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DFT Studies of the Resonance Raman Spectra of Ground and Excited Triplet State Free Base *meso*-Tetraphenylporphyrin (H_2TPP)

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DFT calculations at the B3LYP/6-31G(d) level were carried out for the ground and excited triplet states of free base *meso*-tetraphenylporphyrin, H_2TPP, and its d_2, d_8, d_{10}, d_{20}, d_{22}, and $^{13}C_4$ isotopomers. The agreement between experimental and calculated (scaled with a single factor of 0.973) band positions for the ground state was acceptable (rms $= 9.9$ cm^{-1}). In addition, although the shifts on isotopic substitution were frequently of the same order as this rms error in the absolute positions, it was found that the cancellation of errors in the calculations meant that the direction and magnitude of even small isotope shifts < 10 cm^{-1} were also calculated correctly. In the D_2 symmetry of the calculations the lowest lying triplet state corresponded to a one-electron transition from the b_1 HOMO to a b_3 LUMO. It was found that the calculated changes in cm^{-1} of the vibrational modes on excitation to this triplet (Δ_{S-T}) reproduced the Δ_{S-T} values of the seven bands found in the experimental spectra. Three of these bands (ν_2, ν_{12}, and ν_{15}) moved to lower cm^{-1} on excitation, two were essentially unchanged (ϕ_4 and ν_1), and two moved to higher cm^{-1} (ν_4 and ν_6). Since the Δ_{S-T} values are typically small ($\leq$10's of cm^{-1}), the correct prediction of the pattern of small shifts associated with population of an excited state with a particular electronic configuration is impressive. As before, this improved accuracy presumably arises because errors in the calculations of absolute positions cancel when values for the same modes in different electronic states are subtracted to give shifts on excitation. This level of accuracy is necessary if Δ_{S-T} values are to be used to assign orbital parentage. Surprisingly, for several of the modes the calculated Δ_{S-T} shifts differed dramatically between isotopomers. For example, for ν_2: Δ_{S-T}(calc), $d_0 = -5$ cm^{-1}, $d_8 = -30$ cm^{-1}; Δ_{S-T}(obs), $d_0 = -15$ cm^{-1}, $d_8 = -26$ cm^{-1}. These differences were found to reflect not only the changes in force constants due to promotion to the triplet state (which are the same irrespective of which isotopomer is under consideration) but also changes in the mode composition on excitation which alters the isotope sensitivity. In the case of H_2TPP, the mode compositions change because excitation from $b_1 \rightarrow b_3$ orbitals accentuates the difference in bonding between the pairs of protonated and unprotonated pyrrole rings. In effect, excitation increases the rectangular distortion that is already present in the ground state of free base porphyrins and which distinguishes them from more regular D_{4h} (square) metalloporphyrins. The further distortion causes modes that in the more regular systems involve all four of the pyrrole rings to become increasingly localized on just the protonated or unprotonated pyrroles. More generally, the success of the DFT calculations at this level of theory in predicting frequency shifts on excitation for an extensive series of isotopomers clearly validates the approach. Interpretation of the resonance Raman spectra of the excited states of other tetrapyrroles using DFT calculations is therefore viable, even for systems such as β substituted porphyrins and metalloporphyrins, where much less extensive isotope data are available to aid band assignments.

Introduction

Resonance Raman spectroscopy is well-established as an effective technique for the structural characterization of porphyrins and porphyrin-related materials in their electronic ground state (S_0) while time-resolved resonance Raman (TR^3) spectroscopy is used to great effect for probing the structure of transient species. It was first applied to the excited state of porphyrins in 1989,[1] and since that time there have been several studies of the excited singlet (S_1) and/or triplet (T_1) states of some of the main exemplars of free base and closed-shell metalloporphyrins such as OEP,[2−4] ZnTPP,[1,5,6] ZnOEP,[7−9] and H_2TPP.[4,6,10−12] It is the excited states of these general classes of porphyrins, rather than open-shell metalloporphyrins, that are predominant in the use of porphyrins as excited state reagents in studies of, for example, excited state electron transfer or in the use of porphyrins as sensitizers for photodynamic therapy. There is thus a clear need to understand the electronic structure, as well as the photophysical properties, of these compounds in as much detail as possible. Moreover, the first indications that the orbital character of the excited states can have a direct bearing on their reactivity have begun to emerge.[13]

We have previously published extensive TR^3 investigations on the S_0, S_1, and T_1 states of natural isotopic abundance (na) H_2TPP along with several of its isotopomers; see Figure 1 for the nomenclature of the isotopomers investigated.[10,11,14] Even though the spectra obtained were complex, containing numerous overlapping bands, several bands in the spectra were assigned by using expected shifts on isotopic substitution and/or excitation. There is a need for well-established assignments because, if we are to use the changes in vibrational frequency to understand the structural changes which accompany excitation, the assignments must be reliable, not least because the number of bands which give information useful for this procedure is small. In an effort not only to confirm the band assignments

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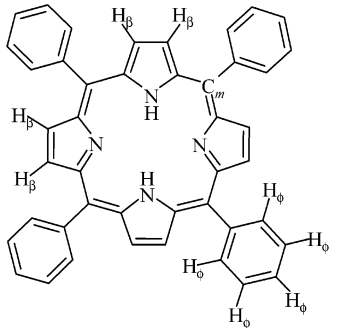

	H_N	H_β	H_ϕ	C_m
na	H	H	H	$^{12}C_4$
d_2	D	H	H	$^{12}C_4$
d_8	H	D	H	$^{12}C_4$
d_{10}	D	D	H	$^{12}C_4$
d_{20}	H	H	D	$^{12}C_4$
d_{22}	D	H	D	$^{12}C_4$
$^{13}C_4$	H	H	H	$^{13}C_4$

Figure 1. Nomenclature of the isotopomers of H_2TPP used here.

made previously but also to extend the work to bands whose assignment had been unclear, we have carried out density functional theory (DFT) calculations on both the ground and excited triplet states of H_2TPP for the na, d_2, d_8, d_{10}, d_{20}, d_{22}, and $^{13}C_4$ isotopomers.

It is now established that a DFT approach to the calculation of the vibrational frequencies using gradient corrected functionals can perform quite satisfactorily on molecules of moderate size.[15−21] Although the resulting vibrational frequencies tend to be higher than those observed experimentally, they are closer to the experimental frequencies than those calculated by semiempirical and Hartree−Fock methods. The remaining overestimation of the vibrational frequencies is mainly due to neglect of anharmonicity, together with incomplete basis sets. One approach to this problem is to use DFT-SQM methods in which the calculated force constants for various bond types are scaled by standard amounts and then used to generate vibrational modes whose position is consistent with experiment.[22−24] An alternative method, which is more straightforward to implement, is to use a single scaling factor for all the vibrational modes,[25−34]and this is the method used here. Similarly, although it has been shown that the intensities of resonance Raman bands can be calculated for porphyrins,[23] for our purposes we have simply used the well-established argument that Soret-excited resonance Raman spectra of porphyrins are completely dominated by totally symmetric (A) vibrational modes and we should therefore assign observed bands with calculated A modes only.

Experimental Section

The density functional calculations were performed in *Gaussian 98* using the hybrid B3-LYP functional and the 6-31G(d) basis set.[35−37] For these calculations on H_2TPP, a modified GDIIS algorithm was used instead of the default rational function optimization (RFO) because the latter did not reach a stationary point under the "tight convergence" conditions used throughout this work. The standard method for calculating Raman intensities in *Gaussian 98* ("freq=Raman" keyword), which calculates intensities for plane-polarized excitation of isotropic samples, was used. All calculated frequencies were scaled by a factor of 0.973. Orbital population analyses were carried out using the pop=reg keyword.

Results and Discussion

Despite the fact that H_2TPP is a relatively large molecule and does not possess the fourfold symmetry of many metalloporphyrins, it was possible to carry out calculations using the reasonably large 6-31G(d) basis set in combination with the B3LYP functional. This method is now well-established as a useful compromise between speed and accuracy in the calculation of the vibrational spectra of medium sized organic molecules. We have previously validated the use of this level of theory, combined with a single scaling factor, rather than a full SQM treatment,[24] for vibrational frequency calculations on porphyrins using the simple model free base porphine (FBP) and several of its isotopomers (d_2, d_4, d_8, and d_{12}).[20] This was a simple way to give an indication of the accuracy that we could expect from this basis set because the resulting vibrational frequencies could be compared to experimental values[38] and to previous calculations that had employed much larger 6-31G(df,p)(5d,7f)[39] basis sets and/or SQM methods.[40]

The experimental resonance Raman spectra for ground state (S_0) na H_2TPP and its d_2, d_8, d_{10}, d_{20}, d_{22}, and $^{13}C_4$ isotopomers were published previously[11] along with the corresponding triplet state (T_1) data. In subsequent work on the excited singlet states of these isotopomers,[14] some additional ground state bands were assigned. Table 1 compares the observed vibrational frequencies taken from refs 11 and 14 with the scaled frequencies from our calculations. For the sake of brevity, we have not included in Table 1 any calculated bands for which we have no experimental data, but a fuller listing is available in the Supporting Information.

Table 1 shows that, in general, the agreement between experimental and calculated (scaled with a single factor of 0.973) band positions for the na isotopomer is very acceptable (rms = 9.9 cm^{-1}). The shifts on isotopic substitution are often of the same order as this rms error, but it is still possible to calculate them with acceptable accuracy because the cancellation of errors in the calculations means that the errors in the calculated isotope shifts are much smaller than those in the absolute positions. For example, Figure 2 compares the observed and calculated isotope shifts for ν_1 and ν_4, and it is clear that despite the fact that the majority of the shifts are <10 cm^{-1} the calculations do reproduce the experimental values.

The combination of reasonably accurate calculated band positions and excellent calculated isotope shifts means that any ambiguities or uncertainties in previous band assignments can be eliminated. For example, a band that was previously observed in the S_0 spectra at 1075 cm^{-1}, but not assigned, we can now attribute to two overlapping modes, ν_9 and ν_{17}, which are calculated to lie within 5 cm^{-1} of each other. These symmetric $C_\beta H$ deformations differ only in their phasing and are sensitive only to d_8 and d_{10} isotopic substitution, where they are calculated to move by >300 cm^{-1} (which is out of the spectral window of the experiments). Similarly, the calculations confirm our original assignment of the band observed at 1552 cm^{-1} as ν_{10}. Although it had been suggested by Verma et al.[41] that this band should be reassigned as ν_{19}, the fact that the only mode of the correct (*A*) symmetry which is calculated to lie near the experimentally determined position is ν_{10} (as confirmed through visualization of the mode) makes our assignment of the band as ν_{10} secure. Finally, visualization of the pair of modes calculated at 961 and 1001 cm^{-1}, which are pyrrole breathing modes, shows that, to be consistent with the standard nomenclature, the lower lying mode in which all four rings are in-phase should be labeled ν_6 while in the higher lying mode the protonated and unprotonated rings breathe with opposite phase and so should be labeled ν_{15}. This is the opposite of previous labeling[10] but is preferred because although both modes have the same (*A*) symmetry in our D_2 calculations (or even in D_{2h} symmetry), in the idealized D_{4h} symmetry used to establish most of the nomenclature ν_6 and ν_{15} have different symmetry and are A_{1g} and B_{1g}, respectively.

TABLE 1: Observed Positions of the Isotopomers of Ground State H_2TPP Taken from Ref 11[a] or Ref 14[b,c]

	d_0		d_2		d_8		d_{10}		d_{20}		d_{22}		$^{13}C_4$	
mode	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
ν_6	963[a]	961	959[a]	957	957[a]	953	953[a]	949	965[a]	957	962[a]	953	959[a]	957
ν_{15}	1003[a]	1001	998[a]	993	998[a]	989	994[a]	983	1001[a]	999	994[a]	991	999[a]	996
ν_1	1238[a]	1226	1236[a]	1225	1235[a]	1224	1235[a]	1223	1184[a]	1175	1182[a]	1174	1230[a]	1218
ν_{12}	1296[a]	1303	1294[a]	1302	1295[a]	1301	1293[a]	1300	1296[a]	1302	1291[a]	1301	1295[a]	1303
ν_4	1362[a]	1359	1358[a]	1353	1351[a]	1350	1352[a]	1343	1360[a]	1358	1353[a]	1351	1358[a]	1359
ν_{11}	1502[a]	1515	1501[a]	1515	1461[a]	1474	1461[a]	1474	1501[a]	1515	1499[a]	1514	1493[a]	1513
ν_{10}	1552[b]	1549	1552[b]	1549	1554[b]	1535	1552[b]	1546	1552[b]	1544	1551[b]	1544	1530[b]	1525
ν_2	1555[a]	1567	1555[a]	1566	1537[a]	1546	1535[a]	1535	1556[a]	1567	1553[a]	1566	1547[a]	1563
ϕ_4	1600[a]	1614	1604[a]	1614	1603[a]	1614	1602[a]	1614	1551[b]	1579	1551[b]	1579	1602[a]	1614

[c] There were minor differences in band position in refs 11 and 14, but for the purposes of this paper, the key parameters are the shifts on excitation to the triplet state. So values for the ground state obtained along with the triplet values are preferred here. Only those bands not originally assigned are taken from ref 14.

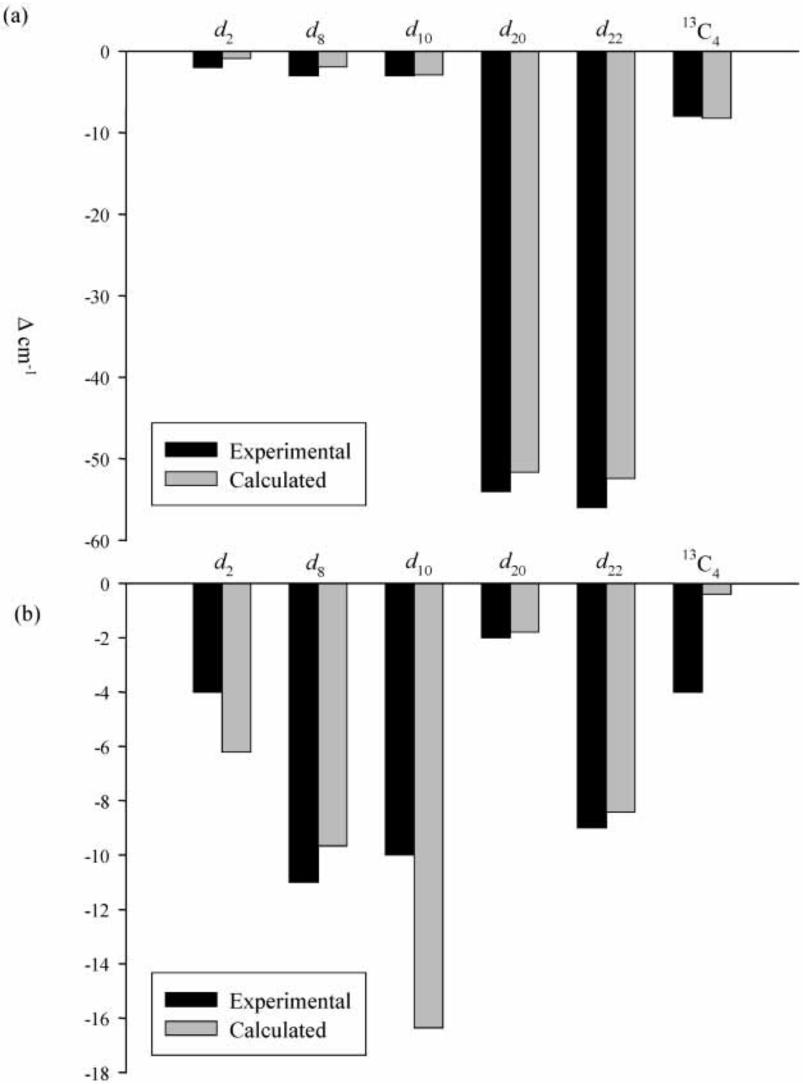

Figure 2. Comparison of ground state experimental and calculated shifts on isotopic substitution for (a) ν_1 and (b) ν_4.

The shifts of the vibrational modes of porphyrins from their ground state positions on electronic excitation are normally interpreted in terms of Gouterman's four orbital (two HOMOs and two LUMOs) model.[42] In this model, porphyrins with idealized D_{4h} symmetry (e.g. idealized metalloporphyrins) have an accidentally near-degenerate a_{1u}, a_{2u} HOMO pair while the LUMOs are a strictly degenerate e_g pair. For singlet excited states, excitation from either of these HOMOs to the LUMOs gives two configurations of similar energy and the same symmetry, which will mix through configuration interaction to give two states, one higher in energy and one lower. This accounts for the strong (Soret) and weak (Q) UV/vis absorption bands of D_{4h} porphyrins. For the triplet state, the situation is much less complex in that the excitation can be modeled as a simple, one-electron promotion between a lower and higher-lying orbital. The model is very similar for H_2TPP, which is normally treated as having an idealized D_{2h} symmetry; that is, the phenyl substituents are treated as points or as being perpendicular to the plane. In D_{2h} H_2TPP the lowering of symmetry lifts the degeneracy of the e_g pair and any one of

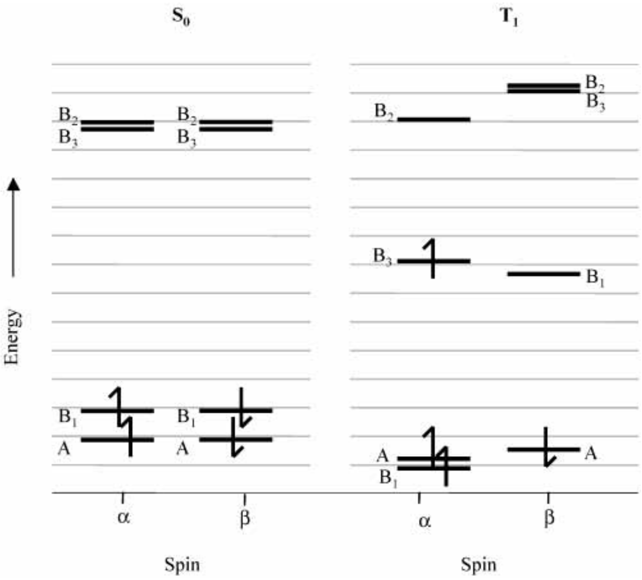

Figure 3. Energies and populations of the frontier orbitals of H_2TPP in the ground (S_0) and lowest-lying triplet (T_1) states.

four possible one-electron transitions from the a_u and b_{1u} HOMOs to the b_{2g}, b_{3g} LUMO pair can now give a low-lying triplet.

Our calculations were on the full H_2TPP molecule in which the phenyl rings are tilted with respect to the porphyrin core; therefore, the molecule has a more realistic D_2 symmetry (rather than the idealized D_{2h} of a free base porphyrin) and there is no mirror plane in the porphyrin core. In this symmetry, the HOMOs are a and b_1 and the LUMOs are b_2 and b_3 but they are effectively equivalent to the orbitals that are seen in the idealized D_{2h} and D_{4h} geometries, with the same patterns of electron density and similarity in energy of the two HOMOs and of the two LUMOs. The DFT calculations give the b_1 orbital as the HOMO and the a as the HOMO-1 (relative energies of the eigenvalues: −0.1810 and −0.1912 hartrees, respectively). The LUMO and LUMO+1 are near-degenerate with the b_3 orbital lying slightly below the b_2 (relative energies of the eigenvalues: −0.0806 and −0.0803 hartrees, respectively).

The most important factor in determining the electronic structure of the lowest-lying triplet state is which two of the four orbitals (i.e. HOMO and LUMO pairs) are involved in the excitation. The DFT calculations predict that the lowest energy triplet excited state is one in which electron promotion is from the b_1 HOMO to the b_3 LUMO, since this state has a singly occupied b_1 orbital, a doubly occupied a orbital, and a singly occupied b_3 orbital (relative energies of the eigenvalues: −0.2013, −0.1979, −0.1947, and −0.1288 hartrees, respectively), as shown in Figure 3. Previous semiempirical calculations[6] also found that the electron promotion is from the b_1 HOMO to the b_3 LUMO; indeed, the changes in bond length predicted by both methods are similar since the form of the calculated orbitals is very similar using either approach. However, because the semiempirical method does not give good vibrational frequencies, it was not possible to translate these calculated changes in bond length directly to changes in vibrational frequency. For this reason, in earlier studies, we were forced to look for consistency between observed shifts and the changes in bonding that would arise from promotion of electrons between different orbitals. Since the expected changes were so dramatically different for different excitations (e.g. $b_1 \rightarrow b_3$ gives decreased bond order in the $C_\beta{-}C_\beta$ bonds of the protonated pyrrole rings but $b_1 \rightarrow b_2$ excitation gives the opposite change), it was possible to distinguish between different possible candidates but not to make any quantitative analysis.

TABLE 2: Observed and Calculated Band Positions of S_0 and T_1 State H_2TPP

	na S_0		na T_1		$T_1 - S_0$	
mode	obs/cm^{-1}	calc/cm^{-1}	obs/cm^{-1}	calc/cm^{-1}	obs	calc
ν_6	963	961	959	954	−4.0	−7.4
ν_{15}	1003	1001	1018	1020	15.0	19.9
ν_1	1238	1226	1233	1221	−5.0	−5.4
ν_{12}	1296	1303	1261	1264	−35.0	−39.0
ν_4	1362	1359	1369	1388	7.0	29.1
ν_{11}	1502	1515	1500	1476	−2.0	−39.7
ν_{10}	1552	1549	1530	1534	−22.0	−14.8
ν_2	1555	1567	1540	1562	−15.0	−5.0
ϕ_4	1600	1614	1600	1612	0.0	−2.4

The main advantage of using DFT rather than semiempirical methods is that with DFT reasonably accurate vibrational frequencies of the ground and excited states of all the isotopomers of interest can be calculated directly. These data can then be used to make secure assignments because not only can the predicted shifts on excitation of each band from its known ground state position (Δ_{S-T}) be compared to the experimental data but so also can the pattern of isotope shifts in the excited state. Table 2 lists the positions of bands assigned for triplet na H_2TPP (which largely agree with those previously published), along with the corresponding ground state bands, while Table 3 gives observed and calculated isotope shifts used to verify the assignments.

Some of the bands are barely perturbed by excitation to T_1. For example, the highest cm^{-1} band is ϕ_4, which is a vibration of the phenyl substituents. Δ_{S-T} is predicted to be just −2 cm^{-1} in the na compound; the observed shift is 0 cm^{-1}. Confirmation of the assignment is provided by the large isotope shifts in the d_{20} and d_{22} isotopomers in both the S_0 and T_1 states (S_0: obs, −49 cm^{-1}; calc, −35 cm^{-1}. T_1: obs, −38 cm^{-1}; calc, −36 cm^{-1}). Similarly, ν_1 (C_m-phenyl) is barely perturbed on excitation (Δ_{S-T}: calc, −5 cm^{-1}; obs, −5 cm^{-1}); again, for this mode, isotopic substitution of the porphyrin core has little effect on the frequency but large shifts to lower cm^{-1} occur on d_{20} and d_{22} substitution where the phenyl rings have been deuterated.

Although some of the bands, such as those discussed above, barely move on excitation and are therefore easy to identify in the excited state spectra, others do shift significantly. The direction of the shift will depend on the orbitals involved in the excitation (as discussed above), so if the correct orbital parentage is used in the excited state calculations, then the predicted Raman shifts on excitation should match those observed. Of course, this will only be the case if the cancellation of errors that allowed small ground state isotope shifts to be determined with better accuracy than absolute band positions also applies to the small shifts of bands between the ground and excited states. The phenyl ring modes already discussed are effectively unchanged on excitation and so do not allow us to test if error cancellation does occur. However, the porphyrin core vibrations are certainly changed on excitation and therefore provide a more rigorous test both that the calculations have predicted the correct orbital occupancy and that the expected error cancellation in the frequency shift between the states does occur.

The most obvious mode to begin with is ν_2, which is predominantly a $C_\beta{-}C_\beta$ stretching mode. The calculations show that $b_1 \rightarrow b_3$ excitation will give an overall decrease in bond order of the $C_\beta{-}C_\beta$ bonds on the protonated rings (bond length increases by 0.027 Å, Table 4) but little change in the equivalent

TABLE 3: Observed and Calculated Isotope Shifts of S_0 and T_1 State H_2TPP

	ground state (S_0)											
	d_2-d_0		d_8-d_0		$d_{10}-d_0$		$d_{20}-d_0$		$d_{22}-d_0$		$^{13}C_4-d_0$	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
ν_6	−4	−5	−6	−8	−10	−13	2	−4	−1	−8	−4	−4
ν_{15}	−5	−8	−5	−12	−9	−18	−2	−2	−9	−10	−4	−5
ν_1	−2	−1	−3	−2	−3	−3	−54	−52	−56	−52	−8	−8
ν_{12}	−2	−2	−1	−2	−3	−3	0	−1	−5	−2	−1	−1
ν_4	−4	−6	−11	−10	−10	−16	−2	−2	−9	−8	−4	0
ν_{11}	−1	0	−41	−41	−41	−42	−1	−1	−3	−1	−9	−2
ν_{10}	0	0	2	−14	0	−3	0	−5	−1	−5	−22	−24
ν_2	0	0	−18	−20	−20	−32	1	0	−2	0	−8	−3
ϕ_4	4	0	3	0	2	0	−49	−35	−49	−35	2	0

	triplet state (T_1)											
	d_2-d_0		d_8-d_0		$d_{10}-d_0$		$d_{20}-d_0$		$d_{22}-d_0$		$^{13}C_4-d_0$	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
ν_6	−11	−3	−5	−7	−8	−11	−1	−3	−5	−9	−5	−5
ν_{15}	−14	−11	−12	−10	−17	−21	−5	−3	−15	−13	−7	−4
ν_1	−1	−1	−1	−3	−2	−3	−51	−49	−51	−49	−7	−7
ν_{12}	0	−2	−4	−3	−7	−5	−9	−1	−5	−3	−8	−1
ν_4	−9	−5	−7	−3	−12	−8	3	8	−16	6	−13	−2
ν_{11}	−9	−1	−21	−23	−41	−25	−2	3	−14	1	−9	−5
ν_{10}		0		−1		−1		−4		−4		−22
ν_2	2	0	−31	−45	−31	−45	0	0	−2	0	−3	−1
ϕ_4	4	0	−1	0	0	0	−38	−36	−38	−36	−1	0

TABLE 4: Bond Lengths for Ground (S_0) State H_2TPP (Crystallographic and Calculated) Compared to Calculated Values for the Triplet (T_1) State[44]

H_2TPP bond[a]	X-ray/Å	calc S_0/Å	calc T_1/Å	$\Delta_{T_1-S_0}$
P-N−C_α	1.374	1.376	1.376	0.000
U-N−C_α	1.364	1.367	1.375	0.008
P-C_α−C_β	1.428	1.434	1.408	−0.026
U-C_α−C_β	1.455	1.460	1.463	0.003
P-C_β−C_β	1.355	1.369	1.396	0.027
U-C_β−C_β	1.347	1.354	1.351	−0.003
P-C_α−C_m	1.397	1.405	1.441	0.036
U-C_α−C_m	1.399	1.411	1.401	−0.010

[a] P = protonated rings; U = unprotonated rings.

bonds of the unprotonated rings. Since ν_2 involves stretching of the $C_\beta-C_\beta$ bonds on both the protonated and unprotonated rings, it would be expected to move to lower cm^{-1} on excitation. Indeed, the observed shift to lower cm^{-1} was one of the reasons that the triplet state was previously assigned as arising from $b_1 \rightarrow b_3$ excitation. In accordance with this orbital picture, the DFT calculations predict shifts to lower cm^{-1} of ν_2 on excitation for the na compound and the isotopomers that are consistent with the experimental data (see Table 5, which brings together the observed and calculated shifts on excitation for all the isotopomers).

It is notable that the magnitudes of the calculated Δ_{S-T} shifts of ν_2 differ dramatically between the isotopomers (Δ_{S-T}(calc): $d_0 = -5$ cm^{-1}, $d_8 = -30$ cm^{-1}) and that the experimental data reflect this pattern (Δ_{S-T}(calc): $d_0 = -15$ cm^{-1}, $d_8 = -26$ cm^{-1}). At first sight this is somewhat surprising since the Δ_{S-T} values are expected to reflect the changes in force constants due to promotion to the triplet state and these are the same irrespective of which isotopomer is under consideration. However, the calculations allow two different effects to be disentangled. First, in those isotopomers where substitution has little effect on the band position (d_2, d_{20}, d_{22}, $^{13}C_4$), the predicted Δ_{S-T} is a remarkably consistent 4 ± 1 cm^{-1}, this value primarily reflecting the reduced force constant of the $C_\beta-C_\beta$ bonds in the triplet state. In contrast, in the d_8 and d_{10} isotopomers Δ_{S-T} is predicted to be much larger (−30 and −18 cm^{-1}, respectively); the calculations show that in these isotopomers the large difference is not due to a reduction in the $C_\beta-C_\beta$ force constants per se but instead arises because the ν_2 frequencies of these isotopomers are sensitive to the change in the mode composition which occurs between the ground and triplet states. In S_0, the ν_2 vibration involves in-phase stretching of the $C_\beta-C_\beta$ bonds on both the protonated and unprotonated pyrrole rings; however, in T_1 it is confined mainly to $C_\beta-C_\beta$ stretching on the unprotonated rings (see Figure 4). This change in the composition of ν_2 is not accompanied by a large change in the frequency in the na isotopomer because the bonds involved are all of similar strength. However, it does mean that the isotope sensitivity of the mode becomes different in the two states; it is calculated to move −20 cm^{-1} on d_8 substitution in the S_0 state but more than twice this (−45 cm^{-1}) on d_8 substitution of T_1. Because of this difference in isotope sensitivity, the Δ_{S-T} values appear to be anomalously high for the d_8 and d_{10} isotopomers in comparison to the values for the other isotopomers.

The second set of bands that have been used to assign orbital parentage of T_1 are ν_6 and ν_{15}, which in S_0 are ring breathing modes involving in-phase and out-of-phase motions of both the unprotonated and protonated rings, with ν_{15} having slightly more protonated character and ν_6 more unprotonated character. However, in T_1 the motions become much more localized on either the protonated or unprotonated rings. This effect is reflected in the isotopomer data where the shifts on d_2 and d_{10} substitution (which of course change predominantly the protonated rings) are similar for both modes in the ground state but much larger for ν_{15} than for ν_6 in the triplet state.

The change in mode composition on excitation also helps to rationalize the different directions of the Δ_{S-T} shifts in ν_6 and ν_{15}. Inspection of the orbital pictures or bond length changes shows that $b_1 \rightarrow b_3$ excitation would be expected to give small changes in the N−C_α bond lengths in the unprotonated and protonated rings (+0.008 Å and 0.000 Å, respectively) and $C_\alpha-C_\beta$ (+0.003 Å) of the unprotonated rings but a significant increase in bond order in the $C_\alpha-C_\beta$ of the protonated rings (−0.026 Å). If both ν_6 and ν_{15} modes were simply in-phase or

TABLE 5: Observed and Calculated Shifts on Excitation (Δ_{S-T}) for All the H_2TPP Isotopomers in This Study

	d_0		d_2		d_8		d_{10}		d_{20}		d_{22}		$^{13}C_4$	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
ν_6	−4	−7	−11	−6	−3	−6	−2	−6	−7	−6	−8	−8	−5	−8
ν_{15}	15	20	10	17	12	21	11	16	16	19	13	16	16	21
ν_1	−5	−5	−4	−5	−3	−6	−4	−6	−2	−3	0	−2	−4	−4
ν_{12}	−35	−39	−33	−40	−38	−40	−39	−41	−44	−39	−35	−40	−42	−39
ν_4	7	29	6	30	15	36	9	37	16	39	4	44	2	28
ν_{11}	−2	−40	−9	−41	19	−22	−1	−23	−2	−37	−12	−38	−1	−42
ν_2	−15	−5	−11	−5	−26	−30	−24	−18	−14	−4	−13	−4	−8	−3
ϕ_4	0	−2	0	−2	−4	−2	−2	−2	11	−3	11	−3	−3	−2

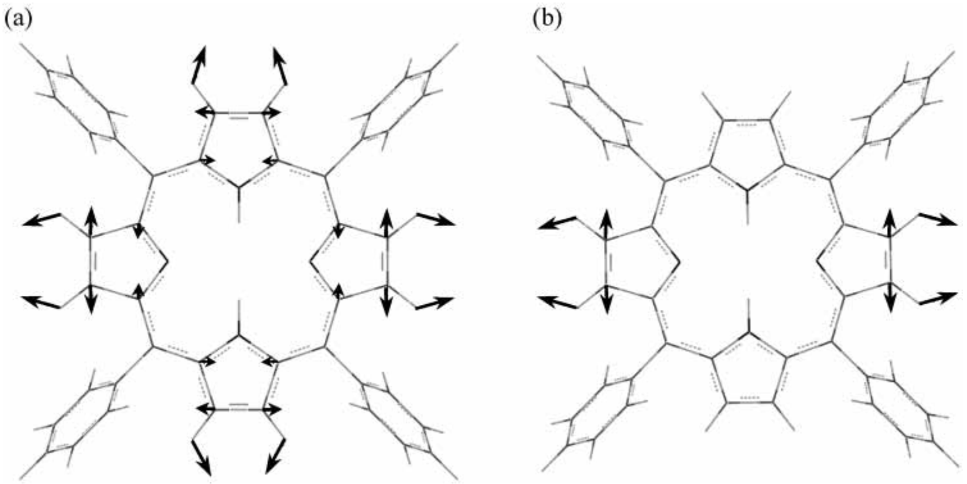

Figure 4. Calculated displacement vectors for ν_2 in the ground (a) and triplet (b) states. Note the increased localization of the modes onto the unprotonated rings in the triplet state.

out-of-phase motions of both the protonated and unprotonated rings, then Δ_{S-T} for both the modes might be expected to reflect the predominant change in bonding, which is an increase of bond order in the $C_\alpha-C_\beta$ of the protonated rings. In this case both modes might be expected to shift to higher cm^{-1} on excitation, but in fact only ν_{15} is observed to shift to higher cm^{-1} (+15 cm^{-1}) on excitation; ν_6 actually shifts -4 cm^{-1} lower. However, the calculations show that excitation to T_1 alters the modes so that ν_6 is more highly localized on the unprotonated rings while ν_{15} is on the protonated rings. This means that ν_{15} will be most affected by the increase in the $C_\alpha-C_\beta$ bonding in the protonated rings and will therefore shift to higher cm^{-1} on excitation while ν_6 will be affected by the much smaller decreases in bonding character of the $C_\alpha-C_\beta$ and the $N-C_\alpha$ bonds in the excited state and shift to slightly lower cm^{-1}. The predicted Δ_{S-T} shifts of +20 and -7 cm^{-1} for ν_{15} and ν_6, respectively, are consistent with these arguments and also agree well with the experimental (+15, -4 cm^{-1}) values.

Several of the remaining bands in the T_1 spectra have been assigned (or reassigned) in light of the calculations. For example, assignment of ν_{12} (a pyrrole half ring vibration) to the bands lying at 1296 and 1261 cm^{-1} in the ground and triplet states, respectively, can be confirmed since the calculations give it at 1303 and 1264 cm^{-1}. This band is very insensitive to isotopic substitution at any of the positions used in this study, but it does show one of the largest Δ_{S-T} shifts: > -35 cm^{-1}.

Although the agreement between calculated and observed Δ_{S-T} shifts is acceptable for most of the modes in the various isotopomers, there are some cases where the discrepancies are anomalously large. In the case of ν_4, the generally poor fit (e.g. Δ_{S-T} in na: obs, 11 cm^{-1}; calc, 29 cm^{-1}) is likely to be simply due to the problem of locating the position of the band in the excited state spectra which display strong broad features in most isotopomers (see Figure 5[43]).

The only band that we need to reassign in the triplet state is ν_{11}, which is the out-of-phase counterpart of ν_2 and lies at 1502 cm^{-1} in the ground state. Previously, a band in the T_1 spectrum of na H_2TPP at 1500 cm^{-1} was assigned as ν_{11}, but this would be a Δ_{S-T} shift of -2 cm^{-1}, quite different from the calculated -40 cm^{-1} value. Since the calculated Δ_{S-T} shifts for the other modes have been shown to be reliable, it seems unlikely that they are in error for just this particular mode, so we interpret the fact that there is no band in the T_1 spectrum at the calculated (1460 cm^{-1}) position to imply that ν_{11} is too weak to observe in the triplet. However, there is clearly a distinct band at 1500 cm^{-1} in the triplet spectrum, and since it is not ν_{11}, we need to find an alternative assignment. The calculations show that ϕ_5, a phenyl ring mode, lies at this position in triplet na H_2TPP, so we can assign the band as ϕ_5, which presumably has gained intensity in the T_1 state in much the same way as ϕ_4, which is also a phenyl ring that is relatively weak in the ground state but has significant intensity in the T_1 spectrum.

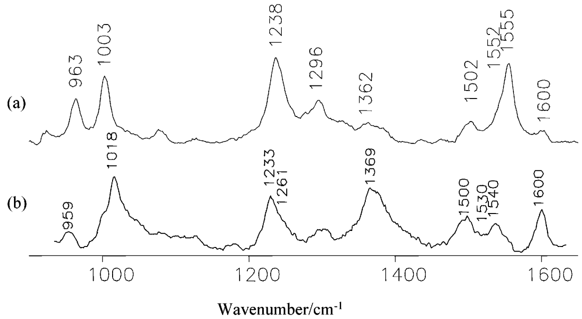

Figure 5. Illustrative resonance Raman spectra of S_0 (a) and T_1 (b) natural isotopic abundance H_2TPP.

Taken as a whole, the data show that although the changes in bonding on excitation of these porphyrins can be predicted simply by inspection of the orbitals involved, or more quantitatively through the changes in bond order on excitation, mapping these differences through shifts in band position in the Raman spectra is not straightforward because the excitation alters the mode compositions as well as the force constants. These effects are very apparent in the H_2TPP studied here. Even in the ground state, the modes of H_2TPP are different from those of D_{4h} porphyrins because there are two pairs of distinct (protonated and unprotonated) rings rather than four identical pyrroles, leading to modes which involve in-phase or out-of-phase vibrations of the pairs of pyrrole rings. These typically have more protonated or unprotonated character, rather than being equally distributed over all four equivalent rings as they are in D_{4h} systems. Importantly, the excitation from $b_1 \rightarrow b_3$ orbitals in H_2TPP accentuates this difference between the two pairs of pyrroles, in effect increasing the distortion from square to rectangular and causing further partitioning of the modes into those associated with each type of ring. The frequency shifts of the modes on excitation are thus a combination of changes in force constant and in mode composition, with some of the modes becoming more sensitive to isotopic substitution in the excited state than they were in the ground state and vice versa.

Conclusion

The DFT calculations at this level of theory (B3LYP 6-31G(d)) provide acceptably accurate vibrational frequencies for the ground state H_2TPP; the rms error (ca. 10 cm^{-1}) is similar to that found for other ground state porphyrins. There is much less published evidence that the same method will provide equally accurate results for the excited states of porphyrins, but if it can, then it will give a simple method for assigning excited state Raman spectra without the need to resort to studies of extensive series of isotopomers. In this work we have found that the calculations do give frequencies which are as good as those of the ground state and also provide predictions of frequency shifts on excitation which are more accurate than the absolute band positions because of cancellation of errors. The predicted shifts on excitation are typically small ($\leq$10's of cm^{-1}) in these molecules because the excitation is delocalized over the entire porphyrin ring system, but the calculations are sufficiently accurate to distinguish between the different patterns of small shifts that would be induced by different excited state orbital occupations. In this case, four bands move to lower cm^{-1} on excitation, two are essentially unchanged, and two move to higher cm^{-1}, a pattern that is accurately reproduced by the DFT calculations. Since there were spectra of a series of isotopomers, there was more data than would normally be available in excited state studies; this in turn gave apparent anomalies that would not normally be observed in studies of single isotopomers. Ultimately, these apparent anomalies were rationalized with the aid of the DFT calculations and were found to be due to subtle changes in mode composition on excitation that occurred in parallel with the changes in bond order. The fact that these subtle effects could be explained with the aid of the DFT calculations is a further validation of the general approach. This means that we can now adopt the same approach to band assignments and interpretation of the Raman spectra of the excited states of other porphyrins, such as β substituted porphyrins and metalloporphyrins, which display different shift patterns on excitation but where extensive isotopic data are unavailable.

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Supporting Information Available: Table of vibrational frequencies for ground state (S_0) na H_2TPP and its d_2, d_8, d_{10}, d_{20}, d_{22}, and $^{13}C_4$ isotopomers along with the corresponding triplet state (T_1) data. This material is available free of charge via the Internet at http://pubs.acs.org.

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