

# CO–NO and CO–O<sub>2</sub> Interactions on Cu(100) between 25 and 200 K Studied with Infrared Reflection Absorption Spectroscopy

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Infrared reflection absorption spectroscopy (IRAS) has been used to study CO–NO and CO–O<sub>2</sub> interactions on Cu(100) between 25 and 200 K. A strong repulsive interaction between CO and NO on Cu(100) at 25 K causes tilting of the CO molecules away from the surface normal and a blue-shift of the CO vibrational frequency. Upon warming and decomposition of the NO, the CO molecules return to a bonding position normal to the surface plane. The vibrational frequency of CO blue-shifts from 2087 to 2136 cm<sup>-1</sup> upon coadsorption with N and O atoms formed from NO decomposition. On the other hand, the interaction of CO with O<sub>2</sub> at 27 K on Cu(100) in the submonolayer regime induces a red-shift of the CO vibrational frequency. Atomic oxygen, formed on Cu(100) by dissociation of O<sub>2</sub> at 95 K, induces a blue-shift of the vibrational frequency of coadsorbed CO to 2116 cm<sup>-1</sup>. The CO vibrational frequency shifts to 2091 cm<sup>-1</sup> when the surface is annealed to 140 K, implying a change in the adsorption geometry of the oxygen atoms on Cu(100).

## 1. Introduction

The interaction of adsorbates with coadsorbed molecules, atoms, and ions is a key to understanding reactions catalyzed by metal and metal oxide surfaces. Infrared reflection absorption spectroscopy (IRAS) is an ideal technique for studying the interaction of CO with coadsorbed species because of the sensitivity of its vibrational frequency to environment.<sup>1–4</sup> The change in the vibrational frequency of CO due to other atomic and molecular adsorbates provides considerable insight into the details of the interaction.

When CO is adsorbed onto most metal surfaces, the CO stretching frequency shifts to a lower frequency (a so-called red-shift) relative to the gas-phase value of 2143 cm<sup>-1</sup>.<sup>5</sup> When CO is adsorbed onto a metal surface without another adsorbate, the vibrational frequency of a molecule is influenced primarily by three contributions: mechanical renormalization, the image dipole, and the chemical bond with the surface.<sup>1</sup> Mechanical renormalization, the so-called “wall effect”,<sup>6</sup> arises because the CO molecular stretch frequency is altered due to the rigid surface to which it is bound. The vibrational frequency shift to a higher frequency (a so-called blue-shift) due to this effect has been estimated to be approximately 50 cm<sup>-1</sup>.<sup>1</sup> The interaction of adsorbed CO with its dipole image in the metal surface plane causes a red-shift of the CO vibrational frequencies of 30–50 cm<sup>-1</sup>.<sup>7</sup> A CO molecule bonds via electron donation from the 5σ orbital to the metal and by back-donation from the metal d-band to the 2π\* orbital.<sup>8,9</sup> The chemical bonding of CO to a metal surface generally weakens the C–O bond and causes a red-shift of the CO vibrational frequency. The strength of this chemical bonding depends critically on the electronic structure of the surface. The vibrational frequency of CO varies, depending on the particular bonding site on the metal surface: typically 2130–2000 cm<sup>-1</sup> for a linear bound species, 2000–1860 cm<sup>-1</sup>

for a 2-fold bridging species, 1920–1800 cm<sup>-1</sup> for a 3-fold bridging configuration, and 1800–1700 cm<sup>-1</sup> for a 4-fold bridging CO.<sup>2</sup>

The vibrational frequency of CO adsorbed on a metal surface can be modified by coadsorbed molecules, atoms, and ions. The various explanations offered for the observed vibrational frequency shifts generally fall into two broad categories: dipole coupling and chemical effects. An adsorbed molecule experiences an electric field originating from surrounding dipoles. The dipole coupling that an adsorbed molecule experiences with these surrounding dipoles can occur either through-space<sup>10,11</sup> or through-bond.<sup>12</sup> Chemical effects include any interaction that affects the bonding of CO to a metal substrate. Several mechanisms have been proposed to explain the interactions between CO and coadsorbed species as well as the effect these interactions have on the shift of the vibrational frequency.<sup>13</sup> These include the following: (a) electron donation from electropositive species to a metal that enhances back-donation leading to a red-shift of the CO vibrational frequency; (b) depopulation of the metal d states by electronegative species giving rise to a blue-shift in the CO frequency; and (c) a strong repulsive interaction that weakens the CO–metal bond with a consequent blue-shift of the CO frequency.

In addition to vibrational frequency shifts, tilting of CO on the surface has been observed as a result of lateral interactions. Frequently, it has been observed that the adsorption geometry of CO is changed from an upright configuration to a tilted one as the CO coverage is increased, that is, CO on Pt(110),<sup>14–16</sup> Pt(111),<sup>17</sup> Pt(112),<sup>18</sup> Pd(110),<sup>19,20</sup> Cu(110),<sup>21</sup> Ni(110),<sup>22,23</sup> Ru(0001),<sup>24</sup> and Mo(110).<sup>25</sup> Interaction with coadsorbed species can also cause tilting of CO on a surface. For example, CO tilts from the surface normal when coadsorbed with K on Ni(110).<sup>22,23</sup> CO also tilts from the surface normal on Mo(110) at low CO coverages; however, when coadsorbed with Cu, CO bonds upright.<sup>25</sup> On Cu(100), tilted CO is stabilized by coadsorbed oxygen;<sup>26</sup> on Pt(533), CO tilts by more than 42° from the surface normal when coadsorbed with butane.<sup>27</sup>

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In this study, IRAS has been used to estimate the tilt angle of CO with respect to the surface normal caused by the interaction of CO with coadsorbed NO and O<sub>2</sub> on Cu(100) between 25 and 200 K. This estimate is based on the surface selection rule,<sup>28,29</sup> where only those vibrations with dipole moments perpendicular to the surface are detected.<sup>1</sup> The interaction between CO and NO on Cu(100) is repulsive and causes significant tilting of CO from the surface normal. The interaction between physisorbed CO and O<sub>2</sub> is weaker than that between CO and NO on Cu(100), whereas oxygen atoms, formed by dissociation of molecular O<sub>2</sub> at 100 K, strongly interact with CO.

## 2. Experimental Section

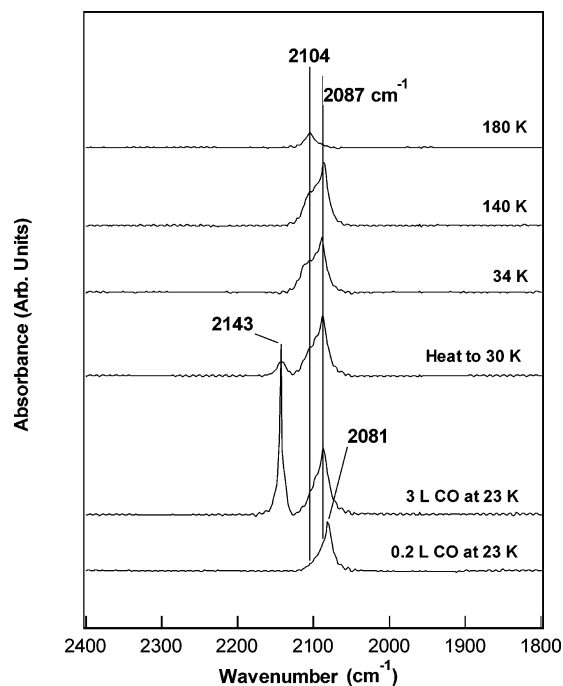
The experiments reported here were carried out in an ultrahigh vacuum (UHV) chamber equipped with IRAS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a quadrupole mass spectrometer. The IRAS spectra were obtained using a Matterson Cygnus 100 spectrometer. The IR beam impinged the sample through a CaF window with an incident angle of 85° with respect to the surface normal. The spectra were acquired with a resolution of 4 cm<sup>-1</sup> using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The instrumentation and data acquisition for IRAS have been described in detail elsewhere.<sup>30</sup>

A Cu(100) sample was mounted on a Vacuum Generators heating and cooling sample stage directly attached to a continuous flow liquid helium cryostat. The sample could be cooled to 21 K and heated to 1100 K. The sample temperature was measured using a K-type thermocouple that was mechanically attached to the top of the sample. The temperature was calibrated using liquid nitrogen and the desorption temperature of multilayer CO.<sup>31</sup> The Cu(100) single-crystal sample was cleaned by repeated cycles of argon ion sputtering at 300 K and an anneal at 750 K. The cleanliness and order of the sample surface were confirmed with AES and LEED. A precision leak valve was used for gas exposures. The purity of the gases was checked with mass spectrometry and with IRAS of the gas condensed on the sample surface at 21 K.

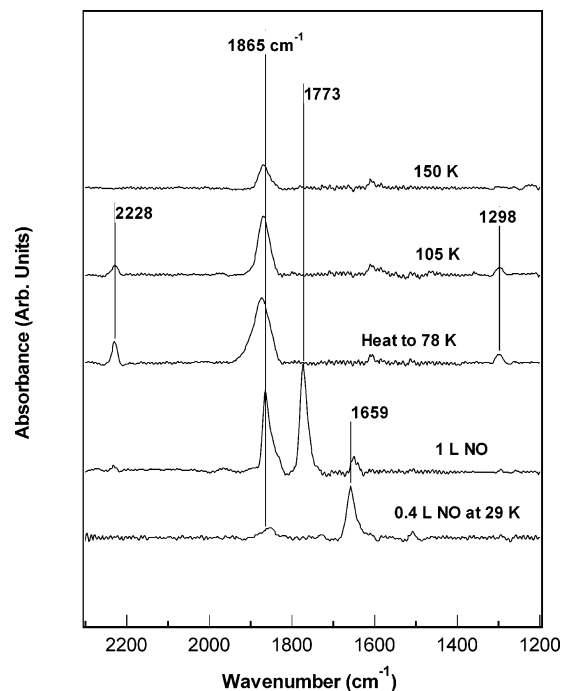
## 3. Results and Discussion

**Adsorption of CO on Cu(100).** Figure 1 shows the IRAS data for CO adsorbed on Cu(100). Upon exposure to 0.2 L of CO at 23 K, an IRAS band is observed at 2081 cm<sup>-1</sup> and is assigned to linearly bound, atop CO.<sup>32,33</sup> With an increase in the CO exposure, the 2081 cm<sup>-1</sup> band shifts to 2087 cm<sup>-1</sup> and a new band appears at 2143 cm<sup>-1</sup>, corresponding to multilayer CO.<sup>34</sup> The blue-shift of the vibrational frequency of chemisorbed CO from 2081 to 2087 cm<sup>-1</sup> is likely due to the formation of a compressed overlayer of CO. CO forms a c(2 × 2) surface structure at 0.5 ML coverage and a compressed (7√2 × √2)-R45° surface structure at higher coverages (~0.57 ML) on Cu(100) at 77 K.<sup>35</sup> Cook and McCash reported the formation of a compressed (7√2 × √2)-R45° CO layer on Cu(100) at 35 K<sup>33,36</sup> on the basis of IRAS data. These authors observed a blue-shift of the CO vibrational mode upon warming the CO multilayer formed at 23 K. This blue-shift was believed to occur by additional adsorption of CO from the CO multilayer prior to desorption or from background CO after desorption.<sup>33</sup>

The shoulder of the chemisorbed CO peak at 2104 cm<sup>-1</sup> is due to CO adsorbed at surface defect sites.<sup>32</sup> Upon warming to 34 K, the multilayer CO band disappears and the CO stretching feature at 2104 cm<sup>-1</sup> becomes more distinct. The main CO stretching feature at 2087 cm<sup>-1</sup> disappears at 180 K, while the



**Figure 1.** IRAS of CO adsorbed on Cu(100) between 23 and 180 K. The spectra were acquired at the temperatures indicated.



**Figure 2.** IRAS of NO adsorbed on Cu(100) between 29 and 150 K.

2104 cm<sup>-1</sup> feature is stable to 190 K, consistent with the assignment of the 2104 cm<sup>-1</sup> band to CO adsorbed at defect sites.

**Adsorption and Reaction of NO on Cu(100).** Figure 2 shows the change of the IRAS features of NO on Cu(100) as a function of exposure and surface temperature. The surface temperature during exposure was 25 K, and the spectra were acquired with the surface temperature indicated in the figure. The initial NO dose produced a band at 1657 cm<sup>-1</sup>, which corresponds to bridge-bonded NO.<sup>37</sup> With an increase in NO exposure, two bands appear at 1865 and 1773 cm<sup>-1</sup> and are assigned to the symmetric ( $\nu_1$ ) and asymmetric ( $\nu_5$ ) stretching modes of the (NO)<sub>2</sub> dimer, respectively.<sup>38,39</sup> Upon warming the

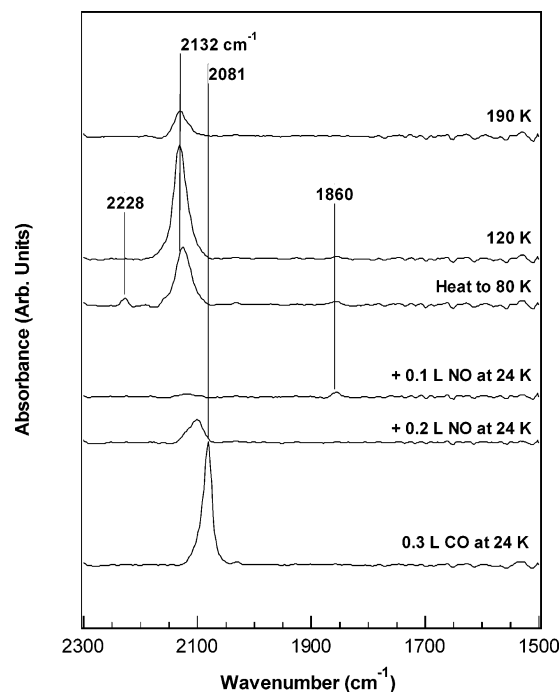


Figure 3. IRAS of coadsorbed CO and NO on Cu(100).

surface above 70 K, new features appear at 2228 and 1296 cm<sup>-1</sup> that correspond to N–N (2228 cm<sup>-1</sup>) and N–O (1296 cm<sup>-1</sup>) stretching modes, respectively, of N<sub>2</sub>O.<sup>40</sup> The N<sub>2</sub>O features disappear upon warming the surface to 150 K. Heating further to 200 K leads to complete decomposition of NO. A trace amount of N<sub>2</sub>O, which is observed at 29 K, is likely related to defect sites. The thermal stability of monolayer and multilayer NO dimers has been described in detail elsewhere.<sup>41</sup>

**Coadsorption of CO and NO.** The coadsorption of CO and NO on Cu(100) was addressed by exposing a CO-covered Cu(100) surface to NO at 24 K, and the IRAS changes were noted (Figure 3). The initial CO exposure of 0.3 L yielded a CO surface coverage of approximately half of the saturation coverage at this temperature. Upon exposure of this CO layer to 0.2 L of NO, the CO stretching feature shifts to a higher frequency with a significant attenuation in its intensity (peak height). With further exposure of this surface to 0.1 L (0.3 L total) of NO, the CO stretching band virtually disappears. The surface coadsorbed with NO and CO was then warmed, and the IRAS spectra were recorded as a function of temperature as shown in Figure 3. Upon warming to 80 K, the CO stretching band reappears at 2130 cm<sup>-1</sup>; at 120 K, the CO stretching feature recovers the intensity of CO adsorbed on the NO-free surface at 24 K.

Similar results are observed when the dosing sequence of CO and NO is reversed. The intensity of the NO stretching band decreases significantly when the NO-covered Cu(100) surface is exposed to CO at 24 K.

The change of the frequency and intensity of the CO vibrational band demonstrates a strong lateral interaction between CO and NO on Cu(100) below 30 K. The blue-shift of the CO vibrational frequency indicates weakening of the Cu–CO bond as a result of repulsive interactions between CO and NO. Several causes could account for the decrease of the CO vibrational band intensity: desorption of CO, formation of the chemical bond between CO and NO, dipole–dipole coupling, depolarization due to weakening of the Cu–CO bond, and tilting of CO. The absence of any characteristic features due to a product species and the full recovery of the CO intensity upon

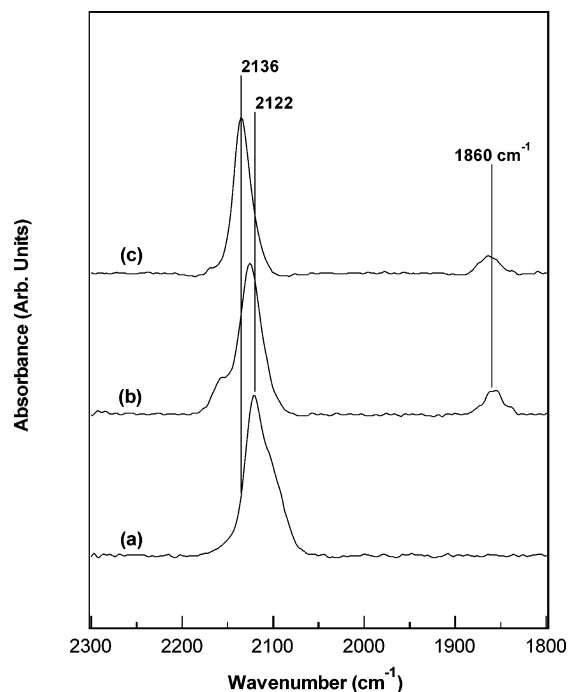


Figure 4. IRAS of CO adsorbed on NO-covered Cu(100). The surfaces were prepared by dosing NO at 25 K followed by heating to 80 K. CO was dosed at 25 K, and the spectra were acquired at 130 K. Initial exposures of NO were (a) 0.3 L, (b) 0.4 L, and (c) 2 L.

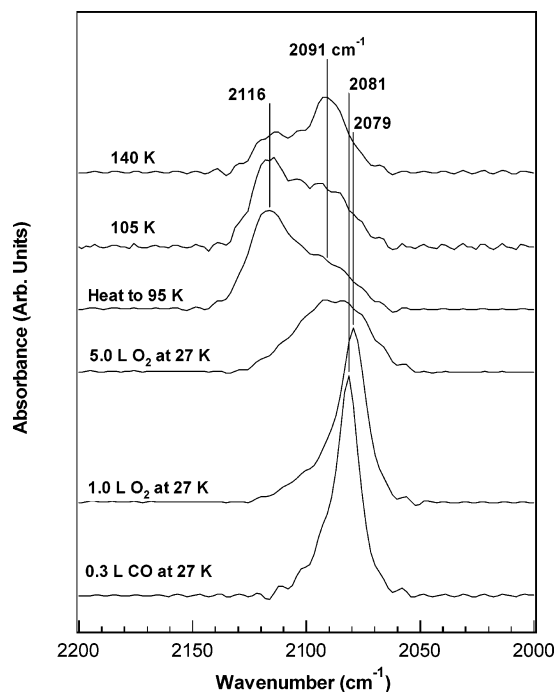
warming argue strongly against the formation of a CO–NO reaction product. Ancillary experiments using <sup>13</sup>C-labeled CO and <sup>15</sup>N-labeled NO support the absence of a reaction product. The effect of dipole coupling between CO and NO should be negligible because significant vibration coupling is generally observed only between two dipoles with very close vibrational frequencies. The most probable reason for the attenuation of the intensity is CO tilting due to the lateral interaction between CO and NO. The intensity of an IRAS feature can be represented as

$$I \propto \cos^2 \theta_{\mu n} \quad (1)$$

where  $\theta_{\mu n}$  is the angle between the dipole moment vector  $\mu$  and the surface normal  $n$ . Significant attenuation of the CO vibration band intensity is consistent with CO tilting away from the surface normal when coadsorbed with NO on Cu(100) below 30 K. The tilt angle of CO on the surface prepared by dosing 0.3 L of CO and 0.2 L of NO is estimated to be more than 50° on the basis of equation (1) and assuming no net change in the dipole moment of the CO. Of course, this approximation cannot be strictly applied because tilting of CO most certainly will attenuate the metal back-donation to CO, leading to a change of its dipole moment.

The recovery of the CO band intensity at 80 K indicates that the CO reorients to the upright bonding configuration as N<sub>2</sub>O is formed. Because the dissociation of NO and N<sub>2</sub>O takes place at temperatures higher than 80 K, the CO vibrational feature assumes its original intensity with a blue-shift to 2132 cm<sup>-1</sup>. The effects of N and O atoms on the CO vibrational frequency were investigated by adsorbing CO on a NO-covered Cu surface. Figure 4 shows the change of the CO IRAS obtained at 120 K as a function of the initial NO exposure. The surface was prepared by dosing the indicated amount of NO at 25 K followed by annealing briefly at 80 K. As the initial coverage of NO increases, the CO vibrational band shifts to a higher frequency. These data indicate that the blue-shift of the CO vibrational





**Figure 5.** IRAS of CO adsorbed on Cu(100) as a function of O<sub>2</sub> exposure and a subsequent anneal.

frequency is due to N and O atoms formed by decomposition of NO and N<sub>2</sub>O. As shown below, the interaction between O atoms and CO on Cu(100) at 120–150 K is relatively weak. These observations suggest that atomic nitrogen is mainly responsible for the blue-shift of the CO vibrational frequency at 120 K on Cu(100) for coadsorbed CO and NO.

**Coadsorbed CO and O<sub>2</sub>.** Figure 5 shows the change of the CO vibrational frequency on Cu(100) as a function of O<sub>2</sub> exposure and surface temperature. At 27 K, the stretching frequency of CO is red-shifted from 2081 to 2079 cm<sup>-1</sup> upon the initial adsorption of O<sub>2</sub>. Further dosing of O<sub>2</sub> causes broadening of the CO stretching band. Although the spectral features broaden, Figure 5 clearly shows that the CO stretching frequency is blue-shifted. Upon heating to 95 K, two vibrational bands appear at 2116 and 2091 cm<sup>-1</sup>. As the surface temperature is increased, the intensity of the 2091 cm<sup>-1</sup> band increases while the band at 2116 cm<sup>-1</sup> attenuates. The vibrational bands of CO disappear at 150 K.

As mentioned earlier, the IRAS of CO on Cu(100) exhibits no significant change between 34 and 140 K. The change of the vibrational features of CO shown in Figure 5 therefore are closely related to the change in the chemical and physical environments caused by a coadsorbed oxygen species. Adsorption and reaction of molecular and atomic oxygen on Cu(100) between 25 and 300 K have been studied in detail by Yokoyama and co-workers using near-edge X-ray absorption fine structure (NEXAFS) and surface-extended X-ray absorption fine structure (SEXAFS).<sup>42,43</sup> These authors have reported that oxygen is physisorbed on Cu(100) below 30 K, whereas chemisorbed molecular oxygen is formed at 44–94 K; dissociation of oxygen takes place above 94 K. The chemical and physical states of physisorbed oxygen below 30 K are very close to those of gas-phase oxygen, that is, the O–O distance is 1.21 Å and the charge transfer from the metal to oxygen is 0.11e.<sup>43</sup> High-resolution electron energy loss spectroscopy (HREELS) studies by Sueyoshi and co-workers showed that the oxygen atoms formed via dissociation at 100 K are adsorbed at low coordination sites, for example, bridge and atop sites.<sup>44</sup> Upon warming to 200 K, oxygen atoms are accommodated into stable, 4-fold hollow sites.

It is generally observed that the CO vibrational frequency blue-shifts when coadsorbed with oxygen on metal surfaces, because electronegative oxygen weakens the metal–CO bond. The initial red-shift of the CO vibrational frequency upon O<sub>2</sub> adsorption on Cu(100) at 27 K implies that the chemical interaction between CO and physisorbed O<sub>2</sub> is relatively weak because the amount of charge transfer from Cu to oxygen molecules is relatively small.<sup>43</sup> The interaction between the CO dipole and the induced dipole in O<sub>2</sub> may be the origin of the CO red-shift. The CO vibrational frequency has been reported to red-shift by as much as 30 cm<sup>-1</sup> upon the coadsorption of a neutral species such as Xe on metal surfaces.<sup>45,46</sup> Both the frequency and intensity of the CO vibrational band are reduced by the interaction of its dynamical dipole with the induced dynamic dipole of Xe atoms coadsorbed with CO.

The blue-shift of the CO vibrational frequency at higher coverages of coadsorbed O<sub>2</sub> implies compression of the CO overlayer. The broadening of the CO vibrational feature indicates inhomogeneous adsorption of CO on the Cu surface coadsorbed with multilayer O<sub>2</sub>. A blue-shift and broadening of the CO vibrational band has been reported when CO was coadsorbed with O<sub>2</sub> on Pt(111) at 25 K.<sup>47</sup>

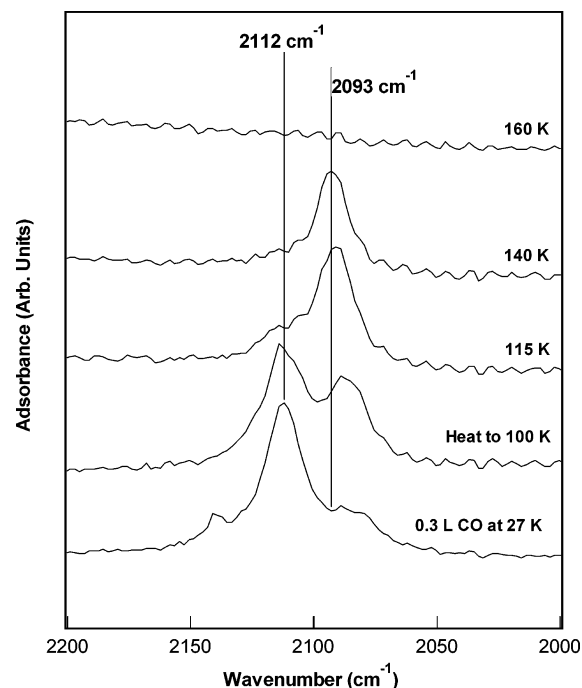
A shift of the CO vibrational frequency to 2116 cm<sup>-1</sup> upon warming the surface to 94 K is consistent with dissociation of molecular oxygen. Bagus and co-workers explained the shift of the CO vibrational frequency caused by ionic coadsorbates in terms of the electric field.<sup>13</sup> The electric field produced by the negative charge on the anionic coadsorbate and the positive image charge below the surface induce a blue-shift of the CO vibrational frequency, a shift strongly dependent on the field strength. These authors have shown that the interaction between the electric field and CO depends strongly on the height of the charge above the surface. In our IRAS experiment of CO coadsorbed with oxygen atoms on Cu(100), the red-shift of the CO vibrational frequency decreases as the surface temperature is increased from 95 to 140 K. This decrease in frequency is consistent with the oxygen atoms rearranging their adsorption sites at 95 K from bridging to 4-fold hollow sites.<sup>44</sup>

The interaction of CO with oxygen atoms formed at 95 K was further investigated. The Cu(100) surface was exposed to 3 L of oxygen at 27 K, heated to 95 K to induce dissociation of oxygen molecules, and then immediately quenched to 27 K. CO was adsorbed on this surface at 27 K, and the change of IRAS was investigated as a function of surface temperature (Figure 6). At 27 K, a strong CO vibrational feature is observed at 2112 cm<sup>-1</sup>. The CO vibrational frequency at 27 K on this surface is very close to that obtained when a surface coadsorbed with CO and O<sub>2</sub> is warmed to 95 K (Figure 5). This result clearly shows that the CO vibrational frequency shift to 2116 cm<sup>-1</sup> in Figure 5 is due to dissociation of O<sub>2</sub> and the interaction of CO with atomic oxygen. A CO stretching band at 2093 cm<sup>-1</sup> grows at the expense of the decrease of the band at 2112 cm<sup>-1</sup> as the surface temperature increases. This result clearly demonstrates that the change of the CO vibrational frequency in the temperature range of 95–140 K is closely related to the change in the oxygen adsorption geometry when CO is coadsorbed with the atomic oxygen that is formed at 95 K on Cu(100).

#### 4. Conclusions

The interaction of CO with NO and O<sub>2</sub> on Cu(100) between 25 and 200 K has been investigated with IRAS. The main conclusions are the following:

(a) There is a strong repulsive interaction between CO and NO on Cu(100) at 25 K that causes tilting of the CO molecules away from the surface normal.



**Figure 6.** IRAS of CO adsorbed on an O-covered Cu(100) surface. The surface was prepared by dosing 3 L of oxygen at 27 K and was followed by warming to 95 K. The surface was quenched immediately, and CO was adsorbed at 27 K. The spectra were acquired while maintaining the temperature indicated.

(b) Both molecular and dissociated NO induce a blue-shift in the CO vibrational frequency.

(c) The interaction of CO and O<sub>2</sub> in the submonolayer regime on Cu(100) at 27 K causes a red-shift and intensity attenuation of the CO vibrational frequency as a result of interaction with the dynamic dipole of oxygen molecules.

(d) Atomic oxygen formed on Cu(100) at 95 K via dissociation of O<sub>2</sub> induces a blue-shift of the vibrational frequency of coadsorbed CO up to 2116 cm<sup>-1</sup>. The CO vibrational frequency shifts to 2091 cm<sup>-1</sup> as the surface is warmed to 140 K, implying a change in the adsorption geometry of the oxygen atoms.

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