BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1266—1267 (1972)

Multiple-Quantum Transitions in the EPR Spectra of Atomic Sulfur

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(Received November 20, 1971)

The multiple-quantum transitions of atoms[1,2] and diatomic molecules[3] in the gas-phase EPR spectra have been reported and have attracted the attention of several scientists both theoretically and experimentally. The two-quantum transitions[1] in the EPR of O($^3P_2$) in the gas phase were among the first multiple-quantum transitions to be observed. The three- and four-quantum transitions to be observed. The three- and four-quantum transitions of O($^3P_2$) and the two-quantum transitions of O($^3P_1$) were observed by McDonald.[4] The EPR multiple-quantum transitions of S atoms have not yet been reported, however, in spite of the observation of the single-quantum transitions of S atoms by Brown[5] in 1966.

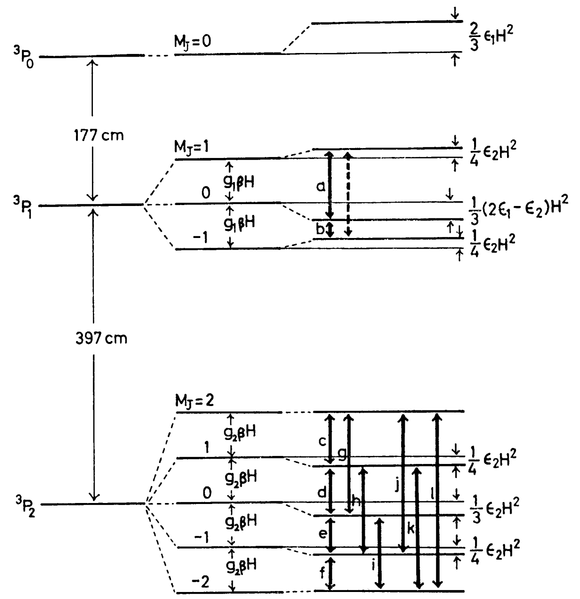

Fig. 1. Magnetic energy levels of the ground ^3P term in S atom (not to scale).
$\varepsilon_1=\beta^2/(177\ \text{hc})$, $\varepsilon_2=\beta^2/(397\ \text{hc})$ erg gauss^{-2}.

We have now observed the multiple-quantum transitions of S($^3P_2$) atoms. S atoms were produced in a 10-mm-i.d. quartz tube which passed through the center of a TE_{011}-mode EPR cavity resonant at 9168.64 MHz. A microwave discharge (2450 MHz, 100 W) was maintained in the flowing of wet H_2 40 cm upstream from the center of the cavity. Hydrogen sulfide was introduced at a point 5 cm upstream.

It is well known that the ground state of S atoms is the ^3P state and that it splits into three levels, $^3P_0$, $^3P_1$, and $^3P_2$, as a result of the spin-orbit interaction in the same manner as the O atom. The energy differences[6] are 177 cm^{-1} ($^3P_0$—$^3P_1$) and 397 cm^{-1}($^3P_1$—$^3P_2$). The energy level diagram is schematically shown in Fig. 1. In the middle the diagram represents the linear Zeeman effect, while the quadratic level displacements are shown on the right side. The observed spectrum of the single-quantum transitions of S atoms is shown in Fig. 2, together with the spectrum of O($^3P_2$) for comparison. The four lines of S($^3P_2$) and the two lines of S($^3P_1$) are labeled from *a* though *f*, corresponding to the transitions shown in Fig. 1. The total pressure was kept at 0.05 Torr in order to achieve a better resolution of the spectra. The information required for its analysis may be obtained from the work of Radford and Hughes[7] on the spectrum of O atoms. As is shown in Table 1, the measured quadratic field splittings are in fair agreement with the spin-orbit coupling predictions, in spite of the possible errors in the measurement of the fine-structure separations of Fig. 1. The magnetic field was measured relative to the line positions of the spectrum of O atoms. The observed *g* factors for the $^3P_1$ and $^3P_2$ states of the S atom were the same as those reported by Brown.[5]

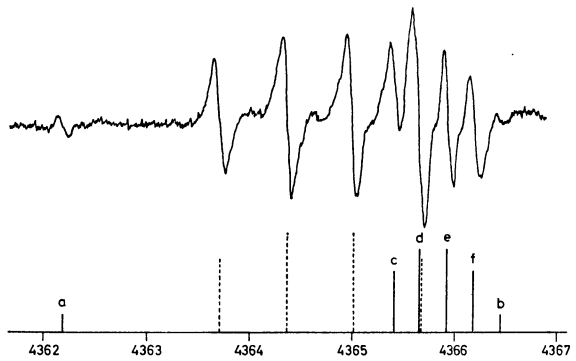

Fig. 2. EPR spectrum of S atom. O atom $J=2$ lines are shown for comparison.

We wish to report on an experiment demonstrating the multiple-quantum transitions among the Zeeman

TABLE 1. COMPARISON OF MEASURED QUADRATIC FIELD SPLITTINGS WITH LS COUPLING THEORY

	Observed (gauss)	Calculated (gauss)
H_b—H_a	4.262±0.01	4.225
H_f—H_c	0.782±0.005	0.766
H_e—H_d	0.262±0.005	0.256

1) V. W. Hughes and J. S. Geiger, *Phys. Rev.*, **99**, 1842 (1955).
2) G. J. Wolga, *ibid.*, **127**, 805 (1962).
3) A. Carrington, D. H. Levy, T. A. Miller, and J. S. Hyde, *J. Chem. Phys.*, **47**, 4859 (1967).
4) C. C. McDonald, *ibid.*, **39**, 3159 (1963).
5) R. L. Brown, *ibid.*, **44**, 2827 (1966).
6) W. L. Wiese, M. W. Smith, and B. M. Miles, "Atomic Transition Probabilities," NSRDS-Natl. Bur. Std. (U. S.) 22, Vol. II (1969), p. 133.
7) H. E. Radford and V. W. Hughes, *Phys. Rev.*, **114**, 1274 (1959).

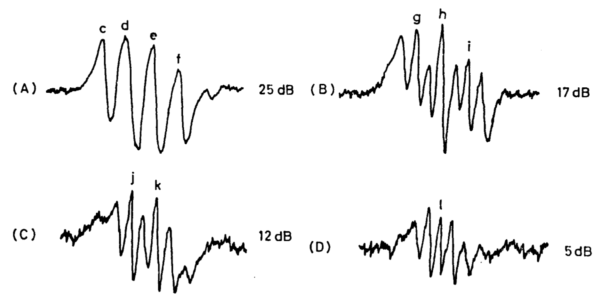

Fig. 3. EPR spectra of $S(^3P_2)$ showing the multiple-quantum transitions at increasing values of incident microwave power. Lines are labeled to correspond with Fig. 1.

levels of $S(^3P_2)$. At the pressure of 0.05 Torr, the spectrum was changed continuously as the microwave power was increased from a 25 to a 5 dB attenuation. The spectra showing the stages of these changes are presented in Fig. 3. At the 25-dB attenuation, only the single-quantum transitions (Fig. 3(A)) were detected. At this pressure, the linewidth of the single-quantum transition was 87 mG, corresponding to the relaxation time of 1.0 μsec. When the power was increased, the single-quantum transitions showed saturation broadening, and three new lines appeared between each two of the four lines of $S(^3P_2)$; the width of these new lines was approximately half the linewidth of the single-quantum transitions. The three new lines were assigned to the two-quantum transitions ($\Delta M_J=\pm 2$), which were more predominant in the spectrum at the 17-dB attenuation (Fig. 3(B)). A further increase in the microwave power produced two additional lines between the three lines of the two-quantum transitions, which could be interpreted as the three-quantum transitions ($\Delta M_J=\pm 3$). The single-quantum transitions vanished in the noise level, and the two-quantum transitions showed saturation broadening. At the 12-dB attenuation, the three-quantum transitions gave the strongest lines in the spectrum (Fig. 3(C)). Finally, between each two of the three-quantum transitions the four-quantum transition ($\Delta M_J=\pm 4$) could be detected at the 5-dB attenuation (Fig. 3(D)). Thus, by virtue of the different saturation properties of the various transitions, all the possible multiple-quantum transitions of $S(^3P_2)$ were observed. The two-quantum transitions of $S(^3P_1)$ were expected to be observable, but they could not be detected, probably because of the lower concentration of $S(^3P_1)$.

The theory of the multiple-quantum transitions in O atoms was developed by Hughes and Geiger,[1] it may be applied here to the case of S atoms. The linewidths of the multiple-quantum transitions were noticeably smaller than those of the single-quantum transitions, as would be expected from their theory. We estimated the minimum linewidths of the single-, two-, three-, and four-quantum transitions to be 87, 45, 35, and 33 mG respectively, though no completely-resolved lines were observed because of the rapid onset of pressure broadening. The three- and four-quantum transition lines may have been less sharpened experimentally than would theoretically be expected because of the 100 kHz modulation. It can also be expected from the theory that the intensities of the two- and three-quantum transitions are proportional to the square and cube of the microwave power respectively. This relation is confirmed by the experimental results shown in Fig. 4 (A) and (B).

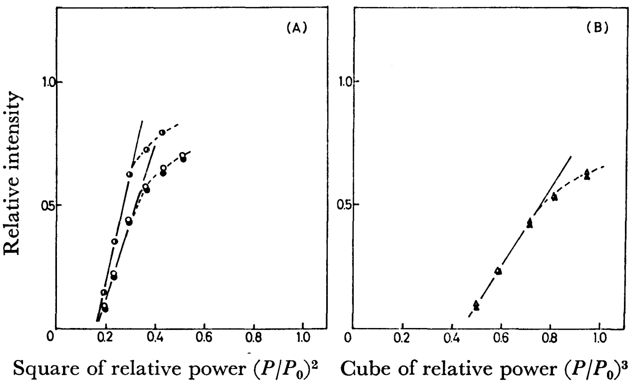

Fig. 4. The microwave power dependence of the intensities of the multiple-quantum transitions of $S(^3P_2)$.
(A) two-quantum transition.
○: $M_J=-2\rightarrow 0$, ◑: $M_J=-1\rightarrow 1$, ●: $M_J=0\rightarrow 2$.
(B) three-quantum transition.
△: $M_J=-2\rightarrow 1$, ▲: $M_J=-1\rightarrow 2$.