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**In Situ FTIR Study of the Adsorption Geometry of Bisulfate  
Ions on a Platinum Electrode**

**by**

**Mahesh G. Samant, Keiji Kunimatsu, Hajime Seki, M. R. Philpott**

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**Abstract** It is shown that a better understanding of the geometry of adsorbed bisulfate species on the surface is gained by simultaneously monitoring more than one vibrational mode of the molecule. We propose that in the double layer region the bisulfate ions are adsorbed via an oxygen atom of its SO<sub>3</sub> unit with the Pt-O-S linkage along the surface normal. In the oxide region the bisulfate ions are adsorbed on the oxygen covered surface of the platinum electrode via the hydrogen atom by hydrogen bonding with the hydrogen bond showing a significant tilt (approximately 60°).

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## Introduction

Recently we reported that, based on a Fourier transform infrared (FTIR) study, a platinum electrode in sulfuric acid/sodium sulfate solution coadsorbs bisulfate and sulfate ions<sup>1,2,3</sup>. The detailed nature of this adsorption is a strong function of the pH of solution and the electrode potential. In addition to the shape of adsorption isotherms for sulfate and bisulfate ions on platinum electrode, we found that the adsorption of these ions on the surface was coupled to the adsorption of water molecules onto the electrode. In the particular case of adsorption from acidified sodium sulfate solution, as the electrode potential became more positive, bisulfate ion adsorption increased with one bisulfate ion displacing a given number of sulfate ions and water molecules over the entire potential range. Since a lot is known about the platinum surface the potential dependence of band position ( $\text{cm}^{-1}$ ) and intensities permitted the most probable orientations of the sulfate/bisulfate ions on the electrode surface to be hypothesized. Additional evidence was necessary to unequivocally support any of these suggested possibilities. Figure 1 (reproduced from the earlier paper<sup>2</sup>) shows some of possible orientations of sulfate and bisulfate ions and water on platinum electrode in sulfuric acid solutions.

One method discussed here which should be effective in restricting the number of possible orientations, involves studying simultaneously more than one IR sensitive vibration of the same molecule. Since the change in dipole moments of these vibrations will most likely be centered at different locations on the molecule and aligned in different directions, the variation of band intensity and position with the electrode potential should be effective in determining the possible orientation of the adsorbed molecule on the surface. This paper presents a study of three IR active vibrational modes of bisulfate ions adsorbed on Pt from 0.5 M sodium sulfate solution as a function of the electrode potential and the pH.

## Experimental

The FTIR spectra were measured using the p-polarized light on a IBM Instruments IR/98 spectrometer. The description of the procedures and the cell used has been detailed earlier<sup>2</sup>. A CaF<sub>2</sub> prism which was used as an IR transparent window in the earlier experiments was replaced with a ZnSe disk which allows transmission of the IR beam down to 700 cm<sup>-1</sup>. The IR spectra shown are difference spectra obtained by ratioing the spectra at sample potential to that one obtained at a potential 50 mV positive of the equilibrium hydrogen electrode potential (The reference potentials versus Ag/AgCl reference electrode were -0.25 V for acidic solution and -0.4 V for the neutral solution). The sodium sulfate solutions were prepared from Na<sub>2</sub>SO<sub>4</sub> (Aldrich, gold label) and Nanopure water (Barnstead Nanopure system). The pH of the solution was altered by addition of necessary quantity of sulfuric acid. The solution thus prepared were (1) 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M H<sub>2</sub>SO<sub>4</sub> and (2) 0.5 M Na<sub>2</sub>SO<sub>4</sub>. In solution 1, the ratio of the concentrations of bisulfate and sulfate ions [SO<sub>4</sub><sup>2-</sup>]:[HSO<sub>4</sub><sup>-</sup>] is approximately 49, while in solution 2 it is 1.2x10<sup>5</sup>. All potentials are referenced with respect to the Ag/AgCl (3M KCl) electrode.

## Results and Discussion

Figure 2 shows the spectra obtained as a function of the electrode potential in the acidified sodium sulfate solution. The features in these spectra are a result of adsorption of various solution species on the electrode. This has been established in the earlier studies<sup>1,2</sup> and was confirmed here following the same procedure of comparing spectra taken by s- and p-polarized light and by comparing spectra taken with and without preadsorbed CO which precluded adsorption of any other solution species. The spectra in Figure 2 indicate in addition to a band at 1600 cm<sup>-1</sup> corresponding to the bending mode of water molecules presence of 4 bands at approximately 1200, 1100, 1050 and 900 cm<sup>-1</sup>. These bands are assigned to vibrations from sulfate and bisulfate ions<sup>4</sup>. The band at 1100 cm<sup>-1</sup> corresponds

to  $\nu_3$ , the asymmetric vibration of the sulfate ions. The bands at 1200, 1050, and 900  $\text{cm}^{-1}$  correspond to  $\nu_4$ , the asymmetric stretch of  $\text{SO}_3$  unit,  $\nu_1$ , the symmetric stretch of  $\text{SO}_3$  unit, and  $\nu_2$ , the S-(OH) stretch of the bisulfate ions respectively<sup>4</sup>. The various vibrations of interest are shown in Figure 3. The dipole moment of the  $\text{SO}_3$  unit and the S-(OH) unit are coaxial with the axis coincident in direction to the S-(OH) bond but are of opposite sense with respect to each other. Figure 3 also includes the approximate location and orientation of the change in dipole moment ( $\delta\mu$ ) resulting from the bisulfate ion vibrations. The  $\delta\mu$  corresponding to the symmetric  $\text{SO}_3$  stretch and S-(OH) stretch are colinear with the S-(OH) bond, whereas  $\delta\mu$  for the asymmetric  $\text{SO}_3$  stretch makes an angle of roughly  $80^\circ$  with the S-(OH) bond axis and lies in the plane defined by the S-(OH) bond and the S-O bond which undergoes the asymmetric vibration.

Figure 2 also indicates the behavior of various bands as a function of the electrode potential. The bands corresponding to bisulfate ions show increasing intensity with the electrode potential indicative of increase in adsorption of bisulfate ions on the electrode. The sulfate band grows in intensity with electrode potential in the opposite direction, which is a result of desorption of sulfate ions. The bands corresponding to the asymmetric vibrations of bisulfate and sulfate ions in these spectra show a dependence on electrode potential in agreement with that described earlier<sup>3</sup>. Previously, it was concluded that the electrode surface in the hydrogen region has substantial amounts of adsorbed sulfate ions which progressively desorb as the electrode potential increases and this is accompanied by adsorption of bisulfate ions. This process is essentially complete in the oxide region where the nature of the platinum surface excludes adsorption of sulfate ions. Figure 4 is the plot of the intensity of various bisulfate bands as a function of the electrode potential. All bands show a similar variation with the electrode potential. Figure 5 shows the plot of the variation of the band position with the electrode potential. The band position of the vibrations corresponding to the  $\text{SO}_3$  unit of the bisulfate ion show very little variation with the electrode potential. The band position of these  $\text{SO}_3$  vibrations appears to show some small dependence on whether the electrode potential is within the double layer region or within the oxide region. Yet within

each of these two regions the vibrational frequency is fairly constant. For example  $\nu_1$  shows a small step between 0.4 and 0.6 V. This feature was found consistently in all our data, see also Figure 8. Similarly the band position of the S-(OH) vibration is fairly independent of electrode potential in the double layer region but shows a substantial dependence on the electrode potential in the oxide region. The frequency of the S-(OH) vibration increases by approximately  $9.5 \text{ cm}^{-1}/\text{V}$  in the oxide region.

The spectra obtained for adsorption of sulfate/bisulfate ions on the platinum electrode in 0.5 M  $\text{Na}_2\text{SO}_4$  (Figure 6) also show presence of four bands. Furthermore, these bands have a dependence on the electrode potential similar to that seen for the acidified sodium sulfate solution. As was the case earlier, the spectra were interpreted to indicate that the sulfate ions are incrementally desorbed as the electrode potential is made more positive and this is accompanied by adsorption of bisulfate ions on the platinum electrode. Figure 7 shows the variation of the intensity of the three bisulfate vibrational bands with electrode potential. No significant adsorption of bisulfate ions was observed on the platinum electrode in the hydrogen region. The bisulfate absorption bands were seen only in the double layer and the oxide region. The intensity variation of bisulfate bands appear to be quite similar to the one seen in Figure 4. The plot of bisulfate band position as a function of the electrode potential is shown in Figure 8. Here again the trends are identical to those seen in Figure 5. The vibrational frequency of asymmetric and symmetric stretches of the  $\text{SO}_3$  unit seem to depend more on the potential region of the electrode and is fairly constant within each region. The vibrational frequency of the S-(OH) stretch displays a significant dependence on the electrode potential in the oxide region with the rate of change of frequency with respect to the electrode potential being  $9.7 \text{ cm}^{-1}/\text{V}$ .

The only significant difference in intensity variation of the sulfate/bisulfate bands in the two solutions involves the electrode potential at which the adsorption of bisulfate ions begins. This is a consequence of much lower concentration of the bisulfate ions in the 0.5 M sodium

sulfate solution as compared to the acidified 0.5 M sodium sulfate. The intensity of the bisulfate bands show a significant dependence on the electrode potential only in the oxide region. This is somewhat more distinct in the case of acidified sodium sulfate solution. Thus based on the intensity variation we note that the increase in adsorbed bisulfate ions on the platinum electrode is minimal in the double layer region but it is quite significant in the oxide region.

The position of the frequency for all three bisulfate ion vibrations in the double layer region show only a slight shift (less than  $5 \text{ cm}^{-1}$ ) with respect to the position of these vibrations for the ions in solution. This implies a weak bonding interaction between the adsorbed bisulfate ion and the Pt electrode surface since a strong bond (covalent or ionic) would undoubtedly result in a large shift because of change in electronic structure or polarization of the ion. Since potential in the double layer region is positive of the pzc, the electrode surface has excess positive surface charge which dictates that the adsorption of the bisulfate ions occur via the electron rich oxygen atoms of the  $\text{SO}_3$  unit. A weak bonding interaction with the surface suggests adsorption predominantly via a single oxygen atom of the  $\text{SO}_3$  unit (i.e. unidentate case). A more detailed understanding of the adsorption geometry can be obtained by considering the variation of vibrational frequency with electrode potential. Interestingly enough in the double layer region the position of the frequency for all three vibrations show a negligible change with electrode potential. This is in spite of a significant increase in surface charge at the platinum electrode in the double layer region<sup>3,5</sup> which should cause a significant increase in the electric field at the electrode surface. The formalism developed for the tuning rate of molecules in presence of an electric field<sup>6</sup> suggests that the geometrical factor governing change in the vibrational frequency is the cosine of the angle between the electric field and the change of the dipole moment caused by vibration of the molecule. Therefore it appears as though the adsorption geometry is such that the interaction between the change in dipole moment corresponding to the vibrations and the electric field is greatly reduced due to presence of a large angle between them. Since the electric field and the surface normal

are coincident, the change in dipole moment due to these vibrations subtends a large angle with the surface normal. This criterion of large angle between the  $\delta\mu$ ' and the surface normal can be used to choose the most reasonable orientation at the surface. The adsorption of bisulfate ion via an oxygen atom of its  $\text{SO}_3$  unit will involve bonding to the surface via the lone pair orbitals of the oxygen atom. Two possibilities exist. First, the adsorption involves just one lone pair orbital. Here the oxygen involved in surface bond should be  $\text{sp}^2$  hybridized. The angle between the Pt-(OS) and (PtO)-S linkages is  $120^\circ$ . The known structure of  $\text{H}_2\text{SO}_4$  molecule<sup>7</sup> can be used to evaluate the angle between the surface normal and the S-(OH) bond as  $48^\circ$ . This value of the angle and the location of the  $\delta\mu$  are such that a measurable shift in vibrational frequency of S-(OH) stretch can be expected. Hence this orientation does not appear to be the most probable. Second, adsorption of bisulfate ion involves both of the lone pairs of electrons on the oxygen atom. In this case the adsorption occurs such that the Pt-(OS) and (PtO)-S linkages are colinear and lie along the surface normal (Figure 9). Again, based on the known structure of the  $\text{H}_2\text{SO}_4$  molecule, the angle (PtO)-S-(OH) should be approximately  $108^\circ$ . Hence, the angle between the electric field (and also the surface normal) and the S-(OH) bond is approximately  $72^\circ$ . Since the  $\delta\mu$  of the S-(OH) and symmetric  $\text{SO}_3$  vibration are colinear with the S-(OH) bond, only a weak interaction between these dipole moments and the electric field is expected. The angle made by  $\delta\mu$  of the asymmetric vibration of  $\text{SO}_3$  unit with surface normal depends on the nature of the vibrational motion of oxygen atom involved in surface bonding. For bonding through the asymmetrically vibrating oxygen this angle is  $27^\circ$  whereas for bonding via either of the two symmetrically vibrating oxygen this angle is  $59^\circ$ . The observation of no change in frequency for all three vibrations with the electrode potential suggests the bonding to the surface is via the symmetrically vibrating oxygen of the  $\text{SO}_3$  unit with all three atoms in the Pt-O-S linkages colinear to the surface normal.

In the oxide region the intensity of all three vibrations increases significantly yet only the vibrational frequency of the S-(OH) unit shows any significant variation with frequency. This

is a result of combination of factors. First, the significant increase in observed intensity is caused by a substantial increase of sulfate ion desorption which is due to covering of the platinum electrode with an oxide layer. This results in a substantial increase of the surface coverage of bisulfate ions. Second, the adsorption of bisulfate ions proceeds in a manner such that the axis along which the change in dipole moments of all three vibrations align closer to the surface normal. This would lead to observation of more enhanced band intensity due to the power law dependence of the measured dipole allowed intensity on the  $\cos^2\alpha$  where the angle  $\alpha$  is the angle between the change in dipole moment and the E-vector of the p-polarized light (also the surface normal). Third, since the electric field strength decreases rapidly with distance from the electrode surface in the compact layer (e.g. see Guoy-Chapman theory<sup>8</sup>) the adsorption occurs with the dipole moments corresponding to the  $\text{SO}_3$  unit lying further away from the surface. This would make the frequency of vibrations of the  $\text{SO}_3$  unit relatively less sensitive to the changes in the potential. This analysis supports the occurrence of adsorption via the hydrogen atom by hydrogen bonding onto the oxygen covered platinum surface which allows for the S-(OH) vibration being influenced more strongly by the electric field due to its proximity to the surface. The adsorption of bisulfate ion via the hydrogen atom was proposed earlier based on pure chemical intuition<sup>3</sup>. In hydrogen bonding of type O-H-O all the 3 atoms are colinear (e.g. structure of ice)<sup>9</sup>. Hence it is expected that (PtO)-H-(OS) to be fairly linear. From the structure of a  $\text{H}_2\text{SO}_4$  molecule it is known that the angle H-O-S should be about  $108.5^\circ$ . Thus if the hydrogen bond were to lie along the surface normal the expected angle between the surface normal and the S-(OH) bond will be approximately  $72^\circ$  (i.e.  $180 - 108.5^\circ$ ). This is same as the angle obtained in the double layer region which yielded no dependence of vibrational frequency on the electrode potential. Therefore it is essential that the hydrogen bond be tilted from the surface normal. This can be achieved if the hydrogen of the bisulfate ion links to a single lone electron pair of oxygen atom belonging to the the surface oxide layer. The lone pairs of this oxygen are expected to make an angle of  $60^\circ$  with respect to the surface normal. Thus the angle between the surface normal and the S-(OH) bond is evaluated to be  $11.5^\circ$ . This small angle between the

electric field and  $\delta\mu$  along with the close proximity of the S-(OH) bond to the surface indicates that there will be a measurable shift in the vibrational frequency of the S-(OH) bond. The orientation of the adsorbed bisulfate ion on the oxide surface of Pt is shown in Figure 9. In this geometry the dipole moments corresponding to the  $\text{SO}_3$  unit are effectively outside the inner Helmholtz plane of the compact layer and hence are influenced quite weakly by the electric field present at the surface.

## Conclusions

The intensity of the adsorbed bisulfate ions increases with potential at the expense of adsorbed sulfate ions. The frequency of vibrations of the asymmetric and symmetric stretches of the bisulfate ions show no change with electrode potential within the double layer region and within the oxide region. The vibrational frequency of the S-(OH) unit though constant in the double layer region increases with potential in the oxide region at the rate of  $9.5 \text{ cm}^{-1}/\text{V}$ . The bisulfate ions adsorb on the platinum electrode via an oxygen atom of the  $\text{SO}_3$  unit with the axis passing through the S-(OH) bond at  $72^\circ$  from the surface normal in the double layer region. In the oxide region the bisulfate ions are hydrogen bonded to the electrode surface. The hydrogen bond is inclined at a significant angle ( $60^\circ$ ) with respect to the surface.

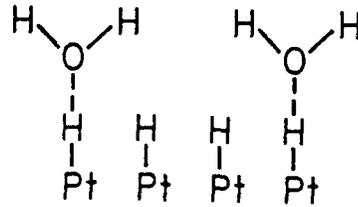
## Acknowledgements

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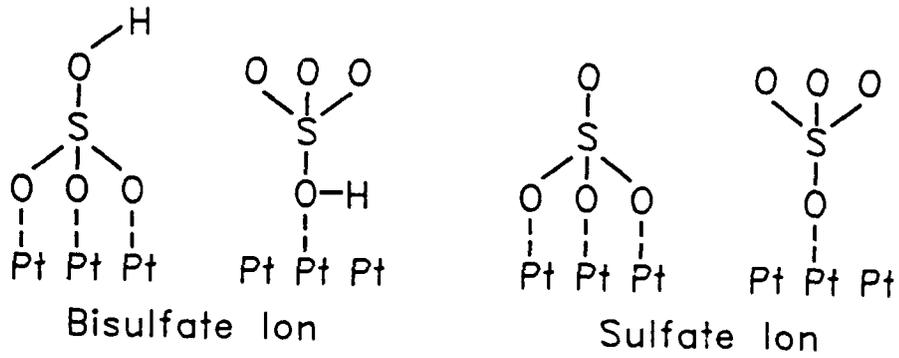
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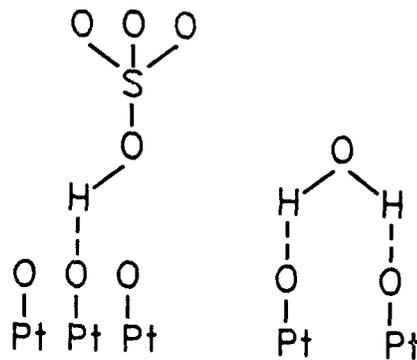
## Hydrogen Region



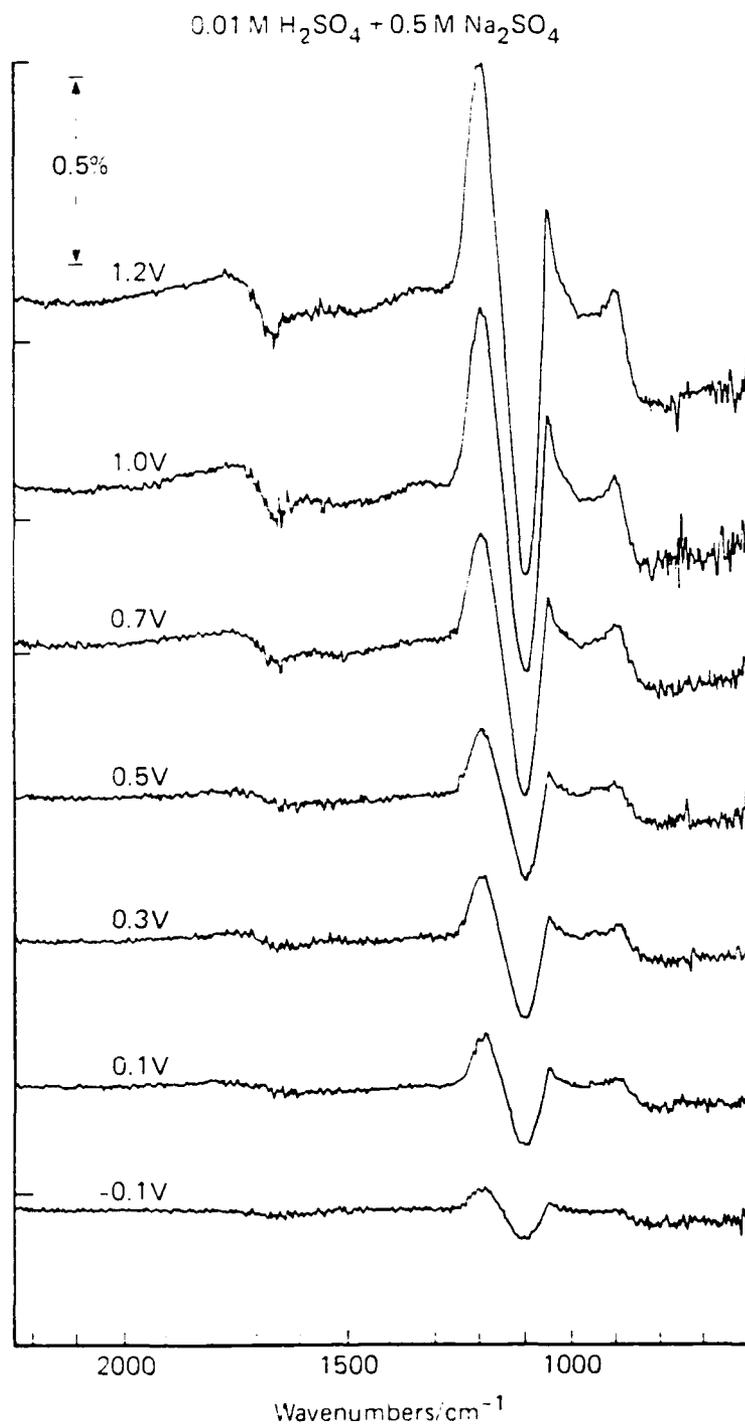
## Double Layer Region



## Oxygen Region



**Figure 1.** The compilation of possible orientations of sulfate bisulfate ions on a platinum electrode surface in sulfuric acid solutions.



**Figure 2.** The absorption spectra of adsorbed sulfate bisulfate ions on a platinum electrode obtained as a function of the electrode potential in 0.01 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{Na}_2\text{SO}_4$  solution.

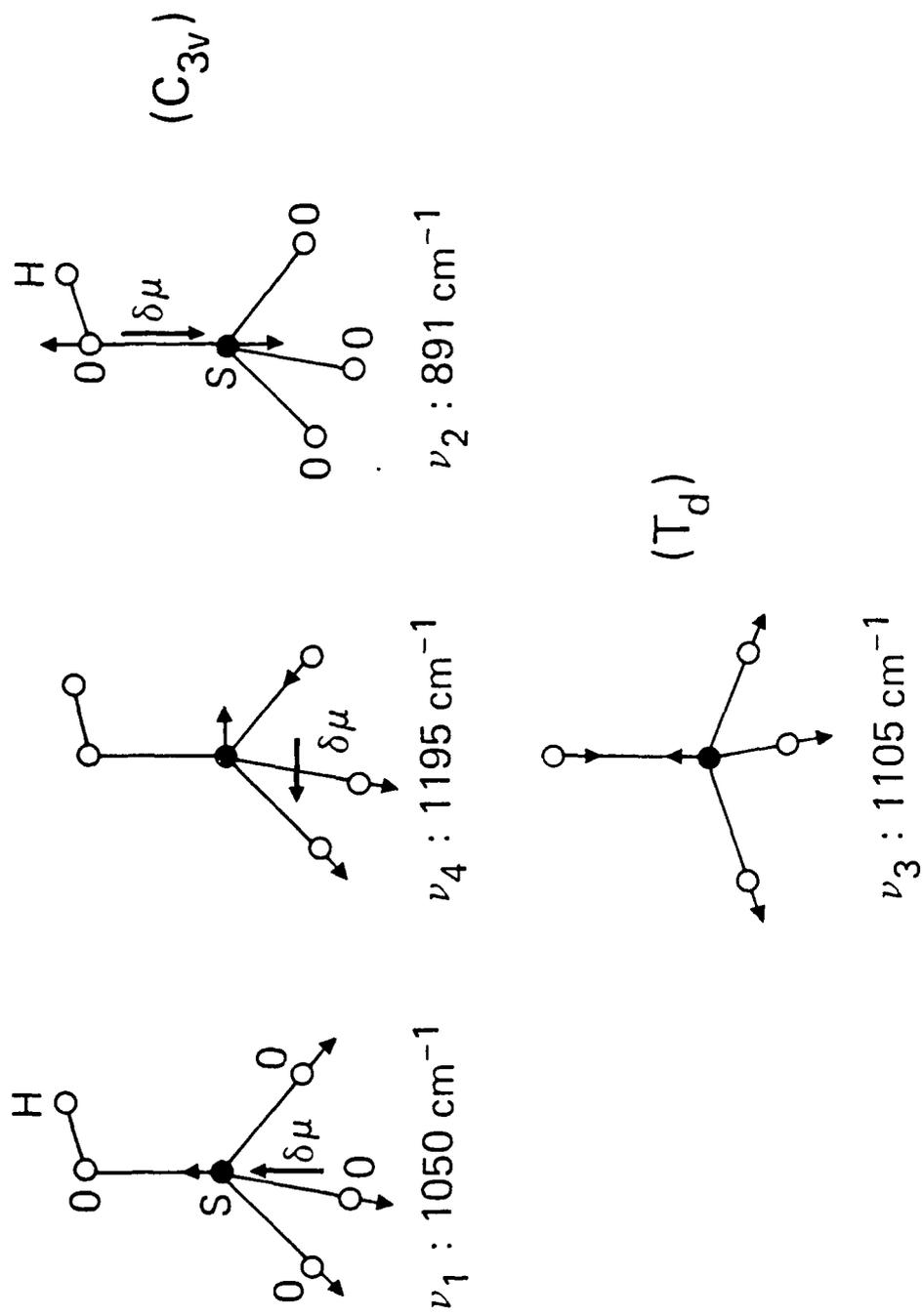
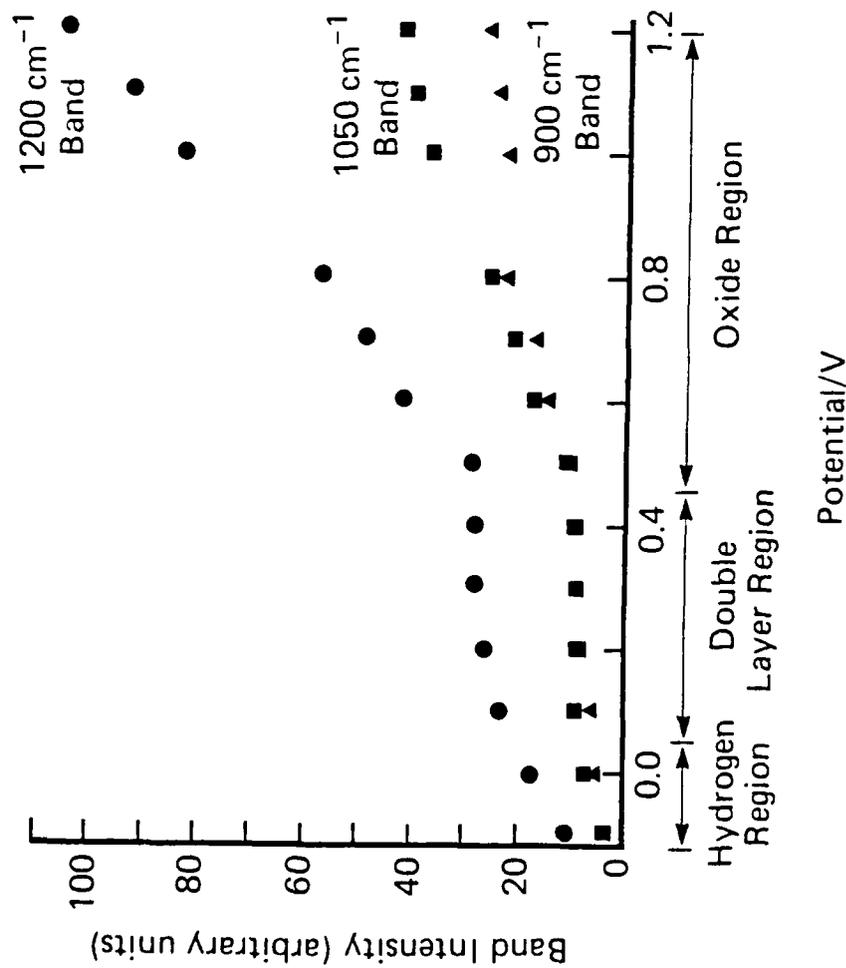
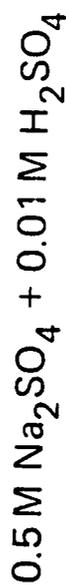
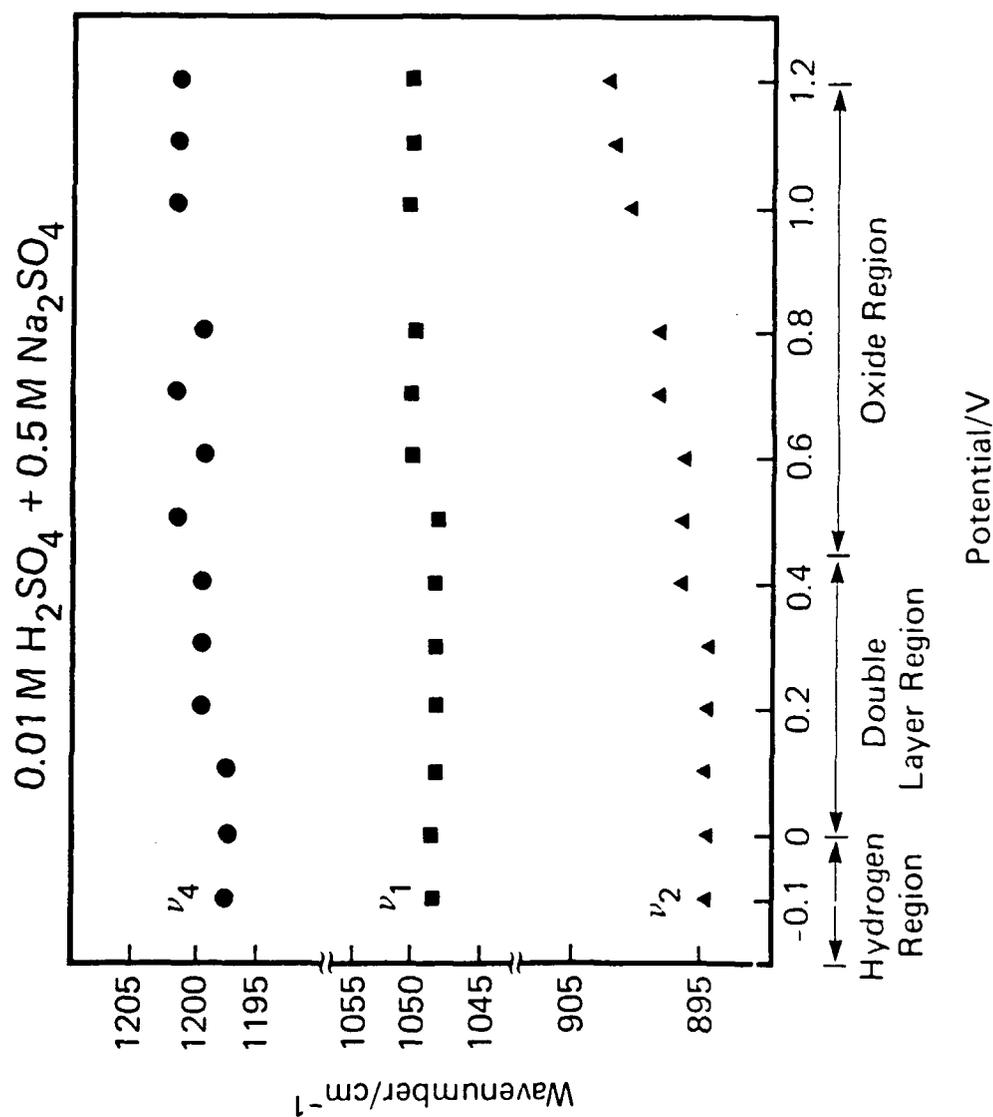


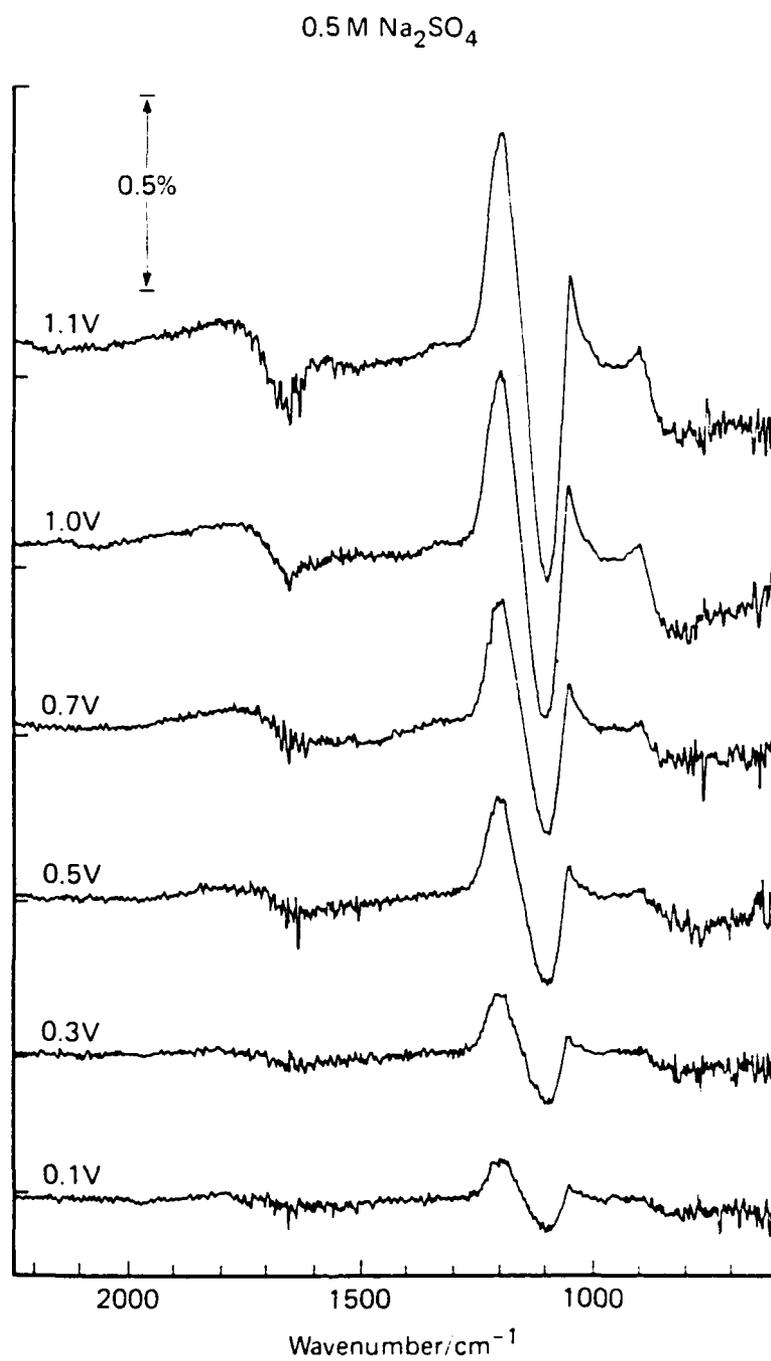
Figure 3. The stretching modes of sulfate/bisulfate ions.



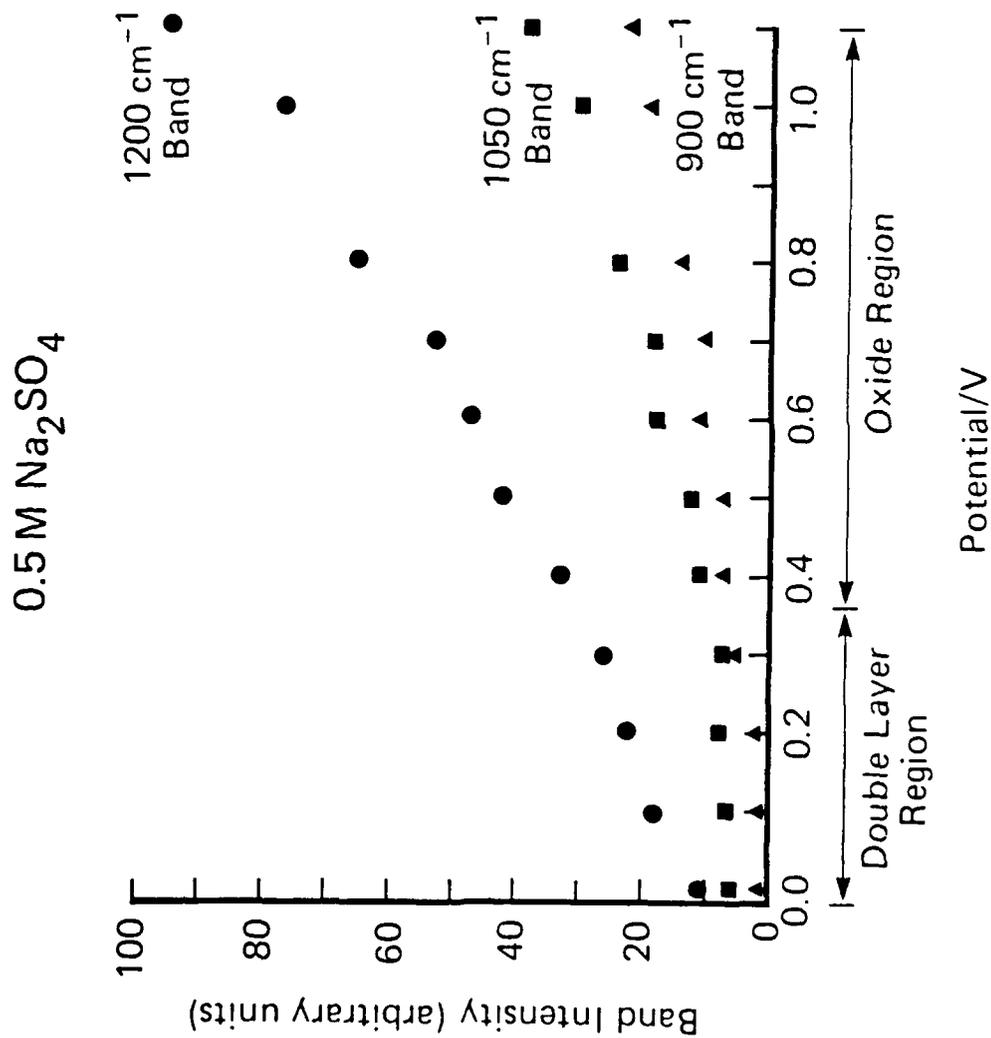
**Figure 4.** The intensity of various bisulfate ion bands obtained as a function of the electrode potential in 0.01 M  $\text{H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$  solution.



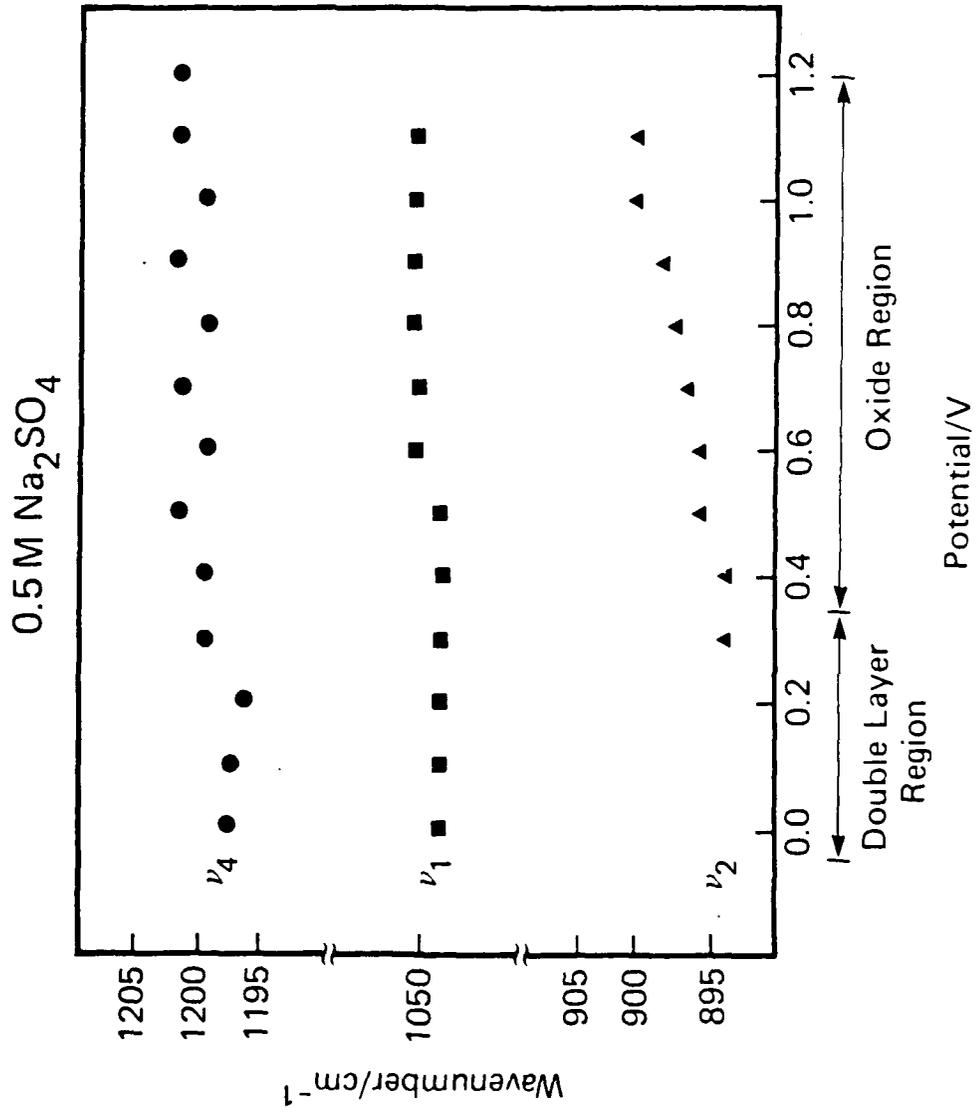
**Figure 5.** The band position of the bisulfate ion bands as a function of electrode potential in  $0.01 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$  solution.



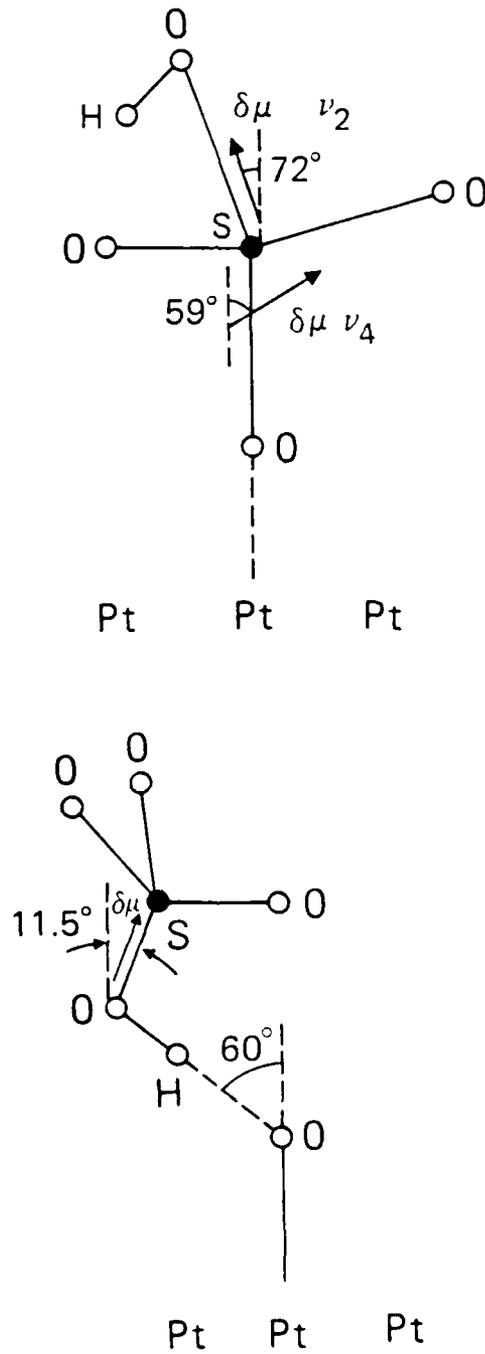
**Figure 6.** The absorption spectra of adsorbed sulfate-bisulfate ions on a platinum electrode obtained as a function of the electrode potential in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution.



**Figure 7.** The intensity of various bisulfate ion bands obtained as a function of the electrode potential in  $0.5 \text{ M Na}_2\text{SO}_4$  solution.



**Figure 8.** The band position of the bisulfate ion bands as a function of electrode potential in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution.



**Figure 9** The orientation of bisulfate ions on a platinum electrode in double layer region and in oxide region.