Infrared Intensity Enhancement of the CN Stretch of HCN by Coadsorbed CO on the Cu(100) Surface

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Reflection absorption infrared spectra reveal a strong enhancement in the intensity of the CN stretch in a mixed ordered overlayer of HCN and CO on the Cu(100) surface. Various combinations of HCN and CO isotopomers show that the intensity enhancement decreases with increasing frequency difference between ν_{CN} and ν_{CO}. The intensity of the 2092 cm^{-1} band of $H^{12}C^{14}N$ is enhanced by a factor of 155 ± 20 through coupling to the 2077 cm^{-1} band of $^{12}C^{16}O$. A simple two-state coupling model explains the isotopomer dependence of the degree of enhancement.

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At the simplest level the vibrational spectrum of a molecule adsorbed on a surface can be understood in terms of the normal modes of an isolated molecule-substrate complex. Corrections to this simple approximation are due both to adsorbate-adsorbate interactions and to anharmonic interactions within the adsorbate-substrate complex. In the latter case, when two vibrational states have similar energies the anharmonic coupling can lead to large shifts in frequency and strong intensity transfer among the states involved. This type of intramolecular coupling is known as a Fermi resonance [1] and is commonly observed in all vibrational spectra, including spectra of surface species. For example, the symmetric CH stretch of molecules containing the CH_3 group often undergoes a Fermi resonance with one or both of the overtones of the CH_3 bending modes [2]. It is not surprising that this general feature of the spectra of CH_3 groups is also observed in surface vibrational spectra [3,4]. The additional vibrational states associated with modes involving displacement of the entire adsorbate molecule relative to the substrate can give rise to Fermi resonances not present in the isolated molecule. Jacob [5] has reported a Fermi resonance between the Ru-CO stretch and a combination band of the hindered rotation plus hindered translation mode of CO on Ru(001). A similar Fermi resonance between the Pt-CO stretch and the CO frustrated translation has been reported for CO on Pt(111) [6]. In addition to these manifestations of anharmonicity within the adsorbate-substrate complex, coverage dependent frequency shifts are commonly observed and are attributed to two effects [7]. The first is due to alterations in the local electronic structure of the adsorbate-substrate complex by neighboring adsorbate molecules. The second is due to vibrational coupling, usually attributed to interactions between the dynamic dipole moments of the molecules. The latter effect is well known in the vibrational spectra of molecular crystals [8], and theories specific to surfaces have been developed [9]. Here we report a type of perturbation in adsorbate vibrational spectra quite distinct from previously considered cases. Like a typical Fermi resonance, the strength of the coupling is due to the near resonance between the states involved. Unlike previous cases, this example involves states of two chemically distinct species: the CO stretch of CO and the CN stretch of HCN in a mixed ordered overlayer on Cu(100).

Our results for CO adsorbed alone on Cu(100) are in general agreement with previous studies [10–15]. Figure 1a shows results from reflection absorption infrared spectroscopy (RAIRS) following a CO exposure that yielded a $c(2 \times 2)$ LEED pattern at 90 K. Although a complete $c(2 \times 2)$ overlayer would correspond to a CO coverage of exactly $1/2$ monolayer (ML), a slightly lower coverage would also be consistent with the results. All spectra reported here were measured with an experimental resolution of 0.5 cm^{-1}. The apparatus used to obtain the spectra and the preparation of the Cu(100) crystal are described in more detail elsewhere [16]. The peak at 2084 cm^{-1} has a full width at half maximum (FWHM) of 4.5 cm^{-1} and corresponds to the CO stretch of molecules adsorbed at on-top sites on the (100) terraces, while the shoulder at 2096 cm^{-1} is due to CO at step sites. As others have noted [10], dipole-dipole coupling between terrace and step CO molecules results in a large transfer of intensity to the step CO, making the 2096 cm^{-1} peak disproportionately large; at saturation the 2096 cm^{-1} peak area is about 30% of the total CO peak area but this corresponds to a step density of at most 3%. In previous RAIRS studies of CO on Cu(100) both lower [12,14] and higher or comparable [11,13] step densities have been reported. Upon exposure to HCN (Fig. 1b), two new peaks at 2092 and 3284 cm^{-1} are seen, with the latter peak due to the CH stretch of HCN. The adsorption of HCN causes ν_{CO} of the terrace site CO to shift to 2078 cm^{-1} and broaden (FWHM = 6.5 cm^{-1}), whereas the 2096 cm^{-1} peak due to CO at the step sites is unaffected. Previous work [15] has shown that at 90 K additional CO can adsorb on the surface to give a saturation coverage of 0.57 ML, in which all of the CO still occupies on-top sites.

Figure 1c shows the spectrum obtained by exposing the crystal to HCN first. The CH stretch is at 3294 cm^{-1} and shows a high frequency tail while no peak is visible in

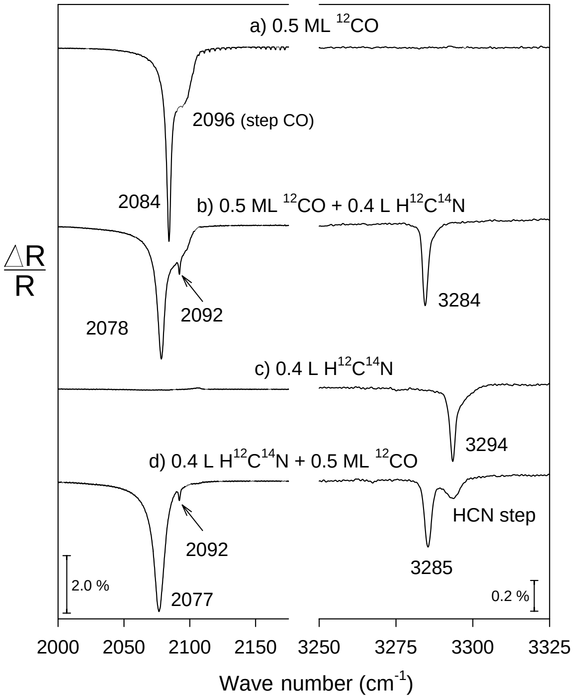

FIG. 1. RAIRS of a mixed ordered overlayer of 0.5 ML of CO with HCN prepared by first exposing to CO (a) followed by HCN (b) compared with first exposing to HCN (c) followed by CO (d). The small ripples in (a) in the 2100–2150 cm^{-1} region are due to gas phase CO generated in the graphite source used for this spectrum. The small feature near 2105 cm^{-1} is due to a low coverage step-site CO peak in the reference spectrum due to background CO adsorption.

the 2000–2200 cm^{-1} region. Although gas phase HCN has a CN stretch frequency of 2089 cm^{-1}, it is anomalously weak with an intensity that is 386 times less than that of the CH stretch [17]. The extreme weakness of the CN stretch of HCN is a characteristic feature of an isolated HCN molecule and the fact that it is unobservable for HCN adsorbed alone on Cu(100) is consistent with the conclusion [18] that HCN weakly interacts with the surface through the nitrogen lone pair with the molecular axis perpendicular to the surface.

Figure 1d shows the result of first exposing the surface to HCN and then dosing the same amount of CO as for Fig. 1a. The reversal of the exposure order has negligible effect on the terrace site CO, whereas the step-site CO peak at 2096 cm^{-1} is completely absent. Instead, the CH stretch now shows a satellite at 3294 cm^{-1}. These results indicate that, when the HCN is first exposed to the clean surface, HCN occupies both terrace and step sites but with a difference in ν_{CH} associated with the two sites too small to resolve. With the HCN blocking the step sites, CO only adsorbs on the terrace sites. A comparison of Figs. 1c and 1d shows that ν_{CH} of terrace HCN redshifts by 10 cm^{-1} in the presence of CO, presumably due to a chemical interaction. The step-site HCN is shifted by a smaller amount and now appears at 3294 cm^{-1}. The fact that the terrace site CO and HCN frequencies are so similar in Figs. 1b and 1d suggests that the same overlayer structure is formed in both cases. In fact, the sharp $c(2 \times 2)$ LEED pattern observed for the conditions of Fig. 1a was unaltered by the 0.4 L (Langmuir; 1 L = 10^{-6} Torr s) HCN exposure used to obtain the spectrum in Fig. 1b. This indicates that the HCN/CO coadsorption system produces a mixed ordered overlayer with the same periodicity as for CO adsorbed alone. Of most significance is the fact that the 2092 cm^{-1} peak is seen regardless of which gas is dosed first, i.e, the 2092 cm^{-1} peak is present even if there is no step-site CO or no step-site HCN. This proves that it is due to a coupling between terrace-site CO and terrace-site HCN.

Figure 2 shows RAIRS results in the CN/CO stretch region for four different pairs of isotopomers. The measured FWHM of the 2092 cm^{-1} peak in Fig. 2a is only 1.4 cm^{-1} (1.3 cm^{-1} with the experimental resolution removed), which further indicates that the HCN is part of a well-ordered overlayer since disordered structures generally give rise to much broader lines. Comparison of the H^{12}C^{14}N/^{12}C^{16}O spectrum with the H^{12}C^{14}N/^{13}C^{16}O spectrum shows that, while ν_{CO} shifts from 2077 to 2026 cm^{-1}, ν_{CN} shifts downward by only 1 cm^{-1}. However, the intensity of the CN stretch, I_{CN}, is substantially reduced. The H^{13}C^{14}N/^{13}C^{16}O spectrum shows that, as the difference in ν_{CN} and ν_{CO} becomes smaller, I_{CN} becomes larger. The I_{CN} intensity enhancement effect appears to depend only on the magnitude of $\nu_{\mathrm{CN}} - \nu_{\mathrm{CO}}$ since, in the H^{12}C^{15}N/^{12}C^{16}O spectrum, ν_{CN} is at a

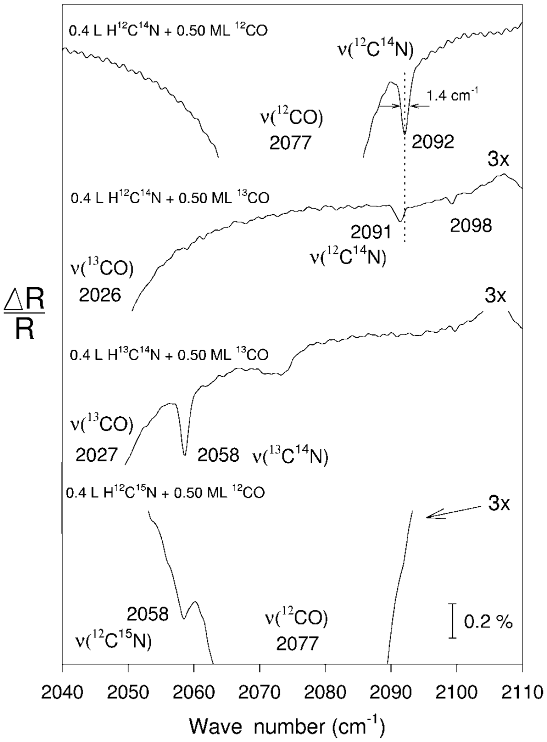

FIG. 2. RAIRS for four different isotopomer pairs of CO and HCN as prepared in Fig. 1d.

lower value than ν_{CO}, yet a strong CN stretch is clearly seen at 2058 cm^{-1}. An enhancement factor, EF, for I_{CN} can be defined as the ratio of CN to CH stretch intensities for HCN coadsorbed with CO on the surface relative to the same intensity ratio in gas phase HCN: $EF = (I_{CN}/I_{CH})_s/(I_{CN}/I_{CH})_g$. The experimental EF values are given in Table I. The intensities are based on fitted peak areas, and the error bars of about 15% reflect different ways of fitting a given spectrum.

The fact that the intensity enhancement is sensitive to $|\nu_{CN} - \nu_{CO}|$ is a clear indication that it is due to vibrational coupling. The dependence of I_{CN} on isotopomer pair is in contrast to the values of ν_{CN} and ν_{CO} in the coadsorption system relative to their frequencies when HCN and CO are adsorbed alone. The fact that ν_{CO} occurs at 2077 cm^{-1} for $H^{12}C^{14}N/^{12}C^{16}O$ and for $H^{12}C^{15}N/^{12}C^{16}O$, even though ν_{CN} is higher than ν_{CO} in the first case but lower than ν_{CO} in the second case, clearly indicates that the shift in ν_{CO} from 2084 to 2078–2077 cm^{-1} when coadsorbed with HCN is due entirely to a chemical effect rather than to vibrational coupling. Thus the vibrational coupling responsible for the large enhancements of I_{CN} has a negligible effect on the frequencies. In general, the near resonant coupling of two states is expected to cause the positions of the states to shift further apart from the values they would have in the absence of a perturbation. But the magnitude of the shift depends on the degree of mixing of the two zero order states. As the treatment given below shows, the mixing of the two states in this case is small enough to have a negligible effect on the frequencies but is still large enough to significantly enhance the extremely low value of I_{CN}. Because the intensity associated with the CO stretch is so much larger than that of the CN stretch, even a very small addition of CO stretch character to the CN stretch vibrational state can have a huge effect on I_{CN}. In principle, the big increase in I_{CN} should be accompanied by a decrease in I_{CO} but this is too small to be detected and virtually all of the intensity of the CO-CN pair is still associated with the CO. This implies that the perturbed and unperturbed CO intensities are equal ($I_{CO} = I^0_{CO}$) and the enhancement factor can equally well be defined as $EF = (I_{CN}/I_{CO})/(I^0_{CN}/I^0_{CO})$. The large effect on I_{CN} is not a consequence of a large mixing of CO and CN vibrational states, rather it is entirely due to the exceedingly small value of I_{CN} in the absence of CO.

TABLE I. Experimental and theoretical enhancement factors for the CN stretch intensity.

Isotopomer pair	$\lvert\nu(\mathrm{CN}) - \nu(\mathrm{CO})\rvert/\mathrm{cm}^{-1}$	Enhancement factor Experiment	Theory
$H^{12}C^{14}N/^{12}C^{16}O$	15	155 ± 20	125
$H^{12}C^{14}N/^{13}C^{16}O$	65	13 ± 2	10
$H^{13}C^{14}N/^{13}C^{16}O$	31	46 ± 7	34
$H^{12}C^{15}N/^{12}C^{16}O$	19	64 ± 10	81

With a few reasonable assumptions, the above arguments can be made more quantitative by applying the same equations used in the treatment of Fermi resonances in molecular crystals, which in turn represent a simple application of first order perturbation theory. For example, the method was used to treat the Fermi resonance between the NCO bend overtone and the NCO symmetric stretch for the cyanate ion in KBr and KCl matrices [19]. The perturbed states, Ψ_{CN} and Ψ_{CO}, can be considered linear combinations of the unperturbed states, Ψ^0_{CN} and Ψ^0_{CO}:

$$\Psi_{CN} = a\Psi^0_{CN} - b\Psi^0_{CO}, \qquad \Psi_{CO} = b\Psi^0_{CN} + a\Psi^0_{CO}.$$

This treatment is the same regardless of whether the unperturbed states refer to states of a single pair of HCN and CO molecules or to a Bloch function with the full two-dimensional periodicity of the layer. In other words, the fact that dipole-dipole coupling leads to a dispersion of ≈ 30 cm^{-1} in ν_{CO} is of little relevance here. The intensity ratio of the perturbed states, I_{CN}/I_{CO}, is given by

$$I_{CN}/I_{CO} = [b + a\mu]^2/[a - b\mu]^2, \tag{1}$$

where μ is the ratio of transition dipole moments for the unperturbed states and is related to the intensity ratio by $\mu^2 = I^0_{CN}/I^0_{CO}$. The a, b coefficients are related to the perturbation matrix element, $W_{12} = \langle\Psi^0_{CN}|W|\Psi^0_{CO}\rangle$, and to the separation of the unperturbed frequencies, δ, by [1]

$$\begin{aligned} a &= \left(\frac{\sqrt{4|W_{12}|^2 + \delta^2} + \delta}{2\sqrt{4|W_{12}|^2 + \delta^2}}\right)^{1/2}, \\ b &= \left(\frac{\sqrt{4|W_{12}|^2 + \delta^2} - \delta}{2\sqrt{4|W_{12}|^2 + \delta^2}}\right)^{1/2}. \end{aligned} \tag{2}$$

The I^0_{CN}/I^0_{CO} ratio is obtained from the observed I_{CH}/I_{CO} ratio and the assumption that the CN stretch to the CH stretch intensity ratio of HCN adsorbed alone on Cu(100) is the same as in gas phase HCN. This then yields $I^0_{CN}/I^0_{CO} = 5.2 \times 10^{-5}$ for $H^{12}C^{14}N/^{12}C^{16}O$. Using the observed ratio of $I_{CN}/I_{CO} = 7.7 \times 10^{-3}$ for the $H^{12}C^{14}N/^{12}C^{16}O$ case in Eq. (1) yields $b/a = 9.5 \times 10^{-2}$ [20]. This confirms that the interaction leads to almost negligible mixing of the two states and that essentially all of the intensity of the 2077/2092 pair is still associated with the CO stretch. Using this b/a ratio and $\delta = 15$ cm^{-1} in Eq. (2) yields $W_{12} = 1.4$ cm^{-1}. Although δ in these equations is the difference between the unperturbed levels, the fact that $\nu(\mathrm{CO}) = 2077 \pm 1$ cm^{-1} regardless of whether $\nu_{CO} < \nu_{CN}$ or $\nu_{CO} > \nu_{CN}$ indicates that ν_{CO} is not measurably shifted by vibrational coupling to the CN stretch. The assumption that ν_{CN} is also the same before and after the vibrational coupling is supported by the analysis below. As Herzberg notes [1], when, as in the case here, δ is large relative to W_{12}, then the perturbed frequencies relative to the unperturbed frequencies are given by

$$\nu_1, \nu_2 = \frac{1}{2}(\nu_1^0 + \nu_2^0) \pm \left(\frac{\delta}{2} + \frac{|W_{12}|^2}{\delta}\right),$$

which in this case yields perturbed frequencies of $\nu_{\mathrm{CO}} = 2076.9$ and $\nu_{\mathrm{CN}} = 2092.1\ \mathrm{cm}^{-1}$, a result that is entirely consistent with the observed spectra. Since $|W_{12}|$ should be the same for all of the isotopomer pairs, we can use the value of $|W_{12}|$ determined for the $\mathrm{H}^{12}\mathrm{C}^{14}\mathrm{N}/^{12}\mathrm{C}^{16}\mathrm{O}$ case to calculate the predicted $I_{\mathrm{CN}}/I_{\mathrm{CO}}$ ratio from Eqs. (1) and (2) for the other isotopomer combinations. Since $4|W_{12}|^2/\delta^2 < 1$ for all pairs of isotopomers, we can simplify the resulting equation by expanding the square root: $(4|W_{12}|^2 + \delta^2)^{1/2} = \delta(4|W_{12}|^2/\delta^2 + 1)^{1/2} \approx \delta + 2|W_{12}|^2/\delta$ to obtain

$$I_{\mathrm{CN}}/I_{\mathrm{CO}} = \left[\frac{|W_{12}| + (\delta^2 + |W_{12}|^2)^{1/2}\mu}{(\delta^2 + |W_{12}|^2)^{1/2} - |W_{12}|\mu}\right]^2.$$

This equation can be further simplified since $|W_{12}|^2 \ll \delta^2$ and $|W_{12}|\mu \ll \delta$ and, if we then divide by μ^2, we get a simple equation with only one adjustable parameter, $|W_{12}|$, for the calculated enhancement factor, EF:

$$EF = \frac{I_{\mathrm{CN}}/I_{\mathrm{CO}}}{I_{\mathrm{CN}}^0/I_{\mathrm{CO}}^0} = \frac{I_{\mathrm{CN}}/I_{\mathrm{CO}}}{\mu^2} = \left(\frac{|W_{12}|}{\delta\mu} + 1\right)^2. \quad (3)$$

Equation (3) indicates that $|W_{12}|$ can be obtained as the slope of the line in a plot of $\sqrt{EF}$ vs $1/\delta\mu$. This yields $|W_{12}| = 1.07\ \mathrm{cm}^{-1}$, which was then used to calculate the theoretical EF values listed in Table I from Eq. (3). The agreement with the experimental values is reasonably good considering the difficulties in measuring intensities accurately and the numerous approximations made in deriving Eq. (3).

The effect observed here is analogous to the sort of vibrational resonance coupling (VRC) that occurs between solute and solvent molecules [21,22]. Unlike the more typical intramolecular Fermi resonance, intermolecular VRC can be due to a perturbation from a term in the potential energy of the form $\partial^2 V/\partial Q_A \partial Q_B$, where Q_A and Q_B are normal modes of two different molecules. When Q_A and Q_B are on the same molecule, by the definition of normal modes, there are no such cross terms in the potential energy. Essentially, VRC associated with such a term is due to the fact that the combined system has normal modes that are different from the normal modes of the two separate molecules. Thus an alternative view of the present system is that the CN and CO stretches can be considered local modes which are only an approximate description of the more rigorous normal modes of the combined HCN/CO/Cu(100) system. The origin of the perturbation that couples the CO and CN stretches could be either a through-substrate mechanical renormalization or a through-space interaction. The latter would likely be dominated by the coupling of transition dipole moments as is usually the case in VRC between different molecules in the liquid phase [22].

The large intensity enhancement observed here should occur whenever there is near resonance between the vibrational frequencies of strong and weak vibrational transitions. It does not require a strong coupling between states and in fact, as in the case here, a weak coupling is preferable so that the strong IR absorber acts only to make otherwise unobservable peaks visible without altering the basic chemisorption properties of the species of interest. Other examples of this effect are currently being investigated.

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