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GAS PHASE OBSERVATION OF THE 1.27-μ EMISSION OF SINGLET DELTA OXYGEN GENERATED AT ATMOSPHERIC PRESSURE BY HETEROGENEOUS PHOTOSENSITIZATION

Walter C. Eisenberg,* Alan Snelson, and James Veltman

IIT Research Institute
Chemistry and Chemical Engineering Research Division
Chicago, Illinois 60616

Robert W. Murray
Department of Chemistry
University of Missouri-St. Louis
St. Louis, Missouri 63121

Abstract. Singlet oxygen was generated in the gas phase using heterogeneous photosensitization and atmospheric pressure. The emission of O_2 ($^1\Delta g \rightarrow {}^3\Sigma g$) at 1.27-μ has been observed.

We have recently reported the gas phase generation of singlet oxygen using heterogeneous photosensitization, intense illumination and atmospheric pressure.[1] Singlet oxygen ($^1\Delta g$) was consistently produced in detectable quantities when air or oxygen was flowed through an irradiated tube coated with Rose Bengal. Evidence for $O_2(^1\Delta g)$ formation was obtained from chemical trapping, product distribution, and physical quenching experiments. We now report the gas phase observation of the 1.27-μ emission of singlet delta oxygen formed by heterogeneous photochemical sensitization at atmospheric pressure.[2]

The detection of the optical emissions from $O_2(^1\Delta g)$ to the ground state[3] provides a rapid accurate method of identifying this excited state. The direct emissions occur at 1.27 and 1.58-μ and correspond to the $^1\Delta g\ (\nu=0) \rightarrow {}^3\Sigma g^-(\nu=0)$ and the $^1\Delta g\ (\nu=0) \rightarrow {}^3\Delta g^-(\nu=1)$ transitions, respectively. The latter transition is weak and difficult to detect. The indirect "dimol" emission $O_2(^1\Delta g) + O_2(^1\Delta g) \rightarrow 2O_2(^3\Sigma\bar{g})$ has been observed at 6340 Å by a number of workers.[4] We were unable to detect the dimol emission by direct visual observation, but are presently modifying our photodetection system to permit observation of this emission. The 1.27-μ band was first identified as a component of the atmosphere airglow by Vallance-Jones and Harrison,[5] and since then there have been numerous reports concerning the presence and intensity of this emission in the airglow.[6]

The previously reported experiments where the 1.27-μ emission was observed were conducted at pressures less than atmospheric.[7(a-f)] Snelling[7(c)] was the first to use the 1.27-μ emission as evidence for the sensitized formation of singlet oxygen in the gas phase using irradiated benzene oxygen mixtures at near atmospheric pressures. Kummler[7(d)] made a similar observation in irradiated benzaldehyde-oxygen mixtures. Kearns[7(e)] and Wasserman[7(f)] identified singlet oxygen in irradiated oxygen sensitizer mixtures at reduced pressures by its characteristic epr spectrum. The emission at 1.27-μ has also been used by Pitts, *et al.*,[7(g,h)] for spectroscopic evidence of the near atmospheric production of $O_2(^1\Delta g)$ by energy transfer using benzene, naphthalene, and benzaldehyde as sensitizers. In addition, Kahn,[8] and Kahn and Kasha[9] have reported the first observation of the 1.27-μ emission in liquid solution at room temperature.

We are presently investigating potential mechanisms for the formation of $O_2(^1\Delta g)$ in the atmosphere, and ultimately we will examine the possibility that reactions involving singlet oxygen may play a role in the health effects related to atmospheric pollution. In our experiments oxygen or air was passed down a Rose Bengal coated generator at a rate of ca. 65 ℓ/min. The generation tube was cooled with a water jacket and irradiated with four 1000w General Electric Model DPT projection lamps. This entire assembly was enclosed in a metal light shield and cooled with a cage blower. At the exit of the generation zone an inlet for the introduction of acceptors and quenchers was attached, followed by a light baffle and the optical detector. In chemical trapping experiments the optical detector was replaced by a reaction zone and product traps.[1] The gas stream exiting from the generator was passed into a detector sample tube fitted with a quartz window through which the emission was observed. The detection system consisted of a light chopper, and interference filter (λ_0 = 1.27-μ, half band with 0.02-μ) and a liquid nitrogen cooled germanium photodiode.[7(h)] The signal was led into a lock-in amplifier and then a strip chart recorder.

The production of detectable quantities of singlet oxygen occurred whenever air or oxygen was flowed down the sensitizer coated generator tube during intense illumination. A record of the 1.27-μ emission of $O_2{}^1\Delta g$ generated during these experiments and measured as the amplified detector signal is presented in Figure 1. When a chemical acceptor such as tetramethylethylene (TME) was introduced following the generator tube the 1.27 emission and thus, the unreacted singlet oxygen reaching the detector decreased substantially (∿90%). Chemical trapping experiments[1] showed that a detector response of ca. 15 mv resulted from a net production rate of ca. 2×10^{-7} moles/min. $^1O_2$. This corresponds to a concentration of ca. 0.4 ppm $^1O_2$ in the gas stream.[10] Similarly, the introduction of a known singlet oxygen quencher, triethylamine, into the gas stream resulted in 90% reduction of the 1.27 emission. The detector signal decreased gradually with time possibly indicating the sensitizer was undergoing oxidation in the generation tube, i.e., a 15% reduction in $^1O_2$ production efficiency occurred after three hours of continuous operation. We are now comparing various sensitizers with respect to their susceptibility to this effect.

Estimates of the intensity of the light source in the generation system indicate that it is approximately ten times the normal solar flux,[7(g)] and may be comparable to the solar flux on a hot summer day. The gas flow in the generator tube is not greater than forty miles per hour. Consequently we have been able to study the reaction of singlet oxygen with a number of chemical substrates including solids under conditions that approximate environmental conditions.

These emission studies coupled with the previously reported chemical acceptor experiments' demonstrate that singlet oxygen can be formed at atmospheric pressure and may implicate it as a low level oxidant in the environment. This appears to be the first observation

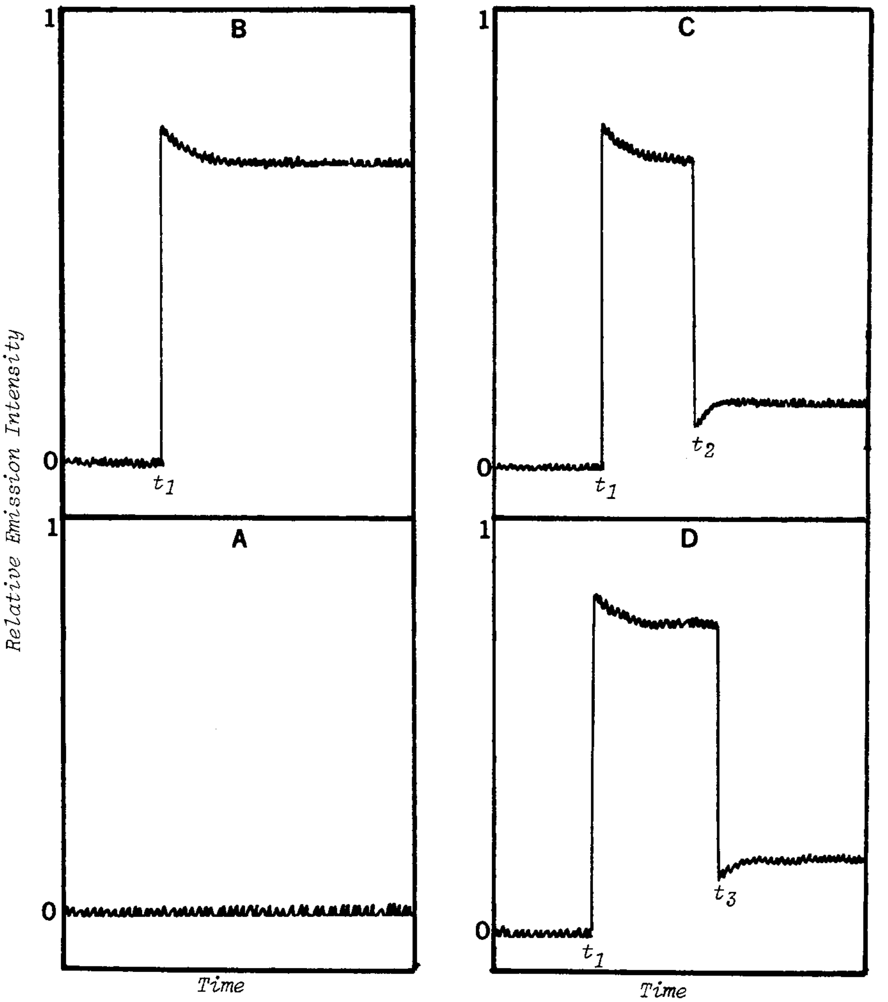

Figure 1. Dye sensitized emission of $O_2(^1\Delta g \rightarrow {}^3\Sigma g)$ at 1.27-μ in the gas phase at atmospheric pressure. (A) blank, air flowing and no illumination; (B) air flowing and illumination, t_1 (C) air flowing and illumination, time t_2, tetramethylethylene added; (D) air flowing and illumination, time t_3, triethylamine quencher added.

of the 1.27-μ emission of singlet oxygen in a heterogeneous gas phase sensitization system at atmospheric pressure. This technique is a direct diagnostic tool for the possible involvement of singlet oxygen in chemical and biological systems. The optical detection of $^1O_2$ has provided us with an extremely convenient method for adjusting the many parameters in our system in order to optimize $^1O_2$ production. Preliminary experiments suggest that this system will permit us to measure: *(1)* sensitizer efficiencies; *(2)* physical quenching rate constants; and *(3)* chemical reaction rate constants. This observation of the production of singlet oxygen under conditions closely approximating those in the environment raises important questions regarding the role of $^1O_2$ in air pollution chemistry. It is possible that oxygenated material present in the atmosphere and known to cause deleterious health effects may be produced by singlet oxygen reaction. Furthermore, it requires that the early suggestions of Pitts *et al.*,[11] regarding the possible sensitized production of $^1O_2$ in polluted atmospheres continue to receive attention.

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