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Fluorescence and nonradiative processes of dioxin vapors



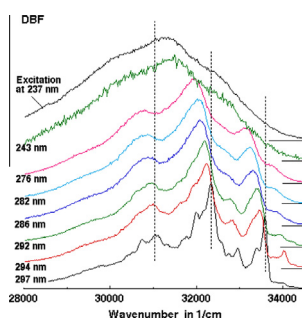
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HIGHLIGHTS

- Fluorescence, excitation and sensitized-excitation spectra of 5 dioxins vapors were measured.
- These are dibenzofuran, chliridibenzofuran, dichlorodibenzofuran, dibenzo-*p*-dioxin and chlorodibenzo-*p*-dioxin.
- Nonradiative rates of dibenzodioxins increase with increasing excitation energy, but those of dibenzofurans are unchanged.
- Main nonradiative process from S_1 of dibenzofurans is intersystem crossing to T_1 and internal conversion to S_0 .
- Main nonradiative process from S_1 of dibenzo-*p*-dioxins is internal conversion to S_0 .

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorescence, fluorescence excitation, biacetyl-sensitized phosphorescence excitation and absorption spectra of five dioxins (dibenzofuran, 2-chlorodibenzofuran, 2,8-dichlorodibenzofuran, dibenzo-*p*-dioxin and 2-chlorodibenzo-*p*-dioxin) have been measured in the vapor phase. The intersystem crossing yields of dioxin vapors have been determined by means of a biacetyl sensitized phosphorescence method. It is shown that the nonradiative rates from the S_1 state of dibenzo-*p*-dioxins increase significantly with increasing excitation energy, while those of dibenzofurans are almost unchanged. It is also shown that the main nonradiative process from S_1 for dibenzofurans is both the intersystem crossing to T_1 and internal conversion to S_0 which includes possible photodecomposition, while that for dibenzo-*p*-dioxins is the internal conversion to S_0 , which also may include possible photochemical decomposition processes.

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Introduction

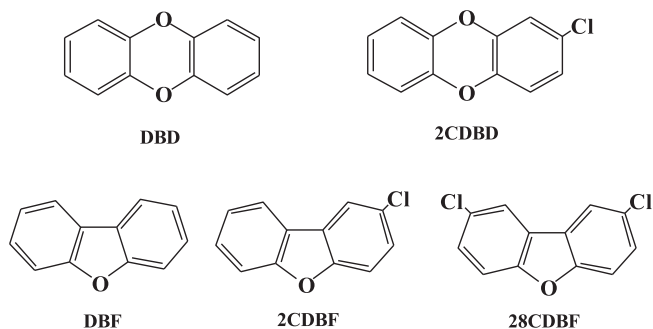
Dioxins are a group of compounds that are formed during combustion processes such as waste incineration and some industrial processes. Some of these compounds are regarded as toxic molecules that are environmental pollutants and persistent organic pollutants [1]. The highest environmental concentrations of dioxins are normally found in soil and sediment, with lower levels in air and water [1]. Dioxins include polychlorinated

dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls. There are 75 and 135 derivatives differing in the number and the location of chlorine atoms, respectively, for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans [1]. Since dioxins have been attracted considerable attention in conjunction with the environmental pollution problems, it is of importance to investigate the photophysics and photochemistry in detail. Most of the spectroscopic studies of dioxins in the vapor phase are focused on unsubstituted dibenzofurans (DBF) or dibenzo-*p*-dioxins (DBD) [2–7], but almost no information is available for the photophysics of dioxins other than parent DBF and DBD.

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In the present study, fluorescence, fluorescence excitation, biacetyl-sensitized phosphorescence excitation and absorption spectra of dibenzofuran (DBF), 2-chlorodibenzofuran (2CDBF), 2,8-dichlorodibenzofuran (28CDBF), dibenzo-*p*-dioxin (DBD) and 2-chlorodibenzo-*p*-dioxin (2CDBD) have been measured in the vapor phase. The intersystem crossing yields of dioxins have been determined by means of a biacetyl sensitized phosphorescence method based on the intermolecular triplet–triplet (T–T) energy transfer. It is shown that the nonradiative rates from the S_1 state of dibenzo-*p*-dioxins increases significantly with increasing excitation energy, while those of dibenzofurans are almost unchanged. It is also shown that the main nonradiative process from S_1 is the intersystem crossing to T_1 for dibenzofurans, while that for dibenzo-*p*-dioxins is the internal conversion to S_0 which may include possible photochemical decomposition processes. Five dioxins treated in the present study are shown below.



Experimental

Sample preparation

Dibenzo-*p*-dioxin (DBD) was obtained from Tokyo Chemical Industry, 2-chlorodibenzo-*p*-dioxin (2CDBD) and dibenzofuran (DBF) were obtained from Aldrich and 2-chlorodibenzofuran (2CDBF) and 2,8-dichlorodibenzofuran (28CDBF) were obtained from Accu Standard. These compounds were purified by repeated recrystallization from benzene followed by vacuum sublimation. It was confirmed that the corrected fluorescence excitation spectra of purified samples in hexane agreed well with the absorption spectra for all the compounds. Further, it was confirmed that the vapor-phase absorption and fluorescence spectra of DBF agrees well with those reported previously [7,8]. A small amount of sample crystal in a quartz cell sealed to a vacuum system was degassed at background pressure less than 10^{-4} Torr. Then, the sample cell was sealed off under vacuum after degassing.

The following procedure was conducted for the preparation of the samples containing both dioxin and biacetyl vapors. Biacetyl sealed in a side arm was degassed by repeated freeze–pump–thaw cycles. A small amount of dioxin crystal in a quartz cell was also degassed by repeated freeze–pump–thaw cycles. Biacetyl used as a sensitizer was admitted into the sample cell after degassing. The pressure of biacetyl was controlled by the temperature of the side arm varied from -20 to 0 °C. The sample cell containing biacetyl vapor was then isolated from biacetyl reservoir, the contents were trapped by liquid nitrogen and the cell was sealed off. By measuring optical density of biacetyl vapor, we estimated the biacetyl pressure.

Measurements

The emission and excitation spectra were measured with a Spex Fluorolog-3 (Model 21-SS) spectrophotometer, 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. Two reflecting mirrors were placed beside the sample cell to intensify the emission signals [9]. For most of the emission measurements square 10-mm path length quartz cells were used. The temperature of the samples was measured with a digital thermometer. A cylindrical quartz cell with a 100-mm path length was also used for measurements of weak absorption.

Fluorescence 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. Excitation spectra were corrected for the spectral intensity distribution of the exciting light with an aqueous solution of rhodamine B as a quantum counter. The emission spectra were corrected for the sensitivity of the detection system by comparing the measured spectrum with the real spectrum using β -naphthol in acetic acid – sodium acetate buffer solution as a standard [10]. 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 [11]. Unfortunately, however, precise values of the fluorescence yields could not be determined due to the low optical densities of the vapor samples, but these values were evaluated to be approximately in the order of 10^{-2} for DBF, 2CDBF and 28CDBF vapors and 10^{-3} for DBD and 2CDBD vapors.

Results and discussion

Fluorescence spectra of five pure dioxin vapors following the excitation at different wavelengths are shown in Figs. 1a–e. The pressures of the samples for spectral measurements are ranging from 0.8 to 0.06 Torr which vary depending on the molecules. Each of the fluorescence spectra is situated in the region adjacent to the corresponding absorption spectrum. It is seen that the fluorescence spectra show red shifts with increasing the excitation energy for all the vapor samples. This observation indicates that the fluorescence originates from the unrelaxed vibronic levels and that the molecules are free from collision during the lifetime of the S_1 state under the present experimental conditions.

Figs. 2a–e show the absorption, corrected fluorescence excitation and corrected biacetyl-sensitized phosphorescence excitation spectra of five dioxin vapors as measured with 0.5 nm excitation bandwidth. It is seen in Figs. 2a–e that the excitation and

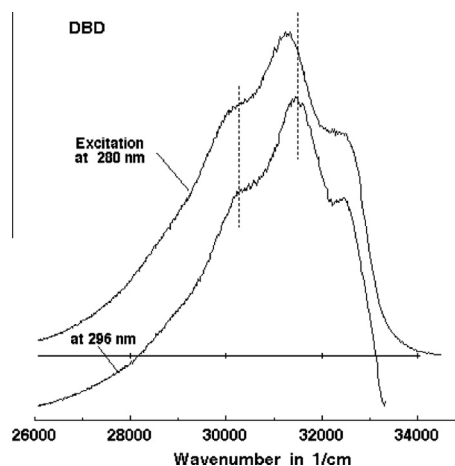


Fig. 1a. Fluorescence spectra of DBD vapor at 0.86 Torr and 90 °C following the excitation at two different wavelengths.

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