VIBRATIONAL ASSIGNMENTS OF RESONANCE RAMAN LINES OF NI(OCTAETHYLPORPHYRIN) ON THE BASIS OF A NORMAL COORDINATE TREATMENT

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Vibrational modes for the resonance Raman lines of Ni(OEP) have been obtained on the basis of a normal coordinate analysis. The Raman line at 1383 cm^{-1}, which corresponds to an oxidation-state marker band of hemoproteins, is mainly due to the breathing mode of the pyrrole rings. The vibrations of the sixteen-membered inner ring contribute to the Raman bands sensitive to the spin-states of the heme iron.

Resonance Raman spectra of hemoproteins have been studied extensively and important suggestions have been made on the symmetry and structure of the heme group,[1-5] the oxidation and spin states of the heme iron,[1,3,6] and the binding nature of the axial ligands.[7,8] Most of the Raman lines are known to arise from the vibrations of the metalloporphyrin chromophore. Therefore, it is quite important to assign the Raman lines to certain vibrational modes for obtaining detailed information about the structure of the heme group.

For this purpose we have studied the resonance Raman spectra of metalloporphyrin complexes as model compounds.[9-11] In the present paper we try to assign the Raman lines of Ni-octaethylporphyrin [Ni(OEP)-h_4] and its meso-deuterated compound [Ni(OEP)-d_4] on the basis of a normal coordinate analysis. Since the resonance Raman spectrum of Ni(OEP)-h_4 is similar to those of hemoproteins, the present assignment can be applied to the Raman lines of hemoproteins. Accordingly, the discussion is focused on the vibrational modes for the Raman lines which correspond to the marker bands for the oxidation or spin states in hemoproteins.

Resonance Raman spectra of Ni(OEP)-h_4 and Ni(OEP)-d_4. According to X-ray analysis[12] the porphynato core of Ni(OEP) in the crystal is in two types of structure, D_{4h} and D_{2d}. However, the patterns of infrared[13] and Raman spectra of solutions indicate that it is only in D_{4h} symmetry. Vibrations of A_{1g}, A_{2g}, and B_{1g} or B_{2g} symmetry can appear in the resonance Raman spectra, corresponding to polarized(p), inversely polarized(ip) and depolarized(dp) lines, respectively. These are all in-plane vibrations. Experimental evidence for distinguishing the vibrations of B_{1g} symmetry from those of B_{2g} was reported previously.[10] Though the vibrational coupling of the porphynato core with peripheral substituents may not be negligible, Raman lines mainly due to the ethyl groups were not recognized in the resonance Raman spectra. Above 1000 cm^{-1} four strong polarized bands, five depolarized bands and four inversely polarized bands were observed for Ni(OEP)-h_4. Four polarized, four depolarized and three inversely polarized bands were seen for Ni(OEP)-d_4. They are listed in Table 1. Meso hydrogen bending vibrations belong to either A_{2g} or

Table 1. Observed and calculated frequencies.

	h4		d4		Isotope shift			h4		d4		Isotope shift	
	Obs.[a]	Calc.[b]	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A_{1g}	1602	1605	1602	1604	0	1	A_{2g}	1603	1602	1580	1593	23	9
	1519	1526	1512	1520	7	6		1397	1407	1397	1406	0	1
	1383	1380	1382	1376	1	4		1309	1299	1202	1224	107	75
	1025	1039	1025	1038	0	1		1121	1103	—	1067	—	36
B_{1g}	1655	1659	1645	1654	10	5	B_{2g}	—	1483	—	1482	—	1
	1576	1561	1576	1555	0	6		—	1402	—	1397	—	5
	1409	1408	1408	1405	1	3		1159	1182	1159	1180	0	2
	1220	1237	—	1165	—	72		—	1041	—	1022	—	19

a) Observed frequencies for Ni(OEP)-h_4 and Ni(OEP)-d_4.

b) Calculated frequencies for Ni(OMP)-h_4 and Ni(OMP)-d_4.

B_{1g} species.   Upon deuteration of the meso positions, two bands at 1220(dp) and 1309 cm^{-1}(ip) for Ni(OEP)-h_4 disappear, while a new band is observed at 1202 cm^{-1} (ip) for Ni(OEP)-d_4.   Besides these bands, the 1519(p), 1655(dp) and 1603 cm^{-1}(ip) bands for Ni(OEP)-h_4 show isotopic frequency shifts.

Normal coordinate treatment of Ni(octamethylporphyrin).   For infrared active bands (E_u species) of metalloporphins, vibrational assignments were made from a normal coordinate analysis.[14]   Using the results of a normal vibration calculation for resonance Raman active species of octamethylporphyrin, Spiro and his coworkers discussed the structure of hemoprotein.[5]   However, a detailed analysis of the vibrational mode for each observed band has not yet been made.   We have calculated the normal vibrations for Ni(OMP)-h_4 and Ni(OMP)-d_4 where molecular symmetry is assumed to be D_{4h} and methyl groups are treated as point masses.   Thirty five in-plane normal vibrations are expected in resonance Raman spectra; $9A_{1g}+9B_{1g}+8A_{2g}+9B_{2g}$.   The potential function used in the calculations consisted of a Urey-Bradley force field modified to take account of chemical resonance(conjugation) by the inclusion of stretching-stretching interaction terms between two adjacent bonds.   Repulsion force constants were transferred from similar molecules and were used without adjustment throughout the calculation.   The stretching(K), bending(H) and stretching-stretching interaction(P) force constants were adjusted by trial and error to fit the calculated frequencies with those of the Raman and infrared bands observed for Ni(OEP)-h_4 and Ni(OEP)-d_4.   The force constants, except those related to the central ion part, are listed in Table 2.   Calculated frequencies and isotopic frequency shifts are

Table 2. Main force constants in mdyn/A.

$K(C_\alpha N)$	4.71	$H(C_\beta C_\beta Me)$	0.40	$P(C_\alpha C_\beta, C_\alpha C_\beta)$	-0.15
$K(C_\alpha C_\beta)$	4.04	$H(C_\beta C_\alpha C_m)$	0.20	$P(C_\alpha N, C_\alpha N)$	0.50
$K(C_\beta C_\beta)$	5.80	$H(C_\alpha C_\beta C_\beta)$	0.18	$P(C_\alpha N, C_\alpha C_m)$	0.21
$K(C_\alpha C_m)$	4.55	$H(C_\alpha C_m C_\alpha)$	0.41	$P(C_\alpha C_m, C_\alpha C_m)$	0.06
$K(C_\beta Me)$	4.00	$H(C_m C_\alpha N)$	0.76	$P(C_\alpha N, C_\alpha C_\beta)$	0.03
$H(C_\alpha N C_\alpha)$	0.33	$H(C_\alpha C_\beta Me)$	0.40	$P(C_\alpha C_\beta, C_\alpha C_m)$	-0.32
$H(N C_\alpha C_\beta)$	0.31	$H(C_\alpha C_m H)$	0.20		
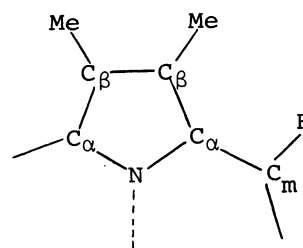
compared with observed frequencies of Ni(OEP) above 1000 cm^{-1} in Table 1. In spite of the many assumptions made, agreement between observed and calculated frequencies is satisfactory. The calculated isotopic shifts will be revised by further refinement of the force field.

Description of vibrational modes.   For ring molecules, it is not always adequate to show vibrational modes in terms of the potential energy distribution, because sometimes it is hard to get appropriate symmetry coordinates for the modes.   In order to obtain precise normal modes, we have calculated elements of the L_x matrix, which give the Cartesian displacements of atoms for each vibration.[15]   The vibrational modes obtained, which are correlated with the Raman lines observed above 1000 cm^{-1} for Ni(OEP)-h_4 are shown in Figure 1. Those of lower frequency bands are reported separately.[11]   The bands at 1602(p), 1383(p) and 1576 cm^{-1}(dp) are due mainly to the pyrrole ring vibrations. The strongly polarized 1383 cm^{-1} band, which has been noted as an oxidation state marker for hemoproteins, is a pyrrole ring breathing mode in which the four pyrrole rings vibrate in-phase and induce the
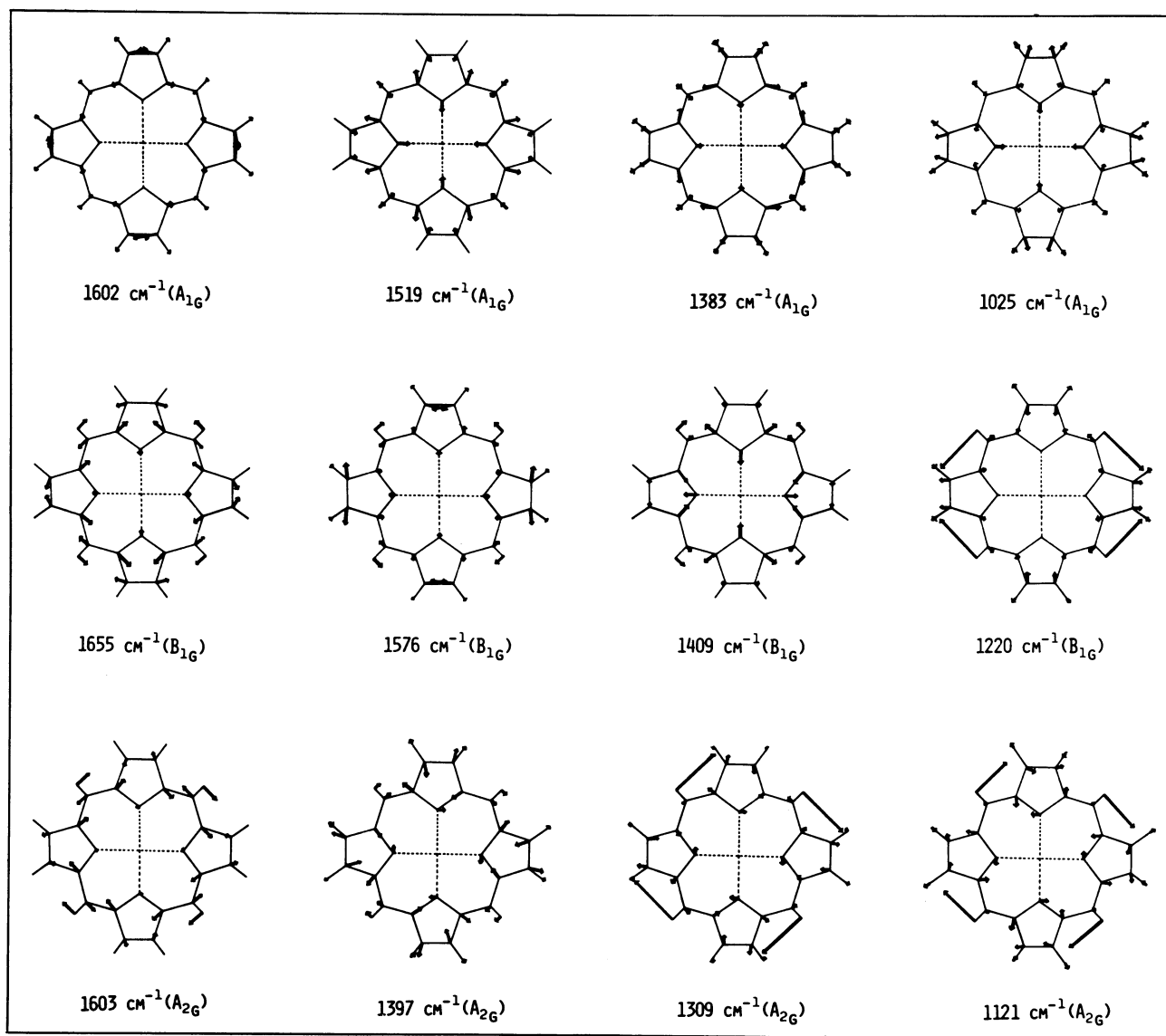

Fig.1 Vibrational modes of the resonance Raman lines observed for Ni(OEP).

methine bridge symmetric stretching vibration. This assignment is likely supported by the fact that the frequency is relatively invariant in a variety of porphyrin complexes of different metals. The frequency of 1383 cm^{-1} is however considerably higher than that of the breathing mode of a free pyrrole molecule.[16] This may be caused by a resonance effect in the conjugated porphyrin ring. The 1602 and 1576 cm^{-1} bands are mainly due to the C_β-C_β stretching modes. Spiro suggested that a depolarized line of hemoproteins near 1550 cm^{-1} could also be used as an oxidation state marker.[4]

The 1519, 1655 and 1603 cm^{-1} bands which correspond to the spin-state sensitive lines of hemoproteins are due to the vibrations of the sixteen membered inner ring. The 1519 cm^{-1} band is mainly due to the C_α-N stretching mode coupled with the methine bridge deformation vibration. On the other hand, the bands at 1655 and 1603 cm^{-1} are mainly due to the methine bridge anti-symmetric stretching modes. As pointed out by Bernstein,[17] the 1655 cm^{-1} band is derived to a greater extent from C_α-C_m bond-stretching than from C_β-C_β bond-stretching motions, though this line has been empirically assigned to the C_β-C_β stretching mode. These three vibrations, in which the movements of the methine bridge carbon atoms (C_m) cause also the movements of hydrogen atoms, show fairly large isotopic frequency shifts upon meso-deuteration.

The 1309 and 1220 cm^{-1} bands are primarily associated with hydrogen deformation modes, in which four hydrogens are displaced in-phase and out-of-phase, respectively. The observed isotopic shift of 107 cm^{-1} for the 1309 cm^{-1} band of A_{2g} symmetry is much smaller than that expected for a pure hydrogen bending vibration. As shown in Table 1 and Figure 1, meso hydrogen bending vibrations are easily coupled with other vibrations. Also in the lower frequency region, a depolarized band which shows a large isotopic frequency shift is observed,[11] which indicates the delocalization of the bending mode. Details of the calculations including infrared active modes will be reported elsewhere.

REFERENCES

1) H.Brunner, A.Mayer, and H.Sussner, J.Mol.Biol., 70, 153 (1972).   2) M.Pézolet, L.A.Nafie, and W.L.Peticolas, J. Raman Spectrosc., 1, 455 (1973).   3) J.Nestor and T.G.Spiro, J.Raman Spectrosc., 1, 539 (1973).   4) T.G.Spiro and T.C.Strekas, J.Amer. Chem.Soc., 96, 388 (1974).   5) P.Stein, J.M.Burke, and T.G.Spiro, J.Amer.Chem.Soc., 97, 2304 (1975).   6) T.Yamamoto, G.Palmer, D.Gill, I.T.Salmeen, and L.Rimai, J.Biol. Chem., 248, 5211 (1973).   7) T.Kitagawa, T.Iizuka, M.Saito, and Y.Kyogoku, Chem.Lett. 849 (1975).   8) T.Kitagawa, Y.Kyogoku, T.Iizuka, M.I.Saito, and T.Yamanaka, J.Biochem. 78, 719 (1975).   9) T.Kitagawa, H.Ogoshi, E.Watanabe, and Z.Yoshida, Chem.Phys.Lett., 30, 451 (1975).   10) T.Kitagawa, H.Ogoshi, E.Watanabe, and Z.Yoshida, J.Phys.Chem., 79, 2629 (1975).   11) T.Kitagawa, M.Abe, Y.Kyogoku, H.Ogoshi, E.Watanabe, and Z. Yoshida, to be published.   12) D.L.Cullen and E.F.Meyer, Jr., J.Amer.Chem.Soc., 96, 2095 (1974).   13) M.Abe, T.Kitagawa, Y.Kyogoku, H.Ogoshi, E.Watanabe, and Z.Yoshida, to be published.   14) H.Ogoshi, Y.Saito, and K.Nakamoto, J.Chem.Phys., 57, 4194 (1972).   15) M.Mikami, I.Nakagawa, and T.Shimanouchi, Spectrochim. Acta, 23A, 1037 (1967).   16) R.C.Lord, Jr. and F.A.Miller, J.Chem.Phys., 10, 328 (1942).   17) S. Sunder, R.Mendelsohn, and H.J.Bernstein, J.Chem.Phys., 63, 573 (1975).