

deviation between experiment and prediction is 1.96 ppm, and the correlation coefficient between experiment and prediction of 0.979 is clearly better than the 0.88 value obtained with the bond energy-bond strength method,⁹ which until now has been the best predictor for ²⁹Si shifts when all types of sites (Q⁰-Q⁴) are considered.

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Resonance Raman Spectra of O₂ Adducts of Cobalt Porphyrins. Enhancement of Solvent and Solute Bands via Resonance Vibrational Coupling

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Abstract: The resonance Raman spectra of O₂ adducts of cobalt porphyrin complexes with a large number of nitrogenous base axial ligands are reported. Evidence is presented for resonance enhancement of certain internal modes of the solvent (toluene or chlorobenzene) and, in some cases, internal modes of excess ligand molecules. The enhancement of these modes is shown to be dependent upon energy matching of the mode with the $\nu(\text{O}-\text{O})$ stretching frequency of the bound O₂. In addition, spectra of picket-fence porphyrin adducts indicate that such enhancement is critically dependent upon close association of the solvent or solute molecule with the bound O₂. These results are interpreted on the basis of resonance vibrational coupling resulting from an intermolecular interaction between bound O₂ and the solute or solvent molecule. Finally, a systematic study of the effect of axial ligand basicity on the frequency of $\nu(\text{O}-\text{O})$ yields a linear relationship between these two parameters over a range of basicities of more than nine orders of magnitude.

The potential of vibrational spectroscopy for the detection of subtle alterations in structure and bonding is well-recognized, and many investigators have applied infrared (IR) and resonance Raman (RR) spectroscopies to the study of oxygen binding to heme proteins and model compounds.¹⁻⁶ In fact, these techniques can provide a direct probe of the metal-oxygen linkage. Thus, the explicit goals of these types of studies are to identify the spectral features associated with the $\nu(\text{O}-\text{O})$, $\nu(\text{M}-\text{O})$, and $\delta(\text{M}-\text{O}-\text{O})$ modes and to precisely define the influence of steric, electronic, and environmental factors on the corresponding vibrational frequencies. Although a good deal of progress has been made recently, full realization of these goals has yet to be attained.

In principle, definitive assignment of the key modes can be made with the aid of isotopic labeling studies. However, correct interpretation of such data may be rendered difficult as a result of the inherent complexities of vibrational spectroscopy, such as vibrational coupling and Fermi resonance.⁷ For example, such

factors complicated the assignment of the $\nu(\text{O}-\text{O})$ in the IR spectra of oxyhemoglobin and model compounds wherein two isotope (¹⁶O₂/¹⁸O₂) sensitive bands were observed near 1100 and 1160 cm⁻¹.^{8,9} Subsequently, Alben and co-workers¹⁰ pointed out that

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such behavior may be reasonably ascribed to Fermi resonance involving the $\nu(\text{O}-\text{O})$ and the first overtone of $\nu(\text{Fe}-\text{O})$ observed at 567 cm^{-1} .¹¹ Similarly, the assignment of this latter band to $\nu(\text{Fe}-\text{O})$, rather than to $\delta(\text{Fe}-\text{O}-\text{O})$, remains controversial at this time.¹²⁻¹⁵

The response of the $\nu(\text{O}-\text{O})$ to slight alterations in structure and bonding has likewise been the subject of some confusion. Thus, multiple bands are sometimes observed which may be interpreted either as evidence for multiple chemical forms or as the result of vibrational coupling.^{16,17} In an attempt to clarify this issue, we had undertaken a systematic study of the RR spectra of oxygen complexes of cobalt porphyrins wherein we carried out strategic isotopic labeling of the key components of each of the systems studied. The essential conclusions of that work, which have been published elsewhere,¹⁸ were as follows: vibrational coupling between $\nu(\text{O}-\text{O})$ and internal modes of the associated axial ligand (usually a nitrogenous base) can give rise to multiple bands; such effects can be easily demonstrated by utilizing selectively deuterated components; finally, such studies greatly facilitate the assessment of steric, electronic, and environmental effects on the $\nu(\text{O}-\text{O})$ frequency.

During the course of that work, we were surprised to obtain evidence for a peculiar type of vibrational coupling between the $\nu(\text{O}-\text{O})$ of the bound O_2 and an internal mode (1155 cm^{-1}) of molecules of the solvent, CH_2Cl_2 . Briefly, it was observed that the spectrum of $\text{Co}([\text{}^2\text{H}_8]\text{TPP})$ in a CH_2Cl_2 solution with added pyridine and $^{16}\text{O}_2$ exhibited two unresolved bands at 1155 and 1143 cm^{-1} . Upon replacement of CH_2Cl_2 with $\text{C}^2\text{H}_2\text{Cl}_2$, the 1155-cm^{-1} shoulder which is assignable to an internal mode of the solvent molecule disappears and, most significantly, the 1143-cm^{-1} band ($\nu(\text{O}-\text{O})$) shifts to 1148 cm^{-1} . The displacement of the $\nu(\text{O}-\text{O})$ from its inherent frequency of 1148 cm^{-1} is due to vibrational coupling, rather than to any possible chemical effects of the solvent change, since no similar shift is observed in the case of $\nu(^{18}\text{O}-^{18}\text{O})$. In addition, these experiments provided evidence of selective enhancement of the 1155-cm^{-1} band of the solvent molecule as a result of this coupling since this band was not observed in the experiment with $^{18}\text{O}_2$, wherein all components were present in comparable concentrations. Finally, comparison of spectra of the complexes in different solvents and the use of various porphyrins indicated that such coupling is facilitated by intimate association of the CH_2Cl_2 solvent molecule (via hydrogen bonding) with the bound O_2 .

The purpose of the present work is to extend these studies in order to evaluate the importance of solvent or solute association with bound O_2 . We have carried out systematic studies in solutions of toluene and present evidence for a vibrational coupling effect which leads to selective enhancement of internal modes of an associated solvent or solute molecule, possibly via resonance vibrational energy transfer as a consequence of a specific intermolecular interaction.

Experimental Section

Compound Preparation. The $^2\text{H}_8$ analogue of tetraphenylporphyrin ($[\text{}^2\text{H}_8]\text{TPP}$) and its cobalt complex ($\text{Co}[\text{}^2\text{H}_8]\text{TPP}$) were prepared as previously described.^{19,20} The cobalt picket-fence porphyrin ($\text{CoT}_{\text{piv}}\text{PP}$)

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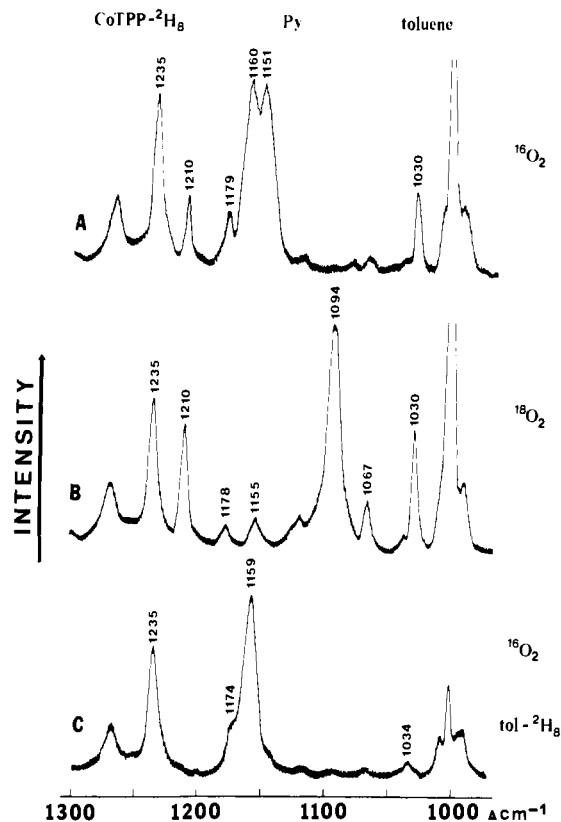


Figure 1. Resonance Raman spectra of $\text{Co}([\text{}^2\text{H}_8]\text{TPP})$ in toluene containing 3% pyridine at $-85\text{ }^\circ\text{C}$ under $\sim 4\text{ atm}$ of O_2 pressure. (A) $^{16}\text{O}_2$; (B) $^{18}\text{O}_2$; (C) $^{16}\text{O}_2$, $[\text{}^2\text{H}_8]\text{toluene}$.

complex was purchased from Midcentury Chem. Co. and used without further purification.

The bases, 4-(dimethylamino)pyridine (4-DMAPy), 3,4-dimethylpyridine (3,4-DMPy), 4-phenylpyridine (4-PhPy), pyridine (Py), $[\text{}^2\text{H}_2]$ -pyridine ($[\text{}^2\text{H}_2]\text{Py}$), 2-formylpyridine (2-FPy), 3-acetylpyridine (3-AcPy), 4-cyanopyridine (4-CNPy), 2-bromopyridine (2-BrPy), and 3,5-dichloropyridine (3,5-DCPy) were purchased from Aldrich Chemical Co. 2,4,6-Trimethylpyridine (2,4,6-TMPy) was obtained from Eastman Organic Chemicals. The liquid bases were purified by distillation. Solid bases, 3,5-DCPy and 4-CNPy, were sublimed prior to use while 4-PhPy was used as supplied. Toluene, $[\text{}^2\text{H}_8]\text{toluene}$, and $[\text{}^2\text{H}_5]\text{monochlorobenzene}$ were purchased from Aldrich Chemical Co. while $[\text{H}_5]\text{monochlorobenzene}$ was supplied by Fisher Scientific Co. Toluene was purified by shaking with calcium hydride (CaH_2) for 24 h, refluxing for 2 h, and then distilling twice. The second distillation was over metallic sodium. Deuterated toluene and monochlorobenzene were used as supplied. Samples of $^{16}\text{O}_2$ (prepurified, Airco Rare and Specialty Gases) and $^{18}\text{O}_2$ (95%, Monsanto Research Corp.) were used as received.

Spectral Measurements. The resonance Raman spectra were recorded on a Spex Model 1401 double monochromator equipped with a Spex DPC-2 digital photometer system. Excitation at 406.7 nm was by a Spectra-Physics Model 164-01 Kr-ion laser. Laser power on the sample was kept below 5 mW . A spectral band-pass of 4 cm^{-1} was used.

Samples for Raman measurements were prepared following the procedure of Bajdor et al.¹⁸ Prepared samples were attached to a copper tip cooled by a CTI Model 21 closed cycle helium cryostat. This allowed us to keep the samples at constant temperature, $-85 \pm 5\text{ }^\circ\text{C}$ (close to the freezing point of toluene), during the measurements. The unperturbed solvent bands (vide infra) were used for calibration. Estimated accuracy of the frequency readings was $\pm 1\text{ cm}^{-1}$.

Results and Discussion

Selective Enhancement of Solvent Bands. The spectra of oxygen adducts with $\text{Co}[\text{}^2\text{H}_8]\text{TPP}$ in toluene are shown in Figure 1. As can be seen in spectrum A, two unresolved, intense bands (1160

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and 1151 cm⁻¹) are observed in the region where $\nu(^{16}\text{O}-^{16}\text{O})$ is expected to occur.¹⁶⁻¹⁸ The appearance of two bands in this region is not due to the presence of two types of oxygen adducts since, as can be seen in spectrum B, only one intense band is observed at 1094 cm⁻¹ when ¹⁸O₂ is employed. The small band at 1067 cm⁻¹ (spectrum B) is due to enhancement of an internal mode of pyridine (vide infra) as has been shown previously by utilization of [²H₅]pyridine.¹⁸ The observation of the strong band at 1151 cm⁻¹ in Figure 1A may be interpreted as a selective enhancement of an internal mode of molecules of the solvent, toluene. This interpretation is supported by the following evidence. The spectrum shown in Figure 1C is that of a solution prepared in an identical fashion to the solution used for the spectrum shown in Figure 1A with the exception that [²H₈]toluene was used in place of the undeuterated toluene. In this case (spectrum 1C), a single intense band, assignable to $\nu(^{16}\text{O}-^{16}\text{O})$, is observed at 1159 cm⁻¹. The small shoulder at 1174 cm⁻¹ is due to an internal mode of [²H₈]toluene.²⁴ There is apparently only a very weak enhancement of the 1174-cm⁻¹ band.

Natural abundance toluene exhibits three bands in this region at 1210, 1178, and 1155 cm⁻¹.²⁴ The relative intensities of these three bands in neat toluene, excited at 406.7 nm, are similar to those observed in the spectrum shown in Figure 1B. In neat toluene the relative intensities are 9:1:1 while in Figure 1B they are approximately 6:1:1. Thus, it is apparent that the occurrence of $\nu(^{16}\text{O}-^{16}\text{O})$ in the vicinity of the internal modes of toluene gives rise to an enhancement of the corresponding toluene bands relative to the band observed at 1210 cm⁻¹. It is equally apparent that if the $\nu(\text{O}-\text{O})$ is displaced to a much lower frequency by substitution of ¹⁸O₂ (Figure 1B), the bands corresponding to these internal modes of toluene are not enhanced significantly. Therefore, the mechanism by which the internal modes of the solvent molecules are selectively enhanced by interaction with $\nu(\text{O}-\text{O})$ evidently is critically dependent upon "energy matching" of the two sets of modes.

In an attempt to provide a more sensitive test of this "energy matching" condition, we have carried out a set of experiments designed to "fine-tune" the $\nu(^{16}\text{O}-^{16}\text{O})$ so as to vary its frequency systematically between the two toluene internal modes at 1178 and 1155 cm⁻¹. Such variation can be accomplished by employing different nitrogenous bases as the axial ligand. Since the bonding in these O₂ adducts can be generally formulated as Co^{δ+}-O₂^{δ-}, it is to be expected that the strength of the Co-O bond, and consequent weakening of the O-O bond, should be sensitive to the basicity of the axial ligand.¹⁻⁶ Although other factors may be important, if these are held constant, the $\nu(\text{O}-\text{O})$ should be sensitive to the nature of the axial ligand (vide infra).

The spectra corresponding to this series of experiments are shown in Figure 2. In trace A, using 4-cyanopyridine (4-CNPy), the $\nu(^{16}\text{O}-^{16}\text{O})$ is observed at 1167 cm⁻¹, a frequency approximately intermediate between the two toluene modes in question. In this case the higher frequency toluene mode (1180 cm⁻¹ in the figure) is enhanced to a degree which is comparable with the enhancement of the lower frequency toluene band (1153 cm⁻¹ in the figure). The spectrum of the complex with pyridine is shown again in Figure 2B wherein the $\nu(^{16}\text{O}-^{16}\text{O})$ is observed at 1160 cm⁻¹, a frequency which is closer in energy to the lower frequency toluene mode (1155 cm⁻¹) than to the 1178-cm⁻¹ mode. Here it is clear that the lower frequency toluene band is enhanced to a much greater extent than that at 1178 cm⁻¹, although this latter band remains enhanced relative to the 1210-cm⁻¹ toluene band. Finally, the spectrum of the complex with 4-(dimethylamino)pyridine (4-DMAPy) is shown in Figure 2C. The $\nu(^{16}\text{O}-^{16}\text{O})$ is observed at 1147 cm⁻¹, a frequency relatively far removed from the 1178-cm⁻¹ toluene band but still close in energy to the lower frequency toluene band at 1155 cm⁻¹. As can be clearly seen in the figure, the lower energy toluene band is definitely enhanced, but the higher energy toluene band at 1178 cm⁻¹ experiences an insignificant enhancement relative to the 1210-cm⁻¹ band. It seems

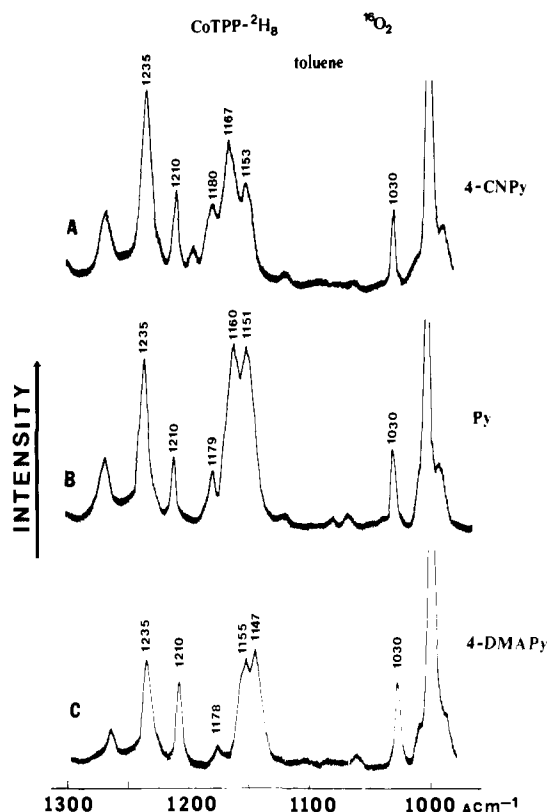


Figure 2. Resonance Raman spectra of Co([²H₈]TPP) in toluene containing 3% 4-cyanopyridine (A), pyridine (B), and 4-(dimethylamino)pyridine (C) at -85 °C under ~4 atm of ¹⁶O₂ pressure.

worthwhile to point out that not only are the intensities of these toluene modes altered via interaction with $\nu(\text{O}-\text{O})$ but also their frequencies may be perturbed. Thus, although only slight shifts are observed, there is an apparent trend in the positions of the 1178- and 1155-cm⁻¹ bands which depend on the frequency of $\nu(\text{O}-\text{O})$. Thus, as $\nu(^{16}\text{O}-^{16}\text{O})$ moves from 1147 cm⁻¹ (trace C) to 1167 cm⁻¹ (trace A) the 1178-cm⁻¹ band shifts to 1180 cm⁻¹, whereas the 1155-cm⁻¹ feature is observed at 1153 and 1151 cm⁻¹ as $\nu(\text{O}-\text{O})$ shifts from 1167 to 1160 cm⁻¹. Thus, the proposed interaction may result in slight frequency shifts of the interacting bands in a manner analogous to other types of vibrational interactions such as Fermi resonance.²¹ However, it must be emphasized that, although there is an apparent trend, such small frequency shifts are close to experimental error and may not be real.

In an effort to effect slight perturbations in the interaction between bound O₂ and toluene molecules it is useful to investigate other solvents, keeping in mind the practical requirement that the solvent remains fluid at low temperatures. For this purpose we have carried out studies in chlorobenzene (ClBz). As is typical of all monosubstituted benzenes, this molecule has two bands (1156 and 1172 cm⁻¹) in the region of $\nu(^{16}\text{O}-^{16}\text{O})$. As can be seen in Table I, an extremely broad band is observed in the case where pyridine serves as the axial ligand. The inherent frequency for $\nu(^{16}\text{O}-^{16}\text{O})$ in this complex is expected to be ~1155 cm⁻¹ based on the value of 1090 cm⁻¹ for the $\nu(^{18}\text{O}-^{18}\text{O})$ analogue ($\Delta\nu = 65$ cm⁻¹). In case of the pyridine complex, $\nu(^{16}\text{O}-^{16}\text{O})$ evidently interacts with both the bound pyridine mode at 1147 cm⁻¹ and the internal mode of ClBz at 1156 cm⁻¹ giving a very broad band which simplifies to two resolved bands if [²H₅]Py is used. In addition, the inherent frequency is seen to occur at 1155 cm⁻¹ in the case of [²H₅]Py in a solution of [²H₅]ClBz (i.e., when both perturbations are removed). It should be emphasized that for the complexes in ClBz, both of the solvent bands (1156 and 1172 cm⁻¹) are enhanced relative to the other solvent bands in the spectrum. Finally, it is noted that the frequency of the [²H₅]Py complexes is 2 cm⁻¹ lower in ClBz than the corresponding inherent frequency (1157 cm⁻¹) in toluene (i.e., [²H₅]Py, [²H₈]toluene).

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Table I

| porphyrin | solvent | base | <i>a</i> | p <i>K</i> _a | $\nu(^{16}\text{O}-^{16}\text{O})$ (cm ⁻¹) | $\nu(^{18}\text{O}-^{18}\text{O})$ (cm ⁻¹) | comments |
|---------------------------------------|--|---|----------|-------------------------|---|---|--|
| Co[² H ₈]TPP | toluene | 4-(dimethylamino)pyridine | 1 | 9.70 | 1147 (1155) | 1091 (1062) | band 1065 cm ⁻¹ for base in toluene |
| Co[² H ₈]TPP | [² H ₈]toluene | 4-(dimethylamino)pyridine | | | 1151 | | |
| Co[² H ₈]TPP | [² H ₈]toluene | 2,4,6-trimethylpyridine | 2 | 7.43 | 1156 | | |
| Co[² H ₈]TPP | [² H ₈]toluene | 3,4-dimethylpyridine | 3 | 6.46 | 1157 | 1096 (1071) | |
| Co[² H ₈]TPP | toluene | 4-phenylpyridine | 4 | 5.55 | 1158 (1152) | 1095 (1067) | |
| Co[² H ₈]TPP | [² H ₈]toluene | 4-phenylpyridine | | | 1159 | | |
| Co[² H ₂₀]TPP | [² H ₈]toluene | 4-phenylpyridine | | | 1159 | | |
| Co[² H ₈]TPP | toluene | pyridine | 5 | 5.25 | 1160 (1151) | 1094 (1067) | |
| Co[² H ₈]TPP | [² H ₈]toluene | pyridine | | | 1159 (1147) | | band 1147 cm ⁻¹ very weak |
| Co[² H ₈]TPP | toluene | [² H ₅]pyridine | | | 1160 (1151) | 1091 | |
| Co[² H ₈]TPP | [² H ₈]toluene | [² H ₅]pyridine | | | 1157 | | |
| Co[² H ₈]TPP | toluene + 20% MeOH | [² H ₅]pyridine | | | | 1089 | |
| Co[² H ₈]TPP | chlorobenzene | pyridine | | | 1154 | 1087 | very broad band |
| Co[² H ₈]TPP | chlorobenzene | [² H ₅]pyridine | | | 1155 (1147) | | band 1167 cm ⁻¹ vs. weak/shoulder |
| Co[² H ₈]TPP | [² H ₅]chlorobenzene | [² H ₅]pyridine | | | 1155 | 1090 | strong, narrow, sym band |
| Co[² H ₈]TPP | [² H ₈]toluene | 2-formylpyridine | 6 | 3.80 | 1162 | | |
| Co[² H ₈]TPP | [² H ₈]toluene | 3-acetylpyridine | 7 | 3.18 | 1163 | | |
| Co[² H ₈]TPP | toluene | 4-cyanopyridine | 8 | 1.90 | 1167 | 1102 (1065) | |
| Co[² H ₈]TPP | [² H ₈]toluene | 4-cyanopyridine | | | 1166 | | |
| CoT _{piv} PP | toluene | 4-cyanopyridine | | | 1161 | | |
| Co[² H ₈]TPP | toluene | 2-bromopyridine | 11 | 0.90 | 1154, 1140 | 1082 | $\nu(^{16}\text{O}-^{16}\text{O}) = 1147 \text{ cm}^{-1}$ (see text) |
| CoT _{piv} PP | [² H ₈]toluene | 2-bromopyridine | 10 | | 1162 | 1093 | |
| CoT _{piv} PP | toluene | 2-bromopyridine | 9 | 0.67 | 1169 | | |

Structural Constraints on Vibrational Coupling. The previous section presented evidence for resonant enhancement of Raman bands corresponding to internal modes of solvent molecules which is induced by vibrational coupling to an internal mode, $\nu(\text{O}-\text{O})$, of the resonant chromophore associated with the Co-O₂ charge-transfer transition. Although the precise mechanisms remain unclear at this time, such behavior implies that the solvent molecules whose internal modes are enhanced are intimately associated with the chromophoric group. In order to define the nature of this association we have carried out studies with cobalt complexes of "picket-fence" porphyrin which possesses four bulky pivaloyl groups on one side of the porphyrin plane. It is generally accepted that these groups restrict close association of all but very small molecules with the bound molecular oxygen.²² Utilizing these complexes, it should be possible to elucidate important structural factors by comparing RR spectra of adducts of the "unprotected" Co([²H₈]TPP) with those of the picket-fence derivatives wherein the bound molecular oxygen may be protected from strong association with the relatively large solvent molecules.

The spectra shown in Figures 1 and 3 provide rather strong evidence that close association of toluene molecules with the bound molecular oxygen is required for induced enhancement of the internal toluene modes. Thus, in trace A of Figure 1, enhancement of toluene modes is clearly evident. If the toluene molecule were directly associated with the bound O₂, it should be expected that such enhancement would disappear for adducts of the picket-fence porphyrin. In this particular case, alterations in vibrational coupling would be difficult to detect since the $\nu(^{16}\text{O}-^{16}\text{O})$ for the picket-fence analogue may be expected to overlap the 1155-cm⁻¹ toluene band. Thus, it was decided to investigate this issue by employing an axial ligand (4-CNPy) which would displace the $\nu(^{16}\text{O}-^{16}\text{O})$ to a slightly higher frequency. The spectra shown in Figure 3 adequately demonstrate the consequence of restricted access of toluene molecules to the bound O₂. Trace A of Figure 3 shows significant enhancement of the toluene bands (1180 and 1153 cm⁻¹). As is shown in trace B, the spectrum of the adduct with Co(T_{piv}PP), obtained under identical conditions, exhibits only one strong symmetrical band in this region (1159 cm⁻¹). As will be shown in the next section, restricted access is also effective in decoupling $\nu(^{16}\text{O}-^{16}\text{O})$ from internal modes of molecules of excess axial ligand. Together, these results indicate that close association of solution components with O₂ is an essential condition for observation of enhancement of the internal modes of the components.

Enhancement of Axial Ligand and Solute Bands. The spectra obtained for O₂ adducts of Co([²H₈]TPP) and Co(T_{piv}PP) with 2-BrPy are shown in Figure 4. The spectrum given in trace A exhibits two strong bands in the region in which $\nu(^{16}\text{O}-^{16}\text{O})$ is

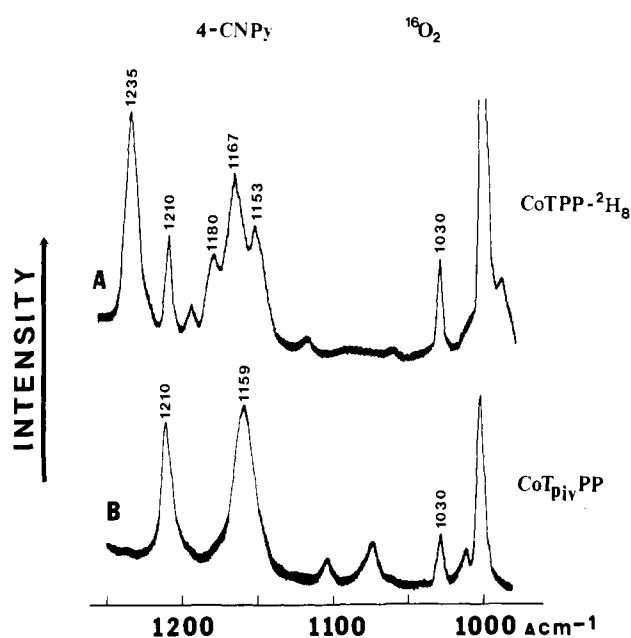


Figure 3. Resonance Raman spectra of Co([²H₈]TPP) (A) and Co(T_{piv}PP) (B) in toluene containing 3% 4-cyanopyridine at -85 °C under ~4 atm of ¹⁶O₂ pressure.

expected to occur. On the other hand, only one strong, symmetrical band is observed at 1082 cm⁻¹ in the case of $\nu(^{18}\text{O}-^{18}\text{O})$ (trace B).

As has been discussed previously,¹⁸ the ¹⁶O₂/¹⁸O₂ isotopic frequency shift for bound molecular oxygen is expected to be 64–66 cm⁻¹. The observed 1082-cm⁻¹ value for $\nu(^{18}\text{O}-^{18}\text{O})$ would correspond to a $\nu(^{16}\text{O}-^{16}\text{O})$ frequency of 1146–1148 cm⁻¹, i.e., a frequency intermediate between the two observed bands at 1154 and 1140 cm⁻¹. The axial ligand in this case, 2-BrPy, possesses an internal, totally symmetric mode whose frequency is 1147 cm⁻¹.²³ The most obvious explanation for the behavior observed for this complex is that the $\nu(^{16}\text{O}-^{16}\text{O})$ has an inherent frequency of 1147 cm⁻¹ but interacts strongly with the 1147-cm⁻¹ internal mode of the 2-BrPy. This interaction displaces both frequencies equally (7 cm⁻¹) to yield two bands at 1154 and 1140 cm⁻¹.

This behavior is reminiscent of previous observations of enhancement of internal modes of pyridine in those cases in which pyridine was added to the solution to serve as the axial ligand.¹⁸ However, the nature of the interaction of added base (2-BrPy or

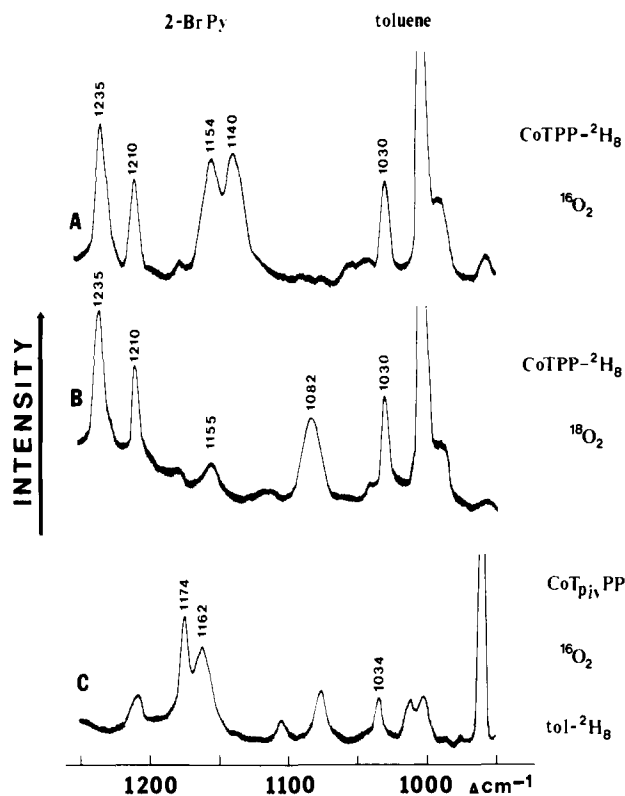


Figure 4. Resonance Raman spectra of Co([²H₈]TPP) in toluene containing 3% 2-bromopyridine saturated with ~4 atm ¹⁶O₂ (A) and ¹⁸O₂ (B) and Co(T_{pv}PP) in [²H₈]toluene containing 3% 2-bromopyridine saturated with ~4 atm ¹⁶O₂, all at -85 °C.

Py) with the bound O₂ which gives rise to enhancement of internal modes of the base is apparently quite different in the two cases. In the case of 2-BrPy, the enhancement is evidently induced by coupling of $\nu(^{16}\text{O}-^{16}\text{O})$ with internal modes of the excess 2-BrPy molecules which are directly associated with the bound O₂ rather than by coupling with modes of 2-BrPy molecules coordinated trans to the O₂. We arrive at this conclusion by recognition of the fact that such coupling disappears for adducts with picket-fence porphyrin. Thus, the spectrum shown in Figure 4C exhibits one strong symmetrical band at 1162 cm⁻¹, whereas the case of "unprotected" O₂ adducts of Co([²H₈]TPP) strong coupling between the 2-BrPy mode and $\nu(^{16}\text{O}-^{16}\text{O})$ was observed. The 1174-cm⁻¹ band in Figure 4C is assignable to ν_8 of [²H₈]toluene.²⁴ If the coupling which gave rise to the two strong bands in Figure 4A involved in a 2-BrPy molecule which is coordinated trans to O₂, it should be expected that such coupling would persist in the spectrum shown in Figure 4C. This behavior is not observed for 2-BrPy adducts. However, as will be shown below, this sort of behavior is observed for pyridine adducts.

In our previous publication¹⁸ we presented evidence for vibrational coupling of $\nu(^{18}\text{O}-^{18}\text{O})$ with the 1067-cm⁻¹ internal mode of pyridine which was added to the solution to serve as the axial ligand. The resulting enhancement of the 1067-cm⁻¹ band can be seen here by referring to Figure 1B. This band is observed only in the spectrum of the ¹⁸O₂ adduct wherein the $\nu(\text{O}-\text{O})$ is in close proximity to the pyridine mode. The band is not enhanced in the ¹⁶O₂ adduct again demonstrating the requirement for "energy matching". The assignment of the 1067-cm⁻¹ band to an internal mode of pyridine was confirmed by its disappearance when employing [²H₅]pyridine.¹⁸ We have also observed enhancement of another internal mode of pyridine (the weak shoulder at 1147 cm⁻¹) by virtue of its coupling with $\nu(^{16}\text{O}-^{16}\text{O})$ as can be seen in Figure 1C wherein the interference from an overlapping toluene band (1155 cm⁻¹) has been avoided by utilizing [²H₈]toluene. Although this 1147-cm⁻¹ feature appears as a weak shoulder, it is present in all such spectra. Furthermore, observation of these pyridine bands at 1147 and 1067 cm⁻¹ cannot be due simply to normal Raman scattering from excess pyridine since,

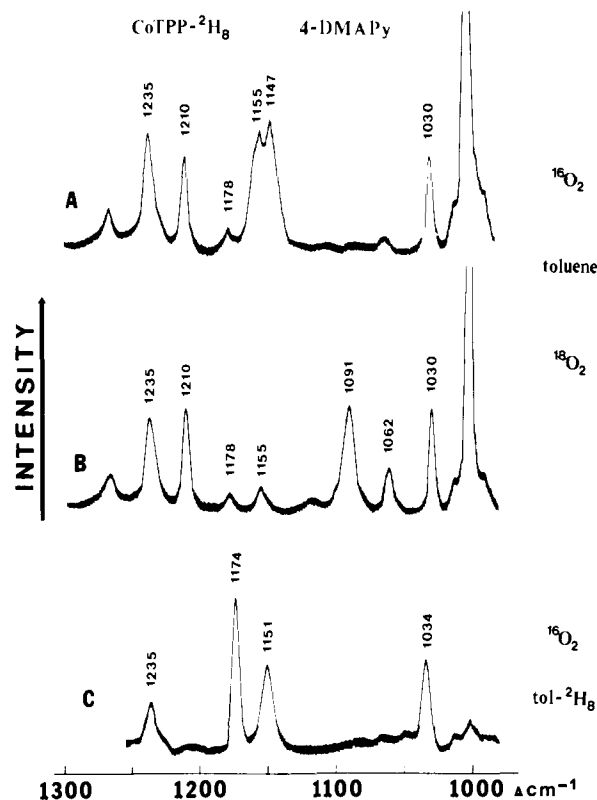


Figure 5. Resonance Raman spectra of Co([²H₈]TPP) in toluene containing 3% 4-(dimethylamino)pyridine at -85 °C under ~4 atm of O₂ pressure: (A) ¹⁶O₂; (B) ¹⁸O₂; (C) ¹⁶O₂, [²H₈]toluene.

if this were the case, one would expect to observe other pyridine bands in this region. That is, in the normal Raman spectrum of pyridine, several other bands are considerably stronger than the 1067-cm⁻¹ band.²⁵

In the earlier report which presented the above data, we attributed this enhancement to vibrational coupling between $\nu(\text{O}-\text{O})$ and the internal modes of a pyridine molecule coordinated trans to the O₂.¹⁸ An alternative explanation would invoke a direct association between the bound O₂ and excess pyridine molecules by analogy with the 2-BrPy adducts discussed above. However, experiments with picket-fence analogues again allow us to distinguish between these mechanisms. In fact, the spectrum of the appropriate adduct has been reported previously.¹⁷ Inspection of Figure 5 of ref 17 clearly demonstrates enhancement of the 1067-cm⁻¹ band in the spectrum of Co(T_{pv}PP) in a methylene chloride solution containing ¹⁸O₂ and pyridine. Again it must be emphasized that the 1067-cm⁻¹ feature of that spectrum cannot be due to normal Raman scattering from excess pyridine since other, stronger, pyridine bands were not observed. To the extent that close association of excess pyridine molecules is restricted in this adduct, the enhancement of the pyridine mode implies coupling with the coordinated ligand. Furthermore, this interpretation receives additional support from the observation that in the case of pyridine with Co[²H₈]TPP in toluene, enhancement of both pyridine and toluene modes was observed. If the excess base is closely associated with bound O₂ then we should not observe toluene enhancement. As can be seen in the case of 2-BrPy, no enhancement of toluene modes was observed (Figure 4A).

It should be pointed out that, provided the energy matching criterion is met, the enhancement of axial ligand modes seems quite general. Thus, we have observed enhancement of the internal mode (at ~1070 cm⁻¹) of the axial ligand with $\nu(^{18}\text{O}-^{18}\text{O})$ for all the substituted pyridines studied which have a mode in this frequency region. In addition, although we have not confirmed the observation by employing isotopically labeled ligand, we have

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obtained preliminary evidence for interaction of $\nu(^{18}\text{O}-^{18}\text{O})$ with an internal mode ($\sim 1080\text{ cm}^{-1}$) of 1-methylimidazole.

A particularly clear demonstration of the necessity for caution in the interpretation of slight frequency shifts in $\nu(\text{O}-\text{O})$ is given by consideration of the data for the case in which 4-DMAPy serves as the axial ligand. For the 4-DMAPy adducts, $\nu(^{16}\text{O}-^{16}\text{O})$ is observed at 1147 cm^{-1} and $\nu(^{18}\text{O}-^{18}\text{O})$ at 1091 cm^{-1} (Figure 5), yielding a $\Delta\nu(^{16}\text{O}_2/^{18}\text{O}_2)$ of only 57 cm^{-1} . However, in $[\text{}^2\text{H}_8]\text{-toluene}$ the inherent $\nu(^{16}\text{O}-^{16}\text{O})$ is seen to be 1151 cm^{-1} (trace C). It is also noted that the $\nu(^{18}\text{O}-^{18}\text{O})$ is evidently perturbed slightly by interaction with an internal mode of 4-DMAPy (the weak band at 1062 cm^{-1} in trace B). The true frequency for this internal mode is observed at 1065 cm^{-1} in a toluene solution of the free ligand; i.e., it is shifted by 3 cm^{-1} . If we assume a comparable shift for the $\nu(^{18}\text{O}-^{18}\text{O})$, its inherent value is 1088 cm^{-1} . Thus the corrected $\Delta\nu(^{16}\text{O}_2/^{18}\text{O}_2)$ for this system is 63 cm^{-1} , a value in reasonable agreement with expectations.

Mechanism of Induced Enhancement. The data presented in the preceding sections provide evidence for selective enhancement of specific internal modes of solvent and excess solute molecules. Such enhancement was seen to be dependent upon several conditions. Perhaps most importantly, the component in question must be closely associated with the bound oxygen molecule. The enhancement of both toluene and 2-BrPy modes disappears for the protected picket-fence analogues. Thus, the first criterion is that there must be an intermolecular interaction. In addition, the degree of the induced enhancement was seen to be critically dependent upon energy matching of vibrational frequencies. That is, both components of the interacting pair (in this case, bound O_2 and a solvent or solute molecule) must possess internal modes exhibiting corresponding frequencies within a rather narrow range (see Figure 2).

Such behavior is apparently similar to that observed for certain internal modes of interacting molecules in associated liquids. Indeed, a large number of theoretical and a fewer number of experimental studies of the effects of intermolecular interactions on IR and Raman band shapes and intensities have been carried out.²⁶⁻³⁰ In the context of the present work, the most important example of such effects is the phenomenon referred to as "resonance vibrational energy transfer" which involves coupling between adjacent molecules via particular vibrational coordinates.³¹ Such coupling is normally considered to be a consequence of the specific type of intermolecular interaction known as the transition-dipole-transition-dipole interaction and may be qualitatively described as induced vibrational excitation of an internal mode of one component of the molecular pair by transfer of energy from the vibrationally excited partner molecule. The efficiency of energy transfer might then be expected to increase in proportion to the dipole moment change associated with a particular vibrational transition. Indeed, on the basis of theoretical considerations, two groups of workers have independently concluded that the effect of this type of interaction on vibrational frequencies depends on the infrared fundamental intensity of the internal mode involved.^{32,33} Inasmuch as the infrared intensities of the toluene modes in question are not substantial, the transition-dipole-transition-dipole interaction mechanism may not be operative in the present case. However, Wang and McHale have pointed out that, in general, vibrational resonance coupling between adjacent oscillators which possess internal modes of comparable energy may result from any type of intermolecular interaction.^{34,35} In any

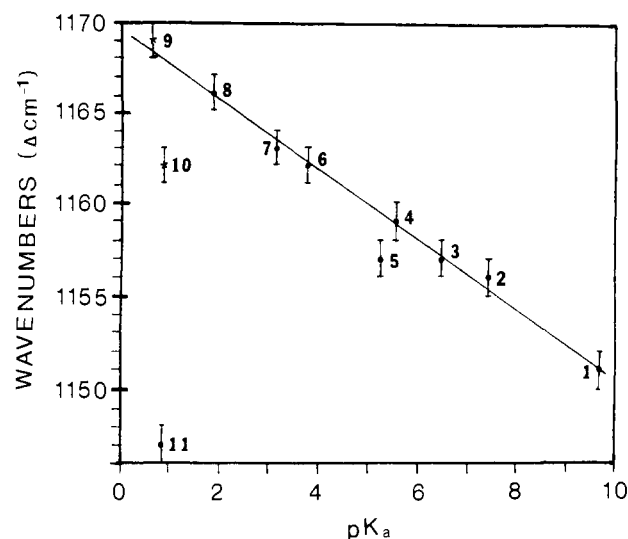


Figure 6. Effect of ligand basicity on $\nu(\text{O}_2)$. For numbering, see Table I.

case, the strength of such interactions is expected to be inversely proportional to the intermolecular distance and critically dependent upon matching of vibrational frequencies.

In the case of self-association,³⁶ as well as in the complexes studied here, the effects of resonance vibrational energy transfer can be eliminated by substitution of an isotopically labeled analogue (i.e., upon elimination of energy matching). The dependence upon intermolecular distance is most clearly demonstrated in the case of self-association of solution components by dilution experiments. Thus, in the well-studied case of benzaldehyde,²⁶ evidence for intermolecular vibrational coupling effects disappears upon dilution in CS_2 (i.e., upon cluster elimination).³⁶ The experiments which we have carried out with the picket-fence complexes are comparable, in terms of purpose, to the dilution experiment with benzaldehyde in CS_2 . Although obvious, it seems worthwhile to emphasize that a static intermolecular interaction is not implied but only that the lifetime of the "solvent (or solute) interaction complex" is long with respect to the time scale of a vibrational transition.

The majority of previous studies of the effects of intermolecular interactions on vibrational spectra have dealt with self-association of solution components wherein the vibrations of adjacent molecules were of identical form and energy. In the present work we are dealing with vibrational coupling between two distinct interacting molecules (e.g., O_2 and toluene). In the type of study described here, evidence for the intermolecular interaction is clearly manifested via selective resonance enhancement of particular internal modes of the associated species. Thus, such studies should represent an especially effective approach for the investigation of the effects of intermolecular interactions on vibrational spectra.

Effect of Axial Ligand Basicity on $\nu(\text{O}-\text{O})$. As was mentioned earlier, based on the $\text{Co}^{3+}-\text{O}_2^{2-}$ formulation of the bonding in these complexes, $\nu(\text{O}-\text{O})$ should be sensitive to the basicity of the coordinated axial ligand, i.e., decreasing with increasing pK_a of the ligand. In a previous publication,¹⁸ we attributed the rather small range of observed shifts within a series of axial ligands to be due to a masking effect of the solvent used in that study (CH_2Cl_2) which results from strong interactions between bound O_2 and the solvent molecules. At that time we suggested that the use of toluene as the solvent would provide a more reliable indication of axial ligand basicity effects. In this section of the present work we present the results of a systematic study of axial ligand variation which confirms these expectations provided that apparently anomalous frequencies are justifiably eliminated on

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the basis that they arise from the vibrational coupling effects described in the previous sections.

The relevant data (including pK_a values of the axial ligands) for all of the complexes studied in this work are given in Table I along with explanatory comments. The dependence of $\nu(^{16}\text{O}-^{16}\text{O})$ frequencies on ligand pK_a value for the complexes of a series of substituted pyridines whose basicities span a range of over nine orders of magnitude ($pK_a = 0.67-9.70$) is demonstrated in Figure 6. With the exception of two points (10 and 11), a linear relationship (correlation coefficient = 0.98) is clearly evident. The low frequency observed for $\nu(^{16}\text{O}-^{16}\text{O})$ in the case of 2-BrPy with "unprotected" $\text{Co}[\text{H}_8]\text{TPP}$ (point number 11) can be ascribed to a strong interaction between the bound O_2 and excess 2-BrPy, as was described in a previous section.

The anomalous frequency for the 2-BrPy complex with the picket-fence porphyrin (point 10) is not fully understood at this time. It may be pointed out, however, that the pK_a data correspond to measurements in aqueous solution. The value of $\nu(\text{O}-\text{O})$ for the 2-BrPy complex indicates that the ligand is a stronger base (lower value for $\nu(\text{O}-\text{O})$) than is implied by the pK_a value. It may be possible that the inherent basicity is underestimated in aqueous solution as a result of stabilization of the base form by tight association of a molecule of water via formation of hydrogen bonds to the nitrogen and the bromo substituent.

Implications for RR Spectra of Heme Protein- O_2 Adducts. Many resonance Raman studies of heme protein complexes with exogenous ligands have been carried out.^{3,16-18} Inasmuch as such studies are generally very useful for detecting slight alterations in structure and bonding parameters of these ligands, it is likely

that future studies will continue to provide useful information. Therefore, it seems important to consider the implication of the present work for these types of investigations.

The first point to be made is that there are, of course, a number of residues in the heme pocket, notably the imidazole group of the distal histidine, which can associate with the bound exogenous ligand.¹⁶ In addition, the demonstrated coupling with internal modes of bound pyridines in this study, as well as in our previous work,¹⁸ implies that, in the case of heme proteins, internal modes of the proximal imidazole may also couple with the exogenous ligand modes. Inasmuch as there is an apparently critical dependence of energy matching of the interacting modes, this phenomenon is presumably decreased in CO derivatives relative to O_2 and NO, which have frequencies closer in energy to internal modes of potentially interacting residues.

In summary, the results presented here show that bands associated with the exogenous ligand (especially O_2 and NO) may be perturbed by vibrational coupling as well as by alterations in structure and bonding. Thus, although certain criteria for effective coupling must be met in order for this to be important, it would seem to be essential to give careful consideration to such possibilities if frequency and/or intensity data are to be interpreted in terms of structural and bonding changes.

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Cycloreversion Induced by Charge-Transfer Excitation of Electron Donor-Acceptor Complexes. Wavelength-Dependent Photochemistry of Dianthracene

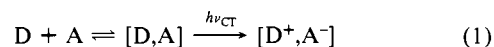
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Abstract: The electron donor-acceptor or EDA complexes of dianthracene (An_2 is the σ -dimer of anthracene) and its derivatives with tetracyanoethylene show two unusually well-resolved charge-transfer (CT) bands. Specific irradiation of each of these absorption bands with monochromatic light at five selected wavelengths ranging from 405 to 577 nm leads to the clean cycloreversion of An_2 to anthracene. The striking wavelength-dependent quantum efficiency for cycloreversion is analyzed in terms of two different CT ion pairs [$\text{An}_2^+, \text{TCNE}^-$] derived from the photoexcitation of the first and second absorption bands, which correspond to electron promotion from the HOMO and SHOMO (second highest occupied molecular orbital) of the dianthracene donor, respectively. Orbital correlations between dianthracene and anthracene π -dimer reveal that electron promotion from the SHOMO of dianthracene leads to an excited radical ion An_2^+ which is more dissociative than that derived from the HOMO transition.

Transient charge-transfer (CT) absorption bands are often observed during the course of many organic and organometallic reactions.¹ These electronic transitions are associated with the presence of metastable electron donor-acceptor or EDA complexes, usually as weakly bound intermediates.² According to Mulliken theory,³ the charge-transfer transitions of EDA complexes involve

the electron promotion from the occupied molecular orbitals of the donor (D) to the unoccupied molecular orbitals of the acceptor (A). In those electron donor-acceptor complexes which have relatively nonpolar ground states $[\text{D}, \text{A}]$, the CT excitation populates an ionic state $[\text{D}^+, \text{A}^-]$ consisting of the radical cation of the donor and the radical anion of the acceptor, i.e.,



Indeed, we recently observed this CT excited state by time-resolved picosecond spectroscopy of a series of anthracene complexes with

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