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Ultrafast dynamics of the excited methylviologen–iodide charge transfer complexes

Włodzimierz Jarzęba^{a,*}, Stanislas Pommeret^b, Jean-Claude Mialocq^b

^a Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

^b CEA/Saclay, DSM/DRECAM/SCM/URA 331 CNRS, F-91191 Gif-sur-Yvette Cedex, France

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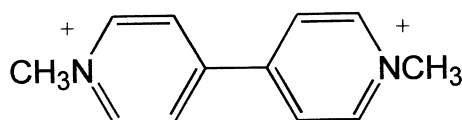
Abstract

The ultrafast dynamics of the excited charge transfer complexes between methylviologen and iodide ions has been investigated in aqueous solutions of potassium iodide using femtosecond transient absorption spectroscopy. Methylviologen and iodide form 1:1 and 1:2 charge transfer complexes characterized by charge transfer bands in the same spectral region. Transient absorption of the complexes has been studied after ultrafast excitation in their charge transfer band. The excitation of the 1:1 complex results in the formation of the $MV^{\cdot+}/I^-$ radical pair while the excitation of the 1:2 complex is leading to the formation of the $MV^{\cdot+}/I^-$ and $MV^{\cdot+}/I_2$ radical pairs. © 2001 Elsevier Science B.V. All rights reserved.

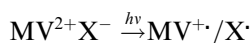
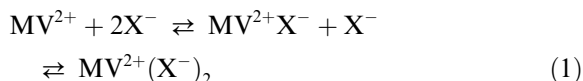
1. Introduction

The photochemistry of methylviologen (MV^{2+}) (1,1'-dimethyl-4,4'-bipyridinium dication or paraquat) is of particular interest because of the great variety of research and applications with viologens in such areas as herbicidal activity [1], photosynthesis, photoelectrochemistry and solar energy conversion [2–6]. Photosensitized reduction of MV^{2+} results in the formation of the methylviologen cation radical $MV^{\cdot+}$, which is a strong reductant capable of reducing a proton to yield molecular hydrogen in neutral to acidic aqueous solutions. The MV^{2+} dication has an absorption peak around 260 nm while the reduced species $MV^{\cdot+}$ has a characteristic absorption spectrum in

the visible with two bands with maxima in water at 396 and 606 nm [7].

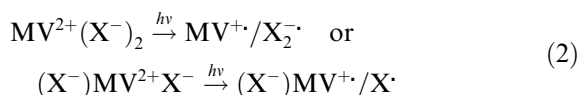


The ground state absorption spectra of the methylviologen halides show the contribution of a characteristic absorption band above 300 nm [8]. This absorption band can be attributed to a charge transfer transition between the halide electron donor and the methylviologen electron acceptor in a contact ion–pair complex.



* Corresponding author. Fax: +48-12-634-0515.

E-mail address: jarzeba@chemia.uj.edu.pl (W. Jarzeba).



The excited state dynamics of these electron donor–acceptor (EDA) complexes can be studied by direct excitation in the charge transfer band. The excited complex subsequently can undergo a nonradiative charge recombination and a charge separation to yield free radical ions and/or free radicals. MV^{2+} complexes with chloride or thiocyanate ions were studied previously by Ebbesen et al. using nanosecond and picosecond laser spectroscopy [9,10]. After excitation in the charge transfer band both complexes give the $\text{MV}^{\cdot+}$ methylviologen cation radical with a quantum yield near 0.2. The dynamics of the $\text{MV}^{\cdot+}$ decay is complex and has been attributed to the presence of 1:1 and 1:2 complexes between MV^{2+} and thiocyanate or chloride ions. Similar studies for Br^- and I^- complexes gave less than 0.01 for the quantum yields of formation of $\text{MV}^{\cdot+}$ which was explained by a much faster charge recombination of the excited complexes [10]. In those picosecond time resolved experiments, the time resolution was too limited to study the excited state dynamics.

Halogen ion complexes with aromatic molecules are interesting model systems for electron transfer (ET) studies as they contain single atom donor and an aromatic acceptor. Recently, ET processes in similar CT complexes of halogen radicals with aromatic molecules have been the subject of experimental and theoretical investigations [11–13].

In this Letter, we report and discuss our results of ultrafast transient absorption studies of 1:1 and 1:2 complexes of methylviologen with iodide ions in aqueous solutions.

2. Experimental

The experiments were performed with a femtosecond laser system described elsewhere [14]. Briefly, the laser pulses were delivered by a modified Ti:Sapphire oscillator (Coherent, Mira),

pumped by an argon ion laser (Coherent, Innova 310) and amplified in a Ti:Sapphire regenerative amplifier (Alpha 1000 US, BM Industries). This laser system provided output pulses of 40 fs duration around 800 nm at a repetition rate of 1 kHz, with energies of about 700 μJ . The pulses were used to generate the second harmonic at 400 nm in a 0.2 mm BBO crystal. A white light continuum, generated by focusing a small fraction of the 800 nm fundamental in a thin rotating fused silica disc, served as a probe. After the sample, the continuum was dispersed in a spectrograph (Spex 270M) and detected using 1024×512 pixels CCD camera (Princeton Instruments). The readout rate of the CCD camera was raised to about 30 Hz using a chopper to modulate the light beam. The instrument response function was derived from two-photon absorption measurements in a 0.15 mm thick glass microscope slide using the second harmonic at 400 nm and the white light continuum [14]. The full width at half maximum (FWHM) of the instrument response function was near 60 fs in the white light continuum spectral range of 400–800 nm. Aqueous solutions of the complexes were prepared by dissolving methylviologen dichloride hydrate (0.03 M) and potassium iodide (0.2–4 M) before experiment. The solutions were flowed in a fused silica cell with 0.25 mm optical path length. The pump energy was set to 10 μJ per pulse and the pump beam diameter was near 2 mm FWHM. At this power density we do not detect measurable transient signal in aqueous solutions of KI. The absorbance of the sample was in the range of 0.3–1.0 at 400 nm, which corresponds to a concentration of the 1:1 complex in the range 0.015–0.02 M. At higher KI concentrations, absorption of the sample increases due to the presence of 1:2 complexes as discussed in the next section. Care was taken to avoid cross phase modulation and the data around the time origin were analyzed carefully. For more details see [15].

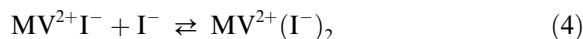
Methylviologen dichloride hydrate (Aldrich, 98%) was used without further purification. Water obtained from a purification system (Waters Millipore) had a resistivity greater than 18 M Ω cm). The experiments were carried out at room temperature (293 K).

3. Results and discussion

The absorption spectra of aqueous solutions containing 0.005 M MVCl₂ and increasing concentration of iodide are shown in Fig. 1. Upon addition of excess I[−] a new absorption band appears between 300 and 500 nm which increases with increasing concentrations of I[−] indicating the formation of a charge transfer complex. For this system a Job plot [16,17] clearly indicates the formation of a 1:1 complex [18]. The association constant K_1 for the equilibrium



and the molar extinction coefficient of the MV²⁺I[−] ion pair were reported [19,20] $K_1 = 6\text{--}7 \text{ M}^{-1}$ and $\epsilon^{350} = 1800 \text{ M}^{-1} \text{ cm}^{-1}$. At higher I[−] concentrations the observed charge transfer absorption cannot be well described as a result of a simple 1:1 complex formation. The presence of 1:2 complexes MV²⁺(I[−])₂ has to be considered. The association constant K_2 of equilibrium



can be evaluated from the fit of the absorption data in the broad range of I[−] concentrations assuming two equilibria (3) and (4) in solution and including activity coefficients $K_1 = 29 \pm 10 \text{ M}^{-1}$ and $K_2 = 0.73 \pm 0.2 \text{ M}^{-1}$ [18]. The extinction coefficients for 1:1 and 1:2 complexes from the fit at

400 nm are $\epsilon_1^{400} = 100 \pm 10 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_2^{400} = 1300 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.

The optical excitation of the MV²⁺I[−] complex at 400 nm is leading to the formation of the radical pair



The iodine atom is very reactive and further reaction with I[−] to form I₂[−] has to be considered. Ebbesen et al. [10] have studied transient absorption spectra of MV²⁺ complexes with Cl[−] and SCN[−]. In both cases, after excitation of the complex, the formation of Cl₂[−] or (SCN)₂[−] has been identified. The total transient absorption spectrum measured in the picosecond and nanosecond time scale was identified as the sum of the absorption spectra of MV^{•+}/X[•] and MV^{•+}/X₂^{•−}. The contribution of the MV^{•+}/X₂^{•−} absorption was increasing with X[−] concentration. The formation of the I₂[−] radicals as a result of the ET from I[−] to an aromatic acceptor was reported in some other studies [21,22].

Fig. 2 shows the time resolved transient absorption spectra observed after excitation of the 0.03 M solution of MV²⁺(Cl[−])₂ in water at 1.5 M KI concentration. Immediately after excitation the characteristic absorption spectrum of MV^{•+} is observed with a peak around 610 nm. However, careful analysis of the transient absorption spectrum indicates, that an additional absorption is

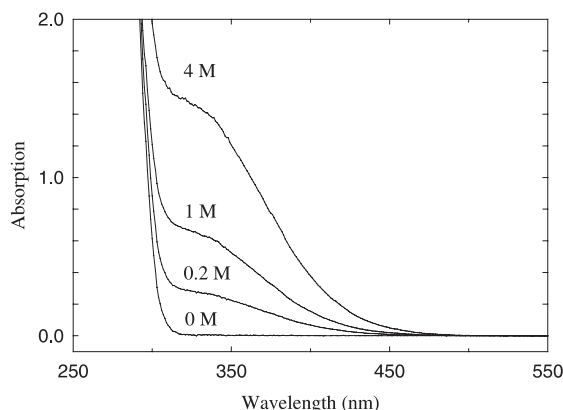


Fig. 1. Absorption spectra of aqueous solutions containing 0.005 M MVCl₂ and increasing concentrations of potassium iodide (0.1 cm cell).

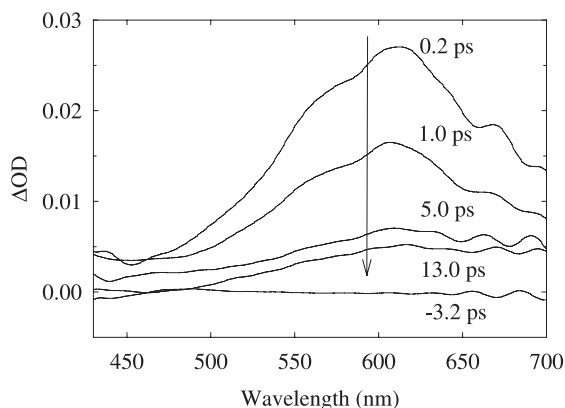


Fig. 2. Time resolved transient absorption spectra observed after excitation of the methylviologen-iodide complex at 400 nm [MV²⁺] = 0.03 M, [KI] = 1.5 M.

present near 450 nm and near 700 nm. This absorption cannot be identified as that of $MV^{+•}$ and indicates the presence of $I_2^{•-}$ with absorption maxima near 390 and 750 nm [23,24]. Two relaxation processes can be distinguished in the decay of the observed transient absorption spectrum. The main part of the band centered near 600 nm and attributed to $MV^{+•}$ decays with a 1 ps relaxation time. The remaining absorption consists of the contributions of $MV^{+•}$ and $I_2^{•-}$ and decays with a characteristic 20 ps lifetime. There is no residual bleach or absorption present on a longer time scale. Fig. 3 shows the decay of the transient absorbance measured at 610 nm in aqueous solutions containing 0.03 M methylviologen and two different concentrations of I^- (0.5 and 4.0 M). In both cases the transients are well represented using a biexponential function with relaxation times near 1 and 20 ps. The contribution of the longer-

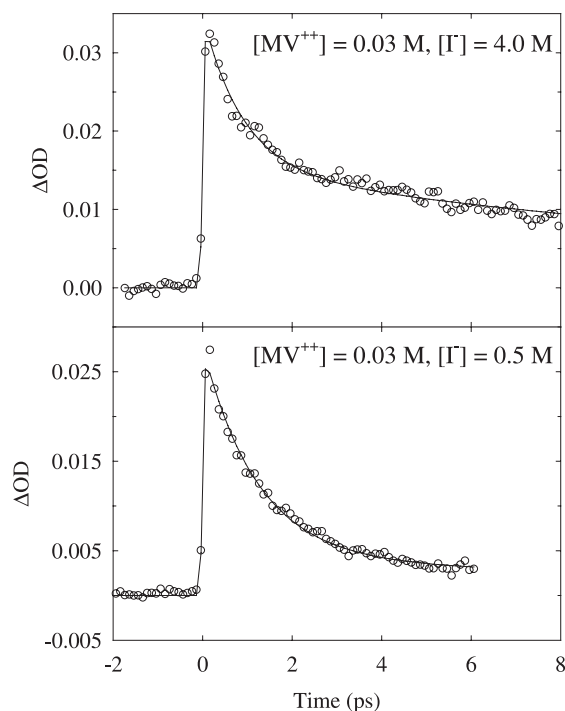


Fig. 3. Decay of the transient absorbance measured at 610 nm in aqueous solutions containing 0.03 M MV^{2+} and various iodide concentrations, after photoexcitation at 400 nm. The solid lines are the best biexponential fits to the data points, with the fitting parameters given in Table 1.

Table 1

Transient absorption decay of the absorbance at 610 nm after ultrafast excitation at 400 nm of aqueous solutions containing 0.03 M methylviologen and increasing concentration of potassium iodide^a

KI concentration (M)	τ_1 (ps)	τ_2 (ps)	A_1/A_2
0.2	1.3	20	$31 \pm 20\%$
0.5	1.2	20	$6.1 \pm 5\%$
1.0	1.1	20	$3.3 \pm 5\%$
1.5	1.0	20	$2.38 \pm 5\%$
4.0	0.9	17	$1.27 \pm 5\%$

^a τ_1 and τ_2 are the relaxation times of the best biexponential fits to the data. A_1 and A_2 are the pre-exponential factors.

lived component increases with I^- concentration as shown in Table 1.

Several processes contribute to the dynamics of the transient absorption of EDA complexes observed in the picosecond and femtosecond time scale [25]. They include decay of the hot-band absorption (vibrational relaxation), decay of the excited state due to back ET, solvation of the excited state, excited state reorganization of the complex, and recovery of the ground state absorption. For the methylviologen-iodide complex, the main contribution to the transient absorption is that of the radical cation $MV^{+•}$. The ground state absorption of the complex recovers completely on the 100 ps time scale due to the back ET process. Interestingly, we do not observe any obvious contribution of ultrafast dynamics (below 1 ps) to the transient absorption, which might be assigned to solvation and reorganization of the complex in the excited state [25]. While solvation should be very fast in water with an average solvation time near 0.5 ps [26] the reorganization of an EDA complex can be much slower on the time scale up to tens of picoseconds [25]. The absorption spectra of $MV^{+•}$ have been studied previously in several polar solvents [7]. The position of the $MV^{+•}$ band changes very little with the change of solvent polarity. Therefore, after the reduction of the MV^{2+} dication, it is very difficult to observe any shift of the $MV^{+•}$ absorption band corresponding to solvent relaxation. Interestingly, we do not observe any dynamics, which can be attributed to a reorganization of the excited state complex either. Careful analysis of the data

measured with ultrashort time resolution shows that there are some difficulties in fitting the transients below 100 fs. However, deviations are relatively small (less than 10%) and therefore difficult to analyze.

The decays of the transient absorption spectra shown in Fig. 2 can be modeled using a biexponential function

$$g(\lambda, t) = g_1(\lambda) \exp(-t/\tau_1) + g_2(\lambda) \exp(-t/\tau_2). \quad (6)$$

This model assumes that the total transient absorption consists of two spectra $g_1(\lambda)$ and $g_2(\lambda)$ assigned to two species decaying with different lifetimes τ_1 and τ_2 . We also assume that the spectral shapes do not change on the observed time scale and within our signal to noise ratio. Therefore, the relaxation times τ_1 and τ_2 have the same values at all wavelengths. The total transient absorption spectrum is reasonably well fitted with the τ_1 and τ_2 values given in Table 1 for solutions containing different KI concentrations. Fig. 4 shows the contributions of the fast component $g_1(\lambda)$ and the slow component $g_2(\lambda)$ to the total transient absorption spectrum at 1.5 M concentration of KI. The $g_1(\lambda)$ spectrum (Fig. 4a) is the characteristic spectrum of the $MV^{+\cdot}$ methylviologen cation radical [7]. The $g_2(\lambda)$ spectrum (Fig. 4b) is similar to the absorption spectrum of $MV^{+\cdot}$ but it contains additional contributions of absorption near 450 and 700 nm. The $g_1(\lambda)$ spectrum decays with a lifetime $\tau_1 \sim 1$ ps while the $g_2(\lambda)$ spectrum decays with a lifetime $\tau_2 \sim 20$ ps. The $g_2(\lambda)$ spectrum can be modeled as the superposition of the absorption spectra of $MV^{+\cdot}$ and $I_2^{\cdot-}$. Assuming that $I_2^{\cdot-}$ does not absorb light at 600 nm the contribution of $MV^{+\cdot}$ ($fg_1(\lambda)$) can be easily subtracted from $g_2(\lambda)$. The resulting spectrum $g_3(\lambda) = g_2(\lambda) - fg_1(\lambda)$ shown in Fig. 4c is the characteristic spectrum of $I_2^{\cdot-}$ [23,24]. The $g_2(\lambda)$ spectrum can be represented as the sum of the contributions of the absorptions of equimolar concentrations of $MV^{+\cdot}$ and $I_2^{\cdot-}$ since it corresponds to the decay of the $MV^{+\cdot}/I_2^{\cdot-}$ radical pair. The ratio of these two contributions was verified using literature values of the extinction coefficients of $MV^{+\cdot}$ ($\epsilon_{606} = 13700 \text{ M}^{-1} \text{ cm}^{-1}$ [7]) and $I_2^{\cdot-}$ ($\epsilon_{450} = 2800 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{700} = 2200 \text{ M}^{-1} \text{ cm}^{-1}$ [24]) in water. In Fig. 4c we also plot the $I_2^{\cdot-}$ absorption spectrum

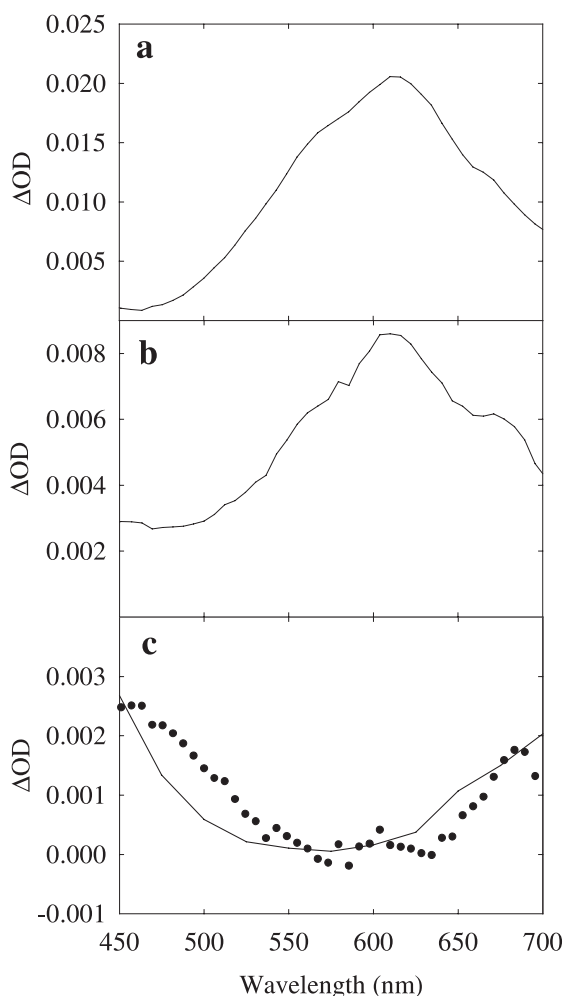


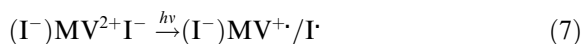
Fig. 4. Comparison between different components of the spectrum in Fig. 2 modeled as $g(\lambda, t) = g_1(\lambda) \exp(-t/\tau_1) + g_2(\lambda) \exp(-t/\tau_2)$; $\tau_1 = 1$ ps, $\tau_2 = 20$ ps. (a) 1 ps – component of the spectrum corresponding to $MV^{+\cdot}$ absorption ($g_1(\lambda)$); (b) 20 ps – component of the spectrum corresponding to $MV^{+\cdot}/I_2^{\cdot-}$ absorption ($g_2(\lambda)$); (c) the difference spectrum $g_3(\lambda) = g_2(\lambda) - fg_1(\lambda)$ corresponds to $I_2^{\cdot-}$ – dots. The $I_2^{\cdot-}$ absorption spectrum from Ref. [19] – solid line.

from Ref. [24]. The deviations between the two spectra given in Fig. 4c are within our experimental error (10^{-3} optical density).

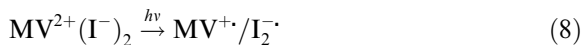
The decay of the transient absorbance measured at 610 nm strongly depends on the KI concentration (Fig. 3). The contribution of the long-lived component of the spectrum $g_2(\lambda)$

corresponding to the decay of the $MV^{+}/I_2^{\cdot-}$ radical pair increases with the KI concentration. The ratio of the pre-exponential factors of both components measured at the maximum of the MV^{+} band are given in Table 1. The data clearly show that a high concentration of iodide ions ($c > 0.1$ M) in solution is necessary to form $I_2^{\cdot-}$ after excitation of the methylviologen aqueous solutions at 400 nm.

Quantum mechanical calculations (AM1, PM3) predict that the most stable structure of the $MV^{2+}(I^-)_2$ complex corresponds to two I^- ions placed on the opposite sides of the MV^{2+} dication, each of them on a different ring. Therefore, the I^- ions are not in close vicinity to form $I_2^{\cdot-}$ immediately after excitation of the 1:2 complex. The excitation of this complex gives the $(I^-)MV^{+}/I^{\cdot-}$ radical pair.



In this case, rotation of one of the pyridinium rings would be necessary to form $I_2^{\cdot-}$. Our experiments show that within our time resolution formation of $I_2^{\cdot-}$ is instantaneous which requires both I^- ions to be in close vicinity already in the ground state of the complex. Two cases can be considered here: (i) two I^- ions are on different aromatic rings but on one side of the MV^{2+} dication, (ii) two I^- ions are in close distance (4–8 Å) but one of the I^- ions is from the solution. The first case corresponds to the formation of thermodynamically less favorable $MV^{2+}(I^-)_2$ complexes with ΔG of formation slightly higher due to coulombic repulsion between the two I^- ions. However, in aqueous solutions this repulsion is relatively weak and a significant population of these complexes can be present. Their excitation might result in ultrafast formation of the radical pair $MV^{+}/I_2^{\cdot-}$.



The second possibility (ii) cannot be excluded particularly at high I^- concentrations, when the probability of finding a second nearby I^- in the solution is significant. In this case, excitation of the complex would also lead directly to the formation of the radical pair $MV^{+}/I_2^{\cdot-}$ as described in Eq. (8). In both processes $I_2^{\cdot-}$ should be formed with an excess of vibrational energy since the initial inter-

nuclear distance is larger than the 3.2 Å equilibrium value [27]. However, in our transient absorption data we do not observe any contribution, which can be assigned to vibrational relaxation of $I_2^{\cdot-}$.

Formation of 1:1 (DA) and 2:1 (D_2A) charge transfer complexes is very common for many donor acceptor systems [28]. The basic charge transfer complex of methylviologen with iodide $MV^{2+}I^-$ is of the 1:1 type. However, methylviologen itself is a double acceptor unit (i.e., A–A) and a 1:2 complex can be easily formed with the structure described as DA–AD.

The relaxation times τ_1 and τ_2 given in Table 1 correspond to the back ET reactions in the radical pairs $MV^{+}/I^{\cdot-}$ and $MV^{+}/I_2^{\cdot-}$, respectively. The rate of the back ET within the $MV^{+}/I_2^{\cdot-}$ radical pair is about 20 times slower than that occurring in the $MV^{+}/I^{\cdot-}$ radical pair. The geometry of the $MV^{2+}(I^-)_2$ excited complex is well defined since the rate of the back ET does not depend on the I^- concentration (Table 1).

It is interesting to compare our results with those obtained by Ebbesen et al. [8–10] for MV^{2+} complexes with Cl^- and SCN^- using picosecond and nanosecond transient absorption spectroscopy. The back ET for these complexes is much slower. Therefore, other processes occurring in the excited states of these complexes have to be considered. Particularly the formation of $X_2^{\cdot-}$ may result from two other excited state reactions. First, $X_2^{\cdot-}$ can be formed in a diffusion controlled bimolecular process $MV^{+}/X^{\cdot-} + X^- \rightarrow MV^{+}/X_2^{\cdot-}$. At high X^- concentrations this reaction pathway can be an important source of $X_2^{\cdot-}$. The second possibility is an excited state intracomplex rearrangement $(X^-)MV^{+}/X^{\cdot-} \rightarrow MV^{+}/X_2^{\cdot-}$ which involves the rotation of one of the pyridinium rings. The contribution of these different processes to the formation of $X_2^{\cdot-}$ can be analyzed using femtosecond transient absorption spectroscopy.

It has been suggested by Ebbesen et al. [8,10] that the ultrafast decay of the excited states of the $MV^{2+}(I^-)_2$ and $MV^{2+}(Br^-)_2$ complexes might be due to efficient intersystem crossing processes. Our studies on the dynamics of the excited $MV^{2+}(I^-)_2$ complex show that the ground state recovery of the complex is too fast to indicate any significant

Table 2

Back ET parameters of the methylviologen–halide complexes

	$E^0(\text{X}/\text{X}^-)^a$ (V)	ΔG_{et} (eV)	λ_s (eV)	k_{et} calc. (s ⁻¹)	k_{et} exp. (s ⁻¹)
Cl [•] /Cl ⁻	2.40	-2.95 ± 0.05	1.4	2 × 10 ¹⁰	>10 ⁹ Ref. [10]
Cl ₂ ^{•-} /2Cl ⁻	2.08	-2.63	0.7	2 × 10 ⁸	4 × 10 ⁸ Ref. [10]
I [•] /I ⁻	1.40	-1.95	1.0	0.9 × 10 ¹²	1.0 × 10 ¹²
I ₂ ^{•-} /2I ⁻	1.12	-1.67	0.4	7 × 10 ¹⁰	5 × 10 ¹⁰

^a From Ref. [35]. The redox potential of methylviologen $E^0(\text{MV}^{2+}/\text{MV}^{•+}) = -0.45$ V vs (n.h.e) [35].

triplet state involvement. Ultrafast back ET in the MV^{2+} complexes with I^- is rather a direct consequence of the energy gap dependence. The free energy of the back ET process ΔG_{et} can be estimated from $\Delta G_{\text{et}} = e(E^0(\text{MV}^{2+}/\text{MV}^{•+}) - E^0(\text{X}^-/\text{X})) + \Sigma \Delta G_a$, where $E^0(\text{MV}^{2+}/\text{MV}^{•+})$ is the redox potential of $\text{MV}^{2+}/\text{MV}^{•+}$ and $E^0(\text{X}^-/\text{X})$ is the redox potential of the electron donor as shown in Table 2. $\Sigma \Delta G_a$ corresponds to the change of the association energy of the donor–acceptor pair between the equilibrium configurations of the excited state and the ground state of the complex. For all donor–acceptor pairs considered in Table 2 we estimate that $\Sigma \Delta G_a$ is not larger than -0.1 eV.

To describe the ET rate the following semi-classical expression is often applied [5,29–31]:

$$k_{\text{et}} = \frac{2\pi}{\hbar} V^2 (4\pi\lambda_s k_B T)^{-1/2} \sum_{m=0}^{\infty} \left[\frac{e^{-S} S^m}{m!} \right] \times \exp \left[-\frac{(\lambda_s + \Delta G_{\text{et}} + m\hbar\nu_v)^2}{4\lambda_s k_B T} \right], \quad (9)$$

$$S = \lambda_v / \hbar\nu_v,$$

where V is the electronic coupling element, λ_s the reorganization energy associated with the solvent and other low-frequency modes, and λ_v is the reorganization energy associated with a single averaged high frequency skeletal mode of frequency ν_v . The other symbols in Eq. (9) are k_B the Boltzmann's constant and m the number of quanta of the ν_v mode. A rough estimate of the solvent reorganization energy can be obtained using the spherical reagent model [32]

$$\lambda = \frac{(\Delta e)^2}{4\pi\epsilon_0} \left[\frac{1}{2a_D} + \frac{1}{2a_A} - \frac{1}{r_{DA}} \right] \left[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_S} \right], \quad (10)$$

where a_D and a_A are the radii of the donor and acceptor, respectively; and r_{DA} is the center-to-center distance between donor and acceptor. In our calculations we assume $a_A = 4$ Å for $\text{MV}^{•+}$, $a_D = 2$ Å for I^- , $a_D = 2.8$ Å for $\text{I}_2^{•-}$, $a_D = 1.67$ Å for Cl^- , $a_D = 2.35$ Å for $\text{Cl}_2^{•-}$ (Cl–Cl distance 2.7 Å from ab initio calculations with 6-31G* basis set) and $r_{DA} = 3.6$ Å for all radical pairs. The calculated solvent reorganization energies are very sensitive to the r_{DA} value and may be endowed with a substantial systematic error. However, the purpose of this calculation is to analyze the energy gap dependence rather than to give correct values for all the parameters in Eq. (9). The λ_s value in Eq. (9) contains also the reorganization energy of low frequency modes which is usually around 0.2 eV for many CT complexes [33]. For the $\text{MV}^{•+}/\text{X}_2^{•-}$ radical pairs the reorganization energy λ_s is slightly higher due to contribution from reorganization of $\text{X}_2^{•-}$ after the ET. This effect is higher for $\text{Cl}_2^{•-}$ and additional contribution of 0.05 eV to λ_s of $\text{MV}^{•+}/\text{Cl}_2^{•-}$ was taken into account. Total solvent and low frequency reorganization energies λ_s are given in Table 2. The ν_v in Eq. (9) was fixed to 1400 cm⁻¹ and the λ_v parameter was assumed to be 0.3 eV. These are typical values used in previous studies of ET in CT complexes [33]. The electronic coupling parameter V was set at 0.025 eV to obtain the best agreement with the experimental data. The calculated ET rate constants are given in Table 2.

The back ET in the excited MV^{2+}X^- or $\text{MV}^{2+}(\text{X}^-)_2$ complexes is observed in the inverted Marcus region [34] (i.e., $-\Delta G_{\text{et}} > \lambda_s + \lambda_v$). For the Cl^- and $\text{Cl}_2^{•-}$ radical pairs with $\text{MV}^{•+}$, the observed ET rates are significantly slower than that for the I^- and $\text{I}_2^{•-}$ radical pairs. The results of calculations given in Table 2 show that the ET rates are well predicted by Eq. (9) and the changes in the ET

rate constants are mainly due to the energy gap dependence. Interestingly, if we compare the ET rate constants between the $MV^{+•}/X^{•-}$ and $MV^{+•}/X_2^{•-}$ radical pairs the rates actually decrease with decreasing energy gap (i.e., normal like behavior). This decrease in the ET rate is also well described by Eq. (9) and results from a significant change of the solvent reorganization energy λ_s .

4. Conclusions

In this Letter, we have reported the observation of two fast back ET processes following the photoinduced instantaneous ET from the iodide electron donor to the methylviologen electron acceptor in 1:1 and 1:2 methylviologen–iodide complexes in aqueous solution. At low I^- concentrations the 1:1 complex is mainly present. At higher I^- concentrations both complexes contribute to the CT absorption. The photoexcitation of the $MV^{2+}I^-$ 1:1 complex is leading to the formation of the $MV^{+•}/I^{•-}$ radical pair which decays with a 1 ps lifetime due to the back ET. The excitation of the CT band of the 1:2 complex results in the formation of $MV^{+•}/I^{•-}$ and $MV^{+•}/I_2^{•-}$ radical pairs. The back ET in the $MV^{+•}/I_2^{•-}$ radical pair is characterized by a 20 ps lifetime. The ultrafast back ET processes in the photoexcited methylviologen–iodide complexes are observed in the inverted region and kinetics can be well described using conventional ET theory.

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