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Time-resolved resonance Raman study of 4-phenylpyridine

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Abstract

The triplet–triplet absorption spectrum of 4-phenylpyridine has been measured and shown to have a maximum at 365 nm with a lifetime of 1.5 μs. TR^3 data for this molecule in the triplet state indicates increasing planarity, relative to its 40° ground state geometry, reflected in the shift of the aromatic C=C vibrational frequency from 1612 cm^{-1} in the ground state to 1578 cm^{-1} in the triplet state. Potential energy surface calculations confirm the quasi-planar nature of the triplet state and the shortening of the inter-ring bond distance in going from the ground state to the lowest triplet. Normal mode calculations identify the specific A-mode vibration, which accounts for the observed enhanced resonance Raman band of the triplet. A single exponential fluorescence decay process is observed only in aqueous solutions, indicating a strongly hydrogen bonded system in the ground state, which facilitates the photoinduced proton transfer upon excitation into the excited singlet state. © 1997 Elsevier Science S.A.

Keywords: Time resolved resonance raman; Triplet–triplet absorption; Potential energy surface calculations; Triplet state geometry; 4-phenylpyridine

1. Introduction

The excited singlet state proton transfer to 4-phenylpyridine from water has been shown to account for its fluorescence ($\Phi_F = 0.20$), which is due to the increased basicity associated with aromatic nitrogen heterocyclics [1]. This molecule is interesting because of its dual character, i.e., its fluorescence is that of a substituted pyridine, while in the triplet state its phosphorescence is that of a substituted benzene with spectroscopic parameters resembling biphenyl. In contrast to the unstructured fluorescence associated with the excited state proton transfer, the phosphorescence shows a structured spectrum with a vibrational band spacing of ≈ 1450 cm^{-1}. Noteworthy, however, is the ≈5000 cm^{-1} shift to lower energies for its phosphorescence 0–0 band relative to other 4-substituted pyridine derivatives, which suggested a planar triplet state.

Semi-empirical CNDO/S calculations of this molecule indicate a $^3A_1$ lowest triplet state [1]. By comparison with biphenyl, which is non-planar in the ground state (D_2) and planar (D_{2h}) in the triplet state, the similarity in phosphorescence behavior for the two molecules suggested that 4-phenylpyridine may also be planar in the triplet state. With this indication of a geometrical change in going from the ground state to the lowest triplet state, we set out to provide independent evidence for this structural change in 4-phenylpyridine by using time-resolved resonance Raman (TR^3) spectroscopy, which is well suited for the investigation of the structure and dynamics of short lived molecular species.

The geometrical change of biphenyl from a twisted (40°) ground state to a planar triplet state has been investigated using Raman techniques, and is summarized up to 1987 by Hamaguchi [2]. In a TR^3 study in which the fourth harmonic (266 nm) of a Nd:YAG laser was used, Buntinx and Poizat [3], observed a ground state Raman band at 1606 cm^{-1}, which shifted to 1570 cm^{-1} in the planar triplet state. The normal mode in this range, which is characteristically the C=C region for a substituted benzene, is also known as the 8a mode in the Wilson notation. They observed the triplet–triplet absorption of biphenyl at 370 nm, which confirmed earlier experiments of Land [4]. The TR^3 study of biphenyl in the singlet state, employing 266 nm excitation, has been reported by Kato et al., [5] and more recently, the picosecond TR^3 study of *p*-terphenyl appeared with emphasis on the time dependent change of Raman band shapes [6].

In view of the low lying triplet state reported for 4-phenylpyridine, and the above geometrical implications, we initiated this study to locate the T–T absorption and carry out the TR^3 experiments of its triplet state. With the aim to supplement our interpretation of experimental data we also

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implemented VAMP calculations using the AM1 Hamiltonian to determine the potential energy surface as a function of torsional angle for the ground state, excited singlet, lowest triplet and protonated ground state. Normal coordinates for the ground and triplet state were also calculated.

2. Experimental section

2.1. Materials

Aldrich supplied 4-phenylpyridine was recrystallized from cyclohexane prior to use, and spectrograde methanol, ethanol, and acetonitrile were used as received after verifying that they did not contribute any impurity emissions. Millipore distilled water was used for aqueous solutions.

2.2. Apparatus and procedures

A 20 ns XeCl (308 nm) excimer laser operating at 10 Hz, together with a continuous analyzing source, was employed to determine the triplet–triplet absorption. The transient spectrum was captured at selected times with a cooled gated diode array system. In the transient Raman studies the pump wavelength was 308 nm, while a second XeCl excimer pumped dye laser operating at 370 nm, delayed by 500 ns, was employed as the probe beam. A concentration of 1.5×10^{-2} M 4-phenylpyridine in 3:1 water–methanol was used, and the Raman signal was captured by the backscattering method. A circulating solution of 4 cm depth was employed for transient absorption and a jet stream was used in the transient Raman experiment. The photodetection system comprised a cooled gated intensified diode array system with a 100 ns window, which was interfaced to a 486 microcomputer. The captured counts versus wavelength data were subsequently used to calculate the triplet absorption spectrum or the Raman spectrum. The transient Raman data were obtained with a double spectrograph employing 1200 lines mm^{-1} gratings. Non-resonant Raman spectra for the ground state in solution were obtained with 370 nm excitation from an excimer pumped dye laser, and at a resolution of 2 cm^{-1} using 514 nm excitation from a CW argon ion laser. Surface enhanced Raman spectra were recorded with a silver sol. Fluorescence spectra were recorded with a Perkin-Elmer LS-50 spectrofluorimeter and UV absorption spectra with a Perkin-Elmer Lambda 2 spectrophotometer. Fluorescence lifetime measurements were made at 308 nm with 5 ps excitation pulses from a frequency doubled rhodamine dye laser synchronously pumped by a mode-locked Nd:YAG laser, and employed photon counting detection.

Semi-empirical potential energy diagrams and normal coordinate calculations were completed with the VAMP quantum mechanical program [7], employing the AM1 Hamiltonian, and vibrational frequencies were scaled to 0.89.

3. Results

3.1. Transient absorption and Raman data

In order to proceed with the TR^3 we initially measured the triplet–triplet absorption of 4-phenylpyridine. Although the UV absorption of the ground state lies below 300 nm in organic solvents, we were able to shift it above 300 nm by dissolving the molecule at a concentration of 1.5×10^{-2} M in a 3:1 water–methanol mixture, where fluorescence is induced by an intermolecular photoinduced proton transfer from water. In this solvent system at the concentration employed the solution is sufficiently basic (pH = 7.1), contains more than 99% neutral molecules and 308 nm excitation can be used, which is not possible with biphenyl where studies have been reported with 266 nm excitation. Although it is difficult to exclude the possibility that some protonated molecules may absorb since the extinction coefficient ratio $\epsilon_{308}(\mathrm{4PhPyH^+})/\epsilon_{308}(\mathrm{4PhPy}) \approx 8\times10^2$, the microsecond time domain of the observed triplet state ensures that the measured transient is that of the neutral molecule. In the case of 4-phenylpyridine hydrogen bonding with water shifts the UV absorption to longer wavelength, thereby making it possible to excite this molecule with a XeCl excimer laser.

In Fig. 1 we see the T–T absorption spectrum of 4-phenylpyridine in a 3:1 water–methanol solution, measured at 1.0, 2.0 and 5.0 μs. The maximum appears at 365 nm and the lifetime is estimated to be 1.5 μs. This transient absorption peak is similar to the known T–T absorption spectrum of biphenyl [3,4]. At such long delay times the molecules in the triplet state will be deprotonated.

The non-resonant ground state Raman spectrum of 4-phenylpyridine measured under a variety of conditions with the 514.5 nm line of an argon ion laser is given in Fig. 2. In a 3:1 water–methanol solution two bands are seen at 1293 and 1612 cm^{-1}, with the latter being the aromatic C=C band. The depolarization ratio for these bands, measured with 370 nm excitation, are as follows: 0.33 for the former and 0.29 for the latter, which indicate that they are symmetric modes that should exhibit resonance enhancement. Noteworthy is that the Raman spectrum of the solid in the 1600 cm^{-1} region shows three resolved bands, in agreement with the 1590, 1602 and 1614 cm^{-1} values reported by Strekas et al. [8]. using 457.9 nm excitation. While water induces fluorescence via an excited state proton transfer, it has the disadvantage that the high frequency modes at ≈ 3000 cm^{-1}, which are usually weak, could not be observed. The 1293 cm^{-1} band was observed in the following fluid solutions: water–methanol, acidic solutions, SERS of the neutral and protonated molecule in an Ag sol; however, it appears to be shifted by 20 cm^{-1} to a lower frequency in the solid state. Noteworthy is that upon protonation the 1612 cm^{-1} band in the ground state is split into two peaks that appear at 1590 and 1635 cm^{-1}, with the latter band assigned to the pyridinium form.

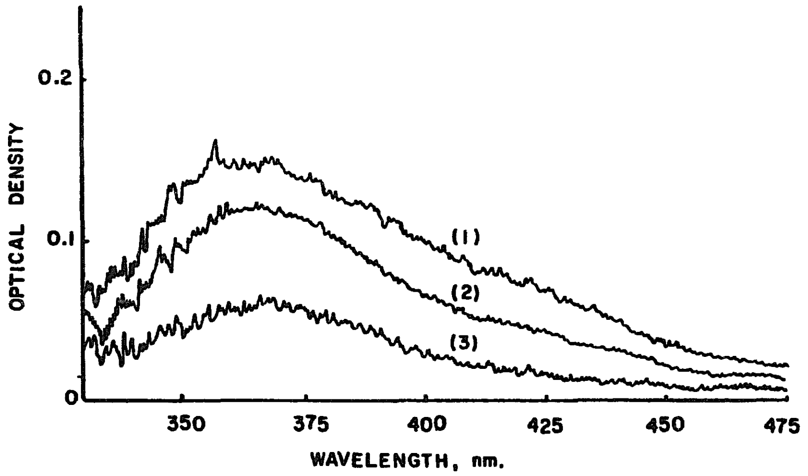

Fig. 1. Triplet–triplet absorption spectrum of 4-phenylpyridine in a 3:1 water–methanol solution measured with a XeCl excimer laser. The delay times for the spectra are: (1) 1.0 μs, (2) 2.0 μs and (3) 5.0 μs.

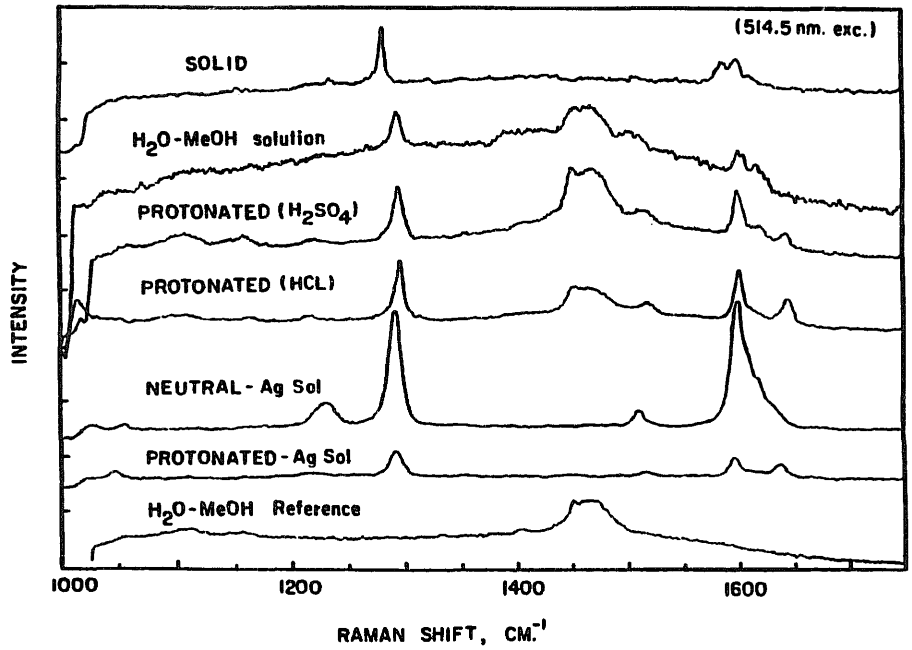

Fig. 2. The Raman spectra for 4-phenylpyridine measured in various media (514.5 nm excitation).

The fluorescence lifetime of 4-phenylpyridine measured in different solvents was observed to give a single exponential decay only for aqueous solutions and its lifetime is 5.30 ± 0.02 ns, which reflects the hydrogen bonding to the nitrogen lone pair on the pyridine ring. Saturating the solution with argon had no effect on the measured lifetime. Noteworthy is that this lifetime is considerably shorter than the 16.0 ns lifetime reported for biphenyl in cyclohexane due to enhanced intersystem crossing associated with n,π–π,π interaction [9]. In acetonitrile the fluorescence exhibited a tri-exponential decay with the following lifetimes: 0.06, 1.3, and 6.3 ns, with the middle component dominant.

The TR^3 experiments with 4-phenylpyridine in 3:1 water–methanol were performed with a 308 nm pump and a 370 nm excimer pumped dye laser as probe laser. The transient Raman of the triplet state is seen in Fig. 3, where it is seen that the C=C Raman band has shifted to 1578 cm^{-1}, clearly indicating a geometrical change relative to its ground state configuration. A second weaker band appears at 1490 cm^{-1}, after subtracting the methanol band at 1450 cm^{-1}. A delay of 500 ns was used between the laser beams to focus on the deprotonated triplet, and the gated detection window was 100 ns.

With the aim of correlating the theoretical and experimental vibrations of 4-phenylpyridine the FTIR spectrum of the solid in a KBr pellet was also measured as a reference. The measured spectrum exhibits four major peaks appearing in the region between 1300–1600 cm^{-1}: 1588, 1544, 1483 and 1410 cm^{-1}.

3.2. Semi-empirical calculations (AM1)

The potential energy surface calculations of the ground and triplet state were performed to determine their optimal

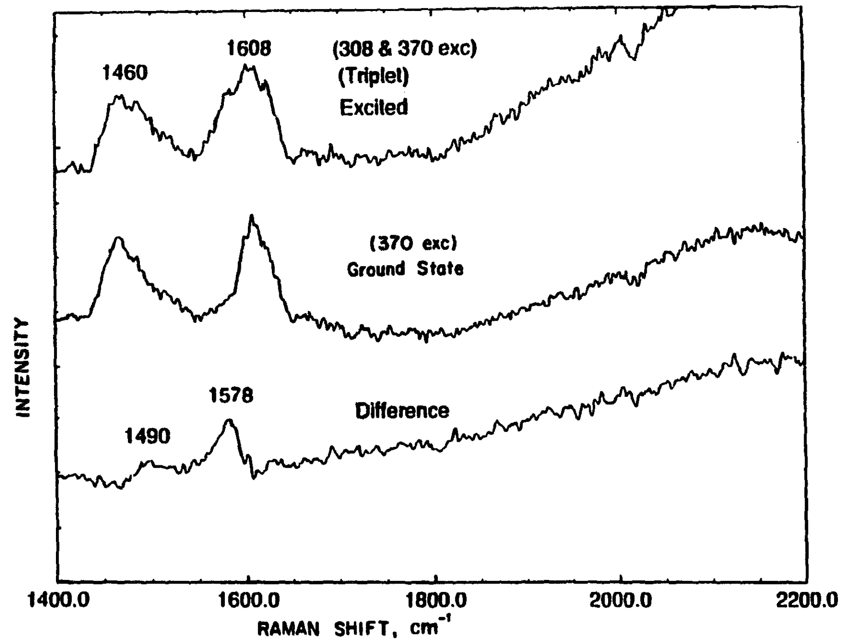

Fig. 3. Transient Raman spectrum for the triplet state of 4-phenylpyridine in a 3:1 water-methanol solution obtained with a XeCl pump laser and an excimer pumped dye laser operating at 370 nm. The difference spectrum shows that the C=C vibrational mode which appears at 1612 cm^{-1} in the ground state is shifted to 1578 cm^{-1} in the triplet state.

geometries. A summary for the ground state configuration is presented in Fig. 4, where it is seen that a 40° configuration with an inter-ring C–C bond distance of 1.46 Å is favored. The torsional energy for a planar state is 1.8 kcal mol^{-1}. The triplet state potential energy surface as a function of torsional angle is also presented in Fig. 4, where an angle of 26.5° and an inter-ring C–C distance of 1.43 Å is predicted. The energy barrier for a planar configuration decreases to 0.8 kcal mol^{-1} and is relatively flat between 0 and 26°. The energy barrier increases rapidly between 85 and 90° due to decoupling of the two aromatic rings. The potential energy value at 90° is 121 kcal mol^{-1}. In the excited singlet state VAMP calculations predict an equilibrium geometry with an inter-ring C–C bond distance of 1.40 Å and a torsional angle of 16.3°.

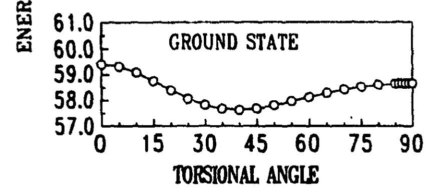

Fig. 4. Torsional energy vs. twist angle plot for 4-phenylpyridine in (1) ground state, (2) triplet state and (3) protonated ground state.

In order to explore the influence of the proton on the ground state torsional energy, calculations were also done for protonated 4-phenylpyridine, which are included in Fig. 4. These calculations indicate that upon protonation the 40° torsional angle of the neutral molecule decreases to 30° and has a torsional energy barrier of 1.0 kcal mol^{-1}.

Calculations of the vibrational modes of 4-phenylpyridine were carried out for the ground and triplet states, which are helpful in assigning the observed Raman bands. In the ground state two vibrations of A-symmetry are predicted at 1587 and 1599 cm^{-1}, while in the triplet they are predicted to be at 1572 and 1663 cm^{-1} as seen in Fig. 5. Noteworthy is that the two A – symmetry vibrations in the triplet state indicate ring breathing modes with vector displacements localized on either the phenyl or pyridyl ring.

4. Discussion

From the above results it is evident that 4-phenylpyridine undergoes a geometrical change reducing the torsional angle in the triplet state, relative to a 40° torsional angle in the ground state. A similar behavior has been reported for biphenyl in the triplet state [3]. Further support comes from the AM1 theoretical calculations, which indicate a torsional energy barrier of 1.8 kcal mol^{-1} in the ground state decreasing to 0.8 kcal mol^{-1} in the triplet state.

It is interesting to note that the vibrational modes involved in the triplet state (see Fig. 5) reflect vector displacements on either the pyridine ring or the phenyl ring, which is consistent with the change from a heterocyclic molecule in the ground and excited singlet state to that of a substituted

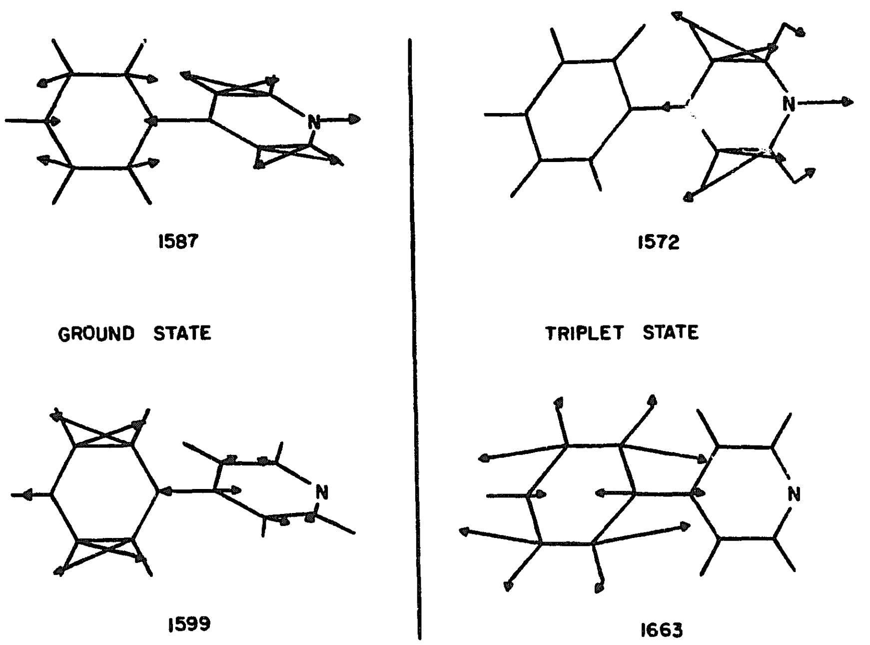

Fig. 5. Calculated symmetric vibrational frequencies and vector displacements associated with the 1600 cm^{-1} region for the ground state and triplet state of 4-phenylpyridine.

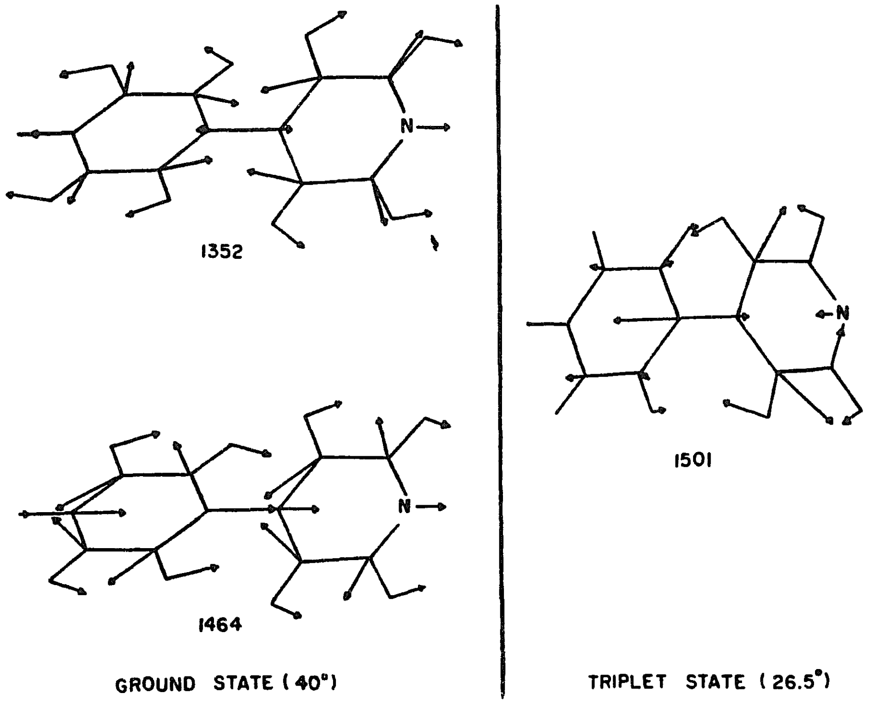

Fig. 6. Calculated symmetric vibrational frequencies and vector displacements associated with the 1450 cm^{-1} region for the ground and triplet state of 4-phenylpyridine.

benzene in the triplet state. The shift in frequency from 1612 cm^{-1} in the ground state to 1578 cm^{-1} in the triplet state is similar to that observed in biphenyl and is consistent with the increased planarity of 4-phenylpyridine in the triplet state. The lower frequency band in the Raman of the triplet correlates well with the calculated value of 1572 cm^{-1} shown in Fig. 5. In fact, our normal coordinate calculations show that this frequency is sensitive to the torsional angle between the two aromatic rings and shifts 44 cm^{-1} to lower frequency when decreasing the torsional angle in the range 70°–0°. Although the optimum geometry predicted (C_2) for the triplet state is 26.5°, the potential energy diagram is relatively flat between 0 and 26.5° thereby making it difficult to exclude a C_{2v} triplet state. Normal coordinate calculations for the triplet predict four totally symmetric, in-plane modes in the region between 1300 and 1700 cm^{-1} (1396, 1501, 1572 and 1663 cm^{-1}), with the second band, shown in Fig. 6, assigned to the symmetric in-plane bending mode that is observed at

1490 cm^{-1} in the transient resonance enhanced Raman experiment, and which appears at 1476 cm^{-1} in biphenyl. The calculated triplet vibration at 1572 cm^{-1}, shown in Fig. 5, represents an in-plane aromatic C=C ring breathing vibration and correlates with the symmetric vibration observed at 1578 cm^{-1} in the TR^3 experiment.

The ground state Raman band seen at 1612 cm^{-1} correlates well with the calculated frequency of 1599 cm^{-1} shown in Fig. 5., which also shows some sensitivity to the torsional angle between the two rings. In contrast the calculated frequency at 1587 cm^{-1} does not show this dependence.

The 1293 cm^{-1} band seen in the non-resonant ground state Raman spectrum correlates well with the symmetric in-plane H-bending mode predicted to be at 1314 cm^{-1} in the 40° configuration of the ground state. The 1483 cm^{-1} band seen in the FTIR spectrum of 4-phenylpyridine correlates well with the symmetric vibrational band seen in its phosphorescence spectrum [1], and also with the calculated symmetric mode at 1464 cm^{-1}, which is shown in Fig. 6.

Since the fluorescence of 4-phenylpyridine in water is due to an inter molecular excited state proton transfer, the issue of protonation in the triplet state should also be addressed. It has long been recognized that the pK_a^* of the triplet state is similar to that of the ground state; therefore we consider it reasonable to conclude that deprotonation occurs during intersystem crossing. In the singlet excited state, the pK_a^* is 9.0, relative to a ground state value of 5.3, which accounts for the excited state proton transfer and fluorescence [1]. The measured monoexponential fluorescence decay time in water of 5.30 ± 0.02 ns is significant in that it shows a tightly bound H-bonded molecule in water, and that the excited state proton transfer in the singlet state occurs from within this hydrogen bonded system. The tri-exponential fluorescence decay time in acetonitrile suggests that photochemical activity may be occurring in this solvent.

In summary our Raman data for 4-phenylpyridine show that the ground state Raman band at 1612 cm^{-1} shifts to 1578 in the triplet state, and reflects a behavior similar to that of biphenyl, where the reported Raman band shifts from 1606 cm^{-1} in the ground state to 1570 cm^{-1} in the triplet state [3]. The triplet Raman band which appears at 1476 cm^{-1} in biphenyl is seen at 1490 cm^{-1} in 4-phenylpyridine, probably due to a greater charge transfer component in the latter molecule, which increases the double bond character of the inter-ring C–C bond. Our calculations show that this bond shortens from 1.46 Å in the ground state to 1.43 Å in the triplet state. The 1490 cm^{-1} band observed in the TR^3 experiment of the triplet correlates with the calculated A-symmetric band predicted at 1501 cm^{-1}, which is shown in Fig. 6, together with the corresponding A-symmetry bands of the ground state. The predicted 1464 cm^{-1} band for the ground state is expected to have a weaker Raman intensity in the non-resonant experiment than in the resonance enhanced experiment and is not observed in the spectra shown in Fig. 2. The above similarities between 4-phenylpyridine and biphenyl indicate that both molecules have a planar quinoidal structure in the triplet state relative to the 40° ground state twist between the two aromatic rings. Finally, the TR^3 experiments presented here confirm the increased planarity of 4-phenylpyridine in the triplet state deduced by phosphorescence measurements of 4-substituted pyridine derivatives.

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