ISOTOPE SHIFT STUDIES OF THE B $^3\Sigma^-$ – X $^3\Sigma^-$ BANDS OF SO

BY K. V. S. R. APPARAO AND N. A. NARASIMHAM, F.A.Sc.

(Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay-74)

ABSTRACT

The $B^3\Sigma^- - X^3\Sigma^-$ bands of SO were excited in an electrodeless microwave (2450 Mc/s) discharge through trace amounts of sulphur enriched with 37% of ^{34}S and oxygen enriched with about 40% of ^{18}O. The emission spectra of $^{32}S^{16}O$, $^{34}S^{16}O$ and $^{32}S^{18}O$ were photographed on a Jarrell-Ash 3·4 m. grating spectrograph at a dispersion of 5 Å/mm. Isotope shift data, obtained from the present studies support the revision of the earlier vibrational scheme (Henri and Wolff, 1929; Martin, 1932) by increasing v''-quantum numbering by two units as suggested by Norrish and Oldershaw (1959).

INTRODUCTION

ONLY one electronic band system is known for the SO molecule. It consists of bands degraded to the red and they lie in the spectral region, 2400 – 4000 Å. The bands were reported in emission by Lowater (1906) and by Johnson and Cameron (1924). Henri and Wolff (1929) obtained them in a spark discharge through SO_2 and proposed vibrational analysis for the bands. Martin (1932) photographed the bands on a 21 ft. grating spectrograph and from an analysis of their rotational structure, showed that they involved a $^3\Sigma - ^3\Sigma$ transition. The corresponding absorption spectrum of SO was observed by Myerson, Taylor and Hanst (1957) and subsequently by Norrish and Oldershaw (1959). These absorption studies gave evidence for the lower state of the $^3\Sigma - ^3\Sigma$ system to be the ground state (X $^3\Sigma^-$) of the SO molecule. In their studies of SO obtained in flash photolysis of SO_2 or SO_3, Norrish and Oldershaw observed, in addition to previously known bands of SO, a number of new bands lying below 2500 Å which could be fitted into the vibrational scheme of the SO bands provided the v''-numbering proposed earlier was increased by two units. McGarvey and McGrath (1964) extended the system to shorter wavelengths, e.g., 1909·2 A (29-0) by observations in absorption following flash photolysis. Abadie and Herman (1964) while studying the microwave discharge

through SO_2 obtained several emission bands of SO above 4000 Å which could be well arranged into the vibrational scheme proposed by Norrish and Oldershaw. Though the revised vibrational numbering gave a satisfactory vibrational analysis of all the emission and absorption bands of SO, the (unlikely) possibility of the existence of even lower vibrational levels of the ground state was mentioned by Norrish and Oldershaw. It was therefore thought desirable to study the emission bands of SO using enriched ^{34}S and ^{18}O isotopes and obtain from them the much desired isotope shift data to provide an unambiguous vibrational assignment for the bands. The present work has indeed supported the revision of v''-quanta by two units. Results of these studies are presented in this communication.

EXPERIMENTAL

The emission spectrum of SO was excited by means of an electrodeless microwave discharge (2450 mc/s) through trace amounts of oxygen and sulphur vapour. The discharge tubes were of quartz, 1 cm. in diameter and 5 cm. in length. They were filled with 1–2 mm. Hg of ultrapure oxygen and about 1 mg. of vacuum distilled sulphur. The discharge tubes were prepared and sealed off under vacuum in a manner described by Tomkins and Fred (1957). In order to obtain the bands due to the isotope molecules, $^{34}S\ ^{16}O$ and $^{32}S\ ^{18}O$, sulphur enriched with 37% of ^{34}S and oxygen enriched with about 40% of ^{18}O were used in preparing the sealed discharge tubes. Moderately intense discharge could be maintained at 30–40 watts power of the microwave oscillator. However, the discharge tubes could emit the SO spectrum steadily for about 30 minutes only. Thereafter the tubes became hard and under higher oscillator power gave only spectra containing carbon and thus necessitated the preparation of fresh discharge tubes. The spectra of SO were photographed on a Jarrell-Ash 3·4 m. grating spectrograph at a dispersion of about 5 Å/mm. The band heads were measured from a number of plates on a Zeiss Abbe-comparator. The sharp heads were estimated to be accurate to about 0·05 Å.

RESULTS

The bands of SO photographed in the present studies extend from 2500 Å to 4600 Å and some of them are shown in Fig. 1. The spectra in (a) are from the discharge tube containing 37% of ^{34}S and hence contains the $^{32}S\ ^{16}O$ bands stronger than those of $^{34}S\ ^{16}O$; Similarly the spectra in (b) are from the discharge tube containing 40% of ^{18}O and therefore contains the $^{32}S\ ^{16}O$ bands stronger than those of $^{32}S\ ^{18}O$. The band heads

TABLE I

Isotope shifts of $B^3\Sigma^-$ — $X^3\Sigma^-$ *bands of SO*

Band		${}^{32}S\,{}^{16}O$		Isotope shifts of bands of ${}^{34}S\,{}^{16}O$ and ${}^{32}S\,{}^{18}O$			
	Rel. int.	λ_{air}	$\nu_{vac.}$	$\nu({}^{34}S\,{}^{16}O) - \nu({}^{32}S\,{}^{16}O)$ in cm.${}^{-1}$		$\nu({}^{32}S\,{}^{18}O) - \nu({}^{32}S\,{}^{16}O)$ in cm.${}^{-1}$	
$v'-v''$		Å	cm.${}^{-1}$	Obs.	Cal.	Obs.	Cal.
0– 3	1	2629·4	38019·6	33·6	35·0	..	..
0– 6	3	2877·8	34738·0	75·0	65·3	254·7	252·1
0– 7	4	2968·6	33676·7	73·6	75·0	390·4	289·3
0– 8	6	3064·1	32626·9	92·7	84·4	332·1	325·6
0– 9	8	3165·0	31586·1	95·9	93·5	359·0	360·9
0–10	10	3271·1	30562·3	99·9	102·4	391·0	395·4
0–11	10	3383·3	29548·8	108·9	111·1	417·9	429·0
0–12	6	3502·1	28345·8	120·1	119·5	467·8	461·6
0–13	4	3627·9	27555·9	135·7	127·7	483·9	493·4
1– 3	2	2588·8	38616·1	33·1	29·1	107·5	112·1
1– 4	4	2664·8	37515·8	45·3	39·4	153·0	152·0
1– 5	5	2743·9	36432·9	52·8	49·3	187·6	190·2
1– 6	6	2827·6	35355·7	61·5	59·4	226·5	229·1
1– 7	7	2914·9	24296·1	74·2	69·0	265·2	266·3
1– 8	6	3007·2	33243·8	79·9	78·4	299·1	302·6
1–11	1	3314·4	30163·1	104·9	105·1	405·2	406·0
1–12	3	3427·8	29164·9	118·4	113·5	446·1	438·6
1–13	5	3548·7	28171·0	121·5	121·7	477·8	470·4
1–14	6	3676·1	27194·9	133·5	129·5	505·0	500·5
1–15	4	3811·2	26230·9	137·9	137·4	..	531·1
1–16	2	3955·1	25276·7	146·1	144·8	564·3	560·2
1–17	2	4107·5	24338·9	153·7	152·1	591·4	588·3
1–18	1	4269·9	23412·9	153·9	159·0	..	615·4
1–19	1	4242·9	22501·1	167·1	165·8	..	641·8

Table I (Contd.)

Band	$^{32}S\,^{16}O$			Isotope shifts of bands of $^{34}S\,^{16}O$ and $^{32}S\,^{18}O$			
	Rel. int.	λ_{air}	$\nu_{vac.}$	$\nu(^{34}S\,^{16}O) - \nu(^{32}S\,^{16}O)$ in cm.$^{-1}$		$\nu(^{32}S\,^{18}O) - \nu(^{32}S\,^{16}O)$ in cm.^{1}	
$v'-v''$		Å	cm.$^{-1}$	Obs.	Cal.	Obs.	Cal.
2– 3	2	2548·4	39228·5	24·1	23·3	91·2	89·9
2– 4	3	2622·0	38126·9	35·6	33·7	128·2	129·8
2– 5	4	2698·9	27040·9	44·6	43·5	173·0	168·1
2– 6	3	2779·9	35961·9	52·8	53·6	201·8	206·9
2– 9	2	3046·1	32818·9	72·5	81·4	309·9	314·3
2–16	3	3861·8	25887·1	139·9	139·0	532·7	538·0
2–17	3	4006·8	24950·3	142·6	146·3	561·9	566·1
2–18	2	4162·9	24014·9	156·6	153·7	586·2	593·2
2–19	1	4326·9	23104·6	156·8	160·0	620·1	619·6
2–20	1	4506·8	22182·6	179·9	169·2	647·3	645·0
3– 3	1	2510·3	39824·7	19·2	17·8	70·3	68·6
3– 4	1	2581·0	38732·8	23·9	28·1	105·8	108·5
3– 5	1	2655·7	37643·9	36·5	38·0	155·9	146·7
3– 9	1	2991·8	33414·7	81·6	76·2	..	294·4
3–17	1	3912·5	25551·9	139·8	140·7	542·6	544·8
3–18	2	4060·4	24620·9	146·1	147·7	569·3	571·9
3–19	3	4216·8	23708·2	151·8	154·5	593·2	598·3
3–20	1	4384·8	22799·6	162·2	161·0	626·8	623·7
3–21	1	4563·2	21908·5	167·0	167·3	643·0	648·1

Average accuracy in the wave-number data of the band heads is no better than 1 cm.$^{-1}$.

due to the three isotopic molecules $^{32}S\,^{16}O$, $^{34}S\,^{16}O$ and $^{32}S\,^{18}O$ can be seen clearly from the juxtaposed spectra in Fig. 1.
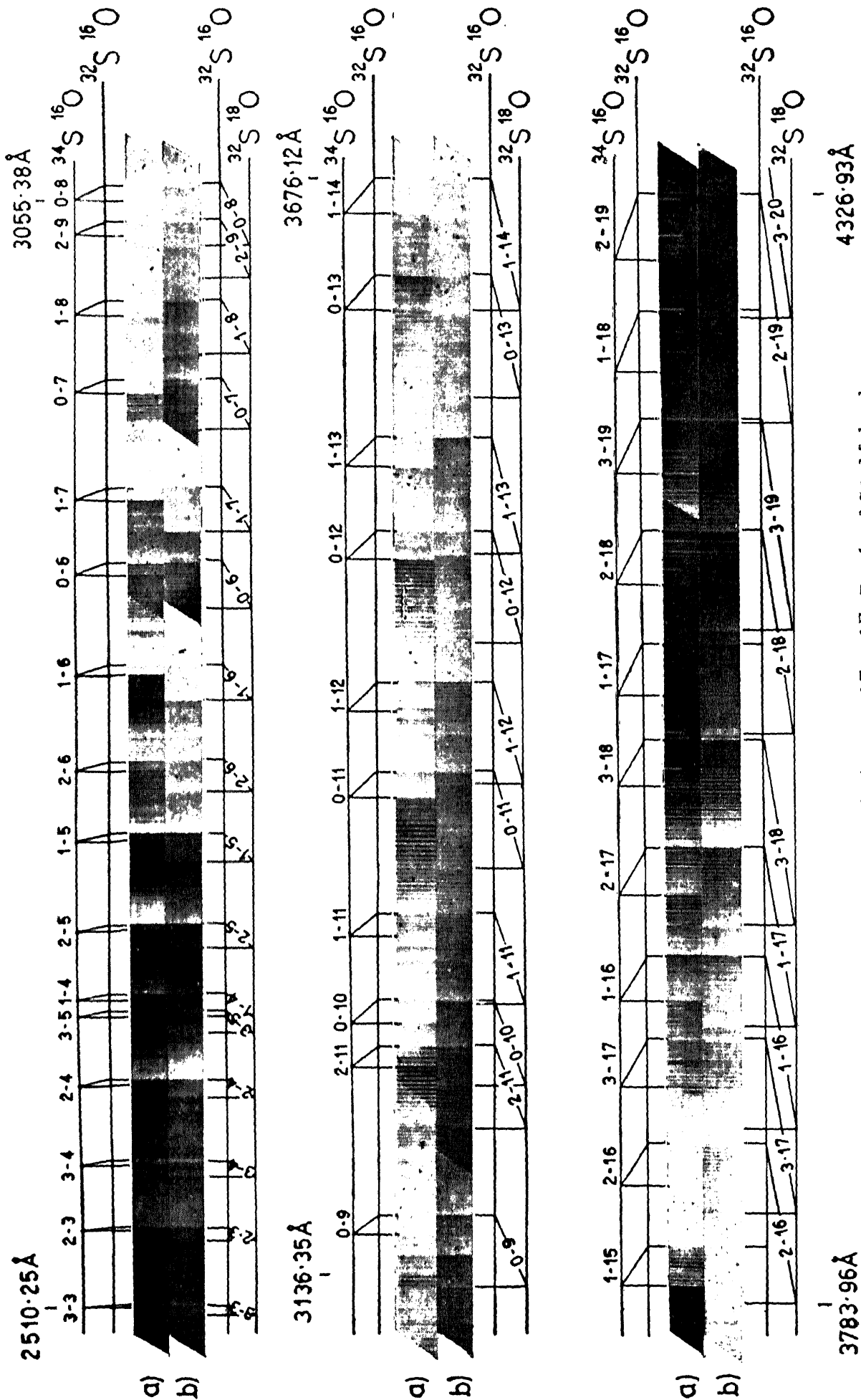
Fig. 1. Isotope Shifts in the $B^3\Sigma^- - X^3\Sigma^-$ Bands of SO Molecule.

The isotope shifts of the bands due to ^{34}S ^{16}O and ^{32}S ^{18}O with respect to ^{32}S ^{16}O are calculated from the relation

$$\nu - \nu^i = (1 - \rho)\{\omega_e'\,(v' + \tfrac{1}{2}) - \omega_e''\,(v'' + \tfrac{1}{2})\}$$

$$- (1 - \rho^2)\{\omega_e' x_e'\,(v' + \tfrac{1}{2})^2 - \omega_e'' x_e''\,(v'' + \tfrac{1}{2})^2\}$$

where $\rho = \sqrt{\mu/\mu^i}$; μ and μ^i are the reduced masses of ^{32}S ^{16}O and ^{34}S ^{16}O or ^{32}S ^{18}O.

If Martin's vibrational data for the upper and lower states are taken to calculate the isotope shifts, there is no agreement with the observed shifts of the band heads. However, if the upper state vibrational constants, *viz.*, $\omega_e' = 628 \cdot 7$ cm.$^{-1}$ and $\omega_e' x_e' = 5 \cdot 65$ cm.$^{-1}$ are retained and the lower state vibrational constants taken as $\omega_e'' = 1148 \cdot 16$ cm.$^{-1}$ and $\omega_e'' x_e'' = 6 \cdot 116$ cm.$^{-1}$ by increasing the older v''-numbering by two units, the isotope shifts for the band heads due to both the molecules ^{34}S ^{16}O and ^{32}S ^{18}O with respect to ^{32}S ^{16}O agree very well, as can be seen from Table I. These isotope shift data, therefore, support the revision of v''-quanta by two units as proposed by Norrish and Oldershaw.

There are a few minor differences between the observed and calculated isotope shifts and these are mainly due to the fact that the calculated shifts are for band origin data while the measured ones for band heads. This is particularly noticeable for bands with large Δv, such as 0–12, 0–13, 1–13, 3–20, 3–21 bands. In a few cases, the inaccuracy is in the measurement of a weak band head overlapped by another band structure.

REFERENCES

1.	Lowater, F.	.. *Astrophys. J.*, 1906, **23**, 324.
2.	Johnson, R. C. and Cameron, W. H. B.	.. *Proc. Roy. Soc.*, 1924, **106 A**, 195.
3.	Henri, V. and Wolff, F.	.. *J. Phys. Radium*, 1929, **10**, 81.
4.	Martin, E. V.	.. *Phys. Rev.*, 1932, **41**, 167.
5.	Myerson, A. L., Taylor, F. R. and Hanst, P. L.	*J. Chem. Phys.*, 1957, **26**, 1309.
6.	Norrish, R. G. W. and Oldershaw, G. A.	*Proc. Roy. Soc.*, 1959, **249**, 498.
7.	McGarvey, J. J. and McGrath, W. D.	*Ibid.*, 1964, **278**, 490.
8.	Abadie, D. and Herman, L.	*J. Quant. Spect. Radi. Trans.*, 1964, 4, 195.
9.	Tomkins, F. S. and Fred, M.	*J. Opt. Soc. Am.*, 1957, **47**, 1037.