ROTATIONAL ANALYSIS OF 2620 Å AND 2760 Å BANDS OF ^{32}S ^{34}S

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INTRODUCTION

IN an earlier paper 'On the fine structure of the ultra-violet bands of S_2' (Narasimham and Brody, 1964) six bands at 2620, 2660, 2760, 2793, 2813 and 2847 Å had been analysed for their rotational structure and assigned to a $^1\Delta_u - {}^1\Delta_g$ transition. From isotope shifts of the band heads of $^{32}S_2$ from those of ^{32}S ^{34}S, it was shown that the bands at 2620 Å and 2760 Å involve 5–1 and 2–2 vibrational transitions respectively. Rotational analysis of the corresponding bands of ^{32}S ^{34}S has now been made, which confirms the earlier vibrational assignment. The results of the rotational analysis are presented in this paper.

EXPERIMENTAL

The ultra-violet bands of S_2 were excited in sealed-off tubes containing traces of sulphur enriched to 44·4% of ^{34}S and 2–3 mm. of argon. The discharge tubes were prepared and the spectra excited by an electrodeless microwave discharge of 2450 mc./s. and photographed in a manner described in the earlier paper.

RESULTS

The vacuum wave-numbers of the P and R branch lines of the bands of ^{32}S ^{34}S are given in Table I. Part of the rotational structure of the bands at 2620 Å and 2760 Å are shown in (*a*) and (*b*) of Fig. 1. The top spectrograms marked (i), in each band, show the P and R branch lines of the bands of $^{32}S_2$. Those marked (ii) show the rotational structure of bands due to both $^{32}S_2$ and ^{32}S ^{34}S. At higher J values, rotational lines of $^{34}S_2$ could also be seen though very weak. As expected the bands of ^{32}S ^{34}S appear stronger in the emission spectrum obtained in a discharge through sulphur containing 44·4% of ^{34}S.

TABLE I

Vacuum wave-numbers (in cm.$^{-1}$) of the ultra-violet bands of ^{32}S ^{34}S

	5–1 band at $\nu_0 = 38141{\cdot}50$ cm.$^{-1}$		2–2 band at $\nu_0 = 36227{\cdot}85$ cm.$^{-1}$	
J	R	P	R	P
25	..	..	..	36 175·81
26	..	..	..	72·04
27	..	..	..	68·24
28	..	..	..	64·49
29	..	..	..	60·15
30	..	..	..	55·99
31	..	38 057·95	..	51·66
32	..	53·20	36 175·00	47·32
33	..	48·15	71·20	42·56
34	..	42·84	67·47	37·77
35	..	37·54	63·61	32·96
36	..	32·02	59·36	27·97
37	38 057·95	26·44	54·95	22·90
38	53·20	20·62	50·55	17·61
39	48·15	15·17	46·09	12·25
40	42·84	08·85	41·45	06·80
41	37·54	02·57	36·70	01·09
42	32·02	37 996·03	31·75	095·38
43	26·44	89·50	26·81	89·55
44	20·62	82·91	21·62	83·68
45	15·17	76·17	16·31	77·49
46	08·85	69·37	10·89	..
47	02·57	62·20	05·52	..
48	37 996·03	55·03	099·64	..
49	89·50	47·69	93·76	..
50	82·91	40·21	87·84	..

TABLE I (*Contd.*)

	5–1 band at $\nu_0 = 38141{\cdot}50$ cm.$^{-1}$		2–2 band at $\nu_0 = 36227{\cdot}85$ cm.$^{-1}$	
J	R	P	R	P
51	76·17	32·54	81·79	..
52	69·37	24·85	75·63	..
53	62·20	17·02	..	..
54	55·03	09·09	..	..
55	47·69	00·95	..	..
56	40·21	892·73	..	..
57	32·54	84·28	..	..
58	24·85	75·78	..	..
59	16·80	66·85	..	..
60	08·70	*	..	..
61	00·48	48·98	..	..
62	892·11	39·71	..	..
63	83·58	30·43	..	..
64	75·13	21·05	..	..
65	66·10	11·37	..	..
66	*	01·60	..	..
67	48·16	791·72	..	..
68	38·94	81·72	..	..
69	29·64	71·54	..	..
70	20·17	61·28	..	..
71	10·51	50·80	..	..
72	00·75	40·19	..	..
73	790·81	29·44	..	..
74	80·75	18·59	..	..
75	70·52	07·57	..	..
76	60·14	696·38	..	..
77	49·67	85·07	..	..
78	39·00	73·58	..	..
79	28·21	..	..	..
80	17·20	..	..	..
81	06·21	..	..	..
82	694·95	..	..	..
83	83·54	..	..	..
84	72·11	..	..	..

* Overlapped but not measured.

TABLE II

B values, in cm.$^{-1}$, of the 5–1 and 2–2 ultra-violet bands of ^{32}S ^{34}S

v'	B′	v''	B″
2	0·214	1	0·283
5	0·213	2	0·278

TABLE III

Band origins and isotope shifts (in cm.$^{-1}$) of the ultra-violet bands

$v' - v''$	$\nu_0{}^i$ ^{32}S ^{34}S	ν_0 $^{32}S_2$	$\nu_0 - \nu_0{}^i$	
			Observed	Calculated
5–1	38 141·50	38 158·77	+17·3	+17·7
2–2	36 227·85	36 218·35	− 9·5	− 9·8

The existence of single series of P and R branches of both odd and even J values for the bands of ^{32}S ^{34}S, just as for $^{32}S_2$, with no detectable Λ-doubling supports the assignment of the bands to a $^1\Delta_u - {}^1\Delta_g$ transition.

The rotational constants, $B_v{}^i$, are obtained from plots of $\Delta_2F/(J + \frac{1}{2})$ against $(J + \frac{1}{2})^2$ and given in Table II. For obtaining the isotope shifts, $\nu_0 - \nu_0{}^i$, the origins of the bands at 2620 Å and 2760 Å of ^{32}S ^{34}S are first determined from the relation

$$R(J-1) + P(J) = 2\nu_0 + 2(B' - B'')J^2$$

and later subtracted from the band origins, ν_0, of corresponding bands of $^{32}S_2$. These $\nu_0 - \nu_0{}^i$ values are given in Table III along with those calculated on the assumption that the bands at 2620 Å and 2760 Å arise out of 5–1 and 2–2 transitions. The agreement between the observed and calculated values supports the vibrational assignments for the bands made earlier.

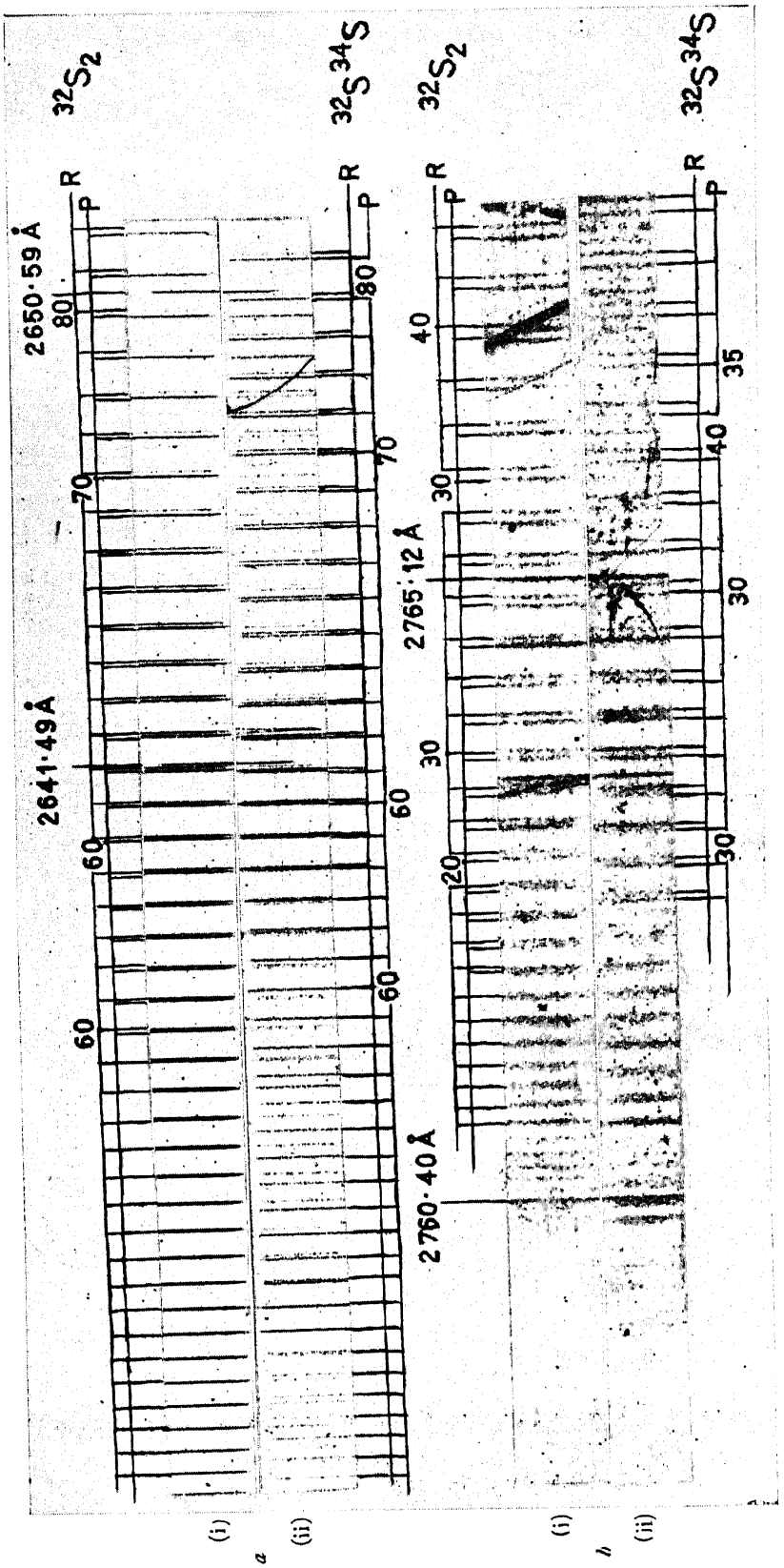

FIG. 1. Rotational structure of the ultra-violet bands of S_2 at (*a*) 2620 Å and (*b*) 2760 Å. Top spectrograms in both the bands marked (*i*) show the P and R branch lines of $^{32}S_2$ while those marked (*ii*) contain the rotational structure of $^{32}S_2$ and $^{32}S\,^{34}S$. The P and R lines of the $^{32}S\,^{34}S$ alone are marked in (*ii*).

SUMMARY

Rotational analysis of bands of $^{32}S\,^{34}S$ at 2620 Å and 2760 Å has been made, which confirms the earlier vibrational assignment of these bands. The band origins and isotope shifts of these bands are

$v' - v''$	ν_0'	Isotope shifts ($^{32}S_2 - {}^{32}S\,{}^{34}S$)	
		Observed	Calculated
5–1	38 141·50	+17·3	+17·7
2–2	36 227·85	− 9·5	− 9·8

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REFERENCE

Narasimham, N. A. and Brody, J. K. *Proc. Ind. Acad. Sci.*, 1964, **59 A**, 345.