

### Rotational Analysis of the $A^2\Pi-X^2\Sigma^+$ System of MgCl

ALTHOUGH the internuclear distances in the diatomic halides of the typical elements of Groups I and III are known, often very precisely, few values are available for the diatomic alkaline earth halides. Following the rotational analysis<sup>1</sup> of the  $C^2\Pi-X^2\Sigma^+$  system of CaCl, we have now completed an analysis of the 0-0 and part of the 0-1 bands of the  $A^2\Pi-X^2\Sigma^+$  system of MgCl, from absorption spectrograms taken in a third order of a 6.5-m. grating instrument.

The analysis of the longer-wave-length sub-bands of the 0-0 and 0-1 bands was straightforward, but lines of the shorter wave-length sub-bands are badly blended and overlapped, and the 1-0 bands are too poorly resolved for analysis. However, a satisfactory check was provided by the analysis of the longer wave-length component of the 0-0 band of  $^{27}\text{MgCl}$ . The bands observed present no unusual features. As in CaCl, the spin-splitting in the ground-state was too small to be detected, so that the satellite branches were everywhere blended with the main branches.  $\Lambda$ -type doubling in the  $^2\Pi$  state is also very small, and the lines in the shorter wave-length sub-bands, presumed to involve  $^2\Pi_{1/2}$ , are too overlapped to show whether this state is, in fact, inverted, as expected from the likely electron configuration.

Table 1. SUMMARY OF CONSTANTS ( $^{24}\text{MgCl}$ )

State	$T_0$	$\Delta G_{01}$	$B_0$	$10^3 a$	$10^7 D$	$r_e, \text{\AA.}$
$A^2\Pi_{1/2}$	26,535.89		0.25116	(1.8)	2.2 <sub>5</sub>	2.171 <sub>4</sub>
$A^2\Pi_{3/2}$	26,481.95		0.24914	(1.8)	2.2 <sub>5</sub>	2.176 <sub>4</sub>
$X^2\Sigma^+$	0	462.12	0.24423	1.5 <sub>4</sub>	2.5 <sub>4</sub>	2.198 <sub>4</sub>

A summary of the constants obtained in the present work is given in Table 1. The value for the internuclear distance in the ground-state is  $r_e = 2.199 \text{\AA.}$ , not significantly different from the value  $2.18 \pm 0.02 \text{\AA.}$  obtained for the gaseous dihalide,  $\text{MgCl}_2$ , by electron diffraction<sup>2</sup>.

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<sup>1</sup> Morgan, E., and Barrow, R. F., *Nature*, **185**, 754 (1960).

<sup>2</sup> Akishin, P. A., et al., see Bastiansen and Lund, *Ann. Rev. Phys. Chem.*, **10**, 43 (1959).

## BIOCHEMISTRY

### Application of Atomic Absorption Spectroscopy to the Determination of Calcium in Saliva

THE importance of salivary calcium concentration of the environment in the solubility of tooth and enamel is readily apparent. As with other biological fluids, numerous methods, ranging from classical oxalate-permanganate titration and emission flame photometry to the more recent complexometric and colorimetric techniques, have been used to estimate the calcium content of saliva. Unfortunately most of these methods have certain disadvantages. The oxalate-permanganate method requires relatively large amounts of saliva, time-consuming centrifugation, washing and titration within a narrow temperature-range. Its accuracy has been questioned because of incomplete precipitation of the oxalate or loss of some calcium oxalate during the washing process<sup>1</sup>. Another devious procedure involves a complexometric analysis of calcium and magnesium in saliva

Table 1. CALCIUM CONTENT (MG/M.100 ML.) OF SALIVA ESTIMATED BY DIFFERENT METHODS

Saliva	Type	(a) Saliva diluted with water	(b) Saliva diluted with ethylenediamine tetraacetic acid	(c) Saliva deproteinized strontium suppressor	(d) Saliva deproteinized lanthanum suppressor	Oxalate permanganate method (Clark-Collip)
H.S.	Whole	—	5.50	5.48	5.68	—
A.T.	saliva*	—	7.25	7.40	7.50	7.42
J.F.	—	—	7.15	7.54	7.50	7.52
E.N.†	—	3.70	5.08	5.15	—	—
E.N.	Par-otid†	2.26	3.35	3.29	—	3.42
A.T.	—	3.39	5.55	5.55	—	—
H.S.	—	2.9	3.7	3.2	—	3.6
H.S.	—	2.46	3.76	3.75	—	3.71
B.G.	—	2.48	4.23	4.13	—	3.99
E.N.	Sub-maxillary‡	4.63	7.39	7.37	—	—
H.S.	—	3.99	6.40	6.40	—	6.95
H.S.	—	5.02	6.55	6.85	—	—

\* Whole saliva was stimulated by paraffin.

† Saliva stimulated by application of citric acid to tongue.

‡ Sample centrifuged to remove particulate matter.

followed by a separate colorimetric determination of magnesium, calcium being obtained as the difference<sup>2</sup>. Several complexon-titration techniques using eriochrome black T, murexide or plasmo corinth indicators were tested on saliva. They were found unsatisfactory because the colour shift at the end-point was either too gradual and indistinct or, in the case of murexide, the colour faded too rapidly.

Willis's method<sup>3</sup> for the determination of calcium in blood serum by atomic absorption spectroscopy has been adapted for salivary calcium analysis and found to be accurate and rapid, requiring as little as 0.1 ml. of saliva. The apparatus used in these experiments has been previously described<sup>4</sup>. A Hilger D 290 monochromator was found satisfactory in this system.

Certain normal constituents of saliva can interfere in the determination of calcium by the atomic absorption method. Sodium enhances calcium absorption, phosphorus depresses the calcium absorption and the interference of protein appears to be variable, depending on the type of flame used<sup>3</sup>. Saliva can be deproteinized by the standard procedure of adding trichloroacetic acid and centrifugation. Large concentrations of  $[\text{Sr}^{++}]$  or  $[\text{La}^{+++}]$  can compete with calcium for combination with phosphorus and suppress this interference. Ethylenediamine tetraacetic acid, by complexing calcium, can also overcome phosphorus interference and presumably compete with proteins for calcium.

The results of calcium estimations on saliva are shown in Table 1. The saliva was diluted 1 : 10 by one of the following methods: (a) direct dilution with water; (b) dilution with water and solution of the disodium salt of ethylenediamine tetraacetic acid, final concentration 10,000 p.p.m. ethylenediamine tetraacetic acid; (c) dilution with water, strontium chloride solution and trichloroacetic acid, final concentration 2,500 p.p.m. strontium and 4 per cent trichloroacetic acid. The sample was centrifuged and measurements made on the supernatant; (d) similar to method (c) but lanthanum chloride was used as a phosphate 'suppressor', final concentration 10,000 p.p.m. lanthanum.

The saliva thus prepared was measured relative to standard calcium solutions containing respectively: (a) 60 p.p.m. sodium (approximate level in 1 : 10 diluted saliva); (b) 10,000 p.p.m. ethylenediamine tetraacetic acid; (c) 5,500 p.p.m. strontium, 60 p.p.m. sodium and 4 per cent trichloroacetic acid; (d) 10,000 p.p.m. lanthanum, 60 p.p.m. sodium and 4 per cent trichloroacetic acid.