Solvent Effect on the $O_2(b^1\Sigma_g^+) \rightarrow O_2(a^1\Delta_g)$ Emission Spectrum

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The effect of solvent on the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ fluorescence spectrum has been examined. The emission maximum in solution is red-shifted relative to the gas-phase value of 1908 nm, and the extent of the shift increases as the refractive index, n, of the solvent increases. This observation is consistent with previously published data on the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition. Although solvent-dependent changes in the *wavelength* of the infrared $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission peak are more pronounced than on the near-infrared $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ peak, the effect of solvent on the respective transition *energies* is roughly equivalent. Plots of the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission maximum against n, or functions of n, indicate that a number of variables likely contribute to the oxygen−solvent interaction.

Introduction

The effect of solvent on radiative transitions in the oxygen molecule,[1−10] or on radiative transitions that depend on the presence of molecular oxygen,[11] remains a subject of great interest. Of particular concern are the near-infrared $[O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)]$ and infrared $[O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)]$ transitions, which are forbidden in the isolated molecule[12,13] but which become significantly more probable as a result of solvent perturbations. Extensive data now exist documenting the effect of solvent on both the probability[2,3] and spectrum[5−8] of the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition. Although some information on the energy and probability of the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition is available,[3,14−16] the effect of solvent has yet to be systematically examined.

Attempts to interpret the existing data have yet to receive universal acceptance.[3,4,9] Although it has been argued that, for $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$, the mechanism by which solvent influences the transition probability differs from that by which solvent influences spectral shifts,[4] it is by no means resolved that these processes are independent. With regard to transition probabilities, one perspective that appears promising is that of Minaev,[10] in which solvent effects on the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition are said to contribute to solvent effects on the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition. Some experimental data have been presented in support of Minaev's argument.[3] Nevertheless, before any further progress can be made documenting either Minaev's perspective or the differences in the way(s) transition probabilities and spectral shifts are influenced by solvent, it is essential to first collect systematic data on the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition in solution. We report herein the results of a study on the effect of solvent on the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission spectrum.

Experimental Section

$O_2(b^1\Sigma_g^+)$ was created by energy transfer from photosensitizers dissolved in the given solvent. A pulsed Nd:YAG laser system was used as the excitation source (Quanta-Ray GCR 230, MOPO 710 optical parametric oscillator). The fluorescence of $O_2(b^1\Sigma_g^+)$ was focused onto the entrance slit of a Photon Technologies, Inc. model 01-001FAST monochromator (grating blazed at 1250 nm, 600 L/mm). A silicon window at the monochromator entrance slit eliminated UV/vis radiation, transmitting only the desired infrared components. A 77 K InSb detector (Judson) was used to detect $O_2(b^1\Sigma_g^+)$ fluorescence. Under all circumstances, the $O_2(b^1\Sigma_g^+)$ signal was limited by the detector time constant of 2 μs, which is expected given the comparatively short $O_2(b^1\Sigma_g^+)$ lifetime.[17,18] $O_2(b^1\Sigma_g^+)$ fluorescence intensities were quantified by integrating this detector-limited signal. Each spectrum was recorded in at least two independent experiments.

The monochromator was calibrated at two wavelengths: (1) 1064 nm, obtained from the fundamental lasing wavelength of the Nd:YAG laser, and (2) 1907 nm, obtained as the first Stokes line by Raman scattering 1064 nm with H_2 gas ($\Delta E = 4155$ cm^{-1}). The spectral response of the monochromator/detector system was ascertained using a calibrated blackbody source. $O_2(b^1\Sigma_g^+)$ spectral bandwidths did not change as the monochromator slits were narrowed from 2 to 0.75 mm.

Solvents (Aldrich) were used as received. 9-Fluorenone, perinaphthenone, and acridine were used as sensitizers. 9-Fluorenone was recrystallized twice from ethanol. Acridine was recrystallized from ethanol/water and then sublimed under vacuum. Perinaphthenone was used as received. In CS_2 and the CS_2/CCl_4 mixtures, where solvent absorption extends to longer wavelengths, 9-fluorenone ($\sim 2 \times 10^{-3}$ M) was irradiated between 430 and 450 nm. Otherwise, sensitizers ($\sim 5 \times 10^{-5}$ M) were irradiated at 355 nm. In all cases, laser energies of ~1−5 mJ/pulse were used. Solutions were air-saturated.

Results and Discussion

Spectral Shift of the Emission Band. In 1961, Noxon[14] reported an emission maximum of 1908 ± 3 nm (5241 ± 8 cm^{-1}) for the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition in the gas phase. Examination[19] of gas-phase data published in 1991 by Fink et al.[16] reveals a $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ maximum centered at about 1912 nm. We recorded the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission

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TABLE 1: Peak Maxima for the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ Transition

solvent	n^a	peak maximum^b
gas phase	1.0000	1908 nm (5241 cm^{-1})
perfluorohexane	1.2515	1914 nm (5225 cm^{-1})
perfluorodecalin^c	1.3145	1917 nm (5217 cm^{-1})
Freon 113^d	1.3580	1920 nm (5208 cm^{-1})
CCl_4	1.4600	1926 nm (5192 cm^{-1})
CCl_4/CS_2 (75:25)^e	1.4826	1928 nm (5187 cm^{-1})
CCl_4/CS_2 (48:52)^e	1.5200	1930 nm (5181 cm^{-1})
CCl_4/CS_2 (25:75)^e	1.5607	1933 nm (5173 cm^{-1})
CS_2	1.6270	1936 nm (5165 cm^{-1})

[a] Solvent refractive index at 20 °C. [b] We estimate our error to be approximately ±1.0 nm. Each number is an average of data obtained from at least two independent measurements. [c] Signal-to-noise levels in this solvent were poor, in part due to an abnormally fast rate of sensitizer degradation. This chemistry may reflect the presence of an impurity in the solvent. [d] 1,1,2-Trichlorotrifluoroethane. [e] Mole fractions of the respective components. In these mixtures, the refractive index is not a linear function of the mole fraction of one component. The refractive indexes were measured using an Abbe refractometer, and the data thus obtained compared well to what has been published.[26]

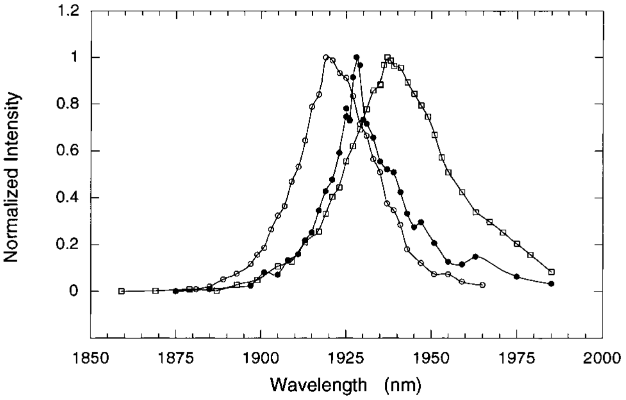

Figure 1. $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission spectrum recorded in three solvents: Freon 113 (○), 0.25 mole fraction CS_2 in CCl_4 (●), and CS_2 (□). Each point was obtained by integrating the signal obtained from the InSb detector. An interpolating function was used to create the lines.

spectrum in eight solvents (Table 1, Figure 1). In all cases, the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ peak maximum is red-shifted relative to the gas-phase values and ranges from 1914 nm in perfluorohexane to 1936 nm in CS_2. Heretofore, the only report of the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission spectrum in solution is that of Chou and Frei[15] in CCl_4. We observe a λ_{max} in CCl_4 that is consistent with the value reported by Chou and Frei.[20]

The effect of solvent on the *wavelength* of the infrared $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ emission maximum is large in comparison to the solvent effect on the near-infrared $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition wavelength.[5-8] For example, relative to the corresponding gas-phase band, the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ maximum in CS_2 is shifted by ~28 nm, whereas the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ maximum is shifted by only ~8.8 nm. The effects of solvent on the transition *energies*, however, are approximately equivalent, 76 and 54 cm^{-1}, for the respective shifts in CS_2.[21,22] From an experimental perspective, use of a more accurate Fourier transform spectrometer[5,6] is thus not as critical for the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ study as it is for the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ study.

Data from $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ studies indicate that, with the exception of a few fluorocarbon solvents, the solvent causes a red-shift of the emission peak relative to the gas-phase value of 1268.6 nm (7882.4 cm^{-1}), and the extent of the shift generally increases as the refractive index of the solvent increases.[5,6] Interpretations of the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ data have focused on the fact that linear correlations may exist when the band maximum is plotted against either the solvent refractive index, *n*, or functions of the refractive index (e.g., the solvent electronic polarizability).[4-6] Such plots nevertheless exhibit a large degree of scatter, and solvents have been identified[23] that clearly do not conform to the proposed linear correlations.[6]

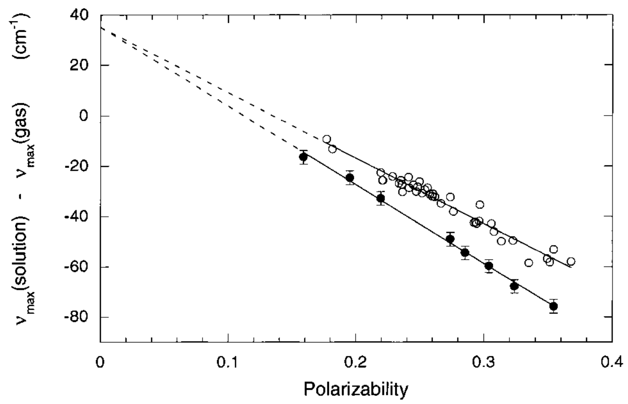

Figure 2. Plot of the difference between the solution- and gas-phase emission maxima as a function of the solvent polarizability for both the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ (●) and $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ (○) transitions. The Noxon value of 5241 cm^{-1} was used for $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ ν_{max}(gas). The $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ data are those of Wessels and Rodgers[6] and exclude the "anomalous" solvents.[23] The solid lines are linear least-squares fits to the data. The polarizability was calculated using the following function of the solvent refractive index, *n*: $(n^2 - 1)/(n^2 + 2)$. Other functions of *n* were also used for the abscissa, including dipolar $[(n^2 - 1)/(2n^2 + 1)]$ and quadrupolar $[(n^2 - 1)/(3n^2 + 2)]$ coupling terms from Kirkwood–Onsager dielectric continuum theories.[11] Differences between these plots were small.

The $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition likewise shifts to lower energy with an increase in *n*, and plots of the emission maximum against *n*, or functions of *n*, yield good linear correlations (Figure 2). Unfortunately, the comparatively short lifetime of $O_2(b^1\Sigma_g^+)$ in solution presently precludes the use of a wider variety of solvents, including those solvents that provide anomalies in analogous plots of the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ data.[23] At least, we are able to conclude from the general dependence of the emission maximum on *n*, and functions of *n*, that the electronic response of the solvent is important in determining the extent to which the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition is perturbed. Such data are consistent with an oxygen–solvent interaction comprised of stabilizing dispersive forces.

If the emission peak maximum indeed depends linearly on *n*, or a function of *n*, our solution-phase data extrapolate to a gas-phase maximum that is blue-shifted relative to the experimentally observed maximum. This is illustrated in Figure 2 where we plot the difference between the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ solution- and gas-phase maxima as a function of the solvent polarizability. The fact that such "Bayliss–McRae" plots do not have an intercept of zero is a common observation.[24,25] Indeed, an analogous plot using the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ data likewise has a nonzero intercept (Figure 2).[4,6] In the latter case, one obtains an intercept of ~35 cm^{-1} and a slope of ~260 cm^{-1}. We obtain an intercept of 35 cm^{-1} and a slope of 313 cm^{-1} from our $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ Bayliss–McRae plot. The fact that these intercepts and slopes are similar indicates that the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition energy responds to the solvent perturbation in much the same way as the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition energy. However, it is important to stress that, for the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ data, the comparatively good linear correlation with the solvent polarizability occurs only upon the exclusion of data.[23] If the experimental limitations can be overcome, it will be important to see how the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition responds to a wider variety of solvents.

A nonzero intercept in a Bayliss–McRae plot may indicate that destabilizing repulsive interactions between the solvent and solute occur along with any stabilizing dispersive interactions.[4,24] In the least, such a nonzero intercept indicates that the solvent–solute interaction is comprised of more than one phenomenon. The comparatively large degree of scatter in the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ data, certainly when plotted with respect to solvent polarizability, supports this latter perspective.

Width of the Emission Band at Half-Maximum. In his gas-phase study, Noxon assigned his observed peak to the Q-branch of the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition.[14] He indicated that the bandwidth at the peak half-maximum is not likely to exceed 20 Å (5.5 cm^{-1}). Spectra published by Fink et al.[16] indicate that the P-, Q-, and R-branches of the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition are subsumed by a broad, pressure-dependent band that appears[19] to have a width at half-maximum in the range 50–70 cm^{-1}. Upon examination of the spectrum reported by Chou and Frei[15] in CCl_4, we discern a bandwidth at half-maximum of ~90 cm^{-1}.[19] Our spectra have bandwidths that fall in the range 50–80 cm^{-1}.

At present, we are unwilling to comment further on the bandwidth, particularly with respect to any correlation, or lack thereof, with either the peak maximum or functions of the solvent refractive index. The accuracy with which this parameter can be measured in our present data is not sufficient to justify discussion.

Conclusions

The dependence of the $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ and $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ emission band maxima on the solvent refractive index, n, and functions of n, shows that (1) the respective transition energies are influenced in a similar manner by solvent perturbations, and (2) the electronic response of the solvent is an important component of the oxygen–solvent interaction. The latter conclusion is consistent with previously published data on the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition *probability*.[2] The spectral shift data, however, indicate that the effect of solvent on these transitions is complex and that variables other than simple dispersion forces likely contribute to the oxygen–solvent interaction.

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(12) Both transitions are forbidden as electric dipole processes. The $O_2(b^1\Sigma_g^+) - O_2(a^1\Delta_g)$ transition has an Einstein A coefficient of 0.0025 s^{-1}, whereas the spin-forbidden $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition has an Einstein A coefficient of 0.000 26 s^{-1}.[13]

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(19) To quantify either the peak maximum or bandwidth, the published spectrum was enlarged and lines were drawn from the spectrum to the abscissa.

(20) Although Chou and Frei report a value of 1.93 μm, examination of the spectrum they published indicates that their λ_{max} may actually be around 1925 nm.[19]

(21) The $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ emission peak in the gas phase is 7882.4 cm^{-1} (1268.6 nm).[22] The value of 54 cm^{-1} was obtained using a peak maximum of 7828.3 cm^{-1} for the $O_2(a^1\Delta_g) - O_2(X^3\Sigma_g^-)$ transition in CS_2.[5,6]

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