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Theoretical Study on Photoinduced Color Change and Charge Transfer of Methylviologen

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Theoretical Study on Photoinduced Color Change and Charge Transfer of Methylviologen[#]

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Abstract

Motivation. Methylviologen dication is easily reduced to a monocation radical, and turned to be blue, forming a charge–transfer complex with a donor molecule. Yoshikawa *et al.* recently reported photo–induced reduction and charge transfer complexes in polycyano–polycadmate host clathrates. We study this reduction using quantum chemical calculations. The energy changes with the torsion angle of the two cations and the spectral change, solvent effect and the charge transfer between the dication and other guest molecules in the clathrates are investigated.

Method. The Hartree–Fock, DFT, CI singles, time dependent DFT calculations are carried out for the ground state and excited states of the two cations. Solvation effect is treated with the polarizable continuum model, and the charge transfer in the clathrates is modeled based on crystal structures determined experimentally.

Results. The optimized geometry of the monocation radical was found to be planar while that of the dication is twisted. These results are consistent with recent calculations for related compounds. The color change upon the photoreduction was reproduced by the calculation. The solvent effect of acetonitrile was found to be small. Charge transfer absorption was reproduced for the mesitylene–methylviologen dication complex in the clathrate host using a small model.

Conclusions. The geometry modification and the color change were reproduced satisfactorily. The TDDFT scheme reproduces the observed spectra better than the CIS scheme, but the latter scheme is still valuable to evaluate qualitative feature of spectra.

Keywords. Viologen; charge transfer; solution; torsion angle; spectra; density functional theory.

Abbreviations and notations

HF, Hartree–Fock	MP2, second order Møller–Plesset perturbation theory
DFT, density functional theory	CIS, configuration interaction with single excitation
TDDFT, time dependent density functional theory	CT, charge transfer
B3LYP, Becke’s three parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional	MV, methyl viologen
HOMO, highest occupied molecular orbital	PCM, polarized continuum model
SOMO, singly occupied molecular orbital	LUMO, lowest unoccupied molecular orbital
UHF, unrestricted Hartree–Fock	RHF, restricted Hartree–Fock
	ROHF, restricted open–shell Hartree–Fock

[#] Dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday.

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1 INTRODUCTION

Methylviologen dication (MV^{2+} = 1,1'-dimethyl-4,4'-bipyridinium dication) shows strong electron accepting character, and is widely used in the fields of photochemistry, electrochemistry, and solar energy conversion [1,2]. MV^{2+} is easily reduced to a monocation radical ($MV^{+•}$) whose color is blue, and forms a charge-transfer (CT) complex with a donor. Yoshikawa *et al.* recently reported reduction of MV^{2+} upon ultraviolet irradiation and charge transfer in polycyano-polycadmate host clathrates [3,4,5].

Using quantum chemical calculations we investigated in this paper the following problems: (1) the potential energy dependence on the torsion angle, which is defined by the dihedral angle between the two pyridinium rings of MV^{2+} or $MV^{+•}$; (2) solvent effect for the spectra of MV^{2+} and $MV^{+•}$; (3) spectral change in the process of the photo-induced reduction from MV^{2+} to $MV^{+•}$; (4) a charge transfer spectrum of a MV^{2+} -mesitylene CT complex trapped in a polycyano-polycadmate host.

2 CALCULATIONS

We employed several *ab initio* methods and the hybrid density functional theory to carry out the calculations for MV^{2+} and $MV^{+•}$. For the ground state we used the Hartree-Fock (HF) and Becke's three parameter hybrid exchange functional with the Lee-Yang-Parr correlation functional (B3LYP) levels of theory [6,7] and the 6-31G(d,p) basis set [8]. In order to calibrate the effects of electron correlation and the diffuse functions on the ground states, the second order Møller-Plesset perturbation theory (MP2)[6] and the 6-31++G basis set were employed [9]. Configuration interaction with single excitation (CIS) [6] and time dependent density functional theory (TDDFT) [10] were used for excited states. The theoretical ultraviolet-visible spectra were obtained using the excitation energy and the oscillator strengths of CIS and B3LYP calculations at the optimized geometries. Tomasi's polarized continuum model (PCM) using the polarizable dielectric model was mainly used to investigate solvation effect [11]. PCM calculations using the polarizable conductor model [12] and using the integral equation formalism model [10] as well as isodensity PCM calculations [14] were also done to check the model dependency of theoretical spectra. In the PCM model, a solute molecule is located in the cavity surrounded by a solvent, and the solvent is represented by the continuum with a given dielectric constant ϵ . The constant ϵ used for acetonitrile is 36.64.

The program Gaussian 98 was used for all the calculations [15]. Calculations were mainly carried out on the SGI Origin 2800 workstation cluster systems at the Research Center for Computational Science, Okazaki National Research Institute, and on the Origin 2000 system at the Information Processing Center of Shizuoka University. A part of calculations were done with the

workstations of our research group equipped with the Intel Pentium 4 and Compaq alpha processors. The graphics of geometrical structures were obtained by MOLDEN [16].

Table 1. The torsion angle at the optimized geometries and the energy differences for the methylviologen dication (MV^{2+}) and monocation radical ($MV^{+\cdot}$) at the R(O)HF, UHF, and B3LYP levels using the 6–31G(d,p) basis set. For $MV^{+\cdot}$, the B3LYP/6–31++G result is also included to investigate the effect of augmentation of diffuse functions.

MV^{2+}	Torsion angle(degree) ^a	V_0-V_{\min} (kJ/mol) ^a	$V_{90}-V_{\min}$ (kJ/mol) ^b
RHF/6–31G(d,p)	49.7	13.4	3.6
B3LYP/6–31G(d,p)	40.3	7.2	7.0
$MV^{+\cdot}$	Torsion angle(degree) ^a	V_0-V_{\min} (kJ/mol) ^a	$V_{90}-V_{\min}$ (kJ/mol) ^b
UHF/6–31G(d,p)	0.0	0.0	62.3
ROHF/6–31G(d,p)	0.0	0.0	93.7
B3LYP/6–31G(d,p)	0.0	0.0	95.2
B3LYP/6–31++G(d,p)	0.0	0.0	92.2

^a The torsion angle is defined as the angle between the two pyridine rings

^b V_{\min} , V_0 , and V_{90} are the potential energies at the optimized geometries, at torsion angle $\tau = 0$, and $\tau = 90^\circ$

3 RESULTS AND DISCUSSION

3.1 Potential Energy Dependence on the Torsion Angle

Table 1 shows the optimized torsion angles and the barrier heights at $\tau = 0$ and $\tau = 90^\circ$ for MV^{2+} and $MV^{+\cdot}$ at the B3LYP level of theory using the 6–31G(d,p) basis set. The torsion angle is defined as the angle between the two pyridine rings. We found that the dication and monocation radical give optimized geometries with τ of 40.3° and 0° , respectively.

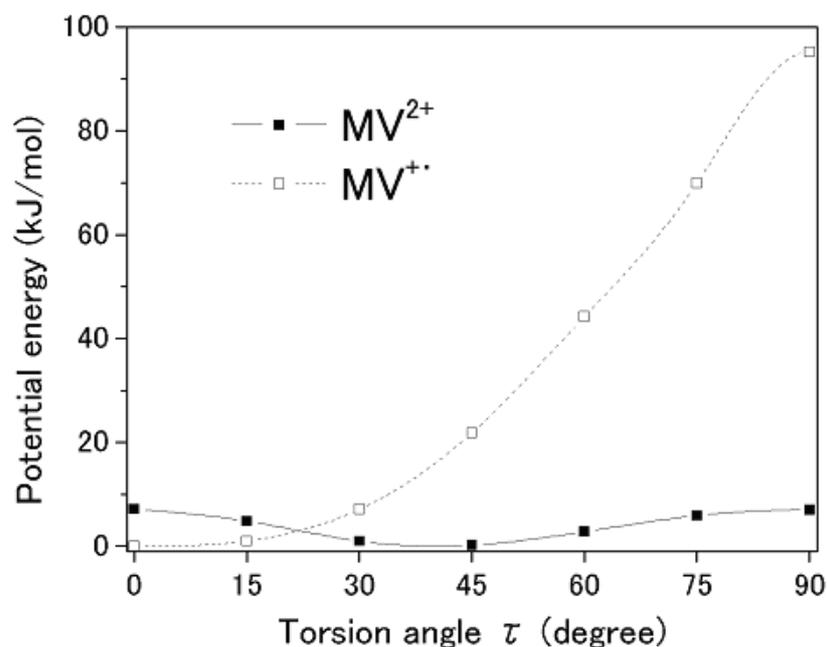


Figure 1. The potential energy curve of MV^{2+} and $MV^{+\cdot}$ for the torsion angle at the HF/6–31G(d,p) level. The torsion angle is defined as the angle between the two pyridine rings.

For MV^{2+} the RHF optimized torsion angle and the potential barriers are not very different from the B3LYP values. The result suggests that the electron correlation is not significant for the closed shell dication. We also carried out the RHF and MP2 calculations using the 3–21G basis set for MV^{2+} , and found that the potential energy curve is close to each other and $\tau = 60.6^\circ$ and 59.8° at the optimized geometries, which supports the view that the electron correlation is not significant for the dication.

For the monocation radical, all the restricted open-shell HF (ROHF), UHF, and (unrestricted) B3LYP schemes give planar optimized geometries. The B3LYP barrier height of 93.7 kJ/mol, and the S^2 values are 0.756–0.758, which indicates the spin contamination is negligible. The ROHF barrier height of 95.2 kJ/mol is comparable to the value of 93.7 kJ/mol in the B3LYP level, although the ROHF calculations were often suffering from the difficulty of convergence. The electron correlation would be small from the comparison of ROHF barrier height with the B3LYP value. The UHF barrier height of 62.3 kJ/mol, on the other hand, is significantly lower than the B3LYP value. The UHF S^2 values are 0.808 at the planar geometry, and become larger with the torsion angle to be 1.191 at $\tau = 90^\circ$. The latter value is significantly deviated from the doublet value of 0.75. We also carried out the MP2 calculation based on the UHF scheme at the optimized UHF geometries at $\tau = 0^\circ$ and $\tau = 90^\circ$, and found that non-projected and projected schemes give the barrier height of 172.5 and 110.4 kJ/mol. The latter barrier height for the projected scheme is comparable to the B3LYP value, but the value for non-projected scheme is much larger. This result again shows that spin contamination should be evaded for reasonable description of the present system. Figure 1 shows the potential energy curves of MV^{2+} and MV^{+} at the B3LYP/6–31G(d,p) level. We optimized the geometries every 15° of the torsion angle: the torsion angle was fixed and all the other geometrical parameters were optimized to obtain each energy. In addition to the partial optimization, we carried out the full optimization of the two molecules.

Wolkers *et al.* obtained a twisted optimized geometry with τ of 15° for MV^{+} at the level of HF/3–21G [17] although the energy difference between the planar and optimized structures was only 0.05 kcal/mol (0.2 kJ/mol). We undertook geometry optimization at the UHF/3–21G level of theory, but still obtained a planar optimized structure with the barrier height of 56.7 kJ/mol. In our result, the energy difference between the planar structure and the twisted structure of $\tau = 15^\circ$ is only 1.0 kJ/mol. The potential curve near the minimum energy structure is also very flat in the present calculation. A different convergence criterion for the geometry optimization, for example, may have led to the different optimized structure in their calculation. The S^2 values are 0.808 at $\tau = 0^\circ$ and 0.807 at $\tau = 15^\circ$. The spin contamination is not serious near the optimized geometry.

We undertook optimization with the 6–31++G because diffuse functions may enhance the bulkiness, that is, repulsion effect between electron clouds around the C–C bond between the pyridinium moieties and lead to a twisted stable structure. However, the B3LYP/6–31++G

calculation still gave a planar optimized structure with a barrier height of 92.2 kJ/mol for MV^{++} .

Castella–Ventura and Kassab calculated several transient species implicated in the photoreduction of 4,4'–bipyridine, and reported the optimized structures of N,N'–diprotonated dication ($44BPYH_2^{2+}$) and N,N'–dihydro cation radical ($44BPYH_2^{+\cdot}$) [18], which give MV^{2+} and $MV^{+\cdot}$ if the hydrogens are replaced with methyl groups. They optimized the geometries at the RHF and B3LYP level using the 6–31G(+*) basis set, in which a polarization function and *sp* diffuse functions are added to the 6–31G basis set on each nitrogen atom. The diprotonated dication had twisted optimized geometries with $\tau = 51.6^\circ$ and 42.2° at the HF and B3LYP levels while the dihydro cation radical was planar at both levels. Ould–Moussa *et al.* reported a planar optimized structure for $44BPYH_2^{+\cdot}$ with the smaller 3–21G(+*) basis set [19]. Our twisted MV^{2+} and planar $MV^{+\cdot}$ structure are consistent with the results of Castella–Ventura and Kassab and Ould–Moussa *et al.* On the other hand, Hofmann *et al.* gave earlier a non–planar $44BPYH_2^{+\cdot}$ structure of $\tau = 11.9^\circ$ at the HF/STO–3G level with partial geometry optimization [20]. The potential energy curve is very shallow at the minimum in MV^{++} and $44BPYH_2^{+\cdot}$, so that the full optimization would be necessary to obtain the correct optimized structure. The low barrier of 7.2 kJ/mol for MV^{2+} enables the torsion angle to have a wide range of values in a crystalline state because of the packing effect as discussed in the previous paper [5]. The torsion angles of MV^{2+} observed in the polycyano–polycadmate host clathrates were in the range of about 0–75°. This observation is consistent with the present calculations. The observed torsion angle for MV^{++} in crystals were 6° and 11° for $[MV^{++}][PF_6^-]$ and 1.8° and 1.2° for $[MV^{++}][Cl^-]$ [16]. The difference between the energies for the planar structure and the geometry of $\tau = 15^\circ$ is only 1.0 kJ/mol. Thus, the twisted structures in the crystals are also explained by the packing effect although the zero point vibrational energy might play a part in this estimation.

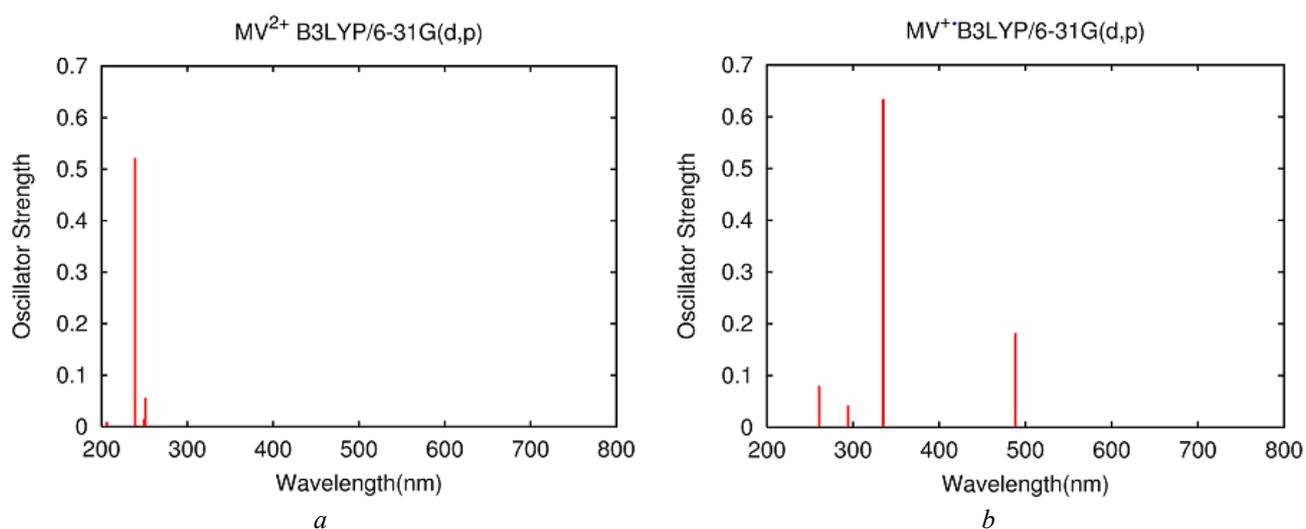


Figure 2. The theoretical spectra in the wave length range of 200–800 nm using the TDDFT scheme for the methylviologen dications (MV^{2+}) (a) and monocation radical ($MV^{+\cdot}$) (b).

3.2 Spectral Change in the Gas Phase and in the Acetonitrile Solution

The theoretical spectra in the ultraviolet–visible region calculated using the TDDFT scheme are shown in Figure 2. The density functional and basis set used are B3LYP and 6–31G(d,p). MV^{2+} shows absorption at 239 nm in the ultraviolet region. The corresponding peak appears at 201 nm in the CIS calculation for MV^{2+} (not shown). These findings are consistent with the fact that MV^{2+} is colorless. On the other hand, $MV^{+•}$ shows a strong absorption at 335 nm in the ultraviolet region and a medium peak at 488 nm in the visible region.

We investigated the solvation effect of acetonitrile on MV^{2+} and $MV^{+•}$ because MV^{2+} is easily soluble to acetonitrile. We tested four different models as described in Calculation Section: PCM using the polarizable dielectric model, polarizable conductor model, and the integral equation formalism, and isodensity PCM. The test calculations were done at the CIS/6–31G(d,p) level for MV^{2+} . The theoretical spectra obtained were very similar to each other. Thus, we decided to use the simplest PCM model to calculate the solvation effects. The theoretical spectrum of MV^{2+} and $MV^{+•}$ in acetonitrile solution based on the TDDFT with the B3LYP functional and the 6–31G(d,p) basis set was close to the spectrum in the gas phase. This result indicates that the solvation effect of acetonitrile is negligible in the dication as well as the monocation radical.

This small solvation effect would be explained by the charge distribution of highest occupied molecular orbital (HOMO) (or SOMO in $MV^{+•}$) and LUMO of the two cations. The HOMO (SOMO) and LUMO are π orbitals of the two cations. The HOMO and LUMO of MV^{2+} are delocalized over the whole molecule, so that the charge separation in the ground state and that in the first excited state are not significant. Thus, the stabilization by the solvation is small for the two states, and this small stabilization for both states leads to the small change of the spectrum in the acetonitrile solution for MV^{2+} . In the case of $MV^{+•}$, the SOMO is localized at one pyridine ring and the LUMO is localized at the other ring. The charge localization in the first excited state is, therefore, similar to that in the ground state. Thus, there is not much difference between the stabilization by polar solvents of the ground state and that of the excited state, and the solvent effect is small. The stabilization of the higher excited states is similar to those of the ground state and the first excited state probably because of a similar reason.

Table 2. Theoretical and observed absorption wave lengths for $MV^{+•}$. The basis set used is 6–31G(d,p).

	Wavelength (nm)	
CIS	325	431
TDDFT B3LYP	335	488
Experiment ^a	396–398	608

^a Ref. [21]. λ_{\max} in dichloromethane, tetrahydrofuran, and acetonitrile solution

Since we have found that the solvation effect is small, we can now safely compare the present results with the values observed in solutions. Table 2 shows comparison of the calculated absorption wavelength with the observation of Bockman and Kochi [21]. Since the solvents other

than acetonitrile have much smaller dielectric constants: $\epsilon(\text{dichloromethane}) = 8.9$ and $\epsilon(\text{tetrahydrofuran}) = 7.6$ compared to $\epsilon(\text{acetonitrile}) = 36.6$, the present argument can apply to the other solvents in Ref. [21]. The comparison of the theory with the observation indicates that the strong absorption at 335 nm corresponds to the sharp peak at 396–398 nm in the experiment and the medium peak at about 488 nm to the broad peak of 608 nm as shown in Table 2.

We calculated the spectrum of MV^{2+} with a planar geometry to examine how large the effect of geometrical change from MV^{2+} to MV^{+} is. It was found that the strong peak at 239 nm of MV^{2+} is shifted to 294 nm. The effect of the geometrical change is significant, but is not enough to lead to the visible absorption of MV^{+} . Several planar MV^{2+} were observed in the polycyano–polycadmate host clathrates [5]. These geometrical changes to planar forms may be the origin of sensitivity of the planar MV^{2+} to the solar light.

In conclusion, the spectra in Figure 2 reproduced the color change accompanying the reduction from MV^{2+} to MV^{+} although the excitation energy was not accurately reproduced. It was also found that TDDFT reproduces the absorption peaks better than CIS in Table 2. The excitation energy was consistently larger in the CIS calculations than in the TDDFT calculations as shown in Table 2. This is due to overestimation of the excitation energy in the CIS scheme. It is noted, however, that the color change is still reproduced in the CIS calculations. This result encourages one to apply the CIS scheme to qualitative evaluation of spectra for larger systems where the TDDFT method is much more difficult to apply.

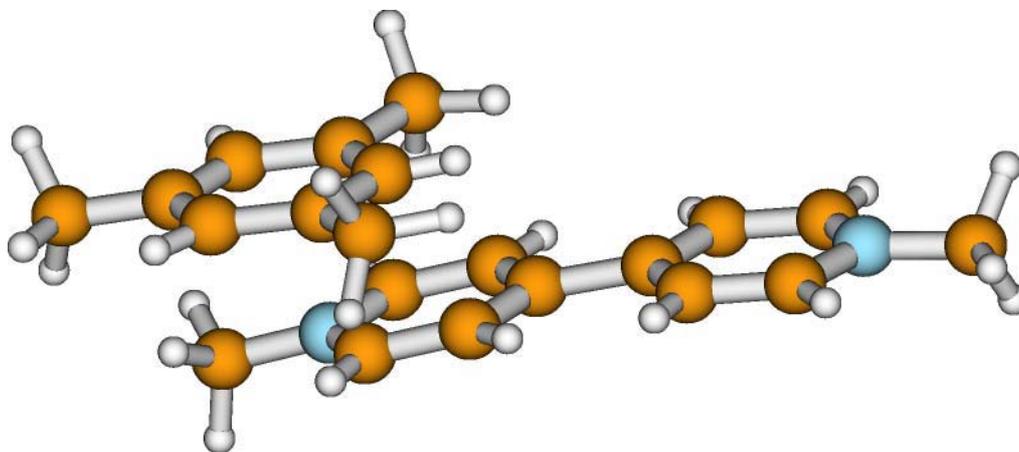


Figure 3. The perspective views of the mesitylene– MV^{2+} CT complex. The brown, blue and white spheres represent carbon, nitrogen and hydrogen atoms, respectively.

3.3 Charge Transfer in Polycyano–Polycadmate Host Clathrates

Yoshikawa *et al.* observed CT complexes in polycyano–polycadmate host clathrates including MV^{2+} . Some of the crystal structures of the clathrates have been determined, and the structure including mesitylene as a CT–donor has been reported [4]. Thus, we calculated the ultraviolet–

visible spectrum of the mesitylene–MV²⁺ complex in the clathrate.

We employed the geometrical parameters of the crystal structures determined by single crystal X-ray diffraction. The positions of hydrogen atoms were generated geometrically. The perspective views of the mesitylene CT complex in the clathrate are shown in Figure 3. The methylviologen moiety is nearly planar in the complex, and the geometry is close to the stable geometry of MV²⁺. This finding suggests that the electronic structures of the moieties are closer to that of MV²⁺ than that of MV²⁺ as indicated in the previous section.

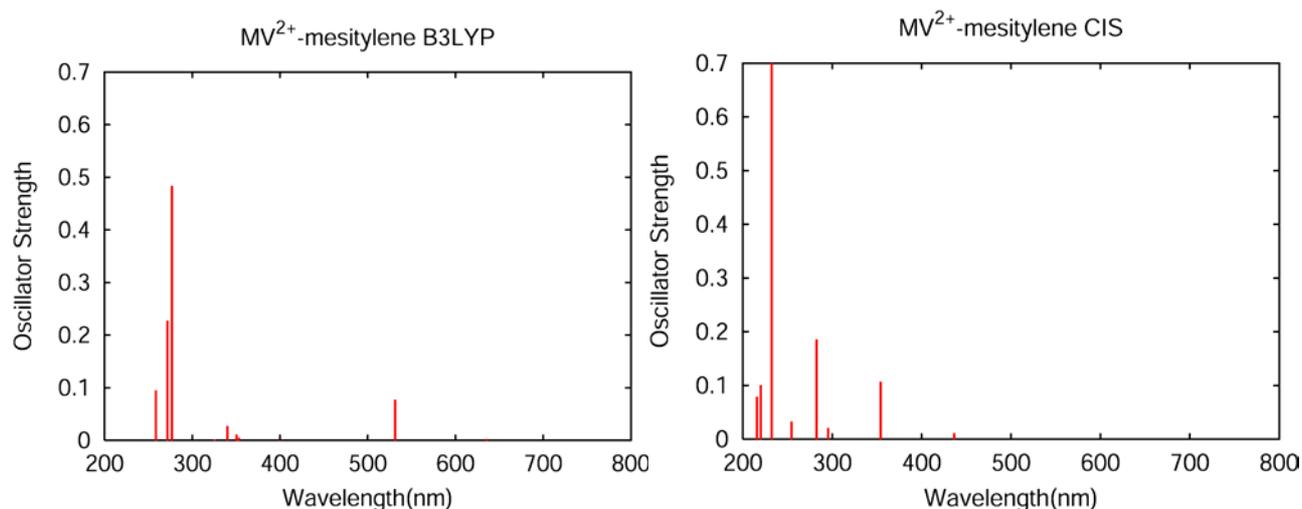


Figure 4. The theoretical spectra in the wavelength range of 200–800 nm at the TDDFT B3LYP and CIS levels for the MV²⁺. The 6–31G(d,p) basis set was used.

Figure 4 shows the theoretical spectra of the MV²⁺–mesitylene complex at the TDDFT B3LYP/6–31G(d,p) and CIS/6–31G(d,p) levels. The significant absorption in the visible area appeared at 531 nm in the B3LYP spectrum. The absorption wavelength is in reasonable agreement with the observed peak (λ_{max}) of 420 nm [4]. CI coefficient analysis reveals that the corresponding excited state is described mainly by the excitation from the mesitylene moiety to the methylviologen moiety. A similar absorption peak appeared at 354 nm in the CIS spectrum, and was found to correspond to the essentially same excitation. Overestimation of excitation energies in CIS calculations would be responsible for the peak appearance at the shorter wave length in the CIS spectrum, but the excitation energy (3.50 eV) is closer to the observed one (2.95 eV) than that in the B3LYP calculation (2.33 eV). Thus, the less expensive CIS scheme is also in reasonable agreement with the experiment in this system. This agreement is due to single excitation character of the relevant excited state.

We also tried a model including two chloride ions (not shown in Figure 3) that are located above the opposite side of the MV²⁺ molecular plane that is in contact with the mesitylene, but no absorption was obtained in the visible area at the TDDFT B3LYP level. This would be due to the false charge transfer from the chloride ions. This result indicates that careful modeling is necessary

for charge transfer in crystals.

4 CONCLUSIONS

The geometry and color change of methylviologen were investigated using *ab initio* and density functional theory. The geometries of MV^{2+} and MV^{+} are found to be twisted and planar. The spin contamination has a significant effect on the potential energy barrier estimate in MV^{+} . The planar geometry of MV^{+} is not in agreement with some earlier calculations. The discrepancy would be due to loose convergence criterion of geometry optimization and/or partial optimization for the shallow minimum of MV^{+} . One should also be careful to evade spin-contamination and should employ full optimization with a reasonable basis set.

The calculated solvent effect of acetonitrile is small. This is explained by the similar stabilization of the ground and excited states for MV^{2+} and MV^{+} . The color change upon photoreduction of MV^{2+} into MV^{+} has been reproduced at the TDDFT and CIS levels of theory. The TDDFT spectra are in better agreement with the observations, but the CIS scheme is still valuable to evaluate qualitative feature of spectra. The visible CT absorption of the MV^{2+} –mesitylene complex in the polycyano–polycadmate host clathrate has been reproduced using a simple model.

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