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**An Infrared Emission Study of the C=O Stretch
Vibration of Bridge-Bonded CO on Pt(111)**

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Abstract

We have studied the C=O stretch vibration of bridge-bonded CO on Pt(111) in the temperature range from 225 K to 300 K. Our spectra are qualitatively different from those previously reported by Hayden and Bradshaw in that we do not observe the line near 1810 cm^{-1} that they attributed to three-fold bonded CO. We observe only a single line at 1849 cm^{-1} . We find that the minimum linewidth occurs for a coverage >0.5 monolayer, which tends to support "fault line" models for the high coverage structure of CO on Pt(111). The width of the line is $11.5 \pm 0.6\text{ cm}^{-1}$ for temperatures below 275 K, rising rapidly to $\sim 34\text{ cm}^{-1}$ at 300 K. This temperature dependence cannot be explained by current models of homogeneous broadening. We attribute it to inhomogeneous broadening associated with an order-disorder transition in the overlayer.

1. Introduction

Carbon monoxide on Pt(111) is one of the most intensively studied chemisorption systems. Virtually the full arsenal of experimental techniques has

been applied in order to understand its properties, including low energy electron diffraction (LEED) [1,2], thermal desorption spectroscopy (TDS) [1-5], ultraviolet photoelectron spectroscopy (UPS) [6], and work function measurements [1]. The study of CO on Pt(111) with vibrational spectroscopies has been particularly extensive. There have been several studies using electron energy loss spectroscopy (EELS) [2,4,7-9], as well as a large number of infrared studies, both on recrystallized ribbons [10-14] and on single crystals [5,15-17]. Recently this system has also been investigated with inelastic helium scattering [18]. With such a broad experimental background, one might expect that this chemisorption system would hold few surprises. Our infrared study of the C=O stretch vibration of bridge-bonded CO, however, demonstrates that qualitatively different results can be obtained in nominally identical experiments with different samples, for reasons that are not understood.

Electron energy loss spectra of CO on Pt(111) at high coverage consistently show two C=O stretch lines, at frequencies of -1870 and -2110 cm^{-1} . The two lines have comparable intensities. The 2110 cm^{-1} line is present at all coverages, while the 1870 cm^{-1} line appears only for $\theta > 0.33$. At $\theta = 0.5$, a $c(4 \times 2)$ overlayer is formed, which is believed to comprise equal numbers of bridge-bonded and terminally bonded molecules [4,8,9,19].

The IR measurements have been less consistent. The line near 2110 cm^{-1} , attributed to terminal CO, is always observed. The 1870 cm^{-1} line, however, has been observed previously only in three studies [5,14,15], and only Hayden and Bradshaw [5] were able to examine it in detail. They studied the line shape as a function of coverage and temperature between 85 K and 300 K.

Essentially the same behavior was observed for all coverages between 0.45 and 0.55. We will briefly summarize their results for a coverage of $\theta = 0.5$.

At 95 K, a single, rather sharp (13 cm^{-1} FWHM) line was found at 1857 cm^{-1} . As the temperature was increased, a second, broader line appeared, centered near 1810 cm^{-1} . By 300 K, the two features merged into a broad ($>50 \text{ cm}^{-1}$ FWHM) line, within which the doublet structure was barely observable. Fig. 1(a) shows some representative spectra, from their paper. The 1857 cm^{-1} line was assigned to bridge-bonded (two-fold) CO. The 1810 cm^{-1} line was assigned to three-fold coordinated CO, and it was postulated that the energy barrier between the bridge and three-fold sites was low enough to permit thermally activated motion between the two sites. The thermally induced disorder observed with LEED between 250 K and 300 K was attributed to the occupation of these three-fold sites.

A similar, though less pronounced doublet structure has been observed for CO on Cu(111) [20]. It has been pointed out that the thermally activated motion between bridge and three-fold sites is equivalent to a dephasing process [21,22]. Dephasing has been found [22] to account for the temperature dependence of the linewidth for bridge-bonded CO on Ni(111), which is expected to be a similar system.

We have reexamined the $1750\text{-}1950 \text{ cm}^{-1}$ spectral region, for CO on Pt(111), using infrared emission spectroscopy. Our findings are radically different from those of Hayden and Bradshaw. Throughout the temperature range from 225 K to 300 K, we observe only a single symmetric line at 1849 cm^{-1} . We do not observe the line near 1810 cm^{-1} attributed by Hayden and Bradshaw to three-fold coordinated CO. We find that the linewidth of the 1849 cm^{-1} line reaches its minimum value at a coverage significantly above $\theta = 0.5$, where the $c(4 \times 2)$

overlayer is complete. This observation tends to support "fault line" models of the high coverage structure of the overlayer. We have also examined the temperature dependence of the linewidth, and we conclude that it is due primarily to inhomogeneous broadening associated with increasing disorder in the overlayer at temperatures above ~ 275 K. The observed temperature dependence is not consistent with any proposed model of homogeneous line-broadening.

2. Experimental

The IR emission technique [23,24] and our methods of surface preparation and characterization [17] have been fully described elsewhere. We refer the reader to these sources for details. The Pt(111) surface was oriented within 0.5° and contained less than 0.01 monolayer carbon, with no other impurities detectable with a commercial cylindrical mirror Auger spectrometer.

The emission technique relies on thermal radiation from the sample as the only IR source in the system. This method offers significant advantages over reflection-absorption spectroscopy [23,24], but it is not well suited for measurements at low sample temperatures. At the frequencies and temperatures of interest in the present work, the emitted power decreases exponentially with decreasing temperature, according to the Planck law. For this reason, we were able to measure spectra only at temperatures >225 K.

3. Results and discussion

3.1. Adsorption sites

Fig. 1(b) shows IR emission spectra for coverages near $\theta = 0.5$, and temperatures from 225 K to 300 K. It is immediately apparent that our results are in qualitative disagreement with those of Hayden and Bradshaw, in that we

do not observe the line near 1810 cm^{-1} attributed to three-fold coordinated CO. Only a single, symmetric line at 1849 cm^{-1} , attributable to bridge-bonded CO, is detected. We have attempted to introduce surface defects by sputtering and have contaminated the surface deliberately with a few percent of a monolayer of carbon, without observing any signal near 1810 cm^{-1} . We have recently learned [25] that Bradshaw and co-workers have reexamined this spectral region, using a different Pt(111) sample. They also find no line near 1810 cm^{-1} . Neither they, nor we, are able to offer an explanation for the discrepancy between these recent observations and the results reported by Hayden and Bradshaw. Evidently the adsorption behavior of CO is so strongly dependent on surface conditions that experiments on different, carefully prepared single crystal samples can show radically different results. It is worth noting in this context that Tobin and Richards [17] found that the linewidth of the molecule-substrate vibration of terminal CO on Pt(111) was very strongly dependent on fine details of the surface condition.

3.2. Coverage dependence

It is well known that adsorbate-adsorbate interactions can give rise to coverage-dependent inhomogeneous broadening [26-28]. It is therefore essential in a study of vibrational linewidths to control the coverage sufficiently carefully that such effects are minimized. In this section we present measurements of the linewidth of the 1849 cm^{-1} line as a function of coverage. These measurements are necessary to an understanding of the temperature dependence of the linewidth, which we will discuss in the next section. They also have implications for the structure of the CO overlayer at high coverage.

In fig. 2 we show the measured linewidth as a function of coverage, for adsorption in the temperature range between 235 K and 250 K. The coverage was determined from the CO exposure by means of a calibration curve, which was based on integrated thermal desorption signals. The uncertainty in the absolute coverage is approximately 10%. The calibration curve, and a detailed description of its measurement, have been given elsewhere [17].

It is apparent from fig. 2 that the minimum linewidth occurs at a coverage of $\theta = 0.54$, which is above the 0.5 monolayer coverage at which the best $c(4 \times 2)$ ordering occurs. This observation is not attributable to uncertainty in the coverage determination. If the LEED pattern is observed at the coverage corresponding to the minimum linewidth, significant elongation of the $(0, 1/2)$ spots is visible. Conversely, IR measurements at the coverage that gives the best $c(4 \times 2)$ LEED pattern show a significantly larger linewidth. Since it is usually assumed that inhomogeneous broadening will be minimal for a well ordered overlayer, it is surprising that in this case the minimum linewidth occurs at a higher coverage. This observation has implications for the structure of the overlayer at high coverages.

There has been some disagreement in the literature regarding the structure of the CO overlayer for $\theta > 0.5$. Several authors [1,2,9] have described the structure in terms of a continuous, uniaxial compression of the $c(4 \times 2)$ unit cell. However, Avery [7] and Biberian and van Hove [19] have proposed "fault line" models, in which all of the molecules remain on high symmetry sites, with higher densities occurring at antiphase boundaries between locally ordered regions. Based on the relative IR intensities of the bridging and on-top C=O stretch vibrations, Hayden and Bradshaw [5] favored the "fault line" model.

Our observation that the C=O stretching vibration of bridge-bonded CO achieves its minimum linewidth for $\theta > 0.5$, and broadens only slightly with further exposure to CO, tends to support the "fault line" models. In a continuously compressed overlayer, the molecules would occupy a variety of sites, rather than identical, high symmetry bridge sites. Since the C=O stretch frequencies for on-top and bridge-bonded CO differ by more than 200 cm^{-1} , one would expect a marked broadening of the line at coverages > 0.5 associated with this distribution of bonding sites. Our measurements, on the contrary, support models in which the molecules remain in registry with the substrate, on well defined bridge sites. In such models, the only broadening would be due to the adsorbate-adsorbate interactions within the fault lines, where the local coverage is very high. The extent of such broadening has not been estimated, but it should be much smaller than that due to actual changes of bonding site. In some models [7], the fault lines contain only terminally bonded molecules, so little broadening of the line due to bridge-bonded molecules is expected.

3.3. Temperature dependence

It is apparent from fig. 1(b) that the width of the 1849 cm^{-1} line is strongly temperature-dependent. Measurements of this temperature dependence are of interest because they can provide important clues to the nature of the line-broadening mechanism [21,29]. In fig. 3 we present the linewidth of the 1849 cm^{-1} C=O stretch vibration as a function of temperature. In order to minimize the effects of inhomogeneous broadening, we varied the exposure at each temperature until the linewidth was observed to increase from its minimum value. The optimal exposure varied somewhat with temperature, from 3.5 L at

250 K to 5.0 L at 300 K. The difference is presumably due either to a lower sticking coefficient or to a higher rate of desorption at higher temperatures. The linewidths in fig. 3 have been corrected for the spectrometer resolution of 7.8 cm^{-1} , which was determined from the angular width of the zero order diffraction peak and confirmed by measurements of water vapor spectra.

The linewidth seems to be constant at $11.5 \pm 0.6 \text{ cm}^{-1}$ at temperatures below 275 K. This value may represent a homogeneous linewidth, caused, for example, by energy relaxation by the excitation of electron-hole pairs. However, it could also represent a residual, temperature-independent inhomogeneous contribution. Our experiments cannot discriminate between these two mechanisms. At higher temperatures, the linewidth increases sharply, reaching approximately 34 cm^{-1} at 300 K. We will show below that this increase is largely reversible and cannot be explained by any proposed model of homogeneous broadening. We attribute it to inhomogeneous broadening associated with the reversible order-disorder transition in the $c(4 \times 2)$ overlayer described by Ertl, et al. [1]. This transition occurs in the temperature range between 275 and 300 K, and is clearly observable with LEED.

Because of the possibility of desorption, and the strong dependence of the linewidth on coverage, it was necessary to investigate the possibility that the apparent temperature dependence of the linewidth is actually due to coverage variations. The experiment summarized in fig. 4 rules out such an effect, for temperatures $< 281 \text{ K}$. The sample was dosed with 3.5 L CO at 241 K to give a linewidth of $14.1 \pm 0.6 \text{ cm}^{-1}$, as shown in curve (a). It was then heated to 281 K, and the spectrum shown as curve (b) was measured at that temperature, giving a linewidth of $20.2 \pm 1.5 \text{ cm}^{-1}$. Finally, the sample was again cooled to

241 K, and the spectrum shown in curve (c) was measured. The linewidth was $13.2 \pm 1.1 \text{ cm}^{-1}$, essentially unchanged from its original value.

When a similar experiment was performed with sample temperatures of 250 K and 300 K, effects due to desorption were observed in addition to reversible temperature-dependent line-broadening. After the sample had been held at 300 K for 30 minutes, the linewidth at 250 K was 20.3 cm^{-1} --smaller than the 35 cm^{-1} linewidths typically observed at 300 K, but significantly larger than the 14.2 cm^{-1} linewidth measured at 250 K before the sample was heated. After the addition of another 1.0 L at 250 K, the linewidth narrowed again to 14.2 cm^{-1} . It is clear from these measurements that most of the temperature-dependent broadening shown in fig. 2 is reversible, although desorption becomes significant at the highest temperatures studied (~300 K).

Three homogeneous line-broadening mechanisms have been proposed that are predicted to show a strong temperature dependence [21,29]: energy relaxation by multiphonon excitation, dephasing by interaction with molecular or lattice vibrations, and dephasing by interaction with electron-hole pairs. None of these processes provides an explanation for our data. The multiphonon process should be negligible for the C=O stretch mode, which has a frequency more than nine times the maximum Pt phonon frequency [30]. The dephasing process, however, might be expected to be important. As we mentioned above, the linewidth of the C=O stretch vibration of bridge-bonded CO on Ni(111) has been attributed to dephasing by interaction with another molecular vibration [22]. This process is characterized by an approximately exponential temperature dependence. It has also been suggested that dephasing by electron-hole pairs, which is characterized by a T^4 dependence, could explain the data for CO on

Ni(111) [31]. The linewidth of the C=O stretch mode of terminally bonded CO on Ru(100) has also been attributed to vibrational dephasing [32].

In the present case of bridge-bonded CO on Pt(111), the observed temperature dependence is inconsistent with dephasing models. The dephasing model of Persson and Ryberg [22,32] predicts the variation of both the linewidth and the vibrational frequency with temperature. Within the experimental error of approximately $\pm 1 \text{ cm}^{-1}$, we observe no change in the vibrational frequency over the temperature range studied. The dotted line in fig. 3 represents the best fit of this model to our linewidth data, subject to our experimental limit on the frequency shift. The essentially exponential dependence predicted by the model is clearly incapable of fitting the abrupt change in the linewidth that we observe. The T^4 dependence predicted for electron-hole pair dephasing [31] is equally unsuccessful in fitting the data; the best fit is shown as the dashed line. A temperature-independent contribution to the linewidth was included in both models, but in each case the best fit was achieved when the value of that contribution was zero.

4. Summary

In summary, we have studied the C=O stretch vibration of bridge-bonded CO on Pt(111) in the temperature range from 225 K to 300 K. We find that the minimum linewidth occurs for a coverage >0.5 monolayer, which tends to support "fault line" models of the high coverage structure. Our spectra are qualitatively different from those of Hayden and Bradshaw [5] in that we observe no line near 1810 cm^{-1} . We observe a single line at 1849 cm^{-1} . The width of the line at the optimal coverage is $11.5 \pm 0.6 \text{ cm}^{-1}$ for temperatures below 275 K, rising rapidly to $\sim 34 \text{ cm}^{-1}$ at 300 K. This temperature dependence cannot be

explained by current models of homogeneous broadening. We attribute it to inhomogeneous broadening associated with an order-disorder transition in the overlayer. We are not able to determine whether the temperature-independent linewidth at temperatures < 275 K is homogeneous or inhomogeneous.

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Figure Captions

Fig. 1. IR spectra of CO on Pt(111) at various temperatures, in the region of the C=O stretch vibration of bridge-bonded CO. (a) As measured by Hayden and Bradshaw [5]. The line near 1810 cm^{-1} was attributed to CO bonded in three-fold sites. (b) As measured in the present work. No line near 1810 cm^{-1} is observed.

Fig. 2. The linewidth of the bridge-bonded CO vibration as a function of coverage, for temperatures between 235 K and 250 K. The minimum occurs at $\theta = 0.54$, which is significantly above the coverage that gives the sharpest $c(4 \times 2)$ LEED pattern.

Fig. 3. The linewidth of the bridge-bonded CO vibration as a function of temperature. The dotted line represents the best fit to a model of dephasing by interaction with other vibrational modes. The dashed line represents the best fit to a model of dephasing by interaction with electron-hole pairs. Neither model adequately fits the data.

Fig. 4. Spectra showing the reversibility of the temperature-dependent line-broadening. (a) Spectrum of 3.5 L CO ($\theta = 0.54$) at 241 K. (b) Spectrum measured at 281 K after dosing at 241 K. (c) Spectrum measured after cooling sample back to 241 K.

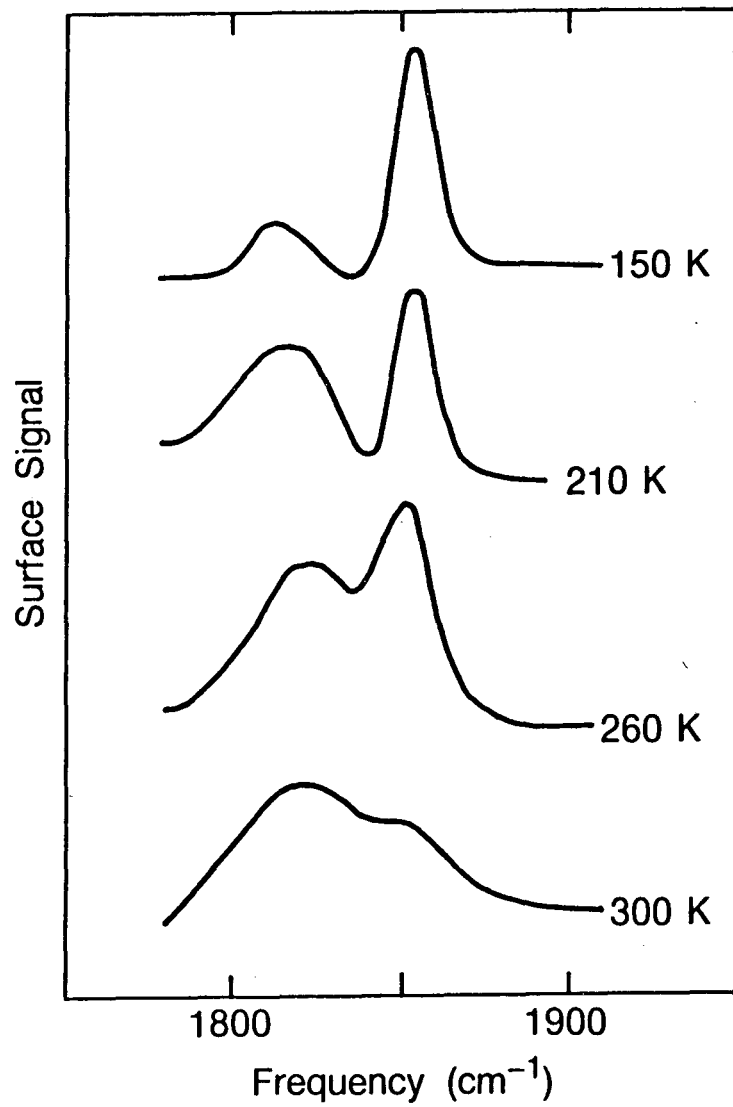


FIGURE 1(A)

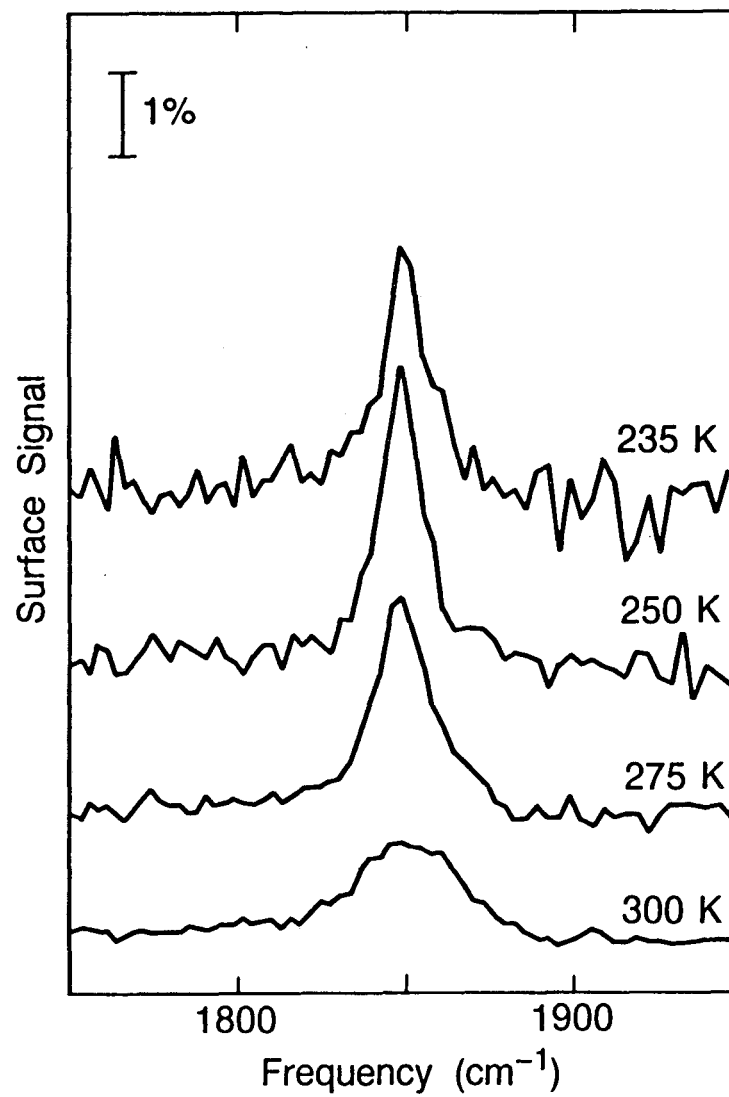
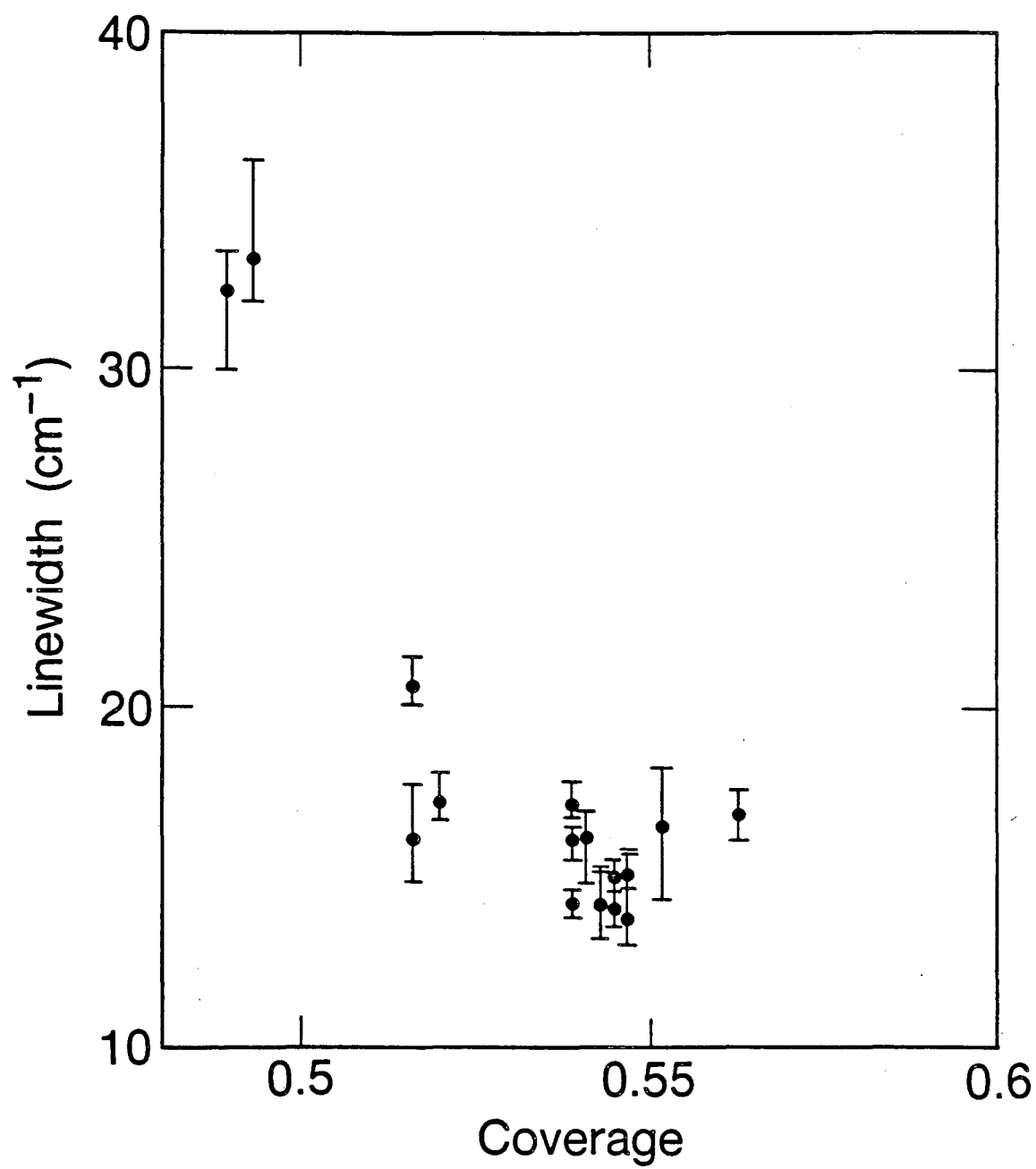


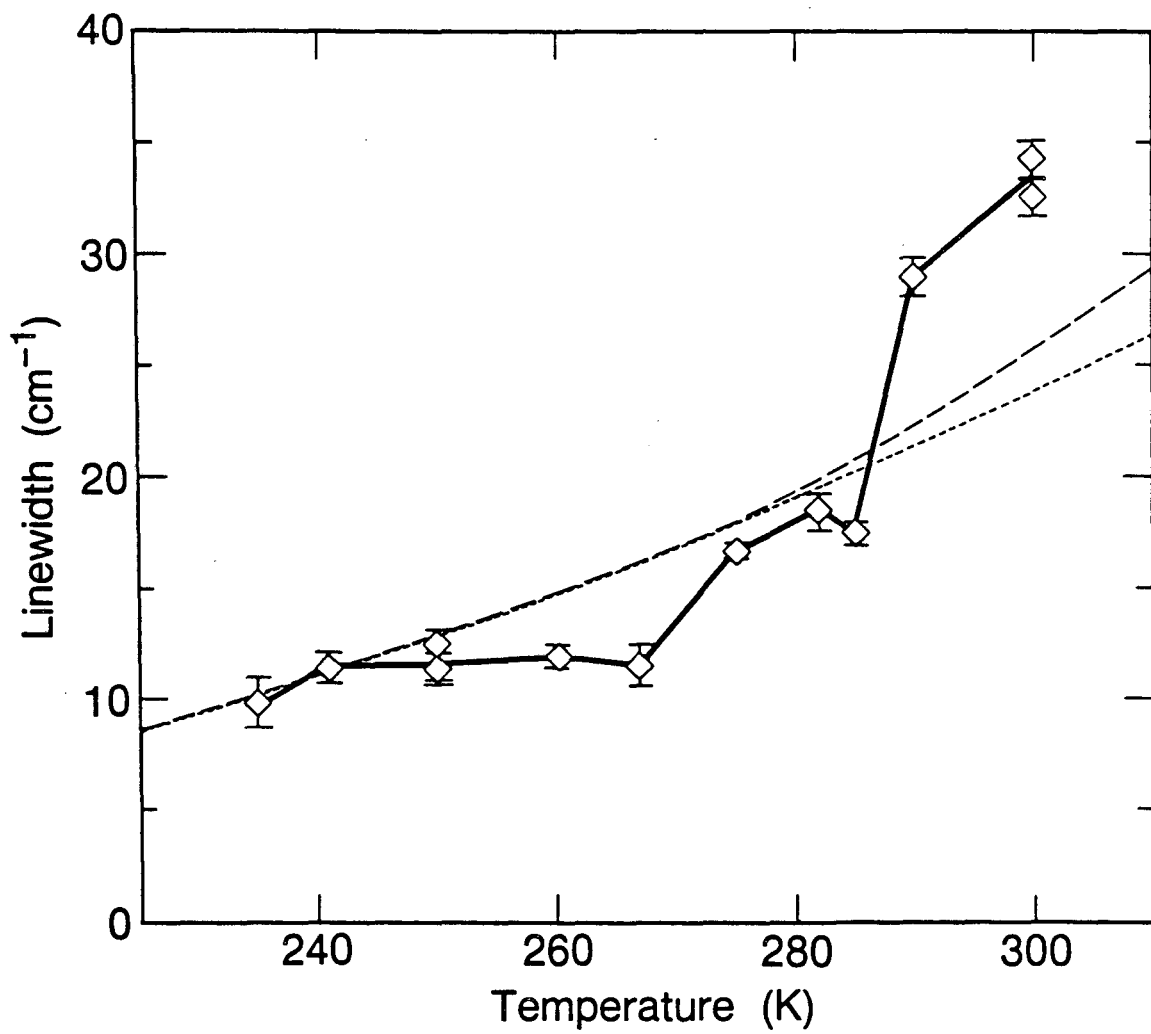
FIGURE 1(B)

XBL 864-7628A



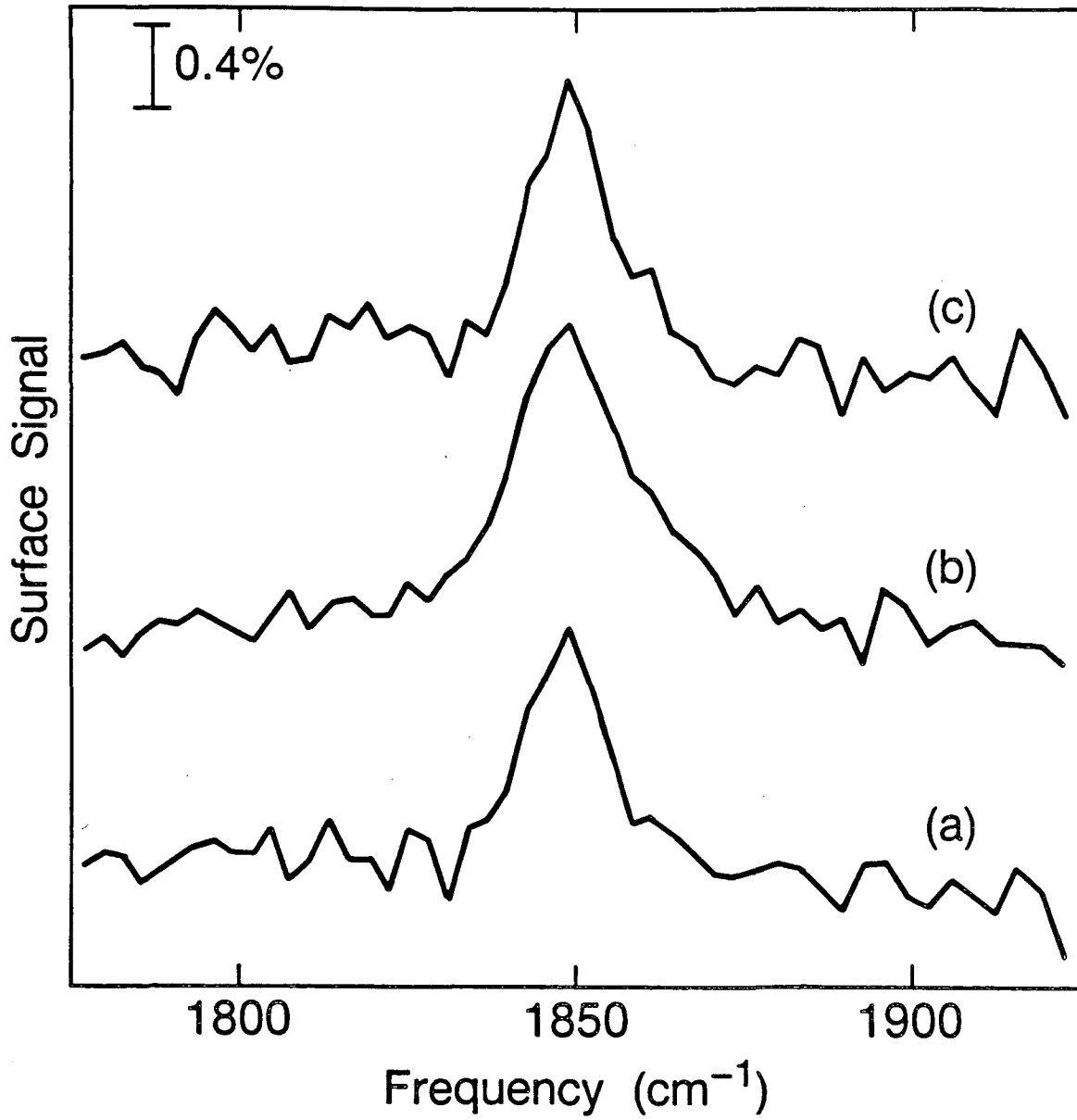
XBL 868-8917

FIGURE 2



XBL 868-8920

FIGURE 3



XBL 868-8918

FIGURE 4

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