

Coadsorption of Oxygen and Water on Ru(001): Vibrational and Structural Properties

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A thermally induced change in the vibrational properties of a coadsorbed oxygen-water overlayer on Ru(001) is attributed to the formation of a local O-H₂O complex. An O-H stretching mode of this complex is observed in electron-energy-loss data, but not in infrared reflection-absorption data available from another laboratory. This provides the first direct experimental evidence of a case in which the surface dipolar selection rule applies in an infrared but not in an energy-loss measurement.

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Recent studies of the coadsorption of oxygen and H₂O on hexagonally close-packed surfaces of Ni, Ru, and Pt have provided several very intriguing results. On Ni, electron-stimulated-desorption ion angular distribution (ESDIAD) measurements¹ indicate that adsorbed molecular water forms structures at 80 K which are azimuthally oriented with respect to the substrate atoms only if oxygen is coadsorbed. In the case of Ru, infrared reflection-absorption spectroscopy (IRAS) showed complete suppression of the infrared activity of the O-H stretching mode of adsorbed water in the presence of a critical coverage of coadsorbed oxygen.² On Pt, vibrational and photoelectron spectra were interpreted as evidence for H₂O dissociation and the formation of hydroxyl species only if oxygen is preadsorbed.³ In all cases, therefore, the presence of adsorbed oxygen exerts a strong effect on the properties of water which is coadsorbed. This effect is evident in the present study also.

We have used electron energy-loss spectroscopy (EELS) to study the vibrational properties of a mixed O-H₂O adlayer on Ru(001). We observe that a critical coverage of oxygen can affect the intermolecular structure of the adsorbed water. The O-H stretching vibration which we observe in EELS for this structure has been shown to be IRAS inactive.² Therefore, different vibrational "selection rules" must be operative in the IRAS and EELS measurements in this case.

The EEL spectra of water adsorbed on clean Ru(001) have been studied extensively in this laboratory, and experimental details have been reported previously.⁴ Specific vibrational features have been shown to reflect the intermolecular and intramolecular structure of the adsorbed H₂O overlayer. The frequencies of the losses due to

frustrated rotations of molecular H₂O depend upon the degree of local order in the adlayer.⁴ Two of the other fundamental vibrations of H₂O, the scissoring mode (v_s) and the O-H stretching mode (v_{OH}), are not sensitive to this type of order. However, v_s can be used as evidence of nondissociative adsorption since it involves the motion of all three atoms in the H₂O molecule. Significant dissociation should affect strongly the intensity of this vibrational feature. The frequency of v_{OH} is sensitive to intermolecular hydrogen bond formation, occurring at 3630–3750 cm⁻¹ for isolated H₂O molecules, and 3000–3600 cm⁻¹ in ice.

Figure 1 shows a series of EEL spectra following sequential adsorption of oxygen and H₂O on Ru(001) at 95 K. The oxygen overlayer was prepared by adsorbing oxygen at 95 K, heating briefly to 350 K to order the adlayer,⁵ and receding in vacuum. Following a low initial exposure of O₂ [0.1 L; 1 L (langmuir)=10⁻⁶ Torr sec] the EEL spectrum, shown in Fig. 1, curve *a*, is similar to that which would be obtained in the absence of oxygen for this exposure of H₂O. The spectrum of pure H₂O for an exposure of 1.1 L at 95 K would show losses due to a frustrated rotation (libration) at 820 cm⁻¹, a combination of a frustrated rotation and a frustrated translation at 460 cm⁻¹, v_s at 1580 cm⁻¹, and v_{OH} at 3350 ± 50 cm⁻¹ with a full width at half maximum (FWHM) of 500 cm⁻¹.⁴ Within experimental uncertainty, the three features highest in frequency are unaffected by the small initial coverage of coadsorbed oxygen in Fig. 1, curve *a*. The lowest frequency occurs at 530–560 cm⁻¹ rather than 460 cm⁻¹, which may be partly due to overlap with the Ru-O vibration of the coadsorbed atomic oxygen occurring at 520–540 cm⁻¹.⁶ This peak

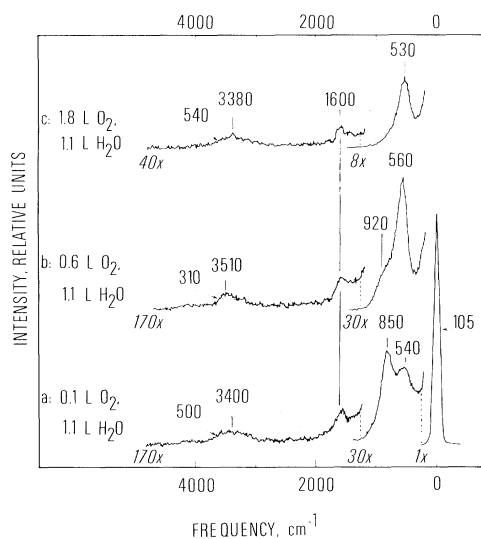


FIG. 1. Coadsorption of H₂O and oxygen at 95 K, for various exposures of oxygen. The peak positions and halfwidths are noted in inverse centimeters.

shifts downward by a factor of 1.21 upon substitution of D₂O, indicating that it contains some combination of contributions from the Ru-OH₂ vibration, the Ru-O vibration, and H₂O libration(s), all of which occur in this frequency range.⁴⁻⁶ This description applies to the 530–560-cm⁻¹ loss in all of the coadsorption measurements of Figs. 1 and 2, based upon similar deuteration results.

The scissoring mode is unaffected by increasing coverages of oxygen, occurring at 1600±10 cm⁻¹ and with constant intensity in Fig. 1, curves *a*–*c*. The ν_{OH} feature is also unchanged in frequency or FWHM, within experimental uncertainty, when the initial exposure of oxygen is ≤ 0.1 L (Fig. 1, curve *a*) or ≥ 1.2 L (Fig. 1, curve *c*). However, at an intermediate initial exposure of oxygen (0.6 L in Fig. 1, curve *b*), the ν_{OH} feature sharpens (FWHM=230–310 cm⁻¹) and shifts upward in frequency to 3480–3530 cm⁻¹ (3510 cm⁻¹ in Fig. 1, curve *b*). This frequency is still in the range of hydrogen-bonded O-H groups, indicative of cluster formation. Moreover, the librational features are influenced strongly by coadsorbed oxygen at exposures greater than 0.1-L O₂: The 850-cm⁻¹ peak of Fig. 1, curve *a* disappears entirely and a single peak at 530–560 cm⁻¹ remains (Fig. 1, curves *b* and *c*). Significantly, there is a small shoulder at 920 cm⁻¹ in Fig. 1, curve *b*, which is observed only at intermediate oxygen coverages and which is associated, therefore, with the changes in frequency

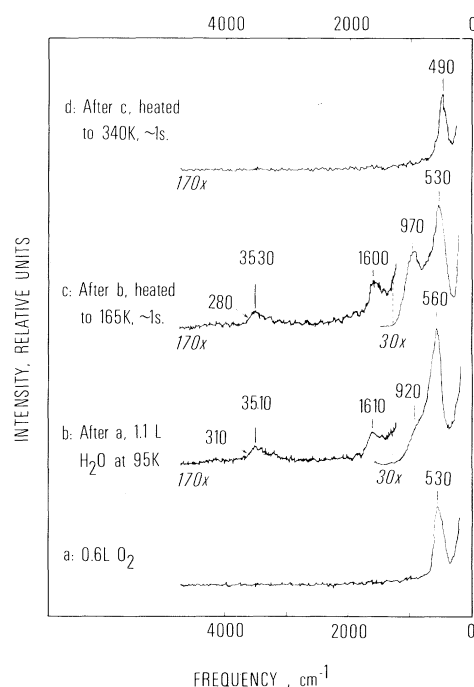


FIG. 2. Coadsorption of H₂O and oxygen at 95 K, followed by sequential heating, as indicated. The peak positions and halfwidths are noted in inverse centimeters.

and FWHM of ν_{OH} .

Figure 2 shows the result of heating the surface of Fig. 1, curve *b*. The small shoulder at 920 cm⁻¹ in Fig. 2, curve *b* (also Fig. 1, curve *b*) develops into an intense peak at 970 cm⁻¹ when the surface is heated to 165 K, as shown in Fig. 2, curve *c*. It disappears only at temperatures above 190 K, leaving a single loss feature due to chemisorbed oxygen at 490 cm⁻¹, shown in Fig. 2, curve *d*. The peak at 970 cm⁻¹ is higher in frequency by 30 cm⁻¹ than any librational feature observed previously for H₂O on clean Ru(001).⁴ EEL spectra obtained for adsorption of D₂O under conditions corresponding to Fig. 2, curve *c* show the feature at 970 cm⁻¹ shifted by a factor of 1.4 to 690 cm⁻¹, confirming its assignment as a librational mode.^{3,4} The feature at 530 cm⁻¹, however, shifts only by a factor of 1.23 to 430 cm⁻¹ upon deuteration and must therefore be of mixed character, as in Fig. 1, curves *a* and *c*. The EELS feature at 970 cm⁻¹ could not be produced by heating if the initial oxygen exposure was ≤ 0.1 L (Fig. 1, curve *a*) or ≥ 1.2 L (Fig. 1, curve *c*), nor if exposures of H₂O greater than 1.1 L were used. This coverage dependence suggests that the 970-cm⁻¹ feature which develops upon heating

to 165 K is associated with the narrow, high-frequency ν_{OH} mode which is apparent already at 95 K under these conditions, i.e., these two effects have the same origin.

The heating sequence of Fig. 2, curves *b* and *c*, leaves the ν_s transition unchanged in intensity or frequency. Consequently, it may be concluded that the frustrated rotation at 970 cm^{-1} in Fig. 2 does not signal an intramolecular change (dissociation), but rather a thermally induced change in the intermolecular structure of the mixed O-H₂O adlayer. The effect of heating to 165 K may be to improve the long-range order of an adlayer structure which has short-range order already at 95 K.

Several comments can be made concerning the structure which forms in Fig. 2, curves *b* and *c*. First, the dependence upon relative coverages of H₂O and O clearly rules out island formation and segregation of the two species. Some mixed structure forms which requires a specific ratio of H₂O and O. ESDIAD has shown that such a structure exists for O and H₂O coadsorbed on Ni(111) at 80 K, with the H₂O arranged in three-fold azimuthal symmetry around a central oxygen adatom.¹ The O-H₂O interaction is proposed to occur via hydrogen bonds between one O adatom and three H₂O admolecules. Such a structure, requiring a particular stoichiometry, could also form on Ru(001). Then, if the initial coverage of O is low (≤ 0.1 L in our experiments), its relative influence would be small, as in Fig. 1, curve *a*. If the initial coverage is high (≥ 1.2 L), it may be sterically unfavorable for these specific H₂O-O complexes to form, as in Fig. 1, curve *c*. Here the influence of the oxygen is still evident, however, in the single low-frequency feature at $530\text{--}560\text{ cm}^{-1}$, compared to Fig. 1, curve *a*. In this context, the low-frequency feature at $530\text{--}560\text{ cm}^{-1}$ is associated with an O-H₂O entity which is not locally well ordered because of the influence of excess oxygen, whereas the 970-cm^{-1} feature signals an O-H₂O complex with a specific local structure. Under the conditions where the latter complex forms in our experiments (Fig. 2, curves *b* and *c*), the oxygen forms a $p(2\times 2)$ lattice⁷ with close to its ideal coverage of 0.25 monolayers, and the H₂O coverage is 0.3–0.4, on the basis of thermal desorption data. With these two facts, a general model can be proposed in which H₂O forms intermolecularly hydrogen-bonded hexamers, each of which is oriented azimuthally on the surface by hydrogen bonding to an underlying triangle of O adatoms from the $p(2\times 2)$ lat-

tice. If all H₂O hexamers are equivalent, the absolute coverage of H₂O is then 0.375, in good agreement with experiment.

Comparison between the IRAS data of Kretzschmar *et al.*² and EELS data is based partly upon the coverage dependences observed in both sets of experiments. Preadsorbed oxygen can suppress completely the ir absorption of ν_{OH} if the coverage of H₂O is less than some critical value, $\Theta_{\text{H}_2\text{O}}^c$. This $\Theta_{\text{H}_2\text{O}}^c$ is itself a function of the coverage of preadsorbed oxygen; for exposures of oxygen equal to zero or above 1.0 L no suppression exists ($\Theta_{\text{H}_2\text{O}}^c = 0$). As oxygen exposure is varied from 0 to 1.0 L, however, $\Theta_{\text{H}_2\text{O}}^c$ first increases smoothly, reaching a maximum of 1.5-L H₂O at 0.5-L O₂, then decreases again to zero at 1.0-L O₂.³ The exposures of O₂ and H₂O at which $\Theta_{\text{H}_2\text{O}}^c$ reaches its maximum value in the IRAS data³ are comparable to the exposures in the EELS experiment of Fig. 1, curve *b*.

Thus, there are three experimental phenomena which are only observed within a limited range of O and H₂O coverages: (1) the suppression of the ir activity of ν_{OH} at 85 K²; (2) the sharp ν_{OH} feature observed at $3480\text{--}3530\text{ cm}^{-1}$ in EELS (Fig. 2, curves *b* and *c*); and (3) the thermally induced rearrangement signaled by the 970-cm^{-1} feature in the EEL spectra. We propose that all three phenomena have the same origin: the formation of a hydrogen-bonded O-H₂O structure with local order at 95 K and long-range order at 165 K. Indeed, Kretzschmar *et al.* proposed that the ir activity of the 3400-cm^{-1} absorption peak was suppressed by coadsorbed oxygen due to a hydrogen-bonded complex between the two adsorbed species.²

A closer examination of ν_{OH} provides more insight into the connection between the IRAS and EELS data. In view of the fact that significant dissociation of H₂O does not occur in our coadsorption experiments, we begin by identifying the sharp ν_{OH} feature at $3480\text{--}3530\text{ cm}^{-1}$ in these experiments as the same feature resolved in off-specular EEL measurements at 3520 cm^{-1} for H₂O on clean Ru(001).⁴ In these previous data, the broad ν_{OH} loss at 3350 cm^{-1} in specular scattering was replaced by two narrower features at 3520 and 3240 cm^{-1} in off-specular scattering, the latter two losses having relatively more isotropic angular intensity distributions. It was postulated⁴ that there is a dipolar-enhanced EEL peak at 3350 cm^{-1} , the intensity of which is maximized in the specular direction,⁸ and two nondipolar features at 3520 and 3240 cm^{-1} . Since the

dipolar selection rule is thought to apply rigorously in IRAS, the two nondipolar losses would be IRAS inactive. This also explains the FWHM of $\nu_{\text{OH}}^{\text{e}}$ in specular EELS compared to the corresponding IRAS band: 500 and 230 cm^{-1} , respectively. The broader halfwidth in specular EELS of pure H_2O is due to three overlapping features, two of which are forbidden in IRAS.

The comparison of the IRAS and EELS data which has been made for pure H_2O can thus be extended to the O- H_2O coadsorption measurements. We propose that the sharp ν_{OH} feature at 3480–3530 cm^{-1} in the EELS data of Fig. 1, curve *b*, which has an isotropic distribution of off-specular intensity similar to that on the clean surface, is not dipolar enhanced and therefore is IRAS inactive. The other two losses, which would occur on clean Ru(001) at 3350 ± 50 and 3240 cm^{-1} , do not appear because of the presence of oxygen. For initial exposures of oxygen $\leq 0.1 \text{ L}$ or $\geq 1.2 \text{ L}$ (cf. Fig. 1, curves *a* and *c*), the influence on ν_{OH} is relatively small, and the dipolar-enhanced (ir-active) mode centered at 3350 cm^{-1} again appears both in the specular EELS and the IRAS data. The observation of ν_{OH} at 3480–3530 cm^{-1} in the EEL spectra but not in the IRAS data² for coadsorbed O and H_2O on Ru(001) is clear experimental evidence of different vibrational scatter-

ing mechanisms in the two types of spectroscopies.

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