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Nonexponential Fluorescence Decay of Diphenylhexatriene Vapor: Influence of Collisions on Vibrational Relaxation in the 2^1A_g Manifold

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Nonexponential decay of the $2^1A_g(S_1) \rightarrow 1^1A_g(S_0)$ fluorescence observed for 1,6-diphenyl-1,3,5-hexatriene (DPH) static vapor in the presence of perfluorohexane used as a buffer gas is shown to be induced by intermolecular collision. The pressure and excitation energy dependence of the decay profiles are interpreted in terms of a simple two-level scheme for the 2^1A_g manifold and are analyzed to evaluate the collision efficiency on the vibrational relaxation, which is found to depend on the excitation energy.

Introduction

Linear polyenes are prototypes of the π-electron conjugation systems for which a number of spectroscopic and quantum mechanical studies have been carried out since around the 1930s, when the applications of spectroscopy or quantum mechanics to molecular systems had just started.[1−3] It was known that linear polyenes exhibit an intense absorption band based on an allowed electronic transition, $^1A_g \rightarrow {}^1B_u(\pi,\pi^*)$.[3] In 1972, however, the existence of an excited state ^1A_g below ^1B_u was pointed out by Hudson and Kohler.[4−6] This finding not only forced a fundamental revision of the accepted molecular orbital picture of polyene electronic structure but also rationalized properties of polyenes that had been termed anomalous. One of the reasons that the idea of the lowest excited 2^1A_g state was not fully accepted initially is probably that the absorption in question is invisible in the optical spectra. The situation is somewhat different from the case of the forbidden $^1(n, \pi^*)$ transitions of carbonyl or aza aromatic compounds, where we can see them clearly in the absorption spectra of high-concentration samples.[7] After the discovery of the 2^1A_g state, the trends of the research on the polyene electronic states soon shifted from the determination of the 2^1A_g-state location and properties to the photophysical and photochemical behavior of that state, as have been reviewed.[8−13]

In the present work, particular attention is focused on the fluorescence decay of 1,6-diphenyl-1,3,5-hexatriene (DPH) vapor. Although DPH is known to exhibit the dual fluorescence $1^1B_u(S_2) \rightarrow 1^1A_g(S_0)$ and $2^1A_g(S_1) \rightarrow 1^1A_g(S_0)$ in room-temperature solution because of the thermal population of the 2^1A_g state,[14−17] the emission so far observed for DPH vapor, both in static and in a supersonic jet expansion, is only the $2^1A_g \rightarrow 1^1A_g$ fluorescence.[18−20] The absence of the $1^1B_u(S_2)$ fluorescence for DPH vapor can be attributed to the large energy separation between the S_1 and S_2 states (3415 cm^{-1}). We have observed distinct nonexponential fluorescence decays for DPH vapor. Pressure and excitation energy dependence of the decay profiles are analyzed on the basis of a simple two-level scheme in the 2^1A_g manifold to investigate the influence of the collision on the vibrational relaxation.

Experimental Section

Diphenylhexatriene was obtained from Aldrich Chemical Co. and was purified by means of repeated recrystallization followed by vacuum distillation. The melting point of the sample crystal was 120−122 °C, in good agreement with that of the all-trans isomer. Further, the absence of any impurity emission from a 77 K solution and verification that the fluorescence and excitation spectra in a glassy matrix at 77 K 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 was used as a buffer gas without purification, after we confirmed that it contained no impurities that emitted under the conditions of the present experiment. The details of the sampling procedures have been described in a preceding paper.[18] However, it should be noted that the amount of DPH crystal sealed in the sample cell was kept as small as possible in order to avoid interference from fluorescence of residual sample crystals and that the cells were heated to 80 °C at a background pressure of 10^{-4} Torr in order to remove a small amount of volatile impurities such as water.

Absorption spectra were measured with a Hitachi 220A spectrophotometer, and emission and excitation spectra were measured with a Spex Fluorolog fluorescence spectrophotometer. Fluorescence decay curves were measured with a pulsed laser (a Quantel YG581-30 Nd:YAG laser pumped dye laser or a Molectron UV24 N_2 laser pumped dye laser), detected using an Amperex XP 1002 photomultiplier and recorded on a Tektronix 7912AD transient digitizer. The temperature of the sample cells was controlled by a thermostated cell holder, of which the lower portion of the cell was maintained at 95 °C and the upper portion at 75 °C. The absorption spectrum of the static vapor was measured at 95 °C using a cylindrical quartz cell with a path length of 100 mm. Digital data were analyzed with a Macintosh Quadra 650 computer.

Results and Discussion

To facilitate the following discussion, the spectroscopic data of DPH vapor are reproduced in Figure 1, which are essentially the same as those shown in a previous paper.[18] As is seen in Figure 1, the fluorescence spectrum of pure DPH shows a red shift and broadens with increasing the excitation energy. The fluorescence spectrum tends to be somewhat structured as the buffer gas pressure is increased, with the spectral shape corresponding closely to that in solution. Further, the excitation intensity at the blue portion decreases significantly with

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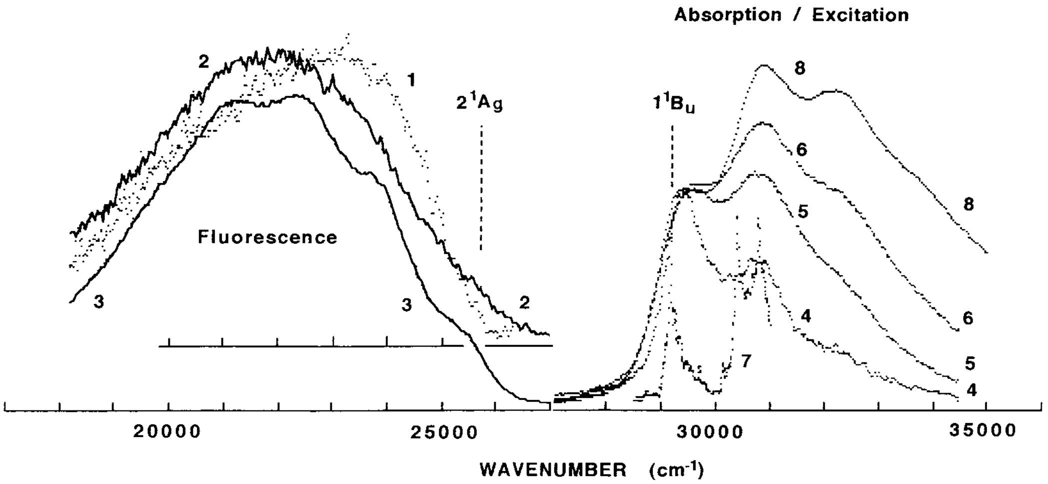

Figure 1. Fluorescence (spectra 1−3), fluorescence excitation (spectra 4−7), and absorption spectra (spectrum 8) of DPH vapor. Pressures of added perfluorohexane are 0 Torr for spectra 1, 2, and 4, 19 Torr for spectrum 5, and 104 Torr for spectra 3 and 6. The excitation wavelengths are 360 nm for spectrum 1 and 320 nm for spectra 2 and 3. Jet spectrum 7 was reproduced from the data used in ref 20. The highest intensities of the fluorescence spectra are normalized to a common magnitude, and the absorption and excitation spectra of the static vapor are normalized at the 1^1B_u origin.

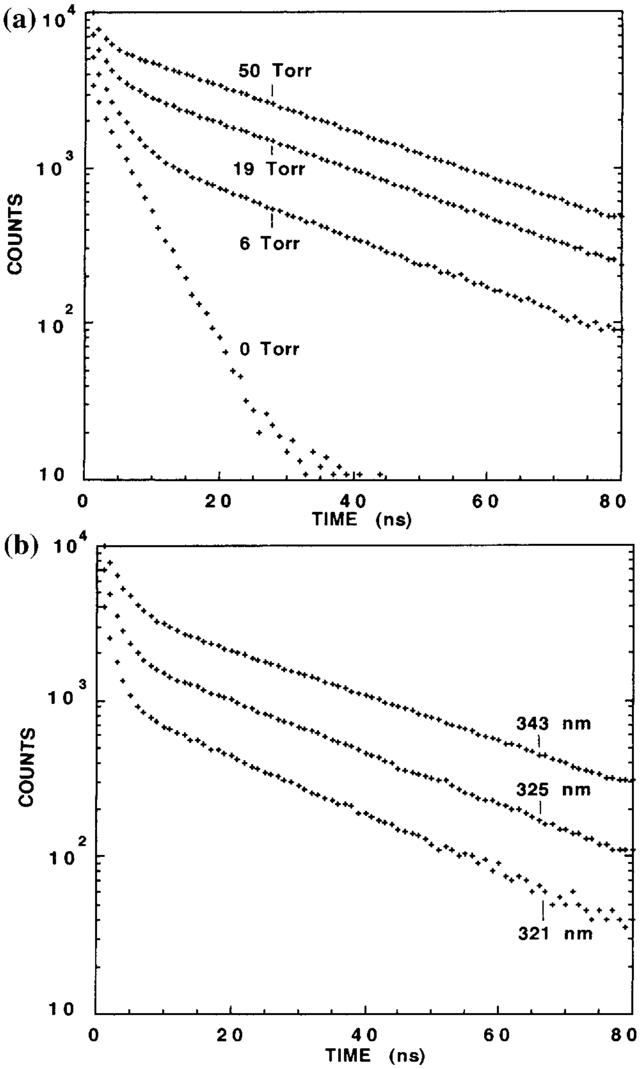

Figure 2. (a) Fluorescence decay profiles of DPH vapor at different perfluorohexane pressures, p, obtained by the excitation at 337.1 nm (1^1B_u excitation region). From upper to lower curves, the pressure is 0, 6, 19, and 50 Torr, respectively. (b) Fluorescence decay profiles of DPH vapor in the presence of 19 Torr perfluorohexane, obtained by the excitation at different wavelengths. From upper to lower curves, the wavelengths are 343 (1^1B_u origin), 325, and 321 nm, respectively.

decreasing the pressure. These spectral changes indicate that at low pressure the fluorescence originates from the unrelaxed vibronic levels of 2^1A_g and that the fluorescence from the relaxed levels increases as the pressure is increased. Figure 1 shows also that at low pressure the fluorescence quantum yield decreases with increasing the excitation energy. By reference to the 1^1B_u optical density of DPH vapor at 95 °C, together with the reported extinction coefficient in the vapor phase ($\sim 3 \times 10^4$ L cm^{-1} mol^{-1} at the 1^1B_u absorption maximum),[20] the vapor pressure of pure DPH under the present experimental conditions is estimated to be about 10^{-2} Torr. The collision interval of pure DPH molecules at this pressure is estimated to be about 10^{-5} s, which is significantly longer than the observed fluorescence lifetime (vide infra). Hence, we can safely say that DPH molecules without buffer gas are free from collisions during the lifetime of the excited 2^1A_g state.

Figure 2a shows the decay profiles of DPH static vapor at different perfluorohexane pressures obtained by the excitation at 337.1 nm (the 1^1B_u excitation region). The decay profile of pure DPH is nearly a single exponential with a lifetime of 4 ± 0.5 ns, but as the pressure is increased, it deviates from the single-exponential curve. As the pressure is further increased, the decay profile again turns out to be a single exponential showing a longer lifetime (~28 ns). At a perfluorohexane pressure above about 100 Torr, all the observed decays are identified as almost single exponential. In light of the pressure and excitation energy dependence of the fluorescence and fluorescence excitation spectra displayed in Figure 1, one can recognize that the observed nonexponential decay curves are due to the superposition of the fluorescence from the different vibronic levels in 2^1Ag, with the lifetimes of the upper levels being shorter.

The decay profiles of DPH vapor in the presence of 19 Torr perfluorohexane obtained by the excitation at different energies are displayed in Figure 2b. The decay curves obtained by the excitation into the 1^1B_u state are all nonexponential, and the lifetimes of both the fast and slow components tend to be shortened as the excitation energy is increased. The fluorescence lifetime of the supersonic jet expansion is reported to be 90.7 ns at the 2^1A_g origin and decreases to 39.1 ns with increasing excitation energy to 5029 cm^{-1} from the apparent 2^1A_g origin (25 742 cm^{-1}).[19,20] Obviously, the lifetime of the 2^1A_g state at

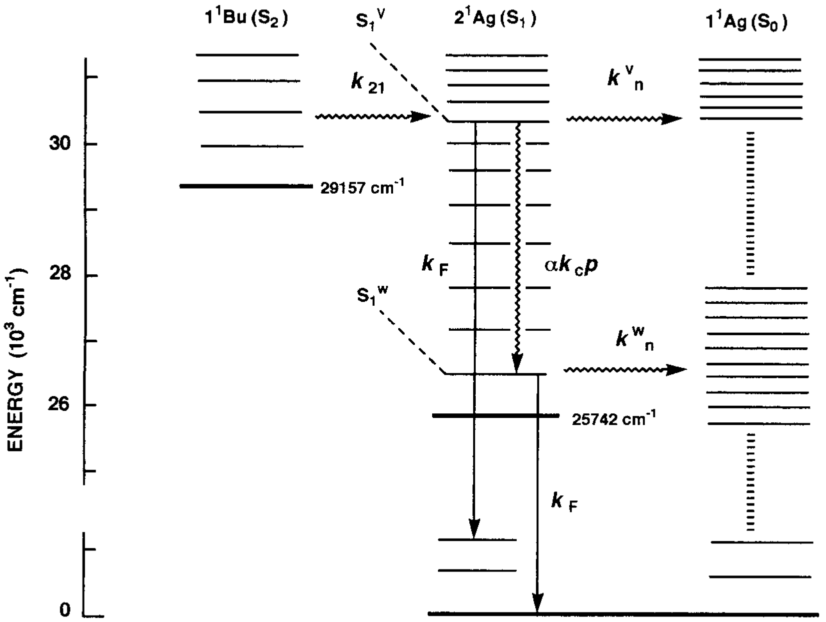

Figure 3. Kinetic scheme and the rate constants for the electronic relaxation processes in DPH vapor.

a particular excitation energy is shorter for the static vapor than for the supersonic jet. Further, the fluorescence lifetime as well as the quantum yield of the static vapor decreases more rapidly than that of the supersonic jet with increasing the excitation energy.[18−20] These observations can be attributed to the existence of thermally activated nonradiative processes from 2^1A_g for the static vapor.

In the following treatment, to a first approximation, the observed decay curves will be tentatively analyzed as being double exponential. In fact, the decay curves fitted by two exponential functions are in good agreement with the observed ones. Of course, it is possible to analyze them with triple- or multiexponential decays, but in such an analysis the accuracy of the obtained parameters may decrease. Thus, the observed decay profiles are approximately given by

$$I_F(t) = I_F^{\text{fast}} \exp(-t/\tau_F^{\text{fast}}) + I_F^{\text{slow}} \exp(-t/\tau_F^{\text{slow}}) \quad (1)$$

where I_F^{fast} and I_F^{slow} are, respectively, preexponential factors for the fast and slow decay components, with τ_F^{fast} and τ_F^{slow} the corresponding lifetimes.

The relaxation model that interprets the observed decay is illustrated in Figure 3. In this simplified model the fluorescence quantum yields for the fast and slow components, respectively, ϕ_F^{fast} and ϕ_F^{slow} at a particular pressure p of the buffer gas, are given by

$$\phi_F^{\text{fast}} = \frac{k_F}{k_F + k_n^{\,v} + \alpha k_c p} \quad (2a)$$

$$\phi_F^{\text{slow}} = \frac{k_F}{k_F + k_n^{\,w}} \frac{\alpha k_c p}{k_F + k_n^{\,v} + \alpha k_c p} \quad (2b)$$

where k_F and k_n are the radiative and nonradiative rate constants for $2^1A_g(S_1)$, respectively, with v and w ($v > w$) denoting the vibrational levels in 2^1A_g. $\alpha k_c p$ represents the effective first-order rate constant at a pressure p for the collisional deactivation from $S_1^{\,v}$ to lower vibrational levels $S_1^{\,w}$, with k_c denoting a bimolecular rate constant for collision and α the probability that one collision relaxes the molecule. It was shown in a previous paper that the observed fluorescence quantum yield, Φ_F, measured as a function of pressure is well reproduced by an equation that is equivalent to $\Phi_F = \phi_F^{\text{fast}} + \phi_F^{\text{slow}}$.[18]

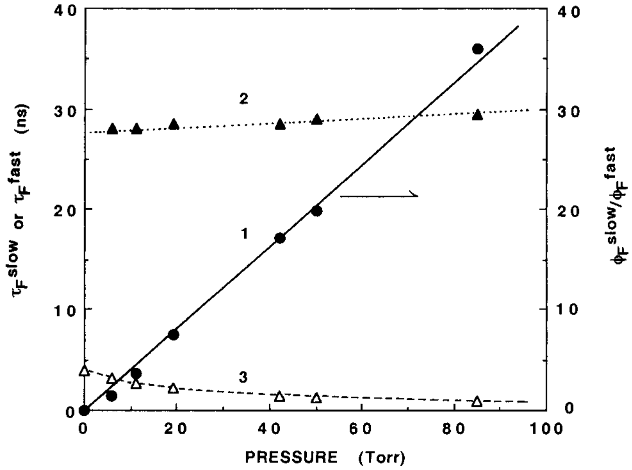

Figure 4. Plots of $\phi_F^{\text{slow}}/\phi_F^{\text{fast}}$ (curve 1), τ_F^{slow} (curve 2), and τ_F^{fast} (curve 3) for DPH vapor at different perfluorohexane pressures obtained by the excitation at 337.1 nm.

It follows from eqs 2a and 2b that

$$\frac{\phi_F^{\text{slow}}}{\phi_F^{\text{fast}}} = \frac{\alpha k_c p}{k_F + k_n^{\,w}} \quad (3)$$

where $\phi_F^{\text{slow}}/\phi_F^{\text{fast}}$ is given by $(I_F^{\text{slow}}/I_F^{\text{fast}})(\tau_F^{\text{slow}}/\tau_F^{\text{fast}})$, which is obtained from the fitted parameters. The decay data analyzed on the basis of eq 3 are shown in Figure 4. The plots of $\phi_F^{\text{slow}}/\phi_F^{\text{fast}}$ against p give a straight line passing through the origin, as may be expected from eq 3. From the slope of the straight line (=0.4 Torr^{-1}), together with the relation $\tau_F^{\text{slow}} = 1/(k_F + k_n^{\,w})$, the value for αk_c is evaluated to be 1.4×10^7 Torr^{-1} s^{-1}. This value is in surprisingly good agreement with 1.3×10^7 Torr^{-1} s^{-1}, which is estimated on the basis of the hard sphere model, assuming the average molecular diameters of DPH and perfluorohexane are 7.6 and 4.8 Å, respectively.[21] This indicates that α is near unity for the excitation at 337.1 nm.

The values for τ_F^{fast} and τ_F^{slow} as well as $\phi_F^{\text{slow}}/\phi_F^{\text{fast}}$ for DPH vapor in the presence of 19 Torr of perfluorohaxane, obtained

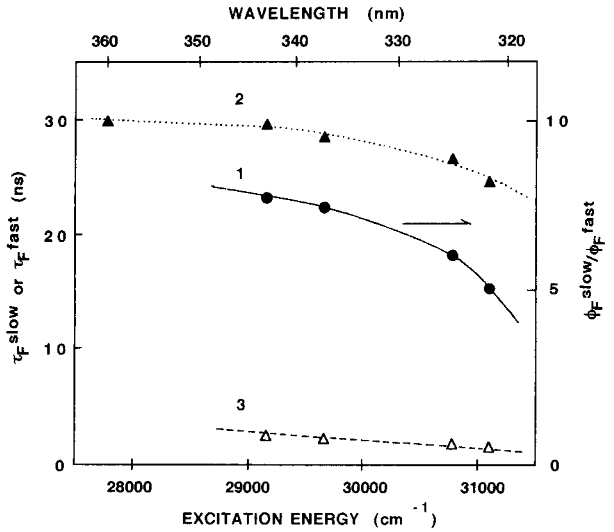

Figure 5. Plots of $\phi_F{}^{slow}/\phi_F{}^{fast}$ (curve 1), $\tau_F{}^{slow}$ (curve 2), and $\tau_F{}^{fast}$ (curve 3) at different excitation energies for DPH vapor in the presence of 19 Torr perfluorohaxane.

by excitation at different wavelengths, are plotted in Figure 5. The lifetime of the slow component measured as a function of the excitation energy shortens slightly at about 5000 cm^{-1} from the 2^1A_g origin. This indicates that highly excited DPH molecules are not totally relaxed to vibratinal levels near the 2^1A_g origin at 19 Torr. Further, since the value for $\phi_F{}^{slow}/\phi_F{}^{fast}$ at a particular pressure is proportional to $\alpha k_c/(k_F + k_n{}^w)$ (cf. eq 3), the change in this value corresponds to that in α. The results in Figure 5 show that the α value decreases with increasing the excitation energy. Referring to the αk_c value obtained from the plots in Figure 4, we obtain the apparent value for α, which changes from 1.1 to 0.7 as the excitation energy is increased from 3400 to 5400 cm^{-1} from the 2^1A_g origin. Perhaps the nonexponential fluorescence behavior of DPH vapor may serve as a method for evaluating the collisiomal efficiency of various buffer gases.

Conclusions

Nonexponential decay of the $2^1A_g(S_1) \rightarrow 1^1A_g(S_0)$ fluorescence observed for 1,6-diphenyl-1,3,5-hexatriene (DPH) vapor is shown to be induced by intermolecular collisions with perfluorohexane used as a buffer gas and is interpreted in terms of a simple two-level scheme in the 2^1A_g manifold. The influence of collisions on vibrational relaxation in the 2^1A_g manifold has been analyzed to evaluate the collision efficiency on the vibrational relaxation. The ineffectiveness of the collisional deactivation of DPH by perfluorohexane at higher excitation energies is demonstrated from the analyses of the decay profiles.

Acknowledgment. This paper is dedicated to the late Professor Bryan E. Kohler on the occasion of a quarter-century anniversary since the discovery of the 2^1A_g state of linear polyenes.

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