

Letters to the Editor.

[The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, nor to correspond with the writers of, rejected manuscripts intended for this or any other part of NATURE. No notice is taken of anonymous communications.]

The Secondary Hydrogen Spectrum.

THE further examination of the secondary spectrum of hydrogen has led to a number of interesting discoveries since my last publication (*Roy. Soc. Proc. A*, vol. 111, p. 714, 1926). It appears that the green and red bands have the same electron jump but correspond to different sets of vibrational transitions, those for the green bands being $0 \rightarrow 0$, $1 \rightarrow 1$, $2 \rightarrow 2$, $3 \rightarrow 3$, and $4 \rightarrow 4$, and those for the red bands $1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 2$, $4 \rightarrow 3$, $5 \rightarrow 3$, and $6 \rightarrow 5$. In addition, there are five other less well developed sets of bands with the same electron jump, two in the infra-red with vibrational transitions $2 \rightarrow 0$, $3 \rightarrow 1$, $4 \rightarrow 2$ and $3 \rightarrow 0$, $4 \rightarrow 1$ respectively, and three on the violet side of the green with the respective sets of vibrational transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$ and $0 \rightarrow 2$, $1 \rightarrow 3$ and $0 \rightarrow 3$. There is an intercombination between the lines of all the above bands and indications of a further combination in the members of the *PR* branches, which, however, are less well developed than the *Q* branches. The second differences of the *Q* branches form a square array with a common vertical difference = 2.4 and a common horizontal difference = 2.8 wave number.

The blue bands have a different electron jump from the foregoing. It appears that there are less well developed bands on the violet side of these, which are connected with them and with the red bands by means of a Rydberg formula. Thus if the first element on the violet side of each band is indicated as usual by the letter *A*, the frequencies of the successive lines *AQ* (*i*) are given by the formula

$$\nu = 109678.3 \times \left\{ \frac{1}{(2 - \mu_1)^2} - \frac{1}{(m - \mu_2)^2} \right\}.$$

The value of μ_1 is approximately 0.067 and μ_2 falls steadily from about 0.063 to 0.058 as *m* increases from 3 to 7. Evidence of the bands can be found for each of the values $m = 3, 4, 5, 6, 7$. When $m = 3$ we get one of Fulcher's red S_3 lines, the one, in fact, nearest the violet end, and when $m = 4$ we get the first line at the violet end of Dieke's blue bands. There is also evidence of the existence of a similar lot of bands connected by a Rydberg formula with the green bands. There can be little doubt, in view of the above equation, that this system constitutes the band analogue of Balmer's series.

O. W. RICHARDSON.

King's College, University of London,
July 11.

Imperfect Crystallisation of Common Camphor.

QUITE recently (*NATURE*, May 22, p. 721) A. Müller described the imperfect crystallisation of behenic acid. The crystals of this substance proved to be built up of small crystal elements which have one direction in common and a random orientation perpendicular to this direction. This seems to be the case with many long-chain compounds.

As another example of such an imperfect crystallisation where, however, the imperfection is still greater, I should like to mention common *d*-camphor (Japan camphor). This substance, which, according to Traube, crystallises in the trigonal-trapezohedral class, was studied in the course of an investigation of the space-groups of some optically active crystals. The

rotatory dispersion of camphor crystals is practically the same as the rotatory dispersion of the substance in the melted, gaseous and dissolved states (L. Longchambon, Thèse, Paris, 1923; *C.R.*, 182 (1926), 769). It was therefore supposed that the crystals might prove to possess no trigonal screw-axes, and thus owe little or none of their rotatory power to the molecular arrangement within them.

Assuming that the crystals are truly trigonal or hexagonal, their tabular form is in favour of this hypothesis. Indeed, the best developed planes in any crystal (here {0001}) are generally those which are the most closely packed with molecules. The presence of a threefold screw-axis would reduce the molecular density of the basal plane to one-third of the value which would hold in the case of a threefold rotation axis.

The crystals used were found in a bottle in which they had been produced by slow sublimation, apparently over a number of years, at room temperature. They consisted of thin hexagonal plates. The X-ray investigation showed, however, that the external form of the crystals is deceiving.

With the Bragg spectrometer never more than three reflections were observed, corresponding to the planes which occur on the crystals. From them the following spacings were deduced: $d_{0001} = 5.80$ Å.U., $d_{10\bar{1}1} = 5.42$ Å.U., $d_{10\bar{1}0} = 6.06$ Å.U. (indices according to Traube). Actually, d_{0001} must be multiplied by 2 to make these spacings consistent. They give for the axial ratio 1.656 (Traube, 1.685). The hexagonal unit calculated from them contains two chemical molecules (1.95). Strange to say, a reflection from {11 $\bar{2}$ 0} was never observed on the spectrometer. Many rotation- and oscillation-photographs were taken with different settings of the crystals (with regard to the outer form). None of these photographs showed the typical hyperbolæ of spots that would be expected. All of them showed only a relatively small number of spots, more or less distributed in a circle round the centre. Although the spots corresponding to the three planes mentioned above were generally found in positions where they would be expected, still no spot that could be definitely identified with {11 $\bar{2}$ 0} was ever found. On the other hand, there were always spots in positions which bore no definite relations to the setting of the crystal. As a consequence it was practically impossible to deduce trustworthy conclusions from the positions of the spots on the plates. Clearly, what are apparently good crystals are in reality no more than conglomerations. Laue photographs seem to confirm this view. Several of them were taken in a direction perpendicular to the basal plane, but a hexagonal or trigonal distribution of spots was never obtained. There were a number of broad spots which appeared to correspond to a more correctly orientated larger part; but mostly the spots were drawn out into lines and located in circles round the centre. It should be noted that no definite indication of a larger constituent could be deduced from the rotation- and oscillation-photographs. The sharp spots must correspond to small crystals having a random orientation.

A small number of spacings were obtained from the oscillation-photographs. Attempts were made to increase this number by taking powder photographs, but a real powder could not be obtained. Rubbing camphor in a mortar effects an orientation of the crystal elements with the basal planes more or less parallel to the surface of the pressed substance. An oscillation photograph of this surface gave a strong reflection corresponding to the spacing of the basal plane. Subliming quickly on a cold surface produced crystals which were too big to be considered as a powder.