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Franck-Condon analysis of the absorption and fluorescence spectra of all *trans* α,ω-diphenylpolyenes with one to seven polyene double bonds

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Fluorescence and absorption spectra have been measured for all-*trans* α,ω-diphenylpolyenes with one to seven polyene double bonds in room-temperature solution, along with the fluorescence spectra of those with one to six polyene double bonds in *n*-alkane matrices at 77 K. All the spectral data were fitted by sums of Gaussians to treat the Franck-Condon envelopes of the measured spectra quantitatively. The Franck-Condon analyses of the spectra in the harmonic limit revealed that the displacements of the C=C and C–C stretching vibrational modes in the 2 Ag state relative to those in the ground state, 1 ^{1}Ag(S_0), increase, while those in the 1 ^{1}Bu state show a slight decrease with the increase of the polyene chain length. It is also shown that the bandwidths of the absorption and fluorescence spectra exhibit a monotonic decrease with the increase of the chain length. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1998830]

I. INTRODUCTION

The spectroscopy of linear polyenes has been the focus of a number of experimental and theoretical studies.[1–6] Because of their stability and finite fluorescence yields, all-*trans* α,ω-diphenylpolyenes are convenient molecules for the systematic determination of how electronic and vibrational properties depend on polyene chain length.[7–13] It is now well established for linear polyenes that there are two low-lying excited electronic states, ^{1}Ag and ^{1}Bu; the former is optically forbidden, but the latter is allowed due to the excited-state symmetry.[1–6] The lowest-energy excited singlet state (S_1) of all-*trans* α,ω-diphenylpolyenes with three to seven polyene double bonds has been assigned to the forbidden 2 ^{1}Ag state in the condensed phase, although in the vapor phase the S_1 state of diphenylbutadiene was also assigned to 2 ^{1}Ag.[14–16] It is of interest to investigate the electronic character of the low-lying excited states and the coupling in these states between the electronic excitation and nuclear motion systematically. The detailed understanding of this coupling is crucial in constructing a clear picture for *cis*-to-*trans* isomerization, which is the characteristic photochemistry of polyenes. Nevertheless, only a few number of reports is found concerning the Franck-Condon analysis of the spectra of polyenes, most of which are on the absorption spectra.[17–19]

In the present work, fluorescence and absorption spectra have been measured for all-*trans* α,ω-diphenylpolyenes with the polyene double bond number (n) from one to seven in room-temperature solution, along with fluorescence spectra of those with n from 1 to 6 in *n*-alkane matrices at 77 K. All the spectral data were fitted by sums of Gaussians to treat the Franck-Condon envelopes of the measured spectra quantitatively. The Franck-Condon analyses of the spectra in the harmonic limit revealed that the displacements of both the C=C and C–C stretching modes relative to those in the ground state, 1 ^{1}Ag(S_0), increase significantly for the 2 ^{1}Ag state, while the displacements decrease slightly for the 1 ^{1}Bu state with the increase of the polyene chain length. The monotonic changes in the bandwidths of the absorption and fluorescence spectra with the change in the chain length are also presented.

II. EXPERIMENT

Stilbene ($n=1$), diphenylbutadiene ($n=2$), diphenylhexatriene ($n=3$), and diphenyloctatetraene ($n=4$) obtained from Aldrich, USA, were recrystallized repeatedly from hexane. Diphenyldecapentaene ($n=5$), diphenyldodecahexaene ($n=6$), and diphenyltetradecaheptaene ($n=7$) were synthesized according to the procedure reported by Spangler *et al.*[20] and recrystallized from a mixture of dimethylformamide and toluene. The solvents used are all of spectroscopic grade.

Absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer. Emission and excitation spectra were measured with a Spex Fluorolog-3 (Model 21-SS) spectrophotometer, equipped with a double-grating excitation monochromator, and a photomultiplier tube (Hamamatsu R928-P) in an electric-cooled housing operated in photon-counting mode. Raman- and Rayleigh-scattering light from the solvents were subtracted from the measured emission spectra. It was confirmed that the excitation spectra of the measured samples agreed well with absorption spectra, as will be described later in detail.

Special care was taken for the correction of the measured fluorescence spectra. Fluorescence spectra were corrected for the spectral sensitivity of the detection system by comparing the measured spectrum with the real spectrum using *N*,*N*-dimethylnitroaniline as a standard which shows emission ranging from 12 000 to 22 000 cm^{-1} in a hexane-benzene mixture.[21] Fluorescence spectra ranging from 18 000 to 25 000 cm^{-1} were corrected using quinine in sul-

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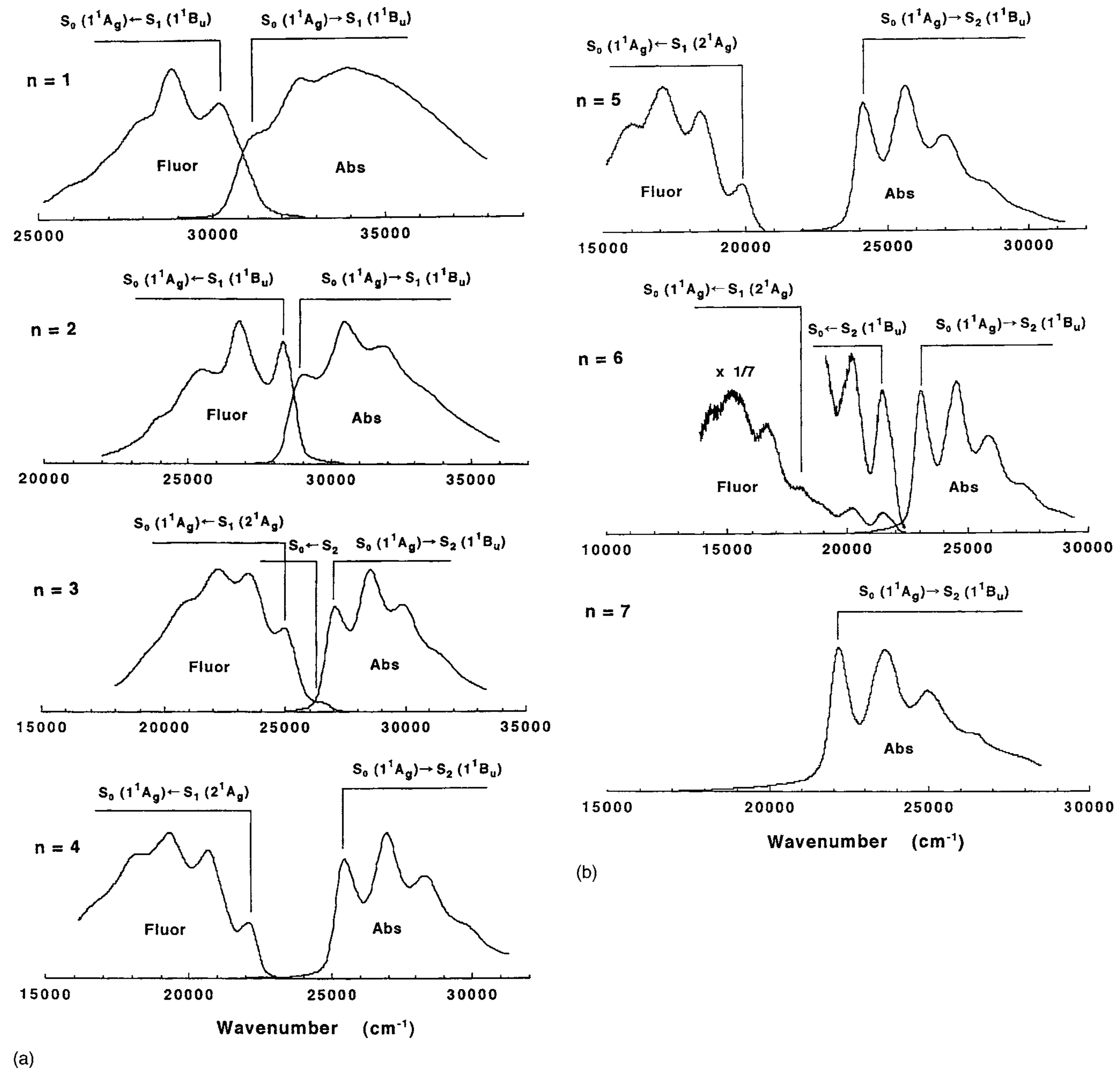

FIG. 1. Corrected fluorescence and absorption spectra of all-*trans* α,ω-diphenylpolyenes with the polyene double bond number (n) from 1 to 4 (a) and from 5 to 7 (b) in n-hexane at 20 °C. Only the absorption spectrum is shown for diphenylpolyenes with $n=7$, since the fluorescence spectrum could not be measured with a reasonable S/N ratio in n-hexane.

furic acid as a standard. It was confirmed that the fluorescence spectra corrected using the former standard agreed well with those using the latter standard in an overlapping range (18 000–22 000 cm^{-1}). The correction of giving the fluorescence intensities $[I(\nu)]$ at a fixed resolution in cm^{-1} was also made using the relation $I(\nu) \sim \lambda^2 I(\lambda)$.[22]

III. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b) we show the absorption spectra of diphenylpolyenes with the polyene double bond number n from 1 to 7 and the corrected fluorescence spectra of diphenylpolyenes with n from 1 to 6 in alkane at room temperature. The excitation spectra of the fluorescence emission were confirmed to agree well with the absorption spectra. Longer diphenylpolyene samples were found to contain trace amounts of shorter and more fluorescent diphenylpolyenes as impurities, which were removed by repeated recrystallizations. In particular, the S_2 fluorescence origin of diphenylpolyene with $n=5$ matches almost exactly the S_1 fluorescence origin of highly fluorescent diphenyloctatetraene ($n=4$). It was confirmed that the measured S_2 fluorescence of the former molecule does not originate from diphenyloctatetraene, based on the measurements of the excitation spectrum and fluorescence spectral shape as well as on the repeated purification-emission measurement cycles.[23,24] The measured emission is assigned as the $1\,^1\mathrm{Bu}(S_1) \rightarrow 1\,^1\mathrm{Ag}(S_0)$ fluorescence for diphenylpolyenes with $n=1$ and 2, as indicated by a good mirror-image relationship and by an overlap between the fluorescence and the $1\,^1\mathrm{Ag}(S_0) \rightarrow 1\,^1\mathrm{Bu}(S_1)$ absorption

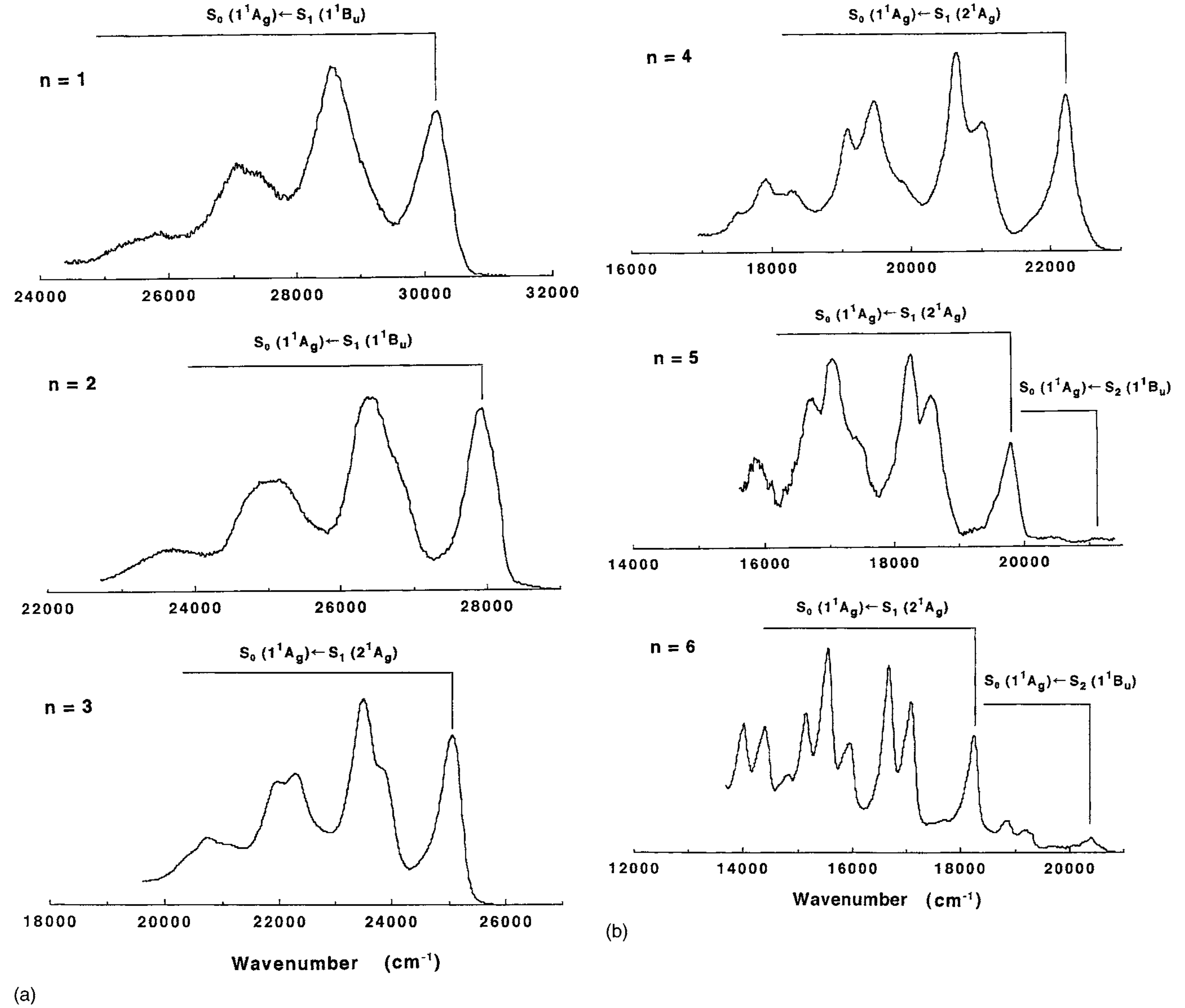

FIG. 2. Corrected fluorescence spectra of all-*trans* α,ω-diphenylpolyenes with n from 1 to 3 (a), and from 4 to 6 (b) in n-alkanes at 77 K. n hexane was used as the solvent for diphenylpolyenes with $n=1$ to 5, while n dodecane was used for diphenylpolyene with $n=6$.

band. On the other hand, the emission consists of mainly the $2\ ^1\mathrm{Ag}(S_1)\rightarrow S_0$ fluorescence accompanied by the weak $1\ ^1\mathrm{Bu}(S_2)\rightarrow S_0$ fluorescence for diphenylpolyenes with n from 3 to 7, although the S_2 fluorescence is not shown in Fig. 1 for diphenylpolyenes with $n=4$ and 5 because of the extremely low intensity.[23–25] It has already been shown in a previous paper that the relative intensity of the S_2 fluorescence depends significantly on the polyene chain length.[24]

Figures 2(a) and 2(b) show corrected fluorescence spectra of diphenylpolyenes with n from 1 to 6 in n-alkane matrices at 77 K. Obviously, the spectral patterns at 77 K are sharpened as compared with those at room temperature. The measured emission is assigned as the $1\ ^1\mathrm{Bu}(S_1)\rightarrow 1\ ^1\mathrm{Ag}(S_0)$ fluorescence for diphenylpolyenes with $n=1$ and 2, while the emission consists mainly of the $2\ ^1\mathrm{Ag}(S_1)\rightarrow S_0$ fluorescence for diphenylpolyenes with n from 3 to 6. The weak

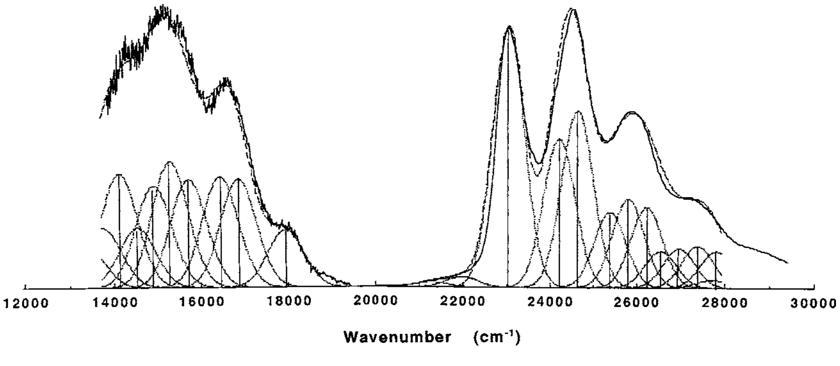

FIG. 3. Corrected S1 fluorescence (left) and absorption spectra (right) of diphenyldodecahexaene ($n=6$) in n-hexane at 20 °C (solid-line spectra), the fitted fluorescence and absorption spectra (broken-line spectra), and Gaussians used for fitting (dotted-line curves). Gaussian amplitudes are indicated by sticks. The S1 fluorescence spectrum is obtained by subtracting the S2 fluorescence spectrum from the measured spectrum.

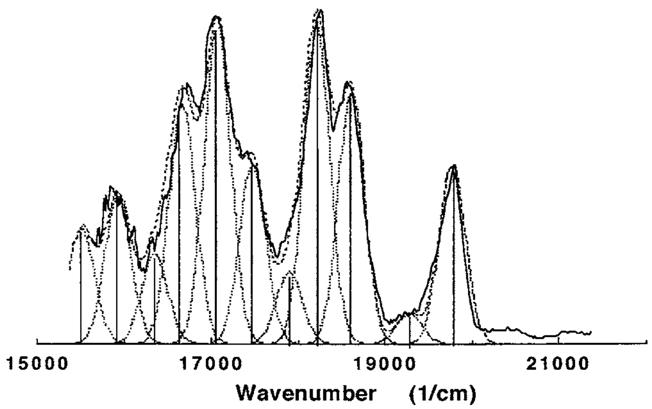

FIG. 4. Corrected fluorescence spectrum of diphenyldecapentaene ($n=5$) in n hexane at 77 K (solid-line spectrum), the fitted fluorescence spectrum (broken-line spectrum), and Gaussians used for fitting (dotted-line curves). The Gaussian amplitudes are indicated by sticks.

$1\ ^1\mathrm{Bu}(S_2) \rightarrow 1\ ^1\mathrm{Ag}(S_0)$ fluorescence is observed as a blue shoulder overlapping the onset of the strong $2\ ^1\mathrm{Ag}(S_1) \rightarrow S_0$ fluorescence for diphenylpolyenes with $n=5$ and 6.

In order to determine the relative intensities for the fluorescence and absorption quantitatively, all the spectral data were fitted by sums of Gaussians, where the intensity $I(\nu)$ at wave number ν was assumed to have the form

$$I(\nu) = I_0(\nu_0)\exp[-(\nu-\nu_0)^2/\sigma^2], \tag{1}$$

where ν_0 is the wave number at the Gaussian center, $I_0(\nu_0)$ is the amplitude, and σ is the width. The spectra were fitted using Gaussians corresponding to the 0-0, 0-1, 0-2, and 0-3 transitions for the C═C (ν_1) and C–C (ν_2) symmetric stretching modes as well as their combination modes by varying $I_0(\nu_0)$ and σ to obtain the Gaussian amplitudes, $I_0(\nu_0)$. The bandwidth σ is kept constant irrespective of the modes for each molecule. In order to derive the most accurate spectral shape estimate of the $2\ ^1\mathrm{Ag}(S_1)$ fluorescence for diphenyloctatetraene ($n=4$) and diphenyldodecahexaene ($n=6$) at room temperature, the $1\ ^1\mathrm{Ag}(S_0) \rightarrow 1\ ^1\mathrm{Bu}(S_2)$ absorption spectrum reflected such that the origin matched the origin of the S_2 fluorescence was subtracted from the measured fluorescence spectrum, and then the resulting difference spectrum was refitted by Gaussians to obtain the integrated intensity of the Gaussian corresponding to the S_1 fluorescence alone. Examples of the calculated fluorescence and absorption spectra in n-hexane at room temperature and the calculated fluorescence spectrum in hexane at 77 K are presented, respectively, in Figs. 3 and 4. These inhomogeneously broadened solution spectra at room temperature can be reproduced reasonably by using only two intrinsic harmonic normal modes. When 12 Gaussians were fitted to the first 6000 cm^{-1} of the absorption spectrum, the measured and calculated spectra were almost indistinguishable from each other. In the case of fluorescence spectra measured at 77 K, the inclusion of the third mode with the frequency of about 700 cm^{-1} improved the calculated line shape, but had no effect on the best-fit C–C and C═C displacements.

In Tables I–III we show amplitudes (I_0) and bandwidths (σ) obtained from Gaussian fittings of the absorption and fluorescence spectra of diphenylpolyenes in n-hexane at room temperature (Tables I and II) and at 77 K (Table III). One can see in Table II that the Franck-Condon envelopes of the fluorescence spectra of shorter diphenylpolyenes are qualitatively different from those of longer ones; both of the ν_1 and ν_2 intensities decrease with the increase of the vibrational quantum number k in the 0-k transition for diphenylbutadiene ($n=2$), while the intensities show a maximum at the 0-1 transition for diphenyldodecahexaene ($n=6$). Furthermore, the bandwidths of the absorption and fluorescence spectra show a monotonic decrease with the increase of the polyene chain length. Similar behavior has been observed for the absorption spectra of unsubstituted polyenes, for which the change in the bandwidth was elucidated in terms of conformational disorder involving static torsions about the ends of the polyene chain.[17]

TABLE I. Amplitudes (I_0) and bandwidths (σ) of the C═C (ν_1) and C–C (ν_2) modes for the Franck-Condon analysis obtained from Gaussian fittings of the $1\ ^1\mathrm{Bu} \rightarrow 1\ ^1\mathrm{Ag}$ absorption of all-*trans* α,ω-diphenylpolyenes with $n=1$–7 in n-hexane at 20 °C.

	I_0[a]						
Assignment	1	2	3	4	5	6	7
$\nu_{0\text{-}0}$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
ν_2	1.07	0.80	0.71	0.67	0.60	0.57	0.50
ν_1	0.67	0.97	0.78	0.72	0.72	0.68	0.58
$2\nu_2$	0.87	0.53	0.39	0.36	0.31	0.29	0.29
$\nu_1+\nu_2$	0.61	0.51	0.44	0.41	0.36	0.34	0.32
$2\nu_1$	0.55	0.51	0.41	0.35	0.33	0.31	0.30
$3\nu_2$	0.51	0.27	0.19	0.17	0.14	0.14	0.15
$2(\nu_1+\nu_2)$	0.49	0.28	0.26	0.19	0.16	0.15	0.16
$\nu_1+2\nu_2$	0.62	0.28	0.21	0.19	0.17	0.16	0.15
$3\nu_1$	0.52	0.35	0.24	0.18	0.16	0.03	0.13
$3(\nu_1+\nu_2)$	0.23	0.11	⋯	⋯	⋯	0.14	0.06
$\sigma(\mathrm{cm}^{-1})$	787.4	692.8	632.4	565.7	538.5	529.2	519.9

[a] +/−0.01

TABLE II. Amplitudes (I_0) and bandwidths (σ) of the C═C (ν_1) and C–C (ν_2) modes for the Franck-Condon analysis obtained from Gaussian fittings of the $1\ ^1\mathrm{Bu} \rightarrow 1\ ^1\mathrm{Ag}$ fluorescence ($n=1$ and 2) and $2\ ^1\mathrm{Ag} \rightarrow 1\ ^1\mathrm{Ag}$ fluorescence ($n=3$–7) of all-*trans* α,ω-diphenylpolyenes in n-hexane at 20 °C.

	I_0[a]						
Assignment	1	2	3	4	5	6	7[b]
$\nu_{0\text{-}0}$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
ν_2	0.63	0.60	0.96	1.26	1.35	1.88	2.42
ν_1	0.82	0.77	1.06	1.32	1.60	1.93	3.88
$2\nu_2$	0.30	0.30	0.80	1.11	1.30	1.88	4.09
$\nu_1+\nu_2$	0.40	0.42	0.88	1.40	1.85	2.19	4.55
$2\nu_1$	0.16	0.38	0.70	0.90	1.01	1.77	3.63
$3\nu_2$	0.09	0.10	0.38	0.50	0.55	1.04	3.03
$\nu_1+2\nu_2$	0.12	0.18	0.66	1.10	1.40	1.98	3.33
$2(\nu_1+\nu_2)$	0.17	0.20	0.57	0.90	0.80	1.04	⋯
$3\nu_1$	0.07	0.04	0.30	0.24	0.40	0.72	⋯
$4\nu_2$	⋯	0.02	0.05	0.24	0.10	⋯	⋯
$\sigma(\mathrm{cm}^{-1})$	692.8	648.0	565.7	547.7	500.2	487.2	⋯

[a] +/−0.01

[b] The Gaussian amplitudes for diphenylpolyene with $n=7$ are taken from Ref. 23.

TABLE III. Amplitudes (I_0) and bandwidths (σ) of the C=C (ν_1) and C–C (ν_2) modes for the Franck-Condon analysis obtained from Gaussian fittings of the 1 ^{1}Bu→1 ^{1}Ag fluorescence (n=1 and 2) and 2 ^{1}Ag→1 ^{1}Ag fluorescence (n=3–7) of all-*trans* α,ω-diphenylpolyenes in n-hexane matrices at 77 K.

	I_0[a]					
Assignment	1	2	3	4	5	6[b]
($\nu_{0\text{-}0}$)	1.00	1.00	1.00	1.00	1.00	1.00
ν_2	0.54	0.65	0.66	0.82	1.38	1.42
ν_1	1.03	0.92	1.15	1.30	1.76	1.79
$2\nu_2$	0.38	0.30	0.37	0.45	0.98	1.05
$\nu_1+\nu_2$	0.39	0.51	0.70	1.01	1.76	2.02
$2\nu_1$	0.43	0.43	0.62	0.80	1.32	1.46
$3\nu_2$	0.14	0.12	0.17	0.21	0.49	0.64
$\nu_1+2\nu_2$	0.16	0.17	0.27	0.40	0.82	1.24
$2(\nu_1+\nu_2)$	0.15	0.19	0.33	0.49	0.60	1.26
$3\nu_1$	0.15	0.12	0.22	0.28	⋯	⋯
σ(cm^{-1})	374.2	316.6	282.8	224.6	212.1	191.4

[a] +/−0.02

[b] In n-dodecane at 77 K.

The vibrational frequencies used for the Franck-Condon analysis are listed in Table IV. The frequencies of the C=C and C–C stretching modes in the ground state of diphenylpolyenes are obtained from the Raman band positions in the literatures.[4,23] The mode frequencies in the 1 ^{1}Bu states are obtained from the spectral fitting procedure assuming that the vibrational structure in the absorption spectra consists of only the C=C (ν_1) and C–C (ν_2) symmetric stretching modes.

The intensity in a given vibronic band, $I_0(\nu_0)$, is assumed to be proportional to the Franck-Condon factor, which is described by the harmonic oscillator wave function basis. Thus, we have

$$I_0(\nu_0) = \text{const.}[\Pi_i|\langle\phi_{i,m}(Q_{i,g})|\phi_{i,n}(Q_{i,e})\rangle|^2], \qquad (2)$$

where i is the number of normal modes, and m and n are the vibrational quantum numbers. The overlap integrals, $\langle\phi_{i,m}(Q_{i,g})|\phi_{i,n}(Q_{i,e})\rangle$, which are a function of displacement of the excited electronic state (e) potential curve for each normal coordinate from the corresponding ground state (g) as well as of the corresponding vibrational frequencies in the excited and ground states, can be simply calculated with the recurrence relations derived by Manneback.[26]

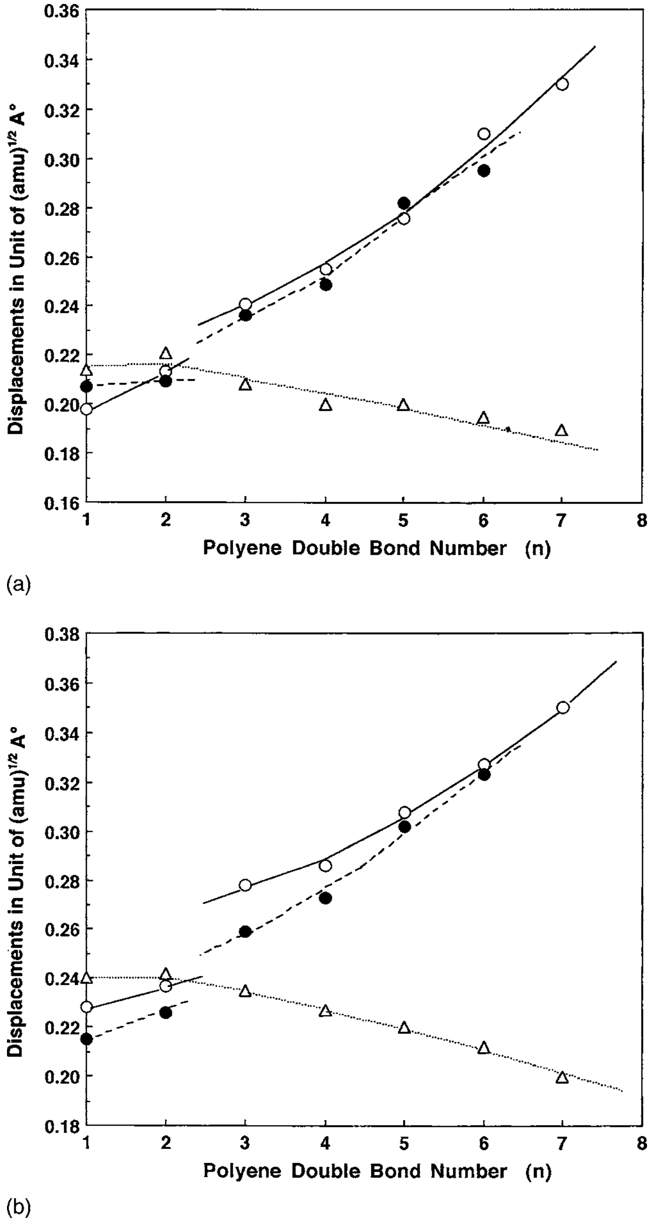

FIG. 5. The C–C (a) and C=C (b) stretching mode displacements in units of (amu)$^{1/2}$ Å from the Franck-Condon fits to the absorption and fluorescence spectra for diphenylpolyenes with n from 1 to 7. The plots indicated by open circles, closed circles, and open triangles, respectively, are obtained from the Franck-Condon fits to the fluorescence at 20 °C, fluorescence at 77 K, and absorption spectra at 20 °C. The mode displacements of diphenylpolyene with n=7 are taken from Ref. 23.

TABLE IV. Mode frequencies for the C=C (ν_1) and C–C (ν_2) symmetric stretching vibrations in the 1 ^{1}Ag(S_0) and 1 ^{1}Bu states of all-*trans* α,ω-diphenylpolyenes (n=1–7) used for the Franck-Condon fits.

State	1 ^{1}Ag		1 ^{1}Bu	
n	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_1 (cm^{-1})	ν_2 (cm^{-1})
1	1641	1180	1590	1190
2	1630	1161	1600	1200
3	1598	1154	1620	1200
4	1576	1148	1620	1200
5	1560	1143	1600	1190
6	1548	1139	1580	1180
7	1536	1136	1540	1170

Figures 5(a) and 5(b) show the displacements of the C=C and C–C stretching modes, respectively, obtained from the Franck-Condon analysis of the fluorescence and absorption spectra. With the increase of the polyene double bond number (n), both of the C=C and C–C stretching mode displacements obtained from fits to the fluorescence increase, while those obtained from fits to the 1 ^{1}Bu absorption decrease slightly. Closer inspection of Fig. 5 shows that there is a sort of discontinuity between n=2 and 3 in the plots of the displacements of the C=C and C–C stretching modes as obtained from the fluorescence spectra. This discontinuity is considered to be caused by the change of the emitting state from 1 ^{1}Bu to 2 ^{1}Ag with n going from 2 to 3. The displacements of the C═C and C–C stretching modes as obtained from the 1 ^{1}Bu absorption are significantly smaller than those from the 2 ^{1}Ag fluorescence for diphenylpolyenes with n from 3 to 7, but correspond closely to the displacements obtained by fitting the fluorescence spectrum for diphenylpolyenes with $n=1$ and 2. This is what we expected when the fluorescencent state is 1 ^{1}Bu and, therefore, when the 1 ^{1}Bu fluorescence and absorption spectra are in a mirror-image relationship for diphenylpolyenes with $n=1$ and 2. Hence, the plots in Fig. 5 show that the displacements of both the C═C and C–C stretching modes relative to those in the ground state, 1 ^{1}Ag(S_0), increase significantly for the 2 ^{1}Ag state, while the displacements decrease slightly for the 1 ^{1}Bu state with the increase the polyene length. The behavior of the displacement in the 1 ^{1}Bu state does not disagree with that observed for unsubstituted linear polyenes, for which the displacements were reported to be almost invariant irrespective of the polyene length.[17] In both the C═C and C–C stretching modes, the displacements in the excited states are shown to be a smoothly varying function of the polyene chain length.

IV. CONCLUSIONS

The displacements of the excited states of diphenylpolyenes with one to seven polyene double bond have been determined through the Franck-Condon analyses and a fit of the geometry to the vibronic intensities of the fluorescence and absorption spectra in the harmonic limit. The displacements of the C═C and C–C stretching vibrational modes in the excited states are shown to be expressed by a smoothly varying function of the polyene chain length. The displacements of these modes in the 2 ^{1}Ag state relative to those in the ground state, 1 ^{1}Ag (S_0), increase with the increase of the polyene chain length. On the other hand, the displacements upon excitation into the 1 ^{1}Bu state decrease slightly as the chain length becomes longer. It is also shown that the bandwidths of the absorption and fluorescence spectra exhibit a monotonic decrease with the increase of the polyene chain length. The observed difference in behavior of the mode displacements between the 2 ^{1}Ag and 1 ^{1}Bu states is considered to be related to their electronic configurations.

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