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STUDY OF ADSORPTION STATES AND INTERACTIONS OF CO ON EVAPORATED NOBLE METAL SURFACES BY INFRARED ABSORPTION SPECTROSCOPY. II. GOLD AND COPPER

P. Dumas, R.G. Tobin and
P.L. Richards

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STUDY OF ADSORPTION STATES AND INTERACTIONS OF CO ON EVAPORATED NOBLE METAL SURFACES BY INFRARED ABSORPTION SPECTROSCOPY

II. GOLD AND COPPER

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Abstract

We have used infrared absorption spectroscopy to study the adsorption of CO at low temperature on evaporated films of gold and copper as a function of the coverage of CO and the deposition temperature of the metal. For both metals we observe two distinct adsorption regimes when the cold metal is exposed to CO gas. These regimes arise depending on whether the deposition temperature of the metal (or the highest temperature at which the metal has been annealed) is above or below a threshold temperature. Gold films deposited at temperatures below 290 K contain chemically active sites at which CO chemisorbs, while films deposited at higher temperatures do not support CO chemisorption. This behavior is very similar to that observed on silver films. Chemisorption of CO occurs on copper films regardless of deposition temperature, but the vibrational spectrum is radically different for films deposited above and below the threshold temperature of 250 K. For both metals, the shift of the vibrational frequency with CO coverage has been analyzed, and the static and dynamic contributions separated. The dynamic shift is found to be very well modeled by dipole-dipole coupling, with no evidence for vibrational coupling through the metal. An analysis of infrared intensities and vibrational polarizabilities shows no evidence for any special infrared enhancement analogous to the large enhancement in Raman cross section peculiar to adsorption on rough metal films, particularly noble metal films, evaporated at low temperatures. Our results are discussed in terms of current theories of the electronic and structural properties of evaporated films, CO chemisorption, and Raman enhancement.

1. Introduction

The aim of this study is to use infrared absorption spectroscopy to elucidate the low temperature adsorption behavior of CO on evaporated gold and copper films deposited at various temperatures. The present work expands upon, and reinforces, our work on silver films, described in the preceding paper [1].

The structural and electronic properties of evaporated films depend strongly on T_D, the temperature of the substrate during the deposition of the film, or equivalently, the highest temperature at which a film deposited at low temperature is annealed. These properties are reflected in the adsorption behavior of CO. In our study of silver films [1], we found that for $T_D < 150$ K, the films contained large numbers of chemically active sites at which CO chemisorbed. Films deposited at higher temperatures did not support chemisorption. In the present study, we find that gold films show almost exactly the same behavior, with a threshold temperature of 290 K for the presence of chemisorption sites. Copper behaves somewhat differently, supporting CO chemisorption for all values of T_D. Nevertheless, changes in film structure as a function of T_D are reflected as significant changes in the vibrational spectrum of adsorbed CO.

The shift in the frequency of a vibrational band with coverage is of interest because it provides a measure of the interadsorbate interactions. Such shifts have been studied in some detail for CO on single crystal copper [2-10], and palladium [11,12]. The shift is commonly found to have two components: a static shift caused by chemical changes induced in an adsorbate by neighboring molecules, and a dynamic shift due to direct electromagnetic interactions between the adsorbates. Dynamic coupling

through the metal has also been suggested [13]. The chemical effect can shift the band either to lower or to higher frequency, depending on the details of the interactions in the system under study. The dynamic shift, on the other hand, always induces a shift to higher frequency with increasing coverage.

These two effects can be separated experimentally by the technique of isotopic substitution. Different isotopes of the same chemical species must have the same chemical interactions, but because their vibrational frequencies differ by more than the linewidth, they can be regarded as vibrationally decoupled [14]. We have performed experiments in which a small quantity of ^{12}CO is adsorbed, and the peak frequency of its vibrational band is followed as increasing amounts of ^{13}CO are coadsorbed. The shift of the ^{12}CO frequency observed in such an experiment represents the effect of the chemical interactions alone. The difference between this chemical shift and the total shift observed for a homogeneous layer of ^{12}CO containing the same number of molecules is attributed to dynamic coupling.

In the preceding paper [1], we showed that for CO chemisorbed on silver films, a negative chemical shift, (a shift to lower frequency with increasing coverage), dominates a positive dynamic shift. We further found that a large part of the chemical contribution could be attributed to the influence of the local work function on the bonding of the CO, and that the dynamic coupling was well described by a dipole coupling model, without any interaction through the metal. In the present work, we demonstrate similar effects in gold and copper films.

We further confirm the applicability of the dipole coupling model by showing that it correctly predicts the relative absorption intensities observed on the three noble metals. No such test of the theory across

different adsorption systems has previously been reported. In general, we find that direct dipole coupling, with physically reasonable values of the relevant parameters, is extremely successful in explaining the observed frequency shifts and intensities. There appears to be no need to invoke any additional mechanism of vibrational coupling.

The interaction of adsorbates with noble metal films deposited at low temperatures is a subject of great interest because such systems are known to exhibit large enhancements in Raman cross section over the values observed either in the gas phase, or for adsorption on smooth single crystals [15]. This phenomenon is known as surface-enhanced Raman scattering, (SERS). It is to be expected that dynamic charge transfer associated with chemisorption on smooth single crystal surfaces or annealed polycrystalline films will give rise to a small increase in the Raman cross section over its gas phase value, much as such charge transfer causes the vibrational polarizability of chemisorbed CO to be greater than that of gas phase CO [15]. We will call this effect a "chemical enhancement." Alone, however, it should not depend strongly on the structure of the film, and cannot explain the very large (10^4-10^6) enhancements of the Raman cross section observed for molecules adsorbed on rough metal surfaces, such as those created when metals are evaporated onto a cold substrate. We will refer to this large enhancement, strongly associated with surface roughness, as a "special" enhancement, to distinguish it from the dynamic charge transfer effects that produce the "chemical enhancement" on smooth surfaces.

A large part of the special enhancement observed on rough films has been attributed to electromagnetic resonances in the films at visible frequencies [15], but it has also been suggested that special Raman-active sites are present in the films [15]. At these sites, if they exist,

dynamic charge transfer processes much stronger than those at typical sites on a single crystal surface would make large contributions to the Raman cross section. Infrared spectroscopy offers a means of separating these two effects, since the charge transfer process at special sites would also be expected to enhance the infrared response of the adsorbate, while the electromagnetic resonances are ineffective at infrared frequencies. In the preceding paper [1], we studied the system of CO on silver films, and found no special enhancement of the infrared cross section. In the present study, we show that gold and copper films, which are also known to show large Raman enhancements, and which also display a strong dependence of adsorption behavior on film deposition temperature, show no evidence of any special enhancement of the infrared absorption cross section.

2. Experimental

These experiments were performed using the same apparatus and techniques as those reported in the preceding paper [1], and we refer the reader to it for a full description.

The films were deposited on a sapphire substrate by evaporation from copper and gold wire, (Johnson Matthey, Ltd., 99.999% and 99.998% purity, respectively), wrapped on a tungsten filament. During deposition the substrate was held at a fixed temperature, T_D, which could be varied between 4 K and 425 K. The deposition rate was 1 Å/s, and no dependence on this rate was found in the range from 1 to 10 Å/s. The film thickness for each deposition was 200 Å.

All infrared data were measured with the sample at 2 K. A germanium thermometer attached to the substrate allowed the temperature change caused

by infrared absorption in the film to be measured, so that the sample itself was used as a bolometric infrared detector. After measurement of a reference spectrum, the sample was exposed to a known quantity of CO from a calibrated effusive beam doser, and additional spectra were measured. The reference spectrum was then subtracted, and the difference divided by the reference, so that the data are presented in the form of fractional absorptances.

The spectra displayed have not been smoothed in any way, and no baseline fitting has been used. An additive constant has been included to clarify the display of multiple spectra. The instrumental resolution was 4 cm^{-1} for all spectra shown.

3. Results

We present here data and conclusions regarding three aspects of CO adsorption on gold and copper films:

1. Adsorption behavior and film structure.
2. Frequency shifts and intermolecular interactions.
3. Integrated vibrational band intensities and enhancement.

We will discuss each topic in turn, presenting the data for gold and for copper, and comparing the results with those of the corresponding experiments on silver, as described in the preceding paper [1].

3.1 Adsorption behavior and film structure

For both gold and copper, we find that the nature of the adsorption of CO depends strongly on T_D, the deposition or highest annealing temperature of the film. In each case, there is a threshold value of T_D, which

separates regimes of strikingly different adsorption behavior. Gold films behave very similarly to silver films in that films deposited or annealed at low T_D contain many sites for CO chemisorption, while those deposited or annealed at high T_D do not. The threshold value of T_D for gold is 290 ± 10 K, compared with 150 K for silver. Copper films, on the other hand, support CO chemisorption for all T_D, but the vibrational spectra indicate that the film structure undergoes a significant transformation near T_D = 250 K.

Fig. 1 shows infrared spectra of 0.1 L and 0.2 L of CO physisorbed at 2 K on a gold film deposited at T_D = 330 K, which is well above the threshold temperature. The narrow band at 2143 cm^{-1}, which does not shift with coverage, is characteristic of physisorbed CO. The identification is confirmed by the observation that the band disappears if the sample is heated to 25 K. The disappearance of the infrared band could be due to desorption of the CO, or to reorientation parallel to the surface, (as apparently occurs in the case of silver [1]). In either case, the behavior is characteristic of physisorption. No vibrational band attributable to chemisorbed CO is observed for films with T_D above the threshold temperature.

Infrared spectra are shown in Fig. 2 for various quantities of CO on a gold film deposited at T_D = 4K, which is far below the threshold temperature. At low coverage, a single broad band due to chemisorbed CO appears at a frequency lower than 2143 cm^{-1}. It grows in intensity and shifts to lower frequency with increasing exposure up to ~0.3 L. The desorption temperature for this feature, 170 K, is in the range

characteristic of chemisorption. At ~0.6 L, a second sharp peak due to physisorbed CO appears at 2143 cm^{-1}.

Based on these results alone, it is clear that gold films deposited at low temperatures contain sites with significantly different electronic structure than those found in annealed films or on single crystals. The nature of these sites is unknown, but it is clear that they are unusually chemically reactive. From the exposure at which the integrated intensity of the chemisorption band reaches its full value, we can estimate the surface concentration of the chemisorption sites to be ~3×10^{14} cm^{-2}, or ~30% of a monolayer on a single crystal surface.

It is tempting to identify these chemisorption sites with the Raman-active sites postulated by some authors [15]. As we will see, however, CO adsorbed at these sites does not exhibit the abnormally high infrared vibrational polarizability suggested by such theories of SERS.

Fig. 3 shows the frequency and integrated intensity of the chemisorption band as a function of CO exposure. The overall frequency shift with coverage is ~15 cm^{-1}, comparable to the shift of ~20 cm^{-1} observed on silver. It is notable that while the intensity of the band appears to saturate at about 0.25 L exposure, the frequency continues to shift until about 0.4 L, and the physisorption band does not appear until 0.6 L. This behavior is surprising; it appears that at exposures between 0.25 L and 0.6 L, added CO is adsorbing in some configuration that does not appear in the infrared spectrum. For example, it could be physisorbing in an orientation parallel to the surface.

The adsorption behavior of CO on copper films has important similarities to the behavior on gold and on silver, but it also shows significant differences. The most significant difference is that copper

films support CO chemisorption regardless of deposition temperature, as we might expect in view of the fact that CO also chemisorbs on single crystal faces of copper [2-10]. Gold and silver films support chemisorption only for low T_D. It seems not to be known whether CO chemisorbs on single crystal gold. It does not chemisorb on single crystal silver [16].

Nevertheless, we observe strikingly different vibrational spectra, depending on whether the substrate temperature during copper deposition was above or below 250 K. Fig. 4 shows infrared spectra for various quantities of CO chemisorbed on a film deposited at T_D = 300 K. The spectrum is characterized by a single broad band with a peak frequency of 2085 cm^{-1}, and a linewidth (FWHM) of 30 cm^{-1}. The frequency remains constant up to 0.3 L, at which point the appearance of a band due to physisorbed CO is accompanied by a shift of the primary band to lower frequency. This shift is probably caused by the change in work function induced by the physisorbed molecules, as we have discussed for CO on silver [1].

When the film is deposited at T_D = 4 K, the corresponding spectra, shown in Fig. 5, are quite different. The single band appears at higher frequency, 2102 cm^{-1}, and is much narrower, with a width of only 17 cm^{-1}. The peak frequencies we observe for the two types of film are fully consistent with those found in earlier studies [9]. It should be noted that much narrower lines have been observed for CO on single crystal faces of Cu [2-10]; the widths observed in the present study are undoubtedly caused by inhomogeneous broadening.

Nevertheless, it is surprising to find a much narrower line on the film evaporated at lower temperature, which is presumably much rougher and more disordered than the film deposited at room temperature. Since the microscopic structure of the films is unknown, we can only speculate as to the cause of the difference in linewidth. Films deposited at high temperatures are likely to be polycrystalline in nature, consisting of

microcrystallites of various orientations, so that the surface consists of a collection of microscopic low-index crystal faces. The infrared bands for CO on such surfaces lie in the frequency range of approximately 2080-2110 cm^{-1} [9], so that an ensemble of such faces could show a broad band such as that seen in Fig. 4. The film deposited at very low temperature, by contrast, could be so rough on an atomic scale that it contains only a rather small number of different types of adsorption site. These sites might be on small clusters of atoms of various sizes. In such a case, it is possible that the linewidth of the vibrational band would be narrower than is seen on polycrystalline films.

The frequency and integrated intensity of the band, for chemisorbed CO on a copper film deposited at $T_D = 4$ K, are shown in Fig. 6, as a function of exposure. The intensity saturates at 0.3 L, which suggests that the maximum coverage attainable on the film is at most only about one third of a monolayer. By contrast, single crystal surfaces can generally hold up to half a monolayer of CO [2-10]. The difference is presumably due to the more complex topography of the evaporated film; significant fractions of its area may be taken up with structures that do not accept CO.

In summary, the dependence of the adsorption behavior on the metal deposition temperature, T_D, is similar for all three noble metals. A significant change in the vibrational spectrum is observed when T_D crosses a threshold. We assume that the change is due to structural features in the films deposited at low temperatures that are removed by annealing at higher temperatures. For silver and gold, films deposited at low T_D contain large numbers of special active sites at which CO chemisorbs, while films deposited at temperatures above the threshold, and single crystal samples of silver [16], do not support chemisorption. Copper differs from the other two metals in that CO does chemisorb on single crystal copper

surfaces, and on films deposited at all temperatures studied. Nevertheless, the vibrational spectra of CO on copper reflect great differences between films deposited at temperatures above and below the threshold.

3.2 Frequency shifts and intermolecular interactions

We have analyzed the frequency shift with coverage for both gold and copper, using the isotopic substitution technique described in the Introduction. We have fitted the vibrational contribution using the dipole coupling model of Persson and Ryberg [17], as described in the preceding paper [1]. In the case of CO on silver [1], we were able to demonstrate that work function changes played an important role in the chemical shift. For gold and copper, the situation is less clear, but we will present indirect evidence for such a role.

Fig. 7 shows a sequence of infrared spectra for 0.02 L ^{12}CO chemisorbed at 2 K on a gold film deposited at T_D = 4 K, with increasing quantities of coadsorbed ^{13}CO. The higher frequency ^{12}CO band shifts to lower frequency due to the chemical effect of the coadsorbed ^{13}CO. The frequency of the ^{12}CO band as a function of exposure is plotted in Fig. 8, together with the total shift, (from Fig. 3), observed for the same exposure of ^{12}CO alone. The size of the chemical shift is nearly twice the total shift. The chemical shift saturates at 0.2 L, similar to the intensity of the chemisorption band, while the total shift continues to change until ~0.4 L. This is another surprising and unexplained feature of the adsorption on gold in the exposure range from 0.2 to 0.6 L.

We attribute the difference between the total shift and the chemical

shift to the effect of vibrational coupling. This shift is plotted, along with the integrated intensity, in Fig. 9. The lines represent our fit to the data using the Persson-Ryberg dipole coupling model [17] with the following values of the adjustable parameters: The vibrational polarizability for chemisorbed CO is $\alpha_v = 0.40 \pm 0.02$ Å^3, and the strength of the dipolar coupling is $\tilde{U}(0) = 0.04 \pm 0.002$ Å^{-3}. The dipole coupling model gives an excellent fit to the frequency shift and intensity variation.

The explanation for the chemical contribution is less clear. The general bonding models advanced to explain such shifts were discussed in the preceding paper [1]; the most likely ones involve changes in the occupation of the CO $2\pi^*$ antibonding orbital as a function of coverage [2]. In the case of CO on silver [1], we found that a large part of the chemical shift was attributable to the work function change caused by neighboring molecules, as indicated by the shift in frequency on physisorption of additional CO and on coadsorption of argon. There was also evidence for a longer range interaction at low coverage, possibly involving overlap of the CO orbitals [2].

In the present case, we again find that the chemical interaction is long range, as there is a strong shift even at very low coverages. This may again be due to overlap of the antibonding orbitals. The evidence regarding the role of the work function is not conclusive. No shift in the frequency of the chemisorption band is observed when a peak due to physisorbed CO appears in the spectrum (Fig. 2), in contrast to the case of CO on silver. We did not perform a coadsorption experiment with argon.

We did, however, perform the following experiment, which was not performed on silver or copper: we deposited the gold film at a substrate temperature $T_D = 280$ K, just below the threshold temperature. When the

film was then cooled to 2 K and exposed to CO, bands due both to chemisorbed and to physisorbed molecules were observed, even at very low coverage. The frequency shift, and the integrated intensity, are shown in Fig. 10 for this unusual case. The chemical shift deduced from an isotopic mixing experiment is also shown. The integrated intensity of the chemisorption band saturates at approximately 0.04 L, indicating that all of the chemisorption sites are filled (unless CO chemisorbs parallel to the surface, which is unlikely). The frequency of the band continues to shift, however, until an exposure of 0.2 L. This shift is most probably caused by physisorbed molecules. The fact that the total shift is nearly identical to the chemical shift is a further confirmation that the physisorbed molecules are responsible; if the chemisorbed species were somehow involved, there should be an offsetting dipole interaction. This evidence is indirect, and other explanations of the data in Fig. 10 may be possible, but we believe that these data provide support for the hypothesis that work function changes play an important role in the chemical shift for CO on gold, as they do for CO on silver.

For CO chemisorbed at 2 K on a copper film deposited at T_D = 4 K, Fig. 6 shows that there is no variation in the peak frequency with coverage. Fig. 11 shows infrared spectra of 0.02 L ^{12}CO with various amounts of coadsorbed ^{13}CO on a similar film. With the vibrational coupling eliminated by the frequency difference between the isotopes, the downward chemical shift can be easily seen. This contribution is plotted in Fig. 12, together with the zero total shift. These isotopic substitution experiments show that the stability of the frequency is due to nearly perfect cancellation of a negative chemical shift and a positive dipole shift. Very similar observations have been made on single crystals [2-10]. No additional experiments were performed on this system to clarify the source of the chemical effect, although the shift seen at high exposures in Fig. 4 points to the role of work function changes.

The vibrational contribution to the frequency shift is shown in Fig. 13, together with the integrated intensity for copper deposited at T_D = 4 K. The lines show our fit to the data using the dipole coupling model, with the parameters $\alpha_v = 0.27 \pm 0.015$ Å^3, and $\tilde{U}(0) = 0.095 \pm 0.005$ Å^{-3}. This value of α_v is identical to that measured for CO on single crystal faces of copper [17].

We can summarize our results as follows: On all three noble metals there is a substantial (20-30 cm^{-1}) negative chemical frequency shift with increasing CO coverage. The magnitude of the chemical shift, the vibrational contribution, and the total shift, are given in Table 1 for all three metals. There is evidence that work function changes play an important role in the chemical shift. The evidence is strongest in the case of silver, but there are circumstantial indications in all cases. The vibrational component of the frequency shift is well explained in all cases by a dipole-dipole coupling model, with no contribution due to coupling through the metal.

Table 2 gives the relevant parameters of the dipole coupling for the three metals. The values of α_v will be discussed in the next section. The values of $\tilde{U}(0)$ are smaller than are typically observed on single crystals. As we discussed in the preceding paper [1], this reduction in $\tilde{U}(0)$ is caused largely by a relatively large separation between adsorption sites. The low exposure at which the chemisorption sites appear to be filled provides evidence for such a separation. The value of $\tilde{U}(0)$ on copper is more than twice the value found for silver and gold. A portion of the difference, (a factor of 1.4), can be attributed to the difference in substrate lattice constant; the remainder may be due to a different distribution of adsorption sites for copper. For example, a tendency of the sites to cluster would produce a larger value of $\tilde{U}(0)$, and might be expected for a metal on which normal lattice sites permit chemisorption.

3.3 Integrated vibrational band intensities and enhancement

Information regarding intensities can be obtained from the values of α_v derived from the vibrational frequency shift and given in Table 2 for the three noble metals. Within the dipole coupling theory of Persson and Ryberg [17], the infrared intensity of a band, for a given fractional site occupation C, is given by:

$$\int \Delta(\omega)\,d\omega \sim \frac{C\alpha_v}{[1 + C\alpha_e \tilde{U}(0)]^2} \qquad (1)$$

where α_e is the electronic polarizability of the molecule, which changes very little on chemisorption from its gas phase value of 3.0 $Å^3$, and the other parameters are as previously defined. In the absence of screening by other molecules, the infrared intensity is directly proportional to α_v. Thus a "special" infrared enhancement associated with special sites on films deposited at low temperature would appear as a value of α_v greater than that observed for chemisorbed CO on single crystals.

Therefore, the first significant point about the values in Table 2 is that the values of α_v are very close to those found on single crystals. The value for CO chemisorbed on copper, for T_D = 4 K, for example, is identical to that found for CO on Cu(100) [17]. Thus, there is no sign of any "special" enhancement of α_v associated with films deposited at low temperatures. The value of α_v is significantly greater for Au than for Ag and Cu; this difference is presumably due to charge transfer between the metal and the CO $2\pi^*$ orbital.

We can make an independent estimate of α_v for CO on gold by comparing the integrated intensities for the same quantity of CO chemisorbed on a film deposited at T_D = 4 K, and physisorbed on a film deposited at

T_D = 300 K. We find that the intensity due to the chemisorbed species is a factor of eight greater than that observed for the physisorbed molecules. If we assume that all of the physisorbed molecules are oriented perpendicular to the surface, so that they contribute to the infrared signal, and that the screening due to α_e is the same for the two species, then the polarizabilities α_v are in the same 8:1 ratio as the intensities. If we then take α_v for the physisorbed species equal to the gas phase value, 0.05 Å^3, we can estimate α_v = 0.40 Å^3 for the chemisorbed CO. This value agrees well with the value deduced from the dipole coupling model.

We have performed the analogous experiment with copper. In this case the CO chemisorbs on both films, and we find that the intensities are equal within 10% for the two films. This experiment constitutes direct evidence that CO chemisorbed on a rough film, deposited at T_D = 4 K, shows no special infrared enhancement compared with a film annealed at room temperature.

We thus find for gold and copper, as we found for silver [1], no sign of any special infrared enhancement on rough films, beyond the chemical enhancement normally observed for chemisorbed CO on single crystals. Our experiments suggest, therefore, that dynamic charge transfer at special sites peculiar to rough films does not contribute significantly to the SERS phenomenon.

The ability of our apparatus to make absolute comparisons of absorbed power on otherwise identical samples of different metals allows us to make a consistency check on the parameters in Table 2. Equation 1 gives an expression for the integrated intensity in terms of parameters that are either known in advance, or deduced from the dependence of the vibrational shift and the intensity on coverage. We can thus predict the ratios of the band intensities for a given exposure of CO on the three metals, and compare it with the experimental values. Fig. 14 shows a set of such

spectra, for an exposure of 0.1 L CO, and Table 3 compares the calculated and measured ratios, which agree very well within experimental error. This result greatly reinforces our confidence in the applicability of the dipole coupling model to our experiment and in the reliability of the parameters that we have deduced from the model. To our knowledge, no such application of the coupling theory across different adsorption systems has previously been reported.

Finally, we would like to compare the results obtained on the three systems when a quantity of CO is chemisorbed at 2 K on a film deposited at T_D = 4 K, and then heated to successively higher temperatures, allowing the molecules to move more freely on the surface. As we reported in the preceding paper [1], an unsaturated layer of CO on silver showed an intensity increase by a factor of 1.4 when it was annealed at 40 K, but displayed no change in the band frequency. We speculated that the molecules were moving to sites at which the electric field was enhanced by the structure of the film. A saturated film, by contrast, showed no change in intensity, but did show a shift to higher frequency. We were not able to offer any explanation for this shift.

Very similar results are observed for CO on gold, as shown in Fig. 15. The increase in intensity for the partially filled surface, on annealing at 150 K, was a factor of 2. For a saturated film, there is little or no intensity change, and no frequency shift until the sample is heated above 40 K; then the band shifts to higher frequency, as was the case with silver films. It should be emphasized that in all cases, annealing the film prior to depositing the CO did not affect the results; thus the enhancements and shifts cannot be attributed to structural changes in the metal film.

The results of a similar experiment on copper, shown in Fig. 16, were different. Little or no intensity change, and no frequency shift, were observed either for a partially or a completely filled surface, for annealing temperatures up to 80 K. At higher temperatures, a decrease in the band intensity was observed, probably due to CO desorption. Whether the difference is due to structural differences between copper films and gold and silver films, or to differences in CO mobility on the different surfaces, is not known.

4. Conclusion

We have used infrared absorption spectroscopy to study the low temperature adsorption behavior of CO on evaporated gold and copper films. This work is an extension of the work on silver films reported in the preceding paper [1], and reinforces the conclusions reached there regarding the structural and electronic properties of the films, the interactions within the adsorbate layer, and the lack of any special infrared enhancement of the sort suggested by some theories of SERS.

Gold films proved to be very similar to silver films. Films deposited at substrate temperatures below 290 K contained chemically active sites at which CO could chemisorb, while those deposited at higher temperatures showed only physisorbed CO. On both silver and gold, the frequency of the chemisorption band shifted to lower values with increasing CO coverage, due to the dominance of a negative chemical interaction over a positive dipolar coupling. The change in work function with the addition of more molecules seems to play an important role in the chemical shift, while the vibrational coupling is very well modeled by simple dipole-dipole coupling. We found no reason to assume any vibrational coupling through the metal.

The adsorption behavior of CO on copper, though similar, differed in detail from that on silver and gold. Chemisorption was observed for all deposition temperatures, but a radical change occurred in the vibrational spectrum at a deposition temperature of 250 K. Films deposited at higher temperatures showed a broad band around 2085 cm^{-1}, while for lower deposition temperatures the band was narrower and peaked at 2102 cm^{-1}. The chemical shift was somewhat smaller, and the dipole shift somewhat larger, than on silver and gold, resulting in essentially no net shift with coverage. As with the other metals, a dipole coupling model accounted well for the dynamic shift.

Because of the suggestion of a special infrared enhancement on rough evaporated films, related to the SERS phenomenon, we have considered the infrared band intensities and vibrational polarizabilities very carefully. We have compared the intensities due to chemisorbed and physisorbed CO on silver and gold, as well as the absorptances of chemisorbed CO on copper deposited at room temperature and at 4 K. We have compared our values for the vibrational polarizability with published values for CO on single crystals. In the preceding paper, we also compared the absorption by CO on silver with that by CO on nickel. In all cases we find no evidence for any special infrared enhancement associated with the special properties of rough evaporated noble metal films deposited at room temperature.

There remain many questions regarding adsorption on evaporated films. The detailed electronic and structural properties of the films are unknown. The nature of the special adsorption sites that are present on silver and

gold films deposited at low temperatures has not been determined. Some of the effects that we have observed, particularly the changes observed in the vibrational spectrum when the sample is heated, remain unexplained. There is a clear need to combine vibrational spectroscopy with other techniques, such as electron microscopy and photoemission, in order to clarify some of these issues.

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Table 1

Chemical, vibrational, and total shift of the CO stretch vibration with coverage, for chemisorbed CO on Ag, Au, and Cu films. T_D = 4 K.

	Chemical shift (cm^{-1})	Vibrational shift (cm^{-1})	Total shift (cm^{-1})
Ag	-34	+12	-26
Au	-30	+17	-13
Cu	-21	+21	0

Table 2

Parameters used in dipole coupling model to fit vibrational shift and intensity variation with coverage, for chemisorbed CO on evaporated Ag, Au, and Cu films. $T_D = 4$ K.

	ω_o (cm^{-1})	α_v (Å^3)	α_e (Å^3)	$\tilde{U}(0)$ (Å^{-3})
Ag	2148	0.27 ± 0.015	3	0.04 ± 0.002
Au	2125	0.40 ± 0.02	3	0.04 ± 0.002
Cu	2102	0.27 ± 0.015	3	0.095 ± 0.005

Table 3

Ratios of infrared intensities for 0.10 L chemisorbed CO on Ag, Au, and Cu films, as predicted by the dipole coupling model, and as measured from Fig. 14. $T_D = 4$ K.

	Theoretical	Experimental
Ag/Cu	0.38 ± 0.08	0.33 ± 0.03
Au/Cu	0.75 ± 0.15	0.72 ± 0.07

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Figure Captions

Fig. 1: Infrared spectra of CO physisorbed at 2 K on a gold film deposited at T_D = 330 K, showing a single narrow band at 2143 cm^{-1}.

Fig. 2: Infrared spectra of CO adsorbed at 2 K on a gold film deposited at T_D = 4K. A broad band due to chemisorbed CO appears at low coverage at 2125 cm^{-1} and shifts to lower frequency with increasing exposure. At 0.6 L a sharp band due to physisorbed CO appears at 2143 cm^{-1}.

Fig. 3: Frequency shift of the CO stretch vibration, and variation of the integrated intensity as a function of exposure, for chemisorbed CO on a gold film deposited at T_D = 4 K. The lines are drawn as a guide for the eye.

Fig. 4: Infrared spectra of CO adsorbed at 2 K on a copper film deposited at T_D = 300 K, as a function of exposure. A broad band due to chemisorbed CO appears at low coverage at 2085 cm^{-1}. At 0.3 L, a sharp band due to physisorbed CO appears at 2143 cm^{-1}, and the chemisorption band shifts slightly to lower frequency.

Fig. 5: Infrared spectra of CO adsorbed at 2 K on a copper film deposited at T_D = 4 K, as a function of exposure. A sharp band due to chemisorbed CO appears at low coverage at 2102 cm^{-1}, and does not shift with coverage. At 0.4 L, a sharp band due to physisorbed CO appears at 2143 cm^{-1}.

Fig. 6: CO stretch frequency and integrated intensity variation for chemisorbed CO on a copper film, T_D = 4 K. The lines are drawn as a guide for the eye.

Fig. 7: Infrared spectra of 0.02 L ^{12}CO coadsorbed with various amounts of ^{13}CO on a gold film deposited at T_D = 4 K. The higher frequency band is due to ^{12}CO. Quantities of coadsorbed ^{13}CO: (a) Zero. (b) 0.02 L. (c) 0.04 L. (d) 0.06 L. (e) 0.08 L. (f) 0.10 L. (g) 0.12 L. (h) 0.18 L.

Fig. 8: Total frequency shift of the CO stretch vibration, and chemical shift as a function of exposure, deduced from Fig. 7. The lines are drawn as a guide for the eye.

Fig. 9: (a) Dynamic contribution to the frequency shift, derived from data in Fig. 8, for chemisorbed CO on a gold film deposited at T_D = 4 K. (b) Integrated band intensity, from Fig. 3. The lines are theoretical fits to the data, using the P-R dipole coupling model with $\alpha_v = 0.40$ Å^3; $\tilde{U}(0) = 0.04$ Å^{-3}.

Fig. 10: Total frequency shift of the CO stretch vibration, chemical shift, and integrated band intensity as a function of exposure for CO chemisorbed on a gold film deposited at T_D = 280 K, which is just below the threshold temperature.

Fig. 11: Infrared spectra of 0.02 L ^{12}CO coadsorbed with various amounts of ^{13}CO on a copper film deposited at T_D = 4 K. The higher frequency band is due to ^{12}CO. Quantities of coadsorbed ^{13}CO: (a) Zero. (b) 0.02 L. (c) 0.04 L. (d) 0.06 L. (e) 0.08 L. (f) 0.10 L. (g) 0.15 L.

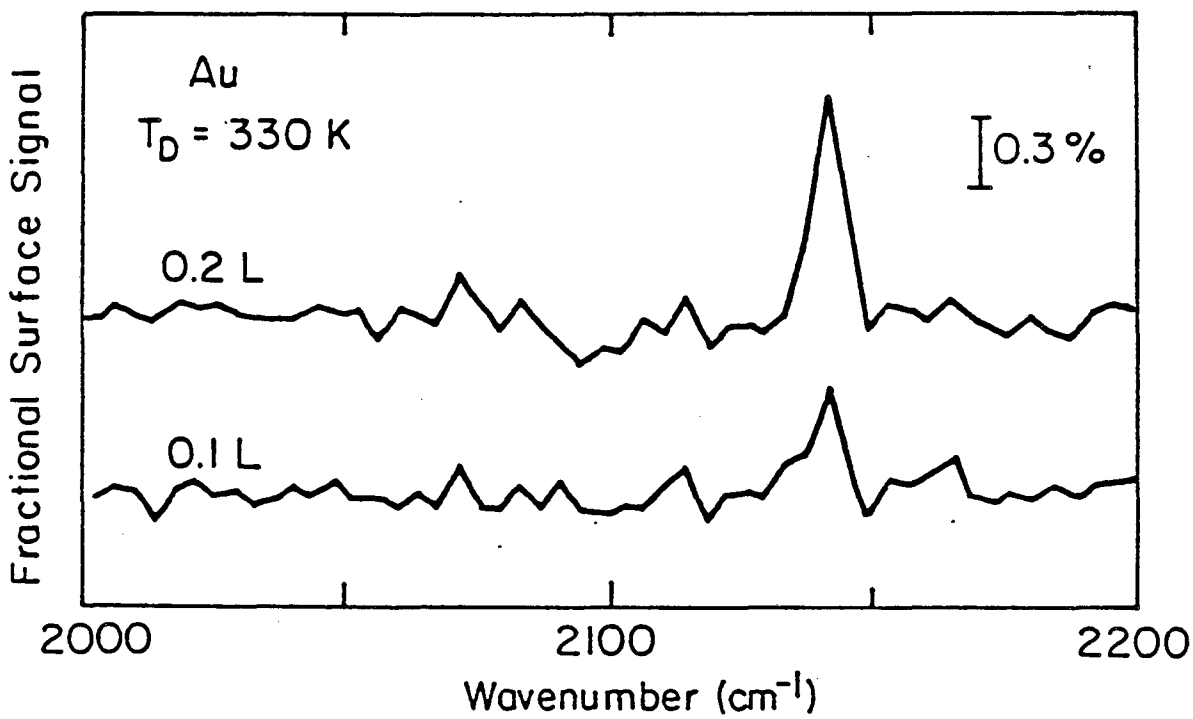
Fig. 12: Total frequency shift of the CO stretch vibration, and chemical shift as a function of exposure, deduced from Fig. 11. The lines are drawn as a guide for the eye.

Fig. 13: (a) Dynamical contribution to the frequency shift, derived from data in Fig. 12, for chemisorbed CO on a copper film deposited at T_D = 4 K. (b) Integrated band intensity, from Fig. 10. The lines are theoretical fits to the data, using the P-R dipole coupling model with $\alpha_v = 0.27$ Å^3; $\tilde{U}(0) = 0.095$ Å^{-3}.

Fig. 14: Infrared spectra of 0.10 L CO chemisorbed on copper, silver, and gold films. T_D = 4 K. The relative intensities are accurately predicted by the dipole coupling model.

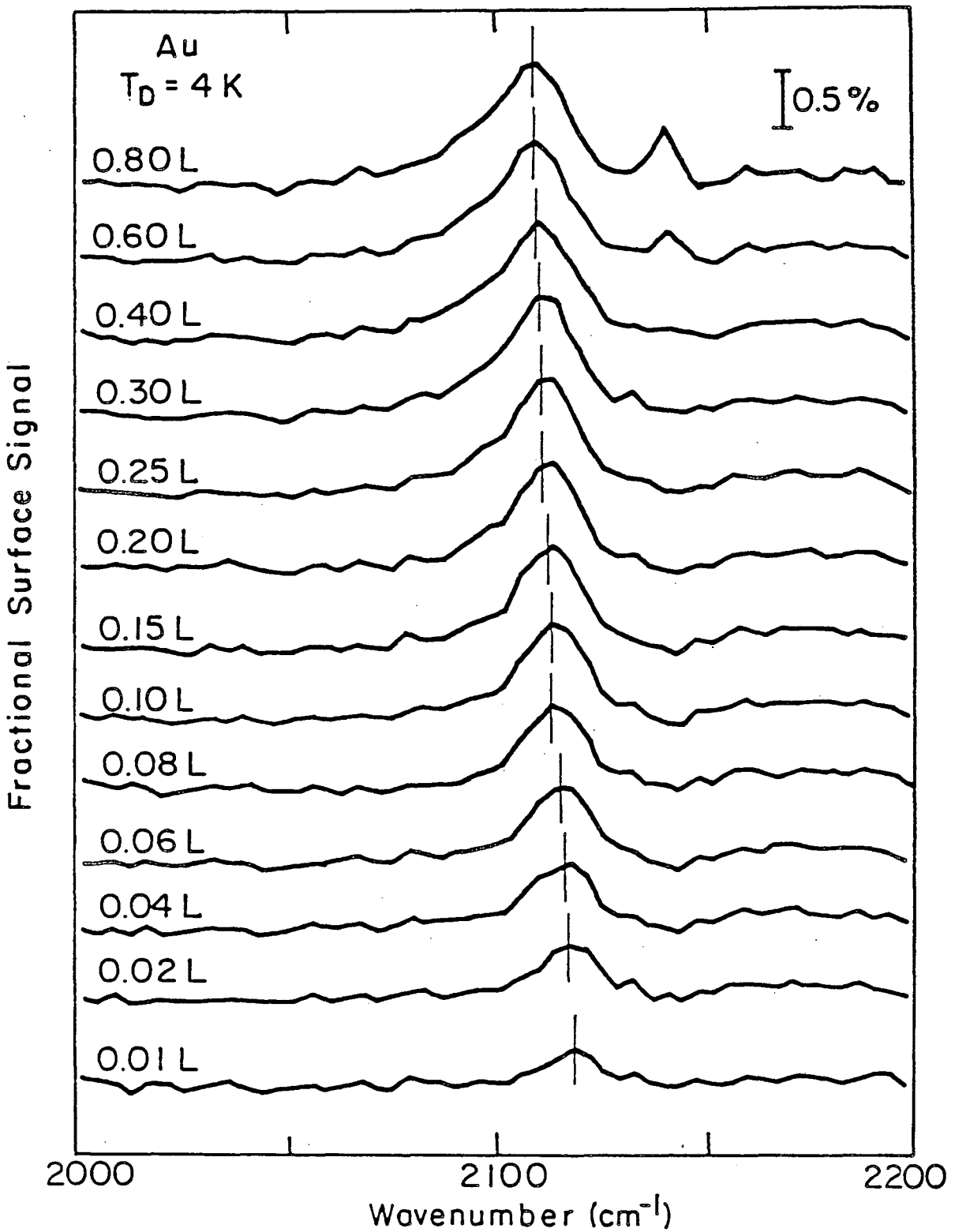
Fig. 15: Infrared spectra of CO chemisorbed at 2 K on a gold film and heated to successively higher temperatures. T_D = 4 K. For 0.025 L CO, the band increases in intensity by a factor of 2, but does not shift in frequency. For 0.5 L CO, the intensity remains constant, but the band shifts to higher frequency.

Fig. 16: Infrared spectra of 0.1 L and 1.0 L of CO chemisorbed at 2 K on a copper film and heated to successively higher temperatures. T_D = 4 K. No significant intensity change or frequency shift is observed.



XBL 854-6067

FIGURE 1



XBL 854-6068

FIGURE 2

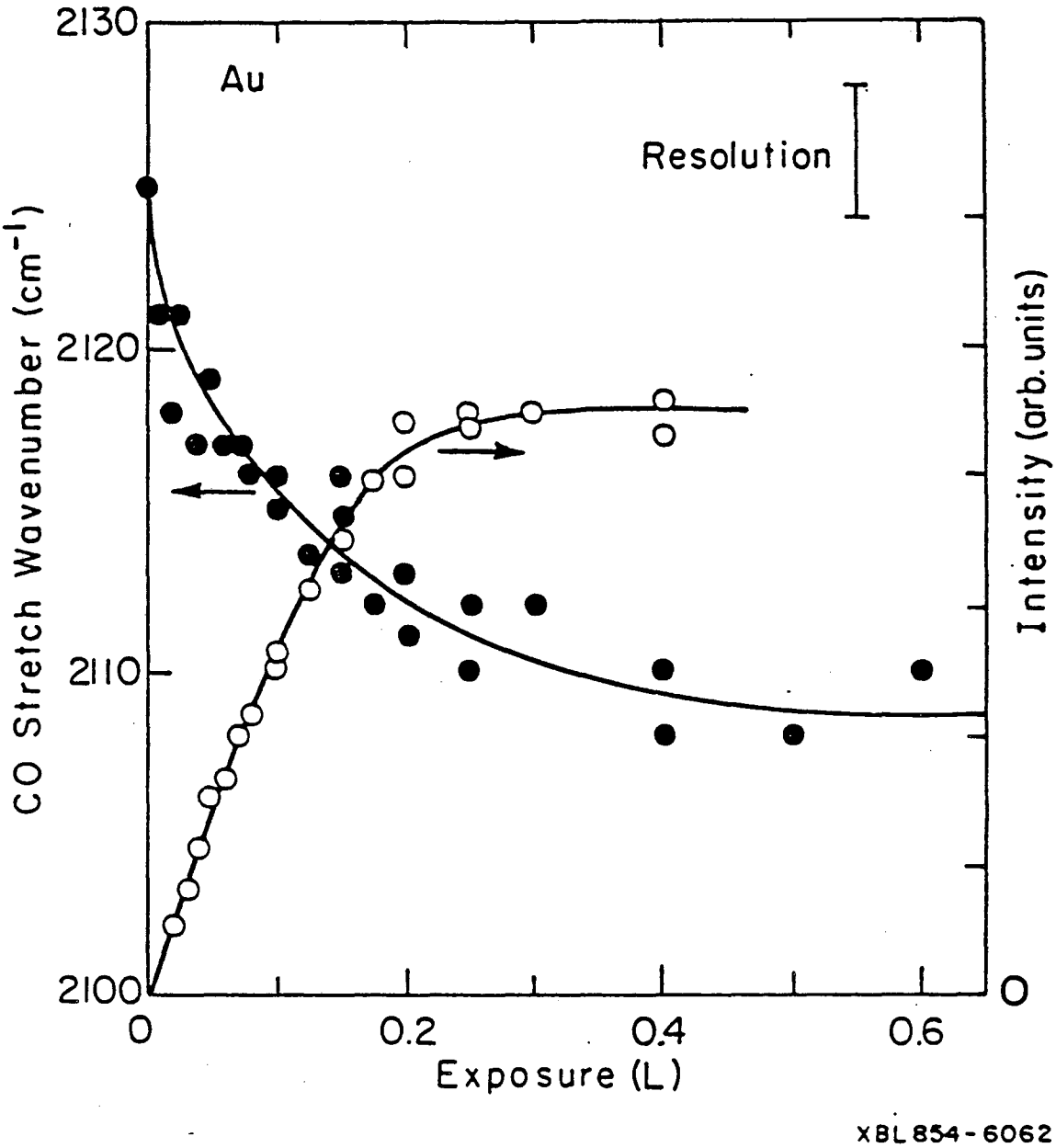

2130
2120
2110
2100
Au
Resolution
CO Stretch Wavenumber (cm^{-1})
Intensity (arb. units)
0
0.2
0.4
0.6
Exposure (L)
XBL 854-6062

FIGURE 3

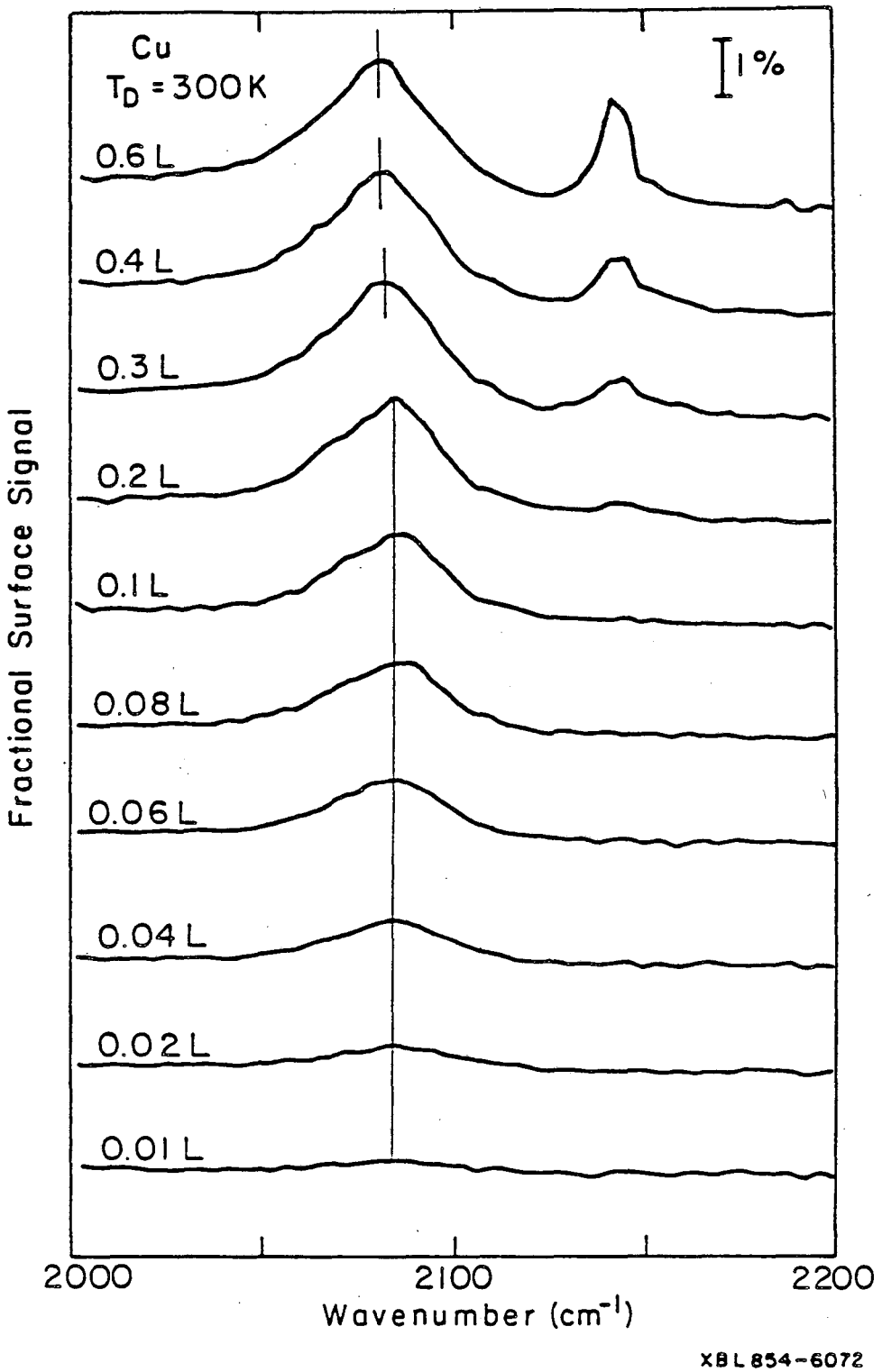
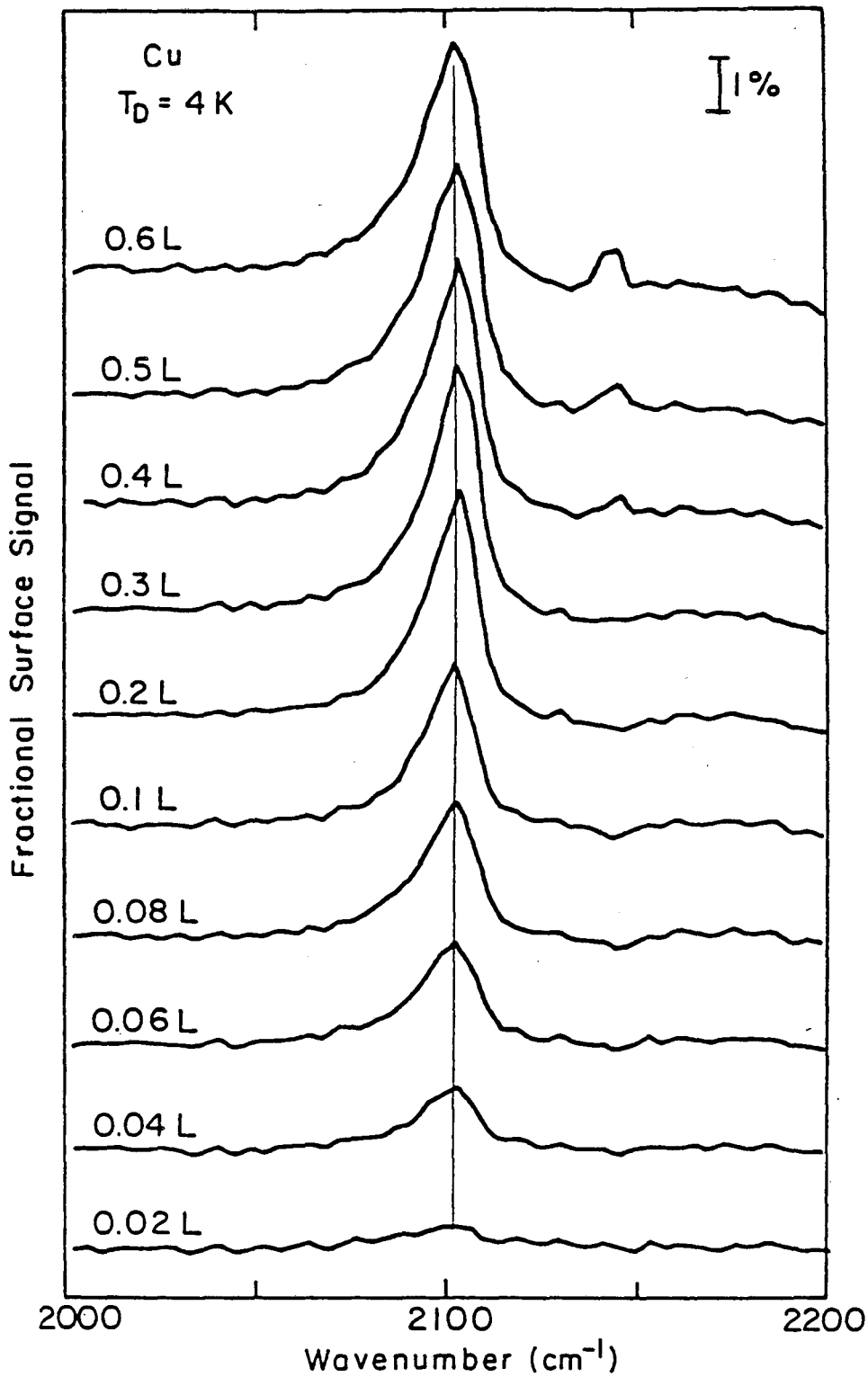

Cu
T_D = 300K
1%
0.6 L
0.4 L
0.3 L
0.2 L
0.1 L
0.08 L
0.06 L
0.04 L
0.02 L
0.01 L
Fractional Surface Signal
2000
2100
2200
Wavenumber (cm^{-1})
XBL 854-6072

FIGURE 4



XBL 854-6073

FIGURE 5

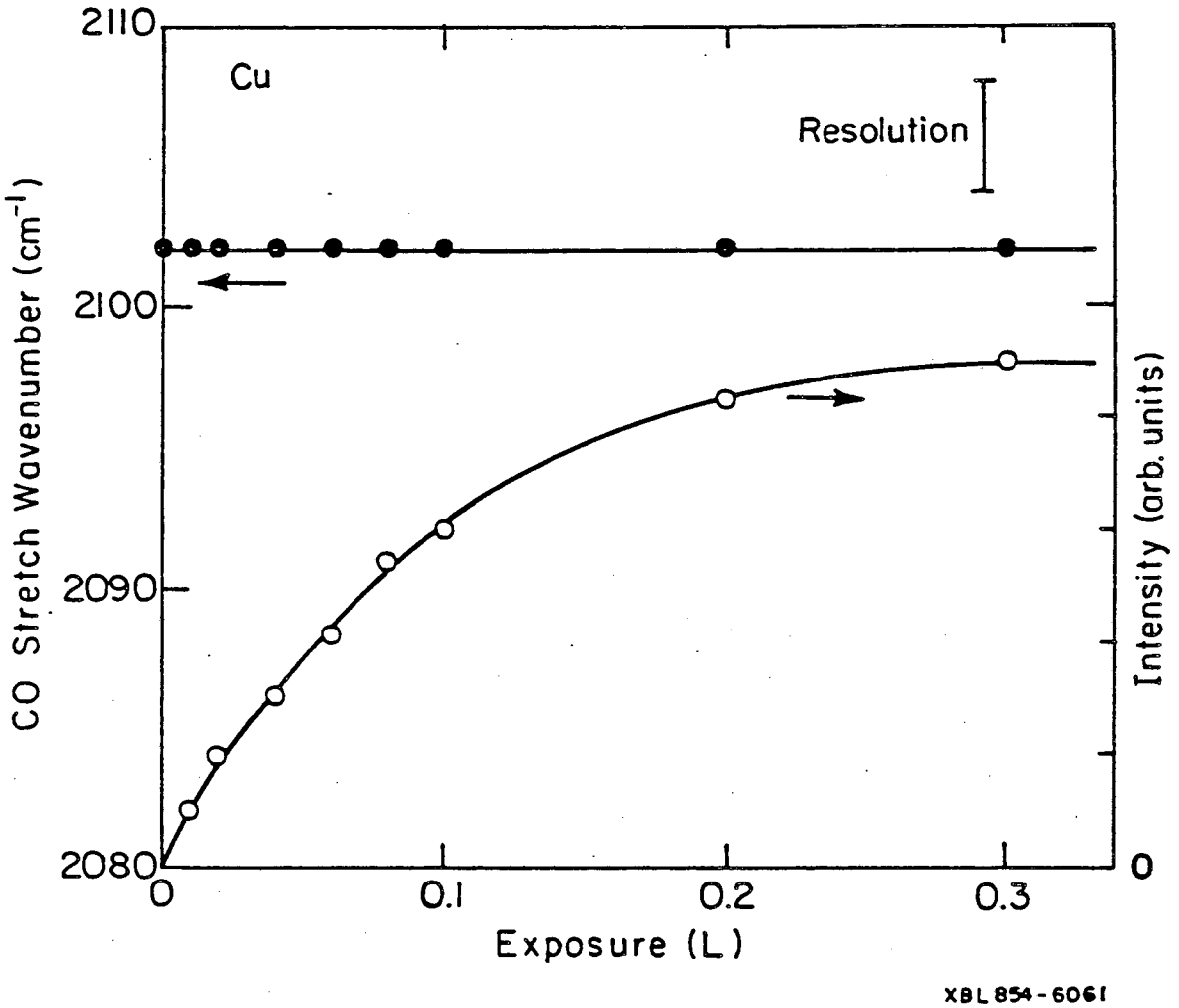

2110
2100
2090
2080
Cu
Resolution
CO Stretch Wavenumber (cm^{-1})
Intensity (arb. units)
0
0.1
0.2
0.3
Exposure (L)
XBL 854-6061

FIGURE 6

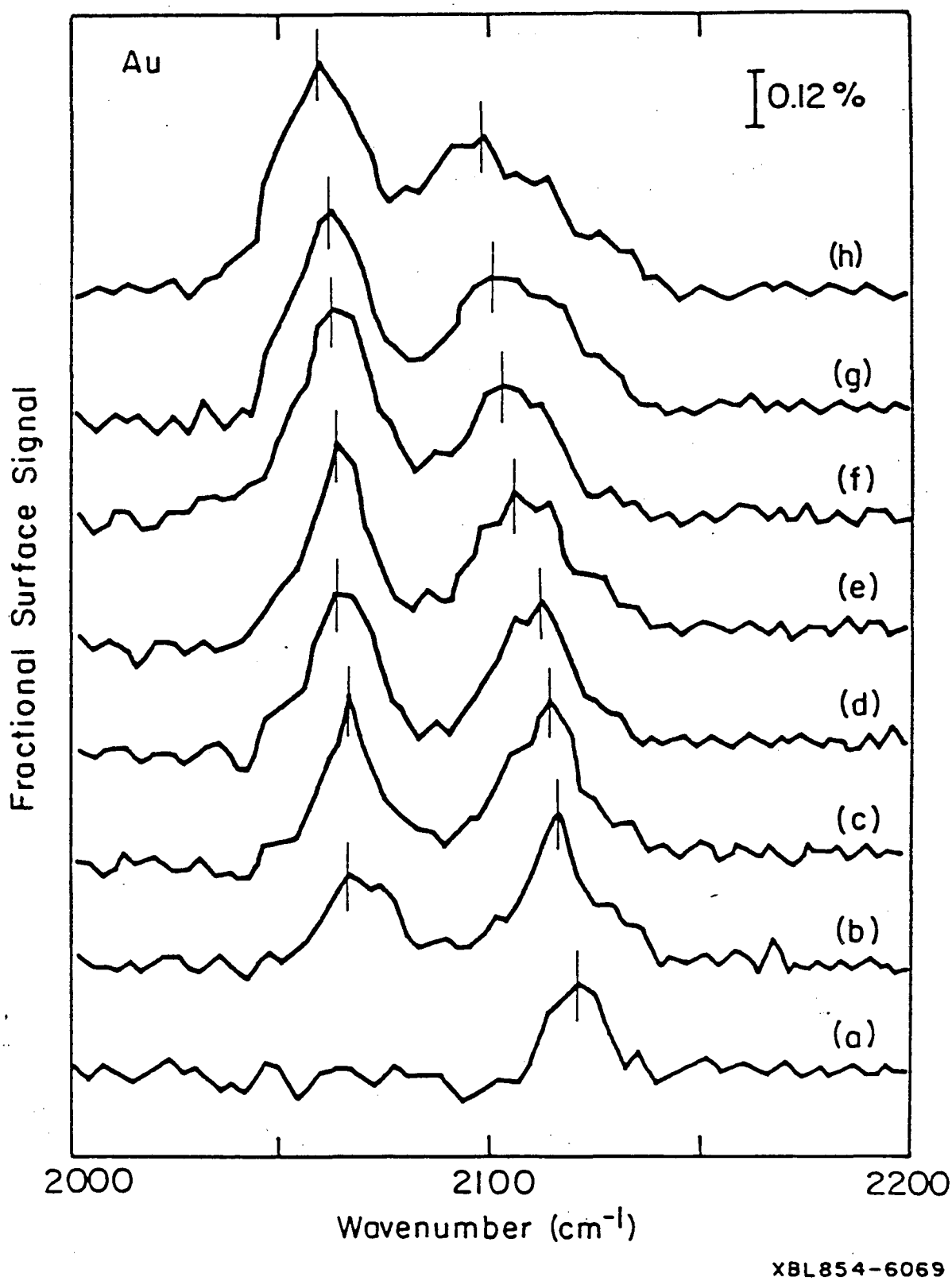

Au
0.12 %
(h)
(g)
(f)
(e)
(d)
(c)
(b)
(a)
Fractional Surface Signal
2000
2100
2200
Wavenumber (cm^{-1})
XBL854-6069

FIGURE 7

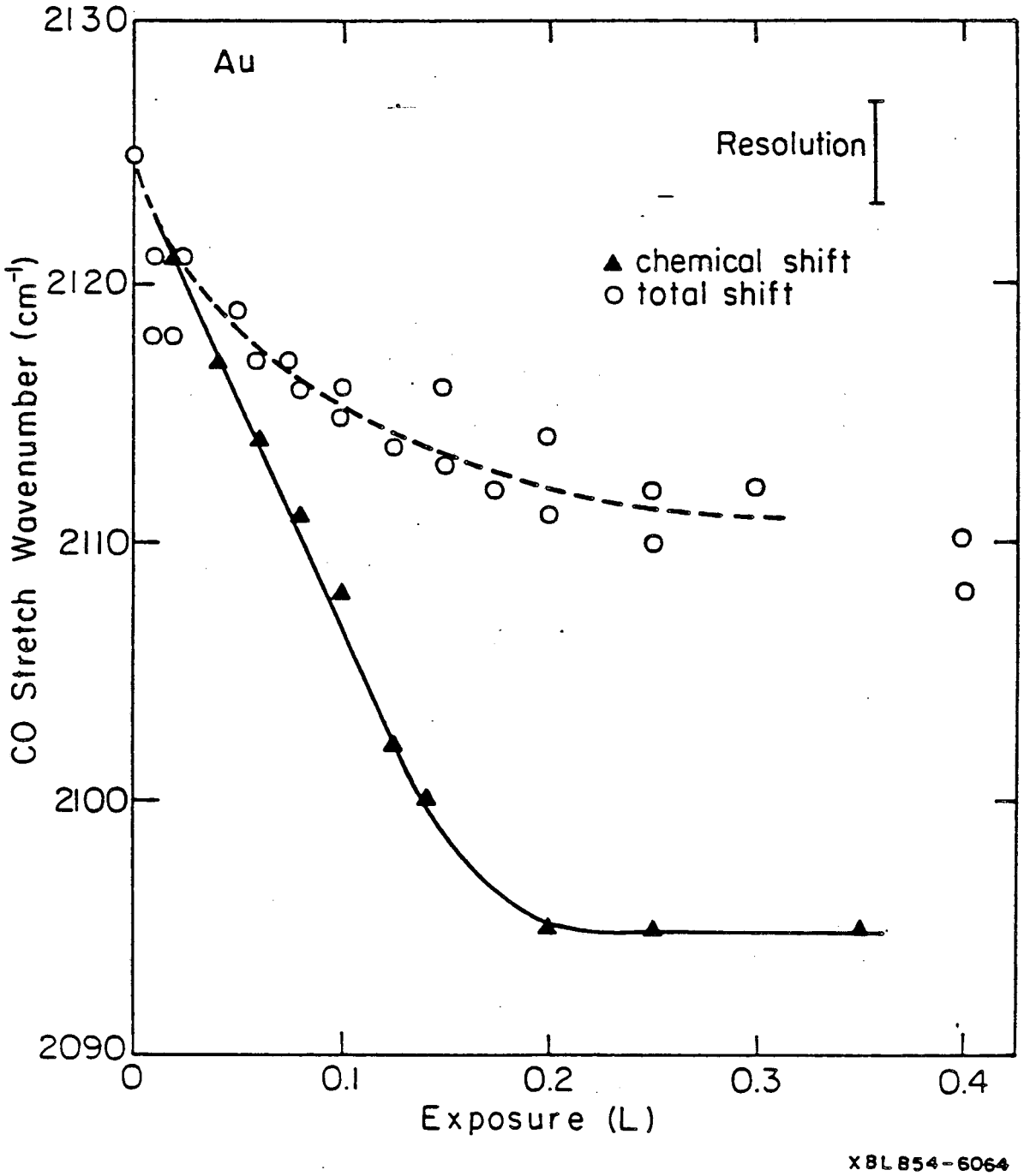
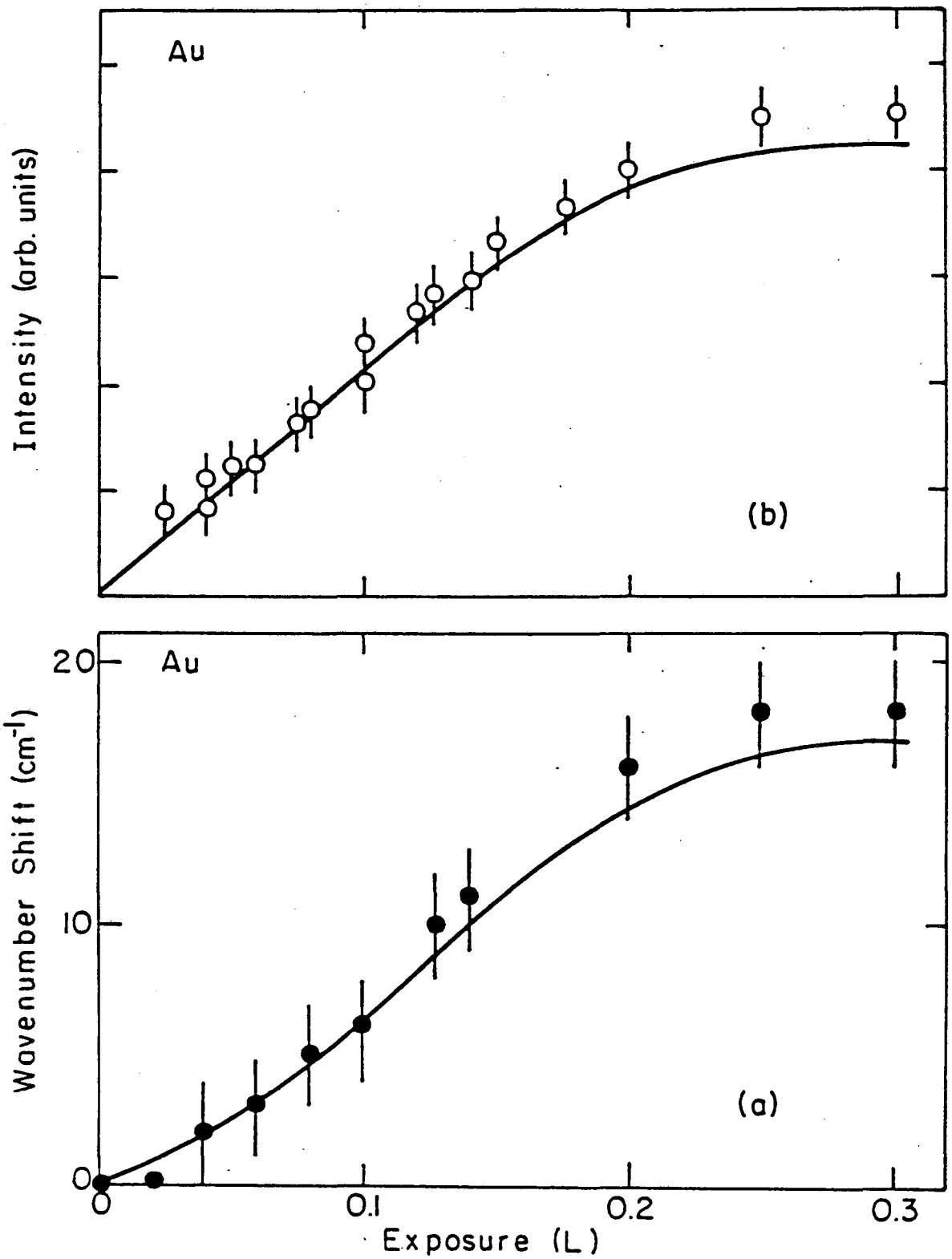

Au
Resolution
▲ chemical shift
o total shift
CO Stretch Wavenumber (cm⁻¹)
2130
2120
2110
2100
2090
0
0.1
0.2
0.3
0.4
Exposure (L)
XBL 854-6064

FIGURE 8



XBL 854-6065

FIGURE 9

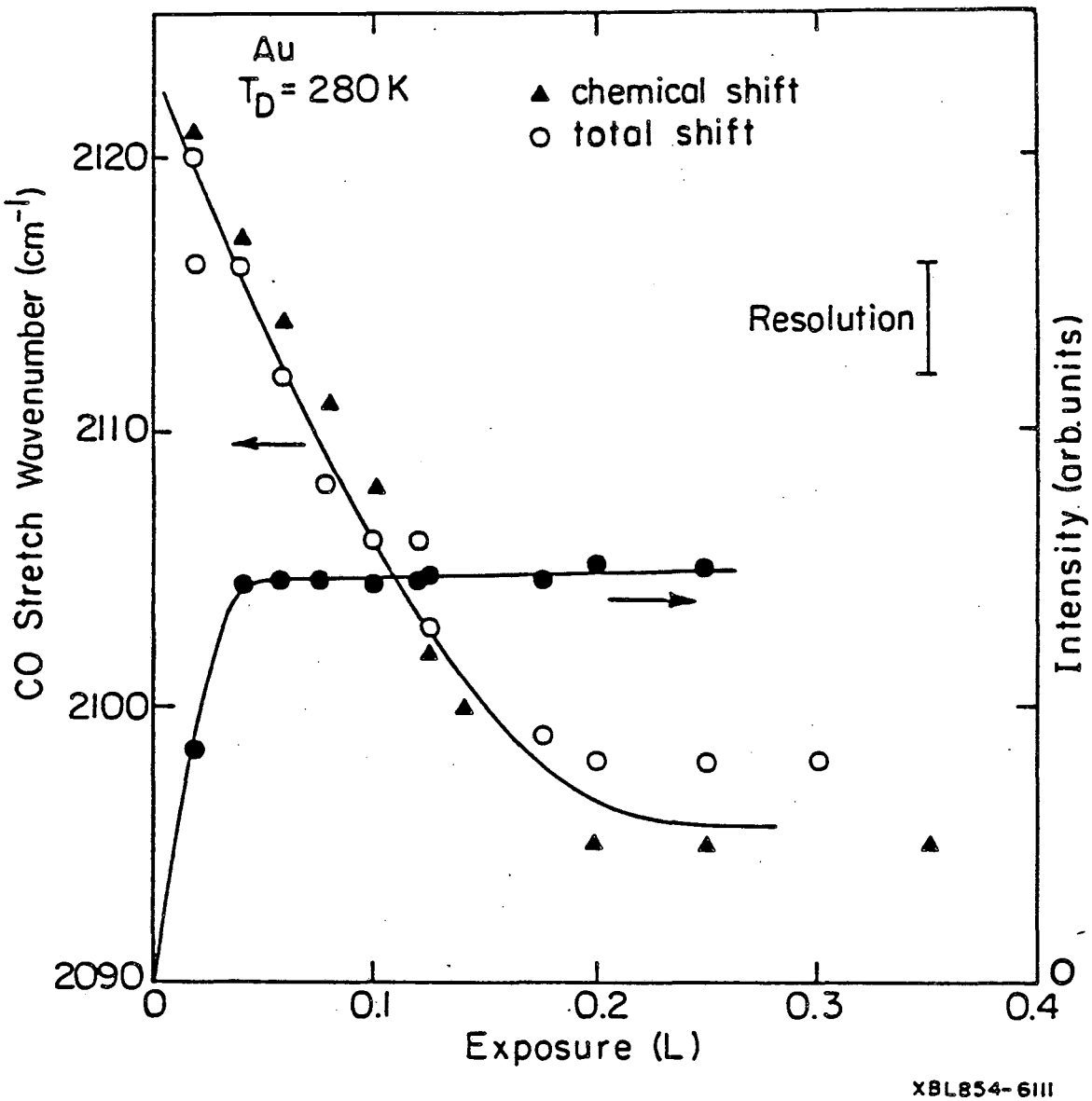
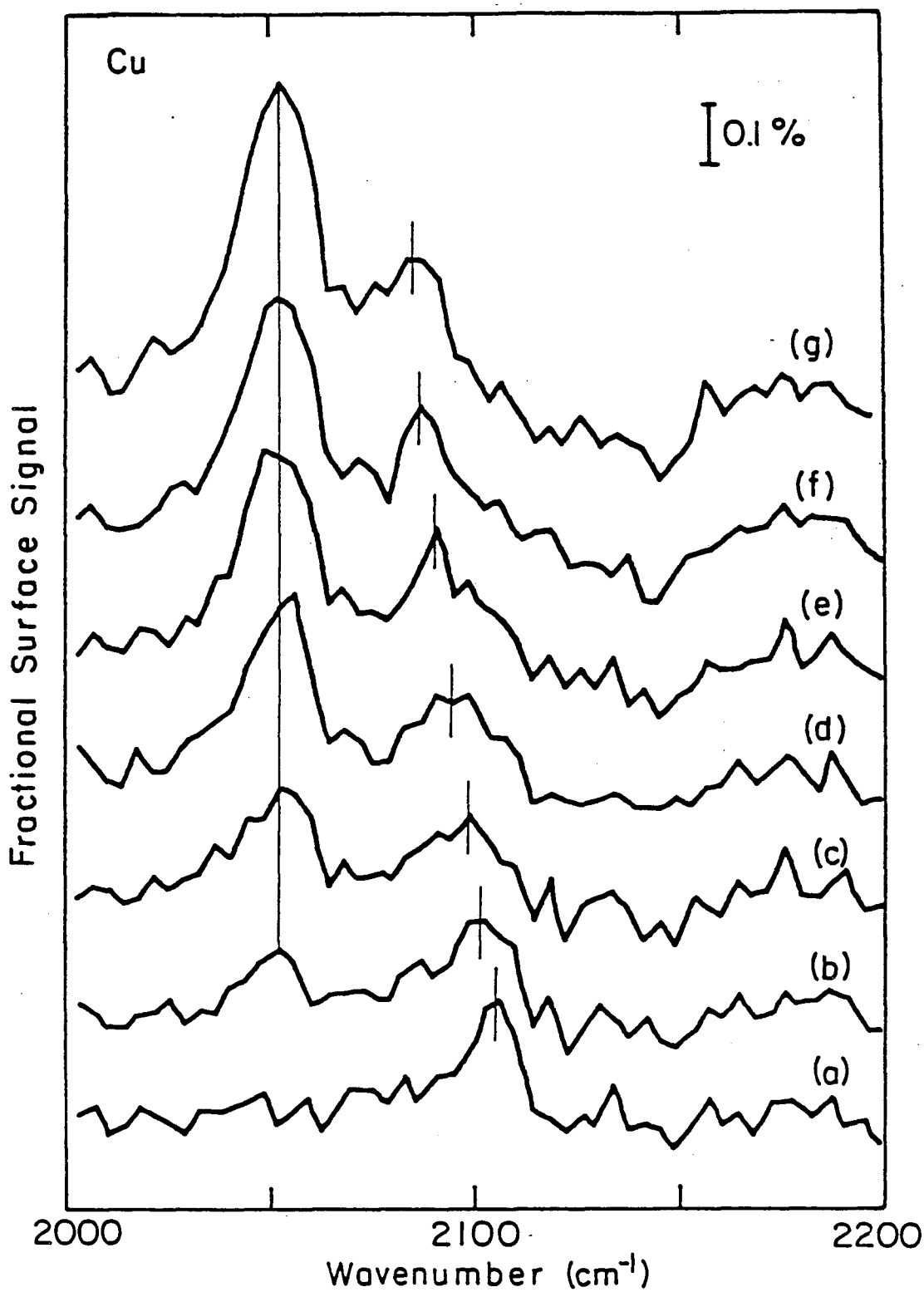
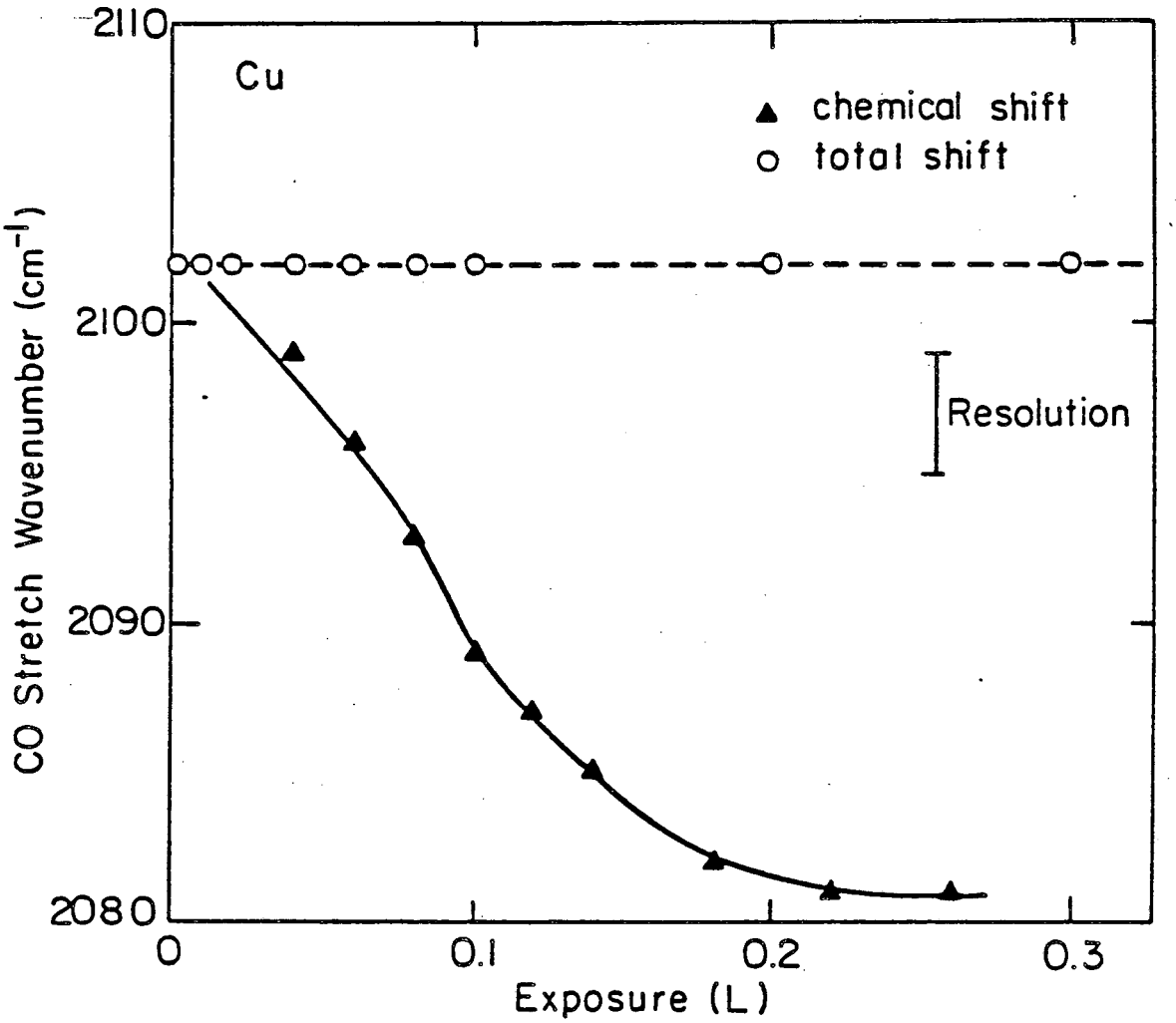

Au
T_D = 280 K
▲ chemical shift
o total shift
Resolution
CO Stretch Wavenumber (cm^{-1})
Intensity (arb. units)
2120
2110
2100
2090
0
0.1
0.2
0.3
0.4
Exposure (L)
XBL854-6111

FIGURE 10



XBL 854-6070

FIGURE 11



XBL854-6063

FIGURE 12

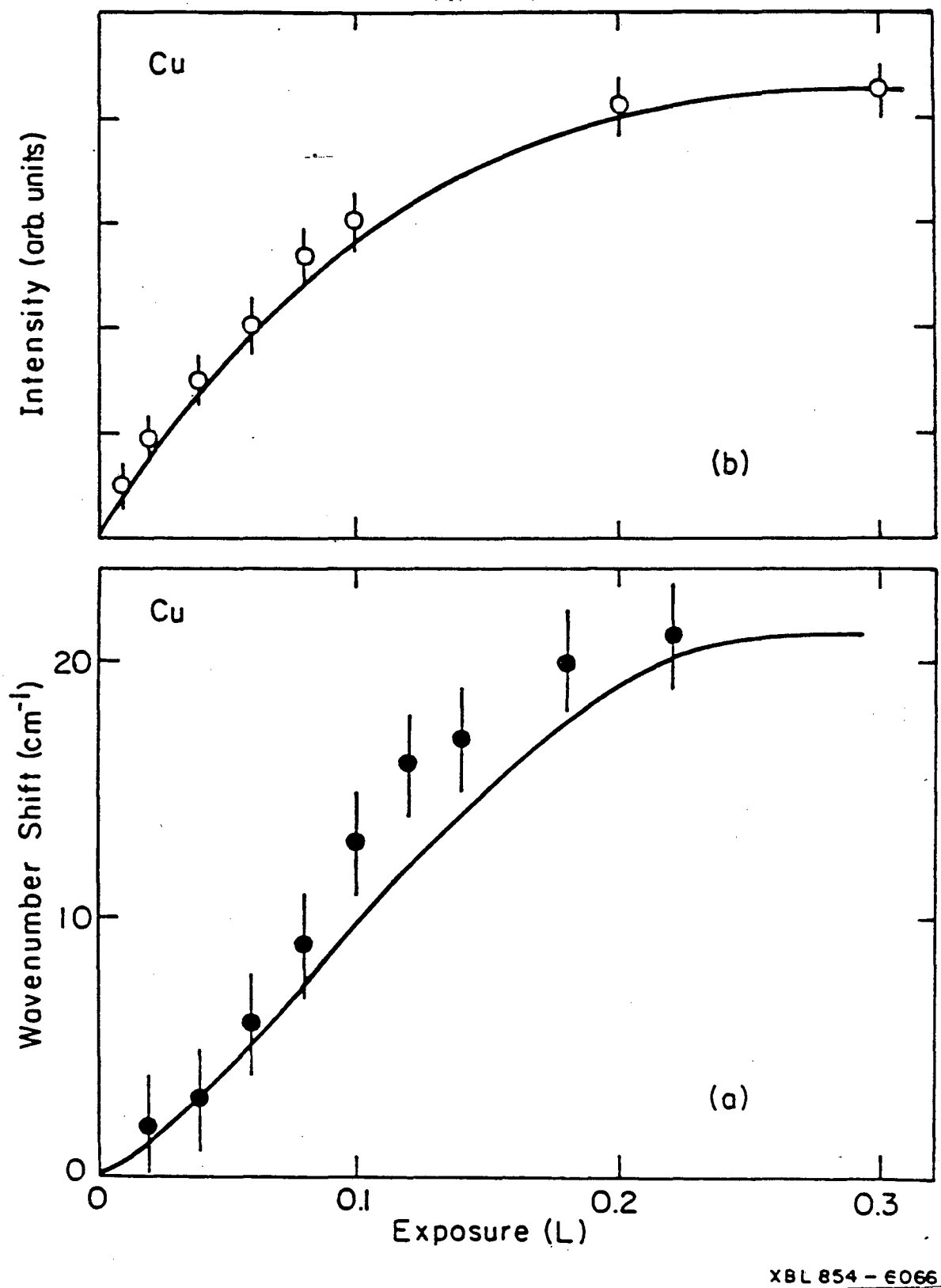

Cu
Intensity (arb. units)
(b)
Cu
Wavenumber Shift (cm^{-1})
20
10
0
(a)
0
0.1
0.2
0.3
Exposure (L)
XBL 854 - 6066

FIGURE 13

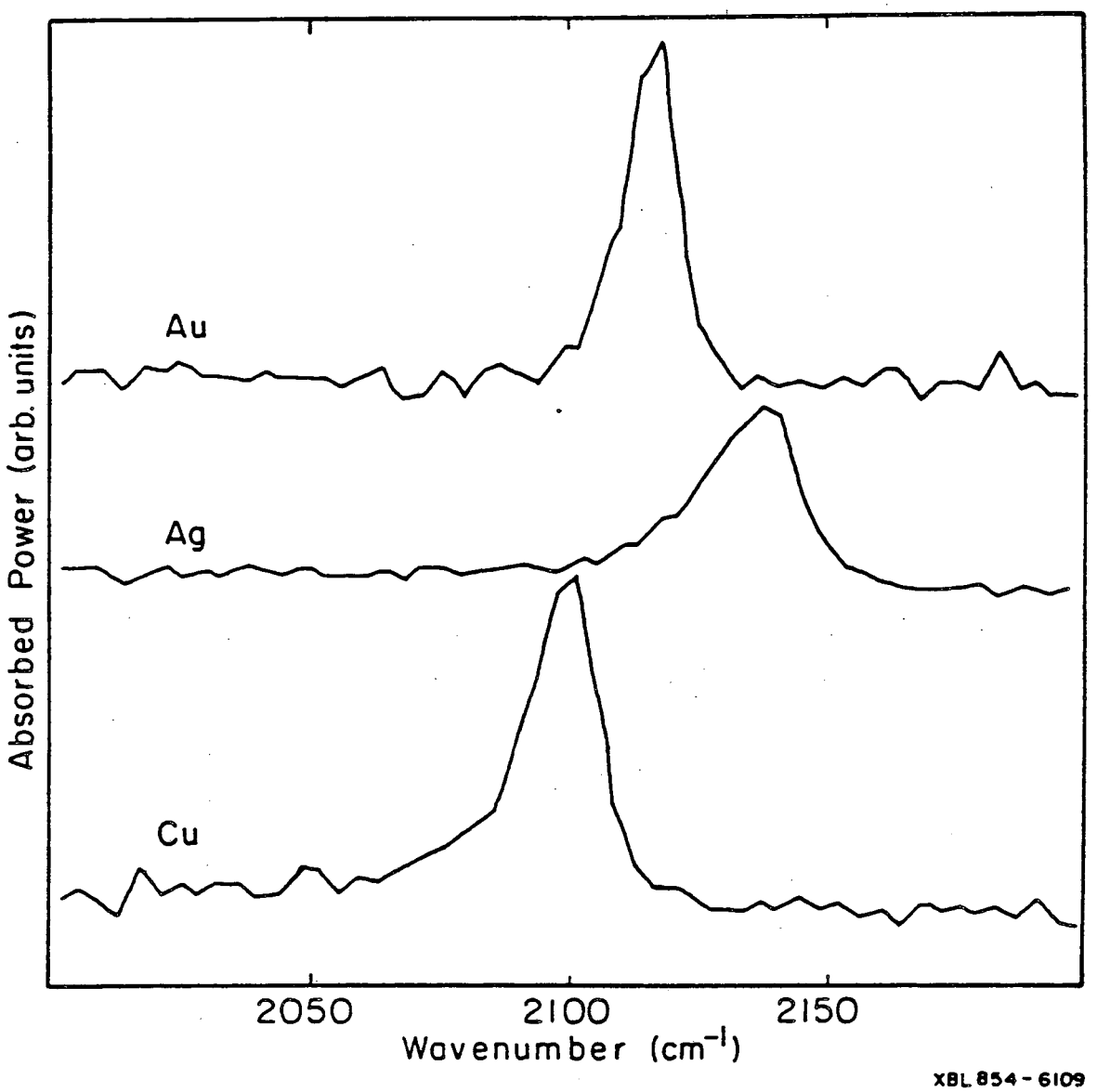

Au
Ag
Cu
Absorbed Power (arb. units)
2050
2100
2150
Wavenumber (cm⁻¹)
XBL 854-6109

FIGURE 14

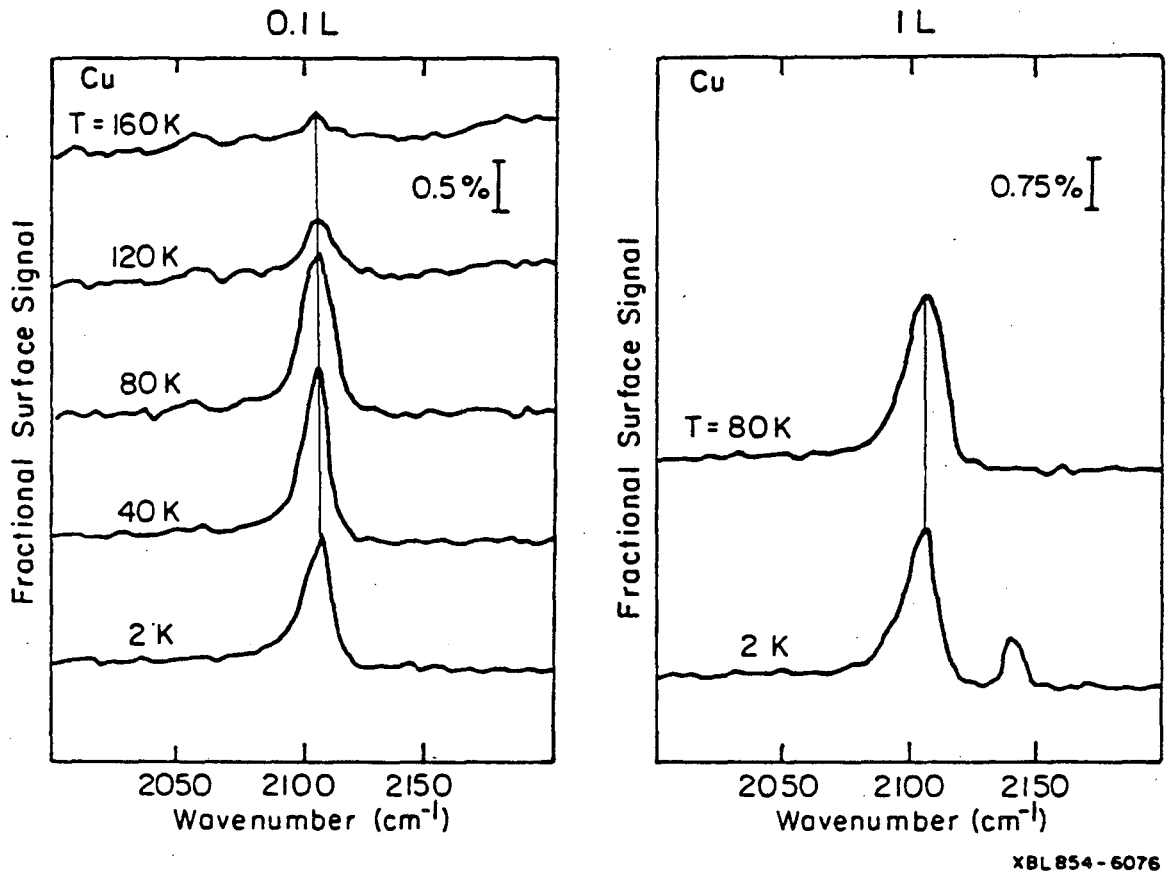

0.1 L
Cu
T = 160 K
0.5 %
120 K
80 K
40 K
2 K
Fractional Surface Signal
2050
2100
2150
Wavenumber (cm⁻¹)
1 L
Cu
0.75 %
T = 80 K
2 K
Fractional Surface Signal
2050
2100
2150
Wavenumber (cm⁻¹)
XBL 854-6076

FIGURE 16

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