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ZEEMAN EFFECT ON PHOSPHORESCENT LIFE-TIME OF MATRIX ISOLATED SO_2

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ABSTRACT

The phosphorescent lifetime of SO_2 as a function of magnetic field has been studied at 4°K in sulfur hexafluoride, oxygen and zenon at zero and 26 kGauss and at 20°K in sulfur hexafluoride between zero and 90 kGauss. At high fields, the decay consists of two lifetime components. One is identical with the zero field lifetime of SO_2; the second has a lifetime of approximately 50% longer, depending on magnetic field.

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Great interest has recently been shown in electronic excitation transfer involving the triplet state of large organic molecules in the presence of a magnetic field[1,2,3]. We report here experiments on SO_2 in which the effect of triplet level splitting on $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ processes are studied. In contrast to large organic molecules, SO_2 has sharp rotational levels in the gas phase. Furthermore, a tentative rotational analysis of T_1 is available[4]; exploratory Zeeman experiments have been performed[5], and the phosphorescent lifetime has been extensively studied in the solid[6] as well as in the gas phase[7]. Due to strong spin orbit coupling the SO_2 lifetime is short for a $T_1 \rightarrow S_0$ transition; 7 msec in the gas phase[7] at 300°K; 11 msec in SF_6 at 77°K, and at 4°K values in rare gas matrices[6] range from 5.6 to 17.5 msec.

The triplet population via $S_1 \rightarrow T_1$ is very sensitive to environment and temperature. In the gas phase phosphorescence occurs only at pressures above 0.01 torr. In solids the triplet population changes by a factor of up to one hundred between 4°K and 100°K.

The experiments were performed in specially designed Dewars which, for the 4°K experiment, fitted in the 1" gap magnet, and for the 20°K experiment, in a five inch 90kGauss magnet. The optical arrangement was similar to that described earlier[6]. The exciting source and the detectors were removed from the magnet area to eliminate the effect of magnetic fields. In the case of the 90kGauss experiment, all electronic equipment was heavily shielded and 15 feet from the magnet core in an area with a residual field of less than 50 Gauss. For efficient light collection, light pipes were used. Decay curves were integrated with the help of a waveform reductor. Care was taken to prove experimentally that no field dependent instrumental effects occurred.

Table I shows the decay time for xenon, sulfur hexafluoride and oxygen at 0 and 26 kG at 4°K. The solvent effect is very pronounced in oxygen. The lifetime is significantly shorter, and the emission is weaker than in any other matrix, indicating that triplet-triplet quenching is efficient. The magnetic effects in all solvents are smaller than 12%.

Table II lists the lifetime at 20°K for fields between 0 and 90 kG. At high field strength, decay curves can be analyzed into two different components. The short lifetime component (τ_1) is similar to that with zero field. Figure 1 shows a log I <u>versus</u> time curve for two typical decays. Long lifetime components (τ_2) account for less than 40% of the initial intensity, regardless of field strength. It is noteworthy that the short lifetime component at high field agrees well with the zero-field lifetime at 20°K and at 4°K, and that all are similar in magnitude to the gas phase value.

In the gas phase, partial rotational analysis[4] indicates that emission originates predominantly from the triplet sublevel F_3. The gas phase

λ value is estimated to be about 1 cm^{-1}. As the zero-field spliting in the solid is not known, one might guess that it is of the same order of magnitude. At the present time it is not known whether $S_1 \rightarrow T_1$ intersystem crossing follows selection rules and populates one triplet sublevel preferentially, or whether all sublevels can be populated independently. The observation that the intensity of phosphorescence does not alter significantly with field, indicates that $S_1 \rightarrow T_1$ processes are not affected by the splitting and shift of triplet sublevels. This might be because T_1 populates only through one, the least shifted, sublevel; it proves in any case that under all conditions T_1 population takes the same path. The Zeeman effect and spin-lattice relaxation (slr) in molecules like SO_2 are not even qualitatively understood. A conclusive description of our observed effects is therefore not yet possible, but we propose the following model which qualitatively explains it.

At 20°K, slr is quick compared to the lifetime of $F_3 \rightarrow S_0$. At zero field, the sublevel splitting, probably a few wavenumbers, is small compared to kT, which is 14 cm^{-1}. The population between the three triplet sublevels will be efficiently redistributed, but almost all radiation will originate from F_3: (the transition $F_3 \rightarrow S_0$ being more allowed than those originating from F_1 or F_2). With zero field the observed lifetime is about the same as in the gas phase. At high field, the sublevel splitting becomes comparable with kT. Because of kT imbalance F_3 emission is now accompanied by either delayed phosphorescence, caused by slow thermal repopulation of F_3, or by emission from F_1 or F_2 to S_o, depending on the relative values of the triplet splitting, slr, and the lifetime of $F_2, F_1 \rightarrow S_o$. Observed effects could be due to very complex processes, because all parameters may change simultaneously. Slr can be a complicated function of temperature[8], and

the lifetimes of the individual sublevels are not known. It is therefore not possible to predict magnetic effects.

We observed experimentally that the emission broadens at 26kGauss by about 30 cm^{-1} (Figure 2). From this we deduce an average value of $g = 2.002$. At high field, the splitting becomes comparable with kT at 20°K. We also observe that the lifetimes change with increasing field. This suggests that above about 50 kG, delayed phosphorescence and/or F_2 or F_1 emission becomes competitive with normal phosphorescence. The largest lifetime observed, 17 msec, is the lower limit of F_2 or $F_1 \rightarrow S_0$. At fields greater than 80 kG, the decay curves show further changes. It is likely that at such high fields spin uncoupling sets in, resulting in a Paschen-Back effect.

At 4°K the situation is different. Slr is slower than triplet decay, and at zero field triplet decay occurs from F_3 directly before sublevel redistribution occurs, very much like in the gas phase. Very high fields would be needed to yield observable amounts of second lifetime components. The small increase of the 0 field lifetime between 20°K and 4°K is probably due to decrease of the non-radiative[6] depopulation of F_3.

Recently, El-Sayed[1], Wolf[3] and van der Waals[2] observed Zeeman effects in organic molecules at 1.6 to 4°K. They explain their observations by assuming that slr dependence on magnetic field, due to triplet splitting, becomes a crucial factor. Slr is expected to be more efficient at larger splittings, at 2°K, and they propose that it becomes significant at high field. Their experiments differ from ours in that we observe our samples at higher temperatures. Their models differ in that organic molecules are observed to have different lifetimes in the solid state above 4°K than at low temperatures. In the case of SO_2, this is not expected

since most emission originates from only one level, even in the gas phase.

For a quantitative description of our model, one would have to take into account that weak decay from F_2 is observed in the gas phase, and may be responsible for the broadening of the emission in the solid. This makes quantitative description unwieldy. Analysis of the polarization of the two lifetime components shows that both are fully depolarized under our conditions. This might, at least partly, be due to exciton transfer.

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Table I

LIFETIMES FOR SO_2 IN SF_6, XENON, AND OXYGEN AT 4°K, WITH AND WITHOUT FIELD

Solvent	Lifetime (msec)	
	zero-field	26 kGauss
SF_6	13.5	14.8
Xenon	5.6	5.8
Oxygen	0.50	0.56

all values ± 5%

Table II

LIFETIMES FOR SO_2 IN SF_6 AT 20°K AS A FUNCTION OF FIELD FROM 0 TO 90 kG

(msec ± 5%)

Field (kG)	τ_1	τ_2	τ_2 % contribution to intensity
0	11.3	-	0
10	12.0	-	0
20	11.5	13.0	20%
30	11.2	13.5	20%
40	11.4	13.5	30-35
50	11.0	13.6	20-33
60	11.5	14.5	30
70	12.5	17.0	30
80	10.0	15.0	30
90	10.2	15.0	30

Figures:

Figure 1: Log I *versus* time of SO_2 in SF_6 at 20°K with 0 and 70 kGauss field.

Figure 2: Part of the $T_1 \rightarrow S_0$ emission of SO_2 in SF_6 at 4°K with fields of 0 and 26 kGauss. The numbers indicate the vibrational assignment of the peaks.

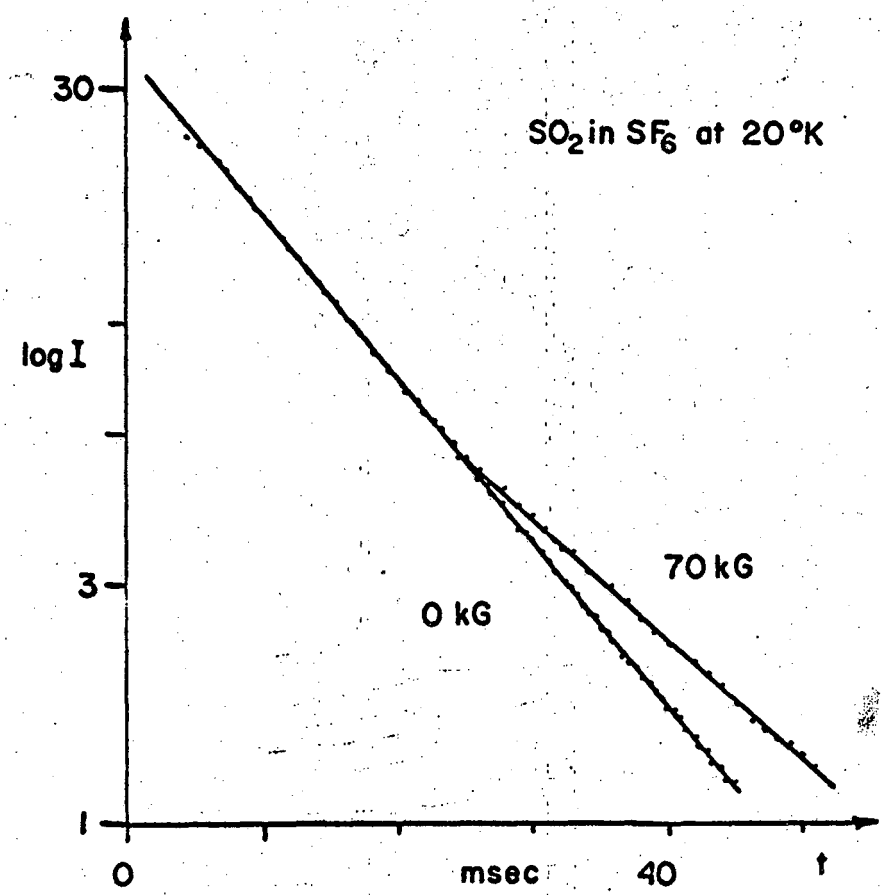

Figure 1

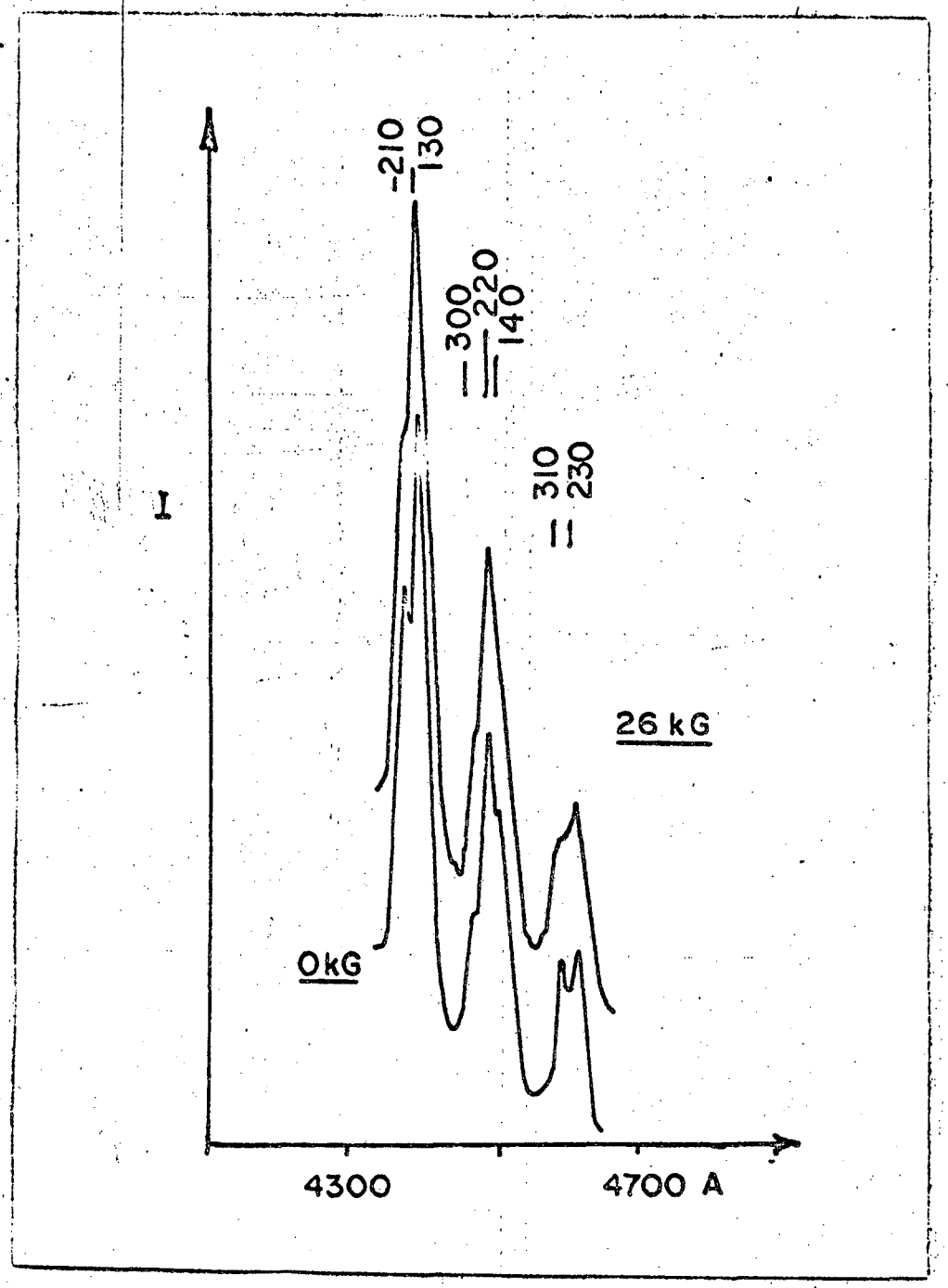

Figure 2

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