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QSPR Analysis of Solvent Effects on the Decay of the $^1\Delta_g$ State of Molecular Oxygen

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QSPR Analysis of Solvent Effects on the Decay of the $^1\Delta_g$ State of Molecular Oxygen[#]

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Abstract

Motivation. Molecular oxygen, O₂, commonly exists as a triplet ($^3\Sigma_g^-$) ground state, but also has two excited singlet states, $^1\Delta_g$ and $^1\Sigma_g^+$, that are of considerable interest due to their biological activities and their possible roles in atmospheric chemistry. In particular, the decay of the $^1\Delta_g$ state has been extensively studied under different conditions and its lifetime is found to vary widely in different solvents. This solvent dependence has been attributed to the involvement of solvent vibrational energy-accepting modes. In the present work a systematic QSPR study of the $^1\Delta_g$ state decay in 54 solvents is presented and observations are made about the factors influencing the decay.

Method. Multiple linear regressions were performed using the SAS statistical program.

Results. A high-quality statistical model with five variables and $R^2 = 0.993$ was obtained for the nonradiative decay rate constant.

Conclusions. Only five solvent features contribute significantly to the nonradiative decay rate of the $^1\Delta_g$ state. Four of these features can be associated with solvent oscillators, and the fifth, previously not well identified, with an external spin-orbit effect. Some solvent data are questionable, and further studies of particular features are recommended.

Keywords. Molecular oxygen; singlet states; phosphorescence decay; multiple linear regression; solvent effects.

Abbreviations and notations

MLR, multiple linear regression

QSPR, quantitative structure–property relationships

1 INTRODUCTION

The photophysical behaviors of the excited singlet $^1\Delta_g$ and $^1\Sigma_g^+$ electronic states of molecular oxygen have been extensively studied for many years because of the presumed involvement of these states in a variety of biological and environmental processes [1–8, and references cited therein]. In particular, the phosphorescence decay $^1\Delta_g \rightarrow ^3\Sigma_g^-$ of the $^1\Delta_g$ state has been of considerable interest due to its extreme sensitivity to solvent perturbation: its decay rate in different solvents is found to

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vary over five orders of magnitude [9]. The radiative $^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition itself is spin-, parity-, and symmetry-forbidden, and in the absence of external influences the intrinsic *radiative* lifetime τ_{rad} of the $^1\Delta_g$ state has been estimated to be of the order of an hour [10, and references cited], whereas the observed lifetime of this state in solution is commonly of the order of microseconds or milliseconds. The observed lifetime τ_Δ in water, for example, is 4 μs , whereas $\tau_\Delta = 55 \mu\text{s}$ in D_2O and 3900 μs in C_6F_6 .

A reasonable conclusion is that *nonradiative* deactivation processes of some sort exert an important influence on the lifetime of the $^1\Delta_g$ state in solution. An important clue to the nature of the specific processes involved came in the early work of Merkel and Kearns [2], who argued that electronic-to-vibrational energy transfer from $^1\text{O}_2(^1\Delta_g)$ to solvent oscillators was the most likely deactivation route. Work in the early 1980s by Hurst and Schuster [4] and by Rodgers [5] extended this concept and showed that the effects of the individual solvent oscillators on the nonradiative deactivation process were at least approximately additive. As a result of these and other studies an attractive picture arose in which the nonradiative decay rate constant k_Δ for $^1\Delta_g$ state deactivation could be regarded as composed of an additive combination of effects from the effective concentrations of the various energy-accepting oscillators in the solvent. Thus,

$$1/\tau_\Delta = k_{\text{decay}} = k_{\text{rad}} + \sum_i n_i \Delta_i [\text{S}] \quad (1)$$

where $k_{\text{rad}} (= 1/\tau_{\text{rad}})$ is the intrinsic radiative rate constant, the n_i are the numbers of each type of oscillator in the solvent molecules, the Δ_i are the specific contributions of these oscillators, the sum is over the solvent oscillator types, and $[\text{S}]$ is the molar concentration of the solvent. In most cases k_{rad} is negligibly small compared to the nonradiative contributions. $[\text{S}]$ can be calculated from the formula weight FW of the solvent and its density ρ using $[\text{S}] = 1000\rho/\text{FW}$. Following Rodgers [5], the bimolecular rate constant for deactivation of the $^1\Delta_g$ state is $k_\Delta = k_{\text{decay}}/[\text{S}] = (10^6/\tau_\Delta)/[\text{S}]$ in units of $\text{M}^{-1}\text{s}^{-1}$.

Based on the above model and the observed lifetimes a number of empirical estimates for the different oscillator contributions Δ_i have been proposed [4–6]. To our knowledge, however, no systematic, quantitative structure–property relationship (QSPR) analysis of this model has been presented. The present work presents such an analysis.

2 METHODS

Decay times τ_Δ for $^1\text{O}_2(^1\Delta_g)$ in 58 solvents were collected from the work of Hurst and Schuster [4] and Rodgers [5]. Two of the reported solvents, *tert*-butanol and cyclohexanol, are solids at 22°C, the temperature at which most of the measurements were carried out. Higher temperatures were required for measurements in these solvents, and these solvents were therefore judged to be unrepresentative and eliminated from the test set. All the solvents considered are listed in Table 1.

Table 1. Experimental Data for the Solvents Studied

No.	Solvent	Formula weight (g)	Density (g/cm ³)	τ_{Δ} μ S	[S] M
1	<i>n</i> -pentane	72.151	0.6262	34.6	8.6790
2	<i>n</i> -hexane	86.178	0.6594	31.4	7.6516
3	<i>n</i> -heptane	100.205	0.6838	29.5	6.8240
4	<i>n</i> -nonane	128.259	0.7176	23.7	5.5949
5	<i>n</i> -decane	142.286	0.7300	27.6	5.1305
6	<i>n</i> -undecane	156.313	0.7402	25.2	4.7354
7	<i>n</i> -dodecane	170.340	0.7487	24.7	4.3953
8	<i>n</i> -tetradecane	198.394	0.7628	24.7	3.8449
9	<i>n</i> -hexadecane	226.448	0.7734	24.3	3.4154
10	methanol	32.042	0.79131	10.4	24.696
11	ethanol	46.069	0.78937	15.3	17.135
12	1-propanol	60.096	0.80375	16.3	13.374
13	1-butanol	74.123	0.8097	17.5	10.924
14	1-pentanol	88.150	0.8148	17.8	9.243
15	1-hexanol	102.177	0.8198	17.9	8.023
16	1-heptanol	116.204	0.8223	18.1	7.076
17	1-octanol	130.231	0.8258	18.5	6.341
18	1-nonanol	144.258	0.8280	18.6	5.740
19	1-decanol	158.285	0.8297	17.8	5.242
20	water	18.015	0.99823	4.2	55.411
21	water-d ₂ ^a	—	—	55.0	55.411
22	acetonitrile	41.050	0.7857	58.3	19.14
23	acetonitrile-d ₃ ^a	—	—	621.0	19.14
24	methanol-d ₄ ^a	—	—	227.0	24.696
25	acetone	58.080	0.7899	50.5	13.60
26	acetone-d ₆ ^a	—	—	585.0	13.60
27	benzene	78.114	0.8765	31.2	11.221
28	benzene-d ₆ ^a	—	—	628.0	11.221
29	2-propanol	60.096	0.78545	22.1	13.07
30	2-butanol	74.123	0.8069	19.7	10.886
31	2-Me-1-propanol	74.123	0.8016	21.1	10.815
32	2-Me-2-propanol ^b	74.123	0.7866	30.8	10.612
33	2,4,4-Me ₃ -pentanol	130.231	0.8330	24.2	6.396
34	cyclohexanol ^b	100.161	0.96244	15.1	9.609
35	ethyleneglycol ^b	62.068	1.1088	7.5	17.864
36	1,4-dioxane	88.106	1.0337	26.7	11.733
37	diethylether	74.123	0.71378	30.4	9.630
38	<i>t</i> -Bu-Me-ether	88.150	0.7405	34.8	8.401
39	isooctane	114.232	0.6919	37.6	6.057
40	3-Me-pentane	86.178	0.6645	32.4	7.711
41	cyclohexane	84.162	0.7785	23.0	9.25
42	methylenchloride	84.933	1.3266	82.9	15.619
43	1,2-Cl ₂ -ethane	98.960	1.2351	63.2	12.481
44	F-benzene	96.104	1.0225	49.0	10.640
45	Cl-benzene	112.559	1.1058	51.0	9.824
46	Br-benzene	157.015	1.4950	50.0	9.521
47	I-benzene	204.010	1.8308	35.0	8.974
48	1,3-F ₂ -benzene	114.094	1.1568	62.0	10.139
49	1,3,5-F ₃ -benzene	132.084	1.2912	99.0	9.776
50	1,2,4,5-F ₄ -benzene	150.074	1.4255	155.0	9.499
51	F ₅ -benzene	168.064	1.5220	317.0	9.056
52	F ₆ -benzene	186.054	1.6184	3900	8.699
53	F-benzene-d ₅ ^a	—	—	1100	10.640

Table 1. (Continued)

No.	Solvent	Formula weight (g)	Density (g/cm ³)	τ_{Δ} μ s	[S] M
54	Cl-benzene-d5 ^a	–	–	1200	9.824
55	Br-benzene-d5 ^a	–	–	812	9.521
56	I-benzene-d5 ^a	–	–	277	8.974
57	chloroform	119.378	1.483	250	12.424
58	chloroform-d ^a	–	–	640	12.424

^aMolarities [S] for the deuterated solvents were set equal to those for their protonated counterparts (see text).

^bNot used in the regression analysis.

Table 2. Solvent features examined in this study

Feature	Feature
NC – number of carbon atoms	NCH2 – number of methylene groups
NH – number of hydrogen atoms	NCH3 – number of methyl groups
NO – number of oxygen atoms	NCH – single C–H bonds (nonaromatic)
NF – number of fluorine atoms	NCHA – aromatic C–H bonds
NCL – number of chlorine atoms	NOH – number of hydroxyl groups
NBR – number of bromine atoms	NCO – number of carbonyl groups
NI – number of iodine atoms	NCD3 – deuterated methyl groups
ND – number of deuterium atoms	NCD – nonaromatic C–D bonds
	NCDA – aromatic C–D bonds
	NOD – number of O–D bonds

Densities for most of the solvents at 20°C were obtained from the *CRC Handbook of Chemistry and Physics* [11]. Because density values for a number of the deuterated solvents were not available, the [S] values for all of the deuterated solvents were set equal to the values determined for their protonated counterparts. This should not introduce any appreciable error: even for the extreme case of water the two values differ by less than 0.5% at 20°C.

A number of structural descriptors for the solvents were examined for possible influence on the decay process. These examined descriptors are summarized in Table 2. The multiple linear regression (MLR) statistical analyses were carried out using the *SAS* [12] statistical analysis program. Covariance statistics were determined using the *QSARIS* software package (*SciVision*, Burlington, MA).

3 RESULTS AND DISCUSSION

Initial analysis of the dependence of k_{Δ} on the solvent descriptors revealed three significant outliers: *n*-nonane, ethyleneglycol, and methanol. Closer examination revealed that the lifetime τ_{Δ} reported in *n*-nonane is not consistent with the values reported for other members of the *n*-alkane series (see Table 1), and its reported τ_{Δ} value is therefore likely be unreliable. Ethyleneglycol is highly viscous compared to many other solvents, and, more importantly, it is subject to internal hydrogen bonding effects that may alter the effectiveness of some of its oscillators. Both compounds were dropped from the list. Methanol was retained, leaving 54 solvents in the data set.

Table 3. Regression results and literature Δ_i values for the solvent parameters

Feature	Study 1	Study 2	Ref. 5 ^a	Ref. 4 ^b	Ref. 6 ^c
	Δ_i	Δ_i	Δ_i	Δ_i	Δ_i
intercept	63 ± 68	39 ± 71			
NCH3	710 ± 36	716 ± 36	550	420 ^d	
NCH2	762 ± 12	763 ± 12	813		390
NCHA	413 ± 27	418 ± 27			470
NOH	2334 ± 81	2345 ± 81	2290	2000	2145–2720
NI	698 ± 211	710 ± 210			
NOD	–	144 ± 133	165	150	156–165
R^2	0.9930	0.9932			
s	283	283			
F	1369	1145			
R_{CV}^2	0.9894	0.9897			

^a Additional values reported: CD3 (15), CH (nonaromatic, 90), C=O (100), C≡N (65).

^b Additional value reported: CD3 (17).

^c Values cited apply to specific compounds; several additional values are given, including N–H (900) and S–H (95).

^d Average value for all C–H.

Table 4. Comparison of the results of Study 1 with the experimental results

Solvent	Exper. k	Calc'd k	Resid.	Solvent	Exper. k	Calc'd k	Resid.
1	3330	3769	–439	30	4663	4579	84
2	4162	4531	–369	31	4382	4579	–197
3	4968	5292	–324	32		4528	
4		6816		33	6460	6761	–301
5	7062	7577	–515	34		6205	
6	8380	8339	41	35		6254	
7	9211	9100	111	36	3192	3110	82
8	10530	10624	–94	37	3416	3007	409
9	12049	12147	–98	38	3421	2905	516
10	3894	3107	787	39	4391	4376	15
11	3815	3869	–54	40	4003	3718	285
12	4587	4630	–43	41	4700	4633	67
13	5231	5292	–61	42	772	825	–53
14	6078	6153	–75	43	1268	1587	–319
15	6963	6916	47	44	1918	2128	–210
16	7808	7677	131	45	1996	2128	–132
17	8525	8438	87	46	2101	2128	–27
18	9367	9200	167	47	3184	2825	359
19	10718	9962	756	48	1591	1715	–124
20	4297	4731	–434	49	1033	1302	–269
21	328	63	265	50	679	889	–210
22	896	774	122	51	348	476	–128
23	84	63	21	52	29	63	–34
24	178	63	115	53	85	63	22
25	1456	1484	–28	54	85	63	22
26	126	63	63	55	129	63	66
27	2856	2540	316	56	402	761	–359
28	142	63	79	57	322	63	259
29	3462	3818	–356	58	126	63	63

When the four solvents mentioned above (*tert*-butanol, cyclohexanol, *n*-nonane, and ethyleneglycol) were removed an excellent statistical model ($n = 54$, $R^2 = 0.9930$, $s = 283.0$, $F = 1369$, $R_{CV}^2 = 0.9894$) for k_Δ was obtained. Five solvent structural features were found to enter with t -test values greater than 3: NCH3 (the number of methyl groups), NCH2 (the number of methylene groups), NCHA (the number of aromatic C–H bonds), NOH (the number of O–H bonds), and NI (the number of iodine atoms). These results, with the corresponding Δ_i values, are summarized in Table 3, and compared with the earlier estimates for these contributions from Hurst and Schuster [4], from Rodgers [5], and from Schmidt and Brauer [6]. Table 4 summarizes the calculated and experimental results for the decay rate constant k_Δ for this analysis (Study 1). These results are also plotted in Figure 1.

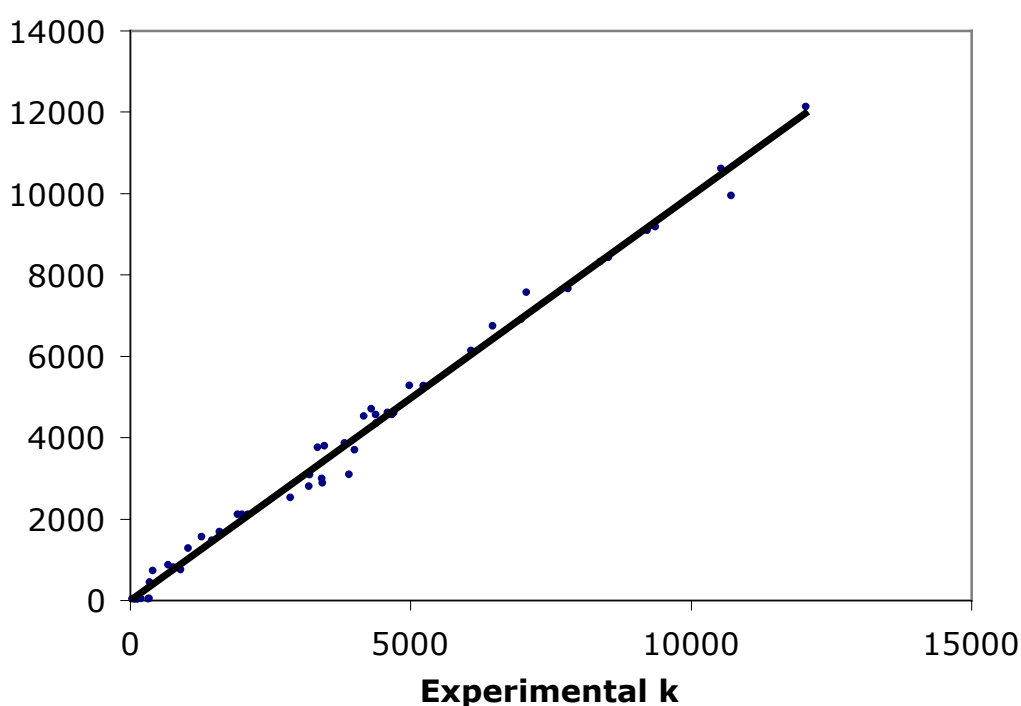


Figure 1. Comparison of calculated and experimental k_Δ values for Study 1.

When the t -test criterion was relaxed to see if other, less statistically sound, contributions could be detected, a contribution from the O–D vibrations, NOD, was found, and the previous Δ_i values were slightly altered. The statistics of the model remained largely the same ($n = 54$, $R^2 = 0.9932$, $s = 282.6$, $F = 1145$, $R_{CV}^2 = 0.9897$). These results are also shown in Table 3 as Study 2.

It is evident from the results in Table 3 that the values obtained from the present analysis agree qualitatively with the earlier, empirical estimates for the contributions of the solvent oscillators proposed by Hurst and Schuster (who did not distinguish different C–H oscillators), Rodgers [5], and Schmidt and Brauer [6]. The high statistical quality of the present results strongly supports the notion that accepting solvent vibrational modes are primarily responsible for deactivation the $^1\Delta_g$ state of molecular oxygen, and the Δ_i values presented in Table 3 give a quantitative measure of the

effectiveness of each type of oscillator in this role. It is to be expected that the highest-energy vibrational modes in the solvents should be most effective in accepting energy from ${}^1\text{O}_2({}^1\Delta_g)$ [6], and this is seen to be the case. The O–H vibrations ($\nu \sim 3400\text{--}3650\text{ cm}^{-1}$) have the largest Δ_i value, and the aromatic C–H stretches ($\nu \sim 3030\text{ cm}^{-1}$) and alkane C–H stretches ($\nu \sim 2850\text{--}2960\text{ cm}^{-1}$) [13] also play significant roles. In contrast, the lower-energy O–D vibrations ($\nu \sim 2200\text{--}2500\text{ cm}^{-1}$) play a much more limited role in deactivating the ${}^1\Delta_g$ state.

The NI parameter represents a much different influence on the ${}^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition from the aforementioned vibrational modes. It represents an external spin–orbit perturbation on the transition [14,15]. The spin–orbit (so-called “heavy atom”) perturbation of the iodine atom acts to partially lift the spin–forbiddenness of the singlet \rightarrow triplet transition. Interestingly, in their original work Merkel and Kearns [2] discussed the possibility of an external heavy–atom effect on the deactivation process, but regarded it as unlikely on theoretical grounds. Hurst and Schuster [4] also considered the possibility of an external heavy–atom effect from iodine, and possibly bromine, but argued that such an effect would be relatively small except for perdeutero compounds. Apparently because of the earlier focus on vibrational deactivation, this feature was not completely explored.

Although nonradiative deactivation processes clearly dominate deactivation of the $\text{O}_2({}^1\Delta_g)$ state in solution, it should be noted that there is evidence that the solvent environment also affects the *radiative* decay of this state. In particular, Ogilby and coworkers have demonstrated solvent effects on the radiative decay rate k_{rad} of the ${}^1\Delta_g$ state [10,16,17]. Others have supported these observations [18,19]. Nonetheless, this effect is small relative to the nonradiative influences described above. Note that the intercept coefficients are small in both studies, indicating that the vibrational descriptors above largely account for the observed variations in the decay.

An advantage of the QSPR approach is that a systematic investigation employing a reasonable selection of structural parameters can provide a largely unbiased, quantitative analysis of the factors influencing an examined phenomenon. A second advantage is that, from the statistical output, one obtains an objective measure of the uncertainty to be associated with the numerical values produced. The regression analysis also calls attention to questionable measurements, which appear as outliers (although, of course these outliers can also arise from shortcomings of the model). Finally, the analysis points to some of the weaknesses in the data set, and hence the model. First, the multiple linear regression model only captures the strongest influences on the decay process, since only such influences acquire statistical significance. Thus the regression analysis will fail to identify smaller influences that might be important in cases where the most influential vibrational features are not present, and the lifetimes are correspondingly longer. Also, in order to obtain a well-characterized value (Δ_i) for a solvent feature, that feature should be well represented in the data set. The Δ_i associated with NI, for example, although it has a relatively large value also displays a large relative uncertainty because there are only two compounds in the data set that contain iodine atoms.

Only two of the solvents in the data set feature O–D oscillators, and just two have bromine atoms. Studies of additional solvents containing these underrepresented features would permit better-defined characterizations of these features. Some such studies have already been carried out [6,18].

Most commonly, QSPR studies of solubility involve studies of different solutes in a common solvent, but studies of a single solute in a variety of solvents can also be highly informative regarding the operating influences in a system. We note, for example, earlier studies of the solvatochromism and thermochromism of rhodamine dyes [20,21], which focused on solvent features favoring either the lactone or zwitterionic forms of these dyes.

4 CONCLUSIONS

A quantitative structure–property analysis of the molecular oxygen $^1\Delta_g \rightarrow ^3\Sigma_g^-$ decay lifetime in 54 solvents reveals that five features of the solvent molecules contribute significantly to enhancing nonradiative deactivation. Four of these features are related to high–frequency vibrational accepting modes of the solvent, which act *via* electronic–to–vibrational energy transfer, and the fifth is related to spin–orbit perturbation of the formally spin–forbidden transition by iodine atoms. Studies of additional solvents containing underrepresented features would further clarify the influence of such features on the $^1\Delta_g$ state lifetime.

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Biographies

Paul G. Seybold is professor of chemistry and biochemistry at Wright State University in Dayton, Ohio, USA. After receiving his B. Engineering Physics from Cornell University, he obtained a Ph.D in biophysics from Harvard University, working with Prof. Martin Gouterman. Dr. Seybold did postdoctoral research with Professor Per–Olov Löwdin at the University of Uppsala, Sweden, Prof. Inga Fischer–Hjalmars, Stockholm, Sweden, and with Prof. Gregorio Weber at the University of Illinois. More recently, he has collaborated on the development of cellular automata models of complex systems with Professor Lemont B. Kier at Virginia Commonwealth University.