University of Groningen

Zeeman Effect in the Electronic Spectrum of Solid CS₂

Hochstrasser, Robin M.; Wiersma, Douwe A.

Published in:
The Journal of Chemical Physics

DOI:
[10.1063/1.1674653](https://doi.org/10.1063/1.1674653)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1971

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Hochstrasser, R. M., & Wiersma, D. A. (1971). Zeeman Effect in the Electronic Spectrum of Solid CS₂. *The Journal of Chemical Physics*, 54(10), 4165-4169. <https://doi.org/10.1063/1.1674653>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Zeeman Effect in the Electronic Spectrum of Solid CS₂*

ROBIN M. HOCHSTRASSER AND DOUWE A. WIERSMA

Department of Chemistry and Laboratory for Research on the Structure of Matter, The University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 14 December 1970)

The lowest-energy $^3A_2 \leftarrow ^1\Sigma_g^+$ singlet-triplet transition of CS₂ has been studied in the CS₂ crystal at 4.2°K. The spectrum consists mainly of progressions in the bending mode ν_2' . The following values for the upper state frequencies have been obtained ($\nu_1' = 677$ cm⁻¹, $\nu_2' = 309$ cm⁻¹) and the unobserved B_2 electronic origin has been calculated to be at 24 739 cm⁻¹. Zeeman studies of the 3676-Å band system have been used to assign a very weak component of a vibronic band of this system as a crystal field induced transition to the (A_1 , B_1) pair of spin sublevels of the triplet state 3A_2 . The zero field splitting (ZFS) parameter of 36 ± 1 cm⁻¹ thus obtained for the vibronic state is comparable with the one calculated by Hougen [J. Chem. Phys. **41**, 363, (1964)] from Zeeman line broadening experiments in the gas phase done by Douglas and Milton [J. Chem. Phys. **41**, 357 (1964)] on comparable vibronic bands. The large value of the ZFS parameter can be explained if it is assumed that the 3A_2 and 3B_2 states are quite nearby.

INTRODUCTION

The electronic absorption spectrum of CS₂ in the region of 4000–3000 Å has been the subject of many gas phase studies. The most comprehensive study is that of Kleman,¹ which also contains an excellent review of previous work. Kleman showed that the transition is of parallel type thus establishing that the upper state total symmetry is B_2 . He was also able to obtain the upper state frequencies and rotational constants from which the upper state SCS angle was computed to be 136°. Furthermore, the simple rotational structure of some bands indicated that the upper state was not spin degenerate.

The magnetic optical rotation studies of Kusch and Loomis² and the Zeeman studies of Douglas and Milton³ argued in favor of an upper state with some spin angular momentum. Assuming the B_2 upper state to be a separated spin sublevel of a 3A_2 triplet state, Hougen⁴ calculated the magnitude of the ZFS parameter for the first vibronic bands of type (0n0) to be between 35 and 40 cm⁻¹ based on the rotational line Zeeman broadening experiments.³

As yet no electronic spectroscopic work has been reported on solid CS₂. One might expect the crystal field to expose the spin substructure of the upper state (if this state in question is a triplet state) so the purpose of this paper is to present and discuss the results of such a solid state study at 4.2°K and to provide a confirmation of the assignment of the upper state as triplet state 3A_2 .

EXPERIMENTAL

Spectrograde quality CS₂ was obtained from Fisher Scientific Company and used without further purification. Samples were sealed in Pyrex tubes after having been degassed on a vacuum line. Optically useful crystalline samples were obtained by lowering these tubes very slowly into a precooled Dewar before adding liquid helium. Due to expansion of the CS₂ crystal at lower temperatures⁵ liquid helium had to

be added very slowly, otherwise the crystal tube shattered. The samples used were about 1 mm thick and displayed strong scattering.

The absorption spectra were photographed on a 3-m concave grating spectrograph (Baird Atomic 6 X-1) having a linear dispersion of 5.1 Å/mm in first order.

The Zeeman spectra were obtained with a split-coil

TABLE I. Absorption of solid CS₂ at 4.2°K; $T_1 \leftarrow S_0$.

I	Å	ν (cm ⁻¹) ^a	Interpretation
		(24 739) ^b	0-0 (B_2)
W	3796.8	26 331	$5\nu_2$ +lattice transitions (B_2)
W	3760.6	26 584	$6\nu_2$ (B_2)
M	3753.3	26 636	$6\nu_2$ +lattice transitions (B_2)
VW	3746.7	26 683	...
M	3718.2	26 887	$7\nu_2$ (B_2)
S	3711.1	26 939	$7\nu_2$ +lattice transitions (B_2)
W	3701.9	27 005	$\nu_1+5\nu_2$ +lattice transitions (B_2)
VVW	3681.7	27 154	$8\nu_2$ (A_1 , B_1)
S	3676.8	27 190	$8\nu_2$ (B_2)
W	3673.4	27 215	$8\nu_2$ +lattice transitions (B_2)
VS	3670.1	27 240	$8\nu_2$ +lattice transitions (B_2)
W	3666.7	27 265	$\nu_1+6\nu_2$ (B_2)
M	3660.8	27 309	$\nu_1+6\nu_2$ +lattice transitions (B_2)
VS	3636.4	27 492	$9\nu_2$ (B_2)
VS	3630.2	27 539	$9\nu_2$ +lattice transitions (B_2)
M	3626.9	27 564	$\nu_1+7\nu_2$ (B_2)
S	3621.4	27 606	$\nu_1+7\nu_2$ +lattice transitions (B_2)

^a Vacuum wavenumbers.^b Obtained from extrapolation.

superconducting magnet (R.C.A.) capable of maintaining fields up to 58 kG in a metal double Dewar with quartz windows. These spectra were photographed on a Jarrel-Ash Fastie Spectrograph, with a dispersion of 0.585 Å/mm at 3670 Å in the 15th order. Kodak 103 AO plates were used to photograph all spectra. In order to obtain sufficient plate blackening with a 1000-W xenon lamp as light source, exposures

FIG. 1. Microdensitometer tracings of photographic plates: (A) the singlet-triplet absorption of the CS_2 crystal at 4.2°K ; (B) the $3670\text{-}\text{\AA}$ band system at high resolution in zero field; (C) the same band system in a 55 kG magnetic field.

up to two hours were needed because of the opacity of the polycrystalline samples.

ABSORPTION SPECTRA

The $T_1 \leftarrow S_0$ absorption spectrum of crystalline CS_2 at 4.2°K is shown in Fig. 1. The crystal spectrum consists mainly of a progression in the upper state bending mode ν_2' ($\sim 305\text{ cm}^{-1}$) and of combination bands of the form $\nu_0 + n\nu_2' + \text{lattice}$ and $\nu_0 + \nu_1' + n\nu_2' + \text{lattice}$. All the absorption lines are rather broad ($\sim 10\text{ cm}^{-1}$) and all the bands emerge from a continuous background which is due to the involvement of the lattice in the electronic excitation, perhaps

complicated by the presence of another electronic state. A significant involvement of the lattice in this transition is not too surprising since it is known that the CS_2 molecule undergoes a significant change in geometry on excitation.¹ Towards wavelengths shorter than $\sim 3600\text{ \AA}$ the spectrum becomes even more diffuse; in solid state spectra such a symptom is often indicative of interference with another electronic state.

A vibrational analysis of the spectrum is given in Table I. The assignments were made by comparing our measured intervals with upper state frequencies obtained from Klemans work.¹ Due to the apparent Franck-Condon forbiddenness of the transition we

TABLE II. Vibrational data^a (in cm⁻¹) for the ³A₂←¹Σ_g⁺ transition of CS₂.

	0, 0	ν ₁	ν ₂	ν ₃
Infrared and Raman (¹ Σ _g ⁺)	...	658.0	395.9	1535.4
Gas phase	26 187±2	691.5±1	310.8±0.5	940±50
Solid state	(24 739±10) ^b	677±4	309±3	...

^a This work and Ref. 1.^b From extrapolation, and assuming that the vibrational numbering is correct.

have not been able to locate the origin, ν₀, of the system. If the Franck-Condon envelope in the solid is the same as that in the gas phase we can extrapolate back to the origin, ν₀=24 739 cm⁻¹. To perform the extrapolation properly the anharmonicity of ν₂' in the solid has to be known. In the gas phase up to 10 quanta of ν₂' have been observed,¹ and we were able to fit the progression to the following relation: ν_{n0}=ν₀+(n+½)ν₂'-b(n+½)²; b=0.138 cm⁻¹ and ν₂'=310.0 cm⁻¹, where the magnitude of ν₂' agrees very well with the one obtained by Kleman from a study of isotopic species (310.8±0.5 cm⁻¹). When it is assumed that the same type of relation holds in the CS₂ crystal, we obtain b=0.043 and ν₂'=309.4 cm⁻¹. The inherent inaccuracy of our spectral measurements (~1 cm⁻¹) is actually larger than b but that b is smaller than in the gas phase is certain, indicating that this molecular vibration is more harmonic in the crystal. Intermolecular repulsive type interactions would produce such an effect. The gas-to-crystal red shift thus deduced is ~1500 cm⁻¹. The Franck-Condon maximum in the gas phase was found from microdensitometer tracings of plates taken of gas phase spectra. The ν₂' progression was identified by comparing the measured positions with those known from Kleman's work.¹ The agreement in line positions was good (±2 cm⁻¹) and the Franck-Condon maximum was found to be at ~9 ν₂'. We have assumed that the line at 27 492 cm⁻¹ is the corresponding Franck-Condon maximum in the solid. The analysis thus obtained, and comparisons with gas phase results are presented in Table II.

CS₂ does not fluoresce or phosphoresce in the solid so we have not been able to confirm the position of the origin from luminescence data. A dilute solution of CS₂ in argon at 4.2°K does display a weak luminescence but it is too broad to contribute usefully to the analysis.

ZEEMAN SPECTRA

We have studied the bands at 3711 and 3670 Å in magnetic fields up to 58 kG and have found no measurable broadening (Δw<1 cm⁻¹) or energy shift of the strong lines. The state is either a singlet or a triplet with its components separated by at least (gβH)²/Δw≈36 cm⁻¹ at 60 kG. If these strong lines

are built on a B₂ spin sublevel, and if the ZFS parameter were ~40 cm⁻¹, as proposed by Hougen,⁴ the second-order Zeeman energy shift of these lines would amount to less than 1 cm⁻¹. A careful study of the 3670-Å band system revealed⁶ the presence of a weak line at 36±1 cm⁻¹ to the low-frequency side of the first strong line. *This line was caused to be undetectable by applying a magnetic field of 55 kG.* The results of this experiment are also shown in Fig. 1. We have concluded that the weak magnetically sensitive line is the crystal field induced transition to the otherwise forbidden (A₁, B₁) pair of spin sublevels of triplet state ³A₂ for the vibronic addition (080), and that the separation between this weak line and the first strong line is the ZFS of CS₂ in this state. Since the broad weak absorption is barely detectable in the absence of the field, the fact that it disappears in the field most likely means that a magnetic field splitting has occurred. It would follow that the A₁ and B₁ spin components are separated by much less than the linewidth at zero field. The crystal field induced line contrast is very much dependent on the quality of the sample. In a sample that scatters too much light, this line is obscured by a steep rising background. The intensity of the magnetically sensitive absorption is about 5%-10% of the main bands.

CRYSTAL EFFECTS

The CS₂ molecule undergoes a large change in geometry on excitation so the exciton states should be treated in the weak coupling limit. No factor group splitting was observed in any vibronic band so it is reasonable to assume that the exciton bandwidth is much less than the ZFS, which means that the spins are best considered as quantized in the molecular rather than the crystal frame.

The crystal field induced intensity in the (A₁, B₁) pair of spin sublevels can be treated as if a triplet excited CS₂ molecule was imbedded in a CS₂ heavy atom solvent. One of the contributions to crystal field induced activity in guest spin sublevels comes from the coupling of a host triplet exciton band with the guest triplet state via the intermolecular potential.⁷ The important selection rule on the intermolecular coupling is concerned with the alignment of the fine-structure axes of nearby molecules. The geometry in

FIG. 2. Correlation diagram, including the effect of spin-orbit coupling, for states deriving from the ${}^3\Delta_u$ state of CS_2 .

solid CS_2 is such that only the interchange equivalent type of interactions can contribute to the intensification of the otherwise inactive spin substates. The active molecular spin substate is T_y in the B_2 component so either the A_1 or B_1 components will become crystal field induced depending upon whether the molecule bends in or out of the bc crystal plane. This is readily deduced from the known⁵ molecular orientations in the crystal.

The intermolecular coupling should vary with the Franck-Condon factor for a particular vibronic transition, so that the crystal field induced lines should be most intense at the maximum of the Franck-Condon envelope. A coupling of $\approx 0.5 \text{ cm}^{-1}$ is needed to provide the observed crystal field induced intensity.⁸

ZERO FIELD SPLITTING

Mulliken⁹ discussed the relative ordering of the states derived from the $\pi_g^3\pi_u$ configuration in molecules like CO_2 and CS_2 and concluded that some of the lowest excited states in these molecules would likely derive from the ${}^3\Delta_u$ state in the linear molecule. Figure 2 gives the correlation diagram that relates the ${}^3\Delta_u$ state of the linear configuration with states of the bent molecule including the effect of spin-orbit coupling. We have calculated the spin-orbit splitting in a ${}^3\Delta_u$ state, assuming that in the π_g MO only the $3p_{x,y}$ orbitals of sulfur are important, and that in the π_u^* MO the electron is localized in the $2p_{x,y}$ orbitals of carbon. Using Garstang's¹⁰ value for the atomic sulfur spin-orbit coupling constant, we compute the total spin-orbit splitting in the ${}^3\Delta_u$ state to be 352 cm^{-1} . A similar calculation performed for the ${}^2\Pi_g$ state of the CS_2^+ ion yields 384 cm^{-1} , and the experimental value is known¹¹ to be 440 cm^{-1} .

Some qualitative insight as to how the inactive (A_1, B_1) pair of spin sublevels of triplet state 3A_2 might separate from the B_2 component can be ob-

tained by considering (for the bent case) the shifts of the 16 states that derive from $\pi_g^3\pi_u$ configuration under the influence of spin-orbit coupling.

The (A_1, B_1) spin substates of triplet state 3A_2 are lowered through interaction with the nearby (A_1, B_1) spin substates of triplet state 3B_2 . This latter possibility has already been recognized by Douglas and Milton. The B_2 spin substate of triplet state 3A_2 spin orbit interacts with a distant singlet state 1B_2 , from which it steals intensity, but this interaction will hardly be expected to shift the zero-order position of the B_2 spin substate. That the (A_1, B_1) spin sublevels do not carry oscillator strength in the free molecule is not surprising, because there are no symmetry appropriate singlets obtainable from the low-energy configurations.

The value of the ZFS parameter for a particular vibronic state of 3A_2 depends critically on the zero-order positions of the vibronic components of the 3B_2 and 3A_2 vibronic states. A ZFS of 36 cm^{-1} can hardly be obtained if in zero order the interacting components are separated by more than a few hundred wavenumbers. Thus in the bent case, the 3A_2 and 3B_2 states must still be quite nearby, and the large ZFS parameter is perhaps best understood as being due to a pseudo-first-order spin-orbit coupling process.

The ZFS parameter also should change with vibrational quantum number depending upon the zero-order positions and analytic form of the potential energy surfaces for the 3A_2 and 3B_2 states. The fact that Douglas and Milton³ found markedly different Zeeman line broadenings for different vibronic lines is consistent with this.

We suggest therefore that the vibronic levels of the triplet states 3A_2 and 3B_2 overlap. 3B_2 cannot show up directly in the absorption spectrum, because it cannot spin-orbit mix with any dipole-allowed singlet, nor can it vibronically mix through the b_2 mode (ν_3) with any triplet state within the group deriving from the $\pi_g^3\pi_u$ configuration.

Recently, a gas phase study of the first excited state of CSe_2 has been published¹² and since the assignment of this state is again uncertain, a similar study as reported here for CS_2 would be very valuable indeed.

* This research was supported in part by a U.S. Department of Health Grant GM-12592-06 and in part by a grant from the Army Research Office—Durham. DA-31-124-ARO(D)-G1115.

¹ B. Klemm, Can. J. Phys. **41**, 2034 (1963).

² P. Kusch and F. W. Loomis, Phys. Rev. **55**, 850 (1939).

³ A. E. Douglas and E. R. V. Milton, J. Chem. Phys. **41**, 357 (1964).

⁴ J. T. Hougen, J. Chem. Phys. **41**, 363 (1964).

⁵ N. C. Baenziger and W. L. Duax, J. Chem. Phys. **48**, 2974 (1968).

⁶ We appreciate the fact that the reader has difficulty in observing the weak line at 36 cm^{-1} to the red of the first strong line in Trace B of Fig. 1. The original microdensitometer tracings, however, show this line very distinctly.

⁷ R. H. Clarke, R. M. Hochstrasser, and C. J. Marzzacco, *J. Chem. Phys.* **51**, 5015 (1959).

⁸ We had to consider an alternative assignment for the absorption bands, in which $n\nu_2'$ is replaced by $\nu_3' + (n-3)\nu_2'$, and $n\nu_2' + \text{lattice}$ is replaced by $n\nu_2'$. This viewpoint was considered unlikely since ν_2' upper states can involve different spin activity, yet no Zeeman splitting was observed; in addition, the vibrationally induced spectrum would emerge as stronger than the allowed portion, whereas in the gas phase there is no ν_3' origin. The appearance of strong lattice bands is not unusual. The peaks correspond to peaks in the density of states for lattice modes, and there is no irregularity associated with having the zero-phonon

lines weaker than the multiphonon bands. In the unlikely event that this alternative assignment were the correct one, the main conclusions of this paper in regard to the zero-field splitting would remain unaltered, except that the measurements would refer to the (160) band, and the values of ν_0 , ν_1' and ν_2' would be slightly altered.

⁹ R. S. Mulliken, *Can. J. Chem.* **36**, 10 (1958).

¹⁰ R. H. Garstang, *Monthly Notices Roy. Astron. Soc.* **111**, 115 (1951).

¹¹ S. Leach, *J. Chim. Phys.* **61**, 1493 (1964).

¹² G. W. King and K. Srikameswaran, *J. Mol. Spectry.* **31**, 269 (1969).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 54, NUMBER 10

15 MAY 1971

Internal Conversion in Benzene, Benzene-*d*₆, and Sulfur Dioxide

WM. HAYDEN SMITH

Princeton University Observatory, Princeton, New Jersey 08540

(Received 21 October 1970)

Lifetime studies of benzene and benzene-*d*₆ at pressures below 1 μ Hg, using an electron beam phase shift method, yield a lifetime of 73.5 ± 8.0 nsec for the measured levels of the ${}^1\tilde{B}_{2u}$ state of benzene and lifetimes varying from 89 ± 9 to 113 ± 11 nsec for essentially the same levels in benzene-*d*₆. From the measured absorption oscillator strength, the nonradiative processes depopulating the ${}^1\tilde{B}_{2u}$ state must proceed at a rate of $1.2 \pm 0.14 \times 10^7$ sec⁻¹. These results are compared with previous theory and experimental data. Radiative lifetime measurements for SO₂ have been extended from those given previously and have been reanalyzed with a model assuming spectral overlap of two different SO₂ upper states. This analysis is shown to be consistent with certain previous discussions of the emission spectrum and, in particular, with those of Douglas³ concerning the anomalous lengthening of the ${}^1\tilde{B}_1$ -state radiative lifetime.

INTRODUCTION

The emission spectra of benzene and sulfur dioxide have been the subject of numerous investigations.¹⁻³ The interpretation of these spectra has been and continues to be a real challenge to spectroscopy. In 1966, Callomon, Dunn, and Mills⁴ made a most impressive study of the benzene ${}^1\tilde{A}_{1g} \rightarrow {}^1\tilde{B}_{2u}$ absorption spectrum and succeeded in unraveling much of the detail of the assignments. The interpretation of the SO₂ spectrum is much more in doubt^{3,5,6} but it is clear that transitions from the ${}^3\tilde{B}_1$, ${}^1\tilde{B}_1$, and ${}^1\tilde{B}_2$ states occupy the region from ~ 2000 – ~ 4000 Å.

Benzene and SO₂ have as a common feature the appearance of a phosphorescent emission, differing in that the phosphorescent state can be reached by benzene from the ${}^1\tilde{B}_{2u}$ state without external perturbation whereas collisions are required by SO₂ for the intersystem crossing ${}^1\tilde{B}_1 \rightarrow {}^3\tilde{B}_1$ to occur. This has led Robinson⁷ to discuss these two molecules in terms of their ability to produce their own "environment" in the isolated state. The conclusion reached is that benzene is either a border-line case or tends to the large molecule limit, whereas SO₂ is a small molecule in that it must be externally perturbed, e.g., by a collision, within the upper state mean lifetime in order to efficiently undergo intersystem crossing.

Lifetime studies of these molecules to provide quan-

titative estimates for these nonradiative processes have not been successfully performed under the necessary experimental conditions so as to dispel various ambiguities among the previous results^{1,2,8-12} which varied by nearly an order of magnitude in the measured lifetime. In particular, the lifetime for the ${}^1\tilde{B}_{2u}$ state in benzene of 590 nsec found by Donovan and Duncan⁸ agrees well with that calculated from the absorption f value of 0.00147,^{1,2} while the lifetimes measured by Chen and Schlag,⁹ Breuer and Lee,¹⁰ and Ludwig,¹¹ Burton and Hunziker¹² and most recently Ware *et al.*¹³ are all on the order of 70 nsec. A preliminary report of our measurements¹⁴ showed agreement with Donovan and Duncan's result.⁸ The present discussion corrects that statement, however, since in the completed analysis we have determined that source conditions play a decisive role in what "lifetime" is measured. We found that secondary excitations become important at electron energies much above 50 eV, and then at pressures above 1 μ Hg. Thus we believe we can resolve the discrepancy noted above and provide accurate lifetimes for various vibronic levels of C₆H₆ and C₆D₆.

For SO₂, we have extended our previous measurements to determine how the SO₂ emission observed in an unmodulated electron beam source at low pressures compares with that found in an rf-modulated source where only species (states) with mean lives less