

FIG. 4. Absorptivity for a few modes in CH_3NH_2 as a function of coverage. The dashed lines represent measured values for gaseous CH_3NH_2 . Note that the absorptivities above 50 L are computed by taking a small difference in a large number and hence, are not accurate.

the same peak in the spectrum of adsorbed ethylidyne has an absorbance of only 0.02% at saturation. One would have expected the intensities of the CH stretching modes to be somewhat different in adsorbed ethylidyne and adsorbed methylamine. However, the fact that there is a factor of 250 difference in the intensities of the peaks is quite surprising.

Figure 3 shows how the peak intensities of a few modes in CH_3NH_2 vary with coverage at 120 K. Very large absorbancies are observed for the first monolayer. The NH_2 wagging mode is much more intense than the largest mode in the spectrum of adsorbed CO, and all of the other modes are also substantially enhanced. The first monolayer makes a large change in the observed absorbance, but additional layers

have a smaller effect. One can quantify the enhancement by calculating a differential absorptivity ϵ defined by

$$\epsilon = \cos(\theta_i) d [\ln(I_0/I)] / dN,$$

where N is coverage, θ_i is the incident angle, and I/I_0 is the attenuation of the infrared beam due to the adsorbed layer.

Figure 4 shows how the differential absorptivity varies with exposure. The gas phase absorptivities are included for comparison. Notice that the absorptivity is enhanced by at least 3 orders of magnitude over that observed in the gas phase for the first monolayer. Thus, the IR spectrum of the first monolayer of methylamine on Pt(111) is significantly enhanced by several orders of magnitude over that expected from simple calculations. The enhancement is difficult to explain. However, it clearly is a surface effect as it only occurs in the first few monolayers. Hence, it appears that this is the first observation of surface enhanced infrared spectroscopy.

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Summary Abstract: Formamide adsorption at 80 K on clean and chemically modified Ru(001) surfaces

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As part of a continuing investigation of the chemistry of various organic functional groups on the hexagonally close-packed Ru(001) surface, we have studied recently the adsorption of formamide on clean Ru(001) (Ref. 1) and on Ru(001) with an ordered $p(1 \times 2)$ overlayer of oxygen adatoms ($\theta_{\text{O}} = 0.5$).^{2,3} The experimental techniques that were utilized are electron energy-loss spectroscopy (EELS) and thermal desorption mass spectrometry. Figure 1 shows the EEL spectra that result when (a) a clean Ru(001) surface and (b) a Ru(001)- $p(1 \times 2)$ -O surface are exposed to 0.5-L NH_2CHO at 80 K, and it is clear that different surface spe-

cies are formed in the two cases. On Ru(001)- $p(1 \times 2)$ -O, formamide is molecularly adsorbed via an electron lone pair on the oxygen atom in an $\eta^1(\text{O})-\text{NH}_2\text{CHO}$ configuration.^{2,3} All of the expected vibrational modes of such a species are observed, including $\nu_a(\text{NH}_2)$, 3490 cm^{-1} ; $\nu_s(\text{NH}_2)$, 3230 cm^{-1} ; $\nu(\text{CH})$, 2940 cm^{-1} ; $\nu(\text{CO})$, 1660 cm^{-1} ; $\delta(\text{NH}_2)$, 1585 cm^{-1} ; $\nu(\text{CN})$ and/or $\delta(\text{CH})$, 1360 cm^{-1} ; and $\rho(\text{NH}_2)$, 1110 cm^{-1} . These frequencies are in good general agreement with those of gas phase⁴ and liquid formamide,⁵ and the assignments have been confirmed by measuring corresponding EEL spectra for ND_2CHO .³ The

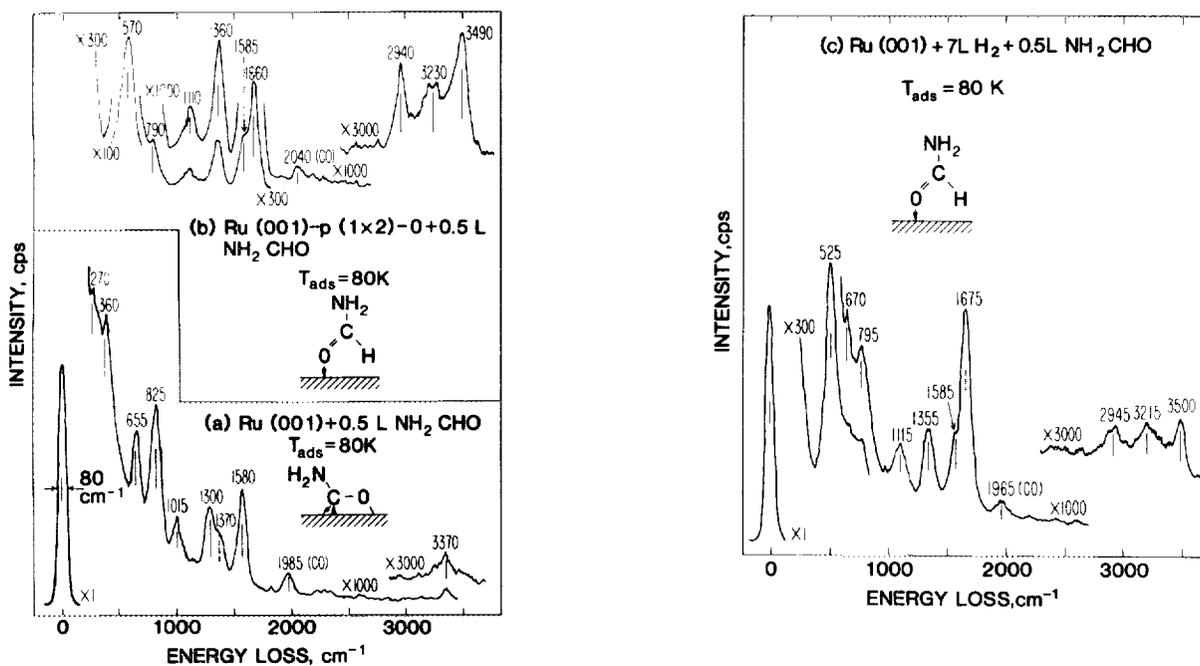


FIG. 1. The EEL spectra that result following 0.5-L formamide exposures to (a) clean Ru(001), (b) Ru(001)- $p(1 \times 2)$ -O, and (c) hydrogen-presaturated Ru(001) at 80 K.

intense loss feature at 570 cm^{-1} is due primarily to ν_s (RuO) of the preadsorbed oxygen adatoms.⁶ The carbonyl stretching frequency of 1660 cm^{-1} is indicative of a carbon-oxygen double bond, and its reduction from the gas phase value of 1734 cm^{-1} is strongly suggestive of O coordination to the surface (rather than N coordination), in analogy to data for organometallic compounds of amides and urea.⁷ A trivial amount of CO is adsorbed from the chamber background but there is no evidence for molecular dissociation.

The EEL spectrum obtained on clean Ru(001) is quite different and is due to the formation of an $\eta^2(\text{C,O})\text{-NH}_2\text{CO}$ species, as has been discussed in detail elsewhere.¹ Note especially the lack of a $\nu(\text{CH})$ loss feature and the absence of the intense $\nu(\text{CO})$ loss feature at 1660 cm^{-1} . Comparison to corresponding EEL spectra for ND_2CHO supports the following mode assignments¹: $\nu_s(\text{NH}_2)$, 3370 cm^{-1} [$\nu_a(\text{NH}_2)$ is resolved near 3500 cm^{-1} in off-specular spectra]; $\omega(\text{NH}_2)$, 825 cm^{-1} ; $\delta(\text{NCO})$, 655 cm^{-1} ; and $\nu(\text{Ru-NH}_2\text{CO})$, 360 and 270 cm^{-1} . The loss features between 1000 and 1600 cm^{-1} involve strongly coupled modes so that specific assignments are less meaningful. For example, the loss feature at 1580 cm^{-1} shifts down to 1440 cm^{-1} upon N deuteration and thus has significant $\delta(\text{NH}_2)$ and $\nu_a(\text{NCO})$ character.¹ In summary, the adsorption of low coverages of formamide on clean Ru(001) at 80 K results in CH bond cleavage and substantial rehybridization of the carbonyl double bond to produce an $\eta^2(\text{C,O})\text{-NH}_2\text{CO}$ species.

The results obtained with formamide on Ru(001) parallel earlier results obtained in the study of acetone⁸ and formaldehyde⁹ on this surface, where at 80 K $\eta^2(\text{C,O})$ bonding predominates on the clean surface but only $\eta^1(\text{O})$ -bonded species are formed in the presence of preadsorbed oxygen (with $\theta_{\text{O}} = 0.25$). This has been rationalized in terms of the electron-withdrawing effect of the electronegative oxygen

adatoms, which increase the surface work function by 1.06 eV (Ref. 10) and thus favor lone pair donor bonding over rehybridization of the carbonyl double bond. Steric effects could also play a role in inhibiting the conversion of $\eta^1(\text{O})\text{-NH}_2\text{CHO}$ to $\eta^2(\text{C,O})\text{-NH}_2\text{CO}$ on Ru(001)- $p(1 \times 2)$ -O. It is thus of interest to investigate the adsorption of formamide on hydrogen-presaturated Ru(001) ($\theta_{\text{H}} \sim 0.85$).¹¹ Unlike oxygen, hydrogen has nearly the same electronegativity as ruthenium and thus has very little effect on the surface work function.¹²

Figure 1(c) shows the EEL spectrum that results following a 0.5-L NH_2CHO exposure at 80 K to a Ru(001) surface that has been presaturated with hydrogen adatoms by exposure to 7-L H_2 .¹³ While there are minor differences in the frequencies and intensities of some modes compared to Fig. 1(b), it is clear that the same $\eta^1(\text{O})\text{-NH}_2\text{CHO}$ species is formed that is formed on Ru(001)- $p(1 \times 2)$ -O. Note especially the carbonyl stretching loss feature at 1675 cm^{-1} and the CH stretching loss feature at 2945 cm^{-1} , which are among the key diagnostic features in distinguishing $\eta^1(\text{O})\text{-NH}_2\text{CHO}$ from $\eta^2(\text{C,O})\text{-NH}_2\text{CO}$. The intense loss feature at 525 cm^{-1} appears to be of a mixed nature³ and probably derives intensity from both the $\delta(\text{NCO})$ and $\omega(\text{NH}_2)$ modes, while the weaker loss features near 670 and 795 cm^{-1} appear to be primarily of NH_2 deformation character, i.e., involving $\tau(\text{NH}_2)$ and $\omega(\text{NH}_2)$.

Since the formation of $\eta^1(\text{O})\text{-NH}_2\text{CHO}$ on hydrogen-presaturated Ru(001) at 80 K cannot be explained in terms of a surface work function change that tends to favor η^1 bonding over η^2 bonding, either a steric effect or another type of electronic effect must be preventing the formation of $\eta^2(\text{C,O})\text{-NH}_2\text{CO}$. In the steric category, hydrogen adatoms could simply block surface sites that are necessary for the formamide carbon atom to coordinate to the surface.