Excitation-energy dependence of the phosphorescence quantum yields of pyridinecarboxaldehyde vapors

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A B S T R A C T

Emission and excitation spectra of 3- and 4-pyridinecarboxaldehyde vapors have been measured at different pressures down to 10^{-2} Torr. The phosphorescence quantum yield measured at low pressure as a function of excitation energy is nearly constant in the range of excitation energy corresponding to the $S_1(n, \pi^*)$ state, but it decreases abruptly at the $S_2(\pi, \pi^*)$ threshold. The onset of the abrupt decrease of the yield corresponds to the location of the S_2 absorption origin of each molecule, indicating that the nonradiative pathway depends on the type of the excited singlet state to which the molecule is initially excited. The relaxation processes are discussed based on the pressure and excitation-energy dependence of the phosphorescence quantum yield.

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1. Introduction

Organic molecules in the vapor phase often exhibit peculiar emission property which cannot be observed in the condensed phases [1]. It is known that the phosphorescence quantum yield of aromatic carbonyl compounds such as benzaldehyde and acetophenone decreases significantly with increasing the excitation energy in the vapor phase at low pressure [2–8]. Two conflicting phosphorescence behaviors are reported for benzaldehyde vapor. It is reported that the abrupt decrease of the phosphorescence quantum yield occurs near both the S_2 and S_3 thresholds [4–6]. However, it is also reported that the drop-offs of the yield is refuted as cell-wall effects and that it decreases monotonically with increasing the excitation energy [7]. It is, therefore, of interest to investigate in detail the excitation-energy dependence of the phosphorescence quantum yield of other aromatic carbonyl compounds in the vapor phase. We have treated here pyridinecarboxaldehydes (C_5NH_4—CHO, referred to as PCA) for which an N atom is included in the ring.

In previous works, we obtained the information on the energy levels of the rotational isomers in the excited and ground states for pyridinecarboxaldehyde vapors through the temperature dependence of the emission and infrared spectral measurements [9,10]. In the present work, the emission and excitation spectra of 3- and 4-pyridinecarboxaldehyde (3- and 4-PCA, respectively) have been

measured in the vapor phase in the presence of an added buffer gas at different pressures from 10^{-2} to 300 Torr. The phosphorescence quantum yields measured at low pressure as a function of excitation energy are nearly constant in the range of excitation energy corresponding to the $S_1(n, \pi^*)$ state, but the yields decrease abruptly near the $S_2(\pi, \pi^*)$ thresholds. The onset of the abrupt decrease of the yield corresponds to the location of the S_2 absorption origin of each molecule, indicating that the nonradiative pathway depends on the type of the excited singlet state to which the molecule is initially excited. The relaxation processes are discussed based on the pressure and excitation-energy dependence of the phosphorescence quantum yield.

2. Experimental

3- and 4-PCA obtained from Aldrich, USA were purified by means of trap-to-trap distillation under vacuum. The absence of any impurity emission in glassy matrix at 77 K and verification that the phosphorescence excitation spectra in the vapor phase agreed well with the corresponding absorption spectrum suggest that the purified samples were sufficiently pure for the experiment. Perfluorohexane obtained from Aldrich, USA was used as a buffer gas.

The samples were degassed by repeating freeze–thaw cycles in an all-glass made vacuum system equipped with a diffusion pump. The pressures of the sample vapors were always kept blow the saturation pressures at the temperatures employed in the present study. We have first determined the vapor pressures of the PCA samples at different temperatures by measuring the absorption intensities.

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Then, the pressures of buffer gas were determined by the temperature of the side arm reservoirs. The sample cell with buffer gas was then isolated from the reservoirs, the contents were trapped by liquid nitrogen, and the cell was sealed off. By measuring the pressure and volume of the buffer and sample gases before trapping and by measuring the volume of the cell, we determined the pressure below the saturation pressure. Vapor pressures of perfluorohexane at different temperatures were obtained from CRC Handbook of Chemistry and Physics. In this way, perfluorohexane pressures were changed from 10 to 300 Torr with keeping the pressure of 3- or 4-PCA vapor almost constant. More details of the sample preparation are described in a foregoing paper [11].

Since all the samples of PCAs are found to be unstable with respect to photon irradiation and degrade during a long-time scanning, all the measurements were carried out only once for each fresh sample just after the preparation. During the measurement, temperature of the sample cell was controlled by a thermostated cell holder. For most of the emission measurements square 10-mm path length quartz cells were used.

Absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer and the emission and excitation spectra were measured with a Spex Fluorolog-3 (Model 21-SS) spectrophotometer. The latter photometer, designed especially for the measurements of weak emission signals, is 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 to detect weak signals. Two reflecting mirrors were placed beside the sample cell to intensify the emission signals [12]. Excitation spectra were corrected for the spectral intensity distribution of the exciting light with an aqueous solution of rhodamine B as a quantum counter.

3. Results and discussion

Emission spectra of 3- and 4-PCA vapors studied are shown in Fig. 1. These emission consist of $T_1(n, \pi^*)$ phosphorescence accompanied by very weak $S_1(n, \pi^*)$ delayed fluorescence, showing a long progression in the C=O stretching vibration in the phosphorescence
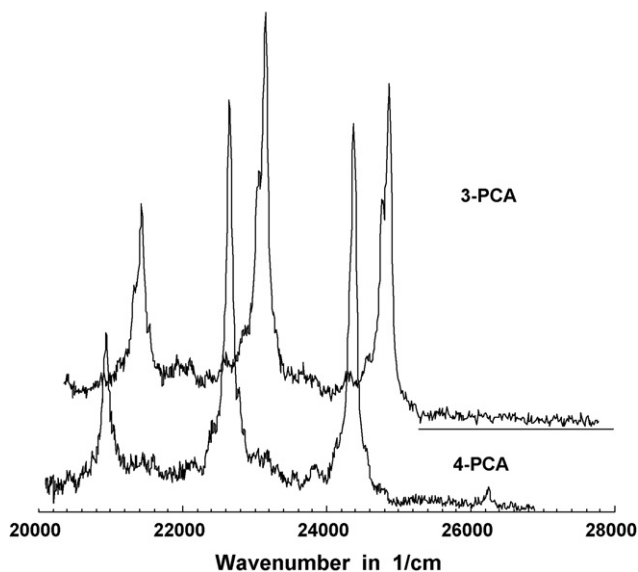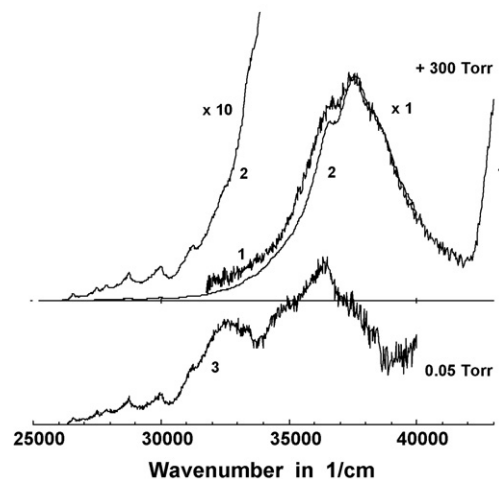
Fig. 2. Absorption (1) and corrected excitation spectra (2 and 3) of 3-PCA vapor at two different pressures.

spectra, as described in a foregoing paper [9]. Although the emission spectrum of 3-PCA vapor consists of that from two rotational isomers, the presence of the two rotational isomers does not affect the photophysical behavior of 3-PCA vapor as far as the temperature is kept constant [9]. The spectral shapes were found independent of the pressure and excitation energy, suggesting that the observed emission is originating from the relaxed T_1 state.

Figs. 2 and 3 show, respectively, the corrected phosphorescence excitation spectra of 3- and 4-PCA vapors at two different pressures. The excitation (or absorption) spectra of these vapors consist of the weak $S_1(n, \pi^*)$ bands starting from about 26,000 cm^{-1} and strong $S_2(\pi, \pi^*)$ bands starting from about 35,000 cm^{-1}. In the presence of high-pressure perfluorohexane as a buffer gas, the excitation spectrum agrees with the corresponding absorption spectrum. It is assumed, therefore, that the corrected excitation spectrum at high total pressure can be used as the substitute for the vapor-phase absorption spectrum. In the case of low-pressure samples,
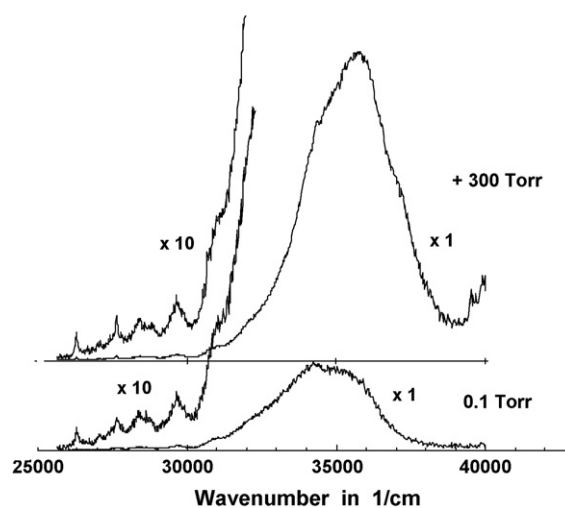
Fig. 1. Emission spectra of 3- and 4-PCA vapors in the presence of 280 Torr perfluorohexane at room temperature.

Fig. 3. Corrected excitation spectra of 4-PCA vapor at two different pressures.

the intensities of the corrected excitation spectra are markedly low in the $S_0 \rightarrow S_2$ region, as compared with those of the absorption spectra.

In Fig. 4, relative phosphorescence quantum yields are shown as a function of the excitation energy for pure PCA vapors at low pressure. These yields were obtained from the comparison of the intensities of corrected excitation spectra at high total pressure with that at low pressure. It should be emphasized that although the phosphorescence quantum yields, Φ_P, are almost constant in the whole range of the excitation energy corresponding to the S_1 state, they undergo an abrupt decrease when the excitation energy is raised to the value corresponding to the S_2 state. Further, the onset of the abrupt decrease of the yield corresponds to the location of the apparent S_2 absorption origin of each molecule. The first S_2 absorption bands of 3- and 4-PCA vapors are observed, respectively, at about 36,500 and 34,400 cm^{-1} and there is about 2000 cm^{-1} difference between the onsets of the S_2 absorption bands. There is also about 2000 cm^{-1} difference between the onsets of the abrupt decrease of the phosphorescence quantum yields. This indicates that the nonradiative pathway depends on the type of the excited singlet state to which the molecule is initially excited. The difference between the locations of the onset of the abrupt decrease of the yield and the apparent S_2 absorption origin is most presumably caused by the presence of the Boltzmann distribution. The mean free path of PCA molecules at 10^{-2} Torr is estimated to be about 10^{-1} cm, suggesting that the wall effect of the cell is not significant at pressures over 10^{-2} Torr.

Fig. 5 shows plots of $\Phi_P(S_2)/\Phi_P(S_1)$ against the pressure of added buffer gas, p, for PCA vapors, where the Φ_P values obtained by the excitation into the S_1 state and at the apparent origin of the S_2 absorption band are denoted by $\Phi_P(S_1)$ and $\Phi_P(S_2)$, respectively. As p is reduced, the ratio $\Phi_P(S_2)/\Phi_P(S_1)$ appears to approach a small value. The pressure dependence of the quantum yield ratio indicates that the step-like decrease of Φ_P caused by changing the excitation from $S_0 \rightarrow S_1$ to $S_0 \rightarrow S_2$ becomes more pronounced as the pressure is lowered.

The nonradiative processes of PCA vapors can be explained by the kinetic scheme shown in Fig. 6. The molecules excited into the S_1 state will be converted to the T_1 molecule through the fast

Fig. 5. Plots of $\Phi_P(S_2)/\Phi_P(S_1)$ against the pressure of added perfluorohexane, p, for 3-PCA (open circles) and 4-PCA (closed circles) vapors. Fitted values are indicated by solid curves.

intersystem crossing. The T_1 molecule formed as the result of the intersystem crossing from S_1 will be deactivated to the lower vibrational levels of T_1 through the collision with the rate $k_C p$, from which the molecule shows the phosphorescence. In the case of the excitation into the S_2 state, the conversion to the intermediate state (Im), is followed by the decomposition with the rate constant k_x at low pressure, but with increasing the pressure collisional deactivation to lower vibrational levels of T_1 competes with the decomposition. Therefore, the phosphorescence quantum yield obtained by the excitation into the S_2 state increases with increasing the pressure, although optical excitation into the S_1 state does not lead to the decomposition. In the case of benzaldehyde and acetophenone vapors, it was reported that excitation into the S_2 state lead to the decomposition to benzene and carbon monoxide and to methyl and benzoyl radicals, respectively, but excitation into the S_1 state does not lead to the decomposition [2,8]. The kinetic scheme accounts for the fact that the quantum yield ratios, $\Phi_P(S_2)/\Phi_P(S_1)$, increase with increasing pressure. As will be mentioned later in detail, the intermediate state is a long-lived state presumably with triplet character. The presence of the decomposing intermediate state of aromatic carbonyl compound vapors has been suggested
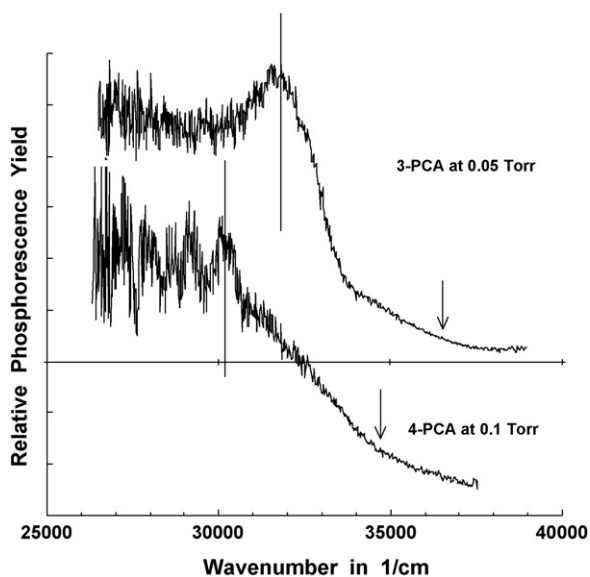

Fig. 4. Relative phosphorescence quantum yields plotted as a function of excitation energy for 3-PCA vapor at 0.05 Torr and 4-PCA vapor at 0.1 Torr. The locations of the apparent S_2 absorption origins are indicated by allows and the onsets of the abrupt decrease of the phosphorescence quantum yields are indicated by solid lines.
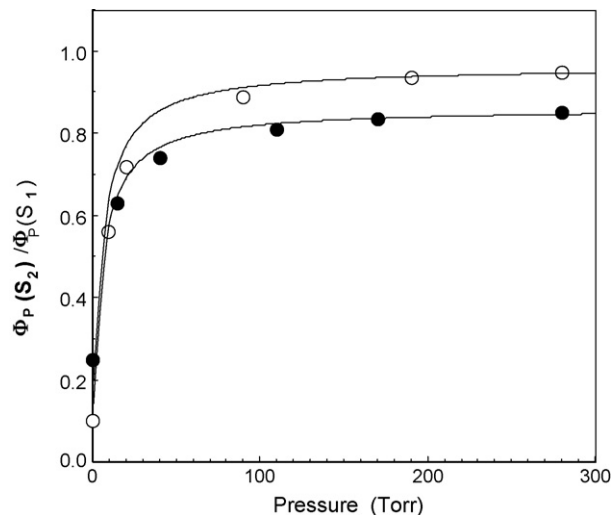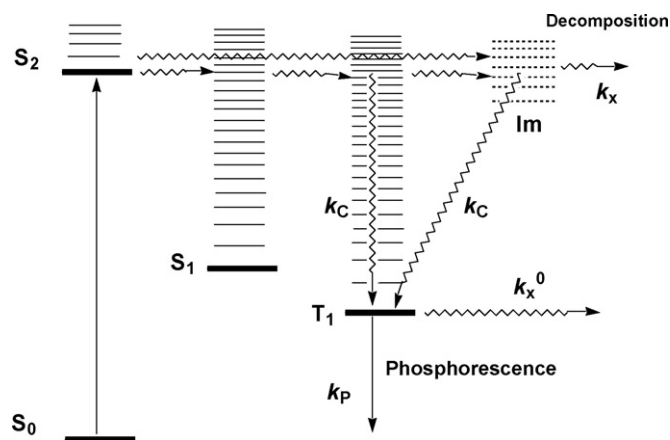

Fig. 6. Kinetic scheme elucidating the pressure and excitation-energy dependence of the phosphorescence quantum yield along with the various rate constants. The collisional deactivation rates of T_1 and Im are treated as almost identical and indicated both by $k_C p$.

not only by photochemical studies but also by the ultrafast electron diffraction measurements [2,5,13]. In a forgoing paper we have reported that 2-PCA vapor dissociates to yield pyridine and carbon monoxide upon UV irradiation in argon matrix [10]. With 3- and 4-PCA, no information is available as to the photochemical products in the vapor phase. However, in light of the decomposition products of 2-PCA and benzaldehyde vapor, the similar photochemical decomposition is considered to occur also for 3- and 4-PCA vapors.

In terms of the scheme shown in Fig. 6, $\Phi_P(S_1)$ and $\Phi_P(S_2)$ are given by,

$$\Phi_P(S_1) = \Phi_{isc}(S_1) \times \frac{k_P}{k_P + k_x^0} \tag{1}$$

$$\Phi_P(S_2) = \Phi_{isc}(S_2) \times \frac{k_C p}{k_C p + k_x} \times \left[\frac{k_P}{k_P + k_x^0} \right] \tag{2}$$

where Φ_{isc} is the quantum yields of the intersystem crossing to T_1 or the overall conversion to Im, and k_P and k_x^0 are the radiative and nonradiative rate constants of the T_1 state, respectively. It follows from Eqs. (1) and (2) that,

$$\frac{\Phi_P(S_2)}{\Phi_P(S_1)} = \frac{\Phi_{isc}(S_2)}{\Phi_{isc}(S_1)} \times \frac{p}{p + k_x/k_C} \tag{3}$$

By fitting the experimental data given in Fig. 5 to Eq. (3), the values for k_x/k_C and $\Phi_{isc}(S_2)/\Phi_{isc}(S_1)$ are evaluated, respectively, to be 2.3 Torr and 0.96 for 3-PCA and 2.9 Torr and 0.89 for 4-PCA.

In terms of the kinetic model, the lifetime of the intermediate state is given by $1/(k_x + k_C p)$. If k_C is assumed to be equal to the bimolecular rate constant for collision ($\sim 10^7$ Torr^{-1} s^{-1}), then the k_x value can be obtained from the k_x/k_C value already determined ($k_x/k_C = 2.3$ Torr for 3-PCA and 2.9 Torr for 4-PCA). The lifetimes of the intermediate state at zero pressure ($1/k_x$) are obtained to be 4.3×10^{-8} and 3.4×10^{-8} s for 3- and 4-PCA vapors, respectively. The fact that fluorescence is observed neither from S_1 nor S_2 means that the lifetimes of these singlet states are much shorter than 10^{-9} s. Thus, the intermediate state cannot be the S_1 nor S_2 state. Taking this into account, the intermediate state should be one of the following states: A dissociative vibrational mode in T_1; a higher triplet state other than T_1, such as $T_i(\pi, \pi^*)$ with $i \geqq 2$; or a reaction intermediate which cannot be identified as any of the excited states of 3- or 4-PCA.

As has been mentioned, Φ_P of 3- and 4-PCA vapors varies according to the nature of the singlet state (S_1 or S_2) to which the molecule is initially excited. This indicates that the molecule excited into S_2 takes a nonradiative pathway different from that taken by the molecule excited optically into the S_1 state. According to the kinetic scheme shown in Fig. 6, the excitation into the S_2 state is followed by the overall conversion to the intermediate state, $S_2 \rightarrow$ Im, while the molecule excited into S_1 converts to the high vibrational levels of T_1. Two pathways are conceivable for the overall conversion to the intermediate state. One is that the molecule excited into S_2 converts to the intermediate state without passing through S_1, and the other is that the S_2 molecule converts to the intermediate state via S_1. In the latter pathway the vibrational redistribution between the optical mode in S_1 and that in S_1 generated as the result of the intersystem crossing should be slow as compared with the conversion to the intermediate state from S_1, there by the molecules retain the memory of the initially excited state. The mechanism mentioned here is also related to the molecular structure formed upon the excitation into the S_2 state, which would be retained during the fast conversion to S_1, T_1 or the intermediate state.

4. Conclusions

The phosphorescence quantum yields of 3- and 4-pyridinecarboxaldehyde (3- and 4-PCA) vapor at low pressure measured as a function of the excitation energy are essentially constant in the whole range of the excitation energy corresponding to the S_1 state, but they undergo an abrupt decrease at the threshold of the $S_1 \rightarrow S_2$ absorption region. The onset of the abrupt decrease of the yield corresponds to the location of the S_2 absorption origin of each molecule, indicating that the nonradiative pathway depends on the type of the excited singlet state (S_1 or S_2) to which the molecule is initially excited. Photophysics of PCA vapors are very similar to that of aromatic carbinyl compounds such as benzaldehyde.

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