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AN INFRARED EMISSION STUDY OF THE MOLECULE-SUBSTRATE MODE OF CO ON Pt(111)

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Abstract

We have used infrared emission spectroscopy to study the molecule-substrate vibrational mode of on-top CO on Pt(111), as a function of coverage and of temperature, in the range from 210 to 400 K. Little change in the line is observed as a function of coverage, except for an abrupt shift, of ~6 cm^{-1}, to lower frequency, at coverages >0.5. The line shape is asymmetric, and the linewidth varies much more slowly with temperature than is predicted by theories of lifetime broadening by phonon emission. Based on these observations, we conclude that the line is inhomogeneously broadened. This is in contrast to suggestions that the corresponding mode of CO on Ni(100) is lifetime broadened by a two-phonon decay process. We also report the observation of the atom-substrate mode of O on Pt(111).

1. Introduction

Infrared spectroscopy has proved to be a valuable tool for probing the dynamics and interactions of molecules adsorbed on metal surfaces [1]. Through careful studies of the frequency shift of the intramolecular C=O stretch vibration of chemisorbed CO, at least two types of interadsorbate interaction have been identified and characterized [2-5]. Careful analysis of the temperature-dependence of the vibrational linewidth has identified the important role played by dephasing [6-8] in the broadening of the C=O stretch band on some metals. Studies [9,10] of vibrational line shapes have shown that energy relaxation by the creation of electron-hole pairs is also important in some cases. In all of these cases, the high resolution (1-5 cm^{-1}) available from a photon spectroscopy provides information unobtainable from electron energy loss spectroscopy (EELS), which achieves 30 cm^{-1} resolution only with difficulty [11].

All of the experiments discussed above involve vibrational modes at frequencies above 900 cm^{-1}. Most vibrations of the bond between the adsorbate and the substrate occur at lower frequencies, and have been largely inaccessible to high-resolution spectroscopy. (An exception is the case of hydrogen, which has an unusually high vibrational frequency [10].) These low frequency modes are expected [12] to interact strongly with substrate phonons, which in metals typically [13] have frequencies less than 300 cm^{-1}. Moreover, adsorbate-substrate vibrational modes play the major role in sticking, desorption, diffusion, and other surface phenomena. For these reasons, it is important to extend the techniques of infrared spectroscopy to the lower frequency regime.

Infrared emission spectroscopy [14,15] is the only technique now capable of resolving low frequency molecule-substrate modes of sub-monolayer coverages of adsorbates on clean, well characterized, metal surfaces. This capability was first used to measure the linewidth of the molecule-substrate mode of CO on Ni(100) [16]. The linewidth contribution due to vibrational decay by two-phonon emission was then calculated by Ariyasu, et al. [17,18]. The results agreed with the experimentally determined linewidth of 15 ± 1 cm^{-1} at 310 K. Fig. 1 shows the calculated linewidth as a function of temperature, together with the experimental result. Also shown, on a different vertical scale, is the result of a calculation using Persson's simplified model [19] of vibrational decay by two-phonon emission. This model gives unreliable quantitative values for the linewidth, but predicts reasonably well the temperature-dependence, which is determined primarily by Bose-Einstein occupation factors for the substrate phonons.

The agreement between theory and experiment for the case of CO on Ni(100) suggests that phonon-mediated decay is an important line-broadening process for low frequency molecule-substrate modes. Experience has shown, however, that erroneous conclusions regarding line-broadening mechanisms are easily reached [20,21], unless great care is taken to exclude inhomogeneous broadening and other complicating effects. In the present case, measurement of the linewidth as a function of temperature is clearly appropriate.

Because of the weak oscillator strength of the molecule-substrate mode for CO on Ni(100), and the relatively high emissivity (~25%) of Ni at near-grazing angles, the temperature-dependence measurement appeared impractical on that system. We report here the results of a detailed study of the corresponding vibrational mode of CO on Pt(111). The oscillator strength of this mode is 5-10 times greater on Pt(111) than on Ni(100). The frequency of the mode on Pt(111), 467 cm^{-1}, is very close to that on Ni(100), 472 cm^{-1}. However, the maximum phonon frequency of 189 cm^{-1} in Pt [22] is substantially smaller than the corresponding frequency, 295 cm^{-1}, in Ni [13]. As a result, the two-phonon decay process that appears to be important on Ni(100) is energetically forbidden on Pt(111); the lowest order allowed process is three-phonon decay. No detailed linewidth calculations exist for the system of CO on Pt(111); however, the model of Persson [19] can be used to estimate approximately the temperature-dependence expected for phonon-mediated lifetime broadening and dephasing.

2. Experimental

2.1. Apparatus

The infrared emission system used in these experiments has been described in detail elsewhere [14,15]. It consists of a liquid helium-cooled grating spectrometer, with an Si:Sb photoconductive detector, coupled to an ultrahigh vacuum chamber. The UHV chamber is equipped with facilities for low energy electron diffraction (LEED), Auger spectroscopy (AES), thermal desorption spectroscopy (TDS), and sample cleaning and dosing. The base pressure of the system is less than 1×10^{-10} torr. Also within the chamber are liquid nitrogen-cooled baffles, which surround the sample during the IR measurements, and a cooled chopper. The sample can be heated to >1300 K for cleaning and annealing, or cooled to 200 K. Within the range from 210 to 400 K, the sample temperature can be regulated within 0.04 K at any temperature.

2.2. Sample preparation and characterization

Two Pt(111) samples were used. Both were cut from a single platinum crystal obtained from Atomergic Chemetals, Inc. They are approximately rectangular, with dimensions 1.5×0.5×0.2 cm, with the normal to the large face oriented within 0.5° of the [111] direction, as determined by X-ray diffraction. No crystallographic faults could be detected with X-ray or low energy electron diffraction. No systematic differences were observed in the IR spectra obtained from the two samples.

The primary contaminants in the crystals, as revealed by AES, were carbon, silicon, calcium, and sulfur. The sulfur and calcium were removed by gentle (250 eV) argon ion sputtering followed by annealing at 1100 K. The carbon could be removed by heating in oxygen (900-1100 K, 5×10^{-8} to 1×10^{-6} torr) for several hours. The last 1-2% of a monolayer of carbon were removed by dosing the sample with 3-5 L of oxygen, and then ramping the sample temperature to 1100 K, while observing the CO partial pressure with a mass spectrometer. The presence of residual carbon was revealed by a characteristic reaction peak near 800 K. Excessive oxygen treatments resulted in residual surface oxygen, which could be detected with AES. Argon ion sputtering, or heating to 1250 K, was then used to remove the oxygen. Sputtering invariably resulted in new carbon contamination, necessitating additional oxygen treatments. With care, a surface could be prepared that had residual concentrations of <0.01 monolayer of both oxygen and carbon. Fig. 2 shows an Auger spectrum of such a surface. Neither a carbon peak (at 272 eV) nor an oxygen peak (at 505 eV) can be detected. However, a small feature due to Si is visible at 92 eV. We estimate that this feature represents ~0.01 monolayer of Si. We were unable to remove this residual Si.

Sputtering of the surface was kept to a minimum, and sputtering energies were kept low (250 eV) in order to avoid surface roughening. In cleaning another Pt(111) sample with extensive sputter treatments, we found that the surface became roughened on the scale of microns. This roughness could be detected as a matte finish on the surface, when it was viewed under oblique illumination with visible light, and it could also be easily seen with a scanning electron microscope. Despite this roughness, the LEED pattern of the sample was excellent, and the Auger spectrum showed no evidence of contamination. Annealing the sample at temperatures up to 1600 K had no effect on the roughness. The samples used for the present experiments show slight evidence of the same behavior--they appear very slightly milky in oblique light--but the roughening is not severe.

It is difficult to detect aluminum and sulfur on platinum with AES, because the primary Auger peaks of these elements overlap prominent Pt peaks. There is, therefore, the possibility that the "clean" platinum surface contained residual aluminum and sulfur. Such undetected contaminants on Pt(100) are thought [23] to be responsible for the complicated reconstructions of that surface. The same study indicated, however, that surface segregation of these impurities is much less severe on the (111) face. The Auger spectrum of fig. 2 can be compared with the published data of Collins and Spicer [24] by taking the ratio of the peak amplitudes between the overlapping peaks and the Pt peak at 237 eV. In each case, the ratio for fig. 2 is smaller than that shown by Collins and Spicer, indicating that the sample used here was no more contaminated by undetected species than those used in other careful studies of Pt(111).

The adsorption of CO, as shown by TDS and LEED, showed the characteristics described in the literature [24-27]. A variety of ordered LEED patterns has been observed for CO on Pt(111), but only the c(4×2) pattern is observable at temperatures between 210 and 300 K. It is sharpest and brightest for a CO coverage of $\theta=0.5$. As the sample is heated above 275 K, the c(4×2) spots become dimmer and fuzzier, until the central spots merge into a hazy ring, near 325 K. This temperature range coincides closely with the onset of desorption. At higher temperatures, a significant coverage of CO can only be maintained by keeping a partial pressure ($\sim 5\times 10^{-8}$ torr) of CO in the chamber; no ordering of the overlayer can be detected with LEED. It is important to keep these temperature-dependent phenomena in mind in interpreting the temperature-dependence of the C-Pt mode linewidth. At temperatures below 250 K, a compressed LEED pattern can be observed at coverages greater than 0.5. This coverage range was not studied in these experiments.

The CO coverage is deduced from the exposure by means of a calibration curve, shown in fig. 3. This curve is obtained by measuring the time integral of the desorption signal for various exposures, and assuming a coverage of $\theta=0.5$ for the exposure that gives the sharpest c(4×2) LEED pattern.

2.3. Experimental procedure

After the sample was cleaned as described above, the clean surface was protected from the accumulation of background contaminants by the adsorption of a saturated layer of CO. Once the surface was cleaned of contaminants, the condition of the surface could be maintained by this method over a period of many days, and through several CO adsorption-desorption cycles, without the buildup of more than a few percent of a monolayer of carbon. The onset of re-contamination could be detected as a degradation in the CO LEED pattern at low temperature. The data shown represent adsorption on surfaces with some variation in the quantity of impurity coverage, but in no case more than 5-10% of a monolayer, and in most cases less than 2%. In addition, the impurity concentration showed some variation across the sample, with the result that thoroughly clean conditions could not always be achieved over the entire surface at once. Since the infrared spectrometer samples essentially the entire surface of the sample, the spectra represent some average over the conditions present on the surface. No systematic dependence of the infrared spectra on these levels of impurities could be identified.

After the sample was heated to desorb the protective CO layer, it was cooled to the desired temperature, and a reference spectrum of the clean surface was measured. This process took ~1 hour. Using TDS, we determined that no more than 0.02 monolayer of CO would accumulate on the surface during that time. Following the measurement of the reference spectrum, the sample was exposed to CO gas, and spectra of the sample with adsorbed CO were measured. For temperatures less than 325 K, a measured exposure of CO was admitted by letting CO into the chamber for a fixed period of time. The chamber was then evacuated, leaving CO on the surface. For higher sample temperatures, adsorbed CO is not stable on the time scale required for the experiment, so this procedure could not be used. Instead, a constant pressure of CO (typically ~5×10^{-8} torr) was maintained in the chamber during the measurement. Little variation in the spectra was found for pressures from 5×10^{-9} to 1×10^{-7} torr. For these temperatures, the CO coverage could not be determined from the exposure; it could only be roughly estimated from the frequency and integrated intensity of the infrared band.

After all infrared measurements were complete, the sample was withdrawn from the baffles and moved in front of the LEED screen. For sample temperatures $\lesssim$ 300 K, the LEED pattern could be observed immediately, and provided a qualitative measure of the degree of ordering present in the last IR spectrum measured. For the data presented here for temperatures of 300 K and below, a distinct c(4×2) pattern was observed. When the IR measurement was made at a higher temperature, the heat was first turned off, and the sample allowed to cool below 300 K, and then exposed to additional CO. The c(4×2) LEED pattern observed was then not characteristic of the state of the overlayer during the IR measurement, but it provided an indication of the state of the Pt surface.

Measurements were made both with ^{12}CO and with ^{13}CO. The choice was solely a matter of experimental convenience; the mass difference between the isotopes is so small that the only difference observable in the spectra is the expected frequency shift. However, a feature in the spectrometer transmittance at the frequency of the ^{12}CO mode occasionally introduced unwanted structure in the baseline, which was less of a problem if ^{13}CO was used.

2.4. Data analysis

The emission spectra of the sample with and without CO were first subtracted point by point, and then divided by the reference spectrum to remove variations due to the spectrometer efficiency and the blackbody spectrum. The data are thus in the form of fractional surface emittances, normalized to the sample emittance (plus a small contribution due to unavoidable leakage radiation). An additive constant has been included in the figures for clarity of presentation. The data have not been smoothed in any way. In most cases a linear slope has been removed from the spectra before plotting. The errors in determining the linewidth are primarily systematic, and arise from uncertainties in the baseline. These errors were estimated by subjectively choosing a range of linear baselines that could be regarded as consistent with the points away from the peak, and determining the full width at half maximum (FWHM) for each choice of baseline. While we cannot place quantitative confidence limits on these error bars, we regard them as very conservative.

The instrumental resolution was 6.1 cm^{-1} for measurements of the C=O stretch mode, and 2.4 cm^{-1} for measurements of the molecule-substrate mode.

3. Results

3.1 The C=O stretch mode

Fig. 4 shows a series of IR emission spectra of the intramolecular C=O stretch mode, at 300 K. The higher frequency band is attributed to on-top CO. The weaker, broad band at

1850 cm^{-1}, observable at the highest coverages, is due to more highly coordinated molecules. These spectra are consistent with previous IR [8,28,29] and EELS [26,27,30,31] studies of CO on single crystal Pt(111). Hayden and Bradshaw [8] found that the "bridging" CO band near 1850 cm^{-1} consists of two bands, which can be resolved at lower temperatures. They attributed the lower frequency band, centered near 1810 cm^{-1}, to three-fold coordinated CO. We have examined this frequency range at temperatures as low as 225 K, and we find only a single band centered at 1850 cm^{-1}. There is no signal in the region around 1810 cm^{-1}. These results will be reported in detail elsewhere [32].

3.2. The molecule-substrate mode

We have studied the molecule-substrate mode as a function of both coverage and temperature. This is the first detailed investigation using high resolution spectroscopy reported for such a mode. Fig. 5 shows a sequence of spectra, for various coverages of ^{13}CO, at 275 K. For $\theta<0.5$, the peak frequency and the linewidth remain constant while the strength of the band increases. At higher coverages, a dramatic shift of the band to lower frequency occurs. This behavior is shown clearly in fig. 6, which shows the peak frequency of the band as a function of coverage. This figure combines data from several separate experiments performed on different days.

The shift of the frequency begins at $\theta=0.5$. It is probably correlated with the abrupt drop in the adsorption energy near $\theta=0.5$ observed by Ertl, et al. [25]. Such a reduction in the adsorption energy, which is related to the depth of the chemisorption well, would be expected to be accompanied by a reduction in the frequency of the molecule-substrate vibration, which depends on the curvature of the well. However, the data of Ertl, et al. [25] indicate a gradual decrease in the adsorption energy with coverage for $\theta<0.5$; it is therefore surprising that no frequency shift was detected in this coverage range. It is worth noting that the magnitude of the frequency shift is only ~6 cm^{-1}. It is unmistakable in the infrared data, but would be undetectable in an EELS experiment, and has not, in fact, been observed previously.

In studies of the intramolecular C=O vibration, it is common to examine frequency shifts further, by using isotopically mixed layers of CO [2-5]. The two isotopes can be effectively vibrationally decoupled [33] and only chemical interactions between the molecules remain. In the present case, the frequencies of the molecule-substrate modes for ^{12}CO and ^{13}CO differ only by approximately one linewidth, so the vibrational coupling is not removed. Such an experiment might be practical using ^{12}C^{16}O and ^{12}C^{18}O, but we have not attempted it.

In the spectra presented in fig. 5, the linewidth does not change appreciably with coverage. This behavior was observed consistently for $\theta<0.5$. At higher coverages, the linewidth was not reproducible, occasionally doubling its low-coverage value. We do not understand these erratic effects at high coverage. The constancy of the linewidth and peak frequency for $\theta<0.5$, however, implies that small variations in the coverage over the course of a spectral measurement should not affect the observed linewidth. Our measurements of the temperature dependence of the linewidth were made in this coverage range.

We have measured the linewidth of the molecule-substrate mode at temperatures from 210 to 400 K. Some representative spectra are shown in fig. 7. The apparent frequency shift seen in fig. 7 between 225 and 300 K is due to the isotope shift; the low temperature spectra shown are for ^{13}CO, while the higher temperature spectra are for ^{12}CO. This shift, incidentally, directly confirms the identification of this mode as the molecule-substrate stretch mode. Spectra were measured over a range of temperatures with both isotopes; as we mentioned above, no systematic difference (other than the frequency shift) was detected. Fig. 8 presents the results of all of our measurements. The method of analysis, and the determination of the error bars, are explained above. For clarity of display, some of the data points in fig. 8 have been slightly displaced horizontally; the sample temperature in each measurement was within 1 K either of 210 K, or of a multiple of 25 K.

Although the error bars in fig. 8 are conservative, in a number of cases they fail to overlap. This lack of reproducibility is particularly severe at temperatures above 325 K. This is the regime in which a pressure of CO was maintained in the chamber during the measurement, in order to achieve a significant CO coverage. As the spectra shown in fig. 7 suggest, the resulting coverage becomes rather low as the temperature is increased. The resulting small signal is responsible in part for the large error bars on the high temperature data points. This method of dosing introduces various possible sources of non-reproducibility, including fluctuations in the pressure of the CO or of contaminant gases in the chamber, and the buildup on the surface of contaminants that bind more strongly than CO. We do not understand the source of the large linewidth variations in this high temperature regime.

At lower temperatures, the variations are less pronounced, but still significant. We have been unable to correlate these variations with any measurable aspect of the surface condition or preparation procedure. It appears that the linewidth is sensitive to fine details of the condition of the surface. This behavior contrasts with that of the molecule-substrate mode of CO on Ni(100). In that case, the linewidth was found to be insensitive to the condition of the surface [16].

4. Interpretation

We conclude, based on our observations, that the linewidth of the molecule-substrate mode for CO on Pt(111) is determined primarily by inhomogeneous broadening. This conclusion is based on three factors: the lack of a strong temperature-dependence, the asymmetry of the line shape, and the sensitivity of the linewidth to surface conditions. We detail these arguments below.

The solid line in fig. 8 is a theoretical prediction for the temperature-dependence of the three-phonon and dephasing contributions (the two are virtually indistinguishable in this temperature range) to the natural linewidth, using the theory of

Persson [19]. We have modified his model slightly by using a representation of the true bulk phonon density of states for Pt [22] rather than a Debye model. The curve has been normalized to the experimental linewidth at 210 K. As in the case of two-phonon broadening illustrated in fig. 1, the linewidths predicted by this simple theory are much greater than the experimental values, but the variation with temperature is likely to be accurate.

The evident discrepancy between theory and experiment in fig. 8 is even more striking when we observe that, in the absence of a line-narrowing mechanism, each measurement places a firm upper limit on the natural linewidth at that temperature. Thus the natural linewidth must lie below the dotted line shown in fig. 8, which is nearly flat compared to the predictions for phonon-decay and dephasing. The observed linewidths clearly cannot represent the effects of these processes.

Lifetime broadening by the electron-hole pair process is essentially temperature-independent [12]. Theories of this process [34], however, suggest that it can account for less than 10% of the observed linewidth. It is therefore unlikely that this process contributes significantly to our data.

The temperature-dependence of inhomogeneous broadening is not well established, but it is generally assumed to be weak [12]. Moreover, it is common for inhomogeneously broadened lines to be asymmetric [12], as are the lines shown in fig. 7. (However, homogeneous line shapes can also be asymmetric [10,35,36].) Taken together, our observations are consistent only with the conclusion that the observed linewidth is inhomogeneous.

Although different isotopes of CO were used, it was not possible to use the mass-dependence of the linewidth as a clue to the broadening mechanism. The fractional change in the linewidth is proportional to the fractional difference in mass between the two isotopes, which in our case is only 0.04. The proportionality constant is between 0 and 2 for most processes [12,37]. Our sensitivity and reproducibility were not sufficient to observe such a small variation in the linewidth.

Our conclusion that the molecule-substrate mode of CO on Pt(111) is inhomogeneously broadened does not necessarily pertain to the system of CO on Ni(100); further investigation of that system is required. Exploration of other low-frequency vibrations is also needed to determine under what conditions, if any, phonon-mediated decay determines vibrational linewidths.

We have examined the system of atomic oxygen on Pt(111), which has many favorable properties [38,39] for a study of line-broadening mechanisms. However, the signal, as shown in fig. 9, is both too weak and too broad for the experiments to be feasible. The peak emittance is a factor of 5 less than that of CO, while the linewidth, 38 cm^{-1}, is more than three times greater. Without further information, it is inappropriate even to speculate as to the cause of this large linewidth.

5. Summary

We have performed the first detailed investigation of a molecule-substrate vibrational mode on a well characterized metal substrate. We have focused particularly on the question of the dominant line-broadening mechanism operating in this system. The issue of line-broadening processes is important to the understanding of surface dynamics, and is an area of considerable theoretical [12] and experimental [37] interest. Although high-frequency vibrations, such as the intramolecular C=O stretch vibration of adsorbed CO, have received considerable attention, little work has been done on low-frequency, adsorbate-substrate vibrations, despite the important role played by these modes in surface dynamics.

Earlier work on CO on Ni(100) suggested that phonons may play an important role in determining the linewidth of such vibrational modes. In the present case of CO on Pt(111), however, we find that the line is inhomogeneously broadened. This conclusion is based on the temperature-dependence of the linewidth, the asymmetry of the line shape, and the sensitivity of the linewidth to undetermined aspects of the surface condition.

In addition, we have examined the variation of the line with coverage. Neither the peak frequency nor the linewidth vary significantly for coverages less than $\theta=0.5$. At higher coverages there is a pronounced frequency shift, by approximately 6 cm^{-1}, to lower frequency.

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FIGURE CAPTIONS

Fig. 1. Theoretical two-phonon linewidth of the C-Ni mode of CO on Ni(100) as a function of temperature. The solid line is the prediction of Ariyasu, et al. [18]. The dotted line is calculated from the theory of Persson [19]. The experimental result of Chiang, et al. [16] is also shown. Both the experimental point and the solid curve refer to the left hand axis; the dotted curve refers to the right hand axis, which has been scaled so that the curves intersect at 300 K.

Fig. 2. Auger spectrum of the clean Pt(111) surface.

Fig. 3. Experimental curve of coverage vs. exposure, determined from integrated thermal desorption signals.

Fig. 4. Infrared emission spectra of the C=O stretch region, for CO on Pt(111), at various coverages: (a) 0.03 (b) 0.10 (c) 0.18 (d) 0.25 (e) 0.50 (f) 0.55.

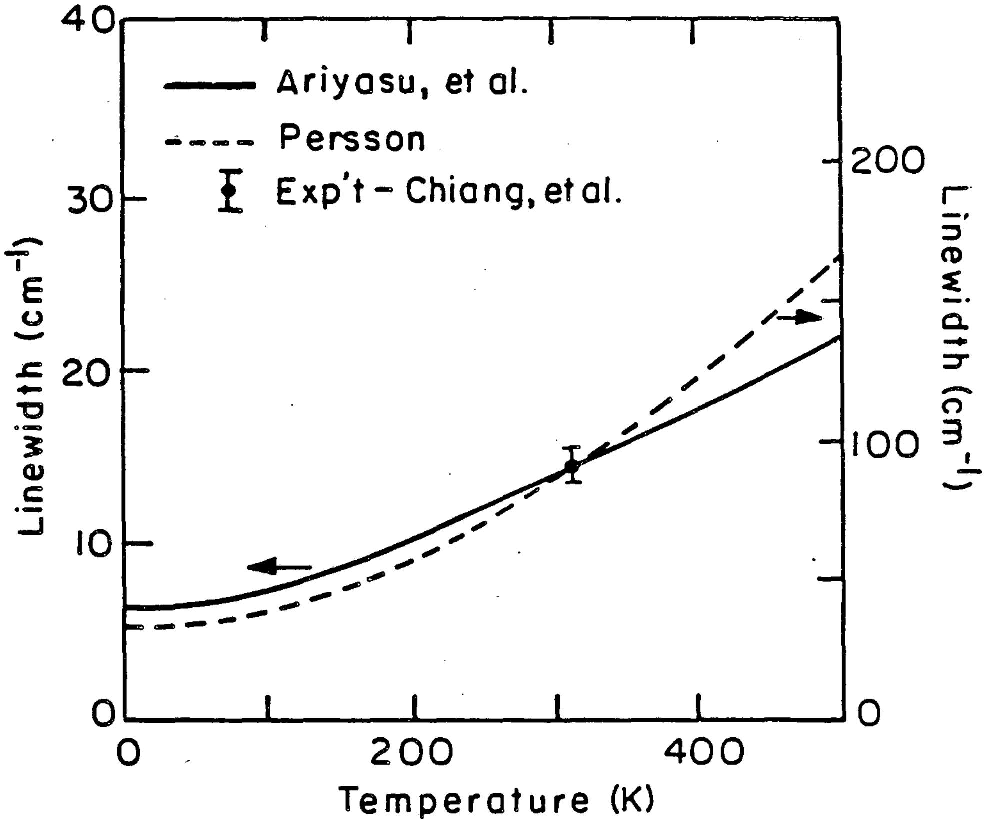
Fig. 5. Infrared emission spectra of the C-Pt stretching vibration of ^{13}CO on Pt(111) at 275 K for various CO coverages: (a) 0.07 (b) 0.14 (c) 0.27 (d) 0.31 (e) 0.50 (f) 0.55.

Fig. 6. Frequency shift of the C-Pt stretch band at 275 K, as a function of coverage.

Fig. 7. Infrared spectra of the C-Pt stretch band of CO on Pt(111) at various temperatures. The two lowest curves are for ^{13}CO; the remaining curves are for ^{12}CO. The observed isotope shift agrees with that predicted for a molecule-substrate stretch mode.

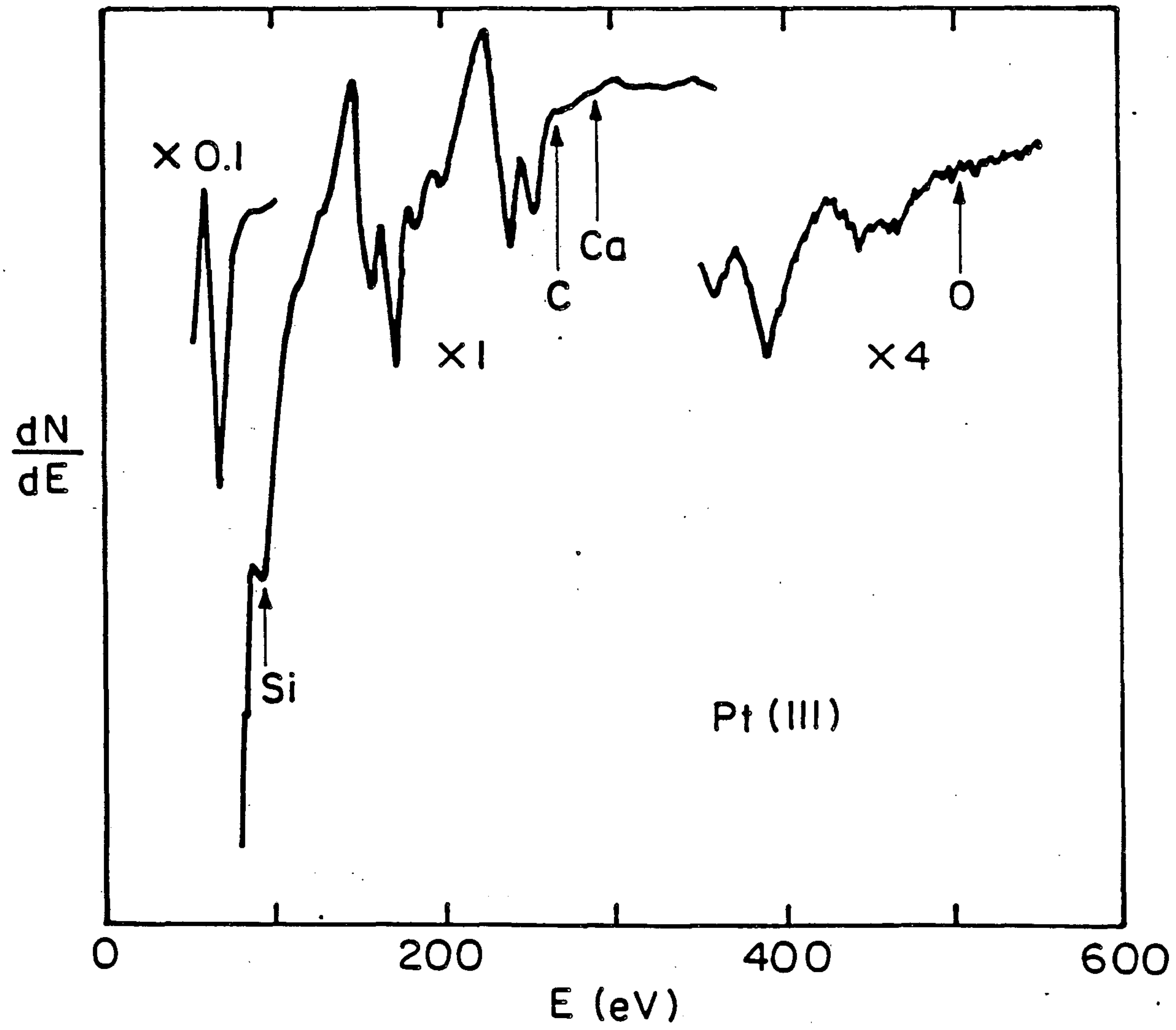
Fig. 8. Linewidth of the C-Pt stretch band as a function of temperature. The method of determining error bars is discussed in the text. The solid line represents the predicted temperature-dependence of the linewidth due to either three-phonon decay or dephasing, calculated within the Persson model [19], and normalized to the experimentally determined linewidth at 210 K. The dotted line represents an upper limit on the natural linewidth of the mode, as discussed in the text.

Fig. 9. Infrared emission spectrum of the O-Pt stretching vibration of $p(2\times2)O$ on Pt(111) at 300 K.



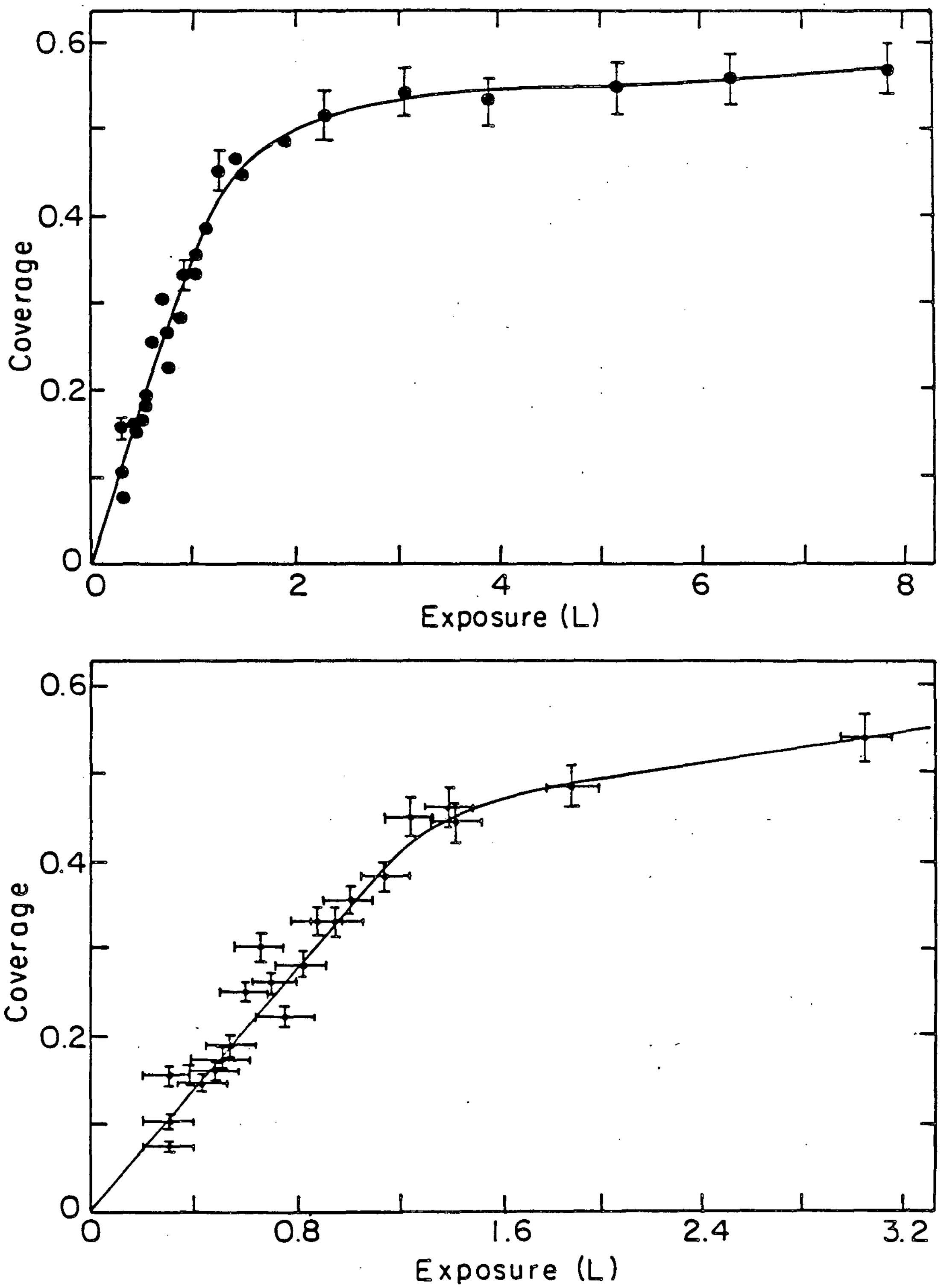
XBL 8510-6727

FIGURE 1



XBL 859-6629A

FIGURE 2



XBL 863-7593

FIGURE 3

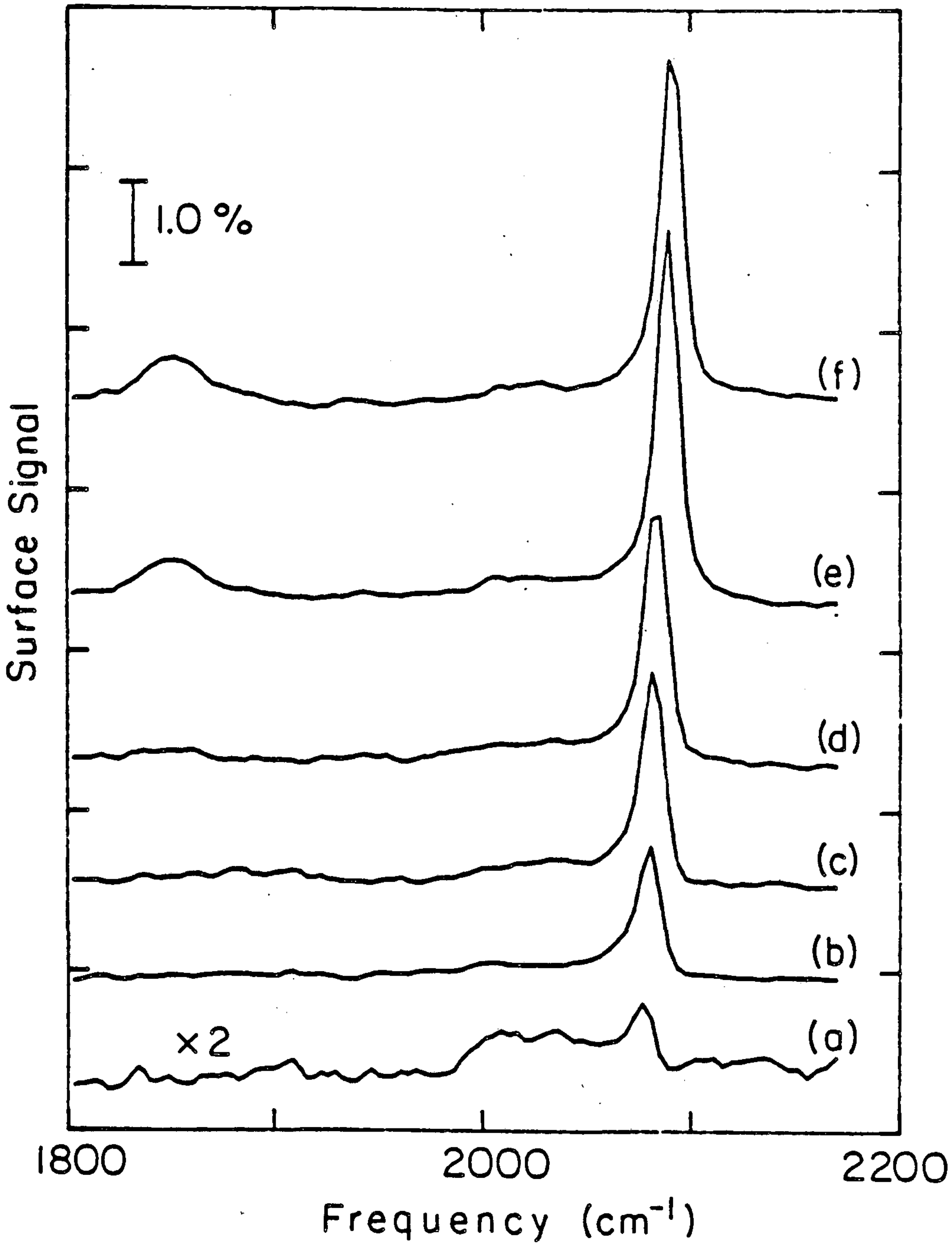


FIGURE 4

XBL 8510-6723

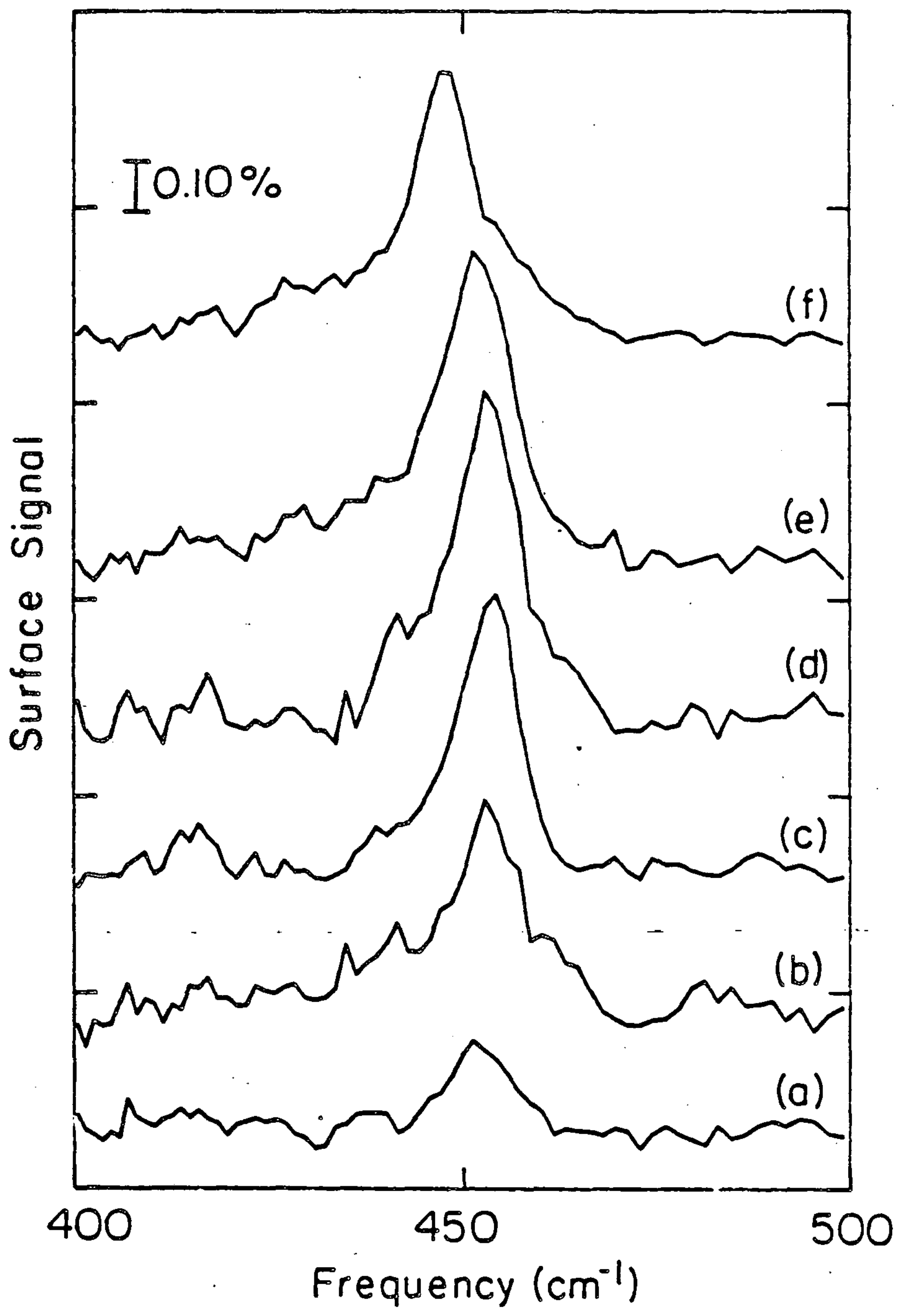

0.10%
Surface Signal
(f)
(e)
(d)
(c)
(b)
(a)
400
450
500
Frequency (cm^{-1})
XBL 8510-6725

FIGURE 5

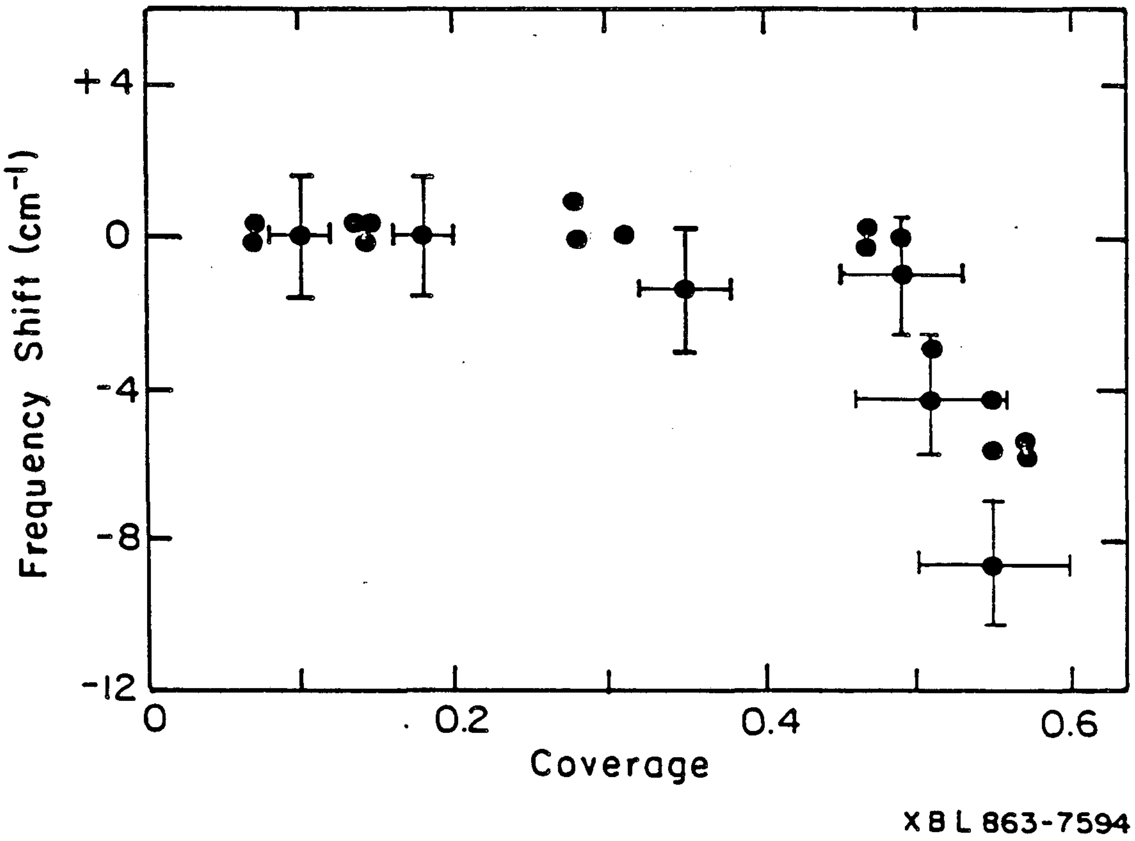
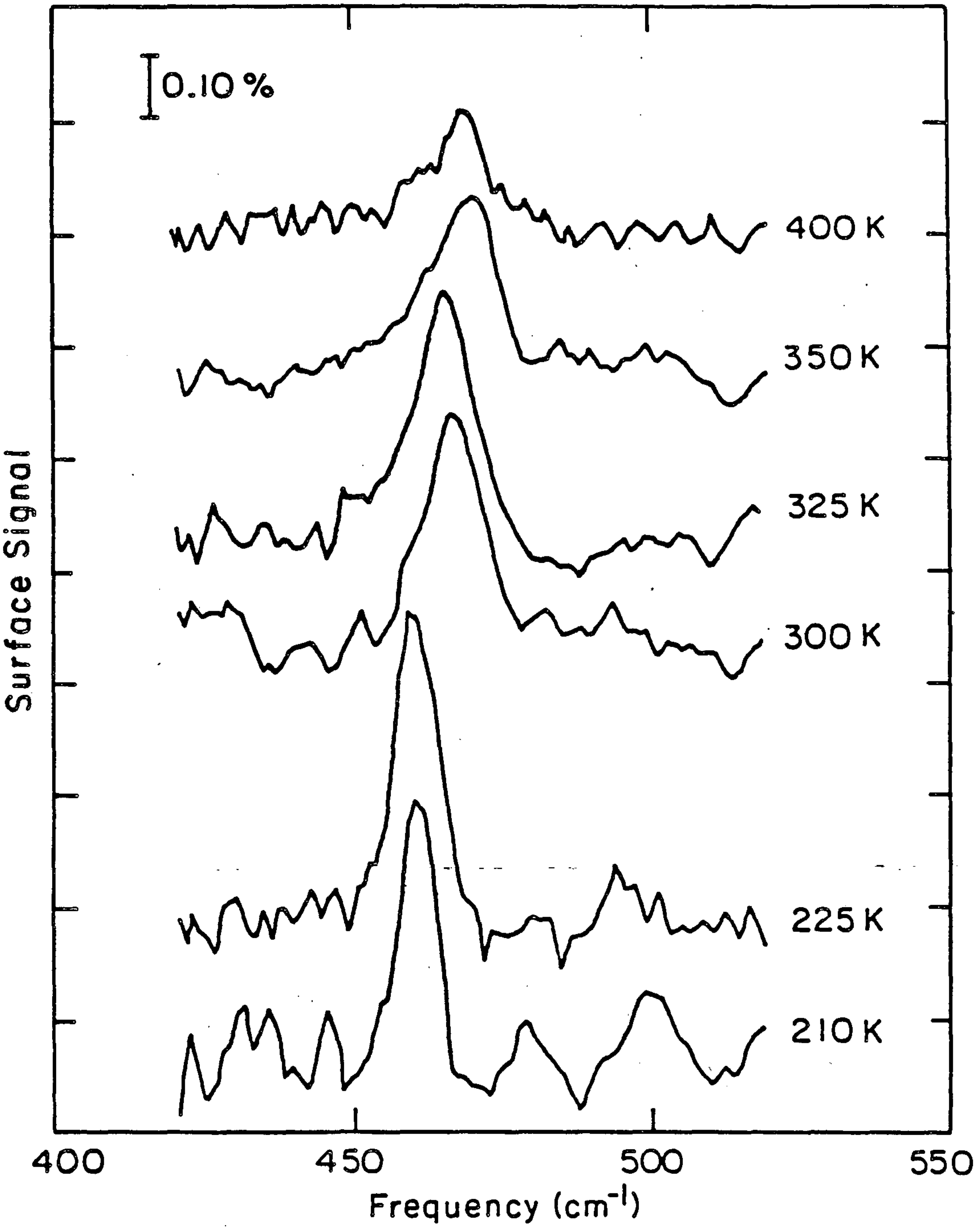
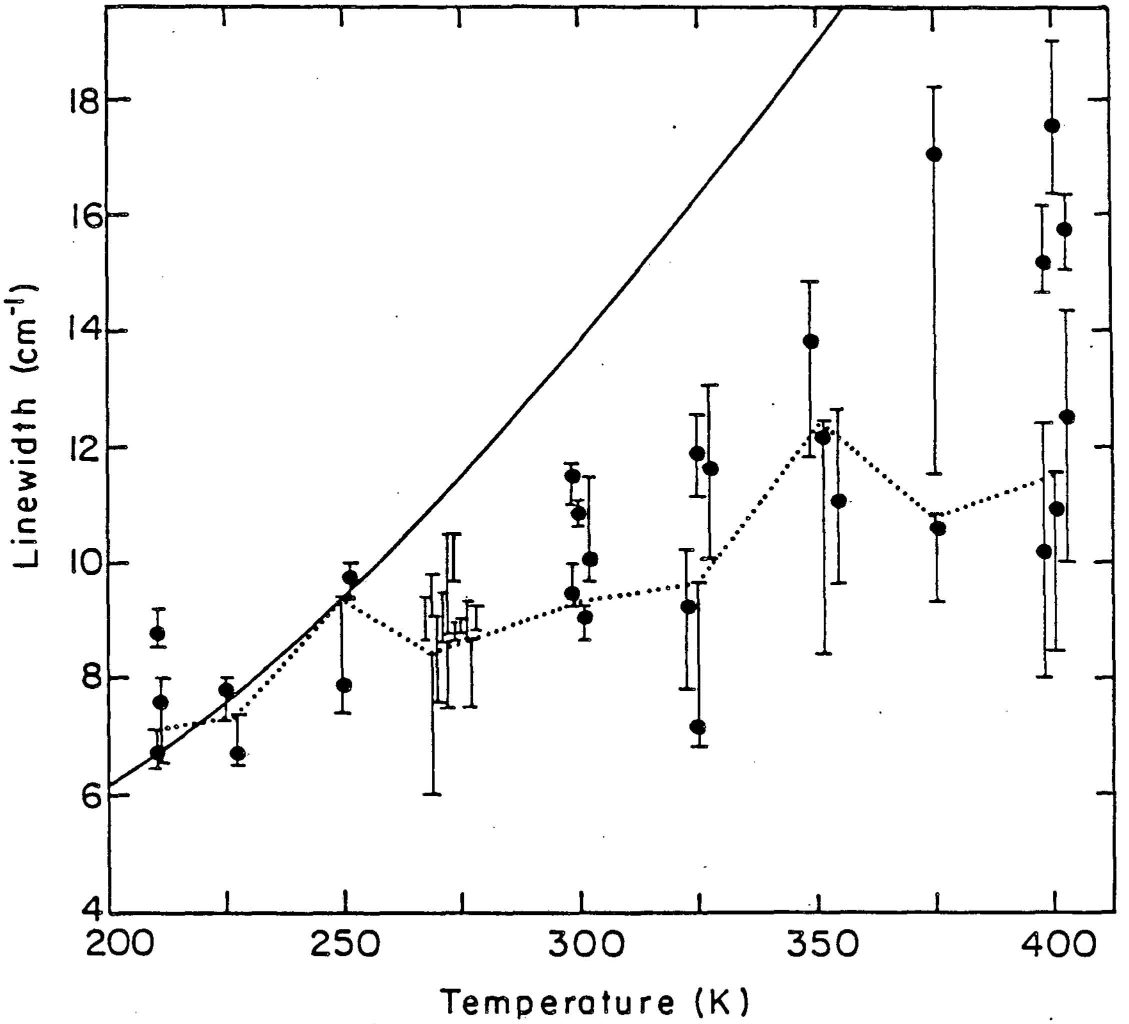


FIGURE 6



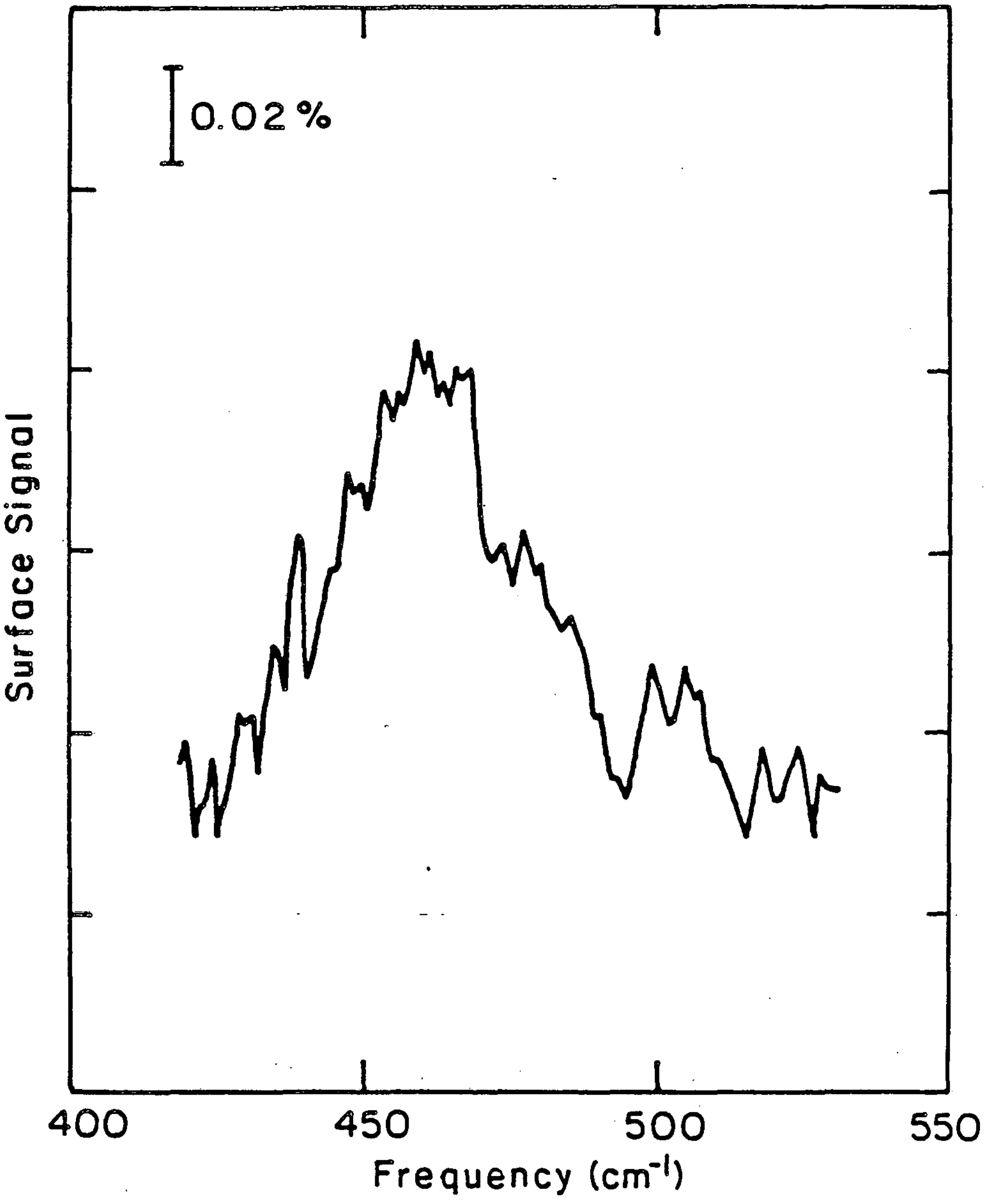
XBL 863-7596

FIGURE 7



XBL 863-7592

FIGURE 8



XBL 863-7595

FIGURE 9

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