

Solvent Effects on the Radiative Transitions of Singlet Oxygen

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Introduction

Molecular oxygen is a ubiquitous, yet very unique, compound that has long provided interesting problems for the chemical community.^{1–4} In recent years, optical spectroscopic studies of solvated oxygen have made dramatic developments possible in fields ranging from medicine to polymer science.^{5–14} To further develop oxygen-specific spectroscopic tools, particularly for time-resolved and spatially resolved studies in heterogeneous media, it is important to understand phenomena that influence oxygen's radiative transitions. As shown in this Account, however, these somewhat esoteric studies also provide a platform for the discussion of a more general issue: the mechanisms by which solvents can perturb solutes.

The effect of solvent on the radiative transitions of a solute is a problem of long-standing interest.¹⁵ Transitions between the three lowest electronic states of oxygen are extremely sensitive to perturbations and thus yield an informative system for a study of equilibrium and non-equilibrium solvent effects. Other features of the oxygen molecule also make it an appealing choice for such a study. Unlike most molecules, oxygen has an open-shell triplet ground state, $O_2(X^3\Sigma_g^-)$. The lowest excited electronic state is a singlet, $O_2(a^1\Delta_g)$, which lies a scant ~ 94 kJ/mol above $O_2(X^3\Sigma_g^-)$. This state has historically been called "singlet oxygen". However, the second excited electronic state of oxygen, $O_2(b^1\Sigma_g^+)$, is also a singlet, and we will thus use the descriptor "singlet oxygen" with reference to both $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$. The $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states in oxygen differ only in the way two electrons occupy degenerate π antibonding orbitals,¹⁶ which is a unique feature that can have important ramifications with respect to oxygen–solvent interactions. Finally, oxygen–solvent model systems are small enough to be amenable to high-level theoretical treatment, thus providing a necessary complement to experimental studies.

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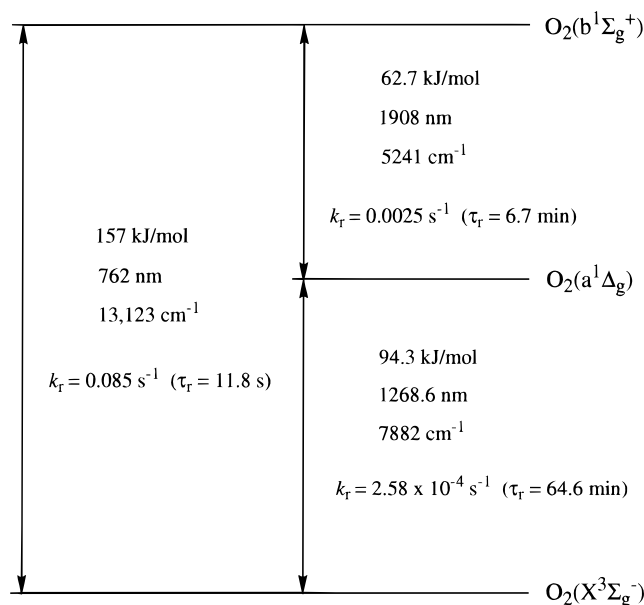


FIGURE 1. Energy level diagram depicting the three lowest electronic states of oxygen. The transition energies and emission rate constants shown are gas-phase values.

Under collision-free conditions, the b – a , a – X , and b – X transitions in oxygen are forbidden as electric dipole processes.² Thus, in low-pressure gas-phase systems, the rate constants, k_r , for excited-state radiative decay are comparatively small (Figure 1). Solution-phase perturbations give rise to three principal changes in these transitions, the extent of which depends significantly on the solvent: (1) The transitions become more probable, as reflected by increases in k_r , (2) the transition energies decrease, as reflected in red-shifted emission spectra, and (3) nonradiative decay channels become accessible and dominate the overall rate constants for $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ deactivation which, in turn, results in emission quantum yields that are quite small ($\sim 10^{-3}$ to 10^{-7}).

The combination of small emission quantum yields, lifetimes in the microsecond to picosecond domain, and transition frequencies in the infrared have made the spectroscopic detection of singlet oxygen in solution difficult. Nevertheless, most measurements are now generally commonplace, principally due to the use of more sophisticated detectors. Indeed, because $O_2(a^1\Delta_g)$ is a reactive intermediate in many systems, the ability to routinely detect the a – X phosphorescence has been useful in a wide range of disciplines.^{5–14,17} Although $O_2(b^1\Sigma_g^+)$ is not known to react with organic molecules in solution,^{18,19} spectroscopic studies of this state are nevertheless also important simply because, in many systems, it is a key precursor of $O_2(a^1\Delta_g)$.^{20–24} In these spectroscopic experiments, the effect of the solvent is thus a critical parameter that can influence conclusions regarding a chemical process.

An appreciable amount of material on singlet oxygen's radiative transitions has accumulated over the past decade, most of it involving the b – a and a – X transitions, and it is on these transitions that our discussion will focus.²⁵ In this Account, we hope to put some key issues

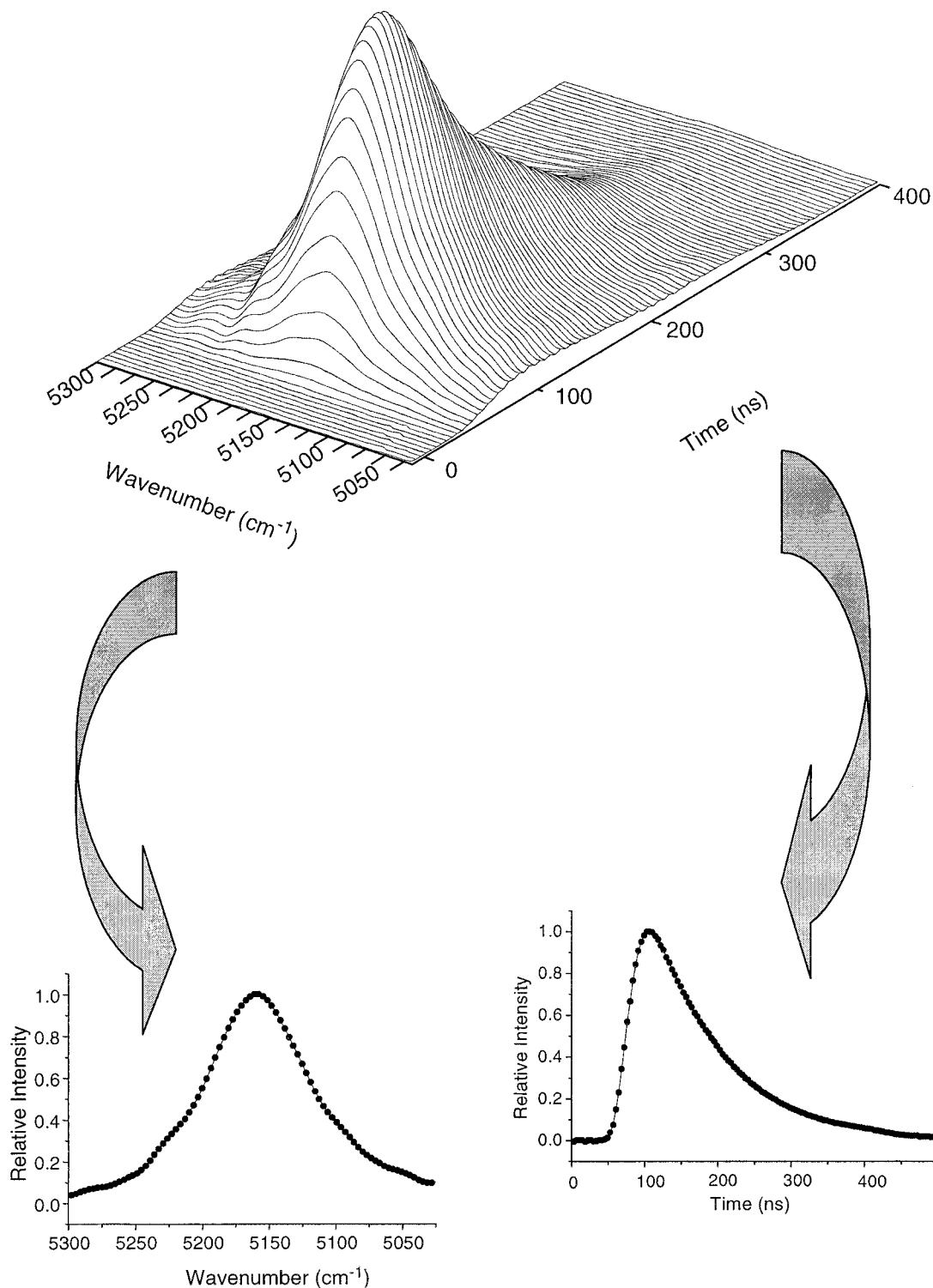


FIGURE 2. Time-resolved O₂(b¹Σ_g⁺) → O₂(a¹Δ_g) emission spectrum in oxygen-saturated CS₂. O₂(b¹Σ_g⁺) was formed by energy transfer from a photosensitizer. The data were recorded using a step-scan Fourier transform spectrometer equipped with a 77 K InSb detector (20 ns response time). The temporal behavior of the signal reflects the convolution of the detector response, the sensitizer decay, and the decay of O₂(b¹Σ_g⁺).³²

into perspective and, in turn, demonstrate that molecular oxygen continues to provide interesting problems for chemical research.

Spectral Shifts

Data. The effect of solvent on the a–X emission spectrum has been examined by a number of groups.^{27–30} The effect

of solvent on the b–a emission spectrum has only recently been reported,³¹ and more comprehensive studies are in progress (Figure 2).³² Data on the b–a transition are presently not as extensive as those on the a–X transition principally because the comparatively short lifetime of O₂-(b¹Σ_g⁺) in solution^{33,34} makes the use of a variety of solvents difficult.

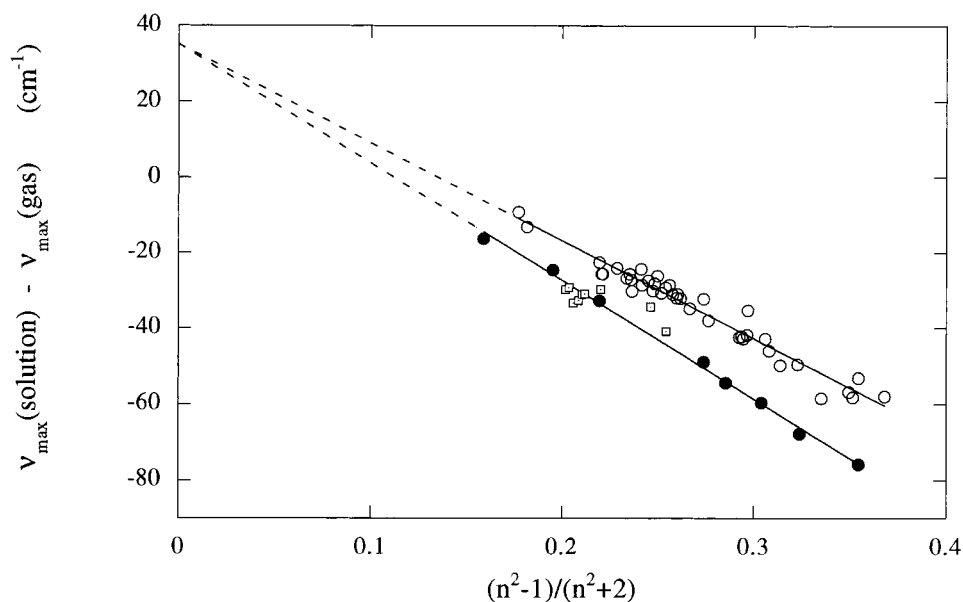


FIGURE 3. Plot of the difference between the solution- and gas-phase emission maxima against a function of the solvent refractive index, n , for both the b-a (●)³¹ and a-X (○)³⁰ transitions. The “anomalous” a-X data, see text, are labeled separately (□). The solid lines are linear least-squares fits to the data and do not include the “anomalous” data. The function of n shown is proportional to the solvent polarizability, α_{sol} .

For both transitions, the solvent causes a red-shift of the emission peak relative to the respective gas-phase values, and the extent of the shift generally increases as the refractive index of the solvent increases (Figure 3). Recent data obtained from a-b absorption experiments are consistent with these observations.³⁵ Moreover, the effects of solvent on the b-a and a-X transition energies are approximately equivalent (Figure 3). Thus, for the a-X transition in the near-infrared, the largest perturbation of $\sim 60 \text{ cm}^{-1}$ corresponds to a wavelength shift of $\sim 9 \text{ nm}$, whereas for the b-a infrared transition, the analogous perturbation corresponds to a wavelength shift of $\sim 28 \text{ nm}$.

Interpretation of Spectral Shift Data. Interpretations of the data have focused on the fact that the spectral shifts correlate reasonably well with either the solvent refractive index, n , or functions of n that reflect, for example, the solvent electronic polarizability, α_{sol} (Figure 3).^{29–31,36} Thus, it appears that the electronic response of the solvent appears to be a significant factor in determining the extent to which the b-a and a-X transitions are perturbed. Such data are consistent with, and thus may indicate, an oxygen-solvent interaction composed of stabilizing dispersion forces.

If the a-X and b-a spectral shifts depend linearly on n , or a function of n , then the solution-phase data extrapolate to gas-phase maxima that are blue-shifted relative to the experimentally observed maxima (Figure 3).^{31,36} This observation is common to many systems^{37,38} and may indicate that, in addition to stabilizing forces, the oxygen-solvent interaction might also consist of a destabilizing repulsive interaction.^{36,37}

On the basis of plots such as those in Figure 3, models have been proposed in which the spectral shift derives

principally from a dispersion interaction with a solvent molecule.^{29,30,36,39} In the most extensive study thus far, Schmidt³⁶ employed the London formula for the solvent-O₂($a^1\Delta_g$) and solvent-O₂($X^3\Sigma_g^-$) interaction energies to calculate the a-X spectral shift, $\Delta\nu_{\text{calc}}^{a-X}$.

$$\Delta\nu_{\text{calc}}^{a-X} = -\frac{1.5\alpha_{\text{sol}}}{R_{\text{int}}^6} \left[\alpha_a \frac{\text{IP}_a \text{IP}_{\text{sol}}}{\text{IP}_a + \text{IP}_{\text{sol}}} - \alpha_X \frac{\text{IP}_X \text{IP}_{\text{sol}}}{\text{IP}_X + \text{IP}_{\text{sol}}} \right] \quad (1)$$

In this expression, R_{int} denotes the interaction distance between oxygen and the perturbing solvent molecule, α_{sol} denotes the polarizability of the solvent, α_X and α_a denote the polarizabilities of the respective states of oxygen, and IP denotes ionization potential of the indicated species.

Despite the apparent success of eq 1 to model the a-X experimental data,³⁶ there are several points which indicate that (1) this equation alone does not accurately reflect the mechanism that gives rise to the trend shown in Figure 3 and (2) plots such as those in Figure 3 mislead one into thinking that dispersion forces are a key factor in defining the oxygen-solvent interaction.

In this application of the London expression, two critical parameters are α_a and α_X , the values of which significantly influence the magnitude of $\Delta\nu_{\text{calc}}^{a-X}$. Unfortunately, polarizabilities have heretofore been available only for gas-phase O₂($X^3\Sigma_g^-$).⁴⁰ Using the gas-phase number, Schmidt³⁶ assumed a value for α_a , with the expectation that α_a should be larger than α_X . We have recently shown, however, that although excited-state polarizabilities are indeed often larger than that of the ground state, α_a is in fact not significantly different than α_X .⁴¹ Moreover, depending on the solvent, α_a can even be smaller than α_X . This result is entirely consistent with the fact that the O₂-($a^1\Delta_g$) and O₂($X^3\Sigma_g^-$) states differ only in the way two

Table 1. Comparison between Experimental and Calculated a–X Spectral Shifts, $\nu_{\max}(\text{solution}) - \nu_{\max}(\text{gas})$

solvent	spectral shifts (cm ⁻¹)	
	experiment ^a	calculated ^b
carbon disulfide	-53.2	-63.4
benzene	-42.9	-39.2
carbon tetrachloride	-32.3	-26.5
acetonitrile	-30.9	-44.4
acetone	-29.8	-28.4

^a Data from an FTIR emission study.³⁰ ^b Average of only several M and O₂ orientation-dependent values.⁴²

electrons occupy degenerate orbitals; in most molecules, electronic excitation results in the occupation of higher energy, more diffuse orbitals, and thus the polarizability of the excited state can be significantly larger than that of the ground state.

Second, although the extensive a–X data show a remarkably good correlation between $\Delta\nu$ and α_{sol} , caution must be exercised in concluding that $\Delta\nu$ is linearly dependent on α_{sol} . Specifically, a–X spectra recorded in water, methanol, acetonitrile, acetone, dioxane, and tetrahydrofuran give rise to data that appear “anomalous” with respect to the proposed linear correlation (Figure 3).³⁰ Because these particular solvents can yield anomalies in such plots,¹⁵ it is indeed tempting to simply neglect the “aberrant” data. However, in light of our oxygen polarizability results, we believe that these “anomalous” data simply indicate that plots of $\Delta\nu$ vs α_{sol} do not properly reflect the mechanism of singlet oxygen perturbation by the solvent.

In an attempt to better understand this phenomenon, we employed ab initio computational methods to characterize complexes between oxygen and a given solvent molecule, M. Specifically, we calculated the energies of a M–O₂(a¹Δ_g) complex that is in equilibrium with its surrounding outer solvent and a M–O₂(X³Σ_g⁻) complex that is not in equilibrium with the outer solvent (i.e., the Franck–Condon state populated in the a → X transition).⁴² We find that these energies depend principally on the quadrupolar coupling term between the complex and the outer solvent, and only minimally on the dipolar coupling term and on dispersion interactions. Most importantly, upon considering multiple M and O₂ orientations, each with a unique a–X energy difference and transition probability, we calculate average spectral shifts that correlate well with experimental data (Table 1). Thus, it appears that the trend observed in plots of $\Delta\nu^{\text{a-X}}$ vs α_{sol} simply reflects the general importance of the solvent’s electronic response in the solvent–solute interaction and that one should be cautious about ascribing such trends solely to a dispersion interaction.

With the recent advance that O₂(a¹Δ_g) can now be detected in time-resolved absorption experiments,³⁵ the Stokes shift between a–b absorption and b–a emission can be obtained (Figure 4). Efforts are currently underway to ensure that our theoretical model can also account for the dependence of these latter data on solvent.

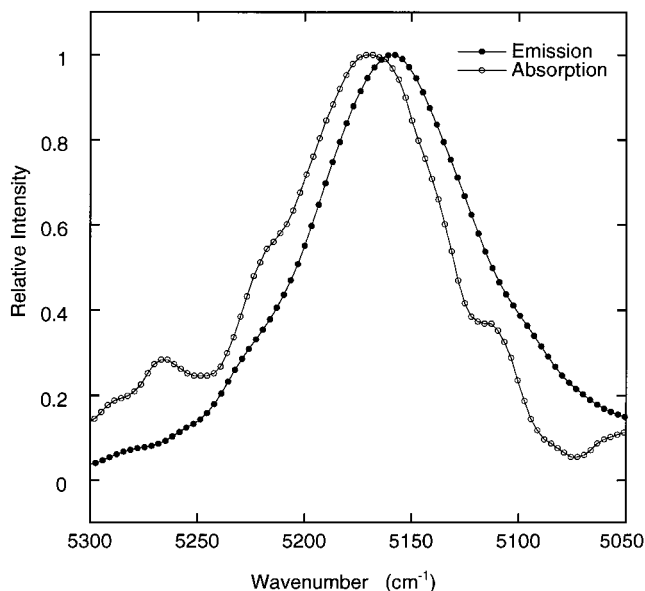


FIGURE 4. Normalized a–b absorption and b–a emission spectra in CS₂.³⁵ The data indicate a Stokes shift of 10.4 cm⁻¹.

Transition Probabilities

Data. The effect of solvent on the rate constant for a–X phosphorescence, $k_r^{\text{a-X}}$, has been examined by a number of groups.^{20,43–50} The data indicate that solvent perturbations cause $k_r^{\text{a-X}}$ to increase $\sim 10^4$ times relative to the gas-phase value⁴⁵ and that the extent of this change increases with an increase in the solvent refractive index, n , or functions of n .⁴⁴ Solvent-dependent differences in $k_r^{\text{a-X}}$ can exceed a factor of 20.^{43–45} Practical applications of this information on the solvent dependence of $k_r^{\text{a-X}}$, and the associated correlation with n , include the ability to (1) normalize data when a–X phosphorescence intensities are used to quantify O₂(a¹Δ_g) yields in different solvents and (2) predict values of $k_r^{\text{a-X}}$ in a medium of refractive index n .¹³ Although this empirical correlation between $k_r^{\text{a-X}}$ and the bulk property n appears to be general, at least for single-solvent systems, caution must nevertheless still be exercised in its use, as recently demonstrated with some binary solvent mixtures.⁵¹

Values of the rate constant for b–a fluorescence, $k_r^{\text{b-a}}$, obtained from solution-phase emission experiments, are limited to one solvent, CCl₄.²⁰ However, because the O₂-(a¹Δ_g) absorption spectrum can now be recorded, it is possible to obtain $k_r^{\text{b-a}}$ from the a–b integrated absorption coefficient.³⁵ Although the data available thus far from these experiments are not extensive, it is clear that (1) $k_r^{\text{b-a}}$ is approximately 1000 times larger than $k_r^{\text{a-X}}$ and (2) $k_r^{\text{b-a}}$ likewise increases with an increase in the refractive index of the solvent.

Interpretation of Transition Probability Data. For any molecule, the rate constant for a radiative transition will depend intrinsically on the solvent. This dependence is embodied by the appearance of the square of the solvent refractive index, n , in the expression of the Einstein coefficient, A , for spontaneous emission from an upper to lower state (eq 2, where Γ is the integrated absorption

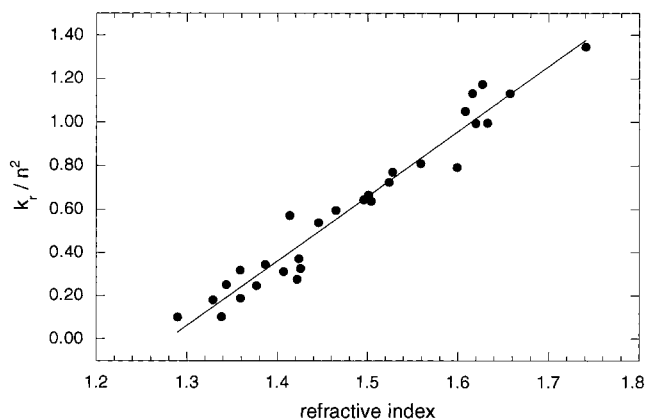


FIGURE 5. Plot of k_r^{a-X}/n^2 vs the solvent refractive index, n . The solid line is a linear least-squares fit to the data. An equally good correlation is observed when k_r^{a-X}/n^2 is plotted against functions of n , such as $(n^2 - 1)/(n^2 + 2)$, that reflect the solvent polarizability, α_{sol} . For this plot, relative k_r^{a-X} values⁴⁴ have been normalized to yield $k_r^{a-X} = 1.5 \text{ s}^{-1}$ in benzene.⁴⁵

coefficient in $\text{M}^{-1}\text{cm}^{-2}$, ν the transition frequency in cm^{-1} , g the degeneracy of the given state, N_A Avogadro's number, and c the speed of light).⁵²

$$A = k_r = n^2 \frac{8\pi c \ln(10)}{N_A} \frac{g_{\text{lower}}}{g_{\text{upper}}} \nu^2 \Gamma \quad (2)$$

The solvent dependence of k_r^{a-X} and k_r^{b-a} actually observed, however, is much larger than that “expected” only on the basis of the factor n^2 . This is illustrated in Figure 5, where values of k_r^{a-X}/n^2 are plotted against n . A number of models have been presented to account for this phenomenon.

It is well-documented that, in the $\text{M}-\text{O}_2$ photosystem, the charge-transfer (CT) state, $\text{M}^+\cdot\text{O}_2^-$, plays an important role.^{53–56} There is certainly sufficient evidence to indicate that $\text{O}_2(\text{a}^1\Delta_g)$ and $\text{O}_2(\text{X}^3\Sigma_g^-)$ can be indirectly coupled through the CT state.^{57–59} Although the CT state can be comparatively high in energy, particularly for molecules typically used as solvents, admixture of CT character into the lower-lying valence states $\text{M}-\text{O}_2(\text{b}^1\Sigma_g^+)$, $\text{M}-\text{O}_2(\text{a}^1\Delta_g)$, and $\text{M}-\text{O}_2(\text{X}^3\Sigma_g^-)$ could give rise to CT-mediated, solvent-dependent changes in k_r^{a-X} and k_r^{b-a} . The extent of such a perturbation would depend on the CT state energy, among other things, and it is thus reasonable to examine how k_r data correlate with changes in the ionization potential (IP) of M . Proponents of this CT thesis claim a linear correlation in plots of k_r^{a-X} vs the gas-phase IP of M .^{47,60} Although a general trend might be discerned in such plots, the claim of a linear correlation is not warranted.⁶¹ To more properly test this thesis, one should consider IPs that have been corrected for the effects of both equilibrium and nonequilibrium solvation.^{61,62} IPs thus modified, however, show equally poor correlations with k_r^{a-X} .^{44,61} Therefore, admixture of CT character is not likely to be a principal factor in changing the $\text{a}-\text{X}$ transition probability. Rather, it appears that the data used by the proponents of the CT thesis simply reflect a transitive effect: the k_r^{a-X} vs IP plot derives from relationships between (1) k_r^{a-X} and n and (2) n and IP.⁶¹

In a second model, it was proposed that coupling between various $\text{M}-\text{O}_2$ states permits forbidden transitions in oxygen to “steal” intensity from allowed transitions in the perturbing molecule M .⁴⁵ Aspects of this argument have been presented in a number of contexts over the past forty years.^{55,63} With respect to the k_r^{a-X} data, the line of reasoning is as follows:⁴⁵ (1) From the Einstein relationships, k_r^{a-X} depends on the oscillator strength, $f_{\text{X-a}}$, of the $\text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{O}_2(\text{a}^1\Delta_g)$ transition. (2) From the intensity stealing argument, $f_{\text{X-a}}$ depends on the oscillator strength, f_{ij} , of a transition $i \rightarrow j$ in M . (3) From the dispersion equations, the molar refraction, and hence the polarizability, of M depends on f_{ij} . However, in a subsequent paper in which some k_r^{b-a} data were also examined, the principal proponents²⁰ withdrew their support for this model in favor of the model described below.

At present, the most promising model that accounts for the effect of solvent on k_r^{a-X} and k_r^{b-a} is that of Minaev.^{64,65} Minaev's thesis is that, by virtue of a spin-orbit interaction that mixes $\text{O}_2(\text{b}^1\Sigma_g^+)$ with $\text{O}_2(\text{X}^3\Sigma_g^-)$, the $\text{a}-\text{X}$ transition can steal intensity from the $\text{b}-\text{a}$ transition. Thus, collision-dependent changes in the $\text{b}-\text{a}$ transition probability will be manifested in the $\text{a}-\text{X}$ transition probability. The mechanism by which the $\text{b}-\text{a}$ transition is proposed to gain intensity involves the solvent-dependent disruption of the cylindrical symmetry in oxygen. Specifically, upon interaction with the perturbing molecule M , a distinction is made between oxygen's normally degenerate π_y and π_x antibonding orbitals which, in turn, gives rise to a dipolar component in the $\text{b}-\text{a}$ transition. In comparison to the unperturbed transition, which is allowed only as an electric quadrupole process, the collision-induced electric dipole character causes a significant increase in the $\text{b}-\text{a}$ transition probability. It is reasonable to expect that the magnitude of this induced dipole would increase with an increase in the polarizability of M , hence providing an explanation for the correlation shown in Figure 5.

Minaev's thesis that solvent-dependent changes in the $\text{a}-\text{X}$ transition probability derive from solvent-dependent changes in the $\text{b}-\text{a}$ transition probability has an interesting consequence, certainly with respect to experimental documentation of the model: the ratio k_r^{a-X}/k_r^{b-a} is predicted to be constant and independent of the perturbing molecule M . Minaev has predicted a value of 3.05×10^{-4} for this ratio, based solely on the introduction of dipolar character in the $\text{b}-\text{a}$ transition.^{65,66} Consideration of other collision-dependent phenomena, including a minor charge-transfer interaction, yields a ratio that is approximately 1.5 times larger.⁶⁵

One argument in support of Minaev has been presented by Schmidt and Bodesheim²⁰ in which gas-phase k_r^{b-a} data⁶⁷ are compared to solution-phase k_r^{a-X} data in logarithmic plots of k_r vs the molar refraction, R , of the perturbing molecule (Figure 6).⁶⁸ Keeping in mind the hazards of comparing such gas- and solution-phase data, it is important to mention several things about Figure 6 that are pertinent to Minaev's theory: (1) the respective

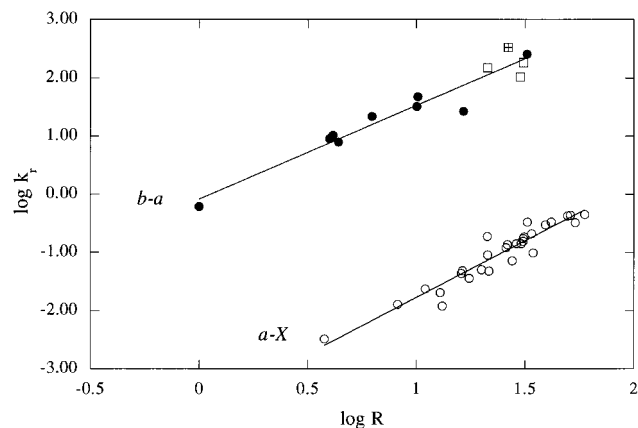


FIGURE 6. Double-logarithmic plot of the bimolecular rate constant, k_r , for singlet oxygen radiative decay ($M^{-1} s^{-1}$) against the molar refraction, R , of the perturbing molecule ($cm^3 mol^{-1}$). The plot is a re-creation of one published by Schmidt and Bodesheim.²⁰ Data for the a-X transition (○) were obtained in liquid solutions⁴⁴ and normalized to yield $k_r^{a-X} = 1.5 s^{-1}$ in benzene.⁴⁵ Data for the b-a transition were obtained from (1) gas-phase emission experiments (●),⁶⁷ (2) emission experiments in liquid CCl_4 (box with grid),²⁰ and (3) a-b absorption experiments in toluene, *n*-hexane, and CS_2 (□).³⁵ The solid lines are linear least-squares fits to the respective data sets and include all of the b-a data (b-a slope = 1.6, a-X slope = 1.9).

data sets appear to respond similarly to changes in the solvent/perturber and (2) the ratio k_r^{a-X}/k_r^{b-a} obtained from linear fits to the data sets is close to the predicted value; for example, at $\log(R) = 1$, the ratio is 5×10^{-4} . Furthermore, it has been noted²⁰ that the slopes of these plots are close to 2, which indicates that, for both transitions, k_r may indeed be proportional to R^2 . Recall that a radiative rate constant is proportional to the square of the transition moment.² Thus, it has been suggested²⁰ that Figure 6 shows that the magnitude of the collision-induced transition dipole in oxygen indeed directly correlates with the molar refraction, R , which, in turn, is proportional to the polarizability of the perturbing molecule.

Also shown in Figure 6 are (1) the k_r^{b-a} value obtained in a solution-phase emission experiment²⁰ and (2) k_r^{b-a} values obtained in solution-phase a-b absorption experiments.³⁵ Although these data do not appear anomalous on the scale of the double-logarithmic plot, which in itself is an important observation, the ratio k_r^{a-X}/k_r^{b-a} is not constant, as predicted, but can vary by as much as a factor of 4 with a change in solvent. This 4-fold change exceeds deviations due to experimental error. Therefore, although Minaev's thesis of intensity stealing appears to be generally correct, some modification in the model is required to account for subtle changes in the k_r^{a-X}/k_r^{b-a} ratio.

Conclusions

Over the past 10 years, much has been learned about the radiative transitions of singlet oxygen in solution and, as a consequence, about solvent effects in general. Nevertheless, some key issues remain to be elucidated, some of which present challenging problems of potential interest

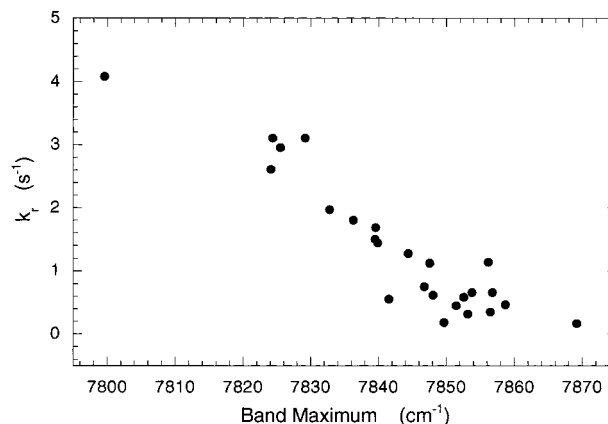


FIGURE 7. Plot of k_r^{a-X} against the band maximum^{30,69} of the $O_2(a^1\Delta_g)-O_2(X^3\Sigma_g^-)$ transition. Of particular interest is the band maximum in CH_2I_2 at $7800 cm^{-1}$ that has heretofore not been published.⁶⁹

to a broad range of chemists. For example, it is important to ascertain whether or not an all-encompassing model can be used to interpret solvent effects on both transition probabilities and spectral shifts. Plots such as that shown in Figure 7, in which k_r^{a-X} appears to correlate well with the a-X emission maxima, indicate that it is reasonable to consider such a model. On the experimental front, much can be gained by optimizing the detection of $O_2(a^1\Delta_g)$ in time-resolved absorption experiments, particularly in systems where emission experiments have limitations. Efforts to understand phenomena that influence the a-b and a-X radiative transitions are a prerequisite for the development of combined time-resolved and spatially resolved studies of singlet oxygen. The latter are expected to be a useful tool for studies in heterogeneous biological and polymeric media. We hope that the discussion in this Account will provide a useful framework to stimulate activity in the field.

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