Phosphorescence emission and excited states of 3- and 4-hydroxybenzaldehyde vapors

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ABSTRACT

Emission spectra of 3- and 4-hydroxybenzaldehyde vapors have been measured along with the excitation and absorption spectra. It is inferred from the temperature dependence of the phosphorescence spectrum that the phosphorescence of 4-hydroxybenzaldehyde vapor originates from the $T_2(n, \pi^*)$ state. In the case of 3-hydroxybenzaldehyde vapor, the emission is shown to consist of that of 3-hydroxybenzaldehyde and benzaldehyde vapors, with the latter molecule being generated as the result of photochemical decomposition of 3-hydroxybenzaldehyde. The interpretation of the emission spectrum of 3-hydroxybenzaldehyde is different from that reported previously. The rotational isomer responsible for appearance of the phosphorescence of 3-hydroxybenzaldehyde vapor is suggested based on DFT calculation and emission spectral data.

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1. Introduction

Some of the aromatic carbonyl compounds such as *p*-methoxybenzaldehyde (anisaldehyde) and *p*-cyanobenzaldehyde are known to exhibit phosphorescence from the second excited triplet state (T_2), as mentioned in a recent review [1]. The reason for the occurrence of the T_2 phosphorescence is that the T_2 and the lowest excited triplet (T_1) states are closely located, with the oscillator strength of the former state being much larger than that of the latter [1–5]. Thus, at temperatures where the Boltzmann distribution is sufficient to populate the upper excited state, the T_2 emission is observable [1]. The T_1 states of some of the derivatives of benzaldehyde, possessing an electron-donating group at para position, are attributed to be $^3(\pi, \pi^*)$ in nature [2–4]. For such molecules the excited state ordering is $S_1(n, \pi^*) > T_2(n, \pi^*) > T_1(\pi, \pi^*)$, so that we can observe the T_1 or T_2 phosphorescence depending on the condition such as temperature as well as an appropriate choice of the host [2–4]. The location of the $T_1(\pi, \pi^*)$ level of 4-hydroxybenzaldehyde vapor cannot be determined, because neither of the $T_1 \rightarrow S_0$ phosphorescence nor the $S_0 \rightarrow T_1$ absorption has been detected in the vapor phase, although in a rigid matrix at 77 K the $T_1(\pi, \pi^*)$ phosphorescence has been reported [6–9]. The excited state ordering of 4-hydroxybenzaldehyde vapor is expected to be $S_1(n, \pi^*) > T_2(n, \pi^*) > T_1(\pi, \pi^*)$, since it possesses an electron-donating group -OH at para position. To the best of our knowledge, the detailed analysis of the emission spectrum of 4-hydroxybenzaldehyde vapor has not been carried out.

In the case of 3-hydroxybenzaldehyde vapor, unlike typical aromatic carbonyl compounds such as unsubstituted benzaldehyde, doublet structures in the C=O stretching bands have been reported in the phosphorescence spectrum [10,11]. Since such a doublet structure is quite anomalous as the band structure of phosphorescence spectrum of aromatic carbonyl molecules, we have investigated this puzzling structure in detail. The T_1 state of 3-hydroxybenzaldehyde vapor is considered to be $^3(n, \pi^*)$ in nature, as in the case of other meta-substituted benzaldehydes, but the detailed information is not available. Since the nature of the T_1 state of aromatic carbonyl compounds often changes depending on the solvent used, it is of importance to determine the energy levels and nature of the T_1 state in the vapor phase, where the molecules suffer no interaction with environment.

In the present work, emission spectra of 3- and 4-hydroxybenzaldehyde (hereafter abbreviated by 3-HOB and 4-HOB, respectively) vapors have been measured along with the excitation and absorption spectra. On the basis of the temperature dependence of the $T_2(n, \pi^*)$ phosphorescence intensities, the energy level of the dark $T_1(\pi, \pi^*)$ states of 4-HOB vapor is shown to be located at about $1550 \pm 100 \, cm^{-1}$ below the $T_2(n, \pi^*)$ level. The reported emission of 3-HOB is shown to be a mixture of the emission from 3-HOB and benzaldehyde vapors, with the latter molecule being generated as the result of photochemical decomposition of 3-HOB vapor. Further, the rotational isomer responsible for appearance of the phosphorescence is suggested for 3-HOB vapor based on the results of the DFT calculation at the B3LYP/ 6-311++G** level and emission spectral data.

2. Experimental and computational

3- and 4-HOB, obtained from Tokyo Chemical Industries (TCI) Japan, was purified by means of repeated recrystallization from carbon tetrachloride and chloroform. Perfluorohexane obtained from TCI was used as a buffer gas as supplied. Perfluorohexane is considered to induce collisional deactivation of the excited vibronic levels of 3- and 4-HOB vapors. The verification that the vapor phase excitation spectra of 3- and 4-HOB in the $S_0 \rightarrow S_2$ region in the presence of added perfluorohexane agreed with the corresponding absorption spectra suggests that the purified samples were sufficiently pure for the experiment. Further, the observed absorption spectra of 3- and 4-HOB in hexane at room temperature, the phosphorescence spectrum of 4-HOB at 77 K in a rigid matrix, and the emission spectrum of 3-HOB vapor are all in agreement with those reported previously [7,12]. The samples were degassed in a vacuum system equipped with a diffusion pump. Details of the sample preparation are described in a foregoing paper [3]. The sample and buffer gas pressure were always kept below the saturation pressures at the temperatures employed in the present study. Since 3-HOB vapor was found to be unstable with respect to photon irradiation and to degrade rapidly during long scan, all the measurements were carried out only once for each fresh sample just after the preparation. During the measurement, the temperature of the sample cell was controlled by a thermostated cell holder that consists of lower and upper parts. The lower part covers most of the quartz square cell for which the emission is detected. The temperature of the upper part of the cell was kept slightly lower than that of the lower part. For most of the emission measurements square 10-mm path length quartz cells were used. A cylindrical 100-mm quartz cell was also used for the measurements of 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. 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 ally-cooled housing operated in photon-counting mode to detect weak signals. With this apparatus the signal from an emitting entity expressed by the product of the emission quantum yield and the optical density being as low as 10^{-7}, can be measured with a reasonable S/N ratio. Two reflection mirrors were attached beside the sample cell holder to intensify the emission signal [13]. In most of the emission measurements, the slit width was kept near 2.0 Å (8.0 cm^{-1} at 500 nm). Wavelength calibration of the spectrophotometer was carried out using a Melles Griot He–Ne green laser (5435 Å). The emission lifetimes were measured with a Fluorolog-3 spectrophotometer in time-intensity measuring mode, with which the lifetime longer than few ms can be measured easily. 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 a standard. 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 [14].

Quantum chemical calculations were carried out using the GAUSSIAN 03 program [15]. Optimized geometry and harmonic vibrational wavenumber in the ground state were obtained by density-functional theory (DFT) calculations at the B3LYP/6-311++G** level. The harmonic wavenumbers, ν_{harm}, were scaled using the relation, $\nu_{calc} = \nu_{harm} \times (1.0087 - 0.0000163 \times \nu_{harm})$, to reproduce the observed vibrational bands [16].

3. Results and discussion

Fig. 1 shows the absorption spectra of 3- and 4-HOB in the vapor phase and in n-hexane at room temperature. The absorption spectra of 3- and 4-HOB vapor in the $S_0 \rightarrow S_1(n,\pi^*)$ region could not be measured because of the low vapor pressure. It is seen that the vapor phase absorption spectra shift slightly to the blue as compared with those in hexane. The apparent $S_1(n,\pi^*)$ origins are seen at 27 000 and 27 500 cm^{-1}, respectively for 3- and 4-HOB in hexane. Weak bands seen at 25 200 and 25 400 cm^{-1}, respectively, for 3- and 4-HOB in hexane with the molar extinction coefficients ε of about 0.3 are due to the singlet–triplet transition. As will be mentioned later in detail, these weak bands can be assigned to the origin bands of $S_0 \rightarrow T_1(n,\pi^*)$ for 3-HOB and $S_0 \rightarrow T_2(n,\pi^*)$ absorption for 4-HOB.

3.1. Emission of 3-hydroxbenzaldehyde (3-HOB) vapor

Fig. 2 shows emission spectrum of 3-HOB vapor at two different temperatures, along with that of pure benzaldehyde vapor. These emission spectra are in general agreement with those reported previously [10]. It is seen that there are doublet structures in the main C=O stretching bands as was reported previously [10]. However, one can notice that one of the peaks in the doublet structure agrees in position with the phosphorescence peak of benzaldehyde vapor. Further, the phosphorescence peak intervals agree exactly with those of benzaldehyde vapor. The locations of the phosphorescence peaks and the peak interval (the C=O stretching frequency) depend rigorously on the molecular species of aromatic carbonyl compounds. It is not conceivable that both the phosphorescence origins and the C=O stretching intervals agree exactly between the two different aromatic carbonyl molecules. Thus, we can safely say that the observed emission involves the peaks originating from benzaldehyde vapor. This interpretation of the emission spectrum is different from that reported previously [10]. The excitation spectrum of the phosphorescence emission agreed with the absorption spectrum of 3-HOB. This observation suggests that benzaldehyde is generated as the result of photochemical conversion in the excited state of 3-HOB vapor. The intensity of the phosphorescence of benzaldehyde vapor was found to increase gradually with increasing irradiation time and temperature, while
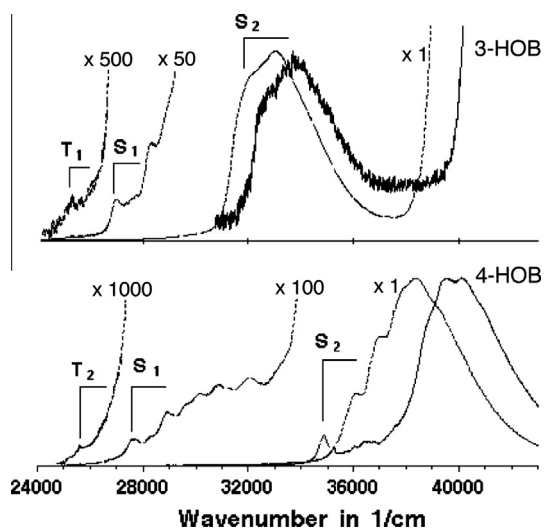

Fig. 1. Absorption spectra of 3- and 4-HOB in n-hexane (broken-line spectra) and in the vapor phase (solid-line spectra). The spectra are normalized to a common magnitude at the $S_0 \rightarrow S_2$ absorption maxima. The molar extinction coefficients ε at the apparent S_1 origins are about 20 for both of 3- and 4-HOB in n-hexane.