Supporting information

Resonant Raman Spectra of Molecules with Diradical Character: Multiconfigurational Wavefunction Investigation of Neutral Viologens

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Detailed analysis of Figure 1

Within the *MP2 approach*, the most intensive peak is mainly associated with the 0-0 transition (FC factor = 2.51E-01). The fundamental vibrational excitations of modes 10 (FC 9.58E-02), 11 (FC 2.26E-02), and 29 (FC 4.31E-02), as well as the overtone $2\nu_{10}$ (FC 1.82E-02) also contribute this vibronic band. The peak at 378 nm represents the second most significant peak in the spectrum and its intensity is very close to the absorption maximum. This vibronic band mainly originated from the fundamental excitations of modes 63 (FC 8.51E-02) and 60 (FC 2.36E-02) and the simultaneous excitation of modes $\nu_{10}+\nu_{63}$ (FC 3.24E-02). The next important contributions to the second peak come from the fundamental excitations of modes 34 (FC 2.08E-02), 39 (FC 1.54E-02), and 43 (FC 1.92E-02), but also from the combinations of bands $\nu_{10}+\nu_{29}$ (FC 1.64E-02) and $\nu_{29}+\nu_{63}$ (FC 1.46E-02). The shoulder at 350 nm is associated mostly with the overtone $2\nu_{63}$ (FC 1.44E-02) but also with several combinations of bands: $\nu_{60}+\nu_{63}$ (FC 7.99E-03), $\nu_{10}+2\nu_{63}$ (FC 5.48E-03) and $\nu_{10}+\nu_{60}+\nu_{63}$ (FC 3.05E-03).

Within the *CASSCF approach*, the single vibronic band peaking at 378 nm originates from the 0-0 transition (FC 1.22 E-01) as well as from fundamental excitations of modes 29 (FC 8.92E-02), 63 (FC 3.19E-02), 10 (FC 2.54E-02), 46 (FC 2.24 E-02) and from the overtone $2\nu_{29}$ (FC 3.27E-02).

Table S1. Optimized bond lengths, R [Å] and dihedral angles θ [°] for the ground state of methyl viologen in different oxidation states as determined at different levels of approximation.

	MV^0	MV^0	MV^{2+}	$MV^{\bullet+}$	MV^0
	SS-CASSCF (14,12)	SS-CASSCF (10,10)	MP2	MP2	MP2
$R(Me-N^1)$	1.446	1.446	1.491	1.469	1.456
$R(N^1-C^1)$	1.391	1.395	1.355	1.368	1.393
$R(C^1-C^2)$	1.350	1.349	1.390	1.373	1.362
$R(C^2-C^3)$	1.467	1.469	1.403	1.429	1.453
$R(C^3-C^{3\prime})$	1.374	1.372	1.482	1.433	1.391

Table S2. SA2-CASSCF vertical excitation energy E_{0e} [eV], wavelength λ_{0e} [nm] and transition dipole moment μ_{0e} [a.u.] of PEV^0. The SA2-CASPT2 values of PEV^0 are obtained by correcting the SA2-CASPT2 results of MV^0 for the effect of the phenylene extension, as determined at the SA2-CASSCF level [$\Delta E_{phenylene}$ = 4.68(PEV^0) - 5.65(MV^0) = -0.97 eV].

	SA2-CASSCF	SA2-CASPT2
E_{0e}	4.68	2.31[†]
λ	265	537
μ	4.23[†]	

[†] Used for the simulations of RR and absorption spectra.

Table S3. Mode labels, vibrational frequencies ω_ℓ [cm^{-1}], and Huang-Rhys factors S_ℓ for the 1st excited state of MV^0 and PEV^0 calculated with the MP2 and SS-CASSCF methods. Only the normal modes with S_ℓ >0.005 are displayed.

MV^0				PEV^0	
MP2		SS-CASSCF		MP2	
$\omega_{sc.}$*	S_ℓ	$\omega_{sc.}$*	S_ℓ	$\omega_{sc.}$*	S_ℓ
241	0.393	270	0.035	58	0.025
277	0.093	291	0.229	63	0.032
469	0.018	652	0.172	70	0.188
668	0.012	766	0.803	109	0.317
791	0.177	852	0.020	218	0.132
812	0.008	976	0.124	268	0.449
994	0.085	1139	0.042	293	0.008
1133	0.063	1200	0.080	335	0.738
1215	0.079	1245	0.202	384	0.007
1254	0.028	1467	0.027	390	0.014
1389	0.010	1489	0.008	418	0.012
1451	0.007	1548	0.150	431	0.136
1545	0.097	1659	0.287	492	0.098
1660	0.349			536	0.019
				570	0.007
				743	0.074
				947	0.063
				987	0.120
				998	0.015
				1234	0.154
				1363	0.066
				1472	0.108
				1487	0.009
				1565	0.107
				1658	0.168

* Scaling factor 0.970
**Scaling factor 0.912

Figure S1. Initial guess for CASSCF calculation on MV^0 (right) and PEV^0 (left). The molecular symmetry of PEV^0 and MV^0 is C_{2v} obtained with the RHF/STO-3G method.
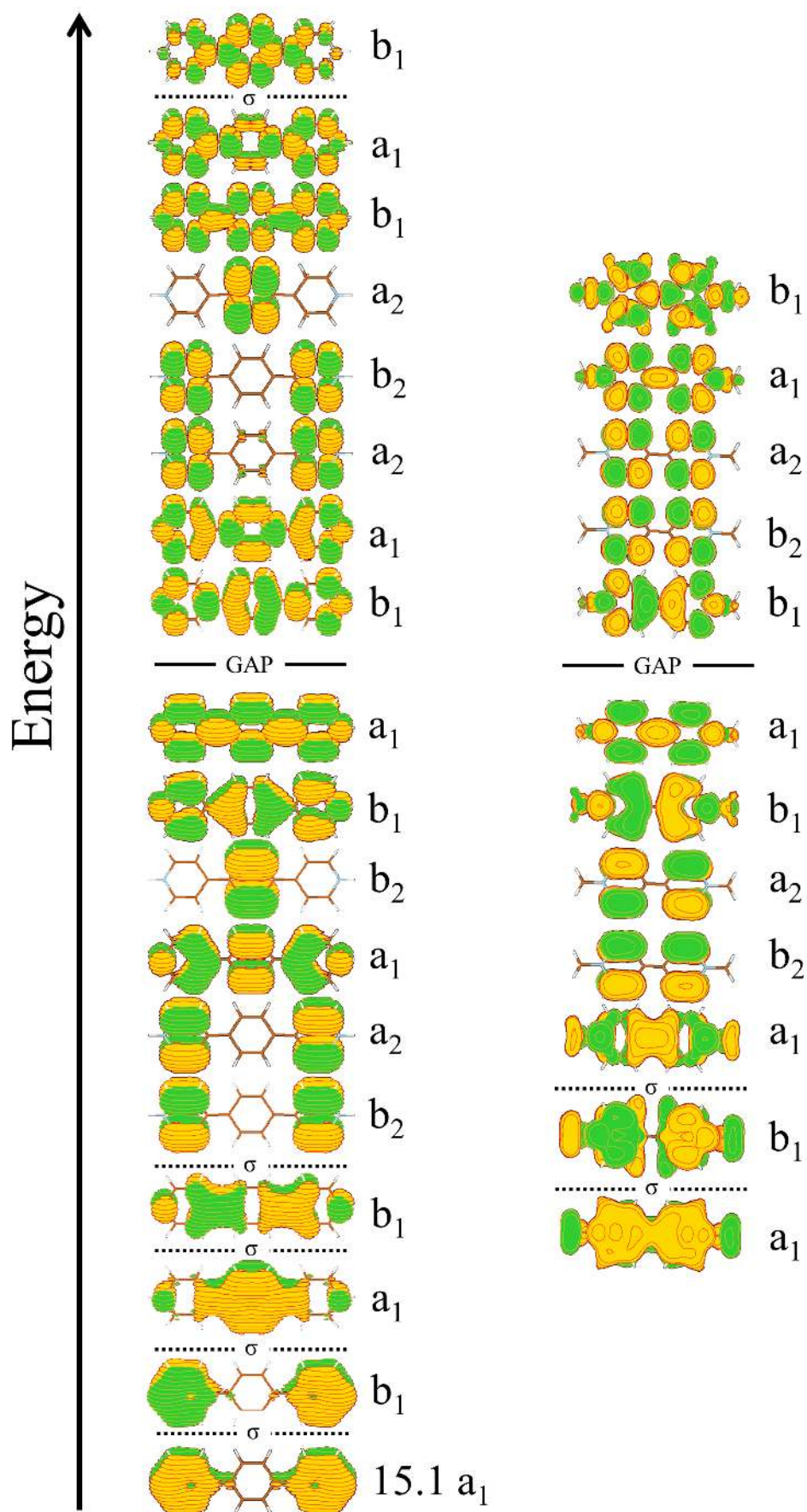
Natural orbitals occupation numbers (ON) from SS-CASSCF(10,10) calculation on the MV^0 ground state:

3 MOs in a_1 (16, ON=1.95; 17, ON=1.85; 18, ON=0.06)

3 MOs in b_1 (15, ON=1.93; 16, ON=0.13; 17, ON=0.04)

2 MOs in b_2 (9, ON=1.92; 10, ON=0.08)

2 MOs in a_2 (9, ON=1.92; 10, ON=0.08).

Natural orbitals occupation numbers (ON) from SA2-CASSCF(10,10) calculation on the MV^0:

3 MOs in a_1 (16, ON=1.96; 17, ON=1.42; 18, ON=0.06)

3 MOs in b_1 (15, ON=1.93; 16, ON=0.56; 17, ON=0.03)

2 MOs in b_2 (9, ON=1.92; 10, ON=0.08)

2 MOs in a_2 (9, ON=1.92; 10, ON=0.08).

Major contributions in the CI vectors from SA2-CASSCF(10,10) calculation on the MV^0:

S_0
22222 00000   0.90
22220 20000 -0.16

S_1
2222a b0000 -0.65
2222b a0000   0.65

Natural orbitals occupation numbers (ON) from SS-CASSCF(16,16) calculation on the PEV^0 ground state:

5 MOs in a_1 (17, ON=1.96; 19, ON=1.93; 20, ON=1.77; 21, ON=0.10; 22, ON=0.05)

5 MOs in b_1 (17, ON=1.95; 18, ON=1.90; 19, ON=0.23; 20, ON=0.06; 22, ON=0.04)

3 MOs in b_2 (12, ON=1.92; 13, ON=1.91; 14, ON=0.09)

3 MOs in a_2 (11, ON=1.92; 12, ON=0.09; 13, ON=0.09).

Natural orbitals occupation numbers (ON) from SA2-CASSCF(16,16) calculation on the PEV^0:

5 MOs in a_1 (17, ON=1.96; 19, ON=1.94; 20, ON=1.36; 21, ON=0.11; 22, ON=0.04)

5 MOs in b_1 (17, ON=1.95; 18, ON=1.91; 19, ON=0.62; 20, ON=0.06; 22, ON=0.03)

3 MOs in b_2 (12, ON=1.92; 13, ON=1.92; 14, ON=0.09)

3 MOs in a_2 (11, ON=1.92; 12, ON=0.09; 13, ON=0.08).

Major contributions in the CI vectors from SA2-CASSCF(16,16) calculation on the PEV^0:
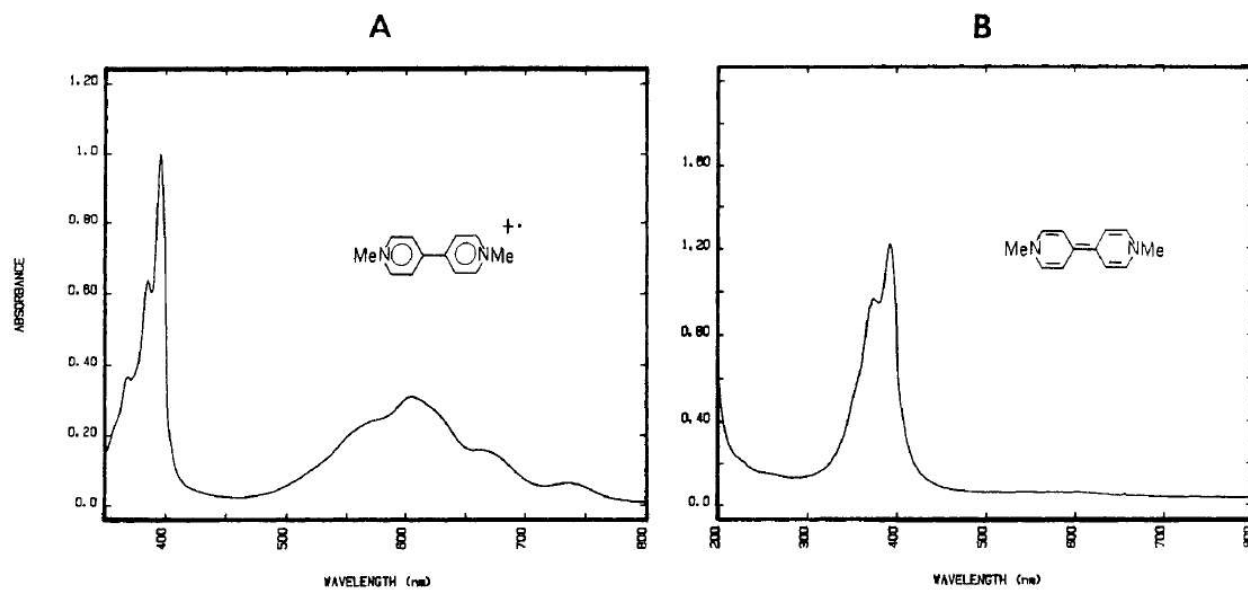
S_0

```
22200 220 22000 200     0.814
22000 220 22200 200    -0.214
```

S_1

```
22b00 220 22a00 200    -0.607
22a00 220 22b00 200     0.607
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Figure S2. MV$^{+\bullet}$ (left) and MV^0 (right) UV/vis absorption spectra from T. M. Bockman and J. K. Kochi, *J. Org. Chem.*, 1990, **55**, 4127.

A

B

Figure 1. Absorption spectrum of (A) 5×10^{-5} M MV$^{\bullet+}$PF$_6^-$ and (B) 3×10^{-4} M MV^0 in dichloromethane.

Figure S3. (Top) RR spectra of MV^0 simulated by using SA2-CASSCF ground and excited state geometries together with MP2 (A) and SS-CASSCF (B) ground state vibrational normal modes. The energy of the incident light was to $E_{0e}+0.30$ eV in order to match the experimental 363.8 nm wavelength. The Raman bands are represented by Lorentzian functions with FWHM set to 10 cm^{-1}. **(Bottom)** Experimental RR spectrum of MV in different oxidation states. (d) corresponds to the RR spectrum of MV^0 prepared by electrolysis in acetonitrile solution, recorded at exciting laser wavelength 363.8 nm from Q. Feng and T. M. Cotton, *J. Phys. Chem.*, 1986, **90**, 983.
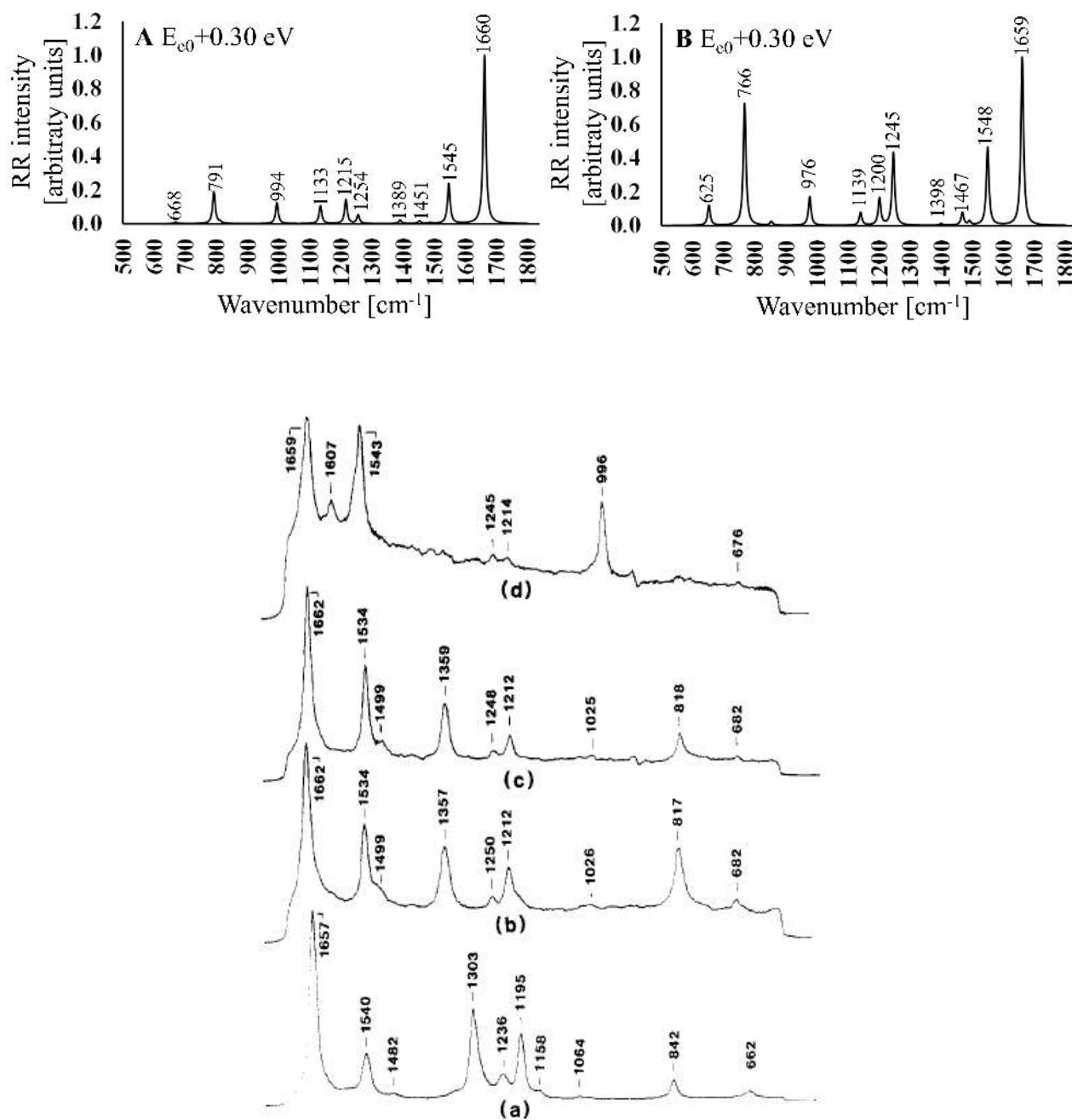
Figure 1. Raman scattering spectra of (a) 0.1 M MV^{2+} in aqueous solution; (b) $MV^{+\cdot}$ in aqueous solution, prepared by reacting 1 mM MV^{2+} with $Na_2S_2O_4$; (c) $MV^{+\cdot}$ prepared by electrolysis of 0.25 mM MV^{2+} in acetonitrile; (d) MV^0 prepared by further electrolysis of c. Exciting laser wavelength 363.8 nm; power 30 mW. The acetonitrile spectrum was subtracted from c and d.