

Vibrational studies of nickel porphins and octaethyl porphyrins

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Abstract. The in-plane vibrational frequencies and assignments of nickel porphin (NiP) and octaethyl porphyrin (NiOEP) and their isotopically substituted derivatives are obtained by using Urey–Bradley potential energy constants. In order to study the core size effects in metalloctaethyl porphyrin (MOEP) systems, the (C_x-C_m) stretching force constants of Co, Cu and ZnOEP are also determined. Structural correlations between these constants and (1) centre-to-pyrrole nitrogen distances and (2) resonance Raman skeletal mode frequencies above 1450 cm^{-1} (ν_2 , ν_3 , ν_{10} , ν_{11} and ν_{19}) indicate the porphyrin core size influence on the (C_x-C_m) stretching force constants and the skeletal mode frequencies.

Keywords. Force field; normal coordinate analysis; nickel porphins and octaethyl porphyrins, core size effects.

1. Introduction

For the proper assignment of the fundamental frequencies and for the interpretation of the vibrational spectra of metalloporphins and octaethyl porphyrins, it is necessary that normal coordinate analysis be performed. Earlier, we have reported the in-plane vibrational frequencies and assignments of copper porphins (Sarma 1987) which were obtained by using the Urey–Bradley force field. In the present investigation, these studies are extended to nickel porphin (NiP) and its isotopomers NiP- d_4 , NiP- d_8 and NiP- d_{12} . Also, nickel octaethyl porphyrin (NiOEP) and its isotopically substituted analogues NiOEP- $^{15}\text{N}_4$ and NiOEP- d_4 are considered.

Vibrational assignments of NiP have been made by Ogoshi *et al* (1972), Verma *et al* (1976) and Susi and Ard (1977). Recently, Li *et al* (1990a) have reported the vibrational data and general valence force constants of nickel porphin and its isotopomers.

Infrared and resonance Raman spectra and tentative band assignments of metalloctaethyl porphyrins have been reported by Ogoshi *et al* (1971), Spaulding *et al* (1975), Kitagawa *et al* (1975, 1976, 1978), Choi *et al* (1982a), Kincaid *et al* (1983) and Lee *et al* (1986). These studies include NiOEP and its isotopically substituted derivatives. Spaulding *et al* (1975) have made a detailed study of the resonance Raman spectra of triclinic (D_{4h}) and tetragonal (D_{2d}) crystal forms of NiOEP and NiOEP- d_4 together with the CH_2Cl_2 solution spectra. They have observed that either crystal form when dissolved resulted in identical solution spectra and from this they concluded that the solution spectrum of NiOEP is that of the D_{4h} planar form examined in the solid phase. Kitagawa *et al* (1978) have made a valuable contribution by presenting

comprehensive data on the resonance Raman spectra of NiOEP, NiOEP- $^{15}\text{N}_4$ and NiOEP- d_4 and proposing vibrational assignments of the fundamental and nonfundamental Raman lines.

Abe *et al* (1978) have carried out normal coordinate calculations for all the in-plane modes of NiOEP and its meso-deuterated and ^{15}N -substituted derivatives by using a modified Urey-Bradley force field and by treating the peripheral ethyl group as a single unit, whereas Li *et al* (1990b) have explicitly included the methylene hydrogen atoms in their general valence force field calculations.

In the present study, the set of Urey-Bradley potential energy constants that were obtained for copper porphins (Sarma 1987), except the ($C_\alpha-C_m$) stretching, ($C_m C_\alpha C_\beta$) bending and repulsive, metal-nitrogen stretching and bending constants; are transferred to calculate the in-plane vibrational frequencies and band assignments of NiP and NiOEP and their isotopically substituted derivatives. Our assignments, in general, agree with those of Li *et al* (1990a, 1990b) except the $\delta(C_m\text{H})$ and $\delta(C_\beta\text{H})$ modes.

In metalloctaethyl and protoporphyrins, it was observed (Spaulding *et al* 1975; Choi *et al* 1982) that the resonance Raman skeletal mode frequencies of the porphyrin macrocycle above 1450 cm^{-1} , show an inverse correlation with core size and this effect was attributed to a dependence on the force constants of the methine bridge bonds ($C_\alpha-C_m$). In the present investigation, core size effects in MOEP (M = Ni, Co, Cu, and Zn) systems are studied using methine-bridge stretching force constants. For this purpose, the ($C_\alpha-C_m$) stretching force constants of Co, Cu and ZnOEP are determined from normal coordinate calculations. These constants are used in obtaining structural correlations between the centre-to-pyrrole nitrogen distances and the resonance Raman bands above 1450 cm^{-1} . These bands, which reflect the porphyrin core geometry, are the three ($C_\alpha-C_m$) stretching (ν_3 , ν_{10} and ν_{19}) and the two ($C_\beta-C_\beta$) stretching (ν_2 and ν_{11}) modes.

2. Procedure of calculation

In this study, only the in-plane vibrations of NiP and NiOEP and their isotopically substituted derivatives are considered and they are grouped into $9A_{1g} + 9B_{1g} + 8A_{2g} + 9B_{2g} + 18E_u$, under D_{4h} point group symmetry. The molecular parameters used for NiOEP are the same as those given by Abe *et al* (1978). The set of Urey-Bradley potential energy constants that were obtained for NiP and NiOEP are given in table 1. The core size dependent stretching force constant ($C_\alpha-C_m$) increases with decrease in M-N bond length. The value of $K(C_\alpha-C_m)$ obtained for NiOEP with M-N bond length of 1.958 \AA is $5.40\text{ m dyn \AA}^{-1}$. The calculated $C_\alpha-C_m$ stretching constants of Co, Cu and ZnOEP are 5.32 , 5.20 and $5.01\text{ m dyn \AA}^{-1}$, with M-N bond lengths of 1.976 , 2.0 and 2.036 \AA respectively. The metal-nitrogen stretching and bending frequencies are mainly dependent on the central metal ion and are not much affected by the M-N bond lengths.

Tables 2 and 3 give a comparison of the observed and calculated frequencies and the potential energy distribution of Ni porphins and octaethyl porphyrins. The observed frequencies are from Li *et al* (1990a, 1990b) and the notation used in numbering the frequencies of NiOEP is that of Abe *et al* (1978).

Table 1. Urey–Bradley potential energy constants for nickel porphins (mdyn Å⁻¹).

Stretching		Bending		Repulsive	
K(Ni–N)	1.35	H(N–Ni–N)	0.10	F(N...Ni...N)	0.03
K(C _α –N)	3.83	H(Ni–N–C _α)	0.06	F(Ni...N...C _α)	0.01
K(C _α –C _m)	5.40	H(C _α –N–C _α)	0.60	F(C _α ...N...C _α)	0.96
K(C _α –C _β)	3.58	H(C _α –C _m –C _α)	0.62	F(C _α ...C _m ...C _α)	0.12
K(C _β –C _β)	5.81	H(C _α –C _m –H)	0.13	F(C _α ...C _m ...H)	0.52
H(C _β –H)	4.88	H(C _m –C _α –C _β)	0.25	F(C _m ...C _α ...C _β)	0.75
K(C _m –H)	4.49	H(N–C _α –C _β)	0.11	F(N...C _α ...C _β)	0.97
		H(N–C _α –C _m)	0.26	F(N...C _α ...C _m)	0.69
		H(C _α –C _β –H)	0.26	F(C _α ...C _β ...H)	0.46
		H(C _β –C _β –H)	0.14	F(C _β ...C _β ...H)	0.18
		H(C _β –C _β –C _α)	0.39	F(C _β ...C _β ...C _α)	0.88
<i>Constants for nickel octaethylporphyrin</i>					
K(C _β –C ₁)	3.98	H(C _α –C _β –C ₁)	0.45	F(C _α ...C _β ...C ₁)	0.10
		H(C _β –C _β –C ₁)	0.13	F(C _β ...C _β ...C ₁)	0.75

3. Results and discussion

Nickel porphins: Earlier, we have assigned the fundamental frequencies of copper porphins (Sarma 1987) and discussed in detail the sensitiveness and form of the modes that shift when the meso-hydrogens and pyrrole hydrogens are replaced by deuterium. The fundamental frequencies of nickel porphins are expected to be nearly the same as those of the copper porphins, except for the metal–nitrogen stretching and bending modes which get slightly shifted. The data presented in table 2 show that most of the modes, except those involving C–H stretching, are highly mixed. The vibrations ν_{11} , ν_{20} and ν_{39} are almost pure C_α–C_m stretching modes of the methine bridges and ν_{12} is relatively a predominant C_β–C_β stretching vibration of the pyrrole ring.

The vibrations ν_{14} , ν_{23} and ν_{45} of Ni porphins can be assigned as bending modes of the meso-hydrogens. ν_6 , ν_{15} , ν_{31} , and ν_{46} are predominantly bending modes of the pyrrole hydrogens. The Ni–N stretching vibrations calculated at 233, 362 and 409 cm⁻¹ in the B_{1g}, A_{1g} and E_u species, respectively, agree with the observed values. The metal–nitrogen bending contributes mostly to ν_{35} . Our assignments for nickel porphins given in table 2, agree with those of Li *et al* (1990a) in general, except the (C_mH) and (C_βH) bending modes belonging to the A_{2g} and E_u species of the deuterated porphins.

NiOEP: The observed and calculated frequencies of NiOEP and its substituted derivatives are given in table 3. The resonance Raman bands between the region 1600–1000 cm⁻¹ are associated with C–C, C_α–N, C_β–C₁ stretching and C_m–H deformation modes. On the basis of the vibrational analysis of NiOEP, four C_α–C_m and two C_β–C_β stretching modes are resonance Raman allowed. Of these, $\nu_{10}(B_{1g})$ and $\nu_{19}(A_{2g})$ are predominantly C_α–C_m stretching modes. The other two C_α–C_m stretching modes are coupled with C_β–C_β and C_α–N stretching in $\nu_3(A_{1g})$ and $\nu_{28}(B_{2g})$. The modes $\nu_2(A_{1g})$ and $\nu_{11}(B_{1g})$ are attributable to C_β–C_β stretching vibrations. The C_α–C_β and C_α–N modes are mixed extensively with the other stretching vibrations

Table 2. Comparison of observed and calculated frequencies (cm^{-1}) of nickel porphyrins.

Sym. No.	Ni-porphin		Potential energy distribution (%)		Ni-porphin- d_4		Ni-porphin- d_6		Ni-porphin- d_{12}	
	Obs. ^(a)	Calc.			Obs. ^(a)	Calc.	Obs. ^(a)	Calc.	Obs. ^(a)	Calc.
A_{1g}	1	...	3118	$\nu(\text{C}_\beta\text{H})92$...	3118	...	2307	...	2307
	2	...	3050	$\nu(\text{C}_m\text{H})88$...	2243	...	3050	...	2243
	3	1574	1543	$\nu(\text{C}_\beta\text{C}_\beta)24, \nu(\text{C}_2\text{C}_m)24$	1566	1538	1552	1526	1546	1520
	4	1459	1426	$\nu(\text{C}_\beta\text{C}_\beta)35, \nu(\text{C}_2\text{N})17, \nu(\text{C}_2\text{C}_m)14$	1456	1420	1431	1414	1427	1409
	5	1376	1385	$\nu(\text{C}_2\text{C}_\beta)25, \delta(\text{C}_2\text{NC}_2)12$	1374	1385	1367	1357	1367	1357
	6	1066	1065	$\delta(\text{C}_2\text{C}_\beta\text{H})50, \delta(\text{C}_\beta\text{C}_\beta\text{H})28, \nu(\text{C}_\beta\text{C}_\beta)17$	1065	1065	775	775	773	774
	7	995	977	$\nu(\text{C}_2\text{C}_\beta)24, \delta(\text{NC}_2\text{C}_\beta)20$	992	973	987	967	985	963
	8	732	713	$\delta(\text{C}_2\text{C}_m\text{C}_2)22, \delta(\text{NC}_2\text{C}_m)19, \nu(\text{C}_2\text{N})18, \delta(\text{C}_2\text{NC}_2)11$	711	695	720	708	709	692
	9	369	362	$\nu(\text{NiN})28, \nu(\text{C}_2\text{C}_m)20, \delta(\text{C}_m\text{C}_2\text{C}_\beta)16, \delta(\text{C}_2\text{C}_m\text{C}_2)10$	367	361	360	356	359	355
B_{1g}	10	...	3118	$\nu(\text{C}_\beta\text{H})92$...	3118	...	2307	...	2307
	11	1650	1649	$\nu(\text{C}_2\text{C}_m)66$	1642	1648	1646	1649	1636	1647
	12	1505	1489	$\nu(\text{C}_\beta\text{C}_\beta)58, \delta(\text{C}_2\text{C}_\beta\text{H})16$	1504	1487	1454	1444	1454	1442
	13	...	1346	$\nu(\text{C}_2\text{N})36; \delta(\text{C}_2\text{C}_m\text{H})20, \nu(\text{C}_2\text{C}_\beta)11$	1321	1325	1324	1344	1315	1322
	14	1185	1191	$\delta(\text{C}_2\text{C}_\beta\text{H})62, \nu(\text{C}_2\text{C}_\beta)12$	938	913	1179	1182	948	910
	15	1060	1063	$\delta(\text{C}_2\text{C}_\beta\text{H})47, \delta(\text{C}_\beta\text{C}_\beta\text{H})25, \nu(\text{C}_\beta\text{C}_\beta)13$...	1079	768	775	768	772
	16	1003	1019	$\nu(\text{C}_2\text{C}_\beta)33, \delta(\text{NC}_2\text{C}_\beta)17$	1020	1049	...	1004	...	1046
	17	732	712	$\delta(\text{C}_2\text{NC}_2)31, \delta(\text{C}_m\text{C}_2\text{C}_\beta)19$	665	640	705	708	655	639
	18	237	233	$\nu(\text{NiN})55, \delta(\text{C}_m\text{C}_2\text{C}_\beta)14, \delta(\text{NC}_2\text{C}_m)13, \delta(\text{NC}_2\text{C}_\beta)10$	237	233	232	229	232	229
A_{2g}	19	...	3126	$\nu(\text{C}_\beta\text{H})91$...	3126	...	2311	...	2311
	20	1611	1597	$\nu(\text{C}_2\text{C}_m)72$	1598	1595	1605	1596	1592	1594
	21	1354	1318	$\nu(\text{C}_2\text{C}_\beta)28, \nu(\text{C}_2\text{N})18, \delta(\text{C}_2\text{C}_\beta\text{H})18$	1347	1326	1256	1224	1189	1207
	22	1317	1338	$\delta(\text{C}_2\text{C}_m\text{H})28, \delta(\text{C}_2\text{C}_\beta\text{H}), \nu(\text{C}_2\text{N})18$	1249	1280	1313	1325	1278	1276
	23	1139	1115	$\delta(\text{C}_2\text{C}_m\text{H})49, \nu(\text{C}_2\text{C}_\beta)17$	910	833	1095	1075	848	827
	24	1005	1000	$\nu(\text{C}_2\text{N})20, \nu(\text{C}_2\text{C}_\beta)16, \delta(\text{C}_2\text{C}_\beta\text{H})16, \delta(\text{NC}_2\text{C}_m)16$	1012	1029	851	849	848	856
	25	806	747	$\delta(\text{C}_\beta\text{C}_\beta\text{C}_2)65$	783	734	788	726	767	716
	26	429	439	$\delta(\text{C}_m\text{C}_2\text{C}_\beta)56, \delta(\text{NC}_2\text{C}_m)15, \delta(\text{NC}_2\text{C}_\beta)14$	419	432	404	418	397	412
	27	...	3126	$\nu(\text{C}_\beta\text{H})91$...	3126	...	2311	...	2311
B_{2g}	28	...	3050	$\nu(\text{C}_m\text{H})88$...	2243	...	3050	...	2243
	29	1505	1470	$\nu(\text{C}_2\text{C}_m)34, \nu(\text{C}_2\text{N})28$	1477	1463	1487	1459	1481	1451

30	1368	1340	$\nu(\text{C}_2\text{C}_\beta)28, \delta(\text{C}_2\text{C}_\beta\text{H})20, \delta(\text{C}_\beta\text{C}_\beta\text{H})12$	1368	1339	1324	1296	1315	1296
31	1193	1177	$\delta(\text{C}_2\text{C}_\beta\text{H})39, \nu(\text{C}_2\text{C}_\beta)17, \nu(\text{C}_2\text{C}_m)15, \delta(\text{C}_\beta\text{C}_\beta\text{H})15$	1193	1177	...	970	948	960
32	...	1005	$\nu(\text{C}_2\text{N})31, \delta(\text{NC}_2\text{C}_m)24, \nu(\text{C}_2\text{C}_m)12, \delta(\text{C}_2\text{C}_m\text{C}_2)12$	1020	988	...	1025	...	1016
33	819	853	$\delta(\text{C}_\beta\text{C}_\beta\text{C}_\beta)53, \delta(\text{NC}_2\text{C}_\beta)14, \delta(\text{C}_2\text{C}_m\text{C}_\beta)10$	815	849	799	781	780	779
34	435	410	$\delta(\text{C}_m\text{C}_2\text{C}_\beta)53, \delta(\text{C}_\beta\text{C}_\beta\text{C}_2)14, \nu(\text{C}_2\text{C}_m)14$	432	410	399	378	399	378
35	197	196	$\delta(\text{NiNi})33, \delta(\text{NiNC}_2)22, \delta(\text{C}_2\text{C}_m\text{C}_2)19$	197	194	197	195	197	193
36	...	3116	$\nu(\text{C}_\beta\text{H})92$...	3116	...	2305	...	2306
37	...	3115	$\nu(\text{C}_\beta\text{H})92$...	3115	...	2301	...	2301
38	...	3051	$\nu(\text{C}_m\text{H})88$...	2246	...	3051	...	2246
39	1624	1632	$\nu(\text{C}_2\text{C}_m)65$	1620	1631	1624	1630	1628	1628
40	1547	1545	$\nu(\text{C}_2\text{C}_\beta)32, \nu(\text{C}_2\text{C}_m)17, \delta(\text{C}_2\text{C}_\beta\text{H})17$	1543	1541	1527	1514	1520	1505
41	1462	1450	$\nu(\text{C}_\beta\text{C}_\beta)23, \nu(\text{C}_2\text{C}_m)22, \nu(\text{C}_2\text{N})18$	1458	1442	1420	1426	1420	1418
42	1385	1376	$\nu(\text{C}_2\text{C}_\beta)30, \nu(\text{C}_2\text{N})18$	1373.	1372	...	1365	...	1357
43	1319	1330	$\nu(\text{C}_2\text{C}_\beta)32, \nu(\text{C}_2\text{N})18$	1315	1314	1265	1318	1265	1298
44	1250	1261	$\delta(\text{C}_2\text{C}_\beta\text{H})28, \delta(\text{C}_2\text{C}_m\text{H})19, \delta(\text{C}_\beta\text{C}_\beta\text{H})18, \nu(\text{C}_2\text{C}_\beta)10$	1261	1237	1192	1204	1123	1128
45	1150	1151	$\delta(\text{C}_2\text{C}_m\text{H})43, \delta(\text{C}_2\text{C}_\beta\text{H})28, \nu(\text{C}_2\text{C}_\beta)11$	910	891	1091	1052	860	874
46	1064	1055	$\delta(\text{C}_2\text{C}_\beta\text{H})40, \delta(\text{C}_\beta\text{C}_\beta\text{H})28, \nu(\text{C}_2\text{C}_\beta)15$	1068	1066	794	806	764	766
47	1033	1034	$\nu(\text{C}_2\text{C}_\beta)22, \delta(\text{NC}_2\text{C}_\beta)22, \nu(\text{C}_2\text{N})14$	1026	1052	914	924	945	928
48	995	1021	$\nu(\text{C}_2\text{N})39, \delta(\text{NC}_2\text{C}_m)16$	999	1021	983	1023	998	1016
49	806	846	$\delta(\text{C}_\beta\text{C}_\beta\text{C}_2)41, \delta(\text{C}_2\text{C}_m\text{C}_2)13$...	840	...	829	...	820
50	745	733	$\delta(\text{C}_m\text{C}_2\text{C}_\beta)21, \delta(\text{C}_2\text{NC}_2)18$	648	673	737	708	648	658
51	420	409	$\nu(\text{NiN})37, \delta(\text{C}_m\text{C}_2\text{C}_\beta)20, \nu(\text{C}_2\text{C}_m)13$...	408	...	399	...	397
52	366	380	$\delta(\text{NC}_2\text{C}_m)36, \delta(\text{C}_2\text{C}_m\text{C}_\beta)29$...	377	...	363	...	360
53	282	279	$\nu(\text{NiN})32, \delta(\text{NiNiN})15, \delta(\text{C}_m\text{C}_2\text{C}_\beta)13$...	277	...	275	...	274

^(a) Observed frequencies are from Li *et al.* (1990a). ν : stretching; δ : bending.

Table 3. Comparison of observed and calculated frequencies (cm^{-1}) of NIOEP, NIOEP- $^{15}\text{N}_4$ and NIOEP- d_4 .

Sym.	NIOEP		NIOEP- $^{15}\text{N}_4$		NIOEP- d_4	
	No.	Obs. ^(a) Calc.	Obs. ^(a) Calc.	Obs. ^(a) Calc.	Obs. ^(a) Calc.	
A_{1g}	1	...	3048	...	3048	...
	2	1602	1565	1601	1565	1601
	3	1520	1479	1519	1477	1512
	4	1383	1400	1376	1391	1382
	5	1138	1136	1131	1127	1138
	6	804	829	799	821	799
	7	674	649	671	648	668
	8	360/343	385	358/342	384	353/343
	9	263/274	269	261/273	268	262/274
	10	1655	1654	1655	1654	1645
	11	1577	1554	1576	1554	1576
	12	...	1345	...	1333	1331
	13	1220	1264	1218	1264	1186
	14	1131	1140	1119	1129	948
	15	751	773	748	773	683
	16	740	692	740	685	762
	17	305	343	305	342	305
	18	168	195	168	194	160
A_{2g}	19	1603	1602	1602	1601	1596
	20	1393	1424	1393	1423	1397
	21	1307	1298	1303	1291	1202
	22	1121	1091	1106	1089	1058
	23	1058	1065	1058	1057	887
	24	597	645	596	641	582
	25	551	536	551	533	545
	26	...	272	...	271	...
	27	...	3048	...	3048	...
	28	1483	1466	1480	1461	1478
29	1407	1414	1406	1413	1405	
B_{2g}	1	2241
	2	1564
	3	1473
	4	1398
	5	1135
	6	819
	7	638
	8	385
	9	269
	10	1648
11	1553	
12	1326	
13	1241	
14	940	
15	638	
16	744	
17	342	
18	194	
19	1581	
20	1397	
21	1202	
22	1089	
23	821	
24	645	
25	529	
26	269	
27	2241	
28	1461	
29	1413	

Potential energy distribution (%)

$\nu(\text{C}_m\text{H})88, \delta(\text{C}_2\text{C}_m\text{H})11$
 $\nu(\text{C}_\beta\text{C}_\beta)52, \nu(\text{C}_\beta\text{C}_1)12$
 $\nu(\text{C}_2\text{C}_m)33, \nu(\text{C}_\beta\text{C}_\beta)11, \nu(\text{C}_2\text{N})11, \nu(\text{C}_\beta\text{C}_1)11$
 $\nu(\text{C}_2\text{C}_\beta)32, \nu(\text{C}_2\text{N})21, \delta(\text{C}_2\text{NC}_2)10$
 $\nu(\text{C}_\beta\text{C}_1)28, \delta(\text{NC}_2\text{C}_\beta)12$
 $\delta(\text{C}_2\text{C}_m\text{C}_2)22, \nu(\text{C}_\beta\text{C}_1)18, \nu(\text{C}_2\text{N})13$
 $\delta(\text{NC}_2\text{C}_m)16, \nu(\text{C}_2\text{C}_\beta)14, \nu(\text{C}_\beta\text{C}_1)14, \nu(\text{C}_2\text{N})10$
 $\delta(\text{C}_2\text{C}_\beta\text{C}_1)28, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)20, \nu(\text{C}_2\text{C}_m)10, \nu(\text{NiN})10$
 $\delta(\text{C}_2\text{C}_\beta\text{C}_1)24, \nu(\text{NiN})13$
 $\nu(\text{C}_2\text{C}_m)67$
 $\nu(\text{C}_\beta\text{C}_\beta)63, \nu(\text{C}_\beta\text{C}_1)18$
 $\nu(\text{C}_2\text{N})38, \delta(\text{C}_2\text{C}_m\text{H})20, \nu(\text{C}_2\text{C}_\beta)10$
 $\nu(\text{C}_2\text{C}_\beta)30, \delta(\text{C}_\beta\text{C}_1)25$
 $\delta(\text{C}_2\text{C}_m\text{H})53$
 $\nu(\text{C}_\beta\text{C}_1)24, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)10$
 $\delta(\text{C}_2\text{NC}_2)21, \delta(\text{C}_m\text{C}_2\text{C}_\beta)16, \nu(\text{C}_2\text{C}_\beta)14, \nu(\text{C}_\beta\text{C}_1)13, \nu(\text{NiN})10$
 $\delta(\text{C}_2\text{C}_\beta\text{C}_1)50, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)37$
 $\nu(\text{NiN})48$
 $\nu(\text{C}_2\text{C}_m)73$
 $\nu(\text{C}_\beta\text{C}_1)34, \nu(\text{C}_2\text{C}_\beta)26, \delta(\text{C}_\beta\text{C}_\beta\text{C}_2)20$
 $\delta(\text{C}_2\text{C}_m\text{H})44, \nu(\text{C}_2\text{N})26$
 $\nu(\text{C}_2\text{C}_\beta)25, \nu(\text{C}_\beta\text{C}_1)24, \nu(\text{C}_2\text{N})17, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)11$
 $\delta(\text{C}_2\text{C}_m\text{H})47, \nu(\text{C}_2\text{N})18$
 $\delta(\text{C}_2\text{C}_\beta\text{C}_1)24, \delta(\text{NC}_2\text{C}_m)18, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)17$
 $\delta(\text{C}_\beta\text{C}_\beta\text{C}_1)46, \nu(\text{C}_\beta\text{C}_1)20, \delta(\text{C}_2\text{C}_\beta\text{C}_1)20$
 $\delta(\text{C}_m\text{C}_2\text{C}_\beta)35, \delta(\text{C}_2\text{C}_\beta\text{C}_1)21, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)11, \delta(\text{NC}_2\text{C}_\beta)10$
 $\nu(\text{C}_m\text{H})88, \delta(\text{C}_2\text{C}_m\text{H})11$
 $\nu(\text{C}_2\text{N})27, \nu(\text{C}_2\text{C}_m)24, \nu(\text{C}_\beta\text{C}_1)10$
 $\nu(\text{C}_2\text{C}_\beta)35, \nu(\text{C}_\beta\text{C}_1)23, \nu(\text{C}_2\text{C}_m)13$

30	1159	1173	$\nu(\text{C}_\beta\text{C}_1)25, \nu(\text{C}_\alpha\text{C}_\beta)18, \nu(\text{C}_\alpha\text{N})17$	1149	1170	1159	1172
31	1015	1000	$\nu(\text{C}_\alpha\text{N})26, \delta(\text{NC}_\alpha\text{C}_m)21, \nu(\text{C}_\alpha\text{C}_m)17, \delta(\text{C}_\alpha\text{C}_m\text{C}_\beta)12$	1006	984	1003	982
32	938	844	$\delta(\text{C}_\alpha\text{C}_\beta\text{C}_1)21, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)21$	938	843	934	842
33	493	496	$\delta(\text{C}_\beta\text{C}_\beta\text{C}_\alpha)38, \nu(\text{C}_\beta\text{C}_1)19, \delta(\text{C}_\alpha\text{C}_\beta\text{C}_1)16$	492	494	490	494
34	197	230	$\delta(\text{C}_m\text{C}_\alpha\text{C}_\beta)20, \delta(\text{C}_\alpha\text{C}_m\text{C}_\beta)14$	197	229	197	229
35	144	163	$\delta(\text{NNiN})28, \delta(\text{C}_m\text{C}_\alpha\text{C}_\beta)20, \delta(\text{NiNC}_\alpha)18$	144	161	141	161
36	...	3048	$\nu(\text{C}_m\text{H})88, \delta(\text{C}_\alpha\text{C}_m\text{H})11$...	3049	...	2244
37	...	1641	$\nu(\text{C}_\alpha\text{C}_m)61$...	1641	...	1636
38	1604	1601	$\nu(\text{C}_\beta\text{C}_\beta)46, \nu(\text{C}_\beta\text{C}_1)14, \nu(\text{C}_\alpha\text{C}_m)12$	1604	1600	1604	1599
39	1501	1493	$\nu(\text{C}_\alpha\text{C}_m)17, \nu(\text{C}_\alpha\text{N})16, \nu(\text{C}_\beta\text{C}_1)16, \delta(\text{C}_\beta\text{C}_\beta\text{C}_\alpha)15$	1501	1491	1494	1487
40	1396	1420	$\nu(\text{C}_\alpha\text{C}_\beta)30, \nu(\text{C}_\alpha\text{C}_m)22, \nu(\text{C}_\beta\text{C}_1)18$	1396	1419	1392	1416
41	...	1371	$\nu(\text{C}_\alpha\text{C}_\beta)27, \nu(\text{C}_\alpha\text{N})25$...	1363	...	1364
42	1231	1270	$\delta(\text{C}_\alpha\text{C}_m\text{H})45, \nu(\text{C}_\alpha\text{N})14, \nu(\text{C}_\beta\text{C}_1)12$	1228	1266	1185	1217
43	1153	1155	$\nu(\text{C}_\beta\text{C}_1)23, \nu(\text{C}_\alpha\text{C}_\beta)11, \delta(\text{NC}_\alpha\text{C}_\beta)10$	1145	1147	1151	1138
44	1133	1109	$\nu(\text{C}_\alpha\text{N})21, \nu(\text{C}_\beta\text{C}_1)18, \delta(\text{C}_\alpha\text{C}_m\text{H})18, \nu(\text{C}_\alpha\text{C}_\beta)14$	1121	1101	948	916
45	996	1026	$\nu(\text{C}_\alpha\text{N})26, \delta(\text{NC}_\alpha\text{C}_m)16, \delta(\text{C}_\alpha\text{C}_m\text{H})15, \nu(\text{C}_\alpha\text{C}_m)11$	991	1011	996	1057
46	927	893	$\nu(\text{C}_\beta\text{C}_1)13, \delta(\text{C}_\alpha\text{C}_m\text{C}_\beta)12, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)10$	924	889	919	834
47	...	751	$\nu(\text{C}_\beta\text{C}_1)25, \nu(\text{C}_\alpha\text{C}_\beta)16, \delta(\text{NC}_\alpha\text{C}_\beta)12$...	745	766	738
48	605	660	$\delta(\text{C}_\beta\text{C}_\beta\text{C}_\alpha)22, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)18, \nu(\text{C}_\beta\text{C}_1)10$	605	659	600	631
49	544	570	$\delta(\text{C}_\alpha\text{C}_\beta\text{C}_1)32, \nu(\text{C}_\beta\text{C}_1)15$	544	568	543	566
50	...	387	$\nu(\text{NiN})25, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)20, \delta(\text{C}_\alpha\text{C}_\beta\text{C}_\alpha)13$...	386	...	386
51	328	305	$\delta(\text{C}_\alpha\text{C}_\beta\text{C}_1)29, \nu(\text{NiN})28, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)13$	328	305	322	305
52	263	287	$\delta(\text{NNiN})14, \nu(\text{NiN})11, \delta(\text{C}_\alpha\text{C}_\beta\text{C}_1)10$	261	288	260	287
53	212	186	$\delta(\text{C}_m\text{C}_\alpha\text{C}_\beta)33, \delta(\text{C}_\alpha\text{C}_\beta\text{C}_1)15, \delta(\text{C}_\beta\text{C}_\beta\text{C}_1)10, \nu(\text{C}_\alpha\text{C}_m)10$	212	186	212	186

^{a)} Observed frequencies are from Li *et al.* (1990b). ν : stretching; δ : bending.

and C_m -H deformations. The bands which contain substantial contributions from C_α - C_β and C_α -N stretching are $\nu_4(A_{1g})$; ν_{12} , $\nu_{13}(B_{1g})$; $\nu_{20}(A_{2g})$ and ν_{28} , $\nu_{29}(B_{2g})$. As in the case of the resonance Raman modes, the stretching vibrations in the infrared active E_u species are highly mixed. Only ν_{37} is relatively a pure C_α - C_m stretching mode.

In NiOEP, Abe *et al* (1978) have chosen a polarized line at 1025 cm^{-1} as ν_5 in preference to another polarized line at 1138 cm^{-1} since the latter is intense with excitation at 488.0 nm but weak with excitation at 514.5 nm . They have assigned the 1025 cm^{-1} line as a mixed mode of C_β -Et and C_α - C_β stretching and the 1138 cm^{-1} line as a combination band. But, the line at about 1025 cm^{-1} is observed only in metal complexes of OEP and is not detected in NiPP (Choi *et al* 1982b), NiTMP (Andersson *et al* 1986) and CuOMP (Sunder *et al* 1975), whereas the line at about 1140 cm^{-1} is seen with various excitations in all these porphyrins. The corresponding observed frequencies in these porphyrins are 1138, 1135, and 1141 cm^{-1} respectively. For this reason, we prefer to use the 1138 cm^{-1} line as ν_5 in NiOEP and assign it as a mixed mode with predominant contribution from C_β - C_1 stretching. This observation agrees with that of Li *et al* (1990b).

For the C_m -H bending vibrations, the results of the present study differ from those of Li *et al* (1990b) in respect of the form of the modes and frequency shifts on meso-deuteration. The potential energy distribution we have obtained and listed in table 3 shows the modes ν_{14} of the B_{1g} species; ν_{21} and ν_{23} of the A_{2g} species; ν_{42} and ν_{44} of the E_u species shift on meso-deuteration. Accordingly, in NiOEP- d_4 we have assigned the observed lines at 948 cm^{-1} as ν_{14} ; 1202 and 887 cm^{-1} as ν_{21} and ν_{23} ; 1185 and 948 cm^{-1} as ν_{42} and ν_{44} . Of these modes ν_{14} and ν_{23} show relatively large isotope shift. The differences between the observed and calculated frequencies in the low frequency region are higher which is the case with the results of Li *et al* (1990b) also. The calculated results of NiOEP- d_4 and NiOEP- $^{15}\text{N}_4$ show distinct isotopic frequency shifts upon meso-deuteration and ^{15}N substitution which were observed experimentally.

The polarized resonance Raman line ν_4 , corresponding to the oxidation state marker of the iron ion in hemoproteins, appears at 1383 cm^{-1} in NiOEP. Sensitivity to oxidation state is ascribed to the alterations in π electronic states of the porphyrin ring, which leads to changes in the frequencies associated with pyrrole breathing. This band ν_4 exhibits a shift of 7 cm^{-1} in NiOEP- $^{15}\text{N}_4$ and almost no shift upon meso-deuteration. This indicates that this band corresponds to a mode involving motion of the four pyrrole nitrogens and connected with C_α -N stretching. This experimental observation is supported by the calculated frequencies of this mode even though the potential energy distribution shows that the contribution of the C_α -N bonds is slightly less than that of the C_α - C_β bonds.

The resonance Raman lines of NiOEP observed at $1520(\nu_3, A_{1g})$ and $1655\text{ cm}^{-1}(\nu_{10}, B_{1g})$ are the corresponding frequencies of hemoproteins that are sensitive to spin states of the heme iron. The transition of the iron atom from the low-spin to the high-spin state lowers the frequencies involving C_α - C_m bonds. These spin state effects have been attributed to the expansion of the porphyrin core due to longer C_α - C_m bonds which produce a weakening of the bonds at the methine bridges and a decrease of the associated frequencies. The modes ν_3 and ν_{10} which are mainly associated with C_α - C_m bonds are spin state sensitive bands and show frequency shifts upon meso-deuteration. The potential energy distribution and the calculated frequencies given in table 1 are consistent with the observed data.

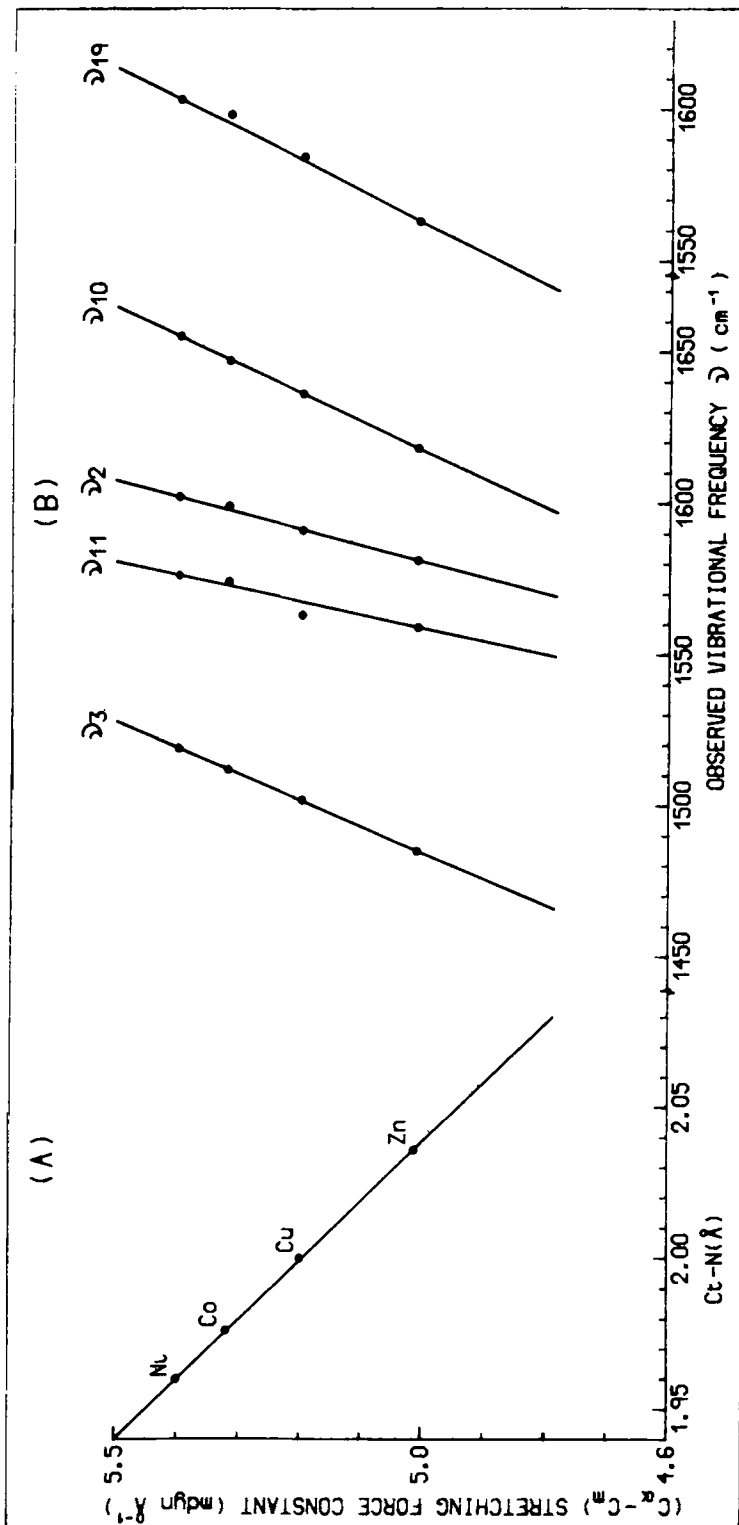


Figure 1. $(C_r - C_m)$ stretching force constants vs (A) porphyrin core size of Ni, Co, Cu and ZnOEP, (B) Resonance Raman frequencies.

Table 4. Observed resonance Raman skeletal mode frequencies (cm^{-1}) of MOEP systems^(a).

OEP	Ct-N (Å)	$K(C_\alpha-C_m)$ (mdyn Å ⁻¹)	ν_3 ($C_\alpha C_m$)	ν_{11} ($C_\beta C_\beta$)	ν_{19} ($C_\alpha C_m$)	ν_2 ($C_\beta C_\beta$)	ν_{10} ($C_\alpha C_m$)
Ni	1.958	5.40	1520	1577	1603	1602	1655
Co	1.976	5.32	1512	1574	1598	1599	1647
Cu	2.000	5.20	1502	1563	1584	1591	1636
Zn	2.036	5.01	1485	1559	1563	1581	1618

^(a)Li *et al* (1990b) and Oertling *et al* (1987).

The $C_\alpha-C_m$ stretching force constants of Ni, Co, Cu and ZnOEP; which were obtained from normal coordinate calculations, and the observed resonance Raman frequencies (Oertling *et al* 1987; Li *et al* 1990b) above 1450 cm^{-1} are given in table 4. These constants are plotted against the porphyrin core size (Ct-N) and the resonance Raman frequencies, in figures 1(A) and 1(B) respectively. To rule out the possibility of dependency of these frequencies on the nature of the central metal ion, we made calculations by changing the metal ion for the same M-N distance and no significant influence on the frequencies above 1450 cm^{-1} was noted. It is evident from these plots, that the resonance Raman frequencies are lowered as the core expands. The modes ν_3 , ν_{10} and ν_{19} , with a larger contribution from $C_\alpha-C_m$ stretching constants, are more sensitive to core size and have higher slopes. The modes ν_2 and ν_{11} , with a predominant $C_\beta-C_\beta$ stretching contribution have lower slopes. The present results establish that as the porphyrin core size increases, the methine-bridge stretching force constants are reduced and the skeletal mode frequencies are lowered.

In conclusion, it can be said that resonance Raman spectroscopy has proven to be an extremely useful probe of the vibrational and electronic structure of metalloporphyrins and hemoproteins; the present studies will help in better understanding and interpretation of their spectra and structure.

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