

IR-spectroscopic study of isotope effects on the NH/ND-stretching bands of meso-tetraphenylporphine and vibrational hydrogen tunneling

Hans-Heinrich Limbach, Jürgen Hennig, and Josef Stulz

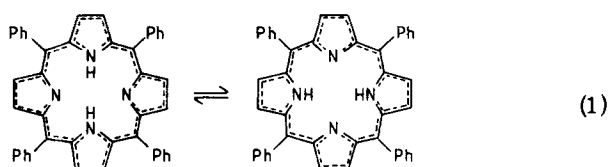
Institut für Physikalische Chemie der Universität Freiburg, Albertstrasse 21, 7800 Freiburg i. Br., West Germany

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The IR spectra of meso-tetraphenylporphine (TPP) dissolved in CCl_4 have been measured in the NH and ND stretching band region as a function of isotopic substitution using a newly constructed vacuum IR cell. Thus, it was possible for the first time to localize the NH and ND stretching bands of TPP-HD, which are characterized by the wave numbers 3335 and 2493 cm^{-1} . TPP- H_2 and TPP- D_2 were found to absorb at lower frequencies, namely 3318 and 2482 cm^{-1} . The observation of this band shift allows one to identify the observed NH and ND stretching bands in TPP- H_2 and TPP- D_2 . They arise from antisymmetric stretching vibrations, the symmetric bands being forbidden in the IR spectra. NH/ND stretching bandwidths of the order of 20 cm^{-1} were observed, which is unusually small for proton transfer systems. This observation further confirms our previous conclusions from the primary HH/HD/DD kinetic isotope effects on the tautomerism in this molecule, namely that the motion of the hydrogen atoms takes place in a coupled manner from discrete vibrational NH stretching levels without substantial coupling to the motion of heavy atoms. Since the symmetric NH stretching vibration has a higher frequency than the antisymmetric stretching vibration, the interaction between the two inner hydrogen atoms in TPP is repulsive.

I. INTRODUCTION

The mechanism of the hydrogen migration in meso-tetraphenylporphine (TPP) and other free base porphines is a matter of continuous experimental¹⁻⁸ and theoretical⁹⁻¹⁴ interest.



The reaction is a model for inter-^{7,15-18} and intramolecular^{7,19,20} double proton transfer reactions in solution,¹⁵⁻¹⁸ the solid state^{21,22} as well as for the tautomerism in biomolecules.²³

By a combination of NMR line shape analysis, selective $T_{1\rho}$ relaxation time measurements^{5,7} and magnetization transfer experiments in the rotating frame,⁸ we have succeeded for the first time in measuring kinetic HH/HD/DD isotope effects (KIE's) of double proton transfer. The TPP tautomerism and the proton exchange between acetic acid and methanol in tetrahydrofuran have served as model reactions. The unexpected high KIE's and the breakdown of the "rule of the geometric mean" (RGM),²⁴ which states for the rate constants of double proton transfer reactions that

$$k^{\text{HD}} = (k^{\text{HH}}k^{\text{DD}})^{1/2}, \quad (2)$$

could not be explained by transition state theory. However, using a simple vibrational model of tunneling based on a resonance tunneling model of Brickman and Zimmerman²⁵ we could accommodate the experimental and the theoretical KIE's calculated in quasiclassical

approximation from the barrier parameters.^{7,9} In the intermolecular case a distribution of symmetrical double minimum potentials had to be taken into account, leading to OH ground state tunneling from intermolecular excited states, whereas a fixed symmetrical double well potential was used for the TPP rearrangement.^{7,9} As a consequence, the TPP rearrangement was described as taking place between the discrete and degenerate vibrational NH-stretching states as shown in Fig. 1. All energies of activation were then given^{5,7,9} by the energy of the NH/ND-stretching frequencies measured first by Mason.²⁶ Whereas in our model the HD and the DD migration take place between the second excited ND-stretching levels which lie at the top of the barrier without an appreciable HD/DD KIE, i.e., with similar frequency factors $A^{\text{HD}} = A^{\text{DD}} = 7 \times 10^{12}\text{ s}^{-1}$, the HH migration proceeds between the first excited NH

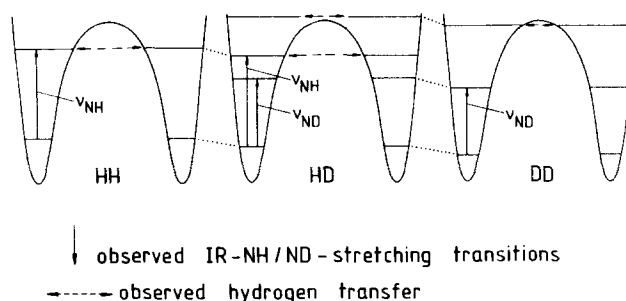


FIG. 1. One dimensional vibrational model of synchronous double hydrogen tunneling in TPP along a fixed symmetrical double minimum potential (schematically), † observed transitions of the NH/ND stretching vibration (probably ν_s for HH and DD), ↔ observed hydrogen transitions. Tunnel splittings are not shown.

stretching levels which lie well below the barrier with $A^{HH} = 10^{10.9} \text{ s}^{-1}$ and $(k^{HH}/k^{HD})_{298\text{K}} = 11$, which indicate tunneling between the first excited NH-stretching states.

Though we are aware that proton tunneling is generally accompanied by a motion of heavy atoms,²⁷⁻³⁰ we neglected^{5,7} this coupling in the case of TPP for two reasons: (i) the presence of such a coupling would reduce the KIE's and (ii) the porphine skeleton has in the solid state a symmetry which is very close to D_{4h} .³¹ On the other hand, an extension of previous CNDO calculations^{11,12} of the energy surface of the porphine rearrangement by Sarai^{13,14} leads to the interesting proposition that the porphine skeleton has only a D_{2h} and not a D_{4h} symmetry. As a consequence, the protons should move in an asymmetric double minimum potential if the heavy atoms remained in a fixed geometry. An energy E_M should, then, be necessary for the change of the porphine skeleton from the D_{2h} to the D_{4h} configuration in which resonance tunneling along a now symmetric double minimum potential could take place. Sarai¹⁴ attributed a considerable part of the experimental energy of activation of the tautomerism to this deformation energy of the skeleton. Using a proton transfer model—which has several features in common with the small polaron hopping theory of hydrogen diffusion in metals²⁷ and the theory of Dogonadze *et al.*²⁸⁻³⁰ of ionic proton transfer in solution coupled to the motion of heavy atoms—Sarai was able to describe the Arrhenius curves of the HH and the DD motion. The parameters used in the calculations were, however, not correlated through the molecular structure, i.e., different barrier parameters had to be assumed for the HH and the DD migration in contrast to our quasi-classical calculations.^{7,9}

Since in the theory of hydrogen bonding it is well known³²⁻³⁴ that a coupling of the proton motion to a heavy atom motion as postulated by Sarai for TPP¹⁴ leads to particularly large AH stretching bandwidths, we undertook the present study of the IR band shapes of the NH/ND stretching bands of TPP as a function of isotopic substitution. A second objective of this study was the question of whether the two NH oscillators are coupled or not. Such a coupling, which would favor a synchronous tunneling process, had been predicted.¹⁰⁻¹³ However, although a number of IR and Raman studies³⁵⁻³⁸ of free base porphines have been carried out this question was still open. By constructing a new all-quartz glass IR vacuum cell with silicon windows and path lengths between 0.1 and 1 mm and by measuring the IR spectra of TPP in CCl_4 we are able to provide in this paper experimental proof of this coupling between the two NH oscillators. The observation of small NH stretching bandwidths will be taken as direct evidence against a substantial coupling of the proton and the heavy atom motion during proton tunneling in TPP, a conclusion which is corroborated by the kinetic data of the tautomerism.

II. EXPERIMENTAL

The IR spectra were measured using a Fourier transform IR spectrometer Bruker IFS 113 V with a resolu-

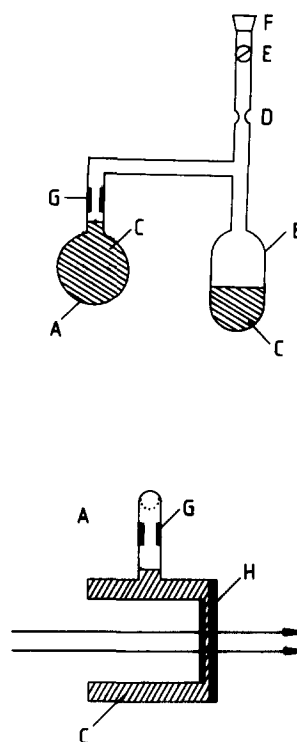


FIG. 2. Vacuum IR sample; A: IR cell with silicon or infrasil windows, B: solution container, C: solution, D: sealing point, E: greasefree stopcock, F: joint to vacuum line, H: windows.

tion of 2 cm^{-1} . In order to obtain and to maintain a defined deuterium content of the samples, a whole Pyrex glass vacuum IR device with silicon windows was constructed as shown in Fig. 2. The windows were sealed to the Pyrex glass by Hellma, Müllheim. They had a thickness of 1 mm. The path length of the cell was 1 mm, however smaller values up to 0.1 mm were also realized. A similar device was constructed with infrasil windows and a quartz-Pyrex transition between the cell and the solvent container B. TPP was synthesized according to Adler *et al.*³⁹ and was deposited in B and the device was attached to a vacuum line. Deuteration was achieved by condensing $\text{C}_2\text{H}_5\text{OD}$ and CCl_4 dried over molecular sieve (Merck, 3 Å) and alumina (Woelm, W 2000, basic), into B followed by the dissolution of TPP and the evaporation of the solvent. This procedure was then repeated with CCl_4 alone in order to remove traces of ethanol. Dried CCl_4 alone was finally condensed into B and the device was sealed at D. From the solution the pure solvent was then condensed into the cell by cooling the tube between the cell and B and the IR spectrum of the solvent was taken and stored in the computer. By means of just a few sample rotations the solution was poured into the cell. The IR spectrum of the solution and of the solvent were then subtracted, thus eliminating cell and solvent bands. Saturated solutions were measured at 303 K. Typical spectra are shown in Fig. 3. For the half deuterated samples a mixture of 1:1 $\text{C}_2\text{H}_5\text{OH}/\text{C}_2\text{H}_5\text{OD}$ was used instead of $\text{C}_2\text{H}_5\text{OD}$. The samples could be stored over months without alteration. The procedure described here is of

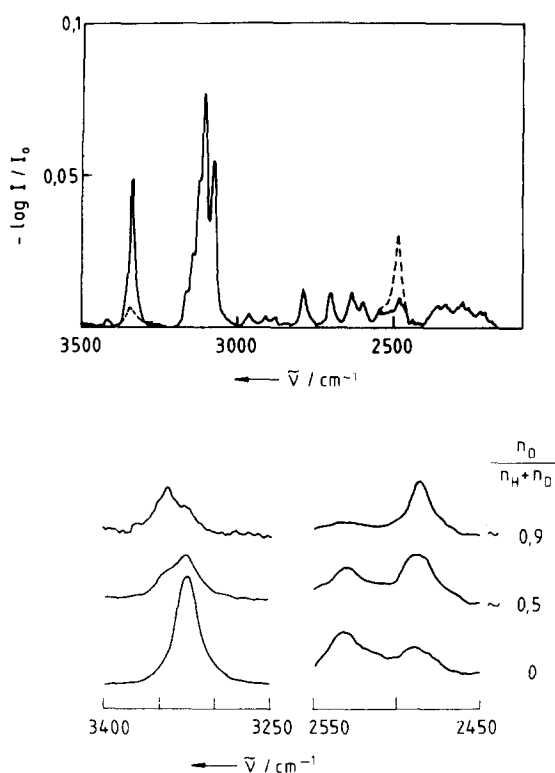


FIG. 3. IR spectra of TPP in CCl_4 at 303 K as a function of the deuterium fraction $n_D/(n_H + n_D)$ of the inner hydrogen atoms.

special use when measuring air sensitive solutions. For quantitative measurements it is possible to calibrate the volume of the cell and of the container.

III. RESULTS AND DISCUSSION

Some typical IR spectra of TPP in CCl_4 are shown in Fig. 3. For TPP- H_2 we find an NH stretching band at 3318 cm^{-1} with a very small bandwidth of 23 cm^{-1} . The ND stretching band was found at 2482 cm^{-1} , which is in good agreement with the corresponding values given by Mason,²⁶ i. e., 3315 and 2478 cm^{-1} . Calibration of our spectrometer with a poly-ethylene foil showed an error of about 1 cm^{-1} for the absolute line positions. The IR spectra of a sample with a deuterium fraction of about 0.5 shows an additional NH and an additional ND-stretching band at higher wave numbers, i. e., at $\nu^{\text{HD}} = 3335 \text{ cm}^{-1}$ and at $\nu^{\text{DH}} = 2493 \text{ cm}^{-1}$ (Fig. 3) which have to be attributed to TPP-HD. The small absorption in the NH stretching band region at $D = 0.99$ arises exclusively from TPP-HD. The NH band of TPP- $^{15}\text{N}_4\text{H}_2$ was found at 3313 cm^{-1} , i. e., a shift of 5 cm^{-1} to lower frequencies as compared to the unlabeled TPP.

These results prove that the two NH oscillators are coupled and that the NH stretching band of TPP- H_2 has to be attributed to the antisymmetric NH-stretching band $\nu_{\text{as}}^{\text{HH}}$, the symmetric band $\nu_{\text{s}}^{\text{HH}}$ being forbidden in the IR spectrum. The frequencies of two coupled AL oscillators where $L = \text{H, D}$ with A atoms of infinite masses characterized by two equal force constants $f_{11} = f_{22}$ and a coupling constant f_{12} are given by

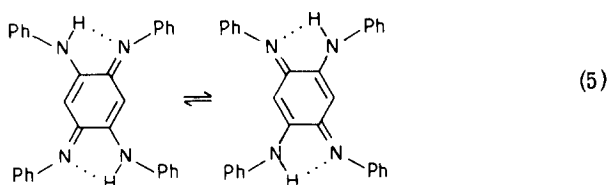
$$4\pi^2\nu_{1,2}^2 = (2m_1m_2)^{-1}(\pm[(f_{11}m_2 - f_{22}m_1)^2 + 4m_1m_2f_{12}^2]^{1/2} + f_{11}(m_1 + m_2)), \quad (3)$$

as can easily be shown by analogy to problems treated by Herzberg.⁴⁰ m_1 and m_2 are the masses of the two L atoms. Equation (3) predicts that

$$\nu^{\text{HD}} - \nu_{\text{as}}^{\text{HH}} = 2^{1/2}(\nu^{\text{DH}} - \nu_{\text{as}}^{\text{DD}}), \quad (4)$$

which is fulfilled experimentally within error limits. From Eq. (3) we can calculate values of $\nu_{\text{s}}^{\text{HH}} = 3352 \text{ cm}^{-1}$ and $\nu_{\text{s}}^{\text{DD}} = 2504 \text{ cm}^{-1}$ for the symmetric NH and ND stretching vibration which are forbidden in the IR but not in the Raman spectrum. Unfortunately, these bands have not yet been observed³⁵⁻³⁸ because of their weakness relative to other bands which are enhanced by the resonance Raman effect. The small NH shift of 5 cm^{-1} after labeling by ^{15}N indicates a small coupling of the motion of the N and the H atoms. The fact that $\nu_{\text{s}}^{\text{HH}} > \nu_{\text{as}}^{\text{HH}}$ means that the interaction between the two inner hydrogen atoms is repulsive. There are two sources which contribute to this interaction: (i) a direct van der Waals interaction between the H atoms and (ii) an indirect interaction via the electronic system of the porphine skeleton. The crystallographic data show an equilibrium NN distance of 410 pm which is slightly greater than the sum of the van der Waals radii of two methyl groups.⁴¹ Since the NH bond lengths are shorter than the CH bond lengths in free base porphines³¹ we estimate that the inner H atoms have van der Waals contact only if they leave their equilibrium positions. Kuzmitsky *et al.*^{13,14} have calculated values of $\nu_{\text{s}}^{\text{HH}} = 3925$ and $\nu_{\text{as}}^{\text{HH}} = 3902 \text{ cm}^{-1}$ using the CNDO method, whereas Almlöf¹⁰ found a value of $\nu_{\text{s}}^{\text{HH}} = 3940 \text{ cm}^{-1}$ in his *ab initio* calculation. This is not the only discrepancy between calculated and experimental data of free base porphines. The calculated CNDO NH bond lengths of 114^{12} and 108 pm^{13} , and the *ab initio* bond length of 102.5 pm^{10} are about 10 to 20 pm too high as compared to the experimental values determined by x-ray analysis,³¹ neutron scattering⁴² in the solid state or by NMR- T_1 relaxation in the liquid.⁴³ The biggest discrepancy is, however, the prediction of barrier heights of the order of 2.5 to 5 eV¹¹⁻¹⁴ as compared to the experimental value of 0.5 eV. Thus, it seems that MO calculations are for the moment not precise enough to predict either the correct positions of the inner hydrogen atoms or the proper values of their motion, i. e., barrier heights and force constants. Conclusions about the mechanism by using results of these methods have, therefore, to be handled with great care, especially the result of Sarai^{13,14} that the porphine skeleton has only a D_{2h} and not a D_{4h} symmetry. The fact that we observe a coupled proton motion in the potential wells supports a coupled hydrogen migration process because this coupling must increase if one of the H atoms is displaced during an early state of the migration process which decreases their internuclear distance. This supports our initial proposition of a synchronous hydrogen migration which was derived from the fact that the probability of tunneling along the synchronous pathway is preferred even if the barrier is higher. Tunneling along the asynchronous pathway is competitive only if the barrier is less than half the barrier of the synchronous process.

The most important result for a discussion of the tunneling process is, however, the observation of the small NH stretching bandwidths which indicate well defined NL stretching states in a fixed double minimum potential. The description of Sarai^{13,14} of the migration process in terms of a heavy atom motion of the porphine skeleton from a D_{2h} to a D_{4h} symmetry and subsequent proton tunneling is, therefore, in contradiction to our IR results. It is known in H-bond theory³²⁻³⁴ that the Hamiltonian as well as the Born-Oppenheimer type separation of the fast proton and the slow heavy atom motion used by Sarai¹⁴ leads to a particular AH-stretching band shape, with a number of discrete lines in the gas phase corresponding to simultaneously excited H bond vibrations and large bandwidths of the order of a few hundredths of wave numbers in solution. Such large bandwidths are absent in the NH stretching bands of TPP. In other words, the potential of the fast proton motion is almost independent of the motion of the atoms of the skeleton in the case of the porphines. The first excited NL stretching states are well defined states with a broadening that does not exceed a value of 10^{-1} kJ mol⁻¹. This indicates an extremely tight double minimum potential for the proton motion, tighter than, e.g., for the proton motion in carboxylic acid dimers even in the solid state.²¹ Therefore, our simple description of the hydrogen migration in terms of tunneling between discrete quantized NL stretching states is corroborated by our IR results. However, we agree that a description of other proton transfer processes has to take into account the heavy atom motion. For the moment, our experimental approach to this problem is to study intramolecular proton transfer in less rigid systems. We have already reported the energy of activation for double proton transfer in azophenine⁷ (AP):



which was given as in the case of TPP by the energy of the NH stretching vibration. We think, however, that the heavy atom motion influences the HH/HD/DD KIE's as well as the NH stretching bandwidth. Up to the present the band shape enlarging mechanism of the AH stretching bands of intramolecular H bonded systems are not well understood. The OH stretching bands in systems of the malondialdehyde (MA) type



range from 100 to 1000 cm⁻¹.^{43,44} The bands may be either broadened by tunnel splitting, intramolecular flexibility of the hydrogen bond distance, or very short lifetimes in the excited state or polarization of the proton potential by solvation.⁴⁴ In any case, tunnel splittings of the ground states of MA has been recently observed

by Baugham *et al.*⁴⁶ Within our simple resonance tunneling model for TPP we calculate from the pre-exponential factor $A^{HH} = 10^{11}$ s⁻¹ a maximum tunnel splitting of $\Delta E = \frac{1}{2} \hbar A^{HH} = 2$ cm⁻¹ which is much smaller than the experimental NH bandwidth of 23 cm⁻¹. The absence of a tunnel splitting in the NH stretching bands of TPP is, therefore, not an argument against the vibrational tunneling model. A greater tunnel splitting should, however, be observed in the NH stretching overtones of TPP. We, therefore, tried to localize these overtones in the FT-NIR spectra of TPP in CCl₄, but without success although an IR cell with a path length of 10 cm was used. Even after 300 scans only the CH overtones of the aromatic CH stretching vibrations were found at 6140 (vw) and 5950 (w) cm⁻¹ which correspond to the fundamentals lying between 3000 and 3100 cm⁻¹. The NH/ND overtones were apparently too weak or too broad.

Finally we want to point out that if one assumes an energy E_m necessary for the excitation of heavy atoms during the hydrogen migration process there is no energy left for the excitation of the NH stretching vibration but only of the NH bending vibration. There is then a great number of states on both sides of the barrier between which tunneling can occur. We have recently shown, using a simple tunneling model which takes into account such continuum of states, that in this case the RGM, i.e., Eq. (1), is fulfilled in approximation, which was also observed experimentally in double and triple proton exchange between acetic acid and methanol in tetrahydrofuran.⁷ However, in the case of TPP the RGM is far from being fulfilled⁷ because $k^{HH} = 10 k^{HD} = k^{DD}$ at 298 K. Only at lower temperatures did we find k^{HD} slightly greater than k^{DD} . This observation is, therefore, also in contradiction to the mechanism of Sarai.

IV. CONCLUSIONS

TPP is the first proton transfer system in which the full HH/HD/DD kinetic isotope effects of the tautomerization process have been measured and which shows at the same time very sharp NH/ND stretching bands which are not broadened by heavy atom motions as in H-bonded complexes. This indicates an extremely tight double minimum potential for the hydrogen motion with discrete vibrational degenerate NL stretching states, between which the reaction proceeds by tunneling. The motion of the two protons is coupled due to a repulsive interaction as shown by IR spectroscopy and as follows from the tunneling model.

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