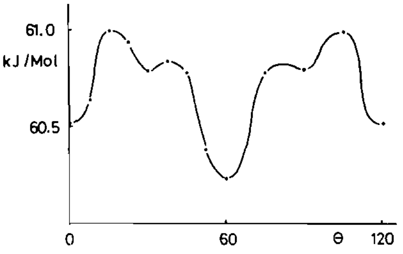
two origins, the crystal packing and the rigidity of the ligand systems. The former is difficult to estimate. The latter however can be calculated using the Consistent Force Field [2] method.

Calculations of this type have been carried out for several ligands such as tacn (1,4,7-triaminocyclononane), tame (1,1,1-trisaminomethyl-ethane) and tach (1,3,5-*cis*, *cis*-triaminocyclohexane) changing the Cu–N reference bond length along the circular path given by the mexican-hat potential. Figure 1 shows the result obtained for Cu(tacn)$_2^{2+}$ in the more stable optical active configuration. The relative energies obtained are a measure for the ease of the ligand, to adapt to the new geometry imposed by the Jahn–Teller distortion, defined by the angle θ [3]. The surprising result of these calculations is, that all three ligands stabilize a compressed tetragonal coordination (θ = 60°) by energies in the order of 1 kJ/mol. The lack of any experimental evidence for tetragonal compressed systems, indicate that for Cu^{2+} this preference of the ligand systems is overridden by other effects.



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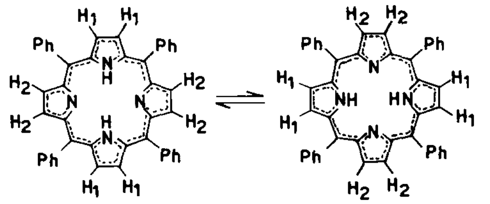
Vibrational Hydrogen Tunnelling in Free Base Porphines

H. H. LIMBACH* and J. HENNIG

Institut für Physikalische Chemie der Universität Freiburg, Albertstr. 21, D-7800 Freiburg i. Br., F.R.G.

The kinetics of the hydrogen and the deuterium migration in *meso*-tetraphenylporphines (TPP) has been studied by a combination of NMR-lineshape analysis and selective T$_{1\rho}$ relaxation time measurements [1]. The anomalous Arrhenius-curves of the migration in TPP–H$_2$, TPP–HD, and TPP–D$_2$ proves that the reaction proceeds by resonance tunnelling between quantized vibrational NH-stretching states. The rate constants are independent of the choice of the solvent which indicates the absence of specific interactions between the inner porphine cavity and the solvent.



The experimental tunnel rates are used to calculate in quasiclassical one-dimensional WKB-approximation the distances over which each hydrogen atom is transported during the reaction [2]. These distances are in good agreement with the crystallographic data for the case of synchronous hydrogen tunnelling.

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^{1}H-NMR Spectroscopic Study of the Thermodynamics of Hydrogen Bonding and the Kinetics of Proton Exchange Between Acetic Acid and Methanol in Tetrahydrofuran-d$_8$

H. H. LIMBACH*, D. GERRITZEN and W. SEIFFERT

Institut für Physikalische Chemie der Universität Freiburg, Albertstr. 21, D-7800 Freiburg i. Br., F.R.G.

The ^{1}H-NMR spectra of the systems acetic acid/methanol/tetrahydrofuran-d$_8$ (THF), acetic acid/THF, and methanol/THF have been measured as a function of the temperature and the concentrations. The kinetics of proton exchange between acetic acid and methanol in THF were determined [1] by NMR-lineshape analysis using the quantum mechanical density matrix formalism [2]. The proton chemical shifts provide the thermodynamic data of the following association reactions between hydrogen bonded species (S = THF):

$$\mathrm{RCOOH\cdots S + RCOOH\cdots S \rightleftharpoons RCOOH\cdots RCOOH\cdots S + S,}$$

$$\mathrm{RCOOH\cdots S + ROH\cdots S \rightleftharpoons RCOOH\cdots ROH\cdots S + S,}$$

$$\mathrm{ROH\cdots S + RCOOH\cdots S \rightleftharpoons ROH\cdots RCOOH\cdots S + S,}$$

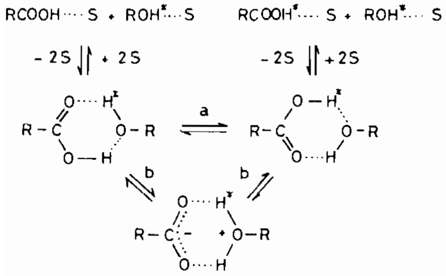
$$\mathrm{ROH\cdots S + ROH\cdots S \rightleftharpoons ROH\cdots ROH\cdots S + S.}$$

By comparison of these data with the thermodynamic data of proton donor dimerisation in other media linear enthalpy–entropy relationships are obtained which are typical for the functional proton donor group and which are useful for estimating the degree of specific solute–solvent interactions

$$\mathrm{AH\cdots S + S' \rightleftharpoons AH\cdots S' + S,}$$

where S, S′ = THF, benzene, CCl_4, cyclohexane.

The thermodynamic and kinetic data lead to the following reaction scheme



The value of the activation entropy provides evidence against the formation of a solvated ion pair as intermediate or transition state. The mechanism of the reaction pathway a is discussed.

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Solvent Effects on Some Optical and Spectroscopic Properties of Aromatic Compounds

J. F. KERUZORE

Laboratoire de Chimie de Coordination, F31030 Toulouse Cedex, France

C. CLEMENT

Centre de Recherche Paul-Pascal, F33405 Talence, France

and J. P. CANSELIER

Institut du Génie Chimique, F31078 Toulouse Cedex, France

In this work we want to report some solvent effects observed during studies on benzenoid and heterocyclic compounds by the Faraday effect and Depolarized Rayleigh Scattering (DRS), and their TCNE-complexes, by UV–visible spectrophotometry.

The measured properties, respectively molecular magnetooptical rotation ($[\rho]_M$), molecular optical anisotropy ($\overline{\gamma^2}$) and maximum absorption wavenumber ($\bar{\nu}_{max}$) undergo rather large changes when moving from gas phase to pure liquid or dissolved state, and vary weakly from a solvent to another one.

As regards weak interactions, the Faraday effect allows essentially to observe internal field changes (Lorentz correction). It is likely that this bulk effect is not restricted to 'aromatic' solutes. Moreover most solute–solvent interactions are masked by this non-specific medium effect, since even with polar solvents ($CHCl_3$, alcohols) no specific interaction given by π-donors and/or polar solutes (*e.g.* halobenzenes, anisole, ...) is detected. So, for a given substance, the true value of $[\rho]_M$ is obtained in the pure liquid state or in a solvent as refractive as the solute.

On the contrary, DRS, very sensitive to oriented interactions, can detect diatropism or paratropism in liquids. Therefore, to get comparable, 'intrinsic' γ^2 values one must not work with pure liquids but rather with dilute solutions in the same 'inert' solvent, that is a non-polar, weakly anisotropic one, containing bonds of the same kind as the solute. Accordingly, for organic compounds (C–H bonds), cyclohexane is preferred to CCl_4 (which may also give specific interactions). On the other hand the molar volume of the solvent need not be taken into account. The cases of benzene and some heterocyclics illustrate these principles.

Finally, spectrophotometric studies of molecular complexes show that the influence of non-polar solvents on $\bar{\nu}_{max}$ generally reduces to a gross medium effect involving a linear function of $(n^2 - 1)/(2n^2 + 1)$. As regards polar solvents, more complex interactions with aromatic compounds and acceptor are likely to occur, and no correlation can be found with polarity parameters like Z or E_T. TCNE-complexes of benzene, benzothiophene (after deconvolution of spectra) and dibenzothiophene are considered.

Two Photon Absorption and Excited Fluorescence of 2,2′-Bipyridine

E. CASTELLUCCI and P. R. SALVI

Istituto di Chimica Fisica dell'Università, Via G. Capooni 9, 50121-Florence, Italy

Two-photon absorption spectroscopy is proving a powerful method to probe one-photon forbidden