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BY ELECTRON ENERGY LOSS SPECTROSCOPY

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Adsorption and Surface Reactions of H$_2$S and SO$_2$ on Cu(100) Studied by Electron Energy Loss Spectroscopy

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ABSTRACT

The adsorption of H$_2$S and SO$_2$ on Cu(100) were investigated using electron energy loss spectroscopy as a function of coverage, temperature and scattering angles. In particular, irreversible dissociation of H$_2$S and the formation of sulphydryl (SH) species at low and intermediate coverage on Cu(100) were observed at low temperature. This was followed by molecular physisorption at higher coverage. In the case of SO$_2$ on Cu(100), decomposition of SO$_2$ and the formation of SO$_3$ surface species at room temperature were observed. A surface reaction involving pre-adsorbed SO$_2$ on Cu(100) with H$_2$S is discussed.

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I. INTRODUCTION

Since the pioneering work of Propst and Piper,1 electron energy loss spectroscopy (EELS)2 has become a popular, non-destructive technique for surface analysis when high surface sensitivity is desired. Detailed information concerning the bonding of various surface adsorbates and their intermediates can be obtained from their characteristic vibrational spectra.3-8 Many surface intermediates9-11, as well as their adsorption and desorption behaviour, have been identified by EELS. Furthermore, recent developments in electron optics have allowed the study of the kinetics of surface reactions involving these surface species.12

The adsorption behaviours of H2S and SO2 on surfaces have attracted a great deal of attention because of the industrial and environmental importance of these molecules. Adsorption properties of H2S on Rh(100),13 Mo(100),14 MoS2,15 Si(111)16 and GaAs17 have been investigated by a variety of techniques including low energy electron diffraction (LEED), photoemission, thermal desorption and EELS. Of particular interest are the photoemission studies of H2S on Ru(110),18 W(100),19 and GaAs surfaces,17 and the electron energy loss studies of H2S on Ni(100)20 and Pt(111),21 which reported the formation of sulfhydryl (SH) species, at low temperature in most cases.18,20,21 Two different interpretations of the corresponding vibrational features were also presented in the latter two EELS studies.20,21

Similarly, a number of studies involving different techniques were reported for the adsorption of SO2 and its reactions on metal surfaces. Blyholder and Cagle showed that the reaction of SO2 on Fe and Ni produced SO4 surface species.22 A similar reaction involving SO4 as a product on Ag was also reported by Barber et al. using secondary ion mass spectroscopy23 and by Lassiter using Auger electron spectroscopy and work function measurements.24 Low, Goodsel and Takezawa, on the other hand, studied the adsorption of SO2 on CaO25 and on MgO26 at room temperature using Fourier transform infrared spectroscopy and suggested SO3 as a possible surface species upon adsorption. Kohler and Wassmuth28 investigated the kinetics of SO2 on Pt(111) using a molecular beam technique and thermal desorption measurements, and further suggested that SO2 adsorbed dissociatively at low temperature for small coverages. Dissociative adsorption involving a
wide range of possible surface species was also observed on other surfaces, including Rh(110),29
Pt(110),29 Pt(111)28 and Pd(100)30 near liquid nitrogen temperatures. However, a recent study by
Hussla and Heidberg27, using far and mid infrared transmission spectroscopy, found no evidence of
dissociative adsorption for SO2 on Cu(100) over a wide temperature range. On Ag(100), Ag(111),
Ag(110),31 and Au,32 molecular adsorption at low temperature and dissociative adsorption at higher
temperature31 were reported.

An earlier publication20 from this laboratory gave a detailed characterization of the
adsorption and decomposition of H2S on Ni(100). In this report, we present a parallel study on the
adsorption of H2S and SO2 on Cu(100) using EELS. Surface species generated from the adsorption
and desorption of H2S and SO2 on Cu(100), as well as from reactions between H2S and a Cu(100)
surface pre-adsorbed with SO2, were characterized using the measured electron energy loss spectra.
Except for the differences in the values of the vibrational frequencies, very similar adsorption and
decomposition behaviours can be inferred from the vibrational spectra associated with these surface
species on Cu(100) and Ni(100)20 in the case of H2S. For SO2, similar adsorption patterns were
found on Cu(100) and Ag(110).31

II. EXPERIMENTAL

The angle-resolved electron energy loss spectrometer was housed in an UHV chamber (base
pressure = 1x10^-10 torr), which was equipped with retarding-field optics capable of LEED and
Auger electron spectroscopy (AES) as well as an ion sputtering gun for sample cleaning. A detailed
description of our modified electron energy loss spectrometer was given elsewhere.33 Briefly, it
consisted of a 2-inch mean diameter double-pass hemispherical monochromator and a 5-inch mean
diameter single-pass hemispherical analyzer. The analyzer was rotatable in both polar and
azimuthal directions with respect to the normal of the crystal to facilitate off-specular measurements
without rotating the sample. Two separate three-aperture lenses were used as the output optics for
the monochromator and as the input optics for the analyzer. In the earlier design, the double
hemispheres of the monochromator were separated by a single aperture. In the present work, the
aperture was replaced by a three-aperture lens to enable the two hemispheres to operate at different
pass energies. This modification improved the signal rate by a factor of 5-10 while maintaining similar energy (40 cm\(^{-1}\) FWHM) and angular (3° half-angle) resolution.

A high purity Cu crystal was cut, polished and oriented to within 1° from the (100) plane by standard methods. It was (pre-)cleaned by a well-known procedure: repeated cycles of Ar ion sputtering at 1 keV followed by annealing at 800 K for 15 minutes. The cleanliness of the sample was checked using retarding-field AES. The sample could be cooled to liquid nitrogen temperature or heated to above 1500 K using electron beam bombardment from the back of the sample plate. The temperature of the crystal was measured using a chromel-alumel thermocouple spot-welded on the sample plate 7 mm above the crystal. The accuracy of the temperature measurements was estimated to be ± 20 K.

Detailed descriptions of the effusive beam dosing procedure as well as the calibration procedure using an ambient dosing technique were given elsewhere. Exposures of H\(_2\)S (Matheson, 99.5% purity) or SO\(_2\) (Matheson, 99.98% purity) was achieved by maintaining an ambient chamber pressure of 1x10\(^{-9}\) torr with the adsorbant for a specified period of time with the sample positioned at 1 cm from an effusive beam doser. Exposures obtained by this beam dosing technique were calibrated with those obtained using an ambient dosing procedure, by comparing the corresponding S(152 eV) to Cu(62 eV) relative Auger intensities. A 1x10\(^{-8}\) torr-sec exposure using the beam dosing procedure corresponded to 0.5-1 L (1 L = 1 x 10\(^{-6}\) torr-sec). A saturation coverage was obtained after 40 L and 20 L exposures of H\(_2\)S and SO\(_2\), respectively. A new sample was prepared for each exposure, to avoid accumulative contamination.

All specular EELS measurements were made at an incident angle of 55° from the surface normal, while off-specular measurements were conducted by rotating the analyser through a fixed angle from the specular direction, away from the surface normal. An impact energy of 1.6 eV was used for all measurements. Individual peaks in the EEL spectra were deconvoluted using a combination of gaussians as well as a background function to approximate the tail of the elastic peak. The accuracy of the reported loss frequencies so determined was estimated to be ± 4 cm\(^{-1}\).
III. RESULTS

A. EELS of H\textsubscript{2}S/Cu(100)

Figure 1 shows the EEL spectra of a Cu(100) surface exposed to a saturation coverage of H\textsubscript{2}S and recorded at (a) 100 K and (b) 300 K in the specular direction. A diffuse p(2x2) LEED pattern with streaks between the quarter and half order spots was observed at both temperatures, with the pattern obtained at 100 K being more diffuse. Further annealing of the sample at 300 K to ca. 500 K for 10 minutes produced a sharp p(2x2) LEED pattern with no observable streaks. Good agreement is observed between the reported p(2x2)S/Cu(100) spectrum\textsuperscript{8} and the room temperature spectrum (Fig. 1b). In particular, the dissociation of H\textsubscript{2}S on Cu(100) is indicated by the strong S-Cu stretch observed at 324 cm\textsuperscript{-1}. The small downward shift (ca. 12 cm\textsuperscript{-1}) relative to the reported S-Cu stretch\textsuperscript{8} can be attributed to possible disorder effects for the dissociated species on Cu(100) at room temperature. There is also some evidence of phonon vibrations,\textsuperscript{7} as indicated by the weak shoulder at 177 cm\textsuperscript{-1}. The spectrum at 100 K (Fig. 1a) shows four additional peaks at 430, 550, 1144 and 2469 cm\textsuperscript{-1}. The two higher vibrational features at 1144 and 2469 cm\textsuperscript{-1} can be readily identified respectively as H-S bending and stretching modes of molecularly adsorbed H\textsubscript{2}S by a comparison with the available vibrational data of free H\textsubscript{2}S molecules.\textsuperscript{35} In the gas-phase data the 1290 and 2611 (2684) cm\textsuperscript{-1} peaks were assigned to H-S bending and symmetric (asymmetric) stretching modes, respectively. The feature at 178 cm\textsuperscript{-1} in the 100 K spectrum can be attributed to either surface phonon vibration as in the room temperature case or hindered translations of molecularly adsorbed H\textsubscript{2}S.

In order to identify the remaining features (i.e. at 430 and 550 cm\textsuperscript{-1}), an EEL spectrum of a saturation coverage of D\textsubscript{2}S on Cu(100) at 100 K was measured (Fig. 2b). The effect of isotopic substitution is to scale the frequencies of the H-related vibrations of H\textsubscript{2}S/Cu(100) with respect to those of the corresponding vibrations of D\textsubscript{2}S/Cu(100) by a factor of \sqrt{2}. The frequencies of these two systems as well as the gas-phase data are given in Table 1. The observed D\textsubscript{2}S/Cu(100) features are consistent with the isotopic substitutional effect, with the scaling factors lying between 1.2 and 1.4. The D-S stretching modes of the molecularly adsorbed D\textsubscript{2}S were not observed, presumably due
to their weak intensities. The broad structure at 317 cm$^{-1}$ may be due to an overlap of two features: the scaled analog of the H$_2$S feature at 430 cm$^{-1}$ and the S-Cu stretch. The features at 430 (317) and 550 (452) cm$^{-1}$ for H$_2$S (D$_2$S) are therefore related to surface vibrations involving H (D) atoms.

Figure 3 shows the EEL spectra of a saturation coverage of H$_2$S on Cu(100) at 100 K measured in the specular and two off-specular scattering geometries. Assuming that the S-Cu stretch (at 320 cm$^{-1}$) is dipole active, one can obtain a qualitative idea of the dipole (infrared) activity of other structures by comparing the changes in their intensities relative to the S-Cu stretch as a function of angle. This comparison confirms that the H-S bend (at 1144 cm$^{-1}$) and H-S stretch (at 2469 cm$^{-1}$) of molecularly adsorbed H$_2$S have non-dipole (i.e. impact-scattering) contributions, as indicated by a large increase in the relative intensities in the 10° off-specular spectrum (note scale change in Fig. 3c). In other words, H$_2$S is adsorbed on the Cu surface such that these vibrations have parallel components in the dipole moments with respect to the surface. Furthermore, the feature at 430 cm$^{-1}$, like the S-Cu stretch (at 320 cm$^{-1}$), is dipole active. Together with the evidence obtained in Fig. 2, we may identify this structure to be H-S stretch of a sulfhydryl (SH) species with S bonded in a head-on configuration perpendicular to the surface. Finally, the angular variation of the remaining feature at 550 cm$^{-1}$ is similar to that of the H-S stretch of the dissociated (SH) species. This may likely be due to a second H-S vibrational mode or a H-Cu vibration. Further evidence is required to distinguish between the two possibilities.

A temperature dependent study is shown in Figure 4. In this experiment, the Cu(100) surface was first exposed with a saturation coverage of H$_2$S at 100 K (Fig. 4a). It was subsequently annealed to the specified temperatures for 5 minutes. The sample was then recooled back to 100 K, at which temperature the EEL spectrum was recorded. It should be noted that a new sample was prepared for each run to avoid accumulative contamination. Fig. 4b shows that the anneal at 130 K removed the two molecular features at high frequency as well as the structure at 430 cm$^{-1}$. The removal of the two high frequency features suggests that H$_2$S was physisorbed on Cu(100) below 130 K. Furthermore, the dissociated SH species, which gave rise to the feature at 430 cm$^{-1}$, was weakly adsorbed. The marked increase in the intensities of the S-Cu stretch and of the vibration at
550 cm\(^{-1}\) (Fig. 4b) further suggests that the SH species may (1) dissociate to form S (abs.) and H (abs.), and/or (2) rearrange itself to a different site or a different vibrational mode. Finally, further annealing to higher temperatures resulted in a gradual decrease in the intensities of the remaining features at 320 and 550 cm\(^{-1}\). A significant depletion in the intensity of the 178 cm\(^{-1}\) peak after the 130 K anneal was also observed, suggesting that the 178 cm\(^{-1}\) peak may have a contribution from the hindered translations of molecularly adsorbed H\(_2\)S. Its residual intensity after the 130 K anneal (Figs. 4c to 4e) can be attributed to phonon vibration. Qualitatively, we may conclude that the adsorption strength of the observed features increases in the following order: \{178, 430, 1144, 2469 cm\(^{-1}\}\} (weak) < 550 cm\(^{-1}\) < 320 cm\(^{-1}\} (strong).

Finally, we present a coverage dependent study (using a beam dosing procedure)\(^{20,33}\) to investigate the early stages of H\(_2\)S adsorption on Cu(100) in Figure 5. The most striking change is the red shift of the feature at 600 cm\(^{-1}\) at low coverage (Fig. 5a) to 550 cm\(^{-1}\) at saturation coverage (Fig. 5e). There is no other noticeable change in the frequencies of the other features with coverage. At low coverages (Figs. 5a and 5b), H\(_2\)S appears to dissociate into S and a species (most likely H) which gives rise to the feature at 550 cm\(^{-1}\) at saturation coverage. These dissociated species saturate at an exposure of about 20 seconds (1-2 L) before the SH species (at 430 cm\(^{-1}\)) and the molecularly adsorbed H\(_2\)S begin to accumulate. This is consistent with the order of adsorption strength of individual species asserted in the temperature dependent study (Fig. 4) above. Furthermore, it confirms that H\(_2\)S dissociates to S (and H) at low coverage on Cu(100) at 100 K.

### B. EELS of SO\(_2\)/Cu(100)

Figure 6 shows the EEL spectra of a saturation coverage of SO\(_2\) on Cu(100) exposed and measured in the specularly reflected direction at two different temperatures. Table 2 summarizes plausible assignments of the observed frequencies, compared with those of free SO\(_2\) molecules and other SO\(_2\) related systems. Except for the low frequency region (<500 cm\(^{-1}\)), two markedly different vibrational spectra were observed. By comparing with the gas-phase data,\(^{35}\) the peaks at 1290, 978 and 515 cm\(^{-1}\) in the 100 K spectrum (Fig. 6a) can be assigned to antisymmetric stretch, symmetric stretch and bending modes respectively. The two S-O stretching frequencies are lower
than the corresponding gas-phase data (c.f. 1362 cm\(^{-1}\) for symmetric stretch and 1151 cm\(^{-1}\) for asymmetric stretch) while the bending frequency at 515 cm\(^{-1}\) is almost identical to the corresponding gas-phase data.\(^{35}\) The remaining broad band is treated as an envelope of two close lying peaks at 346 and 290 cm\(^{-1}\). The feature at 346 cm\(^{-1}\) corresponds closely to the S-Cu stretching frequency of S/Cu(100)\(^{8}\) (c.f. 336 cm\(^{-1}\)) while the peak at 290 cm\(^{-1}\) may be interpreted as either a torsion mode or hindered translations of physisorbed SO\(_2\). The low frequency part of the room temperature spectrum (Fig. 6b) can be assigned in an analogous fashion as the 100 K spectrum. Three different peaks are observed at 859, 613 and 482 cm\(^{-1}\). We postpone discussion of the assignments of these vibrations until later. It should also be noted that the width of the elastic peak changes significantly, from 44 cm\(^{-1}\) FWHM at 300 K to 60 cm\(^{-1}\) FWHM at 100 K. The peak broadening effect is an indication of surface disorder arising from physisorption. This interpretation is supported by an increase in the diffuseness in the observed p(2x2) LEED pattern of the sample at 100 K compared to that at 300 K.

Figure 7 shows the vibrational spectra of SO\(_2\) on Cu(100) at 300 K as a function of coverage obtained using a beam dosing procedure.\(^{20,33}\) The coverages of the 10s, 20s and 30s spectra correspond approximately to 1/3, 2/3 and 1 monolayer, respectively. There is very little change in the spectrum except for the structure at 859 cm\(^{-1}\), which increases proportionally with coverage.

A saturation coverage of SO\(_2\) on Cu(100) at 300 K was annealed to 350 K and 500 K for 5 minutes using electron beam bombardment from the back of the sample. Drastic changes were observed in the vibrational spectra, shown in Figure 8. The low temperature anneal to 350 K completely removed the high frequency features at 613 and 859 cm\(^{-1}\) and sharpened the low frequency band at 324 cm\(^{-1}\). Further annealing to 500 K did not produce any noticeable change. There is also some evidence of a weak shoulder near 172 cm\(^{-1}\) after the anneal. By comparing the annealed spectra with that of S/Cu(100),\(^{8}\) it is clear that the 172 cm\(^{-1}\) feature corresponds to a phonon vibration while the feature at 324 cm\(^{-1}\) is due to S-Cu stretch (Figs. 8b and 8c).

Finally, a saturation coverage of SO\(_2\) on Cu(100) at 300 K was exposed to 12 L of H\(_2\)S using an ambient dosing procedure. The EEL spectrum shown in Figure 9 indicates a very similar
vibrational profile to the spectra of the annealed sample shown in Fig. 8. In particular, the high frequency features are not observed and the feature at 329 cm\(^{-1}\) can again be attributed to S-Cu stretch.\(^8\) Like the annealed spectra (Fig. 8), the weak shoulder at 161 cm\(^{-1}\) provides some evidence of a possible phonon vibration.

IV. DISCUSSION

A. Adsorption of H\(_2\)S on Cu(100)

For C\(_{2v}\) triatomic molecules adsorbed on surfaces, up to 9 vibrational modes may become infrared active. These include 3 normal modes and 6 additional modes including 3 hindered rotations and 3 hindered translations. The assignments of the observed surface vibrations of H\(_2\)S on Cu(100) are consistent with both the gas-phase data\(^35\) and the earlier EELS data of S/Cu(100).\(^8\) In particular, the S-Cu stretch (at 320 cm\(^{-1}\)) is identified by comparison with the reported S/Cu(100) EELS study\(^8\) (Fig. 1a). The assignments of the features at 1144 and 2469 cm\(^{-1}\) to molecular H-S bending and stretching modes respectively are unambiguous. The vibration at 178 cm\(^{-1}\) can be attributed to either phonon vibrations or hindered translations of molecularly adsorbed H\(_2\)S. The latter case is supported by a coordinated increase (Fig. 5) and decrease (Fig. 4) in the intensity of this structure concomitant with the other molecularly adsorbed H\(_2\)S features at 1144 and 2469 cm\(^{-1}\).

The features at 430 and 550 cm\(^{-1}\) are more difficult to interpret. Very similar EELS spectra of H\(_2\)S on Ni(100)\(^{20}\) and on Pt(111)\(^{21}\) were also reported. Both studies assigned the lower frequency peak to H-S stretch\(^{20}\) or H-S bend\(^{21}\) but gave two different assignments to the higher frequency, H-related feature analogous to the one observed at 550 cm\(^{-1}\) in the present work. In particular, Baca \textit{et al.}\(^{20}\) assigned the higher frequency vibration to H-Ni stretch while Koestner \textit{et al.}\(^{21}\) identified the corresponding peak to a second H-S bend. These two studies also reported similar temperature-dependent adsorption behaviours of H\(_2\)S as in the present work, with the higher (lower) frequency vibrations of the respective systems becoming stronger (weaker) at higher temperature. In the case of H\(_2\)S/Pt(111), however, an earlier study by Baro \textit{et al.}\(^{36}\) identified a fairly strong low frequency mode due to H-Pt asymmetric stretch with H adsorbed in a hollow site. This feature persisted in the spectra if the sample was annealed to 220 K, in direct analog with the strong
adsorption of the higher frequency feature observed by Koestner et al. The assignment of Baca et al. (i.e. to H-metal stretch) therefore appears to be more consistent with the data of both Pt(111) studies\(^{36,21}\) and the present case. The assignments of the features at 550 cm\(^{-1}\) and 430 cm\(^{-1}\) to a H-Cu stretch with H in a stable (probably four-fold hollow) site and to H-S vibrations (bend or stretch) of a sulfhydryl species, respectively, are in accord with the observed changes in the relative intensities of the angle-dependent spectra (Fig. 3). The existence of atomic H on Cu(100) is also consistent with an earlier study which suggested that the adsorption of H\(_2\) on Cu(100) involved atomic chemisorption and that activated dissociation was involved.\(^3\) The reported EELS study of H\(_2\) on Cu(100)\(^3\) indicated that H\(_2\) adsorbed molecularly only below 10 K. It should be noted that we cannot, however, rule out an alternative assignment of the feature at 430 cm\(^{-1}\) to hindered rotations of molecularly adsorbed H\(_2\)S. Nevertheless, judging from the small intensity of this peak and the absence of the feature at 178 cm\(^{-1}\) at low coverage (Figs. 5a and b), which we earlier suggested to be due to hindered translations, this assignment appears to be rather unlikely.

Both Fisher\(^{18}\) and Baca et al.\(^{20}\) proposed a similar model for the adsorption of H\(_2\)S on Ru(110) and Ni(100), respectively, at liquid nitrogen temperature. In this model, complete irreversible dissociation of H\(_2\)S into S (ads.) and H (ads.) at low coverage is followed by partial dissociation into H-S (ads.) and H (ads.) at intermediate coverage. The H (ads.) may recombine to form H\(_2\) which is then desorbed from the surface. Finally, molecular adsorption of H\(_2\)S is observed at high coverage, most likely in the form of islands. This model appears to be consistent with the present EELS data of H\(_2\)S on Cu(100) at 100 K, as evidenced by the coverage-dependent study (Fig. 5). Without a detailed calculation of the vibrational spectrum assuming different surface structures, it is difficult to determine the bonding sites or geometries of the observed surface species: S, H, SH and H\(_2\)S from the EELS spectra. The initial dissociation of H\(_2\)S into S and H at low coverage probably leaves the dissociated species in the most stable (four-fold hollow) site which leads to perpendicular surface vibrations. The similarity between the S-Cu stretching frequency in the present case and that of the S/Cu(100) case\(^8\) confirms this model. The small value of the H-Cu stretching frequency also suggests that H is adsorbed in a four-fold site although as pointed out by
Baca et al.\textsuperscript{20} one cannot unambiguously identify the site based only upon the magnitude of the vibrational frequency. At intermediate and higher coverage, it is not clear from the frequencies of the weakly bonded SH and H\textsubscript{2}S species what bonding sites that these species may occupy. In fact the nature of the H-S vibration (i.e. whether it is a stretching or bending mode) is not clear. However, the intensity variation of this feature as a function of scattering angle (Fig. 3) indicates a strong dipole contribution. For the SH species it is therefore more likely, though not conclusively, that the H-S stretching mode is being observed. For the molecular H\textsubscript{2}S species, there are similar difficulties in identifying the adsorption sites, although the associated frequencies allow us to distinguish between the stretching and bending modes.

Unlike H\textsubscript{2}O,\textsuperscript{5,6} for which molecular adsorption on metal surfaces appears to be the rule, the dissociation of H\textsubscript{2}S and the formation of sulfhydryl (SH) species appear to be quite common on most metal surfaces studied to date. Except for W(100)\textsuperscript{19} where it occurred at room temperature, SH formation occurred below 170 K on most metal surfaces, including Rh(100),\textsuperscript{13} Ru(110),\textsuperscript{18} Ni(100),\textsuperscript{20} Pt(111),\textsuperscript{21} and Cu(100). Like molecularly adsorbed H\textsubscript{2}S, the SH species binds weakly to the surface and desorbs easily. This behaviour can be attributed to the much smaller H-S bond energy in H\textsubscript{2}S when compared with the H-O bond energy in H\textsubscript{2}O. The desorption behaviour of H\textsubscript{2}S on Cu(100) is also very similar to that observed on the other metal surfaces,\textsuperscript{13,18,20,21} where H\textsubscript{2} and H\textsubscript{2}S appear to be the only desorption products. In particular, thermal desorption studies of H\textsubscript{2}S on Pt(111)\textsuperscript{21} and on Rh(100)\textsuperscript{13} suggested two molecular H\textsubscript{2}S desorption states: one due to chemisorbed H\textsubscript{2}S interacting with the sulfided metal surfaces and the other due to H\textsubscript{2}S weakly bonded within islands of chemisorbed H\textsubscript{2}S. This picture of weak H\textsubscript{2}S adsorption is consistent with the temperature dependent EELS study in the present work.

B. Adsorption of SO\textsubscript{2} on Cu(100)

In the case of SO\textsubscript{2} adsorption, the three high frequency features at 100 K (Fig. 6a) can be assigned to the corresponding normal modes of free SO\textsubscript{2} molecules by a comparison with the gas-phase data.\textsuperscript{35} (See Table 2). The low frequency features at 346 and 290 cm\textsuperscript{-1} are most likely due to S-Cu stretch and hindered translations, respectively. The similarity of the observed vibrational
features with those of free SO₂ molecules³⁵ and S/Cu(100)⁸ suggests that SO₂ was physisorbed on the surface at 100 K. A similar adsorption pattern was also reported for SO₂ on CsCl films.²⁷ In particular, associative adsorption on CsCl was observed for three different adsorption phases involving different temperature ranges: α phase (220-240 K), β phase (146-205 K), and γ phase (>200 K). The characteristic frequencies corresponding to these phases are given in Table 2. In the case of SO₂ on CsCl,²⁷ only one low-frequency peak, presumably due to S-CsCl stretch, was reported although there were significant backgrounds in these infrared spectra. The assignment of the feature at 290 cm⁻¹ in the SO₂ on Cu(100) case to hindered translation is therefore not unique. Other possibilities include: (1) a torsion mode, and (2) two different adsorption sites for SO₂ molecules which give rise to two possible S-Cu vibrational frequencies. The EEL spectrum of 12 L of SO₂ on Pd(100) recorded at 115 K by Burke and Madix³⁰ was very similar. In both cases, the frequencies of the observed (molecular) features compare favourably with the corresponding ones for solid SO₂.³⁸

The spectral features of the room temperature spectrum (Fig. 6b) are more difficult to interpret. The low frequency features (290 and 340 cm⁻¹) at 300 K could be assigned in a similar fashion as for the low temperature spectrum. No high-frequency peaks (>1000 cm⁻¹), characteristic of the SO₂ internal vibrations that were observed in the low temperature case, were found. The three new features observed at 482, 613 and 859 cm⁻¹ were indicative of different surface species (other than SO₂) resulting from the room temperature adsorption. Previous studies of SO₂ on Fe and Ni,²² Ag films,²³,²⁴ Pt(111),²⁸ Pd(100)³⁰ and p(2x2)S/Pd(100)³⁰ all suggested dissociative adsorption and reported evidence of SO₄ and S as the principal adsorption products, particularly at higher temperatures. Other studies of SO₂ on CaO²⁵ and MgO,²⁶ however, suggested SO₃ as a possible surface species upon adsorption. The EELS study of the oxidation of SO₂ on Ag(110) reported by Outka et al.³¹ suggested the presence of SO₃ and SO₄ at different temperatures. From Table 2, the strong peaks at 859 and 613 cm⁻¹ and the weak feature at 482 cm⁻¹ can be tentatively assigned respectively to symmetric/asymmetric S-O stretch, symmetric S-O bend and asymmetric S-O bend of SO₃. The band at 859 cm⁻¹ is broad and can be attributed to two overlapping bands. Earlier
infrared data relating the SO$_x$ ($x = 3$ or $4$) vibrations suggested that in general the asymmetric S-O stretching frequency is greater than 1100 cm$^{-1}$ for SO$_4$ but smaller than 1100 cm$^{-1}$ for SO$_3$.\textsuperscript{31} The relatively low value of the S-O stretching band at 859 cm$^{-1}$ therefore strongly favours the presence of SO$_3$ rather than SO$_4$.

The sulfite group, SO$_3$, can coordinate to the metal surface as an unidentate or bidentate ligand. Both of these bonding arrangements were considered for the case of SO$_3$ on Ag(110) by Outka et al.,\textsuperscript{31} who concluded from their EEL spectra that unidentate O-bonding occurred between 200-325 K while bidentate bonding was found between 325-500 K. From the infrared data of the coordination complexes compiled by Outka et al.,\textsuperscript{31} O-coordination with SO$_3$ in a pyramidal arrangement (see Table 2) appears to be most likely for Cu(100). This is consistent with Nyberg and Larsson's observation that a strong vibration above 975 cm$^{-1}$ is indicative of S-coordination.\textsuperscript{40} In the case of bidentate geometry, there are at least four possible cases, each involving bonding of a S-O pair or an O-O pair to either one or two metal atoms. From the infrared studies of bidentate coordination complexes of the type [Co(en)$_2$SO$_3$]X where X = ClO$_4^-$, NO$_2^-$, I$^-$ or SCN$^-$, it was found that the spectrum would be more complex due to the existence of many different vibrations.\textsuperscript{37} The simplicity of our spectrum further supports that unidentate coordination through the O atom represents the most probable bonding geometry.

From the observed vibrational spectrum at 300 K, we have already concluded that the reaction: SO$_2$ + SO$_2$ $\rightarrow$ S (abs.) + SO$_4$ (abs.) involving the production of SO$_4$ is unlikely. Instead, surface reactions generating SO$_3$ and S (and/or O) as adsorbed surface species are considered. We therefore propose the following reaction scheme to account for the observed adsorption pattern.

(1) $\text{SO}_2 \rightarrow \text{SO} \text{ (abs.)} + \text{O (abs.)}$

(2) $\text{SO (abs.)} + \text{SO}_2 \rightarrow \text{S (abs.)} + \text{SO}_3 \text{ (abs.)}$

(3) $\text{O (abs.)} + \text{SO}_2 \rightarrow \text{SO}_3 \text{ (abs.)}$

(4) $\text{SO (abs.)} \rightarrow \text{S (abs.)} + \text{O (abs.)}$ at higher coverage or above 350 K

This model (reactions 1-3) is certainly not unique in accounting for the observed S (abs.) and SO$_3$ (abs.) species. It emphasizes dissociative adsorption of SO$_2$ into SO (abs.) and O (abs.)
(reaction 1), which subsequently combines with SO₂ to give SO₃ (abs.) (reaction 3). The reaction of SO (abs.) with SO₂ gives the products S (abs.) and SO₃ (abs.) (reaction 2). As evident from the coverage-dependent spectra (Fig. 7), the increase in the intensity of the S-O stretching modes but not the bending modes at higher coverages suggests the build-up of additional species other than SO₃. In this model, the most likely candidate is SO itself. Furthermore, additional dissociation of SO into S and O (reaction 4 above) cannot be ruled out. It should be noted that both S-Cu⁸ and O-Cu⁹ stretching modes occur at the same frequency and it is therefore impossible to differentiate between the two. The two low frequency features at 296 and 340 cm⁻¹ can also be explained by the presence of two different S-Cu (stretching) vibrations corresponding to Cu-SO or Cu-SO₃. This implies that both SO and SO₃ are present at all coverages and SO continues to build up after the saturation of SO₃ on the surface. With the present resolution of 40 cm⁻¹ FWHM, it is not possible to resolve these two features and investigate their intensity variations as a function of coverage. The surface species (SO or SO₃) appear to be weakly adsorbed because only a small temperature rise is required to remove most of the vibrational features associated with these species (Fig. 8). After annealing, the low frequency band sharpens and can again be attributed to a S-Cu (or O-Cu) stretch. As well, the possibility of dissociation of SO and SO₃ to S and/or O cannot be ruled out.

C. Reaction of H₂S with preadsorbed SO₂ on Cu(100)

Except for the increase in the intensity of the 329 cm⁻¹ peak, an exposure of 12 L of H₂S to preadsorbed SO₂ on Cu(100) at room temperature produced an almost identical spectrum (Fig. 9) to that of the annealed sample (Fig. 8). We suggested above that SO₃ is the most likely surface species upon adsorption of SO₂ on Cu(100) at room temperature. The increase in S-Cu stretch in the resulting vibration spectrum (Fig. 9b) suggests the formation of S (abs.) although it is not possible to identify the reactions involved definitively without other experimental data such as thermal desorption. This spectrum also shows that any reaction involving the formation of SH (abs.) is unlikely because the characteristic vibration at 430 cm⁻¹ is missing. The SH species can, however, act as an intermediate. One possible reaction scheme would involve the dissociation of H₂S to H and SH, which would then undergo further dissociation to H and S (abs.). The dissociation of the
SH species at room temperature is consistent with the earlier temperature-dependent study shown in Fig. 4. The resulting H may combine with SO₃ to form H₂SO₃. Further study is required to substantiate this proposed mechanism.

ACKNOWLEDGEMENTS

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REFERENCES

FIGURE CAPTIONS

Figure 1:
EEL spectra of a saturation coverage of H$_2$S on Cu(100) exposed and recorded at (a) 100 K and (b) 300 K. The FWHMs of the elastic peaks and the peak locations are indicated in cm$^{-1}$.

Figure 2:
EEL spectra of a saturation coverage of (a) H$_2$S and (b) D$_2$S on Cu(100) at 100 K.

Figure 3:
EEL spectra of a saturation coverage of H$_2$S on Cu(100) at 100 K as a function of scattering geometries: (a) specular at 55°, (b) 5° off-specular and (c) 10° off-specular (note the change in the scaling factor for (c) only). The scaling factors of individual parts of the spectra are with respect to the corresponding elastic intensities, which are not normalized to each other.

Figure 4:
EEL spectra of a saturation coverage of H$_2$S on Cu(100) at 100 K after different temperature treatments. The annealing temperature (in K) and time (in seconds) are indicated in each spectrum.

Figure 5:
EEL spectra of H$_2$S on Cu(100) at 100 K as a function of coverage. The number of seconds of exposure using an effusive beam dosing method is indicated in each spectrum. A 10 sec exposure by this procedure corresponds to 0.5-1 L (1 L = 1x10$^{-6}$ torr-sec). The spectrum corresponding to a saturation coverage (~40 L) is given in (e).
Figure 6:
EEL spectra of a saturation coverage of SO$_2$ on Cu(100) exposed and recorded at (a) 100 K and (b) 300 K. The FWHMs of the elastic peaks and the peak locations are indicated in cm$^{-1}$.

Figure 7:
EEL spectra of SO$_2$ on Cu(100) at 300 K at different coverages. The number of seconds of exposure using an effusive beam dosing method is indicated in each spectrum. The spectrum corresponding to a saturation coverage (~20 L) is given in (d).

Figure 8:
EEL spectra of a saturation coverage of SO$_2$ on Cu(100) at 300 K after different temperature treatments. The annealing temperature (in K) and time (in seconds) are indicated in (b) and (c).

Figure 9:
EEL spectra of a saturation coverage of SO$_2$ on Cu(100) at 300 K before (a) and after (b) exposing an additional 12 L of H$_2$S.
Table 1: Comparison of vibrational frequencies (+4 cm\(^{-1}\)) of adsorbed H\(_2\)S and D\(_2\)S on Cu(100) at 100 K with gas-phase data.\(^{35}\)

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Table 2: Comparison of vibrational frequencies (±4 cm⁻¹) of free SO₂, SO₂ adsorbed on metal, and other oxides of sulphur.*

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*Tentative assignments: (b): metal-S stretch; (c), (d): S-O bend; (e), (f), (g): S-O stretch.
Fig. 1 Leung et al.
Fig. 2  Leung et al.
Fig. 3 Leung et al.
Fig. 4 Leung et al.
Fig. 5 Leung et al.
SO$_2$/Cu(100) specular
(b) 300K

Fig. 6 Leung et al.
Fig. 7  Leung et al.
Fig. 8 Leung et al.
SO$_2$/Cu(100)
300K

(b) add 12L H$_2$S

(a) saturation

Fig. 9 Leung et al.