Electronic relaxation processes of *all-trans*-2,4,6,8-decatetraene vapor revealed by the measurements of the S_1 and S_2 fluorescence

TAKAO ITOH

Graduate School of Integrated Arts and Sciences, Hiroshima University,

1-7-1 Kagamiyama, Higashi-Hiroshima City, 739-8521 Japan

E-mail*:* titoh@hiroshima-u.ac.jp

Abstract

Fluorescence and excitation spectra of *all-trans*-2,4,6,8-decatetraene vapor have been measured at different buffer gas pressures from 0 to 1.07×10^5 Pa (800 Torr). The quantum yield of the S_1 fluorescence ($\Phi_F(S_1)$) increases with increasing the buffer gas pressure, while that of the S_2 fluorescence ($\Phi_F(S_2)$) decreases slightly. $\Phi_F(S_1)$ decreases significantly with increasing the excitation energy under the collision free condition, while $\Phi_F(S_2)$ decreases only slightly. The pressure dependence of the fluorescence yields is interpreted in terms of the relaxation model involving the reversible internal conversion between S_1 and S_2 and the vibrational relaxation in the S_1 manifold. The reverse $S_1 \rightarrow S_2$ internal conversion rate is shown to be significantly slow as compared with the forward $S_2 \rightarrow S_1$ internal conversion rate.

Keywords: decatetraene vapor; excited states; S_2 fluorescence; electronic relaxation

1. Introduction

Linear conjugated polyenes have been the subject of a number of spectroscopic investigations, because such studies advance our understanding of not only polyene electronic structure but also the connection between that structure and the electronic relaxation processes [1 - 3]. It is now well-known for unsubstituted polyenes with the polyene double bond number from 3 to 8, that the lowest energy excited singlet state, S_1, is 2^1Ag and that the second excited state, S_2 is 1^1Bu [4 - 9]. In order to obtain a deeper insight into the photophysical processes of linear polyenes, it is of importance to investigate the emission property in the vapor phase where the molecules are not influenced by the environment.

A number of studies have been carried out for the spectroscopy of octatetraene and methyl-substituted octatetraene in the vapor phase and in solution [10-17]. Gavin et al. have measured the absorption and emission spectra of octatetraene along with fluorescence quantum yields and lifetimes in solution and in the static vapor phase [10]. They observed the fluorescence from the 1^1Bu and 2^1Ag states in solution, but observed only the 1^1Bu fluorescence in the vapor phase. Heimbrook et al. measured the emission and excitation spectra of octatetraene in a supersonic jet expansion and assigned the emission as the fluorescence from the $S_2(1^1Bu)$ state [11]. Bouwman et al. reported later the emission spectra of octatetraene and its methyl-substituted octatetraene in the static vapor phase and observed the structured $S_2(1^1Bu)$ fluorescence and the broad $S_1(2^1Ag)$ fluorescence [12]. More recently, Petek et al. reported the similar emission property for methyl-substituted octatetraene vapor in supersonic

molecular beams [13].   The emission properties of octatetraenes reported so far are summarized as follows: In the case of octatetraene, the emission consists mostly of the $S_2(1^1Bu)$ fluorescence accompanied by the weak $S_1(2^1Ag)$ fluorescence in the static vapor phase and in a jet, but in the condensed phases the emission consists solely of the 2^1Ag fluorescence.   In the case of decatetraene, the emission consists of the $S_2(1^1Bu)$ fluorescence accompanied by the $S_1(2^1Ag)$ fluorescence in the vapor phase including supersonic jet condition, while in the condensed phases it consists mostly of the 2^1Ag fluorescence.

Why the S_2 fluorescence is absent or extremely weak in the condensed phases for octatetraene and decatetraene?   In order to elucidate the emission property of octatetraene and its analogues, it is of importance to link the photophysics in the vapor and condensed phases.   In the vapor phase at low pressure, normally the molecules suffer no collisions during the lifetime of the excited states, while in the condensed phases the molecules are relaxed eventually to the lower vibrational levels of the lowest excited states.

In the present work, the fluorescence spectrum of decatetraene $(CH_3-(CH=CH)_4-CH_3)$ vapor has been measured at different buffer gas pressures from 0 up to 1.07×10^5 Pa (~ 800 Torr) and with different excitation energies along with the excitation spectrum.   It is shown that the S_1 and S_2 fluorescence of decatetraene in the static vapor phase originate from the unrelaxed excited levels at low pressure, while a part of the S_1 fluorescence originates from the relaxed levels at elevated pressures.   It is also shown that the quantum yields of both the S_1 and S_2 fluorescence are in the order

of 10^{-5} and that the former yield increases with increasing the buffer gas pressure, while the latter yield decreases slightly.   The S_1 fluorescence quantum yield in the collision free condition is found to decrease significantly with increasing the excitation energy, while the S_2 fluorescence yield decreases only slightly.   The pressure dependence of the observed fluorescence quantum yields is interpreted in terms of the relaxation model involving the reversible internal conversion between the S_1 and S_2 states and the vibrational relaxation in the S_1 manifold.   It is shown that the reverse $S_1 \rightarrow S_2$ internal conversion rate is significantly slow as compared with the forward internal $S_2 \rightarrow S_1$ conversion rate.

2. Experimental

2.1 Materials and Sample Preparation.   *All-trans*-decatetraene was prepared by means of the Witting reaction between hexadienal and crotyltriphenylphosphonium bromide [13].   The product was purified by passing through a silica-gel column using pentane as an eluent followed by the recrystallization at 0 °C from pentane.   This procedure was repeated twice and finally recrystallized from pentane.   The white solid thus obtained was stored in a vial at -5 °C under the dark after being filled by nitrogen gas.   The first strong absorption band of decatetraene in hexane is observed at 310 nm and the emission starts from 350 nm, showing the emission maximum near 420 nm. The absence of any impurity absorption and emission in hexane at room temperature, and verification that the measured excitation spectrum in hexane agreed well with the corresponding absorption spectrum in the 230 – 350 nm region suggest that the purified

sample is sufficiently pure for the experiment.   Perfluorohexane (C_6F_{12}) obtained from Aldrich, USA and N_2 gas were used as buffer gases.

Samples were prepared on an all-glass made vacuum line equipped with a diffusion pump under the dark using the red light. C_6F_{12} sealed in a side arm was degassed by repeated freeze-pump-thaw cycles.   A small amount of sample crystal in a non-fluorescent 10-mm square quartz cell was also degassed by repeated freeze-pump-thaw cycles at a background pressure of less than 0.013 Pa (10^{-4} Torr). C_6F_{12} used as a buffer gas was admitted into the sample cell after degassing.   The pressure of C_6F_{12} was controlled by the temperature of the side arm varied from –25 to –5 °C.   The sample cell with buffer gas was then isolated from C_6F_{12} reservoir, the contents were trapped by liquid nitrogen, and the cell was sealed off.   By measuring the pressure and volume of C_6F_{12} gas before trapping and by measuring the volume of the cell at the end of the experiment, we estimated the buffer gas pressure.   Similar procedure was carried out for adding N_2 gas to the sample for which the N_2 pressure was measured by a Hg gauge before the cell was sealed off.

The sample pressures were always kept blow the saturation pressures at the temperatures used in the present study.   Since the vapor samples were found to be extremely unstable upon photon irradiation, all the measurements were carried out only once for each fresh sample just after the preparation.   In particular, the samples of decatetraene vapor without the buffer gas are found to degrade rapidly upon irradiation. Thus, each emission spectral measurements were carried out within 10 min.   It was confirmed that the absorption spectra measured before and after the emission

measurement did not change throughout the experiment.

2.2 Measurements. Emission and excitation spectra were measured with a Spex Fluorolog-3 (Model 21-SS) spectrophotometer, equipped with a double-grating excitation monochromator, a high-pressure 450-W Xenon lamp as an excitation-light source, and a photomultiplier tube (Hamamatsu R928-P) in an electric-cooled housing operated in photon-counting mode. For most of the emission measurement square 10-mm path length quartz cells were used. Two reflecting mirrors were placed beside the sample cell so as to intensify the emission signal [18]. Absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer. Temperature of the sample cells was controlled by thermostated cell holders. In the emission measurements the temperature of the lower portion of the cell was always kept higher than that of the upper portion by about 5 °C and was measured with a digital thermometer. Background and scattered light were subtracted from the measured spectra. Fluorescence spectra were corrected for the spectral sensitivity of the detection system by comparing the measured spectrum with the real spectrum using β-naphthol in acetic acid- sodium acetate buffer solution as the standard. Excitation spectra were corrected for the spectral intensity distribution of the exciting light with an aqueous solution of rhodamine B as a quantum counter. Emission quantum yields were determined by comparing the corrected emission spectrum of the sample with that of quinine in sulfuric acid used as a quantum counter, which is assumed to have a fluorescence quantum yield of 0.51.

3. Results and discussion

Figure 1 shows the emission spectra of pure decatetraene vapor at 35 °C obtained by excitation at different wavelengths. It is seen that the relative S_2/S_1 fluorescence intensity ratio increases with increasing the excitation energy. Further, the maximum of the broad S_1 fluorescence shift to the red as the excitation energy is increased and that the spectral shape of the S_2 fluorescence changes with varying the excitation energy: It is seen that the S_1 (2^1A_g) fluorescence maximum shifts from about 25000 cm^{-1} for excitation at 31250 cm^{-1} (320 nm) to 22000 cm^{-1} for excitation at 37740 cm^{-1} (265 nm). The observed spectral feature shows that the fluorescence originates from the unrelaxed levels. The red shift of the S_1 fluorescence upon increasing the excitation energy indicates that the fluorescence emission occurs through the transition from the high vibronic levels of S_1 to those of S_0. In light of the boiling point (199.7 °C) and the vapor pressure at 25 °C (63.33 Pa) of decatetraene obtained from registry data in Science Finder Scholar 2007, the vapor pressure at 35 °C is estimated to be about 93.3 Pa (0.7 Torr). The total fluorescence quantum yield (the sum of the quantum yields of the S_1 and S_2 fluorescence) of pure decatetraene vapor at 35 °C in the absence of the buffer gas was evaluated to be 1.3 × 10^{-4}, and each of the S_1 and S_2 fluorescence quantum yields to be in the order of 10^{-5}. Based on the molar extinction coefficient of the S_2 absorption band in hexane at room temperature (ε_{max} at 296 nm = 112000), the intrinsic radiative lifetime of the S_2 state, τ_{F2}^0, is evaluated to be 5.0 × 10^{-10} s. Further, the intrinsic radiative lifetime of S_1, τ_{F1}^0, is reported to be 500 ns [13]. Therefore, if we assume the bimolecular collision rate of about 7.5 × 10^4 s^{-1} Pa^{-1} (1 × 10^7 s^{-1} $Torr^{-1}$),

then pure decatetraene sample is safely regarded as being free from collisions during the lifetimes of the S_1 and S_2 states at 35 °C.

In figure 2, we show the emission spectra of decatetraene vapor in the presence and absence of N_2 as a buffer gas at 35 °C obtained by the excitation into the S_2 origin (288 nm).   One can see that the emission maximum of the broad S_1 fluorescence shifts slightly to the blue and that the relative S_1 fluorescence intensity increases with increasing the pressure: It is seen that the S_1 (2^1A_g) fluorescence maximum shifts from about 22500 cm^{-1} at 0 Pa to 23500 cm^{-1} at 106660 Pa (800 Torr).   The slight blue shift of the S_1 fluorescence with increasing pressure indicates that the molecule tends to emit from the lower vibronic levels of S_1 at elevated pressures.   The emission property at high total pressure was also investigated at different excitation energies (see figure 3). The spectral change similar to that shown in figure 1 is seen at high total pressure, indicating that even at 1.07×10^5 Pa (800 Torr) both of the S_1 and S_2 fluorescence originate, at least in part, from the unrelaxed levels.

Figure 4 shows the corrected excitation spectra of pure decatetraene vapor without buffer gas obtained by monitoring the S_1 and S_2 fluorescence along with the absorption spectrum.   It is seen that the intensity of the excitation spectrum of the S_1 fluorescence decreases significantly with increasing excitation energy as compared with that of the S_2 fluorescence.   This observation suggests the presence of the fast $S_1 \rightarrow S_0$ internal conversion which increases rapidly upon increasing the excitation energy. In figure 5, we show the excitation energy dependence of the S_1 and S_2 fluorescence quantum yields for pure decatetraene vapor.   These yield values are obtained by

division of the corrected excitation spectra of pure decatetraene vapor by the absorption spectrum.   Although both of the S_1 and S_2 fluorescence yields decrease with increasing the excitation energy, the decrease is not significant for the latter yield.

Fluorescence quantum yields of decatetraene vapor obtained at different pressures are plotted in figure 6 for the two-excitation energies.   No appreciable difference is observed between the C_6F_{12} and N_2 pressure dependence of the fluorescence quantum yields.   It is seen in figure 6 that the quantum yield of the S_1 fluorescence, $\Phi_F(S_1)$, increases with increasing the buffer gas pressure, while that of the S_2 fluorescence, $\Phi_F(S_2)$, is nearly constant over whole range of the pressure.

Based on the spectroscopic data and the pressure dependence of the fluorescence quantum yields, the relaxation process of decatetraene vapor can be accounted for by the kinetic model involving the reversible internal conversion between S_1 and S_2 and the vibrational relaxation in the S_1 manifold (see figure 7).   Decatetraene molecules excited into the S_2 state will be converted isoenergetically to the vibronic state of S_1 (S_1^v) through the internal conversion (with the rate constant expressed by k_i), or emits the S_2 fluorescence (k_{F2}).   The molecules in the vibrational levels in the S_1 state (S_1^v) formed as the result of the $S_2 \rightarrow S_1$ internal conversion will be relaxed to the lower vibrational levels in the S_1 state (S_1^0) through the collisional deactivation (k_Cp), converted to the ground state through the $S_1^v \rightarrow S_0$ internal conversion (k_x), or emit the S_1 fluorescence (k_{F1}), with k_C and p denoting the bimolecular rate constant for collision and buffer gas pressure, respectively.   Here, the internal conversion from S_1^v to S_0 implicitly involves the photochemical decomposition from S_1^v including the

isomerization process.　　It is also possible to consider the reverse internal conversion to S_2 from S_1^v (k_r).　　Finally, the molecules relaxed to the lower vibrational levels in S_1 (S_1^0) will be converted to S_0 (k_x^0) or emit the S_1 fluorescence (k_{F1}).

　　　On the basis of the relaxation model illustrated in figure 7, the fluorescence quantum yields obtained by the excitation into the S_2 state are expressed in the forms,

$$\Phi_F(S_1) = k_{F1}k_i \, [1 + k_Cp/(k_{F1} + k_x^0)]/[K(k_{F1} + k_Cp + k_x + k_r)] \qquad (1)$$

$$\Phi_F(S_2) = k_{F2}/K, \qquad (2)$$

where $K = k_{F2} + k_i(k_{F1} + k_Cp + k_x)/(k_{F1} + k_Cp + k_x + k_r)$.

In equation 1, the first term, $k_{F1}k_i \, /[K(k_{F1} + k_Cp + k_x + k_r)]$, corresponds the contribution from the unrelaxed S_1 state, while the second term is the one from the relaxed S_1 state (S_1^0).　　It follows from equations 1 and 2 that

$$\Phi_F(S_1)/ \, \Phi_F(S_2) = (k_{F1}/k_{F2}) \times k_i \times [1 + k_Cp/(k_{F1} + k_x^0)]/(k_{F1} + k_Cp + k_x + k_r) \qquad (3)$$

As was mentioned, the value for k_{F1} is reported to be 2×10^6 s^{-1} ($\tau_{F1}^0 = 500$ ns) and the intrinsic radiative lifetime of the S_2 state τ_{F2}^0 ($= 1/k_{F2}$) is evaluated to be 5×10^{-10} s, which leads the ratio k_{F1}/k_{F2} of about 1×10^{-3}.

　　　In the case of the excitation into the S_2 origin at 34720 cm^{-1} (288 nm) we obtain $k_i/(k_{F1} + k_x + k_r) = 2.0 \times 10^3$, since the value for $\Phi_F(S_1)/\Phi_F(S_2)$ at zero pressure is near 2.0.　　Based on the $\Phi_F(S_2)$ value at $p \approx 0$ Pa ($\approx 4.5 \times 10^{-5}$), the K value at zero pressure is obtained to be 4.4×10^{13} s^{-1}.　　Further, since the K value at zero pressure is expressed approximately by $K \approx k_{F2} + k_i(k_{F1} + k_x)/(k_{F1} + k_x + k_r)$, we obtain $k_i(k_{F1} + k_x)/(k_{F1} + k_x + k_r) \approx 4.4 \times 10^{13}$ s^{-1}.　　Thus, the value for $k_{F1} + k_x$ ($\approx k_x$) is evaluated to be 2.2×10^{10} s^{-1}. By varying the parameters k_i, k_r, and k_x^0 under the condition $k_i > 4.4 \times 10^{13}$ s^{-1}, along

with the assumption $k_C \approx 7.5 \times 10^4$ s^{-1} Pa^{-1} (10^7 s^{-1} Torr^{-1}), the observed $\Phi_F(S_1)$ and

$\Phi_F(S_2)$ values obtained as a function of buffer gas pressure (p) were fitted by the

equations (1), (2) and (3) to obtain the best fitted parameters. The k_i, k_r and k_x^0 values

thus obtained are 6.2×10^{13}, 8.8×10^9 and 8.7×10^9 s^{-1}, respectively, in the case of

excitation into the S_2 origin. In the same way, the values for k_i, k_r and k_x are obtained

to be 5.8×10^{13}, $\sim 2 \times 10^9$ and 3.7×10^{10} s^{-1}, respectively, in the case of the excitation at

36360 cm^{-1} (275 nm). The radiative and nonradiative rate constants thus evaluated are

summarized in Table 1. Although k_r tends to decrease with increasing the excitation

energy, k_i does not show a significant change against the excitation energy.

In light of the relative magnitudes among the rate constants, the value for

$\Phi_F(S_1)/\Phi_F(S_2)$ at zero pressure is now expressed approximately by

$$\Phi_F(S_1)/\Phi_F(S_2) \approx (k_{F1}/k_{F2}) \times k_i /(k_x + k_r) \qquad (4)$$

Since k_{F1} and k_{F2} are the intrinsic radiative rate constants, the quantum yield ratio in

equation 4 corresponds to the ratio $k_i/(k_x + k_r)$. As is seen in figure 5, the quantum

yield ratio $\Phi_F(S_1)/\Phi_F(S_2)$ shows a monotonous decrease with increasing the excitation

energy. This suggests that the value for $k_i/(k_x + k_r)$ also changes against the excitation

energy in the same way as the $\Phi_F(S_1)/\Phi_F(S_2)$ value. Since the k_r value tends to

decrease with increasing the excitation energy (Table 1), the decrease of the $k_i/(k_x + k_r)$

value is probably brought by the increase of the k_x value with increasing the excitation

energy. Further, the present analyses show that the reverse $S_1 \rightarrow S_2$ internal

conversion rate is significantly slow as compared with the forward internal conversion

rate.

In the condensed phases, the S_1 fluorescence quantum yield is in the order of 10^{-1}, suggesting that the k_x and k_x^0 values are much smaller than those in the vapor phase. Further, in the condensed phases the value corresponding to $k_C p$ is considered to be larger than that in the vapor phase. Therefore, it is not unreasonable to detect only the S_1 fluorescence in the condensed phases, where the quantum yield of the S_1 fluorescence is as high as 0.1 and that of the S_2 fluorescence is as low as 10^{-5}.

4. Conclusions

The S_1 and S_2 fluorescence of decatetraene vapor are shown to originate from the unrelaxed excited levels at low pressure, while a part of the S_1 fluorescence originates from the relaxed levels at elevated pressures. The quantum yields of both the S_1 and S_2 fluorescence are in the order of 10^{-5} and the former yield increases with increasing the buffer gas pressure, while the latter yield decreases only slightly. The S_1 fluorescence quantum yield in the collision free condition decreases significantly with increasing the excitation energy, while the S_2 fluorescence yield decreases slightly. The pressure dependence of the observed fluorescence quantum yields is interpreted in terms of the relaxation scheme involving the reversible internal conversion between the S_1 and S_2 states and the vibrational relaxation in the S_1 manifold. The reverse $S_1 \rightarrow S_2$ internal conversion rate is shown to be significantly slow as compared with the forward internal conversion rate. Absence of the S_2 fluorescence in the condensed phases is presumably due to the appearance of the intense S_1 fluorescence from the lower vibrational levels which are populated by the efficient vibrational relaxation in the

S_1 manifold. Further, the weakness of the S_2 fluorescence in the condensed phases is relating also to the fact that the oscillator strengths of S_1 relative to S_2 are comparatively large in the condensed phases due to the small S_1 - S_2 energy separation as compared with that in the vapor phase [19].

References

[1] B. S. Hudson, B. E. Kohler, J. Chem. Phys. **59**, 4984 (1973).

[2] B. S. Hudson, B. E. Kohler, K. Schulten, Excited States **6**, 1 (1983).

[3] B. E. Kohler, Chem. Rev. **93**, 41 (1993).

[4] W. J. Buma, B. E. Kohler, K. Song, J. Chem. Phys. **92**, 4622 (1990).

[5] B. E. Kohler, C. Spangler, C. Westerfield, J. Chem. Phys. **89**, 5422 (1988).

[6] R. L. Christensen, M. G. I. Galinato, E. F. Chu, J. N. Howard, R. D. Broene, H. A. Frank, J. Phys. Chem. A **112**, 12629 (2008).

[7] J. H. Simpson, L. McLaughlin, D, S. Smith, R. L. Christensen, J. Chem. Phys. **87**, 3360 (1987).

[8] R. Snyder, E. Arvidson, C. Foote, L. Harrigan, R. L. Christensen, J. Am. Chem. Soc. **107**, 4117 (1985).

[9] K. L. D'Amico, C, Manos, R. L. Christensen, J. Am. Chem. Soc. **102**, 1777 (1980).

[10] R. M. Jr. Gavin, C. Weisman, J. K. McVey, S. A. Rice, J. Chem. Phys. **68**, 522 (1978).

[11] L. A. Heimbrook, B. E. Kohler, I. J. Levy, J. Chem. Phys. **81**, 1592 (1984).

[12] W. Bouwman, A. Jones, D. Phillips, P. Thibodeau, C. Friel, and R. Christensen, J.

Phys. Chem. **94**, 7429 (1990).

[13] H. Petek, A. Bell, K. Yoshihara, and R. Christensen, J. Chem. Phys. **95**, 4739 (1991).

[14] H. Petek, A. J. Bell, Y. S. Choi, K. Yoshihara, B. Tounge, and R. L. Christensen, J. Chem. Phys. **98**, 3777 (1993).

[15] H. Petek, A. J. Bell, Y. S. Choi, K. Yoshihara, B. A. Tounge, R. L. Christensen, J. Chem. Phys. **102**, 4726 (1995).

[16] J. R. Andrews, B. S. Hudson, Chem. Phys. Lett. **57**, 600 (1978).

[17] M. F. Granville, G. E. Holtom, B. E. Kohler, J. Chem. Phys. **70**, 593 (1979).

[18] T. Itoh, J. Fluores. **16**, 739 (2006).

[19] T. Itoh, J. Chem. Phys. **119**, 4516 (2003).

Figure captions:

Figure 1   Corrected fluorescence spectra of pure decatetraene vapor at 35 °C obtained by the excitation at different energies.   The S_1 (2^1A_g) fluorescence maximum shifts from about 25000 cm^{-1} for excitation at 31250 cm^{-1} (320 nm) to 22000 cm^{-1} for excitation at 37740 cm^{-1} (265 nm).

Figure 2   Corrected fluorescence spectra of decatetraene vapor in the presence and absence of 1.07×10^5 Pa (800 Torr) N_2 as a buffer gas at 35 °C obtained by the excitation into the S_2 origin at 34780 cm^{-1} (288 nm).   The S_1 (2^1A_g) fluorescence maximum shifts with increasing the pressure from about 22500 cm^{-1} at 0 Pa to 23500

cm^{-1} at 106660 Pa.

Figure 3　Corrected fluorescence spectra of decatetraene vapor in the presence of 1.07 × 10^5 Pa (800 Torr) N$_2$ at 35 °C obtained by the excitation at different energies.　The S$_1$ (2^{1}A$_g$) fluorescence maximum shifts from about 24000 cm^{-1} for excitation at 30300 cm^{-1} (330 nm) to 22000 cm^{-1} for excitation at 37740 cm^{-1} (265 nm).

Figure 4 Absorption (1) and corrected excitation spectra of pure decatetraene vapor obtained by monitoring the S$_1$ (3) and S$_2$ fluorescence (2).

Figure 5 Relative S$_1$ and S$_2$ fluorescence quantum yields plotted against the excitation energy for pure decatetraene vapor.

Figure 6　Fluorescence quantum yields (Φ_{F1} (1 and 2) and Φ_{F2} (3 and 4)) of decatetraene vapor at different C$_6$F$_{12}$ (closed circles and triangles) and N$_2$ (open circles and triangles) pressures obtained by the excitation at 34780 cm^{-1} (288 nm) (1 and 3) and 36360 cm^{-1} (275 nm) (2 and 4).　The pressure of decatetraene was kept at 93.3 Pa (0.7 Torr).

Figure 7 Relaxation scheme elucidating the emission properties of decatetraene vapor.

Table 1 The radiative and nonradiative rate constants evaluated for decatetraene vapor.

Rate constant	Excitation energy	
	34780 cm^{-1}(288 nm)	36360 cm^{-1} (275 nm)
k_{F1}	2.0×10^6 s^{-1}	2.0×10^6 s^{-1}
k_{F2}	2.0×10^9 s^{-1}	2.0×10^9 s^{-1}
k_x^0	8.7×10^9 s^{-1}	8.7×10^9 s^{-1}
k_x	8.8×10^9 s^{-1}	3.7×10^{10} s^{-1}
k_i	6.2×10^{13} s^{-1}	5.8×10^{13} s^{-1}
k_r	8.8×10^9 s^{-1}	2.0×10^9 s^{-1}

Figure 1 Corrected fluorescence spectra of pure decatetraene vapor at 35 °C obtained by the excitation at different energies. The S_1 (2^1A_g) fluorescence maximum shifts from about 25000 cm^{-1} for excitation at 31250 cm^{-1} (320 nm) to 22000 cm^{-1} for excitation at 37740 cm^{-1} (265 nm).
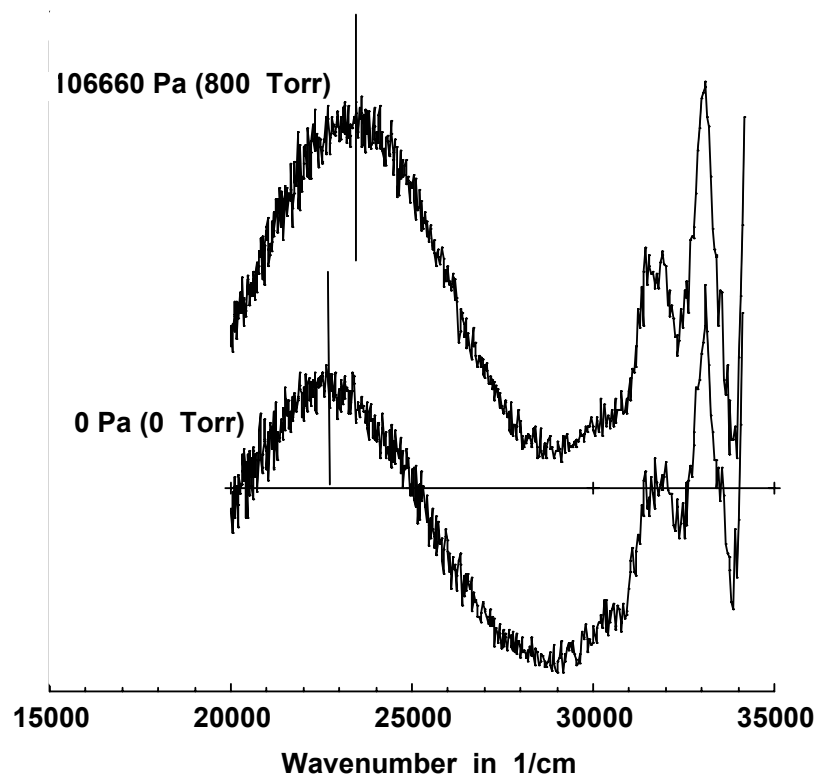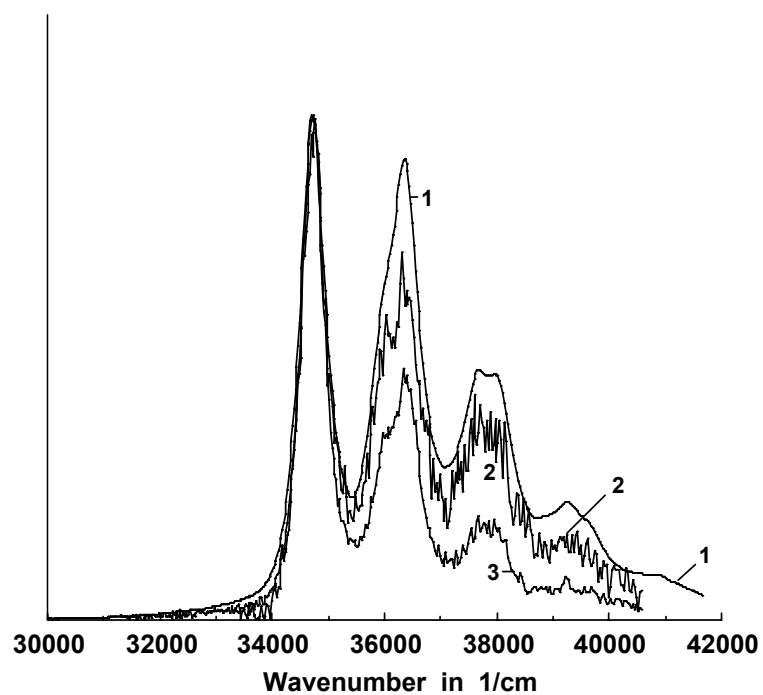
Figure 2   Corrected fluorescence spectra of decatetraene vapor in the presence and absence of 1.07×10^5 Pa (800 Torr) N_2 as a buffer gas at 35 °C obtained by the excitation into the S_2 origin at 34780 cm^{-1} (288 nm). The S_1 (2^1A_g) fluorescence maximum shifts with increasing the pressure from about 22500 cm^{-1} at 0 Pa to 23500 cm^{-1} at 106660 Pa.

Figure 3   Corrected fluorescence spectra of decatetraene vapor in the presence of 1.07 × 10^5 Pa (800 Torr) N$_2$ at 35 °C obtained by the excitation at different energies.   The S$_1$ (2^{1}A$_g$) fluorescence maximum shifts from about 24000 cm^{-1} for excitation at 30300 cm^{-1} (330 nm) to 22000 cm^{-1} for excitation at 37740 cm^{-1} (265 nm).

Figure 4   Absorption (1) and corrected excitation spectra of pure decatetraene vapor obtained by monitoring the S_1 (3) and S_2 fluorescence (2).
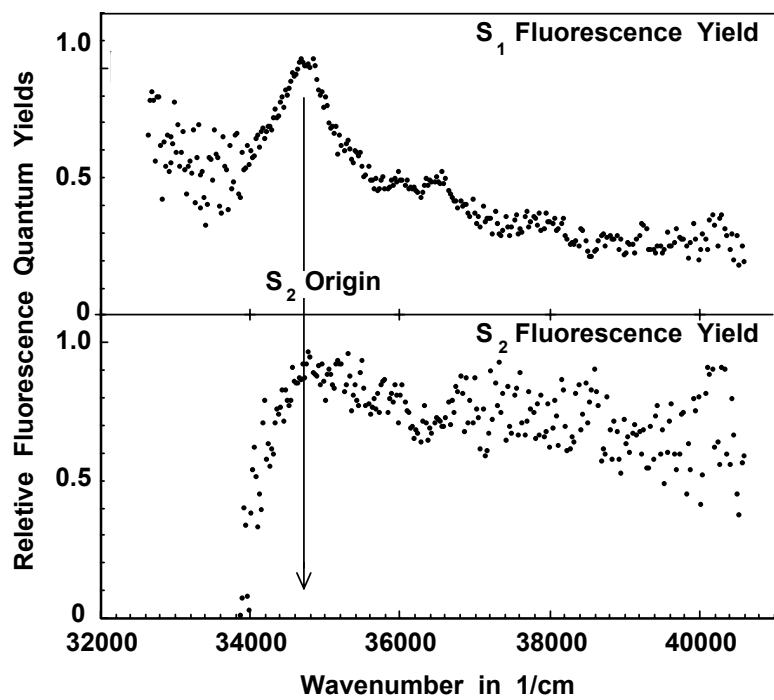
Figure 5   Relative S_1 and S_2 fluorescence quantum yields plotted against the excitation
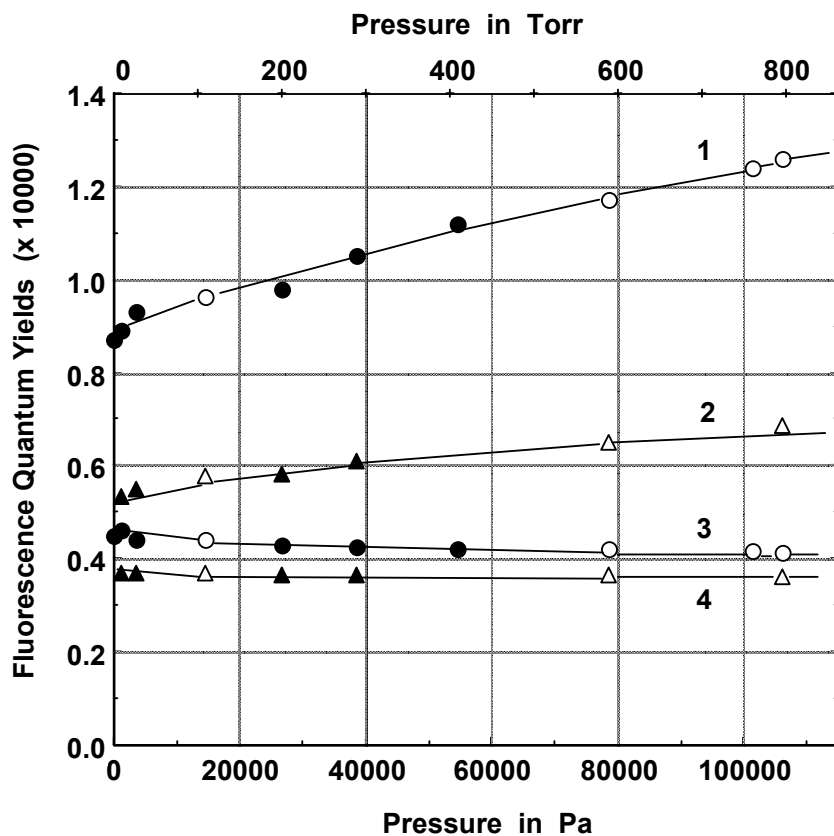
energy for pure decatetraene vapor.

Figure 6　Fluorescence quantum yields (Φ_{F1} (1 and 2) and Φ_{F2} (3 and 4)) of

decatetraene vapor at different C_6F_{12} (closed circles and triangles) and N_2 (open circles

and triangles) pressures obtained by the excitation at 34780 cm^{-1} (288 nm) (1 and 3)

and 36360 cm^{-1} (275 nm) (2 and 4).　The pressure of decatetraene was kept at 93.3 Pa
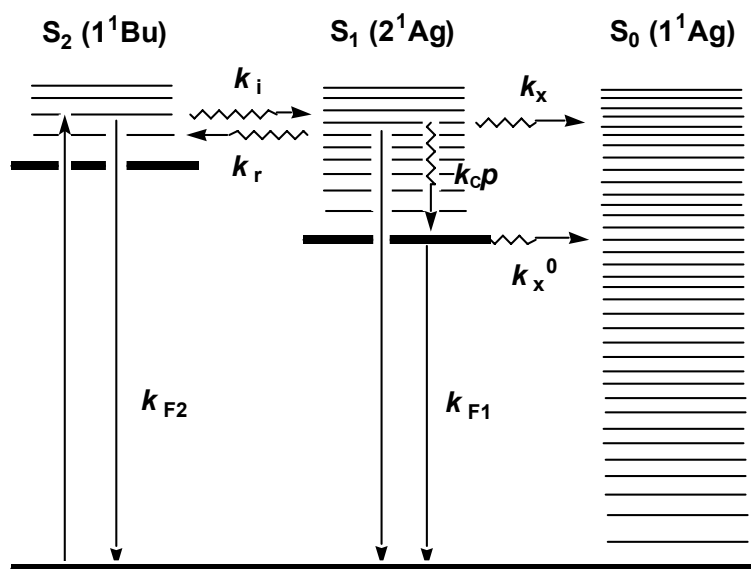
(0.7 Torr).

Figure 7   Relaxation scheme elucidating the emission properties of decatetraene vapor.