the Jahn–Teller stabilization energy E_{JT} never exceeds the energy of a quantum $h\nu$ of the corresponding active vibrational modes substantially. The degree of covalent delocalization of the singly occupied degenerate metal 3d orbital over the ligand rings correlates well with Jahn–Teller distortion increasing strongly along the series $Fe(cp)_2^+ < Mn(cp)_2 < Co(cp)_2 < Ni(cp)_2^+$.

This finding agrees with the predictions of semiempirical MO calculations. In the solid state, by systematic variation of the host lattice we were able to observe a stepwise transition from a purely dynamic Jahn–Teller effect to the static distortion limit in the case of cobaltocene. Alkyl substituents at the rings influenced the cobaltocene EPR spectra in the same way as asymmetric lattice potentials.

Electrical Anharmonicity for the OH Stretching Vibration of Methanol and its Hydrogen Bonded Complexes

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We have calculated the first and second dipole moment derivatives for a number of hydrogen bonded systems involving methanol and a variety of organic bases. Herman and Shuler's [1] expressions for the intensities of fundamental and first overtone are employed for the calculations. Both ++ and +– combinations of experimental values of transition moment integrals R_0^1 and R_0^2 are considered. Given below are the typical values of μ_1 and μ_2 for the two sign combinations in the case of dilute solutions of CH_3OH in CCl_4 representing free OH and CD_3OH in DMSO-d_6 as well as self associated CD_3-OH in CD_3OD. It is found that for all the systems considered both for ++ and +– combinations μ_1 as well as μ_2 increase on hydrogen bonding. Often a reference is made in the literature that the intensity of the first overtone band of XH stretching vibration decreases on hydrogen bonding whereas that of the fundamental increases. On the basis of these observations a decrease in the overtone intensity can be explained on the basis of the fact that the negative contribution to the overtone intensity from an increase in the first derivative of the dipole moment supersedes the positive contribution from the increase in the second derivative of the dipole moment. This explanation is quite justified as it can be noticed from the above values that whereas μ_1 increases about 4 to 5 times on hydrogen bonding in the cases considered in these studies, μ_2 only increases by 50 to 10%.

This observation is similar to the prediction made by Di Paolo, Bourderon and Sandorfy [2] on the basis of their theoretical model calculations on the influence of Electrical Anharmonicity on infrared intensities in hydrogen bonded systems. However, contrary to their predictions it is rather clear from these studies that the decreasing intensities of first overtones on hydrogen bonding can be explained by taking +– combinations as nicely as from ++ combinations of transition moment values.

Methanol in	++ comb.		+– comb.	
	$\mu_1 \times 10^{20}$	$\mu_2 \times 10^{20}$	$\mu_1 \times 10^{20}$	$\mu_2 \times 10^{21}$
CCl_4	4.567	1.017	4.770	8.094
DMSO-d_6	20.443	1.641	20.750	3.943
CD_3OD	23.545	2.033	23.952	4.936

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Synthetic Models for Cytochrome-C Oxidase: Magnetic and Mössbauer Effect Studies of Binuclear Fe(III) Porphyrin–Cu(II) Complexes

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Recent e.s.r., magnetic susceptibility and m.c.d. measurements have indicated the presence of a