stirring for 0.5 h, 7-aminocephalosporanic acid derivatives of **10** (8 mmol) was added to this mixture under ice-cooling. The mixture was stirred for several minutes at room temperature and then worked up as usual method to afford **11**.

Cefpirome-HI salt (8). 3 (3.4 g, 12 mmol) was added with stirring to a mixture of **4** (2.0 g, 10 mmol) and triethylamine (1.5 ml, 11 mmol) in DMF (50 ml) at ice-cold temperature. After 0.5 h, **7** (3.8 g, 8 mmol) was added to this mixture. After stirring for 0.5 h at room temperature, the insoluble meterial was filtered off. DMF was removed by distillation under reduced pressure (2 mmHg), and then isopropyl alcohol (20 ml) was added to the residue to crystalize. After stirring for 0.5 h under ice-bath temperature, The mixture was filtered and dried in vacuo to obtain yellowish crystal of **8** (4.8 g, 93.4%); mp 178-180°C (dec); IR (KBr, cm^{-1}) 1785 (lactam c=o); ^{1}H-NMR (CF$_3$COOD, δ) 2.30-2.85 (2H. m), 3.10-4.05 (6h, m) 4.4 (3H.s) 5.21-6.23 (4H.m) 8.11 (1H.s) 7.65-8.70(3H,m).

References and Notes

1. For general reviews, see; (a) Bodanszky, M.; Hausner, Y. S.; Ondetti, M. A. "Peptide Synthesis"; Wiley: New York, 1976; (b) Ogliaruso, M. A.; Wolfe, J. F. "The Chemistry of Acid Derivatives"; Patai, S., Ed.; Wiley: New York, 1979; Part I; (c) Bodanszky, M. "The Peptides"; Gross, E; Meienhofer, J., Eds.; Academic Press: New York, 1979; Vol. I.

2. H. Gross,; L. Bilk, *Tetrahedron*, **24**, 6935 (1968).

3. M. Itoh,; H. Nojima,; J. Notani,; D. Hagiwara,; K. Takai, *Tetrahedron Lett.*, 3089 (1974).

4. K. Takeda,; I. Sawada,; A. Suzuki,; H. Ogura, *Tetrahedron Lett.*, **24**, 4451 (1983).

5. M. Udea,; H. Oikawa,; T. Takuma, *Synthesis*, 908 (1983).

6. S. Kim,; H. Chang,; Ko, Y. K. *Tetrahedron Lett.*, **26**, 1341 (1985).

7. Brit. UK Pat. Appl. GB 2, 158, 432 (1985).

8. In general, about fifteen hours are required for complete acylation of 7-ACA derivatives by the method of HO BT-DCC ^{9}

9. Ger. Offen. DE 3, 316, 798 (1984).

10. K. Takeda,; K. Tsuboyama, K. Yamaguchi,; Ogura, H. *J. Org. Chem.*, **50**, 273 (1985).

Remarks on Single-Frequency Two-Photon Absorption †

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The single-frequency two-photon absorption tensor is carefully rederived and examined. It is pointed out that the conventionally used tensor, which has been formally deduced from the different-frequency two-photon absorption tensor, can give an incorrect absolute two-photon absorption rate. The identity forbidded selection rule and the polarization ratio expressions are also examined with the new tensor.

Introduction

The expression for the two-photon absorption (TPA) tensor (of rank 2) or the two-photon absorption cross section, is often derived by applying the perturbation technique to the time-dependent Schrödinger equation at the electric-dipole approximation.[1,2] For TPA using two different frequencies (different-frequency two-photon absorption, DFTPA), each Cartesian tensor element contains two terms, each of which is a sum over intermediate states of the product of two dipole transition moments and an energy denominator.[1-5] Since molecular symmetry requires certain relations between the 9 Cartesian tensor elements,[2-4] two-photon transitions can often described by less than 9 independent tensor elements. For example, a transition from the A$_{1g}$ ground state to an A$_{2g}$ vibronic state (one quantum of a b$_{1u}$ vibrational mode in the B$_{2u}$ electronic state) in benzene belonging to the D$_{6h}$ poing group can be described by a single tensor element (the xy or yx element) because the two non-vanishing elements have to

be equal in magnitude and opposite in sign.[2-6] Thus, the TPA tensor for the A$_{1g}$-A$_{2g}$ transition in benzene is traceless and antisymmetric.

When the frequencies of the applied radiation field used in two-photon absorption become identical (single-frequency two-photon absorption, SFTPA), the two-photon absorption tensor expressions are conventionally obtained by simply setting the two frequencies identical in the energy denominators of the DFTPA tensor.[2-4] The conventional Cartesian SFTPA tensor derived in this fashion should be symmetric because the two terms in the tensor element share the same energy denominator.

When the DFTPA tensor is traceless and antisymmetric as for the A$_{1g}$-A$_{2g}$ two-photon transition in benzene, the conventional SFTPA tensor must vanish because of the additional symmetry requirement of the conventional SFTPA tensor. Therefore, such transitions become formally forbidden when the two frequencies are identical. This type of two-photon transitions is known as the *identity forbidden* transitions and the above mentioned A$_{1g}$-A$_{2g}$ transition in benzene is a well-known example of such transtions.[2-6] This transi-

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tion has not been observed either in DFTPA or in SFTPA.[6-7]

A careful derivation of two-photon absorption tensor shows, however, that the *correct* SFTPA tensor has only one term, not the two terms in the conventional SFTPA tensor obtained in the above fashion. Thus, the correct SFTPA tensor need not be symmetric. The difference between the correct and the conventional SFTPA tensor naturally raises questions concerning the validity of some of the results for the SFTPA obtained formally from the conventional tensor. For example, the *absolute* two-photon absorption rate, the identity forbidden selection rule, and the polariztion ratio expressions have been derived formally from the conventional SFTPA tensor. Since the correct SFTPA tensor need not be symmetric, the validity of the identity forbidden selection rule, which is a direct result of the symmetric nature of the conventional tensor, has to be confirmed with the new tensor. The polarization ratio, which is the ratio of two-photon absorption rate of circularly and linearly polarized lights, is an important factor for characterizing two-photon absorption spectra.[6-7]

In this paper, the correct SFTPA tensor is derived and its implication with respect to the above mentioned problems will be discussed.

Single-Frequency Two-Photon Absorption

When the applied radiation field has two different frequency components, one at ω_1 and the other at ω_2, the interaction operator at the electric-dipole approximation takes on the following form,[1,2]

$$H_1(\vec{r},\ t) = -e\vec{r} \cdot \{\hat{e}_1 E_1 \exp(-i\omega_1 t) + \hat{e}_2 E_2 \exp(-i\omega_2 t)\}.$$
(1)

E_1 (E_2) and $\hat{e}_1$ ($\hat{e}_2$) are, respectively, the amplitude and the polarization unit vector, expressed in the molecular frame, of the frequency component ω_1 (ω_2). The complex conjugate parts which do not contribute to the absorption process have been omitted for clarity. The perturbation theory taken to the second order and the use of Fermi's golden rule lead to the following expression for the two-photon absorption rate per unit time,[1,2]

$$\Gamma = (\pi e^4/8\hbar^4)\ [\ |E_1^2 F(\omega_1,\ \omega_1)\ |^2 g(f,\ g;\ \omega_1,\ \omega_1)$$

$$+ |E_1 E_2 \{F(\omega_1,\ \omega_2) + F(\omega_2,\ \omega_1)\}|^2 g(f,\ g;\ \omega_1,\ \omega_2)$$

$$+ |E_2^2 F(\omega_2,\ \omega_2)\ |^2 g(f,\ g;\ \omega_2,\ \omega_2)]$$
(2)

where

$$F(\omega_i,\ \omega_j) = \sum_n \frac{\langle f\ |\ \vec{r}\cdot\hat{e}_i\ |\ n\rangle \langle n\ |\ \vec{r}\cdot\hat{e}_j\ |\ g\rangle}{\omega_{ng} - \omega_j}$$
(3)

and g(f, g; ω_i, ω_j) is a normalized Lorentzian lineshape function peaked at $\omega_i + \omega_j = \omega_{fg}$(i,j = 1,2). In Eqs. (2) and (3), f and g are the final and initial states, respectively. The sum in Eq. (3) is over a complete set of intermediate state n. F(ω_i, ω_j) represents a two-photon absorption process in which the molecule makes a virtual transition from the initial state g to an intermediate state n by absorbing a photon of frequency ω_j and then make a virtual transition to the final state f by absorbing a photon of frequency ω_2. Thus, the first and last terms in Eq. (2) represent, respectively, the two-photon absorption processes of ω_1 only and of ω_2 only. These two terms become important if $\omega_{fg} = 2\ \omega_1$ or $2\ \omega_2$. On the other

hand, the two terms in the middle of Eq. (2) represent the mixed absorption of ω_1 and ω_2 and thus become important when $\omega_{fg} = \omega_1 + \omega_2$. In the second term, a photon at ω_2 is absorbed first and in the third term a photon at ω_1 is absorbed first. Since we are concerned in this paper primarily about the non-resonant two-photon absorption in which there is no intermediate state in resonance with ω_1 or ω_2, the damping effect of intermediate states is not included.

When the two frequencies are different by more than the two-photon absorption band width (DFTPA) and the final state is located at $\omega_{fg} = \omega_1 + \omega_2$, the first and the last terms in Eq. (2) are completely out of resonance and need not be considered. Neglecting these two non-resonant terms, one obtains the following expression for the DFTPA (Cartesian) tensor element. $\bar{S}_{\alpha\beta}(\omega_1,\ \omega_2)$,[1-5]

$$\bar{S}_{\alpha\beta}(\omega_1,\ \omega_2) = \sum_n \frac{\langle f\ |\ \alpha\ |\ n\rangle \langle n\ |\ \beta\ |\ g\rangle}{\omega_{ng} - \omega_2}$$

$$+ \sum_n \frac{\langle f\ |\ \beta\ |n\rangle \langle n\ |\ \alpha\ |\ g\rangle}{\omega_{ng} - \omega_1}$$
(4)

where α and β are the Cartesian components, x, y, or z, in the molecular frame. The absolute two-photon absorption rate with this tensor is given by

$$\bar{\Gamma} = (\pi e^4/8\hbar^4)\ |\ E_1 E_2 \hat{e}_1 \cdot \bar{\underline{S}} \cdot \hat{e}_2\ |^2 g(f,\ g;\ \omega_1,\ \omega_2)$$
(5)

In Eq. (5), $\hat{e}_1 \cdot S \cdot \hat{e}_2$ is identified as F(ω_1, ω_2) + F(ω_2, ω_1) in Eq. (2).

When the two frequencies are identical to ω (SFTPA), the tensor expression is obtained conventionally by simply setting $\omega_1 = \omega_2 = \omega$ in Eq. (4).[2-6] Then, the two sums in Eq. (4) shares the same energy denominator and it is evident from Eq. (4) that the tensor obtained in this fashion should be symmetric with respect to the interchange of two subscripts. Thus, it readily follows that those transitions requiring an antisymmetric and traceless tensor become formally forbidden. Such identity forbidden transitions are a unique feature of multiphoton absorptions where identical Fourier component of the applied field can interact more than once with molecules.[8]

However, when the two frequencies are identical, the first and last terms in Eq. (2), which have been neglected for the DFTPA tensor, show resonance also in the same spectral region as the two terms in the middle and therefore are as important as the other two terms. By properly taking into account these additional two terms, one gets the following form for the SFTPA tensor element, $S_{\alpha\beta}(\omega,\omega)$,

$$S_{\alpha\beta}(\omega,\ \omega) = \sum_n \frac{\langle f|\alpha|n\rangle \langle n|\beta|g\rangle}{\omega_{ng} - \omega}$$
(6)

An immediate consequence of Eq. (6) is that the correct SFTPA tensor does not have to be symmetric like the conventional SFTPA tensor derived from Eq. (4). Therefore, the correct SFTPA tensor does not have to vanish even for the identity forbidden transitions. It is seen that the conventional SFTPA tensor element $\bar{S}_{\alpha\beta}(\omega,\omega)$ deduced from Eq. (4) is simply related to the correct SFTPA tensor elements $S_{\alpha\beta}(\omega,\omega)$ through

$$\bar{S}_{\alpha\beta}(\omega,\ \omega) = S_{\alpha\beta}(\omega,\ \omega) + S_{\beta\alpha}(\omega,\ \omega)$$
(7)

Eq. (6) can also be derived readily by writing the interaction operator in Eq. (1) as following,

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$$H_1 (r, t) = -\hat{e} \; r \cdot e \; E \; \exp \; (-i \omega t). \qquad (8)$$

Here, $\hat{e}$ and E are the polarization unit vector and the amplitude of applied field at frequency ω. It is certainly the correct form when there is only one source of applied field. If there are two different fields at the identical frequency, $\hat{e}E$ is then just the vector sum of the two fields, $\hat{e}_1E_1$ and $\hat{e}_2E_2$:

$$\hat{e} \; E = \hat{e}_1 E_1 + \hat{e}_2 E_2 \qquad (9)$$

with

$$E^2 = E_1^2 + E_2^2 + 2E_1 E_2 \hat{e}_1 \cdot \hat{e}_2 \qquad (10)$$

In other words, the two fields of identical frequency interact with molecules as one combined field whose polarization and amplitude is give as a vector sum of the individual fields.

The absolute rate for SFTPA can be expressed in terms of the tensor;

$$\Gamma = (\pi e^4/8\hbar^4) \left| E^2 \hat{e} \cdot \underline{S} (\omega, \omega) \cdot \hat{e} \right|^2 g (f, g; \omega, \omega) \qquad (11)$$

Thus, it is evident from Eqs. (5), (7), and (11) that the use of the conventional tensor results in the incorrect absolute SFTPA rate, which can differ from the correct one by a factor of 4 when there is a single source of field. Since this constant factor is independent of the polarizations of incident light when a single source of field is used, the polarization ratio expressions derived formally from the conventional tensor remain valid. However, care must be taken if two different sources at the same frequency are used.

When the polarization unit vector $\hat{e}$ is given as

$$\hat{e} = \sum_{\alpha} e_{\alpha} \hat{\alpha} \qquad (12)$$

where $\hat{\alpha}$ is the unit vector along the molecular axes ($\alpha = $x, y, z), Eq. (11) can be rewritten as following

$$\Gamma = (\pi e^4 E^4/8\hbar^4) \left| \sum_{\alpha} e_{\alpha}^2 S_{\alpha\alpha} + \sum_{\alpha > \beta} e_{\alpha} e_{\beta} (S_{\alpha\beta} + S_{\beta\alpha}) \right|^2$$
$$g (f, g; \omega, \omega) \qquad (13)$$

It is evident from Eq. (13) that the SFTPA rate vanishes if the tensor is traceless ($S_{\alpha\alpha} = 0$) and antisymmetric ($S_{\alpha\beta} = -S_{\beta\alpha}$). Therefore, the identity forbidden selection rule remains valid even with the correct SFTPA tensor which need not be symmetric unlike the conventional SFTPA tensor.

The above results can be readily generalized for single frequency m-photon absorption. It can be shown that the tensor element for single frequency m-photon absorption has always a single term, contrary to m! terms as generally accepted.[8] Thus, the simple reduction from the m-frequency m-photon absorption tensor would result in an incorrect absorption rate which can differ from the correct one by a factor of $(m!)^2$. However, the polarization ratio is insensitive to this constant factor when a single source of field is used. The identity forbidden selection rule for multi-photon absorption remain valid not because of the vanishing tensor but because of the vanishing combination of *non-zero* tensor elements when they are projected onto the polarization unit vectors of the incident field.

Concluding Remarks

It has been shown that the correct single-frequency m-photon absorption tensor is composed of a single term regardless of the number of actual sources of applied field. The conventional single-frequency m-photon absorption tensor, which is deduced from the different frequency absorption tensor, can give incorrect absolute transition rates. However, it has been shown that the identity forbidden selection rule, which was formally derived from the conventional tensor, remains valid. Furthermore, the same polarization ratios are derived both from the conventional and correct tensors.

Reference

1. H. Mahr, *Treatis of Quantum Electronics,* Vol. I, pp. 285, ed. by C. L. Tang and H. Rabin (Academic Press, New York, 1975); D. M. Friedlich, *J. Chem. Ed.,* **59**, 472 (1982).
2. W. M. McClain and R. A. Harris, *Excited States,* Vol. 3, pp. 1, ed. by E. C. Lim, (Academic Press, New York, 1977); W. M. McClain, *J. Chem. Phys.,* **55**, 2789 (1971).
3. G. Hohlneicher and B. Dick, *J. Chem. Phys.,* **70**, 5427 (1979); F. T. Marchese, C. J. Seliskar, and H. H. Jaffe, *J. Chem. Phys.,* **72**, 4194 (1980).
4. W. M. McClain, *J. Chem. Phys.,* **57**, 2264 (1972); P. M. Monson and W. M. McClain, *J. Chem. Phys.,* **53**, 29 (1970).
5. D. M. Friedlich and W. M. McClain, *Chem. Phys. Lett.,* **32**, 541 (1975).
6. W. Hampf, H. J. Neusser, and E. W. Schlag, *Chem. Phys. Lett.,* **46**, 406 (1977).
7. L. D. Ziegler and B. S. Hudson, *Excited States,* Vol. 5, pp. 41, ed. by E. C. Lim (Academic Press, New York, (1982).
8. D. M. Friedrich, *J. Chem. Phys.,* **75**, 3258 (1981).