Time-Resolved Absorption Spectrum of Singlet Oxygen in Solution

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Radiative transitions of molecular oxygen in solution continue to be a subject of significant study.[1−9] Most work has focused on the near-infrared phosphorescent transition between the lowest excited state, $O_2(a^1\Delta_g)$, and the ground state, $O_2(X^3\Sigma_g^-)$. More recently, emission from the second excited state, $O_2(b^1\Sigma_g^+)$, has also been studied in both the visible $[O_2(b^1\Sigma_g^+) \rightarrow O_2(X^3\Sigma_g^-)]$[5−7] and infrared $[O_2(b^1\Sigma_g^+) \rightarrow O_2(a^1\Delta_g)]$[3,5] regions of the spectrum. Although these studies have been very informative, limitations inherent to these emission experiments have become increasingly problematic. These limitations include (1) luminescence from other sources that can mask the weak emission of oxygen and (2) a $O_2(b^1\Sigma_g^+)$ lifetime that is short enough to preclude studies in most common solvents, specifically those that contain C−H and O−H bonds.[10,11] To our knowledge, only the *X*−*a* transition has been detected in an absorption experiment on dissolved oxygen, and this study was performed at extremely high oxygen pressures using halogenated hydrocarbon solvents to reduce the dangers of combustion.[12,13] In this paper, we report that $O_2(a^1\Delta_g)$ can be detected in air-saturated hydrocarbon solvents at 1 atm using time-resolved absorption experiments at ~5200 cm^{-1} $[O_2(a^1\Delta_g) \rightarrow O_2(b^1\Sigma_g^+)]$. These experiments not only demonstrate a new method to monitor $O_2(a^1\Delta_g)$ that will be useful in systems where emission experiments are limited, but the technique also yields heretofore unavailable information on the effect of solvent on the *a*−*b* radiative transition.

Using a step-scan Fourier transform infrared spectrometer,[14] absorption spectra were recorded over the range ~5000−5400 cm^{-1} in toluene, *n*-hexane, and CS_2 after irradiation of a $O_2(a^1\Delta_g)$ photosensitizer with a pulsed laser (Figures 1 and 2). The data obtained were assigned to the *a*→*b* transition on the basis of the following points: (1) The observed transient signals decayed with lifetimes identical to those obtained from $O_2(a^1\Delta_g)$ phosphorescence experiments in the same solvents. (2) The absorption signals were absent in nitrogen-saturated samples and samples with a $O_2(a^1\Delta_g)$ quencher. (3) The general position of the absorption maxima are consistent with those expected based on *b*−*a* emission experiments.[3]

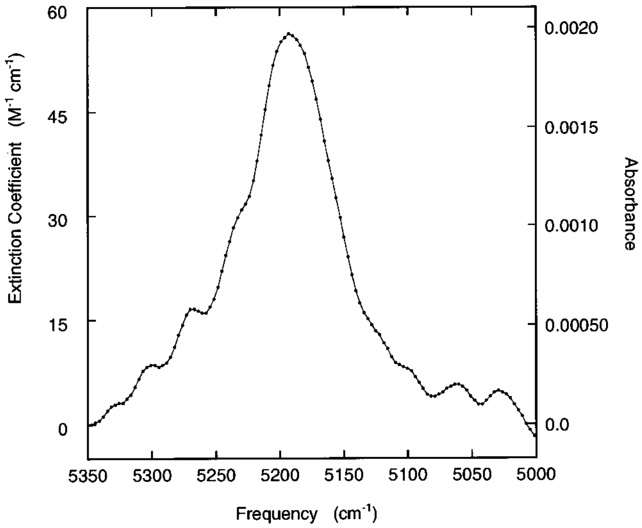

Figure 1. Absorption spectrum of $O_2(a^1\Delta_g)$ in air-saturated toluene at 1 atm over a 1-cm path length. The photosensitizer 9-fluorenone was irradiated at 355 nm (2.7 mJ cm^{-2} pulse^{-1}).

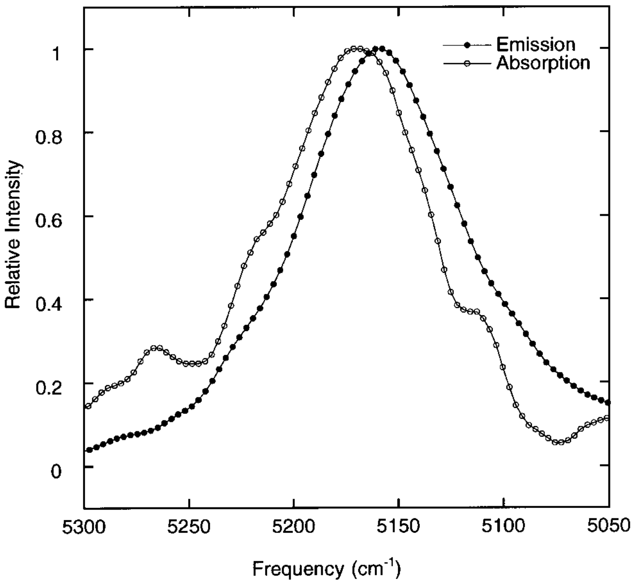

Figure 2. Normalized absorption spectrum of $O_2(a^1\Delta_g)$ and emission spectrum of $O_2(b^1\Sigma_g^+)$ in air-saturated CS_2 at 1 atm over a 1-cm path length. The emission spectrum was likewise obtained using the step-scan Fourier transform spectrometer. Comparison of the *b*−*a* and *a*−*b* spectra indicates a Stokes shift of 10.4 cm^{-1}.

The rate constant, k_{a-X}, for the *a*→*X* radiative transition depends significantly on the solvent.[1,2,4] The interpretation of this phenomenon is important from the general perspective of understanding solvent effects on highly forbidden transitions. At present, the most promising model for the solvent-perturbed oxygen system is that of Minaev in which it is proposed that the *a*→*X* transition steals intensity from the *b*→*a* transition.[15,16] In his presentation, Minaev indicates that the ratio, k_{a-X}/k_{b-a}, of the respective radiative rate constants should (1) not depend on the solvent, and (2) equal $\sim 3 \times 10^{-4}$. The only solution-phase k_{a-X}/k_{b-a} data available are those of Schmidt for which a value of 3.2

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× 10^{-4} is reported based on $b-a$ and $a-X$ emission experiments performed in CCl_4.[5] Schmidt has used this value along with gas-phase data of Fink et al.[17] and 5 K Ar matrix data of Becker et al.[18] to argue in favor of Minaev's thesis.[5] Unfortunately, further tests of Minaev's theory using a range of different solvents, specifically those containing C−H and O−H bonds, will be difficult if k_{b-a} can only be determined in emission experiments.

By using eq 1, in which the $b \rightarrow a$ radiative rate constant, k_{b-a}, is equated to the $a \rightarrow b$ integrated absorption coefficient, Γ_{a-b},[19] data such as those shown in Figure 1 can be used to address Minaev's predictions.

$$k_{b-a} = n^2 \frac{8\pi c \ln(10)}{N_A} \frac{g_a}{g_b} \nu^2 \Gamma_{a-b} \qquad (1)$$

In eq 1, g is the degeneracy of the indicated state, N_A is Avogadro's number, ν is the transition frequency, and n is the solvent refractive index. $O_2(a^1\Delta_g)$ absorption coefficients were assumed to be equivalent to extinction coefficients, and the latter were obtained using Beer's law. The concentration of $O_2(a^1\Delta_g)$ in each of the solvents was determined using the following photosensitized quantum yields: 9-fluorenone in toluene and *n*-hexane, $\phi = 1.0$; C_{60} in CS_2, $\phi = 1.0$. These quantum yields were verified in $O_2(a^1\Delta_g)$ phosphorescence experiments using C_{60}- and phenalenone-sensitized $O_2(a^1\Delta_g)$ emission as a standard.[2,20]

Table 1: Maxima of the $O_2(a^1\Delta_g) \rightarrow O_2(b^1\Sigma_g^+)$ Absorption Band, $\nu_{max}^{a\rightarrow b}$, Maximum Extinction Coefficients of the $O_2(a^1\Delta_g) \rightarrow O_2(b^1\Sigma_g^+)$ Band, $\epsilon_{max}^{a\rightarrow b}$, and Rate Constants for the $O_2(b^1\Sigma_g^+) \rightarrow O_2(a^1\Delta_g)$ and $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$ Radiative Transitions[a]

	$\nu_{max}^{a\rightarrow b}$ (cm^{-1})	$\epsilon_{max}^{a\rightarrow b}$ (M^{-1} cm^{-1})	k_{a-X} (s^{-1})	k_{b-a} (s^{-1})	k_{a-X}/k_{b-a} (× 10^4)
toluene	5192.9	56.3	1.44 ± 0.07	1730 ± 220	8.3 ± 1.5
n-hexane	5197.8	39.7	0.60 ± 0.03	790 ± 130	7.6 ± 1.6
CS_2	5169.8	52.4	3.1 ± 0.2	2460 ± 500	12.6 ± 3.2

[a] The errors shown for k_{a-X} reflect an uncertainty relative to a standard value of k_{a-X} in benzene.[2,21] The error on the absolute value of k_{a-X} in benzene, however, is larger ($k_{a-X}^{benzene} = 1.5 \pm 0.5$ s^{-1}).[4,22]

Values of k_{b-a} determined using eq 1 were then used along with available k_{a-X} data[2,4] to obtain the ratio k_{a-X}/k_{b-a}. For the preliminary experiments reported herein, we find that this ratio (1) is larger than that predicted by Minaev and obtained by Schmidt in CCl_4 and (2) appears to vary with the solvent (Table 1). Although the general thesis of intensity stealing proposed by Minaev is quite reasonable, our data lead us to suggest that some modification in the model is required.

In conclusion, we report that the singlet delta state of oxygen can be detected in time-resolved absorption experiments using the $a-b$ transition at ∼5200 cm^{-1}. This technique will be useful as a general monitor of singlet oxygen, capable of providing heretofore inaccessible information in a wide range of systems.

Note: We have been informed in a recent private communication that A. P. Losev et al. (Minsk) have also been able to detect $O_2(a^1\Delta_g)$ in a solution-phase absorption experiment.

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