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# SIMILARITIES BETWEEN THE INTENSITY-ENERGY RELATION IN SPECTROSCOPIC AND ELECTRODE PROCESSES

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**Abstract**

The similarities and differences between the spectroscopic dipole and electrochemical electron transitions are pointed out with the use of time-dependent perturbation theory. A proof of GURNEY condition of radiationless transition of electron at interfaces is given. An expression for the current density in quantum mechanical term is put forward.

## Introduction

The object in this paper is to point out the correlations (and differences) between the quantum mechanical aspects of the fundamental processes in spectroscopy and the lesser known similar aspects of the emission and acceptance of electrons across the interfaces made by ionic solutions and metals or semi-conductors.

Thus, phenomenologically, the method by which electrode-kinetic results are portrayed is only superficially different from that in which spectroscopic results are shown. The current density used in current-potential diagrams is the analogue of the intensity of the absorption or emission of photons plotted in a spectrum. For the transfer of an electron across an interface, the electrostatic work done is the potential difference multiplied by the electronic charge and this is the analogue of the energy of the photon absorbed in spectroscopic processes. Thus, the intensity-frequency relation in absorption spectroscopy (Fig. 1 a) is the analogue of the current-potential diagram in cathodic electrochemical processes (Fig. 1 b). Qualitatively, after a certain critical energy has been reached, further increase in the photon energy suddenly increases the intensity of absorption of photons by particles in solution (or in the gas phase). Correspondingly, increase in the potential of an electrode beyond a critical value in the negative direction (*i. e.*, increase in elec-

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tron energy in the electrode) suddenly increases the rate of acceptance of electrons from the electrode by acceptors in solution (or their emission from the metal surface). An increase of potential in the positive direction causes an increase in the emission of electrons to the electrode from a donor in solution, in *anodic* electrode process and corresponds to emission of photons from the excited particles.

Thus, qualitatively, there are operational and presentational similarities

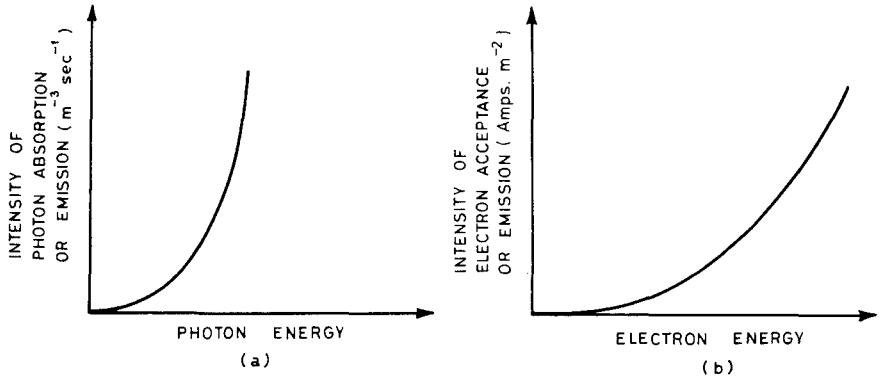


**Fig. 1.** The *initial* trend of increase of intensity in absorption and acceptance of photons and electros as a function of their respective energies.

(a) Increase in intensity of photon absorption or emission with photon energy.

(b) Increase in intensity of electron acceptance or emission with electron energy.

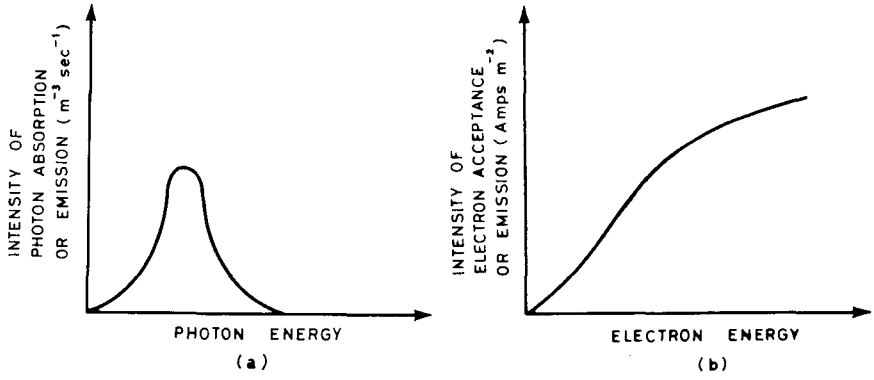


**Fig. 2.** The intensity of absorption and acceptance of photons and electrons as a function of their respective energies, over a wider energy range.

(a) Intensity of photon absorption or emission with photon energy.

(b) Intensity of elecron acceptance or emission with electron energy.[10]

between the individual step in cathodic electrode process and absorption spectroscopy; and anodic electrode processes and emission spectroscopy, respectively.

Moerover, the energy range for absorption spectra in the infra-red region ($10^3\,m^{-1}$ to $10^6\,m^{-1}$), corresponds approximately to $10^{-3}$ eV to 1.0 eV, which roughly covers the range of value of changes in electron energy (due to change in electrode potential) upon passage across the interface in interfacial electrochemistry. There is also similarity in the properties of photons and electrons since both behave as waves and the difference is that the former is Boson and the latter is Fermion.

Correspondingly, there are the following differences in the intensity-energy aspects between spectroscopic and electrochemical phenomena: the spectroscopic situation shows an increase in the rate of transition with respect to energy until a certain maximum with a symmetrical fall of transition rate at higher energies (Fig. 2 a); the electrochemical transition rate also increases with electron energy until a certain current density, after which, at higher energies, it does not undergo a diminution but tends towards a limiting value (Fig. 2 b).

## The Spectroscopic Case

According to time-dependent perturbation theory[1,2] the probability of transition, $P_t$, can be expressed as,

$$P_t = \left| \frac{1}{i\hbar} \int_0^t U_{fi} e^{\omega_{fi}} dt \right|^2 \qquad (1)$$

where $U_{fi}$ is the matrix element of perturbation.

It is well known[1,2] that, using the *time-dependent* perturbating energy corresponding to electromagnetic radiation in Eq. (1), one obtains[2] in spectroscopic case,

$$P_t = \frac{4|U_{fi}^0(x)|^2}{\hbar^2} \left\{ \frac{\sin^2 1/2\,(\omega_{fi}-\omega)t}{(\omega_{fi}-\omega)^2} \right\} \qquad (2)$$

where

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \qquad (3)$$

and $\omega$ is the frequency of the electromagnetic radiation.

Equation (1) indicates that (so long as the transition-moment matrix, $U_{fi}^0(x)$ is non-zero) the probability of transition passes a maximum at $\omega \simeq \omega_{fi} = \omega_0$ *i. e.*, when $E_f - E_i = \hbar\omega_0$, *i. e.*, the Bohr condition[3] is satisfied.

The intensity-energy relation of absorption in spectroscopy (*e.g.* for the *ideal* case in the gas phase) can be expressed[2,4] as,

$$I=\frac{P_t}{t}N_0 e^{-v\hbar\omega_0/kT}$$

$$=\frac{|U^0_{fi}(x)|^2 t}{\hbar^2}\frac{\sin^2\left[\frac{E_f-E_i-\hbar\omega}{2\hbar}t\right]}{\left[\frac{E_f-E_i-\hbar\omega}{2\hbar}\right]^2 t^2}N_0 e^{-v\hbar\omega_0/kT} \qquad (4)$$

where $t$ is the time of a short perturbation (not the linear time) which acts on the system and the martix element of transition,

$$U^0_{fi}(x)=\langle\psi_f|e_0F_0x|\psi_i\rangle \qquad (5)$$

where $e_0$ is the electronic charge, $F_0$ is the field of electromagnetic radiation and $\psi_i$ and $\psi_f$ are respectively the initial and the final state wave functions of the photon absorbing or emitting system, $v$ is the vibrational quantum number, $N_0$ is the number of molecular bonds in their ground vibrational quantum state and $\omega_0$ is the frequency of vibration of the photon absorbing bonds. A plot of Eq. (4) against $\omega$ indicates the spectroscopic intensity-energy relation of the ideal case in the gas phase (Fig. 2 a)*), since the transition moment martrix, $U^0_{fi}(x)$, is independent of $\omega$. This equation (4) represents the essence of the situation in spectroscopy, why the intensity starts to rise but then comes down again around the Bohr condition, within the range of *uncertainty in energy.*

## The Electrochemical Case

The less well known theory of the probability and rate of electron transition at electrified interfaces[5~7] can also be obtained from the general expression (1) but the definitions of the terms, and the nature of the perturbing energy, are radically different from those used in the spectroscopic definition.

The electrochemical case involves a *non-time dependent and non-oscillating* perturbing energy,[8]

$$U^0(r)=e_0X_0r \qquad (6)$$

where $X_0$ is the field across the electrode-solution interface and $r$ is the

*) The solution broadens and complicates the phenomena but the essential feature is given by Fig. 2(a) namely there is a decrease in intensity of absorption or emission after certain increase round about the critical energy, $\hbar\omega_0$.

distance across which the electron travels between the electrode and the acceptor.

Substitution of Eq. (6) in place of the perturbing enery $U_{fi}$ in Eq. (1), gives the probability of an electron transition to an available state across an interface as

$$P_t = \left| \frac{U^0_{fi}(r)}{i\hbar} \int_0^t e^{i\omega_{fi}t}\, dt \right|^2 \qquad (7)$$

where the matrix element of transition is

$$U^0_{fi}(r) = \langle \psi_f | e_0 X_0 r | \psi_i \rangle \qquad (8)$$

where $\psi_i$ represents the initial state of electrons in the metal in the partially filled level and $\psi_f$ is the final state of electron in the acceptor in solution (or vice-versa), $\omega_{fi}$ is the frequency corresponding to the energy difference between the initial and the final state (not to be confused with the $\omega$ used above, which is the frequency of incident electromagnetic radiation, as in Eq. (4)). After intergration Eq. (7) becomes

$$P_t = \left| \frac{U^0_{fi}(r)}{i\hbar} \left[ \frac{e^{i\omega_{fi}t} - 1}{i\omega_{fi}} \right] \right|^2 \qquad (9)$$

On further simplification equation (9) becomes:

$$P_t = \frac{4|U^0_{fi}(r)|^2}{\hbar^2} \left\{ \frac{\sin^2 1/2\omega_{fi}t}{\omega^2_{fi}} \right\} \qquad (10)$$

There are several differences between Eq. (10) (the electrochemical case) and the corresponding Eq. (2) (the spectroscopic case). The matrix element of transition, $U^0_{fi}(x)$ in equation (4) and $U^0_{fi}(r)$ in Eq. (8) and (10) are different in that the spectroscopic case depends on the field of the electromagnetic radiation and the polarizability of the photon-absorbing bonds; and the electrochemical case depends on the electric field in the double layer, and the distance across the interface between the surface electrons in the metal and the first layer acceptors in solution (the transfer rate to those further out in the solution will be negligible).

Equation (10) can be expressed in terms of energy by using Eq. (3). It becomes:

$$P_t = \frac{|U^0_{fi}(r)|^2}{\hbar^2} \left\{ \frac{t^2 \sin^2 \dfrac{E_f - E_i}{2\hbar} t}{\left[ \dfrac{E_f - E_i}{2\hbar} \right]^2 t^2} \right\} \qquad (11)$$

The plot of $\dfrac{t^2 \sin^2 z}{z^2}$ (cf. Eq. (11)) versus $z$ shows a maximum as $z \to 0$, where

$z=(E_f-E_i)t/2\hbar$. Thus, in contrast to the spectroscopic case, the transition probability in the electrochemical case is a maximum when $E_f-E_i\simeq 0$ (or for $E_f\simeq E_i$). Equation (11) represents *the proof given of a suggestion made intuitively many years ago by* RONALD GURNEY concerning the radiationless transition of electrons at the interface.[9] He suggested that electrons would only cross from electrode to solution when $E_i=E_f$, and based upon this (to him obvious) condition, the first paper[9] on the quantum mechanical theory of the rate of a reaction— that of electrons donated to protons at interfaces. At what may, therefore, be called the GURNEY condition ($\Delta E\simeq 0$), the rate of transition of an electron from the metal to an *available* state in the solution becomes:

$$P_t=\frac{P_t}{t}=\frac{2\pi}{\hbar}|U_{fi}^0(r)|^2\rho(E_f) \tag{12}$$

where $\rho(E_f)$ is the density of final electronic states per unit energy.

The dependence of current density on the energy of the electron in the electrochemical case arises from the Boltzmannian population of acceptor molecules in different vibrational-rotational levels in solution.[9] This is

$$N(E)=N(E_g)e^{-\beta(E_g-E)/kT} \tag{13}$$

rather a simple Boltzmann term involving $(E_g-E)$, where $E_g$ is the ground state energy of the acceptor and $E$ is the electron energy. The factor $\beta$, called in electrochemical theory "the symmetry factor",[8] ranges in value between $0<\beta<1$.

Thus, the intensity-energy relation for electron acceptance in the electrochemical case is obtained from Eqs. (12) and (13) as

$$i=\frac{2\pi e_0}{\hbar}|U_{fi}^0(r)|^2\rho(E_f)\,N(E_g)e^{-\beta(E_g-E)/kT} \tag{14}$$

## Discussion

The spectroscopic and electrochemical intensity-energy diagrams (Figs. 2 a and 2 b), namely that the spectroscopic curve *peaks* and the electrochemical one *does not*, springs from differences in expressions (4) and (14), which arise from the fact that spectroscopic transitions (*e. g.*, in the infra red region in solution) involves *excitation* from the lower to higher vibrational quantum state, and such excitations are governed by the transition moment matrix which becomes numerically significant only for transitions between certain vibrational states. In the electrochemical case, there is *no excitation*

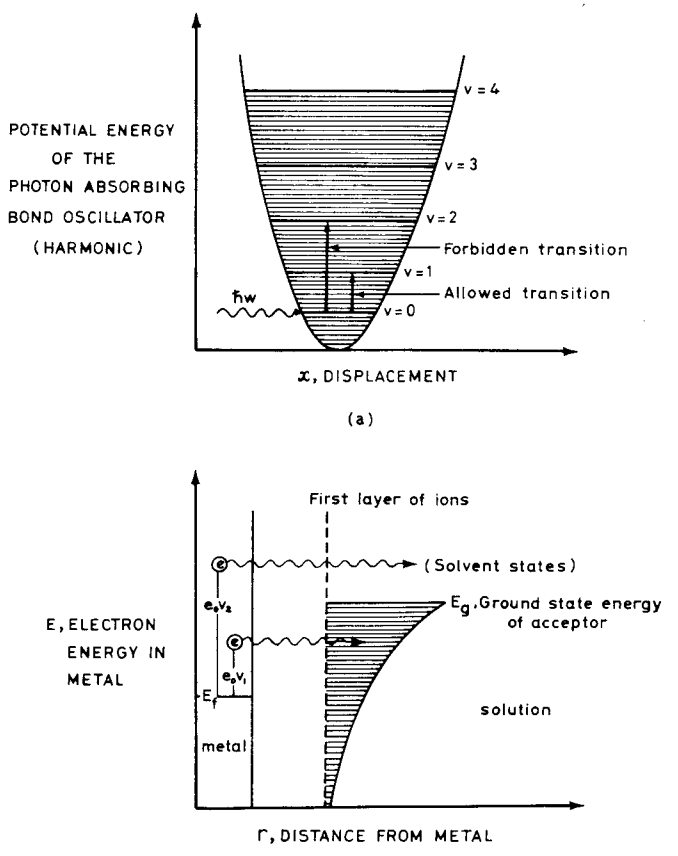


**Fig. 3.** Diagram for photon transition and excitation of bonds (a); and electron transition with no excitation (b).

(a) Shows photon transfer to vibrating bond (*e.g.*, for spectra in solution in an infra red region) and excitation of bonds to higher vibrational quantum state, $v=1$. Transition rates are finite only for certain photon energies.

(b) Shows electron from metal electrode to distributed acceptor states in solution when the electron energy $E$ in the electrode is less than the $E_g$ in solution at potential, $V_1$; and when the electron energy $E$ in the electrode is higher than $E_g$ in solution at potential, $V_2$. If $E>E_g$, there is no longer a Boltzmannian increase of rate with potential (see Fig. 2 b and Eq. (14)). At $E<E_g$, transition rates are finite for all energies.

following upon the process in which the emitted electrons from the metal electrode are accepted by acceptors in solution.

Thus, the selection rule for the spectroscopic (*excitation*) transition arises from the zero and non-zero conditions of the transition moment matrix, $U^0_{fi}(x)$. Thus, using the ground and first excited vibrational state wave functions of the harmonic oscillator[2] in Eq. (5), it is found that $U^0_{fi}(x)$ is non-zero but if the higher quantum states other than the first excited state is used, the transition moment matrix becomes zero[3] and this illustrates the selection rule that $\Delta v = \pm 1$ are the only allowed vibrational transitions (Fig. 3 a).

In the electrochemical case, however, the transition matrix, $U^0_{fi}(r)$, is never zero for the transfer of an electron from the electrode surface to an *available* acceptor state in solution, or vice-versa. This can be proved using the simplifications that the initial state wave function $\phi_i$ is, for the free particle wave of an electron which comes out from the electrode surface,

$$\phi_i = (L_0)^{-3/2} e^{ik\cdot r} \tag{15}$$

where $L_0$ and $k$ are, respectively, the normalization constant and wave vector of the free particle wave; and the final state wave function as the 1s hydrogenic wave function (for the $H_3O^+$ as an acceptor to from H)

$$\phi_f = \left[\frac{\alpha^3}{\pi}\right]^{1/2} e^{-\alpha r} \tag{16}$$

where $\alpha$ is the inverse of the BOHR radius. Then, using (15) and (16) in (8), one obtains

$$U^0_{fi}(r) = A\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r^3 e^{ikr\cos\theta} e^{-\alpha r}\, dr \sin\theta d\theta d\phi = \frac{16\pi i A k^2}{(\alpha^2+k^2)^3} \tag{17}$$

where $A = \left[\frac{\alpha^3}{\pi L_0^3}\right]^{1/2} e_0 X_0$.

Equation (17) shows that the transition matrix for the electrochemical case is not zero and hence no selection rule is involved in transitions between states of *equal* energy.

As there is no selection rule involved in electrochemical transitions (in contrast to those in spectroscopic systems) electrons from the metal electrode can undergo transition to any energy states of the acceptor in solution so long as it is equal to the energy which they have when emitted from the metal electrode, *i. e.*, obeys the GURNEY condition. The population of the corresponding states in solution is given by Eq. (13) (Fig. 3 b).

In solution, collisional interactions cause a lessening of the sharpness of definition of the energy of the vibrational-rotational states, so that there is, in effect, an overlap of the energies of these states which amounts to the existence of quasi-continuous states.[9] This fact, together with the absence of a selection rule, allows the GURNEY condition to be fulfilled at any electron energy, *i. e.*, at any electrode potential, whereas the Bohr condition can exist only for energy transfer for which the transition moment matrix is non-zero, *i. e.*, at the energy at which the selection rules allow transition. Thus, the intensity-energy relation does not peak-out in electrochemical transitions, only again starting to increase when a new energy region is reached which fits the selection rule. With increasing energy of the electronic states in the metal, there will be an exponential increase in the rate of transition (see Eq. (14)). Barring the imposition of factors outside this discussion*), this increase of the rate of transition with increasingly negative electrode potential will continue until the Fermi level in the metal has been shifted to a value equal to that of the ground state of the acceptor (Fig. 3 b). If the electron energy is made still more negative, the electrons have no simple acceptor states in the double layer (*e. g.*, those in an $H_3O^+$ ion) to which to transfer, but it is found experimentally that the current does not peak though it tends to slow its increase[10] and the intensity-energy (*i. e.*, current-potential) relation flattens out (Fig. 2 b). From theoretical computations made of the current-potential relation in photoemission, when incident photons lift electrons in metals above the ground state of $H_3O^+$ ions in solution, it seems likely that the emitted electrons become solvated, diffuse about in solution using up energy, until they can be captured by water molecules, with which they react to generate and then $H_2$.

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*) *e. g.*, the provision by mass transport an insufficient number of states to an interface to accept the electrons at a rate at which the perturbation due to the electric field is producing them.

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