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
ZEEMAN EFFECT ON PHOSPHORESCENT LIFE-TIME OF MATRIX ISOLATED SO₂

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

November 1968
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.
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 $\text{SO}_2$*

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 $\text{SO}_2$ as a function of magnetic field has been studied at $4^\circ\text{K}$ in sulfur hexafluoride, oxygen and xenon at zero and 26 kGauss and at $20^\circ\text{K}$ 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 $\text{SO}_2$; 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
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. We report here experiments on SO₂ in which the effect of triplet level splitting on S₃→T₁ and T₁→S₀ processes are studied. In contrast to large organic molecules, SO₂ has sharp rotational levels in the gas phase. Furthermore, a tentative rotational analysis of T₁ is available; exploratory Zeeman experiments have been performed, and the phosphorescent lifetime has been extensively studied in the solid as well as in the gas phase. Due to strong spin orbit coupling the SO₂ lifetime is short for a T₁→S₀ transition: 7 msec in the gas phase at 300°K; 11 msec in SF₆ at 77°K, and at 4°K values in rare gas matrices range from 5.6 to 17.5 msec.

The triplet population via S₃→T₁ 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. 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 (τ₁) is similar to that with zero field. Figure 1 shows a log I versus time curve for two typical decays. Long lifetime components (τ₂) 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 indicates that emission originates predominantly from the triplet sublevel F₃. 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 \(\text{SO}_2\) 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 \(F_3 \rightarrow \text{S}_0\). 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 \(F_3 \rightarrow \text{S}_0\) 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 \(\text{S}_0\), depending on the relative values of the triplet splitting, slr, and the lifetime of \(F_2 \rightarrow F_1 \rightarrow \text{S}_0\). Observed effects could be due to very complex processes, because all parameters may change simultaneously. Slr can be a complicated function of temperature, 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\(^{\circ}\)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 \(F_1?S_0\). 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\(^{\circ}\)K the situation is different. \(S_{2r}\) 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\(^{\circ}\)K and 4\(^{\circ}\)K is probably due to decrease of the non-radiative 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\(^{\circ}\)K. They explain their observations by assuming that \(S_{2r}\) dependence on magnetic field, due to triplet splitting, becomes a crucial factor. \(S_{2r}\) is expected to be more efficient at larger splittings, at 2\(^{\circ}\)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\(^{\circ}\)K than at low temperatures. In the case of \(S_02\), 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


(3) M. Schwoerer and H. C. Wolf; ibid, page 133


Table I

LIFETIMES FOR $\text{SO}_2$ IN SF$_6$, XENON, AND OXYGEN AT 4°K, WITH AND WITHOUT FIELD

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Lifetime (msec)</th>
<th>zero-field</th>
<th>26 kGauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_6$</td>
<td>13.5</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>Xenon</td>
<td>5.6</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.50</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

all values ± 5%
Table II

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

(msec ± 5%)

<table>
<thead>
<tr>
<th>Field (kG)</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_2$ % contribution to intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.3</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>12.0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>11.5</td>
<td>13.0</td>
<td>20%</td>
</tr>
<tr>
<td>30</td>
<td>11.2</td>
<td>13.5</td>
<td>20%</td>
</tr>
<tr>
<td>40</td>
<td>11.4</td>
<td>13.5</td>
<td>30-35</td>
</tr>
<tr>
<td>50</td>
<td>11.0</td>
<td>13.6</td>
<td>20-33</td>
</tr>
<tr>
<td>60</td>
<td>11.5</td>
<td>14.5</td>
<td>30</td>
</tr>
<tr>
<td>70</td>
<td>12.5</td>
<td>17.0</td>
<td>30</td>
</tr>
<tr>
<td>80</td>
<td>10.0</td>
<td>15.0</td>
<td>30</td>
</tr>
<tr>
<td>90</td>
<td>10.2</td>
<td>15.0</td>
<td>30</td>
</tr>
</tbody>
</table>
Figures:

Figure 1: \textit{Log I versus time of S0}_2 \textit{in SF}_6 \textit{at 20}^{\circ}\textit{K with 0 and 70 kGauss field.}

Figure 2: \textit{Part of the T}_1 \rightarrow \textit{S}_0 \textit{emission of S0}_2 \textit{in SF}_6 \textit{at 4}^{\circ}\textit{K with fields of 0 and 26 kGauss. The numbers indicate the vibrational assignment of the peaks.}
Figure 1

SO$_2$ in SF$_6$ at 20°K

log I

0 mG

70 mG

msec

Figure 1
Figure 2
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.