2P-011

トランス–ドデカペンタエン気体の光物理化学

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Photophysics of all-*trans*-2,4,6,8,10-dodecapataene vapor

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S_1 and S_2 fluorescence and excitation spectra of all-trans-2,4,6,8,10-dodecapataene (P5) vapor have been measured at different N_2 and O_2 gas pressures from 0 to 800 Torr with different excitation energies along with the absorption spectra. Based on the relaxation model, we were able to extracted estimates for the rates that characterize the excited-state dynamical behavior of P5 vapor.

All-trans-2,4,6,8,10-dodecapentaene (P5)
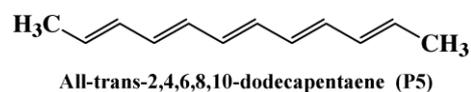
Experimental P5 was synthesized by means of Wittig reaction. The sample was chromatographed on silica gel columns and recrystallized from hexane. Only one peak was detected in HPLC measurements. The absorption and fluorescence spectra of the purified sample in solution agree well with those reported previously. The corrected excitation spectrum in hexane agreed well with the corresponding absorption spectrum. Emission and excitation spectra were measured with a Spex Fluorolog-3 spectrophotometer operated in photon-counting mode.

Results and Discussion **Fig. 1** shows fluorescence spectra of pure P5 vapor at 40 ℃ obtained by excitation at different wavelengths. The red shift of the S_1 fluorescence upon increasing the excitation energy indicates that the fluorescence occurs from the unrelaxed high vibronic levels of S_1.

Fig. 2 shows fluorescence excitation spectra of pure P5 vapor without buffer gas obtained by monitoring the S_1 and S_2 fluorescence along with the absorption spectrum. It is seen that the intensities of the excitation spectra of the S_1 and S_2 fluorescence decrease with increasing excitation energy. In the presence of 800 Torr N_2 gas, the excitation spectrum of the S_1 fluorescence agrees well with the absorption spectrum, but that of S_2 fluorescence is almost the same as the

excitation spectrum measured at low pressure. These observations suggest the presence of the fast $S_2 \rightarrow S_1$ internal conversion.
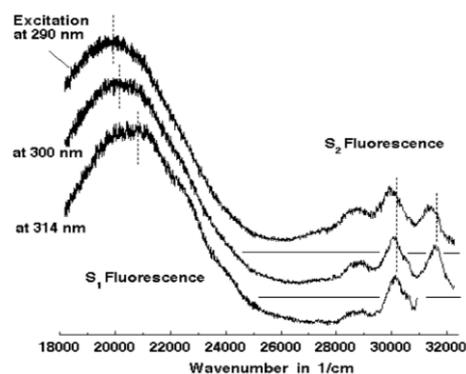
Fig. 1 Corrected fluorescence spectra of pure P5 vapor (0.1 Torr) at 40 ℃ obtained by excitation at different wavelengths. All the spectra are normalized at the highest intensity.
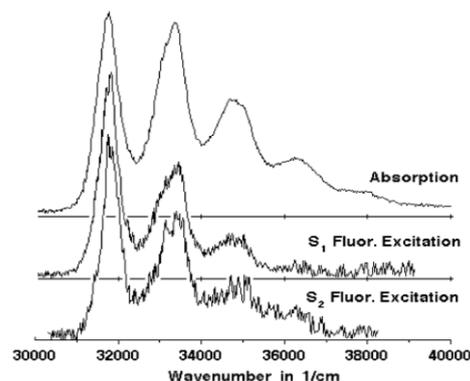
Fig. 2 Corrected fluorescence excitation spectra of pure P5 vapor at 0.1 Torr obtained by monitoring the S_1 and S_2 fluorescence and the absorption spectrum.

In **Fig. 3**, we show the excitation energy dependence of the S_1 and S_2 fluorescence quantum yields for pure P5 vapor along with that of the yield ratio Φ_{F2}/Φ_{F1}. These yield values are obtained by division of the intensity of corrected excitation spectra of pure P5 vapor by that of the absorption spectrum at each wavelength. Although both the S_1 and S_2 fluorescence yields decrease with increasing the excitation energy, the decrease is not significant for the latter yield. In the case of high pressure samples the S_1 fluorescence yield is almost constant regardless of the excitation energy, although the S_2 fluorescence

yield shows a decrease with increasing the excitation energy. The quantum yield of the S_1 fluorescence, Φ_{F1}, was found to increase with increasing N_2 pressure, while that of the S_2 fluorescence, Φ_{F2}, is nearly constant over whole range of the pressure.

Fig. 4 shows fluorescence spectra of P5 vapor in the presence of O_2 and N_2 mixed gas with different O_2 contents, where the total pressures of the buffer gas were always kept at about 800 Torr. The total pressures of the samples were always kept about 800 Torr in order to investigate the effects of added O_2 gas only on the molecules relaxed to lower vibrational levels in S_1. As is seen clearly in Fig. 4, the relative intensity of the S_1 fluorescence decreases systematically depending on the content of added O_2 gas. This observation demonstrates that the fluorescence lifetime of the S_1 state is significantly longer than that of the S_2 state.

Based on the spectroscopic data including the pressure dependence of the fluorescence quantum yields, the relaxation process of P5 vapor can be accounted for by a kinetic shown in Fig. 5. On the basis of the relaxation model illustrated in Fig. 5, the Φ_{F1} and Φ_{F2} fluorescence quantum yields obtained by the excitation into the S_2 state are expressed in the forms,

$$\Phi_{F1} = k_{F1} \times k_{21}/(k_{F2} + k_{21}) \times [1 + k_C p/(k_{F1} + k_{10}^0)]/(k_{F1} + k_{10}^v + k_C p) \quad (1)$$

$$\Phi_{F2} = k_{F2}/(k_{F2} + k_{21}), \quad (2)$$

Under the collision free condition Eq. 1 is approximated by,

$$\Phi_{F1} \cong k_{F1}/(k_{F1} + k_{10}^v) \quad (3)$$

At high total pressure in the presence of 800 Torr N_2 gas, Eq. 1 is approximated by

$$\Phi_{F1} \cong k_{F1}/(k_{F1} + k_{10}^0) \quad (4)$$

It follows from Eqs. 2 and 3 that

$$\Phi_{F2}/\Phi_{F1} = (k_{F2}/k_{F1}) \times (k_{F1} + k_{10}^v + k_C p)/[1 + k_C p/(k_{F1} + k_{10}^0)]/k_{21} \quad (5)$$

Since $k_{F1} \ll k_{10}^v$, under collision-free conditions Eq. 5 can be approximated by

$$\Phi_{F2}/\Phi_{F1} \cong k_{F2}/k_{F1} \times k_{10}^v/k_{21} \quad (6)$$

Further, since $k_{F1} \ll k_{10}^0$ and $k_{F2} \ll k_{21}$, Eqs. 2 and 3 can be approximated, respectively, by

$$\Phi_{F2} \cong k_{F2}/k_{21} \text{ and } \Phi_{F1} \cong k_{F1}/k_{10}^v \quad (7)$$

Hence, the values of Φ_{F2}/Φ_{F1}, Φ_{F2} and Φ_{F1} plotted as a function of excitation energy in Fig. 3 correspond, respectively, to the variation of k_{10}^v/k_{21}, $1/k_{21}$ and $1/k_{10}^v$ against the excitation energy. It is seen in Fig. 3 that

although the values for k_{10}^v and k_{21} increase with increasing excitation energy, the increase of k_{21} is not so significant as that of k_{10}^v.
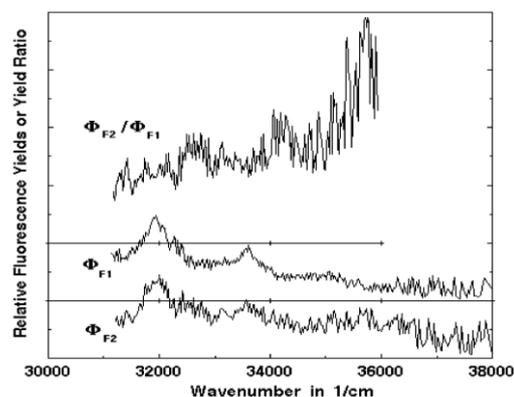
Fig. 3 Excitation energy dependence of the relative S_1 and S_2 fluorescence yields for pure P5 vapor at 0.1 Torr along with that of the yield ratio Φ_{F2}/Φ_{F1}.
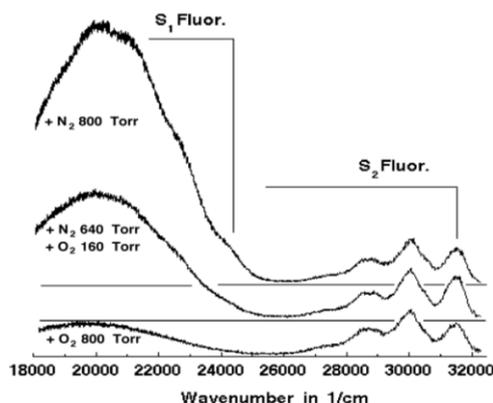
Fig. 4 Corrected fluorescence spectra of P5 vapor in the presence of added buffer gases with different O_2 contents.
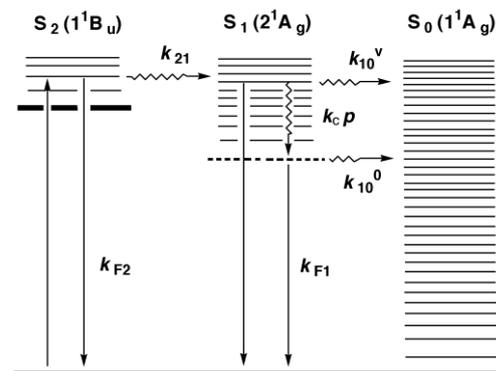
Fig. 5 Scheme showing the electronic relaxation processes of P5 vapor.

Ref. T. Itoh, *Mol. Phys.* **107** (2009) 1705.