Infrared Reflection−Absorption Spectra of C₂H₄ and C₂H₆ on Cu: Effect of Surface Roughness

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Infrared reflection absorption spectroscopy (IRRAS) of the highly symmetric molecules C₂H₄ and C₂H₆ adsorbed as mono- and multilayers onto copper films is studied in relation to the type of metal-film roughness. Spectra of C₂H₄ show Raman lines on cold-deposited Cu films but not on Cu deposited at room temperature. For C₂H₆, the IR spectra from both types of metal films are similar; the surface infrared selection rule holds and no Raman bands are observed. The Raman lines that appear in the IR spectra already at low exposures are attributed to species adsorbed at special defect sites, identical to the so-called active sites in surface enhanced Raman scattering (SERS). The IR excitation mechanism by transient electron transfer to the adsorbate π* state can deliver a discrete vibrational band of a Raman-active vibration only under certain circumstances, for example, for adsorbates at the "SERS-active sites". C₂H₆ at these sites cannot deliver Raman bands in IRRAS, because it has no π* state. We also discuss IRRAS measurements on Cu(111) and Cu(110) single crystals, where Raman bands of C₂H₄ have been observed.

1. Introduction

The IR surface selection rule for molecules at and near a smooth surface of an extended metal[1] is based on the high electronic screening of all metals in the infrared spectral region. Due to the screening currents parallel to the surface within the metal, the electric vector parallel to the surface (this component is continuous across the surface) is very small compared to the vector component above and perpendicular to the surface. Therefore, the incident radiation will nearly exclusively interact with those electric vibration-dipole moments that are oriented perpendicularly to the surface. If the directions of these dipole moments with respect to the molecular symmetry axis and mirror planes are known, the adsorption configuration can be inferred from infrared reflection absorption spectroscopy (IRRAS). We note in passing that also the screening currents do interact with the adsorbates by electronic friction, which can lead to a new channel of exciting vibrations.[2]

First, this article will show for the example of C₂H₆ that the surface selection rule also holds at the local surface of cold-deposited Cu.

Then, we show and explain the breakdown of this rule for C₂H₄. It is well-known for molecular complexes A−B that by transient electron transfer (A−B → A⁺−B⁻ → A−B) Raman-active vibrations of either A or B can be excited with the IR electric vector parallel to the axis from A to B. Devlin and Consani[3] have drawn the attention to "the possibility of strong electron density oscillations between the molecules und the surface regardless of the orientation of the adsorbate molecule. Totally symmetric (adsorbate) modes produce such oscillations

which dominate the infrared spectra of charge-transfer systems and which will be significant in surface enhanced Raman scattering (SERS) as well should the modulation of surface charge density prove to be a contributing factor." This mechanism needs just a little further detail to work. In the system A−B, the electronic hole (state A⁺) "waits" till the electron comes back from B⁻ to end again as AB; the only excitation in the transient electron is the Raman-active vibration. At a smooth metal surface, "the hole has gone"; for example, the hole propagates off the adsorption site with Fermi velocity and does not wait till the electron returns from the π* state of the adsorbate. The end state is a Raman-active vibration of the adsorbate excited and a metallic electron−hole pair of finite energy. Energy conservation requires photon energies with the energies of the fundamental vibration and the energy of the e−h pairs that have a continuous distribution. This does not yield a discrete IR absorption band. Only at so-called "SERS-active sites" is the hole kept for times comparable to the residence times of the electron in the molecule, and there is a chance for electron−hole-pair annihilation, for example, no excitation within the metal. This yields a discrete IR band at the position of a Raman-active mode of the adsorbate. For the case of SERS, this time-domain explanation is given in detail in ref 4. We will explain the IRRAS results for C₂H₄ also in this way. Another way of explanation is based on wave vector conservation in the respective process.[5]

2. Experimental Basics and Metal-Film Preparation

The in situ experiments were performed with a vacuum Fourier transform IR spectrometer (Bruker IFS 66 v/S with midrange mercury−cadmium−telluride detector) attached to an ultrahigh vacuum (UHV) chamber (base pressure < 2 × 10⁻⁸

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Pa). In more detail, the experimental setup is described somewhere else.[6] The Cu films used for infrared reflection absorption spectroscopy (IRRAS) were prepared in the following way: Polished polycrystalline Cu plates as substrates were heated in an UHV to degas them. Copper was thermally evaporated on them, the first part at room temperature and, for cold-deposited films, the second part at a 50 K substrate temperature. These samples are called Cu(50 K) in this work; the films completely grown at room temperature are marked by Cu(300 K). For Cu(50K), the very slow diffusion of Cu on Cu at 50 K is relevant (diffusion barrier of about 0.5 eV[7]), giving roughness on the atomic scale (which we learned for example from the intensity-transfer effect due to dipole−dipole interaction of CO on such surfaces[8]) but the films are almost smooth on a scale beyond some nanometers.[9] Metal-film thicknesses are estimated from the deposition time and the rate (typically 0.1 nm/min assuming Cu bulk density) that was calibrated with a quartz microbalance. Substrate temperatures were measured by a chromel−alumel thermocouple attached to the substrate plate. The film thickness for each deposition step was between 10 and 20 nm. After preparation, the Cu films were exposed to C_2H_4 or to C_2H_6, respectively (purity 99.95 vol % for both gases), with a partial pressure of about 2×10^{-6} Pa at about a 50 K sample temperature. During exposure, we measured the changing reflected intensity of the sample, using p-polarized light at an average angle of 80° with a spectral resolution of 2 cm^{-1}. At least 50 scans per spectrum were sampled with 0.5 s per scan. The reference was the reflected intensity of the copper sample directly before exposure. The exposure is given in langmuirs (L, 1 L = 1.333×10^{-4} Pa·s) with the ion gauge reading corrected by a gauge factor of 2.14 for C_2H_4 and by 2.6 for C_2H_6,[10,11] respectively, and with an accuracy of 0.2 L.

3. Adsorbate Spectra

Figures 1 and 2 show the IRRAS data for C_2H_6 and C_2H_4, respectively, adsorbed at 50 K on Cu films deposited at 50 K and at 300 K. All spectra shown in these figures are shifted against each other. We focus here on the main spectral features around 3000 cm^{-1} for the CH-stretch modes and from about 800 cm^{-1} to about 1650 cm^{-1} for the various other methyl and methylene vibrations and the CC-stretch modes.

Tables 1 and 2 give an overview on the vibration modes of the free molecules, some literature data, and on frequencies from the IRRAS data in this paper and, for C_2H_4, from the so-called surface enhanced IR absorption (SEIRA) data measured by normal transmission of Cu films on transparent substrates. In the tables, we assign spectral features under consideration of much more literature[12−15] than we can show there.

4. Discussion

(a) Ethane (C_2H_6). The direction of the dynamic dipole moments of the IR modes of C_2H_6, either parallel (p) or perpendicular (s) to the CC axis are indicated in Table 1. In the wavenumber range 700−1900 cm^{-1} and at low exposures (first layer signal), only the degenerate modes e_u (CH$_3$ bending, IR-s) at 820 cm^{-1} and e_u (CH$_3$ deformation, IR-s) between 1458 and 1466 cm^{-1} are observed, the polarization of which is perpendicular to the CC axis, different from a_{2u} (CH$_3$ deformation, IR-p) at 1370 cm^{-1}. We use here the notation of the free staggered form of C_2H_6, first because the wavenumber differences with respect to the gas data are small and second because there is a 1:1 relation of the group representations of the vibrations of the staggered (group D_{3d}) and eclipsed (D_{3h}) conformer (Table 104 in ref 16). Therefore, independent from

the conformation, it follows that the CC axis of ethane adsorbed on Cu(50K) and Cu(300K) films is parallel to the surface.

For C_2H_6 on Cu(50K) and Cu(300K), a CH-stretch band at 2958 cm^{-1} is clearly observed at a 0.2 L exposure. We believe that multilayers of C_2H_6 start to grow when the additional bands at 2884 and 2977 cm^{-1} appear, which we assign by comparison with Table 1 to the a_{2u} and e_u CH-stretch mode of the staggered conformation of C_2H_6, respectively. According to this, the transition from adsorption only in the first monolayer to adsorption also in the second layer and to multilayer formation takes place below a 0.7 L exposure to the Cu(300K) film and at about a 1.2 L exposure to the Cu(50K) film. These different exposure values mainly reflect the higher number of surface atoms of the Cu(50K) film per unit area compared to the Cu(300K) film with its more extended smooth terraces, in agreement to thermodesorption measurements of C_2H_6 from copper films deposited at various temperatures.[25,27] The fact that only one CH stretch rather than two is observed at monolayer coverage provides evidence that the CC axis is parallel to the local surface, corroborating the conclusions from the frequency range 700−1900 cm^{-1}. The first layer band at 2958−2960 cm^{-1} is too far from the frequency of the a_{2u} (CH stretch, IR-p) mode to be assigned to this mode. On the other hand, it is close to the e_u (CH stretch, IR-s) mode. Thus, the certain absence of the a_{2u} (CH stretch, IR-p) mode indicates that the C_2H_6 molecules are adsorbed with the CC axis parallel to the local surface. The degeneracy of the e_u (CH stretch, IR-s) mode is broken by adsorption in the first layer, and only the component polarized perpendicularly to the surface is observed, shifted to 2958 cm^{-1}. Hence, the IR surface selection rule (only modes observed with the IR dipole perpendicular to the local surface[1]) holds also for cold-deposited films. The direction of the CC axis parallel to the surface was also proven in ref 28, in the context of near-edge X-ray absorption experiments.

In a forthcoming publication,[17] we will prove, by also considering Raman data (for instance, column 6 in Table 1), that C_2H_6 adsorbs in the eclipsed conformation, whereas it has the staggered conformation in the second and further multilayers.

One should note that no IR bands are observed at the frequency positions of Raman-active vibrations (see Figure 1). This is different for ethylene (C_2H_4).

(b) Ethene (C_2H_4). As demonstrated by near edge X-ray absorption fine structure (NEXAFS) spectroscopy, C_2H_4 adsorbs with the molecular plane parallel to the Cu(100)[28] and Cu(111)[29] planes. On Cu(110), it adsorbs on the ridges, with the molecular plane parallel to the surface, as can be inferred from scanning tunneling microscopy,[30] combined photoemission and photoelectron emission,[31] and X-ray absorption and emission spectroscopy.[32] So-called chemisorbed C_2H_4, predicted by theory, has not been observed.[29] Other bonding configurations on Cu-(110), postulated from IRRAS only,[33,34] are most probably incorrect, because some bands originate from C_2H_4 bonded to defects (see below).

Given the validity of the IR surface selection rule at both kinds of Cu samples as checked with C_2H_6 and given the parallel adsorption of C_2H_4 on Cu, one can start the discussion of the spectra of C_2H_4 in Figure 2. The only IR mode appearing below monolayer coverage is the b_{3u} (CH$_2$ wagging, IR-s) mode, which indicates flat adsorption at flat facets. The IR bands b_{1u} (CH$_2$ scissor, IR-p) at 1436 cm^{-1}, b_{1u} (CH stretch, IR-p) at 2976− 2974 cm^{-1}, and b_{2u} (CH stretch, IR-p) at 3094−3090 cm^{-1} cannot originate from species adsorbed at flat terraces but have to be assigned to species at surface defects or to species in the second or multilayers with the molecular plane no more parallel
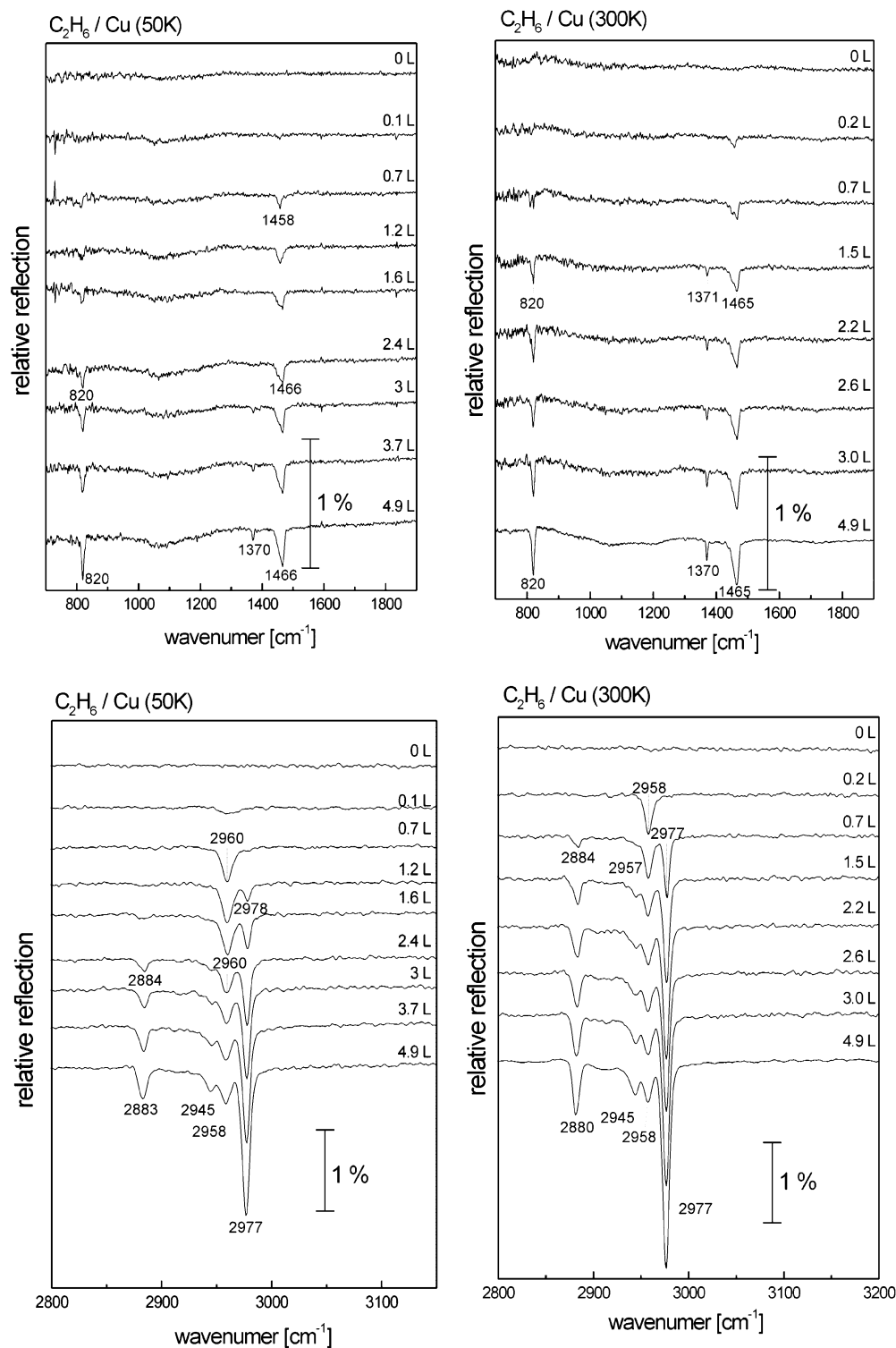
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Figure 1. Development of relative IR reflectance with C_2H_6 exposure: selection of spectra for Cu grown at 50 K (left) and for Cu grown at 300 K (right). The line at 2945 cm^{-1} is attributed to a combination mode.

to the surface. The first possibility is unlikely, because the intensity of the bands of the modes which are IR active in the free molecule (see Table 2) develops in about the same way on the Cu(50K) sample and the Cu(300K) sample, though the latter has much less defects (called "annealable sites"[25]). An extra electromagnetic field enhancement at the Cu(50K) sample with respect to the Cu(300K) sample is not observed in accordance with the low thickness of the cold-deposited film.[9] At an exposure of 4.8 L, the intensity ratio of the four IR bands is about the same as that observed in IR transmission of C_2H_4 ice

condensed at 50K on a KBr(001) substrate.[24] Furthermore, the intensity ratio of these bands for IRRAS to the corresponding ones in transmission on KBr can be explained by the classical theory and the typical IRRAS-enhancement factor.[1]

The significant spectral difference between C_2H_4 adsorbed on the two different Cu samples is the appearance of additional vibration modes already at low exposures to Cu(50K). These modes are exclusively Raman active for the free molecule, the a_g (CH₂ scissor, R) mode at 1279 cm^{-1} and the a_g (CC stretch, R) mode at 1542 cm^{-1}. Their frequencies are observed also in
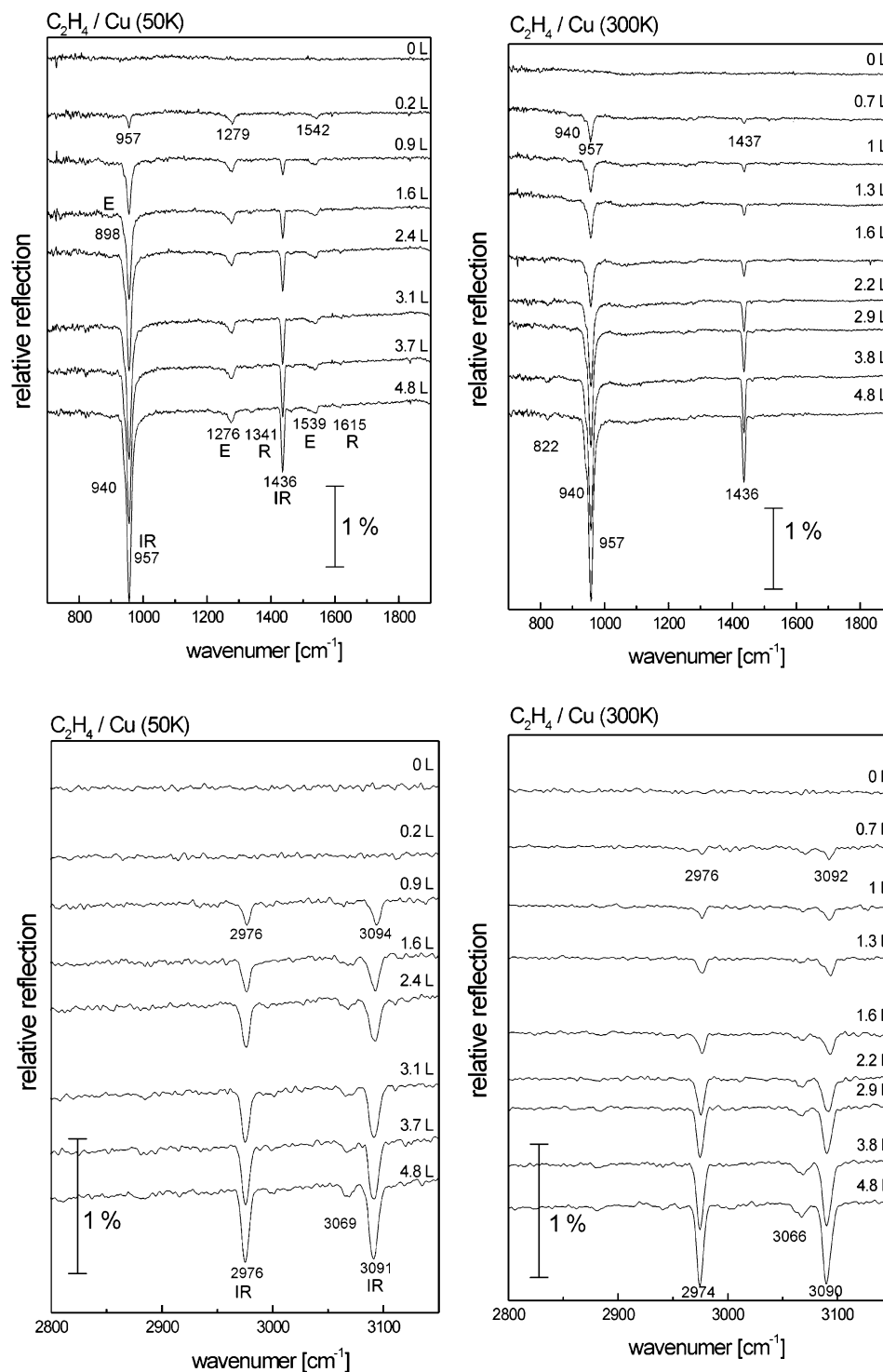
Figure 2. Development of relative IR reflectance with C_2H_4 exposure: selection of spectra for Cu grown at 50 K (left) and for Cu grown at 300 K (right). The line at $3066-3069$ cm^{-1} is a Fermi resonance.

SERS from C_2H_4 on cold-deposited Cu films and assigned to adsorption at so-called annealable sites or SERS-active sites, which disappear by annealing to room temperature.[25] The respective SERS bands have been called E(extra) bands. No Raman modes are observed in the CH-stretch-mode region (see Figure 2).

The band at 957 cm^{-1} already observed at low exposure is attributed to the b_{3u} (CH$_2$ wagging, IR-s) mode, the only mode allowed by the IR surface selection rule. In the transmission spectra of thin Cu films on KBr, more spectral details (including the weak bands R in Figure 2) have been observed,[26] which is described in ref 8 and which will be discussed in more detail

in ref 35. The IR excitation mechanism of the Raman bands of C_2H_4 on cold-deposited copper films is closely related to the SERS mechanism for the E bands.[4] In ref 4, the occurrence of the E bands in SERS is explained in the time domain by a transient electron transfer from so-called surface-resonance states (these are electronic states relatively weakly coupled to the bulk electronic states) to adsorbed C_2H_4, where the electron resides for some femtoseconds in the b_{2g}-π^* state. After retro transfer of the electron to the metal, the electron may "catch" its hole only if the hole lifetime in the surface resonance is of the order of the lifetime of the anionic state. For a half width of ~0.25 eV of the charge-transfer excitation band (for instance, CO on

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TABLE 1: Vibration Frequencies (in cm^{-1}) of C$_2$H$_6$ in Different Environments; Literature Data Compared to IR Data of This Work^a

symmetry and vibration type for the free **ethane** molecule (**staggered** form, D_{3d})	gas data[b]	near normal IR reflectance of solid ethane at 25 K[c]	Raman spectra of solid ethane at 25 K[c]	Raman spectra, ice film on Ag[d]	SERS, 5 L at 40 K on cold-deposited Ag[d]	IRRAS, 1.6 L at 50 K on cold-deposited Cu	IRRAS, 4.9 L at 50 K on cold-deposited Cu	IRRAS, 4.9 L at 50 K on Cu film grown at 300 K
e_u (CH$_3$ bending, IR-s)	822	825, 816, 813			813	820	820	820
a_{1g} (CC stretch, R pol.)	994		996, 993	999	978			
e_g (CH$_3$ bending, R depol.)	1196		1120, 1192, 1185	1194				
a_{2u} (CH$_3$ deformation, IR-p)	1379	1371, 1368				no 1st layer signal	1370 (2nd layer)	1370 (2nd layer)
a_{1g} (CH$_3$ deformation, R pol.)	1397		1376	1405	1304?, 1358?			
e_u (CH$_3$ deformation, IR-s)	1471	1465, 1458, 1456, 1450				1458	1466	1465
e_g (CH$_3$ deformation, R depol.)	1468		1462, 1451, 1447, 1402	1466	1446?			
a_{2u} (CH stretch, IR-p)	2896	2880				no 1st layer signal	2883 (2nd layer)	2880 (2nd layer)
a_{1g} (CH stretch, R pol.)	2897, 2954, FR		2877	2883	2843, 2900?			
e_g (CH stretch, R depol.)	2969			2963	2900 or shoulder above 2900			
e_u (CH stretch, IR-s)	2985	2972				2978 (2nd layer)	2977 (2nd layer)	2977 (2nd layer)
1st layer IR						2960	2958	2958

^{a} Assignment of the vibrations of ethane (without torsional mode) according to Herzberg.[16] Torsions a_{1u} are inactive; see also ref 17. "FR" indicates the Fermi-resonance effect that gives two lines.[18] For the free molecule, the IR and the Raman activity of a mode is indicated by "IR" or "R", respectively; p and s denote directions of the IR dipole parallel and perpendicular to the CC axis, respectively. "pol." and "depol." signify polarized or depolarized Raman scattering. The literature data are rounded to 1 cm^{-1}. ^{b} As summarized in ref 19. ^{c} From ref 20. ^{d} From ref 21.

TABLE 2: Vibration Frequencies (in cm^{-1}) of C$_2$H$_4$ on Copper Films (IR data of this work) Compared to Literature and Previous Data^a

symmetry and vibration type for the free **ethene** molecule	gas data[b]	IR transmittance,[c] ice on KBr at 40 K	Raman,[d] ice film on Cu at 40 K	SERS,[d] 5 L at 40 K on cold-deposited Cu	IRRAS at 100 K,[c] 3.7 L on 13 nm cold-deposited (at 100 K) Cu on Si(111) 7 × 7	SEIRA at 100 K,[c] 6 L on cold-deposited Cu (at 100 K)	SEIRA at 100 K,[c] 9.3 L on cold-deposited Cu (at 50 K)	SEIRA at about 40 K,[c,e] 16.5 L on cold-deposited Cu (at 40 K)	IRRAS of 0.2 L on cold-deposited Cu (at 50 K)	IRRAS at 50 K of 4.8 L on Cu deposited at 300 K
b_{2u} (CH$_2$ rocking, IR-p)	826							819		822
b_{2g} (CH$_2$ wagging, R)	940, 943		940	**902** = E	**922** = E	**896** = E	**893** = E	**898** = E, at about **920** below 1 L		
b_{3u} (CH$_2$ wagging, IR-s)	949	941, 949, doublet				between 950 and 970	970	949, peak appears above 2 L	957	957 with shoulder at 940
b_{3g} (CH$_2$ rocking, R)	1236			1230				1221		
a_g (CH$_2$ scissor, R)	1342		1327, 1345	**1282** = E, 1336 = N	**1289** = E	**1276** = E	**1276** = E	**1276** = E, at 1284 below 1 L, 1338 = N	**1279** = E	
b_{1u} (CH$_2$ scissor, IR-p)	1444	1435				1434 (only above 2 L)	1433	1435 (only above 2 L)		1436
a_g (CC stretch, R)	1623		1614	**1541** = E, 1615 = N	**1551** = E	**1538** = E	**1541** = E	**1537** = E, at **1544** below 1 L, 1615 = N	**1542** = E	
b_{1u} (CH stretch, IR-p)	2989	2973		2972				2971		2974
a_g (CH stretch, R)	3026		2996, 3065	2995						
b_{2u} (CH stretch, IR-p)	3106	3087						3088		3090
b_{3g} (CH stretch, R)	3103									

^{a} For the free molecule, the IR and Raman activity of a mode is indicated by "IR" or "R", respectively. "E" is for extra bands; see text. "N" marks the normal Raman modes of physisorbed species. The symmetry species for the point group D_{2h} are given according to ref 22. ^{b} Taken from refs 12 and 23. ^{c} From ref 24. ^{d} From ref 25. ^{e} From ref 26.

Cu(111)[36]), this time in the π^* state is about 5 fs. At a smooth surface, this electron−hole annihilation is therefore not possible, and an electron−hole pair is left over after the temporary electron transfer. This process however is not Raman scattering. The sites with the electronic surface-resonance states weakly coupled to the bulk electronic states are the so-called SERS-active sites.[4] One should note that the photon did not play a role in this explanation, only the charge transfer back and forth at SERS-active sites. Therefore, the explanation may be used

also for the IR case. It is the mechanism envisioned by Devlin and Consani,[3] but it does not work at a smooth surface, analogous to the case in SERS,[4] because not only a vibration but also an electron−hole pair is excited. The presence of SERS-active sites is a necessary but not in all cases sufficient condition to observe the E bands in infrared spectroscopy of adsorbates. For C_2H_4, the conditions are apparently good. The occurrence of E bands of the b_{2g} CH$_2$ wagging mode and the a_g CH$_2$-scissor and CC-stretch modes is explained by s-wave and d-wave

TABLE 3: Comparison of Experimentally Observed Spectral Lines of C_2H_4 on Copper and Suggested Attribution to Certain a_g Modes of Ethene

vibration type	IRRAS, Cu(111)[39]	IRRAS, Cu(110)[33]	IRRAS, Cu(110)[34]	IRRAS, Cu(110)[40]	SERS cold-dep. Cu[25]	SERS cold-dep. Cu[41]	SERS cold-dep. Cu[42]
a_g (CH$_2$ scissor, R)	1285	1261	1257	1257	1290−1279	1289−1279	1282(5L)
a_g (CC stretch, R)	1535	1522	1522	1519	1546 (5 L)	1551−1545	1541(5L)

resonant scattering, respectively, in the energetically relatively low lying π^*-b_{2g} state.[37] The molecule C_2H_6 has no π^* state but only energetically high lying σ^* states, with residence times of the electron of less than 1 fs.[4] Therefore, the vibration excitation by transient charge transfer becomes negligible with respect to the direct excitation of IR-active modes by the electromagnetic IR field, and Raman-active E modes are not observed.

5. E Bands from Nonideal Single Crystal Surfaces

In ref 38, a typical SERS spectrum of C_2H_4 on cold-deposited Cu is compared with an IRRAS spectrum of C_2H_4 on a Cu(111) single crystal taken with nitrogen cooling of the sample.[39] The strong b_{3u} (CH$_2$ wagging, IR-s) band indicates absorption of C_2H_4 with the molecular plane parallel to the (111) terraces. Weaker bands at 1285 and 1535 cm^{-1} are observed in the IR spectrum,[39] but they are not observed in IR spectra of ethylene on the Cu film grown at 300 K (Figure 2, top right panel), which, at first glance, remains unexplained. These two lines cannot be understood with the IR surface selection rules. In ref 38, these bands were assigned to the E bands of Raman-active modes. In this sense, the room-temperature deposited Cu films despite their azimuthally unordered (111) facets seem to be simpler substrates for IR spectroscopy than not really perfect (111) single crystals, probably because the latter have remaining defects from surface cleaning.

In Table 3, the values of bands in the IRRAS spectra within the spectral range of the a_g (CH$_2$ scissor, R) and a_g (CC stretch, R) vibrations of C_2H_4 on Cu(111) from McCash[39] and on Cu(110) from Jenks et al.,[33] Kubota et al.,[34] and Dumas et al.[40] are compared to the positions of the E bands in SERS of C_2H_4 adsorbed on cold-deposited Cu films from Grewe et al.,[25] Ertürk et al.,[41] and Akemann et al.[42] In the SERS experiments, the exposure was varied, leading to a slight downward shift of the E bands.

The assignment of the IR bands which should not be allowed given the flat orientation of C_2H_4 on Cu(110) (see the discussion above) to adsorption at defect sites is preliminary, as long it is not understood why in the references on Cu(110) (see Table 3) the b_{3u} (CH$_2$ wagging, IR-s) mode of C_2H_4 on clean Cu(110) was not observed. This mode was only observed after an oxygen precoverage of 0.2 L.[34] Unfortunately, a clear spectral analysis of the CH$_2$-wagging range is difficult because of the only small difference of the Raman- and IR-active modes, the adsorption-site dependence of these frequencies, and the dipole−dipole interaction affecting the IR line.[8,35] Thus, we are left with this open problem: We do not understand at the moment why the ethylene molecules which are adsorbed flat on the ridges of the Cu(110) crystals, as seen for instance by scanning tunneling spectroscopy, do not show the IR-active CH$_2$-wagging mode.

The crucial role of surface defects is demonstrated by a careful experiment performed by A. Goussev, published in ref 5. In this reference, it is clearly demonstrated how the E band signals (as the only SERS lines in this case) disappear after 15 cycles of sputtering and heating the sample, but they are still present at only 8 cycles.

6. Summary and Conclusions

The surface infrared selection rule is valid for ethane (C_2H_6) adsorbed on cold-deposited Cu as well as on room-temperature deposited Cu on a copper plate. Ethane adsorbs flat on the local surface. Clearly, ethane has the staggered conformation (D_{3d}) in the second layer and in the further multilayers that form a van der Waals solid. However, in the first monolayer, it adsorbs in a different conformation, probably in the eclipsed one (D_{3h}).[17]

Ethylene (C_2H_4) adsorbs flat on the Cu(300 K) film and shows only the IR modes in IRRAS, but already at low exposures to the cold-deposited Cu(50K) film, the Raman-active CH$_2$-scissor and CC-stretch modes appear, which is assigned to adsorption at SERS-active sites. We explain why transient electron transfer from metal to the molecule yields a dynamical IR moment perpendicular to the surface for Raman-active vibrations of adsorbed C_2H_4 but only leads to a discrete IR band if the molecules are adsorbed at SERS-active sites. Their occurrence is an attribute of cold-deposited copper, for example, and it is correlated to film roughness.[8,35] The only really IR-active mode of free C_2H_4 observed at submonolayer coverage on the Cu-(50K) film, the CH$_2$-wagging mode, originates from majority species which are adsorbed flat on the nanofacets of the film, like they do on the much more extended facets of the Cu(300K) film.[35]

All of these results make an assignment of the other modes observed in IRRAS of C_2H_4 adsorbed on Cu(111) and Cu(110) single crystals to Raman-active modes of molecules at surface defects very likely, rather than explanations by odd bonding configurations at the atomically smooth facets of the single crystals.

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