

LETTERS TO THE EDITOR

ATOMIC POTENTIAL ENERGY DISTRIBUTION FOR XYZ AND XY₃Z TYPE MOLECULES

IN an earlier article¹ the potential energy distribution among atoms for various normal vibrations in some simple molecules were calculated by the method of Kyong². This note reports the extension of the method of determining the atomic potential energy distribution for some XY₃Z and XYZ (bent) type molecules.

Starting from the well-known secular equation in molecular vibration³

$$GFL = LA \quad (1)$$

(where the symbols have their usual meanings) it is easy to arrive at a relation for the distribution of potential energy among atoms² as

$$PED(v_j, a) = \frac{\mu a L_j^{-1} H_a F L_j}{\Lambda_j} \quad (2)$$

wherein the subscripts 'a' and 'j' stand for the atom and the j-th normal vibration under consideration, μ the reciprocal mass of the atom and H_a , in general is a matrix dependent fully on the structural geometry of the molecule.

Making use of the relation given above, the atomic potential energy distribution for different normal vibrations in ONF, ONCl, ONBr, CH₃F, CH₃Cl and CH₃Br molecules were evaluated. In the ONX [X = F, Cl, Br] type molecules it seen that the distribution of potential energy among O and N atoms remains constant throughout for the N-O stretching vibration irrespective of the halogen atom attached to the N-O bond, thereby indicating that the halogen atom does not affect the NO bond. But the potential energy distribution among N and X atoms varies appreciably for the N-X stretching vibration. It is clear from Table I that as the electronegativity of the halogen atom decreases, the contribution of potential energy towards the halogen atom also decreases. This can be attributed to the decrease in the N-halide bond strength as one goes from F to Br. Taking CH₃X (X = F, Cl, Br) type molecules, whereas the above-mentioned trend is noticed for the C-X stretching vibration in 'A' species, the potential energy distribution among C and H atoms for ν_{C-H} stretching vibration remains unaltered by the presence of halogen atom. In general it is seen that atomic potential energy distribution remains constant for a particular normal vibration of a specific chromophoric group in XYZ and XY₃Z type molecules under consideration.

TABLE I
Atomic potential energy distribution for XYZ and XY₃Z type molecules

Type	Molecule	Frequency cm ⁻¹	Atomic P.E.D.		
			X	Y	Z
XYZ	ONF	1844	0.47	0.53	..
		520	..	0.58	0.42
		766	0.26	0.62	0.12
	ONCl	1836	0.47	0.53	..
		336	..	0.71	0.29
		603	0.35	0.60	0.05
XYZ	ONBr	1832	0.47	0.53	..
		269	..	0.85	0.15
		548	0.33	0.65	0.02
	<i>A species</i>	3031	0.02	0.98	..
		1059	0.19	0.81	..
		1490	0.61	..	0.39
XYZ	CH ₃ F	<i>E species</i>			
		3132	0.10	0.90	..
		1498	0.09	0.91	..
	1206	0.13	0.83	0.04	
	<i>A species</i>	2968	0.02	0.98	..
		733	0.19	0.81	..
1355		0.74	..	0.26	
XYZ	CH ₃ Cl	<i>E species</i>			
		3039	0.10	0.90	..
		1452	0.09	0.91	..
	1014	0.10	0.89	0.01	
	<i>A species</i>	3061	0.02	0.98	..
		617	0.19	0.81	..
1333		0.87	..	0.13	
CH ₃ Br	<i>E species</i>				
	3184	0.10	0.90	..	
	1472	0.09	0.91	..	
974	0.08	0.91	0.01		

These results indicate that the atomic potential energy distribution remains the same for the particular chromophoric group and as such it can be used as an additional parameter in molecular vibrational problems.

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PHYSICO-CHEMICAL STUDIES OF THE BIVALENT METAL CHELATES OF SOME MONOPROTIC TRIDENTATE SCHIFF BASES

o-(*N*- α -furfuralideneimino) benzene sulphonic acid (HFB) and *o*-(*N*- α -furfuralideneimino) ethane sulphonic acid (HFE), Schiff bases function as monoprotic tridentate ligands and form solid chelates with Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). These chelates have been characterised by elemental analysis, molecular weight determination, magnetic susceptibility and conductance measurements, electronic absorption and IR spectra. The presence of nitrogen atom of the azomethine group in β -position to the sulphonic group is responsible for the general similarity in the behaviour of the chelates of the two Schiff bases.

A survey of literature^{1,2} shows that no systematic study has been carried out using orthanilic acid and taurine Schiff bases with furfuraldehyde. Taurine and orthanilic acid contain an open chain molecule and phenyl radical, respectively. Both form monoprotic tridentate Schiff bases with furfuraldehyde and these are structurally similar.

HFB and HFE were prepared by the method of Pfeiffer *et al.*³ and their metal chelates with Cr(II), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) were synthesised similar to the procedure described by Yamada *et al.*^{4,5}.

Elemental analysis and molecular weight determinations of the solid chelates indicated 1:2 metal-ligand stoichiometry. Magnetic susceptibility measurements were carried out using Gouy magnetic balance with mercury(II) tetrathiocyanatocobaltate as the reference⁶. The magnetic moments at 308° K of the Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chelates were found 4.84, 5.92, 5.46, 5.18, 3.14 and 1.96 B.M. for HFB chelates and 4.81, 5.91, 5.41, 5.13, 3.12 and 1.92 B.M. for HFE chelates

which indicate the presence of 4, 5, 4, 3, 2 and 1 unpaired electrons, respectively.

The metal chelate solutions in DMF (10⁻³ M) display negligibly small molar conductance values (3.5 to 8.7 ohm⁻¹ cm² mole⁻¹) which suggest the non-electrolytic nature of these compounds.

The electronic absorption spectra of the chloroform solution of the Cr(II) chelates of both the Schiff bases gave one absorption band at ~ 14600 cm⁻¹ ($\epsilon = 43$ – 51 mole⁻¹ cm⁻¹) assignable to the transition ${}^5E_g \rightarrow {}^5T_{2g}$. The Mn(II) chelate solutions gave two bands at ~ 24800 cm⁻¹ ($\epsilon = 52$ – 67 mole⁻¹ cm⁻¹) and ~ 29700 cm⁻¹ ($\epsilon = 70$ – 82 mole⁻¹ cm⁻¹) which can be assigned to the transitions ${}^6A_{1g} \rightarrow {}^4E_g$ (G) and ${}^6A_{1g} \rightarrow {}^4E_g$ (D) respectively. Fe(II) chelates solutions gave one absorption peak at ~ 10700 cm⁻¹ ($\epsilon = 65$ – 73 mole⁻¹ cm⁻¹) assignable to the transition ${}^5T_{2g} \rightarrow {}^5E_g$ (D). The Co(II) chelate solutions gave three bands at ~ 8700 , ~ 19800 ($\epsilon = 67$ – 72 ; 80 – 88 mole⁻¹ cm⁻¹) and ~ 21200 cm⁻¹ ($\epsilon = 92$ – 99 mole⁻¹ cm⁻¹) assignable to the transitions ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{2g}$ (F), ${}^4T_{1g}$ (F) \rightarrow ${}^4A_{2g}$ (F), ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{1g}$ (P), respectively. Similarly the chloroform solutions of the Ni(II) chelates gave three absorption bands with their peaks at ~ 8800 , ~ 13900 ($\epsilon = 69$ – 78 ; 87 – 94 mole⁻¹ cm⁻¹) and ~ 25700 cm⁻¹ ($\epsilon = 98$ – 108 mole⁻¹ cm⁻¹) which can be assigned to the transitions ${}^2A_{2g}$ (F) \rightarrow ${}^3T_{2g}$ (F), ${}^3A_{2g} \rightarrow$ ${}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow$ ${}^3T_{1g}$ (P), respectively. The Cu(II) chelate solutions gave only one absorption band with its peak at ~ 12600 cm⁻¹ ($\epsilon = 118$ – 130 mole⁻¹ cm⁻¹) assignable to the transition ${}^2E_g \rightarrow {}^2T_{2g}$. These data including the low molar extinction coefficient values suggest octahedral structure for all the metal chelates under investigation.

IR spectra of HFB and HFE consist of two bands in the narrow ranges of 1150–1140 cm⁻¹ and 1610–1600 cm⁻¹ assignable, respectively to ν -SO₃H and ν C=N. In the spectra of the metal chelates the bands in the range of 1150–1140 cm⁻¹ are absent suggesting co-ordination through sulphonic group. ν C=N of HFB and HFE in the range of 1610–1600 cm⁻¹ was shifted to lower frequency side on complexation suggesting participation of azomethine nitrogen in co-ordination. The appearance of two new bands in the ranges of 620–610 cm⁻¹ and 550–540 cm⁻¹ in the metal chelates indicate the formation of M-O and M-N bonds, respectively, in them.

Based on the above data the metal chelates may have the structure as shown in Fig. 1.

The results so far obtained conclusively show that the general similarities of the chelates of HFB and HFE are not due to the presence or absence of an open chain or a six-membered ring but it is due to the presence of nitrogen atom of the azomethine group in β -position to the sulphonic group. This result is also in agreement with an earlier finding⁷.