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HREELS study of the interaction of aniline with Cu(110)

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Abstract

The adsorption and reaction of aniline on Cu(110) was studied using a combination of high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). HREEL spectra with an energy resolution of $\sim 13 \text{ cm}^{-1}$ were obtained for both multilayer and monolayer aniline-derived surface species permitting a comprehensive comparison with the infrared spectra of liquid and gaseous aniline. The experimental results indicate that aniline forms randomly-oriented multilayers upon adsorption at 100 K, while at 300 K aniline adsorbs dissociatively forming stable $\text{C}_6\text{H}_5\text{NH}$ surface species. This species decomposes between 525 and 875 K producing gaseous H_2 and N_2 and adsorbed carbon.

Keywords: Amines; Copper; Electron energy loss spectroscopy; Low index single crystal surfaces; Vibrations of adsorbed molecules

1. Introduction

High resolution electron energy loss spectroscopy (HREELS) is a powerful technique for characterizing the vibrational structure of adsorbed surface species. In the past, the major disadvantage of HREELS compared to other vibrational spectroscopies, such as Raman and infrared (IR) spectroscopy, has been its inherently low resolution. However, recent improvements in the design and construction of HREEL spectrometers has made it possible to achieve energy resolution approaching that obtained in IR spectroscopy [1]. In the present investigation we demonstrate how this new generation of HREEL spectrom-

eters allows for the characterization of the vibrational modes of adsorbed species in unprecedented detail. The system of study in this investigation was the interaction of aniline ($\text{C}_6\text{H}_5\text{NH}_2$) with Cu(110).

The interaction of aniline with metal surfaces has been the subject of several recent investigations [2–5]. These studies have been motivated by interest in the structure and properties of thin films of polyaniline, a conducting polymer, and by the fact that aniline is a subunit of polyimides. Ramsey et al. demonstrated that aniline adsorbs dissociatively on Pd(110) forming a stable $\text{C}_6\text{H}_5\text{NH}$ species [4]. The dehydrogenation of adsorbed aniline was observed on Pt(111) at temperatures between 350 and 450 K [2], while on Ni(100) and Ni(111) surfaces, aniline was found to polymerize with the resulting polymer being stable to temperatures in excess of 700 K [3,5]. The HREELS and TPD results presented below indi-

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cate that aniline also adsorbs dissociatively on Cu(110).

2. Experimental

The HREELS experiments were performed in an ultra-high vacuum chamber equipped with an LK Technologies model 3000 spectrometer. The design of this spectrometer is described in detail by Ibach [1]. The vacuum chamber containing the HREEL spectrometer was also equipped with LEED/AES optics (OCI). TPD experiments were carried out in a separate ultra-high vacuum chamber equipped with a mass spectrometer (UTI) and an AES spectrometer (Omicron).

Prior to use, the Cu(110) single crystal was polished with diamond paste until optically smooth. In-situ cleaning of the surface was achieved by cycles of Ar^+ sputtering and annealing. A cycle consisted of sputtering for 15 min at a beam energy of 1 keV and a sample temperature of 300 K, followed by sputtering for 30 min at a sample temperature of 600 K, and then annealing at 900 K for 15 min. This procedure produced a clean surface that exhibited a sharp (1×1) LEED pattern.

Aniline was obtained from Fisher Scientific and was purified by numerous freeze-pump-thaw cycles prior to use. The HREEL spectrometer was operated with an electron beam energy of 4.0 eV and all spectra were collected in the specular direction with the electron beam directed 60° from the surface normal. The elastic peak obtained from the Cu(110) surface was typically 100–150 kHz in intensity with a full width at half maximum (FWHM) of 1.6–2.0 meV.

3. Results and discussion

The interaction of aniline with Cu(110) was initially studied using TPD. Fig. 1 displays a TPD spectrum obtained after dosing 20 L of aniline onto the Cu(110) surface at 100 K. The most prominent feature in the TPD spectrum is a narrow aniline desorption peak ($m/e = 93$) centered at 195 K. The abrupt leading edge of this peak and its narrow width

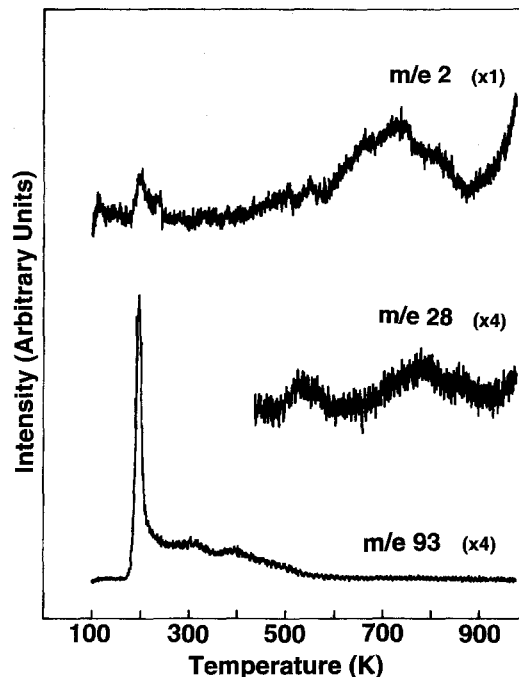


Fig. 1. TPD data obtained from Cu(110) dosed with 20 L of aniline at 100 K. Mass-to-charge ratios 2, 28, and 93 correspond to hydrogen, nitrogen, and aniline, respectively.

suggest a zero-order process which is typical of the desorption of weakly-bound multilayers. A broad tail on the aniline desorption peak extending up to approximately 500 K is also observed.

In addition to aniline, both N_2 and H_2 were detected as products during the TPD experiments. Hydrogen desorption was observed in the 180–250 K and 500–875 K regions. The low-temperature H_2 desorption feature appears to consist of two overlapping peaks centered at 195 and 235 K. The low-temperature peak is coincident with the aniline multilayer desorption feature and therefore could be due to a cracking fragment of aniline. The smaller peak at 235 K can be assigned to the recombinative desorption of adsorbed hydrogen atoms. The production of H_2 at low temperature suggests that a portion of the adsorbed aniline dissociates. Nitrogen desorption was observed in two peaks at 525 and 775 K. The desorption of NH_3 , C_2H_2 and C_6H_6 was also monitored, but these products were not detected within the sensitivity limits of the mass spectrometer.

AES spectra collected after TPD indicated that the surface was partially covered with a layer of carbon.

Molecular aniline can bind to metal surfaces by interactions with the π -electron system of the aromatic ring and the lone pair electrons on the amine nitrogen. Previous studies of related molecules have shown that neither mechanism produces a particularly strong bond to the Cu(110) surface [6–8]. For example, the desorption temperature for C_6H_6 on Cu(110) is less than 270 K [8], while NH_3 desorbs from Cu(110) below 255 K [6,7]. This suggests that the TPD products detected above 300 K do not result from adsorbed molecular aniline. It has been reported that aniline adsorbs dissociatively on both Pd(110) and Pt(111) surfaces to form stable C_6H_5NH species [2,4]. Since alcohols and carboxylic acids are known to adsorb dissociatively on Cu(110) [9–12], it would not be surprising if aniline also adsorbs dissociatively on this surface. This possibility is consistent with the presence of a low-temperature H_2 desorption feature in the TPD results. Another possibility that would account for the thermal stability of the surface species formed from aniline is that adsorbed aniline undergoes a polymerization reaction. It has been postulated that aniline reacts to form polyaniline on both Ni(100) and Ni(111) surfaces, with the resulting polymer being stable to temperatures in excess of 700 K [3,5].

In order to identify the stable species formed on the aniline-dosed Cu(110) surface, vibrational spectra of the adsorbed species were collected using HREELS. The results of these experiments are summarized in Fig. 2. The lower spectrum in this figure corresponds to that of the clean Cu(110) surface. The only feature present in this spectrum is a small peak centered at 155 cm^{-1} which has been previously assigned to a surface phonon mode by Baddorf et al. [13].

Fig. 2c corresponds to HREEL spectrum obtained after exposure to 20 L of aniline at 100 K. Based on the TPD results, this dose is sufficient to produce adsorbed multilayers. The high resolution of this spectrum (13 cm^{-1}) allows a comprehensive comparison to be made with IR spectra of liquid and gaseous aniline [14,15]. The assignment of the vibrational peaks are listed in Table 1. As shown in this table, the peak positions in the HREEL spectrum of condensed aniline are in excellent agreement with

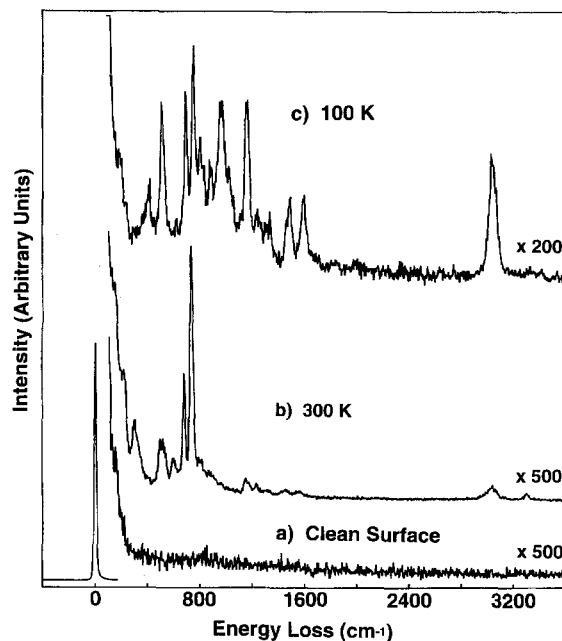


Fig. 2. HREELS spectra for (a) clean Cu(110), (b) Cu(110) saturated with aniline at 300 K, and (c) Cu(110) dosed with 20 L of aniline at 100 K.

those of the infrared spectra of the molecular species. By comparison to the IR spectra, the peaks in the HREEL spectrum of the adsorbed multilayer can be assigned in the following manner. The peaks centered at 3400 and 3310 cm^{-1} correspond to asymmetric and symmetric NH_2 stretching modes. The loss at 3070 cm^{-1} is consistent with a CH stretching mode. Note that in the IR spectrum of gaseous aniline, there are three CH stretching modes, one symmetric and two asymmetric. These separate modes cannot be distinguished in the HREEL spectrum of the surface species. However, the peak at 3070 cm^{-1} is rather broad compared to that of the elastic peak suggesting that it is comprised of several overlapping features. The small shoulder at 1600 cm^{-1} corresponds to an NH_2 scissor mode, while losses in the region 1580 – 1335 cm^{-1} can be assigned to aromatic ring stretches. The peak at 1270 cm^{-1} and the shoulder at 1065 cm^{-1} result from a CN symmetric stretch and an NH_2 twist, respectively. In-plane and out-of-plane CH bending modes can be assigned to the peaks between 1270 and 750 cm^{-1} , while the loss at 802 cm^{-1} corresponds to a

combination of a CN stretch and a ring stretch. The peaks at 645 and 400 cm^{-1} can be attributed to an NH_2 wag and a CN rock, respectively.

A HREEL spectrum of the Cu(110) surface saturated with aniline at 300 K is shown in Fig. 2b. Since the aniline multilayer desorption temperature is below room temperature, this spectrum corresponds to that of the chemisorbed species. An identical spectrum was obtained from a sample that was dosed with aniline at 100 K and then heated to room temperature. Comparison of the spectra of the chemisorbed species and the condensed multilayers reveals several differences, the most noticeable being the intensities of the various peaks. The differences

in the relative peak intensities can be attributed to different orientations for the physisorbed and chemisorbed species relative to the metal surface. Based on the surface dipole selection rule, only those modes which have a component of their oscillating dipole moment perpendicular to the surface have a non-zero cross-section for dipole scattering. Oscillating dipoles oriented parallel to the surface are screened by an induced image dipole in the metal. Since image dipole effects are expected to be less pronounced for multilayers and the condensed layer is likely to be disordered, the intensities obtained in the multilayer spectrum can be assigned to randomly oriented molecules. This is further supported by the

Table 1
Assignment of vibrational modes

Vibrational mode ^a	Gas phase ^b	Liquid phase ^b	Monolayer ^c	Multilayer ^d
NH_2 asym. str.	3500	3440		3400
NH_2 sym. str.	3418	3360		3310
NH str.	—	—	3300	
CH asym. str.	3089	3088		
CH sym. str.	3047	3072	3036 ^e	3070 ^e
CH asym. str.	3025	3010		
NH_2 scissor	1619	1618		1600sh
Ring str.	—	1586		1580
NH bend	—	—	1565	
Ring str.	1503	1500	1460	1495
Ring str.	—	1468		1470sh
Ring str.	—	1330		1335
CH i.p. bend	—	1312	1320	1310
CN sym. str.	1279	1278	1236	1270
CH i.p. bend	1173	1175	1154	1165
CH i.p. bend	1084	1118		1100sh
NH_2 twist	—	1050		1065sh
CH i.p. bend	1028	1028		1020sh
Ring breathing	990	996		970
CH o.p. bend	874	880	890	875
CH o.p. bend	825	826		820sh
CN str. ring str.	812	810	800	802
CH o.p. bend	750	751	740	750
Ring o.p. def.	690	691	680	690
NH_2 wag	664	670		645
NH def.	—	—	600	
Ring o.p. def.	500	501	510	505
CN rock	390	390	305	400

^a i.p. = in-plane; o.p. = out-of-plane; def. = deformation; str. = stretch; sh = shoulder.

^b Values from Ref. [14].

^c Data for saturation coverage at room temperature.

^d Data for multilayers condensed at 100 K.

^e Broad peak indicates multiple components.

fact that there is an excellent one-to-one correspondence between the peak positions in the condensed layer spectrum and the IR spectrum of liquid aniline.

The two most intense peaks in the spectrum obtained at 300 K are centered at 680 and 740 cm^{-1} . These peaks can be assigned to an out-of-plane ring deformation and a CH out-of-plane bending mode, respectively (see Table 1). The high intensity of these two peaks relative to that of the other ring modes indicates that these vibrational modes are directed more perpendicular to the surface. This would be the case if the aromatic ring of the adsorbed species is oriented approximately parallel to the surface. The assignment of the remaining modes involving the aromatic ring is detailed in Table 1.

Although the intensities of the ring modes vary significantly between the spectra obtained at 100 and 300 K, it is important to note that the frequencies of these modes remain fixed. It has previously been shown that bonding of an aromatic ring to a metal surface produces a shift in the frequency of the out-of-plane CH bending modes relative to those of the gas phase molecule [8,16]. The magnitudes of these shifts have been used to estimate the strength of the metal–ring interaction [8,17]. Virtually no shift in frequency is observed for weakly interacting molecules, such as benzene on Cu(111), whereas for strongly interacting molecules, these shifts can be on the order of 50–150 cm^{-1} [8,16]. In the 300 K spectrum, the CH bending mode occurs at 740 cm^{-1} , a value only 10 cm^{-1} lower than that for the gas phase molecule. This indicates that the aromatic ring interacts rather weakly with the Cu(110) surface. This result also suggests that the chemisorbed species is not a polymerized form of aniline. Formation of polyaniline would considerably alter the structure of the aniline ring, transforming a mono-substituted phenyl ring into a 1,4-di-substituted species. This would be expected to cause a measurable shift in the frequencies of the ring modes compared to those for molecular aniline in the multilayer spectrum. The C–H bending mode would also be expected to shift to approximately 800 cm^{-1} , which is where this mode appears in the IR spectrum of fully reduced polyaniline [18,19].

More definitive clues as to the mode of interaction of the room temperature aniline species with the surface can be obtained by examining the NH

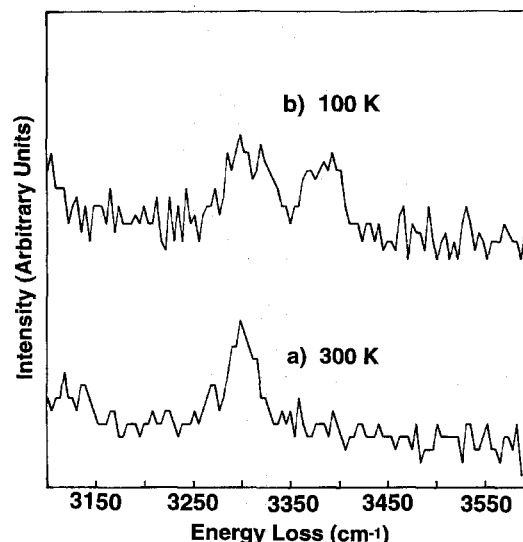


Fig. 3. N–H stretching region of the HREEL spectrum of (a) Cu(110) saturated with aniline at 300 K and (b) Cu(110) dosed with 20 L of aniline at 100 K.

stretching region of the spectra. An expanded view of this portion of the spectrum for both the 100 and 300 K species are displayed in Fig. 3. The spectrum at 100 K corresponds to that of the condensed species and contains two separate NH stretching modes centered at 3400 and 3310 cm^{-1} . As noted previously, these peaks can be assigned to NH_2 asymmetric and symmetric stretches, respectively. The spectrum at 300 K corresponds to the chemisorbed species, and, in contrast to the multilayer spectrum, only a single NH stretching mode at 3300 cm^{-1} is observed. The absence of a peak near 3400 cm^{-1} due to the NH_2 asymmetric stretch indicates either that this mode is not dipole-active for the chemisorbed species or that aniline adsorbs dissociatively on Cu(110) to form a secondary amine, characterized by a single NH stretch near 3300 cm^{-1} [20]. The latter explanation is most plausible since an aniline bonding configuration in which the aromatic ring is oriented nearly parallel to the surface would require the oscillating dipole of the NH_2 asymmetric stretching mode to have a component oriented perpendicular to the surface, and thus be dipole-active. The frequencies of the CN stretching and rocking modes of the adsorbed species also suggest a change in the chemical structure of the amine functionality. For the chemisorbed

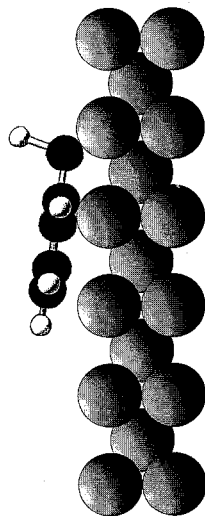


Fig. 4. Postulated bonding geometry for C_6H_5NH on Cu(110).

species, the CN stretch occurs at 1236 cm^{-1} and the CN rock at 305 cm^{-1} , which are 34 and 95 cm^{-1} lower in energy, respectively, than the corresponding modes in the multilayer spectrum.

The TPD and HREELS results clearly indicate that aniline adsorbs dissociatively on Cu(110) at room temperature to form C_6H_5NH which bonds in a configuration in which the phenyl ring is nearly parallel to the surface. This species is similar to that formed by the reaction of aniline on Pt(111) and Pd(110) [2,4]. A possible bonding configuration for C_6H_5NH on the Cu(110) surface is presented in Fig. 4. A slight tilting of the molecule into the grooves on Cu(110) allows for bonding via the nitrogen while maintaining interaction between the phenyl ring and the surface. This bonding configuration is the same as that proposed for C_6H_5NH on Pd(110) [4]. The slight tilt of the ring explains the low intensities of the majority of the in-plane modes of the phenyl group in the HREEL spectrum of the chemisorbed species. If the aromatic ring were oriented completely parallel to the surface these modes would be expected to be absent from the spectrum, as is the case for low coverages of C_6H_6 on Cu(111) [16].

The aforementioned tail on the aniline desorption peak in the TPD spectrum indicates that a portion of the adsorbed C_6H_5NH recombines with surface hydrogen and desorbs as aniline between 250 and 500 K. Some of the adsorbed C_6H_5NH species, however,

are stable to higher temperatures as indicated by the desorption products detected above 500 K and the fact that carbon is deposited on the surface. The presence of N_2 and H_2 desorption peaks near 525 K in the TPD results suggests that the onset of the decomposition of the C_6H_5NH occurs near this temperature. The N_2 peak at 775 K is at a temperature near that reported for the recombinative desorption of nitrogen atoms from Cu(110) [21].

4. Conclusions

The results of this investigation demonstrate that aniline forms randomly oriented multilayers upon adsorption on Cu(110) at 100 K, while dissociation occurs at 300 K to form stable C_6H_5NH species. The vibrational spectrum of this species indicates that its adsorption geometry is such that the aromatic ring is situated nearly parallel to the surface. Adsorbed C_6H_5NH decomposes between 525 and 875 K producing gaseous N_2 and H_2 and adsorbed carbon. This study also demonstrates the capabilities of the latest generation of HREEL spectrometers for the characterization of the vibrational structure of complex organic molecules on metal surfaces.

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