Resonance Raman Spectra of Ferrylporphyrins and Related Compounds in Dioxygen Matrices

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Resonance Raman (RR) spectra are reported for three ferryl compounds: (TPP)FeO, (OEP)FeO, and (salen)FeO (where TPP = tetraphenylporphyrinato anion, OEP = octaethylporphyrinato anion, and salen = N, N'-ethylenebis(salicylideneaminato)anion). (TPP)FeO and (OEP)FeO were formed via laser photolysis (406.7-nm line) of cocondensation products of Fe(TPP) and Fe(OEP), respectively, with dioxygen at 15 K. In both cases, the ferryl stretching (ν (FeO)) bands appear at 852 cm⁻¹ as the O-O bond cleavage reaction proceeds and their intensities reach maxima after about 20 min of laser irradiation (1-2-mW power). This photolysis does not occur with other exciting lines. In the case of Fe(salen), similar photolysis occurs readily with laser lines in the range from 457.9 to 514.5 nm as evidenced by the appearance of the ν (FeO) at 851 cm⁻¹. In contrast, attempts to prepare (Pc)FeO (Pc = phthalocyanato anion) by similar procedures were not successful although all lines in the region from 406.7 to 676.4 nm were employed. Instead, these excitations produced the RR spectrum of $Fe(Pc)O_2$ which exhibited the ν (Fe-O₂) and δ (FeOO) at 488 and 279 cm⁻¹, respectively. The oxidation and/or spin state marker bands were observed at 1375 (band A), 392 (band E), and 1575 cm⁻¹ (band D) for (TPP)FeO and at 1379 (v₄), 1507 (v₃), and 1643 $cm^{-1}(v_{10})$ for (OEP)FeO. These frequencies indicate that the iron atom in the ferrylporphyrins is low-spin with formal oxidation state close to Fe(IV). Furthermore, the FeO stretching force constant obtained (5.32 mdyn/Å) is much larger than the FeO single-bond stretching force constant $(3.80 \text{ mdyn}/\text{\AA})$. On the basis of these and other results, we propose to formulate the five-coordinate ferrylporphyrin as $PFe^{IV} \leftrightarrow O^{2^{-}}$ (P = porphyrin) which involves one σ and two π bonds. The marked enhancement of the v(FeO) relative to porphyrin core vibrations suggests the possibility of direct resonance excitation via an electronic transition involving FeO charge transfer which is located near 406.7 nm, the wavelength of the laser line used for excitation.

Introduction

The activation of molecular oxygen has been a subject of considerable interest in recent years.^{2,3} Biological systems are able to incorporate readily and efficiently one or both atoms of dioxygen into a substrate in a highly specific manner.^{2,4} For example, cytochrome P-450 catalyzes the necessary function of substrate hydroxylation in living organisms.⁵ Its active site is protoporphyrin IX which is commonly found in hemoproteins such as hemoglobin, myoglobin, or peroxidases. During the catalytic cycle, cytochrome P-450 forms a dioxygen adduct which is converted into a ferryl species via the O-O bond cleavage. This ferryl species is unstable and releases the activated oxygen atom which is capable of hydroxylating even the C-H bond of a substrate molecule. Such ferryl species are also involved in the reactions of horseradish peroxidases and cytochrome oxidases.⁴

The electronic structures of the "ferryl compounds" have been studied extensively by using various spectroscopic techniques. Mössbauer studies on horseradish peroxidase compound I (HRP-I) and compound II (HRP-II)^{6,7} showed that the iron atoms in these compounds are in the Fe(IV) state. Subsequent studies with ESR,⁸ magnetic susceptibility,⁹ NMR,¹⁰ and ENDOR¹¹ as well as the-

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oretical studies^{12,13} are consistent with the description of HRP-I as a Fe(IV) (S = 1) porphyrin π cation radical. On the other hand, HRP-II is regarded as a Fe(IV) (S = 1) without π cation character according to MO calculations.¹² However, Morishima and Ogawa¹⁴ on the basis of heme methyl proton shifts in the ¹H NMR spectra have proposed an alternative structure. According to these workers, HRP-I involves a Fe(IV) (S = 2) configuration with a single electron distributed not on the porphyrin ring but on the protein. The electronic structure of ferrylmyoglobin, which is formed by the oxidation of oxymyoglobin or metmyoglobin at alkaline pH, has been studied by ESR,¹⁵ Mössbauer,¹⁶ magnetic susceptibility,¹⁷ and electronic spectra¹⁶ and magnetic circular dichroism.¹⁸ These results show that it is a Fe(IV) (S = 1) protein similar to HRP-II.

Extensive studies have been carried out to mimic hydroxylation reactions of cytochrome P-450 using model systems. For example, Groves and co-workers^{19,20} have shown that hydrocarbons can be epoxidated and/or hydroxylated by using iodosylbenzene or organic peroxy acids as oxygen donors and metalloporphyrins such as Fe(TPP)Cl as the catalyst. The proposed mechanisms of these reactions involve the formation of ferrylporphyrin (or its equivalent) whose oxygen atom is utilized for oxygen insertion. Mössbauer studies^{19,20} as well as optical measurements²¹ show that the intermediate species involves the Fe(V) $(S = \frac{3}{2})$ or Fe(IV) porphyrin π cation radical. Recently, we²² made a preliminary report on a ferrylporphyrin, (TPP)FeO, which was formed by laser irradiation of $Fe(TPP)O_2$ in O_2 matrices at 15 K. The band at

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852 cm⁻¹ observed in RR (resonance Raman) spectra has been assigned to ν (FeO) (ν , stretching) based on the oxygen and iron isotope shifts. Subsequently, the ν (FeO) band of HRP-II was located at 787 cm⁻¹ (isoenzyme C) by Hashimoto et al.²³ and at 779 cm⁻¹ (isoenzyme A-1) by Terner et al.²⁴ by RR spectroscopy. Recently, Sitter et al.²⁵ observed that HRP-II (isoenzymes B and C) exhibits the ν (FeO) at 779 cm⁻¹ in acidic solution but at 789 cm⁻¹ in alkaline solution. These workers assigned the former to the ferryl group which is hydrogen bonded to the distal imidazole and the latter to the ferryl group which is free from such hydrogen bonding. The ν (FeO) band is also reported to be at 797 cm⁻¹ in ferrylmyoglobin.²⁶

In this paper, we report the RR spectra of (TPP)FeO, (OEP)FeO, and (salen)FeO which are formed by laser irradiation of corresponding dioxygen adducts in O₂ matrices at 15 K. The electronic structure of the ferryl group in the former two compounds will be discussed based on ν (FeO) as well as several porphyrin core vibrations which are known to be sensitive to the change in the oxidation and/or spin state of the iron atom. Possible mechanisms of resonance enhancement of the ν (FeO) band near 852 cm⁻¹ will be proposed. In the case of Fe(Pc)O₂, laser irradiation does not produce the ferryl species. Instead, we²⁷ obtain the RR spectra of the dioxygen adducts whose ν (Fe-O₂) and δ (FeOO) (δ , bending) vibrations have been assigned based on oxygen isotope shifts and normal-coordinate calculations.

Materials and Methods

Tetraphenylporphyrin (H₂TPP) and octaethylporphyrin (H_2OEP) were obtained from Midcentury, Posen, IL. H_2TPP was purified by literature methods²⁸ and then chromatographed on alumina to remove traces of tetraphenylchlorin.²⁹ H₂OEP was used without further purification. Fe(TPP)Cl and Fe(OEP)Cl were prepared by the method of Chang et al.³⁰ $Fe(TPP)(pip)_2$ (pip = piperidine) and $Fe(OEP)(py)_2$ (py = pyridine) were synthesized by using the methods of Epstein et al.³¹ and Bonnett and Dimsdale,³² respectively. Iron(II) phthalocyanine (FePc) was purchased from Eastman Kodak Co. and purified by sublimation. The pyridine complex of N,N'-ethylenebis(salicylideneaminato)iron(II), Fe(salen)(py), was prepared according to Niswander and Martell.³³ The gases ¹⁶O₂ (99,99%, Matheson), $^{17}O_2$ (~77%, Monsanto Research), and $^{18}O_2$ (95.91%, Monsanto Research) were used without further purification. A mixture of ${}^{16}O_2$, ${}^{16}O^{18}O$, and ${}^{18}O_2$ was prepared by electrical discharge of an equimolar mixture of ${}^{16}O_2$ and ${}^{18}O_2$. Ozone produced during the process was decomposed on activated 4A molecular sieves (Aldrich Chemicals). The mixing ratio of these isotopic molecules was determined by Raman spectroscopy.

The iron complexes were placed in a miniature oven under the cold tip of our matrix isolation Raman apparatus.³⁴ The graphite oven was heated up to 450 K under vacuum (10^{-5} torr) by laser to remove adsorbed water and piperidine or pyridine from the complexes. The "base-free" complexes thus obtained were vaporized by heating the oven to 500 K and cocondensed with dioxygen on the inclined surface of the cold tip which was cooled

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Figure 1. Resonance Raman spectra of Fe(TPP) cocondensed with dioxygen at 15 K (406.7-nm excitation) with (A) ${}^{16}O_2$, (B) ${}^{18}O_2$, and (C) ${}^{16}O_2/{}^{16}O_1{}^{18}O_2$ (1/2/1 ratio).

to 15 K by a CTI Model 21 closed-cycle helium refrigerator.

RR spectra of the cocondensation products were measured on a Spex Model 1401 double monochromator. Spectra-Physics Models 164-01 Kr-ion and 164-08 Ar-ion lasers were used as the exciting sources. RR spectra of the dioxygen adducts of iron porphyrins were excited by 406.7-nm radiation (Kr-ion laser), while those of Fe(salen) and FePc complexes were excited by 457.9-nm (Ar-ion laser) and 676.4-nm (Kr-ion laser) radiation, respectively. The power of the laser used was 1-2 mW throughout the experiments. The accuracy of frequency reading was ± 1 cm⁻¹.

Results

(*TPP*)FeO. We have demonstrated previously³⁵ via IR studies that matrix cocondensation reactions of Fe(TPP) with dioxygen at 15 K produce five-coordinate "base-free" Fe(TPP)O₂. The 1:1 (O₂/Fe(TPP)) stoichiometry was confirmed by the observation that essentially the same spectra were obtained by changing the O₂/Ar dilution ratio in a wide range from pure O₂ to 1/1000 (O₂/Ar) while maintaining the same vaporization conditions of Fe(TPP). The Fe(TPP)O₂ thus obtained is a mixture of two isomeric forms; the major product is an end-on isomer which exhibits the ν (O₂) at 1195 cm⁻¹ while the minor product is a side-on isomer with the end-on isomer when the matrix is warmed up to 100 K.

As stated in our previous communication,²² laser irradiation (406.7 nm) of $Fe(TPP)O_2$ in pure O_2 matrices yields ferryltetraphenylporphyrin, (TPP)FeO, via the O-O bond cleavage of dioxygen. It should be noted that this O-O bond cleavage reaction proceeds photochemically as the ferrylporphyrin is not formed with other laser lines of much higher power (20-30 mW). Figure 1A shows the RR spectrum of (TPP)FeO thus obtained. The strongest band at 852 cm⁻¹ is assigned to the ν (FeO) since it is shifted to 818 cm⁻¹ by ${}^{16}O_2 - {}^{18}O_2$ substitution (Figure 1B). The magnitude of this shift is in good agreement with that expected for a Fe-O harmonic oscillator. When similar experiments are made with a 1:2:1 isotopic mixture of ${}^{16}O_2$: ${}^{16}O^{18}O_2$, only two ν (FeO) bands are observed at 852 and 818 cm⁻¹ as shown in Figure 1C. These results clearly indicate that the bands at 852 and 818 cm⁻¹ are due to the ν (Fe¹⁶O) and ν Fe(¹⁸O) of (TPP)FeO, respectively. Further support for these assignment is provided by the high-frequency shifts (4 cm^{-1}) of these bands by ${}^{56}\text{Fe}-{}^{54}\text{Fe}$

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Figure 2. Resonance Raman spectra of Fe(OEP) cocondensed with dioxygen at 15 K (406.7-nm excitation) with (A) ¹⁶O₂, (B) ¹⁸O₂, and (C) ¹⁶O₂/¹⁶O¹⁸O/¹⁸O₂ (1/2/1 ratio).

isotopic substitution.²² The intensity of the ν (FeO) band is time-dependent and reaches the maximum after ca. 20 min when the laser power is kept at 1-2 mW. A plot of the relative intensity of the ν (FeO) band vs. time of laser irradiation shows that the above photolysis follows first-order kinetics.²²

The most striking features of Figure 1A,B are the high intensities of these ν (FeO) bands which surpass all porphyrin core vibrations. In Figure 1C, the TPP band at 392 cm⁻¹ is slightly stronger than that of the ν (FeO) since the former is an overlap of two bands due to the TPP vibration of the ¹⁶O and ¹⁸O species. The relatively strong appearance of the TPP band at 1374 cm⁻¹ in Figure 1C can also be explained in a similar manner. Other strong bands observed at 1551, 1507, and 1463 cm⁻¹ (marked by asterisks) are due to the stretching vibrations of unbound dioxygen, ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂, respectively.

Recently, Balch et al.³⁶ observed by using ¹H NMR spectroscopy that (TMP)FeO is formed via the O-O bond cleavage of (TMP)Fe-O-O-Fe(TMP) upon warming its toluene solution to $-30 \degree C$ (TMP = tetramesitylporphyrinato anion). However, we³⁵ could not find any indication of such dimerization in our previous IR matrix experiments. Thus, the possibility of forming the ferryl species via the O-O bond cleavage of such a dimer seems to be remote in our case.

(OEP)FeO. Similar to the case of $Fe(TPP)O_2$, cocondensation reactions of Fe(OEP) with dioxygen at 15 K yield a mixture of end-on and side-on dioxygen adducts, Fe(OEP)O2, which exhibit the $\nu(O_2)$ at 1190 and 1104 cm⁻¹, respectively.³⁵ Ågain, the latter is converted into the former at 100 K. When these dioxygen adducts are irradiated by the 406.7-nm line of a Kr-ion laser, the RR spectra such as shown in Figure 2A-C are obtained. The strong bands at 852 and 817 cm⁻¹ are assigned to the ν (FeO) of (OEP)Fe¹⁶O and its ¹⁸O analogue which are formed by the O-O bond cleavage of the bound dioxygen. In this case, resonance enhancement of these ν (FeO) bands relative to OEP vibrations is less dramatic than that of (TPP)FeO discussed above. Again, the O-O bond cleavage by laser irradiation follows first-order kinetics and the ν (FeO) band intensity reaches the maximum after ca. 20 min (1-2 mW). Similar to ferryltetraphenylporphyrin, (OEP)FeO is formed only when the dioxygen adduct is irradiated with the 406.7-nm line of a Kr-ion laser.



Figure 3. Resonance Raman spectra of Fe(salen) cocondensed with dioxygen at 15 K (457.9-nm excitation) with (A) ¹⁶O₂, (B) ¹⁸O₂, and (C) ${}^{16}O_{2}/{}^{16}O^{18}O/{}^{18}O_{2}$ (1/2/1 ratio).

(salen)FeO. We³⁵ have shown previously that the cocondensation product of Fe(salen) with O_2/Ar is Fe(salen) O_2 which exhibits the $\nu(O_2)$ at 1106 cm⁻¹ in IR spectra and that the structure-spectra relationship derived from published data suggests a side-on structure. When Fe(salen)O₂ thus formed is irradiated by the 457.9-nm line of an Ar-ion laser (1-2 mW), the spectrum shown in Figure 3A is obtained. The band at 851 cm⁻¹ is shifted to 816 cm⁻¹ by ${}^{16}O_2 - {}^{18}O_2$ substitution (Figure 3B), and a mixture of ${}^{16}O_2/{}^{16}O_1{}^{18}O_2$ yields only two bands at these frequencies (Figure 3C). The RR spectrum of Fe(salen) thin film shows no such bands in the 800-900-cm⁻¹ region. These results clearly indicate that the bands at 851 and 816 cm-1 are due to the $\nu(\text{Fe}^{16}\text{O})$ and $\nu(\text{Fe}^{18}\text{O})$ of (salen)FeO, respectively.

Different from the ferrylporphyrins discussed previously, (salen)FeO is formed immediately by laser irradiation. Furthermore, the 406.7-nm line used for the photolysis of oxo(porphyrinato)iron does not produce (salen)FeO. With the 457.9-nm excitation the ν (FeO) band is most strongly enhanced. Even so, it is not as strong as those of the ferrylporphyrins discussed earlier. In fact, the Fe(salen) bands at 1585 and 619 cm⁻¹ are stronger than the ν (FeO) band at 851 cm⁻¹. Only a weak band is observed at 851 cm⁻¹ when the laser line is chosen near 515 nm.

(Pc)FeO. The IR spectrum of Fe(Pc)O₂ exhibits the ν (O₂) at 1207 cm⁻¹ which is the highest among those we studied previously.³⁵ This result indicates that the O-O bond in $Fe(Pc)O_2$ is the strongest since higher $\nu(O_2)$ implies less electron density in the 2p π^* orbitals of the dioxygen. Apparently, a large π -conjugated system of the Pc ring is responsible for the decrease in the electron density on the Fe atom which, in turn, decreases electron donation to the dioxygen. We have attempted to prepare ferrylphthalocyanine using the laser photolysis technique described earlier. However, no ferryl species was formed in spite of our effort to cleave the O-O bond with all available laser lines between 406.7 and 676.4 nm. Instead, we were able to obtain the RR spectrum of $Fe(Pc)O_2$ which will be discussed later.

Discussion

Structure-Sensitive Bands of (TPP)FeO. RR spectra of Fe-(TPP) complexes exhibit three bands in the regions 1370-1340 (band A), 1570-1540 (band D), and 390-370 cm⁻¹ (band E) which are known to be sensitive to the change in the oxidation and/or spin state.³⁷⁻⁴¹ Table I lists the frequencies of five Fe(TPP)

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TABLE I: Oxidation/Spin State Sensitive Bands in Resonance Raman Spectra of Fe(TPP)LL' Series $(cm^{-1})^d$

| | CN | state | oxidn state | spin state | band | | | | |
|-------------------------|----|--------------------------------------|------------------|---------------|------|------|-----|-----|--|
| L, L' | | | | | D | A | E | ref | |
| μ -N ^a | 5 | CS ₂ soln | +3.5 | l.s. | 1567 | 1367 | 386 | 42 | |
| μ -C ^a | 5 | solid | +4 | l.s. | 1571 | 1370 | 394 | 43 | |
| | 5 | CH ₂ Cl ₂ soln | +4 | 1.s. | 1568 | 1365 | 392 | 44 | |
| μ -N ^{+ a} | 5 | CH_2Cl_2 soln | >+4 | l.s. | 1560 | 1370 | 389 | 44 | |
| Ō | 5 | O_2 matrix | ≥+4 ^b | 1.s. | 1575 | 1374 | 392 | С | |
| μ -O ^a | 5 | thin film | +3 | h.s. | 1554 | 1363 | 391 | С | |
| | 5 | CH ₂ Cl ₂ soln | +3 | h.s. | 1553 | 1359 | 390 | 38 | |
| Cl | 5 | thin film | +3 | h.s. | 1554 | 1362 | 390 | С | |
| | 5 | N_2 matrix | +3 | h.s. | 1556 | 1364 | 391 | С | |
| | 5 | CH ₂ Cl ₂ soln | +3 | h.s. | 1555 | 1366 | 390 | 38 | |
| Im. Im | 6 | CH ₂ Cl soln | +3 | l.s. | 1568 | 1370 | 390 | 38 | |
| , | 4 | thin film | +2 | i.s. | 1562 | 1367 | 390 | С | |
| | 4 | Ar matrix | +2 | i.s. | 1565 | 1370 | 391 | с | |
| | 4 | CH ₂ Cl ₂ soln | +2 | i.s. | 1565 | 1370 | 392 | 38 | |
| CO, CO | 6 | CO matrix | $+2^{-}$ | l.s. | 1568 | 1369 | 392 | С | |
| NO, NO | 6 | NO matrix | $+\bar{2}$ | l.s. | 1569 | 1369 | 391 | с | |

^a(TPP)Fe-X-Fe(TPP) where X is shown. ^bSee text. ^cThis work. ^dAbbreviations: Im, imidazole, l.s., h.s., and i.s. denote low, high, and intermediate spin, respectively; CN, coordination number.

| L, L' | CN | state | oxidn state | spin state | band | | | |
|---|----|--------------------------------------|-----------------|---------------|-----------------|-----------------|-----------------------------|-----|
| | | | | | $\nu_3(A_{lg})$ | $\nu_4(A_{lg})$ | $\nu_{10}(\mathbf{B_{lg}})$ | ref |
| μ -N ^a | 5 | CS_2 soln | +3.5 | l.s. | 1513 | 1378 | 1647 | 52 |
| 0 | 5 | O_2 matrix | +4 ^b | l.s. | 1507 | 1379 | 1643 | с |
| μ -O ^a | 5 | thin film | +3 | h.s. | 1492 | 1377 | 1624 | С |
| μ -O ^a | 5 | CS_2 soln | +3 | h.s. | 1495 | 1377 | 1627 | 52 |
| Cl | 5 | thin film | +3 | h.s. | 1495 | 1377 | 1630 | с |
| Cl | 5 | CH ₂ Cl ₂ soln | +3 | h.s. | 1493 | 1374 | 1629 | 49 |
| F | 5 | CH_2Cl_2 soln | +3 | h.s. | | 1375 | 1629 | 53 |
| Br | 5 | CH_2Cl_2 soln | +3 | h.s. | | 1373 | 1631 | 53 |
| I | 5 | CH_2Cl_2 soln | +3 | h.s. | | 1374 | 1631 | 53 |
| Im, Im ^d | 6 | CH_2Cl_2 soln | +3 | l.s. | 1504 | 1374 | 1640 | 49 |
| ClÓ₄ | 5 | CH_2Cl_2 soln | +3 | i.s. | 1513 | 1377 | 1645 | 54 |
| 4-CNpy, ClO₄ | 6 | CH_2Cl_2 soln | +3 | i.s. | 1507 | 1376 | 1637 | 54 |
| ••• | 4 | thin films | +2 | i.s. | 1509 | 1378 | 1646 | с |
| | 4 | N_2 matrix | +2 | i.s. | 1510 | 1378 | 1644 | с |
| | 4 | Ar matrix | +2 | i.s. | 1511 | 1379 | 1647 | С |
| NO, NO | 6 | NO matrix | +2 | 1.s. | 1495 | 1377 | 1643 | с |
| CO, CO | 6 | CO matrix | +2 | l.s. | 1510 | 1378 | 1638 | с |
| py, py | 6 | KBr disk | +2 | l.s. | 1493 | 1365 | 1621 | С |
| pip, pip | 6 | KBr disk | +2 | l.s. | 1493 | 1359 | 1625 | с |
| py, ĊŎ | 6 | KBr disk | +2 | l.s. | 1503 | 1380 | 1636 | 48 |
| 2-MeIm | 5 | CH ₂ Cl ₂ soln | +2 | h.s. | 1488 | 1359 | 1608 | С |
| S(CH ₂) ₃ CH ₃ ^e | 5 | THF soln | +2 | h.s. | 1476 | 1362 | 1606 | с |
| SC,H. | 5 | THF soln | +2 | h.s. | 1476 | 1358 | 1605 | с |

^a (OEP)Fe-X-Fe(OEP) where X is given. ^bSee text. ^cThis work. ^dClO₄ salt. ^ePotassium 18-crown-6 salt. ^fAbbreviations: pip, piperidine; pv, pyridine; CN, coordination number; h.s., l.s., and i.s. denote high spin, low spin, and intermediate spin, respectively.

complexes we observed in thin films or in gas matrices together with those in the literature. Our values are in good agreement with those obtained in solution and in the solid state.

Band A originates from $\nu(C_{\alpha}-N) + \delta(C_{\beta}-H)$ (where C_{α} and C_{β} refer to those at the α and β positions of the pyrrole ring respectively), and its frequency is known to depend upon the electron density on the π^* (eg) orbital of the porphyrin core.^{38,39} In general, this frequency becomes higher in going to higher oxidation state complexes since the electron density in this orbital decreases as the oxidation state becomes higher. However, it does not necessarily reflect the oxidation state of the Fe atom involved. For example, a square-planar Fe(TPP) (Fe(II), intermediate spin) exhibits band A at 1367 cm⁻¹ in a thin film, at 1369 cm⁻¹ in a pure N_2 matrix, and at 1370 cm⁻¹ in a pure Ar matrix. These frequencies are higher than those of Fe(III) high-spin complexes

(1362 cm⁻¹) and close to those of Fe(III) low-spin complexes (1370 cm^{-1}). This phenomenon is also seen for the corresponding OEP complexes. (Table II). The electronic configuration of intermediate-spin Fe(II) and low-spin Fe(III) complexes are similar $((d_{xy})^2(d_{\pi})^3(d_{Z^2})^1$ and $(d_{xy})^2(d_{\pi})^3$, respectively, ^{45,46} and the $d_{x^2-y^2}$ orbital is empty).⁴⁶ These configurations minimize π back-bonding to the porphyrin π^* orbital and raise band A to near ~1370 cm⁻¹.

Thus far, only a few RR data are available for the high-oxidation-state Fe(TPP) complexes. Recently, (tetraphenylporphyrinato)iron dimers bridged by the nitrogen or carbon atom have been prepared. The series of compounds ((TPP)Fe)₂N, ((TPP)Fe)₂C, and ((TPP)Fe)₂N⁺ contain low-spin Fe atoms, and Mössbauer data show increasing charge at the iron atom in the above order; the formal oxidation state of iron is +3.5 for the μ -nitrido dimer, +4 for the μ -carbido dimer, and higher than +4 for $((TPP)Fe)_2N^{+.47}$ The RR spectra of these compounds show band A at 1367,⁴²⁻⁴⁴ 1370,^{42,44} and 1370 cm⁻¹,⁴² respectively, as shown in Table I. The observed frequency (1374 cm⁻¹) of (TP-

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Figure 4. Structure-sensitive bands in the RR spectra of Fe(OEP)-LL'type complexes. HS, LS, and IS denote high spin, low spin, and intermediate spin, respectively.

P)FeO is higher than that of these high-oxidation-state compounds and suggests the oxidation state of Fe(IV) or higher.

Band E is assigned to a porphyrin core deformation mode and was thought to be an oxidation-state marker.³⁸ All Fe^{III}(TPP) complexes exhibit this band in the 388-391-cm⁻¹ range, while Fe¹¹(TPP) complexes show it in the 376-384 cm⁻¹ range.⁴⁰ However, this band appears near 390-392 cm⁻¹ in some Fe(II) complexes listed in Table I. Also, its frequency decreases in the order of $((TPP)Fe)_2C$ (392-396 cm⁻¹) > $((TPP)Fe)_2N^+$ (389 cm^{-1} > ((TPP)Fe)₂N (386 cm⁻¹) although the formal oxidation statse of the Fe atoms in these compounds do not decrease in the same order. So the frequency of this band seems to depend not only on the oxidation state but also on the spin state and the nature of the axial ligand. Hence, the frequency of 392 cm⁻¹ observed for (TPP)FeO does not necessarily reflect its high oxidation state.

Band D was assigned to $\nu(C_{\beta}-C_{\beta}) + \nu(C_{\beta}-H)$ by Burke et al.³⁸ It has been well established³⁸⁻⁴⁰ that this band serves as a spin state marker: 1542-1554-cm⁻¹ range for high-spin complexes and 1553-1572 cm⁻¹ for low-spin complexes regardless of the oxidation state of iron. The (tetraphenylporphyrinato)iron dimers ((TP-P)Fe)₂N, $((TPP)Fe)_2C$, and $((TPP)Fe)_2N^+$ contain low-spin iron atoms and exhibit band D at 1567, 1571, and 1560 cm⁻¹, respectively.⁴²⁻⁴⁴ (TPP)FeO exhibits this band at 1575 cm⁻¹ which is the highest among all Fe(TPP) complexes and shows conclusively that it is a low-spin complex.

Structure-Sensitive Bands of (OEP)FeO. Extensive studies have already been made on the oxidation and/or spin state marker bands for Fe(OEP) complexes.48,49 These studies show that $\nu_3(A_{1g})$ (1475-1515 cm⁻¹) and $\nu_{10}(B_{1g})$ (1605-1650 cm⁻¹) ae sensitive to the change in the oxidation as well as spin state while $\nu_4(A_{1g})$ (1355–1380 cm⁻¹) is sensitive to the change in the oxidation state only. Table II summarizes the frequencies of these three vibrations obtained for more than 20 compounds, and Figure 4 plots these frequencies.

The v_4 corresponds to band A of Fe(TPP) complexes and to band IV of hemoproteins.⁴⁹ This vibration is due to $\nu(C_{\alpha}-N)$ coupled with $\delta(C_{\alpha}-C_m)$ (C_m, meso carbon) which involves in-plane displacements of all four pyrrole nitrogen atoms toward the central metal.^{50,51} Its frequency reflects the electron population in the π^* (e₂) orbital of the porphyrin core. As discussed earlier, decreasing charge transfer from the $d_{\pi}(Fe)$ to the $\pi^*(porphyrin)$

orbital causes shortening of the C_{α} -N bond, leading to an increase in the ν_A frequency. As is shown in Figure 4, both high- and low-spin Fe^{III}(OEP) complexes exhibit ν_4 at 1373–1377 cm⁻¹. The ν_4 of ((OEP)Fe)₂N (formal oxidation state, +3.5) is at 1378 cm⁻¹,⁵² while that of (OEP)FeO we obtained by laser photolysis is at 1379 cm^{-1} , indicating an oxidation state higher than +3.5. Similar to the case of Fe^{II}(TPP), some Fe^{II}(OEP) complexes of intermediate spin exhibit the v_4 band in the range of Fe^{III}(OEP) low-spin complexes. Also, a number of Fe^{II}(OEP) low-spin complexes containing strong π -acceptor ligands (CO, NO, etc.) raise v_4 close to 1378 cm⁻¹ while those containing π -donor ligands (SR⁻) lower it near 1360 cm^{-1.37} Thus, the v_4 frequency does not always reflect the real oxidation state of the Fe atom. 49,55,56

The ν_3 and ν_{10} vibrations are sensitive to both oxidation and spin states of the heme iron atom and correspond to bands III and I of hemoproteins, respectively.⁴⁹ These vibrations are due to $\nu(C_{\alpha}-C_{m})$ coupled with $\nu(C_{\alpha}-C_{\beta})$. The large size of the Fe atom in the high-spin complexes causes expansion or out-of-plane deformation of the porphyrin core, either of which would product a weakening of the methine bridge bonds and decrease the ν - $(C_{\alpha}-C_{m})$.^{49,51} As is shown in Figure 4, however, these vibrations are also sensitive to the oxidation state because the $C_{\alpha}-C_{m}$ bond order is affected by the electron density on the porphyrin π^* (e_g) orbital. Thus, it is not possible to make clear-cut predictions on the oxidation and spin states based on these frequencies. It is seen in Figure 4, however, that the v_3 (1507 cm⁻¹) and v_{10} (1643 cm⁻¹) of (OEP)FeO are in and above the Fe(III) low-spin range, respectively, and definitely higher than those of Fe(III) high-spin complexes. On the basis of the three frequencies mentioned above, we conclude that (OEP)FeO is a low-spin complex with the oxidation state close to Fe(IV). Similar conclusions have been drawn previously for HRP-II which exhibits the v_4 and v_3 at 1379 and 1509 cm⁻¹, respectively.²³

Electronic Structure of Ferryl Group. As discussed above, the RR data suggest that the five-coordinate ferrylporphyrins we obtained in O₂ matrices involve low-spin Fe atoms with oxidation state close to Fe(IV). Furthermore, these ferryl complexes exhibit the ν (FeO) at 851-852 cm⁻¹ regardless of the nature of the inplane chelating ligand. This result indicates that there is no appreciable vibrational coupling between the ν (FeO) and in-plane ligand modes. Simple diatomic calculations yield a force constant of 5.32 mdyn/Å for the ν (FeO). This value is much larger than the FeO single-bond stretching force constant of (Fe(TPP))₂O $(3.80 \text{ mdyn/Å})^{57}$ and indicates substantial π bonding between the iron and oxygen atoms of the ferryl group. Using Badger's rule, we estimate the FeO distance of (TPP)FeO to be 1.67 Å. This value is close to 1.70 Å assumed by Strich and Veillard⁵⁸ in their MO calculations of ferrylporphyrins and is much shorter than 1.763 Å obtained for (Fe(TPP))₂O.⁵⁹

On the basis of these observations, we propose to express the ferrylporphyrin as $PFe^{IV} \leftrightarrow O^{2-}$ (P = porphyrin) which involves one σ bond (d_z²-p_z overlap) and two π bonds (d_{xz}-p_x and d_{yz}-p_y) overlap). The equivalence of the orbitals in the x and y directions in the five-coordinate species necessitates this triple-bond formulation. Here, the broken lines imply that these π bonds are relatively weak due to poor overlap of the orbitals involved. This may occur when the porphyrin core of the five-coordinate complex is domed. In fact, the Fe atoms in ((TPP)Fe)₂C,⁶⁰ ((TPP)Fe)₂N,⁶¹

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TABLE III: Comparison of Frequency, Force Constant, and Formulation



and ((TPP)Fe)₂O⁶¹ show marked vertical deviations from the center of the porphyrin plane (0.26, 0.32, and 0.5 Å, respectively).

As stated earlier, the ν Fe(O) of HRP-II and ferrylmyoglobin are at 787²³ and 797 cm⁻¹,²⁶ respectively. These values yield the force constants of 4.45 and 4.66 mdyn/Å, respectively. The weakening of the FeO bond in these biological systems is apparently due to the presence of the proximal imidazole at the trans position to the ferryl group which hinders electron donation via the $d_{z^2}(Fe) \leftarrow p_z(O)$ bond. The ferryl bond of these six-coordinate species has been expressed by using a variety of formulations: (L)(P)Fe^V= \ddot{O} :²⁻, (L)(·P⁺)Fe^{IV}= \ddot{O} :²⁻, (L)(P)Fe^{IV}- \ddot{O} -, and (L)(P)Fe^{III}- \ddot{O} :, where L and P denote the axial ligand and the porphyrin ring, respectively.⁶² Among them, the first two have been preferred by some workers.^{19,20} We prefer the (N)(P)- Fe^{IV} $\rightarrow O^{2-}$ formulation in which the σ bond is weakened by the electron donation from the base ligand. Table I compares the ν (FeO), FeO stretching force constant, and FeO bond formulation for the μ -oxo complex, HRP-II, and the ferrylporphyrins we studied.

Mechanisms of RR Enhancement. As shown in Figures 1 and 2, the ν (FeO) vibrations of ferrylporphyrins are markedly enhanced by the Soret excitation (406.7 nm). Thus far, at least three mechanisms have been proposed to account for resonance enhancement of axial vibrations such as ν (FeO). Kitagawa et al.⁵³ proposed that, in Fe(OEP)L₂ (D_{4h} symmetry) and Fe(OEP)L (C_{4v} symmetry), the out-of-plane vibrations (A_{1g} and A_1 , respectively) can couple with in-plane porphyrin core vibrations of the same symmetry and borrow intensity from the latter. Spiro³⁷ suggests, however, that such vibrational coupling would be weak since the internal coordinates are orthogonal or close to orthogonal. He prefers direct coupling of the axial vibration to the in-plane electronic transition. In addition to these indirect mechanisms, there is a possibility of direct resonance excitation of the ν (FeO) which occurs when the laser frequency coincides with that of the Fe-O charge-transfer (CT) transition.

The indirect mechanism proposed by Spiro requires coupling of v(FeO) to the in-plane electronic transition. In the C_{4v} point group of (porphyrin)FeO, the ν (FeO) of the A₁ symmetry can be enhanced by the $\pi - \pi^*$ transition which alters the Fe-O bond length.³⁷ If so, its excitation profile should follow the electronic absorption spectrum; the enhancement should be the strongest in the Soret region and become much weaker in the Q region. Even in the Soret region, however, excitation of the v(FeO) is expected to be rather weak since the $\pi - \pi^*$ transitions are highly localized on the porphyrin plane. In such a case, the shift of the equilibrium position in going from the ground to the excited state $(\hat{\Delta} \text{ shift})^{63}$ is small and the Franck-Condon factor in A term resonance⁶⁴ is not significantly large. Thus, only the ν (FeO) fundamental should be observed in the RR spectra.

The direct mechanism assumes the presence of Fe-O CT transition in the Soret region. In iron porphyrins, axial ligand



Figure 5. Resonance Raman spectra of Fe(Pc) cocondensed with dioxygen at 15 K (676.4-nm excitation) with (A) ${}^{16}O_2$, (B) ${}^{18}O_2$, (C) ${}^{16}O_2/{}^{16}O_1{}^{18}O/{}^{18}O_2$ (1/2/1 ratio), and (D) ${}^{17}O_2$.

 \rightarrow Fe CT transitions may occur from filled σ or π ligand orbitals to vacant d orbitals whereas $Fe \rightarrow axial ligand CT$ transitions may occur from the partially filled d orbitals to π^* ligand orbitals.³ Since such a CT transition is localized in the Fe-axial ligand linkage, its distance is expected to change appreciably when the laser wavelength is chosen in the region of the corresponding CT band (large Δ shift). Although we have not been able to measure the electronic spectra of (porphyrin)FeO in O₂ matrices, we anticipate the presence of a strong Soret band between 390 and 430 nm and much weaker Q bands in the 500-600-nm region.⁶⁵ The fact that ν (FeO) vibrations are strongly enhanced by 406.7-nm excitation seems to suggest that there is a Fe-O CT transition in the Soret region. This is also supported by our observation that the first overtone of the ν (FeO) of (TPP)FeO is at 1697 cm⁻¹ (1627 cm⁻¹ for the ¹⁸O species). Although these bands are very weak, it does not preclude the possibility of direct excitation since the intensity of the overtone band in the A-type resonance depends markedly on the magnitude of the Δ shift.^{63,64} It is interesting to note that the ν (FeO) of HRP-II is also resonance enhanced by 406.7-nm excitation and that the magnitude of resonance enhancement relative to porphyrin core vibrations is much less than that of the five-coordinate ferrylporphyrin.^{23,44} This may suggest that the nature of the Fe-O CT transition is affected markedly by the coordination of the base ligand at the trans position to the ferryl group. Finally, the FeO CT band of OFe(salen) is probably shifted near 460 nm as its ν (FeO) is strongly enhanced by 457.9-nm excitation.

Resonance Raman Spectra of Oxy(phthalocyanato)iron. Figure 5 shows the RR spectra of $Fe(Pc)O_2$ in O_2 matrices. The 676.4-nm line of a Kr-ion laser gave the best resonance enhancement among the lines used. By combining oxygen isotopic shift data with normal-coordinate calculations, we have demonstrated previously that the bands at 486 and 279 cm⁻¹ of Fe(Pc)O₂ (Figure 5A) are due to the ν (Fe–O₂) and δ (FeOO), respectively.²⁷ This was the first observation of two O_2 -related vibrations in the

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low-frequency spectra of dioxygen adducts. Thus, the present discussion is limited to FePc vibrations observed in the higher frequency region.

The most prominent band at 1540 cm⁻¹ can be assigned to ν (C–N) coupled with δ (NCN) and δ (CNC) vibrations.⁶⁶ The position of this band is sensitive to the nature of the central metal in the macrocyclic system and varies from 1506 (MgPc)⁶⁷ to 1553 cm⁻¹ (NiPc).⁶⁸ Careful examination of our spectra shows that this band appears at 1533 cm⁻¹ in a thin film of FePc and shifts to 1540 cm⁻¹ upon oxygenation. Some differences in intensity and frequency are noted between our spectra and those obtained by other workers^{66,68} which are also different from each other. For example, Alexandrov et al.⁶⁸ and Melendres and Maroni⁶⁶ observed it at 1520 and 1530 cm⁻¹, respectively, both in KBr pellets. Apparently, the frequency of this band depends upon the pressing conditions and/or the relative concentration of FePc in KBr.⁶⁶ Melendres and Maroni suggest that the observed lowfrequency shift of this band may be due to the reaction of FePc with KBr to form FeBr_2 and $K_2(\text{Pc})$. Such a reaction cannot occur in noncoordinating solvents or in gas matrices. It is also possible that the large frequency shift observed between KBr pellet and the matrix-isolated state is due to the difference in the crystal modifications (α and β) as observed in IR spectra.⁶⁹

Other bands of medium to strong intensity are observed 1343, 1142, 754, 686, and 595 cm⁻¹ as shown in Figure 5. These bands are due to coupled modes among ν (C–N), ν (C–C), and various bending modes.⁶⁶ The most intense band at 686 cm⁻¹ is assigned to the ring breathing vibration of the 16-membered Pc ring.⁷⁰ All these vibrations are not metal-sensitive.67-71

Summary. It is expected that the donation of negative charge from the in-plane ligand to the dioxygen decreases in the order $Fe(salen)O_2 > Fe(porphyrin)O_2 > Fe(Pc)O_2$, since the extent of the π conjugation increases in going from salen (18 π electrons) to porphyrin (24 π electrons) to Pc (40 π electrons). Thus, the dioxygen in Fe(salen) O_2 is most negative and that in Fe(Pc) O_2 is least negative while the dioxygen in $Fe(porphyrin)O_2$ is intermediate between these extreme cases. As the negative charge on the dioxygen becomes large, the $\nu(O_2)$ becomes lower and the O-O bond becomes weaker. This is reflected on the order of $\nu(O_2)$ observed previously,³⁵ Fe(salen)O₂ (1106 cm⁻¹) < Fe(porphyrin) O_2 $(1195 \text{ cm}^{-1}) < \text{Fe}(\text{Pc})O_2 (1207 \text{ cm}^{-1})$, and also on the order of ease of the O-O bond cleavage by laser photolysis observed in this work. Thus, $Fe(salen)O_2$ readily produces and $Fe(Pc)O_2$ does not produce the ferryl species while Fe(porphyrin)O2 produces ferrylporphyrin after ca. 20 min of laser irradiation (406.7 nm). We plan to carry out a more quantitative study to confirm such a relationship.

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Ligand Charge Localization in Tris(2-(2'-pyridyl)quinoline)ruthenium(II), Tris(2,2'-biquinoline)ruthenium(II), and Their First Three Reduction Products

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The extent of localization of the redox orbitals of tris(2-(2'-pyridyl)quinoline)- and tris(2,2'-biquinoline)ruthenium(II) was investigated through the first three reduction products. Using cyclic voltammetry, UV/visible/near-IR absorption spectroscopy, and resonance Raman spectroscopy, we found that the added electrons continued to be localized on single ligands. Moreover, the redox electrons were further confined to a "quinoline" (predominately the fused benzene ring) portion of the ligand for the first two reduction products. Electrostatic repulsion in the three-electron products appears to place the third electron onto a different set of π orbitals which appear to be localized on the metal-bipyridine portion of the third ligand.

Introduction

Previous studies of reduced tris(diimine)ruthenium(II) complexes in solution have shown that an electrochemically added electron occupies a spatially isolated orbital (redox orbital) localized on a single ligand¹⁻⁷ which results in lowering of the molecular symmetry. The mechanism governing this symmetry breaking remains unclear, and the identification of a system with delocalized redox orbitals could add to the understanding of the process.

Vibronic coupling and solvent interactions are two mechanisms for redox orbital localization. Theoretical models⁸⁻¹³ for dimeric and trimeric systems, as in the Creutz-Taube complex, predict a competition between the delocalizing effect of electronic interaction and the localizing effect of vibronic interactions. The solvent may insulate one ligand from another by penetrating into

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