Electronic Structure of Cytochrome *f* and Its Oxidation Potential

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The electronic structure of turnip cytochrome *f* has been investigated by CNDO method. The crystallographic coordinates were obtained from the Protein Data Bank at Brookhaven National Laboratory. The protein chain was truncated to separate the entity Cyt-*f* that retains the essential structural features of cytochrome *f*. Thus Cyt-*f* consists of the basic heme unit, one water molecule hydrogen bonded to a carboxylic acid substituent of the heme unit, and one tyrosine residue and one histidine residue along the axial positions on top and below the iron atom, respectively. The central metal atom's orbital angular momenta are found to be fully quenched. The HOMOs and the first few LUMOs are basically the π orbitals of the porphyrin macrocycle. Since the latter orbitals are quasi-degenerate, the Fe complex always has a high-spin ground state. Both heme and Cyt-*f* have pentet ($2S + 1 = 5$) ground states. The CNDO calculations indicate that the quartet ($2S + 1 = 4$) state is slightly more stable than the hextet ($2S + 1 = 6$) state for the oxidized forms of heme and Cyt-*f*; but the relative stability is so small that even the inclusion of only the monatomic exchange integrals would lead the spin hextets to clearly emerge as the ground states of respective cations. Hence the redox potentials were calculated with the pentet states of the reduced forms and the hextet states of the oxidized species. The reduction potential calculated for Cyt-f^+ in an aqueous solution at pH 7 is 0.295 V at 25 °C. This is in excellent agreement with the experimentally determined midpoint potential 0.365 V for the reduction of cytochrome *f* cation. The calculated potential for the species in the condensed phase of thylakoid is 0.398 V which agrees with the placement of cytochrome *f* in Z-scheme. Significant deviations in calculated potentials can be observed in the absence of histidine and tyrosine residues, which indicates the importance of these axial ligands in the evolution of the redox properties of cytochrome *f*.

1. Introduction

Cytochrome *f* is a 285-residue protein subunit anchored in the thylakoid membrane of chloroplast, which acts as a high-potential electron acceptor and as an electron donor to plastocyanin in the Z-scheme of photosynthesis. Spectroscopic studies on the soluble redox-active 252-residue lumen-side polypeptide have shown that cytochrome *f* is a c-type cytochrome with an absorption maximum at 554 nm and a midpoint oxidation potential of −365 mV at pH 7.[1] The redox partners of cytochrome *f* are its donor, the Rieske iron−sulfur protein, and its acceptor, the soluble copper protein plastocyanin.

The intact chloroplast cytochrome b_6f complex has one copy of the four polypeptides with cytochrome *f* being the largest of the four (31 289 Da), the other three being the heme containing cytochrome b_6, the Rieske protein (2Fe−2S complex), and the cofactor-free subunit IV. Cytochrome *f* contains the characteristic fingerprint sequence Cys-X-Y-Cys-His of c-type cytochromes which is responsible for covalent attachment of heme group (Figure 1).[2] The oxidation−reduction mechanism of the above cytochrome is of immense interest to both theoretical and experimental chemists.

As part of our ongoing investigations on the redox processes occurring in the Z-scheme,[3−8] we have theoretically determined the redox potential of cytochrome *f* by using the CNDO method. Section 2 describes the crystallographic molecular structure selected for our quantum chemical investigation. Section 3 discusses the calculation procedure. The computed results are presented in section 4. The energies and the molecular orbitals computed in this work will be used to determine the rate of electron transfers from the iron−sulfur protein to cytochrome *f* cation and from cytochrome *f* to plastocyanin in a work to be published elsewhere.

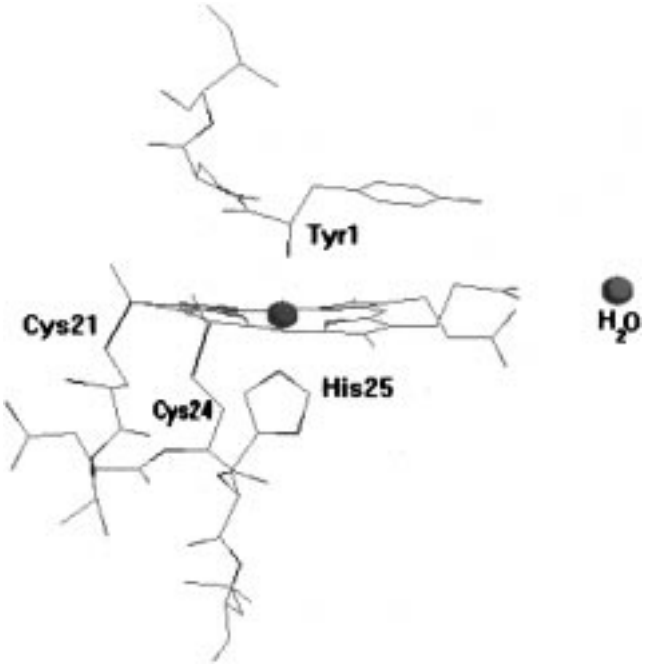

Figure 1. Cys-X-Y-Cys-His linkage in cytochrome *f*. Cys21, Cys24, the ligands [heme, tyrosine (Tyr1), and histidine (His25)] and one of the water molecules of the protein are shown here.

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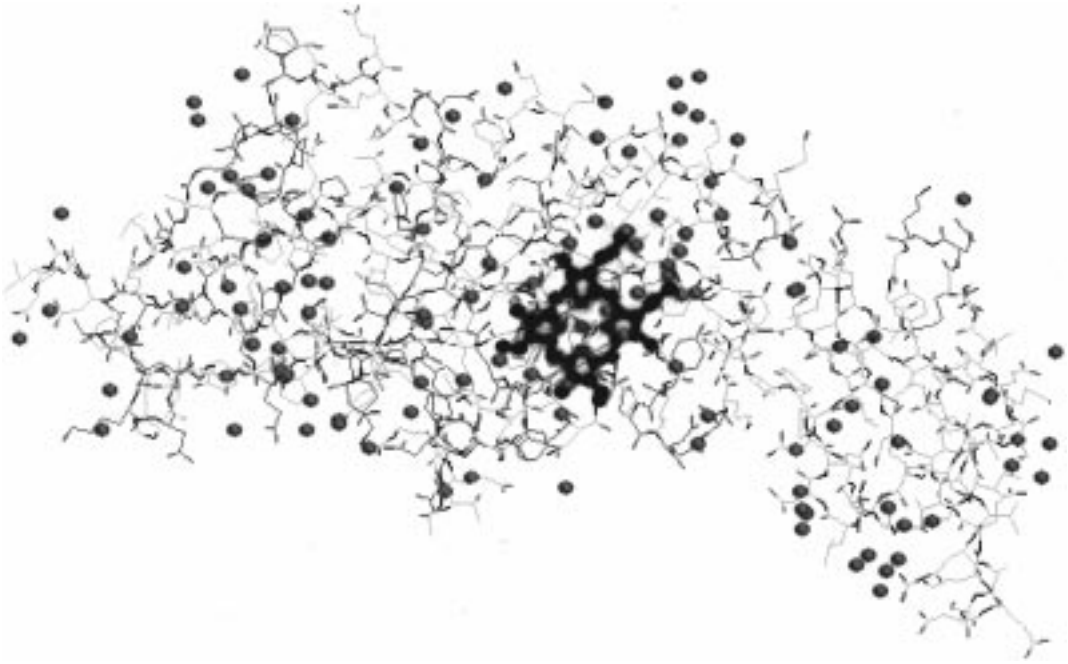

Figure 2. Position of heme group and all the water molecules in cytochrome *f*.

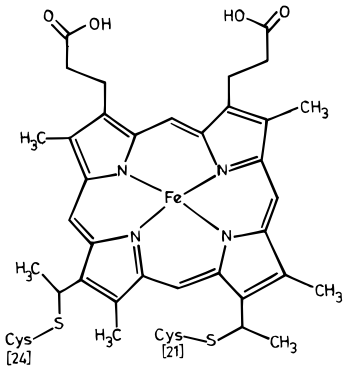

Figure 3. Heme in the native protein (the axial ligands are removed for clarity).

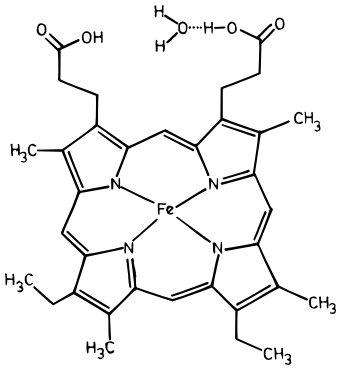

Figure 4. Heme of Cyt-*f* used for calculations. Note that the sulfide linkages are substitued with hydrogen atoms and the axial ligands (not shown for clarity, but see Figure 5) are converted into the respective amino acids.

2. Molecular Geometry

The crystallographic coordinates were downloaded from the Protein Data Bank at Brookhaven National Laboratory (file 1CTM of the reduced form of cytochrome *f* of turnip *Brassica rapa*; http://pdb.pdb.bnl.gov/bsm/pdbsum/1ctm.promotif.html). Figure 2 shows the wire model of the protein, the position of the heme moiety and the position of all the water molecules (solid spheres) in the protein. Almost all the water molecules lie far away from the iron atom but a few are close to the COOH group of the heme.

The ferrous ion in cytochrome *f* is octahedrally coordinated with four of its ligands being the four nitrogen atoms of the porphyrin ring and rest being the nitrogen of the imidizole ring of His 25 and the nitrogen of the α-amino group of Tyr 1 (Figure 1).[2]

As the protein is too big for any presently feasible quantum chemical calculation of reliable accuracy, we have in our study modified the metalloporphyrin by substituting the two connecting cystine linkages with hydrogen atoms. See Figures 3 and 4 for comparison. The two axial ligands tyrosine and histidine residues which are coordinated to the iron of heme are modified to the respective amino acids (see Figure 5, edge view). The model also includes a single water molecule lying entirely in the plane of the heme, which was taken into consideration while keeping in mind its vicinity to one of the COOH groups of the heme. This includes the possibility of hydrogen bonding of type $COOH\cdot\cdot OH_2$ (see Figure 4). For the calculations we have used the widely accepted value of 8.5 as the dielectric constant of the condensed phase of the photosystems.[6−8]

Figure 5 shows the front and the edge views of the modified cytochrome *f* moiety (Cyt-*f*) that has been used for the calculations. It also shows the position of the water molecule with respect to the porphyrin ring.

3. Method of Calculation

In our earlier work[4−9] we have consistently found that the CNDO/2 and INDO methods[10] yield good values of thermochemical properties. The INDO method is known to yield very accurate free energy changes,[4−8] but the CNDO method nevertheless yields reasonably good values.[4−6,9] A transition metal (iron) is involved in the species under investigation. We relied on the CNDO calculation because of two reasons: (i) INDO methods for transition elements are often specific for the calculation of spectroscopic properties (e.g., the calculation by ZINDO); and (ii) of course, our own CNDO program has not been extended for INDO calculations on third-row elements such

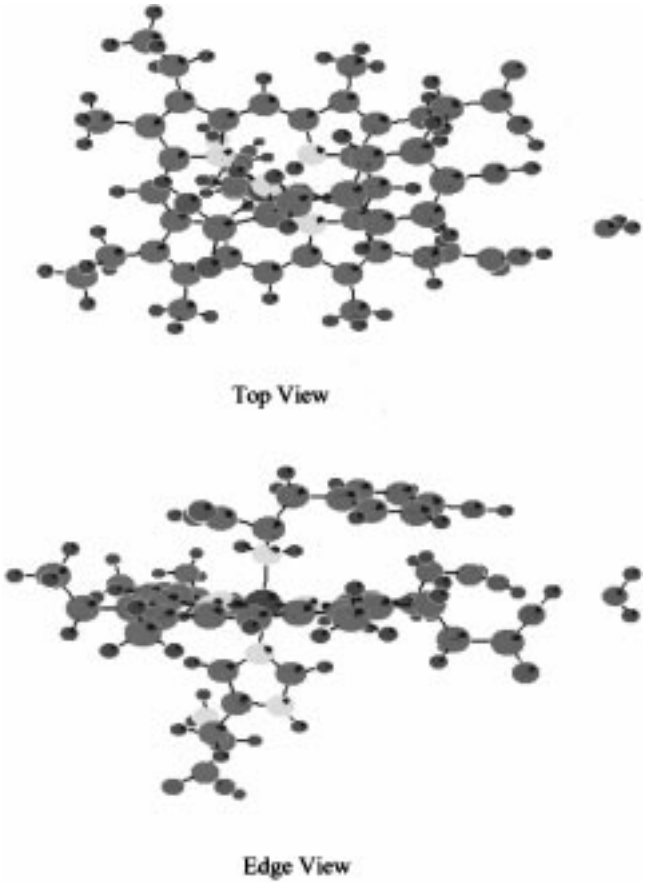

Figure 5. Top and side views of the model Cyt-*f* used for calculation.

as those belonging to the first transition series. Our CNDO program had been modified for the estimation of medium polarization effects[9] in terms of the Born term and Onsager's energy correction due to the feedback field. We have made an explicit use of G92W software[11] to compute the Onsager radius. The presence of iron atom hindered the calculation of thermal energies of the main species by G92W. But the thermal energy difference between a metalloporphyrin and its cation is known to be small, of the order of 1 kcal mol $^{-1}$ or about 0.05 eV. This is to be compared with the range of error of CNDO values for the concerned energy differences, which is of the order $\pm$0.1 eV.

In all the calculations we took the kinetic energy of the free (gaseous) electron into account and neglected all the small (*PV*−*TS*) terms. Since the same value were adopted for the oxidation (reduction) of the hydrogen molecule, there should be no error in the evaluation of the oxidation (reduction) potential. The latter property is always scaled with the oxidation (reduction) potential of hydrogen in normal state being set at zero.

Atomic coordinates of molecules H_2, H_2O, H_3O^+, and $H_2O\cdot H^+\cdot H_2O$ were optimized by G92W and then the respective dipole moments were calculated by executing our own CNDO program as discussed in ref 9.

4. Results and Discussion

For the calculation of redox potentials one needs to know the standard change in free energy $\Delta G^0_{^1/_2H_2(g)\rightarrow H^+(g)}$ corresponding to the process

$$^1/_2H_2(g) \rightarrow H^+(aq) + e^-(g) \qquad (1)$$

TABLE 1: Computed Molecular Characteristics of the Species under Investigation[a]

species[b]	spin multiplicity	Hartree−Fock total energy (au)[c]	Onsager radius (Å)[d]	dipole moment (D)[c]
histidine	1	−121.2077		4.0608
tyrosine	1	−131.0960		6.8377
porphyrin	1	−409.2505		3.4894
$[Por]^{-2}$	1	−409.3502	6.41	13.1439
heme	1	−431.2837	6.41	3.5116
	3	−431.2674	6.41	3.5137
	5	−431.3469	6.41	3.5356
$[Heme]^+$	4	−431.1130	6.41	8.1279
	6	−431.0969	6.41	8.1215
Cyt-*f*	1	−691.6878	7.32	7.5833
	3	−691.6726	7.32	7.5768
	5	−691.7514	7.32	7.1172
$[Cyt\text{-}f]^+$	4	−691.5327	7.32	6.8387
	6	−691.5179	7.32	6.8231

[a] Molecular geometries are fixed and correspond to cytochrome *f* crystallographic geometry that was obtained from the Protein Data Bank as discussed in the text. [b] Por represents the prophyrin residue inclusive of one water molecule and heme is the Fe−Por complex in Cyt-*f*. Cyt-*f* also contains histidine and tyrosine as axial ligands. [c] CNDO results. [d] Calculated by using G92W, without iron.

A *semiempirical estimate* of the free energy can be made by averaging the free energies of the reactions

$$^1/_2H_2(g) + H_2O(aq) = H_3O^+(aq) + e^-(g) \qquad \Delta G_1^0 \quad (2)$$

$$^1/_2H_2(g) + 2H_2O(aq) = H_2O\cdot H^+OH_2(aq) + e^-(g) \qquad \Delta G_2^0 \quad (3)$$

Using the data from ref 9 we get $\Delta G_1^0 = 6.619$ eV and $\Delta G_2^0 = 4.475$ eV when the kinetic energy of the free (gaseous) electron is taken into account but the small (*PV*-*TS*) terms are neglected. The CNDO estimate $\Delta G^0_{^1/_2H_2(g)\rightarrow H^+(g)} = 5.547$ eV is about 25% larger than the experimental value 4.479 eV.[12] Comparing with the INDO estimate 4.529 eV, we conclude that the error 1.1 eV in the CNDO estimate is mostly an artifact of the neglect of monatomic exchange integrals. As such, semiempirical parametrization leads to reliable thermochemical changes.

The rather large error 1.1 eV cannot greatly influence the calculation of redox potentials. The reason is as follows. The oxidation of Cyt-*f* in the condensed phase (s) corresponds to the process

$$Cyt\text{-}f(s) = Cyt\text{-}f^+(s) + e^-(g) \qquad \Delta G^0_{Cyt-f\rightarrow Cyt-f^+} \quad (4)$$

This ΔG^0 would also be in error by about the same amount (1.1 eV).[13] In fact, the oxidation potential is to be evaluated as the differential free energy change

$$(\Delta G_{Cyt-f\rightarrow Cyt-f^+} - \Delta G_{^1/_2H_2(g)\rightarrow H^+(aq)})$$

that corresponds to the reaction

$$Cyt\ f(s) + H^+(aq) = Cyt\ f^+(s) + {}^1/_2H_2(g) \qquad (5)$$

Several pioneering researchers have pointed out that the errors created in quantum chemical calculations of the energies of reactant molecules largely cancel the errors in the energies of product species so that the energy change remains more or less unaffected by a change in the methodology or by the choice of the basis set.[14] The logic used in this work is indeed familiar in quantum chemistry literature.[15]

TABLE 2: Orbital Energies of a Few Species of Interest

		orbitals of spin α			orbitals of spin β		
species	spin multiplicity	no.	nature	energy (au)	no.	nature	energy (au)
histidine	1	31	π LUMO	0.1493	31	π LUMO	0.1493
		30	π HOMO	−0.4185	30	π HOMO	−0.4185
tyrosine	1	36	π LUMO	0.1367	36	π LUMO	0.1367
		35	π HOMO	−0.4260	35	π HOMO	−0.4260
porphyrin	1	115	π	0.0285	115	π	0.0285
		114	π	0.0277	114	π	0.0277
		113	π LUMO	−0.0921	113	π LUMO	−0.0921
		112	π HOMO	0.3136	112	π HOMO	0.3136
		111	π	0.3917	111	π	0.3917
		110	π	0.3947	110	π	0.3947
$[Por]^{-2}$	1	115	π	0.2646	115	π	0.2446
		114	π LUMO	0.2639	114	π LUMO	0.2639
		113	π HOMO	−0.0080	113	π HOMO	−0.0080
		112	π	−0.0223	112	π	−0.0223
		111	π	−0.1511	111	π	−0.1511
		110	π	−0.1545	110	π	−0.1545
		109	π	−0.1619	109	π	−0.1619
heme	5	120	π	−0.0041	116	π	−0.0045
		119	π LUMO	−0.0053	115	π LUMO	−0.0061
		118	π HOMO	−0.2842	114	π HOMO	−0.2837
		117	π	−0.3334	113	π	−0.3335
$[Heme]^{+}$	4	119	π	−0.1354	117	π	−0.0965
		118	π LUMO	−0.1373	116	π LUMO	−0.0977
		117	π HOMO	−0.4329	115	π HOMO	−0.2188
		116	π	−0.4541	114	π	−0.4880
$[Heme]^{+}$	6	121	π	0.0158	115	π	0.0975
		120	π	0.1352	114	π LUMO	−0.2185
		119	π LUMO	−0.1370	113	π HOMO	0.4481
		118	π HOMO	0.4327	112	π	0.5383
Cyt-*f*	5	185	π	0.0096	181	π	0.0096
		184	π LUMO	0.0075	180	π LUMO	0.0067
		183	π HOMO	−0.2700	179	π HOMO	−0.2697
		182	π	−0.3013	178	π	−0.3017
$[Cyt\text{-}f]^{+}$	4	184	π	−0.1179	182	π	−0.0791
		183	π LUMO	−0.1197	181	π	−0.0808
		182	π HOMO	−0.4153	180	π LUMO	−0.2016
		181	π	−0.4183	179	π HOMO	−0.4578
					178	π	−0.5171
$[Cyt\text{-}f]^{+}$	6	185	π	0.1176	180	π	0.0805
		184	π LUMO	−0.1194	179	π LUMO	−0.2012
		183	π HOMO	0.4148	178	π HOMO	0.4576
		182	π	0.4180	177	π	0.5172

Computed molecular characteristics of all the involved species including Cyt-*f* and its cation Cyt-f^{+} are given in Table 1. The HOMOs and the LUMOs of each iron complex have been identified as π orbitals of the porphyrin ring. See Table 2. Orbital energies corresponding to the molecular orbitals which can be identified as primarily orbitals of the metal atom are given in Table 3. This table makes it clear that the orbital angular momentum of the metal atom has been fully quenched in heme, $heme^{+}$, Cyt-*f*, and Cyt-f^{+} in different spin states. But 4s and 4p orbitals of Fe are relatively higher in energy and contribute to a few LUMOs. Similarly, the unoccupied 3d orbitals of β spin contribute to the low-lying unoccupied molecular orbitals. Molecular orbital energy level diagrams for a few species of interest are shown in Figure 6, a and b. These exhibit features which are generally in agreement with the trends expected from a qualitative molecular orbital treatment.

Table 1 exhibits an interesting feature. For heme as well as Cyt-*f*, the pentet state is far more stable than the triplet state. This makes sense because, although the total orbital angular momentum of Fe atom is fully quenched, the HOMOs and LUMOs are mostly π orbitals of the macrocycle ligand (prophyrin) and these orbitals are quasi-degenerate so that the electron−electron repulsion forces the state with the highest spin multiplicity to appear as the ground state in an open-shell calculation. For the monopositive cations $heme^{+}$ and Cyt-f^{+}, the doublet calculation becomes oscillatory, hinting at the stability of the higher spin states, but the quartets appear to be more stable than the hextet spin states! This is not surprising at all, for the hextet−quartet energy difference is less than 0.02 au and the CNDO calculation neglects all the exchange integrals. Even if only the monatomic exchange integrals were retained as it is done in an INDO calculation, the hextet states would have clearly emerged as the ground states. Because of this fact we have taken the spin hextets as the ground states of cations in our calculation of redox potentials.

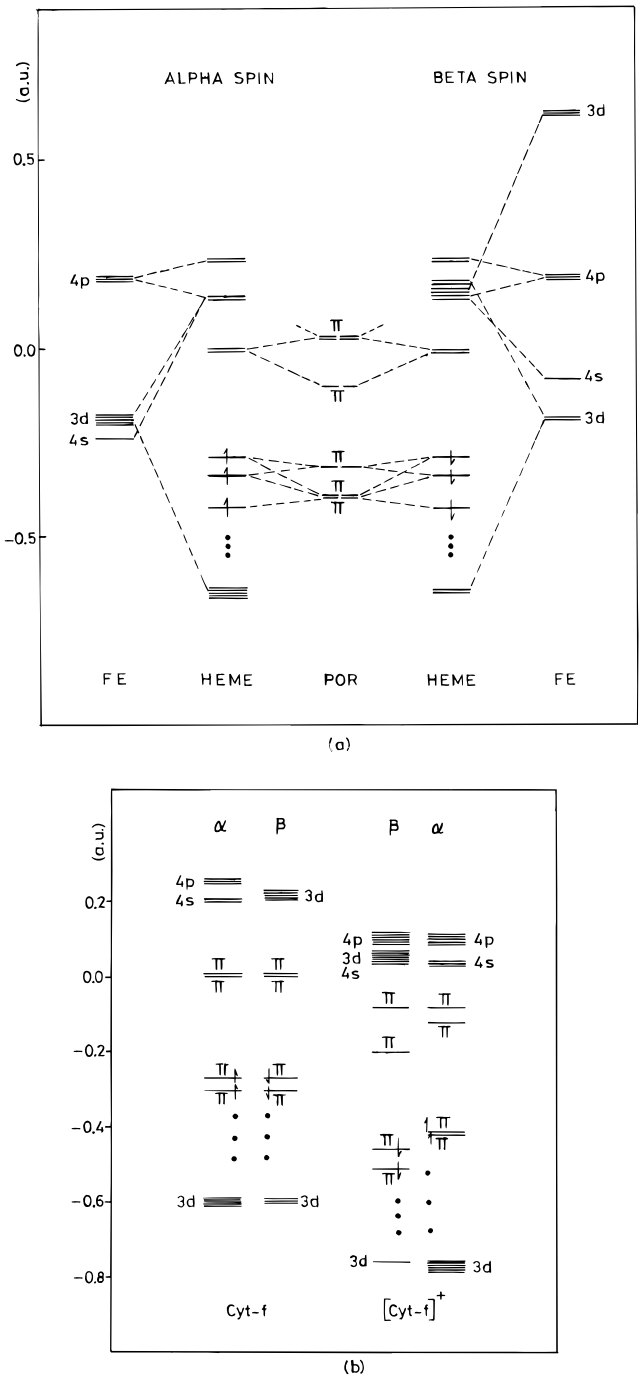

Figure 6. (a) Formation of the energy levels in heme. (b) Molecular orbital energy level diagrams for Cyt-*f* ($2S + 1 = 5$) and its cation Cyt-f^{+} ($2S + 1 = 6$). Energy levels for molecular orbitals having large contributions from the orbitals of the metal atom are indicated by writing the name of the major contributing central atom orbital (3d, 4s, or 4p) by the side of the energy levels.

The calculation of the oxidation potential of cytochorme *f* (rather, that of the reduction potential of cytochrome *f* monopositive cation), is illustrated in Table 4. Here, in analogy with our previous discussion[5−8] on the determination of redox potentials of electron-carrying agents in thylakoid membrane,

TABLE 3: Orbital Energies for Orbitals with Large Contributions from Iron Orbitals

		orbitals of spin α			orbitals of spin β		
species	spin multiplicity	no.	nature	energy (au)	no.	nature	energy (au)
heme	5	78	$3d_{x^2-y^2}$	−0.6551	79	$3d_{xz}$	−0.6423
		81	$3d_{xy}$	−0.6423	80	$3d_{xz}$	−0.6411
		82	$3d_{xz}$	−0.6416	118	4s	0.1324
		83	$3d_{yz}$	−0.6409	119	$4p_z$	0.1391
		84	$3d_{z^2}$	−0.6369	120	$3d_{x^2-y^2}$	0.1641
		122	$4p_z$	0.1366	121	$3d_{yz}$,$3d_{xy}$	0.1708
		123	4s	0.1405	122	$3d_{yz}$,$3d_{xy}$	0.1709
		132	$4p_x$,$4p_y$	0.2379	124	$3d_{z^2}$	0.1794
		133	$4p_x$,$4p_y$	0.2405	132	$4p_x$,$4p_y$	0.2389
					133	$4p_x$,$4p_y$	0.2415
$[Heme]^+$	6	73	$3d_{x^2-y^2}$	−0.7948	76	$3d_{xz}$	−0.7646
		74	$3d_{x^2-y^2}$	−0.7816	118	4s	0.0084
		75	$3d_{xz}$	−0.7754	119	$4p_z$	0.0139
		77	$3d_{xy}$,$3d_{yz}$	−0.7667	120	$3d_{x^2-y^2}$	0.0411
		78	$3d_{xy}$,$3d_{yz}$	−0.7654	121	$3d_{xy}$	0.0477
		79	$3d_{xz}$	−0.7643	122	$3d_{yz}$	0.0480
		81	$3d_{xy}$,$3d_{yz}$	−0.7603	123	$3d_{z^2}$	0.0556
		122	$4p_z$	0.0134	129	$4p_x$,$4p_y$	0.1131
		123	4s	0.0160	130	$4p_x$,$4p_y$	0.1159
		129	$4p_x$,$4p_y$	0.1121			
		130	$4p_x$,$4p_y$	0.1145			
		131	$4p_x$,$4p_y$	0.1154			
Cyt-*f*	5	135−139	3d	−0.5994 to −0.5904	133−135	$3d_{xz}$	−0.5995, −0.5979, −0.5923
		201−202	4s	0.2017, 0.2034	199	$3d_{x^2-y^2}$	0.2113
		211−213	$4p_x$,$4p_y$	0.2555, 0.2591, 0.2628	200,204	$3d_{yz}$	0.2137, 0.2260
					201	$3d_{z^2}$	0.2151
					202	$3d_{xy}$	0.2168
$[Cyt\text{-}f]^+$	6	118−126	3d	−0.7808 to −0.7568	124	$3d_{xz}$	−0.7553
		190−192	4s	0.0385, 0.0404, 0.0439	186−188	4s	0.0391, 0.0407, 0.0442
		198−200	$4p_z$	0.0813, 0.0932, 0.0949	189	$3d_{x^2-y^2}$	0.0474
		201	$4p_x$	0.1008	190−192	$3d_{z^2}$,$3d_{yz}$	0.0503, 0.0521, 0.0524
		202	$4p_y$	0.1030	193	$3d_{xy}$	0.0537
					199−205	4p	0.0958 to 0.1115

TABLE 4: Calculation of the Reduction Potential (*E*) of Cytochrome *f* Cation at 25 °C[a]

phase[b]	ΔE_{CNDO} (au)	$\Delta E_{solution}$ (au)	ΔE_{total} (eV)[c]	*E* (V)[d]
		Species X: heme		
aqueous	−0.2500	0.0430	−5.6693	0.536
condensed	−0.2500	0.0384	−5.7965	0.663
		Species X: Cyt-*f*		
aqueous	−0.2236	0.0356	−5.4279	0.295
condensed	−0.2336	0.0318	−5.5306	0.398

[a] The reaction studied is X^+ ($2S + 1 = 6$) + e^- = X ($2S + 1 = 5$), where X is either heme or Cyt-*f*. [b] Dielectric constant is 78.5 for the aqueous phase and 8.5 for the condensed phase inside the thylakoid membrane. [c] The kinetic energy of the free electron 0.03855 eV has been subtracted to obtain the total ΔE. [d] This *E* refers to the midpoint potential at pH 7 in an aqueous phase, and to the reduction potential shown in the Z-scheme when referred to the condensed phase of the thylakoid membrane in equilibrium with the surrounding solvent phase at physiological pH.

we have adopted the dielectric constant 8.5 for the membrane phase. Similarly, for the aqueous phase we have retained the static dielectric constant of 78.5 at 298.15 K.[9] The CNDO estimate for $\Delta G_{^1/_2H_2 \rightarrow H^+(aq)}$ at 298.15 K at pH 7 is 5.133 eV. The latter quantity has been used throughout in our calculation.

The reduction potential calculated for Cyt-f^+ in aqueous phase at pH 7 is 0.295 V. This is in excellent agreement with the experimentally determined midpoint potential for the reduction of cytochrome *f* cation, 0.365 V.[1] The condensed phase value 0.398 V also agrees very well with the placement of cytochrome *f* in Z-scheme at around 0.4 V. Table 4 also manifests that when the histidine and tyrosine ligands are not considered (that is, when the species X is heme), the calculated potentials differ from the observed ones by more than 0.2 V. This is in general in agreement with the recent finding by Rovira et al.[16] that an imidazole ligand induces significant changes in the properties of iron porphyrin−(AB) complexes with AB = O_2, CO, and NO. Any investigation of electron transfer from cytochrome *f* or to its cation will remain inconclusive unless one takes into consideration the presence of the two ligands tyrosine and histidine above and below the plane of the heme.

5. Conclusions

In this work we have presented a semiempirical evaluation of the oxidation potential of cytochrome *f*. As the molecule is too large for our own computing abilities, we have truncated the protein chain while leaving aside the essential structural features of cytochrome *f*. The CNDO calculation indicates that the oxidation potential would be about −0.3 V (±0.1 V) which is in extremely good agreement with the experimentally determined midpoint value of −0.365 V at pH 7. The difference is less than 0.003 au, which, in spite of the highly complex nature of effects arising out of different dynamics, is remarkably small. Similarly, the reduction potential calculated for the condensed phase in equilibrium with the surrounding aqueous medium at physiological pH is about 0.4 V, which matches excellently with the placement of cytochrome *f* in Z-scheme of green-plant photosynthesis. This success is not astonishing at all—we have repeatedly demonstrated that the Pariser−Parr−Pople development of semiempirical theories is ideally suitable for thermochemical calculations. The results are good enough to indicate that the CNDO estimate of $\Delta G_{^1/_2H_2(g) \rightarrow H^+(aq)}$ has been quite correct. We have not explicitly taken into account the thermal energy differences between the metal complexes and

their cations, and neglected all ($PV-TS$) terms. These effects can lead to a change in the calculated potentials by about ± 0.1 V.

In summary, the calculated semiempirical electronic structures are indeed good approximations to the electronic structures in the real specimens. Our ultimate objective is to determine the rates of electron transfer from (Fe−S) complex to cytochrome f^+ and from cytochrome f to plastocyanin. This work clearly forms the basis of our future investigation.

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References and Notes

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(12) ΔG_f^0 for H(g) is 203.25 kJ mol^{-1} and ΔE_{sol} for H^+(g) is 1090 kJ mol^{-1} as documented by: Barrow, G. M. *Physical Chemistry*, 5th ed.; Tata-McGraw-Hill: New Delhi, 1992. These data were used to calculate the experimental value while the exceedingly small *TS* terms were neglected.

(13) This would hold good as the HOMOs are expected to be the π orbitals delocalized on the ligand atoms and with very little contributions from the iron atomic orbitals. The situation would change if, for example, the Fe atom is replaced by a rare earth.

(14) One of the authors (S.N.D.) first learned it from H. Eyring in 1976. Handy, Hirshfelder, Lykos, Simons, and Trular have discussed this point in various lectures. For instance, J. Simons mentioned the same observation while discussing the problems associated with the investigation of negative ion ground states in the International Symposium on Aspects of Many Body Effects in Molecules and Extended Systems held at IACS, Calcutta, in 1988. K. Raghavachary discussed the contribution of Pople to the investigation of isodesmic processes in XII International Conference on Computers in Chemical Research and Education held in Pune in 1998.

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