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# Thermodynamic analysis of some electrochemical properties of transition metal complexes in electronically excited states

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**Abstract**

A theoretical treatment is presented of the relationship between absorption and emission maxima for (0–0) electronic transitions in transition metal complexes such as the ruthenium(II) polypyridyl chromophores used as dye sensitizers in photovoltaic cells, and the corresponding shift in standard redox (or half-wave) potential of these ionic complexes. It is shown that the potential shift is proportional to the average of absorption and emission wavenumbers for oxidized or reduced forms, a result that follows from a detailed analysis of medium relaxation effects, based on the Onsager cavity model, and attendant solvatochromic shifts. It is also shown how additional thermodynamic properties (reaction entropies and enthalpies) pertaining to the half reaction if the reactants are present in solution can be obtained from observation of the variation of spectra with temperature.

For the case of reactants present in an insoluble monolayer, a general expression is derived for the Gibbs energy change that results from the promotion of all absorbing species to an excited state, and the changes in Gibbs energy resulting from the processes that return the system to ground-state equilibrium.

*Keywords:* Photoelectrochemistry; Photovoltaics; Standard redox potential; Thermodynamic cycle; Franck–Condon principle; Onsager cavity model; Solvatochromic shifts; Reaction entropy; Reaction enthalpy; Monolayer

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## 1. Introduction

The conversion of solar radiation to electrical currents, a field of study generally referred to as photovoltaics or photoelectrochemistry, continues to be the focus of a major research effort towards the development of efficient, cheap solar cells. The attention is concentrated on the anodes of these cells, semiconductors such as $TiO_2$, which are characterized by a wide band gap that is associated with high resistance against photocorrosion. Direct use of sunlight to create the electron–hole pairs in the semiconductor which generate the photo-currents would require ultraviolet light, and would thus underutilize the available energy. Hence the use of dye-sensitizers, that are deposited on the anode in the form of a monolayer, which absorb in the visible region and are excited into electronic states that are quenched by injecting electrons into the conduction band of the electrode. Polypyridyl complexes of ruthenium have proved to be particularly suitable for this purpose [1]. In regenerative-type cells, the oxidized form in its ground state is subsequently reduced by a dissolved reductant species of a mediator redox couple that returns the electrons to the dye after their passage through an external circuit and release at the metallic cathode.

The effect of illumination is to raise the standard redox potential of the dye with respect to the anode, or, equivalently, lower the potential of the anode with respect to a plane passing through the redox centers in the monolayer, thus increasing the cell voltage.

This study considers two separate cases. In the first, the effect of electronic excitation on the standard potential of a dissolved metal complex redox couple is determined, and the relationship between the shift in standard potential and the absorption and emission frequencies of oxidized or reduced forms is examined. It seeks to determine which part of the energy absorbed by a transition metal complex is used to effect the change in standard potential and which part is dissipated as a result of medium relaxation, consequent upon the non-equilibrium, or Franck–Condon, state attained by the complex immediately after absorption of a photon.

The present treatment closely follows that of a similar study of the acidity of electronically excited molecules or ions [2],

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which leads to a modification of the so-called Förster equation, from which the effects of medium relaxation are likewise eliminated so as to arrive at a proper thermodynamic concept of acidity constants in electronically excited states. Again, use is made of the Onsager cavity model [3] and basic electrostatics to derive the relevant free energies. As is to be expected, there is a close link between this theory and the phenomenon of solvatochromism [4], the fundamental equations for which have been derived previously, but a considerably simplified and more concise derivation will be given in Section 3.

An additional advantage of the present, fundamental approach is that it readily allows for the determination of relevant thermodynamic parameters, such as entropy and enthalpy changes accompanying the half reaction in the excited state, simply by repeating spectral measurements at different temperatures and combining this information with the corresponding ground-state values for these quantities. The argument will be based on a simple thermodynamic cycle, which is the analogue of the well-known Förster cycle [5,6] employed in the derivation of excited-state acidity constants.

The treatment of excited electro-active complexes that are present in the form of an insoluble monolayer is fundamentally different and will be taken up in Section 4. There, expressions are derived for the free energy changes accompanying the promotion of all absorbing species to an excited state and the subsequent relaxation back to the ground state of the monolayer.

## 2. Thermodynamic cycle and standard states

The shift in standard redox potential for the half reaction $\mathrm{O}+ne^- \rightleftarrows \mathrm{R}$ will be calculated based on an analysis of the thermodynamic cycle shown in Fig. 1, which pertains to the case of oxidative quenching.

In the following discussion it will be assumed that oxidized and/or reduced species are luminescent and capable of attaining relatively long-lived excited states. Strictly speaking, the electronic transitions that are considered here are those that occur between the lowest vibrational levels in the two electronic states (0–0 transitions). The cycle will be analyzed in terms of the standard Gibbs energy since once this function has been evaluated, it can subsequently be used to generate additional thermodynamic information associated with the half reaction.

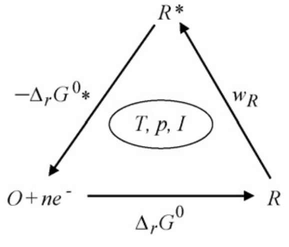

Fig. 1. Thermodynamic cycle with photochemical step (oxidative quenching) for a dissolved or adsorbed redox couple O/R at constant temperature, pressure and ionic strength. Standard free energies for the different stages of the cycle are indicated.

First, it is necessary to elaborate somewhat on the notion of "standard state" in this context [2]. In general, the compound, in most cases of practical importance this will be a transition metal complex, will possess both a charge and a permanent dipole moment which tend to polarize the (aqueous or non-aqueous) environment. This polarized environment will, in turn, give rise to an additional, induced, dipole moment through the reaction field it generates at the location of the complex. In the case of soluble redox-active species, the solute–solvent interactions and interactions between solute dipole moment and charges on other solutes are contained in the "standard" part $\mu_i^0$ of the chemical potential:

$$\mu_i = \mu_i^0 + kT\ln\left(\frac{y_i c_i}{c^\theta}\right) \tag{1}$$

where $c_i$ is the molarity of solute species $i$, $c^\theta$ denotes the standard concentration, conventionally set equal to 1 mol dm$^{-3}$. Ion–ion interactions among solutes are formally accounted for by the term $kT\ln y_i$, which, in the case of an extremely dilute electrolyte solution, is given explicitly in terms of temperature and parameters characterizing the medium, *viz.* dielectric constant of the solvent, $\varepsilon$, and ionic strength, $I$, by the well-known Debye–Hückel expression. The argument of the logarithm in Eq. (1) is usually abbreviated as $a_i$, the activity of solute $i$. Based on the above definition of solute standard potential, $\mu_i^0$ is expected to also depend on ionic strength which, throughout the cycle of Fig. 1, is supposed to be kept constant (by adding an inert supporting electrolyte), along with temperature and pressure, as indicated. Another implication of these definitions is that the $y_i$ are independent of the electronic state of the ion, i.e. $y_i^* = y_i$.

If the two members of the redox couple O/R are both present in their respective electronic ground states, the condition for equilibrium between electrode and solution with respect to the half reaction can be formulated as

$$\mu_\mathrm{R}^0 - \mu_\mathrm{O}^0 - n\bar{\mu}_\mathrm{e} + kT\ln\left(\frac{a_\mathrm{R}}{a_\mathrm{O}}\right) = 0 \tag{2}$$

where $\bar{\mu}_\mathrm{e} = \mu_\mathrm{e} - e\phi^M$ is the electrochemical potential, or Fermi level, of an electron inside the electrode, with $\phi^M$ denoting the electrostatic potential of the electrode with respect to the bulk of the solution (which is arbitrarily chosen to be at the zero level). If oxidized and reduced species are confined to a monomolecular layer adsorbed onto the electrode, the relevant potential difference is that between electrode and the plane passing through the redox centers, $\phi^M - \phi'$ (see Section 4).

The analogous expression for the equilibrium involving the excited-state reductant is

$$\mu_\mathrm{R}^{0*} - \mu_\mathrm{O}^0 - n\bar{\mu}_\mathrm{e}^* + kT\ln\left(\frac{a_\mathrm{R}}{a_\mathrm{O}}\right) = 0 \tag{3}$$

After substitution for $\bar{\mu}_\mathrm{e}$ and $\bar{\mu}_\mathrm{e}^*$, Eqs. (2) and (3) assume the forms

$$\phi^M = \phi^0 + \frac{kT}{ne}\ln\left(\frac{a_\mathrm{O}}{a_\mathrm{R}}\right) \tag{4}$$

and

$$\phi^{M*} = \phi^{0*} + \frac{kT}{ne}\ln\left(\frac{a_\mathrm{O}}{a_\mathrm{R}}\right) \tag{5}$$

respectively, defining “standard potentials” as

$$\phi^0 = \frac{\mu_{\mathrm{O}}^0 + n\mu_{\mathrm{e}} - \mu_{\mathrm{R}}^0}{ne} = \frac{-\Delta_{\mathrm{r}}G^0}{ne} \tag{6}$$

where the “standard Gibbs energy of the half reaction”, $\Delta_{\mathrm{r}}G^0$, has been defined, and, analogously

$$\phi^{0*} = \frac{\mu_{\mathrm{O}}^0 + n\mu_{\mathrm{e}} - \mu_{\mathrm{R}}^{0*}}{ne} = \frac{-\Delta_{\mathrm{r}}G^{0*}}{ne} \tag{7}$$

Similar expressions apply if the redox couple is confined to an adlayer, in which case the standard state is defined as one in which the surface concentrations $\Gamma_{\mathrm{O}}$ and $\Gamma_{\mathrm{R}}$ are equal, with all excitable redox centers either in the ground state or in the excited state. This is therefore a purely hypothetical state because in reality the reactants spontaneously distribute themselves between oxidized and reduced states.

Eqs. (4) and (5) are recognized as forms of the Nernst equation pertaining to the local electrode/solution equilibrium with oxidant and reductant in the ground state or reductant in the excited state.

Introducing the standard free energy:

$$w_{\mathrm{R}} = \mu_{\mathrm{R}}^{0*} - \mu_{\mathrm{R}}^0 \tag{8}$$

inspection of the cycle of Fig. 1 readily leads to the following relationship between the standard free energies defined above:

$$\Delta_{\mathrm{r}}G^{0*} = \Delta_{\mathrm{r}}G^0 + w_{\mathrm{R}} \tag{9}$$

Based on definitions (6) and (7) and a more practical expression for the shift in standard potential (which has absolute significance, independent of the choice of zero level for potential), $\phi^{0*} - \phi^0 = E^{0*} - E^0$, where $E$ is the electrode potential measured with respect to an arbitrary reference electrode, Eq. (9) can be written in the equivalent form:

$$E^{0*} = E^0 - \frac{w_{\mathrm{R}}}{ne} \tag{10}$$

The free energy change $w$ can be interpreted as the reversible work of promoting an ion to an excited state from the electronic ground state, such that the ion is understood to be in equilibrium with the surrounding medium in both states. In practice, the promotion to the excited state involves absorption of a photon of frequency $\nu_{\mathrm{a}}$ (different from the frequency $\nu_0$ at which the ion would absorb *in vacuo*) and subsequent relaxation of the medium from a non-equilibrium Franck–Condon state to equilibrium, provided that the excited state is sufficiently long-lived. The change in the medium is brought about by a sudden change in the dipole moment, $\vec{\mu}$, on the ion as a result of a redistribution of its electronic charge. In the next section, the relationship between the work $w$ for either the oxidized or reduced form and the photon energies for absorption and emission (which are in general different) is established using a simple electrostatic model.

## 3. Calculation of promotion free energy and related thermodynamic properties: connection with solvatochromic shifts

In order to compute the free energy $w$ for promoting an ionic complex to an excited state while maintaining equilibrium with its environment, it is necessary to introduce a model to describe the electrostatic interaction between the charge distribution on the solute and the rest of the solution. To this end, we shall adopt the model introduced by Onsager in 1936 as part of a general treatment of dielectrics [3], according to which the solute ion is, on average, contained in a spherical cavity of radius $a$, of the order of the ionic complex’s radius, while the surrounding solvent is modeled as a uniform dielectric with relative permittivity $\varepsilon$. The charge $q$ and dipole moment $\vec{\mu}$ on the ion are represented by a point charge and point dipole superposed at the center of the cavity (see Fig. 2). This dipole moment polarizes the solution in the immediate vicinity of the ion, thus creating a uniform reaction field inside the cavity that can be shown to be equal to [7]:

$$\vec{E}_{\mathrm{r}} = \frac{2\vec{\mu}}{a^3}\frac{\varepsilon' - 1}{2\varepsilon' + 1} \tag{11}$$

where

$$\varepsilon' = \varepsilon\left(1 + \frac{(\kappa a)^2/2}{1 + \kappa a}\right) \tag{12}$$

is an effective dielectric constant, in which the second term arises as a result of the contribution to the reaction field due to the redistribution of ions (represented as point charges in this model) surrounding the dipole. The factor $\kappa$ is the inverse Debye length, defined as $\kappa = (2e^2 N_{\mathrm{A}} I/\varepsilon\varepsilon_0 kT)^{1/2}$, with $I$ the ionic strength of the solution, and other symbols having their usual meanings.

The net dipole moment can be considered as a sum of a permanent dipole moment and a dipole moment induced by the reaction field, hence, if $\alpha$ is the polarizability of the ion, which will be taken to be scalar, it can be written as $\vec{\mu} = \vec{\mu}_{\mathrm{p}} + \alpha\vec{E}_{\mathrm{r}}$. If dipole and surrounding solvent are in equilibrium, substitution of this expression into Eq. (11) and solving the resulting equation for the equilibrium reaction field, that we shall denote by

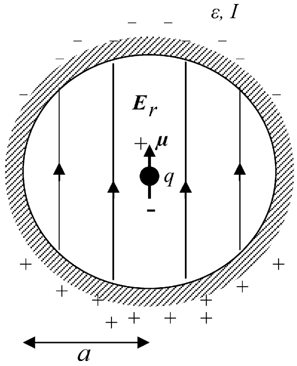

Fig. 2. Onsager cavity model for an ionic compound with permanent dipole moment, showing relevant model parameters.

$\vec{E}_0$, gives

$$\vec{E}_0(\vec{\mu}_\mathrm{p}) = \frac{2(\varepsilon'-1)}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)}\frac{\vec{\mu}_\mathrm{p}}{a^3} \tag{13}$$

where a dimensionless polarizability $\alpha' = \alpha/a^3$ has been introduced.

When, consequent upon the absorption of a photon, the ionic complex is promoted to an excited state in which it has permanent dipole moment $\vec{\mu}_\mathrm{p}^*$, the rapid change in the dipole moment elicits a response of the surrounding medium in the form of an adjustment of the electronic part of the polarization field, on account of the Franck–Condon principle, which is described in terms of the high-frequency ("optical") dielectric constant, $n^2$, with $n$ the refractive index of the solution. More generally, if the dipole moment changes instantaneously from the ground-state value $\vec{\mu}_\mathrm{p}$ to some intermediate value $\vec{\mu}'_\mathrm{p}$, the non-equilibrium reaction field is the sum of the initial equilibrium field given by Eq. (13) and that due to the excess dipole moment $\vec{\mu}'_\mathrm{p} - \vec{\mu}_\mathrm{p}$, as follows:

$$\vec{E}_\mathrm{r}(\vec{\mu}'_\mathrm{p}) = \vec{E}_0(\vec{\mu}_\mathrm{p}) + \frac{2(n^2-1)}{2n^2+1-2\alpha'(n^2-1)}\frac{\vec{\mu}'_\mathrm{p}-\vec{\mu}_\mathrm{p}}{a^3} \tag{14}$$

provided that it can be assumed that $\alpha^* \cong \alpha$, or that at least some average polarizability can be used. It is possible, in principle, to account for the (likely) change in polarizability following excitation [7], but the resulting expressions, which contain the difference $(\alpha^* - \alpha)$, are rather unwieldy. Moreover, to this author's knowledge, no excited-state polarizability values for the relevant compounds have been reported.

The energy absorbed during the transition in solution differs from that *in vacuo* by an amount equal to the electrostatic interaction energy between the excess dipole and its surroundings, i.e. the reversible work done in creating this excess dipole if the medium only responds to its presence via electronic polarization. The change in absorbed radiation energy thus equals the difference in electrostatic stabilization energy between permanent dipoles $\vec{\mu}_\mathrm{p}$ and $\vec{\mu}_p^*$:

$$h\Delta\nu_\mathrm{a} = -\int_{\vec{\mu}_\mathrm{p}}^{\vec{\mu}_\mathrm{p}^*} \vec{E}_\mathrm{r}(\vec{\mu}'_\mathrm{p})\cdot \mathrm{d}\vec{\mu}'_\mathrm{p} \tag{15}$$

Substitution of Eqs. (13) and (14) in the integrand then produces the following expression for the solvatochromic shift in the case of absorption [7]:

$$\begin{aligned} h\Delta\nu_\mathrm{a} &= -\frac{\vec{\mu}_\mathrm{p}^* - \vec{\mu}_\mathrm{p}}{a^3}\cdot\left\{\frac{2(\varepsilon'-1)}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)}\vec{\mu}_\mathrm{p}\right. \\ &\quad \left. + \frac{(n^2-1)(\vec{\mu}_\mathrm{p}^*-\vec{\mu}_\mathrm{p})}{2n^2+1-2\alpha'(n^2-1)}\right\} \end{aligned} \tag{16}$$

If the compound is an emitter, and if the excited-state exists long enough for the medium to attain equilibrium, the analogous expression for the solvatochromic shift for luminescence is obtained by simply reversing the roles of ground state and excited state in Eq. (16), which gives

$$\begin{aligned} h\Delta\nu_\mathrm{f} &= -\frac{\vec{\mu}_\mathrm{p}^* - \vec{\mu}_\mathrm{p}}{a^3}\cdot\left\{\frac{2(\varepsilon'-1)}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)}\vec{\mu}_\mathrm{p}^*\right. \\ &\quad \left. - \frac{(n^2-1)(\vec{\mu}_\mathrm{p}^*-\vec{\mu}_\mathrm{p})}{2n^2+1-2\alpha'(n^2-1)}\right\} \end{aligned} \tag{17}$$

For a fluorescing compound, the vacuum absorption and emission frequencies are equal if we consider only the 0–0 transition, so that $\Delta\nu_\mathrm{a,f} = \nu_\mathrm{a,f} - \nu_0$ in that case. These solvatochromic shifts have often been used to determine excited-state dipole moments of molecules in solution [8], as an alternative to the method based on the normal Stark effect, which is applicable only to gaseous samples. The above treatment is expected to remain valid for transitions to higher vibrational levels in the ground or excited state only as long as the contribution of the inner-sphere modes to the Franck–Condon energy is relatively small. Otherwise, corrections to the vacuum frequencies will become necessary, while it can be assumed that corrections to the permanent dipole moments are insignificant.

We now return to the problem of computing the reversible work $w$ of forming the excited state from the ground state in solution. *In vacuo*, $w = h\nu_0$, but in solution an electrostatic term must be added, equal to the work done against the reaction field in changing the permanent dipole moment from $\vec{\mu}_\mathrm{p}$ to $\vec{\mu}_\mathrm{p}^*$ (compare Eq. (15)):

$$\begin{aligned} w &= h\nu_0 - \int_{\vec{\mu}_\mathrm{p}}^{\vec{\mu}_\mathrm{p}^*} \vec{E}_0(\vec{\mu}'_\mathrm{p})\cdot \mathrm{d}\vec{\mu}'_\mathrm{p} \\ &= h\nu_0 - \frac{\mu_\mathrm{p}^{*2} - \mu_\mathrm{p}^2}{a^3}\frac{\varepsilon'-1}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)} \end{aligned} \tag{18}$$

where use has been made of Eq. (13).

If this result is compared with Eqs. (16) and (17), we obtain for a fluorescing compound the following simple relationship [2]:

$$w = h\frac{\nu_\mathrm{a}+\nu_\mathrm{f}}{2} \equiv hc\bar{\tilde{\nu}} \tag{19}$$

introducing the average wavenumber for absorption and emission, $\bar{\tilde{\nu}}$, which roughly coincides with the point at which absorption and emission spectra intersect.

The relationship among the energies (which are, strictly speaking, *free* energies) $h\nu_\mathrm{a}$, $h\nu_\mathrm{f}$ and $w$ is illustrated in Fig. 3.

Substitution of the above expression for $w$ into Eq. (10) gives for the standard potential of a redox couple which has its reduced form present in an electronically excited state:

$$E^{0*} = E^0 - \frac{hc}{ne}\bar{\tilde{\nu}}_\mathrm{R} \tag{20}$$

The case of reductive quenching can be treated in an analogous manner, which leads to an expression similar to Eq. (20), with $\bar{\tilde{\nu}}_\mathrm{R}$ replaced by $-\bar{\tilde{\nu}}_\mathrm{O}$, so that our results may be summarized in the following form:

$$E^{0*} = E^0 \pm \frac{0.124\,\mathrm{mV}}{n}\bar{\tilde{\nu}}_\mathrm{O,R}/\mathrm{cm}^{-1} \tag{21}$$

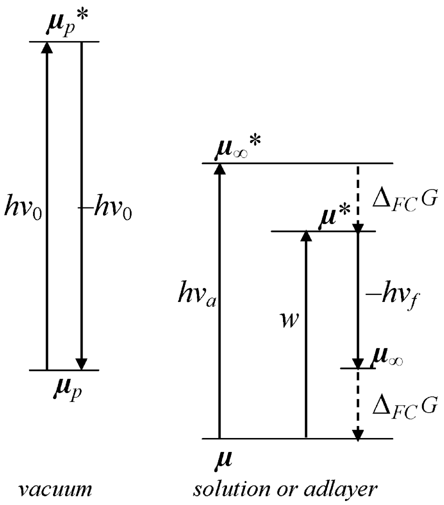

Fig. 3. Relationships among free energies for an absorption/emission process (0–0 transition) with medium relaxation. Net dipole moments at each stage are indicated, with $\vec{\mu}^*_\infty$ and $\vec{\mu}_\infty$ the values in “Franck–Condon states”, immediately after absorption or emission of a photon, respectively.

where the positive sign and subscript ‘O’ pertain to reductive quenching, and *vice versa*.

It should be noted that the averaging of absorption and fluorescence wavenumbers serves to eliminate the contribution to the absorption and emission energies $h\nu_a$ and $h\nu_f$ due to the creation of a non-equilibrium configuration of solvent molecules and ions around the complex in the “Franck–Condon state”, the free energy of this fluctuation, $-\Delta_{FC}G = h(\nu_a - \nu_f)/2$, being subsequently liberated in the form of heat as the medium relaxes to its new equilibrium configuration (see Fig. 3).

For a compound that absorbs and emits in the visible range of the spectrum (ca. 14,000–24,000 $\text{cm}^{-1}$) the shift in standard potential could easily amount to a value in the order of volts, according to Eq. (21). For reversible electron transfer processes, $E^0$ is usually very close to the half-wave potential $E_{1/2}$ obtained from voltammetric measurements, and shifts of the predicted order of magnitude and (negative) sign have indeed been observed in photoelectrochemical studies of the oxidation of excited transition metal complexes such as $\text{Ru(bipy)}_3{}^{2+*}$ to $\text{Ru(bipy)}_3{}^{3+}$ [9].

Additional information on thermodynamic properties may be gleaned from observations of the temperature dependence of electrode potentials and absorption/emission spectra, based on basic thermodynamic relationships. For example, the molar entropy of the half reaction in the excited state of dissolved reactants simply follows by taking the temperature derivative of Eq. (9) (or its reductive quenching analogue) after substitution of Eq. (19), and adding terms associated with deviations from standard conditions (which are common to both ground and excited states), as

$$\Delta_r\bar{S}* = \Delta_r\bar{S} \pm N_A hc\left(\frac{\partial\bar{\tilde{\nu}}_{O,R}}{\partial T}\right)_{p,I} \qquad (22)$$

The difference in reaction entropies can be attributed mainly to changes in the arrangement of solvent molecules and ions in the neighborhood of the complex resulting from the change in its dipole moment.

Likewise, the difference in molar reaction enthalpies can be found from Eqs. (9) and (19) through application of the Gibbs–Helmholtz equation, which leads to

$$\Delta_r\bar{H}* = \Delta_r\bar{H} \pm N_A hcT^2\left(\frac{\partial\left(\bar{\tilde{\nu}}_{O,R}/T\right)}{\partial T}\right)_{p,I} \qquad (23)$$

It must be remembered that the above relationships (Eqs. (21)–(23)) are applicable to dissolved chromophores such as polypyridyl complexes of ruthenium(II).

In the case where these complexes are anchored to the surface of a wide-bandgap semiconductor anode (typically $\text{TiO}_2$) of a photoelectrochemical, or photovoltaic, cell, where they act as dye-sensitizers [10]; however, these results are of little practical interest because, among other things, of the impossibility to maintain a standard state (with equal numbers of oxidized and reduced species) in both the presence and absence of radiation under open-circuit conditions.

A discussion of some of the issues involved in this more practically relevant situation is presented, again from a thermodynamic point of view, in the next section.

## 4. Calculation of the free energies of excitation and equilibration of redox centers in a monolayer adsorbed on an electrode

The treatment given here is analogous to that followed in a recent study on the thermodynamics of insoluble redox-active self-assembled organothiol monolayers at electrode surfaces [11].

The system under consideration is a two-electrode cell where one electrode is covered by a monolayer containing electroactive species, O and R, present at surface concentrations $\Gamma_O = N_O/A$ and $\Gamma_R = N_R/A$ ($A$ = electrode area) and characterized by electrochemical potentials:

$$\bar{\mu}_{O,R} = \mu^0_{O,R} + kT\ln\left(\frac{\Gamma_{O,R}}{\Gamma_T}\right) + z_{O,R}e\phi' \qquad (24)$$

where the $\mu^0_{O,R}$ refer to states in which the monolayer is either fully oxidized or fully reduced, $\Gamma_T = \Gamma_O + \Gamma_R$ and $\phi'$ is the average local potential in the plane through the redox centers. The cell voltage $E$ is taken as the difference between the potential of the film-covered electrode and that of the counter-electrode.

Next we imagine the surface area $A$ to be expanded infinitesimally while keeping all intensive parameters (temperature $T$, pressure $p$, cell voltage $E$, interfacial tension $\gamma$ and the $\bar{\mu}_{O,R}$) constant. This change is accompanied by a change in the cell's Gibbs energy equal to

$$(\mathrm{d}G)_{T,p} = \gamma\,\mathrm{d}A + (\bar{\mu}_O + n\bar{\mu}_e)\,\mathrm{d}N_O + \bar{\mu}_R\,\mathrm{d}N_R + E\,\mathrm{d}Q' \qquad (25)$$

where $\mathrm{d}Q'$ is a small quantity of charge flowing into the electrode via the external circuit. If we assume that the redox-active species is introduced in reduced form and subsequently oxidized (or not), this means that the net charge on the electrode surface can be written as $Q = Q' - neN_O$.

At constant $T$, $p$, $A$, $N_{\mathrm{T}}$ and $Q'$ (the latter condition implies an open circuit), Eq. (25) simplifies to

$$(\mathrm{d}G)_{T,p,A,N_{\mathrm{T}},Q'} = (\bar{\mu}_{\mathrm{O}} + n\bar{\mu}_{\mathrm{e}} - \bar{\mu}_{\mathrm{R}})\,\mathrm{d}N_{\mathrm{O}} \tag{26}$$

which should vanish on account of the condition of internal equilibrium between adlayer and electrode, hence

$$\bar{\mu}_{\mathrm{O}} + n\bar{\mu}_{\mathrm{e}} = \bar{\mu}_{\mathrm{R}} \tag{27}$$

which is the Nernst equation, as expected, and, after substitution of Eq. (24), equivalent to [12]:

$$\phi^M = \phi^0 + \phi' + \frac{kT}{ne}\ln\left(\frac{\Gamma_{\mathrm{O}}}{\Gamma_{\mathrm{R}}}\right) \tag{28}$$

with $\phi^0$ as defined previously. A similar expression holds for the excited state.

Assuming this condition to be fulfilled at all times, Eq. (25) becomes

$$(\mathrm{d}G)_{T,p} = \gamma\,\mathrm{d}A + \bar{\mu}_{\mathrm{R}}\,\mathrm{d}N_{\mathrm{T}} + E\,\mathrm{d}Q' \tag{29}$$

This equation may be readily integrated, based on the imaginary surface expansion process described earlier, to yield the expression for the Gibbs energy of the cell:

$$G = G_0 + \gamma A + \bar{\mu}_{\mathrm{R}}N_{\mathrm{T}} + EQ' \tag{30}$$

Here, the integration constant $G_0$ denotes the contribution to $G$ due to the other parts of the cell, i.e. electrodes and solution.

If, under open-cell conditions, the monolayer is subsequently exposed to light of appropriate frequency such that the reduced complexes are all promoted to an excited state, the cell's Gibbs energy, in the first instance, increases by an amount $N_{\mathrm{R}}h\nu_{\mathrm{a}}$, leading to a non-equilibrium (Franck–Condon) state. After the source of the light is removed, the system subsequently relaxes to a new state, labeled (1), with Gibbs energy $G^{(1)} = G + N_{\mathrm{R}}(h\nu_{\mathrm{a}} + \Delta_{\mathrm{FC}}G) = G + N_{\mathrm{R}}w_{\mathrm{R}}$, as discussed in Section 3, and from there to a state in which the equilibrium between electrode and monolayer is restored, characterized by a Gibbs energy:

$$G^* = G^0 + \gamma^* A + \bar{\mu}^*_{\mathrm{R}}N_{\mathrm{T}} + E^* Q' \tag{31}$$

Using the fact that the net charge on electrode and adlayer is fixed (no current is allowed to flow through the cell), the diffuse part of the double layer and, in particular, the diffuse layer potential $\phi'$ is left unaffected, and we can write for the difference in Gibbs energy between initial and final states per unit electrode area, using Eqs. (8), (19), (24), (30) and (31), and the fact that $E^* - E = \phi^{M*} - \phi^M$:

$$\begin{aligned}\frac{(\Delta G)_{T,p,A,N_{\mathrm{T}},Q'}}{A} &= -\Delta\Pi_{\mathrm{mono}} + \left(hc\bar{\tilde{\nu}}_{\mathrm{R}} + kT\ln\left(\frac{\Gamma^*_{\mathrm{R}}}{\Gamma_{\mathrm{R}}}\right)\right)\Gamma_{\mathrm{T}}\\ &\quad +(\phi^{M*} - \phi^M)q'\end{aligned} \tag{32}$$

defining $q' = Q'/A$ and $\Delta\Pi_{\mathrm{mono}} = \gamma - \gamma^*$. The first contribution gives the change in interfacial tension consequent upon absorption, which is due primarily to the exchange of electrons between metal and redox centers that follows the absorption process, and can be identified as minus the change in the lateral surface pressure exerted by this layer and, if the electrode is a semiconductor, the space charge layer.

The free energy difference between the final state and state (1) is found from $\Delta_{\mathrm{FC}}G^{(1)} = G^* - G^{(1)}$, as

$$\begin{aligned}(\Delta_{\mathrm{FC}}G^{(1)})_{T,p,N_{\mathrm{T}},A,Q'} &= (\gamma^* - \gamma)A + (\bar{\mu}^*_{\mathrm{R}} - \bar{\mu}_{\mathrm{R}})N_{\mathrm{T}} - w_{\mathrm{R}}N_{\mathrm{R}}\\ &\quad +(E^* - E)Q'\\ &= -\Delta\Pi_{\mathrm{mono}}A + kTN_{\mathrm{R}}\ln\left(\frac{\Gamma^*_{\mathrm{R}}}{\Gamma_{\mathrm{R}}}\right)\\ &\quad +(\bar{\mu}^*_{\mathrm{R}} - \bar{\mu}_{\mathrm{R}})N_{\mathrm{O}} + (\phi^{M*} - \phi^M)Q'\end{aligned} \tag{33}$$

where Eqs. (8) and (24) have been used.

In the course of the equilibration process, some of the reduced species become oxidized, so $\Gamma^*_{\mathrm{R}} < \Gamma_{\mathrm{R}}$ and $\phi^{M*} < \phi^M$. From the treatment of organothiol monolayers [11] it furthermore follows that, for a rigid monolayer:

$$\Delta\Pi_{\mathrm{mono}} = \int_{\phi^M}^{\phi^{M*}} q\,\mathrm{d}\phi = q'(\phi^{M*} - \phi^M) - ne\int_{\phi^M}^{\phi^{M*}} \Gamma'_{\mathrm{O}}\,\mathrm{d}\phi \tag{34}$$

the so-called Maxwell pressure [13], where $\Gamma'_{\mathrm{O}}$ varies between $\Gamma_{\mathrm{O}}$ and $\Gamma^*_{\mathrm{O}}$. The factor of $N_{\mathrm{O}}$ in Eq. (33) can also be written, using Eq. (27) and its excited-state counterpart, as

$$\bar{\mu}^*_{\mathrm{R}} - \bar{\mu}_{\mathrm{R}} = kT\ln\left(\frac{\Gamma^*_{\mathrm{O}}}{\Gamma_{\mathrm{O}}}\right) - ne(\phi^{M*} - \phi^M) \tag{35}$$

After making these substitutions, the reorganization Gibbs energy per unit area becomes

$$\begin{aligned}\frac{(\Delta_{\mathrm{FC}}G^{(1)})_{T,p,N_{\mathrm{T}},A,Q'}}{A} &= ne\left(\Gamma_{\mathrm{O}}(\phi^M - \phi^{M*}) - \int_{\phi^{M*}}^{\phi^M} \Gamma'_{\mathrm{O}}\,\mathrm{d}\phi\right)\\ &\quad -kT\left(\Gamma_{\mathrm{O}}\ln\left(\frac{\Gamma_{\mathrm{O}}}{\Gamma^*_{\mathrm{O}}}\right) + \Gamma_{\mathrm{R}}\ln\left(\frac{\Gamma_{\mathrm{R}}}{\Gamma^*_{\mathrm{R}}}\right)\right)\end{aligned} \tag{36}$$

From the previous discussion it is clear that the first contribution is negative, and a straightforward analysis shows that also the second is strictly negative, subject to the constraints mentioned after Eq. (33), so that the reorganization Gibbs energy is indeed negative, as it should be for a spontaneous process.

In the absence of an external radiation source, the $N^*_{\mathrm{R}}$ reductants will emit the absorbed energy, instantaneously decreasing the cell's Gibbs energy by $N^*_{\mathrm{R}}h\nu_{\mathrm{f}}$, and a further $N^*_{\mathrm{R}}\Delta_{\mathrm{FC}}G$ following medium relaxation. Finally, the electrode/adlayer system relaxes back to the equilibrium ground state, with an accompanying change in the Gibbs energy denoted by $\Delta_{\mathrm{FC}}G^{(2)}$, which can be shown by arguments analogous to those leading to Eq. (36) to be equal, per unit area, to

$$\begin{aligned}\frac{(\Delta_{\mathrm{FC}}G^{(2)})_{T,p,N_{\mathrm{T}},A,Q'}}{A} &= ne\left(\int_{\phi^{M*}}^{\phi^M} \Gamma'_{\mathrm{O}}\,\mathrm{d}\phi - \Gamma^*_{\mathrm{O}}(\phi^M - \phi^{M*})\right)\\ &\quad -kT\left(\Gamma^*_{\mathrm{O}}\ln\left(\frac{\Gamma^*_{\mathrm{O}}}{\Gamma_{\mathrm{O}}}\right) + \Gamma^*_{\mathrm{R}}\ln\left(\frac{\Gamma^*_{\mathrm{R}}}{\Gamma_{\mathrm{R}}}\right)\right)\end{aligned} \tag{37}$$

and is again found to be strictly negative.

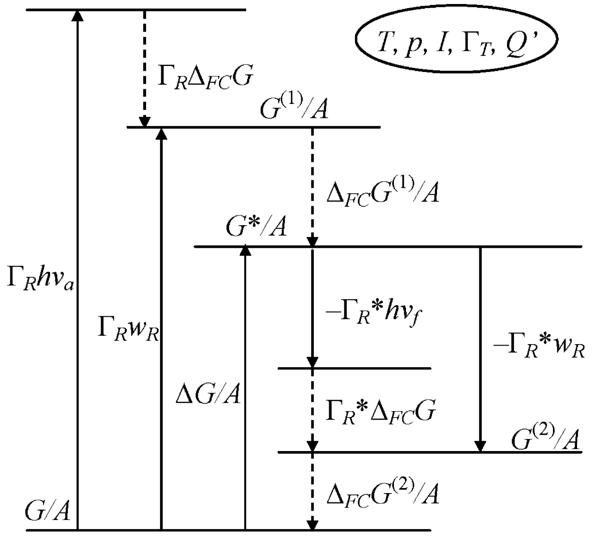

Fig. 4. Scheme showing the relationships among the various Gibbs energies (referred to a unit of electrode area) associated with absorption, emission and dissipation processes when the cell initially absorbs radiation that promotes all reduced species in the monolayer to an excited state, and subsequently returns to its equilibrium ground state. Symbols are defined in the text.

Eqs. (34) and (35) also allow Eq. (32) to be cast in a similar form, as

$$\frac{(\Delta G)_{T,p,N_\mathrm{T},A,Q'}}{A} = ne\left(\Gamma_\mathrm{T}(\phi^M - \phi^{M*}) - \int_{\phi^{M*}}^{\phi^M} \Gamma'_\mathrm{O}\,\mathrm{d}\phi\right) + kT\Gamma_\mathrm{T}\ln\left(\frac{\Gamma^*_\mathrm{O}}{\Gamma_\mathrm{O}}\right) \tag{38}$$

which, based on earlier remarks, is obviously positive.

The relationships among the various free energy changes are summarized in Fig. 4.

The set of expressions for the free energies absorbed, emitted and dissipated in the film is a potentially useful starting point for thermodynamic investigations of these systems. Further elaboration would require rather detailed modeling of the interfacial region, as was done in [11] for electro-active organothiol monolayers, which would lead to a more explicit form of these functions and would allow computation of the corresponding entropy and enthalpy changes, but this will not be pursued further here.

## 5. Discussion

The thermodynamic study presented in the preceding sections considers two distinct cases of heterogeneous equilibrium between a redox couple with one member present in an excited state and a (semiconductor) electrode. In the first, the redox couple is soluble, while in the second it is immobilized in a monolayer covering the electrode, typically a wide-bandgap semiconductor in which a photocurrent is generated via injection of electrons by the excited reductant which subsequently quenches the excited state, producing the ground-state oxidized form. The latter arrangement is more common in photovoltaic cells, where the photo-anode is covered with a dye. Moreover, in recent years, the use of nano-crystalline semiconductor materials has led to vast improvement in the efficiency of these cells and significant reduction in the cost of their manufacture [14].

In this contribution, a detailed analysis is presented of the effects of medium relaxation on the free energy balance of the cell, and their connection with solvatochromism in the common situation where the ion undergoes a sudden change of dipole moment upon absorption or emission of a photon. This allows us to account for the fraction of absorbed radiation that is ultimately dissipated as a result of the relaxation of the solvent and ions in the vicinity of an excited dipole consequent upon an absorption or emission event. It has been shown that the relaxation effects can be simply eliminated by using the average of absorption and emission energies to give the free energy difference between ground and excited state in which the dipole moment remains in equilibrium with its surroundings. Similar corrections were applied to the photon absorption and emission energies of acids and bases to obtain improved estimates for excited-state acidity constants. As argued previously [2], the averaging of frequencies leads to an overestimate of the free energy of excitation if the compound fluoresces before equilibrium is reached.

The present application leads to an expression for the light-induced shift in (standard) redox potential in terms of these averaged photon energies, for either oxidative or reductive quenching.

From the temperature dependence of the spectra, the corresponding differences in other thermodynamic parameters, such as reaction enthalpy and entropy, can be inferred.

The more practical situation of the electro-active species adsorbed onto the anode in the form of a closely packed monolayer requires a somewhat different approach, as in this case the excitation of the reductant will be accompanied by a change in composition and electrode potential. Unless the redox centers are in direct contact with the electrode, the development of a rather detailed model of the interface becomes necessary, in order to describe the potential distribution between electrode and solution. This problem can be treated in a manner analogous to that employed in the case of an electrode modified with an organic monolayer with embedded electro-active species [11]. This approach will enable the computation of the potential shift that results from excitation of redox centers, as well as the concomitant change in Gibbs energy of the cell (assuming the cell terminals to have been disconnected). The latter could be used to find the corresponding changes in other thermodynamic quantities, based on a temperature study and using standard methods. The same considerations pertaining to the role of medium relaxation in dissipation of the absorbed energy that applied in the case of soluble reactants are equally pertinent here.

It is expected that the theory outlined in this study will find use in analyses of the energy balance and efficiency of photoelectrochemical cells as it provides a fairly detailed breakdown of the contributions to the free energy that is absorbed from radiation, into dissipated and stored fractions. This will also provide theoretical background material for the calculation of the steady-state composition of the monolayer under finite-current conditions, as based on the principle of minimum entropy production [15] for small departures from equilibrium, and as a reference for kinetic studies.

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