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３－と４－ヒドロキシベンズアルデヒド気体のリン光と励起状態

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

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Introduction The location of the T_1 (π, π^*) level of 4-hydroxybenzaldehyde (4-HOB) vapor has not been determined, because neither of the T_1 phosphorescence nor the T_1 absorption has been detected in the vapor phase. In the case of 3-hydroxybenzaldehyde (3-HOB) vapor, doublet structures in the C=O stretching bands have been reported in the phosphorescence spectrum. It is shown, based the temperature dependence of the phosphorescence spectrum, that the phosphorescence of 4-HOB vapor originates from the T_2 (n, π^*) state. In the case of 3-HOB vapor, the emission is shown to consist of that of 3-HOB and benzaldehyde vapors, with the latter being generated as the result of decomposition of 3-HOB. The rotational isomer responsible for appearance of the phosphorescence of 3-HOB vapor is suggested based on spectral measurements and DFT calculation.

Experimental and Computational Emission, excitation spectra and lifetimes were measured with a Spex Fluorolog-3 (Model 21-SS) spectrophotometer. In most of the emission measurements, the silt width was kept near 2.0 A°. Harmonic vibrational wavenumber were obtained by DFT B3LYP/ 6-311++G** level calculations.

Results and Discussion **Emission of 3-HOB vapor:** Fig. 1 shows emission spectrum of 3-HOB vapor at two different temperatures, along with that of benzaldehyde vapor. It is seen that there are doublet structures in the main C=O stretching bands. One can notice that one of the peaks in the doublet structure agrees exactly in position with the phosphorescence peak of benzaldehyde vapor. Further, the phosphorescence peak intervals agree exactly with those of benzaldehyde vapor. Thus, we can safely say that the observed mission involves the peaks originating from benzaldehyde vapor. 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. Thus, the phosphorescence peak seen at 25010 cm^{-1} can be assigned as the T_1 phosphorescence origin of 3-HOB vapor, which agrees in position with the T_1(n, π^*) absorption origin in hexane. The weak delayed S_1(n, π^*) fluorescence band of 3-HOB vapor also agrees with the S_1(n, π^*) absorption origin in hexane. There are four possible metastable rotamers for 3-HOB (Fig. 2). DFT calculations indicate that among the four rotational isomers of 3-HOB, the C=O-syn-OH-syn conformer is the most stable rotamer. Further, the observed C=O stretching frequency in the phosphorescence of 3-HOB vapor is 1725 cm^{-1} which agrees favorably with the calculated frequency of 1728.9 cm^{-1} obtained for the most stable C=O-syn-OH-syn conformer, while those of the C=O-syn-OH-anti, C=O-anti-OH-anti and C=O-anti-OH-syn conformers are calculated to be 1735.1, 1735.7 and 1735.7 cm^{-1}, respectively. Thus, the observed phosphorescence of 3-HOB vapor is considered to originate from the C=O-syn-OH-syn conformer.

Emission of 4-HOB vapor: Fig. 3 shows the emission spectrum of 4-HOB vapor along with that of 4-HOB in rigid glass at 77 K. The emission of 4-HOB is considered to consist of the T_2 (n, π*) phosphorescence accompanied by weak thermally activated S_1 (n, π*) delayed fluorescence, while the emission at 77 K was assigned to the T_1 (π, π*) phosphorescence. The phosphorescence in the vapor phase exhibits a prominent feature of the C=O stretching vibration with the frequency of 1720 cm^{-1}. The phosphorescence origin in the vapor phase is seen at 25710 cm^{-1}, while that in a rigid glass at 77 K is seen at 24000 cm^{-1}. The phosphorescence origin of 4-HOB vapor agrees with the T_2 band in hexane. The phosphorescence lifetime of 4-HOB was obtained to be 0.35 s in a rigid glass at 77 K with the quantum yield of about 0.1, suggesting that the T_1 state is $^3(\pi, \pi^*)$ in nature. Both of the phosphorescence and fluorescence intensities of 4-HOB vapor are found to increase upon elevation of temperature. This observation supports the T_2-phosphorescence assignment for 4-HOB vapors. The measured emission intensities were analyzed quantitatively.

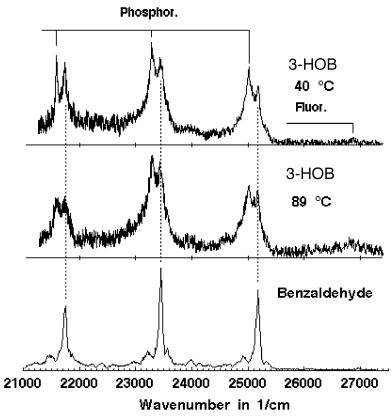

Fig. 1 Emission spectra of 3-HOB vapor at two different temperatures and the phosphorescence spectrum of benzaldehyde vapor.

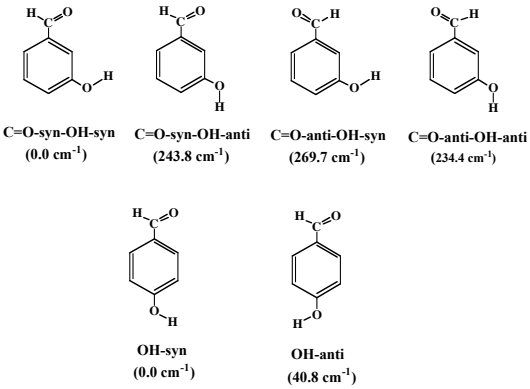

Fig. 2 Possible rotational isomers of 3- and 4-HOB. The energy values in parentheses indicate the DFT calculated energy differences between the most stable isomer and each isomer in the ground state.

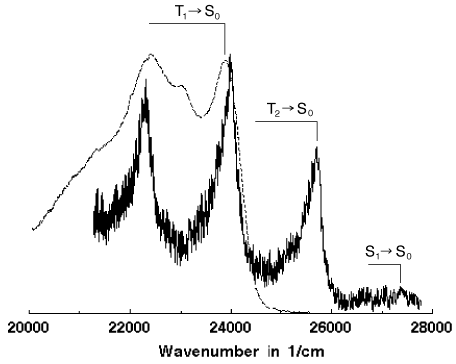

Fig. 3 Corrected emission spectrum of 4-HOB vapor at 90 °C (solid-line spectrum) and the phosphorescence spectrum of 4-HOB in an isopentane-methycyclohexane mixture at 77 K (broken-line spectrum).

Ref. T. Itoh, Chem. Rev., 112 (2012) 4541.

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