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K-Band Electron Paramagnetic Resonance of Sulfur Monoxide in the Gaseous Phase

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Four K-band electron paramagnetic resonance transitions of ${}^3\Sigma^-$ ${}^{32}S^{16}O$ in the gas phase have been observed. One of these occurs between the Zeeman levels of the $K=1$, $J=0 \rightarrow K=0$, $J=1$ states and three between the Zeeman levels of the $K=2$, $J=2 \rightarrow K=3$, $J=2$ states. The analysis of the spectra has led to the g values of $g_s{}^e$, $g_l{}^e$, and g_r (in accordance with the notation by Tinkham and Strandberg). Knowledge of the rotational magnetic moment gave the equilibrium internuclear distance of $R_e=1.48101\pm0.00006$ Å.

Two electric dipole EPR transitions of ${}^3\Sigma^-$ ${}^{32}S^{16}O$ in the gas phase were first detected by McDonald.[1] Subsequently, another two transitions were observed by Daniels and Dorain[2] and another one by Carrington, Levy and Miller.[3] These five lines occur between levels characterized by $K=1$ and $J=1$ and by $K=2$ and $J=1$, and are observable by using a conventional X-band spectrometer. Several other transitions are expected to be detected at the K-band frequencies. In the present study, four K-band transitions of ${}^3\Sigma^-$ ${}^{32}S^{16}O$ were observed among the Zeeman levels of $K=1$, $J=0 \rightarrow K=0$, $J=1$ and $K=2$, $J=2 \rightarrow K=3$, $J=2$.

Recently, detailed analyses of the X-band spectrum were carried out by Daniels and Dorain[4] and by Carrington, Levy, and Miller[5] using the theory of the oxygen molecule presented by Tinkham and Strandberg.[6,7] Since the sign of the g value of the rotational magnetic moment, g_r, is different between their results, it would be desirable to analyze the K-band spectra independently of the X-band lines, in order thus to determine the sign of g_r. In this study, the g values of the electron spin, the orbital, and the rotational magnetic moments were determined by means of the K-band data. The rotational magnetic moment gave the equilibrium

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1) C. C. McDonald, *J. Chem. Phys.*, **39**, 2587 (1963).

2) J. M. Daniels and P. B. Dorain, *ibid.*, **40**, 1160 (1964).

3) A. Carrington, D. H. Levy and T. A. Miller, *Proc. Roy. Soc. (London)*, **A293**, 108 (1966).

4) J. M. Daniels and P. B. Dorain, *J. Chem. Phys.*, **45**, 26 (1966).

5) A. Carrington, D. H. Levy and T. A. Miller, *Proc. Roy. Soc. (London)*, **A298**, 340 (1967).

6) M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, **97**, 937 (1955). This is referred to as TS I.

7) M. Tinkham and M. W. P. Strandberg, *ibid.*, **97**, 951 (1955). This is referred to as TS II.

internuclear distance, R_e, by the use of the equilibrium *interatomic* distance, r_e, obtained by Amano, Hirota and Morino.[8)]

Experimental

A modified Japan Electron Optics Laboratory ESR spectrometer with a 100 kHz field modulation was used in conjunction with a 12-in electromagnet yielding a maximum field of 10000 G. The K-band experiments were performed with a cylindrical TE_{012}-mode detection cavity, the parallel endplates of which were replaced by some with 8 mm-i.d. holes and with collars to prevent any leakage of the cavity radiation. A cavity with a 7.5-mm-o.d. quartz flow tube inserted was adjusted to resonate at 24.9 GHz. The magnetic field was measured with a Hewlett-Packard 5245 L electronic counter by counting the proton magnetic resonance frequency of the water contained in a probe just outside the detection cavity. The field measurements were corrected for the small field differential that existed between the cavity center and the position of the magnetometer probe. The microwave frequencies were determined with reference to the transition frequencies of the atomic hydrogen observed simultaneously with those of SO. The required g factor was taken from the work of Beringer and Heald.[9)] A trace amount of hydrogen was added to the oxygen upstream of a microwave discharge cavity in order to generate the atomic hydrogen.

Sulfur monoxide was produced by mixing the product of a microwave discharge in the oxygen gas with carbonyl sulfide at a point just upstream from the detection cavity and was pumped through a quartz flow tube whose inner diameter was 6.5 mm into a K-band spectrometer detection cavity. The gaseous flow through the tube was maintained by means of a Tokuda 500-*l*/min mechanical pump. A waveguide-type discharge cavity was placed 20 cm upstream from the detection cavity and was powered by a Toshiba 2M89 magnetron operated at a frequency of 2450 MHz.

The observation of the SO lines in the K-band region was difficult compared with that in the X-band region. This difficulty was mainly caused by the restriction on the maximum flow rate because of the small size of the flow tube through the K-band cavity. Moreover, the adhesions of sulfur and sulfuric acid inside the flow tube decreased the spectrometer sensitivity and shifted the resonant frequencies, though the sulfur coating was slight at a low partial pressure of carbonyl sulfide. In this study, the partial pressure of carbonyl sulfide was about 3×10^{-2} mmHg, and that of oxygen was about 2×10^{-1} mmHg. Sulfuric acid was formed because of the grease used. By the use of Dow-Corning silicone grease, the sulfuric acid became scarcely discernible. The flow tube was washed with detergent before each measurement. This procedure was indispensable to avoid large noises caused by the free electrons introduced into the spectrometer cavity.

Description and Analysis of the Spectra

Four transitions, $K,J,M=1,0,0\rightarrow0,1,-1$, $2,2,1\rightarrow3,2,2$, $2,2,2\rightarrow3,2,1$, and $2,2,2\rightarrow3,2,2$, were observed in the K-band region. These transitions are shown in Fig. 1. The position of each line was determined as follows: immediately after a transition of SO was measured, a transition of the atomic hydrogen and again the same transition of SO were successively recorded. The frequencies thus determined are listed in Table 1. The experimental uncertainty in the magnetic field is the difference between the two measurements of the field value of a transition of SO plus the error for

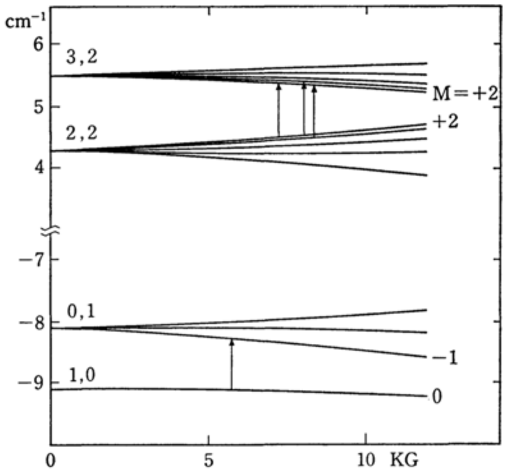

Fig. 1. An energy-level diagram of the magnetic-field splitting of the $K,J=1,0$; $0,1$; $2,2$ and $3,2$ levels of $^{32}S^{16}O$. The observed transitions are indicated.

TABLE 1. $^3\Sigma^-$ $^{32}S^{16}O$ SPECTRA IN THE K-BAND REGION

K,J,M	H(obs)	ν(obs)	ν(calcd)[a)]
$1,0,0\rightarrow0,1,-1$	5743.4 ± 0.4	24932.1 ± 0.3	24931.9
$2,2,2\rightarrow3,2,2$	7240.8 ± 0.2	24906.2 ± 0.3	24906.3
$2,2,2\rightarrow3,2,1$	8026.2 ± 0.2	24901.9 ± 0.3	24901.7
$2,2,1\rightarrow3,2,2$	8333.1 ± 0.2 G	24908.8 ± 0.3 MHz	24908.7 MHz

a) Frequencies were calculated by using $g_s{}^e=2.00199$, $g_l{}^e=0.00364$, and $g_r=0.00011$.

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8) T. Amano, E. Hirota and Y. Morino, *J. Phys. Soc. Japan,* **22**, 399 (1967).

9) R. Beringer and M. A. Heald, *Phys. Rev.,* **95,** 1474 (1954).

reading the position of a peak. The designated uncertainty in the microwave frequency is based on an estimated error in measuring the position of a peak of atomic hydrogen. Under optimum conditions the strongest band of the $1,0,0 \rightarrow 0,1,-1$ transition was observed at a 1-sec time constant with a signal-to-noise ratio of 100. The microwave frequency used was 24.9 GHz. The slight difference in microwave frequency for each measurement was due to the slight difference in the position of the quartz-flow tube inserted in the spectrometer cavity. The $2,2,1 \rightarrow 3,2,1$ and $2,2,1 \rightarrow 3,2,0$ transitions could not be detected.

The observed spectra were analysed according to the thory of molecular oxygen proposed by Tinkham and Strandberg.[6,7] Recently, Kayama and Baird[10] have shown that several modifications of the theory proposed by Tinkham *et al.* are indispensable. Therefore, we follow the formulation by Tinkham and Strandberg so as not to conflict with the theory of Kayama and Baird. The modifications given by Kayama and Baird will be discussed later. The effective Hamiltonian for $^3\Sigma^-$ molecules were derived[6,7] as:

$$\begin{aligned}\mathscr{H} &= P_R{}^2/2M + \frac{1}{2}M\omega_e{}^2R_e{}^2\xi^2 + b\xi^3 \\ &\quad + B\mathfrak{R}^2 + \frac{2}{3}\lambda(3S_z{}^2 - \boldsymbol{S}^2) + \mu\mathfrak{R}\cdot\boldsymbol{S} \\ &\quad + (g_s{}^e - g_r)\beta HS_z + g_l{}^e\beta H\sum_{g=x,y}\phi_{Zg}S_g \\ &\quad + g_r\beta HM, \qquad (1)\end{aligned}$$

where:

$$B = B_N - B'',\ \lambda = \lambda' + \lambda'' \text{ and } \mu = \mu' + \mu''.$$

Since the Hamiltonian (1) is integrated over the electron coordinates, the ξ dependence of the parameter λ as well as B must be taken into account:

$$B = B_e(1 - 2\xi + 3\xi^2),\quad \lambda = \lambda_e + \lambda_{(1)}\xi + \lambda_{(2)}\xi^2. \qquad (2)$$

No similar expansion for the parameter, μ, was found to be necessary for this experiment. The meanings of the various notations used above are the same as those given by Tinkham and Strandberg, except that the gyromagnetic ratios, $g_s{}^e$, $g_l{}^e$, and g_r, are opposite in sign.

The analysis was carried out by setting up a secular equation of $\mathscr{H}$ with respect to Hund's Case b wavefunctions. The matrix elements off-diagonal in the vibrational quantum number, v, were eliminated by the Van Vleck transformation. This procedure shows that large vibration-dependent terms can be taken out by defining the v-dependent constants, λ_v and B_v, as in the (3) equations:

$$\left.\begin{aligned}B_v &= B_e[1 + (2v + 1)(3\varepsilon + 12b\varepsilon^3B^{-1})], \\ \lambda_v &= \lambda_e - 6(2v + 1)b\varepsilon^3B^{-1}\lambda_{(1)},\end{aligned}\right\} \qquad (3)$$

although higher-order centrifugal distortion terms cannot be eliminated in this way.

The matrix elements in Hund's Case b representation have been given in Eqs. (52) and (60) of TS I and Eq. (24) in TS II. The elements with $\Delta K = \pm 2$ and $\Delta J = 0, \pm 1$, which are introduced by the term $g_l{}^e\ \beta H \sum_{g=x,y} \phi_{Zg}S_g$ and which are not listed in TS II, are given in the $(K', J', M|\mathscr{H}_{ml}|K, J, M)$ form as:

$$\left.\begin{aligned}&(J-1, J, M|\mathscr{H}_{ml}|J+1, J, M) = \\ &\qquad -g_l{}^e\beta HM/\{(2J+1)[J(J+1)]^{1/2}\} \\ &(J-2, J-1, M|\mathscr{H}_{ml}|J, J, M) = \\ &\qquad -g_l{}^e\beta H[(J^2-1)(J^2-M^2)]^{1/2}/ \\ &\qquad \{(2J-1)[J(2J+1)]^{1/2}\}, \\ &(J-1, J-1, M|\mathscr{H}_{ml}|J+1, J, M) = \\ &\qquad -g_l{}^e\beta H[(J^2-1)(J^2-M^2)]^{1/2}/ \\ &\qquad \{(2J+1)[J(2J-1)]^{1/2}\}\end{aligned}\right\} \qquad (4)$$

where:

$$\mathscr{H}_{ml} = g_l{}^e\beta H\sum_{g=x,y}\phi_{Zg}S_g. \qquad (5)$$

The required 19-dimensional matrix for a given value of M was diagonalyzed by using an IBM 7090 computer. The values of field-free parameters used in this study were: $B_{v=0} = 21523.6$, $\lambda_{v=0} = 158256$, $\mu_{v=0} = -168.5$, and $\lambda_{(1)} = 2.1 \times 10^5$, in units of megahertz. They were obtained by Amano, Hirota, and Morino[8] by analyzing the microwave spectra of $^{32}S^{16}O$.

The computation was made point by point for various values of the field H and of the g values, $g_s{}^e$, $g_l{}^e$, and g_r. The most probable g values obtained by fitting the K-band $^{32}S^{16}O$ resonances are given in Table 2. The quoted errors reflect the experimental uncertainties both in the magnetic field and in the microwave frequency. The experimental and calculated EPR results are shown in Table 1.

Discussion

It may be seen from Table 1 that the observed EPR transitions in the K-band region can be explained by the theory of Tinkham and Strandberg. Table 2 indicates that the g values, $g_s{}^e$, $g_l{}^e$, and g_r, obtained in the present study are almost in agreement with those given by Daniels and Dorain. The negative sign of g_r proposed by Carrington, Levy, and Miller[5] does not describe the observed K-band spectra.

All this while the theory of Tinkham and Strandberg was followed. As has been mentioned above, Kayama and Baird pointed out that the contribution of $^1\Sigma_g{}^+$ to the $^3\Sigma_g{}^-$ ground state of O_2 cannot be ignored. They re-examined the theory of Tinkham *et al.* by the use of the "true microscopic" spin-orbit interaction Hamiltonian and modified the results given in TS I and II. Their results

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[10] K. Kayama and J. C. Baird, *J. Chem. Phys.*, **46**, 2604 (1967).

TABLE 2. g VALUES OF SO

g Value	Present study	Daniels and Dorain[4]	Carrington, Levy and Miller[5,a]
g_s^e	2.00199 ± 0.00010	2.00197 ± 0.0001	2.0023
g_l^e	0.00364 ± 0.00020	0.00371 ± 0.0005	0.0040 ± 0.0003
g_r	0.00011 ± 0.00007	0.00019 ± 0.0002	-0.00020 ± 0.00020

a) g Values listed here are all opposite in sign to those of Carrington, Levy and Miller.[5]

revealed that, first, the value of λ'' should be given by the sum of λ''_Π and λ''_r, where λ''_Π is the contribution to λ'' from the $^3\Pi_g$ symmetry state and λ''_r from the $^{2S+}\Pi^1_g$ ($S=0, 2$) and $^{2S+1}\Sigma_g^+$ ($S=0, 1, 2$) states, and, second, as a result of the mixing of the $^1\Sigma_g^+$ state with the $^3\Sigma_g^-$ ground state, the λ_v, μ, and g_l^e parameters in Eqs. (1) and (3) should be interpreted as $\tilde{\lambda}_v$, $\tilde{\mu}$, and $\tilde{g}_l^e$, which depend on the state-mixing as expressed by:

$$\left.\begin{aligned} \tilde{\mu} &= \mu + 2\alpha\Big(B_v - \frac{1}{2}\mu\Big), \\ \tilde{\lambda}_v &= \lambda_v - \frac{2}{3}\alpha(2\lambda_v + \zeta_v) + \alpha\Big(B_v - \frac{3}{2}\mu\Big) \\ \tilde{g}_l^e &= g_l^e - \alpha g_s^e, \end{aligned}\right\} \qquad (6)$$

where 2α represents the $^1\Sigma_g^+$ character in the ground state and ζ, the contribution to λ'' from the $^1\Sigma_g^+$ state.

In the case of sulfur monoxide, there is no g or u symmetry, and the physical interpretation of the parameters introduced by Kayama and Baird must be different from that for the oxygen molecule. Nevertheless, the (6) equations seem valid phenomenologically and we shall not discuss this difference any further. In these circumstances, such physical interpretations of the λ and μ paramters as those given by Daniels and Dorain seem meaningless unless the correct estimates of ζ and μ' or α are made. It is more proper to express the molecular constants, μ' and μ'' in the following form, including α as a parameter:

$$\left.\begin{aligned} \mu' &= -0.0004 + 1.4\alpha \pm 0.0003 \\ \mu'' &= -0.0052 - 2.9\alpha \pm 0.0003\ \mathrm{cm}^{-1}. \end{aligned}\right\} \qquad (7)$$

Kayama and Baird[10] estimated the 2α value of oxygen to be $(3.0\text{—}4.0) \times 10^{-4}$. The 2α value for sulfur monoxide should be of the same order of magnitude as that for oxygen. Therefore, the second-order contrubution, $-2Bg_l^e$, constitutes the main part of μ. In fact, the fact that the value, $-2Bg_l^e = -0.0052 \pm 0.0003\ \mathrm{cm}^{-1}$, determined from the electron resonance is almost equal to the value of $\mu = -0.0056\ \mathrm{cm}^{-1}$ determined through microwave spectroscopy provides a welcome check on the consistency of the electron resonance and the microwave spectra, as was pointed out by Carrington, Levy, and Miller.[5]

The contribution of the electronic mass to the rotational constant is:

$$B'' = B(g_r - g_r^n) = 0.00027 \pm 0.00005\ \mathrm{cm}^{-1}. \qquad (8)$$

This leads to the value of $0.721087 \pm 0.000055\ \mathrm{cm}^{-1}$ of B_{Ne}, the rotational constant of the bare nuclei, when the B_e value of $0.720817 \pm 0.000005\ \mathrm{cm}^{-1}$ obtained by Amano, Hirota, and Morino is used. The B'' value of $0.00027\ \mathrm{cm}^{-1}$ is a correction of 370 ppm (parts per million). The usual procedure of using atomic rather than nuclear masses reduces this correction 270 ppm, leaving 100 ppm. The equilibrium internuclear distance, R_e, was estimated to be 1.48101 ± 0.00006 Å by using the nuclear masses and the latest values of the universal constants. The difference of 0.00007 Å between r_e and R_e is somewhat larger than the experimental errors. Carrignton, Levy, and Miller[5] concluded that the internuclear distance R_e coincided with the interatomic distance r_e within the limits of experimental error. The contradiction between the two experiments occurs mainly from the different signs of the values obtained for g_r. Most molecules will have $g_r > 0$ because the electronic contribution slightly outweighs that of the bare nuclei.[11] A sizable correction of the electronic contribution must be made for the rotational constant, B_e, in order to determine the internuclear distances to the full accuracy of the data. The correction of +370 ppm for B_e in the sulfur monoxide in the present study is of reasonable order of magnitude compared with the correction of +400 ppm in the oxygen molecule.[6]

The author wishes to express his gratitude to Professor Yonezo Morino for his encouragement throughout this work. His thanks are also due to Dr. K. Kayama for helpful suggestions on improving the experimental accuracy.

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11) M. Tinkham, "Group Theory and Quantum Mechanics," McGraw-Hill Book Company, Inc., New York (1964), p. 263.