

# ISOTOPE SHIFTS ( $C^{32}S - C^{34}S$ ) IN THE BANDS OF THE $A^1\Pi - X^1\Sigma^+$ SYSTEM OF $CS^*$

ONLY one emission band system in the ultra-violet is known for the  $CS$  molecule. Rotational analysis<sup>1</sup> of the bands showed that they arise from an initial  $^1\Pi$  to the final  $X^1\Sigma^+$ , ground state of the molecule. In the present investigation, vibrational isotope shifts of the bands are studied. Spectra of  $C^{32}S$  and  $C^{34}S$  are excited in an electrodeless, microwave (2450 mc./s.) oscillator discharge through sulphur, enriched to 44% of  $^{34}S$  and photographed at a dispersion of 0.89 Å/mm. Figure 1 shows some of the bands

due to  $C^{32}S$  and  $C^{34}S$ . The  $R_1$  heads of both the isotopic molecules are measured and their differences, in vacuum wave numbers, are given in Table I. Isotope shifts for the bands are calculated from the following expression and given in column 4 of Table I.

$$\nu - \nu' = (1 - 0.9919) \{1073.4 (v' + \frac{1}{2}) - 1285.1 (v'' + \frac{1}{2})\} - (1 - 0.9919^2) \{10.1 (v' + \frac{1}{2})^2 - 6.4_6 (v'' + \frac{1}{2})^2\}$$

The vibrational frequencies and anharmonic constants of the  $^1\Pi$  and  $^1\Sigma^+$  states given above are those derived by Barrow, Dixon, Lagerquist and Wright.<sup>2</sup> A comparison of the observed and calculated isotope shifts shows a good agree-

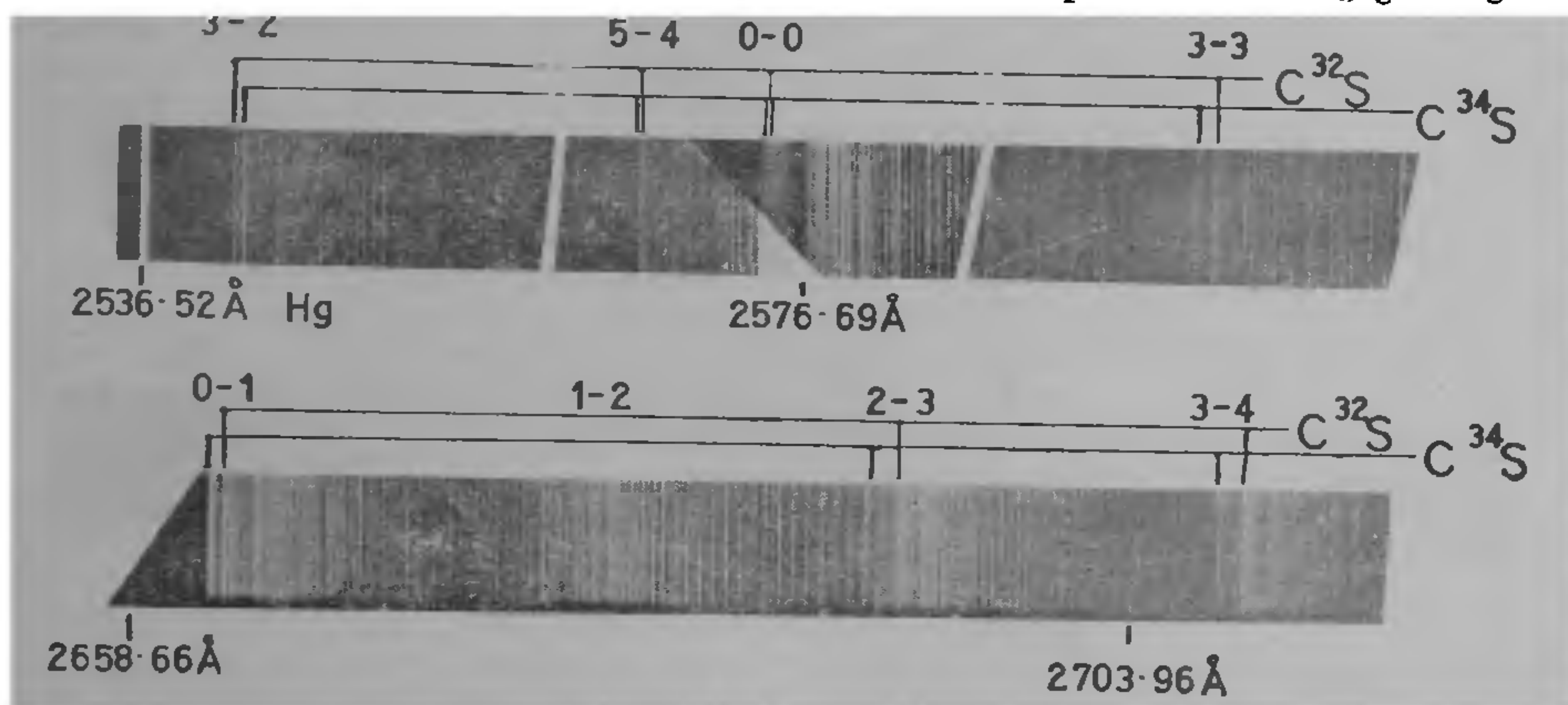


FIG. 1. Emission bands of  $C^{32}S$  and  $C^{34}S$ .

TABLE I

Isotope Shifts,  $\nu^1 (C^{32}S) - \nu^1 (C^{34}S)$  of the band heads of the  $^1\Pi - X^1\Sigma^+$  system

$v' - v''$	$R_1$ band heads of $C^{32}S$ in Å.U	Isotope Shifts in $cm^{-1}$ Observed	Calculated
3-1	2460.3	+13.5	+12.9
4-2	2477.0	+10.4	+10.5
5-3	2493.7	+ 8.5	+ 7.8
2-1	2523.2	+ 7.1	+ 5.3
3-2	2538.7	+ 3.7	+ 3.1
5-4	2572.7	- 1.9	- 1.8
0-0	2575.9	•	- 0.9
3-3	2621.5	- 6.3	- 6.8
0-1	2662.8	-11.1	-11.1
2-3	2693.3	-13.2	-14.4
3-4	2708.9	-15.7	-16.3
4-5	2726.6	(-13.4)	-18.3
5-6	2743.8	-20.5	-20.4
0-2	2754.7	-19.6	-21.1
1-3	2768.9	-21.8	-22.5
2-4	2785.1	-23.7	-24.0
3-5	2801.6	-25.1	-25.7

\* The  $C^{34}S$  head could not be correctly located because of strong intensity of the  $C^{32}S$  head.

ment which confirms the vibrational assignment of the bands.

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\* Preliminary results on eight bands were reported at the Indian Science Congress, 1963.

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## RELAXATION TIMES AND ACTIVATION ENERGIES OF SOME DIPOLAR MIXTURES

THE present communication reports the results of dielectric relaxation and activation energies for some simple dipolar mixtures in dilute solutions in the 3 cm. microwave region at the temperature of 20° C. The method employed was the same as reported earlier.<sup>1</sup>

TABLE I  
Values of relaxation time ( $\tau$ ) and free energy of activation

Polar components	$\tau \times 10^{12}$ sec.	$H_f$ (K.cal./mole)	Dipolar mixture	$\tau \times 10^{12}$ sec.	$H_f$ (K.cal./mole)	$H_\eta$ (K.cal./mole)
Anisaldehyde ..	14.94	2.63	Anisaldehyde + salisaldehyde	11.62	2.48	2.90
Salisaldehyde ..	6.87	2.18	Salisaldehyde + o-chlorobenzaldehyde	9.54	2.37	2.90
Chlorobenzaldehyde ..	11.60	2.48	Anisaldehyde + o-chlorobenzaldehyde	14.79	2.62	2.90

Kadaba<sup>2</sup> has suggested that when the absorption regions of two polar liquids are quite close to each other, one may expect a single relaxation time for their mixture in non-polar solvents. Keeping this in view, the relaxation times of mixtures of anisaldehyde, salisaldehyde and o-chlorobenzaldehyde have been determined.

Five solutions of increasing concentrations were made by mixing equal volumes of the two components of the dipolar liquids in benzene. The relaxation time and activation energy for these dipolar mixtures and for their components as observed are given in Table I.

The experimental results for mixtures suggest that for every pair of dipolar mixture in benzene, the relaxation time obtained is the average of two individual relaxation times. These results also show that there is no association in the mixture. This conclusion is in conformity with the fact that in dilute solutions, dipole-dipole interaction is considerably reduced.

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#### CHEMICAL COMPONENTS OF VATERIA INDICA SEEDS

*Vateria indica* (dipterocarpaceae) is a large ever-green tree indigenous to South-Western India, Kanara and Travancore. It is the source of the Indian Copal resin of commerce. The seeds which are enclosed in a thick hard shell contain usually from 22 to 27% of what is called Malabar or Piney Tallow (Dhupa fat). This oil is credited with medicinal properties. It is used as a local application in chronic rheumatism and other painful afflictions.<sup>1</sup>

With a view to study the non-fatty components of this oil, a sample of the seeds was obtained

from Shimoga, Mysore. The shell was separated from the kernel and the latter (2.5 kg.) coarsely ground and extracted with a succession of solvents in an extractor. (i) Light petroleum (b.p. 60–80°) yielded only the fat (250 g., 10%). (ii) Subsequent ether extraction at room temperature afforded a small amount (ca. 0.5 g.) of a compound which had no definite m.p. but charred and left a residue on ignition. (iii) Extraction with acetone at room temperature yielded a deep red extract. On partial concentration a viscous brown-red mass was obtained which deposited a small amount of fat and a colourless crystalline compound. The fat was removed by repeated washing with ether and the crystalline compound collected by decantation and washing with methanol (Yield 7 g.; m.p. 155–156°). Complete removal of acetone from the decanted solution gave a dark brown resinous solid which could not be crystallised. The colourless compound crystallised from water or aqueous ethanol in stout rectangular prisms, m.p. 155–156°. Drying at 120° in vacuum for three hours raised the m.p. to 226–228° (Found on dried material: C, 48.9; H, 5.4. Calc. for  $C_{14}H_{16}O_9$ ,  $1H_2O$ : C, 48.5; H, 5.2%). The compound did not give Molisch test and dissolved in cold sodium hydroxide solution from which it could be recovered on acidification. It dissolved slowly in aqueous sodium bicarbonate and more easily in sodium carbonate, the colourless solution becoming violet on keeping. An alcoholic solution of the compound gave a light green colour with ferric chloride.

Acetylation with sodium acetate and acetic anhydride (140°, 3 hr.) yielded a pentaacetate which crystallised from methanol as colourless hexagonal plates, m.p. 205–206° (Found: C, 53.7; H, 5.0; COMe, 40.9. Calc. for  $C_{14}H_{11}O_9$  (COMe)<sub>5</sub>: C, 53.5; H, 4.8; COMe, 39.9%).

A solution of the compound in ethanol showed blue fluorescence in UV light;  $\lambda_{max}$  275 m $\mu$ ,  $\lambda_{inflex}$  310 m $\mu$  (Methanol medium). The IR spectrum had the following peaks: 2.85, 3.02  $\mu$  (hydroxyl); 3.35, 3.62  $\mu$  (chelated hydroxyl);