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Direct Spectroscopic Evidence of Photosensitized O_2 765 nm ($^1\Sigma^+{}_g \rightarrow {}^3\Sigma^-{}_g$) and O_2 Dimol 634 and 703 nm (($^1\Delta_g)_2 \rightarrow ({}^3\Sigma^-{}_g)_2$) Vibronic Emission in Solution

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Only recently has the investigation of the second low-lying O_2 $^1\Sigma^+{}_g$ state in solution become possible with the detection of the O_2 ($^1\Sigma^+{}_g \rightarrow {}^1\Delta_g$) 1930 nm emission.[1,2] Unfortunately, due to the slow response limit of infrared detectors (>2 μs), these studies were unable to directly resolve the relaxation dynamics of the $^1\Sigma^+{}_g$ state. To overcome this barrier, Schmidt and Bodesheim[3−5] photosensitized O_2 and monitored the emission decay within the 765 nm region, which has been attributed, on the basis of gas phase studies,[6,7] to the $^1\Sigma^+{}_g \rightarrow {}^3\Sigma^-{}_g$ emission. Therefore, the time resolution can be achieved by a fast-response photomultiplier. Using an interference filter to isolate the emission at 765 ± 19 nm and applying a multistep analysis that involved both the subtraction of background as well as deconvolution, they were capable of extracting a portion attributed to the $^1\Sigma^+{}_g$ decay. On the other hand, collision between two O_2 $^1\Delta_g$ molecules in the gas phase results in dimol emission with principal maxima at 634 and 703 nm.[7] Recently, many attempts have been made to measure $O_2(^1\Delta_g)$ dimol luminescence upon photosensitization in solution. Several reports of $O_2(^1\Delta_g)$ dimol emission in solution were attributed to $O_2(^1\Delta_g)$ dimol interacting with photosensitizers and/or their oxygenation products.[8−10] Based on the $O_2(^1\Delta_g)$ dimol sensitizing tetra-*tert*-butylphthalocyanine (PC) luminescence Krasnovsky and Foote[11] reported the time-resolved study of the $O_2(^1\Delta_g)$ dimol. Since the monitored decay dynamics originate from the $O_2(^1\Delta_g)$ dimol sensitizing PC luminescence, the complexity of this system required a nontrivial numerical solution of the differential equation.

We report here the direct, unambiguous spectroscopic evidence of $O_2(^1\Sigma^+{}_g)$ emission (765 nm) and $O_2(^1\Delta_g)$ dimol emission (634 and 703 nm) in solution. Consequently, the decay dynamics of the $O_2(^1\Sigma^+{}_g)$ state and the $O_2(^1\Delta_g)$ dimol in solution can be monitored directly by time-dependent spectral evolution. In this study, 1H-phenalen-1-one (PH)[12] was chosen as a sensitizer for $^1O_2$ generation. PH has been reported to produce $O_2(^1\Sigma^+{}_g)$ and $O_2(^1\Delta_g)$ states in yields of 0.62 and 0.93, respectively.[3,4] We applied a red-sensitive intensified charge coupled detector (ICCD, Princeton Instrument, Model 576G/1) coupled with either an Ar^+ laser (351−363 nm) for the steady-state measurement or a Nd:YAG laser (355 nm, 5 ns) for the time-resolved measurement. The inset in Figure 1 shows the non-time-resolved PH-sensitized $^1O_2$ emission spectrum in the region of 600−800 nm. Apparently, in addition to a smooth declining background emission resulting from the PH phosphorescence, three narrow-bandwidth humps with maxima at ∼630, ∼700, and ∼765 nm were observed. Upon degassing, these three vibronic peaks disappear accompanying an enhancement of the PH phosphorescence. Consequently, subtraction of the PH phosphorescence background between oxygenated and degassed spectra to resolve the $^1O_2$ emission spectra is difficult. Taking the quenching rates of methanol for the O_2 $^1\Sigma^+{}_g$ and $^1\Delta_g$ states to be 2.2×10^9 M^{-1} s^{-1} [5] and 3890 M^{-1} s^{-1},[13] we calculate that, by adding 5 vol % methanol, >99% of $O_2(^1\Sigma^+{}_g)$ and ∼90% of $O_2(^1\Delta_g)_2$ in CCl_4 will be quenched whereas the PH phosphorescence intensity changes slightly. As a result, Figure 1 shows the $^1O_2$ emission spectrum after subtracting the spectrum with 5 vol % methanol added. Three vibronic emission maxima at 634, 703, and 765 nm were resolved, which exactly correspond to $^1O_2$ dimol (($^1\Delta_g)_2(0,0) \rightarrow ({}^3\Sigma^-{}_g)_2(0,0)$ and ($^1\Delta_g)_2(0,0) \rightarrow ({}^3\Sigma^-{}_g)_2(0,1)$) emission and O_2 ($^1\Sigma^+{}_g(0) \rightarrow {}^3\Sigma^-{}_g(0)$) emission, respectively, in the gas phase.[7]

We have performed the decay dynamics of $O_2(^1\Sigma^+{}_g)$ and O_2($^1\Delta_g$) dimol emissions by monitoring the time-dependent spectral evolution at 600−800 nm. Figure 2 shows the time-dependent 765 nm emission spectra from 50 ns to 1.0 μs. A plot of the 765 nm intensity versus the delay time (insert in Figure 2) gives both rise and decay components. The formation and decay dynamics of the $^1\Sigma^+{}_g$ state are depicted in Scheme 1 (eqs 1−3). With a pseudo-first-order approximation, the rise and decay of the 765 nm emission ($[O_2(^1\Sigma^+{}_g)]_t$) can be fitted by eq I.

Scheme 1

$$\mathrm{PH} \xrightarrow[(>10^{10}\ \mathrm{s}^{-1})]{h\nu\quad \text{intersystem crossing}} \mathrm{PH^*(T)} \tag{1}$$

$$\mathrm{PH^*(T)} + O_2(^3\Sigma^-{}_g) \xrightarrow{k_c} O_2(^1\Sigma^+{}_g) + \mathrm{PH}(S_0) \tag{2}$$

$$O_2(^1\Sigma^+{}_g) \xrightarrow{k_d} O_2(^1\Delta_g) \text{ or } O_2(^3\Sigma^-{}_g) \tag{3}$$

$$O_2(^1\Delta_g) \xrightarrow{k_p} O_2(^3\Sigma^-{}_g) \tag{4}$$

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \underset{k_{-ac}}{\overset{k_{ac}}{\rightleftharpoons}} (O_2(^1\Delta_g))_2 \tag{5}$$

$$(O_2(^1\Delta_g))_2 \xrightarrow{k_{dim}} (O_2(^3\Sigma^-{}_g))_2 \tag{6}$$

$$[O_2(^1\Sigma^+{}_g)]_t = \{A_0k_r/(k_d - k_r)\}[e^{-k_rt} - e^{-k_dt}] \tag{I}$$

$$k_r = k_c[O_2(^3\Sigma^-{}_g)]$$

In this iterative fitting procedure, the oxygen concentration ($[O_2(^3\Sigma^-{}_g)]$) is taken to be 1.24×10^{-2} M in CCl_4 at 1 bar of oxygen pressure.[14] With the best fit, the decay rate k_d of the $^1\Sigma^+{}_g$ state is calculated to be 8.20×10^6 s^{-1}, which corresponds to a lifetime of 122 ns. This value is within the same magnitude as that reported by previous methods.[3−5] However, our time-dependent spectral evolution of the 765 nm emission simultaneously provides both spectral and dynamic evidence of the O_2 $^1\Sigma^+{}_g \rightarrow {}^3\Sigma^-{}_g(0)$ transition in solution. k_c is calculated to be 2.0×10^9 s^{-1}, consistent with the theoretical ∼1/9 of the diffusion-controlled rate of forming a PH- -O_2 collisional complex in CCl_4.

Both 703 and 634 nm emission bands undergo slower decay dynamics, and the rate is determined to be 1.2×10^3 s^{-1} (833 μs) in CCl_4. A similar measurement was performed in oxygen-saturated C_6F_6, and the decay was calculated to be 4.35×10^2 s^{-1} (2.3 ms). We also performed the lifetime study of O_2 $^1\Delta_g \rightarrow {}^3\Sigma^-{}_g(0)$ 1270 nm emission in oxygenated CCl_4 and C_6F_6 solution.[15] Under the same excitation energy as that used in the $O_2(^1\Delta_g)$ dimol studies the lifetimes are measured to be 1.7 and 4.7 ms, respectively.[16] These lifetimes are approximately twice as long as the lifetime of $O_2(^1\Delta_g)$ dimol emission, which is consistent with Krasnovsky and Foote's results based on the $O_2(^1\Delta_g)$ dimol sensitized PC luminescence.[11] This result can

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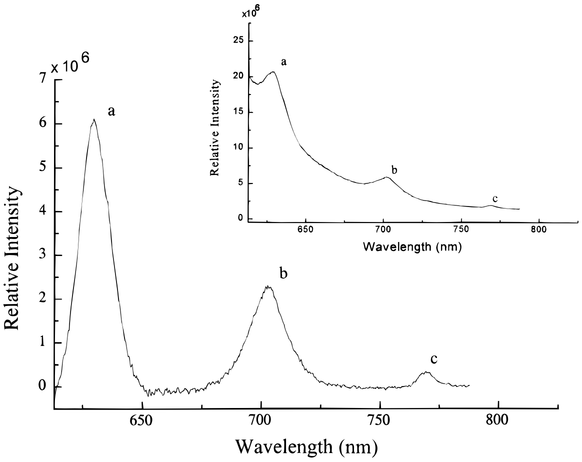

Figure 1. Emission spectrum of O_2 (1.24×10^{-2} M) sensitized by PH in CCl_4 at 25 °C. Peaks a and b correspond to the $O_2(^1\Delta_g)$ dimol transition $(^1\Delta_g)_2 \rightarrow (^3\Sigma^-_g)_2$, and peak c corresponds to the $^1\Sigma^+_g \rightarrow {}^3\Sigma^-_g$ single-molecule emission. The PH was excited by a CW Ar^+ laser (351−363 nm, 150 mW with a beam diameter of 1.5 mm). The inset shows the emission spectrum within the 620−800 nm region before subtracting the background luminescence (see the text).

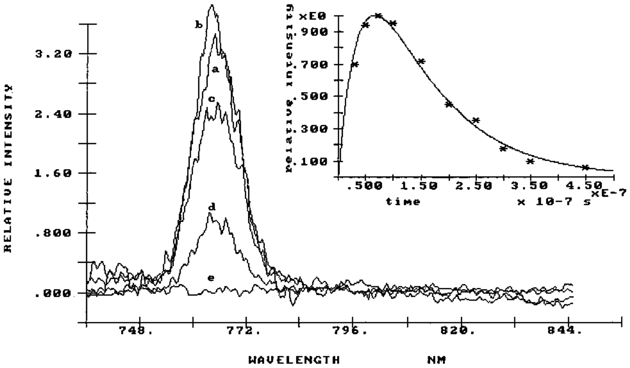

Figure 2. Time-resolved spectra of O_2 $^1\Sigma^+_g$ at several selected delay times: (a) 50, (b) 75, (c) 150, (d) 250, and (e) 1000 ns. The inset shows a plot of the integrated 765 nm emission intensity versus various delay times. In this experiment the third harmonic of a Nd:YAG laser (355 nm, 1.5 mJ with a beam diameter of 2.0 mm) was used as an excitation source.

be rationalized by the formation and decay dynamics of the $O_2(^1\Delta_g)$ dimol species depicted in Scheme 1 (eqs 4−6). Since dimol formation does not lead to the quenching of the $^1\Delta_g$ lieftime, Krasnovsky and Foote conclude that the rate of dissociation (k_{-ac}) of the $^1O_2$ dimol to $^1O_2$ monomer should be much faster than the rate of dimol formation (k_{ac}). Accordingly, the time-dependent dimol concentration can be expressed as in eq (II). Therefore, the dimol signal decay reflects the slow and

$$[(^1\Delta_g)_2]_t = \frac{k_{ac}[^1O_2]^2(t=0)}{(k_{-ac} + k_{dim} - 2k_p)} e^{-2k_p t} \qquad \text{(II)}$$

limiting annihilation of two $^1\Delta_g$ molecules, which actually corresponds to twice the decay rate of the $^1\Delta_g$ species.

An important scientific problem, raised by Krasnovsky et al., is the exact nature of the emitting dimol species: whether it is free or resulting from the collisional complex with the sensitizer.[9] In an attempt to resolve this controversy we have performed the photosensitization experiment using 1′-acetonaphthone and 2′-acetonaphthone as sensitizers. Table 1 clearly shows that the spectral features (e.g., the emission peak wavelength, bandwidth, and 703 nm/634 nm intensity ratio) of the dimol emission are nearly identical between PH and 1′-acetonaphthone (or 2′-acetonaphthone). One may argue that this result may simply indicate a similar interaction between $O_2(^1\Delta_g)$ dimol species and various sensitizers with the ketone group. To resolve this inquiry we have studied the $^1O_2$ emission expelled from photoeliminating 1,4-dimethylnaphthalene endoperoxide (DMN-O_2)[19] and found that the spectral features of the $O_2(^1\Delta_g)$ dimol emission are also identical with those measured by the photosensitization method (Table 1). Thus, we conclude that 634 and 703 nm emission bands result from a freely solvated $O_2(^1\Delta_g)$ dimol but not from a collisional complex between $O_2(^1\Delta_g)$ dimol and sensitizers used in this study. We also performed an experiment using porphyrin-based sensitizers such as tetraphenylporphine and the dimethyl ester of protoporphyrin IX. The resulting spectra in the 600−800 nm region are complicated due to the dominant delayed fluorescence of the sensitizer and possibly the photoproduct. It is also noteworthy that no 765 nm emission was observed by photoeliminating DMN-O_2. This result is consistent with our previous report that the generation of the O_2 $^1\Sigma^+_g$ state by photoeliminating DMN-O_2 is at least 70 times less than that of the photosensitization method.[1,20]

Table 1

	λ_{max}, nm (fwhm, cm^{-1})			
	$^1\Delta_g \rightarrow {}^3\Sigma^-_g$	$^1\Sigma^+_g \rightarrow {}^3\Sigma^-_g$	$(^1\Delta_g)_2 \rightarrow (^3\Sigma^-_g)_2$	$I_{634}:I_{703}:I_{765}$[b]
PH	1270 (140)	765 (133)	634 703 (368)	1:0.63:0.09
2′-acetonaphthone	1270 (138)	765 (135)	633 703 (370)	1:0.63:0.1
1′-acetonaphthone	1270 (140)	765 (135)	633 703 (370)	1:0.63:0.09
DMN-O_2[a]	1273 (140)	*c*	634 703 (370)	1:0.65

[a] For DMN-O_2 the Nd:YAG laser (266 nm) was used as a photoelimination source. [b] The ratio of emission intensity for three peaks is calculated after correcting the wavelength-dependent responsivity of our detection system. [c] The 765 nm emission was not observed.

Taking advantage of our spectral resolution of ~20 cm^{-1} in the CW measurement, the full width at half maximum (fwhm) of the 765 nm emission was measured to be ~135 cm^{-1}, which is nearly the same as that of the $^1\Delta_g$ 1270 nm emission band (~140 cm^{-1}; see Table 1). Since the $O_2(^1\Delta_g)$ dimol emission requires a simultaneous transition of two $^1\Delta_g$ state O_2 molecules, the fwhm of dimol emission is estimated to be in the range of 280 cm^{-1}. Therefore, the observed fwhm of ~370 cm^{-1} of the 635 and 703 nm bands (Table 1) is intriguing. If the interaction energy of O_2−O_2 pairs is extremely weak, the result may indicate that the rate of dissociation (k_{-ac}) of the $O_2(^1\Delta_g)$ dimol to the monomer is ultrafast, resulting in the spectral broadening. Assuming that the additional ~45 cm^{-1} broadening for each $^1\Delta_g$ emission in the dimol corresponds to $(2\pi c\tau)^{-1}$, where τ is lifetime of the dimol species, k_{-ac} (~$1/\tau$) is estimated to be 8.5×10^{12} s^{-1}.[21,22] Taking the diffusion-controlled rate of ~2.0×10^{10} s^{-1} as an upper limit for the rate (k_{ac}) of dimol formation in CCl_4, k_{-ac} is more than 2 orders of magnitude faster. The result further supports the assumption of $k_{-ac} \gg k_{ac}$ in deriving eq II.

In conclusion, we report direct, unambiguous spectral evidence of solution-phase photosensitized $O_2(^1\Sigma^+_g)$ and $O_2(^1\Delta_g)$ dimol emissions in the visible region. The capability of monitoring dynamics of relaxation and time-dependent spectral evolution simultaneously may provide novel information on the photophysics and photochemistry of the solvated singlet molecular oxygen.

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(16) The measured $O_2(^1\Delta_g)$ lifetime of 4.7 ms in C_6F_6 is close to those reported previously (~5.0 ms[11] and 3.9 ms[17]). On the other hand, the observed lifetime in CCl_4 has been known to be strongly excitation-energy dependent. Our measured lifetime of 1.7 ms is between the reported values of 700 μs[1] and 26 ms.[18]

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