada, I. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2999.
- (4) Akita, M.; Hiramoto, S.; Osaka, N.; Itoh, K. *J. Phys. Chem. B* **1999**, *103*, 10189.
- (5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Gaussian, Inc.: Pittsburgh, PA, 1998.
- (6) Matsuura, H.; Yoshida, H. *Handbook of Vib. Spectrosc.*; 2001; Vol. 3, S4203.
- (7) Greenler, G. R. *J. Chem. Phys.* **1966**, *44*, 310.
- (8) Perchard, J. P. *Spectrochim. Acta* **1970**, *26A*, 707.
- (9) Wetterer, S. M.; Lavrich, D. J.; Cummings, T.; Bernasek, S. L.; Scoles, G. *J. Phys. Chem. B* **2000**, *102*, 9266.