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Excited-state levels and relaxation processes of chromone and 6-fluorochromone vapors

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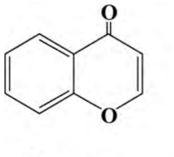
ABSTRACT

Emission and excitation spectra of chromone and 6-fluorochromone have been measured in the vapor phase at different temperatures and pressures along with the absorption spectra. The emission is shown to consist of the $^3(n, \pi^*)$ phosphorescence accompanied by weak $S_1(n, \pi^*)$ delayed fluorescence. It is inferred from the temperature dependence of the phosphorescence intensity that the $^3(n, \pi^*)$ state is located at energies below the $^3(\pi, \pi^*)$ state for chromone and 6-fluorochromone vapors. The relaxation processes in the vapor phase are discussed based on the pressure and excitation energy dependence of the relative phosphorescence yields. The data include the vibrational analyses of the emission spectra based on the results of the DFT calculations at the B3LYP/6-311 + G(p, d) level.

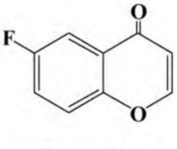
1. Introduction

Photochemical behavior of chromone has been investigated intensively, and the nature of the lowest excited state T_1, $^3(n, \pi^*)$ or $^3(\pi, \pi^*)$, has been discussed based on the photoproducts [1–7]. It is known that normally the type of photoproduct of the carbonyl compounds differs significantly depending on the nature of the T_1 state. The T_1 state of chromone has been investigated also spectroscopically [8–12]. It was reported that the T_1 state of chromone is of $^3(\pi, \pi^*)$ type in polar solvents such as ethanol, but is of $^3(n, \pi^*)$ type in non-polar solvents such as 3-methypentane at 77 K [7]. However, it was also suggested based on the high-resolution experiments at He temperature that the T_1 state of chromone is of $^3(\pi, \pi^*)$ type in non-polar solvents such as 3-methylpentane and methylcyclohexane [9]. In any case, the lowest $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$ states of chromone are considered to be located very closely to each other, but the ordering of these two triplet states seems to be still in controversy. It is, therefore, of importance to determine the state ordering as well as the accurate location of the triplet states of chromone in the vapor phase where the molecules suffer no interaction from the environment. Nevertheless, at present no information is available for the emission and absorption spectral data of chromone in the vapor phase. This is presumably due to the low emission quantum yield and low vapor pressure as well as to the chemical instability of chromone vapor with respect to photon irradiation.

In general, the phosphorescence spectral data of organic molecules in the vapor phase are scarce. In addition, only some of the phosphorescent molecules show detectable sharp emission bands in the vapor phase. Nevertheless, without the acquirement of the emission spectra showing sharp bands, it is almost impossible to investigate the interaction between the electronic and vibrational states. In order to obtain vibrationally resolved spectra, therefore, it is of importance to access the molecules which show the sharp phosphorescence bands in the vapor phase.



Chromone



6-Fluorochromone

In the present study, vibrationally resolved emission spectra have been measured for chromone and 6-fluorochromone vapors at different temperatures. The latter molecule is expected to possess the excited-state electronic structure similar to that of chromone. It is shown that chromone and 6-fluorochromone exhibit comparatively sharp phosphorescence bands in the vapor phase. The emission is shown to consist of the $^3(n, \pi^*)$ phosphorescence accompanied by the weak $S_1(n, \pi^*)$ delayed fluorescence. The locations of the $T_1(n, \pi^*)$ and $S_1(n, \pi^*)$ origins have been determined in the vapor phase. The vibronic bands in the emission spectra were assigned based on the results of the DFT calculations at the B3LYP/6-311 + G(p, d) level. It is inferred from the temperature dependence of the phosphorescence intensity that the $^3(n, \pi^*)$ state is located at energies below the $^3(\pi, \pi^*)$ state for chromone and

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6-fluorochromone vapors. The relative phosphorescence quantum yields are found to decrease with increasing excitation energy and with decreasing pressure. The relaxation processes in the vapor phase are discussed based on the pressure and excitation energy dependence of the relative phosphorescence yield.

2. Experimental and computational methods

Chromone obtained from Tokyo Chemical Industry, Japan, and 6-fluorochromone obtained from Aldrich were purified by means of repeated recrystallization from hexane. Absence of any impurity emission in glassy matrix at 77 K and verification that the excitation spectra in the vapor phase agreed well with the corresponding absorption spectra suggest that the purified samples are sufficiently pure for the experiment. Perfluorohexane obtained from Aldrich, USA, was used as a buffer gas. The sample was carefully degassed by repeating freeze–thaw cycles in an all-glass made vacuum system equipped with a diffusion pump: a small amount of the sample crystal was put into the cell and then the buffer gas was introduced to the sample cell after degassing of the crystal as well as the buffer gas. The details of the sample preparation method are described in a foregoing paper [13]. The samples were found to be unstable with respect to photon irradiation and to degrade during long-time measurements. Thus, all the measurements were carried out only once for each fresh sample just after the preparation. It took about 100 min for measuring each emission spectrum and about 60 min for measuring each excitation spectrum. It was confirmed that no appreciable change was detected for the spectral intensities before and after the measurement. In most of the spectral measurements, square 10-mm path length quartz cells were used and the temperature of the cell was controlled by a thermostated cell holder. A cylindrical 100-mm path length quartz cell was used for measuring weak absorption spectra.

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. Two reflection mirrors were placed beside the sample cell holder to intensify the emission signals [14]. The slit width used for measuring the absorption, emission and excitation spectra is kept 2.0 Å. The wavelength calibration was carried out using a Melles Griot He–Ne green laser. Emission spectra were corrected for the spectral sensitivity of the detection system by comparing the measured spectrum with the real spectrum using quinine in sulfuric acid 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.

Quantum chemical calculations were carried out with the density-functional theory (DFT) using GAUSSIAN 03 program [15]. Optimized geometries, total energies and harmonic wavenumbers in the ground state, $\nu_{\rm harm}$, were obtained by the DFT calculations at the B3LYP/6-311 + G(d, p) level. The calculated wavenumbers, $\nu_{\rm calc}$, in the ground state were scaled using the relation, $\nu_{\rm calc} = \nu_{\rm harm} \times (1.0087 - 0.0000163 \times \nu_{\rm harm})$, to reproduce the anharmonicity of observed vibrations, where $\nu_{\rm harm}$ denotes the harmonic frequency obtained by the DFT calculation [16].

3. Results and discussion

3.1. Emission spectra and the electronic-state ordering

Absorption spectra of chromone and 6-fluorochromone in hexane at room temperature are shown in Fig. 1a and b, respectively. In hexane, the absorption spectrum of chromone consists of the weak $S_0 \rightarrow {}^3(n, \pi^*)$, $S_0 \rightarrow S_1(n, \pi^*)$ and comparatively strong $S_0 \rightarrow S_2(\pi, \pi^*)$ bands with the origins seen at 26,300, 27,700 and 33,100 cm^{-1}, respectively, and with the molar extinction coefficients of the origin bands of 0.3, 5.0 and 6450. The absorption spectrum of 6-fluorochromone resembles that of chromone and the origin bands of the ${}^3(n, \pi^*)$, $S_1(n, \pi^*)$ and $S_2(\pi, \pi^*)$ states are seen at 26,100, 27,550 and 32,280 cm^{-1}, respectively, with the molar extinction coefficients of the origin bands of 0.4, 10.0 and 5900. The absorption spectra in solution provide the approximate locations of the excited triplet and singlet (n, π*) states, but may not provide the information on the locations of the triplet (π, π*) states.

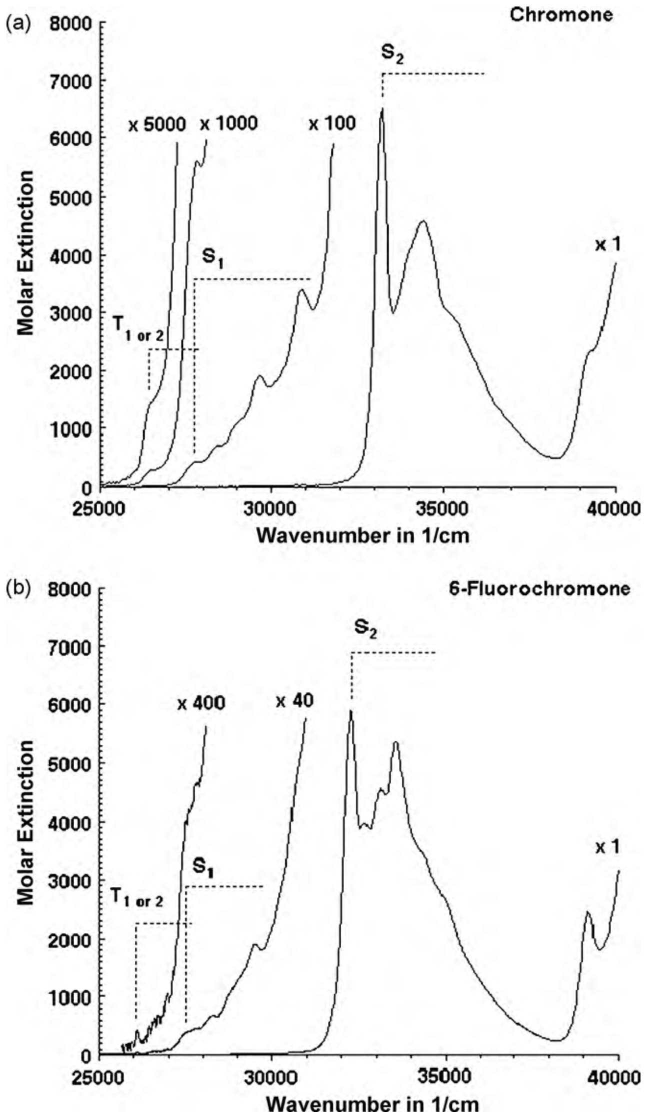

Fig. 1. Absorption spectra of chromone (a) and 6-fluorochromone (b) in hexane at room temperature. The concentrations of chromone and 6-fluorochromone in hexane are below 10^{-3} mol/l.

The emission spectra of chromone and 6-fluorochromone vapors in the presence of 250 Torr perfluorohexane at different temperatures are shown in Fig. 2a and b, respectively. In the present experiment, a buffer gas was added to the samples, since the emission of the samples is weak without buffer gas and since addition of buffer gas induces the efficient collisional relaxation to the lower-lying excited states. As will be shown later in detail, the excitation spectra of the observed emission agree well with the absorption spectra. The emission of chromone and 6-fluorochromone vapors consists of the weak fluorescence from $S_1(n, \pi^*)$ and phosphorescence from ${}^3(n, \pi^*)$, showing a prominent progression in the C=O stretching vibration in the phosphorescence spectra. The