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I. SILVER

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

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Abstract

We have used infrared absorption spectroscopy to study the adsorption of CO at low temperature on evaporated silver films as a function of the coverage of CO and the deposition temperature of the silver. We observe two adsorption regimes when a cold silver film is exposed to CO gas. If the silver deposition temperature, (or the highest temperature at which the silver has been annealed), is above the threshold temperature of 150 K, then only physisorbed CO is observed. For sample temperatures below 25 K, these physisorbed molecules are oriented perpendicular to the metal surface. Films deposited at temperatures below 150 K, however, contain ~0.4 monolayer of chemically active sites at which CO chemisorbs. The infrared band due to chemisorbed CO shifts to lower frequency with increasing coverage. We have analyzed this shift and separated the static and dynamic contributions. The static, chemical shift is caused in part by the change in work function induced by surrounding adsorbates. The dynamic shift is fully explained by a dipole-dipole interaction; we find no evidence for a vibrational coupling through the metal. We have analyzed the vibrational polarizability and infrared absorption strength of the adsorbed CO, and find no evidence for the infrared enhancement suggested by some theories of surface enhanced Raman scattering.

1. Introduction

The aim of this study is to use infrared absorption spectroscopy to elucidate the low temperature adsorption behavior of CO on evaporated silver films deposited at various temperatures. The aspects of adsorption that we have investigated are: the nature of the adsorption site, the interadsorbate interactions, and the integrated intensity of the vibrational band.

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 this study, we find that for $T_D < 150$ K, the films contain large numbers of chemically active sites at which CO chemisorbs. Chemisorption does not occur on films deposited at higher temperatures.

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 [1-9], and palladium [10,11]. 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 [12]. 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 [13]. 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.

We find 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 find that a large part of the chemical contribution can be attributed to the influence of the local work function on the bonding of the CO, and that the dynamic coupling is well described by a dipole coupling model, without any need to invoke an interaction through the metal.

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 [14]. 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

infrared vibrational polarizability of chemisorbed CO to be greater than that of gas phase CO [14]. 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 small "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 [14], but it has also been suggested that special Raman-active sites are present in the films [14]. 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 not excited at infrared frequencies. We find that for chemisorbed CO on silver, there is no "special" enhancement of the infrared cross section.

2. Experimental

The absorption of electromagnetic radiation by molecules adsorbed on the surface of a solid populates vibrational or electronic states of the adsorbate. Relaxation proceeds mainly by transfer of energy to the substrate, leading to a small temperature rise. In our experiment we measure this rise at low substrate temperature with a sensitive thermometer, thus using the sample itself as a bolometric infrared detector. This thermal detection technique was developed by Bailey et al. [15], and a detailed description of the apparatus can be found in their publication. Compared with reflection-absorption spectroscopy, this technique has the advantage that the adsorbate signal is superimposed on the small background absorption of the substrate, rather than on the larger reflected signal.

The sample design is based on a type of composite bolometer developed for far-infrared astronomy [16]. It consists of a gallium-doped germanium thermometer attached to the back of a sapphire substrate. The metal film to be studied is deposited on the front surface of the substrate. Copper leads to the thermometer provide a thermal link to a heat sink at 1.2 K. The assembly is supported by tungsten wires, which also provide the means to heat the sample to temperatures as high as 425 K. A copper-constantan thermocouple is attached to the sample to monitor its temperature during heating.

The sample is surrounded by radiation shields both at liquid helium and at liquid nitrogen temperatures. These shields are necessary to prevent radiation from the room temperature surroundings from reaching the sample.

Small amounts of warm radiation would cause additional photon noise, while large amounts could saturate the sensitive bolometer. Cryopumping by the shields also helps to maintain UHV conditions in the vicinity of the sample. Without cryopumping, the diffusion pumped UHV chamber has a base pressure in the 10^{-10} torr range. In the present apparatus, the shields prevent the use of analytical tools other than infrared spectroscopy, which could provide for a better characterization of the surface.

Unpolarized infrared radiation from an EOCOM 7001P Rapid Scan Fourier Transform Spectrometer enters the UHV chamber through an indium-sealed KRS-5 window, and is incident on the sample at an angle of approximately 82° to the surface normal. The average absorbed power of 16 μW raises the sample temperature by 0.6 K above the heat sink temperature. The sensitivity of the detector is limited by photon noise, with an NEP of 8×10^{-13} W/√Hz. As an example of the high sensitivity of this detection technique, we show in Fig. 1 the signal from 0.001 L of chemisorbed CO on an evaporated silver film deposited at $T_D = 4$ K. This spectrum required approximately 40 min. of integration time to obtain the signal to noise ratio of about 3 that is shown. The resolution for this spectrum was 8 cm^{-1}.

The experimental procedure was as follows. First a silver film approximately 200 Å thick was deposited at a rate of about 1 Å/s by evaporation from a tungsten filament wrapped with silver wire, (99.998% purity, Johnson Matthey Ltd.). No dependence of the results on evaporation rate was observed, for rates between 1 and 10 Å/s. During the deposition of the silver, the heater was used to maintain the substrate at a temperature T_D, which could be varied from 2 K to 425 K. The pressure measured in a warm region of the chamber that was far from the sample never

exceeded 10^{-9} torr during the evaporation. It is safe to assume that the pressure inside the cold shields was much lower.

When the heater was turned off, the substrate cooled within a few minutes to 1.8 K. A reference spectrum of the clean film was measured. The sample was then exposed to CO gas from an effusive beam doser. The exposure, expressed in Langmuir, (1 L = 10^{15} molecules/cm^2), was calculated from the known geometry, and the calibration was checked by measurements of CO adsorption on Ni films [15,17]. The sample temperature was maintained at 1.8 K during adsorption. Because of the low sample temperature, it is safe to assume a sticking coefficient very close to unity. A spectrum of the film with adsorbed CO was then measured. The reference spectrum was subtracted, and the result divided by the reference, so that the final absorptance is expressed as a fraction of the bulk film absorptance. In some cases, the film was heated before the spectrum was measured, to allow desorption, annealing, or molecular rearrangement to occur. In all cases, the sample was returned to 1.8 K for infrared measurements. We assume that the arrangement of the molecules on the surface at the higher temperature is preserved when the sample is cooled.

With the exception of the spectrum shown in Fig. 1, all the data presented represent about 10 min. of integration per spectrum, and an instrumental resolution of 4 cm^{-1}. All data are displayed as measured; there has been no smoothing, and no baseline fitting. An additive constant has been included to clarify the display of multiple spectra.

3. Results

We present here data and conclusions regarding three aspects of CO adsorption on silver:

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

Each aspect will be discussed in turn.

3.1. Adsorption behavior and film structure

We find that the nature of the adsorption of CO depends strongly on T_D, the substrate temperature during deposition of the silver film, or, equivalently, the annealing temperature for a film deposited at low temperature. When a film deposited at $T_D > 150$ K is exposed to CO at 2 K , only physisorbed CO can be detected. For lower T_D, chemically active sites that support CO chemisorption are present in the film in substantial concentration, ($\sim 4 \times 10^{14}$ cm^{-2}). These observations imply that there are major structural differences between films deposited at low temperatures and those deposited or annealed at temperatures above 150 K.

Fig. 2 shows infrared spectra of increasing amounts of CO adsorbed on a silver film deposited at $T_D = 300$ K, well above the threshold. The frequency of the single band, 2143 cm^{-1}, is equal to that for gas phase CO. This frequency, and the lack of any frequency shift with increasing coverage, are characteristic of physisorption. This result is consistent with the known behavior of CO on single crystal silver surfaces, which also do not support CO chemisorption [18]. Due to the infrared selection rules, the observation of an infrared signal from physisorbed CO implies that at

least some of the physisorbed molecules have their axes perpendicular to the surface. We will show below that there is reason to believe that nearly all of the physisorbed molecules are in such an orientation. This is in contrast to recent photoemission results, which suggest that physisorbed CO on silver single crystals at 40K is bonded either with its axis parallel to the surface, or in a random orientation [18]. We find that the infrared signal vanishes when the sample is heated to 25 K after CO adsorption, (Fig. 3). These two results could be reconciled if the physisorbed CO undergoes a transition from a perpendicular to a parallel orientation near 25 K.

For a silver deposition temperature $T_D = 4$ K, well below the threshold, the spectra are quite different, (Fig. 4). At low coverages, a single band due to chemisorbed CO is observed, as has been previously shown with infrared [2], and Raman [19-24], spectroscopies. The band appears initially at 2148 cm^{-1}, as can be seen more clearly in Fig. 1. The shift from the gas phase value of 2143 cm^{-1} indicates the formation of a chemical bond with the surface. Moreover, the band shifts to lower frequencies with increasing coverage. Such a shift, as we will discuss in detail later, can only occur in the presence of chemical bonding to the surface. Furthermore, we find that this band persists until the sample is heated above 80 K, (Fig. 5). It is clear, therefore, that CO chemisorbs on silver films deposited at low temperature, in marked contrast to its behavior on films deposited at room temperature and on single crystals.

The observation of a C=O stretch frequency higher than the gas phase frequency is unusual. On transition metals, the frequency is typically shifted down by 50-300 cm^{-1} for the chemisorbed species, and sometimes

even further. This downward shift arises from two effects: the partial filling of the CO $2\pi^*$ antibonding orbital on adsorption [1], and the "self-image" effect caused by the electrostatic response of the metal [25,26]. An effect that tends to shift the frequency upward is that of dynamic coupling between the C=O stretching mode and the stretching vibration of the C-metal bond [4]. In typical cases of strong chemisorption, this upward shift is small compared to the first two effects. In the present case of weak CO chemisorption on silver, the dynamic effect is apparently dominant.

The band due to chemisorbed CO is much broader than that due to physisorbed CO, (Fig. 2), and it is asymmetric, with a tail to lower frequencies. For a film that is certainly rough, there is every reason to believe that the lineshape represents inhomogeneous broadening.

After an exposure of 0.4 L, a second, much sharper band appears at 2143 cm^{-1}. This band is due to physisorbed CO; it can be removed by heating the sample to 40 K. The fact that a band due to physisorbed CO is observed only after the chemisorption band has saturated implies some mobility for molecules on the surface. At 2 K, virtually all molecules that strike the surface stick, and those that do not initially hit chemisorption sites must be mobile enough to migrate to such sites. Since the density of such sites is large, the CO molecules do not need to migrate very far. As we will show, additional rearrangement of the overlayer can be induced by heating the sample after adsorption.

From the radically different behavior of CO on silver films deposited at T_D = 2 K and at T_D = 300 K, it is clear that the two films must have significantly different chemical and structural properties. In particular,

films deposited at low temperature include reactive sites on which CO readily chemisorbs, while films deposited at room temperature do not. Moreover, these sites are present in substantial concentration. Based on the exposure at which the chemisorption band ceases to increase in intensity, we conclude that the surface density of such sites is approximately 4×10^{14} cm^{-2}. This is equivalent to ~40% of a monolayer on a silver single crystal surface. We have investigated CO adsorption on silver films deposited at various substrate temperatures in the range $4 < T_D < 300$ K. We have found that the transition temperature between the two types of behavior is 150 ± 10 K. For higher values of T_D, no chemisorbed CO is detected.

It is tempting to identify these chemically reactive sites in the films deposited at low temperature with the Raman-active sites that have been postulated to account for the large enhancement of the Raman cross section observed for molecules on such films [14]. We will show later that such an identification is not supported by our measurements.

3.2. Frequency shifts and intermolecular interactions

An inspection of Fig. 4 shows that the center frequency of the infrared band changes from about 2143 cm^{-1} at low coverage, to 2123 cm^{-1} after an exposure of 0.4 L. The frequency as a function of exposure is shown in Fig. 6, along with the integrated intensity of the band. We have analyzed the chemical and dynamic contributions to the shift, using the isotopic substitution technique described in the Introduction. We find that the chemical contribution is largely caused by the change in the work function due to coadsorbed molecules, and is a long-range interaction. We will

present a qualitative model of the chemical shift based on ideas of Otto, et al. [26]. The vibrational coupling is well described by dipole-dipole coupling; there is no evidence of a vibrational coupling through the metal.

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. 6) observed for a homogeneous layer of ^{12}CO. The size of the chemical shift (-34 cm^{-1}) is substantially greater than that of the total shift, (-26 cm^{-1}).

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. We will return to Fig. 9, but first we wish to discuss the sources of the chemical shift.

The most popular explanation of a chemical effect on the C=O stretch frequency is due to Blyholder [27,28], and involves the effect of backdonation of metal electrons into the antibonding $2\pi^*$ orbital of CO. Because the orbital is antibonding, such backdonation reduces the C=O stretch frequency, and changes in the amount of backdonation with coverage can cause frequency shifts. For example, a positive frequency shift, (an increase in the vibrational frequency with increasing coverage), which is observed for CO on Pd [10,11], is explained in terms of competition for backdonated electrons. When more molecules have to "share" the metal's donated electrons, the backbonding is reduced. The resulting decrease of the population of the $2\pi^*$ orbital causes a shift of the band to higher

frequency. A quantitative relationship between CO stretch frequency and $2\pi^*$ occupation has been obtained by Baerens et al. [29], who compared $2\pi^*$ populations obtained from LCAO-HF calculations, with experimental C=O stretch frequencies for a series of carbonyl complexes. Unfortunately, there is as yet no quantitative theory for the relationship between $2\pi^*$ occupation and coverage.

In order to explain the negative shift observed in the present experiment with this model, we need to explain an increase in $2\pi^*$ occupation with increasing coverage. Such an explanation has been advanced by Woodruff et al. [1]. They assume that the interaction with the metal causes the $2\pi^*$ orbitals to have a large spatial extent, so that they overlap even at rather low coverage. The overlap further broadens the orbital in energy, which could cause the amount of backdonation to increase, as more of the orbital lies below the Fermi level in energy.

An alternative argument, not based on $2\pi^*$ backdonation, has been offered by Pritchard and coworkers [2,8], to explain the downward frequency shift observed for CO adsorbed on silver and gold films. They argue that for these systems backdonation should be unimportant, because the metal d-band, which is responsible for backdonation on transition metals, lies four eV below the Fermi level in noble metals. Instead, they argue that charge transfer from the molecule to surface metal atoms weakens the σ bond between the carbon atom and the metal, and this in turn lowers the C=O stretch frequency. The assumption that backdonation is insignificant seems untenable, however. As we will show, the vibrational polarizability of the adsorbed CO is substantially enhanced over its gas

phase value; this is most easily explained by dynamic charge transfer between the metal and a partially occupied molecular orbital at the Fermi level [1]. Moreover, recent angle-resolved photoemission experiments for CO on copper directly show occupation of the $2\pi^*$ orbital [30].

Both of the above mechanisms invoke a chemical interaction between the adsorbates, either direct or substrate-mediated, to account for changing adsorption chemistry, and thus for the chemical shift. We will now argue, however, that a large portion of the chemical shift occurs <u>even when the coadsorbed molecules do not interact chemically with the surface.</u>

The first evidence for this statement is seen in Fig. 6, in which the appearance of physisorbed CO in the spectrum is accompanied by an additional shift in the frequency of the band due to chemisorbed CO. The effect is shown even more dramatically in Fig. 10. The bottom curve shows the spectrum for a film saturated with chemisorbed CO, but without any physisorbed molecules. In the middle curve, another 0.625 L CO have been added, giving a strong peak due to physisorbed CO and shifting the band due to chemisorbed CO to lower frequencies. The sample was then heated to 40 K, desorbing the physisorbed molecules. The chemisorbed band returned to its original frequency.

Fig. 11 shows that similar results are observed when the coadsorbate is an inert gas. In this experiment, 0.1 L CO was chemisorbed on a silver film deposited at $T_D = 4$ K, and increasing amounts of argon were coadsorbed, up to an exposure of 1 L. A shift in the C=O stretch frequency of $-16\ cm^{-1}$ is observed. No shift was detected, however, for Ar exposures less than 0.1 L.

We will propose a qualitative model to explain these results in terms of the effect of work function changes on $2\pi^*$ backdonation. It is known that physisorbed CO on Ag(111) [11], and chemisorbed CO on copper [7], decrease the work function by 0.8 eV and 0.4 eV, repectively. It seems reasonable to assume that chemisorbed CO on silver films deposited at low temperatures has a similar effect. Adsorption of rare gases also generally lowers the work function [31].

We model the effect of the change in the work function, $\Delta\phi$, on the occupation of the $2\pi^*$ level in terms of the model presented by Otto, et al. [26], for the energy of a molecular orbital. The energy separation of the orbital from the metal Fermi level can be written, (see Fig. 12):

$$\Delta E = \phi + B$$

where ϕ is the work function, and B is the binding energy of the orbital relative to the vacuum. If the orbital is broad and partially overlaps the Fermi level, a decrease in ΔE will cause an increase in the occupation of the orbital. This could come about through a change in B due to a chemical interaction with other adsorbates. It could also occur, however, through a change in ϕ, as shown schematically in Fig. 12(b) and in Fig. 13.

Such a model accounts qualitatively for our experimental results, but it appears surprising that the change in the work function due to a coadsorbed atom or molecule would extend far enough to have a significant effect at very low coverages. Indeed, it appears that Ar coadsorption has little effect on the C=O frequency at exposures less than 0.1 L. It is possible that the shift seen at very low coverages is due primarily to a true chemical interaction mediated by a partially filled electronic surface band in the metal; the strength of such an interaction has been predicted to vary as r^{-2} [32,33].

The effect of vibrational coupling on the frequency shift and on the integrated intensity of the band can be analyzed using the theory of Persson and Ryberg, (P-R) [34]. This theory assumes pure dipole interactions between molecules adsorbed randomly on sites in a periodic lattice. It is not immediately clear that such a model is applicable to the present case, in which the surface structure is certainly complex and the distribution of sites is unknown. In fact, however, we find that the model accounts quite well for our experimental observations, which is probably an indication that the chemically active sites are rather uniformly distributed over the surface. The success of the model, with physically reasonable parameters, also suggests that vibrational interactions mediated by the metal, such as those suggested by Moskovitz and Hulse [12], are not of importance.

The primary results of the P-R model are contained in the equations for the frequency and integrated intensity as a function of coverage:

$$\frac{\Omega}{\omega_0} = 1 + \frac{C\alpha_v \tilde{U}(0)}{1 + C\alpha_e \tilde{U}(0)} \qquad (1)$$

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

where:

C = fractional occupation of adsorption sites

Ω = frequency of the molecules for concentration C

ω_0 = singleton frequency, (frequency at C = 0)

α_v = vibrational polarizability of the molecule

α_e = electronic polarizability of the molecule

$\Delta(\omega)$= infrared absorption intensity at frequency ω

$\tilde{U}(0)$= interaction potential for the two dimensional wavevector q=0. This term represents the dipole part of the electromagnetic interaction between a molecule and all the surrounding molecules, including the response of the metal. The vibrational polarizability α_v is the polarizability as modified by the interaction with the metal, and including any dynamic charge transfer between the substrate and a partially filled orbital, as well as the "image dipole."

We have used the P-R model to fit the data shown in Fig. 9 for the vibrational frequency shift and the integrated intensity of the band. We have assumed that α_e is unchanged from its gas phase value of 3 $Å^3$, which is consistent with results for other systems [34]. The singleton frequency ω_o = 2148 cm^{-1} was taken from the observed frequency at 0.001 L exposure, (Fig. 1), and also agrees with the value obtained by extrapolating the frequency versus exposure data in Fig. 6 to zero exposure. The fit then involves only two adjustable parameters, α_v and $\tilde{U}(0)$. The best fit is shown as the lines in Fig. 9; the parameters are:

$$\alpha_v = 0.27 \pm 0.015\ Å^3$$

$$\tilde{U}(0) = 0.04 \pm 0.002\ Å^{-3}.$$

This value of α_v is the same as that obtained for CO adsorbed on Cu, (0.27 $Å^3$) [34,36]. It is substantially larger than the gas phase polarizability of CO, 0.05 $Å^3$. This increase in the vibrational polarizability on chemisorption represents the normal chemical enhancement due to dynamic charge transfer between the molecule and the metal as the partially filled $2\pi^*$ orbital is perturbed by the motion of the molecule.

We can make an independent estimate of α_v by comparing the integrated intensities for the same quantity of CO chemisorbed on a film deposited at low temperature, and physisorbed on a film deposited at high temperature. We find that the intensity due to the chemisorbed species is a factor of four greater than that observed for the physisorbed molecules. If we assume that all of the physisorbed molecules are oriented perpendicular to the surface, and that the screening due to α_e is the same for the two species, then the polarizabilities α_v are in the same 4:1 ratio as the intensities. If we take the polarizability of the physisorbed species to be the same as that of gas phase CO, 0.05 $Å^3$, we then estimate $\alpha_v = 0.20$ $Å^3$ for the chemisorbed species. The agreement with the value deduced from fitting the frequency shift confirms that most of the physisorbed molecules must indeed be oriented normal to the film surface, at least for temperatures below 25 K. Our value of $\tilde{U}(0)$ is quite low compared to those obtained for CO adsorbed on monocrystalline copper and ruthenium surfaces, (0.3 $Å^{-3}$ and 0.17 $Å^{-3}$ respectively). This difference can be understood, at least semi-quantitatively, by considering the expression for $\tilde{U}(0)$ in an approximation that treats the surrounding molecules as point dipoles, and the substrate response in the image approximation:

$$\tilde{U}(0) = \frac{1}{a^3} \sum \left[\frac{1}{|x_{ij}|^3} + \frac{1}{|x_{ij}+D|^3} - \frac{3D^2}{|x_{ij}+D|^5} \right] \quad (3)$$

where:

x_{ij} = distance between adsorption sites i and j

D = distance between a dipole and its image

and all distances are measured in terms of the constant, a, that describes the lattice of adsorption sites. In the case of a single crystal, the proper value for a is the normal surface lattice constant. However, in the present case, the concentration of adsorption sites on the surface is only ~40%, so the proper value for a is larger by a factor of ~1.6. Thus we expect a value of $\tilde{U}(0)$ on the order of 4 times smaller than is typically observed on single crystals, and that is approximately the ratio that we find. Since we have virtually no information about the actual structure of the film or the distribution of adsorption sites, such an argument is necessarily imprecise. Certainly they are not located on a periodic lattice. Because the substrate imposes a minimum site spacing, assuming a broad distribution of spacings tends to reduce $\tilde{U}(0)$ slightly. The basic argument remains unaffected, however, by such a distribution.

The P-R model of vibrational coupling thus seems to give a good account of the observed data, with values of α_v that are physically reasonable and consistent with the other information available for the system.

3.3. Integrated vibrational band intensities and enhancement

As we have already suggested, it is important to consider the possibility that our observation of special adsorption sites on silver films deposited at low temperatures is related to the phenomenon of surface enhanced Raman scattering, (SERS). If these adsorption sites are the special Raman-active sites postulated by Otto [14], we would expect dynamic

charge transfer to produce a "special" enhancement of the infrared intensity, beyond the chemical enhancement seen on single crystals and polycrystalline films.

Information regarding the infrared intensity is contained in the value of α_v derived from the vibrational frequency shift. Other parameters being equal, equation (2) shows that integrated intensity of the infrared band is proportional to α_v. Thus a "special" infrared enhancement associated with special sites on rough films deposited at low temperature would appear as a value of α_v greater than that observed for chemisorbed CO on single crystals.

We have already shown that the value of α_v deduced from the dynamic frequency shift is no greater than that observed on single crystal copper. This deduced value of α_v accounts well for the observed intensities, (Fig. 9). There is thus no evidence for any "special" infrared enhancment associated with the special structure of the rough film.

We have also made a more direct test of this claim, by directly comparing the power absorbed by equal quantities of CO on a silver film and on a nickel film. Since CO adsorbs at normal lattice sites on nickel, while on the silver film it chemisorbs only at special sites, not present on single crystals or annealed films, any "special" infrared enhancement due to the special character of the silver adsorption sites should appear as extra integrated intensity in the band.

Fig. 14 shows the result of such an experiment. We first deposited a nickel film at $T_D = 4$ K and exposed it to 0.1 L of CO. The spectrum is shown as the lower curve in Fig. 15. We then evaporated silver onto the substrate at $T_D = 4$ K, and deposited the same quantity of CO. The upper

curve shows the infrared spectrum. We have integrated the area under the peaks in the two curves, and found them to be equal within 10%. We thus find no evidence for any "special" infrared enhancement beyond the chemical enhancement normally associated with chemisorption on single crystal metals.

Under certain conditions, we do observe an increase in the integrated intensity of the band when the sample is heated after CO adsorption. This effect is shown in Fig. 5(a), where the spectrum of 0.04 L chemisorbed CO is shown after deposition at 2 K and after heating to 20 K, 40 K, and 80 K. Annealing at 40 K produces an increase in the infrared intensity by a factor of 1.4. The absence of any frequency shift excludes the possibility of additional CO adsorption during heating; it also tends to exclude the possibility that the molecules are moving to sites of substantially different chemistry. Annealing the clean film prior to depositing the CO does not produce the enhancement. We do not know what causes this effect, but we speculate that the molecules may be migrating to chemically equivalent sites that are located in regions of enhanced electric field. Such sites might be located in microscopic pores [37,38], cavities [39], or at steps [40].

Such an interpretation is supported by the observation that a saturated film, (Fig. 5(b)), does not show any intensity increase, as would be expected since all sites are already filled. The saturated film does, however, show a shift of the band to higher frequency and a band narrowing. We do not understand these effects; they indicate the complexity of the true nature of the evaporated films.

4. Discussion

Our results clearly show that films deposited at $T_D < 150$ K contain chemically active sites that are not present in films deposited at higher temperatures. The concentration of such sites is rather high, ~40% of a monolayer, and is essentially independent of T_D below the threshold temperature. These sites are certainly electronically distinct from the sites on a smooth silver surface, and it is likely that they are also structurally distinct, at least on an atomic scale. Our data do not permit any detailed conclusions regarding either the electronic or the structural nature of these sites, but we will review here what is known and speculated about the nature of such films.

The precise structure of silver films deposited at low temperatures is not known, since there has apparently been no detailed microscopic investigation of such films. There is some experimental evidence that silver films deposited at low temperatures are porous [37,38]. The evidence is based on observations of the photoelectron spectra of Xe on silver films deposited at different temperatures. The intensity of the Xe $5p_{3/2}$ $5p_{1/2}$ doublet is strongly dependent on the structure of the film. It is strongly suppressed for low film deposition temperatures. The intensity difference is explained in terms of incorporation of Xe atoms into pores, from which the photoelectrons cannot escape. The pores are thought to be of only atomic scale width, and they are eliminated if the film is annealed in the temperature range between 170 and 250 K [37]. It has been calculated that the electric field must be enhanced inside such pores [37]. Otto *et al.* [26], have made the specific suggestion that the pores occur at the

boundaries between microcrystallites. Seki and Chuang [39], have suggested the existence of chemisorption sites inside larger scale cavities, with widths of 10-30 Å, and depths of ~150 Å.

There is little experimental information regarding the electronic structure of the chemisorption sites. No drastic difference in the photoemission spectra exists between silver films deposited at room temperature and those deposited at low temperatures [38,41]. An intensity change is observed at the upper d-band edge at 4.2 eV below E_F. This extra structure has been assigned to localized d-electron states of surface defects. The work function of the silver films is 4.4 ± 0.1 eV and does not depend either on the deposition temperature or on the annealing condition. However, one might expect a different local work function at defect sites [42].

There are two suggested changes in the electronic structure at defects that could allow the formation of a bond with CO. The d-band at active sites might be closer to the Fermi level, as it is in transition metals, and mix with the 5σ orbital of CO to form a bond. Alternatively, Otto et al. [26] argue that a quasi-atomic Ag 5s state may exist at defect sites, and may not have been detected by photoelectron spectroscopy due to a very low photoionization cross section. They suggest that such a localized 5s electronic state at E_F could play a role in binding with the CO 5σ orbital. There is currently no experimental evidence to confirm or refute either explanation.

Finally, we would like to discuss the surface Raman data obtained by Seki [32] and by Wood, et al. [22], for CO adsorbed at low temperature on

silver films deposited at 150 K and at 120 K, in light of our results. Seki measured the Raman spectrum of about 1 monolayer of CO adsorbed at 10 K. Only a band located at 2143 cm^{-1} was detected on the Raman spectrum. By comparison with our results, the observation of this frequency after such a high exposure indicates the presence of physisorbed CO. This result is not surprising in view of our observation that films evaporated at T_D > 150 K do not support chemisorption. On the other hand, Wood et al. [22], in a similar experiment using a deposition temperature of 120 K, observed a negative frequency shift of the C=O band with coverage, indicating the presence of chemisorbed CO, as we would expect.

It seems, then, that the molecules observed in these SERS experiments show the same adsorption behavior as those that we detect with infrared spectroscopy. There is no evidence for special Raman-active sites that dominate the SERS spectrum while contributing negligibly to the infrared data. It seems clear, then, in view of our observation of no significant "special" infrared enhancement, and the fact that Seki's measurement of the temperature dependence of the Raman enhancement bears no relation to the temperature dependence of the concentration of chemisorption sites, that there is no significant charge transfer contribution to the special Raman enhancement for this system. A more definitive measurement of the contribution of a charge transfer mechanism could be obtained by a quantitative comparison of the Raman intensity for physisorbed CO on a film deposited at T_D > 150 K with that for chemisorbed CO on a film deposited at lower temperature.

5. Conclusion

Infrared absorption spectroscopy, using a thermal detection technique, has allowed us to investigate different aspects of the interaction of CO molecules with evaporated silver films as a function of coverage and film deposition temperature. The sensitivity of our technique is high enough to detect a coverage as low as 10^{-3} monolayer.

Silver films deposited at temperatures below 150 K exhibit chemically active sites at which CO molecules can chemisorb. These active sites are in relatively high concentration (~40% of a monolayer). For higher deposition temperatures, only physisorbed CO is detected.

An overall downward shift of 26 cm^{-1} is observed in the vibrational frequency between zero coverage and saturation. The chemical and dynamic contributions to the shift have been separated by coadsorbing isotopes. At low coverages, the shift is dominated by a long range chemical interaction, at least a part of which is attributable to the work function change caused by coadsorbed molecules. At higher coverage, an offsetting dynamic shift becomes significant. The dynamic shift is well described by a model of dipole-dipole coupling, with physically reasonable parameters. There is no evidence for a dynamic coupling through the metal.

We have found no evidence for a "special" infrared enhancement associated with the chemisorption sites, beyond the chemical enhancement normally found for chemisorbed CO on single crystals. Considering previous Raman measurements for CO on evaporated silver in the light of our results, we find that the dramatic "special" enhancement of the Raman cross section observed on rough films, as compared with annealed films and single

crystals, is not caused in any significant degree by charge transfer effects at special sites.

Our results on physisorbed CO clearly show that most, and probably all of the molecules are oriented perpendicular to the surface. Above 25 K, no signal is detected from physisorbed CO, indicating that the molecules have either desorbed, or have reoriented parallel to the surface, as suggested by other studies.

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Figure Captions

Fig. 1: Infrared spectrum of 10^{-3} L CO chemisorbed at 2 K on a silver film deposited at T_D = 4 K, showing a single band at 2148 cm^{-1}. The integration time was ~40 min. The resolution was 8 cm^{-1}; all other spectra shown in this paper have a resolution of 4 cm^{-1}.

Fig. 2: Infrared spectra of CO physisorbed at 2 K on a silver film deposited at T_D = 300 K, as a function of exposure, showing a single narrow band at 2143 cm^{-1}.

Fig. 3: Infrared spectra of 0.2 L CO physisorbed at 2 K on a silver film deposited at T_D = 300 K. The signal vanishes when the film is heated to 25 K.

Fig. 4: Infrared spectra of CO chemisorbed on a silver film deposited at T_D = 4 K. A broad band due to chemisorbed CO appears at low coverage at 2148 cm^{-1}, and shifts to lower frequency with increasing exposure. At 0.4 L, a sharp band due to physisorbed CO appears at 2143 cm^{-1}, and the band due to chemisorbed CO shifts further to low frequency.

Fig. 5: Infrared spectra of chemisorbed CO on a silver film after heating to various temperatures: (a) 0.04 L; (b) 0.4 L. T_D = 4 K.

Fig. 6: CO stretch frequency and integrated intensity variation for chemisorbed CO on a film deposited at T_D = 4 K. The lines are drawn as a guide for the eye. The arrow indicates the exposure at which a peak due to physisorbed CO first appears in the spectrum.

Fig. 7: Infrared spectra of 0.02 L ^{12}CO coadsorbed with varying amounts of ^{13}CO, showing the chemical frequency shift. The higher frequency band is due to ^{12}CO. $T_D = 4$ K. Quantities of coadsorbed ^{13}CO: (a) Zero. (b) 0.01 L. (c) 0.02 L. (d) 0.03 L. (e) 0.04 L. (f) 0.06 L.

Fig. 8: Total frequency shift of the CO stretch vibration, from Fig. 6, and chemical shift deduced from Fig. 7, as a function of exposure. 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 silver film, $T_D = 4$ K. (b) Integrated band intensity, from Fig. 6. The lines are theoretical fits to the data, using the P-R dipole coupling model with $\alpha_v = 0.27$ A^3 and $\tilde{U}(0) = 0.04$ A^{-3}.

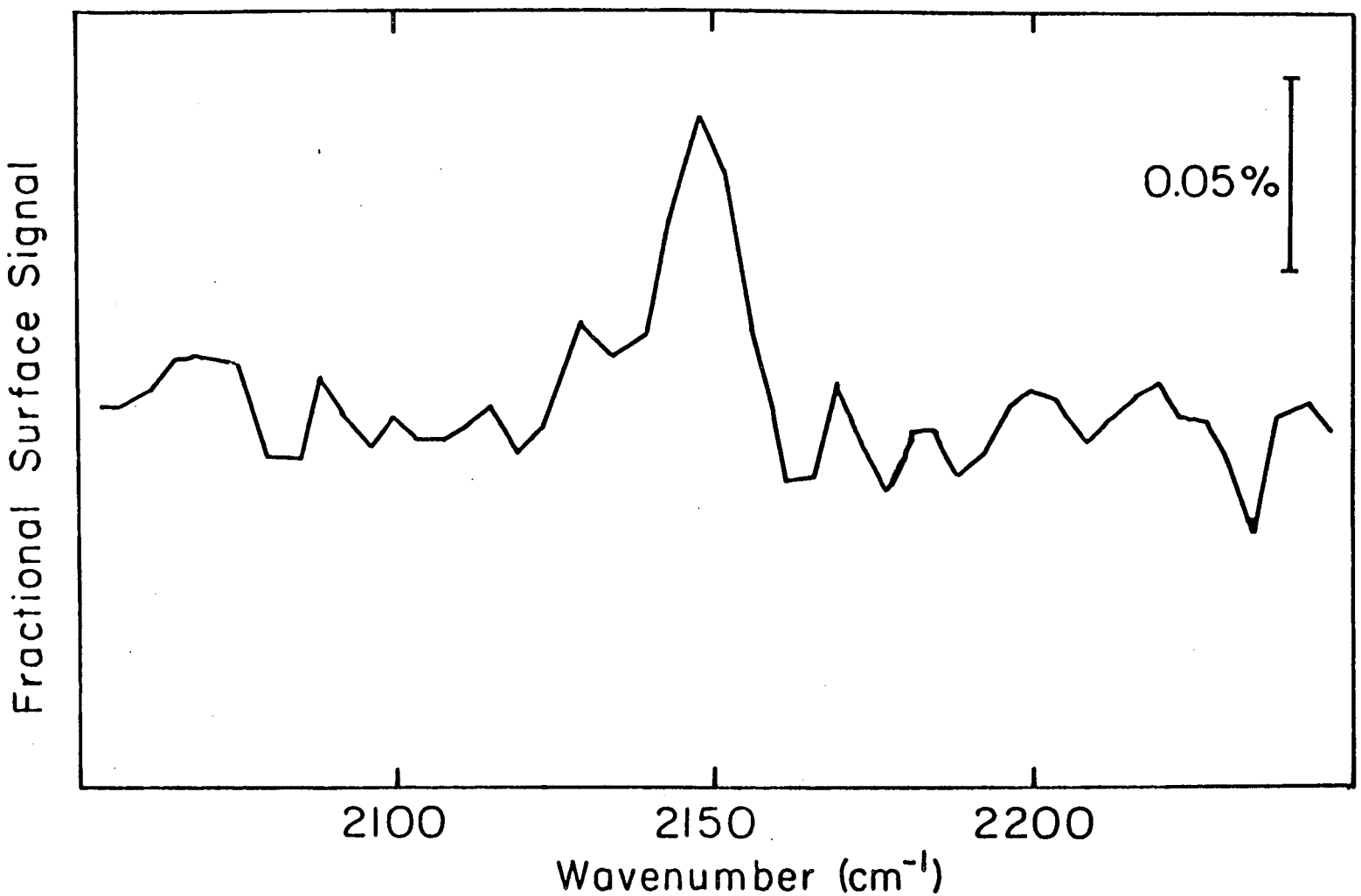
Fig. 10: Effect of physisorbed CO on frequency of the chemisorption band. (a) Saturation coverage of chemisorbed CO. (b) Spectrum after addition of 0.625 L physisorbed CO. (c) After heating to 40 K to remove physisorbed species.

Fig. 11: Infrared spectra of 0.01 L chemisorbed CO coadsorbed with various amounts of argon: (a) Zero. (b) 0.2 L. (c) 0.4 L. (d) 0.6 L. (e) 1.0 L. $T_D = 4$ K. Although the argon is chemically inert, it induces a chemical shift in the frequency of the CO stretch vibration.

Fig. 12: Schematic depiction of the effect of a change in work function on the position of a molecular affinity level.

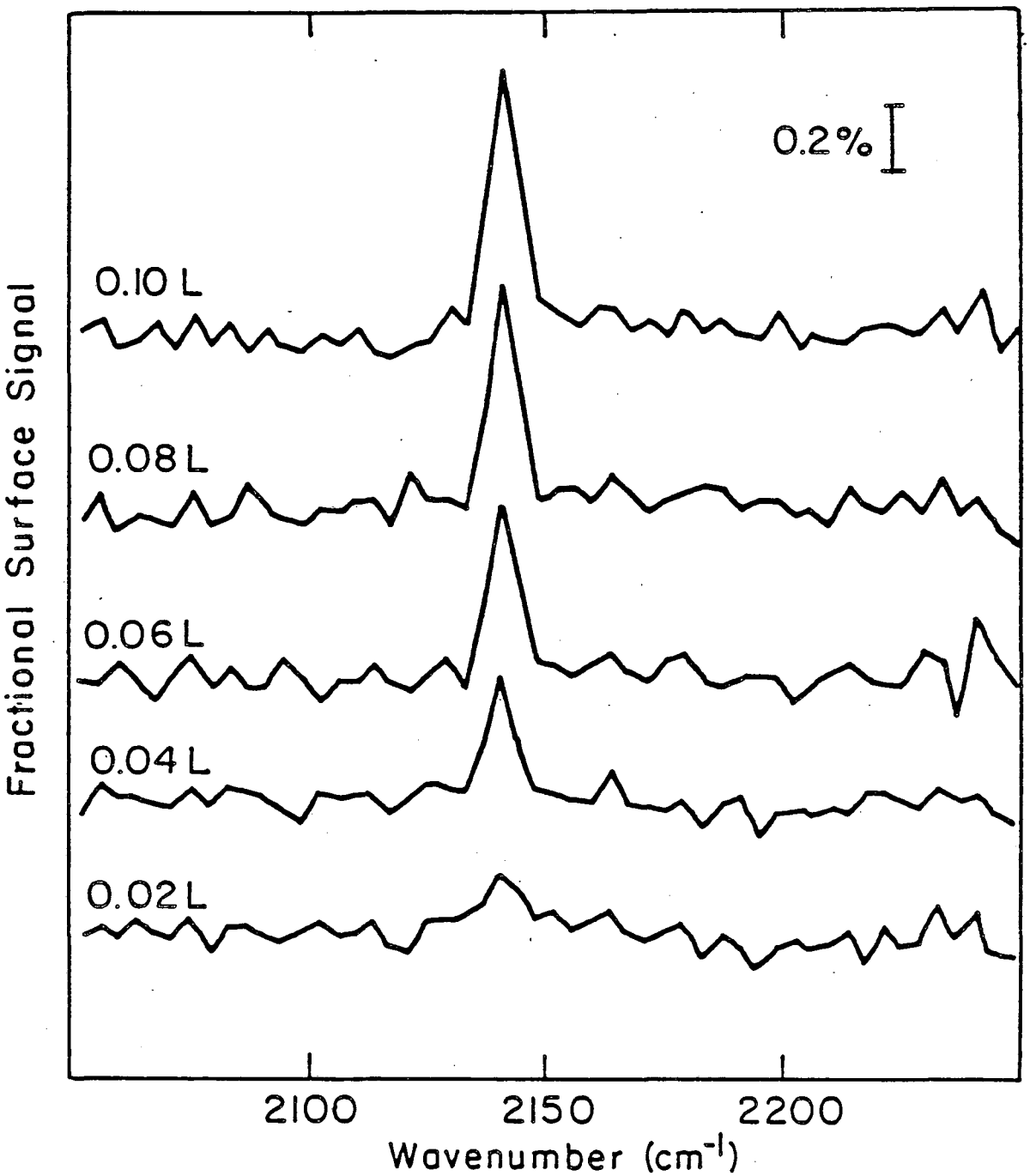
Fig. 13: Schematic depiction of the change in occupation of the broadened CO $2\pi^*$ orbital due to a shift in the energy level.

Fig. 14: Infrared spectra of 0.1 L CO chemisorbed on (a) Evaporated nickel deposited at $T_D = 4$ K. (b) Evaporated silver deposited at $T_D = 4$ K. The integrated intensities for the two spectra are equal within 10%.



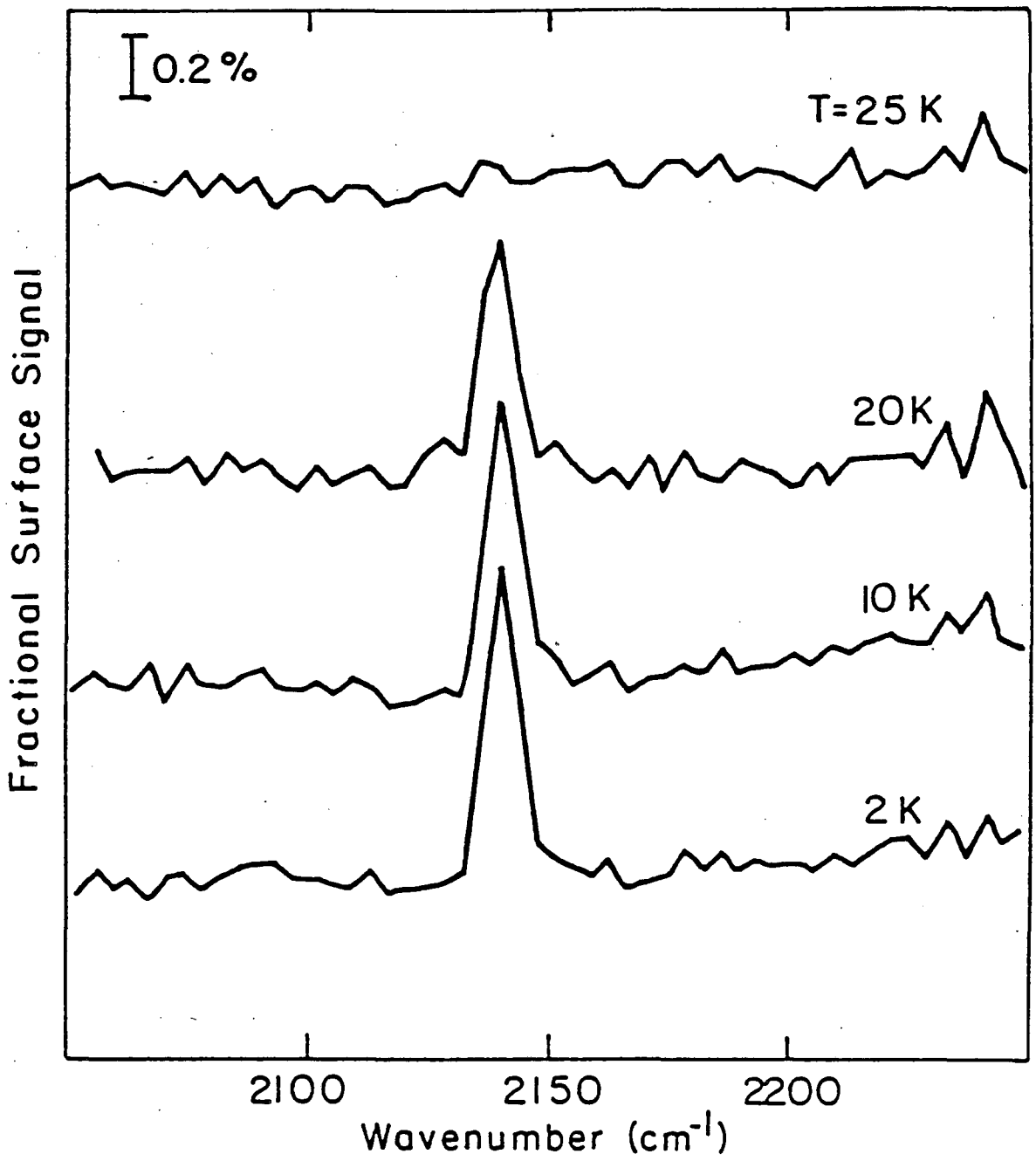
XBL 854-6053

FIGURE 1



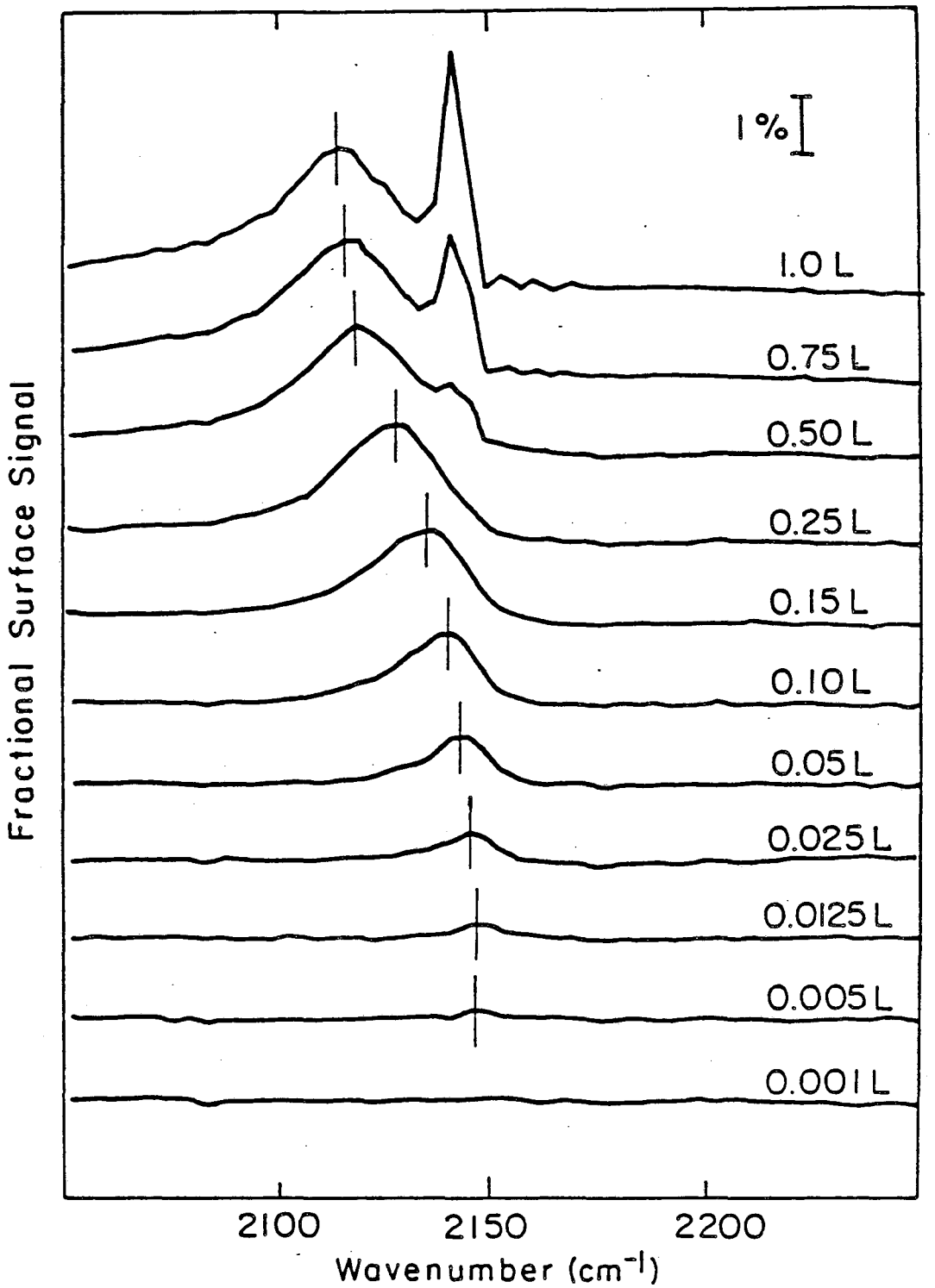
XBL 854-6055

FIGURE 2



XBL 854-6059

FIGURE 3



XBL 854-6052

FIGURE 4

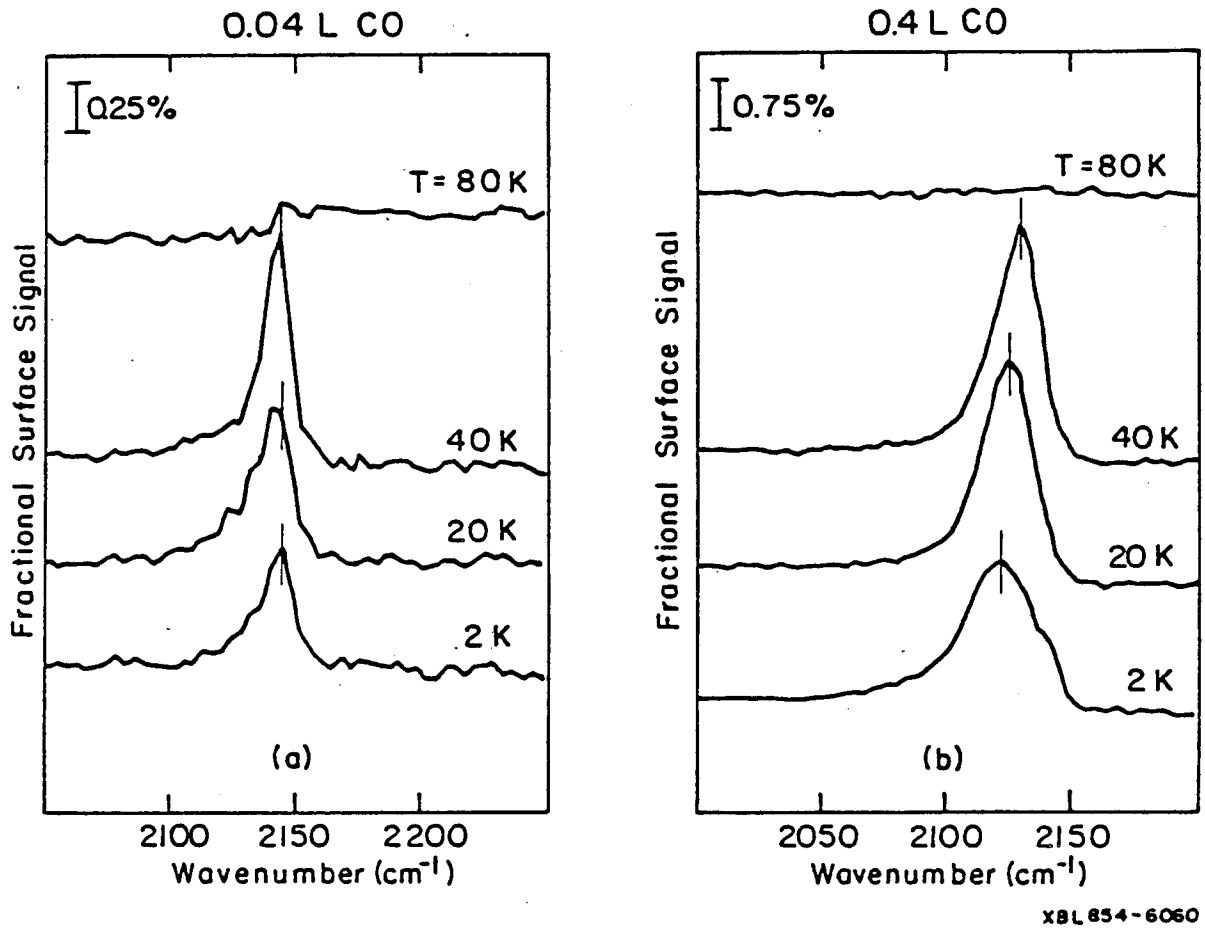

0.04 L CO
0.25%
T = 80 K
40 K
20 K
2 K
(a)
Fractional Surface Signal
2100
2150
2200
Wavenumber (cm⁻¹)
0.4 L CO
0.75%
T = 80 K
40 K
20 K
2 K
(b)
Fractional Surface Signal
2050
2100
2150
Wavenumber (cm⁻¹)
XBL 854-6060

FIGURE 5

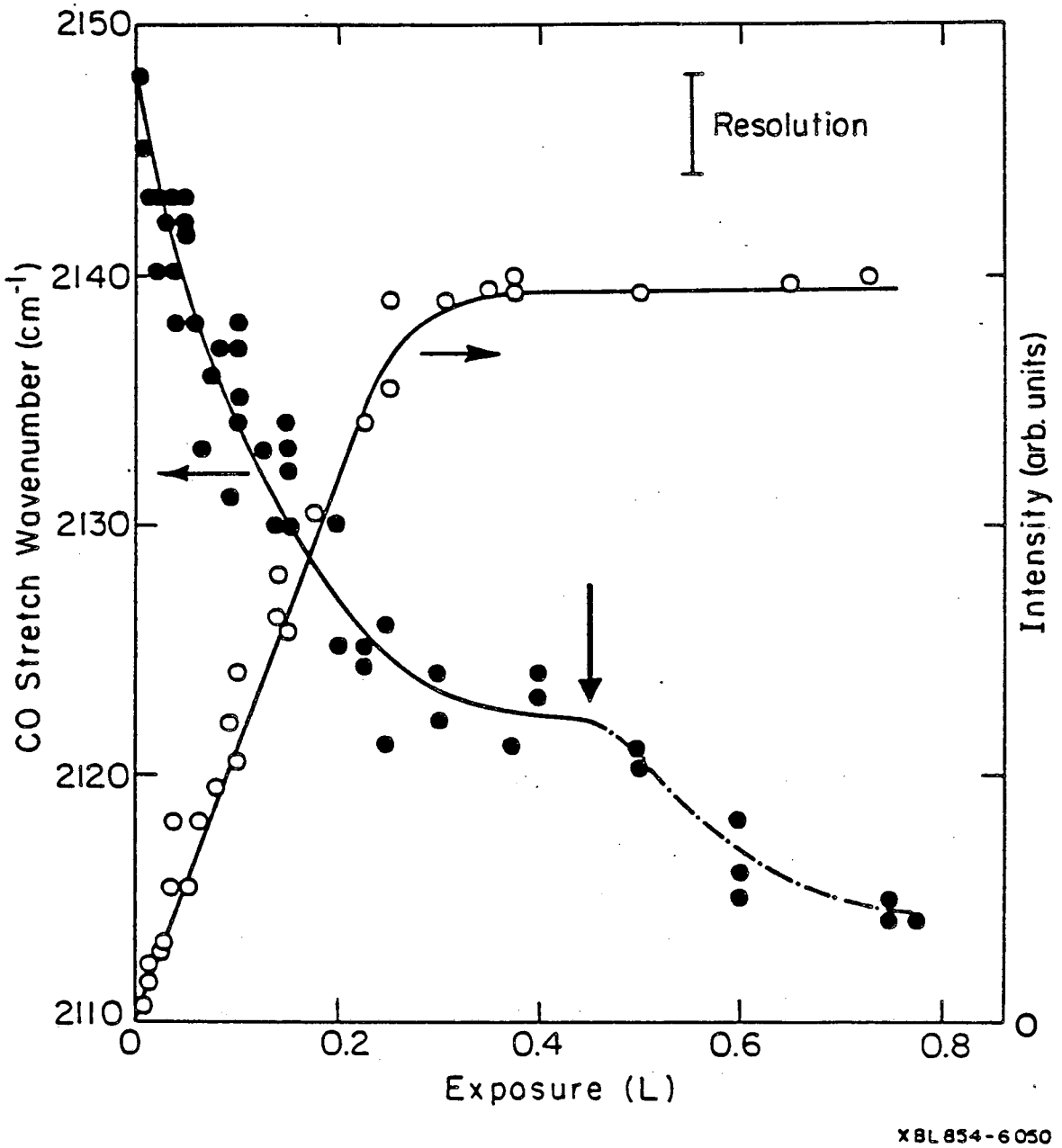
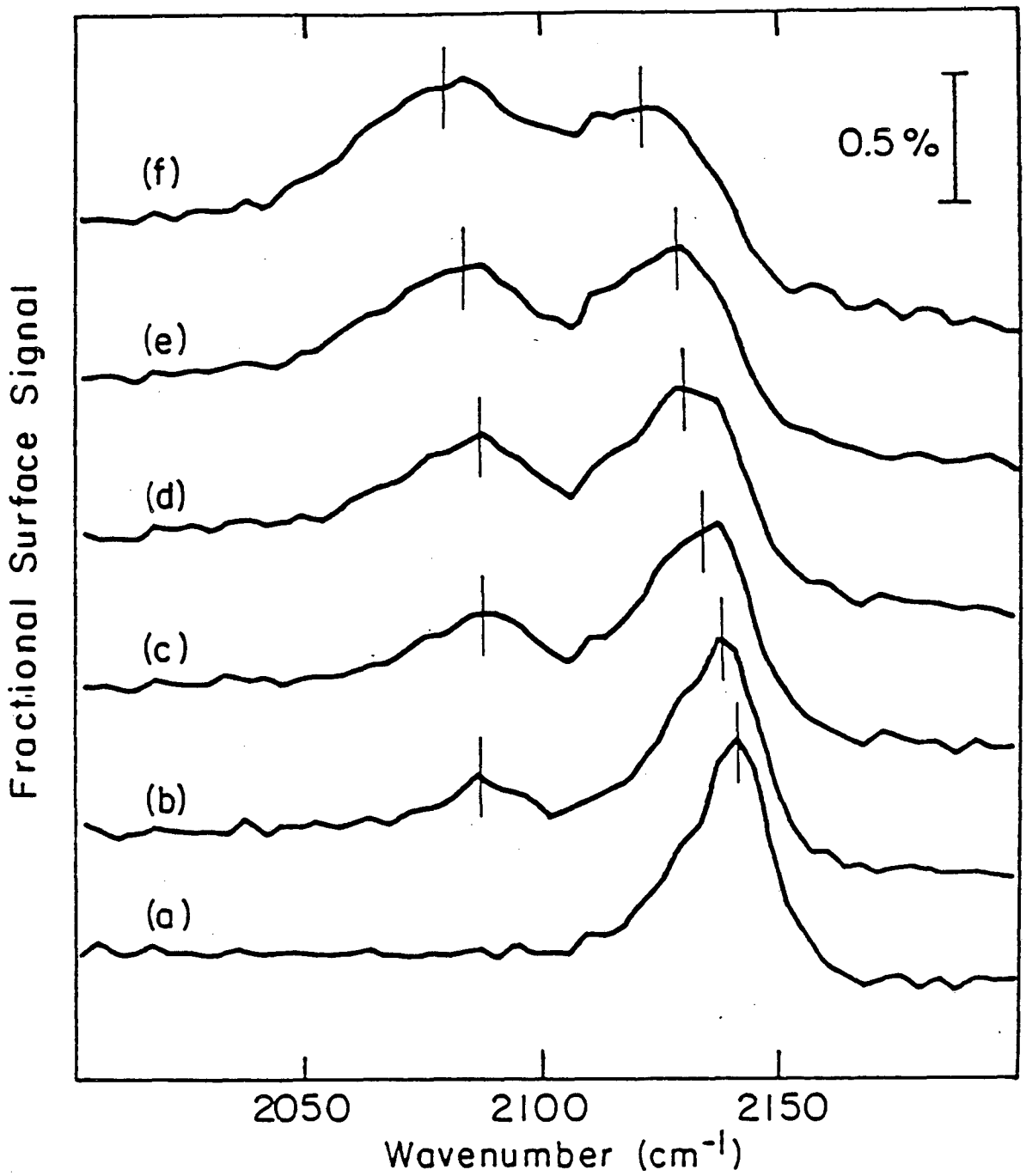

2150
2140
2130
2120
2110
CO Stretch Wavenumber (cm^{-1})
Resolution
Intensity (arb. units)
0
0.2
0.4
0.6
0.8
Exposure (L)
XBL 854-6050

FIGURE 6



XBL854-6057

FIGURE 7

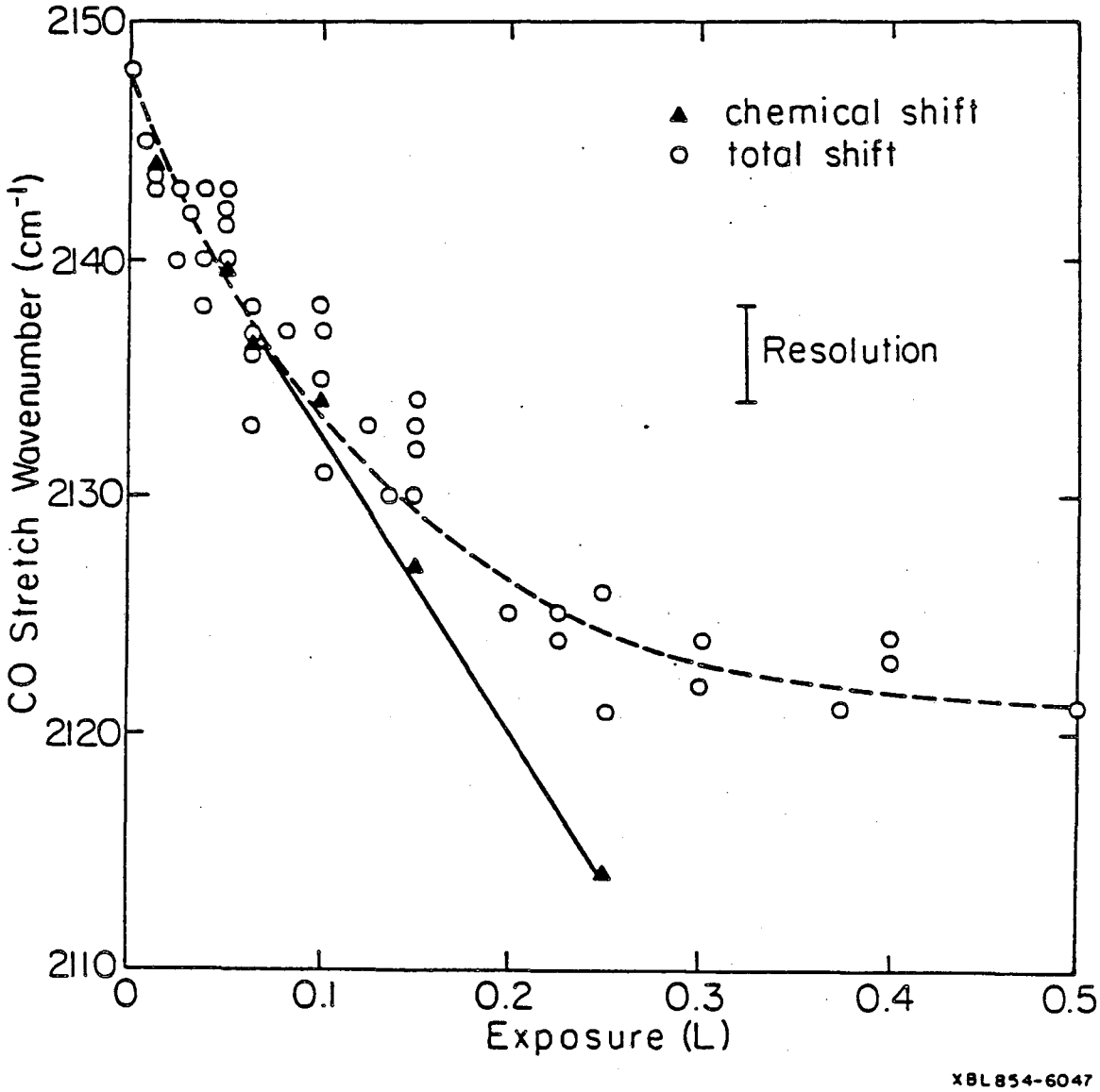

2150
2140
2130
2120
2110
CO Stretch Wavenumber (cm⁻¹)
0
0.1
0.2
0.3
0.4
0.5
Exposure (L)
chemical shift
total shift
Resolution
XBL854-6047

FIGURE 8

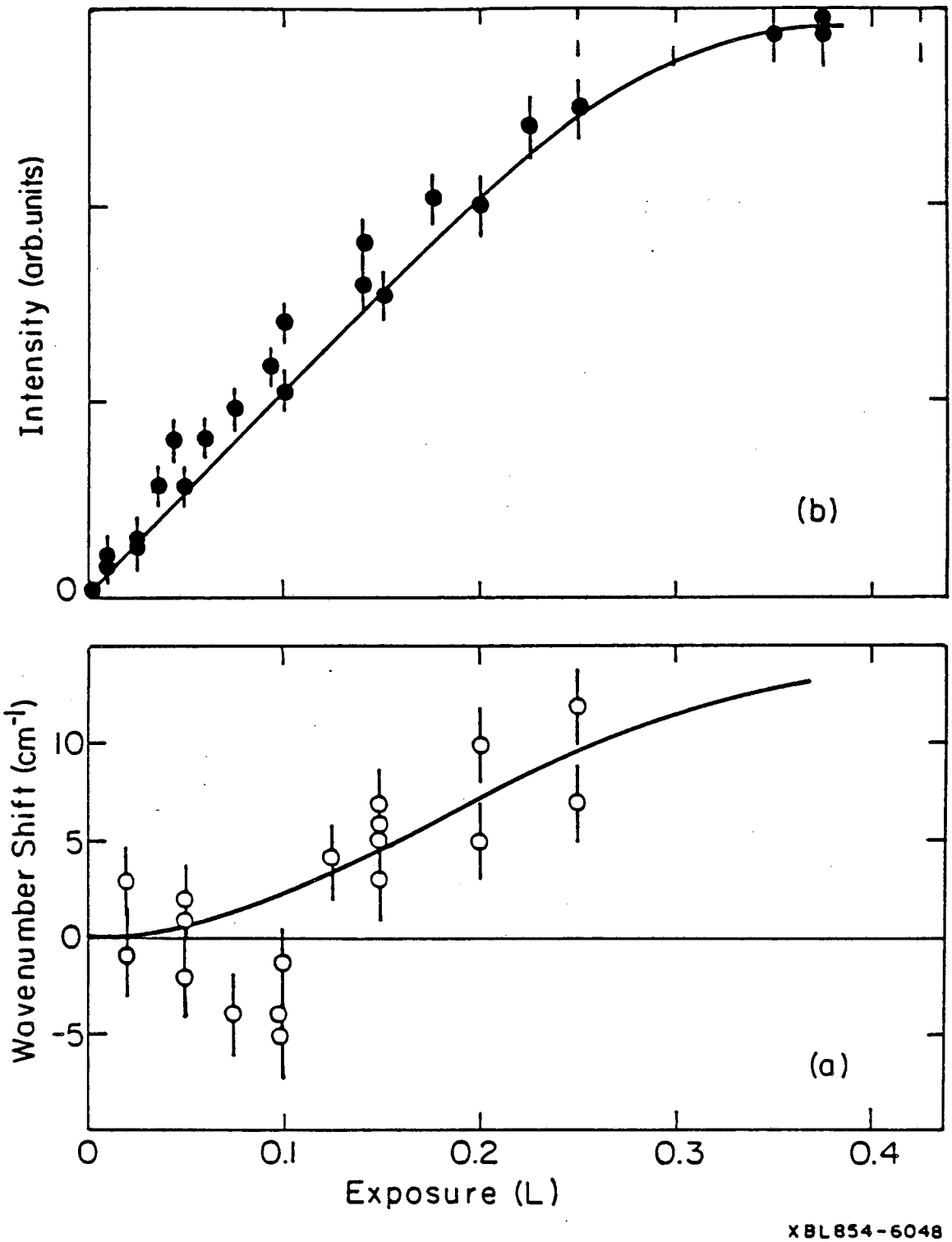

Intensity (arb.units)
0
(b)
Wavenumber Shift (cm⁻¹)
10
5
0
-5
(a)
0
0.1
0.2
0.3
0.4
Exposure (L)
XBL854-6048

FIGURE 9

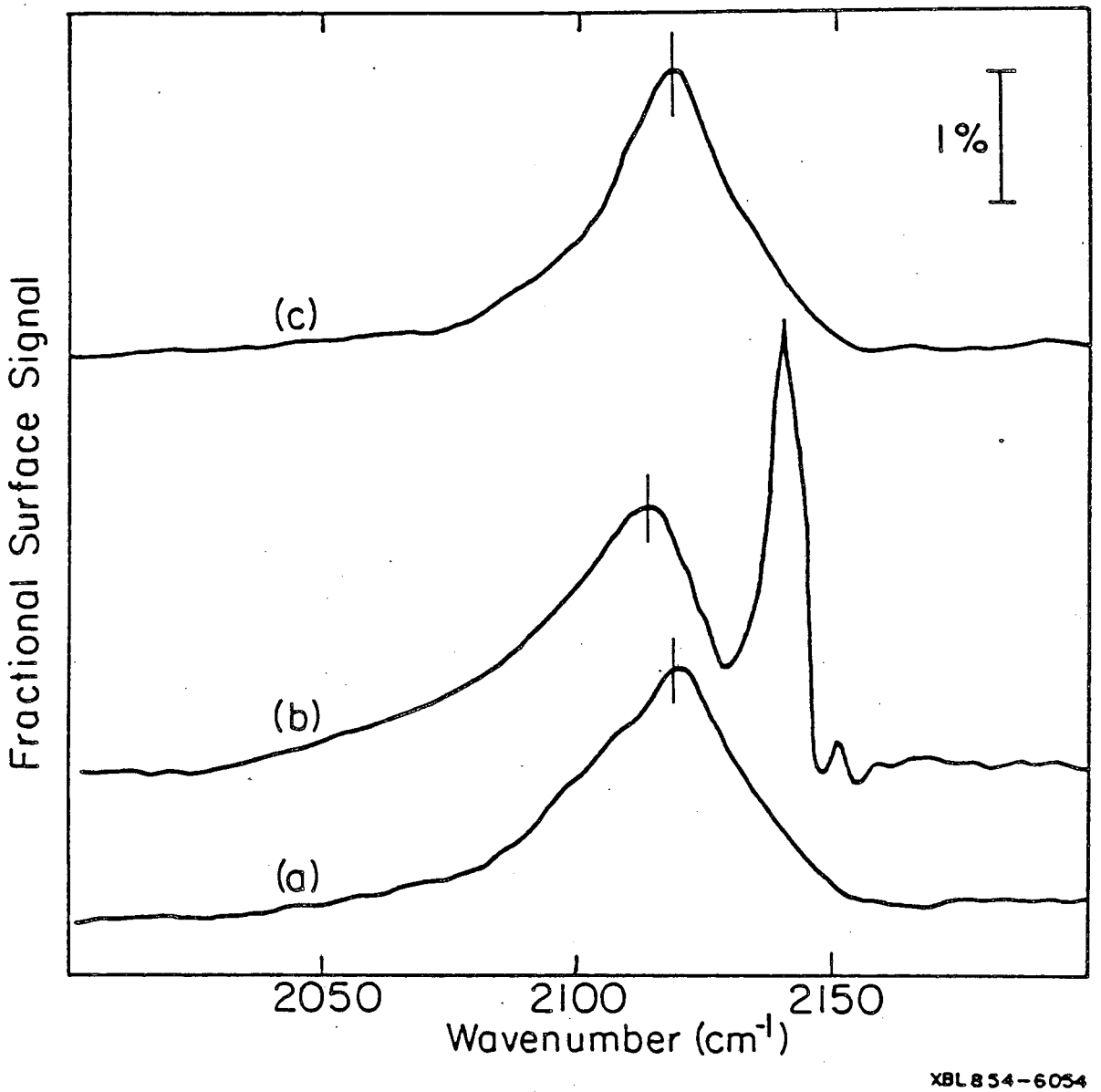
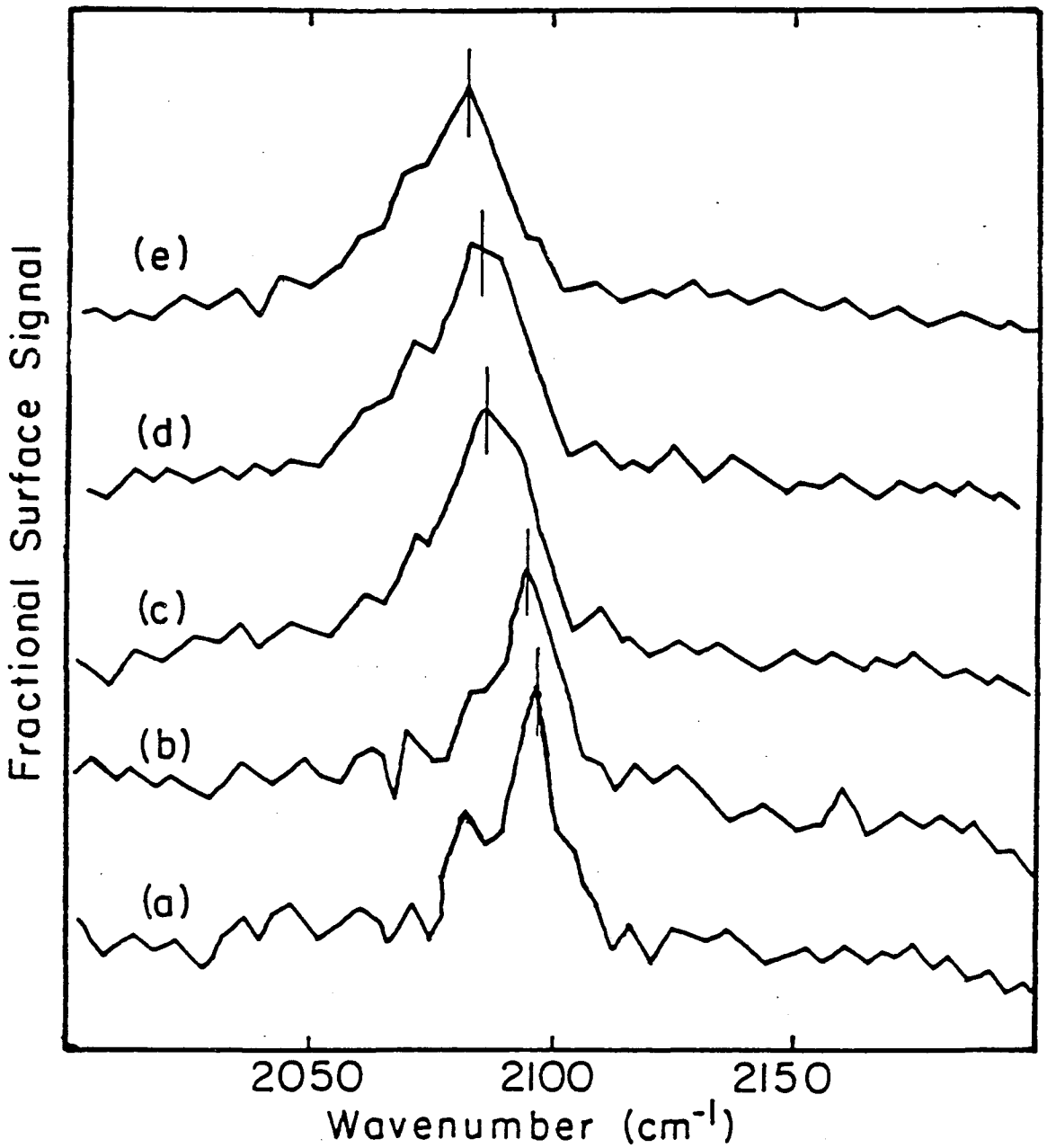
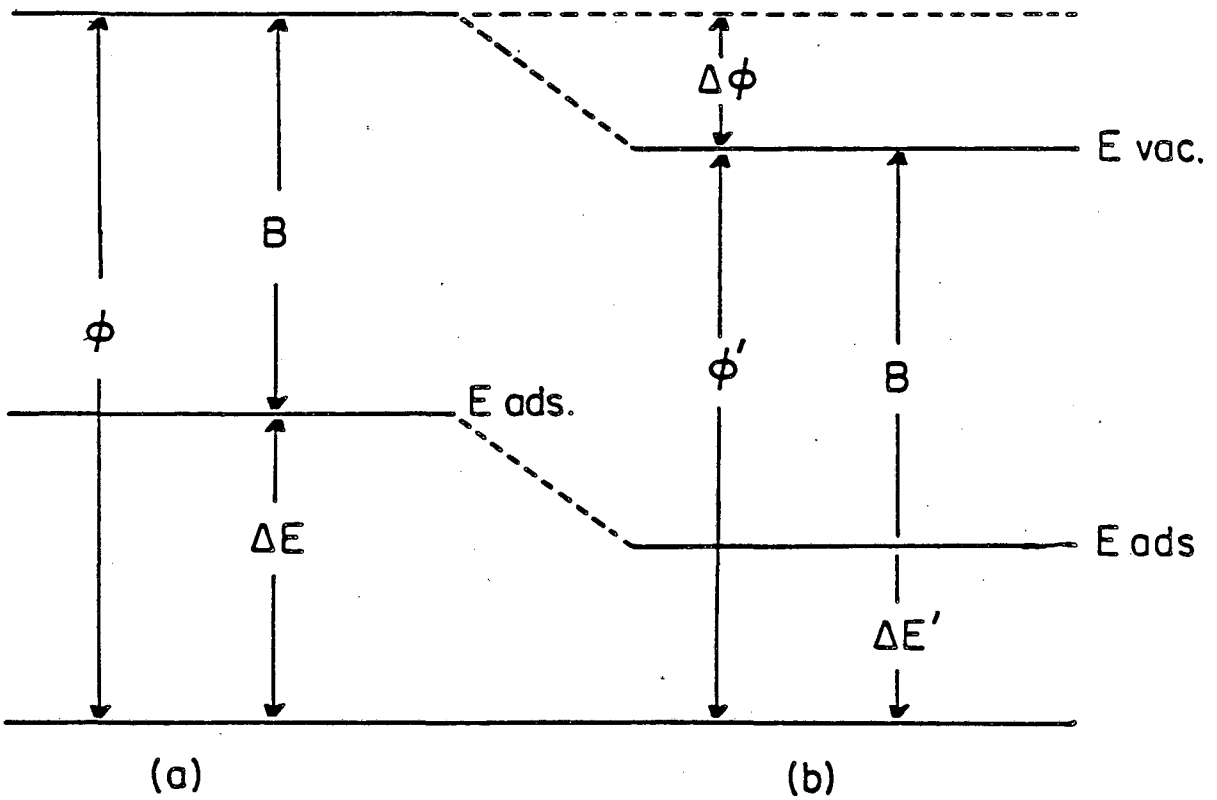

1%
(c)
(b)
(a)
Fractional Surface Signal
2050
2100
2150
Wavenumber (cm^{-1})
XBL 854-6054

FIGURE 10



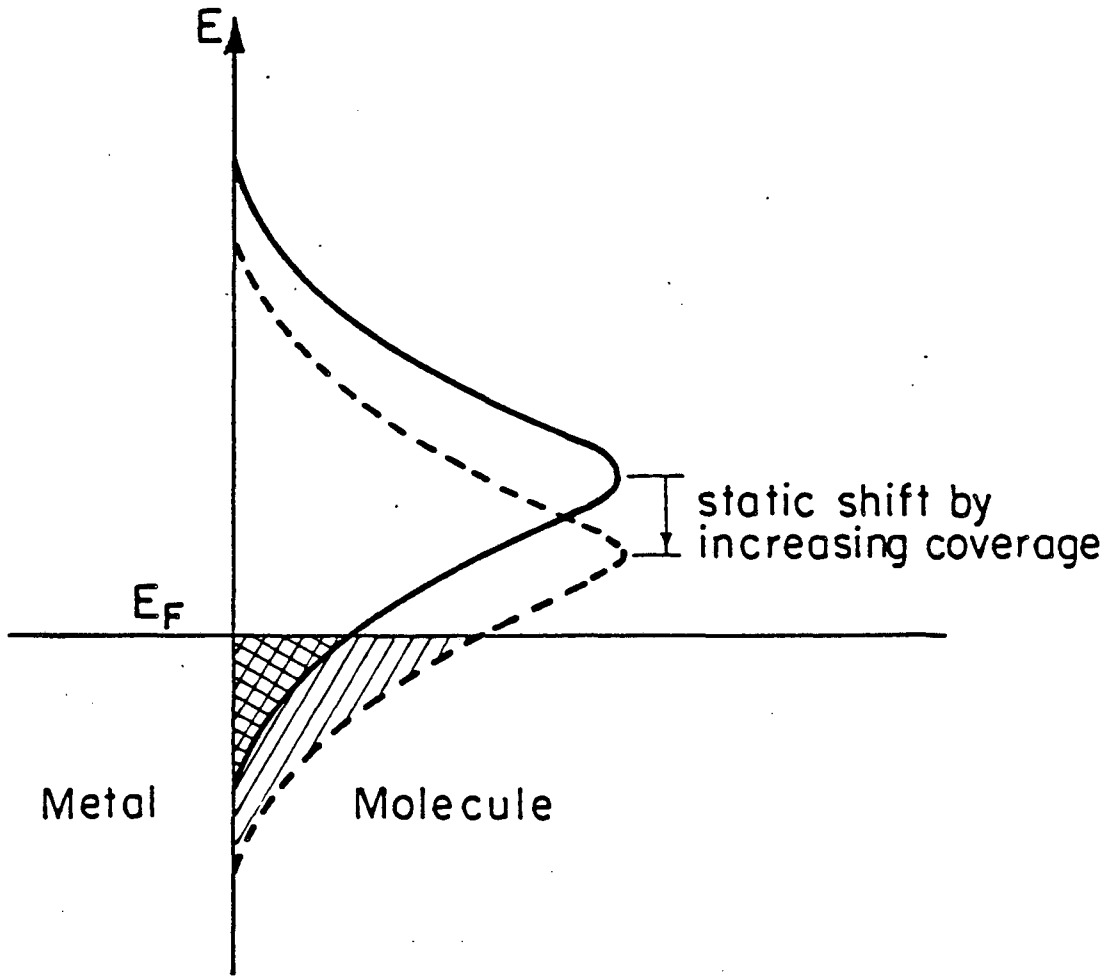
XBL 854-6110

FIGURE 11



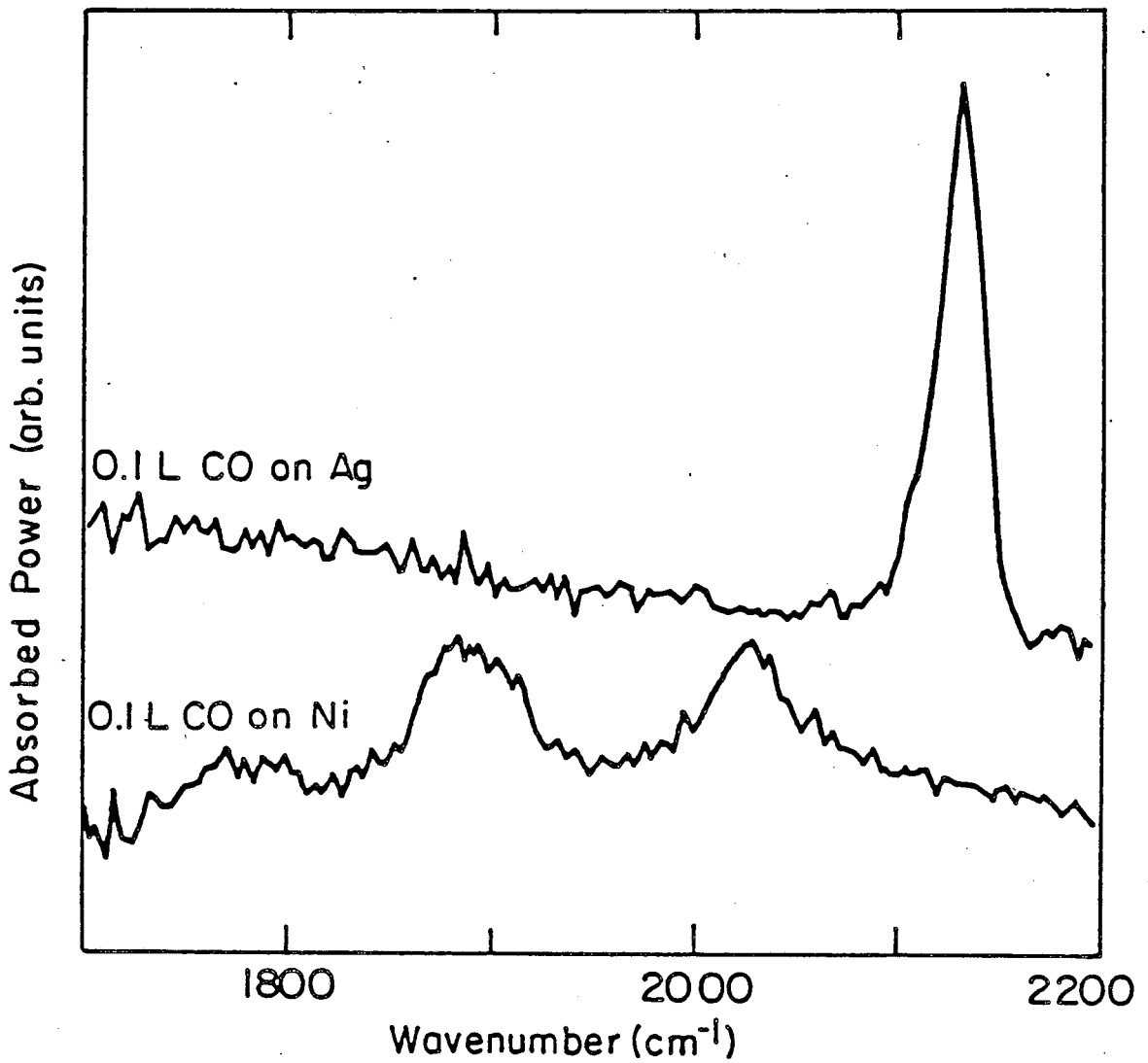
XBL 855-2664

FIGURE 12



XBL854-6049

FIGURE 13



XBL 854-6056

FIGURE 14

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