

# Resonance Raman Spectra of Dioxygen Adducts of Cobalt Porphyrins. Spectroscopic Manifestation of Vibrationally Coupled Dioxygen and Energy Matching of Interactive Modes

Leonard M. Proniewicz,<sup>†</sup> Kazuo Nakamoto, and James R. Kincaid\*

Contribution from the Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233. Received November 2, 1987

**Abstract:** Resonance Raman spectra of dioxygen adducts of cobalt porphyrin complexes with 3,5-dichloropyridine (DCP) are reported. When  $^{16}\text{O}_2$ ,  $^{18}\text{O}_2$ , and "scrambled" oxygen (i.e.,  $^{16}\text{O}_2$ : $^{16}\text{O}^{18}\text{O}$ : $^{18}\text{O}_2$ ) are used, evidence is obtained for vibrational coupling of  $\nu(\text{O}-\text{O})$  with an internal mode of axially coordinated DCP. This coupling is manifested spectroscopically by shifts of the coupled modes from their inherent frequencies and/or by intensity enhancement of the coupled internal mode relative to noncoupled ligand modes. The magnitude of the perturbation is shown to be dependent upon energy matching of the interacting modes through a series of studies in which the frequency of the  $\nu(\text{O}-\text{O})$  is varied by controlled alterations in structure and solution environment.

The utility of resonance Raman (RR) spectroscopy as a probe of the structure and bonding of exogenous ligands of heme proteins has been impressively demonstrated by many investigators.<sup>1</sup> In favorable cases, the presence of charge-transfer transitions, which are accessible with conveniently available laser-excitation wavelengths, facilitates direct resonant enhancement of modes associated with the metal-ligand fragment. Unfortunately, the  $\text{O}_2$  adducts of the oxygen-transport proteins, hemoglobin (Hb) and myoglobin (Mb), do not fall in this category, and the  $\nu(\text{O}-\text{O})$  is not enhanced in the native (iron) proteins.<sup>1</sup> However, Tsubaki and Yu<sup>2</sup> demonstrated that  $\nu(\text{O}-\text{O})$  modes of the dioxygen adducts of the corresponding cobalt-substituted proteins are effectively enhanced with 406.7-nm excitation, presumably via a charge-transfer transition located near the intense Soret band in this region.

Given the inherent sensitivity of vibrational frequencies to subtle alterations in structure and bonding, such studies may provide detailed information about these parameters. Thus, it is important to critically assess all factors that may influence the vibrational characteristics of the exogenous ligand in these and other adducts. Clearly, the most effective approach involves the study of well-designed model systems wherein the structural, electronic, and environmental factors can be relatively easily controlled. While our initial efforts<sup>3,4</sup> in this area did permit an evaluation of these important issues, they also provided evidence for vibrational coupling of  $\nu(\text{O}-\text{O})$  with internal modes of the axial nitrogenous bases coordinated trans to the dioxygen. Perhaps more surprisingly, certain modes ascribed to an associated solvent molecule (methylene chloride or toluene) were shown to be enhanced via vibrational coupling with the bound dioxygen.<sup>4</sup>

Specifically, in the case of the  $\text{O}_2$  adduct of the cobalt tetraphenylporphyrine complex with pyridine (i.e.,  $\text{CoTPP}(\text{py})\text{O}_2$ ), an internal mode of the coordinated pyridine ( $1067\text{ cm}^{-1}$ ) is enhanced but only in the spectrum of the  $^{18}\text{O}_2$  adduct, wherein  $\nu(^{18}\text{O}-^{18}\text{O})$  occurs at  $\sim 1080\text{ cm}^{-1}$ .<sup>3</sup> In the spectrum of the  $^{16}\text{O}_2$  adduct, wherein  $\nu(^{16}\text{O}-^{16}\text{O})$  is observed at  $\sim 1150\text{ cm}^{-1}$ , no enhancement of this  $1067\text{-cm}^{-1}$  mode is observed. Similar observations were made during the study of the 1,2-dimethylimidazole adducts.<sup>3</sup> However, in this case, the coupling of  $\nu(^{16}\text{O}-^{16}\text{O})$  with the  $1155\text{-cm}^{-1}$  internal mode of the 1,2-dimethylimidazole gave rise to a strong doublet in the  $^{16}\text{O}_2$  adduct while only a single strong symmetrical band was observed at  $1079\text{ cm}^{-1}$  in the  $^{18}\text{O}_2$  adduct.

Further documentation of such behavior and eventual elucidation of the factors that control the extent of such coupling are therefore essential in order to properly interpret vibrational data in these systems. The present work describes a thorough study of the RR spectra of  $\text{O}_2$  adducts of several cobalt porphyrin

complexes with 3,5-dichloropyridine and presents evidence for especially strong coupling of  $\nu(\text{O}-\text{O})$  with an internal mode of this axial ligand. In this particular case, the vibrational interaction is of adequate strength to permit a systematic investigation of the energy-matching dependence of the interacting modes over a controlled range of frequency separations. The results of such studies demonstrate that the behavior of the coupled modes is consistent with theoretical predictions.

## Experimental Section

**Compound Preparation.** The pyrrole-deuteriated analogue of tetraphenylporphyrine ( $\text{H}_2\text{TPP-}d_8$ ) and its cobalt complex ( $\text{CoTPP-}d_8$ ) as well as  $\text{CoTPP}$  were prepared according to the method described previously.<sup>5</sup> The cobalt picket-fence porphyrin ( $\text{CoT}_{\text{piv}}\text{PP}$ ) was purchased from Midcentury Chemical Co. and used without further purification. The base, 3,5-dichloropyridine (DCP), was purchased from Aldrich Chemical Co. and was purified by sublimation prior to use. Toluene, deuteriated toluene (toluene- $d_8$ ), and deuteriated methylene chloride ( $\text{C}^2\text{H}_2\text{Cl}_2$ ) were purchased from Aldrich Chemical Co. Toluene was purified by shaking with calcium hydride ( $\text{CaH}_2$ ) for 6 h, refluxing for 2 h, and then distilling twice. The second distillation was over metallic sodium. Deuteriated toluene and deuteriated methylene chloride were used as supplied.

The gases  $^{16}\text{O}_2$  (99.99% Matheson) and  $^{18}\text{O}_2$  (98.15% Monsanto Research) were used without further purification. Samples of "scrambled" oxygen ( $^{16}\text{O}_2$ : $^{16}\text{O}^{18}\text{O}$ : $^{18}\text{O}_2$ , 1:2:1 and 1:1:1) were prepared by electrical discharge of an equimolar mixture of  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ . Ozone produced during the process was decomposed by including a small amount of activated 4A molecular sieve (Aldrich Chemical Co.) in the flask used for the scrambling process. The mixing ratio of these isotopic molecules was determined by Raman spectroscopy.

**Spectral Measurements.** Spectral measurements were carried out by using the "minibulb" technique.<sup>6</sup> About 0.3 mg of solid cobalt porphyrin ( $\text{Co}(\text{TPP-}d_8)$  or  $\text{CoT}_{\text{piv}}\text{PP}$ ) and 2-10 mol equiv of DCP were placed into a glass minibulb, which was then attached to a vacuum line. The water-free solvent was degassed by several freeze-pump-thaw cycles and then distilled under vacuum to the sample bulb, which was immersed in liquid nitrogen. After distillation of solvent, the temperature of the minibulb was raised to room temperature to allow cobalt porphyrin and the base to dissolve efficiently. The sample was then frozen again in

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(3) Bajdor, K.; Kincaid, J. R.; Nakamoto, K. *J. Am. Chem. Soc.* **1984**, *106*, 7741.

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(7) La Lau, C.; Snyder, R. G. *Spectrochim. Acta, Part A* **1971**, *27A*, 2073.

(8) The Raman spectrum of 3,5-DCP was measured in  $\text{CH}_2\text{Cl}_2$  at room temperature with the 488-nm argon-ion laser line. The  $702\text{-cm}^{-1}$  solvent band was used as a frequency standard.

(9) Collman, J. P.; Halbert, T. R.; Suslick, K. S. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980; Vol. 2, p 1.

<sup>†</sup> Permanent address: Regional Laboratory of Physicochemical Analyses and Structural Research, Jagiellonian University, Cracow, Poland.

liquid nitrogen, and oxygen was transferred to the minibulb via vacuum line. The pressure of  $O_2$  was estimated to be approximately 4 atm at  $-90^\circ C$  (i.e., the temperature at which the sample was liquified). After oxygen was introduced to the sample, the stem of the glass bulb was sealed while the body of the bulb was kept in liquid nitrogen. In as short a period of time as possible, the sealed bulb was attached to a cooled ( $-150^\circ C$ ) copper tip,<sup>6</sup> which was connected to the cooling head of a CTI Model 21 closed-cycle helium cryocooler. This unit permits effective temperature control, and all spectra were obtained from samples at  $-90^\circ C$  unless otherwise noted. The temperature of the solution is readily determined from the relative intensities of the Stokes and anti-Stokes Raman lines of the solvent.

The RR spectra were recorded on a Spex Model 1401 double monochromator equipped with a Spex DPC-2 digital photometer system. Some of the measurements were carried out on a Spex Model 1403 double monochromator connected to a Spex Laboratory Coordinator DM1B, and data were stored on floppy disks. Excitation lines were from a Spectra-Physics Model 164-01 krypton ion laser (406.7 nm), a Coherent Model 1100-K3 krypton ion laser (406.7, 413.1, 415.4 nm), a Liconix Model 4240 NB He: Cd laser (441.6 nm), or a Spectra-Physics Model 2025-05 argon ion laser (454.5 and 457.9 nm). A spectral band-pass of  $4\text{ cm}^{-1}$  was used during measurements. The unperturbed solvent bands were used for frequency calibration. Accuracy of the frequency readings was  $\pm 1\text{ cm}^{-1}$ .

## Results and Discussion

### Dioxygen Adducts of $Co(TPP-d_8)(DCP)$ in Methylene Chloride.

The spectra of the  $O_2$  adducts of  $Co(TPP-d_8)$  in deuteriated methylene chloride ( $C^2H_2Cl_2$ ) are shown in Figure 1. As was explained in the earlier reports,<sup>3,4</sup> the  $d_8$  analogue of TPP was utilized in order to avoid interference of a strong  $1084\text{-cm}^{-1}$  band characteristic of  $CoTPP$  which is substantially shifted to lower frequency in the  $d_8$  analogue. In addition,  $C^2H_2Cl_2$  is used in order to avoid interference and possible coupling<sup>3</sup> of the  $1156\text{-cm}^{-1}$  mode of  $CH_2Cl_2$  with the  $\nu(^{16}O-^{16}O)$  of the  $^{16}O_2$  adduct. The spectrum of the  $^{16}O_2$  adduct [ $Co(TPP-d_8)(DCP)^{16}O_2$ ] is given in Figure 1A. A strong isolated band is observed at  $1160\text{ cm}^{-1}$ . In addition, a weaker band is observed at  $1112\text{ cm}^{-1}$ . In the spectrum of the  $^{18}O_2$  adduct (Figure 1B), the strong  $1160\text{-cm}^{-1}$  band and the weak  $1112\text{-cm}^{-1}$  band disappear and are replaced by bands occurring at  $1121\text{ cm}^{-1}$  (weak) and  $1086\text{ cm}^{-1}$  (strong).

One possible interpretation of these observations is that the dioxygen adduct exists in two chemical forms which exhibit  $\nu(^{16}O-^{16}O)$  frequencies at  $1160$  and  $1112\text{ cm}^{-1}$ . The corresponding  $^{18}O_2$  adducts would also be expected to exhibit two  $\nu(^{18}O-^{18}O)$  bands, and two bands are indeed observed at  $1121$  and  $1086\text{ cm}^{-1}$ . According to this interpretation, the form exhibiting the highest frequency  $\nu(O-O)$  would yield a  $\Delta\nu(^{16}O_2-^{18}O_2)$  of  $39\text{ cm}^{-1}$  ( $1160 \rightarrow 1121\text{ cm}^{-1}$ ) and the second form (lower frequency  $\nu(O-O)$ ) would yield a  $\Delta\nu(^{16}O_2-^{18}O_2)$  of only  $26\text{ cm}^{-1}$  ( $1112 \rightarrow 1086\text{ cm}^{-1}$ ). These  $\Delta\nu(^{16}O_2-^{18}O_2)$  values are quite small compared to that predicted ( $64\text{--}66\text{ cm}^{-1}$ ) by the harmonic approximation. Furthermore, given the observed intensities of these bands, this approach would also require that either the relative populations or the inherent scattering efficiencies of the two isotopic species are different. That is, it would be necessary to consider the higher frequency form to predominate for the  $^{16}O_2$  adduct and the lower frequency form to be the major form for the  $^{18}O_2$  adduct. Alternatively, it would require that  $\nu(^{16}O-^{16}O)$  has an inherently greater scattering efficiency in one chemical form but that  $\nu(^{18}O-^{18}O)$  has a greater efficiency in the second chemical form.

These tenuous arguments can be avoided by invoking vibrational coupling of  $\nu(^{18}O-^{18}O)$  with an internal mode of the (trans) coordinated DCP. The spectrum of free DCP in  $CH_2Cl_2$  exhibits, among others, two strong bands of comparable intensity at  $1109$  and  $1012\text{ cm}^{-1}$ . While small shifts may be associated with coordination of DCP, it is thus reasonable to expect internal ligand modes to occur near these  $1110\text{-}$  and  $1010\text{-cm}^{-1}$  regions in the spectra of the dioxygen adducts. Consideration of these facts leads naturally to the following interpretation of the observed spectra of the adducts. The strong  $1160\text{-cm}^{-1}$  band (Figure 1A) is assigned to  $\nu(^{16}O-^{16}O)$  and the weaker  $1112\text{-cm}^{-1}$  feature to an enhanced internal mode of the coordinated DCP. Given a  $\nu(^{16}O-^{16}O)$  value of  $1160\text{ cm}^{-1}$ , the harmonic approximation predicts the occurrence of  $\nu(^{18}O-^{18}O)$  at  $1094\text{ cm}^{-1}$  (i.e.,  $\Delta\nu(^{16}O_2-^{18}O_2) = 66\text{ cm}^{-1}$ ). This

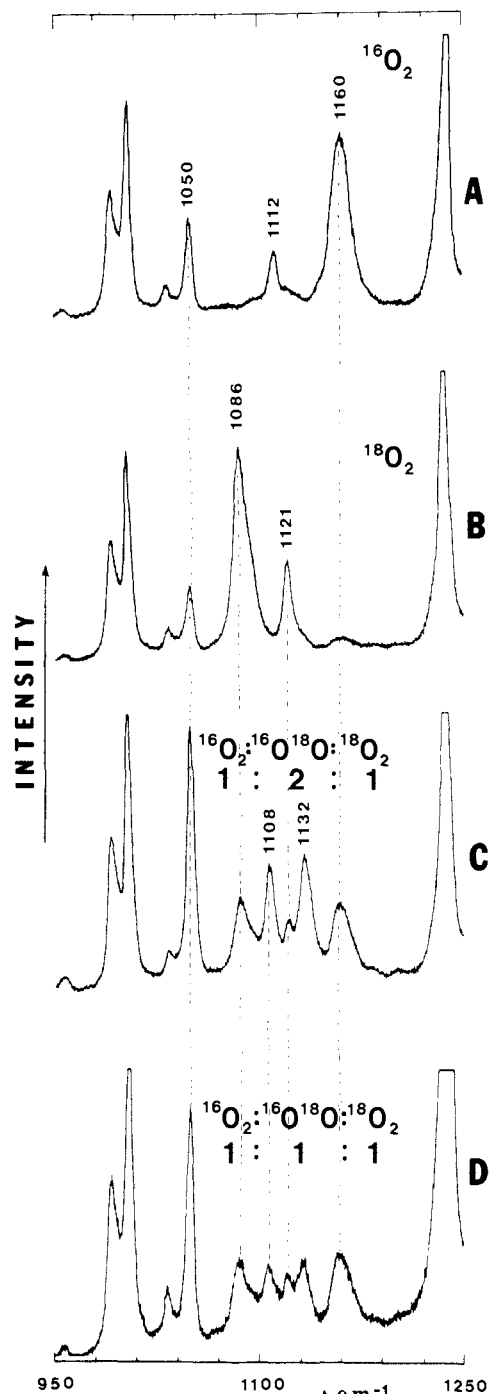
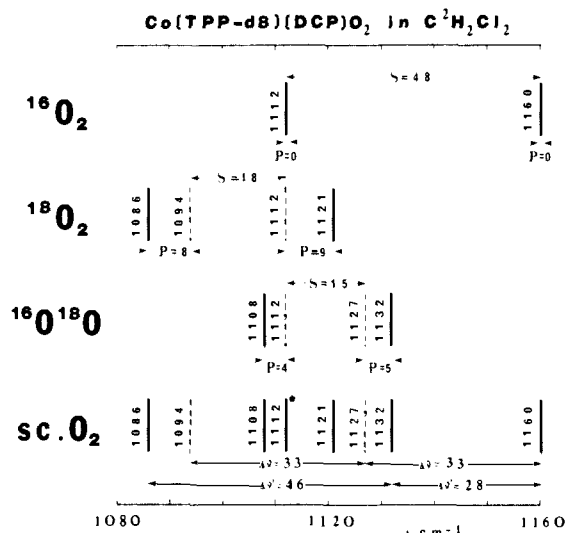


Figure 1. Resonance Raman spectra of  $Co(TPP-d_8)(DCP)O_2$ : (A)  $^{16}O_2$ ; (B)  $^{18}O_2$ ; (C)  $^{16}O_2:^{16}O^{18}O:^{18}O_2$  (1:2:1); (D)  $^{16}O_2:^{16}O^{18}O:^{18}O_2$  (1:1:1). Solvent  $C^2H_2Cl_2$ .

latter frequency is similar in energy to the internal ligand mode at  $1112\text{ cm}^{-1}$ . Interaction of these modes yields two Raman lines, which are shifted from their inherent frequencies by  $\sim 8\text{ cm}^{-1}$  (i.e., lines are observed at  $1121$  and  $1086\text{ cm}^{-1}$ ).

Further confirmation of this coupling and a clear demonstration of the spectroscopic complexity that may result from such behavior are provided by the study of adducts formed with scrambled oxygen ( $^{16}O_2:^{16}O^{18}O:^{18}O_2$ ). The spectrum of the solution containing the adducts formed in the presence of 1:2:1 scrambled oxygen (i.e.,  $^{16}O_2:^{16}O^{18}O:^{18}O_2$ , 1:2:1) is shown in Figure 1C. In this figure, the band observed at  $1160\text{ cm}^{-1}$  is readily assignable to the  $^{16}O_2$  adduct while the  $1121\text{-}$  and  $1086\text{-cm}^{-1}$  features are attributable to the  $^{18}O_2$  adduct. However, new features are observed at  $1132$  and  $1108\text{ cm}^{-1}$ . The  $1108\text{-cm}^{-1}$  line overlaps and obscures the band expected at  $1112\text{ cm}^{-1}$  (i.e., the weak ligand mode associated with the  $^{16}O_2$  adduct). This complex spectroscopic

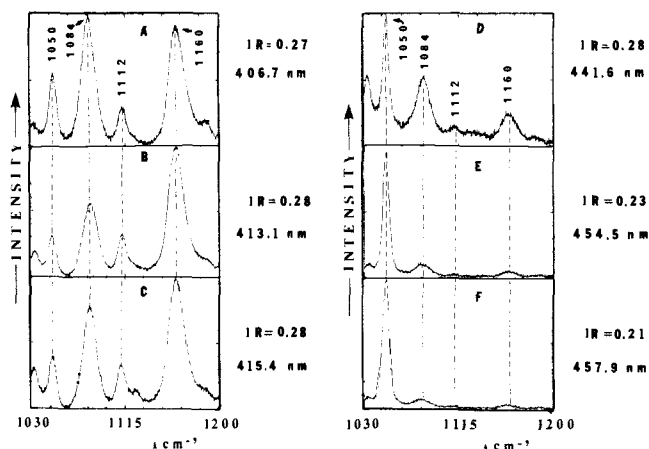


**Figure 2.** Schematic diagram of observed spectral patterns:  $S$  = inherent frequency separation;  $P$  = induced perturbation; sc = scrambled. Note: All frequencies shown have units of reciprocal centimeters. The line labeled with \* corresponds to the undetected 1112-cm<sup>-1</sup> ligand mode, which is obscured by the 1108-cm<sup>-1</sup> band.

pattern is entirely consistent with the above stated interpretation of the spectrum of the  $^{18}\text{O}_2$  adduct. Thus, given a  $\nu(^{16}\text{O}-^{16}\text{O})$  frequency of 1160 cm<sup>-1</sup>, the harmonic approximation would yield a  $\nu(^{16}\text{O}-^{18}\text{O})$  frequency of 1127 cm<sup>-1</sup> (i.e., a 33-cm<sup>-1</sup> isotopic shift). This frequency is within 15 cm<sup>-1</sup> of the inherent frequency of the coordinated ligand mode, and these may vibrationally couple. Therefore, interaction of the (lower frequency)  $\nu(^{18}\text{O}-^{18}\text{O})$  with the 1112-cm<sup>-1</sup> ligand mode results in splitting of the coupled modes to 1121 and 1086 cm<sup>-1</sup>. On the other hand, interaction of the (high frequency)  $\nu(^{16}\text{O}-^{18}\text{O})$  with the 1112-cm<sup>-1</sup> ligand mode results in shifts of the coupled modes by +5 cm<sup>-1</sup> (1127–1132 cm<sup>-1</sup>) and –4 cm<sup>-1</sup> (1112–1108 cm<sup>-1</sup>) from their inherent frequencies. That is, while interaction of the  $\nu(^{18}\text{O}-^{18}\text{O})$  induces an upshift in the 1112-cm<sup>-1</sup> mode to 1121 cm<sup>-1</sup>, interaction of the  $\nu(^{16}\text{O}-^{18}\text{O})$  results in a corresponding downshift of the 1112-cm<sup>-1</sup> mode to 1108 cm<sup>-1</sup>. Further support of this explanation is provided by the spectrum of the 1:1:1 scrambled adduct shown in Figure 1D, which confirms the “linkages” of the 1132- and 1108-cm<sup>-1</sup> features. Thus, in this case the relative intensities of these two bands remain similar to those observed in the 1:2:1 scrambled case but are proportionately decreased relative to those associated with the adducts of  $^{16}\text{O}_2$  (i.e., 1160 and 1112 cm<sup>-1</sup>) and  $^{18}\text{O}_2$  (i.e., 1121 and 1086 cm<sup>-1</sup>).

In order to further clarify our interpretation of the complex spectral patterns obtained for these dioxygen adducts, a diagrammatic representation of the observed spectral features and their corresponding inherent frequencies for each of the dioxygen (isotopomer) adducts are given in Figure 2. In the figure, the inherent frequencies are depicted with dotted lines while the solid lines represent the observed (i.e., perturbed) frequencies. The inherent frequency separation ( $S$ ) and the induced perturbation ( $P$ ) are also indicated. Also, as shown in the figure, such vibrational coupling can yield *apparent* isotopic frequency shifts ( $\Delta\nu'$ ) that are substantially different from those theoretically predicted ( $\Delta\nu$ ). In addition, it should be emphasized that the diagram is included to depict the observed frequency perturbations and is not intended to provide an accurate representation of the observed relative intensities.

It is important to comment on the occurrence of the weak 1112-cm<sup>-1</sup> band in the spectrum of the  $^{16}\text{O}_2$  adduct. We have confirmed that the observation of this line cannot be attributed to the presence of excess base. Its intensity, relative to the 1160-cm<sup>-1</sup> mode, remains constant as the ligand (DCP) concentration is varied. Furthermore, in the spectrum of the free ligand a slightly stronger band is observed at 1012 cm<sup>-1</sup>, which is not observed in the spectrum of the  $^{16}\text{O}_2$  adduct studied here. Thus,



**Figure 3.** Resonance Raman spectra of  $\text{CoTPP(DCP)(}^{16}\text{O}_2\text{)}$  with different excitation wavelengths. The abbreviation IR is the  $I_{1112}/I_{1160}$  ratio discussed in the text. Note: The IR values for E and F were obtained from spectra that exhibited higher signal to noise. The spectra shown here for cases E and F were normalized with respect to the 1050-cm<sup>-1</sup> solvent band to illustrate relative enhancement.

the 1112-cm<sup>-1</sup> internal mode of DCP undergoes enhancement either as a consequence of vibrational coupling with  $\nu(\text{O}-\text{O})$  or as a result of direct resonance with a CoDCP charge-transfer transition. In the cases of  $\nu(^{16}\text{O}-^{18}\text{O})$  and  $\nu(^{18}\text{O}-^{18}\text{O})$ , vibrational coupling is manifested by the observed frequency perturbations (shifts of the 1112-cm<sup>-1</sup> mode to 1108 and 1121 cm<sup>-1</sup>, respectively). However, the  $\nu(^{16}\text{O}-^{16}\text{O})$  at 1160 cm<sup>-1</sup> is relatively far removed from the 1112-cm<sup>-1</sup> DCP mode and, to the extent that the frequencies are not perturbed from their inherent values, there exists no definitive evidence for vibrational coupling of these modes.

In order to investigate this issue further, it was decided to obtain spectra with multiple excitation lines. Indirect (i.e., vibrational coupling) enhancement of the internal DCP mode should be expected to yield nonvariant relative intensities (i.e.,  $I_{1112}/I_{1160}$ ), whereas direct resonance enhancement via a separate CoDCP electronic transition may lead to varying relative intensities. While instrumental limitations restrict the number of excitation lines available to us in the 400-nm region, the results obtained provide no support for the direct enhancement mechanism. Thus, as can be determined from inspection of the spectra given in Figure 3, the  $I_{1112}/I_{1160}$  ratio (abbreviated as IR in Figure 3) remains relatively constant between 406.7 and 457.9 nm. The actual values measured for  $I_{1112}/I_{1160}$  are given in the figure.

The conditions employed to obtain the spectra shown in Figure 3 provide a convenient means for obtaining particularly well-calibrated relative enhancement measurements of bands associated with the different molecular fragments of the  $\text{O}_2$  adduct. Thus, the 1084-cm<sup>-1</sup> band corresponds to the (nondeuterated) CoTPP, the 1112-cm<sup>-1</sup> band to coordinated DCP, and the 1160-cm<sup>-1</sup> band to  $\nu(^{16}\text{O}-^{16}\text{O})$  of the bound  $^{16}\text{O}_2$ . In addition, the 1050-cm<sup>-1</sup> solvent ( $\text{C}_2\text{H}_2\text{Cl}_2$ ) band serves as a reliable frequency and intensity (internal) standard. While the number of data points in the region of 400 nm is relatively limited, it is interesting to note that the  $\nu(^{16}\text{O}-^{16}\text{O})$  and the 1112-cm<sup>-1</sup> bands reach maximum intensities at 413.1 nm, while the 1084-cm<sup>-1</sup> macrocycle mode undoubtedly maximizes at the Soret band maximum. Inasmuch as the Soret band for this adduct occurs at 426 nm, these preliminary data provide evidence for a  $\text{CoO}_2$  charge-transfer transition in the vicinity of 413 nm, although further work involving extended and higher resolution excitation profile studies will be needed to confirm this.

The experiments described above indicate that the 1112-cm<sup>-1</sup> DCP band observed in the spectrum of the  $^{16}\text{O}_2$  adduct gains intensity as a consequence of vibrational coupling with  $\nu(^{16}\text{O}-^{16}\text{O})$ , yet the coupling does not lead to the measurable frequency perturbations. In the cases of the  $^{18}\text{O}_2$  and scrambled (i.e., the  $^{16}\text{O}-^{18}\text{O}$ ) oxygen adducts, coupling is manifested by both intensity borrowing and frequency perturbation. In these cases, the separation of interacting modes is  $\sim 15$  cm<sup>-1</sup>, whereas in the case

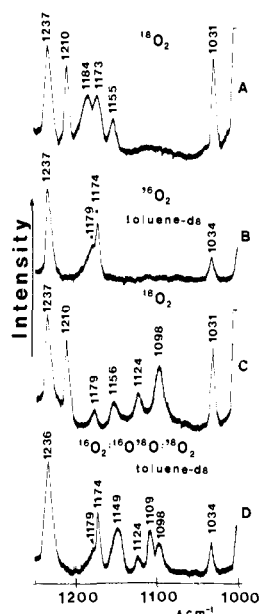


Figure 4. Resonance Raman spectra of  $\text{Co}(\text{TPP-}d_8)(\text{DCP})\text{O}_2$  in toluene: (A)  $^{16}\text{O}_2$ , toluene; (B)  $^{16}\text{O}_2$ , toluene- $d_8$ ; (C)  $^{18}\text{O}_2$ , toluene; (D)  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$ ,  $^{18}\text{O}_2$  (1:2:1), toluene- $d_8$ .

of the  $^{16}\text{O}_2$  adduct the separation is  $48\text{ cm}^{-1}$  ( $1160\text{--}1112\text{ cm}^{-1}$ ). While the electronic and molecular structures, as well as the precise form of the interacting ligand mode, are undoubtedly important in determining the coupling strength, it may also be expected that energy matching of the interacting modes plays an important role.<sup>10</sup> Such dependence is generally difficult to evaluate in most systems inasmuch as the relevant modes are usually stationary. However, dioxygen adducts such as those studied here provide a unique opportunity to investigate this issue because the frequency of  $\nu(\text{O--O})$  can be relatively conveniently tuned by controlled perturbations in macrocycle structure and environmental conditions. For this reason we have included studies of  $\text{O}_2$  adducts of several cobalt porphyrin complexes of DCP under various solution conditions.

**Dioxygen Adducts of  $\text{Co}(\text{TPP-}d_8)(\text{DCP})$  in Toluene.** The spectrum of the  $^{16}\text{O}_2$  adduct [ $\text{Co}(\text{TPP-}d_8)(\text{DCP})^{16}\text{O}_2$ ] in toluene is given in Figure 4A. Two strong unresolved bands having peak maxima at  $1184$  and  $1173\text{ cm}^{-1}$  are observed along with a weak band at  $\sim 1155\text{ cm}^{-1}$ . As was fully discussed in our earlier work,<sup>4</sup> toluene possesses weak bands at  $1179$  and  $1156\text{ cm}^{-1}$  which may be enhanced by coupling with  $\nu(\text{O--O})$ . The  $1210\text{-cm}^{-1}$  band is attributable to a noninteracting toluene mode. When toluene- $d_8$  is used as the solvent (Figure 4B), the  $\nu(^{16}\text{O--}^{16}\text{O})$  is observed at  $1179\text{ cm}^{-1}$  as a shoulder on the  $1174\text{-cm}^{-1}$  band, the latter of which is a characteristic band of toluene- $d_8$ .<sup>7</sup> The most reasonable interpretation of Figure 4A is that the inherent frequency of the  $\nu(^{16}\text{O--}^{16}\text{O})$  of this complex is  $1179\text{ cm}^{-1}$  but that it is coupled to the  $1179\text{-cm}^{-1}$  internal mode of toluene, giving rise to two bands that are shifted from the  $1179\text{-cm}^{-1}$  coincident frequency of  $+5$  and  $-6\text{ cm}^{-1}$ . As will be discussed below, further support for an inherent  $\nu(^{16}\text{O--}^{16}\text{O})$  of  $1179\text{ cm}^{-1}$  is provided by consideration of the data for the  $^{18}\text{O}_2$  and scrambled ( $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$ ,  $^{18}\text{O}_2$ ) adducts. While the  $\nu(^{16}\text{O--}^{16}\text{O})$  couples with the  $1179\text{-cm}^{-1}$  toluene mode, giving rise to a shift (to  $1184\text{ cm}^{-1}$ ) and enhancement of this band (relative to the  $1210\text{-cm}^{-1}$  toluene band), it apparently does not couple with the  $1174\text{-cm}^{-1}$  mode of toluene- $d_8$ . Future work involving additional careful experiments and detailed calculations will be necessary to satisfactorily elucidate the nature of this coupling and define the differences in the natural abundance and perdeuterated toluene cases.

In comparison with the toluene solution, wherein  $\nu(^{16}\text{O--}^{16}\text{O})$  is observed at  $1179\text{ cm}^{-1}$ , the  $^{16}\text{O}_2$  adduct in methylene chloride

solution exhibits an  $18\text{-cm}^{-1}$  lower frequency for  $\nu(^{16}\text{O--}^{16}\text{O})$ , i.e.,  $1160\text{ cm}^{-1}$ . This  $18\text{-cm}^{-1}$  shift can be attributed to a chemical effect, as has been discussed previously.<sup>3,4</sup> Thus,  $\text{CH}_2\text{Cl}_2$  (or  $\text{C}^2\text{H}_2\text{Cl}_2$ ) stabilizes the charge separation in the  $\text{Co}^{\delta+}\text{O}_2^{\delta-}$  formulation via hydrogen bonding and solvent dipole orientation, giving rise to stronger  $\text{O}_2$  bonding (lower  $\nu(\text{O--O})$ ) relative to the toluene solutions.

With regard to the issue of interest here (i.e., the factors that control coupling with internal ligand modes), this solvent effect permits an examination of the role of energy matching in determining the magnitude of frequency and intensity perturbations of the coupled modes. Given an inherent  $\nu(^{16}\text{O--}^{16}\text{O})$  of  $1179\text{ cm}^{-1}$ , the harmonic approximation yields a predicted  $\nu(^{18}\text{O--}^{18}\text{O})$  of  $1113\text{ cm}^{-1}$ , a frequency which is essentially identical with the inherent frequency of the DCP internal mode. As can be seen by inspection of the spectrum of the  $^{18}\text{O}_2$  adduct in toluene (Figure 4C), interaction of these energy-matched modes leads to a substantial frequency perturbation, yielding two bands with frequencies displaced by  $\sim 13\text{ cm}^{-1}$  ( $1124$  and  $1098\text{ cm}^{-1}$ ) from their inherent value of  $\sim 1112\text{ cm}^{-1}$ .

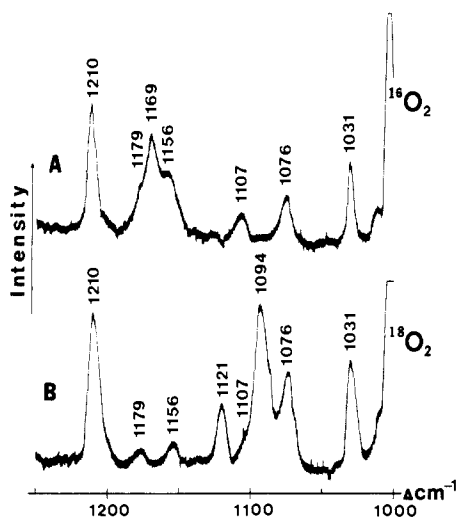
As is shown in Figure 4D, the spectroscopic behavior of solutions prepared with the 1:2:1 scrambled oxygen is also consistent with the proposed vibrational coupling scheme and provides further information regarding the dependence of frequency perturbation on energy matching. Thus, the  $\nu(^{16}\text{O--}^{18}\text{O})$  is observed as a rather strong band at  $1149\text{ cm}^{-1}$ , slightly higher ( $3\text{ cm}^{-1}$ ) than that predicted by the harmonic approximation ( $1179 - 33\text{ cm}^{-1} = 1146\text{ cm}^{-1}$ ), i.e., half of the  $\Delta\nu(^{16}\text{O}_2\text{--}^{18}\text{O}_2)$ . It is also noted that a new band is observed at  $\sim 1109\text{ cm}^{-1}$  which is attributed to coupling of the  $1112\text{-cm}^{-1}$  DCP mode with the  $\nu(^{16}\text{O--}^{18}\text{O})$ . The inherent frequency of  $\nu(^{16}\text{O--}^{18}\text{O})$  ( $1146\text{ cm}^{-1}$ ) is  $34\text{ cm}^{-1}$  higher than the interacting ligand mode, and only a small frequency perturbation is noted. Nevertheless, it is clear that  $\nu(^{16}\text{O--}^{18}\text{O})$  is coupled with the internal DCP mode inasmuch as this extra feature (i.e., that at  $1109\text{ cm}^{-1}$ ) is observed only in the spectrum of the scrambled oxygen adduct. It is noted that in the case of the  $^{16}\text{O}_2$  adduct in toluene there is no evidence for enhancement of the DCP internal mode at  $1112\text{ cm}^{-1}$ . This is not surprising inasmuch as the  $\nu(^{16}\text{O--}^{16}\text{O})$  is separated from the latter mode by  $67\text{ cm}^{-1}$  in this case.

In summary of the studies in toluene solution, it has been shown that the large ( $67\text{-cm}^{-1}$ ) separation of  $\nu(^{16}\text{O--}^{16}\text{O})$  from the DCP internal mode prevents effective coupling. The inherent  $\nu(^{16}\text{O--}^{18}\text{O})$  separated by  $34\text{ cm}^{-1}$  from the DCP mode, is seen to be coupled to the extent that the DCP mode is enhanced, but the observed frequency perturbations ( $3\text{ cm}^{-1}$ ) are relatively small. Quite substantial frequency perturbation ( $13\text{ cm}^{-1}$ ) and DCP mode enhancement are observed for the  $^{18}\text{O}_2$  adduct, wherein the interacting modes are perfectly energy matched.

**Dioxygen Adducts of  $\text{Co}(\text{T}_{\text{pv}}\text{PP})(\text{DCP})$ .** The dioxygen adducts of  $\text{Co}(\text{T}_{\text{pv}}\text{PP})(\text{DCP})$  were also studied to provide an example wherein the  $\nu(\text{O--O})$  of the bound dioxygen exhibits a frequency that is intermediate between those observed for the  $\text{Co}(\text{TPP-}d_8)(\text{DCP})$  complex in toluene and methylene chloride. In addition, the observation of mode coupling in this system (see below) establishes the fact that the interaction involves the internal mode of coordinated DCP (rather than a molecule of excess ligand which may be associated with the bound dioxygen of the  $\text{Co}(\text{TPP-}d_8)$  complex). This conclusion stems from our earlier studies of  $\text{Co}(\text{T}_{\text{pv}}\text{PP})$ , which has shown that molecules as large as toluene (and therefore DCP) are effectively excluded from direct association with the bound dioxygen.<sup>3,4</sup>

The spectra of the dioxygen adducts of this cobalt porphyrin are given in Figure 5. The  $\nu(^{16}\text{O--}^{16}\text{O})$  is observed as a strong band at  $1169\text{ cm}^{-1}$  which is overlapped with the weak toluene modes at  $1179$  and  $1156\text{ cm}^{-1}$  (Figure 5A). This frequency is  $\sim 10\text{ cm}^{-1}$  lower than  $\nu(^{16}\text{O--}^{16}\text{O})$  observed in the spectrum of the corresponding  $\text{CoTPP}$  complex (in toluene), indicative of stronger  $\text{O}_2$  bonding in the picket-fence analogue, as was previously discussed.<sup>3,4</sup> With regard to the issue of current interest, the observation of  $\nu(^{16}\text{O--}^{16}\text{O})$  at  $1169\text{ cm}^{-1}$  leads to an expected frequency of  $\sim 1103\text{ cm}^{-1}$  for  $\nu(^{18}\text{O--}^{18}\text{O})$  (i.e.,  $\Delta\nu(^{16}\text{O}_2\text{--}^{18}\text{O}_2) = 66$

(10) Herzberg, G. *Molecular Spectra and Structure*; Van Nostrand Reinhold: New York, 1945; Vol. 2, p 215.



**Figure 5.** Resonance Raman spectra of  $\text{Co}(\text{T}_{\text{piv}}\text{PP})(\text{DCP})\text{O}_2$ : (A)  $^{16}\text{O}_2$ ; (B)  $^{18}\text{O}_2$ . Solvent: toluene.

$\text{cm}^{-1}$ ). As can be seen in Figure 5B, two new bands are observed at 1121 and 1094  $\text{cm}^{-1}$  in the spectrum of the  $^{18}\text{O}_2$  adduct. We note that the weak band observed at 1107  $\text{cm}^{-1}$  in the spectra of both the  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$  adducts is readily assignable to a noninteracting mode of the  $\text{Co}(\text{T}_{\text{piv}}\text{PP})$  moiety. Thus, the most reasonable interpretation is that the  $\nu(^{18}\text{O}-^{18}\text{O})$  with an inherent frequency of 1103  $\text{cm}^{-1}$  couples with the axial ligand mode at 1112  $\text{cm}^{-1}$ , giving rise to two bands at frequencies that are higher and lower than the inherent frequencies by equivalent amounts (9  $\text{cm}^{-1}$ ).

### Summary and Conclusions

Clearly, the propensity of bound dioxygen to vibrationally couple with internal modes of trans-coordinated axial ligands may complicate the interpretation of slight frequency shifts or intensity changes in these systems, including the cobalt-substituted heme proteins.<sup>11</sup> It is therefore important to thoroughly characterize this behavior by extensive experiments with model compound systems employing carefully controlled conditions and strategic isotopic labeling.

In an extension of earlier work,<sup>3,4</sup> the studies reported herein document especially strong vibrational coupling of bound dioxygen with the trans-coordinated ligand 3,5-dichloropyridine. In addition, controlled variation of solution conditions and the use of dioxygen isotopomers provide a set of data wherein the energy of  $\nu(\text{O}-\text{O})$  is conveniently altered relative to the energy of the interacting

ligand mode. The results indicate that while internal DCP mode enhancement is not observed when the inherent frequencies of the interacting modes differ by  $\sim 66 \text{ cm}^{-1}$  (i.e.,  $\text{Co}(\text{TPP}-d_8)(\text{DCP})^{16}\text{O}_2$  in toluene), definite enhancement is observed for a  $\sim 50\text{-cm}^{-1}$  separation ( $\text{Co}(\text{TPP}-d_8)(\text{DCP})^{16}\text{O}_2$  in  $\text{C}^2\text{H}_2\text{Cl}_2$ ). As the inherent energies of the interacting modes approach one another, frequency perturbations (relative to the inherent frequencies) are observed that are seen to increase, reaching a maximum (13  $\text{cm}^{-1}$ ) at the point of accidental degeneracy (i.e.,  $\text{Co}(\text{TPP}-d_8)(\text{DCP})^{18}\text{O}_2$  in toluene). For example, where the separation of the inherent frequencies is  $\sim 10 \text{ cm}^{-1}$  ( $\text{Co}(\text{T}_{\text{piv}}\text{PP})(\text{DCP})^{18}\text{O}_2$ ), the perturbation is 9  $\text{cm}^{-1}$ . Perturbations of 5 and 8  $\text{cm}^{-1}$  are observed where the inherent frequencies are separated by 15–18  $\text{cm}^{-1}$  (i.e.,  $\text{Co}(\text{TPP}-d_8)(\text{DCP})$  in  $\text{C}^2\text{H}_2\text{Cl}_2$  with  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ ). On the other hand, only a 3- $\text{cm}^{-1}$  perturbation is observed for an inherent frequency separation of 34  $\text{cm}^{-1}$  ( $\text{Co}(\text{TPP}-d_8)(\text{DCP})(^{16}\text{O}^{18}\text{O})$  in toluene). While it is probably not strictly valid to assume that the inherent coupling strength does not change for the three situations studied, it is important to note that this behavior approximates that expected for mode coupling of fixed strength and varying energy separation.<sup>10</sup> However, while approximate compliance with the model is observed, it is necessary to point out that the 5- and 8- $\text{cm}^{-1}$  perturbations observed for the  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}_2$  adducts of  $\text{Co}(\text{TPP}-d_8)(\text{DCP})$  in  $\text{C}^2\text{H}_2\text{Cl}_2$  are apparently reversed (i.e., the perturbation should be larger for  $\nu(^{16}\text{O}-^{18}\text{O})$  than for  $\nu(^{18}\text{O}-^{18}\text{O})$ ). While this apparent discrepancy might be the result of the combined error in the experimental frequencies (i.e., the perturbations might actually be comparable), it is possible that the simple model is inadequate for these complexes. In this regard, we have noted the apparently anomalous enhancement of the axial ligand mode in the case of the  $^{16}\text{O}^{18}\text{O}$  adduct relative to its intensity in the spectrum of the  $^{18}\text{O}_2$  adduct.

Further studies involving a larger number of axial ligands and carefully controlled stereochemical relationships will be needed to elucidate electronic and structural parameters which dictate the inherent coupling strength. In addition, revelation of the subtle details of such interactions involving a particular ligand will undoubtedly require adequate normal-mode descriptions. Such studies, including those involving imidazole derivatives (i.e., histidine analogues), are currently under way in our laboratory.

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(11) Bruha, A.; Kincaid, J. R., submitted for publication.