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# An Empirical Relation between Oscillator Strengths Calculated from the Dipole Length and Dipole Velocity Formalisms in the Optical Absorption of Conjugated Molecules

Toshiaki Kakitani and Hiroko Kakitani

Department of Physics, Nagoya University, Nagoya, Japan

It is found that a ratio between the oscillator strengths of the optical absorption calculated from the dipole length formalism and those calculated from the dipole velocity formalism is almost constant for many conjugated molecules if the calculation is made using the theoretically obtained transition energy. The value of the ratio becomes very sensitive to the molecular geometry if the calculation is made using the experimentally obtained transition energy. The origin of the constancy of the ratio is discussed.

**Key words:** Empirical relation of the oscillator strengths $f_1$ and $f_2$ – Empirical and semi-empirical $\pi$-electron theories

## 1. Introduction

Although absorption wavelengths of many conjugated molecules have been predicted satisfactorily by the semi-empirical theory of $\pi$-electrons [1, 2], calculations of oscillator strength in the optical absorption were not successful. It is generally recognized that the calculated values of the oscillator strength are 1–5 times as large as the experimental values. The oscillator strength is usually calculated by either the dipole length formalism $f_1$ or the dipole velocity formalism $f_2$, which are defined in the following:

$$f_1 = (2m\,\Delta E_{ba}/3\hbar^2)\cdot\left|\left\langle b\left|\sum_i \boldsymbol{r}_i\right|a\right\rangle\right|^2 \tag{1.1}$$

$$f_2 = (2\hbar^2/3m\,\Delta E_{ba})\cdot\left|\left\langle b\left|\sum_i \nabla_i\right|a\right\rangle\right|^2 \tag{1.2}$$

where $m$, $\hbar$ and $\Delta E_{ba}$ are the electron mass, Planck's constant and the transition

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energy from the ground state $|a\rangle$ to the excited state $|b\rangle$, respectively. If the electronic wavefunctions are exact, an equality $f_1 = f_2$ should hold by virtue of an off-diagonal hypervirial theorem [3],

$$\left\langle b \left| \sum_i \nabla_i \right| a \right\rangle = -\frac{m}{\hbar^2} \Delta E_{ba} \left\langle b \left| \sum_i r_i \right| a \right\rangle \tag{1.3}$$

However, in the actual calculation, $f_1$ becomes considerably larger than $f_2$ in most molecules.

Chong [4] and Yue and Chong [5] investigated which is better, $f_1$ or $f_2$, in order to explain the experimental values of the oscillator strengths of polyenes and $\alpha$, $\omega$-diphenyl-polyenes by the simple molecular orbital theories. The results were that $f_2$ agrees with the experimental values much better than $f_1$ for the transition to the lowest excited state. The similar calculations were made by McHugh and Gouterman on polyacenes [6]. The results were also that $f_2$ is better than $f_1$ to explain the experimental data of the transitions to some lower excited states. It should be mentioned here that all these calculations were made by the method so called semi-empirical one in which the experimentally obtained value of $\Delta E_{ba}$ is used in Eqs. (1.1) and (1.2).

The effect of the electron correlation on $f_1$ and $f_2$ was also investigated by the configuration interaction (CI) method [7], and by the many-electrons theory [8, 9]. The doubly-excited CI causes to decrease the values of $f_1$ and $f_2$ together [10]. Although the calculated values of $f_1$ become considerably closer to the experimental values by taking into account electron correlation effects, satisfactory agreement between the calculation and the experiment has not yet been obtained for most molecules [11].

In this paper, we investigate the relation between the calculated values of $f_1$ and $f_2$. However, we do not intend to fit the calculated values to the experimental values. No systematic studies of this problem have been done so far. We do this systematically for many conjugated molecules using the theoretically obtained transition energy in Eqs. (1.1) and (1.2), which is called the theoretical method. We compare these results with those obtained using the semi-empirical method of the transition energy. The effect of the molecular geometry is also investigated.

## 2. Method of Calculation

When the wavefunction of the excited state $|b\rangle$ is obtained by an electron transition from an occupied molecular orbital $\psi_j$ to an unoccupied molecular orbital $\psi_k$, we get

$$\left\langle b \left| \sum_i r_i \right| a \right\rangle = \sigma_j \int \psi_k^* \, r \psi_j \, d\tau \tag{2.1}$$

$$\left\langle b \left| \sum_i \nabla_i \right| a \right\rangle = \sigma_j \int \psi_k^* \, \nabla \psi_j \, d\tau \tag{2.2}$$

where

$$\sigma_j = \begin{cases} \sqrt{2} & \text{if } \psi_j \text{ is occupied by two electrons,} \\ 1 & \text{if } \psi_j \text{ is occupied by one electron.} \end{cases} \tag{2.3}$$

When the excited state wavefunction is expressed by the one in which CI is taken, the two transition vectors become

$$\left\langle b \left| \sum_i \boldsymbol{r}_i \right| a \right\rangle = \sum_j^{\text{occ}} \sum_k^{\text{unocc}} A^*_{bj \to k} \sigma_j \int \psi_k^* \boldsymbol{r} \psi_j \, d\tau \tag{2.4}$$

$$\left\langle b \left| \sum_i \nabla_i \right| a \right\rangle = \sum_j^{\text{occ}} \sum_k^{\text{unocc}} A^*_{bj \to k} \sigma_j \int \psi_k^* \nabla \psi_j \, d\tau \tag{2.5}$$

where $A_{bj \to k}$ is a coefficient of the configuration mixing in the excited state.

Writing the molecular orbital $\psi_l$ as

$$\psi_l = \sum_p C_{lp} \chi_p \tag{2.6}$$

where $\chi_p$ and $C_{lp}$ are the atomic orbital centered at $P$ and a coefficient, respectively, we obtain

$$\boldsymbol{D}_{kj} \equiv \int \psi_k^* \boldsymbol{r} \psi_j \, d\tau = \sum_p \sum_q C_{kp}^* C_{jq} \boldsymbol{T}_{pq} \tag{2.7}$$

$$\boldsymbol{V}_{kj} \equiv \int \psi_k^* \nabla \psi_j \, d\tau = \sum_p \sum_q C_{kp}^* C_{jq} \boldsymbol{W}_{pq} \tag{2.8}$$

where

$$\boldsymbol{T}_{pq} \equiv \int \chi_p^* \boldsymbol{r} \chi_q \, d\tau$$

$$= \tfrac{1}{2}(\boldsymbol{R}_p + \boldsymbol{R}_q) S_{pq} + \boldsymbol{M}_{pq}, \tag{2.9}$$

$$\boldsymbol{W}_{pq} \equiv \int \chi_p^* \nabla \chi_q \, d\tau = - \int \chi_q^* \nabla \chi_p \, d\tau \tag{2.10}$$

with

$$S_{pq} = \int \chi_p^* \chi_q \, d\tau \tag{2.11}$$

$$\boldsymbol{M}_{pq} = \int \chi_p^* \boldsymbol{r}' \chi_q \, d\tau \tag{2.12}$$

In Eq. (2.9), $\boldsymbol{R}_p$ and $\boldsymbol{R}_q$ are position vectors of the atomic centers $P$ and $Q$, and $\boldsymbol{r}'$ is the position vector relative to the middle point of $P$ and $Q$.

When we adopt the leading terms in Eqs. (2.9) and (2.10), we obtain

$$\boldsymbol{D}_{kj}=\sum_{p} C^{*}_{kp} C_{jp} \boldsymbol{R}_{p} \tag{2.13}$$

$$\boldsymbol{V}_{kj}=\sum_{p>p}\sum \delta_{p,q'}(C^{*}_{kp} C_{jq}-C^{*}_{kq} C_{jp}) \boldsymbol{W}_{pq} \tag{2.14}$$

where $q'$ denotes the neighboring atomic site to $q$. The approximation used in obtaining (2.13) and (2.14) is consistent with the usual approximation that the overlap integral $S_{pq}(p \neq q)$ is neglected in solving the secular equation

$$|\boldsymbol{F}-\varepsilon \boldsymbol{S}|=0 \tag{2.15}$$

where $\boldsymbol{F}$ is the Fock operator or the one electron Hamiltonian in the Hückel theory, and $\varepsilon$ and $\boldsymbol{S}$ are the orbital energy and the overlap integral matrix, respectively.

The atomic orbitals are assumed as the Slater-type $2p_z$ orbitals, whose orbital exponents $\mu$'s are 1.625, 1.950 and 2.275 for carbon, nitrogen and oxygen atoms, respectively [12].

Analytical formulas for $\boldsymbol{W}_{pq}$, the two-center moment integral $\boldsymbol{M}_{pq}$ and the overlap integral $S_{pq}$ are given by Kral [13], Suzuki *et al.* [14] and Mulliken [12], respectively.

In this paper, the molecular orbitals and the transition energies of conjugated molecules are obtained by the self-consistent HMO theory [15]. An essential part of the theory is to use a pseudoresonance integral which includes the effect of the electron–electron interaction as follows:

$$\beta^{*}_{pq}=\left\{\beta_{pq}(R_{pq})-\zeta(2p_{pq}-\sum_{(rs)}^{\text{neigh.}} p_{rs}|\cos\theta_{rs}|\right\}\cdot|\cos\theta_{pq}| \tag{2.16}$$

where $\beta_{pq}(R_{pq})$, $p_{pq}$, $\theta_{pq}$ and $\zeta$ are a function of a bond length $R_{pq}$, bond order, torsional angle and a constant, respectively. The summation over the bond $rs$ is taken for the neighboring bonds of $pq$. The molecular orbital and the molecular geometry are simultaneously determined by satisfying the relation between the bond order and the bond length which is obtained from the condition of the total energy minimum. This theory was considerably improved in the parametrization [16], and was successful in predicting the molecular geometries in the ground state [16] and the excited state [17] together with the absorption wavelength [16] and the fluorescence wavelength [17] of many conjugated molecules.

## 3. Empirical Relation between $f_1$ and $f_2$

Using the approximations (2.13) and (2.14) and the improved version of the self-consistent HMO theory [16], we calculated the oscillator strengths $f_1$ and $f_2$ of many groups of conjugated molecules. We did this by adopting the theoretically obtained transition energy $\Delta E_{ba}$ (theoretical method) in (1.1) and (1.2). The calculated values of $f_1$ and $f_2$ are listed in Table 1 together with the absorption wavelength $\lambda$ and the difference of the direction of the two transition vectors $\delta$ for the first allowed $\pi$–$\pi^*$ transition. It is found from this table that the values of

$f_1/f_2$ are almost the same for aromatic hydrocarbons, carotenoids except for smaller ones such as ethylene and butadiene, hydrocarbons with 5- and 7-members conjugated rings except for fulvene and azulene, hetero-cyclic conjugated molecules, aromatics substituted by heteroatomic groups, cations, anions, radicals except for fluorene, and the other conjugated molecules of the group H. In Fig. 1, we illustrate the relation between $f_1$ and $f_2$. It seems to be peculiar that such a simple empirical relation holds between $f_1$ and $f_2$ for almost all the species of conjugated molecules.

It should be also noticed in Table 1 that the value of $\delta$ does not exceed two degrees for almost all the conjugated molecules. This means that the direction of the transition vector $\langle b|\sum_i r_i|a\rangle$ is almost parallel to that of $\langle b|\sum_i \nabla_i|a\rangle$.

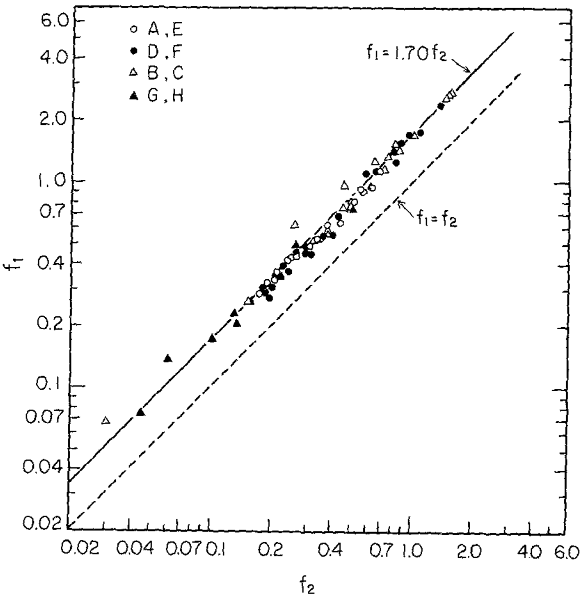

**Fig. 1.** Graph of $f_1$ vs $f_2$ in the first allowed transition. Letters A–H denote the groups of molecules. It is seen that the plotted points nearly hit a line $f_1 = 1.70 f_2$

## 4. Effects of Transition Energy and Molecular Geometry

Yue and Chong calculated $f_1$ and $f_2$ of polyenes by the semi-empirical method using the Hückel theory. Their calculated values of $f_1/f_2$ were 4.07, 5.18, 6.65 and 8.20 for butadiene, hexatriene, octatetraene and decapentaene, respectively. Our present results do not agree with these values. This large discrepancy mainly comes from the different transition energies used in the two calculations. We can easily see from Eqs. (1.1) and (1.2) that the ratio $f_1/f_2$ is dependent upon the square of the transition energy. In the HMO theory, the calculated transition energies of the polyenes are considerably smaller than the experimental values. If we calculate $f_1/f_2$ by the theoretical method, it becomes the same value of 1.72 for the four polyenes, and this result is consistent with the present one.

The similar situation can be found in the study of the effect of the molecular

**Table 1.** The calculated values of the absorption wavelength $\lambda$, the oscillator strengths $f_1$ and $f_2$, the ratio $f_1/f_2$ and the difference between the directions of the two transition vectors $\delta$ for the first allowed transition

| Molecules[a] | $\lambda(m\mu)$ | $f_1$ | $f_2$ | $f_1/f_2$ | $\delta$(deg.) |
|---|---|---|---|---|---|
| A. *Aromatic hydrocarbons (6-member rings)* | | | | | |
| naphthalene | 287 | 0.421 | 0.240 | 1.75 | 0 |
| anthracene | 383 | 0.365 | 0.211 | 1.73 | 0 |
| naphthacene | 488 | 0.322 | 0.190 | 1.69 | 0 |
| pentacene | 604 | 0.288 | 0.173 | 1.66 | 0 |
| phenanthrene | 301 | 0.916 | 0.542 | 1.69 | 0 |
| chrysene | 339 | 0.622 | 0.379 | 1.64 | 0 |
| pyrene | 376 | 1.12 | 0.686 | 1.64 | 0 |
| perylene | 445 | 0.898 | 0.579 | 1.55 | 0 |
| 1,2-benzanthracene | 368 | 0.416 | 0.250 | 1.66 | 0.6 |
| ovalene | 519 | 0.941 | 0.627 | 1.50 | 0 |
| biphenyl | 252 | 0.801 | 0.512 | 1.56 | 0 |
| B. *Polyenes and carotenoids (hydrocarbons)* | | | | | |
| ethylene | 157 | 0.618 | 0.255 | 2.43 | 0 |
| butadiene | 219 | 0.954 | 0.457 | 2.09 | 2.0 |
| hexatriene | 273 | 1.25 | 0.640 | 1.95 | 1.6 |
| octatetraene | 318 | 1.52 | 0.805 | 1.88 | 1.2 |
| vitamin $A_1$ | 325 | 1.52 | 0.815 | 1.87 | 1.1 |
| vitamin $A_2$ | 329 | 1.52 | 0.822 | 1.85 | 0.8 |
| $\beta$-carotene | 460 | 2.57 | 1.44 | 1.78 | 0.6 |
| $\gamma$-carotene | 473 | 2.62 | 1.48 | 1.77 | 0.5 |
| $\varepsilon_1$-carotene | 456 | 2.53 | 1.42 | 1.79 | 0.7 |
| $\alpha$-carotene | 458 | 2.55 | 1.43 | 1.79 | 0.6 |
| lycopene | 484 | 2.69 | 1.53 | 1.76 | 0.4 |
| styrene | 256 | 0.749 | 0.454 | 1.65 | 1.1 |
| stilbene | 317 | 1.14 | 0.720 | 1.58 | 1.1 |
| diphenylbutadiene | 351 | 1.41 | 0.860 | 1.64 | 0.8 |
| diphenylhexatriene | 381 | 1.69 | 1.00 | 1.69 | 0.3 |
| C. *Hydrocarbons with 5- and 7-members conjugated rings* | | | | | |
| fulvene | 292 | 0.068 | 0.030 | 2.27 | 0 |
| azulene | 457 | 0.137 | 0.061 | 2.23 | 0 |
| pentalene[b] | 473 | 0.558 | 0.374 | 1.49 | 0 |
| heptalene[b] | 677 | 0.797 | 0.499 | 1.60 | 0 |
| sesquifulvalene | 464 | 0.958 | 0.615 | 1.56 | 0 |
| heptafulvalene | 465 | 1.31 | 0.757 | 1.73 | 0 |
| *s*-indacene[b] | 721 | 0.961 | 0.624 | 1.54 | 0 |
| fluoranthene | 358 | 0.768 | 0.490 | 1.57 | 0 |
| acenaphthylene | 336 | 0.519 | 0.321 | 1.62 | 0.1 |
| pyracylene[b] | 369 | 0.585 | 0.373 | 1.57 | 0 |
| D. *Hetero-cyclic conjugated molecules* | | | | | |
| pyridine | 226 | 0.456 | 0.294 | 1.55 | 0 |
| pyrimidine | 225 | 0.493 | 0.298 | 1.65 | 0 |
| quinoline | 288 | 0.398 | 0.229 | 1.74 | 0 |
| thymine | 276 | 0.533 | 0.316 | 1.69 | 2.3 |
| cytosine | 287 | 0.276 | 0.194 | 1.42 | 1.7 |
| adenine | 280 | 0.543 | 0.359 | 1.51 | 0.8 |
| guanine | 315 | 0.447 | 0.312 | 1.43 | 0.3 |
| purine | 269 | 0.558 | 0.396 | 1.41 | 0.5 |
| acridine | 387 | 0.348 | 0.204 | 1.71 | 0 |
| phenazine | 397 | 0.307 | 0.180 | 1.71 | 0 |
| 9-aminoacridine | 391 | 0.450 | 0.291 | 1.55 | 0 |

Table 1—*continued*

| Molecules[a] | $\lambda(m\mu)$ | $f_1$ | $f_2$ | $f_1/f_2$ | $\delta$(deg.) |
|---|---|---|---|---|---|
| lumiflavine | 443 | 0.646 | 0.441 | 1.46 | 0.3 |
| furan | 218 | 0.297 | 0.186 | 1.60 | 0 |
| imidazole | 208 | 0.308 | 0.200 | 1.54 | 0 |
| pyrrole | 212 | 0.352 | 0.212 | 1.66 | 0 |
| indole | 266 | 0.480 | 0.307 | 1.56 | 0 |
| E. *Aromatics substituted by heteroatomic groups* | | | | | |
| phenol | 228 | 0.437 | 0.262 | 1.67 | 0 |
| aniline | 255 | 0.338 | 0.206 | 1.64 | 0 |
| benzoic acid | 260 | 0.638 | 0.418 | 1.53 | 0.3 |
| benzaldehyde | 266 | 0.437 | 0.262 | 1.67 | 0 |
| 1-naphthol | 300 | 0.436 | 0.257 | 1.70 | 0 |
| 1-naphthoic acid | 328 | 0.493 | 0.307 | 1.61 | 0 |
| 1-naphthaldehyde | 335 | 0.517 | 0.317 | 1.63 | 0.1 |
| 1-naphthylamine | 327 | 0.433 | 0.256 | 1.69 | 0 |
| 2-naphthol | 294 | 0.420 | 0.248 | 1.69 | 1.4 |
| 2-naphthoic acid | 317 | 0.521 | 0.324 | 1.61 | 3.1 |
| 2-naphthaldehyde | 323 | 0.415 | 0.263 | 1.58 | 1.5 |
| 2-naphthylamine | 320 | 0.424 | 0.262 | 1.80 | 1.8 |
| F. *Other heterconjugated molecules* | | | | | |
| p-benzoquinone | 325 | 1.13 | 0.646 | 1.76 | 0 |
| p-naphthoquinone | 345 | 0.519 | 0.343 | 1.51 | 0 |
| tropolone | 347 | 0.689 | 0.423 | 1.63 | 0.5 |
| retinal$_1$ | 382 | 1.57 | 0.877 | 1.79 | 0.5 |
| 11-*cis* retinal$_1$ | 347 | 1.10 | 0.579 | 1.89 | 0.7 |
| retinal$_2$ | 385 | 1.57 | 0.878 | 1.79 | 0.6 |
| $R_1SB$ | 365 | 1.71 | 0.941 | 1.82 | 0.9 |
| $R_2SB$ | 368 | 1.72 | 0.948 | 1.81 | 0.8 |
| canthaxanthin | 464 | 2.38 | 1.35 | 1.76 | 0.3 |
| benzalazine | 331 | 1.27 | 0.813 | 1.56 | 1.8 |
| cinnamalazine | 385 | 1.75 | 1.07 | 1.64 | 0.2 |
| peptide | 195 | 0.458 | 0.266 | 1.72 | 0 |
| formic acid | 172 | 0.428 | 0.252 | 1.70 | 1.0 |
| urea | 196 | 0.364 | 0.244 | 1.49 | 0 |
| G. *Cations and anions* | | | | | |
| acridinylium | 412 | 0.260 | 0.152 | 1.71 | 0 |
| lumiflavine cation | 368 | 0.736 | 0.507 | 1.45 | 0.2 |
| phenate | 267 | 0.259 | 0.158 | 1.64 | 0 |
| benzoate | 279 | 0.202 | 0.133 | 1.52 | 0 |
| tropolonate | 418 | 0.344 | 0.223 | 1.54 | 0 |
| $PR_1SB$ | 442 | 1.43 | 0.807 | 1.77 | 0.4 |
| $PR_2SB$ | 447 | 1.41 | 0.798 | 1.77 | 0.3 |
| H. *Radicals* | | | | | |
| benzil rad. | 392 | 0.075 | 0.045 | 1.67 | 0 |
| naphthyl rad. | 476 | 0.227 | 0.129 | 1.76 | 0 |
| pentatrienyl rad. | 355 | 0.491 | 0.265 | 1.85 | 0 |
| indene | 363 | 0.169 | 0.101 | 1.69 | 0.9 |
| fluorene | 416 | 0.050 | 0.011 | 4.55 | 0.9 |

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[a] For the polyenes and the carotenoids, all-*trans* form is assumed except for 11-*cis* retinal$_1$. $R_1SB$, $PR_1SB$, $R_2SB$ and $PR_2SB$ denote retinal$_1$ Schiff-base, protonated retinal$_1$ Schiff-base, retinal$_2$ Schiff-base and protonated retinal$_2$ Schiff-base, respectively.

[b] The transition to the lowest excited state is forbidden.

geometry by the self-consistent HMO theory. When the calculation was made by the semi-empirical method, the value of $f_1/f_2$ was affected considerably by the variation of the molecular geometry. On the contrary, when the calculation was made by the theoretical method, it was little affected.

As a conclusion, the near constancy of the values of $f_1/f_2$ for many conjugated molecules seems to hold only when we use the electronic wavefunction and the transition energy both of which are obtained by solving a model Hamiltonian for a given molecular geometry.

## 5. Discussion

In this paper, it was shown that an approximate constancy holds in the calculated values of $f_1/f_2$ among many conjugated molecules if the theoretically obtained transition energy was used.

In the following, we try to search the physical meaning of the constant value of $f_1/f_2$ under the hypothesis that the π-electron Hamiltonian is expressed by the perfectly independent particle model as given by the self-consistent HMO theory. Furthermore, we assume that the π-electron has an effective mass $m^*$. This is considered to be the effect of the renormalization due to the π–π interaction, σ–π interaction, electron-vibration interaction and so on. Then, the oscillator strengths are written as

$$f_1^* = (2m^* \Delta E_{ba}/3\hbar^2) \cdot \left| \left\langle b \middle| \sum_i r_i \middle| a \right\rangle \right|^2 \tag{5.1}$$

$$f_2^* = (2\hbar^2/3m^* \Delta E_{ba}) \cdot \left| \left\langle b \middle| \sum_i \nabla_i \middle| a \right\rangle \right|^2 \tag{5.2}$$

and then,

$$f_1^*/f_2^* = (m^*/m)^2 (f_1/f_2) \tag{5.3}$$

where $f_1$ and $f_2$ are the ones defined in (1.1) and (1.2).

Now, we assume our wavefunctions are exact for our π-electron Hamiltonian. Then, $f_1^* = f_2^*$ should hold. From (5.3), we get

$$m^*/m = \sqrt{f_2/f_1} \tag{5.4}$$

When we put $f_1/f_2 = 1.7$, we obtain $m^* = 0.75m$. This result means that if the π-electron Hamiltonian is expressed by the independent particle model, the effective mass of the π-electron should be a little smaller than $m$. In this case, the theoretical oscillator strength is expressed by $f_1$ and $f_2$ as follows

$$f_1^* = f_2^* = \sqrt{f_1 f_2} \tag{5.5}$$

Eq. (5.5) is the same as given by Hansen intuitively [10]. The idea of the effective mass is, of course, one of possibilities to analyze the origin of the constant value of $f_1/f_2$. The effect of the electron correlation on the value of $f_1/f_2$ is also worth studying. This is a future problem.

We also calculated $f_1/f_2$ of polyenes by the PPP theory with and without CI. As a result, it was found that the approximate constancy also holds for the calculated values of $f_1/f_2$, which are a little larger than the present ones, and that the effect of the singly-excited CI upon the value of $f_1/f_2$ is small.

In this paper, we have not compared the calculated values with the experimental values. Our theoretical method is primitive and then the accuracy of the calculated values is not good for many molecules compared with other detailed calculations. However, some results obtained by our systematic calculations for many conjugated molecules would hold true even in the detailed calculations with the $\pi$-electron approximation.

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