Solvent Shift of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ Phosphorescence of O₂

Reinhard Schmidt

Institut für Physikalische und Theoretische Chemie, J. W. Goethe-Universität, Marie-Curie-Strasse 11, D60439 Frankfurt am Main, Germany

Received: February 15, 1996[⊗]

Literature data of the 0−0 transition energy ν_{max} of the collision induced $^1\Delta_g$ phosphorescence of O₂ in solution are analyzed. It is shown that the solvent shift of ν_{max} is composed additively of a red-shift, caused by dispersive interactions between the solvent in the surrounding of the colliders O₂($^1\Delta_g$) and solvent molecule, and a blue-shift which is due to the inherent collision induced nature of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition and due to changes in the repulsive part of the effective intermolecular potential in the condensed phase with electronic excitation.

Introduction

Recently, Wessels and Rodgers reported about the influence of the solvent on the 0−0 transition energy ν_{max} of the $^1\Delta_g$ phosphorescence of O₂ in solution.[1] They observed by means of a Fourier transform luminescence spectrometer a small variation of ν_{max} by only 0.63% between 7873.2 (trifluoroacetic acid) and 7823.9 cm⁻¹ (diiodohexane). In 44 out of 50 solvents a strongly linear correlation between ν_{max} and the bulk polarizability $P = (n^2 - 1)/(n^2 + 2)$, with n being the solvent refractive index, was observed. Extrapolation to $P = 0$ resulted in 7916.7 cm⁻¹, which was assumed to be the energy of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition of the O₂ molecule. However, the comparative value of 7918.1 cm⁻¹ taken from Herzberg[2] is only the energy gap between the potential minima of the $^1\Delta_g$ and $^3\Sigma_g^-$ states. Considering the different zero vibrational energies of both states, one obtains as 0−0 transition energy 7882.4 cm⁻¹.[2] Thus, the extrapolated energy either contradicts the assumption of Wessels and Rodgers of a general strictly linear correlation between ν_{max} and P or indicates that besides attractive dispersive interactions additional repulsive interactions contribute to the solvent dependence of ν_{max}. In fact, the authors did not present the physical reason why a strictly linear correlation between ν_{max} and P should result, on the basis of which the differentiation between the six anomalous solvents and the rest of solvents could be made. However, they demonstrated qualitatively and in accordance with others[3−5] that primarily dispersion interactions cause the very small red-shift of ν_{max} by 50 cm⁻¹ with increasing P.

The solvent influences also the rate constant k_r of the radiative $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition by dispersion interactions.[6−9] However, the variation of k_r is by orders of magnitude stronger than that of ν_{max}. k_r varies by a factor of about 20.[6,8,9] On search for a relation between the solvent effects on the energy and the probability of the 0−0 transition Wessels and Rodgers correlated k_r with ν_{max}. It was stated that in resemblance to the energy gap law for radiationless transitions, the exponential relation $k_r = a e^{-\Delta E/\gamma}$ with a and $\gamma = 18$ cm⁻¹ being constants and $\Delta E = \nu_{max}$ describes the functional dependence of k_r on ν_{max}. To underline the physical relevance of the exponential relation, it was pointed out that the value of γ of 18 cm⁻¹ is within the order of magnitude of London dispersion interactions, i.e., the driving force for the perturbation-induced intensity enhancement of the forbidden $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition. It was not mentioned that the experimental data could be described only if the constant

a takes the physically unreasonable value of $a = 2.0 \times 10^{189}$ s⁻¹. The fastest optical events occur in the order of magnitude of about 10^{15} s⁻¹. Thus, the empirical exponential relation lacks any physical significance.

It is the aim of the present letter to interpret the solvent effect on ν_{max} on a physically more meaningful basis. Data of ν_{max} have also been determined by Macpherson et al.[5] Some of these data differ distinctly from the data of Wessels and Rodgers. Therefore it is not possible to mix the data. Since the better overlap of data of k_r with values of ν_{max} is given for the solvents investigated by Wessels and Rodgers, only these data will be discussed.

Discussion

Correlation of ν_{max} with P. It is assumed that the main reason for the solvent shift of ν_{max} are dispersion interactions between O₂ and solvent molecules.[1,3−5] The volume polarizability in cm⁻³ is defined as $\alpha' = 3R_m/(4\pi N_A)$ with R_m, N_A, and V_m being the molar refraction $R_m = V_m P$, Avogadro's number, and the molar volume, respectively. The energy V_Σ of dispersion interaction between the ground-state O₂ molecule (Σ) and a solvent molecule (S) is approximatively given by the London eq 1 in cm⁻¹ units, if I_Σ and I_S denote the respective

$$V_\Sigma = -1.5\alpha_\Sigma' \alpha_S' d_C^{-6} I_\Sigma I_S/(I_\Sigma + I_S) \tag{1}$$

ionization potentials in cm⁻¹ and d_C is the distance of both molecules in cm, each of which is assumed to be spherical: $d_C = (d_\Sigma + d_S)/2$.[10]

The ionization potential I_Δ of O₂($^1\Delta_g$) is lower than $I_\Sigma = 12.07$ eV by its excitation energy of 0.98 eV.[11] Dipole interactions contribute to the solvent-induced red-shift for allowed transitions with large transition dipole moments.[12] The $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition is strongly forbidden for electric dipole radiation. The radiative lifetime of O₂($^1\Delta_g$) reaches in solution maximum values of only 3−4 s⁻¹.[8,9] Therefore eq 2 may serve as an approximation for the calculation of the polarizability dependent red-shift $\Delta\nu^c = \nu^c_{max} - 7882.4$ in solution.

$$\Delta\nu^c = V_\Delta - V_\Sigma =$$
$$-1.5\alpha_S' d_C^{-6}\{\alpha_\Delta' I_\Delta I_S/(I_\Delta + I_S) - \alpha_\Sigma' I_\Sigma I_S/(I_\Sigma + I_S)\} \tag{2}$$

Values $I_\Delta I_S/(I_\Delta + I_S)$ and $I_\Sigma I_S/(I_\Sigma + I_S)$ are practically equal for a given solvent. Moreover, values of $I_\Sigma I_S/(I_\Sigma + I_S)$ decrease only by 20% in the series of solvents of Table 1 in going from
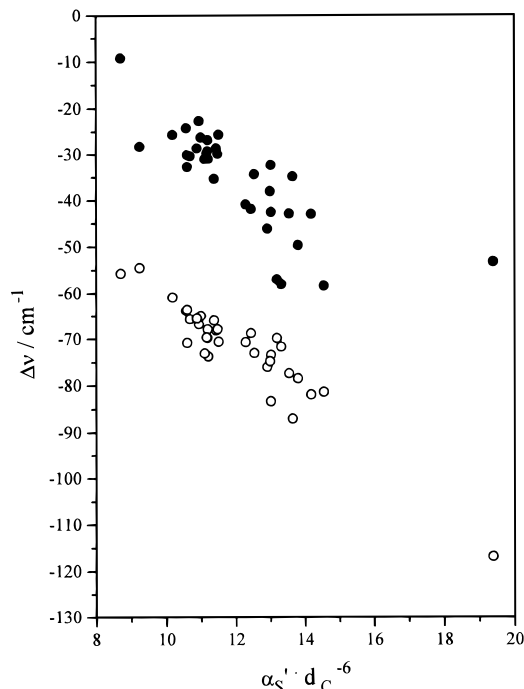
Figure 1. Plot of experimental $\Delta\nu$ (full circles) and calculated red-shifts $\Delta\nu^c$ (open circles) versus $\alpha_S' d_C^{-6}$.

TABLE 1: Compilation of 0−0 Transition Energies ν_{max}, Volume Polarizabilities α_S', Ionization Potentials I_S, Colliding Distances d_C, Solvent Molarities V_m^{-1}, Bulk Polarizabilities P, and Values of $k_r[S]$

solvent[a]	ν_{max},[b] cm⁻¹	$10^{24}\alpha_S'$, cm⁻³	I_S,[c] eV	$10^8 d_C$,[d] cm	V_m^{-1}, M	P	$k_r[S]$,[e] M s⁻¹
F$_3$CCO$_2$H	7873.2	5.18	11.46	4.26	12.98	0.169	
CF$_3$CH$_2$OH	7869.2	5.26		4.24	13.72	0.181	2.26
pentane	7859.8	10.06	10.35	4.58	8.68	0.219	
hexane	7858.2	11.92	10.13	4.74	7.65	0.229	
octane	7858.0	15.59		5.01	6.15	0.241	
ethanol	7856.8	5.18	10.47	4.06	17.01	0.221	5.87
heptane	7856.8	13.73	9.92	4.88	6.83	0.235	4.50
CF$_3$C$_6$H$_5$	7856.2	12.15	9.69	4.72	8.21	0.250	9.36
1-propanol	7855.6	6.97	10.22	4.29	13.38	0.234	
hexene	7855.2	11.63		4.68	8.00	0.234	
nonane	7855.0	17.44		5.13	5.60	0.245	
decane	7854.2	19.23	9.65	5.25	5.13	0.248	
cyclohexane	7853.8	11.02	9.86	4.61	9.26	0.256	6.11
1-butanol	7853.8	8.82	10.06	4.48	10.93	0.242	
methanol	7853.2	3.27	10.85	3.78	24.78	0.203	7.81
dodecane	7853.1	22.96		5.45	4.40	0.254	
methanol-d	7852.7	3.26	10.85	3.78	24.62	0.202	
acetone	7852.6	6.43	9.71	4.22	13.62	0.220	7.97
1-pentanol	7852.3	10.72	10.00	4.65	9.20	0.248	
butyl formate	7852.1	10.83	10.50	4.65	8.73	0.238	
1-hexanol	7851.7	12.59		4.80	7.97	0.252	
acetonitrile	7851.5	4.40	12.20	3.97	19.15	0.212	8.62
acetonitrile-d	7851.4	4.37	12.20	3.97	19.15	0.210	
hexadecane	7851.3	30.40		5.81	3.41	0.261	
1-octanol	7851.2	16.18		5.07	6.35	0.258	
1-nonanol	7850.4	18.06		5.18	5.73	0.260	
1-decanol	7850.2	19.92		5.29	5.24	0.262	
CCl$_4$	7850.1	10.53	11.47	4.48	10.36	0.274	9.63
D$_2$O	7849.7	1.46	12.61	3.34	55.13	0.203	9.95
THF	7848.1	7.98	9.41	4.31	12.29	0.246	7.56
CHCl$_3$	7847.6	8.82	11.37	4.32	12.08	0.268	13.59
C$_2$Cl$_4$	7847.1	10.68	9.32	4.59	9.79	0.262	
C$_6$H$_5$F	7844.4	10.34	9.20	4.47	10.64	0.276	13.57
dioxane	7841.6	8.64	9.19	4.38	11.71	0.254	6.50
xylene	7840.6	14.42	8.50	4.76	8.19	0.297	
toluene	7839.9	12.36	8.82	4.60	9.41	0.292	13.55
C$_6$H$_5$Cl	7839.6	12.40	9.06	4.57	9.82	0.306	16.50
C$_6$H$_6$	7839.5	10.43	9.25	4.41	11.25	0.295	16.87
benzonitrile	7836.3	12.52	9.62	4.62	9.79	0.308	17.63
C$_6$H$_5$Br	7832.8	13.50	8.98	4.63	9.53	0.323	18.73
benzyl alcohol	7832.5	12.92		4.67	9.66	0.314	
CS$_2$	7829.2	8.50	10.07	4.05	16.60	0.354	51.55
CH$_3$C$_{10}$H$_7$	7825.5	19.76	7.85	4.97	7.04	0.349	20.80
BrC$_{10}$H$_7$	7824.4	20.39	8.09	4.98	7.19	0.368	22.33
C$_6$H$_5$I	7824.1	15.57	8.69	4.70	8.97	0.351	23.41
diiodohexane	7823.9	22.00		5.14	6.07	0.335	

[a] Designation of solvents of ref 1. [b] Reference 1. [c] Reference 11. [d] Calculated with $d_\Sigma = 3.46$ Å from vdW volumes given by Bondi.[13] [e] Values of k_r from ref 9.

D$_2$O ($I_S = 12.6$ eV) to 1-methylnaphthalene ($I_S = 7.85$ eV). Thus, $\alpha_\Delta' I_\Delta I_S/(I_\Delta + I_S) - \alpha_\Sigma' I_\Sigma I_S/(I_\Sigma + I_S)$ varies only little and a roughly linear correlation of the experimental red-shift $\Delta\nu = \nu_{max} - 7882.4$ with $\alpha_S' d_C^{-6}$ is expected on the basis of eq 2, if dispersion interactions cause the variation of $\Delta\nu$ with solvent. Figure 1 compares for the solvents, for which values of I_S are known, values of $\Delta\nu$, derived from the work of Wessels and Rodgers, with the values of $\Delta\nu^c$, calculated by eq 2 with the data of α_S', d_C, and I_S of Table 1 and $\alpha_\Sigma' = 1.6 \times 10^{-24}$ cm³ and $\alpha_\Delta' = 2.6 \times 10^{-24}$ cm³. In fact, the experimental values $\Delta\nu$ correlate roughly linearly with $\alpha_S' d_C^{-6}$. The correlation becomes worse if the long-chain aliphatic hydrocarbons and alcohols of Table 1, for which values of I_S are missing, are included. Presumably, the assumption of spherical shape is too far apart from reality for these molecules. α_Δ' is a fit parameter which is used to adjust the slope of the correlation $\Delta\nu^c \propto \alpha_S' d_C^{-6}$. With $\alpha_\Delta' = 2.6 \times 10^{-24}$ cm³ the dependences of $\Delta\nu$ and $\Delta\nu^c$ on $\alpha_S' d_C^{-6}$ become similar. Actually, a slightly larger polarizability is expected for O$_2$($^1\Delta_g$) than for O$_2$($^3\Sigma_g^-$) because of its lower ionization potential. The values of $\Delta\nu^c$ are in the mean by about 40 cm⁻¹ more negative than $\Delta\nu$, indicating a corresponding blue-shift of the experimental data due to additional repulsive interactions which are not considered in eq 2.

We note a quite good linear correlation of the values of d_C^{-6} of Table 1 with the reciprocal molar solvent volumes V_m^{-1} corresponding to d_C^{-6} (cm⁻⁶) $\approx 1.25 \times 10^{43} V_m^{-1}$ (M). This correlation is a consequence of the size of d_Σ and d_S. d_C^{-6} would linearly correlate with V_m^{-2} for $d_\Sigma \ll d_S$, d_C^{-6} would be practically constant for $d_\Sigma \gg d_S$. Because $d_C^{-6} \propto V_m^{-1}$, the proportionality $\alpha_S' d_C^{-6} \propto R_m/V_m = P$ holds approximatively true in the series of solvents investigated. Therefore, since $\alpha_\Delta' I_\Delta I_S/(I_\Delta + I_S) - \alpha_\Sigma' I_\Sigma I_S/(I_\Sigma + I_S)$ is approximately constant, a linear correlation of $\Delta\nu$ or ν_{max} with P can actually be expected in the liquid phase. This kind of correlation is given in Figure 2 and was first noticed by Wessels and Rodgers.[1] The correlation is much better than the one of $\Delta\nu$ with $\alpha_S' d_C^{-6}$ of Figure 1. Probably different inaccuracies of the model fortuitously cancel in part by the approximations made above. It is

interesting to note that also the long-chain aliphatic hydrocarbons and alcohols of Table 1 fit into the linear correlation. Thus, the physical basis for the linear correlation of ν_{max} with the bulk polarizability P is shown. However, there is no reason to expect a strict linearity. The deviation of the data points for D$_2$O, methanol, acetonitrile, acetone, tetrahydrofurane, and dioxane are not large enough to justify a discrimination between anomalous and normal solvents. In particular, there are no physical or chemical properties of solvent molecules supporting such a differentiation. Figure 2 shows in addition the dependence of $\Delta\nu^c$ on P. In the calculation of these values $1.25 \times 10^{43} V_m^{-1}$ was substituted for d_C^{-6} in eq 2. $\Delta\nu^c$ depends in a very similar way on P as $\Delta\nu$. The slope amounts to -230 cm⁻¹, demonstrating that the dispersion-influenced solvent shift of ν_{max} is very weak as a consequence of a small difference of polarizabilities of O$_2$ in the $^1\Delta_g$ and $^3\Sigma_g^-$ states of about 1.0×10^{-24} cm³. However, again a blue-shift of the experimental data of 40 cm⁻¹ is observed. Therefore, it is concluded that
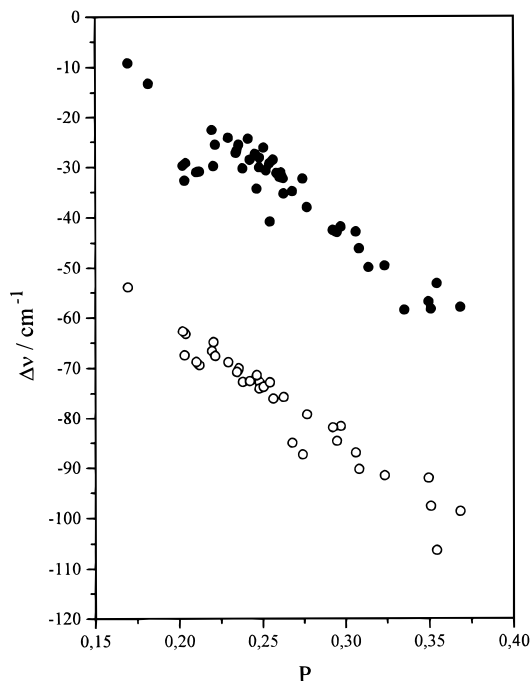
Figure 2. Plot of experimental $\Delta\nu$ (full circles) and calculated red-shifts $\Delta\nu^c$ (open circles) versus P. Values $\Delta\nu^c$ differ from the $\Delta\nu^c$ data of Figure 1 since $1.25 \times 10^{43}V_m^{-1}$ was substituted for d_C^{-6} in eq 2.

different kinds of interactions contribute to the solvent shift of ν_{max}. Besides dispersive interactions, which are the only ones considered in eq 2 and which cause the variation of ν_{max} with P, additional repulsive interactions must take place.

The radiative transitions $^1\Delta_g \leftrightarrow {}^3\Sigma_g^-$ aquire intensity in collisions. It was shown by Wildt et al.[14] by gas-phase experiments that the rate constant of the collision induced emission $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ amounts to $k^c_{a-X} = 0.020$ M^{-1} s^{-1} if O$_2$ is the collider. Already earlier Badger et al.[15] demonstrated that in the gas phase the discrete line bands of the $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ absorption are underlaid by a continuous absorption band caused by collision-induced absorption. The absorption coefficient increases with increasing O$_2$ pressure. The corresponding rate constant of collision-induced absorption amounts to $k^c_{X-a} = 0.024$ M^{-1} s^{-1}. Of course, repulsive interactions become effective in collisions. If these repulsive interactions influence the 0−0 transition energy, a blue-shift of the continuous absorption or emission bands should be observable. As a matter of fact, Badger et al. pointed out that the maximum of the collision-induced 0−0 absorption band is blue-shifted by 13 cm^{-1} to 7895 cm^{-1} for O$_2$ as collider. From the gas-phase emission spectra recorded by Wildt et al.[14] the 0−0 energy of the collision-induced emission can be estimated as 7905 cm^{-1}, if NO is the collider. Thus, a blue-shift of the collision induced radiative transitions $^1\Delta_g \leftrightarrow {}^3\Sigma_g^-$ of about 20 cm^{-1} is actually observed already in the gas phase, where $P \approx 0$. It is assumed that a blue-shift of this size is inherent also to the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ emission induced by binary collisions of O$_2$ with solvent molecules. A second contribution to the overall blue-shift could result from the changes in the repulsive part of the effective intermolecular potential upon electronic excitation in the condensed phase. Because of the small charge expansion of the π-electronic system repulsive interactions are expected to increase leading to a slight blue-shift.[16] Hence, we conclude that the solvent-shift $\Delta\nu$ is caused by the combination of attractive dispersive interactions between O$_2$ and solvent molecules and repulsive interactions due to the inherent collision induced nature of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition and due to changes in the repulsive part of the effective intermolecular potential
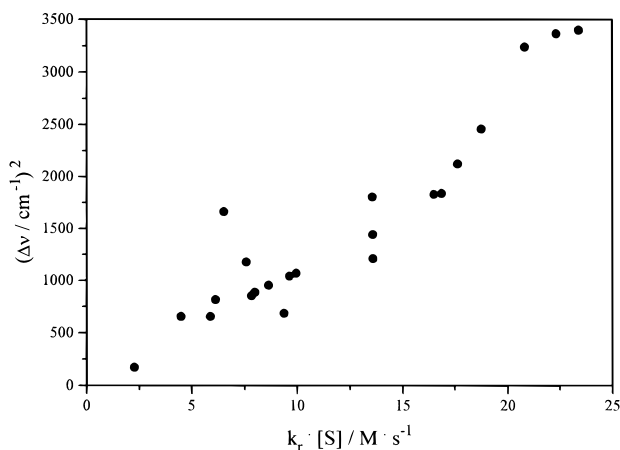

Figure 3. Plot of $\Delta\nu^2$ versus $k^c_{a-X}[S]^2 = k_r[S]$.

with electronic excitation. The first contribute to $\Delta\nu$ by a bulk polarizability-dependent red-shift, the latter by a more or less constant blue-shift of about 40 cm^{-1}.

Correlation of $\Delta\nu = \nu_{max} - 7882.4$ with k_r. A linear fit of all data of Figure 2 results in $\Delta\nu = 23.5 - 223P$ cm^{-1}. With the exception of CF$_3$CH$_2$OH, the bulk polarizabilty P of the solvents, in which k_r has been determined, is distinctly larger than 0.205 and lower than 0.368. In this range of P values we find a rather good linearity between $\Delta\nu^2 = (23.5 - 223P)^2$ and $P^2 = R_m^2/V_m^2$. We have recently shown that the bimolecular rate constant $k^c_{a-X} = k_r/[S]$ of the collision-induced radiative transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ is directly proportional to the square of the molar refraction: $k^c_{a-X} \propto R_m^2$.[17] Since the solvent molarity is the reciprocal solvent molar volume, $[S] = V_m^{-1}$, eq 3 is obtained as the relation between the dispersion-interaction-induced red-shift and the probability of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ radiative transition.

$$\Delta\nu^2 \propto k^c_{a-X}[S]^2 = k_r[S] \qquad (3)$$

Values of $\Delta\nu^2$ are plotted in Figure 3 versus the corresponding data of $k_r[S]$. The data point for CS$_2$ ($\Delta\nu^2 = 2830$ cm^{-2}, $k_r[S] = 51.6$ M s^{-1}) basing on $k_r = 2.07$ s^{-1} from ref 9 has been omitted.[18] A reasonable linear correlation can be noted. Equation 3 leads to the expectation that the red-shift linearly depends on the collider concentration: $\Delta\nu = const\cdot(k^c_{a-X})^{0.5}[S]$. This holds true for one-component collider systems because $(k^c_{a-X})^{0.5} \propto R_m$ and $[S] = P/R_m$. Of course, this is only an indirect effect on the 0−0 transition energy caused by the bulk polarizability of the surrounding of the colliders. Thus, eq 3 represents no really new functionality but is only a different formulation of the relation $\Delta\nu \propto -P = -R_m[S]$. This conclusion is further supported by the analysis of the solvent shift $\Delta\nu$ in solvent mixtures. The bulk polarizability of the mixture is given in a good approximation by $P = R_{m,1}[S_1] + R_{m,2}[S_2]$, as long as the molar refractions $R_{m,1}$ and $R_{m,2}$ of both components remain constant in the mixture. Then, the red-shift can approximatively be described by $\Delta\nu \approx const_1'\cdot[S_1] + const_2'\cdot[S_2]$, where the constants $const' = \Delta\nu/[S] = const\cdot(k^c_{a-X})^{0.5}$ are calculated for each pure solvent component from the values of $\Delta\nu$ and $[S]$. We calculate from the data of Table 1 for pentane $const_1 = -2.61$ cm^{-1} M^{-1} and for toluene $const_2 = -4.52$ cm^{-1} M^{-1}. Using these numbers, it is possible to reproduce the linear shift of ν_{max} from 7839.9 to 7859.8 cm^{-1} observed by Wessels and Rodgers for pentane/toluene mixtures with increasing mole percent pentane.[1]

The 0−0 transition is in mixtures of pentane and toluene not formed as an addition of two line bands caused by collisions of

$O_2(^1\Delta_g)$ either with pentane or toluene molecules. If this would be the case, then the volume polarizability of each collider would influence directly the value of ν_{max}. Then, at 50 mol % pentane both bands should have about half the shifts in the pure solvents, i.e., the band orginating from collisions with pentane molecules should be shifted by 11.3 cm^{-1}, the band caused by collisions with toluene molecules should be shifted by 21.3 cm^{-1}. Since both bands would overlap the overall shift of ν_{max} would be between 16.3 and 21.3 cm^{-1} depending on the relative size of the k_r values in pentane and toluene. However, $\Delta\nu \approx 32$ cm^{-1} was found.[1] Therefore, the effect of polarizability on ν_{max} is not a direct one, caused by the molecular polarizability of the molecule colliding with $O_2(^1\Delta_g)$ and inducing the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ radiative transition, but is an indirect one, caused by the bulk polarizability of the solvent molecules surrounding the colliding pair.

The radiative transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ is a collision induced process in solution.[14,17,19] The transition steals intensity in collisions from the radiative transition $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$, which for the isolated O_2 molecule is a pure quadrupole transition. An asymmetric charge shift occurs from the MOs of the collider to the $\pi_{g,z}$ and $\pi_{g,y}$ MOs of O_2, which induces electric dipole character into the $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ transition in collisions, resulting in a strong enhancement.[19] We found that the induced transition dipole moment is directly proportional to the molecular polarizability of the collider leading to the relation $k^c_{a-X} \propto R_m^2$.[17] Thus, the molecular polarizabilty of the colliding molecule influences strongly and directly the radiative probability of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition. In contrast, the effect of the polarizability on the shift of the 0−0 transition is only small and indirect. Therefore, the mechanisms by which the polarizability of the solvent influences $\Delta\nu$ and k_r or k^c_{a-X} are distinctly different.

References and Notes

(1) Wessels, J. M.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 17586.

(2) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950; p 560.

(3) Bromberg, A.; Foote, C. S. *J. Phys. Chem.* **1989**, *93*, 3968.

(4) Byteva, I. M.; Gurinovich, G. P.; Losev, A. P.; Mudryi, V. A. *Russ. Opt. Spectrosc.* **1990**, *68*, 317.

(5) Macpherson, A. N.; Truscott, T. G.; Turner, P. H. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1065.

(6) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599.

(7) Schmidt, R. *Chem. Phys. Lett.* **1988**, *151*, 369.

(8) Schmidt, R.; Afshari, E. *J. Phys. Chem.* **1990**, *94*, 4377.

(9) Scurlock, R. D.; Nonell, S.; Braslavsky, S. E.; Ogilby, P. R. *J. Phys. Chem.* **1995**, *99*, 3521.

(10) Atkins, P. W. *Physikalische Chemie*; VCH: Weinheim, Germany, 1988; p 600.

(11) *CRC Handbook of Chemistry and Physics*, 74th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993.

(12) Longuet-Higgins, H. C.; Pople, J. A. *J. Chem. Phys.* **1957**, *27*, 192.

(13) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(14) Wildt, J.; Fink, E. H.; Biggs, P.; Wayne, P. R. *Chem. Phys.* **1992**, *159*, 127.

(15) Badger, R. M.; Wright, A. C.; Whitlock, R. F. *J. Chem. Phys.* **1965**, *43*, 4345.

(16) Leutwyler, S. *Chem. Phys Lett.* **1984**, *107*, 284.

(17) Schmidt, R.; Bodesheim, M. *J. Phys. Chem.* **1995**, *99*, 15919.

(18) CS_2 is the only solvent for which strongly differing values of k_r have been reported in the literature, which are ranging from 0.3 to 2.33 s^{-1}.[9] The CS_2 value would fit into the linear correlation with $k_r = 1$ s^{-1}, indicating that the recommended value of $k_r = 2.07$ s^{-1} could be too large.

(19) Minaev, B. F. *J. Mol. Struct. (THEOCHEM)* **1989**, *183*, 207.

JP960464C