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Franck-Condon Analysis for the Carbonyl Stretching Progression Bands in Phosphorescence Spectra of 4-Chromanone at 4.2 K

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Abstract

Phosphorescence spectra of 4-chromanone have been studied optically at 4.2 K in methylcyclohexane host. The energy level of the lowest excited triplet state is determined. The Franck-Condon envelope of the 4-chromanone phosphorescence exhibits predominantly a three quanta $\nu_{C=O}$ progression. The observation of the $\nu_{C=O}$ sequence bands suggests a geometry change between the ground and T_1 states involving the carbonyl local site. From the Franck-Condon analysis for $\nu_{C=O}$ sequence bands, the stable C=O bond distance in the phosphorescent state is estimated to be lengthening by 6.2 per cent of the ground state equilibrium distance upon electronic excitation to the T_1 state.

Introduction

A discussion of aromatic carbonyl spectra from the view-point of the molecular geometry of the photo-excited states and the form of the potential surfaces is clearly required to understand relaxation phenomena of photo-excited molecules. An important problem in considering relaxation of excited electronic states is interstate coupling which is important in considering photophysical processes involving the low lying electronic states of aromatic carbonyls.^{1,2)} The photo-excited molecule experiences some internal or external perturbation on the phosphorescent processes because of relative long lifetime. Generally, the lowest excited triplet state may play an important role in the initial stage for the photochemical reactions of aromatic carbonyls.³⁾ The phosphorescence spectra and their excitation spectra give us many informations for the excited electronic states and their photophysical behaviors of photo-excited molecules. From these points of view, we carry out the Franck-Condon analysis for the $\nu_{C=O}$ progression bands in the phosphorescence spectra of 4-chromanone and attempt to do discussions for the geometry change in the photo-excited triplet 4-chromanone.

Experimental

4-Chromanone (Aldrich) was purified by repeated vacuum distillation. It was found to be free of luminescence impurities at a desired sensitivity setting of the detector unit. Methylcyclohexane (Dotite spectrocol) was used without farther purification and no impurity emission was detected in this solvent. The phosphorescence measurements were carried out using 4-chromanone concentrations 10^{-2} to 10^{-4} (most usually 10^{-3} mol/mol ratio). A sample was supported with a cell holder connected with an acryl resin stick and immersed in liquid helium. A 500 W xenon arc lamp was used as an excitation source. Phosphorescence spectra were resolved with a Spex 0.85 M modified Czerny-Turner mount double spectrometer in the first order with an EMI 6256S photomultiplier tube. The signals

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were led to a preamplifier and then fed to an NF Circuit Design Block lock-in-amplifier. The other experimental details are similar to those reported previously.⁴⁾

Theoretical

Invariable methods of the Franck-Condon analysis have been presented by Smith and Warsop for emission and absorption spectra of polyatomic molecules with a considerable geometry change between the relevant two electronic states.⁵⁾ Here let us start with adapting their treatment. The most prominent spectral feature in the phosphorescence spectra of 4-chromanone is a long progression of the $\sim 1670\text{cm}^{-1}$ C=O stretching vibrational mode with remarkable intensity. If we are allowed to assume that the transition intensity comes from the same type of the transition nature of aromatic carbonyl having the $n\pi^*$ character of emitting state, the phosphorescence transition is polarized along the C=O axis. Given that the electronic transition moment is expanded as a power series of normal coordinates around the zeroth equilibrium configuration of the ground state, the intensity contour will be expressed by the pure electronic integral part and the Franck-Condon overlap integral part. The Franck-Condon factor gives a vibronic band intensity distribution in emission and absorption spectra in general. The relative intensity of the progression bands ν , that of the origin band is then given by

$$\frac{I(0 \rightarrow m)}{I(0 \rightarrow 0)} = \left[\frac{\nu_{0-m}}{\nu_{0-0}} \right]^4 \left[\frac{R(m \rightarrow 0)}{R(0 \rightarrow 0)} \right]^2, \quad (1)$$

where the ratio $[R(m \rightarrow 0)/R(0 \rightarrow 0)]$ is described by the Hermite polynomial of degree m , i. e., H_m .

$$\frac{I(0 \rightarrow m)}{I(0 \rightarrow 0)} = \frac{2^{-m/2} (-i)^m (1 - \beta^2)^{m/2} H_m(i\beta^2 \gamma) (1 - \beta^4)^{-1/2}}{(m!)^{1/2} (1 + \beta^2)^{m/2}}, \quad (2)$$

where the following definitions are employed:

$$\beta = (\alpha' / \alpha'') = (\nu' / \nu'')^{1/2} \quad (3)$$

$$\alpha^2 = 4 \pi^2 \nu c / h \quad (h: \text{Planck's constant}; c: \text{light velocity}) \quad (4)$$

$$\gamma = \alpha'' d \quad (d: \text{the reduced normal coordinate}). \quad (5)$$

For cases of $m = 1$ and $m = k$, eq.(2) may be expressed as follows:

$$\frac{R(0 \rightarrow 1)}{R(0 \rightarrow 0)} = \frac{2^{1/2} \beta^2 \gamma}{1 + \beta^2} \quad (6)$$

$$\frac{R(0 \rightarrow k+1)}{R(0 \rightarrow 0)} = \frac{2^{1/2} \gamma}{(1 + \beta^2) (1+k)^{1/2}} + \frac{m^{1/2} R(0 \rightarrow k-1) (1 - \beta^2)}{(1+k)^{1/2} R(0 \rightarrow k) (1 + \beta^2)}, \quad (7)$$

In eqs. (3) and (5), prime (') and double prime (") discriminate between the upper and lower states, respectively. For the ν_{0-0} normal coordinate, let us take an approximate relation as follows:

$$\gamma = \alpha'' \Delta Q = (\Delta r) [4 \pi^2 c \nu m_c m_o / (m_c + m_o) h]^{1/2}, \quad (8)$$

where $\Delta r = r_{c-o}' - r_{c-o}''$ (r_{c-o}' and r_{c-o}'' : the stable C=O distance in the T_1 state and in the ground state, respectively); m_c and m_o are the atomic weight of carbon and oxygen atoms, respectively. The value $\Delta r / r_{c-o}''$ is a good measure of the geometry change

between the two zero-vibrational levels.

Results and Discussion

Phosphorescence Spectra. The T→S phosphorescence spectrum of 4-chromanone in methylcyclohexane host at 4.2 K is shown in Fig. 1. It may be assured that the phosphorescence emission originates from two emitting sites in the crystal lattices. However, almost all fundamental and combination bands in the phosphorescence system are sharp

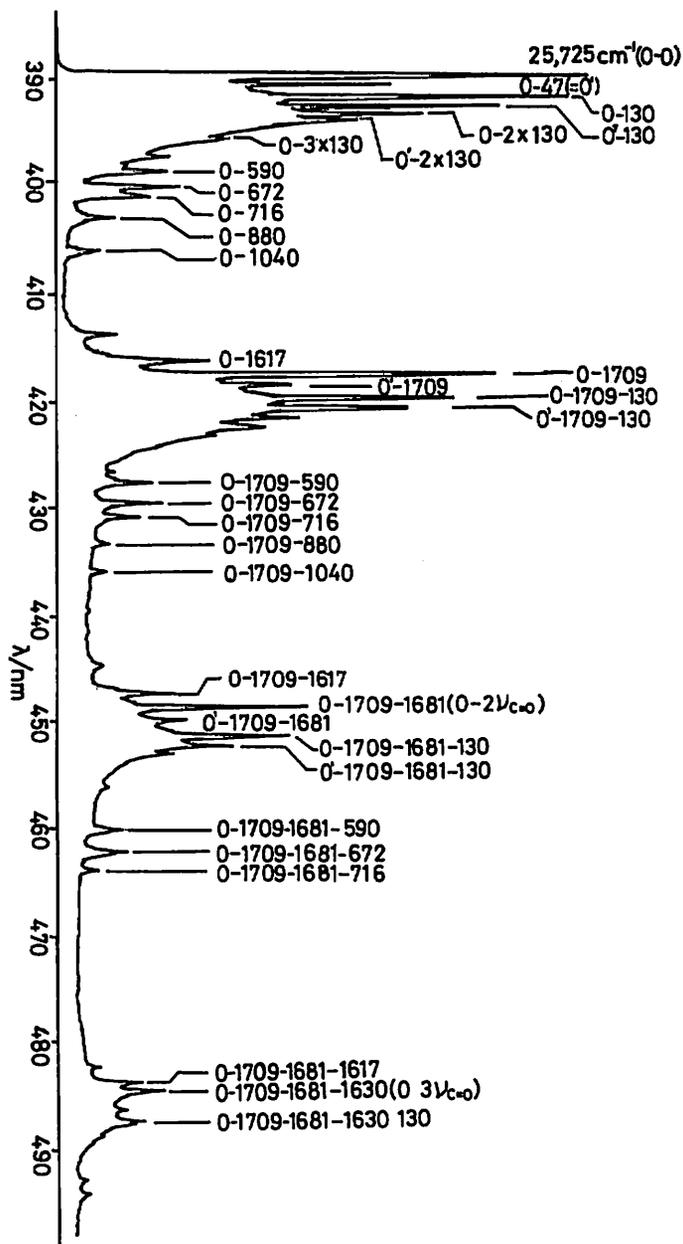


Figure 1. Phosphorescence spectrum of 4-chromanone in methylcyclohexane at 4.2 K

enough to be discriminated from two different sites. The first sharp band at $25,725\text{cm}^{-1}$ is taken as the origin band of the system. The 0-47 band is ascribed to the origin (0') band of another dominant site emission. The appearance of the strong 0-0 band and predominant $\nu_{\text{C=O}}$ progression bands therefrom are a characteristic manifestation that the transition seems to be of $^3n\pi^*$ state. Each progression band separation amounts to $1,709\text{cm}^{-1}$, $1,681\text{cm}^{-1}$, $1,630\text{cm}^{-1}$, respectively, and then the energy spacing decreases in the higher vibrational quantum states. Absence or weakness in intensity of the ring and C-H vibrational modes also suggest that the emitting state is a $n\pi^*$ character. From a viewpoint of the phosphorescence lifetime observed, however, we suppose that the lowest excited triplet state of 4-chromanone is of mixed $n\pi^* - \pi\pi^*$ character in methylcyclohexane host.

Another notable aspect of the phosphorescence spectrum is in the appearance of sub-progression bands with the band spacing of 130cm^{-1} . This sequence band shows three or four quanta in the phosphorescence spectra and fluorescence excitation spectra in the mixed crystal system.⁶⁾ Particularly, This vibrational mode is very active and forms a prominent sequence bands or combination bands with $\nu_{\text{C=O}}$ mode in the one- and two-color multiphoton ionization spectra in the jet-cooled system.⁷⁾ Therefore, it is suggested that this vibrational mode may play an important role in the vibronic relaxation processes of the photo-excited 4-chromanone.

Franck-Condon Analysis. From the present phosphorescence emission data and phosphorescence excitation spectral data of 4-chromanone in the mixed crystal at 4.2 K, we may take $\nu_{\text{C=O}}'' = 1709\text{cm}^{-1}$ and $\nu_{\text{C=O}}' = 1271\text{cm}^{-1}$. The eq. (8) is approximately described by $\Delta r/r_{\text{eq}}'' \sim \gamma/18.31r_{\text{eq}}''$. By means of this relation, we calculated the intensity distributions of several $\nu_{\text{C=O}}$ progression bands and compared them with the observed relative intensities. The results are in part shown in Fig. 2. Here, the intensities of the origin bands are normalized as unity both in the calculated and observed spectra. The values of the plausible deviation factor γ thus drop within 1.45 and 1.49, which means that the relative lengthening of the C=O bond distance in the lowest excited triplet state amounts to 6.2 per cent of the ground state equilibrium distance. The results obtained here are close to the reported value for $^3n\pi^*$ aromatic carbonyls.⁸⁻¹¹⁾ It is manifestation that the lengthening of the C=O bond appears to be closely associated with the appearance of sequence band of C=O stretching vibrational mode in the phosphorescence spectra. Besides, remarkable frequency decrease of the $\nu_{\text{C=O}}$ mode in the T_1 also supports that a significant geometry change occurs in the carbonyl local site of the phosphorescent 4-chromanone.

Concluding Remarks

From the available optical data, the phosphorescent state of 4-chromanone may be described by

$$T_1 = a \ ^3n\pi^* + b \ ^3\pi\pi^* \quad (9)$$

If it is true in the real system, it is interest to note that the carbonyl oxygen of the chromophore loses its π -electron density in the lowest excited triplet state, unlike many other aromatic carbonyl molecules.¹²⁾ However, the mixing coefficient a in eq. (9) is so substantial that many of the properties of T_1 are very far from that normally observed

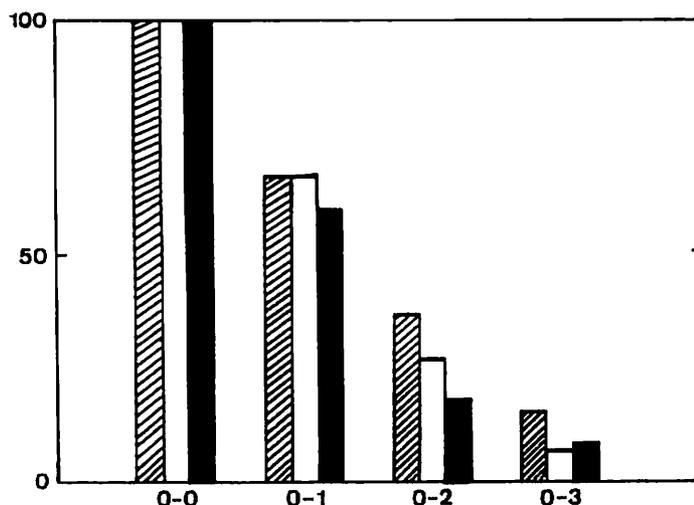


Figure 2. Franck-Condon analysis for phosphorescence spectrum of 4-chromanone at 4.2 K. Bundled columns for each band 0-n ($n=0, 1, 2, 3$) from the left to the right denote the calculated intensity at $\gamma=1.49$ (the shaded columns), the observed spectrum (the white ones) and the calculated spectrum at $\gamma = 1.45$ (the black ones).

for a ${}^3\pi\pi^*$ state, e. g., the prominent $\nu_{C=O}$ progression, the phosphorescence lifetime at 4.2 K of only ~ 10 msec.

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