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(22) An analogous peak is present in chloroperoxidase, but with lowered relative intensity. Horseradish peroxidase, another high-spin ferric heme protein, shows some very weak low frequency structure but essentially no enhancement at 351 cm^{-1}.
(23) The fact that the resonance Raman intensities are sensitive to the absorption envelope does complicate matters. We should point out that a substantial change in the overall absorption spectrum accompanies the conversion of $P450_{cam}$ to the P420 form.[2] In the region of the Raman excitation (3638 Å), however, there is little change in the total absorbance and we feel that this small difference, by itself, cannot explain the selective deenhancement of the modes at 351 and 691 cm^{-1}.
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The Raman Spectrum of Adsorbed Iodine on a Platinum Electrode Surface

Sir:

Laser Raman spectroscopy has been employed in a number of recent investigations of chemical processes at working electrode surfaces.[1-4] In the present investigation, Raman spectroscopy has been employed to examine the nature of adsorbed iodine on platinum electrodes in an acidic medium. The essential electrode processes involved in this investigation have been identified by electrochemical and radiochemical techniques.[5]

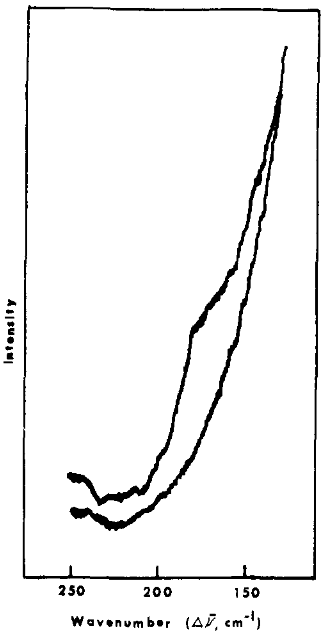

Figure 1. The Raman spectra from the surface of a platinized Pt electrode in 2 × 10^{-3} M KI, 0.1 M H_2SO_4 at +500 mV (upper trace) and +200 mV (lower trace). Exciting line: 514 nm Ar^+ (130 mW). Intensity of the 174-cm^{-1} line after background correction is ca. 250 counts s^{-1}.

Raman spectra were recorded using a modified Coderg T800 spectrometer coupled to a Spectra Physics 170 argon ion laser. A slit width of 6 cm^{-1} was used. The photometric system of the spectrometer consisted of an EMI 9789B S-11 phototube and a Brookdeal Ortec 5C1 photon counter. The signal-to-noise ratio was enhanced, where necessary, using a Hi-Tek PA1 signal averager. The electrochemical equipment including the spectroscopic cell has been described previously.[2] Potentials in the present study were measured relative to a saturated calomel reference electrode (SCE).

For Raman work it is usually essential that the electrode have a high surface area and be relatively reflecting. The gray-bronze colored platinized platinum electrodes used here were prepared by electrolysis of a lead-free chloroplatinic acid solution.[6,7] The electrodes were cycled in 1 M H_2SO_4 between hydrogen and oxygen evolution for about 15 min prior to commencing the spectroscopic experiments. The final pretreatment cycle was terminated cathodically, and weighed quantities of solid KI were added to the solution in the cell. The working solution (2 × 10^{-3} M KI, 1 M H_2SO_4) was purged with N_2 before and during the spectroscopic experiments to prevent oxidation of iodide to iodine. The profile of the cyclic voltammograms recorded using the platinized electrodes closely resembled (except for the quantity of current flowing) those recorded using smooth electrodes and also those in the literature.[5]

As the potential of the working electrode was adjusted from hydrogen evolution to +400 mV (vs. saturated calomel electrode) no potential sensitive features were observed in the Raman spectrum between $\Delta\bar{\nu}$ = 90 and 350 cm^{-1}. According to Johnson,[5] inter alia, the surface in this potential region holds adsorbed iodide ions. At an applied potential of +500 mV a band appeared at $\Delta\bar{\nu}$ = 174 cm^{-1} which was not detectable at potentials of ≥700 mV. The potential at which this line was observed coincides with the voltammetric prewave attributed to the oxidation of I^- from the bulk solution at the electrode surface and the subsequent adsorption of the I_2 produced.[5] Similar results to these have been obtained for neutral 0.1 M

KF solutions containing 2×10^{-3} M KI (Figure 1). The frequency of the Raman line argues against its assignment to I_3^- (115 cm^{-1})[8] or PtI_4^{2-} (126 cm^{-1}).[9] There are no reports in the literature of Raman spectra of PtI_2 and PtI_4, and it was not possible to obtain spectra of these compounds under conditions similar to those existing in the electrochemical experiments. Also, the ultraviolet-visible absorption spectrum of the solution after standing at +500 mV indicated that I_3^- ions were present. The disappearance of the 174 cm^{-1} band at $E \geq 700$ mV is assumed to result from the absorption of incident and scattered light by the I_3^- solution species. The observations above tend to rule out the possibility of platinum corrosion of the type previously identified electrochemically in related systems by Argue and Banewicz.[10] The assignment of the line to adsorbed I_2 is supported not only by the line position (see above) but also by the limiting adsorption data taken from the isotherms of Johnson.[5] These data favor adsorbed I_2 rather than I_3^-. In other experiments, the failure to detect adsorbed Br_2 in experiments with 0.1 M KF, 2×10^{-3} M KBr solutions is consistent with the tendency[5] of Br^- to be oxidized to BrO^- rather than Br_2.

Turning to the molecular vibrational frequency (174 cm^{-1}) which has been assigned to adsorbed iodine: the displacement of the frequency from its gas phase value (213 cm^{-1}) to that of the crystal (180 cm^{-1}) has been attributed by Anderson and Sun[11] to the influence of intermolecular forces in the crystal. The comparable but slightly larger decrease observed in the present study for adsorbed iodine suggests that both iodine-iodine and platinum surface-iodine interactions are important. In contrast to the observations for I_2 in the crystal phase,[11] the stretching fundamental for adsorbed I_2 does not appear to be split by intermolecular coupling. The breadth of the 174-cm^{-1} band in the present study may reflect a range of intermolecular interactions present in the adsorbed phase. The displacement of the I_2 fundamental is unlikely by itself to be diagnostic of sideways or end-on coordination with the surface. Both configurations would be expected to lead to a reduction in the force constant and therefore in the fundamental frequency. However, the stereochemistry[12] of numerous 1:1 donor-acceptor complexes suggests that end-on coordination would be favored.

We conclude with a comment regarding the sensitivity of Raman spectroscopy in experiments of the type reported here. The technique, while relatively insensitive, is feasible if sophisticated technique is combined with careful electrode preparation. The sensitivity of the method is far greater for systems which exhibit resonance enhancement. However, such enhancement is restricted to molecules which specifically absorb the source radiation, and hence a distorted picture of relative populations of species may result. Resonance enhancement did not appear to be a significant factor in the present study as the intensity of the 174-cm^{-1} band was not very sensitive to a change in exciting radiation from 514 to 488 nm. Also the first overtone of the 174-cm^{-1} band was not detectable. Further, the overtone peak of crystalline I_2 has been reported as very weak in intensity.

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Coordination Isomers of Biological Iron Transport Compounds. 8.[1] The Resolution of Tris(hydroxamato) and Tris(thiohydroxamato) Complexes of High-Spin Iron(III)

Sir:

Tris metal chelates in which two different donor atoms in the chelate ring coordinate to the metal ion can exist in two geometrical isomers. We previously have designated these as the cis and trans forms—both of which can exist as either Δ or Λ optical isomers.[2] These are diagramed in Figure 1 for the cis geometrical isomers. The x-ray structure analysis of tris(benzohydroxamato)iron(III), $Fe(PhC(=O)N(-O)H)_3$, found a preferred cis geometry for this complex.[3] This geometry also has been found in the potassium salt of tris(thiobenzohydroxamato)chromium(III) $Cr(PhC(=S)N(-O)H)_3$,[4] and the isostructural ferric complex.[5] The ferric ions in both the hydroxamate and thiohydroxamate complexes are high spin with magnetic moments of 5.4-5.8. μ_B.[6-8] Thus there is no ligand field stabilization energy for these d^5 metal complexes, which have been considered to be kinetically labile.[9] Both the hydroxamate and thiohydroxamate functional groups are found in a series of compounds, called the siderophores, which are manufactured by microbes as iron transport agents.[1,10] Earlier we resolved tris(hydroxamato)chromium(III)[10] and tris(thiohydroxamato)chromium(III) and -cobalt(III).[5] *To our surprise we find the corresponding ferric complexes are resolvable by the same procedure and are very stable.* To our knowledge this is the first report of the resolution of a high-spin ferric complex which is stable in solution under ambient conditions.

The tris(thiobenzohydroxamato)iron(III) was prepared from sodium thiobenzohydroxamate and ferric nitrate in acetone, methanol, or buffered aqueous solutions. In all cases a dark green product was obtained. However, a dark violet compound was obtained from the aqueous solution of sodium thiobenzohydroxamate and ferric nitrate as described earlier.[8,11] The green and the violet products have comparable analytical data: Anal. Calcd for $Fe(PhC(=S)N(-O)H_3 \cdot H_2O$: C, 47.6; H, 3.8; N, 7.9. Found, green form: C, 47.8; H, 3.6; N, 8.2. Found, violet form: C, 47.7; H, 3.5; N, 7.8.

They also have similar IR spectra in the region 400-1200 cm^{-1}, and room temperature magnetic susceptibilities (Gouy technique, $\mu = 5.4$-$5.8\ \mu_B$) and EPR spectra characteristic of high-spin iron(III) complexes. Both colored forms dissolve in concentrated potassium hydroxide solution to give the dark red-orange potassium salt, $K_3[Fe(PhC(-S)=N(-O))_3]$, which, upon careful neutralization, gives back the green form of the neutral complex . Both the tris(benzohydroxamato) iron(III) and its trisodium salt were prepared as described earlier.[12]

The tris(thiobenzohydroxamato)iron(III) was resolved by the precipitation of the double salt of its trianion with Λ or Δ-tris(ethylenediamine)cobalt(III) iodide, $[Co(en)_3]I_3$, from strongly basic solution. The neutral chelate was then extracted