

MAGNETIC DEPOLARIZATION OF CS₂ VAPOR FLUORESCENCE *

J. W. MILLS **

Department of Chemistry, Drew University, Madison, New Jersey, USA

and

R. N. ZARE ***

Department of Chemistry, Columbia University, New York, New York, USA

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The CS₂ V system (2900–3300 Å) has been excited using a high-pressure xenon lamp in conjunction with a fast monochromator and the degree of polarization of the resulting fluorescence has been measured. From the depolarization of the fluorescence ($\lambda_{\text{ex}} = 3200$ Å) with applied magnetic field the product $\bar{g}\tau = 7.3 \pm 0.9 \times 10^{-9}$ sec has been determined from level-crossing studies. Using the radiative lifetime $\tau = 1.5 \times 10^{-5}$ sec, the average effective g value of the excited state is estimated to be $\bar{g} = 4.9 \pm 0.6 \times 10^{-4}$.

1. INTRODUCTION

Since the early work of Fortrat [1] it has been recognized that the perturbed lines of a molecular spectrum are much more strongly influenced by a magnetic field than are their neighboring normal lines in the same band. The reason for this is based on the fact that only magnetic sublevels with the same value of M can perturb each other [2]. If the Zeeman splitting of the perturbed state differs from that of the perturbing state, then the interaction causing the perturbation between the individual M components will be quite sensitive to an applied magnetic field. Measurement of this variation gives detailed information about the character of the perturbing states. Thus far, however, almost no data are available for this purpose. The most likely explanation for this lack is the smallness of the splitting combined with the multiplicity of magnetic sublevels, which together cause most Zeeman patterns of molecules to appear broadened

and incompletely resolved even when the highest dispersion spectrographs and the largest magnetic fields readily available are used.

A case in point is the absorption spectrum of carbon disulfide vapor in the region 2900–3900 Å, which has been analyzed and divided by Kleman [3] into two systems: (1) the weaker R system (3300–3900 Å) showing orderly, well-resolved rotational structure; and (2) the much stronger V system (2900–3300 Å) which Kleman describes as having a 'dense, complex and apparently irregular structure'. In the latter system Douglas [4] found the radiative lifetime to be anomalously long, $\tau = 1.5 \times 10^{-5}$ sec, and he cites the CS₂ V system as a classic case of massive perturbations in small polyatomics.

In 1939 Kusch and Loomis [5] studied the magnetic rotation spectrum (MRS) of CS₂ in the 2900–3900 Å region. They found intense MRS in the region 3355–3640 Å of the R system and a very much weaker MRS in the region 3125–3250 Å of the V system. MRS work on the V system has been continued by Palatnick [6] using a 3.4 m spectrograph and a magnetic field of 3650 G, but he could not establish a detailed correlation between the MRS and the absorption spectrum. These MRS studies clearly establish the existence of a magnetic moment in the R and V systems, but the magnitude of the magnetic moment could not be determined from this method.

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** Postdoctoral Research Associate, 1968–1969, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado, USA.

*** Alfred P. Sloan Fellow.

In 1958 Douglas [7] studied the Zeeman splitting of the CS₂ absorption spectrum using a 10 m spectrograph and magnetic fields varying from 15 000 to 40 000 G. Although he was unable to resolve any Zeeman components, Douglas observed a broadening of the 3600 Å band lines in the R system. The breadth was proportional to the product of the magnetic field strength and the rotational quantum number. This has been interpreted [8-10] as evidence for a magnetic moment which arises from rotational distortion. However, inspection of Douglas' plates shows no Zeeman effect for any of the lines of the V system [6].

We describe here the application of molecular level-crossing spectroscopy [11] to the CS₂ V system, whereby a field of less than 10 G causes magnetic depolarization of the molecular fluorescence. This demonstrates the increased sensitivity of this new technique as compared to high-resolution Zeeman studies of molecular spectra.

2. PHOTOSELECTION OF CS₂ VAPOR

Photoselection by excitation with a beam of polarized light is well-known for polyatomic molecules in condensed media [12], and for diatomic molecules in the gas phase [11, 13]. Detection of the latter through the degree of polarization of the fluorescence, first observed by Wood [13], is possible because the rotational motion of a free symmetric top is not random and partially preserves the preferred direction(s) of excitation. Such detection of gas phase photoselection should also be feasible in polyatomic molecules (at pressures sufficiently low so that the excited state lifetime is less than the collision time) although the degree of photoselection is expected to be reduced in general by the more complete directional averaging caused by 1) the rotational motion of an asymmetric top and by 2) the vibrational motions of the polyatomic that distort its conformation.

A schematic diagram of the experimental set-up is shown in fig. 1. Fluorescence is excited in CS₂ using a 600 W high-pressure xenon lamp (Hanovia 970C-1) in conjunction with a high intensity UV monochromator (Bausch and Lomb). The slits of the monochromator are adjusted between 55 and 110 Å FWHM corresponding to zero-intensity widths of 100 and 260 Å, respectively. The monochromator output, which is about 50% plane-polarized, is focused onto the fluorescence cell about 1125 cm away.

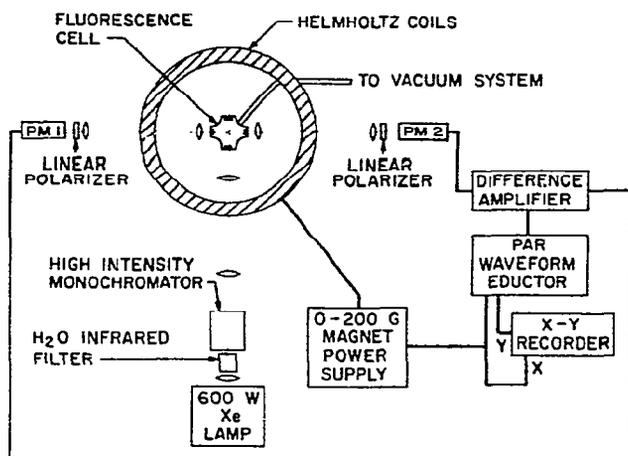


Fig. 1. Level-crossing apparatus. The magnetic field is perpendicular to the plane of the figure.

The fluorescence cell is a pyrex cross (4 cm ID) with Suprasil I windows mounted with torr-seal epoxy. Attached to the cell is a mercury- and grease-free vacuum system using sorption pumps, teflon stopcocks and viton O rings. Pressures are measured with a thermocouple gauge which has been calibrated for CS₂ against a McLeod gauge on a separate vacuum system. Liquid CS₂ was degassed by repeated freezing-pumping to a background pressure of 1 millitorr. No evidence was found of chemical attack by CS₂ on any of the vacuum system components.

The fluorescence spectrum [14] excited by light in the 2900-3300 Å region covers the range 3800-6500 Å with a broad maximum in the 4300-4800 Å region. No fluorescence below 3800 Å is observed. The total fluorescence intensity is greatest when the excitation is in the region 3100-3200 Å, decreasing by about 70% at 100 Å on either side.

Absolute polarizations are measured by inserting linear polarizers before the entrance and exit windows of the fluorescence cell. The incident polarizer is UV transmitting (Polacoat Corporation) while the analyzing polarizer is simply a Polaroid sheet. Only one of the pair of photomultipliers (RCA 1P28) is necessary for the polarization measurement. It is located 3 cm from the cell at right angles to the incident light beam. Care is taken to use only strain-free quartz and pyrex lenses. Appropriate filters reduce scattered light to less than 8% of the weakest fluorescence signal levels used in these polarization measurements. Observed degrees of polarization [13], $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ are

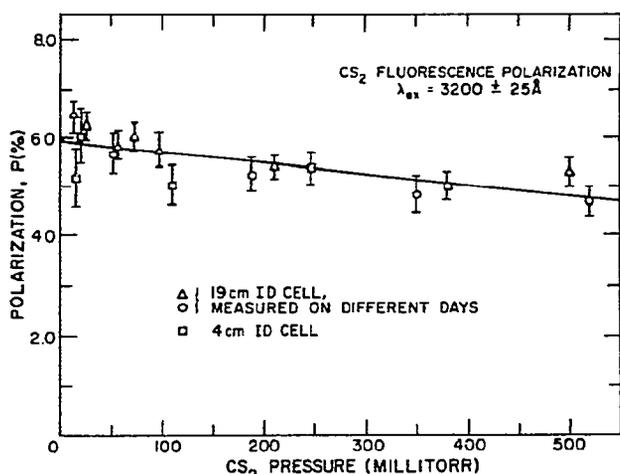


Fig. 2. CS₂ fluorescence polarization as a function of CS₂ pressure. Error bars are mean deviations of a set of approximately 20 measurements. The solid line is a weighted least squares fit to the data.

corrected for the polarization of the scattered light, cell windows, filters and response of the detector. As a further check that we have caused photoselection in CS₂ vapor, P was also measured for several CS₂ pressures with the incident beam polarized only 50%. The resulting reduction in the degree of polarization of the fluorescence was found to agree well within experimental error with that predicted by a classical Hertzian oscillator model for polarized fluorescence [11, 13].

Fig. 2 presents the degree of polarization of the CS₂ fluorescence excited by $\lambda_{ex} = 3200 \pm 25 \text{ \AA}$. Extrapolation to zero CS₂ pressure gives $P = 5.95 \pm 0.13\%$ where the error represents one standard deviation. The degree of polarization was remeasured with a second fluorescence cell to determine the importance of wall collisions as a depolarization mechanism. This cell was a 19 cm ID pyrex sphere with 4 cm OD quartz windows. Fig. 2 indicates that cell size had no effect on the observed degree of polarization. This result suggests that either the natural lifetime of the excited state is less than about $1 \times 10^{-5} \text{ sec}$ [15], or the wall collisions produce predominantly electronic relaxation. Previous work [14] supports the latter conclusion.

The degree of polarization is observed to vary nearly linearly from $P = 4.5\%$ at 3000 \AA to $P = 7.5\%$ at 3400 \AA , using an excitation bandwidth of 55 \AA and a CS₂ pressure of 250 millitorr.

3. MAGNETIC FIELD LEVEL CROSSINGS

In the absence of a magnetic field the photo-selection caused by irradiation with nonisotropic light causes the degenerate magnetic sublevels to be excited with certain phase relations (coherence) that result in the polarization of the re-radiated light. Application of a magnetic field with sufficient strength to split ('uncross') the magnetic sublevels by more than their natural linewidth destroys their coherence and causes the fluorescence to become depolarized (the so-called zero field level crossing or Hanle effect). For the right-angle geometry shown in fig. 1, the fluorescence intensity, I_{\perp} , has a Lorentzian dependence on the applied field H given by

$$I_{\perp} = a + \frac{b}{1 + (2g\beta_0\tau H/\hbar)^2}, \quad (1)$$

where a and b are constants, g is the Landé g factor, τ the radiative lifetime and β_0 the electronic Bohr magneton. From a measurement of the magnetic field halfwidth, $H_{1/2}$, the product $g\tau$ can be obtained from

$$g\tau = \hbar/2\beta_0 H_{1/2}. \quad (2)$$

Eqs. (1) and (2) assume that the magnetic moment of the excited state level does not depend on the strength of the applied field.

The experimental arrangement for the CS₂ level-crossing study is pictured in fig. 1. A dc magnetic field is produced by a pair of water-cooled Helmholtz coils 50 cm in diameter that are capable of producing a 300 G field which is homogeneous to better than 0.1% over a 200 cm³ volume located at its center. The field axis is perpendicular to the plane of fig. 1 and the incident light is plane-polarized with its electric vector perpendicular to the field direction.

The fluorescence is monitored by a pair of photomultipliers operated as an optical bridge [16]. One photomultiplier detects I_{\parallel} , the fluorescence polarized along the field direction (which is independent of the applied field); the other detects I_{\perp} , the fluorescence polarized perpendicular to the applied field (which is responsible for the level-crossing signal). The photomultiplier outputs are subtracted by a high-impedance difference amplifier. The photomultiplier sensitivities are matched by adjusting their photocathode voltages to produce a null difference in their output at zero field. Use of the optical bridge thus reduces the noise on the fluorescence signal from about 15% to less than 2% of the total signal. Even without filters, the

scattered light could be made less than 1% of the fluorescence signal.

The difference amplifier output is stored in the memory of a PAR waveform eductor as the field is repetitively swept in 10 sec periods. A voltage ramp formed by the eductor, inverted and appropriately biased, drives the magnet power supply (Nobatron DCR 150-10A). The dc

field is measured to within 0.5% with a Hall probe. The zero-field level-crossing signal from 36 scans is averaged and displayed on an X-Y recorder, the X axis of which is driven by the voltage ramp of the eductor.

Recorder traces of the level-crossing signal are shown in fig. 3a for selected pressures. The magnetic field halfwidths at half maximum, $H_{1/2}$, were determined by a least squares fit of each trace to a Lorentzian profile. Fig. 3b shows the pressure dependence of $H_{1/2}$. At zero CS_2 pressure, $H_{1/2} = 7.8 \pm 1.0$ G.

The use of broad-band excitation causes each trace to represent the weighted sum of different level-crossing signals from all the excited states that contribute to the fluorescence process. The rough fit of the traces to a Lorentzian shape encourages us to analyze the data using eqs. (1) and (2) even though for certain levels the magnetic moment may be somewhat field-dependent. From the measured value of $H_{1/2}$ we obtain $\bar{g}\tau = 7.3 \pm 0.9 \times 10^{-9}$ sec. If the value of $\tau = 1.5 \times 10^{-5}$ sec [4] is taken as the appropriate lifetime of the magnetically sensitive levels, the average effective molecular g value is estimated to be $\bar{g} = 4.9 \pm 0.6 \times 10^{-4}$. Such a small magnetic moment is consistent with the failure to detect Zeeman splittings in the CS_2 V system.

From the intensity of the level-crossing signal and the magnitude of the degree of polarization, it is concluded that only 25% of the molecular levels excited at 3200 Å undergo magnetic depolarization in a field corresponding to $6H$. An attempt was made to measure $H_{1/2}$ as a function of excitation wavelength. It could be qualitatively concluded that $H_{1/2}$ varies in an irregular manner. The feasibility of molecular level-crossing studies of polyatomic systems is clearly demonstrated by this work. However, the analysis of the CS_2 V system by this technique must await the development of sufficiently intense excitation sources so that the level crossings can be studied under high resolution.

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REFERENCES

- [1] R. Fortrat, Compt. Rend. Acad. Sci. (Paris) 156 (1913) 1459; Ann. Phys. (Paris) 3 (1915) 345; F. H. Crawford, Rev. Mod. Phys. 6 (1934) 90.

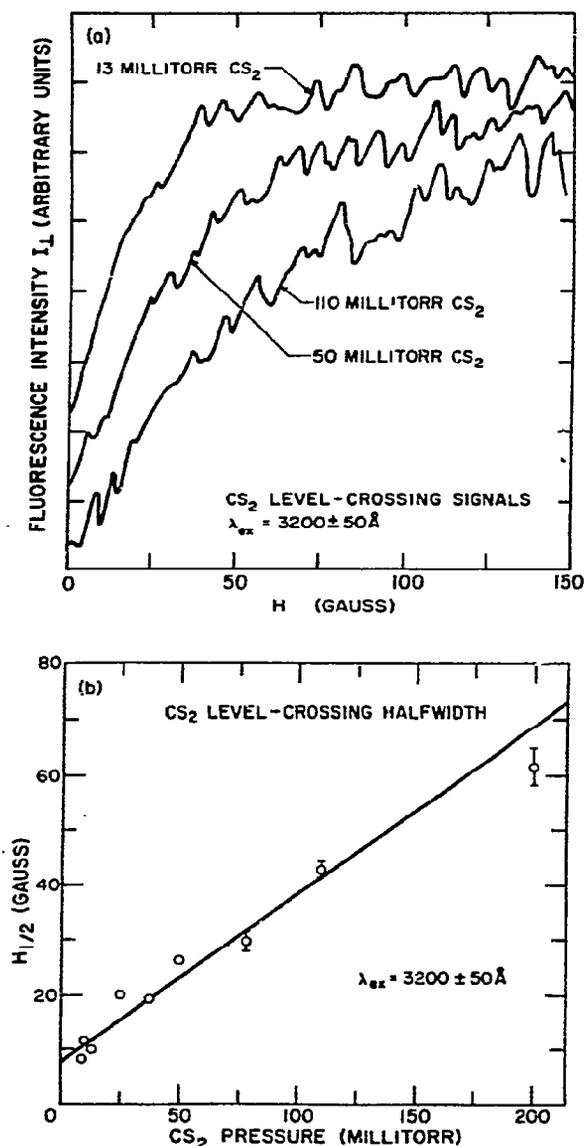


Fig. 3. CS_2 level-crossing signals; a) recorder traces for selected CS_2 pressures; b) plot of $H_{1/2}$ as a function of CS_2 pressure. In a) the recorder traces have been arbitrarily offset for clarity. In b) error bars are shown only where they exceed the diameter of the open circles.

- [2] R. De L. Kronig, Band spectra and molecular structure (Cambridge University Press, London, 1930) pp. 40-44.
- [3] B. Kleman, Can. J. Phys. 41 (1963) 2034.
- [4] A. E. Douglas, J. Chem. Phys. 45 (1966) 1007.
- [5] P. Kusch and F.W. Loomis, Phys. Rev. 55 (1939) 850.
- [6] B. Palatnick, Ph. D. Thesis, Columbia University (1968), unpublished.
- [7] A. E. Douglas, Can. J. Phys. 36 (1958) 147.
- [8] P. Kusch, J. Mol. Spectry. 11 (1963) 385.
- [9] A. E. Douglas and E. R. V. Milton, J. Chem. Phys. 41 (1964) 357.
- [10] J. T. Hougen, J. Chem. Phys. 41 (1964) 363.
- [11] R. N. Zare, J. Chem. Phys. 45 (1966) 4510.
- [12] A. C. Albrecht, J. Mol. Spectry. 6 (1961) 84.
- [13] P. P. Feofilov, The physical basis of polarized emission (Consultants Bur., New York, 1961); R. W. Wood, Physical optics, 3rd Ed. (Macmillan, New York, 1934).
- [14] J. Heicklen, J. Am. Chem. Soc. 85 (1963) 3562.
- [15] F. W. Byron, M. N. McDermott, R. Novick, B. W. Perry and E. B. Saloman, Phys. Rev. 134 (1964) A47.
- [16] K. R. German and R. N. Zare, Phys. Rev. 186 (1969) 9; Phys. Rev. Letters 23 (1969) 1207.