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R.G. Tobin

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Vibrational Linewidths of Adsorbed Molecules:
Experimental Considerations and Results

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Abstract

The current understanding of the causes of vibrational line-broadening in adsorbates is discussed, with particular emphasis on experimental considerations. Recent experimental determinations of line-broadening mechanisms are reviewed. While there has been great progress in the theoretical understanding of line-broadening by energy and phase relaxation, it remains difficult to determine experimentally the relative importance of the various proposed mechanisms. Inhomogeneous broadening, which is certainly important in many cases, has received little theoretical attention.

1. Introduction

One of the most striking features of the infrared vibrational spectra of chemisorbed molecules is the large width of the vibrational lines. For example, the linewidth of the C=O stretching vibration of chemisorbed CO is typically $\sim 10 \text{ cm}^{-1}$. The natural linewidth of the same vibration in the gas

phase is some 10^{10} times smaller. In recent years, the study of these linewidths has been an area of intense experimental [1-16] and theoretical [3,17-43] interest. Nevertheless, a clear understanding of the important line-broadening mechanisms is only beginning to emerge.

Much of the research into vibrational linewidths is motivated by the possibility that they are determined by the finite lifetime of the vibrationally excited state. The vibrational lifetime is a measure of the rate of energy transfer between the adsorbed molecule and the substrate. This energy transfer plays a crucial role in such surface phenomena as sticking [42,44], desorption [45], diffusion [46], and surface chemical reactions [45]. The understanding of the dynamics of these processes requires a detailed knowledge of the rates and mechanisms of energy transfer that operate at surfaces. The calculation of vibrational lifetimes has thus received considerable attention [17].

Linewidth measurements offer the prospect of a static measurement that yields information about energy transfer processes that occur on the picosecond time scale. It is certain, however, that many experimentally observed linewidths are determined by effects other than lifetime broadening. The determination of the dominant line-broadening mechanism for a particular vibrational mode is a difficult experimental problem. In this paper, I will briefly review the current theoretical understanding of vibrational line-broadening, and discuss in some detail the experimental considerations that affect the identification of line-broadening mechanisms. Finally, I will review those experiments in which a broadening mechanism has been at least tentatively identified, and discuss the basis for the identification.

2. Theoretical Background

An excellent review of the theory of line-broadening mechanisms has been given by Gadzuk and Luntz [17]. The processes can be broadly classified as lifetime broadening, dephasing, and inhomogeneous broadening.

2.1. Lifetime Broadening

The vibrational decay process that leads to lifetime broadening can be characterized by the type of excitation that is created to carry off the vibrational energy. The most important ones are photons, phonons, adsorbate vibrational modes other than the one under study, and electron-hole pairs (for metal substrates).

2.1.1. Photons

Radiative decay is entirely negligible as a mechanism of line-broadening. A simple estimate of the radiative lifetime of the C=O stretch mode of CO-- which has a rather high oscillator strength--using a charged harmonic oscillator model, gives a value of 10^{-1} s. The lifetimes implied by adsorbate vibrational linewidths are some 10^{10} times shorter.

2.1.2. Phonons

The role of substrate phonons in vibrational decay is of much greater importance, but it has received relatively little theoretical attention, because of a shortage of relevant experimental data. Metiu and Palke [26], in one of the earliest attempts to account for adsorbate vibrational linewidths, estimated the phonon contribution to the linewidth of the C=O stretch mode of adsorbed CO. They found the broadening due to vibrational decay by phonon emission to be insignificant. Tully, et al. [3], in a much more sophisticated calculation for H on Si(100), arrived at the same conclusion. This result is due primarily to the energy mismatch: the vibrational frequencies are

$\sim 2000 \text{ cm}^{-1}$, while typical maximum phonon frequencies [6,47,48] are $200\text{-}500 \text{ cm}^{-1}$. The very high order process of 5- to 10-phonon emission occurs only at a very slow rate. On insulating substrates, where vibrational decay into electron-hole pairs is not a possibility, phonon emission is likely to determine the vibrational lifetime at all frequencies, as Casassa, et al. [49] have shown for OH on SiO_2 . Dephasing and inhomogeneous broadening, however, will normally determine the linewidth in such cases. At lower frequencies, where decay into one, two, or three phonons is energetically possible, the process could contribute significantly to the linewidth.

The problem of phonon-mediated decay for low frequency, adsorbate-substrate modes has been analyzed by Persson [21] and by Ariyasu, et al. [28,29]. Persson used a simple model to show that decay into phonons and dephasing could give linewidths of $1\text{-}100 \text{ cm}^{-1}$ for frequencies less than three times the maximum substrate phonon frequency. Linewidths in this range have been observed experimentally [13,14], as I will discuss below.

Persson's rough, but intuitive treatment of the problem is useful, but more detailed calculations are needed for comparison with experiment. Ariyasu, et al., have performed a sophisticated calculation, with no adjustable parameters, of the two-phonon contribution to the linewidth for oxygen and sulfur on Ni(100) and (111) and for CO on Ni(100). In each case, linewidths of $\sim 10 \text{ cm}^{-1}$ were found, and the value for CO at 300 K was in close agreement with that observed experimentally [14]. Thus it is clear that phonon-mediated lifetime broadening can be significant for modes with vibrational frequencies less than two or three times the maximum substrate phonon frequency. For higher frequency modes, the lifetime is expected to increase exponentially with the number of phonons required to absorb the vibrational energy [17].

2.1.3. Other adsorbate vibrations

The de-excitation of a vibrational mode by the excitation of other adsorbate vibrational modes, accompanied by the emission or absorption of one or more substrate phonons, is a process that has received relatively little attention. It is difficult to explore experimentally, since the frequencies of all the modes are rarely known, and cannot be determined with IR spectroscopy due to the surface selection rule [50]. Modes that are not IR-active can be detected with EELS, but the signal is usually very weak [51]. The process can be treated theoretically only in a full dynamical calculation such as that carried out by Ariyasu, et al. [29]. Nevertheless, it may be an important process to consider, particularly if the homogeneous linewidth seems anomalously large. For example, Andersson, et al. [52], using electron energy loss spectroscopy (EELS), deduced a linewidth of 40 cm^{-1} for $p(2 \times 2)0$ on Ni(100), even though the vibrational frequency is so high that decay into two substrate phonons has almost zero probability [28]. Ariyasu, et al. [29], were able to account for the linewidth by including coupling to other vibrational modes of the adsorbed atom.

2.1.4. Electron-hole pairs

On metallic substrates, electron-hole pairs provide an additional channel for vibrational decay. Since the number of accessible electron states increases with the energy of the vibration, the decay rate for this process increases with vibrational frequency. It is therefore most likely to dominate the linewidth for high frequency modes, well above the maximum substrate phonon frequency. It is precisely these modes--most notably the C=O stretching vibration of chemisorbed CO--that have received the greatest experimental attention.

Calculation of the electron-hole pair contribution to the linewidth is difficult. A good discussion of the problem is given by Avouris and Persson [20]. A complete treatment requires inclusion of the dynamics of charge transfer between the adsorbate and the substrate, the non-local dielectric response of the metal, and the fact that the boundary between the metal and the vacuum is not abrupt [20,25]. A number of authors [32-42] have treated the problem in varying approximations, but fully detailed, realistic linewidth predictions still appear to be out of reach. The models that are most suitable for the analysis of experiments are phenomenological.

Persson and Persson [34] have emphasized the role of adsorbate-induced resonances in the electronic density of states at the Fermi level. The existence of such a resonance has been confirmed for CO both theoretically [53,54] and experimentally [55,56]. When the molecule is vibrationally excited, the orbital is perturbed by the changes in the atomic positions, and its occupation oscillates at the vibrational frequency. This oscillation represents a resonant dynamic transfer of charge between the metal and the molecule, and has two observable effects. It enhances the dynamic dipole moment, and thus the oscillator strength, of the vibrational mode. In addition, it enhances the coupling of the vibrational motion to the electrons in the metal, and thereby increases the rate of energy transfer. The magnitude of the oscillation can be estimated from the chemisorption-induced change in the dynamic dipole, which can be measured experimentally. This deduced value can then be used to estimate the vibrational lifetime. Applying this analysis to CO on Cu(100), Persson and Persson [34] estimated a linewidth contribution within a factor two of the experimentally observed value.

Langreth [23] has taken a different approach, based on the same idea of an adsorbate-induced resonance near the Fermi level. Rather than estimate the lifetime, he calculated the line shape, and found that the electron-hole pair mechanism necessarily produces a characteristic, asymmetric shape. This result contrasts with the prevailing assumption [4,17] that a lifetime-broadened line should be Lorentzian in shape.

2.2. Dephasing

In addition to lifetime broadening, dephasing can provide a substantial contribution to the homogeneous linewidth. The process of dephasing is well known in other fields, including magnetic resonance and optical spectra of defects in crystals. Gadzuk and Luntz [17] provide a review of some of the literature, and a summary of the concepts and formalism.

Persson's model [21] for phonon broadening can also be used to estimate the dephasing contribution to the linewidth, for the adsorbate-substrate mode coupled to the phonons. In this model, the dephasing process is regarded as an elastic collision in which a phonon scatters off the vibrating molecule, disrupting its phase without changing its energy.

Other work on vibrational dephasing has dealt with modes at frequencies much greater than phonon frequencies [3,5,11,18,19]. In some cases, the dephasing is dominated by a single adsorbate vibrational mode at lower frequency, which is strongly damped by coupling to substrate phonons [5,18,19]. The excitation of the low-lying mode--frequently a frustrated translation or rotation of the molecule--modulates the resonant frequency of the high frequency mode. This frequency is very sensitive to the location of the molecule parallel to the surface. As a result [18,19], the high frequency mode is broadened and shifted in frequency. The magnitude and temperature dependence

of the broadening and of the shift can be estimated with an analytical model based on work by Shelby, et al. [57]. This model includes two adjustable parameters, which represent the coupling of the low frequency mode to the high frequency mode and to the phonon continuum.

Tully, et al. [3], have taken another approach to the problem, treating the dephasing of the Si-H stretch vibration of Si(100)-(2 × 1)H with a molecular dynamics simulation. This approach entails important approximations, but it involves no adjustable parameters. All of the vibrational modes and their couplings are included, but it was found that a single mode (the Si-H bending mode) dominates the dephasing process. These results will be discussed below.

Recently, Morawitz [43] has pointed out that dephasing can also occur by the interaction of the adsorbate vibration with electron-hole pairs, and has estimated that this process may be a significant source of line-broadening.

2.3. Inhomogeneous Broadening

Only a few workers [10,22,30] have made estimates of inhomogeneous broadening, despite its undoubted importance in many experimental situations. In each case, the analysis has dealt with incomplete monolayers, in which variations in local environment, and thus in the degree of dipolar coupling to nearby molecules, cause the adsorbed molecules to have a range of vibrational frequencies, resulting in a broadened, and usually asymmetric infrared line. The inhomogeneous contribution to the linewidth, for complete, well ordered overlayers is unknown [17].

In the ideal case of a perfectly clean, atomically flat surface of infinite extent covered with a defect-free, single-domain ordered overlayer, no inhomogeneous effects are expected. Real substrates are finite, and always

contain a non-zero density of defect sites and contaminants. These are likely to perturb the local chemistry, and therefore the vibrational frequency of nearby adsorbates. Moreover, adsorbate overlayers often consist of many domains, and molecules at or near domain boundaries will experience different dipole interactions, as well as different static lateral interactions, from those adsorbed far from the boundaries. The result of either type of inhomogeneous effect will be a broadened, and possibly asymmetric vibrational line, but neither the linewidth nor the line shape has been predicted [17]. In general, one expects that the extent of inhomogeneous broadening will be sensitive to the number, nature, and distribution of defects and contaminants. Inhomogeneous broadening is therefore likely to depend sensitively on the preparation of the surface.

3. Experimental Considerations

3.1. Instrumental Broadening

Instrumental broadening is not a significant factor in any of the experimental linewidth studies discussed in this work. Most infrared spectrometers readily achieve the resolution ($1-5\text{ cm}^{-1}$) required to resolve adsorbate vibrational modes, which typically have linewidths of $5-30\text{ cm}^{-1}$. Electron energy loss spectroscopy (EELS), on the other hand, achieves 30 cm^{-1} resolution only with great difficulty; 50 cm^{-1} is more typical [51]. The superior resolution of IR spectroscopy is one of the major motivations for IR surface studies, offsetting the advantages of EELS in surface sensitivity, spectral range, and convenience.

3.2. Determination of the line-broadening mechanism

It is difficult to determine experimentally the dominant broadening mechanism for a given line. The evaluation of the role of inhomogeneous broadening is particularly problematic. In some instances [58] it has simply been assumed that observed linewidths are due to lifetime broadening. This point of view is being increasingly questioned. In this section, I will discuss various means of distinguishing the different line-broadening mechanisms, and particularly of identifying or avoiding inhomogeneous effects.

At a minimum, it is essential to work on systems as well characterized as possible: smooth, uncontaminated surfaces, as determined by x-ray diffraction and Auger electron spectroscopy (AES) and ordered adsorbate overlayers, as determined by low energy electron diffraction (LEED). It has been shown both theoretically [22] and experimentally [4,10,15] that the disorder inherent in an incomplete layer can produce substantial inhomogeneous broadening due to adsorbate-adsorbate interactions. Control of the surface coverage, and evaluation of the effect of coverage on the linewidth are therefore crucial. Contamination can also introduce inhomogeneous broadening [15], so the effect of residual contaminants on the linewidth should also be investigated. Even in the best characterized system, however, the possibility of inhomogeneous broadening remains, and other means of isolating the homogeneous contribution must be found. The primary experimental techniques are measurements of the line shape and of the mass and temperature dependence of the linewidth. Gadzuk and Luntz [17] have summarized the expected outcomes of these measurements for the various proposed line-broadening mechanisms.

3.2.1. Line shape measurements

The shape of a vibrational line may give a clue to its origins. Inhomogeneously broadened lines are often asymmetric [4,10,15,22,30], and it is often assumed [17] that, if they are symmetric, the line shape will be Gaussian. Homogeneous broadening, by contrast, is expected to give a Lorentzian line shape [17]. However, as I mentioned earlier, Langreth [23] has argued that electron-hole pair decay necessarily produces a distinctive asymmetric line shape and Sorbello [24] has shown that a similar shape occurs for coupling to optical phonons. Metiu [27] has also derived asymmetric line shapes for broadening by phonon-mediated decay, in certain circumstances. An additional complication is that the theories of vibrational line shapes frequently deal with isolated molecules, while experiments are invariably performed on overlayers of interacting molecules [4]. These interactions can affect the line shape, even for very dilute overlayers [18,22]. The theoretical situation regarding line shapes is thus unclear.

Experimentally, line shape measurements require very high signal-to-noise ratios and excellent baseline subtraction unless a strong and distinctive asymmetry is predicted or observed. The Gaussian and Lorentzian shapes, for example, differ significantly only in the wings of the line, where the signal is much smaller than the signal at the peak.

3.2.2. Isotope effects

Since isotopic substitution allows the mass of an adsorbate to be changed without affecting the chemistry, it can provide another tool for distinguishing among the various line-broadening processes. The nature of the isotope effect for various broadening mechanisms, however, is controversial and complex [17]. The mass dependence of the linewidth can be characterized by the quantity $\alpha =$

$(\partial \ln \gamma / \partial \ln \mu)$, where γ is the linewidth, and μ is the reduced mass of the vibrational mode.

Certain theories [6,37] of electron-hole pair decay predict $\alpha = -1$, but this prediction is not obvious, and is not universally accepted. The isotopic dependence of phonon-mediated broadening is difficult to predict [17]. In Persson's model [21], α depends strongly on the vibrational frequency, and can range from nearly zero to greater than two. Persson's approach to dephasing due to phonons predicts $\alpha = -1$, but a much more complex dependence is to be expected when other vibrational modes of the adsorbate are involved.

Inhomogeneous broadening due to defects and impurities should be characterized by $\alpha = -0.5$, since the chemical effect on the force constant should be mass-independent, while the frequency is proportional to $\mu^{-1/2}$. I argue that the same dependence should occur for domain boundary inhomogeneity, despite the claim of Gadzuk and Luntz [17] that $\alpha = 0$ in this case. If the lateral interactions are predominantly chemical in nature, the argument given for defects applies. For dipolar coupling, the frequency shift for a molecule with a given array of identical neighboring molecules is proportional [22] to the vibrational frequency, and therefore to $\mu^{-1/2}$. Since it is precisely these shifts that give rise to the broadening, $\alpha = -0.5$ in this case, as well.

The greatest value of isotopic substitution, in principle, is thus the confirmation or exclusion of inhomogeneous broadening. Even for this purpose, however, considerable care is required, and errors of interpretation are possible.

Measuring the mass dependence of the linewidth can pose problems for the experimentalist. Except for low mass adsorbates, like hydrogen, the change in

the linewidth due to isotopic substitution is very small. Very high resolution and excellent signal-to-noise ratios are required. Even if the experimental apparatus is adequate, moreover, isotopic impurities may be sufficient to obscure the effect [4].

I am aware of only one case in which the isotope effect on the linewidth has been measured and used to determine the line-broadening mechanism. The linewidths of the C-H stretch modes of CH_3O on $\text{Cu}(100)$ were found to exhibit $\alpha \sim -1$, which was taken as evidence for electron-hole pair broadening [6]. Certainly the data seemed to exclude the possibility of inhomogeneous broadening. Recently, however, these modes have been remeasured [4,59] and the linewidths are found to be much narrower than in the original experiment, with little difference in linewidth between the CH_3 and CD_3 modes. The authors now attribute these linewidths to inhomogeneous broadening, but neither the strong apparent isotope dependence observed originally, nor the lack of any isotope dependence in the later measurement has been explained. This example illustrates the difficulty of clearly determining the source of vibrational line-broadening, even in apparently unambiguous experimental situations.

3.2.3. Temperature dependence

The most fruitful experimental method to date for determining line-broadening mechanisms has been the measurement of the linewidth as a function of temperature. Since the energy scale characterizing electrons in a metal is the Fermi energy, lifetime broadening by electron-hole pair generation should be essentially temperature-independent [17] at typical chemisorption temperatures (<1000 K). Dephasing by interaction with electron-hole pairs, however, is predicted to show a T^4 dependence [43]. For phonon broadening and dephasing, the characteristic energies are adsorbate or substrate vibrational

energies, so these processes are strongly temperature-dependent in the 100-500 K range. Furthermore, at least approximate predictions of the form of the temperature dependence are available [5,18,21,29]. In the high temperature limit, both processes lead to an exponential dependence [5,49] on temperature.

One difficulty in interpreting linewidth variations with temperature is that the temperature dependence of inhomogeneous broadening is uncertain. It is generally believed [17] that inhomogeneous broadening is nearly temperature-independent, since it does not involve dynamics. This argument should be correct for inhomogeneity due to crystallographic defects or contaminants on the surface, since their concentration should generally be insensitive to the temperature (unless, for example, contaminants accumulate more rapidly on a colder surface). Inhomogeneity due to lateral interactions within the overlayer, on the other hand, could certainly be temperature-dependent. Small variations in surface coverage with temperature can cause linewidth changes that mimic a true temperature dependence [12]. Even if the coverage is properly controlled, the density of faults in the packing of the overlayer could vary with temperature. It can be imagined that the creation of such faults could be an activated process characterized by the energy required to create them. In such a case, inhomogeneous broadening might mimic the dependence predicted for dephasing and phonon-mediated broadening. This comment is speculative, but suggestive that a temperature-dependent linewidth may not be sufficient evidence to exclude inhomogeneous effects.

3.3. Direct measurement of the lifetime

Given the evident difficulty of isolating the lifetime contribution to the linewidth for a given vibrational line, one is driven to ask whether direct

measurements of vibrational lifetimes are feasible. Casassa, et al. [49,60-63] have performed a series of such experiments on OH and OD chemisorbed on high-surface-area fumed silica (SiO_2). Using picosecond infrared pulses, they have directly measured vibrational relaxation times in the 50-200 ps range [62]. The temperature dependence of the lifetime suggests a multi-phonon decay process [49].

To date, this approach has been limited to relatively high vibrational frequencies, long lifetimes, and high-surface-area, transparent dielectric substrates. The extension of time-resolved spectroscopy to adsorbates on single crystal metal samples is planned [64,65], and will certainly shed light on the issues of line-broadening discussed here.

4. Experimental results

In this section, I will review those experiments in which the various techniques discussed above have been used to isolate the dominant line-broadening process for a vibrational mode. As we will see, not all of these identifications can be regarded as conclusive, but this summary will indicate the current state of experimental linewidth studies.

4.1. Electron-hole pairs

Two modes have been identified experimentally as examples of lifetime-broadening by the electron-hole pair mechanism: the C=O stretch mode of CO on Cu(100) [4], and the wagging mode of H on W(100) [2]. Both identifications are based on analysis of the shape and temperature dependence of the vibrational line.

The intramolecular stretch mode of CO on Cu(100) is an exceptionally strong absorber; at the peak its absorptance [7] is ~15%. Ryberg [4] has

measured the line shape of this mode with extremely high signal-to-noise ratio. The measured line shape, with best-fit Gaussian and Lorentzian functions, is shown in Fig. 1. The linewidth was found to be temperature-independent over the range from 20 to 130 K, which excludes the dephasing and phonon mechanisms. The essentially Lorentzian line shape, and the poor fit obtained with a Gaussian function, were used as arguments against a significant inhomogeneous contribution to the linewidth. The significant high frequency tail is unexpected; Langreth's theory [23] predicts, on the contrary, a tail to lower frequency for this system [4]. This discrepancy is speculatively attributed to adsorbate-adsorbate interactions, which are not included in the theory [4].

This example illustrates the fact that careful experimental technique makes it possible to draw conclusions about line-broadening mechanisms. The invariance of the linewidth over a substantial temperature range conclusively excludes dephasing and phonon decay. As is often the case, however, the argument against inhomogeneous broadening is weaker, not because of any deficiency in experimental technique, but because the current understanding of inhomogeneous broadening on surfaces is incomplete. It is not well established that inhomogeneous line shapes are necessarily Gaussian, or that they cannot approximate Lorentzian functions near the line center. These assumptions, however, provide the sole basis for rejecting inhomogeneous broadening in this experiment.

A measurement of the isotope effect on the linewidth could resolve the question of inhomogeneity, at least in principle [4]. Assuming that $\alpha=-1$ for electron-hole pair broadening, the linewidths for $^{12}\text{C}^{16}\text{O}$ and for $^{13}\text{C}^{18}\text{O}$ would differ by 0.3 cm^{-1} . The latter isotope is not available in sufficiently high purity, however, for this effect to be observed experimentally [4].

The characteristic line shape predicted by Langreth [23] has been observed by Chabal [2] for the overtone of the wagging mode of H on W(100). Fig. 2 shows the measured spectrum, with a fit to Langreth's model. The broad line near 1100 cm^{-1} is the W-H stretch vibration, which will be discussed below. The linewidth of the wagging mode at 1270 cm^{-1} is temperature-independent, as expected for the electron-hole pair mechanism, and the distinctive line shape convincingly rules out a dominant inhomogeneous contribution. The observed isotope dependence of the line shape does not appear to be consistent with the theory [66], but this uncertainty is unlikely to affect the basic interpretation.

The W-H stretch mode shown in Fig. 2 is extremely broad, with a linewidth of $\sim 100\text{ cm}^{-1}$. For comparison, the electron-hole pair contribution to the linewidth has been estimated [36,37] to be $\sim 15\text{ cm}^{-1}$. The line-broadening mechanism for this mode has not been identified, but the isotope dependence of the linewidth, and experiments involving isotopically mixed layers, appear to exclude the possibility of significant inhomogeneous broadening [1,66]

4.2. Dephasing

The C=O stretching mode of bridge-bonded CO on Ni(111) has been studied by Persson and Ryberg [5] and by Trenary, *et al.* [11]. Both groups measured the temperature dependence of the linewidth, and concluded that dephasing is the predominant line-broadening mechanism. Both groups also observed that the linewidth of the mode due to on-top CO did not vary appreciably with temperature, which suggests that dephasing is not important for the on-top species, but they did not determine the broadening mechanism for that mode. Despite the similar conclusions drawn by the two groups, there are important differ-

ences in the results of the two experiments. Fig. 3 compares their data for the bridge-bonded species.

Persson and Ryberg [5] found that the linewidth varied from 6 to 22 cm^{-1} between 30 and 300 K, while the peak frequency shifts by 8 cm^{-1} , from 1897 to 1905 cm^{-1} . These changes are well explained by a dephasing process mediated by a mode at 210 cm^{-1} , reasonably close to the expected frequency of the frustrated rotational mode, 184 cm^{-1} . The values obtained for the adjustable coupling parameters also appear to be reasonable.

The frustrated rotation frequency for bridge-bonded CO is lower than the maximum phonon frequency in Ni [47], which is 295 cm^{-1} . This mode should therefore be strongly damped. For on-top CO, the corresponding mode has a frequency of 411 cm^{-1} , well above the substrate phonons. The resulting weak damping of the frustrated rotation may explain why dephasing does not appear to contribute significantly to the linewidth for the on-top species [5].

The results of Trenary, et al. [11] are qualitatively similar, but there are important differences. They find a linewidth variation from 18 cm^{-1} to 48 cm^{-1} between 80 K and 300 K. Both the linewidths and the strength of the temperature dependence are much greater than found by Persson and Ryberg [5]. The frequency shift, on the other hand, is less than 6 cm^{-1} , and appears to be in the opposite direction from that observed by Persson and Ryberg. The data cannot be explained by a dephasing process involving a single intermediate mode; a number of modes must be included, with frequencies between 600 cm^{-1} and 800 cm^{-1} . Furthermore, Persson and Ryberg [19] have shown that physically unreasonable values of the coupling and damping parameters are required to fit the data with a dephasing model.

Evidently the two experiments on CO on Ni(111) are inconsistent. Both cannot be measurements of the homogeneous linewidth of the mode on a clean Ni(111) surface. Either the dephasing dynamics are significantly different for the two samples used, or at least one set of results must represent inhomogeneous broadening. Because the measured linewidths are smaller, and the fit to the dephasing model is better, preference must be given to the experiment of Persson and Ryberg. However, if the lines measured by Trenary, et al., are inhomogeneously broadened, then this type of broadening can evidently show a strong temperature dependence. If such is the case, then the possibility of inhomogeneous broadening cannot be absolutely excluded in either experiment. As in the case of electron-hole pair broadening, the uncertainty arises less from experimental problems than from a lack of understanding of the properties of inhomogeneous broadening.

Dephasing has also been used to explain the linewidth of on-top CO on Ru(100) [16], although in this case the linewidth only varies from 4 to 7 cm^{-1} over the temperature range from 100 to 400 K. The strongest evidence for the dephasing mechanism for this system comes from the shift of the vibrational frequency with temperature.

Results similar to those from CO on Ni(111) were obtained by Hayden and Bradshaw [9] for the C=O stretch mode of CO on Pt(111). The mode due to on-top CO did not change significantly with temperature, but the lower frequency line exhibited complicated temperature-dependent structure, and clearly consisted of at least two strongly coupled modes. The line shape variations were interpreted in terms of thermally activated movement between bridging and three-fold sites. This process can be regarded [17] as an extreme case of de-

phasing involving motion parallel to the surface. Very similar effects have also been observed [8] for CO on Cu(111).

Recent IR emission measurements of the same system [12], however, show only a single line due to bridging CO, with a linewidth of $\sim 20 \text{ cm}^{-1}$. No evidence for the occupation of three-fold sites, or for thermally activated movement of the CO is found. Evidently the effects observed by Hayden and Bradshaw are strongly dependent on properties of the sample that have not yet been identified.

The linewidth of the Si-H stretch mode of Si(100)-(2 × 1)H has also been attributed primarily to dephasing, in the study by Tully, et al. [3] discussed earlier. The calculated linewidths are compared in fig. 4 with the experimental values, after the subtraction of a temperature-independent inhomogeneous contribution of 0.9 cm^{-1} . The homogeneous contribution to the linewidth clearly shows an exponential dependence on temperature, characteristic of an activated process. The experimental and theoretical linewidths differ by about a factor two, which the authors regard as quite good in view of the approximations inherent in the calculations. The slopes of the lines in fig. 4, which are indicative of the frequency of the mode primarily responsible for the dephasing, agree with each other, and with the frequency of the Si-H bending mode, within experimental and theoretical error.

4.3. Phonons

There has been relatively little experimental work on linewidths at frequencies below 1000 cm^{-1} , where phonon-mediated decay is likely to be an important broadening mechanism. There are as yet no cases in which this mechanism has been conclusively shown to dominate the linewidth. The molecule-substrate stretch mode of CO on Ni(100), however, is a promising candidate.

The experimental work on this system was carried out by Chiang, et al. [14]. We found a linewidth of $15 \pm 1 \text{ cm}^{-1}$ at a temperature of 310 K. The width proved to be insensitive to the state of the surface, as fig. 5 illustrates. The figure compares the spectrum for a well ordered $c(2 \times 2)$ overlayer of CO on a clean surface with that for a surface contaminated with a few percent of a monolayer of carbon, on which no ordered CO LEED pattern was observed. Because of the experimental difficulty of measuring this weak vibrational mode, no more detailed investigation (e.g., temperature dependence or isotope effect measurements) have yet been performed.

Ariyasu, et al. [29] have calculated the linewidth contribution due to two-phonon decay for the molecule-substrate mode of CO on Ni(100), as a function of temperature. Their result is shown in fig. 6, along with the experimental value at 310 K. The agreement is excellent. Linewidth measurements at other temperatures will be needed to confirm the mechanism, however. Fig. 6 also shows the results of Persson's [21] model for two-phonon broadening, on a compressed vertical scale. This simpler model seriously overestimates the linewidth, but the predicted temperature dependence is similar to that obtained from the detailed theory.

4.4. Inhomogeneous broadening

In an extension of the work on CO on Ni(100), we have recently shown that the molecule-substrate mode of CO on Pt(111) is inhomogeneously broadened [13]. This conclusion is based on the asymmetry of the line shape, the weak temperature dependence of the linewidth, and the sensitivity of the linewidth to the condition of the surface. Fig. 7 shows several spectra of the

molecule-substrate mode, measured at various temperatures. The asymmetry of the line is apparent.

Fig. 8 displays the results of a large number of linewidth measurements at temperatures between 210 and 400 K. The scatter in the data, even for well ordered layers on a clean surface at 210 K, indicates the sensitivity of the linewidth to minute changes in surface conditions. The solid line represents the temperature dependence predicted by Persson's [21] model for either three-phonon broadening (two-phonon decay is energetically forbidden for this system) or dephasing; the two are indistinguishable in this temperature range. The curve has been normalized to the experimental linewidth at 210 K. The discrepancy between theory and experiment is even more striking when it is noted that each linewidth measurement places a firm upper limit on the natural linewidth of the mode. It is clear that the observed widths do not represent natural linewidths caused by dephasing or phonon decay. The data do not exclude electron-hole pair decay, but theories of that process [34] suggest a linewidth contribution at least an order of magnitude smaller than the observed widths. The most likely line-broadening mechanism is therefore inhomogeneous broadening.

As I discussed in section 3.2.2, inhomogeneities have also been found [59] to account for the observed linewidths of the C-H stretch modes of CH₃O on Cu(100), which were initially attributed to electron-hole pair broadening [6], although the observed isotope effects remain unexplained.

Tully et al. [3] found a temperature-independent contribution to the linewidth of the H-Si stretch mode of H on Si(100), which becomes dominant below 250 K as the broadening due to dephasing decreases. They attribute this temperature-independent term to inhomogeneous broadening. The dominance of

inhomogeneity at low temperature is to be expected for this system, since the electron-hole pair decay channel is missing, and the decay rate into phonons is very slow because of the high frequency of the vibrational mode.

5. Summary

The possibility of obtaining useful dynamical information about adsorbate-substrate and adsorbate-adsorbate interactions from measurements of the vibrational line shape has been recognized for many years. As the theoretical understanding of these line shapes and the experimental techniques for their study have become more sophisticated, it has become clear that great care must be taken in determining the broadening mechanism for any particular line. Where it was once assumed that lifetime broadening was the primary process, we now recognize that dephasing and inhomogeneous broadening can often play important roles. A reliable determination can be made only by careful experimentation combined with comparisons with theoretical predictions. This combination, as I have indicated, is beginning to bear fruit, as convincing examples of the various broadening processes are offered. There is no doubt that further experimental and theoretical advances will provide additional insights into surface dynamics.

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REFERENCES

- [1] D.M. Riffe, L.M. Hanssen, A.J. Sievers, Y.J. Chabal and S.B. Christman, *Surface Sci.* **161** (1985) L559.
- [2] Y.J. Chabal, *Phys. Rev. Lett.* **55** (1985) 845.
- [3] J.C. Tully, Y.J. Chabal, K. Raghavachari, J.M. Bowman and R.R. Lucchese, *Phys. Rev.* **B31** (1985) 1184.
- [4] R. Ryberg, *Phys. Rev.* **B32** (1985) 2671.
- [5] B.N.J. Persson and R. Ryberg, *Phys. Rev. Lett.* **54** (1985) 2119.
- [6] B.N.J. Persson and R. Ryberg, *Phys. Rev. Lett.* **48** (1982) 549.
- [7] R. Ryberg, *Surface Sci.* **114** (1982) 627.
- [8] B.E. Hayden, K. Kretzschmar and A.M. Bradshaw, *Surface Sci.* **155** (1985) 553.
- [9] B.E. Hayden and A.M. Bradshaw, *Surface Sci.* **125** (1983) 787.
- [10] H. Pfnur, D. Menzel, F.M. Hoffmann, A. Ortega and A.M. Bradshaw, *Surface Sci.* **93** (1980) 431.
- [11] M. Trenary, K.J. Uram, F. Bozso and J.T. Yates, Jr., *Surface Sci.* **146** (1984) 269.
- [12] R.G. Tobin, R.B. Phelps and P.L. Richards, to be published.
- [13] R.G. Tobin and P.L. Richards, to be published.
- [14] S. Chiang, R.G. Tobin, P.L. Richards and P.A. Thiel, *Phys. Rev. Lett.* **52** (1984) 648.
- [15] R.G. Tobin, S. Chiang, P.A. Thiel and P.L. Richards, *Surface Sci.* **140** (1984) 393.
- [16] F.M. Hoffmann and R. de Paola, to be published.
- [17] J.W. Gadzuk and A.C. Luntz, *Surface Sci.* **144** (1984) 429.
- [18] B.N.J. Persson, F.M. Hoffmann and R. Ryberg, to be published.

- [19] B.N.J. Persson and R. Ryberg, Phys. Rev. **B32** (1985) 3586.
- [20] Ph. Avouris and B.N.J. Persson, J. Phys. Chem. **88** (1984) 837.
- [21] B.N.J. Persson, J. Phys. C **17** (1984) 4741.
- [22] B.N.J. Persson and R. Ryberg, Phys. Rev. **B24** (1981) 6954.
- [23] D.C. Langreth, Phys. Rev. Lett. **54** (1985) 126.
- [24] R.S. Sorbello, Phys. Rev. **B32** (1985) 6294.
- [25] T. Maniv and H. Metiu, J. Chem. Phys. **72** (1980) 1996.
- [26] H. Metiu and W.E. Palke, J. Chem. Phys. **69** (1978) 2574.
- [27] H. Metiu, J. Chem. Phys. **68** (1978) 1453.
- [28] J.C. Ariyasu, D.L. Mills, K.G. Lloyd, and J.C. Hemminger, Phys. Rev. **B28** (1983) 6123.
- [29] J.C. Ariyasu, D.L. Mills, K.G. Lloyd, and J.C. Hemminger, Phys. Rev. **B30** (1984) 507.
- [30] P. Hollins, Surface Sci. **107** (1981) 75.
- [31] G.P. Brivio and T.B. Grimley, J. Phys. C **10** (1977) 2331.
- [32] B.N.J. Persson and N.D. Lang, Phys. Rev. **B26** (1982) 5409.
- [33] J.W. Gadzuk, Phys. Rev. **B24** (1981) 1651.
- [34] B.N.J. Persson and M. Persson, Solid State Commun. **36** (1980) 175.
- [35] B.N.J. Persson and M. Persson, Surface Sci. **97** (1980) 609.
- [36] B. Hellsing, M. Persson and B.I. Lundqvist, Surface Sci. **126** (1983) 147.
- [37] M. Persson and B. Hellsing, Phys. Rev. Lett. **49** (1982) 662.
- [38] P. Apell, Solid State Commun. **47** (1983) 615.
- [39] H. Ueba, J. Chem. Phys. **77** (1982) 3759.
- [40] L.E. Brus, J. Chem. Phys. **73** (1980) 940.
- [41] M.A. Kozhushner, V.G. Kustarev and B.R. Shub, Surface Sci. **81** (1979) 261.
- [42] G.P. Brivio and T.B. Grimley, Surface Sci. **89** (1979) 226.

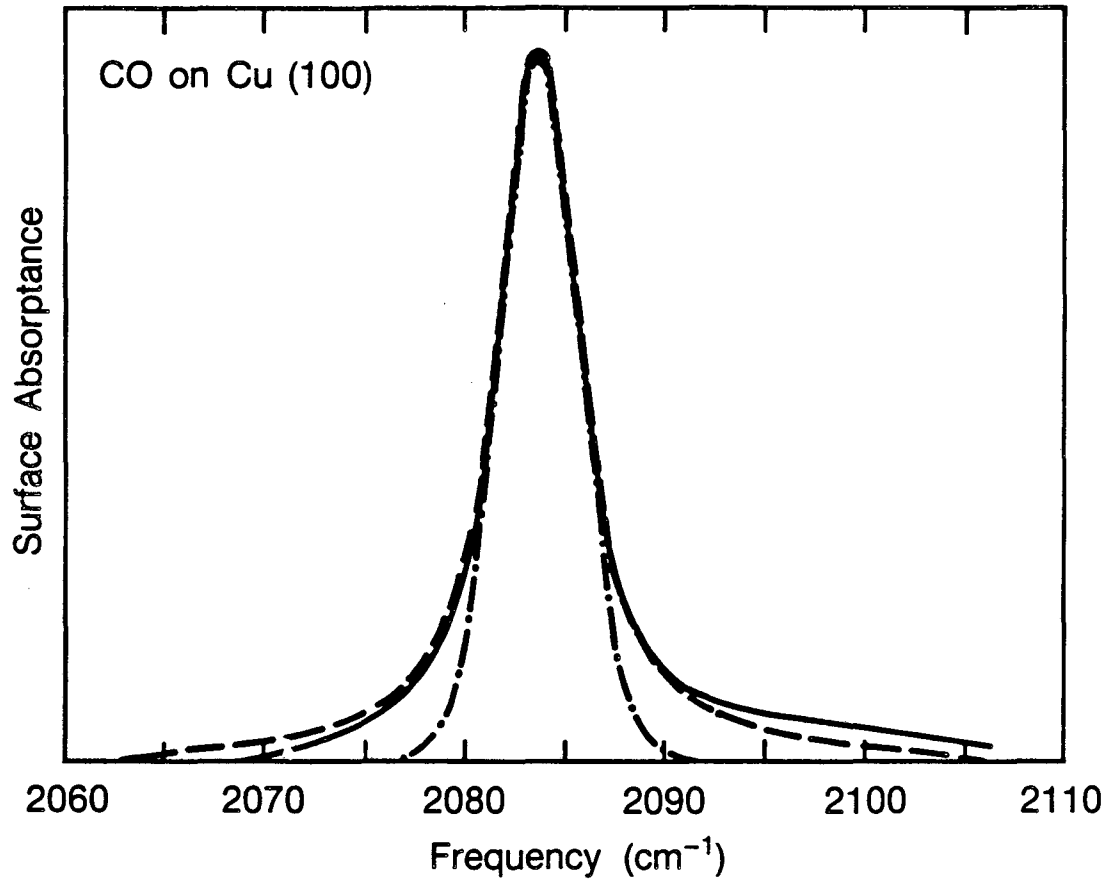
- [43] H. Morawitz, to be published.
- [44] J.K. Nørskov and B.I. Lundqvist, *Surface Sci.* **89** (1979) 251.
- [45] T.J. Chuang, *Surface Sci. Rep.* **3** (1983) 1.
- [46] A.G. Naumovets and Yu. S. Vedula, *Surface Sci. Rep.* **4** (1984) 365.
- [47] R.J. Birgenau, J. Cordes, G. Dolling and A.D.B. Woods, *Phys. Rev.* **136** (1964) A1339.
- [48] R. Ohrlich and W. Drexel, *Inel. Scatt. Neut. Symp. Copenhagen 1* (1968) 203.
- [49] M.P. Casassa, E.J. Heilweil, J.C. Stephenson and R.R. Cavanagh, *J. Chem. Phys.* **84** (1986) 2361.
- [50] F. M. Hoffmann, *Surface Sci. Rep.* **3** (1983) 107.
- [51] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, (Academic Press, New York, 1982).
- [52] S. Andersson, P. A. Karlsson and M. Persson, *Phys. Rev. Lett.* **51** (1983) 2378.
- [53] E. J. Baerends and P. Ros, *Mol. Phys.* **30** (1975) 1735.
- [54] I. P. Batra and P. S. Bagus, *Solid State Commun.* **16** (1975) 1097.
- [55] D. E. Eastman and J. K. Cashion, *Phys. Rev. Lett.* **27** (1971) 1520.
- [56] J. Lee, C. P. Hanrahan, J. Arias, R. M. Martin, and H. Metiu, *Phys. Rev. Lett.* **51** (1983) 1803.
- [57] R.M. Shelby, C.B. Harris, and P.A. Cornelius, *J. Chem. Phys.* **70** (1979) 34.
- [58] R. Ryberg, in *Vibrations at Surfaces*, edited by R. Caudano, J.-M. Gilles and A.A. Lucas (Plenum, New York, 1982) 309.
- [59] R. Ryberg, *J. Chem. Phys.* **82** (1985) 567.

- [60] E.J. Heilweil, M.P. Casassa, R.R. Cavanagh and J.C. Stephenson, J. Chem. Phys. **81** (1984) 2856.
- [61] M.P. Casassa, E.J. Heilweil, J.C. Stephenson and R.R. Cavanagh, J. Vac. Sci. Technol. **A3** (1985) 1655.
- [62] E.J. Heilweil, M.P. Casassa, R.R. Cavanagh and J.C. Stephenson, J. Chem. Phys. **82** (1985) 5216.
- [63] E.J. Heilweil, M.P. Casassa, R.R. Cavanagh and J.C. Stephenson, J. Vac. Sci. Technol. **B3** (1985) 1471.
- [64] R.R. Cavanagh, private communication.
- [65] H.W.K. Tom and S. Chu, private communication.
- [66] Y.J. Chabal, private communication.

FIGURE CAPTIONS

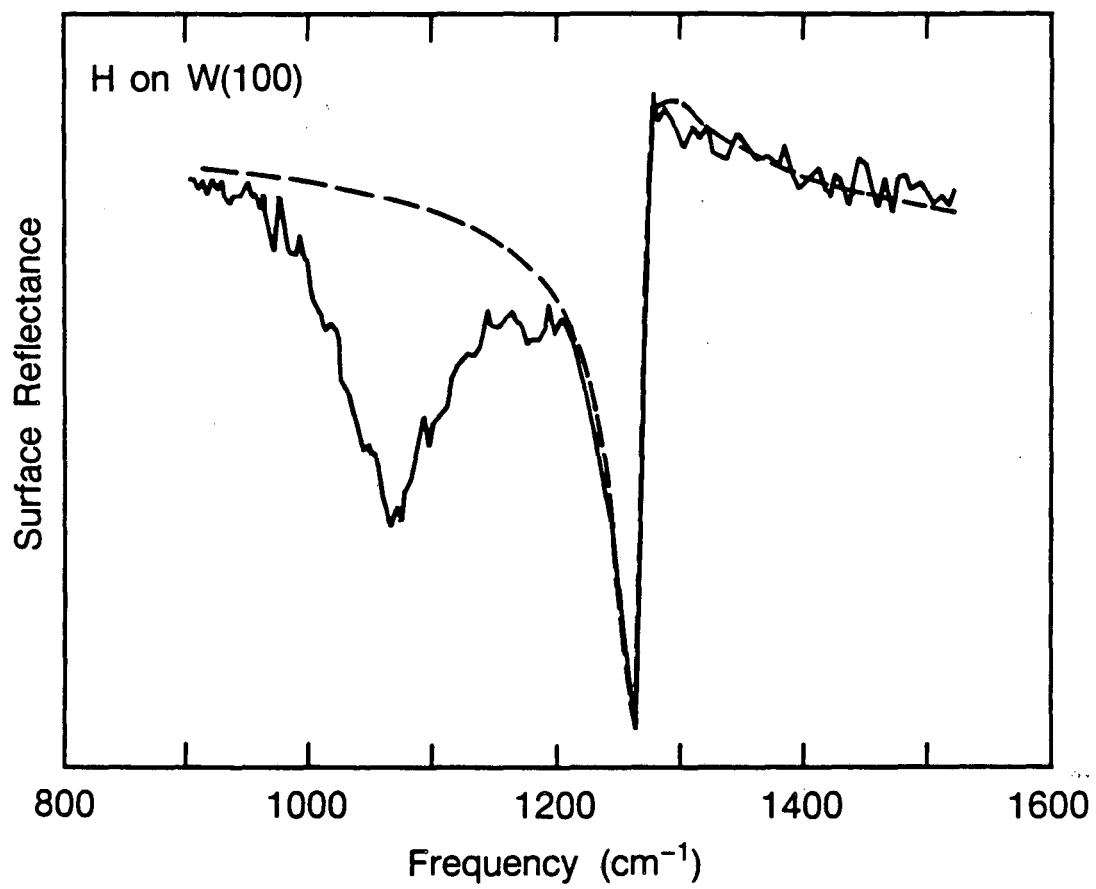
- Fig. 1. The C=O stretch mode line shape of $c(2 \times 2)\text{CO}$ on Cu(100) at 100 K, as measured by Ryberg [4]. Lorentzian (- - -) and Gaussian (- · - ·) fits are also shown.
- Fig. 2. Vibrational spectrum of H on W(100) at saturation coverage, as measured by Chabal [2]. The broad line near 1100 cm^{-1} is due to the W-H stretch mode. The asymmetric line near 1270 cm^{-1} is the first overtone of the W-H wagging mode. The dashed line is a fit to the line shape predicted by Langreth [23] for electron-hole pair broadening.
- Fig. 3. The measured linewidth of the C=O stretch vibration of bridging CO on Ni(111), as a function of temperature. The lower set of points was measured by Persson and Ryberg [5], and the line through those points represents a fit to a dephasing model for the linewidth. The upper set was measured by Trenary, et al. [11]; the line represents an Arrhenius function.
- Fig. 4. Theoretical and experimental values of the linewidth of the Si-H stretch mode of $(2 \times 1)\text{H}$ on Si(100), obtained by Tully, et al. [3]. A temperature-independent contribution of 0.9 cm^{-1} has been subtracted from the experimental linewidths. The frequencies corresponding to the slopes of the lines are shown.

- Fig. 5. Vibrational spectra of the molecule-substrate mode of CO on Ni(100) at 310 K, as measured by Chiang, et al. [14]. (a) Spectrum of a disordered CO layer on a surface partially contaminated with carbon. (b) Spectrum of an ordered $c(2 \times 2)$ CO overlayer on a clean surface.
- Fig. 6. Theoretical two-phonon linewidth of the molecule-substrate mode of CO on Ni(100) as a function of temperature. The solid line is the prediction of Ariyasu, et al. [29]. The dotted line is calculated from the theory of Persson [21]. The experimental result of Chiang, et al. [14] 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. 7. Vibrational spectra of the molecule-substrate mode of CO on Pt(111) at various temperatures. The two lowest curves are for ^{13}CO ; the remaining curves are for ^{12}CO . From Tobin and Richards [13].
- Fig. 8. Linewidth of the molecule-substrate mode of CO on Pt(111) as a function of temperature, measured by Tobin and Richards [13]. The solid line represents the predicted temperature dependence of the linewidth due to either three-phonon decay or dephasing, calculated within the Persson model [21], and normalized to the experimentally determined linewidth at 210 K. The dotted line represents an upper limit on the natural linewidth of the mode.



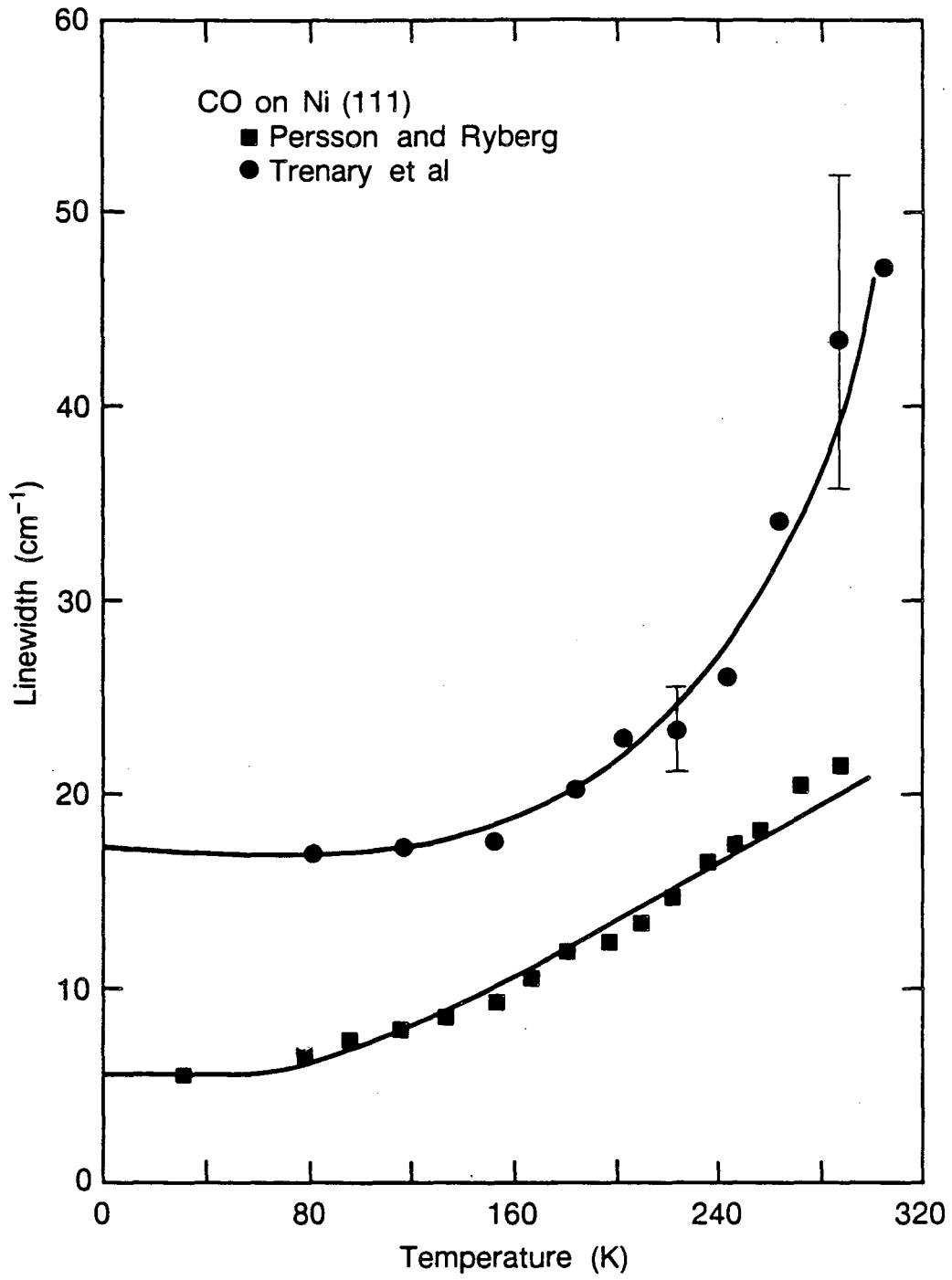
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FIGURE 1



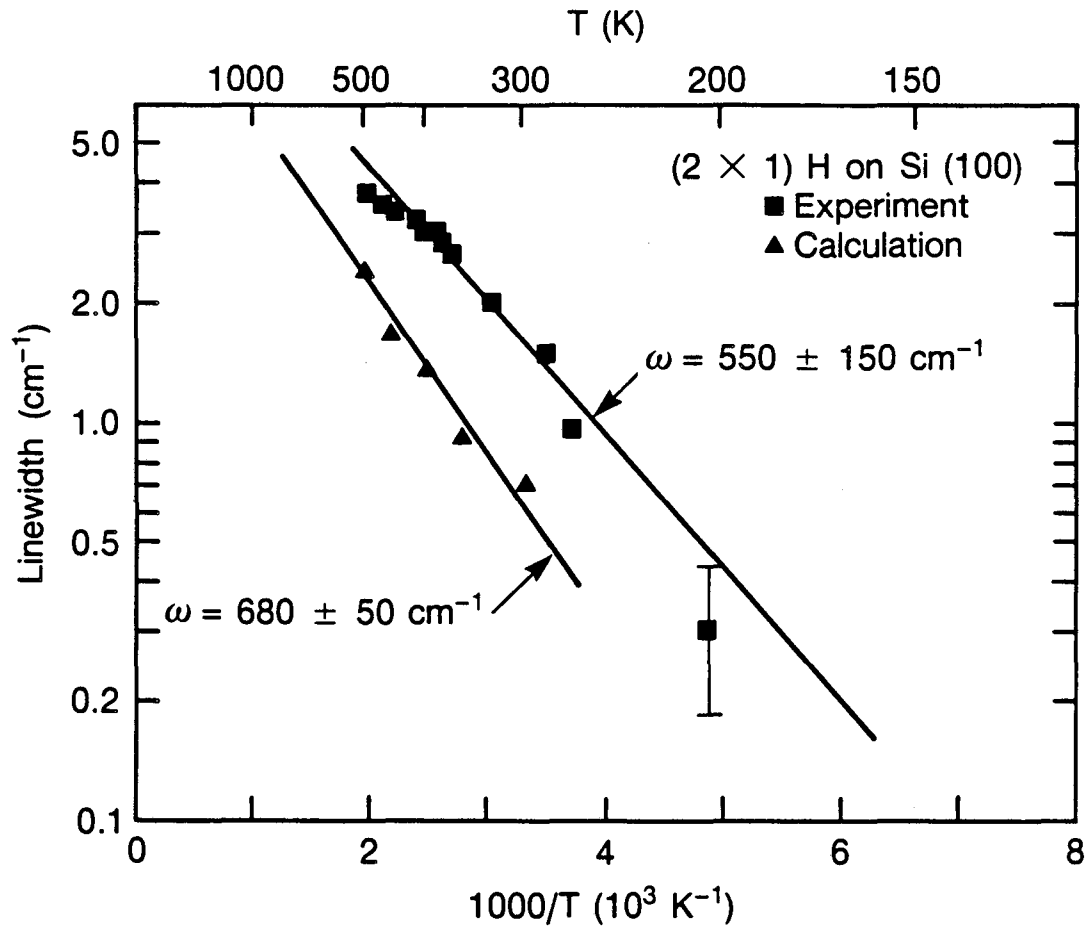
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FIGURE 2



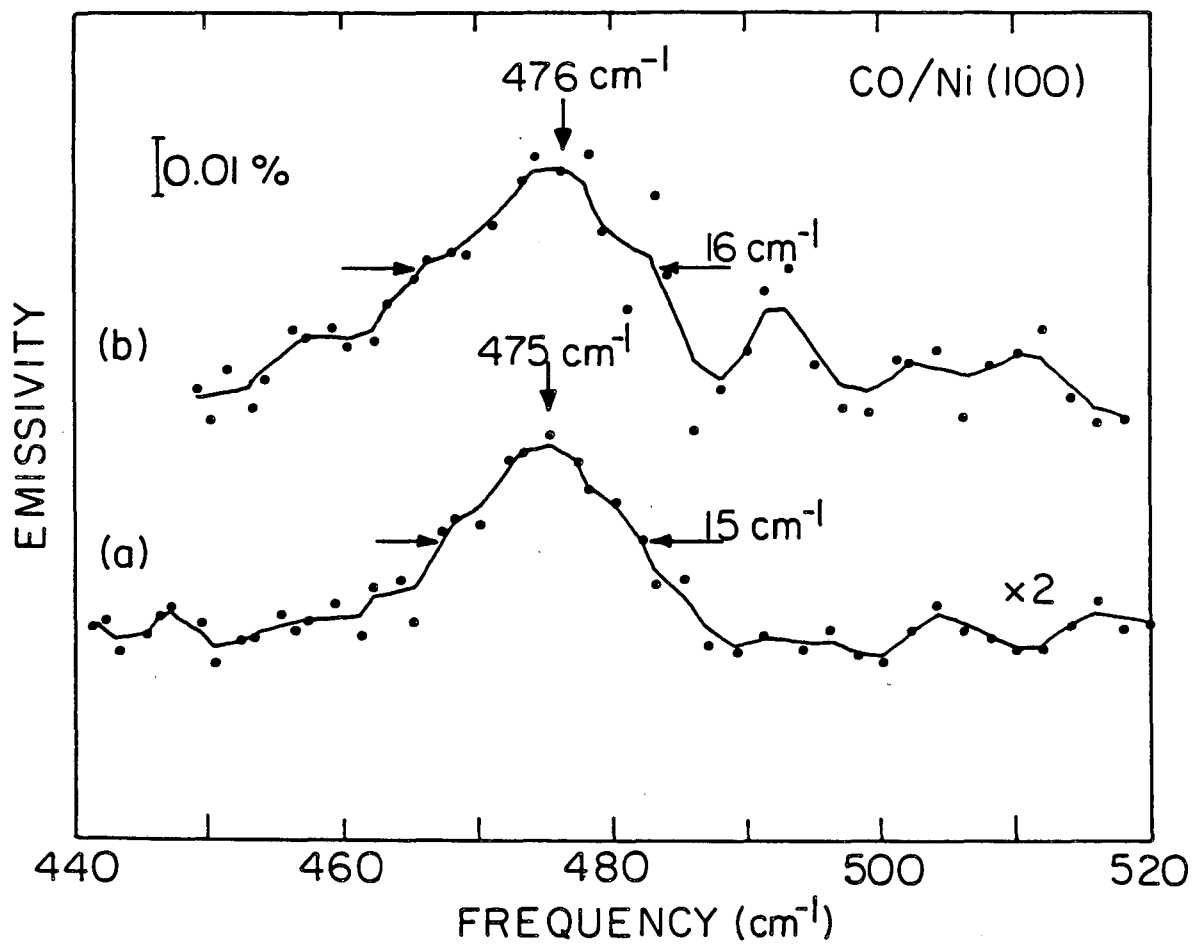
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FIGURE 3



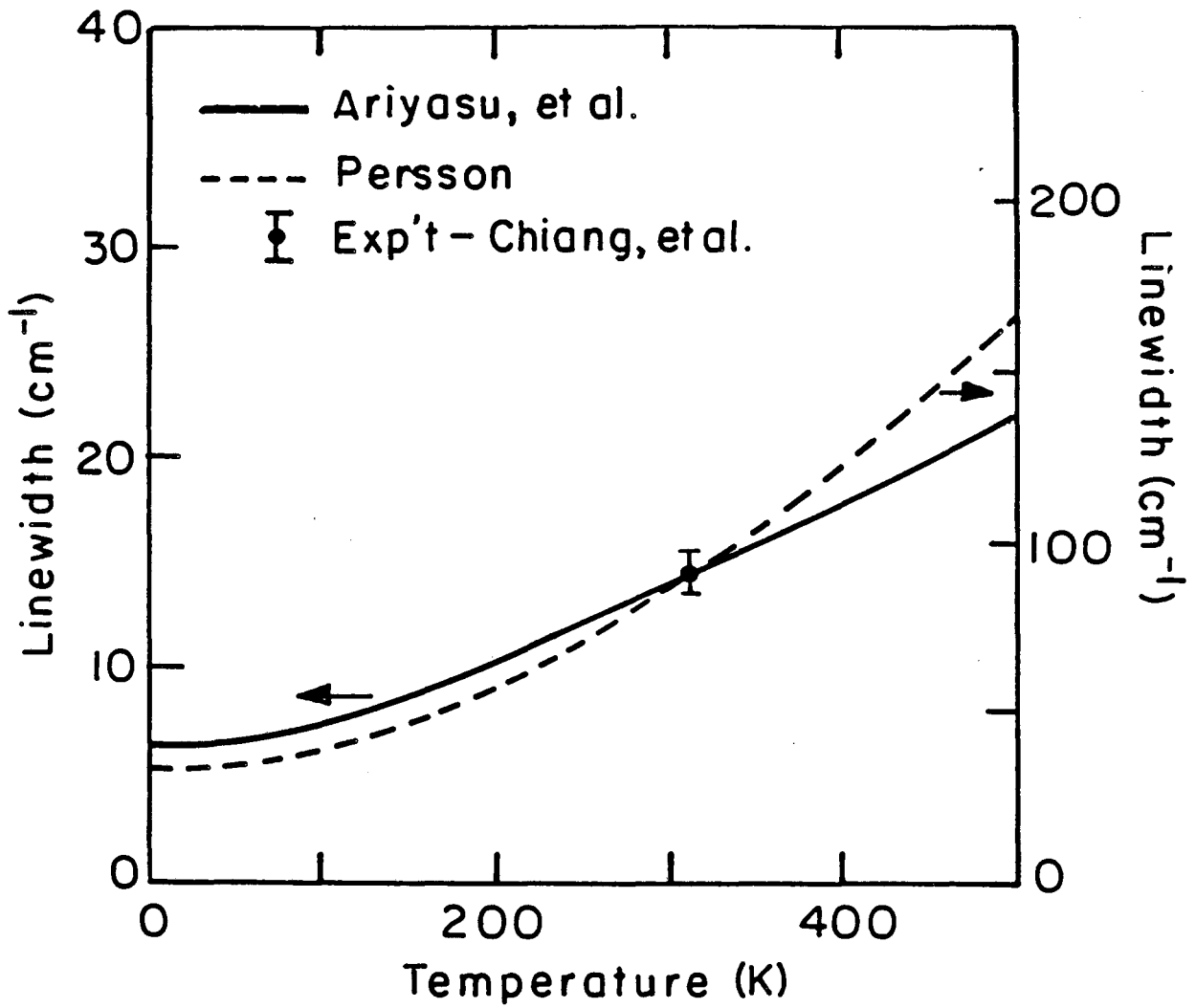
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FIGURE 4



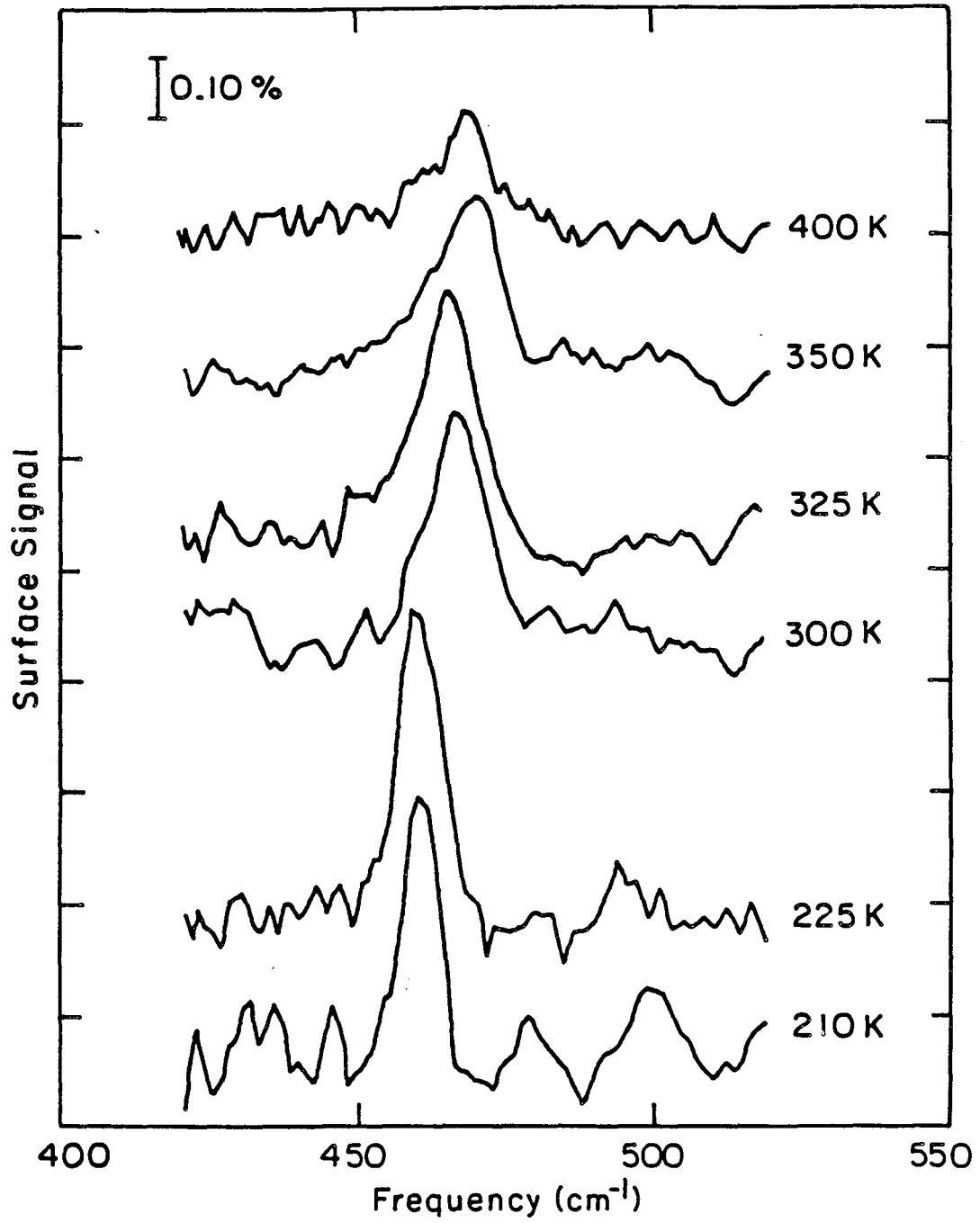
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FIGURE 5



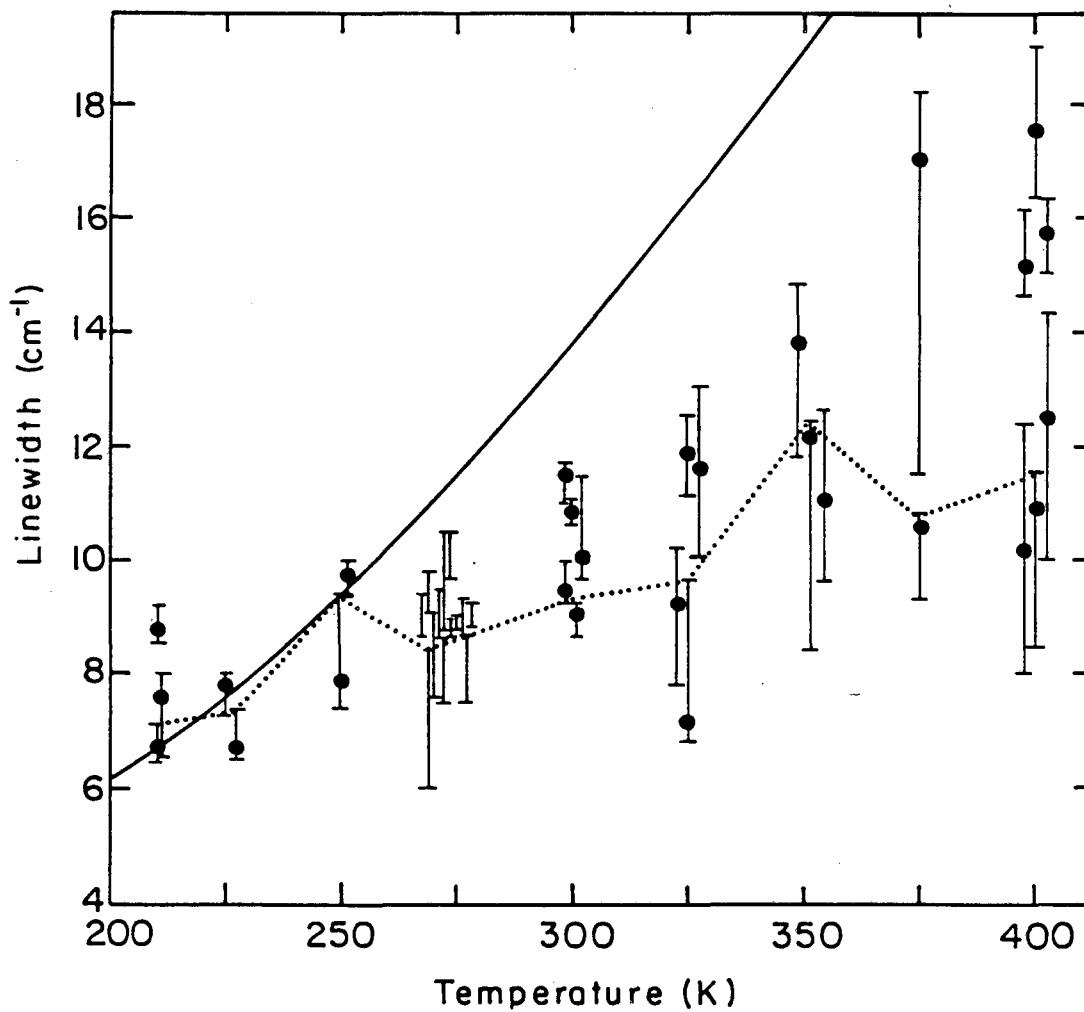
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FIGURE 6



XBL 863-7596

FIGURE 7



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