Singlet Oxygen Emission at 1270 nm in Protoporphyrin Solution Excited by Argon Laser

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TORINUKI, W. and MIURA, T. Singlet Oxygen Emission at 1270 nm in Protoporphyrin Solution Excited by Argon Laser. Tohoku J. exp. Med., 1983, 140 (3), 297-299 — The direct observation of dye-photosensitized 1270 nm emission of the $^1A_g \rightarrow ^3\Sigma_g^-$ transition of molecular oxygen in liquid solution is reported. Singlet oxygen was photosensitized by argon laser excitation of protoporphyrin in carbon tetrachloride.

It is generally accepted that the interaction of molecules excited to the triplet state with molecular oxygen results in a transition of the latter to the singlet excited state $^1O_2$ (Kearns 1971). The singlet oxygen plays an important role in many photochemical and photobiological processes, including skin photosensitivity in porphyria (Lamola et al. 1973). We report here the direct spectroscopic detection of the $^1A_g \rightarrow ^3\Sigma_g^-$ infrared emission band at 1270 nm arising from molecular oxygen in a protoporphyrin solution under argon laser excitation.

MATERIALS AND METHODS

Carbon tetrachloride (CCl₄; Wako Pure Chemical Co., Japan) was used as the solvent of protoporphyrin dimethyl ester (Sigma Chemical Co., USA), because the lifetime of $^1O_2(^1A_g)$ has been determined in CCl₄ in which the duration of the oxygen luminescence was greater than $10^{-4}$ sec (Merkel and Kearns 1972). The purity of the porphyrin was 90% as examined by the combined technique of thin layer chromatography and fluorescent scanning (Miura and Torinuki 1977).

Our experimental setup (Fig. 1) consisted of argon laser equipment (model 164; Spectra-Physics Co., USA), germanium photodiode cooled by liquid nitrogen with spectral response of infrared region and a Shimadzu sensitive near-infrared spectrophotometer. Protoporphyrin dimethyl ester ($5 \times 10^{-4}$M in CCl₄) was excited with the argon laser light (400 mW; a blue-green beam). Tank oxygen was bubbled through the solution under excitation. The signal from the sample was analyzed by the spectrometer and detected by germanium photodiode. The output of the photodiode detector was fed to a strip-chart recorder via a lock-in amplifier and the emission spectrum was recorded.

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**RESULT**

Fig. 2 shows near-infrared emission (1270 nm) corresponding to the (0,0) band of the $^1A_g \rightarrow ^3\Sigma_g^-$ transition of molecular oxygen observed for protoporphyrin-sensitizer, obtained by using the apparatus shown in Fig. 1. The (0, 1) band of the $^1A_g \rightarrow ^3\Sigma_g^-$ transition (at 1580 nm) was not clearly detected because of the edge of the grating limited instrument capability.

**DISCUSSION**

Erythropoietic protoporphyria is an inherited disorder of porphyrin metabolism in which the major clinical manifestation is cutaneous photosensitivity, but the molecular mechanism of the photosensitivity is not known in detail. The skin
reaction involves the energy transfer from triplet state protoporphyrin to ground state oxygen (Spikes 1975). The triplet state energy is sufficient to generate singlet oxygen (Lamola 1974) and it has been assumed that singlet oxygen is the primary toxic component.

The transient presence of singlet oxygen can be deduced from chemical products, scavenger trapping, or other secondary evidence. However, many of these secondary effects can also be an indication for other reactive intermediates such as superoxide radical and therefore, a direct spectroscopic technique for the detection of singlet oxygen is desirable. Krasnovsky (1979) and Khan and Kasha (1979) demonstrated the singlet oxygen infrared emission at 1270 nm by direct spectroscopic observation using various chlorophylls and related molecular dyes as sensitizers. Here we have observed the emission corresponding to the $^{1}A_g(0) \rightarrow ^{3}e_g(0)$ transition of molecular oxygen in protoporphyrin solution under laser excitation. The result obtained in this study may have many useful extensions in photochemical and biological researches of skin photosensitivity in porphyrias.

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References