

THE LESS REFRANGIBLE BANDS IN THE
SPECTRUM OF TIN MONOCHLORIDE

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ABSTRACT

Four groups of bands previously obtained by Jevons in a discharge through SnCl_4 vapor are now found also in streaming active nitrogen. Two groups, α and β , were previously classified as a $^2S \rightarrow ^2P$ transition in SnCl ; with the help of new measurements, and from an examination of the band structure, it is concluded that the other two groups, $\lambda 3500$ and $\lambda 3800$, are a $^2D \rightarrow ^2P$ transition with the same 2P state as the α and β bands. The chlorine isotope effect confirms the identity of the emitter as SnCl and confirms the vibrational quantum number assignments. The vibrational intensity distribution (intensity concentrated in $\Delta n = 0$ sequence) is in qualitative agreement with theory, for the ratio of ω_0'' to ω_0' . An attempt was made to obtain analogous bands by introducing SnI_4 vapor into active nitrogen, but no new bands were obtained.

INTRODUCTION AND EXPERIMENTAL PROCEDURE

IN AN uncondensed discharge through the vapor of SnCl_4 Jevons¹ has found four groups of bands, and two continuous bands. He obtained equations representing the α and β groups and found the isotope effect of chlorine for SnCl . These groups were later classified by Mulliken² as a $^2S \rightarrow ^2P$ electronic transition. Two groups, near $\lambda 3800$ and $\lambda 3500$, shaded toward the red, were unidentified by Jevons; these are the object of the present paper. Strutt and Fowler³ describe the spectrum of chlorides of tin in streaming active nitrogen, mentioning only a continuous band and a band group in the region $\lambda 4768 - \lambda 4430$. The present work is a continuation of that last mentioned, but evidently with a more intense exposure. The band group, however, does not appear in the region $\lambda 4768 - \lambda 4430$. The present spectrum corresponds with that obtained by Jevons (Plate 2)¹ in the uncondensed discharge, except in particulars to be discussed below. The measured spectrum was obtained with a quartz spectrograph giving a dispersion of from 8A per mm to 11A per mm in the region investigated. An Eastman 40 plate was used with an exposure of three hours. The pressure in the afterglow tube was about 15 mm. At high pressure the continuous band of the region $\lambda 3300 - \lambda 3600$ was found to be weaker relative to the $\lambda 3500$ group.

STRUCTURE AND INTERPRETATION

No rotational lines were resolved in any of the less refrangible bands. An intensity minimum is observed near the head of each in a few of the most intense bands, apparently giving two heads. The obvious interpretation, however, is that each band has an R head and a Q head, the intensity mini-

¹ W. Jevons, Proc. Roy. Soc. **A110**, 365 (1926).

² R. S. Mulliken, Phys. Rev. **28**, 481 (1925).

³ R. J. Strutt and A. Fowler, Proc. Roy. Soc. **A86**, 105 (1912).

$$\text{SnCl}^{35} \begin{cases} \lambda 3500 \text{ group: } \nu = 28665.3 + 296.2n' - 4.2n'^2 - 350.7n'' + 1.1n''^2 \\ \lambda 3800 \text{ group: } \nu = 26579.1 + 297.5n' - 4.1n'^2 - 349.5n'' + 1.0n''^2 \end{cases}$$

These completely agree with a ${}^2D \rightarrow {}^2P$ transition. The initial state coefficients in both groups are very nearly the same, indicating states closely related, like ${}^2D_{1\frac{1}{2}, 2\frac{1}{2}}$. The final state coefficients indicate final levels in common with Jevons' β and α groups, respectively, equations for which are:

$$\text{SnCl}^{35} \begin{cases} \beta: \nu = 33622.6 + 431.3n' - 1.2n'^2 - 351.4n'' + 1.2n''^2 \\ \alpha: \nu = 31262.5 + 431.3n' - 1.2n'^2 - 353.5n'' + 1.0n''^2 \end{cases}$$

(Agreement in case of the $\lambda 3800$ group is much closer if R branch heads are used. This may be due to the present method of ascertaining Q heads for that group). Further confirmation of vibrational quantum number assignments is given by the isotope effect (see below).

The distribution of intensity in a single band from a ${}^2D \rightarrow {}^2P$ transition can be estimated theoretically from formulas given by Mulliken.⁴ With a reasonable assumption as to the temperature (of active nitrogen) and as to the size of the SnCl molecule, this distribution was calculated;

and the relative intensity of P , Q , and R branches agrees with that observed as well as could be expected. Calculations show that the Q branch reaches high intensity very close to the origin. (Intensity of the P branch is very small compared to the Q branch). The R branch for ${}^2D_{1\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}$ is less intense than the Q branch; and for ${}^2D_{2\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}$ the R branch intensity is greater—possibly greater than the Q branch. In either case the R branch near the origin shows an intensity minimum, leaving an open region. The different appearance of these same bands as photographed by Jevons in a discharge can be satisfactorily accounted for also. For a higher temperature (as in a discharge) the R branch will have a strong maximum at its head (“line-like”); and the Q branch will be weaker relative to the R branch; (the Q branch in the $\lambda 3800$ group is barely visible in Jevons' reproduction).

The intensity in each group is concentrated in the $\Delta n = 0$ sequence, falling off rapidly toward the $+1$ and $+2$ sequences. Only one minus sequence in each group is observed,—for very few and weak bands. In view of the ratio of final to initial vibrational frequencies this distribution is compatible with Condon's⁵ theory, resembling the case of SiN; but the asymmetry about the zero sequence is striking and indicates peculiar $V(r)$ curves.

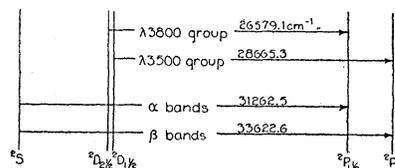


Fig. 1. Electronic energy levels and transitions in SnCl. To scale, except ${}^2P - {}^2D$ separation is shown half size.

⁴ R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

⁵ E. U. Condon, Phys. Rev. **28**, 1182 (1926).

ISOTOPE EFFECT

In several instances weak band heads were associated with the stronger heads recorded above. The displacements of these weaker heads from the stronger were measured and are recorded in Table II. The isotopic coefficient⁶ ρ for SnCl^{37} compared to SnCl^{35} is 0.9791. The theoretical displacement of a SnCl^{37} band head from a SnCl^{35} band head is therefore 0.0209 of the distance of the latter from the group origin. Measured and theoretical isotopic displacements are recorded in Table II. (For the $\lambda 3800$ group, displacements of R heads were observed).

TABLE II. Measured and theoretical isotopic displacements.

$\lambda 3500$ group ($\nu_0 = 28665.3$)					$\lambda 3800$ group ($\nu_0 = 26579.1$)		
n'	n''	$\nu(\text{SnCl}^{35})$	$\Delta\nu$ obs. $\text{SnCl}^{37} - \text{SnCl}^{35}$	$\Delta\nu$ calc. .0209($\nu_0 - \nu$) SnCl^{35}	$\nu(\text{SnCl}^{35})$	$\Delta\nu$ obs. $\text{SnCl}^{37} - \text{SnCl}^{35}$	$\Delta\nu$ calc. .0209($\nu_0 - \nu$) SnCl^{35}
3	3				26395.4	4.6	3.8
4	4	28397.	6.	5.6	321.0	8.2	5.4
0	1	315.7	7.1	7.3	230.3	7.6	7.3
1	2	260.9	8.8	8.4		*	
2	3	198.8	11.1	9.7	118.0	12.7	9.6
3	4	131.9	11.1	11.1	052.2	12.0	11.0
4	5	056.	14.	12.7	25982.	14.	12.5

* masked by NO band structure

The measured displacements agree within experimental error with the calculated values. This agreement proves the identity of the emitter as SnCl . It also proves the correctness of the assignment of vibrational quantum numbers. The tin isotope effect, discussed fully by Jevons, was not resolved with the dispersion here employed.

EXPERIMENT WITH TIN IODIDE

The above experiment was repeated using stannic iodide (SnI_4) in active nitrogen. It produces no characteristic spectrum in the region $\lambda 7000 - \lambda 1900\text{A}$. The tin and iodine line spectra and bands of iodine appear rather strong, iodine lines being photographed at $\lambda\lambda 1844$ and 1830 in 30 minutes.

The writer wishes to express his thanks to Professor R. S. Mulliken for suggesting this problem, and also for his generous advice in the progress of the work.

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NEW YORK UNIVERSITY,
June, 1928.

⁶ R. S. Mulliken, Phys. Rev. 25, 119 (1925).