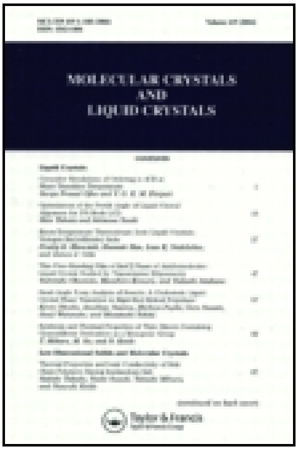

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Photophysical Evaluation of Second-Order Molecular Hyperpolarizabilities of Organic Nonlinear Optical Materials. Application of the Three-Level Model to Systems with Low Energy Double Transitions

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Photophysical Evaluation of Second-Order Molecular Hyperpolarizabilities of Organic Nonlinear Optical Materials. Application of the Three-Level Model to Systems with Low Energy Double Transitions

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The second-order molecular hyperpolarizabilities of 4-aminostilbene, p-nitroaniline and 2-methyl-4-nitroaniline were calculated using photophysical parameters obtained by electronic spectra measurements and the effects of solvents on the spectra. The lowest energy absorption band of the molecules was found to be composed of two transitions, indicating that the well-known two-level model does not apply well to these molecules. The three-level model was developed to evaluate the second-order molecular hyperpolarizability for systems having low energy double transitions. In it the second excited state is explicitly taken into account in the calculation, in addition to the first excited and ground state. The second-order molecular hyperpolarizabilities calculated using the three-level model gave excellent agreement with the observed values determined by the dcSHG technique.

Keywords: second-order molecular hyperpolarizabilities, two-level model, three-level model, low energy double transition systems, photophysical properties

INTRODUCTION

Nonlinear optical properties of organic molecules have been under intensive investigations for potential applications in the area of opto-electronic devices.[1,2] It is well known that conjugated organic molecules exhibit very large optical nonlinearities, especially when they have donor and acceptor substituents at each end of the systems. This originates from an efficient intramolecular charge transfer through a highly polarizable π-electron system. Although both microscopic and macroscopic properties must be considered and optimized for second-order nonlinear effects such as second harmonic generation (SHG), the first step to reach suitable materials for such applications is to evaluate their quadratic molecular hyperpolarizabilities.

Since photophysical properties of conjugated organic systems are also dominated by π-electronic delocalization of the systems, it would be of great importance to investigate them. The relationship between photophysical and quadratic nonlinear optical properties of organic molecular crystals has been investigated in our laboratory.[3-5] The results have shown the importance of photophysical evaluations for understanding the optical nonlinearities of conjugated organic systems at the molecular level.

In this paper, the second-order molecular hyperpolarizabilities are calculated for 4-aminostilbene (4-AS), p-nitroaniline (p-NA) and 2-methyl-4-nitroaniline (MNA) using photophysical parameters obtained by electronic spectra measurements and the effect of solvents on the spectra. Ever since Oudar successfully evaluated the second-order molecular hyperpolarizabilities for stilbene[6] and p-nitroaniline[7] derivatives by the two-level (TW) model, it has been regarded as a simple and convenient method for evaluation of quadratic molecular hyperpolarizabilities. It was found, however, that the lowest energy absorption band is composed of two electronic transitions for the systems investigated in this study. Thus it is doubtful if the TW model is applicable to systemse with low energy double transitions such as 4-AS and p-NA derivatives. By explicitly taking into account the second excited state in the calculation, in addition to the first excited and ground states, the three-level (TH) model was developed. It is especially suitable for the evaluation of the second-order molecular hyperpolarizability for systems having low energy double transitions.

EXPERIMENTAL

Commercially available 4-aminostilbene was purified by repeated recrystallization from ethanol. All solvents were spectroscopic grade and were used as purchased.

Spectroscopic measurements were carried out using a Hitachi 330 spectrophotometer and a Hitachi 4000 fluorescence spectrophotometer. Fluorescence spectra were corrected for both the intensity of the light source and the spectral sensitivity of the monochromator-photomultiplier combination using ethylene glycol solution of rhodamine B as a quantum counter. All sample solutions were degassed by repeated freeze-pump-thaw cycles and all measurements were performed at room temperature.

The 0—0 band of the lowest energy absorption band, whose position was determined by means of the mirror-image relationship between the absorption and fluorescence spectra, was taken as a transition energy. Oscillator strengths of the band were evaluated by numerically integrating the band area fitted by the spline function.

DERIVATION OF THE THREE-LEVEL MODEL

The hyperpolarizability tensor $\beta_{ijk}{}^{2\omega}$ for the second-harmonic generation relates the peak amplitude $p_i{}^{2\omega}$ of the second-harmonic dipole to the peak amplitude E_j^{ω} of the fundamental electric field.

$$p_i{}^{2\omega} = \beta_{ijk}{}^{2\omega} E_j^{\omega} E_k^{\omega} \tag{1}$$

where ${\beta_{ijk}}^{2\omega}$ is expressed[8-10] by

$$\beta_{ijk}^{2\omega} = \frac{1}{2\hbar^2}\sum_{p,q}\left[\mu_{0p}^{i}\left(\mu_{pq}^{j}\mu_{q0}^{k} + \mu_{pq}^{k}\mu_{q0}^{j}\right)\frac{\omega_p\omega_q + 2\omega^2}{\left(\omega_p^2 - 4\omega^2\right)\left(\omega_q^2 - \omega^2\right)} + \mu_{0p}^{k}\mu_{pq}^{j}\mu_{q0}^{j}\frac{\omega_p\omega_q - \omega^2}{\left(\omega_p^2 - \omega^2\right)\left(\omega_q^2 - \omega^2\right)}\right] \tag{2}$$

In Equation (2) the sum runs over all energy states of the system, and the excited states energy: $\hbar\omega_p = E_p - E_0$ and the dipole operator between states p and q: $\mu_{pq}^{i} = \langle p|i|q\rangle$.

In the TW model, the sum is restricted to only two levels, the ground state $|0\rangle$ and the first excited state $|1\rangle$, and the assumption is made of simple dispersion behaviour for $i = j = k$. The expression for the second-order hyperpolarizability by the TW model is given by

$$\beta^{2\omega} = \frac{3\,\Delta\mu_1 m_1}{2\hbar^2}\,\frac{\omega_1^2}{(\omega_1^2 - 4\omega^2)(\omega_1^2 - \omega^2)} \tag{3}$$

where $m_1 = \mu_{01}$ and $\Delta\mu_1 = \mu_{11} - \mu_{00}$.

In the three-level (TH) model, the second excited state $|2\rangle$ is explicitly taken into account, in addition to the states $|0\rangle$ and $|1\rangle$. Assuming simple dispersion behaviour for $i = j = k$ as in the case of the TW model, we obtain the expression for the second-order hyperpolarizability by the TH model, considering $\mu_{12} = 0$, as follows:

$$\beta^{2\omega} = \frac{3\,\Delta\mu_1 m_1}{2\hbar^2}\,\frac{\omega_1^2}{\left(\omega_1^2 - 4\omega^2\right)\left(\omega_1^2 - \omega^2\right)} + \frac{3\,\Delta\mu_2 m_2}{2\hbar^2}\,\frac{\omega_2^2}{\left(\omega_2^2 - 4\omega^2\right)\left(\omega_2^2 - \omega^2\right)} \tag{4}$$

where $\Delta\mu_2 = \mu_{22} - \mu_{00}$ and $m_2 = \mu_{02}$. The assumption of $\mu_{12} = 0$ means that the oscillator strength of the transition between the first and second excited states is zero. This has been verified experimentally[11] and theoretically[12] at least for the systems investigated in this paper. Of course, the TH model could be expanded also to systems with nonzero values of μ_{12} quite easily. Therefore it is necessary to obtain the transition energy, oscillator strength and dipole moment change both for $|1\rangle \leftarrow |0\rangle$ and $|2\rangle \leftarrow |0\rangle$ transitions to evaluate the second-order molecular hyperpolarizabilities by the TH model.

Photophysical evaluation of second-order molecular hyperpolarizabilities

4-Aminostilbene It has been reported that 4-AS is a fairly efficient nonlinear optical material for both second and third harmonic generation.[13] The electronic absorption spectrum of 4-AS closely resembles that of trans-stilbene, except for the positional red-shift and the increase of the oscillator strength. The electronic spectra of trans- and cis-stilbene, and their derivatives have been the subject of extensive investigations both experimentally and theoretically. The existence of a second component in the lowest energy absorption band of trans-stilbene has been suggested as a result of MO calculations by Jaffé and co-workers.[14] They have shown that the transition for the lowest energy absorption band of trans-stilbene has a low intensity short wavelength component due to the $^1G^- \leftarrow {}^1A$ transition in addition to the main $^1B \leftarrow {}^1A$ transition. Bernstein later showed spectroscopic evidence for the presence of the second transition in the lowest energy absorption band of some trans-stilbene derivatives by means of absorption and fluorescence spectra measurements.[15] It is therefore expected that the lowest energy absorption band of 4-AS should also be composed of two transitions.

In all the solvents, the bandwidths of the lowest energy absorption are about twice as wide as those of the corresponding fluorescence. This suggests the presence of multiple transitions under the first absorption band. Further evidence for the presence of a second transition in the absorption band was found after considering that the band shape was strongly dependent on the solvents used. The influence of the band shape can be demonstrated in three groups (group I, II and III). A typical spectrum from each group is shown in Figure 1 for *n*-hexane (group I), benzene (group II) and ethanol (group III) solution. In addition, only the lower energy part of the first absorption band was found to coincide with the mirror image of the fluorescence spectrum for the three groups. The deconvoluted first absorption band by the mirror image of the fluorescence spectrum reveals the

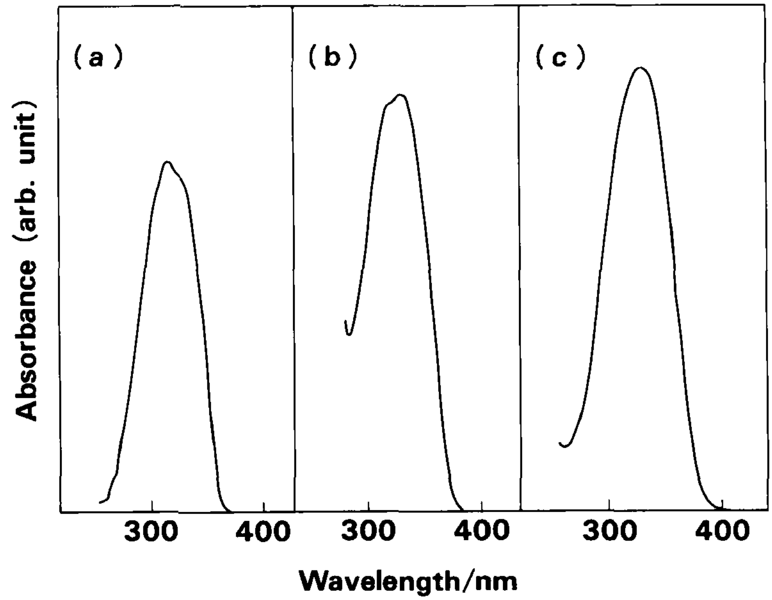

FIGURE 1 Solvent effects on the band shape of the lowest energy absorption of 4-AS (a) in *n*-hexane (group I), (b) in benzene (group II), and (c) in ethanol (group III).

presence of an additional absorption band associated with the second transition, as shown in Figure 2. The band shape (Figure 1) depends on the relative intensity of the two transitionse in the solvents used.

Solvatochromic shifts of the absorption and fluorescence spectra can be expressed by the following equations.[16-18]

$$hc(\nu_a - \nu_f) = 2F(\epsilon, n)(\mu_e - \mu_g)/a^3 + \text{const.} \tag{5}$$

$$F(\epsilon, n) = [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)] \tag{6}$$

where: ν_a and ν_f are the wavenumbers of the peaks of the absorption and fluorescence bands, respectively; ϵ and n are the dielectric constant and refractive index of the solvent; and a is the cavity radius in Onsager's theory of the reaction field. The plot of $(\nu_a - \nu_f)$ against $F(\epsilon, n)$ is slightly scattered for two main reasons: firstly because hydrogen bonds are formed between the solute and solvent molecules such as alcohol and ether solutions, and second because the band shape of the first absorption changes with solvent as shown above. Based on the least squares fit of the plot, the $(\mu_e - \mu_g)$ value of 4-AS is calculated as 3.5 D, assuming a = 3.0 Å. The value of a is calculated according to Suppan's method.[19] Table I lists the photophysical parameters of 4-AS determined in this study.

First the second-order molecular hyperpolarizability was calculated by the TW model using the photophysical parameters listed in Table I and Equation (3). The determined values are also listed in Table I. The values calculated by the TW model are much larger than the observed values obtained by the dcSHG Technique.[6] The disagreement is, however, reasonable because the presence of the two transitions

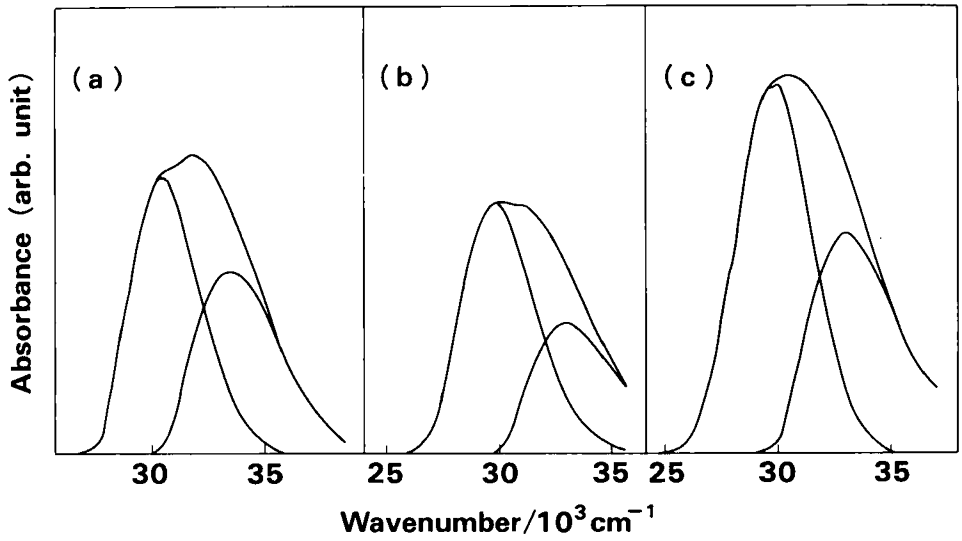

FIGURE 2 Deconvoluted first absorption band by the mirror image of the fluorescence spectrum of 4-AS (a) in *n*-hexane (group I), (b) in dichloromethane (group II), and in ethanol (group III).

TABLE I

Photophysical parameters and second-order hyperpolarizabilities by the two-level models.

	4-AS	p-NA	MNA
f	0.791	0.318	0.365
$\Delta\mu$ (D)	3.5	10.1	9.6
W (nm)	374	431	436
β_{TW}[a] (10^{-30}esu)	18.5	49.0	56.5
β_{ob}[b] (10^{-30}esu)	12	34.5	42

[a]Calculated by the two-level model.
[b]Observed values by Oudar *et al.*[6,7].

under the first absorption band is neglected in the calculation. In applying the TH model to 4-AS, it was possible to determine experimentally the photophysical parameters except for $\Delta\mu_1$ and $\Delta\mu_2$ as shown in Table II. It was found, however, that the bandwidths are almost independent of the solvents used for the first absorption band. This observation indicates that the difference of the dipole moments is small between the two excited states corresponding to the two transitions. Thus the values of both $\Delta\mu_1$ and $\Delta\mu_2$ can be taken as 3.5 D. The second-order molecular hyperpolarizability was calculated by the TH model using the parameters listed in Table II and Equation (4). The value calculated by the TH model gave a better agreement with the observed values than that by the TW model, as can be seen from Table II.

p-NA DERIVATIVES The spectral featues of the lowest energy absorption band of p-NA and MNA are summarized in Table I. Both p-NA and MNA were found to be practically non-fluorescent at room temperature. In this case, solvent effects on the absorption spectrum can be related to the solvent polarity by Equations (7), (8)

$$hc\Delta\nu_a = (\mu_e - \mu_g)(\mu_g/a^3)f(\epsilon) \tag{7}$$

$$f(\epsilon) = 2(\epsilon - 1)/(2\epsilon + 1) \tag{8}$$

TABLE II

Photophysical parameters and second-order hyperpolarizabilities by the three-level models.

	4-AS		p-NA		MNA	
f	0.500	0.291	0.240	0.078	0.265	0.100
$\Delta\mu$ (D)	3.5	3.5	9.9	10.1	9.6	5.9
W (nm)	374	329	431	323	436	338
β_{TH}[a] (10^{-30}esu)	14.7		36.3		44.6	
β_{ob}[b] (10^{-30}esu)	12		34.5		42	

[a]Calculated by the three-level model.
[b]Observed values by Oudar *et al.*[6,7].

where the symbols have the same meanings as Equations (5) and (6). The plot of the maximum position of the lowest energy absorption band against the solvent polarity for MNA is shown in Figure 3. The first absorption bands show a large red-shift with the increase in solvent polarity, indicating that the transitions are associated with the intramolecular charge transfer from the donor to acceptor substituent. The $\Delta\mu$ values were calculated as shown in Table II using a = 3.45 Å[20] and μ_g = 6.5 D for MNA. The parameters for p-NA were taken from those by Oudar and co-workers.[7] Table I collects the photophysical parameters determined in this study.

By means of the photophysical parameters listed in Table I, the second-order molecular hyperpolarizabilities of *p*-NA derivatives were calculated by the TW model. The calculated values were also much larger than the observed values obtained by the dcSHG technique.[7]

It is well-known that the first absorption band of *p*-nitroaniline derivatives consists of two transitions, as shown experimentally by the polarized absorption measurement for the single crystal[21] and the electric dichroism measurement.[22] Molecular orbital calculations by the CNDO/S-CI method have been carried out by Mori[12] for p-NA and MNA. According to those MO results, the lowest energy absorption band of p-NA and MNA is composed of two transitions, and the second transition of p-NA is negligible in the calculation because the transition moment lies toward the short molecular axis. In applying the TH model to p-NA and MNA, the photophysical parameters have been calculated using the following procedures:

1. Transition energy: the 0—0 band of the first transition in acetonitrile solution was taken as ω_1, and the ω_2 value was obtained by the sum of ω_1 and the energy difference between the second and third excited states in the MO results.
2. Oscillator strenght; the experimental value for acetonitrile solution was proportionally divided into f_1 and f_2 in proportion to the values obtained by the MO calculation.
3. Dipole moment; the values calculated by Mori were used.

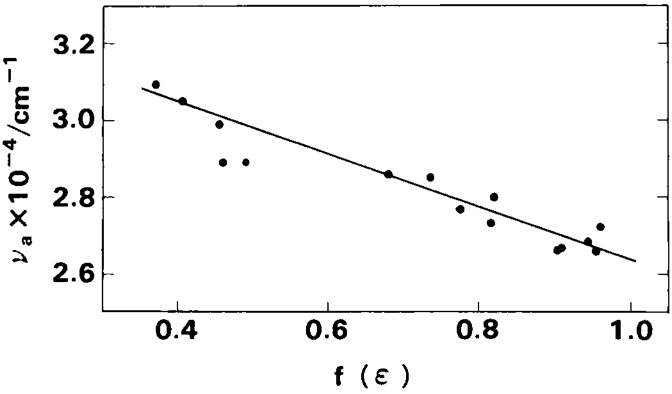

FIGURE 3 Solvatochromic shift of the lowest energy absorption band of MNA on the solvent polarity.

Table II lists the photophysical parameters thus determined for the first and second transitions, and the second-order molecular hyperpolarizabilities by the TH model. The second-order molecular hyperpolarizabilities calculated by the TH model agree very well with the observed values measured by the dcSHG technique.[7] This shows that, as in the case of 4-AS, it is crucial to allow explicitly for the presence of multiple transitions under the first absorption band.

Finally the difference should be mentioned between the β values measured by Oudar and Chemla in methanol (p-NA:34.5, MNA:42 (10^{-30} esu)),[7] and those by Teng and Garito in 1,4-dioxane (p-NA:16.9, MNA:16.7 (10^{-30} esu))[23] for the fundamental frequency of ω = 1.06 μm. As also shown in this paper, the lowest energy absorption band of p-NA derivatives has long been known to show a large red-shift with the increase in solvent polarity. The peak position of the band of MNA, for example, shifts from 356 nm in 1,4-dioxane (ϵ = 2.209) to 376 nm in methanol (ϵ = 33.7). The solvent-induced red-shift in excitation energy of the band causes the β values to increase because the excitation energy approaches 2ω. In addition, it has been noted that 1,4-dioxane behaves like a more polar solvent with polar solute than its bulk dielectric properties imply.[24] This 'dioxane anomaly' was also observed in the absorption spectra of p-NA and MNA, suggesting that there is a special solvent-solute interaction in 1,4-dioxane solution which could influence the β values measured by dcSHG technique.

CONCLUSION

The second-order molecular hyperpolarizabilities has been calculated for 4-aminostilbene, *p*-nitroaniline and 2-methyl-4-nitroaniline using photophysical parameters obtained by electronic spectra measurements and the effects of solvents on the spectra. The lowest energy absorption band of the molecules was found to be composed of two transitions, indicating that the well-known two-level model does not apply well to these molecules. The three-level model has been developed to evaluate the second-order molecular hyperpolarizability for systems having low energy double transitions. In the three-level model, the presence of the second excited state, in addition to the first excited and ground states, is explicitly taken into account in the calculations. The second-order molecular hyperpolarizabilities calculated by the three-level model agreed very well with the observed values determined by the dcSHG technique.

Stilbene and p-NA derivatives are typical for organic nonlinear optical materials and therefore the three-level model has significant importance for the quantitative evaluation of second-order hyperpolarizabilities. Molecular orbital calculation often gives spectral features quite different from the observed ones for molecules of sizes similar to those of typical organic nonlinear materials. It is desirable, therefore, as demonstrated in this study, to use the experimental photophysical parameters as much as possible.

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References

1. D. J. Williams, "Nonlinear Optical Properties of Organic and Polymeric Materials," ACS Symposium Series 233 (ACS, Washington, D.C., 1983).
2. D. S. Chemla and J. Zyss, "Nonlinear Optical Properties of Organic Molecules and Crystals," 2 Vols (Academic Press, Orlando, FL, 1987).
3. H. Suzuki and K. Sukegawa, *Appl. Phys. Lett.*, **51**, 401 (1987).
4. H. Suzuki, T. Kurihara, T. Kaino and F. Ebisawa, *Acta Cryst.*, **C44**, 484 (1988).
5. H. Suzuki and H. Hiratsuka, *Proc. SPIE*, **971**, 97 (1988).
6. J. L. Oudar, *J. Chem. Phys.*, **67**, 446 (1977).
7. J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977).
8. J. A. Armstrong, N. Bloembergen, J. Ducuing and P. Pershan, *Phys. Rev.*, **127**, 1918 (1962).
9. F. N. H. Robinson, *Bell. Syst. Tech. J.*, **46**, 913 (1967).
10. J. L. Oudar and J. Zyss, *Phys. Rev.*, **A26**, 2016 (1982).
11. K. Yoshihara, A. Namiki, M. Sumitani and N. Nakashima, *J. Chem. Phys.*, **71**, 2892 (1979).
12. Y. Mori, The 54th Spring Annual Meeting of the Chemical Society of Japan, (1987) and private communication.
13. S. Tomaru, M. Kobayashi and T. Edahiro, The 30th Spring Meeting of The Japan Society of Applied Physics, (1983).
14. D. L. Beveridge and H. H. Jaffé, *J. Am. Chem. Soc.*, **87**, 5340 (1965).
15. J. Bernstein, *Spectrochim. Acta*, **29A**, 147 (1973).
16. E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955).
17. E. Lippert, *Z. Electrochem.*, **61**, 962 (1957).
18. N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **29**, 465 (1956).
19. P. Suppan, *Chem. Phys. Lett.*, **94**, 272 (1983).
20. S. Millefiori, G. Favini, A. Millefiori and D. Grasso, *Spectrochim. Acta*, **33A**, (1977).
21. J. Tanaka, *Bull. Chem. Soc. Jpn.*, **36**, 833 (1963).
22. H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **46**, 1314 (1963).
23. C. C. Teng and A. F. Garito, *Phys. Rev. B*, **28**, 6766 (1983).
24. M. B. Ledger and P. Suppan, *Spectrochim. Acta*, **23A**, 3007 (1967).