

FIG. 4. Absorptivity for a few modes in  $\text{CH}_3\text{NH}_2$  as a function of coverage. The dashed lines represent measured values for gaseous  $\text{CH}_3\text{NH}_2$ . 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  $\text{CH}_3\text{NH}_2$  vary with coverage at 120 K. Very large absorbancies are observed for the first monolayer. The  $\text{NH}_2$  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  $\epsilon$  defined by

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

where  $N$  is coverage,  $\theta_i$  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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<sup>1)</sup> Correspondence should be addressed to this author.

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

J. E. Parmeter, U. Schwalke, and W. H. Weinberg

*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125*

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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 ( $\theta_{\text{O}} = 0.5$ ).<sup>2,3</sup> 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  $\text{NH}_2\text{CHO}$  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.<sup>2,3</sup> All of the expected vibrational modes of such a species are observed, including  $\nu_a(\text{NH}_2)$ , 3490  $\text{cm}^{-1}$ ;  $\nu_s(\text{NH}_2)$ , 3230  $\text{cm}^{-1}$ ;  $\nu(\text{CH})$ , 2940  $\text{cm}^{-1}$ ;  $\nu(\text{CO})$ , 1660  $\text{cm}^{-1}$ ;  $\delta(\text{NH}_2)$ , 1585  $\text{cm}^{-1}$ ;  $\nu(\text{CN})$  and/or  $\delta(\text{CH})$ , 1360  $\text{cm}^{-1}$ ; and  $\rho(\text{NH}_2)$ , 1110  $\text{cm}^{-1}$ . These frequencies are in good general agreement with those of gas phase<sup>4</sup> and liquid formamide,<sup>5</sup> and the assignments have been confirmed by measuring corresponding EEL spectra for  $\text{ND}_2\text{CHO}$ .<sup>3</sup> The

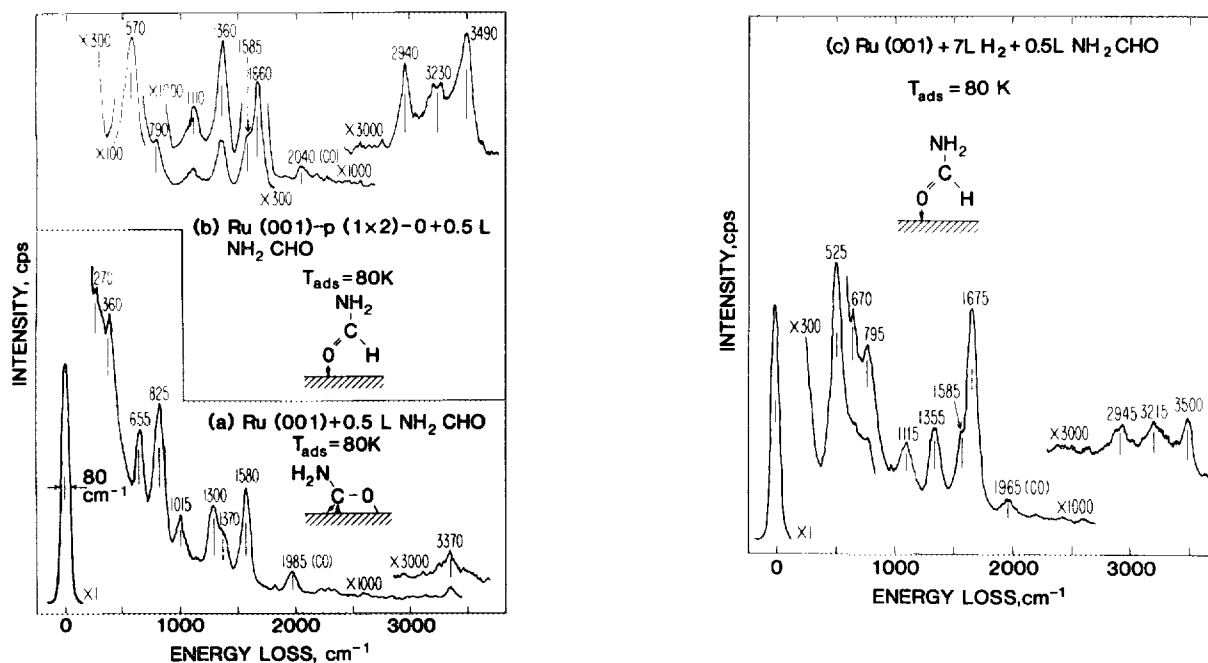


FIG. 1. The EEL spectra that result following 0.5-L formamide exposures to (a) clean Ru(001), (b) Ru(001)- $p(1 \times 2)$ -O, and (c) hydrogen-presaturated Ru(001) at 80 K.

intense loss feature at  $570 \text{ cm}^{-1}$  is due primarily to  $\nu_s$  (RuO) of the preadsorbed oxygen adatoms.<sup>6</sup> The carbonyl stretching frequency of  $1660 \text{ cm}^{-1}$  is indicative of a carbon-oxygen double bond, and its reduction from the gas phase value of  $1734 \text{ cm}^{-1}$  is strongly suggestive of O coordination to the surface (rather than N coordination), in analogy to data for organometallic compounds of amides and urea.<sup>7</sup> 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.<sup>1</sup> Note especially the lack of a  $\nu(\text{CH})$  loss feature and the absence of the intense  $\nu(\text{CO})$  loss feature at  $1660 \text{ cm}^{-1}$ . Comparison to corresponding EEL spectra for  $\text{ND}_2\text{CHO}$  supports the following mode assignments<sup>1</sup>:  $\nu_s(\text{NH}_2)$ ,  $3370 \text{ cm}^{-1}$  [ $\nu_a(\text{NH}_2)$  is resolved near  $3500 \text{ cm}^{-1}$  in off-specular spectra];  $\omega(\text{NH}_2)$ ,  $825 \text{ cm}^{-1}$ ;  $\delta(\text{NCO})$ ,  $655 \text{ cm}^{-1}$ ; and  $\nu(\text{Ru-NH}_2\text{CO})$ ,  $360$  and  $270 \text{ cm}^{-1}$ . The loss features between  $1000$  and  $1600 \text{ cm}^{-1}$  involve strongly coupled modes so that specific assignments are less meaningful. For example, the loss feature at  $1580 \text{ cm}^{-1}$  shifts down to  $1440 \text{ cm}^{-1}$  upon N deuteration and thus has significant  $\delta(\text{NH}_2)$  and  $\nu_a(\text{NCO})$  character.<sup>1</sup> 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 acetone<sup>8</sup> and formaldehyde<sup>9</sup> 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) ( $\theta_{\text{H}} \sim 0.85$ ).<sup>11</sup> Unlike oxygen, hydrogen has nearly the same electronegativity as ruthenium and thus has very little effect on the surface work function.<sup>12</sup>

Figure 1(c) shows the EEL spectrum that results following a 0.5-L  $\text{NH}_2\text{CHO}$  exposure at 80 K to a Ru(001) surface that has been presaturated with hydrogen adatoms by exposure to 7-L  $\text{H}_2$ .<sup>13</sup> 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  $1675 \text{ cm}^{-1}$  and the CH stretching loss feature at  $2945 \text{ cm}^{-1}$ , 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  $525 \text{ cm}^{-1}$  appears to be of a mixed nature<sup>3</sup> and probably derives intensity from both the  $\delta(\text{NCO})$  and  $\omega(\text{NH}_2)$  modes, while the weaker loss features near  $670$  and  $795 \text{ cm}^{-1}$  appear to be primarily of  $\text{NH}_2$  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  $\eta^1$  bonding over  $\eta^2$  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.