

# Resonance Raman Spectra of Nickel(II) Acetyl and Formyl Deuteroporphyrins. Effects of Selective 2 vs. 4 Substitution and Altered Electron-Withdrawing Capability of Conjugating Groups

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**Abstract:** Infrared and visible excitation (selective B state and throughout the Q state) resonance Raman (RR) spectra are reported for a series of Ni(II) acetyl and formyl DP complexes (DP = deuteroporphyrin IX dimethyl ester). These include Ni(DP), Ni(2-acetylDP), Ni(4-acetylDP), Ni(2,4-diacetylDP), Ni(2,4-diformylDP), the acetyl and formyl deuterated derivatives of the two disubstituted complexes, and meso-deuterated- $\beta$ -pyrrole-deuterated Ni(DP). Virtually all of the in-plane porphyrin skeletal modes and a number of the internal vibrations of the conjugating groups are assigned on the basis of deuteration shifts, comparison of the spectra of the different Ni(II) DP derivatives, and comparison of these spectra with those of Ni(OEP) (OEP = octaethylporphyrin). Specific effects of the conjugating groups include (a) RR enhancement and splittings of degenerate IR-type  $E_u$  modes, (b) RR enhancement of the internal modes of the acetyl and formyl groups, and (c) perturbation of the porphyrin skeletal modes by kinematic mixing with the internal modes of the conjugating groups. RR activity is observed for out-of-plane modes in all the Ni(II) DP derivatives, indicating a distortion of the porphyrin cores from planarity. For Ni(2-acetylDP) and Ni(4-acetylDP), the vibrational frequencies,  $E_u$  mode splittings and RR enhancements are virtually identical, indicating that substitution of the conjugating group at the two different porphyrin ring positions results in essentially identical perturbations on the porphyrin  $\pi$ -electronic structure. For Ni(2,4-diacetylDP) and Ni(2,4-diformylDP), the  $E_u$  mode B-state RR enhancements are significantly larger than for the monoacetyl derivatives. It is suggested that this enhancement results from in-phase mixing of the two components of the degenerate mode facilitated by coupling to the in-phase combination of the two carbonyl stretches. Comparison of the Q-state excitation profiles for the RR bands of the mono and dicarbonyl derivatives suggests that the vibronic coupling between the Q and B states is comparable in the two sets of complexes. The splitting between  $Q_x$  and  $Q_y$  is also comparable in the mono- and dicarbonyl derivatives and is estimated to be 300–400  $\text{cm}^{-1}$ .

## I. Introduction

Many biologically important porphyrins contain peripheral substituent groups which can conjugate into the  $\pi$ -electron system of the porphyrin ring. Protoporphyrin IX (PP) with 2,4-divinyl substituents is the most common natural porphyrin. Variants of this moiety are also prevalent in natural systems, for example, sirographis and heme *a*, which contain 2-formyl-4-vinyl and 4-vinyl-8-formyl substituents, respectively.<sup>2</sup> The presence of conjugating groups affords the opportunity for control of the physical and chemical properties of the porphyrin ring via substituent interactions with the amino acid residues of the protein.<sup>3-11</sup> Such interactions have been proposed for the vinyl groups of protoheme in hemoglobin<sup>5-7</sup> and cytochrome *b*,<sup>8</sup> and for the formyl group of heme *a* in cytochrome *c* oxidase.<sup>9-11</sup>

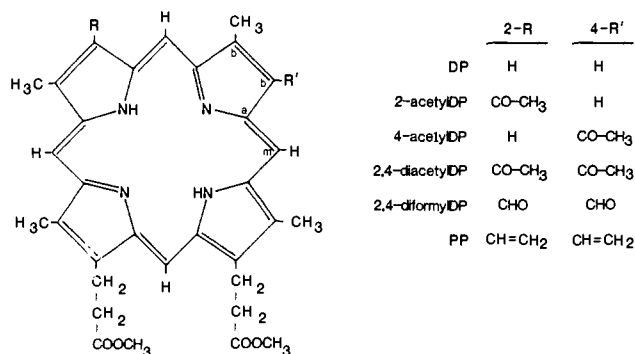
Resonance Raman (RR) spectroscopy is a particularly sensitive probe of the  $\pi$ -electronic structure of porphyrins<sup>12,13</sup> and the effects of conjugating substituents.<sup>14-16</sup> Recent RR studies of myoglobin

reconstituted with sirographis heme<sup>17</sup> and protoheme containing deuterated vinyl groups<sup>18</sup> have revealed various substituent group-protein interactions. The interpretation of the RR data from these studies was greatly facilitated by the availability of detailed vibrational spectra<sup>19</sup> and normal coordinate calculations<sup>20</sup> for the highly symmetrical Ni(II) octaethylporphyrin complex [Ni(OEP)]. The RR study of protoheme by Spiro and co-workers was accompanied by vibrational assignments for Ni(PP) and its divinyl deuterated derivatives<sup>21</sup> which were made largely by analogy to those of Ni(OEP). These Ni(PP) assignments in turn provided the basis for the interpretation of the protoheme vibrational spectra.

Despite the recent progress in the assignment of metalloporphyrin vibrational spectra and particularly the contribution of conjugating substituents to the RR spectra, there have been no vibrational studies probing the effects of either selective 2-R vs. 4-R' substitution or changes in the electron-withdrawing capability of conjugating groups. The characterization of such specifically substituted porphyrins is necessary before position-specific and substituent-specific porphyrin-protein interactions can be sorted out. To this end, we report detailed RR and IR studies of the Ni(II) complexes of the series of 2- and 4- and 2,4-substituted deuteroporphyrin IX dimethyl esters shown in Figure 1. These include deuteroporphyrin (DP), 2,4-di-deuterioDP-*meso-d*<sub>4</sub> (DP-*d*<sub>6</sub>), 2-acetylDP (2-AcDP), 4-acetylDP (4-AcDP), 2,4-diacetylDP (2,4-AcDP), 2,4-di(acetyl-*d*<sub>3</sub>)DP

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**Figure 1.** Structure of deuteroporphyrin IX dimethyl ester with atom-labeling scheme. The 2-R/4-R' substituents are shown to the right of the structure.

(2,4-AcDP-*d*<sub>6</sub>), 2,4-diformylDP (2,4-FDP), and 2,4-di(formyl-*d*)DP (2,4-FDP-*d*<sub>2</sub>).

We first present the results of the vibrational study and summarize the assignments for the porphyrin skeletal modes and the internal vibrations of the conjugating substituents. Next we discuss the vibrational assignments and the influence of the substituent groups on the porphyrin vibrational spectra. Finally we comment on position-specific substituent group-protein interactions as a means of controlling functional activity.

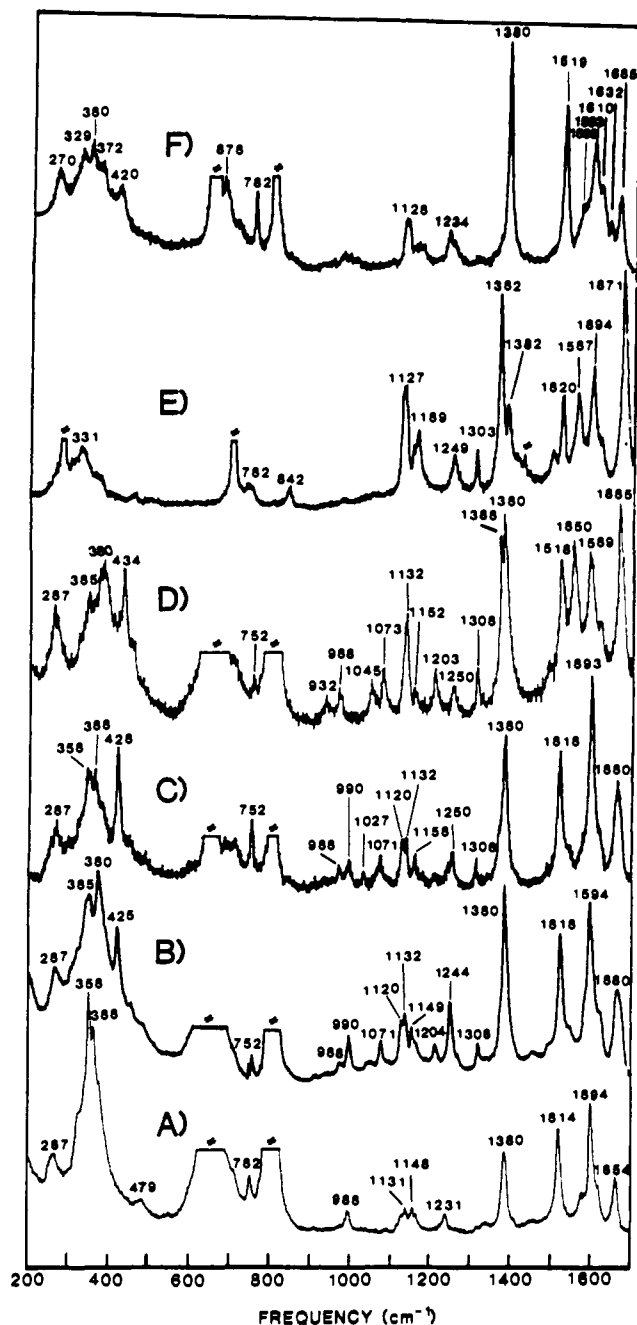
## II. Experimental Section

The free-base porphyrins DP, 2,4-AcDP, 2,4-FDP, and PP were obtained from Midcentury (Posen, IL). The free bases of 2-AcDP and 4-AcDP were the generous gift of Professor K. M. Smith. The diacetyl deuterated derivative, 2,4-AcDP-*d*<sub>6</sub>, was prepared as described by Budd et al.<sup>22</sup> The diformyl deuterated derivative, 2,4-FDP-*d*<sub>2</sub>, was prepared by an osmium tetroxide catalyzed periodate oxidation<sup>23,24</sup> of PP containing  $\alpha$ -deuterated vinyl groups. The latter material was prepared by the method of Budd et al.<sup>22</sup> The 2,4-FDP-*d*<sub>2</sub> was purified on activity III alumina, eluting with CHCl<sub>3</sub>. The meso-deuterated  $\beta$ -pyrrole deuterated derivative, DP-*d*<sub>6</sub>, was prepared by stirring DP in 90 wt % D<sub>2</sub>SO<sub>4</sub>/MeOD for 18 h.<sup>25</sup> NMR spectroscopy established the extent of deuteration at 90% or greater for each of the three deuterated derivatives described above. The metal was inserted into the various DP derivatives according to published procedures.<sup>26,27</sup>

The RR spectra were recorded with the optics in a 90° scattering configuration on a computer-controlled Spex Industries Ramalog 6 spectrometer equipped with a thermoelectrically cooled Hamamatsu R955 photomultiplier tube and a photon-counting detection system. Excitation wavelengths were provided by a tunable dye laser (Coherent Radiation Model 590) utilizing the tuning ranges of Rhodamine 6G and Coumarin 6 dyes (Exciton Chemical Co.) and by the discrete lasing outputs of Ar ion (Spectra-Physics Model 164-05) and Kr ion (Coherent Radiation Model CR-2000K) lasers. RR spectra were collected at 2-cm<sup>-1</sup> intervals at a rate of 2 s/point. The incident laser power ranged from 50 to 150 mW and the spectral slit width from 3 to 5 cm<sup>-1</sup>. Solution samples (CS<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub>) were contained in sealed capillary tubes and prepared to give an absorbance of 1.0/mm as measured at either the B(0,0) or Q(0,0) absorption maxima. Solid samples were prepared in KBr pellets (1 mg/100 mg of KBr). Excitation profiles were obtained in CS<sub>2</sub> solutions and measured with respect to the 656- and 796-cm<sup>-1</sup> solvent bands. The profiles are corrected for the  $\nu^4$  dependence of scattered light, sample reabsorption, and instrument and photomultiplier responses. All IR spectra were recorded on solid samples in KBr pellets on a Perkin-Elmer 283B spectrometer. The spectral resolution is 2 cm<sup>-1</sup>.

## III. Results

Representative RR spectra of the Ni(II) complexes of DP, 2-AcDP, 4-AcDP, 2,4-AcDP and 2,4-FDP obtained with excitation near the maxima of the B(0,0) and Q(0,0) absorption bands are



**Figure 2.** B-state excitation RR spectra of the Ni(II) DP derivatives: (A) Ni(DP),  $\lambda_{ex}$  4154 Å; (B) Ni(2-AcDP),  $\lambda_{ex}$  4131 Å; (C) Ni(4-AcDP),  $\lambda_{ex}$  4154 Å; (D) Ni(2,4-AcDP),  $\lambda_{ex}$  4131 Å; (E) Ni(2,4-FDP),  $\lambda_{ex}$  4154 Å; (F) Ni(PP),  $\lambda_{ex}$  4131 Å. Spectra A, B, C, D, and F were recorded in CS<sub>2</sub> solutions and spectrum E was recorded in CH<sub>2</sub>Cl<sub>2</sub> solution. The solvent peaks are denoted by #. See Experimental Section for spectral conditions.

shown in Figures 2 and 3, respectively. The exact excitation wavelengths are given in the figure legends. For comparison, RR spectra of Ni(PP) are also shown in the two figures. The IR spectra of all six complexes are shown in Figure 4. The frequencies we observe for the RR and IR bands of Ni(PP) and the IR bands of Ni(DP), Ni(2,4-AcDP), and Ni(2,4-FDP) are in reasonably good agreement with those previously reported for these complexes.<sup>21,28,29</sup> The high- and low-frequency RR spectra of Ni(DP) and Ni(DP-*d*<sub>6</sub>) are compared in Figures 5 and 6, respectively. The high-frequency RR and IR spectra of Ni(2,4-FDP) and Ni(2,4-FDP-*d*<sub>2</sub>) are compared in Figures 7 and 8, re-

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Table I. Fundamental Raman and IR Bands (cm<sup>-1</sup>) Assignable to In-Plane Skeletal Modes

assignment <sup>a</sup>		Ni(OEP)		Ni(DP)		Ni(2-AcDP)		Ni(4-AcDP)		Ni(2,4-AcDP)		Ni(2,4-FDP)		Ni(PP)		
sym	no.	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	
A <sub>1g</sub>	$\nu_2$	1602		1594		1594		1593		1589		1594		1593		
	$\nu_3$	1519		1514		1518		1518		1518		1520		1519		
	$\nu_4$	1383		1380		1380		1380		1380		1382		1380		
	$\nu_5$	1025								1045						
	$\nu_6$	806		818 <sup>b</sup>								822		798		
	$\nu_7$	674				672		672		670				675		
	$\nu_8$	344		355		355		355		355		347 <sup>b</sup>		350		
	$\nu_9$	226		223		(212) <sup>c</sup>		(212) <sup>c</sup>		(217) <sup>c</sup>				220		
	$\nu_{10}$	1655		1654		1654		1654		1654		1654		1655		
B <sub>1g</sub>	$\nu_{11}$	1576		1572		1572		1572		1572		1572		1575		
	$\nu_{13}$	1220		1231		1244		1240		1244		1249		1234		
	$\nu_{16}$	751		752		752		752		752		752		752		
	$\nu_{18}$	(187) <sup>d</sup>		(183) <sup>c</sup>		(190) <sup>c</sup>		(183) <sup>c</sup>		(190) <sup>c</sup>						
	A <sub>2g</sub>	$\nu_{19}$	1603		1602		1602		1602		1602		1602		1603	
		$\nu_{21}$	1308		1306		1306		1306		1306		1303		1305	
		$\nu_{22}$	1121		1116		1120		1120		1120		1127		1125	
		$\nu_{23}$	(1022) <sup>d</sup>				(1014) <sup>c</sup>		(1014) <sup>c</sup>		(1015) <sup>c</sup>					
		B <sub>2g</sub>	$\nu_{28}$	(1469) <sup>d</sup>		1482		1482		1482		1482		1482		1482
$\nu_{29}$			1409		1404		1404		1404		1398		1412		1401	
$\nu_{30}$			1159		1148		1156		1156		1152		1146		1167	
$\nu_{32}$			785				782		782		784					
$\nu_{33}$			(536) <sup>d</sup>				(535) <sup>c</sup>		(535) <sup>c</sup>		(537) <sup>c</sup>					
$\nu_{35}$	(182) <sup>d</sup>					(190) <sup>c</sup>		(190) <sup>c</sup>		(190) <sup>c</sup>						
E <sub>u</sub>	$\nu_{37}$			1604				1622		1622		1622		1620		1610
	$\nu_{38}$			1557		1573	1540	1540	1540	1545	1550	1553	1557	1551	1566	1567
	$\nu_{39}$			1487		1456		1455		1459		1455		1456		1456
	$\nu_{40}$		1443		1442		1442		1442		1442		1442		1440	
	$\nu_{41}$		1362	1366	1367		1388		1388		1388		1395		1377	
	$\nu_{42}$		1268		1268		1268		1268		1268		1258		1262	
	$\nu_{43}$		1148		1178		1165		1175		1175		1178		1167	
	$\nu_{44}$		1113		1135		1122		1122		1128		1128		1118	
	$\nu_{45}$		993	986	987		990		990		971		968		998	
	$\nu_{46}$		924	909	909		932	972	930	968	932	932	898		984	
	$\nu_{47}$		726	898	897		906	930	902	930	932	932	898		963	
	$\nu_{52}$		264	287 <sup>e</sup>	267		267		267		267		268 <sup>b</sup>		270	

<sup>a</sup> Skeletal mode numbering and assignments follow Kitagawa et al.<sup>19</sup> <sup>b</sup> Frequency observed in a KBr pellet. <sup>c</sup> Not observed; frequency determined on the basis of combination or overtone frequencies given in Table II. <sup>d</sup> Not observed for Ni(OEP); calculated value.<sup>20</sup> <sup>e</sup> Observed in the IR spectrum of Ogoshi et al.<sup>30</sup>

Table II. Nonfundamental Raman Bands (cm<sup>-1</sup>) Assignable to In-Plane Skeletal Modes

assignment <sup>a</sup>		Ni(OEP)	Ni(DP)	Ni(2-AcDP)	Ni(4-AcDP)	Ni(2,4-AcDP)	Ni(2,4-FDP)	Ni(PP)
sym	no.							
A <sub>1g</sub>	$\nu_5 + \nu_9$	1261		~1250	~1250	~1250	~1250	1254
	$\nu_6 + \nu_8$	1138	1131	1132	1132	1132	1132	1130
	$2\nu_{33}$			1071	1071	1073		
	$\nu_{32} + \nu_{35}$	963	968	968	968	968	968	968
	$2\nu_9$			425	425	434		
	$2\nu_{35}$			380	380	380	378 <sup>b</sup>	372
	$2\nu_{18}$	361	366		366			
B <sub>1g</sub>	or $\nu_{35} + \nu_{23}$			1204	1204	1203		
	B <sub>2g</sub>	$\nu_{18}$		1328	1328	1328		
	?							

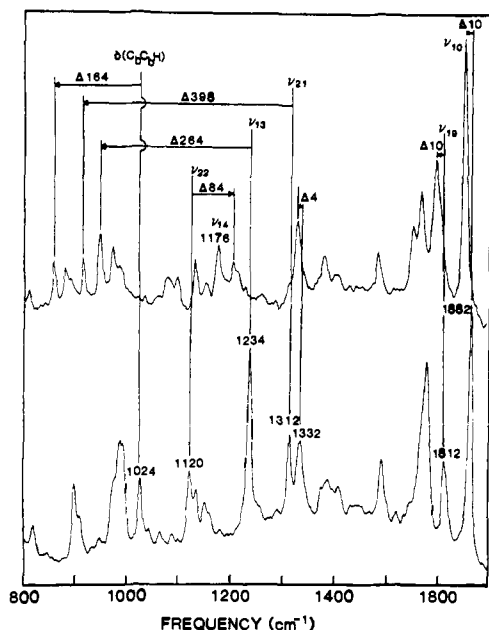
<sup>a</sup> Skeletal mode numbering and assignments follow Kitagawa et al.<sup>19</sup> <sup>b</sup> Frequency observed in a KBr pellet.

spectively. Bands which undergo substantial shifts upon formyl group or porphyrin ring deuteration are indicated in the figures. The RR and IR spectra of Ni(2,4-AcDP-*d*<sub>6</sub>) are not shown. The frequencies of all the RR bands and the IR bands not associated with the C-H motions of the acetyl methyl groups of this complex were found to be identical with those of Ni(2,4-AcDP). Finally, visible-region excitation profiles for Ni(DP), Ni(4-AcDP), and

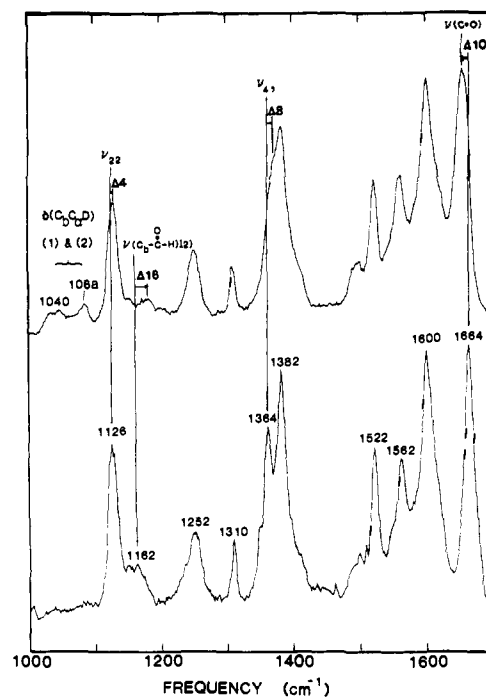
Ni(2,4-AcDP) are shown in Figure 9. Profiles were also obtained for Ni(2-AcDP) and Ni(2,4-FDP). The profiles for these complexes are virtually identical with those of Ni(4-AcDP) and Ni(2,4-AcDP) and are not shown.

The observed RR and IR bands assignable to fundamental in-plane porphyrin skeletal modes of the various DP complexes are given in Table I. Assignments for observed Raman com-

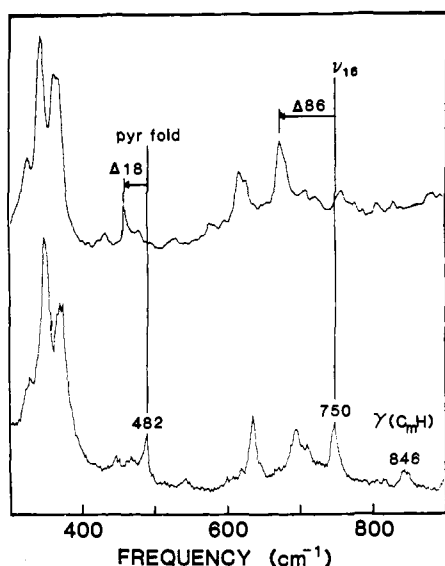




**Figure 5.** High-frequency RR spectra of Ni(DP) (bottom) and Ni(DP- $d_6$ ) (top) in KBr pellets;  $\lambda_{\text{ex}}$  5682 Å. Note that the frequencies observed for the solid samples shown in this figure and Figures 6, 7, and 8 are slightly different from those observed for solution samples (Figures 2 and 3, Table I).

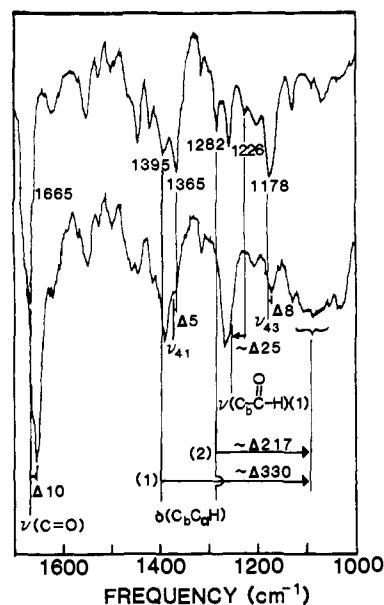


**Figure 7.** High-frequency RR spectra of Ni(2,4-FDP) (bottom) and Ni(2,4-FDP- $d_2$ ) (top) in KBr pellets;  $\lambda_{\text{ex}}$  4131 Å.



**Figure 6.** Low-frequency RR spectra of Ni(DP) (bottom) and Ni(DP- $d_6$ ) (top) in KBr pellets;  $\lambda_{\text{ex}}$  4131 Å.

the porphyrin core is strictly planar.<sup>19</sup> On the other hand, naturally occurring metalloporphyrins such as the 2-R/4-R' substituted DP complexes do not possess higher than  $C_2$  symmetry owing to the inequivalence of the  $C_b$  substituent groups (Figure 1). Previous studies of metalloporphyrins have revealed that in the low-symmetry environment substituent-induced perturbations can be manifested in the vibrational spectra in several ways.<sup>11,15-18,21,31-36</sup>



**Figure 8.** High-frequency IR spectra of Ni(2,4-FDP) (top) and Ni(2,4-FDP- $d_2$ ) (bottom) in KBr pellets.

(1) The stretching and bending modes of the asymmetrically distributed  $C_b$  substituents can mix with the other porphyrin modes in a fashion substantially different from symmetrically distributed substituents, thus significantly altering the skeletal frequencies. In the extreme, symmetry lowering by either kinetic or potential energy effects may induce Raman activity into IR modes and vice versa and lift the degeneracy of  $E_u$  modes. (2) The internal modes of conjugating substituents may become resonance enhanced in the Raman spectra with porphyrin Q- and B-state excitation. Also, the internal modes of the conjugating groups can mix with the porphyrin skeletal modes, perturbing their frequencies. All of these effects are observed in the vibrational spectra of the Ni(II) DP derivatives. In sections IV.A and IV.B below, we discuss the assignments for the porphyrin skeletal modes and the internal vibrations of the conjugating substituents. The specific effects of the substituents on the porphyrin vibrational spectra and electronic structure are discussed in section IV.C.

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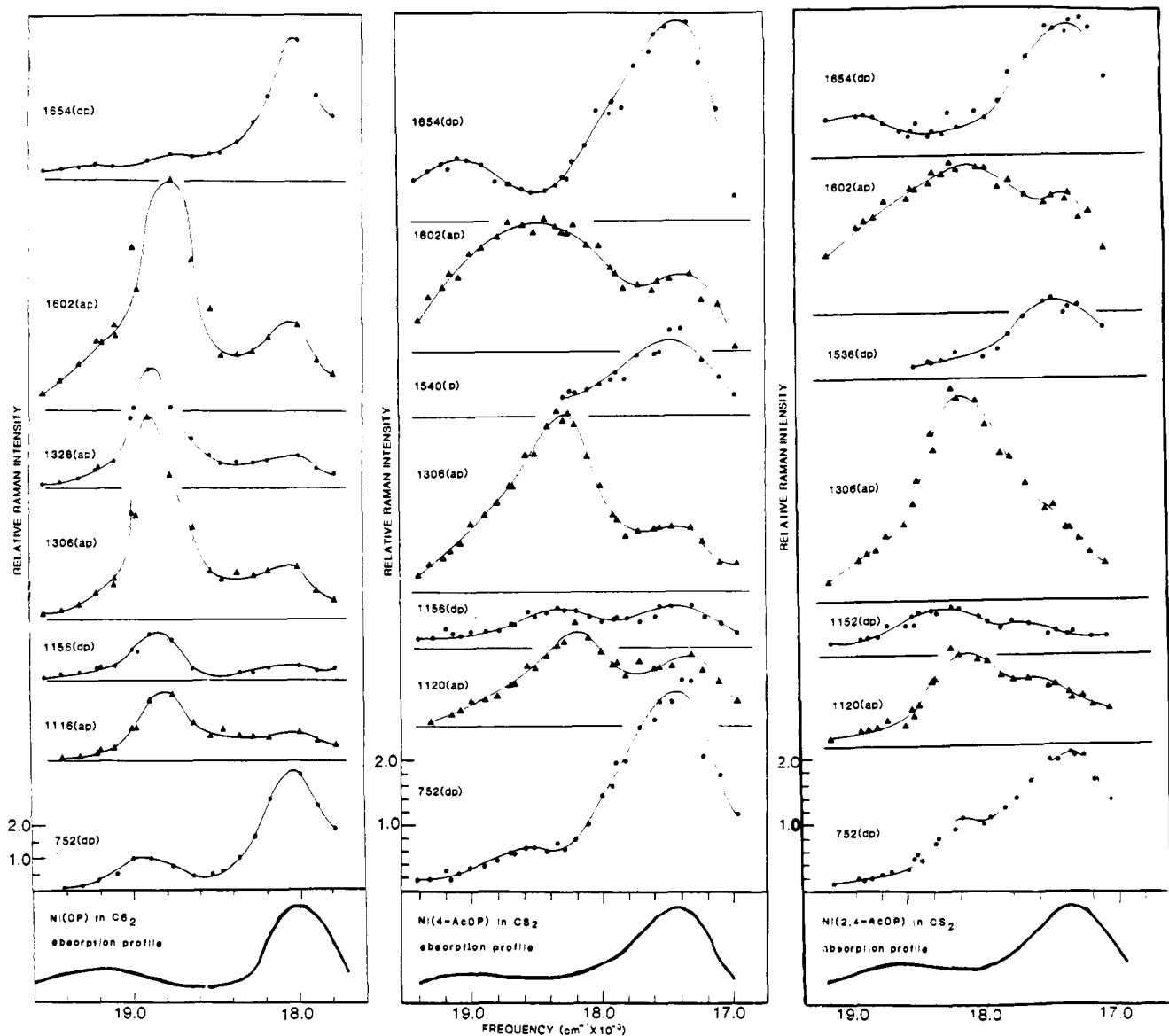


Figure 9. Q-state excitation profiles of Ni(DP) (left), Ni(4-AcDP) (center), and Ni(2,4-AcDP) (right) in CS<sub>2</sub> solution. The intensities are plotted on a linear scale and the frequencies are given in cm<sup>-1</sup>. The profiles are displaced vertically and plotted by using alternate circles (●) and triangles (▲) for clarity of presentation. The Q-state absorption profile is also shown. Abbreviations used: p, polarized; dp, depolarized; ap, anomalously polarized.

Table IV. Raman and IR Bands (cm<sup>-1</sup>) Associated with the 2-R and 4-R' Substituents

assignment	Ni(DP)		Ni(2-AcDP)		Ni(4-AcDP)		Ni(2,4-AcDP)		Ni(2,4-FDP)	
	R	IR	R	IR	R	IR	R	IR	R	IR
$\nu(\text{C}=\text{O})$ $\begin{cases} (1) \\ (2) \end{cases}$			1660 <sup>b</sup> 1656 <sup>c</sup>	1649	1660 <sup>b</sup> 1656 <sup>c</sup>	1652		1663		1674
$\nu(\text{C}_{\text{b}_2}\text{-acetyl}) (\nu_{43})$			n.o. <sup>e</sup>	1165			~1165	1656	1671 <sup>d</sup>	1665
$\nu(\text{C}_{\text{b}_4}\text{-acetyl}) (\nu_{43})$					n.o.	1175	n.o.	1175		
$\nu(\text{C}_{\text{b}}\text{-formyl})$ $\begin{cases} (1)(\nu_{42}) \\ (2)(\nu_{43}) \end{cases}$									n.o.	1226
									1159	n.o.
$\delta(\text{C}_{\text{b}}\text{C}_{\alpha}\text{R})$ $\begin{cases} (1) \\ (2) \end{cases}$			n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	f	1395 1282
$\delta(\text{C}_{\text{b}}\text{C}_{\text{b}}\text{H})$	1022	1025	1034	1032	1027	1029				
$\delta(\text{C}_{\text{b}}\text{C}_{\text{b}}\text{C}_{\alpha}) (\nu_9)$			212 <sup>g</sup>		212 <sup>g</sup>		217 <sup>g</sup>		n.o.	

<sup>a</sup> (1) and (2) refer to the out-of-phase and in-phase motions for Ni(2,4-AcDP) and Ni(2,4-FDP). <sup>b</sup> Frequency observed in CS<sub>2</sub> solution. <sup>c</sup> Frequency observed in a KBr pellet. <sup>d</sup> Frequency observed in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>e</sup> Not observed. <sup>f</sup> These bands are not observed for Ni(2,4-FDP) but are observed for Ni(2,4-FDP-d<sub>2</sub>) at 1088 and 1040 cm<sup>-1</sup> (Figures 7 and 8). <sup>g</sup> Not observed; frequency determined on the basis of combination and overtone frequencies given in Table II.

Table V. Depolarization Ratios ( $\rho$ ) of the Raman Bands ( $\text{cm}^{-1}$ ) at Selected Excitation Wavelengths

assignment <sup>a</sup>		Ni(DP)				Ni(2-AcDP)				Ni(4-AcDP)				Ni(2,4-AcDP)				Ni(2,4-FDP)				
		$\lambda_{\text{ex}}$ (Å)				$\lambda_{\text{ex}}$ (Å)				$\lambda_{\text{ex}}$ (Å)				$\lambda_{\text{ex}}$ (Å)				$\lambda_{\text{ex}}$ (Å)				
sym	no.	$\bar{\nu}$	4154	5309	5540	$\bar{\nu}$	4131	5309	5682	$\bar{\nu}$	4154	5309	5682	$\bar{\nu}$	4131	5309	5654	$\bar{\nu}$	4154	5309	5799	
A <sub>1g</sub>	$\nu_2$	1594	0.23			1594	0.26			1593	0.28			1589	0.41			1594	0.28			
	$\nu_3$	1514	0.18			1518	0.23			1518	0.25			1518	0.22			1520	0.35			
	$\nu_4$	1380	0.20			1380	0.18	0.45		1380	0.18	0.53		1380	0.10	0.33	0.61	1382	0.33	p	p	
	$\nu_5 + \nu_9$					~1250	0.36	p	p	~1250	0.33	p		~1250	0.3			~1250	0.3			
	$\nu_6 + \nu_8$	1131		p	p	1132	0.32	p	p	1132	w (sh)			1132	p	p	p	1132	<0.1			
	$2\nu_{33}$					1071	0.2	p	p	1071	<0.1		p	1073	0.39	p	0.16					
	$\nu_5$													1045	0.36							
	$\nu_{32} + \nu_{35}$	968	w (sh)	w (sh)		968			0.3	968	<0.1		0.3	968	0.25		0.54	968		p	0.6	
	$\nu_6$	818	b											670		p	p	822	p	p		
	$\nu_7$					672	b			672	b			434	0.2							
	$2\nu_9$					425	0.30	p		425	0.2		0.5	380	0.3							
	$2\nu_{35}$					380	0.18	p	p	380	p			380	0.3				378	b		
	$2\nu_{18}$	366	0.1	<0.1	p					366	0.24			355	p				347	b		
	$\nu_8$	354	0.1	<0.1	0.3	355	0.28	p	p	355	0.23	p	p	355	p							
$\nu_9$	223			p																		
B <sub>1g</sub>	$\nu_{10}$	1654	0.8	0.8	0.68	1654		0.7	0.4	1654		0.8	0.3	1654		0.75	0.8	1654		0.7	0.8	
	$\nu_{11}$	1572			0.72	1572			0.6	1572			0.5	1572			0.7	1572			dp	
	$\nu_{13}$	1231	0.8	0.75	0.64	1244			0.7	1244			0.7	1244		0.7	0.75	1249		0.6	0.7	
A <sub>2g</sub>	$\nu_{16}$	752	0.8	0.8	0.75	752	0.7	0.7	0.7	752	0.5		0.6	752	0.7	0.7	0.75	752			0.75	
	$\nu_{19}$	1602		15.2	5.1	1602		1.3	2.2	1602		2.7	1.4	1602		2.9	3.0	1602		2.2	2.2	
	$\nu_{21}$	1306		13.8	6.6	1306	0.54	3.5	3.0	1306	0.33	2.3	2.2	1306	0.13	2.4	5.2	1303	0.5	2.0	3.0	
B <sub>2g</sub>	$\nu_{22}$	1116		6.2	1.2	1120	0.37	1.3	0.6	1120	p	1.5	0.71	1120	0.75	1.4	1.0	1127		p	0.75	
	$\nu_{28}$	1482			0.72	1482			dp	1482			w	1482			0.75	1482			0.75	
	$\nu_{29}$	1404			dp	1404			dp	1404			0.8	1398		dp	dp	1412			dp	
	$\nu_{18} + \nu_{23}$					1204	0.7	dp		1204			0.6	1203		0.7	0.7					
	$\nu_{30}$	1148	dp	0.75	0.60	1156	dp	0.8		1156			0.6	1152	0.54	0.80	0.75	1146	0.3	0.7	0.7	
	$\nu_{32}$					782			b	782			b	784			b					
	$\nu_{38}$					1540			0.46	1540			0.27	1550	0.20				1557	0.40		
E <sub>u</sub>	$\nu_{41}$	1366			p	1370			p	1368			0.4	1368	0.10	p	0.7	1546			0.8	
	$\nu_{45}$	986	1.0	0.75	0.74	990	0.23		0.5	990	0.2		0.5			p	p	1362	0.24	p	dp	
	$\nu_{46}$	909		w (sh)	w	932			0.3				0.3	932	0.2		0.75					
	$\nu_{47}$	898			0.4	906			0.3	902												
	$\nu_{52}$	271	0.1	0.6		708	b			710	b			701	b							
$\nu(\text{C=O})$					267	<0.1	p	p	267	0.17		p	267	0.2	p							
?		1328		7.4	1.6	1328		1.6	0.6	1328		1.4	1.0									
$\delta(\text{C}_b\text{-H})$		1022			0.4	1034			0.47	1027			0.30									
$\gamma(\text{C}_m\text{-H})$		842	p															842	0.2		0.37	
pyr fold		479	p			479		p	p	478	b							458	b			

<sup>a</sup> Skeletal mode numbering and assignments follow Kitagawa et al.<sup>19</sup> <sup>b</sup> Band observed in KBr pellet: depolarization ratio not measured.

**A. Porphyrin Skeletal Modes. 1. RR- and IR-Active In-Plane Fundamental Modes.** The fundamental RR- ( $A_{1g}$ ,  $A_{2g}$ ,  $B_{1g}$ ,  $B_{2g}$ ) and IR- ( $E_u$ ) active in-plane porphyrin skeletal vibrations can be assigned fairly readily by analogy to those of Ni(OEP),<sup>19,20</sup> despite the substantial deviations of the Ni(II) DP derivatives from the idealized  $D_{4h}$  model (Figures 2–4, Table I). This is particularly true for the RR modes where all but a few of the bands of the Ni(II) DP derivatives are within 5  $\text{cm}^{-1}$  of the analogous bands of Ni(OEP), the clear exceptions being  $\nu_2$ ,  $\nu_8$ , and  $\nu_{13}$ . The  $\nu_5$  and  $\nu_6$  bands of the Ni(II) DP complexes also appear to be at frequencies different from those of Ni(OEP), but these bands are not observed for all the DP derivatives and trends cannot be ascertained. The depolarization ratios of the RR bands of the Ni(II) DP derivatives (Table V) also correlate reasonably well with those of the analogous RR bands of Ni(OEP). The Ni(DP) complex exhibits  $\rho$  values essentially identical with those of Ni(OEP) for bands of all polarization, including the  $A_{2g}$  modes which are quite sensitive to perturbation of the porphyrin  $\pi$ -electronic structure.<sup>31</sup> The  $\rho$  values for the  $A_{2g}$  modes of the acetyl and formyl derivatives are substantially different from those of Ni(OEP), reflecting the symmetry lowering resulting from conjugation of the carbonyl group with the porphyrin aromatic system. Also, the  $A_{1g}$  modes of these complexes, although clearly polarized, exhibit  $\rho$  values somewhat larger than those of the totally symmetric modes of Ni(OEP).

The correlation of the IR bands of the Ni(II) DP derivatives with those of Ni(OEP) is not nearly as straightforward as for the RR bands. The IR spectra are quite complex owing to the activity of out-of-plane porphyrin modes and internal vibrations of the  $C_b$  substituents. Nonetheless, the examination of the various Ni(II) DP derivatives, including the deuterated species, allows assignments to be made for the  $E_u$  modes with reasonable confidence. In general, the IR-active modes appear to be much more sensitive to the effects of the  $C_b$  substituents than the RR bands. Most of the  $E_u$  modes of the Ni(II) DP derivatives occur at frequencies different from those of Ni(OEP), the only universal exception being  $\nu_{40}$ . Also, many of the  $E_u$  modes, including  $\nu_{38}$ ,  $\nu_{41}$ ,  $\nu_{43}$ , and  $\nu_{46}$ , show clear evidence of doubling, indicating their degeneracy has been lifted. It should be noted that the doubled IR bands cannot be attributed to internal vibrations of the methyl or propionic acid ester groups since Ni(DP), which contains these groups, does not exhibit the split bands (with the possible exceptions of  $\nu_{44}$  and  $\nu_{46}$ ). Deuterium substitution in the acetyl and formyl substituents indicates that the extra bands cannot be attributed to internal vibrations of these substituents.

**2. RR-Active  $E_u$  Modes.** The RR spectra of the Ni(II) DP derivatives are considerably richer than those of Ni(OEP), in large part owing to the activity of  $E_u$  modes (Figures 2 and 3, Table I). This is most clearly seen in the B-state excitation spectra of Ni(2,4-AcDP) and Ni(2,4-FDP) where the  $\nu_{38}$  and  $\nu_{41}$   $E_u$  modes are observed at 1550 and 1368  $\text{cm}^{-1}$  and 1557 and 1362  $\text{cm}^{-1}$  for the two complexes, respectively. The  $\nu_{38}$  mode is split for both Ni(2,4-AcDP) and Ni(2,4-FDP) and the second component is observed in the Q-state excitation spectra at 1536 and 1546  $\text{cm}^{-1}$ , respectively. The IR spectra of the two complexes indicate that the  $\nu_{41}$  mode is also split (Figure 4); however, in the RR spectra the second component of this mode falls in a congested region and cannot be clearly identified. The  $\nu_{38}$  and  $\nu_{41}$  modes are also observed in the Q-state excitation spectra of Ni(2-AcDP) and Ni(4-AcDP) at 1540 and  $\sim 1370$   $\text{cm}^{-1}$ , respectively, for each complex. Apparently  $\nu_{38}$  is not split for the monoacetyl derivatives in that no second component is observed in either the RR or IR spectra. On the other hand, the IR spectra indicate that the  $\nu_{41}$  mode is split (Figure 4), but the second component cannot be identified in the RR spectra. A RR band is also observed at 1366  $\text{cm}^{-1}$  in the Q-state excitation spectrum of Ni(DP) coincident with the strong unsplit  $\nu_{41}$  IR mode. This RR band is quite weak, as are the RR enhancements of the  $\nu_{41}$  modes of the two monoacetyl derivatives, in contrast to the strong enhancements observed for the diacetyl and diformyl derivatives.

A final note regarding the appearance of forbidden bands in the vibrational spectra is that despite the strong activity of certain

of the  $E_u$  modes in the RR spectra there is little if any evidence for IR activity of the  $A_{1g}$ ,  $A_{2g}$ ,  $B_{1g}$ , or  $B_{2g}$  vibrations (Figure 4). A similar observation was made by Spiro and co-workers<sup>21</sup> in their study of Ni(PP). These workers attributed the one-sided breakdown of symmetry selection rules to much stronger conjugation of the vinyl groups into the porphyrin  $\pi$ -electronic excited state than into the ground state. Apparently, this is also the case for the acetyl and formyl derivatives.

**3. RR-Active Combination and Overtone Modes.** A number of bands are observed in the RR spectra of the Ni(II) DP derivatives which cannot be assigned either as fundamental in-plane porphyrin skeletal modes or internal vibrations of the 2-R and 4-R' substituents. About half of these bands exhibit frequencies similar to RR bands of Ni(OEP) which have been assigned to combination or overtones of the in-plane skeletal modes.<sup>19</sup> We have made analogous assignments for the Ni(II) DP derivatives (Table II). The remaining RR bands are principally observed in the spectra of the acetyl derivatives and include bands near 1070 (p), 430 (p), 380 (p), and 1204 (dp)  $\text{cm}^{-1}$  for all three complexes and a band at  $\sim 1330$   $\text{cm}^{-1}$  for the two monoacetyl derivatives. None of these bands are observed for Ni(DP) or Ni(2,4-FDP) with the exception of the 1330- $\text{cm}^{-1}$  band which is observed for the former complex and the 380- $\text{cm}^{-1}$  band which is observed for the latter. Deuteration of the acetyl and formyl groups does not result in any discernible shifts in any of these bands nor does deuteration of the porphyrin ring  $C_b$  and meso positions.

The assignments for the 1330-, 1204-, 1070-, 430-, and 380- $\text{cm}^{-1}$  RR bands of the Ni(II) DP derivatives are not entirely clear. It is possible that some of the RR bands are combination and overtone vibrations of the in-plane porphyrin skeletal fundamentals which are activated in the low-symmetry environment. In this connection, we have indicated in Table II possible nonfundamental assignments for most of the "extra" RR bands. The assignments as combination and overtones of skeletal fundamentals do, however, present some difficulties. For example, the ring deuteration experiment renders the consistent assignment of the 1330- $\text{cm}^{-1}$  band as nonfundamental in-plane skeletal vibration nearly impossible (Figure 5). Consequently, we suggest no assignment for this band in Table II. If the 1330- $\text{cm}^{-1}$  and other RR bands of the Ni(II) DP derivative are not due to fundamental or nonfundamental in-plane porphyrin skeletal modes or internal vibrations of the 2-R and 4-R' substituents, the only other possible assignments are out-of-plane vibrations for the low-frequency bands ( $< 500$   $\text{cm}^{-1}$ ) and internal vibrations of the methyl and propionic acid methyl ester groups for the high-frequency bands ( $> 1000$   $\text{cm}^{-1}$ ). Out-of-plane modes have been observed previously in the RR spectra of metalloporphyrins,<sup>12,37–39</sup> and indeed we observe several bands in the RR spectra of the Ni(II) DP derivatives which can be confidently assigned as out-of-plane vibrations (see section IV.A.4). However, the RR intensity for the out-of-plane modes are quite low, significantly less than that of either the 430- or 380- $\text{cm}^{-1}$  bands. The possibility that the high-frequency RR bands of the Ni(II) DP derivatives are due to internal vibrations of the methyl or propionic acid methyl ester groups is quite interesting, since these modes have not been identified previously in metalloporphyrin RR spectra. Such an assignment is particularly intriguing for the 1330- $\text{cm}^{-1}$  band in that this mode also exhibits significant IR intensity (Figure 4), unlike either the 1204- or 1070- $\text{cm}^{-1}$  bands. Clearly, the participation of internal vibrations of saturated substituent groups in metalloporphyrin RR spectra needs to be investigated further.

**4. RR-Active Out-of-Plane Modes.** Out-of-plane modes have been observed in the RR spectra of several protoheme derivatives.<sup>12,37,39</sup> Recently, Choi and Spiro<sup>37</sup> have discussed their mechanisms of resonance enhancement and have assigned a number of these vibrations including methine hydrogen deformations,  $\gamma(C_m-H)$ , at  $\sim 840$   $\text{cm}^{-1}$ , pyrrole folding modes between 400 and 500  $\text{cm}^{-1}$ , and methine bridge deformations,  $\gamma(C_m-C_a)$ ,

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	R	R	
		CH <sub>3</sub>	H
$\nu(\text{C}=\text{O})$		1685	1694
$\nu(\text{C}_\alpha-\text{R})$		955	
$\nu(\text{C}_\beta-\text{COR})$		1265	1206
$\delta(\text{C}=\text{O})$		590	653
$\delta(\text{C}_\beta\text{C}_\alpha\text{R})$		368	1395
$\delta(\text{C}_\beta\text{C}_\alpha\text{H})$		226	221

**Figure 10.** Schematic diagram of the in-plane acetyl and formyl modes. The frequencies given for the modes are typical values and not those actually observed for the Ni(II) DP derivatives.

at  $\sim 320\text{ cm}^{-1}$ . The RR spectra of the Ni(II) DP derivatives exhibit weak bands around 840, 480, and  $325\text{ cm}^{-1}$  (Figures 2 and 3). These bands are insensitive to deuteration of the acetyl and formyl groups. However, deuteration of the meso and  $\text{C}_\beta$  ring positions of Ni(DP) results in substantial frequency downshifts of the bands. The shift observed for the  $\sim 840\text{-cm}^{-1}$  band is similar to that observed for  $\gamma(\text{C}_m\text{-H})$  in protoheme complexes (Figure 6).<sup>12,37</sup> Consequently, we have assigned the three low-frequency bands of the Ni(II) DP derivatives by analogy to those assigned by Choi and Spiro (Table III). The RR activity of the out-of-plane modes of the Ni(II) DP derivatives is probably due to a slight ruffling of the porphyrin cores.<sup>40-42</sup>

**B. 2-R and 4-R' Substituents.** We observe a number of RR-active acetyl and formyl group vibrations in the Ni(II) DP derivatives and have assigned these (Table IV) via deuteration shifts, comparison of the RR spectra of the various DP complexes, and comparison with the vibrational spectra of the simple olefins acetophenone<sup>43</sup> and benzaldehyde<sup>44</sup> for which complete vibrational assignments have been given. Our RR studies reveal that Raman activity is limited to the in-plane motions of the acetyl and formyl substituents, excluding all C-H stretching vibrations and C-H bending modes of the acetyl methyl group. The lack of RR activity for the C-H stretches and acetyl methyl bends is expected since the former vibrations are decoupled from the other internal modes of the substituent group while the latter involve atoms not bonded to the conjugating group.<sup>12</sup> The lack of RR activity for the out-of-plane deformations of the acetyl and formyl groups is not entirely expected since a number of out-of-plane vinyl group deformations have been observed in the RR spectra of Ni(PP)<sup>21</sup> and protoheme derivatives.<sup>18</sup>

The in-plane motions of the acetyl and formyl groups, excluding the C-H stretches and acetyl methyl bends, are shown diagrammatically in Figure 10 along with typical values for their frequencies.<sup>43,44</sup> These modes include the carbonyl stretch and bend,  $\nu(\text{C}=\text{O})$  and  $\delta(\text{C}=\text{O})$ , the acetyl methyl stretch and bend,  $\nu(\text{C}_\alpha-\text{C}_\beta)$  and  $\delta(\text{C}_\beta\text{C}_\alpha\text{C}_\beta)$ , and the formyl hydrogen bend,  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$ . In addition to these internal modes, there are two in-plane vibrations which involve the acetyl and formyl groups

as a whole. These are the  $\text{C}_\beta$ -acetyl/formyl stretch and bend,  $\nu(\text{C}_\beta-\text{COR})$ , and  $\delta(\text{C}_\beta\text{C}_\alpha\text{C}_\beta)$ . Note that these two modes are also formally included as in-plane skeletal vibrations when the  $\text{C}_\beta$  substituents are treated as part of the porphyrin structure. In the case of Ni(DP), Ni(2-AcDP), and Ni(4-AcDP), one or both of the ring-2-R/4-R' stretching and bending modes involves a hydrogen atom. RR activity is expected for the  $\text{C}_\beta$  hydrogen bend,  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$ , but not for the  $\text{C}_\beta$ -H stretch. In the following sections, we discuss in more detail the in-plane internal motions of the acetyl and formyl groups.

**1.  $\nu(\text{C}=\text{O})$ .** The  $\nu(\text{C}=\text{O})$  bands of Ni(2-AcDP), Ni(4-AcDP), Ni(2,4-AcDP), and Ni(2,4-FDP) are observed in the B-state excitation RR spectra at 1660, 1660, 1665, and  $1671\text{ cm}^{-1}$ , respectively (Figure 2). These modes are not observed with Q-state excitation. The selective B-state RR activity for  $\nu(\text{C}=\text{O})$  in the Ni(II) DP derivatives is in accord with that previously found for formyl carbonyl stretching modes in heme *a*<sup>32-36</sup> and spirographis heme.<sup>17</sup> The  $\nu(\text{C}=\text{O})$  IR bands of Ni(2,4-AcDP) and Ni(2,4-FDP) show an additional feature not observed in the RR spectra, a slight splitting with the components separated by 7 and  $9\text{ cm}^{-1}$ , respectively. We attribute this separation to the in-phase and out-of-phase combinations of the carbonyl stretch in the two disubstituted complexes. The single RR-active  $\nu(\text{C}=\text{O})$  band of Ni(2,4-AcDP) and Ni(2,4-FDP) corresponds to the lower frequency IR component (Table IV). This band in the dicarbonyl derivatives is attributed to the symmetric in-phase combination of the carbonyl stretches on the basis of the small  $\rho$  value ( $\sim 0.2$ ) compared with that observed for the two monocarbonyl complexes ( $\sim 0.5$ ) (Table V).

**2.  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$ .** The formyl hydrogen deformation in benzaldehyde is observed at  $1395\text{ cm}^{-1}$  and shifts to  $1046\text{ cm}^{-1}$  upon deuteration.<sup>44</sup> Spiro and co-workers<sup>36</sup> have assigned  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$  for the single formyl group in heme *a* as  $\sim 1390\text{ cm}^{-1}$  on the basis of a slight D/H shift of a skeletal fundamental which obscures the hydrogen deformation. Deuteration of the formyl hydrogens in Ni(2,4-FDP) results in a substantial narrowing and a  $6\text{-cm}^{-1}$  downshift of the higher frequency ( $1395\text{ cm}^{-1}$ ) IR-active component (Figure 8) of the split  $\nu_{41}$  mode and an  $8\text{-cm}^{-1}$  upshift of the lower frequency ( $1365\text{ cm}^{-1}$ ) IR- and RR-active component (Figures 7 and 8). Deuteration also results in the complete disappearance of the IR band at  $1282\text{ cm}^{-1}$  and the appearance of two new bands in both the IR and RR spectra at  $\sim 1088$  and  $1040\text{ cm}^{-1}$  (Figures 7 and 8). These observations suggest that one of the  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$  modes is obscured by and slightly to the blue of the  $\nu_{41}$  component at  $\sim 1395\text{ cm}^{-1}$  while the other  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$  deformation is at  $1282\text{ cm}^{-1}$ . The very large splitting of these two modes as well as the  $\delta(\text{C}_\beta\text{C}_\alpha\text{D})$  vibrations ( $\sim 1088$  and  $1040\text{ cm}^{-1}$ ) must arise from very strong differential interactions of the in-phase and out-of-phase combinations with the porphyrin skeletal modes.

**3.  $\nu(\text{C}_\beta-\text{COR})$ .** The  $\text{C}_\beta$ -acetyl/formyl stretches of the Ni(II) DP derivatives are expected in the frequency range  $1100\text{-}1300\text{ cm}^{-1}$  (Figure 10).<sup>43,44</sup> Spiro and co-workers<sup>36</sup> have assigned the  $\text{C}_\beta$ -formyl stretch of heme *a* as  $1220\text{ cm}^{-1}$  on the basis of a substantial D/H upshift in this mode which occurs upon uncoupling of the higher frequency formyl  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$  motions. There are several skeletal vibrations of Ni(2,4-FDP) which are sensitive to formyl group deuteration. These include the  $\nu_{41}$  ( $\text{E}_u$ ) modes discussed in section IV.B.2, the  $\nu_{22}$  ( $\text{A}_{2g}$ ) mode, and the  $\nu_{42}$  and  $\nu_{43}$  ( $\text{E}_u$ ) modes. The  $\nu_{22}$  vibration exhibits only a slight D/H upshift ( $\sim 4\text{ cm}^{-1}$ ) while the  $\nu_{42}$  and  $\nu_{43}$  modes are shifted dramatically (Figures 7 and 8). The  $\nu_{42}$  IR mode appears to be split into two components at  $1258$  and  $1226\text{ cm}^{-1}$ . Deuteration of the formyl group collapses this mode into a slightly split band centered at  $\sim 1265\text{ cm}^{-1}$  (Figure 8). The  $\nu_{43}$  mode is observed in the IR spectrum of Ni(2,4-FDP) at  $1178\text{ cm}^{-1}$  and downshifts  $8\text{ cm}^{-1}$  upon formyl deuteration. A second band, observed at  $\sim 1162\text{ cm}^{-1}$  in the RR spectrum undergoes a  $16\text{-cm}^{-1}$  D/H upshift (Figure 7). These two bands are attributed to the two components of the  $\nu_{43}$  mode, split by interactions with  $\delta(\text{C}_\beta\text{C}_\alpha\text{H})$ . The large D/H upshifts of the lower frequency components of  $\nu_{42}$  ( $1226 \rightarrow \sim 1250\text{ cm}^{-1}$ ) and  $\nu_{43}$  ( $\sim 1162 \rightarrow 1178\text{ cm}^{-1}$ ) are consistent with these modes having a substantial  $\text{C}_\beta$ -formyl stretching component.

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The contribution of  $C_b$ -acetyl stretching motions to the skeletal modes are somewhat difficult to ascertain since this mode is not expected to exhibit a significant shift upon acetyl methyl group deuteration ( $\sim 2\text{ cm}^{-1}$ ).<sup>43</sup> Indeed, none of the porphyrin skeletal modes of Ni(2,4-AcDP- $d_6$ ) are observed at frequencies different from those of Ni(2,4-AcDP). However, the  $\nu_{43}$  vibrations of the acetyl DP derivatives do appear to be specifically sensitive to substitution at the 2 vs. 4 position. This mode is observed as a single band in the IR spectra of Ni(2-AcDP) and Ni(4-AcDP) at 1165 and 1175  $\text{cm}^{-1}$ , respectively (Figure 4, Table I). The  $\nu_{43}$  mode of Ni(2,4-AcDP) is observed as an IR band at 1175  $\text{cm}^{-1}$ . A RR band observed at  $\sim 1165\text{ cm}^{-1}$  as a weak shoulder on the 1152- $\text{cm}^{-1}$   $\nu_{30}$  ( $B_{2g}$ ) mode may correspond to the second component of  $\nu_{43}$  for the diacetyl derivative (Figure 3). These observations suggest that the  $C_b$ -acetyl and  $C_b$ -acetyl stretches are both associated with  $\nu_{43}$  (Table IV). The relatively small splitting ( $\sim 10\text{ cm}^{-1}$ ) of the two  $C_b$ -acetyl stretching combinations in Ni(2,4-AcDP) is attributed to their mixing with the same porphyrin skeletal mode rather than different modes, as is the case for the  $C_b$ -formyl motions of Ni(2,4-FDP).

4.  $\delta(C_bC_bH)$ . The in-plane deformations of the  $C_b$  hydrogen atoms of unsubstituted metalloporphyrin complexes have been observed in the IR spectra between 1000 and 1200  $\text{cm}^{-1}$ .<sup>45</sup> Bands appear in both the RR and IR spectra of Ni(DP), Ni(2-AcDP), and Ni(4-AcDP) at 1022, 1034, and 1027  $\text{cm}^{-1}$ , respectively, which are not observed for Ni(2,4-AcDP) or Ni(2,4-FDP). These modes are assigned as  $\delta(C_bC_bH)$  on the basis of the shift of the 1022- $\text{cm}^{-1}$  band of Ni(DP) to 860  $\text{cm}^{-1}$  upon  $C_b$  deuteration (Figure 5, Table IV). There is no clear evidence for a second  $\delta(C_bC_bH)$  mode in the RR and IR spectra of Ni(DP).

5.  $\delta(C_bC_bC_\alpha)$ . The bending deformations of the acetyl and formyl groups as a whole are expected to be associated with low-frequency skeletal modes (Figure 10) and exhibit moderate to small shifts upon substituent deuteration.<sup>43,44</sup> There are no bands observed in the spectra of Ni(2,4-FDP) assignable to  $\delta(C_bC_bC_\alpha)$ . The only low-frequency band in the spectra of the acetyl DP derivatives sensitive to the 2-R/4-R' substituents is the RR mode observed at 425  $\text{cm}^{-1}$  for Ni(2-AcDP) and Ni(4-AcDP) and at 434  $\text{cm}^{-1}$  for Ni(2,4-AcDP). This mode is assigned tentatively as  $2\nu_9$  (section IV.A.3, Table II) which could conceivably be mixed with  $\delta(C_bC_bC_\alpha)$ .

6. **Other Modes.** The internal motions of the substituents which remain to be assigned are the acetyl and formyl carbonyl bends  $\delta(C=O)$  and the acetyl methyl stretching and bending modes,  $\nu(C_\alpha-C_\beta)$  and  $\delta(C_bC_\alpha C_\beta)$ . The two types of bending modes are expected between 400 and 700  $\text{cm}^{-1}$  while the stretch is expected around 1000  $\text{cm}^{-1}$  (Figure 10). All three modes are expected to show substantial deuteration shifts.<sup>43,44</sup> The lack of such shifts for any of the observed RR bands indicates these modes are not enhanced. We are also unable to make any unambiguous assignments for these vibrations in the IR.

C. **Substituent Influences on Porphyrin Vibrational Spectra and Electronic Structure. 1. Classification of the Substituent Effects.** The porphyrin skeletal modes of the Ni(II) DP derivatives can be classified into three basic categories according to the influence of the  $C_b$  substituents on their vibrational frequencies and RR activities. The first category consists of modes which are basically insensitive to the substituent groups and any symmetry lowering induced by their asymmetric distribution or by conjugation effects. Each mode of this type has a frequency the same for all the Ni(II) DP derivatives and also Ni(OEP). These vibrations include most of the RR-type modes ( $A_{1g}$ ,  $A_{2g}$ ,  $B_{1g}$ ,  $B_{2g}$ ), except  $\nu_2$ ,  $\nu_8$ ,  $\nu_{13}$ , and possibly  $\nu_{30}$ , but only one of the IR-type modes ( $E_u$ ),  $\nu_{40}$ . The second category of skeletal modes are those which are relatively insensitive to specific substitution at the 2 and 4 positions but are quite sensitive to changes in the vibrational Hamiltonian resulting from replacement of symmetrically distributed substituents of the same mass with asymmetrically distributed substituents of different mass. The in-plane modes in this category have frequencies the

same for all the Ni(II) DP derivatives, including Ni(DP), but different from those of Ni(OEP) and include  $\nu_2$ ,  $\nu_8$ ,  $\nu_{37}$ , and  $\nu_{39}$ . The out-of-plane skeletal deformations of the Ni(II) DP derivatives are also included in the second category. These modes do not necessarily have frequencies different from Ni(OEP), but do exhibit RR activity, unlike their counterparts in the symmetrical complex. The third category consists of vibrations which are quite sensitive to the 2-R/4-R' substituent groups. These modes exhibit frequency differences between the various Ni(II) DP derivatives and, in the case of  $E_u$  modes, RR activity and/or loss of degeneracy. Vibrations in this category include  $\nu_{13}$ ,  $\nu_{38}$ ,  $\nu_{41}$ ,  $\nu_{43}$ ,  $\nu_{44}$ ,  $\nu_{45}$ , and  $\nu_{46}$ .

2. **General 2-R/4-R' Substituent Effects.** The porphyrin skeletal modes in the third category can be further classified according to whether they are influenced by the 2-R/4-R' substituents through kinetic and/or potential energy terms in the vibrational Hamiltonian. Kinetic energy effects appear to be quite important in determining the frequencies of the  $\nu_{13}$  and  $\nu_{38}$  vibrations which vary dramatically between Ni(DP) and the other derivatives. The former vibration is observed at 1231  $\text{cm}^{-1}$  for Ni(DP), 1220  $\text{cm}^{-1}$  for Ni(OEP), and between 1240 and 1250  $\text{cm}^{-1}$  for the acetyl and formyl complexes while the latter is observed at 1573  $\text{cm}^{-1}$  for Ni(DP), 1557  $\text{cm}^{-1}$  for Ni(OEP), and between 1535 and 1555  $\text{cm}^{-1}$  for the acetyl and formyl derivatives. The frequency variation observed for  $\nu_{38}$  impinges on the characterization of this motion. Abe et al.<sup>20</sup> attribute  $\nu_{38}$  and  $\nu_{37}$  to predominantly  $C_bC_b$  and  $C_bC_m$  stretches, respectively. Spiro and co-workers<sup>21</sup> have suggested that this assignment should be reversed. Our study of the Ni(II) DP derivatives suggests that the original assignment of Abe et al. is correct. The frequencies of the  $\nu_{37}$  bands of the Ni(II) DP derivatives are essentially identical, while the frequencies of the  $\nu_{38}$  bands show wide variation. For the acetyl and formyl complexes,  $\nu_{38}$  is split and exhibits RR activity. This behavior seems more commensurate with that expected for a  $C_bC_b$  stretch, which involves bonds directly perturbed by the carbonyl substituents.

Kinematic effects are also undoubtedly important in determining the frequencies of the  $C_b$ -acetyl ( $\nu_{43}$ ) stretches of Ni(2-AcDP), Ni(4-AcDP), and Ni(2,4-AcDP) and the  $C_b$ -formyl ( $\nu_{42}$  and  $\nu_{43}$ ) stretches of Ni(2,4-FDP). Differential kinetic interactions of the in-phase and out-of-phase  $C_b$ -formyl stretches with the skeletal modes of Ni(2,4-FDP) result in a substantial splitting of these modes which does not occur for the two  $C_b$ -acetyl stretches of Ni(2,4-AcDP). The internal modes of the formyl groups in Ni(2,4-FDP) also kinematically mix with the skeletal vibrations. Mixing of  $\delta(C_bC_\alpha H)$  with  $\nu_{41}$ ,  $\nu_{42}$ , and  $\nu_{43}$  is clearly responsible for the increased splitting of these modes in Ni(2,4-FDP) relative to Ni(2,4-AcDP) (see section IV.B.3).

It is not clear to what extent kinetic energy effects are responsible for RR activity and loss of degeneracy of the  $E_u$  modes. Perturbations on the  $E_u$ -type vibrations are most strongly manifested in the acetyl and formyl derivatives, suggesting that carbonyl conjugation, which alters the electronic structure and vibrational potential energy, is responsible for these effects. This is particularly apparent in the  $\nu_{38}$   $C_bC_b$  stretches and  $\nu_{41}$   $C_\alpha N$  stretches. The  $\nu_{38}$  vibration is RR inactive in Ni(DP) but becomes RR active upon the addition of a single acetyl group. The addition of the second acetyl group results in a loss of degeneracy of the mode with RR activity in both components (Figures 2-4, Table I). The  $\nu_{41}$  mode is degenerate for Ni(DP) but highly split for all the acetyl and formyl derivatives. The low-frequency component of this mode ( $\sim 1370\text{ cm}^{-1}$ ) is weakly RR active for the two monoacetyl derivatives but is quite intense for the two dicarbonyl derivatives (Figure 2).

3. **Specific 2-R vs. 4-R' vs. 2,4-R Substituent Effects.** The comparison of the vibrational spectra of the Ni(II) DP derivatives and the determination of the 2-R/4-R' substituent-induced perturbations allows the evaluation of the effects of 2 vs. 4 substitution of the conjugating groups. In this connection, the skeletal mode frequencies, RR intensities, and  $E_u$  mode splittings and RR activities are essentially identical for Ni(2-AcDP) and Ni(4-AcDP). The only exceptions are the  $\nu_{13}$  and  $\nu_{43}$  modes which are kinematically influenced in a slightly different manner in the

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two complexes. Also, the carbonyl stretching frequencies and RR activities are identical for the two different monoacetyl derivatives. All of the above observations together suggest that substitution of a conjugating group at the 2 or 4 position is indistinguishable in terms of the influence of the group on the ground and excited  $\pi$ -electronic states of the porphyrin ring.

The presence of a second carbonyl group on an adjacent pyrrole ring modifies the perturbation of the porphyrin  $\pi$ -electronic structure induced by the first carbonyl group. Both the ground and excited electronic states are affected as is evidenced by the splitting of the  $\nu_{38}$  C<sub>b</sub>C<sub>b</sub> stretching modes of Ni(2,4-AcDP) and Ni(2,4-FDP) (absent in Ni(2-AcDP) and Ni(4-AcDP)) and the increased RR activity of these modes as well as for the  $\nu_{41}$  C<sub>a</sub>N motion. Interestingly, the increased RR activity of the E<sub>u</sub> modes appears only to occur with B-state excitation (Figure 2). The Q-state activities of these modes are essentially identical for the mono- and dicarbonyl complexes (Figure 3). These observations suggest a mechanism for the perturbation of the  $\pi$ -electronic structure in the dicarbonyl derivatives. The  $\nu(\text{C}=\text{O})$  modes of the two dicarbonyl complexes are coupled through the porphyrin  $\pi$  system as is evidenced by the 10-cm<sup>-1</sup> splitting of the in-phase and out-of-phase combinations (Table IV). (Note also that the  $\sim 8\text{-cm}^{-1}$  upshift in the average frequency of  $\nu(\text{C}=\text{O})$  for Ni(2,4-AcDP) relative to Ni(2-AcDP) and Ni(4-AcDP) indicates that the second electron-withdrawing group reduces the electron-withdrawing capability of a given group in the diacetyl derivative relative to the monoacetyl derivatives.) The coupling of the  $\nu(\text{C}=\text{O})$  modes on adjacent pyrrole rings implies that the two components of an E<sub>u</sub> mode can also mix. The in-phase and out-of-phase combinations of the two components of the degenerate mode are of the appropriate symmetry to mix with these same phases of the two coupled  $\nu(\text{C}=\text{O})$  modes.<sup>45</sup> This could split  $\nu_{38}$  in the ground (and excited) electronic state. Also, the large B-state RR activity of one component of  $\nu_{38}$  and  $\nu_{41}$  parallels the strong activity of the in-phase combination of  $\nu(\text{C}=\text{O})$ , suggesting that the origin shifts of the in-phase combinations of the components of the E<sub>u</sub> porphyrin vibrations are increased via mixing with this latter motion. On the other hand, the Q-state RR activity of the out-of-phase combination of the components of  $\nu_{38}$  and  $\nu_{41}$  is consistent with these motions being more vibronically active. The fact that the Q-state RR activity for the two E<sub>u</sub> modes of Ni(2,4-AcDP) is comparable to that of these modes of Ni(2-AcDP) and Ni(4-AcDP) suggests that the vibronic coupling between the Q and B states is not altered by the presence of the second carbonyl group.

The relative vibronic activity of the porphyrin vibrations in the mono- and dicarbonyl derivatives is better reflected in the excitation profiles of the Ni(DP) complexes (Figure 9). As can be seen, the profiles of Ni(4-AcDP) and Ni(2,4-AcDP) are essentially identical, indicating similar vibronic coupling strength of analogous vibrations in the two complexes. The general features of the profiles of the mono- and dicarbonyl derivatives and also Ni(DP) itself are similar to those observed for other metalloporphyrins.<sup>13,46-49</sup> However, the Q(0,0) and Q(0,1) maxima are broader and more poorly resolved.<sup>50,51</sup> The separation between the maxima for many of the RR bands is also significantly less than expected on the basis of the vibrational frequencies. This

latter feature could reflect strong vibronic coupling<sup>47</sup> in the asymmetric electronic environment. The Q(0,0) and Q(0,1) peaks observed in the profiles for the RR bands of Ni(4-AcDP) and Ni(2,4-AcDP) are comparable in breadth, but are much broader than those of Ni(DP). The widths at half-height of many of the peaks of the carbonyl derivatives exceed 1000 cm<sup>-1</sup>. This broadening suggests a splitting of at least 300–400 cm<sup>-1</sup> between Q<sub>x</sub> and Q<sub>y</sub> for the mono- and dicarbonyl complexes. The splitting of Q<sub>x</sub> and Q<sub>y</sub> is also reflected in the increased width of the absorption maximum of these complexes relative to Ni(DP) (Figure 9). The 300–400-cm<sup>-1</sup> splitting, although substantial, is significantly less than is observed for heme *a* (1600–2000 cm<sup>-1</sup>).<sup>36</sup> This derivative has formyl and vinyl substituents on opposite pyrrole rings which greatly enhances the Q-state asymmetry relative to mono- or adjacent pyrrole disubstituted systems.

## V. Summary and Conclusions

The observed IR and Raman frequencies and RR enhancements of the porphyrin skeletal modes and internal vibrations of the acetyl and formyl substituents indicate that the conjugating groups significantly affect both the ground and excited porphyrin  $\pi$ -electronic states. The effects of conjugation are greatest in the excited state as is evidenced by the strong RR activity of IR-type modes but little if any IR activity for Raman-type modes. The in-plane asymmetry of the Ni(II) DP derivatives in conjunction with slight deviations from planarity of the porphyrin cores is also apparently responsible for substantial RR activity of out-of-plane skeletal modes. The virtually identical spectral features of Ni(2-AcDP) and Ni(4-AcDP) indicate that conjugation at the two different porphyrin ring positions results in essentially identical perturbations of the porphyrin  $\pi$  system. The presence of a second conjugating group on an adjacent pyrrole ring modifies the perturbation of the ground state and B-state electronic structure induced by the first conjugating group. On the basis of the RR excitation profiles, the vibronic activity for analogous vibrations of the mono- and dicarbonyl derivatives is similar. Likewise, the splitting between Q<sub>x</sub> and Q<sub>y</sub> for the mono- and dicarbonyl systems is comparable and is estimated to be 300–400 cm<sup>-1</sup>.

The essentially identical electronic structures of Ni(2-AcDP) and Ni(4-AcDP) suggests that protein interactions with a given conjugating group at the 2 vs. 4 position in a heme moiety cannot provide an effective means of differential control over biological processes. However, protein interactions with one vs. both groups in a disubstituted system do provide a mechanism for influencing the electron density at the metal center in a stepwise fashion. The degree of control could be further regulated in a system containing two different conjugating groups such as heme *a*. The differential interaction of these groups with the amino acid residues of the protein could provide a means of fine-tuning the electron density at the metal center and, hence, the ligand binding affinity and redox chemistry.

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**Registry No.** Ni(OEP), 24803-99-4; Ni(DP), 15892-10-1; Ni(2-AcDP), 88200-53-7; Ni(4-AcDP), 88200-54-8; Ni(2,4-AcDP), 14057-09-1; Ni(2,4-FDP), 19440-09-6; Ni(PP), 15304-70-8.

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