We therefore conclude that CNDO/2-computed charges for **1** (Figure 2) do not correspond to the actual pattern of induced charges in the molecule.

Summaries of the most significant point charge interactions for **1** and **2**, using SRME charges, are given in Tables III and IV. In addition to the Cl···C-1 interaction[17] and the Cl···H-2*cis* interaction,[10,18] the attractive Cl···C-2 interaction makes an important contribution to stabilization of axial relative to equatorial chlorine in **1** and **2**.[19] However, we stress that calculation of the electrostatic component of the conformational energy by the charge interaction model should include *all* pairwise interactions in the molecule.[14]

In summary, an analysis of the electrostatic component of the conformational enthalpy change for **1** by the point charge interaction model leads us to conclude that the induced-charge alternation (Figure 1) predicted by CNDO/2 theory may be an artifact of the calculations rather than a molecular property. CNDO/2-computed charges are not consistent with experiment, whereas charges which conform to the classical model of the inductive effect (SRME charges[13]) give results which account reasonably well for the experimental data.

For **1** and **2**, we plan to compare the CNDO/2-predicted charges with MNDO-predicted charges.[20] We believe such a comparison will be of interest because for 1,1,1-trifluoroethane the CNDO/2-predicted negative charge on C-2 is −0.108 electron unit,[1] while the MNDO-predicted charge on C-2 is slightly positive (0.008 electron unit[21]).

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Heme Asymmetry in Deuterohemin-Reconstituted Cytochrome *c* Peroxidase

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In the course of a comprehensive study of the proton NMR spectrum[1-4] of cytochrome *c* peroxidase (EC 1.11.1.5; CcP) we have observed that reconstituting the native apoprotein with deuterohemin IX (IB) doubles the number of certain assignable hyperfine-shifted proton resonances. This indicates the presence of heme asymmetry, which may be relevant to the function of this protein. CcP is a ferriheme enzyme isolated from baker's yeast by standard procedures.[5] Its function is to catalyze the oxidation of ferrocytochrome *c* by hydrogen peroxide and as such it plays an important role in cellular electron transport. Its enzymic cycle may involve ligand binding as well as electron transfer so that the

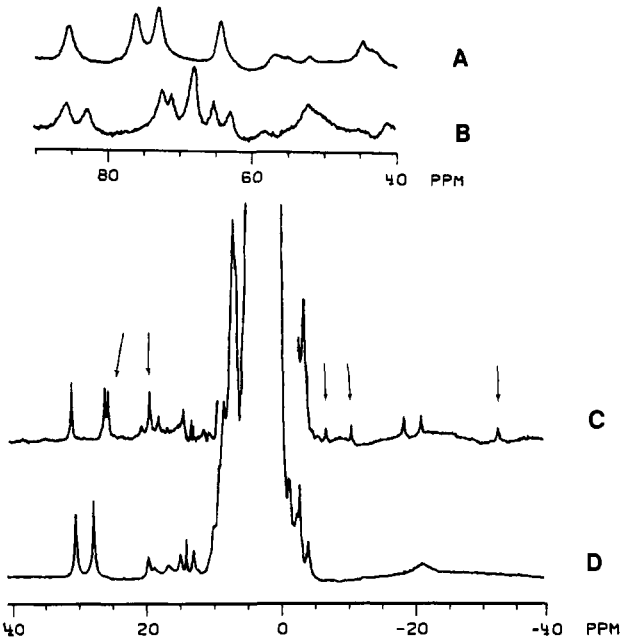
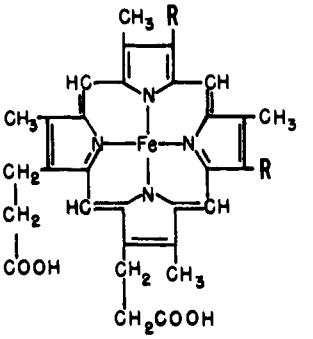


Figure 1. Downfield portion of the proton spectrum of the aquo forms of CcP (A) and deuterohemin-reconstituted CcP (B) showing double the number of peaks in the hemin methyl region between 60 and 90 ppm. C and D illustrate the effect of reconstitution upon the spectrum of the cyanide-ligated forms of the enzyme. D shows the spectrum of native CcP-CN with the two characteristic hemin methyl resonances between 26 and 31 ppm. In the deuterohemin CcP-CN spectrum (C) double the number of hemin methyl resonances indicates the heme heterogeneity. The upfield portion of spectrum C shows four instead of the expected two pyrrole 2,4 protons, further establishing this heterogeneity. Peaks comprising the minor fraction at 28 °C are indicated by arrows and include the tentatively assigned methine resonance at −5.6 ppm. All spectra were obtained on a Nicolet 360-MHz spectrometer. Samples were prepared in 0.1 M KNO_3 at pH 7.4, 25 °C. Shifts were referenced to residual water and are reported relative to external 2,2-dimethyl-2-silapentane-5-sulfonate.

observation of two sets of heme resonances presents a mechanism whereby the protein's reactivity may be subject to regulation.



IA, R = vinyl
B, R = H

The observation of two sets of hyperfine resonances appears to be related to dual sets of proton[6,7] and carbon[8] resonances which were observed for *C. thummi thummi* hemoglobin fractions and duplicity in the hyperfine resonances of both native and reconstituted sperm whale myoglobin.[9] Such previous spectral anomalies were interpreted as originating from two orientations of the heme group within the heme pocket. These orientations

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differ by 180° rotations about one of the heme pseudo-C_2 axes. In addition, an earlier report of two forms of cytochrome b_5 is further evidence of the generality of this phenomenon and suggests the possibility that such heme asymmetry could modulate electron-transfer properties as well as ligand binding.[10]

We have not yet observed such heterogeneity in native CcP but, Figure 1 demonstrates that reconstituting CcP with deuterohemin IX produces such heterogeneity. Consider Figure 1A, the spectrum of native CcP. It is similar to that of most other met-aquo heme proteins. The four intense resonances between 45 and 90 ppm downfield from 2,2-dimethyl-2-silapentane-5-sulfonate[11] were previously assigned to the peripheral methyl substituents of protohemin IX (IA).[1] Reconstitution doubles the number of methyl resonances in this region, indicating heme asymmetry. Comparison of the cyanide-ligated forms of the native and reconstituted protein (Figure 1C,D) makes this clearer.

In Figure 1D the spectrum of the cyano-native protein displays two of the protohemin methyls[12] which are shifted away from the diamagnetic envelope (30.4, 27.4 ppm). Reconstitution (Figure 1C) produces twice the number of downfield methyl resonances (31.8, 26.9, 26.4, 20.2 ppm). In the upfield region where the 2,4 protons of deuterohemin characteristically resonate[7,10] the reconstituted protein displays four resonances instead of the expected two (−9.5, −17.4, −19.7, −31.3 ppm). The peak at −5.6 ppm is assigned to a single hemin meso proton based on its integrated intensity and assignments made in model compounds. These peaks may be assigned to one component or the other on the basis of their temperature-dependent intensities, and those of the minor components at 28 °C are indicated by arrows.

Besides demonstrating that the relative concentrations of each component depend upon temperature, our preliminary work indicates their sensitivity to pH and treatment of the apoprotein. Work currently under way is designed to quantitate this behavior, elucidate the mechanism by which the heme asymmetry is established, and define the nature of the asymmetry. Whether such asymmetry exists in the native protein is particularly important. Although its presence has not yet been established, if the concentration of the asymmetric component were small, as in the case of sperm whale myoglobin, it may be difficult to detect except under more severe treatment of the protein.

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Silicon Photocathode Behavior in Acidic V(II)-V(III) Solutions

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The p-Si/VCl_3–VCl_2–HCl/C cell shows 2.8% light-to-electrical conversion efficiency at 101 mW cm^{-2} of natural sunlight with improved output retention relative to previous aqueous Si-based photoelectrochemical cells. Over a 0.5-V range, the open-circuit photovoltage follows the redox potential of the solution, ruling out, for this system, pinning of the p-Si surface Fermi level as proposed by Bocarsly et al.[1]

Photocathode-based semiconductor–liquid junction solar cells differ fundamentally from photoanode-based cells in that illumination confers cathodic protection rather than intensifying the problem of anodic photocorrosion. Reductive degradation of silicon (as to SiH_4) is kinetically difficult. n-Si photooxidizes in acid solution to form an insulating SiO_2 layer which makes Si photoanodes inactive in short order. Derivatization of the surface leads to increased stabilization but, so far, not to efficient cells.[2] For p-Si, Bookbinder et al. have shown that stable currents may be drawn for at least 24 h in mixed acetonitrile–water–NaI with organic redox couples and 2.4% conversion efficiency for 6328-Å light[3] can be reached.

According to these groups[1-4] higher efficiencies (i.e., photovoltage) cannot be reached because of "pinning" of the Fermi level at the interface. We find this explanation inconsistent with several well-established features of the surface chemistry of silicon. Si, upon exposure to air or water, readily forms an oxide layer which "unpins" the surface Fermi level.[5] A wide literature and technology of Si MIS and MOS (metal–insulator–semiconductor and metal–oxide–semiconductor) solar cells amply demonstrate that there is no pinning at the $Si/SiO_x/SiO_2$ interface. Indeed, modern silicon technology is highly dependent on the quality of this interface with respect to a low density of surface states in the forbidden gap.

Recently we reported that, by using a relatively concentrated V^{2+}/V^{3+} redox couple with p-InP, we could achieve 9.4% solar-to-electrical conversion efficiency. With p-InP, as Si, pinning is likely to be overcome by an air-formed interfacial layer (possibly also by adsorbed cations in solution). Measurements of the voltage of the p-InP/VCl_2–VCl_3–HCl/C cell as a function of the redox potential of the solution, while varying the latter, indicate that the surface Fermi level is substantially unpinned. We show that the same holds also for p-Si and, in addition, that the interface is more stable than in any other previously reported Si-based photoelectrochemical cell. We note that effects of solvents other than water[1] may produce different results and are concerned here only with aqueous environments. Indeed, in some solvents, an interfacial oxide may not be produced.

The open-circuit voltage of the cell p-Si/V^{n+}–$V^{(n+1)+}$–HCl/C, under tungsten–halogen illumination equivalent to AM1 solar, was recorded while the $n/(n+1)$ species ratio was being increased by zinc metal or decreased by access to air. Since vanadium has three (V^{3+}/V^{2+}, V^{4+}/V^{3+}, V^{5+}/V^{4+}) well-defined one-electron couples, each separated by about 0.5 V over its 2+ to 5+ oxidation states, the redox potential could be varied with ease over a wide range. Reduction by zinc metal produces equivalently concentrated Zn^{2+} solutions which may have small effects on equilibria and redox potentials. The result of the experiment is shown in Figure 1. A simple linear dependence of cell photovoltage on solution redox potential is found over a Nernst potential range of −0.4 to +0.1 V vs. SCE. Slices of a standard semiconductor grade p-Si wafer B-doped to 7×10^{15} cm^{-3}, with bulk resisivity of 3 Ω cm have been used as photocathodes. (100) faces were employed after conventional slicing and polishing, with 30% HF or with CP-4, an etchant consisting of 25 mL of HNO_3, 15 mL of CH_3COOH, 15 mL of HF, and 1% bromine. When the redox potential in a 0.35 M total vanadium solution was −0.47 ± 0.01 V vs. SCE (adjusted by access of air or by zinc reduction, as necessary), no weight loss (±10 mg cm^{-2}) was detectable after

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