Vibronically Induced Two-Photon Transitions in Benzene

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The strengths of two-photon transitions from the ground state to excited vibronic states in benzene are calculated by using the CNDO/2-U wave functions. The role of vibronic coupling in two-photon absorption process is discussed. The A_{1g}^{-}-A_{2g}^{+} two-photon transitions, which are forbidden by the identity-forbidden selection rule in single frequency two-photon absorption, are too weak to be experimentally observed even when two photons of different energies are used. It is because the transitions are forbidden also by the pseudo-parity selection rule which are applicable for alternant hydrocarbons such as benzene. It is also shown that the vibronic coupling is not very effective in altering the pseudo-parity property of the electronic state. The strength of the vibronically induced two-photon absorption is strongly affected by the presence of an electronic state from which two-photon absorption can borrow the intensity. It is pointed out that the pseudo-parity selection rule may be violated in such cases.

Introduction

Two-photon absorption (TPA) spectroscopy has been one of the powerful nonlinear spectroscopies for probing excited molecular states ever since TPA was first observed experimentally in early 1960's.[1] By using TPA, it becomes possible to reach those high lying excited states which are not usually accessible by the conventional linear one-photon absorption (OPA) spectroscopy. However, much of its advantage over OPA arises from the differences in the selection rules for TPA and OPA. For example, the parity selection rule for TPA is exactly opposite to the parity selection rule for OPA. Therefore, it is possible to probe by TPA the excited molecular states which are inaccessible by OPA.[2]

Two-photon absorption experiments can be carried out either with a single laser or with two different lasers. When a single laser is used, two photons of the same frequency and polarization are absorbed (single frequency two-photon absorption or SFTPA). SFTPA is experimentally easier than different frequency two-photon absorption (DFTPA) experiment in which two lasers of different frequencies and polarizations are used. However, some two-photon transitions are allowed only in DFTPA because of the identity-forbidden selection rule in SFTPA. Furthermore, more versatile combinations of polarizations and frequencies of laser lights in DFTPA can give more detailed information about the molecular excited states.

The strength of TPA can be described in terms of the two-photon absorption tensor of rank 2 which has 9 independent Cartesian elements in the most general case.[3] In many cases, however, TPA tensor elements are related to one another due to molecular symmetry. When TPA tensor is traceless and antisymmetric, the TPA transition becomes forbidden when the two photons absorbed are identical as in SFTPA. This type of selection rule, which is called identity-forbidden selection rule[3] for obvious reason, are common in multiphoton absorption processes in which more than two photons of the same kind are absorbed by molecules.[4] For identity-forbidden transition, each of the absorption tensor elements was usually thought as vanishing when the frequencies of the photons absorbed are identical.[3] However, it has been pointed out that the correct tensor elements have nonvanishing values even in SFTPA.[5] Nevertheless, the identity-forbidden selection rule is valid because the polarization vectors are common to both photons absorbed, resulting in vanishing transition probability. The traceless and antisymmetric scattering tensor are also related to the unique inverse polarization effect in resonance Raman scattering process,[6] which is useful for identifying certain vibrational modes in Raman spectra.

In benzene belonging to the D_{6h} point group, the transition from the ground electronic state (A_{1g}) to the lowest excited electronic state (B_{2u}) is group theoretically forbidden both in OPA and the TPA, and the lowest electric dipole allowed electronic state is the E_{1u} state. In OPA, the transitions to the various vibronic states in the B_{2u} electronic manifold become allowed by borrowing intensity from the nearby E_{1u} state through coupling of the electronic motion with the vibration motions of nuclei. Likewise, two-photon transitions to the B_{2u} electronic manifold are also possible through vibronic coupling. The two-photon transitions from the A_{1g} ground state to the E_{2g}, A_{1g}, and A_{2g} states are group theoretically allowed. Among these two-photon allowed transitions, the transitions of the A_{2g} vibronic states are forbidden in SFTPA by the identity-forbidden selection rule. In fact, these transitions have been experimentally observed neither in SFTPA nor in DFTPA.[2,3] The absence of these transitions in SFTPA can be understood as a result of the identity-forbidden selection rule.[3] However, the absence in DFTPA has not been clearly understood yet.

In this study, we have calculated the two-photon absorption strengths of benzene by using wave functions obtained from the semi-empirical CNDO 2-U method. The role of the vibronic coupling in two-photon absorption process will be studied in detail. Also, the reason for the experimental absence of the transitions to the A_{2g} vibronic states will be discussed.

Two-Photon Absorption. The possibility of two-photon absorption, in which molecules absorb two photons simultaneously to make a transition to an excited state, was first predicted theoretically in 1930's.[7] Two-photon absorption rate is proportional to the square of the incident light intensity, unlike conventional one-photon absorption in which the absorption rate increases linearly with the incident intensity. However, since TPA rate is too small to be observed under normal conditions, the experimental verification of TPA was achieved only after laser, a powerful tunable light source, became available in 1960's.[1] Since then, TPA has been widely used as a powerful spectroscopic tool for probing molecular excited states.

Two-photon absorption rate is usually described by the two-photon absorption cross section, $\sigma_{TPA}(\omega_1,\omega_2)$, which is typically on the order of 10^{-50} cm^4 sec/(photon molecule).[2,4] In SFTPA, ω_1 and ω_2 are the same, while they are different in DFTPA. The cross section for the transition from the initial (ground) state i to a final state f, in turn, can be expressed in terms of the two-photon absorption tensor of rank 2, $S^{if}(\omega_1, \omega_2)$,[3]

$$\sigma^{if}_{TPA}(\omega_1, \omega_2) = (8\pi^2 e^4 \omega_1 \omega_2 / c^2)\,|\,\hat{\lambda}\cdot\mathbf{S}^{if}(\omega_1, \omega_2)\cdot\hat{\mu}\,|^2 \; g(\omega_{fi};\, \omega_1, \omega_2) \tag{1}$$

Here, $\hat{\lambda}$ and $\hat{\mu}$ are the polarization unit vectors of the incident lights of the frequencies ω_1 and ω_2, respectively. And, $g(\omega_{fi};\omega_1, \omega_2)$ is the Lorentzian line shape function with the dimension of sec.

The density matrix approach has been proved as the most accurate way of finding quantum mechanical expression for the TPA tensor.[8] Within the electric dipole approximation, a Cartesian DFTPA tensor element takes on the following form:

$$S^{if}_{\alpha\beta}(\omega_1, \omega_2) = \sum_n \Big[\frac{<i|\hat{\alpha}|n><n|\hat{\beta}|f>}{E_n - \hbar\omega_1} + \frac{<i|\hat{\beta}|n><n|\hat{\alpha}|f>}{E_n - \hbar\omega_2}\Big] \tag{2}$$

In Eq. (2), $\hat{\alpha}$ and $\hat{\beta}$ are the Cartesian components (x, y, or z) of the polarization unit vectors of the incident lights. E_n represents the energy of the intermediate state measured from the ground state. The transition dipole matrix elements in the numerator represent the coupling of molecular states through the electric dipole operator. The summation in Eq. (2) is over the complete set of molecular eigenstates including the continuum. The first term in Eq. (2) represents the process in which molecule makes a virtual transition first from the initial state i to the intermediate state n by absorbing a photon of ω_1 and then to the final state f by absorbing a photon of ω_2. For the second term, the sequence is reversed. The energy conservation condition is not required for the virtual transitions to the intermediate states. However, the sum of two photon energies corresponds to the energy gap between the initial and final states, i.e. $E_f = \hbar(\omega_1 + \omega_2)$.

For SFTPA, in whch $\omega_1 = \omega_2 = \omega$, the tensor takes on a slightly different form from the DFTPA tensor.[5] Unlike the DFTPA tensor in Eq. (2), the SFTPA has a single term in the summation as a following:

$$S^{if}_{\alpha\beta}(\omega, \omega) = \sum_n \Big[\frac{<i|\hat{\alpha}|n><n|\hat{\beta}|f>}{E_n - \hbar\omega}\Big] \tag{3}$$

The difference between Eqs. (2) and (3) arises from the fact that photons of the same energy are indistinguishable. Therefore, the two terms in Eq. (2) cannot be distinguished from each other. It has been pointed out that the correct form in Eq. (3) shoud be used to calculated absolute two-photon transition rate and the polarization ratio for SFTPA.[5]

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The Cartesian form of TPA tensor has 9 independent elements in the most general case.[3] The patterns of the TPA tensor, which can be derived by using group theory, play an important role in interpreting TPA spectra. As a special case, when TPA tensor is traceless ($S_{\alpha\alpha} = 0$) and antisymmetric ($S_{\alpha\beta} = -S_{\beta\alpha}$), the two-photon transition becomes forbidden when two frequencies are identical as in SFTPA. It is known as the identity forbidden selection rule.[3]

The electronic of molecule are usually classified to their group theoretical properties. However, the electronic states of alternant hydrocarbons such as benzene can also be classified by the pseudo-parity property.[9] Alternant hydrocarbon is a group of conjugated hydrocarbons in which two groups of carbon atoms, "starred" and "unstarred", are alternating each other. For these molecules, the energies of Hückel molecular orbitals are always symmetric with respect to the nonbonding orbital. In this case, the excited electronic states are always degenerated, resulting in the "plus" and "minus" pseudo-parity property. The non-degenerate ground electronic state is usually classified as a minus state. It has been shown that the electric dipole operator can couple the states with different pseudo-parity.[9] Therefore, the transitions to the plus states are allowed in OPA, while the transitions to the minus states are allowed in TPA. Although the pseudo-parity selection rule is not so powerful as the group theoretical selection rule, it is quite useful in identifying vibronic spectra of alternant hydrocarbons.[10] The pseudo-parity of an electronic state can be altered by coupling with the vibrational modes. For example, among the in-plane vibrational modes of cyclic polyenes, those modes with tangential nuclear motions conserve the pseudo-parity of the electronic state. On the other hand, those modes with radial vibrational nuclear motions alter the pseudo-parity.[10] In benzene, the b_{2u} vibrational modes (ν_9 and ν_{10}) belong to the former case and the b_{1u}(ν_5 and ν_6) are the example of the latter case.

Calculation of Two-Photon Absorption Strength. Two-photon absorption strengths for π-electron systems have been successfully calculated by using the wave functions from the semi-empirical CNDO method. In this work, we have used the empirical parameters for the CNDO method employed by Del Ben *et al.*[11]

In order to calculate the TPA tensor in Eq. (2) or Eq. (3), it is necessary to calculate the transition dipole moments between the electronic states. The CNDO wave function for an excited electronic state is represented as a linear combination of the Slater determinants $\{V_l(n\text{-}n')\}$. The antisymmetrized Slater determinant $V_l(n\text{-}n')$ represents the electronic configuration in which an electron is excited from an occupied one-electron molecular orbital ϕ_n to an unoccupied orbital $\phi_{n'}$. Thus, the electric dipole transition moment between the electronic states j and k is given as[9]

$$<j|\hat{\alpha}|k> = \sum_l \sum_m D^*_{jm} D_{kl} < V_m(q-q')\,|\,\hat{\alpha}\,|\,V_l(p-p')> \tag{4}$$

Here, D_{kl} is the coefficient of the l-th configuration in the k-th electronic state. The integral in the right hand side of Eq. (4) can be simplified in terms of the one-electron transition dipole moments as following,[9]

$$<V_m(q-q')\,|\,\hat{\alpha}\,|\,V_i(p-p')> = \begin{cases} M^{\alpha}_{pp}+M^{\alpha}_{p'p'}+2\sum_{r\neq p} M^{\alpha}_{rr} & \text{for } p=q \text{ and } p'=q' \\ -M^{\alpha}_{pp} & \text{for } p\neq q \text{ and } p'=q' \\ M^{\alpha}_{p'q'} & \text{for } p=q \text{ and } p'\neq q' \\ 0 & \text{otherwise} \end{cases} \tag{5}$$

Within the zero differential overlap approximation, in which the contributions from the basis functions centered at different nuclei are entirely neglected, the one-electron transition moment, M^{α}_{rs} between the molecular orbitals ϕ_r and ϕ_s can be written as following,

$$M^{\alpha}_{rs}=\sum_{a}\sum_{b} C^{*}_{ra} C_{sb}\,\alpha^{c}_{a}\,\delta_{ab} \tag{6}$$

Here, α^{c}_{a} is the α component of the coordinate of the center of the basis function. In the case of benzene with the center of inversion, there is no contribution to the transition dipole moment from nuclear motions.

The transition dipole moment from the ground electronic state V_i is given as[9]

$$<V_i\,|\,\hat{\alpha}\,|\,V_i(p-p')>=\sqrt{2}M^{\alpha}_{pp'} \tag{7}$$

The extra factor of $\sqrt{2}$ is introduced because of the different normalization constants between V_i and $V_i(p\text{-}p')$. In the CNDO method, the ground electronic state which has closed shell configuration is represented by a single Slater determinant. On the other hand, the excited states with open shell configuration are represented by sets of two Slater determinants.

Eqs. (4) through (7) can be sued to calculate the TPA tensor elements in Eqs. (2) and (3). In our calculations for benzene, we have used only the molecular orbitals of the $\pi\pi^{*}$ type with the zero differential overlap approximation. Furthermore, the summations in Eqs. (2) and (3) are limited to those π states obtained in the CNDO method. These have been typical approximations used in many successful calculations of two-photon absorption strengths for aromatic compounds.[12]

When molecules are randomly oriented, the TPA strength is better represented by taking an average of the TPA corss-section over all possible molecular orientations. According to Monson and McClain[3], the orientation averaged TPA strength can be written as

$$\delta=<|\,\hat{\lambda}\cdot S\cdot\hat{\mu}\,|^{2}>_{av}=F\delta_F+G\delta_G+H\delta_H \tag{8}$$

where

$$\delta_F=\sum_{\alpha}\sum_{\beta} S_{\alpha\alpha}S^{*}_{\beta\beta} \tag{9a}$$

$$\delta_G=\sum_{\alpha}\sum_{\beta} S_{\alpha\beta}S^{*}_{\alpha\beta} \tag{9b}$$

$$\delta_H=\sum_{\alpha}\sum_{\beta} S_{\alpha\beta}S^{*}_{\beta\alpha} \tag{9c}$$

and F, G, and H are the parameters representing the polarization unit vectors. For TPA with parallel linear polarizations ($\delta_{\uparrow\uparrow}$), $F=G=H=2$. For perpendicular polarizations ($\delta_{\uparrow\rightarrow}$), $F=H=-1$ and $G=4$. For the transitions forbidden by the identity forbidden selection rule, $\delta_{\uparrow\uparrow}$ vanishes because $\delta_F=0$ and $\delta_G=-\delta_H$.

The TPA strengths for the transitions to various vibronic states of benzene are calculated by using the wave functions obtained from benzene distorted according to the given normal modes of vibration. The nuclei of benzene are placed at the positions which are displaced by the root-mean-square displacements from the undistorted positions. The electronic wave functions calculated in this fashion should include the effect of vibronic motions in an average way.

Table 1. Vibronically Induced Two-Photon Absorption Strengths for A^{-}_{1g}-A^{-}_{1g}

Final State	E_f (eV)	$\delta_{\uparrow\uparrow}$ (10^{-41} cm^6)		
		20^a	30^a	50^a
$B^{-}_{2u}\times b_{2u}(\nu_9)$	4.866	3.57	3.11	0.700
$B^{-}_{2u}\times b_{2u}(\nu_{10})$	4.971	6.98	6.03	1.35
$B^{+}_{1u}\times b_{1u}(\nu_5)$	5.787	0.0174	0.0127	0.0102
$B^{+}_{1u}\times b_{1u}(\nu_6)$	5.785	0.0616	0.0452	0.00900

[a] $\hbar\omega_1/E_f$(%).

Table 2. Vibronically Induced Two-Photon Absorption Strengths for A^{-}_{1g}-A^{+}_{2g}.

Final State	E_f(eV)	$\delta_{\uparrow\rightarrow}$($10^{-45}$ cm^6)		
		20^a	30^a	$50^{a,b}$
$B^{+}_{1u}\times b_{2u}(\nu_9)$	5.837	0.111	0.234	0.0
$B^{+}_{1u}\times b_{2u}(\nu_{10})$	5.888	0.454	0.635	0.0
$B^{-}_{2u}\times b_{1u}(\nu_5)$	4.760	4.71	1.78	0.0
$B^{-}_{2u}\times b_{1u}(\nu_6)$	4.753	16.5	6.23	0.0

[a] $\hbar\omega_1/E_f$(%) [b] This is forbidden by the identity-forbidden selection rule.

Table 3. Vibronically Induced Two-Photon Absorption Strengths for A^{-}_{1g}-E^{+}_{2g} and A^{-}_{1g}-E^{-}_{2g}

Final State		E_f(eV)	$\delta_{\uparrow\uparrow}$ (10^{-41} cm^6)		
			20^a	30^a	50^a
$E^{+}_{1u}\times b_{2u}(\nu_9)$	$[E^{+}_{2g}]$	7.321	0.655	0.326	0.0530
$E^{+}_{1u}\times b_{2u}(\nu_{10})$	$[E^{+}_{2g}]$	7.333	1.04	0.512	0.0831
$E^{+}_{1u}\times b_{1u}(\nu_5)$	$[E^{-}_{2g}]$	7.310	0.0264	0.0102	0.00540
$E^{+}_{1u}\times b_{1u}(\nu_6)$	$[E^{-}_{2g}]$	7.300	0.0941	0.0365	0.00483

[a] $\hbar\omega_1/E_f$(%).

Results and Discussions

The calculated orientation averaged two-photon absorption strengths in Eq. (8) are listed in Tables 1-3. The final vibronic states are identified by the irreducible representations for the undistorted benzene. The photon energy $\hbar\omega_1$ is given as a fraction of the energy difference E_f between the ground and final states, and thus $\hbar\omega_2=E_f-\hbar\omega_1$.

In undistorted benzene, the E_{2g} state, the superscript representing the pseudo-parity property, is the lowest electronic state to which TPA transition from the A_{1g} ground state is allowed by the group theoretical selection rule as well as by the pseudo-parity selection rule. The E_{2g} state is located 8.213eV above the ground state in the CNDO calculation.

The orientation averaged TPA strengths in Eq. (8) are on the order of 10^{-39} cm^6 which can be regarded as the typical order of magnitude of the allowed TPA strength for benzene. The TPA strength is weaker in general in SFTPA than in DFTPA. However, the weakness in SFTPA can be easily compensated by long path length of laser light in experiment.

On the other hand, the strengths for vibronically induced two-photon absorptions are at least 100 times smaller than the allowed TPA strengths as can be seen in Tables 1-3. Here, the b_{2u} (ν_9 and ν_{10}) and b_{1u} (ν_5 and ν_6) vibrational modes, which are known to conserve and alter, respectively, the pseudo-parity of the electronic state, are considered. It is found that the TPA strengths are not so sensitive to the amount of nuclear displacements. Furthermore, the TPA cross-section is the largest when the incident lights are linearly polarized to the same direction.

Among the in-plene vibrational modes considered in this work, the b_{2u} modes, in which the nuclei are displaced to the tangential directions to the benzene ring, are found as to be more effective in shifting electronic energy levels as can be seen in Table 1-3. In undistorted benzene, the B_{2v}, B_{1u}, and E_{1u} states are located 4.762, 5.788, and 7.314 eV above the ground state, respectively. The result appears to be due to the fact that all of these excited electronic states have the electronic configurations obtained from $\pi\pi^*$ transitions and that the π orbital energy is more sensitive to the distance between two adjacent carbon atoms.

Tables 1 and 2 show that the vibrational coupling is not very effective in modifying the pseudo-parity character of the electronic state. In other words, the TPA strength for a transition to vibronic state is dominated mostly by the pseudo-parity property of the unperturbed from the pseudo-parity allowed B_{2u}^- electronic state are stronger than the transitions to the vibronic states of the pseudo-parity forbidden B_{1u}^+ state. This is interesting because the E_{1u} electronic state, which serves as the most important intermediate state, lies closer to the B_{1u} state. And, in group theoretically allowed two-photon transitions, it is normally expected that the transition to the state close to the important intermediate state becomes stronger because of the small energy denominator in Eq. (2) or Eq. (3). This, if the energy denominator is the dominant factor for determining the TPA strength, the transitions to the B_{1u}^+ manifold are expected to be stronger than those to the B_{2u}^- manifold.

The TPA strengths in Table 2 are much smaller than the other vibronically induced TPA strengths in Tables 1 and 3 by a factor of 10^{-4}. The TPA tensor for $A_{1g}^- - A_{2g}^+$ transitions in Table 2 is traceless and antisymmetric as discussed in Section 2. Thus, the two-photon transition is forbidden by the identity-forbidden selection rule when two photon energies are identical as in SFTPA. The two-photon transitions are also forbidden when photons of the parallel linear polarization are used in DFTPA since $F=G=H=2$ and $\delta_F=0$ and $\delta_G=-\delta_H$ in Eq. (8). Thus, these transitions can only be detected experimentally when the polarizations of the photons are perpendicular to each other. However, these transitions are too weak to be observed experimentally even in DFTPA because they are forbidden by the pseudo-parity selection rule.

In Table 3, the TPA strengths for the transitions to the vibronic states in the E_{1u}^+ state are listed. Here, the pseudo-parity forbidden $A_{1g}^- - E_{2g}^+$ transitions are stronger than the pseudo-parity allowed $A_{1g}^- - E_{2g}^-$ transitions. And, the pseudo-parity selection rule does not seem to work for these transitions. Although it can be regarded as an indication that the radial nuclear displacements are less effective in modifying the pseudo-parity property of the electronic state, the more important reason is the presence of the two-photon allowed E_{2g}^- electrionic state within 1 eV range from the E_{1u}^+ state.

The two-photon transition to a vibronic state in a forbidden electronic manifold can be regarded as borrowing the intensity from the transition to nearby allowed state through vibronic coupling. According to the Herzberg-Teller formalism for the vibronic coupling,[13] the degree of mixing of nearby electronic state due to the vibronic coupling depends inversely on the energy gap between the two electronic states. Thus, the presence of the E_{2g}^- state has little effect on the transitions to the B_{2u}^- and B_{1u}^+ manifold which are located more than 2.4 eV below the E_{2g}^- state. However, it can bring significant amount of the allowed character into the close-lying E_{1u}^+ state through vibronic coupling.

In fact, the E_{1u}^+ wave function has about 10% of the E_{2g}^- character when it is coupled with the b_{2u} vibrational modes. On the other hand, the b_{1u} vibrational modes bring only a few percent of the allowed character into the E_{1u}^+ state. According to the Herzberg-Teller theory, the magnitude of the allowed character reflects the steepness of the electronic potential surface with respect to the vibrational coordinate.[13] In other words, the potential energy surface in benzene is more sensitive to the b_{2u} normal modes of vibration than to the b_{1u} modes. The more steepness of the electronic potential energy surface with respect to the b_{2u} vibrational modes can be also seen from the fact that the b_{2u} modes are more effective in shifting energy levels as discussed above. Thus, the TPA strengths depends significantly on the nature of the electronic potential energy surface with respect to the normal mode of vibration when there is a nearby electronic state from which the two-photon transition can borrow the intensity.

In this work, the role of vibronic coupling in two-photon absorption is studied by using CNDO wave functions. In benzene, the TPA strengths for vibronically induced transitions are at least 100 times smaller than the allowed transitions. The pseudo-parity property of the vibronic state is an important factor for the TPA strengths. However, the dependence of the electronic energy surface on the vibrational modes is also important when an electronic state from which the two-photon transition can borrow the intensity is located very close to the final state.

Acknowledgement. This work was supported by the Korea Science and Enegineering Foundation and the Korea Research Foundation.

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Species Selective Spectroelectrochemistry Employing Derivative Absorbance Signals

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Received March 6, 1989

Species selective spectroelectrochemistry (SSSE) is described by relating the derivative absorbance (*dA/dt*) signals with electrochemical currents for conventional transient electrochemical experiments. Expressions relating the currents with the *dA/dt* signals were obtained. From these expressions, physical constants such as diffusion coefficients and molar absorptivities of electrogenerated species can be determined. By obtaining both derivative absorbance and current signals concurrently and comparing them, one can perform the SSSE experiments. The utility of the SSSE in sorting out electrochemical information is demonstrated.

Introduction

Although the concept of the species selective electrochemistry (SSSE) has been recognized in the earlier literature[1-5] on spectroelectrochemical techniques, the general comparison of absorbance and current signals has not been made explicitly so that the SSSE may be implemented in conventional transient electrochemical experiments. Bancroft *et al.*[6] reported a spectroelectrochemical experiment equivalent to cyclic voltammetry by obtaining the *dA/dE* signal, where *A* and *E* represent the absorbance and the potential, respectively. The *dA/dE* signal has the identical shape to the cyclic voltammetric current, but the two showed different scan rate dependencies. These authors also demonstrated that the double layer charging current can be eliminated by running chronoabsorptometry instead of chronocoulometry,[7] if the electrogenerated species absorbs photons.

We have recently developed near normal incidence reflectance spectroelectrochemical (NNIRS) techniques using a bifurcated optical fiber probe.[8] This system is a modified version of the experimental arrangement reported by McCreery *et al.*[9] such that the angle of the probing beam would be nearly normal to the reflective working electrode. The NNIRS technique offers simplicity at the expense of sensitivity, when compared to the system described by McCreery *et al.*[9] Its fully supported microcomputer controlled data acquisition system allows easy treatment of the data. Due to the fast and undistorted electrochemical responses owing to its favorable cell geometries, this system is suitable for making nonequilibrium spectroelectrochemical measurements. Its utility for studying electrochemically generated intermediates, both solution and surface bound species such as oxide and polymer films formed on electrode surfaces, has been demonstrated.[10-13]

In our current communication, we describe equations relating *dA/dt* signals with currents for transient electrochemical experiments, and discuss the concept of the SSSE from the results obtained using the NNIRS system. Thus, the concurrent measurement of optical and electrochemical signals allows us to carry out the SSSE for traditional transient electrochemical experiments such as cyclic voltammetry, chronoamperometry/chronocoulometry, and chronopotentiometry. The SSSE can be a powerful tool for studying complex electrochemical reactions.

Experimental

The chemicals were all ACS reagent grade or better, and were used as received without further purification. Doubly distilled, deionized water was used for preparing solutions. Solutions were deaerated by bubbling with nitrogen gas, and the nitrogen atmosphere was maintained throughout the ex-

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