

Lawrence Berkeley National Laboratory

Recent Work

Title

ZEEMAN EFFECT ON PHOSPHORESCENT LIFETIME OF MATRIX ISOLATED SO₂

Permalink

<https://escholarship.org/uc/item/4d363265>

Authors

Conway, John G.

Meyer, B.

Smith, J.J.

et al.

Publication Date

1968-11-01

ey. Z

ZEEMAN EFFECT ON PHOSPHORESCENT LIFE-
TIME OF MATRIX ISOLATED SO₂

John G. Conway, B. Meyer, J. J. Smith,
and L. J. Williamson

November 1968.

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-18657
UC-4 Chemistry
TID-4500 (52nd Ed.)

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

ZEEMAN EFFECT ON PHOSPHORESCENT LIFETIME
OF MATRIX ISOLATED SO₂

John G. Conway, B. Meyer, J. J. Smith, and L. J. Williamson

November 1968

ZEEMAN EFFECT ON PHOSPHORESCENT LIFETIME OF MATRIX ISOLATED SO_2 *

John G. Conway
Lawrence Radiation Laboratory, University of California, Berkeley

and

B. Meyer, J.J. Smith and L.J. Williamson #
Chemistry Department, University of Washington, Seattle, and Inorganic
Materials Research Division, Lawrence Radiation Laboratory, University of
California, Berkeley

ABSTRACT

The phosphorescent lifetime of SO_2 as a function of magnetic field has been studied at 4°K in sulfur hexafluoride, oxygen and xenon 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.

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

NSF Undergraduate Research Fellow

ZEEMAN EFFECT ON PHOSPHORESCENT LIFETIME OF MATRIX ISOLATED SO_2^*

J.G. Conway

Lawrence Radiation Laboratory, University of California, Berkeley

and

B. Meyer, J.J. Smith, and L.J. Williamson #

Chemistry Department, University of Washington, Seattle, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley

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 available⁴; exploratory Zeeman experiments have been performed⁵, and the phosphorescent lifetime has been extensively studied in the solid⁶ as well as in the gas phase⁷. 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 phase⁷ at 300°K; 11 msec in SF_6 at 77°K, and at 4°K values in rare gas matrices⁶ 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 earlier⁶. 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 versus 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 analysis⁴ 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 splitting 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_0 , depending on the relative values of the triplet splitting, slr, and the lifetime of $F_2, F_1 \rightarrow S_0$. Observed effects could be due to very complex processes, because all parameters may change simultaneously. Slr can be a complicated function of temperature⁸, 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-radiative⁶ depopulation of F_3 .

Recently, El-Sayed¹, Wolf³ and van der Waals² 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.

ACKNOWLEDGEMENT:

The authors wish to thank professor Leo Brewer for advice and support, and Mr. Chiladakis for assistance with high field experiments.

Professor R. Myers contributed in discussion.

References

- (1) L. Hall, A. Armstrong, W. Moomaw and M. A. El-Sayed; J. Chem. Phys. 48, 1395, (1968)
- (2) J. H. v.d. Waals and M. S. de Groot; Proc. Int. Conference Triplet State, American University, Beirut, 1967 pg. 118
- (3) M. Schwoerer and H. C. Wolf; *ibid*, page 133
- (4) A. J. Merer; Dis. Faraday Soc. 35, 127 (1963)
- (5) A. E. Douglas, Can. J. Phys. 36, 147 (1958)
- (6) B. Meyer, L. F. Phillips and J. J. Smith; Proc. Nat. Acad. Sciences 61, 7 (1968)
- (7) S. J. Strickler and D. B. Howell, J. Chem. Phys. 49, 1947 (1968)
- (8) A. A. Manenkov and A. M. Prokhorov; Proc. Int. Conference Paramagnetic Resonance, Jerusalem 1962; W. Low editor, Academic Press 1963; page 425

Table I

LIFETIMES FOR SO₂ IN SF₆, 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 \pm 5%

Table II

LIFETIMES FOR SO₂ IN SF₆ AT 20°K AS A FUNCTION
OF FIELD FROM 0 TO 90 kG

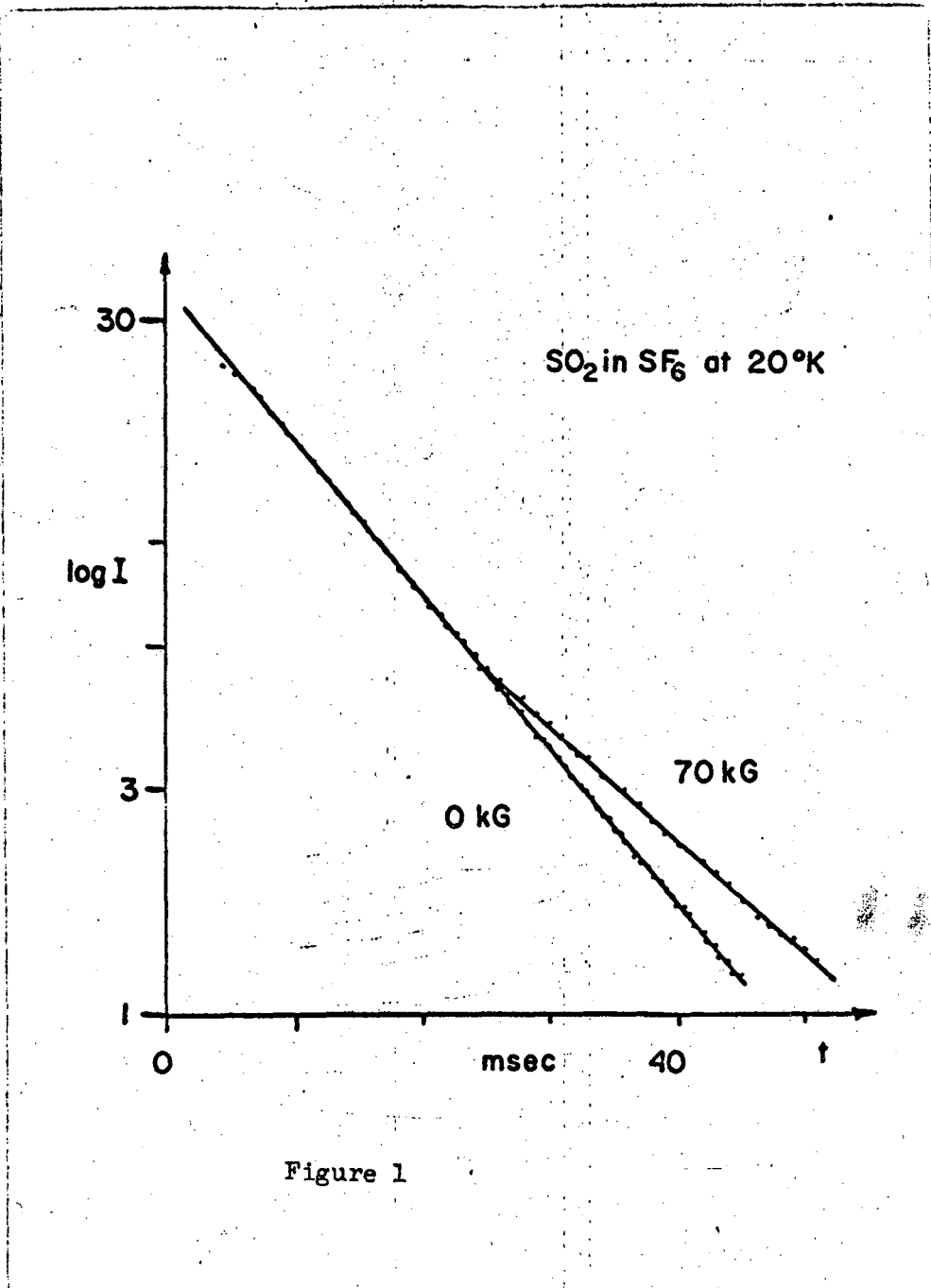
(msec ± 5%)

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 $\text{T}_1 \rightarrow \text{S}_0$ 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.



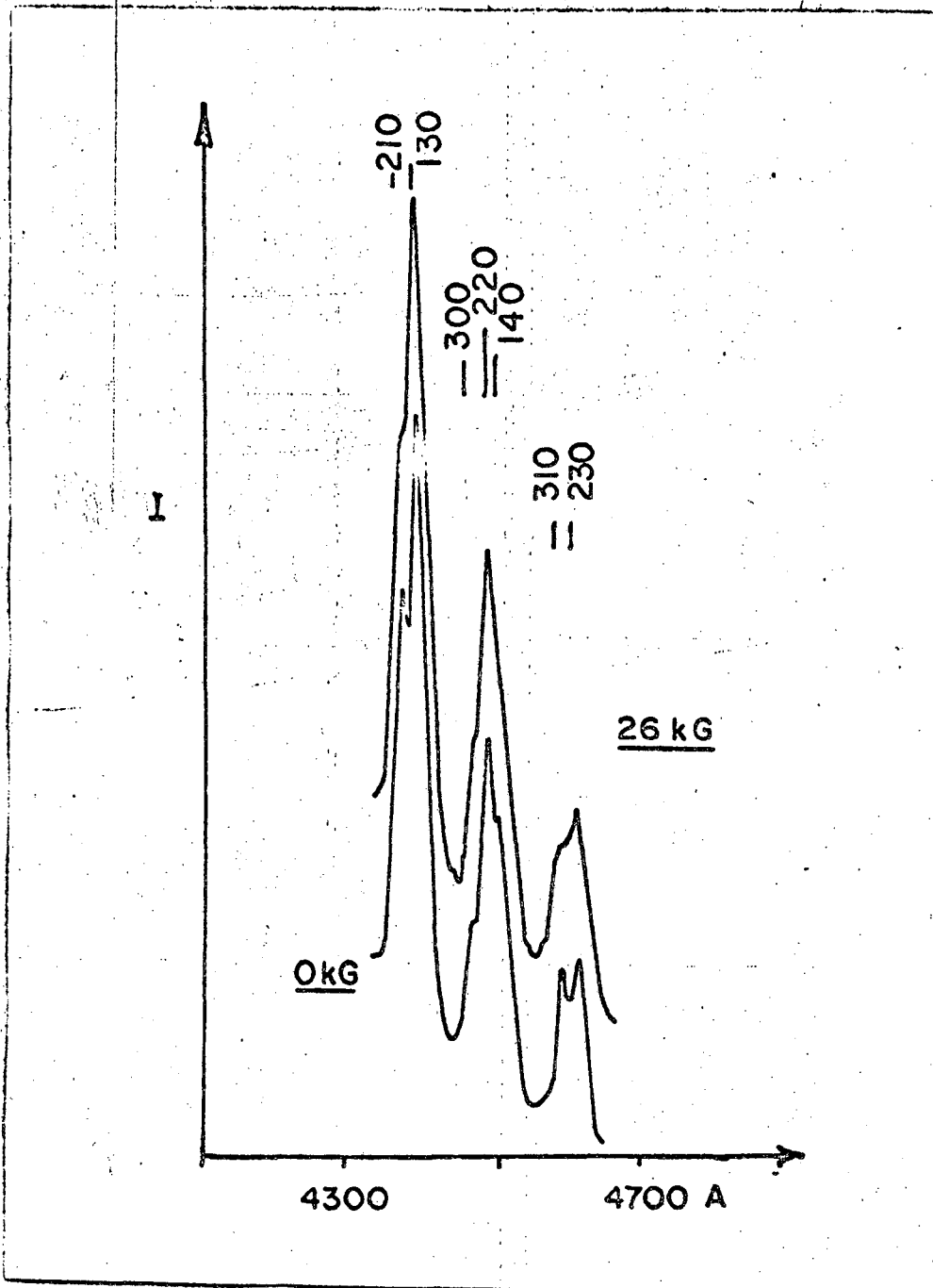


Figure 2

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720