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Electron energy loss spectroscopy of H₂S adsorbed on Ni(100)

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H₂S adsorption has been studied on Ni(100) at temperatures between 110–295 K by means of electron energy loss spectroscopy, low-energy electron diffraction and Auger spectroscopy. Coverage dependence of the H₂S adsorption has been studied at 110 K. At low coverages H₂S dissociates to S_{ads} + H_{ads}. At higher coverages two distinct molecular species are observed; H₂S with C_{2v} symmetry (highest coverages) and either HS or H₂S with C_s symmetry (intermediate coverages). H_{ads} coexists with the two molecular species and S_{ads}, and a H–Ni stretching frequency of 650 cm^{−1} suggests a four-fold hollow site for H_{ads}. A saturation coverage is reached which produces a faint c(2×2) LEED pattern, and a comparison with D₂S is made at this coverage. The temperature-dependent spectra shown dissociation of the molecular species at ~170 K and H_{ads} recombining and leaving the surface at 220 K.

I. INTRODUCTION

The role of sulfur-containing compounds in atmospheric pollution and the related necessity of removing sulfur from coal and petroleum products hardly need stressing. In addition, many reactions transforming coal and petroleum products into more valuable chemicals use catalysts of rare or costly materials that are eventually poisoned by sulfur. The need for understanding the chemistry of sulfur on metal surfaces and its relation to the above problems is widely understood, and a lot of effort is being expended in this area. However, the vast majority of the work so far has dealt with atomic sulfur on various metal surfaces.¹ Little work has been done on the adsorption and subsequent reactions of molecular sulfur-containing compounds which are more relevant to the actual process of sulfur extraction. It is generally necessary to carry out such studies at low temperatures in order to observe stable molecular adsorption on a time scale of a surface measurement. These studies include spectroscopic studies^{2–4} and nonspectroscopic studies on W,⁵ Ag,⁵ Ni,⁶ and Pb.⁷ The spectroscopic studies all used ultraviolet photoelectron spectroscopy (UPS) as the primary tool which identifies molecular and atomic species on the surface. Fisher studied the coverage dependence of H₂S/Ru(110)² at 80 K. Bhattacharaya³ found a small amount of molecular HS on W(100) at room temperature. On polycrystalline Ni, Brundle and Carley⁴ found that at 120 K molecular adsorption was occurring, though some degree of dissociation was considered possible.

We report a fairly complete characterization of the adsorption and decomposition reactions of H₂S on Ni(100). Electron energy loss spectroscopy (EELS) has been used to characterize the coverage dependence of this system at 110 K (Sec. III A) and the temperature dependence of the high coverage sample (Sec. III B). Like the abovementioned UPS studies, EELS has proven to be very useful for identifying both molecular and atomic species. In addition, direct spectroscopic information for hydrogen adsorption is reported, which gives qualitative structural information.

II. EXPERIMENTAL

Measurements were taken with an EEL spectrometer recently constructed in our laboratory.⁸ Briefly, the design is

based on an electron monochromator with two sets of hemispheres of 1 in. mean radius and an analyzer with a single set of 2 1/4 in. mean radius hemispheres, rotatable about two perpendicular axes and covering a solid angle of 2 π . The electron impact energy was nominally 1.60 eV and a resolution of 50 cm^{−1} was typically obtained. All spectra were taken in the specular direction with an incident angle of 55° from the normal.

A high-purity nickel crystal, oriented and cut to within 1° of the (100) plane, was mounted in an ultrahigh vacuum chamber having a base pressure of 1×10^{−10} Torr. The crystal was cleaned by a previously described procedure.⁹ Carbon, oxygen, and sulfur impurity levels were less than detection limits of retarding field Auger spectroscopy, and no impurities other than small amounts of CO in some EEL spectra were observed. Spectroscopic grade H₂S obtained from Matheson was directed at the liquid nitrogen cooled surface by means of an effusive beam. A one second exposure to the effusive beam corresponds to ~0.05–0.1 L (1 L = 1 Langmuir = 10^{−6} Torr s). The D₂S used (98% D) was obtained from Stohler Isotopes. Purity was checked *in situ* by means of a residual gas analyzer (Inficon IQ200) during exposures. Recording the time of exposure for reproducible sample coordinates at a given chamber pressure (1.0×10^{−9} Torr of H₂S) was found to give adequately reproducible exposures. Low-energy electron diffraction (LEED) and Auger measurements of an overlayer of H₂S were taken after an EEL spectrum. These corresponded well to LEED and Auger measurements obtained for freshly prepared, equivalent exposure samples. Heating was carried out by resistively heating the sample plate, and temperature measurements were made by means of a chromel-alumel thermocouple attached to the sample plate near the Ni(100) crystal. All EEL spectra were taken at 110 K.

III. RESULTS

A. 110 K coverage dependence

When H₂S is exposed to the clean Ni(100) surface at 110 K, a saturation coverage is attained. Further exposure to H₂S leads to no further increase in the S Auger signal, as well

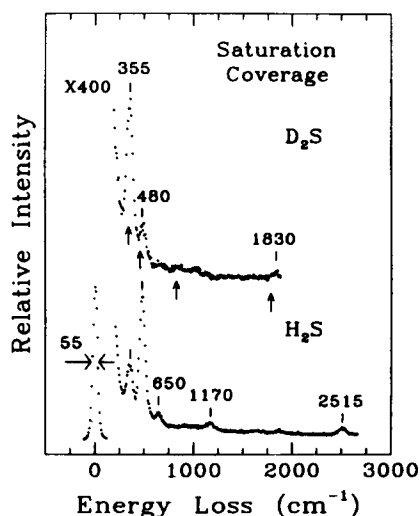


FIG. 1. The EEL spectra for a saturation coverage of H₂S and D₂S on Ni(100) at 110 K. The arrows point to $\omega/\sqrt{2}$ for a given frequency ω in the H₂S spectrum. $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

as no further changes in a $c(2 \times 2)$ LEED pattern observed under these conditions. The $c(2 \times 2)$ LEED pattern is of poor quality with very faint and diffuse $c(2 \times 2)$ spots and a high background of scattered electrons between diffraction spots. At 110 K it appears that the degree of order is not very great. The Auger spectra show the same dependence of the S(LMM) intensity for a 110 K exposure as that shown by a room temperature exposure followed by a 470 K anneal. This and the $c(2 \times 2)$ LEED pattern indicate a saturation coverage of $1/2$ monolayer is reached at 110 K with an exposure of ~ 3 – 6 L.

The EEL spectrum of H₂S and D₂S at saturation coverage is shown in Fig. 1. The frequency shifts upon deuteration of the loss peaks at 2515, 1170, 650, and 480 cm^{-1} indicate that these features involve primarily hydrogen motion, although the shifts of the 1170 and 650 cm^{-1} peaks, which should occur near 830 and 460 cm^{-1} (near the arrows in Fig. 1), are not readily discernible due to the uneven background of the D₂S spectra. A comparison of these spectra to gas phase H₂S and D₂S is given in Table I. The gas phase spectra show three vibrational modes: symmetric (ν_1) and asymmetric (ν_3) stretches, and an SH₂ (SD₂) deformation or "scissoring" mode (ν_2). The observation of ν_1 and ν_2 indicates the presence of molecular H₂S, the surface frequencies being downshifted by ~ 100 cm^{-1} . The ν_3 mode on the surface is

TABLE I. A comparison of gas phase H₂S and D₂S to surface spectra.

	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$
H ₂ S (gas)	2611 ^a	1290 ^b	2684 ^b
H ₂ S (surface)	2510	1170	...
D ₂ S (gas)	1892 ^a	934 ^c	1999 ^c
D ₂ S (surface)	1830

^aG. M. Murphy and J. E. Vance, *J. Chem. Phys.* **6**, 426 (1938).

^bA. D. Sprague and H. H. Nielsen, *J. Chem. Phys.* **5**, 85 (1937); C. R. Bailey, J. W. Thompson, and J. B. Hale, *ibid.* **4**, 625 (1936).

^cC. R. Bailey, J. W. Thompson, and J. B. Hale, *J. Chem. Phys.* **4**, 625 (1936); A. H. Nielsen and H. H. Nielsen, *ibid.* **5**, 277 (1937).

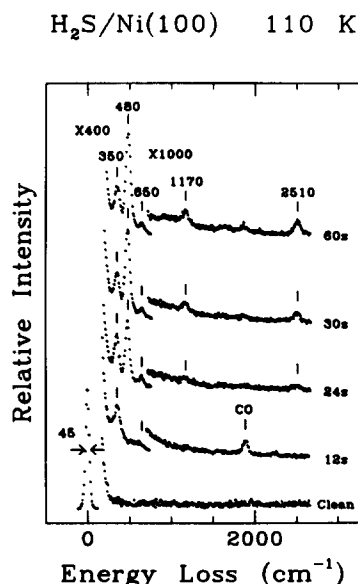


FIG. 2. Coverage-dependent spectra for H₂S/Ni(100) at 110 K. The number of seconds of exposure to an effusive beam of H₂S is listed at the right of each trace. $1 \text{ s} \sim 0.05$ – 0.1 L. $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

dipole inactive (absent in the specular direction). This is expected if the molecular symmetry is C_{2v} or C_s with a mirror plane normal to the surface bisecting the H atoms. The aspect of molecular symmetry and our assignment will be addressed more fully in Sec. IV.

Coverage dependent spectra at 110 K are shown in Fig. 2. The spectra show a trend of decreasing dissociative adsorption as the coverage is increased. At the lowest exposure of 12 s, H₂S is dissociated on the Ni(100) surface. The S–Ni stretch at 350 cm^{-1} agrees well with the value Andersson has reported for S/Ni(100) at room temperature.¹⁰ The broad shoulder centered at 560 cm^{-1} is identified as a H–Ni stretch. Evidence supporting this by a comparison to 1 L of H₂/Ni(100) is shown in Fig. 3.

A small amount of CO adsorbed from the residual gas of the chamber during the 60–90 min required to collect a

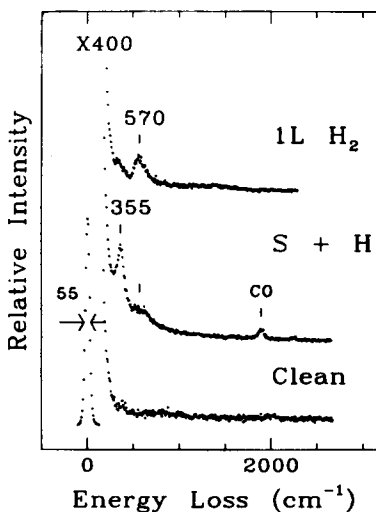


FIG. 3. Comparison of the lowest exposure (12 s) of H₂S/Ni(100) at 110 K to an exposure of 1 L of H₂ on Ni(100) at 110 K. $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

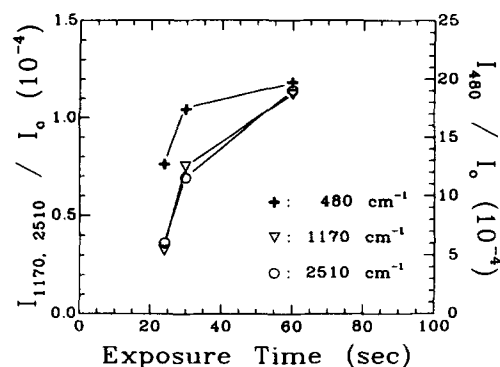


FIG. 4. Intensity vs H₂S exposure for the 480 cm⁻¹ (+), 1170 cm⁻¹ (∇), and 2510 cm⁻¹ (O) peaks.

spectrum is seen in the 12 s exposure in Fig. 2. Its intensity is comparable to other features in the spectrum because of the large dipole derivative of CO. It is not seen in the higher coverage spectra for the following reasons. Each spectrum was obtained after exposure to a freshly cleaned surface, i.e., impurities do not build up from one exposure to the next. At the higher coverages less sites are available for CO and other impurities to adsorb during the time it takes to collect a spectrum. In addition, less time is required to collect a spectrum at higher coverages.

At higher exposures of H₂S gas four additional features appear in the loss spectrum at 480, 650, 1170, and 2510 cm⁻¹, the latter two previously attributed to H₂S. The likely candidates responsible for the high coverage spectrum are H₂S and a mixture of H₂S and HS. The loss at 480 cm⁻¹ has a different coverage dependence than the 1170 and 2510 cm⁻¹ losses as seen in Fig. 4. This could result from a different chemical identity of the 480 cm⁻¹ feature (HS) or a different molecular orientation of H₂S (C_s vs C_{2v}) at different coverages. These possibilities are discussed at length in Sec. IV. For the present it suffices to note that we observe two different species. It should also be noted that EELS intensities depend not only on the number of dipole oscillators and oscillator strength but also on the degree of surface order, which in general changes with coverage. However, if the 480, 1170, and 2510 cm⁻¹ losses are due to one species, one would not expect any intensity ratio differences vs coverage due to the degree of order.

B. Temperature dependence

The temperature dependence of the high coverage spectrum from 0–1000 cm⁻¹ is shown in Figs. 5 and 6. The spectra were recorded by annealing to the indicated temperature for 5 min and cooling back down to 110 K before collecting the spectrum. The feature at 480 cm⁻¹ is seen to disappear by 170 K while the feature at 650 cm⁻¹ persists until 220 K. This is interpreted as the dissociation of H₂S (or HS) and the desorption of hydrogen, respectively. We only observe that hydrogen leaves the surface; however Fisher's thermal desorption data confirm our interpretation.¹¹ A complete spectrum from 0–2800 cm⁻¹, taken after a 150 K anneal, shows the disappearance of the 1170 and 2510 cm⁻¹ features as well, which indicates that the two different molecular species have approximately the same temperature dependence.

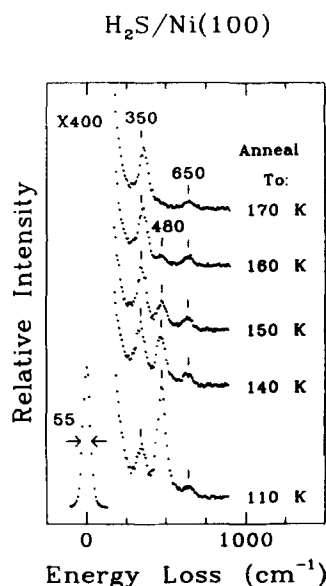


FIG. 5. Temperature dependence of a saturation coverage of H₂S/Ni(100) from 110–170 K. Each spectrum was obtained after annealing to the given temperature for 5 min and then cooling back down to 110 K. $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

Further evidence for assigning the 650 cm⁻¹ feature to a H–Ni stretch is given in Fig. 7. The spectrum obtained by annealing a saturation coverage of H₂S to 170 K, lowest trace, is compared with a spectrum generated by adding 5 L of H₂ to the S/Ni(100) surface at 110 K, middle trace, and a spectrum of 1 L of H₂ adsorbed on Ni(100). The loss features in the range 570–650 cm⁻¹ are thus correlated to surface hydrogen.

We prepared a sample with fewer surface species by carrying out the following experiment. A c(2×2) S/Ni(100) overlayer annealed to 470 K (equivalent to annealing a saturation coverage of H₂S at 110 K to 470 K as LEED and

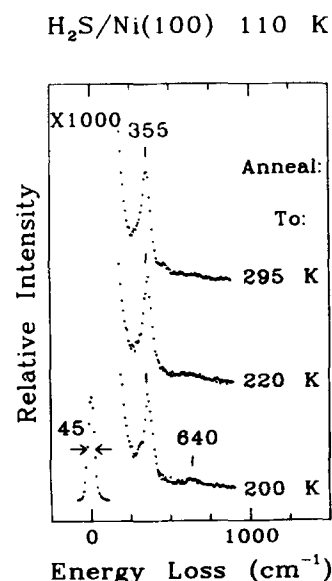


FIG. 6. Temperature dependence of a saturation coverage of H₂S/Ni(100) from 200–295 K. Each spectrum was obtained after annealing to the given temperature for 5 min and then cooling back down to 110 K. $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

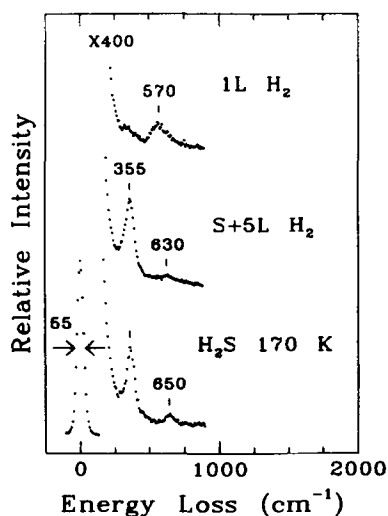


FIG. 7. A comparison of the following surfaces: a surface obtained by annealing a saturation coverage of H₂S/Ni(100) to 170 K (lowest trace), a surface of 1/2 monolayer of S/Ni(100) cooled to 110 K to which 5 L of H₂ has been added (middle trace), and 1 L of H₂ on Ni(100) at 110 K (upper trace). $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

Auger show) was cooled to 110 K and further exposed to a large amount of H₂S (25 \times saturation coverage). The count rate of the elastic peak of the resulting surface was reduced by a factor of 10 even after extensive retuning, indicating that some change on the surface had taken place. The spectrum collected under these conditions is shown in Fig. 8. Two features at 1210 and 2520 cm⁻¹ can be assigned to H₂S, and no feature is seen at 480 cm⁻¹. This is further evidence that two molecular species exist on the surface at different coverages, and that the higher coverage species (H₂S, C_{2v} symmetry) can be isolated as the only molecular species.

IV. DISCUSSION

One can think of three possibilities for H₂S orientation on Ni(100) as shown in Fig. 9. However, only (a) and (b) are

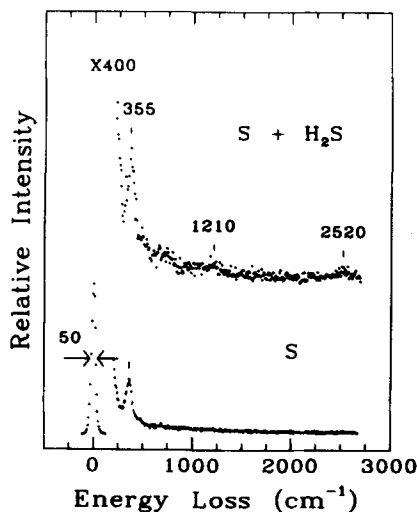


FIG. 8. A comparison of a surface to which a very large exposure (25 \times saturation) has been added to c(2 \times 2) S/Ni(100) at 110 K. $E_i = E_r = 55^\circ$, $E_0 = 1.6$ eV.

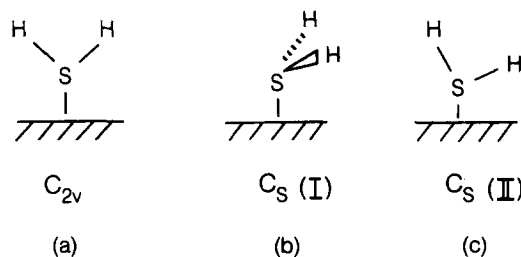


FIG. 9. Three possible orientations of H₂S/Ni(100), (a) C_{2v} symmetry; (b) C_s symmetry with a mirror plane bisecting the H atoms; and (c) C_s symmetry with a symmetry plane containing the H₂S molecule.

consistent with the absence of an asymmetric SH₂ stretch at ~ 2600 cm⁻¹. The orientation with C_{2v} symmetry has only two vibrational modes that are dipole allowed, i.e., that have a change in dipole moment perpendicular to the surface. These are the SH₂ symmetric stretch and scissor modes. Other possible normal modes are the SH₂ rock, wag, and twist. The rocking mode becomes dipole active for orientation (c), which has already been ruled out, while the wag is dipole active for orientation (b). We observe three modes with the same or similar temperature dependence at 480, 1170, and 2510 cm⁻¹, which could be a mixture of orientations (a) and (b). Alternatively we have the possibility of two molecular surface species H₂S in C_{2v} symmetry, having modes at 1170 and 2510 cm⁻¹, and SH with modes at 480 and 2510 cm⁻¹. Our data allow either possibility; however the results of two previous workers^{2,12} may tend to favor SH. Fisher observed SH at intermediate coverages on Ru(110) by means of difference spectra in UPS and comparison with the UPS spectra of H₃SiSH.¹³ Interestingly he observed dissociation of H₂S at low coverages and molecular H₂S at high coverages, much as in the present work. Fisher and Sexton¹² identified an OH species on Pt(111) in the presence of coadsorbed O using EELS by exposing a surface containing O to H₂O at 110 K and heating to 155 K. Their assignment did not have the alternate possibility we have because there was no H₂O simultaneously present under the conditions they observed OH. However, a striking similarity is observed between this work and OH/Pt(111). The loss observed at 1015 cm⁻¹ due to the OH bend is much stronger than any other feature in the spectrum. On Ni(100) the loss at 480 cm⁻¹ is correspondingly more intense than all other features. To our knowledge there are no vibrational data for inorganic compounds of HS or H₂S bonded to transition metals available for comparison. The closest possibility is (CH₃)₃SiSH,¹⁴ which contains no mention of an SH bend. Since we have no basis of comparison for assigning the 480 cm⁻¹ mode to an HS bend, or an SH₂ wag, we are left with only indirect evidence; the fact that the coverage dependences on Ru(110) and Ni(100) at liquid nitrogen temperatures are nearly identical if HS is the intermediate species on Ni(100), and the observation that the intensity ratio of the OH bend to the OH stretch on Pt(111) is similar to that of the presumed HS bend to the HS stretch (and H₂S symmetric stretch) on Ni(100).

It is interesting to note the similarities between H₂S adsorption on Ru(110) and the present work. In both cases there is complete dissociative adsorption at low tempera-

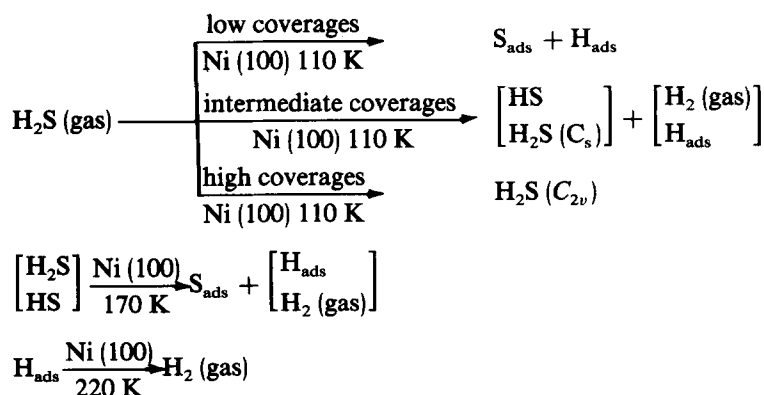
tures and low coverages, with hydrogen remaining on the surface. At higher coverages on Ru(110) first HS then H₂S was observed at 80 K, similar to what we observe. The Ru(110) surface is much more open than the more densely packed Ni(100) surface. In order to dissociate H₂S an activation barrier must be overcome by some means as a large amplitude vibrational motion which will bring hydrogens in close proximity to the metal surface. It is easy to imagine such a mechanism to be surface structure sensitive. In fact the great similarities between H₂S/Ru(110) and H₂S/Ni(100) suggest that a mechanism for dissociation is not surface structure dependent but electronic structure dependent. This is consistent with Fisher's observation that large changes in the work function as a function of coverage occur up to the point where molecular species began to adsorb and then gradually level off.

Free surface hydrogen can take part in a variety of interesting processes including bond-forming reactions, modification of surface electronic properties, etc. For example, in the case of bond-forming reactions, the activation energy for bond formation should depend critically on the hydrogen site. Yet structural information which could shed light on these processes is difficult to come by. Current structural measurements are not applicable to hydrogen because it is a $Z = 1$ element. Qualitative structural information that can be obtained by vibrational spectroscopy is difficult to come by for hydrogen when there are several surface species present because M-H stretching frequencies are both very weak and lie in a region where there are many other modes present; e.g., for hydrocarbons there are many CH_x bending modes in the range 600–1500 cm⁻¹. Even in cases where hydrogen is known to be on the surface at temperatures below the desorption threshold, such as methoxy on Ni(111)¹⁵ where there is only one methoxy frequency at 1020 cm⁻¹ in the range 600–1500 cm⁻¹, surface hydrogen is not observed by EELS. The present case is a fortunate example where a H-Ni stretch at 650 cm⁻¹ can be discerned in the presence of three other surface species. The low frequency for the H-Ni

stretch suggests that H lies in a fourfold hollow site. For inorganic complexes, metal-hydrogen (M-H) stretching frequencies greater than 1600 cm⁻¹ have been found by many workers to result from linear M-H bonds, and frequencies in the range 800–1300 cm⁻¹ correspond to bridge sites.^{16,17} Although there is not yet a wide body of information available on surfaces, data from inorganic complexes give a good qualitative guide. Since the 650 cm⁻¹ frequency on Ni(100) lies below the accepted range for a bridge site, an assignment of a fourfold hollow site can be made for H on Ni(100). In addition, data by Andersson¹⁸ for H/Ni(100) and a theoretical study by Upton and Goddard¹⁹ on a Ni₂₀H cluster support such a conclusion. However, the situation is not so simple. The site designations atop, bridge, threefold, and fourfold hollows are more appropriate for larger atoms where hard sphere radii designations are valid. Were a hard sphere radius appropriate for hydrogen, the hydrogen would either fit solidly in the fourfold hollow ($r_H > \sim 0.51$ Å) site or have the possibility of bonding atop to the atom below or in a threefold site with the atom below and two of the surface Ni atoms ($r_H < \sim 0.51$ Å). However, a hard sphere model is inappropriate for a proton with its surrounding electron density largely blending into the surface. In addition, sites intermediate to bridge and threefold have been reported for H/Ni(110).^{20,21} This leads us to conclude that while the 650 cm⁻¹ H-Ni stretch indicates a high degree of coordination, probably fourfold, this does not unambiguously determine the hydrogen site. The nature of this site is changing, as evidenced by the narrowing and upward shift of the H-Ni frequency (Fig. 6). What is causing this change is unclear.

SUMMARY

We have carried out a fairly complete characterization of the adsorption and decomposition of H₂S on the Ni(100) surface. The reaction steps listed below indicate species that we have been able to identify using EELS under various conditions of coverage and temperature.



Future experiments using HDS would be useful in determining the identity of the intermediate coverage species. Adsorbed hydrogen is observed in the presence of three other surface species. Desorption of H₂ is inferred from the disappearance of the H-Ni stretch and is confirmed by the thermal desorption data of Fisher.¹¹

ACKNOWLEDGMENTS

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