THE MAGNETIC MOMENT OF THE DIATOMIC SULFUR MOLECULE

By E. J. Shaw and T. E. Phipps
Department of Chemistry, University of Illinois

(Received May 20, 1931)

Abstract

The magnetic properties of the diatomic sulfur molecule have been investigated by means of the Stern-Gerlach molecular-ray method. The diatomic sulfur was prepared by heating sulfur vapor at a pressure of 0.3 mm of mercury to temperatures of 300–450°C. At the higher temperature, the magnetic fields attainable were insufficient to break down the coupling between the rotational axis of the molecule and the spin axis of the electrons and only broadening of the image resulted. At 300°C the image was split into two lines, one at the position of the line obtained in the absence of a magnetic field and the other on the side of the stronger field. The results prove that the diatomic sulfur molecule possesses a magnetic moment due to electron spin; the indicated configuration is a $^3\Sigma$.

Introduction

SINCE the original application of the molecular-ray method for the determination of magnetic moments by Stern and Gerlach in 1922,[1] all applications of this method have been to atoms. However, a study of the magnetic properties of the molecules of paramagnetic gases would seem to be of interest. No satisfactory means of detecting a beam of oxygen or nitric oxide has been developed as yet. The diatomic sulfur molecule may be readily investigated by this method, detection consisting merely of condensation on a liquid air cooled surface until an image of sufficient depth to photograph is obtained.

Theoretical

The spectrum of the diatomic sulfur molecule has been investigated by Rosen[2] and by Henri and Teves[3] and has been found to be quite similar to that of oxygen which is known to have a $^3\Sigma$ ground state. Rompe[4] has analyzed the spectrum and drawn the conclusion that the ground state of S_2 is a $^1\Sigma$. There is some doubt concerning this analysis, since as Rompe points out, Rosen's results show a Q branch in what Rompe's conclusions indicate is a $^1\Sigma - {}^1\Sigma$ transition. More recently Naudé and Christy[5] have published a preliminary note on the analysis of the S_2 spectrum using much higher dispersion than Rompe did, and have found that the ground state is a $^3\Sigma$.

A $^1\Sigma$ state for the S_2 molecule is not in accord with its chemical behavior;

[1] W. Gerlach, and O. Stern, Zeits. f. Physik **8**, 110 (1922) ibid. **9**, 349 (1922).
[2] B. Rosen, Zeits. f. Physik **43**, 69 (1927); ibid. **48**, 545 (1928).
[3] Henri and Teves, Comptes Rendus **179**, 1156 (1924); Nature **114**, 894 (1924).
[4] R. Rompe, Zeits. f. Physik **65**, 404 (1930).
[5] Naudé and Christy, Phys. Rev. **36**, 1800 (1930).

the strong tendency which it shows to polymerize indicates an unsaturation such as might be expected from "unclosed shells," to use Mulliken's terminology. Also, its close relationship to O_2 would lead one to expect it to have a $^3\Sigma$ ground state. Unfortunately its magnetic susceptibility has not been determined.

The Stern-Gerlach experiment provides a convenient means of determining whether or not a molecule has a magnetic moment. A beam of $^1\Sigma$ molecules would be expected to pass undeflected thru an inhomogeneous magnetic field just as a beam of ^1S atoms would. Any other type of molecule would

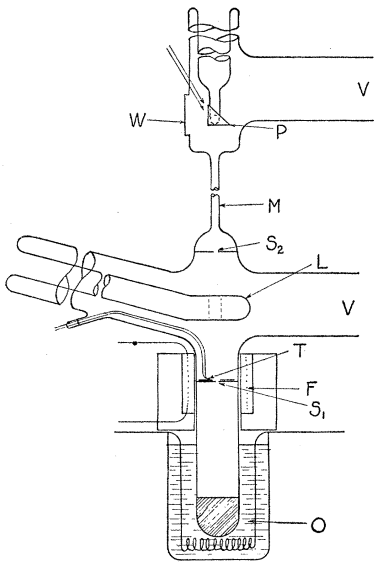


Fig. 1. Apparatus.

suffer deflection. A molecule with magnetic moment due to orbital electronic motion could not be expected to give a split image, since attainable magnetic fields would be far too low to uncouple the orbital axis from the molecular axis. In the case of Σ molecules, however, with a magnetic moment due to electron spin, it should be possible, at least in low rotational states, to uncouple the spin axis from the rotational axis of the molecule and obtain a split image. From this point of view, S_2 is not an ideal molecule to investigate, since sulfur vapor, even at the low pressure used in the Stern-Gerlach experiment, must be heated to about 300°C in order to give any considerable concentration of diatomic molecules; hence, low rotational states will not be favored. Splitting of the image is not necessary to show that a molecule is magnetic; broadening is sufficient to prove that.

The reader is referred to a preliminary note on this research for a further discussion of the theory.[6]

[6] E. J. Shaw, T. E. Phipps, and W. H. Rodebush, Phys. Rev. **35**, 1126 (1930).

EXPERIMENTAL

The apparatus is shown in Fig. 1. An electrically heated oil bath, O, stirred by means of a stream of air bubbles, maintains the sulfur at 155°C, at which temperature its vapor pressure is 0.3 mm.[7] The vapor passes up to the source slit, S_1, which is heated by means of an electric furnace, F, to a temperature of 300–450°C as measured by means of the platinum platinum-rhodium thermocouple, T. The thermocouple is welded to an annular sheet of platinum which serves to hold it in position and to make thermal contact with the glass. The thermocouple leads are brought out through separate small tubes sealed with deKhotinsky cement. The second slit, S_2, allows a beam of sulfur vapor to proceed through the tube, M, which passes between the pole-pieces of a large electromagnet, to the collecting surface on P, a liquid air cooled Pyrex prism. Between S_1 and S_2 is a liquid air cooled surface, L, which aids in removing the sulfur vapor which does not go through S_2 directly, and thereby prevents its undirected escape through S_2 and consequent fogging of the image. L also condenses any material which might volatilize from the deKhotinsky cement used to make the seals where the thermocouple leads leave the vacuum. The slits are 1.6 mm long and 0.03 mm wide, the distance between them being 70 mm. The distance from the second slit to the prism is about 85 mm. In front of the prism is an optical Pyrex window which makes possible the observation and photographing of the image at any time during the course of an experiment. The best visibility was obtained with light from the direction indicated by the parallel arrows.

The pole pieces used to produce the inhomogeneous magnetic field were the same as those used by Kurt and Phipps in their determination of the magnetic moment of the oxygen atom.[8]

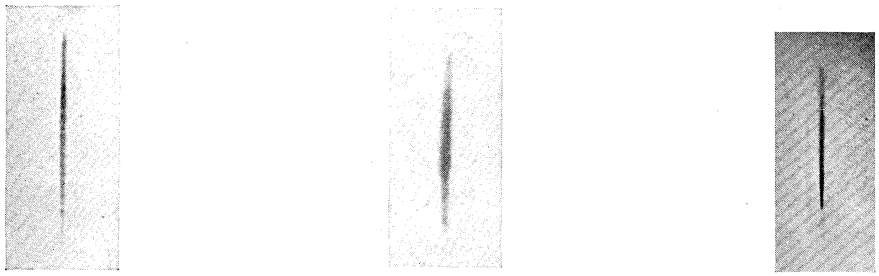
Experimental procedure.

The vacuum pumps were started and the oil bath brought up to temperature. After pumping three or four hours, the furnace was brought to the desired temperature, liquid air was put in L, the current started through the magnet winding, and the prism cooled by means of liquid air. After two or three hours the line on the prism was visible. In order to develop side lines however, it is usually necessary to continue the experiment about five times as long as is required for the undeviated line. The experiment was usually terminated at the end of 14 hours.

At first it was believed that it would be desirable to have practically complete dissociation into S_2, so a temperature of 450°C was used at the bottom slit. Repeated attempts showed, however, that although in every case a widening of the central image was obtained, it was impossible to obtain the side lines that one would expect from a $^3\Sigma$ molecule. The temperature of the source slit was therefore lowered to 300°C so as to decrease the average rotational quantum number of the S_2 molecules. The concentration of the heavier

[7] O. Ruff, and H. Graf, Ber. D. Chem. Ges. **40**, 4199 (1907).
[8] O. E. Kurt, and T. E. Phipps, Phys. Rev. **34**, 1357 (1929).

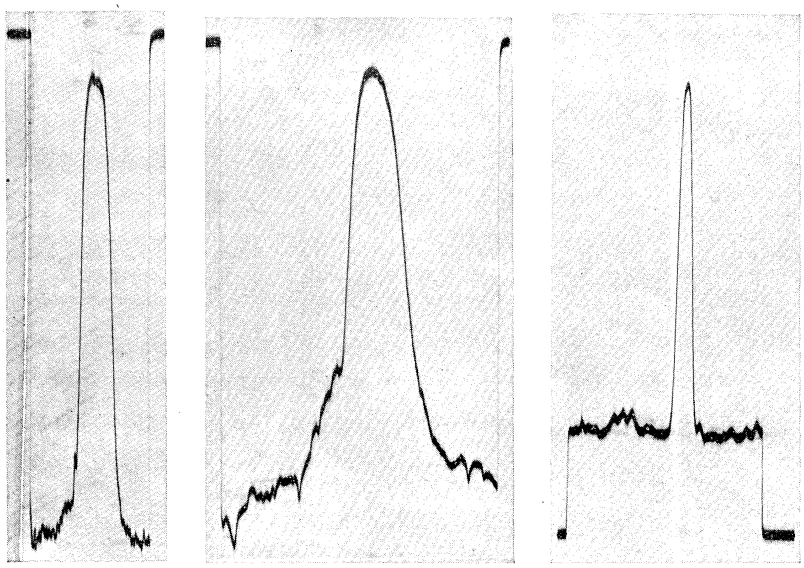
allotropic forms becomes rather high at this temperature, but this should serve only to make the undeviated line more pronounced. Under these conditions one side line was obtained and that on the side toward the higher field



a *b* *c*

Fig. 2. Images obtained. a, without field. b, field on, and source at 450°C. c, field on, and source at 300°C.

strength. This result indicates that the field strength at the normal position of the beam was just sufficient to uncouple the spin from the rotational axis in the case of the molecules in the lower rotational states. Those initially deflected in the direction of weaker field coupled again before passing through



a *b* *c*

Fig. 3. Microphotometer records of images obtained.

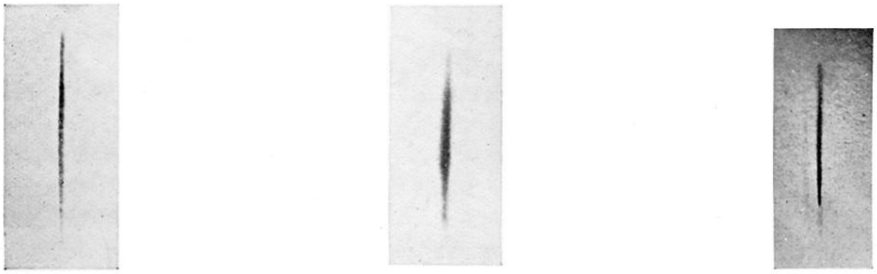
the region of the field, and hence gave no line on that side. In order to show that the side line was caused by S_2, an experiment was made with the source slit at 200°C. The image obtained was indistinguishable from that obtained with no magnetic field.

Fig. 2 shows 10× magnifications of three characteristic results of experiments. *a* is the result obtained when no magnetic field was applied. *b* is an image obtained with the magnetic field and a source temperature of 450°C. *c* shows the split image obtained with the source at 300°C. Fig. 3 *a*, *b*, and *c* show microphotometer records of the corresponding photographs of images shown in Fig. 2.

It would seem desirable to determine the actual magnetic moment by comparing the deflection obtained with that obtained with a hydrogen atom. As the result of the form of the apparatus this could not be done with assurance that the beam would pass through the same part of the magnetic field as the sulfur beam did. A comparison of the deflection obtained with that obtained with hydrogen in a different apparatus with the same pole pieces indicates that the magnetic moment of S_2 is approximately 2 Bohr magnetons. This is the magneton value to be expected from a $^3\Sigma$ state.

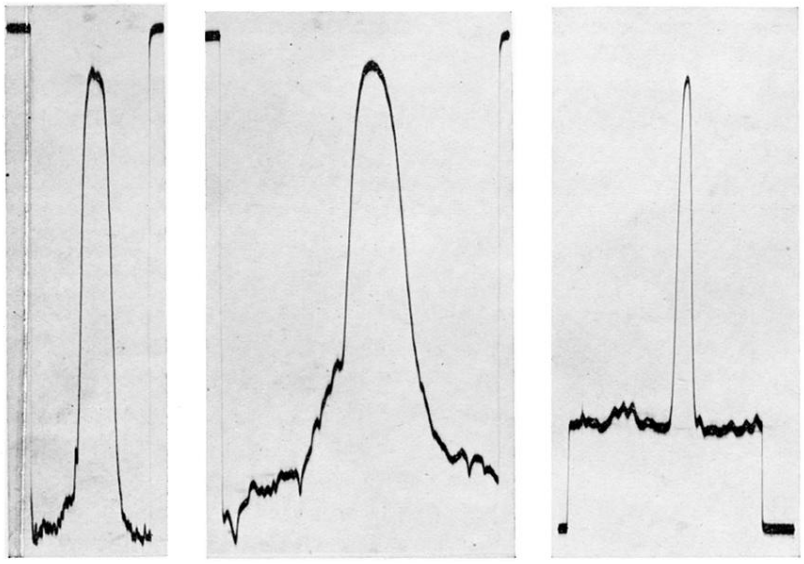
Conclusion

The Stern-Gerlach experiment has been used to demonstrate that the ground state of the diatomic sulfur molecule is magnetic. The observation of a split image shows that it must be a Σ molecule, and since even multiplicities are excluded, the indicated conclusion is that the molecule is a $^3\Sigma$. This conclusion agrees with what would be predicted from the close relationship of S_2 to O_2, and with chemical and spectroscopic observations.



a *b* *c*

Fig. 2. Images obtained. a, without field. b, field on, and source at 450°C. c, field on, and source at 300°C.



a *b* *c*

Fig. 3. Microphotometer records of images obtained.