

# Photosensitized luminescence of vibrationally excited singlet-oxygen molecules [ ${}^1\Delta_g(V=1)$ ] in solution

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A photoinduced luminescence accompanied by a transition of the oxygen molecules from the singlet vibrationally excited state [ ${}^1\Delta_g(V=1)$ ] to the triplet ground state [ ${}^3\Sigma_g^-(V=0)$ ] has been observed in solutions of a photosensitizer. This emission is shown to result from a photosensitized filling of the [ ${}^1\Delta_g(V=0)$ ] level followed by a thermally induced transition of the molecules to the [ ${}^1\Delta_g(V=1)$ ] state.

The photosensitized formation of the singlet state ( ${}^1\Delta_g$ ) of molecular oxygen ( ${}^1\text{O}_2$ ) in the gas phase or in solution is accompanied by a luminescence, whose spectrum has two groups of bands. At  $\lambda \leq 1000$  nm are the peaks of “dimols” ( ${}^1\text{O}_2$ )<sub>2</sub>, while at  $\lambda \geq 1200$  nm are the peaks of “unimols”  ${}^1\text{O}_2$ . The unimol luminescence spectrum has a primary peak at 1270 nm and a large number of longer-wavelength bands of much lower intensity.<sup>1-5</sup> All the bands of the unimol luminescence which have been described previously, however, have resulted from the decay of the zeroth vibrational level of the  ${}^1\Delta_g$  state [ ${}^1\Delta_g(V=0)$ ]. In this letter we are reporting the observation of a new type of photosensitized luminescence of  ${}^1\text{O}_2$  unimols, which corresponds to a decay of vibrationally excited molecules of singlet oxygen [ ${}^1\Delta_g(V=1)$ ]. This emission was detected in aerobic solutions of photosensitizers.

The measurements were carried out on an apparatus with mechanical phosphoroscopes with a time resolution of 1 ms (Ref. 6). The photodetectors were FEU-83 photomultipliers with an S-1 spectral characteristic. The solvents were  $\text{CCl}_4$  and hexafluorobenzene, additionally purified by distillation. As photosensitizers we used 2,3,7,8-dibenzopyrene-1,6-quinone, tetraphenylporphin, pheophytin *a*, and bacterio-pheophytin *a*. The pigment concentration in the experiments was  $\approx 10^{-6}$  M. The excitation intensity did not exceed 100 mW/cm<sup>2</sup>.

In agreement with the results of earlier studies, we observed a luminescence with a primary peak at 1272 nm in aerobic solutions of all the photosensitizers which we used.<sup>1-3</sup> In addition, we detected in all cases a faint emission peaking at 1073 nm (Fig. 1). At room temperature the intensity of this emission was  $(2.5 \pm 1) \times 10^{-5}$  of the intensity of the band at 1272 nm.

In addition to this band, the emission spectra of the  $\text{CCl}_4$  solutions of the photosensitizers have a very faint but reliably observable band at 1160 nm. As detected on the apparatus which we used (20°), this band is about an order of magnitude weaker than the band at 1073 nm. After a correction for the spectral sensitivity of the photomultiplier, however, this band turned out to be ten times as intense as the band at 1073 nm (Fig. 1). The band at 1160 nm could not be detected reliably in the hexafluorobenzene solutions of the photosensitizers.

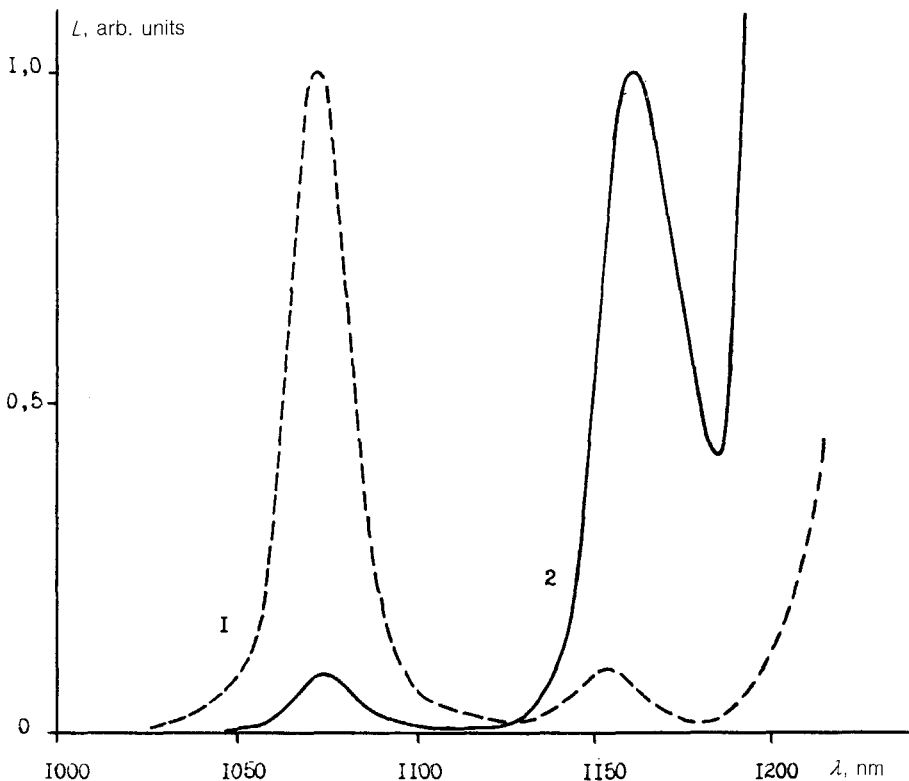


FIG. 1. Spectrum of photosensitized luminescence of singlet molecular oxygen in an air-saturated  $\text{CCl}_4$  solution of dibenzopyrene (1) before and (2) after correction for the spectral sensitivity of the luminescence apparatus used. Here  $L$  is the luminescence intensity. The primary luminescence peak, at 1270 nm, is not shown here.

The intensity of each band is a linear function of the intensity of the exciting light. The lifetime of the afterglow at the peak of the band at 1073 nm is close to the lifetime of the luminescence at the peak at 1270 nm (about 20 ms in  $\text{CCl}_4$  and  $\text{C}_6\text{F}_6$ ). The difference is less than 15%. An estimate puts the lifetime corresponding to the band at 1160 nm at approximately the same value.

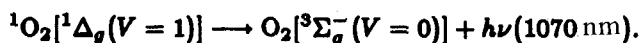
The addition of a  $^1\text{O}_2$  quencher, namely acetone, to the solutions resulted in a sharp attenuation of all the afterglow bands. At acetone concentrations  $\geq 10\%$ , none of these bands could be detected at all. It had been shown previously that at such acetone concentrations the  $^1\text{O}_2$  lifetime decreases to  $\leq 0.5$  ms, at which it is impossible to detect the emission on our apparatus, with mechanical phosphoroscopes.<sup>5</sup>

Purging the oxygen from the solutions by bubbling argon through them or by hooking up a vacuum pump erased all these afterglow bands.

Analysis showed that the intensity of the band at 1270 nm depends only weakly on the temperature. As the temperature is varied from  $-20^\circ\text{C}$  to  $+70^\circ\text{C}$ , the inten-

sity of this band decreases by a factor of about 1.5. As the temperature is raised, the band at 1073 nm grows sharply. The activation energy for the ratio of the intensities of the bands at 1073 and 1273 nm ( $I_{1070}/I_{1270}$ ) is  $4.5 \pm 0.5$  kcal/mole, according to our data. An estimate of the corresponding activation energy for the band at 1160 nm yields a value about half as large.

Note that the band at 1073 nm is observed in the absorption spectra of molecular oxygen in solution and in the gas phase. It corresponds to a filling of the [ $^1\Delta_g(V=1)$ ] state.<sup>6</sup> One would thus naturally conclude that this absorption band and the luminescence band which we observed at 1073 nm belong to the same electronic-vibrational transition:



Theoretically, one could think of several mechanisms for a photosensitized filling of the [ $^1\Delta_g(V=1)$ ] state. The experimental data, however, agree with the scheme in Fig. 2, according to which [ $^1\Delta_g(V=1)$ ] is filled as a result of a thermally induced transition from the [ $^1\Delta_g(V=0)$ ] state. The filling of the [ $^1\Delta_g(V=0)$ ] state is known quite well to result from a transfer of energy to oxygen from triplet photosensitizer molecules.<sup>1</sup> The decisive argument in favor of this mechanism is the strong temperature dependence of the band at 1073 nm, with the corresponding activation energy  $\approx 5$  kcal/mole, which is close to the energy distance between the peaks of the bands at 1272 and 1073 nm (4.2 kcal/mole).

In this case, the band at 1160 nm can also be explained in a simple way (Fig. 2).

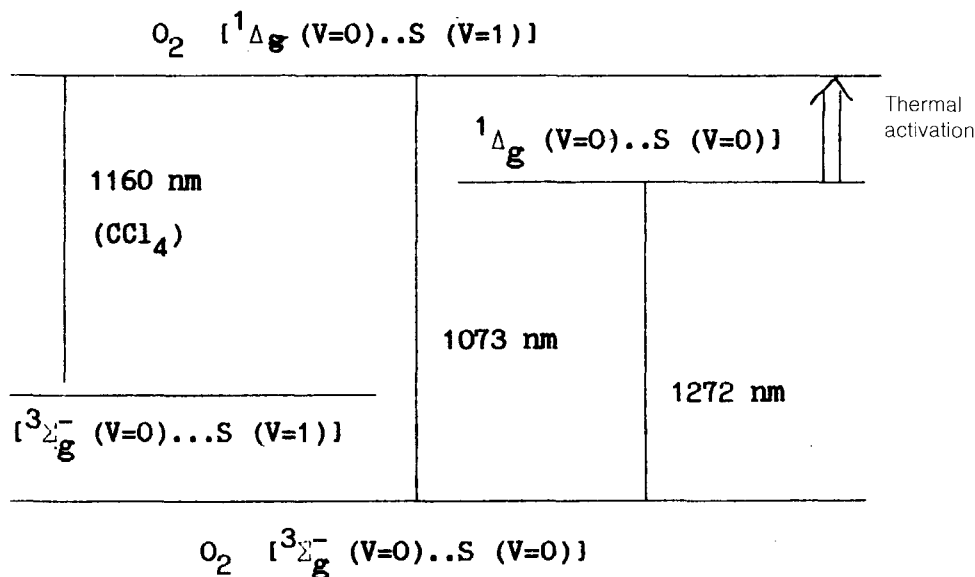
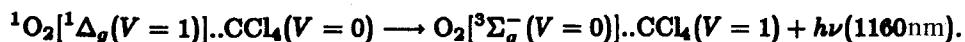


FIG. 2. Mechanism for the photosensitized luminescence of vibrationally excited  ${}^1\text{O}_2$  molecules; here  $S$  is a solvent molecule.

The fundamental frequency of C–Cl vibrations corresponds to<sup>7</sup> 780 cm.<sup>-1</sup> The energy distance between the bands at 1073 and 1160 nm corresponds to 700 cm.<sup>-1</sup>, i.e., to very nearly the same value. One is led to suggest that the band at 1160 nm corresponds to the transition



This luminescence band thus probably accompanies a decay of the [<sup>1</sup>Δ<sub>g</sub>(V=1)] state, with a simultaneous excitation of vibrations of the solvent molecules. The fundamental C–F vibration frequency is ≈ 1000 cm.<sup>-1</sup>, while that for C–D vibrations is ≈ 1600 cm.<sup>-1</sup> (Ref. 7). The implication is that corresponding bands could be observed at ≈ 1200 nm in the hexafluorobenzene. In this region, the sensitivity of the photomultiplier is lower than that at λ 1160 nm by a factor of several units, so it is essentially impossible to observe this band on our apparatus. According to the interpretation proposed here, the band at 1160 nm is thus similar to the band at 1350 nm which was described in Ref. 4. There is the difference that the first of these bands corresponds to a decay of the [<sup>1</sup>Δ<sub>g</sub>(V=1)] state, while the second corresponds to the decay of [<sup>1</sup>Δ<sub>g</sub>(V=0)].

<sup>1</sup>A. A. Krasnovsky, Jr., *Photochem. Photobiol.* **29**, 29 (1979).

<sup>2</sup>A. U. Khan, *Chem. Phys. Lett.* **72**, 112 (1980).

<sup>3</sup>K. I. Salokhiddinov, B. M. Dzagarov, I. M. Byteva, and G. P. Gurinovich, *Chem. Phys. Lett.* **76**, 85 (1980).

<sup>4</sup>P.-T. Chou and A. U. Khan, *Chem. Phys. Lett.* **103**, 281 (1984).

<sup>5</sup>A. A. Krasnovsky, Jr., and K. V. Neverov, *Chem. Phys. Lett.* **167**, 591 (1990).

<sup>6</sup>C. Long and D. R. Dearn, *J. Chem. Phys.* **59**, 5729 (1973).

<sup>7</sup>K. Nakanisi, *Infrared Spectra and Structure of Organic Compounds* [Russian translation], Mir, Moscow, 1965.

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