Fluorescence spectra of *all trans* 1,4-diphenylbutadiene obtained by the two-photon excitation into the 2^1Ag state

Takao Itoh(1)*, Yasushi Numata(2) and Isamu Suzuka(2)

1) *Graduate School of Integrated Arts and Sciences, Hiroshima University,*
1-7-1 Kagamiyama, Higashi-Hiroshima City, 739-8521 Japan
2) *Department of Materials Chemistry and Engineering, College of Engineering, Nihon University, Koriyama, 963-8642 Japan*

*To whom the correspondence should be addressed.
Electric mail:* titoh@hiroshima-u.ac.jp

The fluorescence spectra obtained by the two-photon excitation into the 2^1Ag state of diphenylbutadiene (DPB) have been measured in room temperature solutions, along with the one- and two-photon absorption spectra. It is shown that DPB molecule excited into the two-photon allowed 2^1Ag state through the two-photon process exhibits the fluorescence from the two-photon forbidden 1^1Bu state irrespective of the solvent polarizability. Relaxation processes followed by the two-photon excitation into the 2^1Ag state, and the shape of the two-photon absorption spectra measured when the 2^1Ag origin is located below the 1^1Bu origin are discussed.

1. Introduction

Diphenylbutadiene (DPB) is a typical polyene for which considerable attention has been paid on the lower-lying excited electronic states [1 - 13]. It is now well established that in the vapor phase the origin of the 2^1Ag state of DPB lies below the origin of the 1^1Bu state [1 - 6]. However, in solution these two excited states are nearly isoenergetic, so that the apparent order can differ in different experiments [7 - 9]. The two-photon absorption spectra demonstrated that the two origins are nearly degenerate in cyclohexane,[8] but the 2^1Ag state lies above the 1^1Bu state by about 2000 cm^{-1} in CCl_4.[9] In perfluorohexane, as well as in other low-polarizability solvents such as pentane, DPB excited into the 1^1Bu state exhibits the emission which has been assigned to the 1^1Bu → 1^1Ag fluorescence at temperatures near room temperature [10, 11]. Hence, it is of interest to determine the location of the 2^1Ag state of DPB in low-polarizability solvents. Further, the fluorescing state responsible for the two-photon absorption detection has not been clarified for DPB in solution. In a foregoing paper, it was suggested that in perfluorohexane and perfluoropentane the 2^1Ag state of DPB is located at energies slightly lower than the 1^1Bu state [10]. More recently, this excited-state ordering was reconfirmed also by fluorescence quantum yield and lifetime measurements.[12]

In order to determine the location of the 2^1Ag state of DPB in low-polarizability solvents, we have tried to measure the two-photon absorption spectrum in perfluorohexane at room temperature. Unfortunately, however, the measurement accompanied some difficulties probably due to the low solubility of the sample. Thus, we have measured the two-photon absorption spectra of DPB in a perfluorohexane-pentane mixture where the solubility of DPB increases approximately by a factor of 10 as compared with that in perfluorohexane alone. In the present paper, evidence is given for DPB that the molecule excited into the 2^1Ag state through the two-photon process exhibits the fluorescence from the 1^1Bu state. Relaxation processes followed by the two-photon excitation into the 2^1Ag state, and the shape of the two-photon absorption spectra measured when the 2^1Ag origin is located below the 1^1Bu origin are discussed.

2. Experimental

Diphenylbutadiene (DPB) was obtained from Aldrich Chemical Co., USA and purified by means of repeated recrystallization. The absence of any impurity emission in glassy matrices at 77 K and verification that the fluorescence and excitation spectra in 77 K matrices agreed well, respectively, with the reported emission and the corresponding absorption spectra suggest that the purified samples were sufficiently pure for the experiment. Perfluorohexane obtained from Alfa products USA and n-pentane obtained from Wako Pure Chemicals, Japan was used without purification, after we confirmed that these solvents contained no impurities that emitted under the conditions of the present experiment. The concentrations of the samples for two-photon measurements were kept near 10^{-3} mol/l, while those for one-photon measurements were kept below 10^{-5} mol/l.

One-photon absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer and conventional one-photon excited fluorescence and excitation spectra were measured with a Hitachi 650-10S spectrophotometer. For most of the emission measurements square 10-mm path length quartz cells were used. Temperature of the sample cells was controlled by a thermostated cell holder.

A YAG laser (Continuum PL8010) pumped dye laser (Continuum Jaguar) was used for the excitation light source for the two-photon measurements. The fluorescence generated by the two-photon excitation was dispersed by a monochromator

(Nikon P250). The power of the laser pulse used for the excitation was monitored with a photodiode. The two-photon spectral intensity was obtained by dividing the integrated fluorescence intensity by square of the laser power at each wavelength.

3. Results and discussion

In Fig. 1 we show the fluorescence spectra obtained by the two-photon excitation into the 2^1Ag state measured in different solvents at room temperature. The absence or stunt of the first fluorescence band of the measured spectra is due to the high concentration of the sample. The fluorescence spectra, corrected with respect to the re-absorption of the fluorescence emission are shown also in Fig. 1. It is clearly seen in Fig. 1 that the corrected fluorescence spectra shift to the red with increasing the solvent polarizability and that there are sufficient overlapping between the fluorescence and the 1^1Bu absorption bands, forming good mirror image relationships between them. Hence, we can say that the measured fluorescence spectra are originating from the 1^1Bu state.

Fig. 2(a) shows the two-photon excitation spectra of DPB in a perfluorohexane-pentane (1:1) mixture and in benzene at room temperature. The first weak band of the two-photon spectrum in a perfluorohexane-pentane (1:1) mixture is seen vaguely at around 29500 cm^{-1}, which coincides with the first 1^1Bu absorption band seen at 29500 cm^{-1}. The two-photon excitation spectrum does not show a significant change with varying the solvent. Based on the data on the excited-state energies as a function of solvent polarizability shown in a previous paper [10], the 2^1Ag state is expected to be located at about 100 cm^{-1} below the 1^1Bu state in a perfluorohexane-pentane (1:1) mixture. The laser power dependence of the two-photon excitation intensity shown in Fig. 2(b) indicates that the signal intensity depends almost linearly on the square of the laser power for the excitation, suggesting that the observed signals are generated by two-photon process. However, we can say nothing more than that the 2^1Ag and 1^1Bu states are almost degenerate in a perfluorohexane-pentane mixture so far as Fig. 2(a) is concerned.

The relaxation processes followed by the two-photon excitation into the 2^1Ag state of DPB in various solvents are displayed in Fig. 3(a). We consider two cases depending on the state ordering: One is that the 1^1Bu state is located below 2^1Ag (case 1) and the other is that 2^1Ag is located below 1^1Bu (case 2). In case 1, DPB molecule excited into the 2^1Ag state through two-photon excitation is followed by the fast internal conversion to the 1^1Bu state, from which the molecule shows the fluorescence. In case 2, DPB molecule excited into the 2^1Ag state through two-photon excitation is followed by the thermal population to the 1^1Bu state, along with accompanying nonradiative processes. In both cases, the observed emission is the 1^1Bu fluorescence, since the 1^1Bu/2^1Ag oscillator strength ratio is considered to be much larger than unity. Therefore, in case 2 the intensity of the 1^1Bu fluorescence generated as the result of two-photon excitation will be decreased by a factor of $\exp(-\Delta E/kT)$ at energies below the 1^1Bu origin, where ΔE is the energy separation between the two excited states, k is the Boltzmann constant and T is the absolute temperature. The calculated two-photon absorption spectrum expected for case 2 is demonstrated in Fig. 3(b), where the broken-line spectrum is the expected real spectrum and the solid-line spectrum is the measured spectrum. As one can see in Fig. 3(b), the measured spectral intensity tends to be decreased at energies below the 1^1Bu origin, and the absorption maximum tends to match the 1^1Bu origin. Further, the two-photon transition, although symmetry allowed for the g - g transition, is forbidden by Pariser parity, and besides the spectra in solution at room temperature are broad as compared with those in a jet or in a low-temperature matrix. These are probably the reasons why the measurements of the two-photon absorption spectrum of DPB in low-polarizability solvents accompany difficulties. Of course, the analysis for case 2 does not apply to jet-cooled DPB vapor, for which the observed major emission is the 2^1Ag fluorescence [2 - 6].

4. Conclusions

It is shown that DPB molecule excited into the 2^1Ag state through the two-photon process exhibits the fluorescence from the 1^1Bu state in room-temperature solutions. Relaxation processes followed by the two-photon excitation into the 2^1Ag state are discussed. It is indicated that the shape of the two-photon absorption spectra obtained by monitoring the fluorescence is distorted, in case the 2^1Ag origin is located below the 1^1Bu origin,

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Figure captions:

Fig. 1 Fluorescence spectra of DPB obtained by the two-photon excitation into the 2^1Ag state (solid- and broken-line spectra), along with the absorption (solid-line spectra) and fluorescence spectra obtained by the one-photon excitation (dotted-line spectra) in different solvents at room temperature: The solid- and broken-line fluorescence spectra present, respectively, the measured and corrected spectra obtained by the two-photon excitation into the 2^1Ag state.

Fig. 2 (a) Two-photon excitation (1 and 2) and one-photon absorption (3) spectra of DPB in a perfluorohexane-pentane (1:1) mixture (1 and 3) and in benzene (2) at room temperature.

(b) Laser power dependence of the signal intensity for the excitation at 675 nm ($2 \times \nu = 29630$ cm^{-1}) for DPB in a pentane-perfluorohexane (1:1) mixture at room temperature.

Fig. 3 (a) Schema showing the relaxation processes following the two-photon excitation into the 2^1Ag state of DPB; E(2^1Ag) > E(1^1Bu) (case 1) and E(2^1Ag) < E(1^1Bu) (case 2). (b) Modeled two-photon absorption spectra generated by sum of two Gaussians; (1) the real absorption spectrum and (2) the measured absorption spectrum. The 2^1Ag origin is assumed to be located at 29500 cm^{-1}, and the 2^1Ag - 1^1Bu energy separation (ΔE) is assumed to be 200 cm^{-1}. The broadness of the 1^1Bu state is not taken into account.

Fig. 1

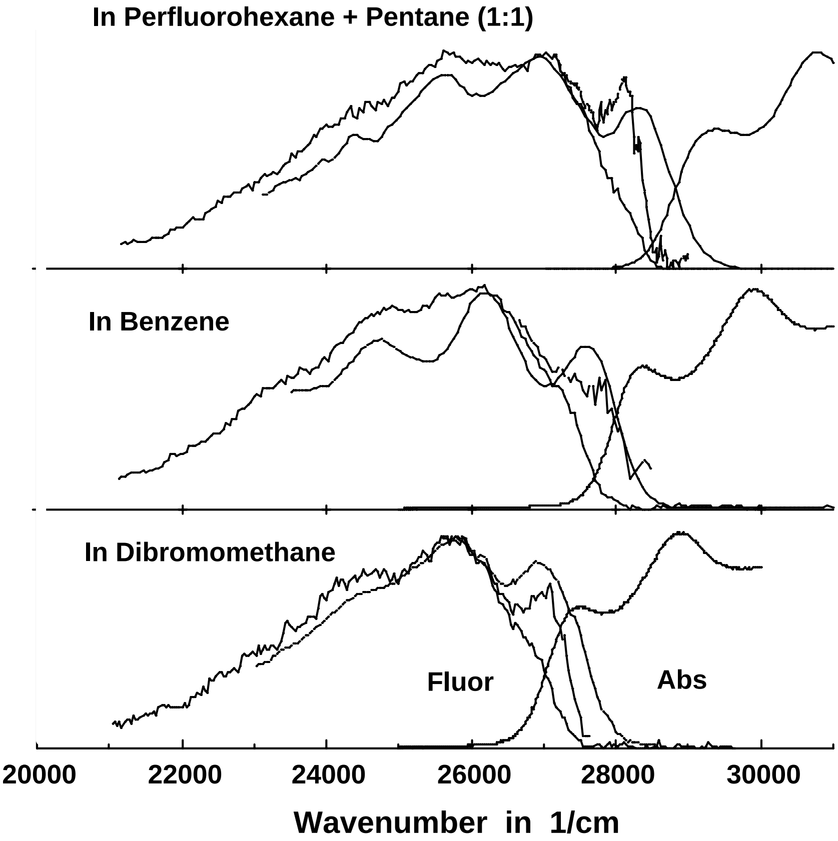

In Perfluorohexane + Pentane (1:1)
In Benzene
In Dibromomethane
Fluor
Abs
20000
22000
24000
26000
28000
30000
Wavenumber in 1/cm

Fig. 2(a)

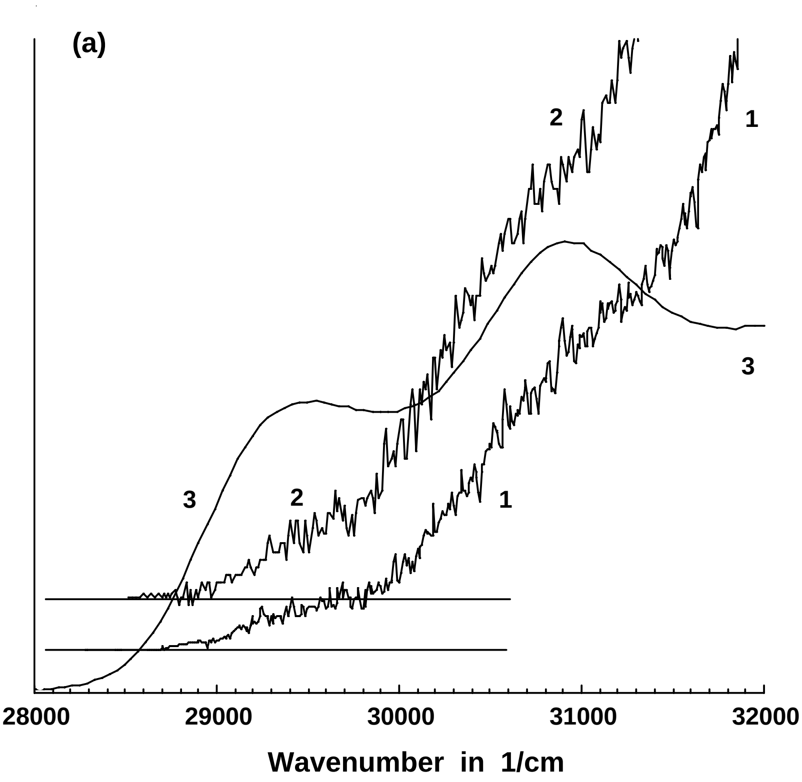


Fig. 2(b)

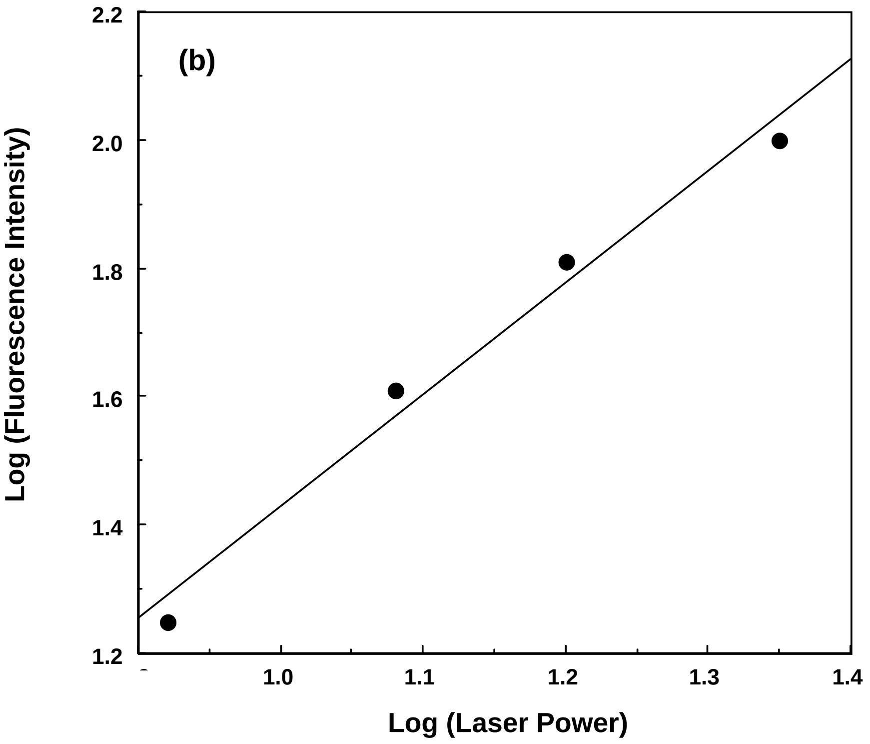

(b)
Log (Fluorescence Intensity)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
1.1
1.2
1.3
1.4
Log (Laser Power)

Fig. 3(a)

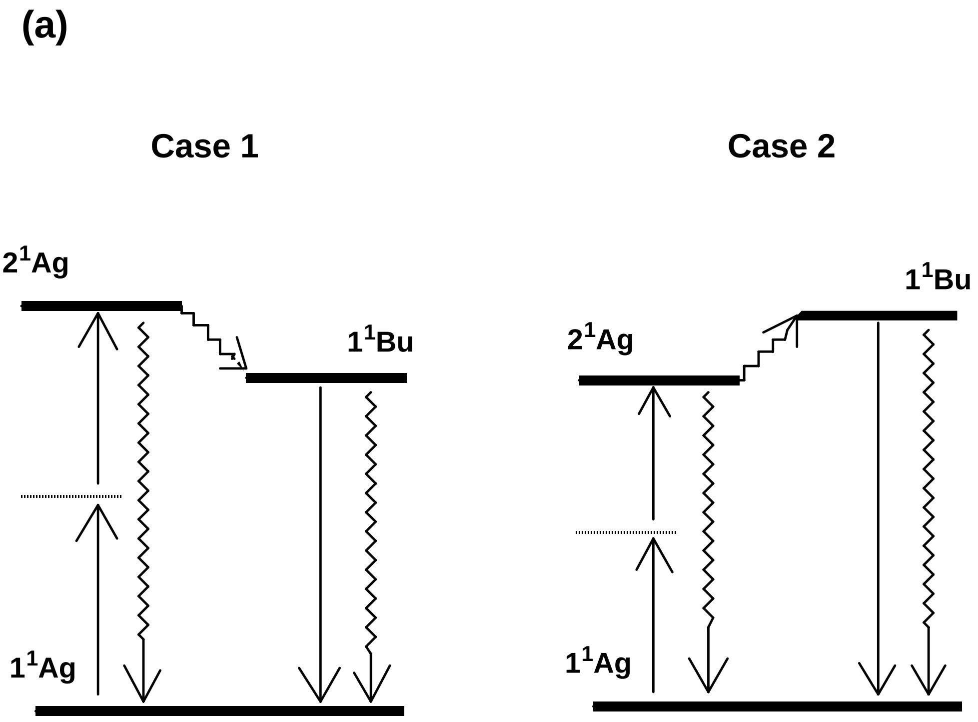
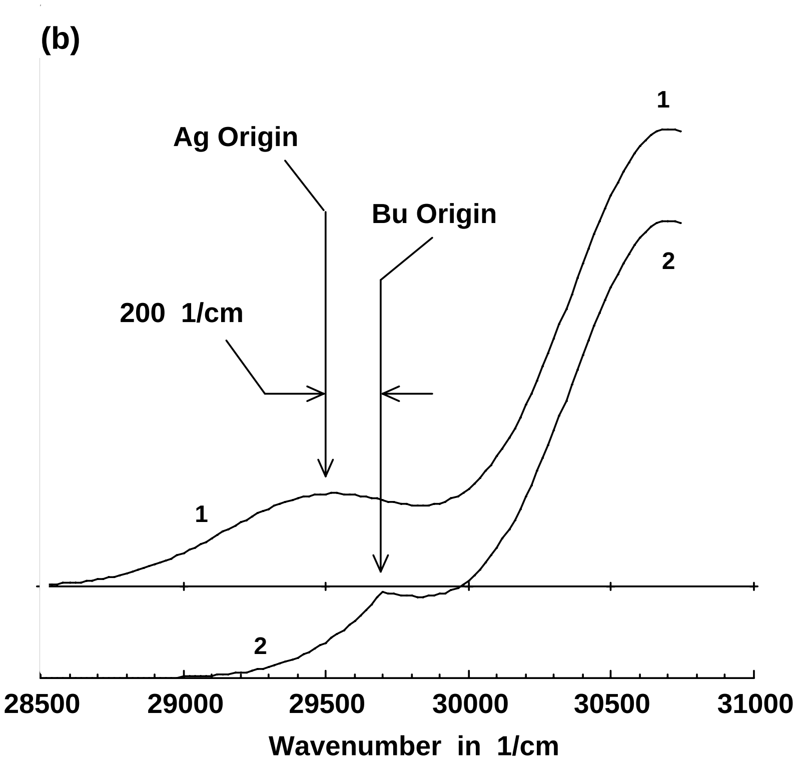


Fig. 3(b)


(b)
1
Ag Origin
Bu Origin
2
200 1/cm
1
2
28500
29000
29500
30000
30500
31000
Wavenumber in 1/cm