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Resonant enhancement of second-harmonic generation of electric quadrupole origin in phthalocyanine films

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Second-harmonic-generation (SHG) resonance spectra were measured in thin films of centrosymmetric copper phthalocyanine and metal-free phthalocyanine. A sharp peak was observed at the high-energy edge of the Q-absorption band using 1100-nm fundamental light, and was attributed to the resonant enhancement of the electric-quadrupole transition based on an orientation gas model. The SHG resonance spectra provide us with a useful tool for studying electric-dipole-forbidden states. [S0163-1829(96)51520-1]

Considerable attention has been paid to the relatively strong optical second-harmonic generation (SHG) in thin films of centrosymmetric molecules such as C_{60} and copper phthalocyanine (CuPc). Theory of SHG in centrosymmetric media was developed in the 1960's.[1–4] Adler[2] classified the origin of sum-frequency generation in a dielectric into five possible mechanisms [the electric dipole (ED) mechanism, the magnetic dipole coupling (MDC) mechanism, the magnetic dipole (MD) mechanism, the electric quadrupole coupling (EQC) mechanism, and the electric quadrupole (EQ) mechanism], in which the last four mechanisms are also allowed in a centrosymmetric system.

Koopmans *et al.*[5,6] demonstrated that the resonant SHG in C_{60} thin films is of bulk character and is due to the MDC mechanism at 689 nm fundamental wavelength. They obtained an effective $\chi^{(2)}$ value (1.8×10^{-8} esu). Wilk *et al.*[7] indicated that the resonant SHG in C_{60} films at 1064 nm fundamental wavelength originates from the ED transition and the vibration-assisted ED transition at the second-harmonic (SH) frequency (the MDC mechanism and the EQC mechanism) and the EQ transition at the SH frequency (the EQ mechanism).

Kumagai *et al.*[8] obtained a $\chi^{(2)}$ value (4.5×10^{-8} esu) at 1064 nm fundamental wavelength in CuPc films assuming the ED mechanism as a bulk property. We have also investigated the thickness dependence of SHG in CuPc thin films using 1064 nm fundamental wavelength.[9,10] The experimental results were reproduced with the MDC, EQC, or EQ mechanism under $D_{\infty h}$ symmetry, though it was assumed that the SHG is nonresonant.[10] Thus, further studies are required to clarify the origin of the SHG.

In this paper, we report the SH spectra in a CuPc film and a metal-free H_2Pc film. A sharp resonant peak at 550 nm SH wavelength was observed in both films. We discuss the origin of the resonance from microscopic views and propose that the dominant origin of the resonant SHG is the electric quadrupole mechanism.

The sample films were prepared by vacuum evaporation in a vacuum chamber the base pressure of which was 2×10^{-6} Torr. The film thickness was monitored by Leybold Inficon XTM/2 and was calibrated by a direct observation of the film thickness by means of an atomic force microscope (Seiko SPI-3700). The film thickness for the present experiments was about 110 nm. The SHG measurement was carried out without exposing the film to atmosphere.[11]

The fundamental light ranging from 1010 to 1310 nm was obtained by the optical parametric oscillation of a beta-barium-borate (BBO) crystal (BMI OP 901.355/70) pumped by the third-harmonic light of a Nd:YAG laser (Quanta Ray DCR-11). The fundamental light of 3–5 mJ/pulse ran at a repetition frequency of 10 Hz. The p- or s-polarized fundamental light was obtained by a combination of a phase compensator and a polarizer. The fundamental light after passing through a planoconvex lens and a color filter to remove SH light from optical components was cast upon the film. The fundamental light was impinged on the film side with an incident angle of 45°. The p-polarized SH light filtered through a color filter to remove the fundamental light, an analyzer, a lens, and a monochromator (Ritsu MC-10N) was detected by a photomultiplier (Hamamatsu R955) in the transmission direction. The frequency and the polarization dependence of the effective efficiency for the detector system were carefully calibrated using a standard halogen lamp. The frequency dependence of the fundamental light power was calibrated using a power meter (Gentec TPM-310).

In general, a bulk optical nonlinear polarization in centrosymmetric K_h and $D_{\infty h}$ symmetries is written in the form $P_i=g_{ijkl}E_j\nabla_kE_l$ and the nonzero g components are characteristic in the four mechanisms. The notations in this paper are the same as those in our previous paper.[10] We describe the resonant terms of microscopic expressions for four mechanisms.[2,7] The MDC mechanism or the EQC mechanism is due to a MD transition or an EQ transition at one input field, respectively, and an ED transition at the other input field, as illustrated in Figs. 1(a) and 1(b). The MD mechanism or the EQ mechanism is due to ED transitions at both of the input fields and a MD transition or an EQ transition at the output field, respectively, as illustrated in Figs. 1(c) and 1(d). Among them, the MD mechanism can be ruled out from a symmetrical consideration as shown in our previous paper.[10]

The SH resonance spectra and the absorption spectra for a CuPc film and a H_2Pc film are displayed in Figs. 2(a) and 2(b), respectively, where $I(s,p)$ stands for p-polarized SH intensity under the incidence of s-polarized fundamental light, as illustrated in Fig. 2. It was confirmed that $I(p,s)$ and

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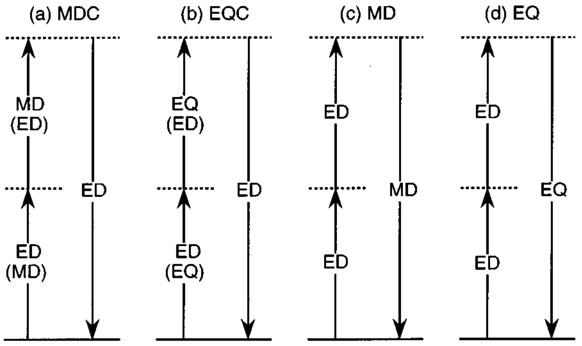

FIG. 1. Schematic illustration of microscopic views of four SHG processes: (a) the magnetic dipole coupling mechanism, (b) the electric quadrupole coupling mechanism, (c) the magnetic dipole mechanism, and (d) the electric quadrupole mechanism.

$I(s,s)$ are negligible as expected from a symmetrical consideration. A sharp resonance peak was observed at the high-energy edge (550 nm) of the Q-absorption band in both films.

Let us first examine the effect of the absorption on the SH intensity. Not only the frequency dispersion of the nonlinear susceptibility but also the dispersion of a dielectric constant influence the SH intensity. Debe *et al.*[12] measured a dielectric dispersion in the visible region for a CuPc film. We estimated the influence of dielectric dispersion using their values as follows. For the geometry of $I(s,p)$, the bulk nonlinear polarization P involves P_1 and P_3, where the 3 axis is along the film surface normal and the 1 axis is parallel to the film surface and to the optic plane. They are expressed as

$$\begin{aligned}P_1&=\Gamma_{1212}E_2\partial_1E_2+\Delta_{1212}E_2\partial_1E_2-\Lambda_{1122}\partial_1E_2E_2\\&=(\Gamma_{1212}+\Delta_{1212}-2\Lambda_{1122})E_2\partial_1E_2\\&=g_{1212}E_2\partial_1E_2,\end{aligned}$$

$$\begin{aligned}P_3&=\Gamma_{3232}E_2\partial_3E_2+\Delta_{3232}E_2\partial_3E_2-\Lambda_{3322}\partial_3E_2E_2\\&=(\Gamma_{3232}+\Delta_{3232}-2\Lambda_{3322})E_2\partial_3E_2\\&=g_{3232}E_2\partial_3E_2,\end{aligned}$$

where Γ, Δ, and Λ are nonlinear susceptibilities for the MDC, EQC, and EQ mechanisms, respectively. The electric field E of fundamental light in the film is expressed as a sum of the forward and the backward waves, that is,

$$E_2=E_2^f+E_2^b.$$

In order to examine the effect of dielectric dispersion, we assumed K_h symmetry, in which the relation $g_{1212}=g_{3232}$ exists. We calculated $I(s,p)$ at two wavelengths, 550 nm (SH resonance peak) and 620 nm (absorption peak), only by taking account of the dielectric dispersion assuming that g has no frequency dependence. The calculation was performed by solving the wave equations at ω and 2ω subject to the Maxwell boundary conditions.[13] In the calculation, we used the values $\epsilon_1(550\text{ nm})=2.3+0.3i$, $\epsilon_3(550\text{ nm})=1.9+0.7i$, $\epsilon_1(620\text{ nm})=2.0+1.6i$ and $\epsilon_3(620\text{ nm})=3.4+4.2i$. For dielectric constants at 1100 and 1240 nm, a value at 1064 nm $[\epsilon_1(1064\text{ nm})=3.3]$ obtained by Kumagai *et al.*[8] was used. The calculation leads to $I^{620\text{ nm}}(s,p)/I^{550\text{ nm}}(s,p)=0.65$ for the film of 110 nm thickness. The value 0.65 is solely caused by the dielectric dispersion. However, $I^{620\text{ nm}}(s,p)/I^{550\text{ nm}}(s,p)=0.036$ obtained by the experiment is much smaller than the simulation. The fact indicates that the influence of the absorption in the film exists but is not serious since the film is not thick, and that a frequency dispersion of the nonlinear susceptibility plays an important part in the present SH spectra.

Let us discuss the SH resonant spectra based on an orientation gas model in which optical properties of a free molecule directly reflect to bulk optical properties through a molecular orientation distribution function. The energy diagram for a free CuPc molecule is shown in Fig. 3. The relative energy intervals between the levels correspond to the energy diagram given in Ref. 14. Although one electron is located on the metal dominant $b_{1g}(d_{x^2-y^2})$ level according to their results, this level has no influence upon the present SH optical process, since the SH resonance peak appears at the same wavelength in a H_2Pc film as well as in CuPc. Since the Q-absorption band originates from the lowest π-π^* transition, $a_{1u}(\pi)$-$e_g(\pi^*)$, there are no energy levels which contribute to the resonance in the fundamental frequency region used in this experiment, including MD, EQ, and ED transitions. Furthermore, the resonance wavelength 550 nm is far from the peak of the Q-absorption band, indicating that the resonant excited state must be for the ED forbidden transition. Judging from the energy diagram, the EQ and MD allowed transitions, $b_{2g}(Np\sigma)\rightarrow e_g(\pi^*)$, $e_g(Np\sigma)\rightarrow e_g(\pi^*)$, and $a_{1g}(Np\sigma)\rightarrow e_g(\pi^*)$ are the candidates for the resonance at the SH frequency, since $b_{2g}(Np\sigma)$, $e_g(Np\sigma)$, and $a_{1g}(Np\sigma)$ levels exist near the

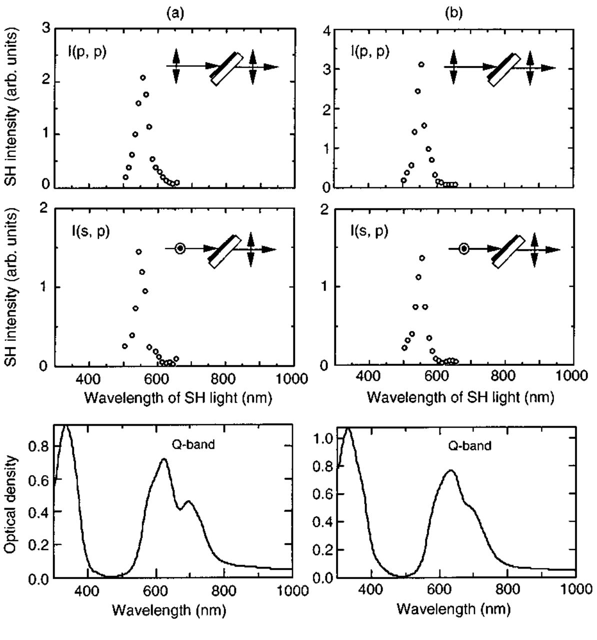

FIG. 2. SH spectra and linear absorption spectra in (a) a CuPc film and (b) a H_2Pc film. The SH intensities, $I(p,p)$ and $I(s,p)$, are plotted for the SH wavelength.

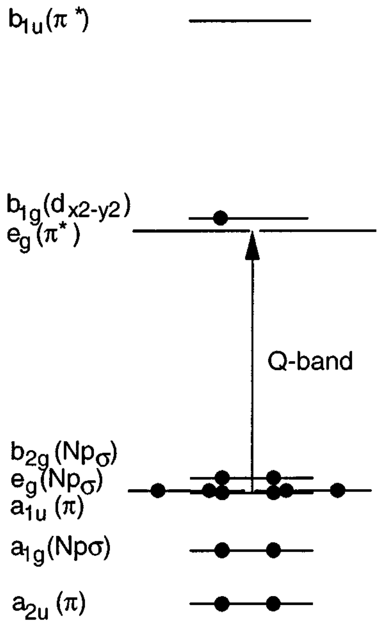

FIG. 3. The energy diagram for a free CuPc, which is quoted from Ref. 14.

$a_{1u}(\pi)$ level. However, the energy-level calculation for the $Np\sigma$ orbitals in various phthalocyanines has poor reliability.[14] In fact, such σ orbitals exist lower than the $a_{2u}(\pi)$ level, according to a recent calculation for magnesium phthalocyanine (MgPc).[15] Moreover, it is questionable whether the large nonlinearity occurs in the optical process, which includes the localized σ-orbital electron excitation. The EQ allowed transition $[a_{1u}(\pi)\text{-}b_{1u}(\pi^*)]$ can contribute to the resonance at SH frequency, since the $b_{1u}(\pi^*)$ level exists at a reasonable position according to the recent calculation.[15]

An alternative interpretation for the resonance peak is the one based on charge transfer (CT) excitons[16,17] in phthalocyanine crystals. Tokura *et al.*[18,19] measured an electro-absorption (EA) spectrum and suggested the existence of an antisymmetric CT exciton state. Since this state is ED-transition forbidden and lies above the main absorption band, the observed resonance SHG may be attributed to the EQ transition to this state. However, this idea can be ruled out by the observation of in-plane anisotropy of SHG in copper phthalocyanine films epitaxially grown by molecular-beam epitaxy, as briefly mentioned in the following.

Epitaxial CuPc films on a KCl(100) substrate surface have D_{4h} symmetry.[20,21] In D_{4h} symmetry, $I(s,p)$ is expressed as a sum of φ-independent and φ-dependent terms in the EQ mechanism, where φ is a rotation angle about the film surface normal. In the experiment using 1064 nm fundamental wavelength, we observed large φ-dependent SHG with 90° periodicity.[20] According to the detailed analysis, in-plane components of Λ in the crystal coordinate system play an important role in the SHG. The planelike CuPc molecules tend to lie parallel to the KCl(100) plane,[21] so that in-plane components in the crystal coordinate system are related to in-plane components of the molecular coordinate system. The resonance at SH frequency due to the EQ allowed transition $[a_{1u}(\pi)\text{-}b_{1u}(\pi^*)]$ produces dominant tensor components $[\lambda_{11qq}=\lambda_{22qq}$ ($q=1$, 2, or 3)], where λ_{mnop}'s are microscopic susceptibility tensor components for the EQ mechanism. For $I(s,p)$, the terms $\lambda_{1111}=\lambda_{2222}$ and $\lambda_{1122}=\lambda_{2211}$ mainly contribute to the angle dependence. Thus, rotational-angle-dependent SHG is also consistent with the interpretation of the SH spectrum based on the orientation gas model. In the case of CT exciton states, on the other hand, out-of-plane components must play a role, since CT exciton states have large anisotropy to the direction of stack axis.[18]

In conclusion, we observed SH resonance spectra for H_2Pc and CuPc films and discussed the origin based on an orientation gas model. The sharp peak observed in the SH spectra was attributed to the resonance enhancement of the electric quadrupole transition. The SHG resonance spectrum in centrosymmetric systems will help us to investigate forbidden states, as well as sophisticated methods such as electro-absorption spectrum, two-photon absorption, electric-field-induced second-harmonic generation, and third-harmonic generation resonance spectrum. It is also interesting to apply SH resonance spectrum measurement to various π-conjugate systems.

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