Infrared Reflection−Absorption Spectroscopic Study on the Adsorption Structures of 1,3-Butadiene at Au(111) and Ag(111) Surfaces

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Infrared reflection−absorption spectroscopy (IRAS) was applied to study the adsorption structures of 1,3-butadiene on Au(111) and Ag(111) in the temperature range from 25 to 95 K. On increasing exposures from 0.01 to a few langmuirs (langmuir = 10^{-6} Torr·s) at 40 K, the adsorbates on both substrates take on discrete adsorption states, as clearly probed by IR bands associated with CH_2 twisting ($\tau(CH_2)$) and CH_2 wagging ($\omega(CH_2)$) modes. The frequencies of these bands indicated that the adsorbates are weakly π-bonded to the substrates. At low exposures (0.04−0.2 langmuir) 1,3-butadiene on both substrates takes an s-trans form and occupies two kinds of adsorption sites; the adsorbate at one site (α-state) gives rise to the $\omega(CH_2)$ band at 916 cm^{-1} on Au(111) and at 908 cm^{-1} on Ag(111), and the adsorbate at another site (β-state) gives the $\omega(CH_2)$ band at 908 cm^{-1} on Au(111) and at 905 cm^{-1} on Ag(111). The adsorbate in the α-state, which lies parallel to the substrate surfaces, is predominant at a lower temperature (25−30 K), and upon raising the temperature up to 90 K, the α-state is partially converted to the β-state. The conversion accompanies a tilting of the molecular plane, keeping the C=C bonds parallel to the surfaces. The enthalpy difference between the α- and β-states on Ag(111) was estimated to be about 170 J/mol. At 0.3−0.5 langmuir the adsorbates saturate on the surfaces, giving the $\tau(CH_2)$ and $\omega(CH_2)$ bands at 1005 and 914 cm^{-1} on Au(111) and at 1002 and 906 cm^{-1} on Ag(111). When the exposure is increased further (1−4 langmuirs), the adsorbates on both substrates form ordered multilayers, giving doulets bands at 1022 and 1016 cm^{-1} for the $\tau(CH_2)$ band and those at 920 and 916 cm^{-1} for the $\omega(CH_2)$ band. Both the monolayer coverage and the multilayered states mainly consist of the s-trans form. A second conformer (s-cis or gauche form) was found to exist only in a few monolayers which exist between the monolayer coverage state and the multilayered state.

Introduction

Infrared reflection−absorption spectroscopy (IRAS) has been applied to study the chemisorption structures of organic molecules such as ethylene[1−5] and formic acid[6−8] on transition metals. On the other hand, IRAS has been applied only a little to the study of physisorption structures of the adsorbates on inert substrates, such as graphite, silver, and gold surfaces,[9−13] where adsorbate−substrate interactions are due to weak chemical interactions as well as electrostatic and dispersive or van der Waals interactions. These interactions are of crucial importance for association−dissociation equilibria, surface diffusion and migration processes, and self-assembling process at two-dimensional surfaces.[14,15] In the previous paper we applied IRAS to study the adsorption structures of acrolein at an evaporated gold film as well as at an Au(111) surface under ultrahigh-vacuum conditions.[13] The results indicated that the adsorbate on Au(111) takes discrete adsorption states successively with increasing exposure, i.e., an isolated state, associated states with a two-dimensional arrangement, a monolayer coverage state, and an ordered multilayered state. Each state gives characteristic IR bands in the CH and CH_2 out-of-plane bending vibration regions, providing direct clues to elucidate lateral interactions between the adsorbates as well as interlayer interactions between the layered adsorbates.[13] In the present paper we measured the exposure dependence of the IR spectra of 1,3-butadiene adsorbed on Au(111) and Ag(111) in the temperature range 25−95 K. If we neglect a deviation from

the planality of the ethylenic moiety caused by adsorbate−substrate interactions, we can consider three kinds of conformations as possible adsorption geometries, i.e., planar s-trans (C_{2h}) and s-cis (C_{2v}) forms and a nonplanar gauche form (C_2, see Figure 1). The geometry of the most stable conformer has shown to be s-trans for gaseous and Ar-matrix states.[16,17] An analysis of the torsional vibration[18] of 1,3-butadiene indicated that the enthalpy difference between the s-trans form and a less stable one (s-cis or gauche) is 13.1 kJ/mol. So questions addressed by the present paper are 2-fold. First, what kind of conformer of 1,3-butadiene is stabilized on adsorption to the substrates? Second, do the adsorption structures of 1,3-butadiene exhibit discrete changes such as those observed for acrolein on Au(111) and Ag(111)? The results of the this paper present explicit answers to the questions, giving a general view of adsorption characteristics of 1,3-butadiene on relatively inert substrates such as the Au(111) and Ag(111) surfaces.

Experimental Section

Materials. 1,3-Butadiene was purchased from Takachiho Chemicals Co. Ltd. The sample was proved to have the purity larger than 99.9% by gas chromatography and used without further prurification.

Preparation of Substrates. The Au(111) and Ag(111) surfaces were prepared following the procedure already reported.[13] Briefly, a thick film of gold (or silver) was evaporated on a mica sheet (10 × 20 mm), which was cleaved just before

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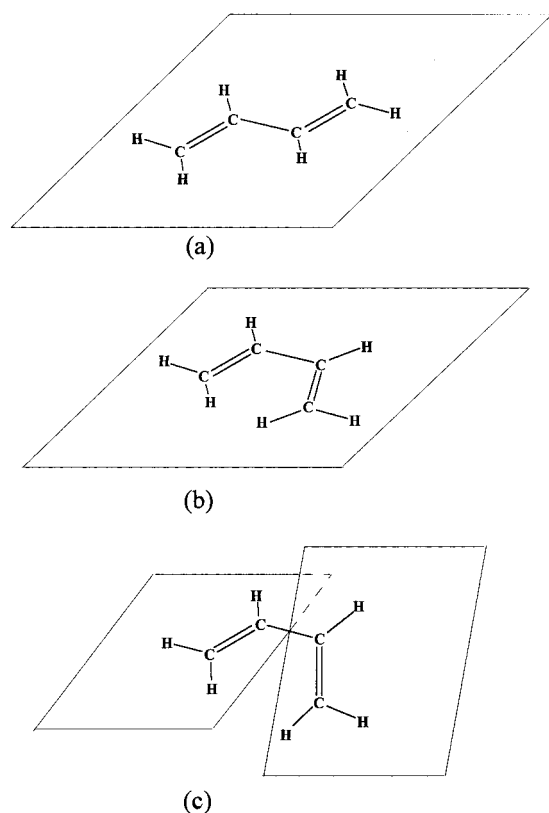
Figure 1. Possible conformers of 1,3-butadiene: (a) s-trans (C_{2h}) form, (b) s-cis (C_{2v}) form, (c) gauche (C_2) form.

Figure 2. Exposure dependence of the IR spectra of 1,3-butadiene on Au(111) at 40 K. The number at the right-hand side of each spectrum indicates the exposure. The vertical line indicates a scale for the ordinate of the spectra. The spectra in the 3150−2950 cm^{-1} region are shown by multiplying their ordinates by 7.5.

the evaporation, keeping the temperature of the sheet at 600 K. The film of gold (or silver) was annealed at 700 K for 48 h. Both films gave LEED patterns characteristic of the (111) surface. An AFM observation indicated that the surface of the Au(111) film consists of terraces with an average area of 4000 × 4000 Å^2.

Measurement of IR Spectra. The apparatus used to record the IR spectra was virtually the same as that already reported.[9,10,13] In the present study, however, a closed cycle helium cryostat (Iwatani Cryo. Co. Ltd., model D-3) was added to keep the substrate temperature in the range 25−95 K. The base pressure of the UHV chamber was kept under 1 × 10^{-10} Torr. The IR spectra were recorded in a single reflection mode at an incidence angle of 80° with a liquid nitrogen cooled MCT detector. All the spectra were given by −log(R/R_0) as a function of wavenumbers in the 4000−750 cm^{-1} region, where R and R_0 indicate measured reflected intensities of the IR beam from a substrate with and without an adsorbate, respectively. Each reflected intensity was recorded by adding 1000 scans at the resolution of 4 cm^{-1}. Exposure of the sample to the substrates was performed through a variable leak valve positioned at a distance of 2 cm from the substrates. The amount of the exposure was expressed by uncorrected langmuir units (1 langmuir = 1 × 10^{-6} Torr·s).

Results and Discussion

IR Spectra of 1,3-Butadiene on Au(111). Figure 2 illustrates the coverage dependence of the IR spectra observed for 1,3-butadiene on Au(111) at 40 K.[19] The spectra show appreciable changes in the 3088−2972, 1022−1005, and 920−908 cm^{-1} regions. The analyses of the IR and Raman spectra of 1,3-butadiene performed by Furukawa et al.[20] indicates that the IR bands observed in the 3088−2972 cm^{-1} region are
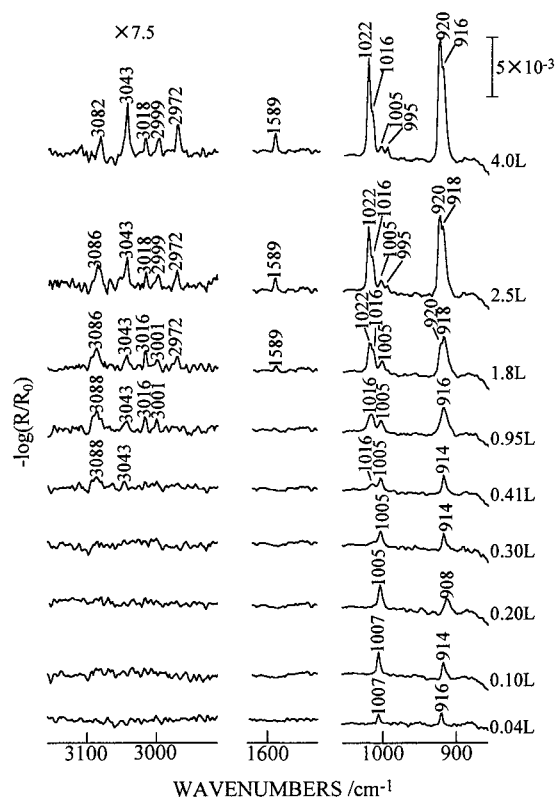
ascribable to CH and CH$_2$ in-plane stretching vibrations, those in the 1022−1005 cm^{-1} region to a CH$_2$ twisting mode coupled with a CH bending vibration (hereafter, it is designated τ(CH$_2$) for simplicity), and those in the 920−908 cm^{-1} region mainly to a CH$_2$ out-of-plane wagging mode (ω(CH$_2$)). In the case of the gauche form (see Figure 1), which does not have a molecular symmetry plane, the "in-plane" means atomic displacements within a plane of the ethylenic moiety and "out-of-plane" means the displacements perpendicular to the plane. The IR bands at 1589 and 995 cm^{-1}, which appear at exposures larger than 1.8 langmuirs, are due to C=C stretching (ν(C=C)) and in-plane CH$_2$ rocking (ρ(CH$_2$)) vibrations, respectively.[20]

Adsorption Structures on Au(111) at Exposures below 0.3 langmuir. Among three kinds of possible conformers in Figure 1, the s-trans form is thermodynamically the most stable, and the IR spectrum of 1,3-butadiene in a low-temperature argon matrix prepared by passing the sample through a nozzle at a room temperature consists mainly of bands ascribable to the s-trans form, while the spectrum of 1,3-butadiene in the Ar matrix prepared by using a nozzle at an elevated temperature (e.g., 800 °C) gives IR bands ascribable to a less stable conformer (s-cis or gauche) in addition to the bands due to the s-trans form.[17,20] Furukawa et al.[20] performed detailed normal coordinate analyses on 1,3-butadiene with the s-trans, s-cis, and gauche forms and assigned the IR bands associated with the s-trans form. In addition, the authors reported that the calculated normal frequencies for the gauche form give better fit with the additional IR bands than those for the s-cis form, concluding that the second conformer takes on a nonplanar gauche form. The s-trans form in the Ar matrix gives rise to the τ(CH$_2$) and ω(CH$_2$) bands at 1022 (a$_u$) and 905 cm^{-1} (a$_u$), respectively, while the second conformer gives the τ(CH$_2$) bands at 983 and

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TABLE 1: Comparison of the $\tau(CH_2)$ and $\omega(CH_2)$ frequencies (cm^{-1}) Observed for 1,3-Butadiene Adsorbed on Au(111) and Ag(111) in Various States (See Text) with the Corresponding Frequencies of 1,3-Butadiene in an Argon Matrix State

	Au(111)		Ag(111)	
	$\tau(CH_2)$	$\omega(CH_2)$	$\tau(CH_2)$	$\omega(CH_2)$
α-state	1007	916	1007	908
β-state	1005	908	1005	905
monolayer coverage state	1005	914	1002	906
multilayers in an ordered state	1016, 1022[a]	916, 920[a]	1016, 1022[a]	914, 922[a]
Ar matrix[b]	1022	905		

[a] Doublet bands. [b] Data taken from ref 20.

996 cm^{-1} and the $\omega(CH_2)$ bands at 915 and 914 cm^{-1}. If 1,3-butadiene takes on the s-cis form, the 983 and 915 cm^{-1} bands belong to the a$_2$ species and the 996 and 915 cm^{-1} bands to the b$_2$ species, while, if the sample takes the gauche form, the former set of bands are classified to the a species and the latter to the b species.

Figure 2 indicates that at exposures smaller than 0.3 langmuir the adsorbate gives rise to a single peak due to the $\tau(CH_2)$ mode at 1007−1005 cm^{-1} and that due to the $\omega(CH_2)$ mode at 916−908 cm^{-1}. The frequencies of the $\tau(CH_2)$ and $\omega(CH_2)$ bands are close to those observed for *s-trans*-1,3-butadiene in the Ar matrix (1022 and 905 cm^{-1}), suggesting that the adsorbate on Au(111) at the lower exposures take on mainly a structure similar to the s-trans form with the C_{2h} symmetry. From Figure 2 it is also clear that the adsorbate at the lower exposures exhibits neither IR bands due to in-plane stretching modes of the C=C, CH, and CH$_2$ groups nor those due to in-plane bending modes of the CH and CH$_2$ groups. These spectral features should be interpreted in terms of a site (or local) symmetry assumed by the adsorbate on the substrate. A coupling of one of the in-plane vibrations of the adsorbate itself with an adsorbate−substrate mode such as a C=C···Ag stretching vibration may cause a transition moment component parallel to the surface normal of the substrate, resulting in the appearance the in-plane vibration in the IRAS spectrum. This has been actually observed for a di-σ-complex of ethene on Ni(111).[2] In the case of 1,3-butadiene on Au(111), however, the coupling of the in-plane vibration with the adsorbate−substrate mode can be neglected, because the adsorbate−substrate interaction is small, as deduced from the small frequency shifts of the IRAS bands due to the $\tau(CH_2)$ and $\omega(CH_2)$ modes compared to the corresponding bands observed for the Ar matrix. Then, according to the surface selection rule,[21] we interpreted the absence of the IR bands assigned to the in-plane modes in Figure 2 as due to a flat orientation of the s-trans adsorbate on the substrate surface. On the basis of these results, we concluded that the adsorbate at the lower exposures (0.04−0.30 langmuir) takes on mainly the s-trans form lying nearly flat on Au(111).

As can be seen from Figure 2, the 1007 ($\tau(CH_2)$) and 916 cm^{-1} ($\omega(CH_2)$) bands observed at the lowest exposure (0.04 langmuir) shift to 1005 and 908 cm^{-1}, respectively, upon increasing the exposure to 0.20 langmuir.[22] At the exposure of 0.30 langmuir the $\omega(CH_2)$ band appears at 914 cm^{-1}, while the $\tau(CH_2)$ band remains at 1005 cm^{-1}. On subsequent increase of the exposure (0.41−4.0 langmuirs) the intensities of the 1005 and 914 cm^{-1} bands remain almost constant, indicating that these bands are ascribable to *s-trans*-1,3-butadiene forming a monolayer coverage on the substrate. (The constant intensity of the 914 cm^{-1} band at exposures larger than 0.30 langmuir is not clear from the spectra measured at 0.41−4.0 langmuirs. It can be proved, however, by a curve resolution procedure, the result of which is not shown in this paper.)

The 1007 ($\tau(CH_2)$) and 916 cm^{-1} ($\omega(CH_2)$) bands observed at the lowest exposure (0.04 langmuir) are ascribable to the

adsorbate occupying an isolated site (abbreviated to α-state), since there should be no lateral interaction between the adsorbates at the exposure level. In Table 1 the frequencies of the IR bands due to $\tau(CH_2)$ and $\omega(CH_2)$ in various adsorption states are summarized together with the corresponding frequencies observed for 1,3-butadiene in an argon matrix.[20] From the table it is clear that the $\tau(CH_2)$ frequency for the α-state is lower than that observed for the argon matrix ($\Delta\nu = -15$ cm^{-1}), while the $\omega(CH_2)$ frequency for the adsorbate is higher than that for the argon matrix ($\Delta\nu = +11$ cm^{-1}). These frequency shifts observed for the CH$_2$ group adjacent to the C=C bonds indicate the existence of a weak π-bonding interaction between the adsorbate and the Au(111) surface, as observed for the CH$_2$ wagging vibrations of olefins on Ag(110).[23]

As already explained, the $\tau(CH_2)$ and $\omega(CH_2)$ bands for the α-state shift their frequency to 1005 and 908 cm^{-1}, respectively, upon increasing the exposure (0.04 → 0.20 langmuir) in Figure 2. Frequency shifts of adsorbates induced by coverage increase have been extensively studied for CO adsorbed on transition metals[24] and explained in terms of two factors, i.e., a chemical shift,[25] due to changes in substrate−adsorbate bonding, and a coupling shift,[26] due to electrodynamic interactions between the oscillating molecules. The coupling effects usually cause frequency increase upon increasing coverage, which does not conform to the results for the $\tau(CH_2)$ and $\omega(CH_2)$ bands. It thus seems likely that the main reason is ascribable to the first factor and that the adsorbate in the α-state is converted to another adsorption site in which the adsorbate−substrate bonding interaction is slightly different from that of α-state. Hereafter, the new adsorption state is called the β-state. From Figure 2 (0.10−0.20 langmuir) it is clear that the intensities of the $\tau(CH_2)$ and $\omega(CH_2)$ bands remain almost constatnt during the α- to β-state conversion. This result suggests that the molecular plane of *s-trans*-1,3-butadiene in the α-state is parallel to the Au(111) surface, while that in the β-state tilts the molecular plane to a certain extent, keeping the C=C bonds parallel to the surface. This tilting should cause the appearance of the $\rho(CH_2)$ band. This band, however, could not be observed, which may be ascribable to its low intensity. The conversion between the two states was studied further by measuring the temperature dependence of the IR spectra at lower coverages, as will be explained in a following section.

When the adsorbates saturate on the surface, lateral adsorbate−adsorbate interactions may alter the adsorbate−surface registry, resulting again in the change of adsorbate−substrate bonding to increase the $\omega(CH_2)$ band from 908 to 914 cm^{-1} (see Table 1). The fact that the $\tau(CH_2)$ and $\omega(CH_2)$ bands do not show appreciable intensity change during the conversion from the β to monolayer coverage state, as can be seen from Figure 2 (0.20−0.30 langmuir), indicates that there occurs a further tilting of the molecular plane with the C=C bonds parallel to the substrate surface.

It is certain that some fraction of the thermodynamically less stable isomer is present in an initially dosed sample. So there

may be two factors to explain why the adsorbate gives only the IR bands due to the s-trans form at the lower exposures. First, the intensities of the bands due to the less stable isomer are too small to be detected, even if the adsorbate contains the isomer. Second, an interaction with the substrate assists the less stable isomer to overcome an enthalpy barrier between the isomer and the s-trans one, resulting in the conversion from the less stable isomer to the s-trans one during the adsorption process. The true reason, however, remains unknown.

Adsorption Structures on Au(111) at Exposures from 0.41 to 0.95 langmuir. In addition to the IR bands associated with the monolayer coverage, new bands appear at 1016 ($\tau(CH_2)$), 3088, and 3043 cm^{-1} at the exposure of 0.41 langmuir, and the intensities of these bands increase at 0.95 langmuir, where the corresponding $\omega(CH_2)$ band appears at 916 cm^{-1}. These band are ascribable to the adsorbates forming a overlayer on the top of the monolayer coverage on Au(111). The 3088 and 3043 cm^{-1} bands correspond the 3103 and 3062 cm^{-1} bands, respectively, which are observed for *s-trans*-1,3-butadiene in the Ar matrix and assigned to a CH_2 asymmetric stretching (ν_{as}-(CH_2), b_u) and CH stretching ($\nu(CH)$, b_u) modes, respectively.[20] In addition to these bands, the IR spectrum measured at 0.95 langmuir gives rise to bands at 3016 and 3001 cm^{-1}. 1,3-Butadiene in the less stable state (s-cis or gauche) should give rise to two IR bands due to $\nu(CH)$; i.e., the s-cis form gives the a_1 and b_1 modes and the gauche form the a and b modes. The IR spectrum of the Ar matrix gives one of the IR bands at 3014 cm^{-1},[20] which corresponds to the 3016 cm^{-1} band in the IR spectrum measured at 0.95 langmuir. The counterpart of the 3001 cm^{-1} band, however, has not been observed in the IR spectrum of the Ar matrix. Presumably the 3001 cm^{-1} band is ascribable to another one of the IR bands associated with the $\nu(CH)$ of the less stable or second form. Thus, the IR spectrum measured at 0.95 langmuir indicates that the overlayer consists of the s-trans and second forms. The appearance of the CH_2 and CH stretching bands of the s-trans form at exposures larger than or equal to 0.41 langmuir can be explained by considering that the molecular plane is more or less tilted from the parallel orientation, giving perpendicular components with respect to the surface normal to the transition moments associated with these bands. As already explained, the $\tau(CH_2)$ and $\omega(CH_2)$ bands are observed as a single peak at 1016 and 916 cm^{-1}, respectively, and these frequencies resemble those (1022 and 905 cm^{-1}, vide supra) observed for *s-trans*-1,3-butadiene in the Ar matrix, indicating that the bands are ascribable to the s-trans form. The reason for the absence of the $\tau(CH_2)$ and $\omega(CH_2)$ bands due to the second form may be explained as follows. If either the molecular plane of the s-cis form or the C_2 axis of the gauche form is perpendicular to the substrate surface, the transition moments of the $\tau(CH_2)$ and $\omega(CH_2)$ bands are parallel to the surface, resulting in the extinction of the IR bands in the surface spectra.[21] The second form may take a more or less perpendicular orientation. This is consistent also with the appearance of the 3016 and 3001 cm^{-1} bands associated with the $\nu(CH)$ modes.

Adsorption Structures on Au(111) at Exposures above 1.8 langmuir. At the exposure of 1.8 langmuirs the $\tau(CH_2)$ and $\omega(CH_2)$ bands (1016 and 916 cm^{-1}) of the s-trans form increase intensity and split to doublets; the former give the doublets at 1022 and 1016 cm^{-1} and the latter the doublets at 920 and 916 cm^{-1}. As explained below, the doublets are explained as due to a crystal field splitting, indicating that *s-trans*-1,3-butadiene forming a multilayer exists in an ordered or crystalline state. The $\nu(C=C)$ and $\rho(CH_2)$ bands appear at 1589 and 995 cm^{-1},
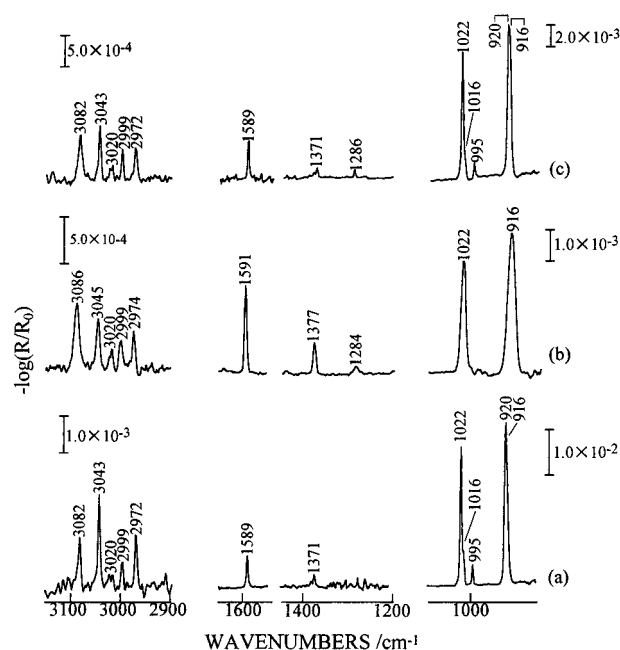
Figure 3. IR spectra measured at 40 K for (a) 1,3-butadiene (10 langmuirs) on a Au(111), (b) 1,3-butadiene (14 langmuirs) on an evaporated or polycrystalline silver film, and (c) the sample of (b) annealed at 95 K. The vertical lines at the left- and right-hand sides of the spectra indicate scales of the ordinates of the spectra in the 3150–2900 and 1650–900 cm^{-1} regions, respectively.

respectively, coincident with the doublets. These bands are the counterparts of the 1597 and 988 cm^{-1} bands, which are observed for the Ar matrix and assigned to the $\nu(C=C)$ and the $\rho(CH_2)$ mode of the b_u species of the s-trans form.[20] The IR spectrum in the CH and CH_2 stretching region measured at 1.8 langmuirs gives features similar to those observed at 0.95 langmuir, except for an IR band at 2972 cm^{-1}. This band is the counterpart of the 2986 cm^{-1} observed for the Ar matrix and assigned to a CH_2 symmetric stretching mode ($\nu_s(CH_2)$, b_u) of the s-trans form.[20] As can be seen from the IR spectra measured at 2.5 and 4.0 langmuirs in Figure 2, when the exposure is increased further, the IR bands associated with the s-trans form increase their intensities, while the intensities of the $\nu(CH)$ bands near 3016 and 3000 cm^{-1} associated with the second form (*s-cis* or gauche) remain almost constant. This result indicates that the second form is almost confined in a few monolayers, which exist between the monolayer on the substrate and the ordered multilayer.

In Figure 3 the IR spectrum (a) of 1,3-butadiene on Au(111) measured at the exposure of 10 langmuirs is compared with the spectrum (b) of 1,3-butadiene adsorbed on an evaporated silver film at the exposure of 14 langmuirs and the spectrum (c) recorded after annealing the sample of Figure 3b at 95 K. The IR spectrum in Figure 3a gives similar features to those observed at 4.0 langmuirs in Figure 2, except for a band at 1371 cm^{-1}, which corresponds to the 1381 cm^{-1} band due to CH_2 scissoring ($\delta(CH_2)$, b_u) mode of *s-trans*-1,3-butadiene in the Ar matrix.[20] On the other hand, the IR spectrum in Figure 3b gives broad bands at 1591, 1377, 1022, and 916 cm^{-1}, which are due to $\nu(C=C)$, $\delta(CH_2)$, $\tau(CH_2)$, and $\omega(CH_2)$, respectively. These frequencies resemble the corresponding ones (1597 (b_u), 1371 (b_u), 1022 (a_u), and 905 cm^{-1} (a_u)) observed for *s-trans*-1,3-butadiene in the Ar matrix.[20] The spectrum gives broad bands also in the CH_2 and CH stretching region; i.e., 3086 ($\nu_{as}(CH_2)$, s-trans), 3045 ($\nu(CH)$, s-trans), 3020 ($\nu(CH)$, a second form), 2999 ($\nu(CH)$, a second form), and 2974 ($\nu_s(CH_2)$, s-trans). As can be seen from Figure 3b,c, the annealing makes all the IR

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bands much sharper than before, causing doublet features at 1022 and 1016 cm^{-1} (τ(CH$_2$)) and those at 920 and 916 cm^{-1} (ω(CH$_2$)), which are similar to those observed for the spectra in Figure 2 (4.0 langmuirs) and Figure 3a. These results indicate that the sample of Figure 3b is in an amorphous state, while those of Figure 3a,c (and those of Figure 2 (4.0−1.8 langmuirs)) form an ordered or crystalline state. The amorphous state was observed also for acrolein adsorbed on an evaporated or polycrystalline silver.[13] An irregular morphology of the evaporated surface may be one of the prerequisites for the formation of the amorphous state. Thus, the doublets observed for the τ(CH$_2$) and ω(CH$_2$) bands in Figure 2 (4.0−1.8 langmuirs) are ascribed to the crystal field splitting. The adsorbates in the amorphous state (Figure 3b) are more or less randomly oriented, which conforms to the fact that the intensity of the in-plane ν(C=C) band and those of the out-of-plane τ(CH$_2$) and ω(CH$_2$) bands are similar to each other in Figure 3b. The relative intensity of ν(C=C)/ω(CH$_2$) in Figure 3c is much smaller than that in Figure 3b, indicating that the annealing results in the increase in the amount of the adsorbates with their molecular plane parallel to the substrate surface. The intensity ratios of the ν(CH) bands ascribable to the second form to the CH and CH$_2$ stretching bands due to the s-trans form in Figure 3b are similar to those in Figure 3c, indicating that the content of the second form (and probably the structure of a few monolayers on the top of the monolayer coverage) is not affected by annealing.

As explained above, the multilayered state consists of only *s-trans*-1,3-butadiene, as far as the IRAS spectra can tell within their detection limit. Since the predosed sample contains a certain amount of the thermodynamically less stable isomer (s-cis or gauche form), the result suggests that there occurs either a selective adsorption of the s-trans isomer or a conversion from the less stable isomer to the s-trans one during the formation process of the multilayered state. Although it is unknown which is the most important factor, the result indicates the importance of a molecular packing effect in determining the multilayered structure.

IR Spectra and Adsorption Structures of 1,3-Butadiene on Ag(111). To know whether the discrete changes of the adsorption structure observed for 1,3-butadiene on Au(111) take place also on Ag(111), we measured the exposure dependence of the IR spectra of 1,3-butadiene on Ag(111) at 40 K. As can be seen from Figure 4, the spectra exhibit discrete changes similar to those observed for the adsorbate on Au(111) in the CH and CH$_2$ stretching region (3088−2972 cm^{-1}) as well as the ν(C=C) (1589 cm^{-1}), τ(CH$_2$) (1022−1002 cm^{-1}), and ω-(CH$_2$) (922−905 cm^{-1}) regions. IR bands near 1371 and 1286 cm^{-1}, which are observed at larger exposures (2.0−5.0 langmuirs), are the counterparts of IR bands at 1381 and 1297 cm^{-1}, which are observed for the IR spectrum of the Ar matrix and assigned to CH$_2$ scissoring (δ(CH$_2$), b$_u$) and CH in-plane bending (δ(CH), b$_u$) modes, respectively, of *s-trans*-1,3-butadiene.[20] The facts clarified from Figure 4 can be summarized as follows: (i) The 1007 and 908 cm^{-1} bands observed at the lowest exposure (0.03 langmuir) are the counterparts of the 1007 and 916 cm^{-1} bands in Figure 2 (0.04 langmuir) and can be assigned to the s-trans form in the α-state. (ii) On increasing the exposure from 0.03 to 0.20 langmuir, the τ(CH$_2$) band shifts to 1005 cm^{-1} and there appears a shoulder ω(CH$_2$) band at 905 cm^{-1}, which can be compared with the shifts of 1007 → 1005 cm^{-1} (τ(CH$_2$)) and 916 → 908 cm^{-1} (ω(CH$_2$)) observed for the adsorbate on Au(111) by increasing the exposure from 0.04 to 0.20 langmuir. Presumably, the 1005 and 905 cm^{-1} bands
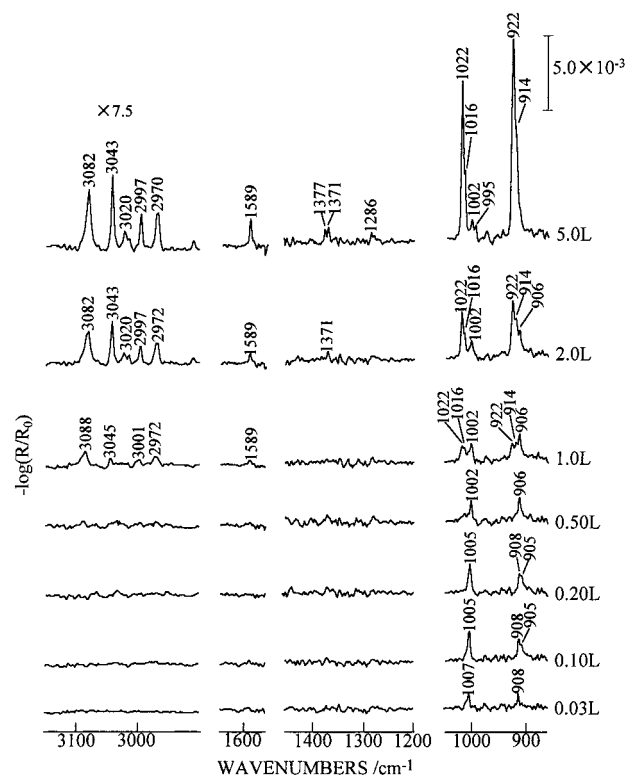
Figure 4. Exposure dependence of the IR spectra of 1,3-butadiene on Ag(111) at 40 K. The number at the right-hand side of each spectrum indicates the exposure. The vertical line indicates a scale for the ordinate of the spectra. The spectra in the 3150−2950 cm^{-1} region are shown by multiplying their ordinates by 7.5.

observed for the adsorbate on Ag(111) are ascribable to the s-trans form in the β-state. (iii) At the exposure of 0.50 langmuir the shoulder band at 905 cm^{-1} disappears, and at the same time there appear new τ(CH$_2$) and ω(CH$_2$) bands at 1002 and 906 cm^{-1}; the intensities of the latter bands remain almost constant upon further exposure (0.50−5.0 langmuirs). These bands, which correspond to the 1005 and 914 cm^{-1} bands observed for the adsorbate on Au(111) at the exposure of 0.30−4.0 langmuirs, are ascribable to the adsorbates forming a monolayer coverage on Ag(111). The formation of the monolayer coverage associated with the exposure increase from 0.20 to 0.50 langmuir does not cause any intensity increase for the τ(CH$_2$) and ω-(CH$_2$). This can be explained by considering that the process accompanies a tilting of the molecular plane, keeping the C=C bonds parallel to the substrate surface, as in the case of the adsorbate on Au(111). (iv) The absence of IR bands ascribable to in-plane vibrations at exposures less than or equal to 0.50 langmuir indicates that the adsorbates in the α- and β-states and those forming the monolayer coverage have the molecular plane nearly parallel to the surface. (v) The doublets (τ(CH$_2$)) at 1022 and 1016 cm^{-1} and those (ω(CH$_2$)) at 922 and 914 cm^{-1} appear at 1.0 langmuir, and the intensities of the doublets increase with exposure (1.0−5.0 langmuirs). (vi) The IR spectrum measured at 5.0 langmuirs is almost identical with those in Figure 3a and Figure 2 (4.0 langmuirs), indicating that the doublets in Figure 4 can also be ascribed to multilayered adsorbates in the ordered or crystalline state on Ag(111). (vii) At exposures larger than or equal to 1.0 langmuir there appear IR bands near 3088, 3045, and 2972 cm^{-1}, which are due to the ν_{as}(CH$_2$), ν(CH), and ν_s(CH$_2$) bands of the s-trans form, and IR bands near 3020 and 3000 cm^{-1}, which are due to the ν(CH) bands of the second form (s-cis or gauche). Upon increasing the exposure up to 5.0 langmuirs the intensities of
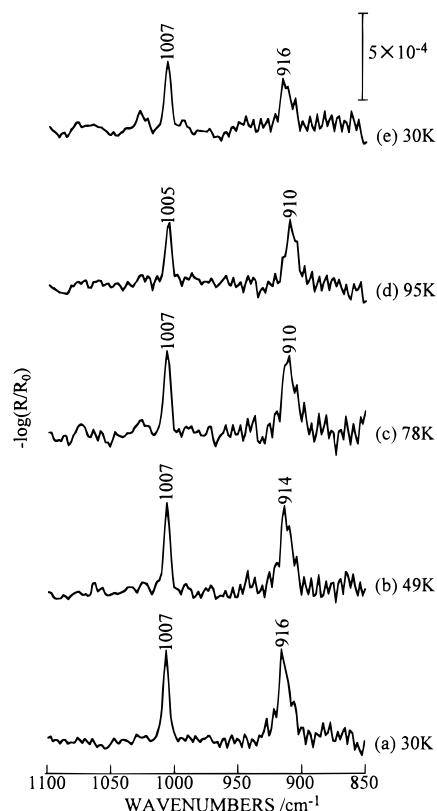
Figure 5. Temperature-dependent IR spectra of 1,3-butadiene on Au-(111) at 0.01 langmuir. The vertical line indicates a scale for the ordinate of the spectra.
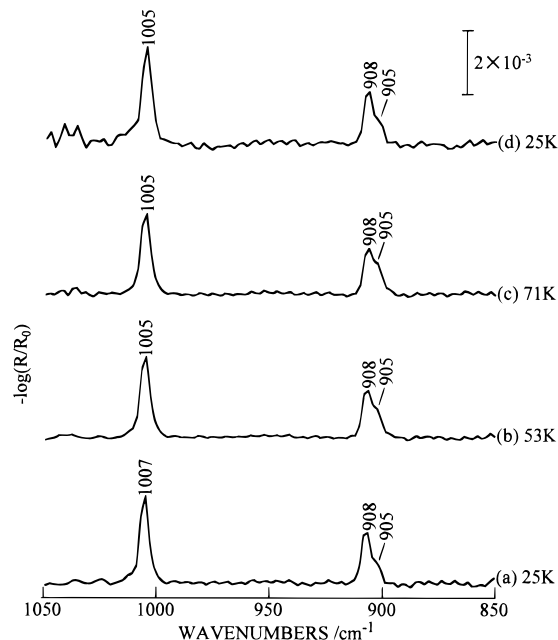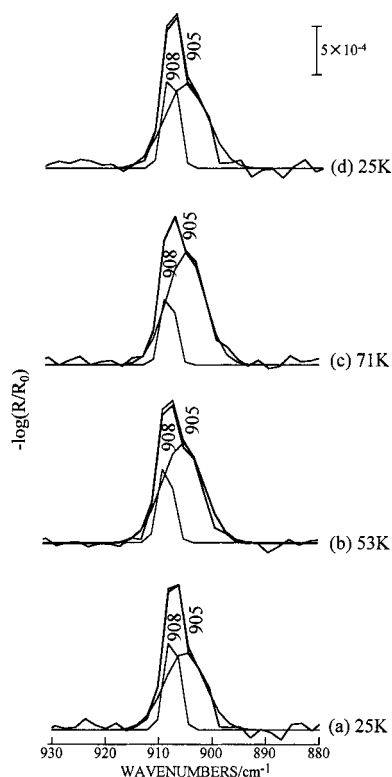

Figure 6. Temperature-dependent IR spectra of 1,3-butadiene on Ag-(111) at 0.15 langmuir. The vertical line indicates a scale for the ordinate of the spectra.

the IR bands associated with the s-trans form increase at a much faster rate than those of the second form, indicating that the adsorbates forming the ordered multilayer assume mainly the s-trans form.

Thus, the discrete changes in the adsorption state on Ag-(111) correspond well with those on Au(111), although there are several discrepancies. As can be seen from Table 1, there exist frequency differences in the $\tau(CH_2)$ and $\omega(CH_2)$ bands of each adsorption state. This may be ascribed to differences in the π-bonding interaction between the adsorbates on Au(111) and those on Ag(111). The adsorbate on Ag(111) does not exhibit the $\tau(CH_2)$ and $\omega(CH_2)$ bands ascribable to a few monolayers on the top of the monolayer at saturation coverage. These bands are observed at 1016 and 916 cm^{-1} in Figure 2 (0.95 langmuir). This is due to an experimental artifact, because if the exposure to the Ag(111) substrate was performed at a more reduced rate than that employed for the measurement of the spectra in Figure 4, the broad bands appear in the 1022−1016 and 922−914 cm^{-1} regions.

As indicated by result ii, the IR spectra proved the existence of two kinds of adsorption sites (α- and β-states) at low coverages. To elucidate the nature of the adsorption states, the temperature dependence of the IR bands at lower exposures was investigated.

Temperature Dependence of the IR Spectra of 1,3-Butadiene on Au(111) and Ag(111). Figure 5a is the IR spectrum in the $\tau(CH_2)$ and $\omega(CH_2)$ band regions observed for 1,3-butadiene on Au(111) at 30 K and the exposure of 0.01 langmuir. The 1007 and 916 cm^{-1} bands are assigned to the α-state. As can be seen from Figure 5b−d, when the substrate temperature is increased, these bands shift to the lower frequency side, giving the bands at 1005 and 910 cm^{-1} at 95 K, which correspond to the 1005 and 908 cm^{-1} bands assigned to the

β-state in Figure 2. Upon reducing the temperature again to 30 K, the bands moves to 1007 and 916 cm^{-1} (Figure 5e), which are almost identical with those in Figure 5a. Thus, the conversion from the α- to β-state, which is originally observed by increasing the exposure, is observed also by raising the substrate temperature, and the conversion takes place reversibly with temperature. The temperature-dependent reversible conversion between the two states was observed also for the adsorbate on Ag(111).

Figure 6 illustrates the temperature dependence in the 25−71 K region observed for the $\tau(CH_2)$ and $\omega(CH_2)$ bands of 1,3-butadiene on Ag(111) at the exposure of 0.15 langmuir. At 25 K (Figure 6a) the $\tau(CH_2)$ and $\omega(CH_2)$ bands are observed at 1007 and 908 cm^{-1}, which are ascribable to the α-state. The 908 cm^{-1} band accompanies a shoulder band at 905 cm^{-1}. On increasing the substrate temperature to 71 K (Figure 6c), the 1007 cm^{-1} band shifts to 1005 cm^{-1} and the shoulder band increases its intensity. When the temperature is reduced again to 25 K (Figure 6d), the intensity of the shoulder band decreases, giving an IR band feature due to $\omega(CH_2)$ almost identical with that in Figure 6a. (The $\tau(CH_2)$ band at 1005 cm^{-1} does not recover the original feature at 1007 cm^{-1}. This may be due to an experimental artifact.) The temperature dependence of the relative intensities of the 905 and 908 cm^{-1} bands was determined by a curve resolution procedure performed under the assumption that the bands are composed of two Gaussian components at 908 and 905 cm^{-1}. As shown in Figure 7, the procedure reproduces the observed bands appreciably well, proving the validity of the assumption. The results indicate the following facts: (i) The relative intensity ($I(905$ cm$^{-1}/908$ cm^{-1})) increases upon raising the substrate temperature. (ii) The relative intensity changes reversibly with temperature. (iii) Arrhenius plots of ln($I(905$ cm$^{-1}/908$ cm^{-1})) vs $1/T$ give the enthalpy difference between the α-state (associated with the 908 cm^{-1} band) and the β-state (associated with the 905 cm^{-1} band) to be about 170 J/mol, the former state being more stable than the latter. (iv) The bandwidth due to the β-state is larger than that of the α-state. (As shown in Figure 5a−c, the $\omega(CH_2)$ band of the adsorbate on Au(111) seems to show similar

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Figure 7. Results of the curve resolution procedure performed on the $\omega(CH_2)$ bands in Figure 6 (see text). The vertical line indicates a scale for the ordinate of the spectra.

broadening upon temperature increase from 30 to 78 K. The broadening, however, is not clear on further temperature change of 78 → 95 → 30 K (Figure 5c−e), because of the intensity decrease of the $\omega(CH_2)$ band due to partial desorption.) The frequency lowering of the $\tau(CH_2)$ and $\omega(CH_2)$ bands corresponds well to that observed by increasing the exposure level from 0.03 to 0.2 langmuir in Figure 4, i.e., 1007 → 1005 cm^{-1} for $\tau(CH_2)$ and 908 → 905 cm^{-1} for $\omega(CH_2)$ in Figure 4. Thus, the adsorbates on Ag(111) undergo the conversion between the two adsorption states (or sites), which is similar to that for the adsorbate on Au(111). (The continuous frequency lowering of the $\omega(CH_2)$ band in Figures 2 and 5 can be interpreted as due to the decrease in the relative population of the 916 cm^{-1} component with respect to the 910 cm^{-1} one. The curve resolution procedure could not be performed because of low signal-to-noise ratios for the $\omega(CH_2)$ bands in Figure 5.)

The temperature- and coverage-dependent interconversions among several adsorption states have been well proved for simple molecules such as CO on low-index clean transition-metal surfaces.[24,27,28] In the case of CO on Ni(100), at a low temperature below 100 K, the adsorbates predominantly occupy the bridged site at a lower coverage and at higher coverage also on the terminal or on-top sites. The relative occupation for the two sites was measured from 80 to 220 K, indicating that the energy difference between the two adsorption states is 1.06 kJ/mol.[28] The difference is 1 order larger than that observed for the energy difference (170 J/mol) between the two adsorption states of 1,3-butadiene on Ag(111) in line with much smaller adsorbate−substrate interaction on Ag(111). As explained in the Experimental Section, the AFM observation indicated that the Au(111) surface consists of terraces with an average area of 3000 × 3000 Å. Presumably, at low exposures (ca. 0.1 langmuir) the adsorption initially takes place into the terrace site, forming the α-state. Increasing the substrate temperature may increase surface mobility to cause the conversion to some

defect sites consisting of step and/or kink sites. The broad features observed for the $\omega(CH_2)$ band due to the β-state suggest that a variety of different types of defect site are occupied. A reversible spectral change due to the conversion between the terrace and defect sites has been observed also for the linear or on-top adsorption state of CO on Pt(111).[27] To get more detailed information about the nature of the α- and β-states, we need to perform STM observation, which is under way in our laboratory.

Conclusion

The spectra especially in the $\tau(CH_2)$ and $\omega(CH_2)$ vibration regions clarified the adsorption states of 1,3-butadiene, one of the simplest olefins with conjugated C=C bonds, on Au(111) and Ag(111). The adsorbates on both surfaces take on a common series of discrete states as the exposure increases, that is, α-state, in which the adsorbate occupies a terrace site, β-state, in which the adsorbate probably occupies defect sites (e.g., kink and step sites), a monolayer coverage state, and multilayers with an ordered or crystalline state. The α- and β-, monolayer coverage, and multilayered states take the s-trans form. The second conformer (s-cis or gauche form) is assumed only by the adsorbates forming a few monolayers which exist between the monolayer coverage state and the multilayered state. The molecular plane of the adsorbate in the α-state is parallel to the substrate surfaces, while those in the β- and saturation coverage states take on a tilted orientation keeping the C=C bonds parallel to the surfaces. The α- and β-states are in a thermal equiriblium in the 25−90 K region. Although the mode of the adsorbate−substrate interactions still remains unknown, the results in the present paper clarified the general characteristics of the adsorption process of a planar molecule such as 1,3-butadiene at relatively inert substrates such as Au(111) and Ag(111) and indicated that the analysis of the IR spectra especially in the CH$_2$ out-of-plane bending vibration region provides valuable information about surface diffusion and migration processes of 1,3-butadiene at the two-dimensional surfaces.

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