

Resonant Electron Scattering of 11-Mercaptoundecanoic Acid Self-Assembled Monolayer Adsorbed on Au (111)

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Received: September 27, 2002; In Final Form: January 15, 2003

We present a High-Resolution Electron Energy Loss study of an 11-mercaptoundecanoic acid self-assembled monolayer (SAM) adsorbed on Au(111). This work has to be placed in the general context of the study of thin organic layers by HREELS and of low-energy interaction mechanisms of electrons with large organic molecules. Evidence is presented here for two resonance phenomena, at ~ 1.5 eV and at ~ 6 eV, respectively. The first one is attributed to a negative ion resonance involving the carboxylic group, and the second one is the well-known resonance of CH_2 . From the angular distribution of the elastically scattered electrons the crystalline domain size of the monolayer is estimated to be about 100 Å.

1. Introduction

High-Resolution Electron Energy Loss Spectroscopy (HREELS) was developed for the study of metallic and semiconductor surfaces as well as for the characterization of small molecules adsorbed on crystalline surfaces.^{1–3} By selecting appropriate experimental conditions, HREELS can indeed bring information about electronic transitions or vibrational properties of adsorbed molecules. When used for vibrational studies, HREELS has the advantage of being extremely surface sensitive: submonolayer coverage are almost routinely studied, and the information often comes exclusively from the outmost layer of adsorbed molecules.⁴ Moreover, complementary to optical (Infrared and Raman) spectroscopies, HREELS can evidence excitations at lower frequency than infrared spectroscopy.

For large chemisorbed or condensed molecules, one can cite without being exhaustive, studies on benzene,^{5–7} formic acid,^{8–11} pyridine and cyclohexane,¹² cyclopropane,¹³ tetrahydrofuran,¹⁴ furan,¹⁵ hydrocarbons,¹⁶ and deuterated eicosanoic acid.¹⁷ As for polymers, the paucity of published papers reflects the difficulty in studying insulating materials; nevertheless, some data are available on polyethylene,^{18–19} polycarbonate,^{18–21} poly(tetrafluoroethylene),^{21,22} and polystyrene.²³ In this work, we focus our attention on the study of 11-mercaptoundecanoic acid in a wide range of electron impact energy, extending it particularly to very low (1 eV) electron energy.

The interaction of low energy electrons with molecules has recently attracted a lot of interest as it can trigger excitation processes or chemical reactions, which are influenced by the molecular environment. The central question in this context concerns the importance of negative ion resonance states as intermediate steps in the vibrational or electronic excitation of a molecule, and/or in its electron-induced dissociation. More complex phenomena such as intermolecular electron transfer and substrate-mediated processes are also studied; they do

convey real practical applications, e.g., in electron damage of biological polymers, or environmental science.²⁴

In High-Resolution Electron Energy Loss Spectroscopy, the ability to tune the electron impact energy allows us to study the energy dependence of the induced process(es). A comparison between gas-phase resonances, and phenomena observed in physisorbed systems and for chemisorbed species allows us to disclose the effect of image potential (on metal substrates), of chemical bonding, and interactions with coadsorbed molecules¹² on the shift in energy of the resonance and on its lifetime. This may be useful to selectively control specific surface events under resonance. It should be noted that HREELS resonance analyses may be complemented by studies of resonance electron capture (electron attachment) and/or of ion emission (desorption).

Three interaction mechanisms are known to play a significant role in electron scattering: dipole and impact interactions, and resonant scattering. The latter is a particular case of impact scattering. In the resonant interaction, the electron is captured in an affinity state of the molecule which becomes a temporary negative ion. First evidences of this phenomenon were presented in the late sixties for molecules in the gas phase. The observation of resonances is by now well established since exhaustive reviews exist for gas-phase diatomic²⁵ and adsorbed molecules.¹² However, to our knowledge very few resonance studies have been performed on large organic molecules adsorbed/condensed on crystalline surfaces.

We chose in this work to study resonances in a self-assembled monolayer of an alkanethiol terminated by a carboxylic group (11-mercaptoundecanoic acid) on Au(111), which from its well-defined composition, thickness, and molecular structure provide a particularly well-suited reference sample.²⁶ Indeed, no charging effect can be evidenced due to the limited and well-controlled thickness of the organic layer and the structural organization of such layer contributes to improve the resolution.^{17,27} Moreover, due to self-organization, the extreme surface is essentially composed of the $-\text{COOH}$ groups. This work will thus allow us to make a comparison with former studies of resonances in CO in the gas phase,²⁵ in physisorbed^{12,29–32} or

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chemisorbed^{28,33,34} layers on different substrates, in physisorbed CO₂,^{28,35} and in adsorbed HCOOH overlayers.^{8,36,37} Other works³⁸ dedicated to HREELS studies of the thermal stability of alkanethiol SAMs should also be mentioned.

Concerning their physical properties, alkanethiol self-assembled monolayers have been characterized in depth by a complete set of surface analysis techniques. However, to our knowledge, there are only a few works that provide HREELS information: an explorative paper of the vibrational fingerprint of very short chains,³⁹ a study of the correlation between surface order and layer preparation (substrate, immersion time),⁴⁰ and an investigation of the negative ion resonances in an octadecanethiol monolayer on Au(111) and Au(100).⁴¹

Our work consists of an analysis of spectra obtained in the specular geometry for primary energies of the incident electrons ranging from 1 to 10 eV. We first attribute the loss peaks observed in the HREELS spectra through comparison with IRAS data. Afterward, we give an estimation of the size of the coherent domain size, i.e., of the order in the thiolate layer. Finally, by studying the vibrational peak intensities as a function of electron primary energy we give evidence of resonances; this is corroborated by a study of the overtones.

2. Experimental Section

Materials. The 11-mercaptoundecanoic acid molecule was synthesized from 11-bromoundecanoic and mercaptoacetic acid according to the procedure which has been described elsewhere.⁴² Octadecanethiol (Aldrich, 98%) and absolute ethanol (Merck, 99.8%) were used as received.

Preparation of the Monolayer. Self-assembled monolayers are formed by the spontaneous adsorption of alkanethiol molecules onto gold substrates.²⁶ The substrate, a Au(111) single crystal, was cleaned by Ar⁺ sputtering–annealing cycles in a UHV chamber until a good low energy electron diffraction pattern was obtained and no trace of contaminants that could be detected by HREELS. After this treatment, the crystal was removed from the vacuum chamber and immediately was immersed for 2 h in a 10^{−3} mol/L 11-mercaptoundecanoic acid solution using absolute ethanol as solvent. The sample was copiously rinsed with absolute ethanol and dried in an argon stream prior to the IRAS analysis or to the introduction into the vacuum chamber of the HREELS spectrometer.

HREELS Measurements. The HREELS experiments were performed in a two-chamber UHV system equipped with a high-resolution spectrometer (ISA-Riber). The base pressures in the analysis and preparation chambers were 4 × 10^{−11} and 3 × 10^{−10} Torr, respectively. The spectrometer consists of two identical hemispherical electrostatic selectors, one acting as monochromator, the other as analyzer. The energy of the incident electron beam can be varied from $E_p = 0.5$ eV up to 150 eV. The spectrometer has an effective acceptance angle of 1.2°. For the study of vibrational properties of organic monolayers, the energy resolution measured as full width at half-maximum of the elastic peak was about 14 meV. All the HREELS spectra presented in this paper were carried out in the specular reflection geometry ($\theta_i = \theta_r = 45^\circ$) with an electron beam current on the sample of the order of 10^{−10} A.

IRAS Measurements. The IRAS spectrum was recorded on a Biorad FTS 60A FT-IR spectrometer equipped with a variable incidence angle accessory and a liquid nitrogen-cooled MCT detector. The system was purged with dried air to eliminate water vapor and carbon dioxide. The resolution was set to 4 cm^{−1}.

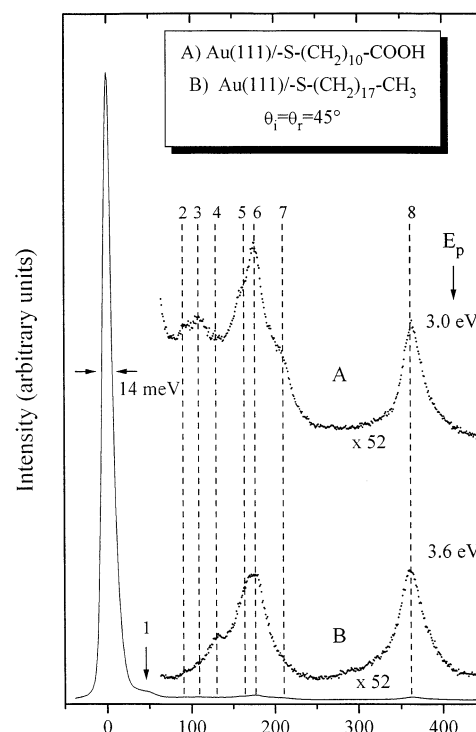


Figure 1. HREELS spectra of the 11-mercaptoundecanoic acid (A) and the octadecanethiol (B) monolayer recorded in the specular geometry ($\theta_i = \theta_r = 45^\circ$).

TABLE 1: Position and Assignment of the Observed HREELS Vibrational Losses of the 11-Mercaptoundecanoic Acid Self-Assembled Monolayer

peak no.	energy loss (meV)	frequency (cm ^{−1})	assignments
1	49	395	skeletal deformation
2	89	718	CH ₂ rocking, C–S stretching
3	108	871	OH–O wagging
4	131	1057	C–C stretching
5	163	1315	CH ₂ wagging, C–OH stretching
6	177	1428	CH ₂ scissoring, C–O–H bending
7	210	1694	C=O stretching
8	363	2928	C–H stretching

3. Results and Discussion

3.1. Vibrational Bands. Figure 1 presents HREELS spectra of a 11-mercaptoundecanoic acid ($E_p = 3.6$ eV) and for comparison, of an octadecanethiol monolayer ($E_p = 3.0$ eV). In both spectra, the intensities are normalized by setting the total area under the spectrum to one; they are then magnified by the same factor. From this comparison, we can assign all the vibrational losses of the 11-mercaptoundecanoic acid monolayer. At least 8 loss features, appearing as peaks and shoulders (numbered from 1 to 8) are observed. Their positions and assignments are summarized in Table 1.

Let us first observe that no S–H stretching band (expected at about 320 meV) is observed in the spectrum; this rules out the possibility of having a double layer structure (with hydrogen bonding between both layers); this is also a first indication of the good anchoring and order of the layer (see the next section).

Peak 1 is detected at 49 meV and falls in the frequency range where one expects the Au–S stretching³⁹ and the skeletal deformations of the C–C backbone chain.⁴³ However, there are several arguments against an assignment to the Au–S stretching: Nuzzo et al. observed it at ~28 meV on the HREELS spectrum of methanethiol and dimethyl disulfide monolayers on gold³⁹, and unpublished theoretical calculations for a CH₃S–Au system

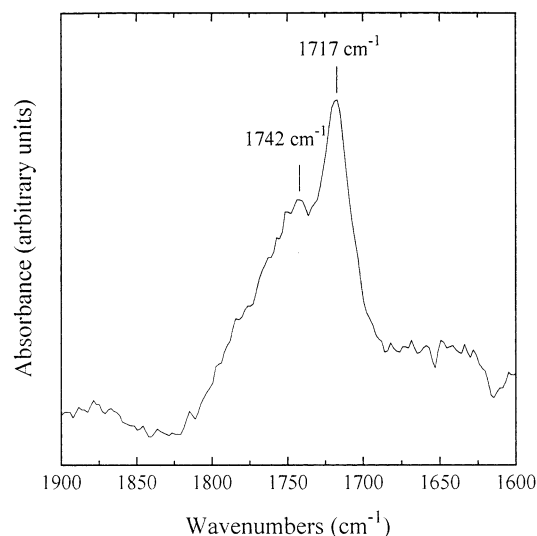


Figure 2. IRAS spectrum of the 11-mercaptoundecanoic acid monolayer in the C=O stretching region.

gives a value of ~ 35 meV.⁴⁴ Moreover, this loss is not seen systematically for all the alkanethiol molecules adsorbed on gold studied so far.⁴⁰ We therefore tentatively attribute the loss peak at 49 meV to skeletal deformations of the C–C backbone. These deformations are chain expansion–contraction motions where all C–C–C angles change in-phase. It has been shown that the frequency of these modes depends on the carbon number in the paraffin chain as well as on the presence of gauche sequences.⁴³ For an alkane chain with 11 carbon atoms in all-trans conformation, the vibration is observed at 206 cm^{-1} (~ 25 meV) in the Raman spectrum.⁴³ The peak is shifted toward higher frequency when gauche defects appear in the chain or when the alkane chain is shorter. The value observed for the 11-mercaptoundecanoic acid monolayer (49 meV) could therefore point to the presence of gauche defects in the alkane chain. Such defects are probably responsible for the disorder in the monolayer which is evidenced by the fact that the off-specular spectra present in this energy range exactly the same structures as the specular ones.⁴¹

Peak 2 at 89 meV corresponds to the CH₂ rocking and the C–S stretching modes. The next peak at ~ 108 meV, which is absent in the spectrum of the octadecanethiol monolayer, is attributed to the OH- -O wagging of the carboxylic groups. It is indeed well-known that in condensed systems carboxylic groups often assemble as dimers.^{45,46} To confirm the existence of such dimers in our monolayer we also collected the infrared spectrum presented in Figure 2. It shows two peaks in the 1700–1750 cm^{-1} region: the C=O stretching mode of the isolated C=O group appears at 1742 cm^{-1} while the hydrogen-bonded one is at 1717 cm^{-1} .⁴³ The molecules in the ideal (defect-free) overlayer must therefore present the geometrical arrangement shown in Figure 3.

Returning to the attribution of the spectral features of Figure 1, we note that band #4 appearing at 131 meV corresponds to the C–C stretching mode of the carbon skeleton. The next three features may be attributed on the basis of the IR and Raman literature as follows:⁴³ the shoulder at 163 meV corresponds to the wagging mode of the CH₂ groups but contains probably also a contribution of the C–O stretching mode which cannot be resolved. The loss peak at 178 meV is a mixing of CH₂ scissoring and C–O–H bending modes and the marked shoulder at 210 meV is due to the C=O stretching mode of the carboxylic

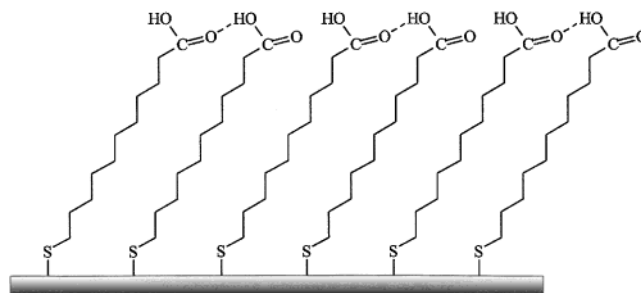


Figure 3. Representation of the 11-mercaptoundecanoic acid self-assembled monolayer.

groups. The latter assignment is confirmed by the absence of the 210 meV feature in the octadecanethiol spectrum (Figure 1, curve B).

Finally, the broad structure at 363 meV is a fingerprint of the C–H stretching modes. However, it contains not only the symmetric and antisymmetric C–H stretching modes but also a contribution of the O–H stretching modes due to carboxylic groups involved in hydrogen bonds, as well as the first harmonic of the peak at 178 meV (i.e., CH₂ scissoring and C–O–H bending modes).

3.2. Domain Size. The angular distribution of the elastically scattered electrons was measured on the 11-mercaptoundecanoic monolayer to obtain some information about the organization of the layer. Following LEED theory and assuming circular domains, one may, in fact, obtain a rough estimate of the domain size, D (Å), from the angular width at half-maximum (fwhm) of the elastic peak, $\Delta\theta$ (rad)⁴⁷:

$$D \cong \frac{\lambda}{2\Delta\theta \cos\theta}$$

where θ (rad) is the angle of incidence and λ (Å) is the wavelength of the incident electrons of energy E_p (eV):

$$\lambda(\text{\AA}) = \frac{12}{\sqrt{E_p(\text{eV})}}$$

A typical angular distribution is presented in Figure 4, wherefrom a fwhm of 3.5° is calculated, leading to an estimate of the coherent domain size of ~ 95 Å. This value is slightly lower but comparable to the one obtained for a monolayer of simple alkanethiols containing approximately the same number of carbon atoms (decanethiol, 106 Å).⁴¹ This seems to suggest that the carboxylic groups have no negative effect on the organization of the overlayer. However, larger domain sizes have been obtained with longer alkane chains,⁴⁰ implying that the 11-mercaptoundecanoic acid monolayer is less organized, probably due to its relatively short carbon chain length and/or to dimer formation.

3.3. Resonant Excitation. The resonant excitation represents an additional channel for the appearance of a vibrational loss which is present only when the energy of the probing electron matches that of an affinity state of the molecule. In the HREELS spectra, it shows up as an increase in intensity for a particular vibrational loss which persists over a range of primary energies. To identify a resonant excitation one has therefore to monitor the intensity of the various features in the HREELS spectrum of the 11-mercaptoundecanoic acid monolayer as a function of the primary energy of the incident electrons. The spectra are presented in Figure 5. Two enhancements of the loss intensities are easily identified, one around 1.5 eV primary energy, the second one starting above 5 eV; both resonances are ac-

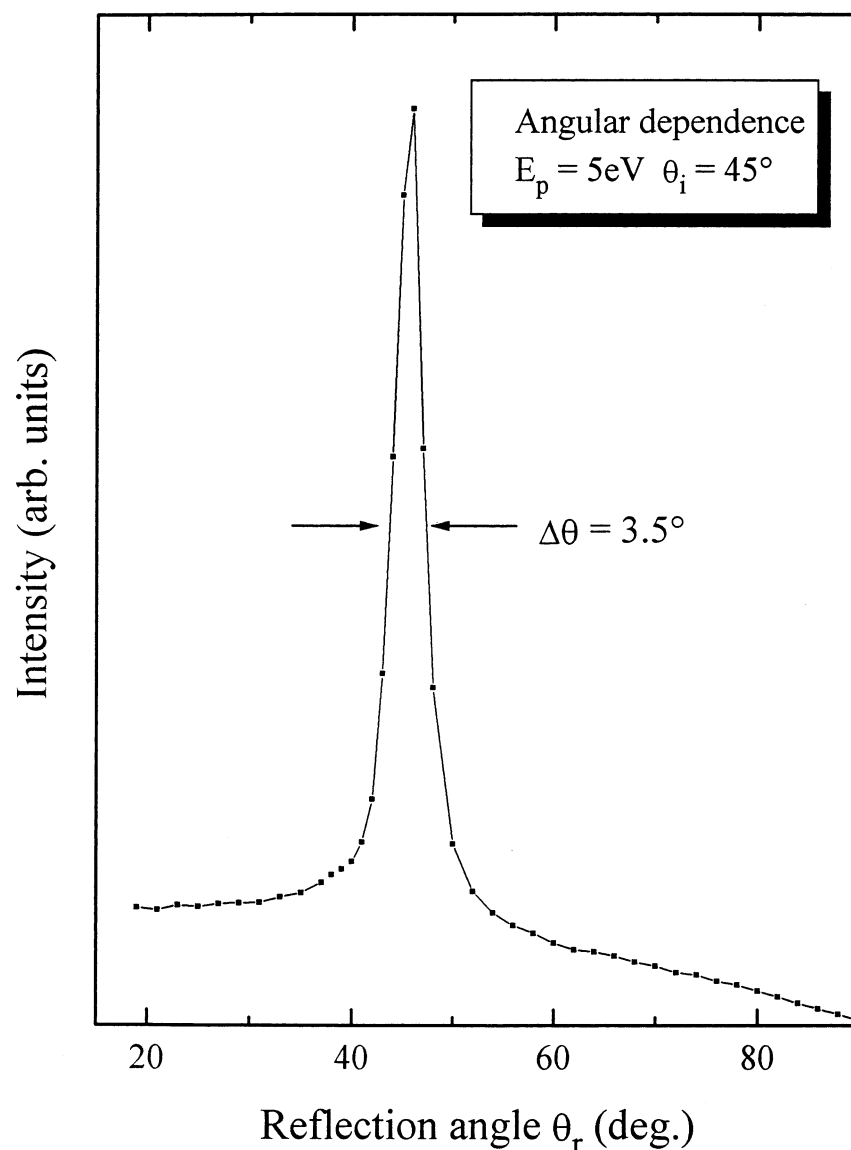


Figure 4. Angular distribution curve around the specular direction (45°) of the HREELS elastic peak intensity recorded on the 11-mercaptoundecanoic acid monolayer.

accompanied by an enhancement of the overtone intensities. This behavior is typical for a negative ion resonance. In fact, the excited vibrational state is created in the de-excitation of the negative ion state and this channel follows different selection rules than the direct excitation one.¹² The resonances are observed over a range of energies which is rather narrow for the first one at $E_p = 1.5$ eV, while it is very broad for the second one starting at 5 eV.

These are probably not the only resonances which exist for this layer, but we did not investigate primary energies higher than 13 eV since we noticed that electron-induced sample damage occurred for values of $E_p > 13$ eV.

To identify the affinity state into which the primary electron is trapped, the relative intensity variation of each loss feature was determined over the whole primary energy range from 0.7 to 13 eV. The result is presented in Figure 6. These intensities were obtained as peak heights after normalizing the area of the whole HREELS spectrum taken at a particular E_p to unity. The curve corresponding to the C=O stretching mode at 210 meV clearly shows the strongest enhancement around 1.0–1.5 eV primary energy. This phenomenon is also seen for the C–OH stretching mode at 163 meV.

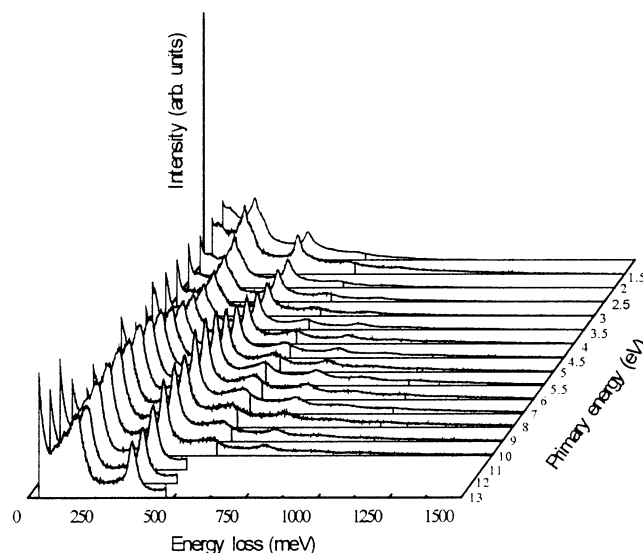


Figure 5. HREELS spectra of the 11-mercaptoundecanoic acid monolayer recorded in the specular geometry ($\theta_i = \theta_r = 45^\circ$) for different electron primary energies.

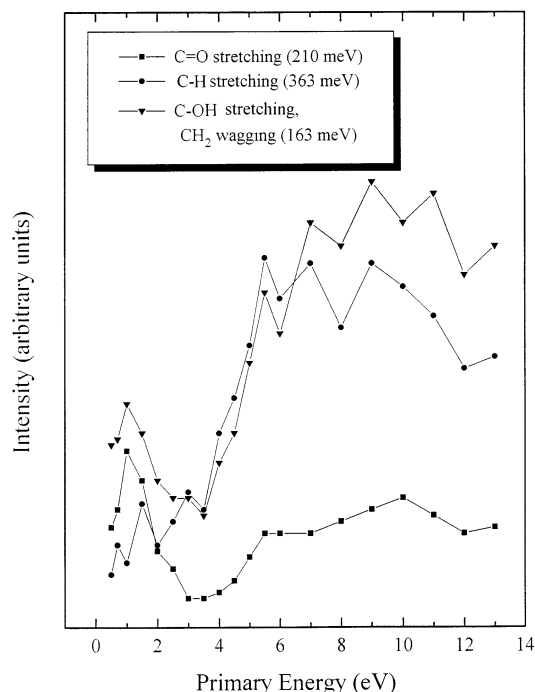


Figure 6. Loss probabilities of the vibrational modes detected at 210, 363, and 163 meV on the 11-mercaptoundecanoic acid monolayer HREELS spectra versus electron primary energy.

There are very scarce literature values on resonance energies at low electron energy; most of the data were collected on small (diatomic in most cases) molecules, and they are not relevant here. For large condensed or chemisorbed molecules, a NIR (negative ion resonance) has been observed for benzene on Pd(100) at 2.7 eV;⁵ benzene on Pt(111) at 2.1 eV;⁶ formic acid at 1.8 eV;⁹ acetaldehyde, formaldehyde, and acetone at 1.3, 1.3, and 1.5 eV, respectively;⁴⁸ and butadiene at 1 eV.⁴⁸

With Ben Arfa et al., we attribute the 1.5 eV resonance in 11-mercaptoundecanoic acid to a π^* -shape resonance ($C=O$ antibonding state) in the carboxylic end group. No resonance has been reported up to now at such a low energy for linear hydrocarbon chains, except for the small ethylene molecule (π^* - $C-C$ resonance between 1 and 3 eV⁴⁸). This π^* -shape resonance in the carboxylic end group at 1.5 eV may be compared to NIR values measured for condensed chemisorbed formic acid molecules on Al (a resonance seen at 3.5 eV¹¹) whereas in polycarbonate, a $O-C-O$ resonance has been measured also at 3.5 eV.²⁰ It seems thus that the very low energy value of the observed NIR is really intrinsic to the quasi free carboxylic end group, terminating the 11-mercaptoundecanoic acid chain, far from the gold substrate.

For the resonance at higher energy, the CH_2 modes do experience the strongest enhancement as can be seen from the curve relative to the $C-H$ stretching at 363 meV in Figure 6. The maximum of this broad resonance is reached at 6 eV, a value which points to a σ^* resonance of the $C-H$ bond widely described in the literature.^{12,49,50}

In Figure 6, one sees clearly that the $C=O$ band intensity, if the largest around 1.0–1.5 eV (at the resonance), becomes the smallest above 6 eV impact energy; the reverse is true for the $C-H$ stretch band intensity: it is the most intense at 6 eV and above, and small at 1 eV. It seems that there is thus no clear-cut in the symmetry of the empty orbitals participating to the resonances: that may imply some kind of delocalization of the electrons in these empty states. As for the band at 163 meV, it is more equally intense at both impact energies, with a sharp

resonance at 1 eV and a broad one above 6 eV; this is probably a confirmation of this band assignment, which is composed of both $C-OH$ stretch and CH_2 wag intensities.

4. Conclusions

We have studied the high-resolution electron energy loss spectra of a self-assembled monolayer of 11-mercaptoundecanoic acid on Au(111). Low-energy negative ion resonances are observed at 1.0–1.5 and above 6 eV, involving respectively a π^* -shape resonance in the carboxylic end group, and a σ^* resonance of the $C-H$ bond.

Our spectroscopic analysis including FT-IR allowed also to evidence the formation of dimers in the monolayer. Finally, the analysis of the angular distribution of the elastically scattered electrons allowed us to get some information about the structural organization of the layer, leading to an estimate of a coherent domain size of about 100 Å, quite in the range of what is obtained for other alkanethiols.

Acknowledgment. This work has been supported by different research funding agencies; we acknowledge support of the Interuniversity Research Project PAI 4/10 on “Reduced Dimensionality System” sponsored by the Belgian Prime Minister’s Office; the FRFC research convention no. 2.4544.98 on “Electron-molecules resonances”; the Region Wallonne research convention 3119 on “ultra thin-films”; and the EU-HCM-NIR (Negative ion resonances of adsorbed molecules on surfaces) network ERB-CHRX-CT 93-0326.

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