

Electronic spectroscopy of polyatomic molecules

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Abstract : Spectroscopy created a new horizon in the field of atomic study. Its identity could establish as basic need of ours. It might be the prospect of concrete platform of panoramic view of coming scientific future. It would be involved day by day and time to time stepwise. Bond length, Bond angle, Bond energy, natural & desirable efficiency of bond, direction of bond, dimensions of atomic bonds and atomic arrangement within the polyatomic molecules might be established through this technology. Spectroscopy would be fruitful in the field of pharmacy in various medicinal systems for manufacturing of targeted drugs and chemicals for specific conditions. Maleimide ($C_4H_2O_2NH$), Cyclopentene ($C_5H_4O_2$) and maleic anhydride ($C_4H_2O_3$) were chosen for experimental observations since 1st Jan to 31st Dec. 2017 and 1st Jan to 31st December 2018 successively. Development of this technology would uplift the health conditions of coming human generations.

(Keywords : Polyatomic molecules, Maleimide ($C_4H_2O_2NH$), Cyclopentene ($C_5H_4O_2$) and Maleic Anhydride ($C_4H_2O_3$), RINDO/S -Method.)

Introduction

By the use of RINDO/S - method the ground and excited state of Polyatomic molecules like Maleimide($C_4H_2O_2NH$), Cyclopentene ($C_5H_4O_2$) and Maleic anhydride ($C_4H_2O_3$) to know the bond efficiency and their identity at NTP laboratory condition, which will help in manufacturing of targeted drugs and chemicals. During the process of screening $\pi(\pi)$ and $\sigma(\sigma)$ bond were identified on the basis of their bond energy and Bond length. The valence basis set and extended basis set can be understood as follows:-

Valance basis

H : 1s
 C : 2s, 2p_x, 2p_y, 2p_z
 N : Do
 O : Do
 F : Do

Extended basis

1s, 2s, 2p_x, 2p_y, 2p_z
 2s, 2p_x, 2p_y, 2p_z, 3s,
 3p_x, 3p_y, 3p_z
 Do
 Do
 Do

It is important to note that it includes only H, C, N, O and F atom. The use of extended basis set is important in the sense that it accounts for higher excited states of polyatomic molecules. Higher excited states means the Rydberg state which correspond to the Rydberg (outer) atomic orbitals considered for H-F atoms. In our calculation in addition to valence excitations emphasis is given on Rydberg (outer) orbitals and it is found that some excitations lead to an excited state with considerable Rydberg character.

Ground State Properties:

It contains charge distribution and Ionization Potentials of Molecule under consideration. The net charge distribution does indicate that which of the atom in a molecule are donors or acceptors. If a +ve positive charge is developed on an atom then it is an acceptor and a donor otherwise.

I.P of Molecule is calculated using Koopman's theorem which states that the negative of Molecules orbital energy is taken as I.P of the Molecule.

The no. of I.Ps of molecules depends on its total no, of occupied MO_s The Ist I. P. of the

molecule is the negative of the lowest occupied MOs energy.

The importance of calculating net charge distribution is as follows:

- A. It gave the donor and acceptor characters of atoms in the molecules.
- B. From charge distribution one may account for electric dipole moment of the molecules.

Excited- State Properties:

This includes singlet excitations, triplet excitations and S-T splitting. In addition it accounts for transitions energy, frequency of transitions, Oscillator strength'. Polarization of the transition and percentage of Rydberg character. oscillator strength of a particular transition is directly proportional to its intensity and hence it plays very important role in experimental assignment of the transitions. The Rydberg character is indicating of the fact that wheather the transition is a Rydberg transition or valence transitions.

If a transition is a Rydberg transition then its membership corresponding to ns, np and nd Rydberg Series is determined by calculating its Quantum defect determined by the formulas.

$$\Gamma.v = \frac{R}{(n - \sigma)^2}$$

Where I = I.P (Ist)

$\mathfrak{Q}$ = Frequency of the transitions

R = Rydberg Const. (10937.5cm⁻¹)

n = S (Principal Quantum No.)

which is used generally in our calculation

If we calculate electronic excitations of an atom containing only H atom then n=2.

The small values of $\delta = 0.1$ to 0.2

correspond to nd Rydberg series.

Some greater values of $\delta = 0.3$ to 0.5 correspond to np Rydberg series.

And still greater values of $\delta = 0.9$ to 1.2 correspond to ns Rydberg series.

If however the values of δ lie between 0.5 & 0.9 than the Rydberg series is assigned from the electron population on Atomic orbital of the relevant MO.

In our calculation we evaluated 30 eigen values for 30SCF (Self Consistent Field) states. So, we diagonalies 30/30 mattice. Since a mattice cannot be completely diagonalies hence we use a cut-off = 0.001; the process which we use for diagonalisation Jacobi diagonalisation.

The trial and error wave function is considered and SCF wave functions is obtained by using iterations process. For obtaining SCF wave functions we use SCF cut-off = 0.01 i.e of the order 10^{-2} . It is found that after some iterations convergence is obtained and the energy as eigen values are calculated by the computer.

The first calculation is the ground state energy of the system. The lower is the ground state energy the higher is stability of the molecule. Then after Mos (molecules orbital) are calculated which result from linear combination (LCAO) of Atomic orbital. Each MO is followed by its eigen values and the Atomic Orbitals are followed by eigen vectors which are treated as population of electrons on Atomic orbitals. After calculating energies of all MO_s singlet and triplet excitation energies are calculated with SCF states in our calculation we have considered 30SCF states.

When excitation takes place then an electron from bonding MO goes to an anti-bonding MO. The overall symmetry of the excited state is determined by the direct product of the symmetries of bonding and anti-bonding MOs. For Ex:-. Let us consider a molecule which belongs

to molecular point group C_{2v} . If the symmetry of bonding MO is b_1 and that of anti-bonding MO is a_2 then overall symmetry of the excited state be B_2 . Actually we calculate transition energy by solving Schrodinger Eqn viz $H\psi = E\psi$

Where, H is the Hamiltonian of the system and E is the energy eigen values of the system. The Hamiltonian of a system is the total energy of the system. In classical mechanics H is simply an energy while in Quantum Mechanics it becomes an operator which operates on an appropriate wave functions. The reason of becoming operator is that the momentum which is a vector in classical mechanics, behaves like an operator in Quantum mechanics. The momentum P in Quantum Mech. is written as

$$\vec{P} = -i\hbar\vec{\nabla}$$

Where $\vec{\nabla}$ is called del vector and it is written as (in 3-dimension)

$$\vec{\nabla} = \frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}$$

So that

$$\nabla^2 = \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

We know that the total energy of the system is nothing but the addition of K.E and P.E

Thus we can write

$$H = K.E + P.E.$$

$$= \frac{1}{2}mv^2 + v$$

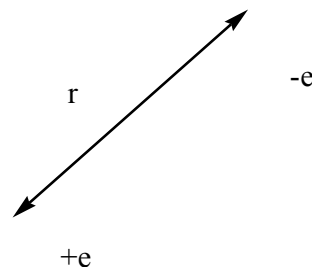
$$= \frac{1}{2m}m^2v^2 + v$$

$$= \frac{1}{2m}p^2 + v$$

$$= \frac{1}{2m}(-i\hbar\vec{\nabla}) \cdot (-i\hbar\vec{\nabla}) + v$$

$$H = -\frac{1}{2m}\hbar^2\nabla^2 + v$$

For calculating Hamiltonian of hydrogen atom we proceed as follow :



Hydrogen atom contains 1 Proton in nucleus and 1 electron at a distance of r from it. Hence the Hamiltonian of the system can be calculated as follows :

$$H = K.E \text{ (of electron)} + v$$

$$= \frac{1}{2}mv^2 + v$$

$$= -\frac{1}{2m}\hbar^2\nabla^2 - \frac{e^2}{r} \quad (i)$$

On atomic scale unit $m=\hbar=e=1$, $4\pi\epsilon_0=1$ & $e=1$

Hence we obtain

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\psi = e^{i(p_x x - Et)/\hbar} \quad \text{in 1-dimension}$$

$$= e^{i(\vec{p} \cdot \vec{r} - Et)/\hbar} \quad \text{in 3-dimension}$$

$$\vec{p} = p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$$

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$\vec{p} \cdot \vec{r} = (p_x\hat{i} + p_y\hat{j} + p_z\hat{k}) \cdot (x\hat{i} + y\hat{j} + z\hat{k})$$

$$\vec{p} \cdot \vec{r} = p_x x + p_y y + p_z z$$

Table - 1
The Lowest Ionization Potentials For
Maleimide And Its Isoelectronic Molecule

Molecules	Exptl.* IP	RINDIO/S-CI (Present Work) I.P Symmetry
 $C_4H_2O_3$ (C_2V)	10.98	10.77 $A_1(\pi)$
		11.35 $A_1(\pi)$
		12.57 $B_1(\sigma_\pi)$
		13.67 $B_2(\sigma_\pi)$
		15.63 $A_1(\sigma)$
		21.58 $A_1(\pi)$
		29.21 $A_2(\sigma)$
		42.31 $A_1(\pi)$
 $C_4H_3O_2N$ (C_2V)	10.00	9.51 $A_1(\pi)$
		10.77 $A_2(\sigma_\pi)$
		11.71 $A_2(\pi)$
		13.21 $A_1(\sigma_\pi)$
		15.16 $B_1(\pi)$
		18.62 $A_1(\sigma)$
		22.08 $B_2(\sigma)$
		28.41 $B_2(\sigma)$
 $C_3H_4O_2$ (C_2V)	9.41	43.63 $B_1(\sigma)$
		9.37 $A_1(\sigma)$
		11.06 $A_1(\pi)$
		13.45 $B_2(\pi)$
		16.04 $B_2(\sigma_\pi)$
		18.92 $B_2(\sigma)$
		27.05 $B_1(\pi)$
		36.82 $B_1(\sigma)$
		41.32 $A_1(\sigma)$

Material Method:

Borosil Glass Wires and BDH & Merch were used as lab materials and methods were continuously applied during 1st January 2017 to 31st December 2017 and 1st Jan 2018 to 31st

December 2018 at NTP laboratory condition. The total work were based on various observations on Maleimide($C_5H_4O_2NH$), Cyclopentene ($C_5H_4O_2$) and Maleic anhydride ($C_4H_2O_3$)

Results and Discussion

Since the starting of spectroscopic screening Molecules, Bio-Molecules as well as polyatomic molecule were targeted for acknowledgment of the bonding symmetry of Molecule. The bond arrangement, directions and dimension were found responsible for the change of chemical nature and their properties also. Brundle et.al.(1) (1969) supported the change of core configuration of polyatomic molecules. Charan et.al.(2) (1995) were involved themselves the basic screening of Bio-molecules through SEM (Screening Electron Microscope). Knoop et.al.(3) (1969) established the coordination between bond length and bond energy.

During (1996) Abha et.al.(4) were also included in this arena. The work of R. Mason(5) (1956) were found associated with spectroscopic of Molecules again Marsh et.al.(6)(1962) calculation of Pandey et.al.(7)(1995) were presented similar results. Prasad et.al.(8) (1995).Robin et.al.(9) (1970)- (1975). Seliskar et.al.(10)(1971), (1972A), (1972B) Postulated many assumptions on the basis of spectroscopic. Finally Singh et.al.(11) (1989) confirmed spectroscopic calculations on maleimide, cyclopentene, Maleic anhydride.

Conclusion

The targeted molecules are phenolic compounds most of secondary meta-bodies are used up drug in various Medicinal systems. Traditional drug delivery systems are replaced by targeted drugs in record according era to the revolution of time acts modern medicinal systems prefers the targeted drug for the eradication of particular elements and microbial contagious diseases even viral diseases.

Table - 2

Molecule	Exptl. ΔE	CNDO/S*			RINDO/S-CI (Present Work)			% Rydber Character									
		f	Symm.	ΔE	f	Symm.	ΔE	f	Symm.	C	H	O	N	T			
1 Maleic anhydride (C ₄ H ₂ O ₃)	2			5	6	7	8	9	10	11	12	13	14	15			
	3.3 ^a	8x10 ⁻⁵	A ₁ ($\pi \rightarrow \pi^*$)	2.96	0.00	B ₂ ($\pi \rightarrow \pi^*$)	3.02	0.00	B ₂ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
	3.9 ^a	0.24	A ₁ ($\pi \rightarrow \pi^*$)	3.22	0.00	A ₂ ($\pi \rightarrow \pi^*$)	4.12	0.00	A ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
	5.6 ^a	0.31	B ₂ ($\pi \rightarrow \pi^*$)	5.62	0.14	B ₁ ($\pi \rightarrow \pi^*$)	5.26	0.07	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
				5.84	0.00	B ₂ ($\pi \rightarrow \pi^*$)	5.97	0.00	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
4 Cyclopenten e 2,5-dione (C ₄ H ₄ O ₂ CN)				6.01	0.26	B ₁ ($\pi \rightarrow \pi^*$)	6.37	0.02	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
				7.60	0.15	B ₁ (Ryd.)	7.91	0.00	A ₁ ($\pi \rightarrow \sigma^*$)	2	9	1	0	12			
				8.5	0.25	B ₁ (Ryd.)	8.21	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	18	70	5	0	93			
				9.8	0.27	A ₁ (Ryd.)	8.50	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	25	54	2	0	82			
							8.67	0.01	B ₁ ($\pi \rightarrow \pi^*$)	18	79	2	0	99			
							9.00	0.00	A ₁ ($\pi \rightarrow \sigma^*$)	0	28	14	0	4			
							9.22	0.02	B ₁ ($\pi \rightarrow \pi^*$)	0	1	1	0	02			
							9.48	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	0	99	1	0	100			
							9.65	0.00	B ₂ ($\pi \rightarrow \pi^*$)	15	82	2	0	99			
							9.86	0.26	B ₂ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							10.09	0.04	A ₁ ($\pi \rightarrow \sigma^*$)	29	48	5	0	82			
							10.28	0.00	B ₁ ($\pi \rightarrow \pi^*$)	14	81	3	0	98			
							10.39	0.02	A ₁ ($\pi \rightarrow \sigma^*$)	1	1	0	0	02			
							10.54	0.16	B ₂ ($\pi \rightarrow \pi^*$)	35	33	0	0	68			
							3.12	0.00	B ₂ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							3.22	0.00	B ₂ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
Maleic anhydride (C ₄ H ₂ O ₃)							4.60	0.01	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							5.10	0.00	A ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0	0			
							5.74	0.09	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							6.13	0.12	A ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0	0			
							6.59	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	3	1	1	2	7			
							7.1	0.02	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							7.80	0.01	A ₁ ($\pi \rightarrow \sigma^*$)	20	43	22	5	90			
							8.12	0.02	A ₂ ($\pi \rightarrow \sigma^*$)	21	40	33	6	100			
							8.30	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	16	32	17	0	75			
							8.67	0.01	A ₂ ($\pi \rightarrow \pi^*$)	2	0	3	5	10			
							9.10	0.06	B ₁ ($\pi \rightarrow \pi^*$)	31	24	4	12	91			
							9.28	0.16	B ₁ ($\pi \rightarrow \pi^*$)	18	31	2	6	80			
							9.41	0.00	B ₁ ($\sigma \rightarrow \sigma^*$)	25	42	5	6	78			
							9.91	0.14	A ₁ ($\pi \rightarrow \sigma^*$)	30	16	20	16	82			
							10.25	0.08	A ₁ ($\pi \rightarrow \sigma^*$)	0	0	0	0	0			
							10.41	0.00	A ₂ ($\pi \rightarrow \sigma^*$)	15	16	12	14	57			
							3.82	0.00	B ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							4.27	0.00	A ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							4.86	0.00	A ₁ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							5.94	0.01	A ₂ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							6.72	0.14	A ₂ ($\pi \rightarrow \pi^*$)	0	0	0	0	0			
							6.90	0.08	A ₁ ($\pi \rightarrow \pi^*$)	2	1	1	0	4			
							7.48	0.00	A ₁ ($\pi \rightarrow \sigma^*$)	25	43	30	0	98			
							7.90	0.02	B ₁ ($\pi \rightarrow \pi^*$)	20	37	25	0	82			
							8.10	0.03	B ₁ ($\pi \rightarrow \sigma^*$)	21	40	38	0	99			

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