

## MO Calculations to Interpret Optical Spectra of MV: and related species

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**Summary:** The higher reduction products of dications of methyl viologen (MV<sup>2+</sup>), diquat (DQ<sup>2+</sup>) and *n*-butyl viologen (BV<sup>2+</sup>) i.e. MV; DO; and BV; respectively were prepared and their spectra recorded. MO calculation have been carried out to interpret the optical spectra of MV; and DQ: A good agreement was obtained between experimental and predicted singlet transitions for MV: while in case of DQ: the agreement for singlet transition at longer wave length was at variance.

In case of MV:(I) the observed transition are 3.1307 and 3.3056 eV while calculated one are 3.1352 (B<sub>2u</sub>) and 3.4006 (B<sub>3u</sub>) eV respectively where as in case of DQ: (II) the observed transitions are 3.0228 and 3.1307 eV while the calculated one are 2.6032 (B<sub>1</sub>) and 3.0873 (A<sub>1</sub>) eV respectively.

### Introduction

Methyl Viologen Neutral (MV:) a name proposed by the present worker [1] for the higher reduction product of 1,1'-dimethyl-4,4'-bipyridinium dication, is a chemical reactive intermediate [2,3]. Its mediating property is further being investigated by Crumbliss *et al.* [4].

Methyl Viologen dichloride or paraquat is an interesting and important member of the viologen family [5]. Some of the members of the family exhibit herbicidal activity [6]. Besides these compounds have been investigated for electrochromic properties and has been used as probe e.g. to investigate the properties of clay and polymer electrode, catalytic production of hydrogen and micelle formation [7]. In one of the recent interesting studies [8] electrochemical deposits of neutral forms of methyl viologen have been investigated by cyclic voltammetry (CV), rotating ring-disk electrode (RRDE) voltammetry, and double potential step chronocoulometry (DPSC) in aqueous medium, it was noted that neutral form of viologens is always insoluble in aqueous solutions.

The higher reduction product, MV: was isolated and the optical and NMR spectra were reported [1]. In this report the optical spectra of the neutral species of Methyl Viologen (MV:I) and Diquat (DQ:II) and M.O. calculations of their transitions in the  $\pi$  orbital frame work are reported.

The  $\pi$ - frame work calculations in the Pariser, Parr and Pople prescription is an old tested M.O. calculation [9-20]. It (Pariser-Parr-Pople, PPP method) has been successfully exploited in calculation pertaining to the electronic structure of molecule e.g. electronic charge densities, bond orders etc. It has been reported that predication regarding the UV/Visible spectra of conjugated  $\pi$ -electronic system is carried out better by PPP method than CNDO's method [8]. Hence the PPP method is employed here to interpret the optical spectra of above mentioned moieties (I,II).

It may be noted that these "neutral species" are closed shell system hence the theory of closed shell system with configuration interactions (CI) (in  $\pi$ -frame work) were utilized to interpret the optical spectra.

Details of the theory are available in standard books [10]. It is summarized below:

In LCAO-MO approximation one has  $\psi$ , the M.O. in terms of atomic orbital  $\phi$ 's as:

$$\psi = \sum_{r=1}^N C_{ij} \phi_r \quad (1)$$

which leads to the secular equation

$$\sum C_{ip} (H_{pq} - \epsilon_i S_{pq}) = 0 \quad (2)$$

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where  $S_{pq}$  is the overlap integral,  $\epsilon_i$  is the one electron energy,  $C_{ip}$  is the coefficient and  $H_{pq}$  is given as:

$$H_{pq} = \int \phi_p H \phi_q d\tau \quad (3)$$

The matrix elements in the familiar notation are given below:

$$H_{pp} = \alpha_{pp} + \frac{1}{2} P_{pp} \gamma_{pp} + \sum_{p \neq q} P_{pq} \gamma_{pq} \quad (4)$$

and

$$H_{pq} = \beta_{pq} - \frac{1}{2} P_{pq} \gamma_{pq} \quad (5)$$

Here  $\beta_{pq} = 0$  for non contiguous atoms and  $\alpha_{pp}$  is further expressed as:

$$\alpha_p = \omega_p + (p \sum_{p \neq q}^N v \setminus p) \quad (6)$$

Where  $\omega_p$  is the core potential at the atom  $p$ , the second term is the potential of an electron in the orbital of atom  $p$  in the field of core at position  $q$ .

The final of LCAO-MO-SCF matrix are:

$$\begin{aligned} H_{pp} &= \omega_p + \frac{1}{2} P_{pp} \gamma_{pp} + \sum_{p \neq q} (P_{pp} - Z_p) \gamma_{pq} \\ H_{pq} &= \beta_{pq} - \frac{1}{2} P_{pq} \gamma_{pq} \end{aligned} \quad (7)$$

The above equation (7) can be represented as Roothan's equations(8).

$$\sum_q H_{pq} C_q = \epsilon C_p \quad (p, q = 1, 2, \dots, N) \quad (8)$$

The eigen values  $\epsilon$  are distributed about the energy  $\omega_c + 1/2\gamma_{cc}$ . Computation can be simplified by subtracting this term from diagonal elements of LCAO-MO-SCF matrix elements (eq 7), with no damage done with the calculated energies of transitions.

The final form of equation comes out to be:

$$\begin{aligned} H_{pp} &= (\omega_p - \omega_c) + (\frac{1}{2} P_{pp} \gamma_{pp} - \gamma_{cc}) + \sum_{p \neq q} (P_{pp} - Z_p) \gamma_{pq} \\ H_{pq} &= \beta_{pq} - \frac{1}{2} P_{pq} \gamma_{pq} \quad (9) \\ d\omega &= \omega_p - \omega_c \end{aligned}$$

Where  $P_{pq}$  is the bond order and  $\gamma_{pq}$  the coulomb repulsion integral. To solve the secular equation (2), the various integrals of equations (9) have to be known. These are either available in the literature or chosen such as to reproduce the optical spectra [11].

A brief discussion about the choice and evaluation of integrals are given in Appendix.

Simple LUMO  $\rightarrow$  HOMO  $\psi_m \rightarrow \psi_{m+1}$  transition is inadequate to interpret the optical spectra, hence configuration interaction is recommended and utilized.

The CI type of calculation involves the expanded basis set, the basis of this method is to couple linearly all the possible solutions of Schrodinger wave equation. A better result towards the true energy is expected by a function made up of configurational functions [12].

$$\xi_{CI} = \sum_i C_i \chi_i \quad (10)$$

$\chi_i$ 's are the functions which represent the configurations of electrons in various SCF levels, with the same symmetry.

Since the individual configurations are orthonormal therefore in general:

$$\sum_i C_i^2 = 1 \quad (11)$$

The ground state configuration is given by [13].

$$\chi_0 = \frac{1}{\sqrt{N}} \text{Det} \left| \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_m \bar{\psi}_m \dots \psi_m \bar{\psi}_m \right| \quad (12)$$

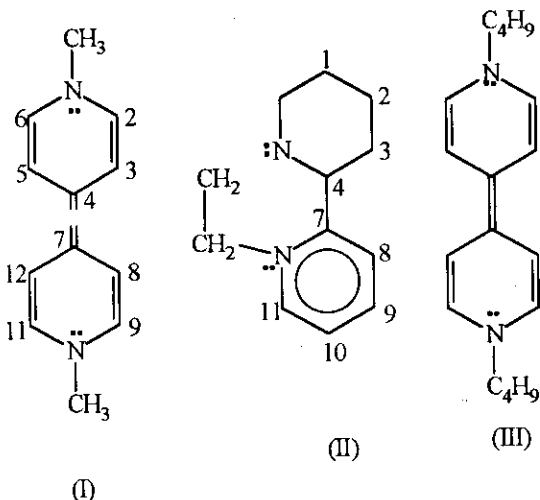
(where  $m$  represents the occupied MO)

Since an electron may or may not change spin during excitation from bonding MO to antibonding or virtual orbital MO the excitation are of singlet-singlet and singlet-triplet type.

The singlet-singlet excitation from bonding molecular orbital "i" to antibonding molecular orbital or virtual orbital "j" is given by:

$$x_{i,j} = \frac{1}{\sqrt{N}} \left( \frac{1}{\sqrt{2}} \text{Det} |\psi_1 \overline{\psi_1} \psi_2 \overline{\psi_2} \dots \psi_i \overline{\psi_i} \dots \psi_j \overline{\psi_j}| - \frac{1}{\sqrt{2}} \text{Det} |\psi_1 \overline{\psi_1} \psi_2 \overline{\psi_2} \dots \psi_i \overline{\psi_i} \dots \psi_j \overline{\psi_j}| \right) \quad (13)$$

This configuration means an electron from SCF MO "i" has been excited to MO "j". The linear combination is required because the situation when excited electron to the MO "j" has  $\beta$  spin while remaining electron in the MO "i" has  $\alpha$  spin is equivalent to situation when the excited electron in the MO "j" has  $\alpha$  spin and the remaining electron in the MO "i" has  $\beta$  spin. The minus sign is required to antisymmetrize the wave functions.



## Results and Discussion

The spectra of (I) and (III) resemble with each other to the extent that both gave  $\lambda_{\max}$  around 390 nm and 370 nm (Table-6). The similar spectra stems that the  $-\text{CH}_3$  and  $-\text{C}_4\text{H}_9$  substituents have virtually the same inductive effect and cause same polarization to the  $\pi$  molecular orbitals. One can therefore safely use the same parameters for hetro atom N and  $\text{N}^{+2}$  core.

With the integral values given in Table-1 and in the appendix, LCAO-MO-SCF calculations were carried out and the SCF energies and symmetries are collected in Table-2 and 3 for MV:(I) and DQ:(II) respectively.

The MO computer program as given by Greenwood [13] was modified for our system and the main computer (NEC-610) of our computer centre

Table-1: Parameter values

Core	Method	$-d\omega$ (eV)	$\gamma_{pq}$ (eV)	p-q	$-\beta_{pq}$
$\text{C}^{+1}$	Mataga	0.000	11.130	C-C <sup>a</sup>	2.390
$\text{N}^{+2}$		14.850	14.800	C-N <sup>a</sup>	1.912
$\text{C}^{+1}$	Charge Sphere	00.000	10.530	C-C <sup>b</sup>	2.395
$\text{N}^{+2}$		16.830	12.270	C-N <sup>b</sup>	1.912

a) See Reference [14]

b) See Reference [15]

Table-2: MO's, SCF energy levels (in eV) for MV: (I) calculation according to Mataga-Nishimoto method.

No.	SCF Levels (Symmetry)	Wave Functions
1.	-9.918 B <sub>1u</sub>	0.617 ( $\phi_1 + \phi_{10}$ ) + 0.209 ( $\phi_2 + \phi_6 + \phi_9 + \phi_{11}$ ) + 0.114 ( $\phi_3 + \phi_5 + \phi_8 + \phi_{12}$ ) + 0.113 ( $\phi_4 + \phi_7$ )
2.	-9.863 B <sub>3g</sub>	0.630 ( $-\phi_1 + \phi_{10}$ ) + 0.206 ( $-\phi_2 - \phi_6 + \phi_9 + \phi_{11}$ ) + 0.091 ( $-\phi_3 - \phi_5 + \phi_8 + \phi_{12}$ ) + 0.044 ( $-\phi_4 + \phi_7$ )
3.	-7.440 B <sub>1u</sub>	0.246 ( $-\phi_1 - \phi_{10}$ ) + 0.066 ( $\phi_2 + \phi_6 + \phi_9 + \phi_{11}$ ) + 0.281 ( $\phi_3 + \phi_5 + \phi_8 + \phi_{12}$ ) + 0.522 ( $\phi_4 + \phi_7$ )
4.	-5.380 B <sub>3g</sub>	0.255 ( $1\phi_1 - \phi_{10}$ ) + 0.195 ( $-\phi_2 - \phi_6 + \phi_9 + \phi_{11}$ ) + 0.355 ( $\phi_3 + \phi_5 - \phi_8 - \phi_{12}$ ) + 0.335 ( $\phi_4 - \phi_7$ )
5.	-4.893 B <sub>2g</sub>	0.000 ( $\phi_1 + \phi_{10}$ ) + 0.362 ( $-\phi_2 + \phi_6 - \phi_9 + \phi_{11}$ ) + 0.344 ( $-\phi_3 + \phi_5 - \phi_8 + \phi_{12}$ ) + 0.000 ( $\phi_4 + \phi_7$ )
6.	-4.888 A <sub>u</sub>	0.000 ( $\phi_1 + \phi_{10}$ ) + 0.361 ( $-\phi_2 - \phi_6 + \phi_9 + \phi_{11}$ ) + 0.345 ( $\phi_3 + \phi_5 - \phi_8 - \phi_{12}$ ) + 0.000 ( $\phi_4 + \phi_7$ )
7.	-1.676 B <sub>1u</sub>	0.227 ( $-\phi_1 - \phi_{10}$ ) + 0.340 ( $\phi_2 + \phi_6 + \phi_9 + \phi_{11}$ ) + 0.182 ( $\phi_3 + \phi_5 + \phi_8 + \phi_{12}$ ) + 0.389 ( $\phi_4 - \phi_7$ )
8.	3.365 B <sub>3g</sub>	0.189 ( $-\phi_1 + \phi_{10}$ ) + 0.379 ( $\phi_2 + \phi_6 - \phi_9 - \phi_{11}$ ) + 0.113 ( $-\phi_3 - \phi_5 + \phi_8 + \phi_{12}$ ) + 0.390 ( $-\phi_4 + \phi_7$ )
9.	5.045 A <sub>u</sub>	0.000 ( $\phi_1 + \phi_{10}$ ) + 0.346 ( $-\phi_2 + \phi_6 + \phi_9 - \phi_{11}$ ) + 0.362 ( $\phi_3 - \phi_5 - \phi_8 + \phi_{12}$ ) + 0.000 ( $\phi_4 + \phi_7$ )
10.	5.057 B <sub>2g</sub>	0.000 ( $\phi_1 + \phi_{10}$ ) + 0.344 ( $\phi_2 - \phi_6 + \phi_9 - \phi_{11}$ ) + 0.217 ( $-\phi_8 + \phi_9 - \phi_{11} + \phi_{12}$ ) + 0.000 ( $\phi_4 + \phi_7$ )
11.	6.102 B <sub>1u</sub>	0.154 ( $-\phi_1 - \phi_{10}$ ) + 0.291 ( $\phi_2 + \phi_6 + \phi_9 + \phi_{11}$ ) + 0.344 ( $-\phi_3 - \phi_5 - \phi_8 - \phi_{12}$ ) + 0.264 ( $\phi_4 + \phi_7$ )
12.	6.203 B <sub>3g</sub>	0.073 ( $-\phi_1 + \phi_{10}$ ) + 0.164 ( $\phi_2 + \phi_6 - \phi_9 - \phi_{11}$ ) + 0.304 ( $-\phi_3 - \phi_5 + \phi_8 + \phi_{12}$ ) + 0.505 ( $\phi_4 - \phi_7$ )

Table-2A: Singlet transition energies (in eV) for MV:(I) calculations are according to Mataga-Nishimoto Method.

Calcd	Obs	Contributing Configurations
3.1352 <sup>a</sup>	3.1307	0.9877 $\chi_{7-8}$ + 0.1094 $\chi_{6-10}$ + 0.0993 $\chi_{5-9}$
(B <sub>2u</sub> )		+0.0288 $\chi_{4-11}$ + 0.0086 $\chi_{7-12}$ + 0.0242 $\chi_{3-8}$
		-0.0282 $\chi_{3-12}$ + 0.0137 $\chi_{2-11}$ + 0.0070 $\chi_{1-8}$
		-0.0143 $\chi_{1-12}$
3.4006 <sup>b</sup>	3.3056	0.9845 $\chi_{7-10}$ + 0.1441 $\chi_{6-8}$ + 0.0602 $\chi_{4-9}$
(B <sub>3u</sub> )		-0.0231 $\chi_{5-11}$ + 0.0055 $\chi_{6-12}$ + 0.526 $\chi_{3-10}$
		-0.0361 $\chi_{2-9}$ - 0.0411 $\chi_{1-10}$

a) Polarized along +Y-axis

b) Polarized along +X-axis

Both Mataga-Nishimoto potential and charged sphere model were used for MO calculations. Tables 2A and 3A contain the first two singlet-singlet transition energies along with them configuration contributing for MV:(I) and DO:(II) respectively. Of 35 (the maximum

Table-3: MO's, SCF Energy levels (in eV) for DQ: (II) calculation according to Mataga-Nishimoto method

No.	SCF Levels (Symmetry)	Wave Functions
1.	-10.202 B <sub>2</sub>	0.092 ( $\phi_1 + \phi_{10}$ ) + 0.751 ( $\phi_2 + \phi_9$ ) +0.124 ( $\phi_3 + \phi_8$ ) + 0.291 ( $\phi_4 + \phi_7$ ) +0.092 ( $\phi_5 + \phi_{12}$ ) + 0.075 ( $\phi_6 + \phi_{11}$ )
2.	-9.721 A <sub>2</sub>	0.109 ( $-\phi_1 + \phi_{10}$ ) + 0.695 ( $-\phi_2 + \phi_9$ ) +0.078 ( $-\phi_3 + \phi_8$ ) + 0.146 ( $-\phi_4 + \phi_7$ ) +0.637 ( $-\phi_5 + \phi_{12}$ ) + 0.223 ( $-\phi_6 + \phi_{11}$ )
3.	-6.601 B <sub>2</sub>	0.217 ( $\phi_1 + \phi_{10}$ ) + 0.367 ( $\phi_2 + \phi_9$ ) +0.388 ( $\phi_3 + \phi_8$ ) + 0.278 ( $\phi_4 + \phi_7$ ) +0.301 ( $-\phi_5 - \phi_{12}$ ) + 0.009 ( $\phi_6 + \phi_{11}$ )
4.	-6.357 A <sub>2</sub>	0.368 ( $-\phi_1 + \phi_{10}$ ) + 0.433 ( $-\phi_2 + \phi_9$ ) + 0.321 ( $-\phi_3 + \phi_8$ ) + 0.052 ( $-\phi_4 + \phi_7$ ) +0.216 ( $\phi_5 - \phi_{12}$ ) + 0.156 ( $\phi_6 - \phi_{11}$ )
5.	-5.726 B <sub>2</sub>	0.414 ( $\phi_1 + \phi_{10}$ ) + 0.184 ( $\phi_2 + \phi_9$ ) 0.126 ( $-\phi_3 - \phi_8$ ) + 0.386 ( $\phi_4 + \phi_7$ ) +0.013 ( $\phi_5 + \phi_{12}$ ) + 0.359 ( $\phi_6 + \phi_{11}$ )
6.	-4.291 A <sub>2</sub>	0.333 ( $\phi_1 - \phi_{10}$ ) + 0.139 ( $-\phi_2 + \phi_9$ ) +0.400 ( $-\phi_3 + \phi_8$ ) + 0.222 ( $\phi_4 - \phi_7$ ) +0.079 ( $-\phi_5 + \phi_{12}$ ) + 8.393 ( $\phi_6 - \phi_{11}$ )
7.	-1.847 B <sub>2</sub>	0.171 ( $\phi_1 + \phi_{10}$ ) + 0.352 ( $-\phi_2 - \phi_9$ ) +0.217 ( $-\phi_3 - \phi_8$ ) + 0.379 ( $\phi_4 + \phi_7$ ) +0.227 ( $-\phi_5 - \phi_{12}$ ) + 0.323 ( $\phi_6 + \phi_{11}$ )
8.	3.225 A <sub>2</sub>	0.096 ( $\phi_1 - \phi_{10}$ ) + 0.398 ( $\phi_2 - \phi_9$ ) +0.289 ( $\phi_3 - \phi_8$ ) + 0.296 ( $-\phi_4 + \phi_7$ ) +0.175 ( $\phi_5 - \phi_{12}$ ) + 0.371 ( $-\phi_6 + \phi_{11}$ )
9.	4.400 B <sub>2</sub>	0.313 ( $\phi_1 + \phi_{10}$ ) + 0.176 ( $\phi_2 + \phi_9$ ) +0.409 ( $-\phi_3 - \phi_8$ ) + 0.174 ( $\phi_4 + \phi_7$ ) +0.062 ( $\phi_5 + \phi_{12}$ ) + 0.411 ( $-\phi_6 - \phi_{11}$ )
10.	5.689 A <sub>2</sub>	0.428 ( $-\phi_1 + \phi_{10}$ ) + 0.211 ( $\phi_2 - \phi_9$ ) +0.111 ( $\phi_3 - \phi_8$ ) + 0.385 ( $-\phi_4 + \phi_7$ ) +0.008 ( $\phi_5 - \phi_{12}$ ) + 0.334 ( $\phi_6 - \phi_{11}$ )
11.	6.968 B <sub>2</sub>	0.381 ( $-\phi_1 - \phi_{10}$ ) + 0.413 ( $\phi_2 + \phi_9$ ) +0.321 ( $-\phi_3 - \phi_8$ ) + 0.121 ( $\phi_4 + \phi_7$ ) +0.065 ( $-\phi_5 - \phi_{12}$ ) + 0.248 ( $\phi_6 + \phi_{11}$ )
12.	7.802 A <sub>2</sub>	0.223 ( $-\phi_1 + \phi_{10}$ ) + 0.303 ( $\phi_2 - \phi_9$ ) +0.367 ( $-\phi_3 + \phi_8$ ) + 0.436 ( $-\phi_4 + \phi_7$ ) +0.102 ( $-\phi_5 + \phi_{12}$ ) + 0.150 ( $\phi_6 - \phi_{11}$ )

possible) configuration the contribution of some of them are zero due to symmetry [14]. Tables 4A and 4B contain the result using charged sphere model.

The calculations according to charged sphere model are unable to reproduce the spectra of these species (I) and (II), it is probably due to larger  $\gamma_{pq}$ 's. The calculations with the Mataga-Nishimoto formulation brought closer agreement to the experimental spectra.

Experimentally these neutral species MV:(I) and DQ:(II) exhibit two adsorption peaks. The position of absorption peaks are collected in Table-6.

In Table 2A and 3A the singlet-singlet transition due to all configuration are laid down for molecules (I) and (II) respectively according to Mataga-Nishimoto formulation along with the experimental values.

Table-3A: Singlet transition energies (in eV) for DQ: (II) calculations are according to Mataga-Nishimoto Method.

Calcd	Obs	Contributing configuration
2.6032 <sup>a</sup>	3.0238	0.9820 $\chi_{7-8}$ - 0.0525 $\chi_{6-9}$ + 0.1480 $\chi_{7-11}$
(B <sub>1</sub> )		- 0.0282 $\chi_{5-8}$ - 0.0410 $\chi_{5-10}$ - 0.0225 $\chi_{4-9}$ + 0.0189 $\chi_{4-11}$ - 0.0378 $\chi_{7-12}$ + 0.0554 $\chi_{3-8}$ + 0.0196 $\chi_{5-12}$ + 0.0303 $\chi_{3-10}$ - 0.0267 $\chi_{3-12}$ + 0.0273 $\chi_{2-9}$ + 0.0099 $\chi_{2-11-8}$ - 0.105 $\chi_{1-8}$ - 0.0094 $\chi_{1-10}$ + 0.0141 $\chi_{1-12}$
3.0873 <sup>b</sup>	3.1307	0.9691 $\chi_{6-9}$ + 0.1722 $\chi_{6-8}$ - 0.0964 $\chi_{6-9}$
(A <sub>1</sub> )		- 0.1137 $\chi_{5-9}$ - 0.0288 $\chi_{7-11}$ - 0.0154 $\chi_{4-8}$ + 0.0229 $\chi_{5-11}$ + 0.0182 $\chi_{4-10}$ + 0.0158 $\chi_{6-12}$ + 0.0651 $\chi_{3-9}$ + 0.0080 $\chi_{4-12}$ - 0.0203 $\chi_{3-11}$ + 0.0035 $\chi_{2-8}$ + 0.0395 $\chi_{2-10}$ - 0.0092 $\chi_{2-12}$ - 0.0172 $\chi_{1-9}$ - 0.0142 $\chi_{1-11}$

a) Polarized along +Y-axis

b) Polarized along -X-axis

Table-4A: Singlet transition energies (in eV) for MV:(I) calculations are according to Charge Sphere Method.

Calcd	Obs	Contributing configurations
3.4181 <sup>a</sup>	3.1307	0.9918 $\chi_{7-8}$ + 0.0783 $\chi_{6-10}$ - 0.0676 $\chi_{5-9}$
(B <sub>2u</sub> )		-0.0702 $\chi_{4-11}$ - 0.0238 $\chi_{7-12}$ - 0.0082 $\chi_{3-8}$ -0.0017 $\chi_{3-12}$ + 0.0045 $\chi_{2-11}$ - 0.003 $\chi_{1-8}$ + 0.0061 $\chi_{1-12}$
3.3484 <sup>b</sup>	3.3056	0.9801 $\chi_{7-10}$ - 0.0388 $\chi_{6-8}$ + 0.1757 $\chi_{4-9}$
(B <sub>3u</sub> )		-0.0552 $\chi_{5-11}$ - 0.0210 $\chi_{6-12}$ - 0.0265 $\chi_{3-10}$ -0.0364 $\chi_{2-9}$ - 0.0395 $\chi_{1-10}$

a) Polarized along +Y-axis

b) Polarized along +X-axis

Table-5A: Singlet transition energies (in eV) for DQ:(II) calculations are according to Charge Sphere Method.

Calcd	Obs	Contributing configurations
2.7179 <sup>a</sup>	3.0238	0.9608 $\chi_{7-8}$ - 0.2080 $\chi_{6-9}$ + 0.1560 $\chi_{7-11}$
(B <sub>1</sub> )		-0.0027 $\chi_{5-8}$ + 0.0232 $\chi_{5-10}$ - 0.0178 $\chi_{4-9}$ +0.0332 $\chi_{4-11}$ - 0.0404 $\chi_{7-12}$ + 0.0278 $\chi_{3-8}$ +0.0257 $\chi_{5-12}$ + 0.0425 $\chi_{3-10}$ + 0.0077 $\chi_{3-12}$ +0.0411 $\chi_{2-9}$ + 0.0098 $\chi_{6-10}$ - 0.0226 $\chi_{1-8}$
3.4039 <sup>b</sup>	3.1307	0.9745 $\chi_{7-9}$ - 0.0383 $\chi_{6-8}$ - 0.1597 $\chi_{6-9}$
(A <sub>1</sub> )		-0.0675 $\chi_{5-9}$ - 0.0438 $\chi_{7-11}$ - 0.0017 $\chi_{4-8}$ +0.0668 $\chi_{5-11}$ - 0.0270 $\chi_{4-10}$ + 0.0052 $\chi_{6-12}$ +0.0900 $\chi_{3-9}$ - 0.0120 $\chi_{4-12}$ - 0.0025 $\chi_{3-11}$ +0.0154 $\chi_{2-8}$ + 0.0466 $\chi_{2-10}$ - 0.0158 $\chi_{2-12}$ -0.0256 $\chi_{1-9}$ - 0.0128 $\chi_{1-11}$

a) Polarized along +Y-axis

b) Polarized along -X-axis

The calculated triplet - triplet transition, does not confer to the experimental results. The same conclusions were drawn earlier from pure experimental results [1]. It is also to be noted that using Charged Sphere Model for  $\gamma_{pq}$ , the calculated spectra are at variance with the experimental spectra (See Table 4A for calculated and experimental transition energies), whereas the Mataga-Nishimoto integrals for  $\gamma_{pq}$  leads to two transition which are closer to the experimental values. Thus through the theoretical calculations we establish that I and II exist as closed shell singlet molecules. It is, therefore, to be noted that for the pi-electrons frame work calculation, complete planar structure for all the moieties were assumed. In case of DQ(II) both of its rings were assumed to have aromatic character.

In case of DQ:(II), the transition at 410 nm is not reproduced precisely. The reason might be that parameters selected better suited to the lower wave length (UV or near UV) transitions or other possibility might be that in it's case the electronic charge density is not distributed symmetrically as in MV:(I).

Table-6: Position of  $\lambda_{max}$  and experimental extinction coefficients

Molecule	Position (nm)	Extinction Coefficients
MV:(I)	396	27100
	376	20000
DQ:(II)	410	27800
	396	14500
BV:(III)	390	25700
	372	22500

### Experimental

$MV^{2+}$  can be reduced in two steps by one electron addition in each step (eq. I and eq. II) either by electrochemical or chemical means.



Chemical method is adopted to reduce all the species methyl viologen dication ( $MV^{2+}$ ), diquat dication ( $DQ^{2+}$ ), diquat dication ( $DQ^{2+}$ ) and n-butyl viologen dication ( $BV^{2+}$ ) by taking

magnesium as reducing agent in acetonitrile solvent.

Details of preparation of MV:(I), DO:(II) and BV:(III) are the same described before [1] except that in the present case the reactants were stirred for 5-9 hours and the progress was monitored by taking UV visible spectra time to time. The mixture changed colour, dark blue to yellowish red in case of ( $MV^{2+}$ ) and ( $BV^{2+}$ ) while green to yellowish brown in case ( $DQ^{2+}$ ).

### Appendix

#### The choice of integrals

While applying Charged Sphere Model, the values of  $\gamma_{cc}$  is taken to be equal to 10.53 eV [15] while  $\beta_{\alpha} = -2.390$  eV as suggested by Parr [16].

The two centre  $\gamma_{cc}$  integrals are given in Table-A-1. The basis of integrals is outlined below:

For interatomic distances greater than 2.80 Å the two centre repulsion integrals  $\gamma_{cc}$  are calculated according to eq. A-2 [17] based upon the interaction of two uniformly charged spheres of diameter:

$$D_p = \frac{4.597}{Z_p} \text{ \AA} \quad (A-1)$$

where  $Z_p$  is the effective nuclear charge for the  $2p_z$  atomic orbital denoted by  $\phi_p$ .

$$\gamma_{pq} = \frac{7.1975}{r_{pq}} \left[ \left\{ 1 + \left( \frac{D_p - D_q}{2r_{pq}} \right)^2 \right\}^{-\frac{1}{2}} + \left\{ 1 + \left( \frac{D_p + D_q}{2r_{pq}} \right)^2 \right\}^{-\frac{1}{2}} \right] \quad (A-2)$$

For distances less than 2.80 Å the repulsion integrals  $\gamma_{pq}$  are calculated by extrapolation method.

$$\gamma_{pq} = \frac{1}{2} (\gamma_{pp} + \gamma_{qq}) + C_1 r_{pq} + C_2 r_{pq}^2$$

The two constants  $C_1$  and  $C_2$  are calculated by solving the two equations simultaneously obtained from eq. A-3 by substituting the  $\gamma_{pp}$  and  $\gamma_{qq}$  values obtained from eq. A-2 for  $r_{pq} = 2.80$  Å and  $r_{pq} = 3.70$  Å respectively.

Table-A-1: One and two centre  $\gamma_{cc}$  integrals for MV:(I) and DQ:(II) according to Charged Sphere Model ( $Z_C = 3.25$ )

Distance	Repulsion integral
0.000	$\gamma_{11} = 10.530 = \gamma_{55}$
1.395	$\gamma_{12} = 7.285 = \gamma_{54}$
2.416	$\gamma_{13} = 5.441 = \gamma_{53}$
2.790	$\gamma_{14} = 4.879 = \gamma_{52} = \gamma_{512}$
4.185	$\gamma_{17} = 3.123 = \gamma_{511}$
5.029	$\gamma_{18} = 2.809$
6.393	$\gamma_{19} = 2.225$
6.975	$\gamma_{110} = 2.043$

Table A-2: One and two centre  $\gamma_{cc}$  integrals for MV:(I) and DQ:(II) according to Mataga-Nishimoto method ( $I_C = 11.16$ )

Distance	Repulsion integral
0.000	$\gamma_{11} = 12.130 = \gamma_{55}$
1.395	$\gamma_{12} = 5.355 = \gamma_{54}$
2.416	$\gamma_{13} = 3.881 = \gamma_{53}$
2.790	$\gamma_{14} = 3.526 = \gamma_{52} = \gamma_{512}$
4.185	$\gamma_{17} = 2.628 = \gamma_{511}$
5.029	$\gamma_{18} = 2.277$
6.393	$\gamma_{19} = 1.873$
6.975	$\gamma_{110} = 1.741$

Table-A-3: Modified repulsion integrals  $\gamma_{CN}$  integrals for MV:(I) according to Mataga-Nishimoto method ( $I_N = 19.72$ )

Distance	Repulsion integral
0.000	$\gamma_{11} = 14.800$
1.395	$\gamma_{12} = 5.744$
2.416	$\gamma_{13} = 4.082$
2.790	$\gamma_{14} = 3.691$
4.185	$\gamma_{17} = 2.718$
5.029	$\gamma_{18} = 2.344$
6.393	$\gamma_{19} = 1.919$
6.975	$\gamma_{110} = 1.811$

While in case of Mataga-Nishimoto method [19], which gives generally better agreement [20] the two centre repulsion or coulomb integrals  $\gamma_{pq}$  have been calculated by the expression:

$$\gamma_{pq} = \frac{14.3986}{R + r_{pq}} \quad (\text{A-4})$$

where

$$R = \frac{14.3986}{\frac{1}{2}(I_p + I_q) + (E_p + E_q)} \quad (\text{A-5})$$

and  $r_{pq}$  is the distance between atom  $p$  and  $q$ .  $I_p$  is the valence state ionization potential of atom  $p$  and  $E_p$  is the electron affinity of the same atom.

Table-A-4: Modified repulsion integrals  $\gamma_{CN}$  for DQ:(II) according to Mataga-Nishimoto method ( $I_N = 19.72$  eV)

Distance	Repulsion integral
0.000	$\gamma_{55} = 14.800$
1.395	$\gamma_{54} = 5.744$
2.416	$\gamma_{53} = 4.082$
2.790	$\gamma_{52} = 3.691$
4.185	$\gamma_{511} = 2.718$
4.185	$\gamma_{512} = 3.825$

One enter two electron repulsion integrals  $r_{pq}$  were calculated according to expression [14].

$$\gamma_{pq} = I_p + E_q \quad (\text{A-6})$$

The values of  $I_c$  and  $E_c$  are obtained from Hinze and Jaffe's table. The resonance integrals  $\beta_{cc}$  is taken to be -2.390 eV as already mentioned.

#### Modification for hetro atom

While applying Charged Sphere Model (eq. A-1, A-2) the one centre two electron repulsion integral  $\gamma_{NN}$  was taken to be 12.27 eV [1]. For the purpose to calculate two centre two electron repulsion integral  $\gamma_{CN}$ ,  $Z_N$  was taken to be 4.25,  $d\omega_N$  was varied and adjusted at -16.83 eV to reproduce the first singlet state of MV:(I) to its best, while taking care of allowed symmetry type of the transition. (The calculated integrals are not included in the Appendix).

While applying Mataga-Nishimoto Method the one centre repulsion integral are calculated according to the expression A-6. The valence state ionization potential  $I_N$  was taken to be equal to 19.72 eV and the electron affinity was taken to equal to -4.92 eV. [21]  $d\omega_N$  integral was varied to reproduce the first singlet of MV:(I), in this method it was set at -17.25 eV. The integrals  $\gamma_{CN}$  are listed in Table A-3. The resonance integrals  $\beta_{CN}$  is related to the standard resonance integrals  $\beta$  in the usual Huckel formulation [22] (eq. A-7) for both the models.

$$\beta_{CN} = k_{CN}\beta \quad (\text{A-7})$$

where  $k_{CN}$  is equal to 0.8 and  $\beta$  or  $\beta_{cc}$  is equal to -2.390 eV.

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