trated aqueous solutions of borates [1, 2]. The ^{11}B nuclear magnetic resonance spectra of sodium, potassium and ammonium polyborates in D_2O solutions, – as a function of concentration and pH value –, provide information of the hydrolysis equilibria. Two NMR signals are observed in the aqueous solutions of the pentaborates $Na[B_5O_6(OH)_4]$, $K[B_5O_6(OH)_4]$ and $NH_4[B_5O_6(OH)_4]$, while only one NMR line is recorded in the solutions of the tetraborates $Na_2[B_4O_5(OH)_4]$ and $(NH_4)_2[B_4O_5(OH)_4]$. A solution of $(NH_4)_2[B_4O_5(OH)_4]$ at pH 7 shows two lines again [3].

The next step was to study the Raman spectra of solid H_3BO_3, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$, $K[B_5O_6(OH)_4]\cdot 2H_2O$ and of $Na[B(OH)_4]$ as well as of borax in aqueous solutions as a function of concentration and pH, recorded between 300 and 1500 cm^{-1}.

For comparisons the Raman spectra of solid $(NH_4)_2[B_4O_5(OH)_4]\cdot 2H_2O$, β-$NH_4[B_5O_6(OH)_4]\cdot 2H_2O$, $NH_4[B_5O_6(OH)_4]\cdot 0.67H_2O$ and $NH_4[B_5O_6(OH)_4]$ were considered. In solution, all lines in the Raman spectra could be assigned and the degree of depolarization measured. The assigned Raman frequencies can be used for the identification of unknown B–O lines and therefore of unknown borate structures [4].

In the last step the influence of some series of foreign electrolytes in various concentrations of the equilibria of the borate species in a 0.5 *M* solution was investigated by Raman spectroscopy.

On the one hand, addition of the foreign electrolyte solutions has a dilution effect, so that in many of these systems there exists only the $[B(OH)_4]^-/B(OH)_3$ equilibrium without polyborates. On the other hand, the effect is sometimes a forcing of the equilibrium in favour of the polyborate formation with the triborate ions $[B_3O_3(OH)_4]^-$ and $[B_3O_3(OH)_5]^{2-}$ as predominant species. The tetraborate ion $[B_4O_4(OH)_5]^{2-}$ is present only to a minute extent, while the formation of the pentaborate ion $[B_5O_6(OH)_4]^-$ is repressed the most [5].

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A Chemical Interpretation of the Intense Raman Spectra Observed at a Silver Electrode in the Presence of Chloride Ion and Pyridine: Formation of Radicals

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During the past five years, a large number of researchers have been interested in the Raman spectroscopic study of the phenomena involved at a silver electrode immersed in an aqueous chloride solution containing pyridine. We feel that the numerous interpretations proposed (1 to 9 and references therein) to explain the 'giant' intensity enhancement of the Raman spectra observed at the silver electrode solution interface are not convincing.

The aim of this work is to show that the observed phenomenon may be explained by a simple resonance Raman effect due to radical species formed at the silver electrode–solution interface during the oxidation–reduction cycle. In the case of KCl, pyridine solution, the bands observed in Raman and electroreflectance spectroscopy at 227 cm^{-1} and 750 nm ($\Delta R/R$) are assigned to the presence of $Cl_2^{\overline{\cdot}}$ radical anions. The band at 1025 cm^{-1} and the bands at 1008 and 1036 cm^{-1} as well as the shoulder at 650 nm ($\Delta R/R$) are attributed respectively to the formation of pyridinium radical cations and pyridinyl radical anions.

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Ligand Effects on Jahn–Teller Distortions. Consistent Force Field Calculations of Cu(II) Complexes

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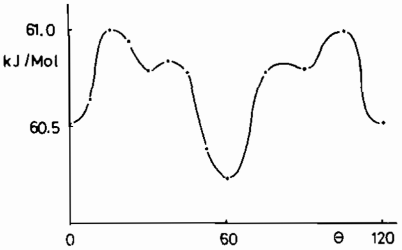
The structural and electronic properties of Cu(II) complexes with symmetric tridentate facially coordinating ligands have recently been studied with respect to their Jahn–Teller distortions [1]. In such systems the forces opposing the Jahn–Teller distortion are of two origins, the crystal packing and 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

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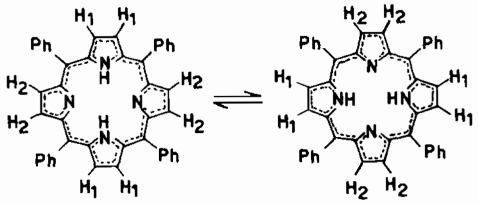
The kinetics of the hydrogen and the deuterium migration in *meso*-tetraphenylporphines (TPP) has been studied by a combination of NMR-lineshape analysis and selective $T_{1\rho}$ relaxation time measurements [1]. The anomalous Arrhenius-curves of the migration in TPP–H_2, TPP–HD, and TPP–D_2 proves 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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¹H-NMR Spectroscopic Study of the Thermodynamics of Hydrogen Bonding and the Kinetics of Proton Exchange Between Acetic Acid and Methanol in Tetrahydrofuran-d_8

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The ¹H-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):