Infra-red Absorption Spectra of Ammonia, Phosphine, and Arsine.

IN the *Proceedings of the Royal Society* for August (vol. 120, pp. 128-210) will be found a series of communications from the Government Laboratory on the infra-red spectra of the three gases, ammonia, phosphine, and arsine, by Sir Robert Robertson and Dr. J. J. Fox.

In the first two papers of this series are described in some detail the apparatus and arrangement, as it was represented to the authors that it would be of interest to others working in this field to give an account of their technique. In the third paper are given numerical data at gas pressures of 1, $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{1}{16}$ atm. for the position of the oscillation bands, and for the rotation-oscillation bands when they have been resolved, together with curves illustrating these. The fourth paper contains a discussion of the molecular structure of the three gases as deduced from their band spectra.

A Hilger No. 2 infra-red spectrometer with wavelength drum engraved for a rock-salt prism was used. Both to calibrate the engraving of the drum and to obtain the values of the markings for use with prisms of quartz (up to 3 μ) and of fluorite (from 3 μ to 8 μ), these values were experimentally determined in terms of angles of rotation of the prism table. It is considered that when prisms of different materials are employed, engraving on the drum would have been more convenient if it had been in terms of angles. To obviate the effect of variations of air pressure on the thermopile, this was enclosed in a specially designed air-tight casing with rock-salt windows.

In work in the infra-red region, the importance of taking into account the high temperature coefficient of refractive index of rock-salt and also of fluorite has been insufficiently recognised. This temperature coefficient has been determined by Liebreich, and as Sir Robert Robertson and Dr. Fox have already directed attention to this subject in this journal (NATURE, June 4, 1927, p. 818) it is sufficient to say that not only was the temperature of the prism taken periodically throughout each experiment and allowance made for any deviation from a standard temperature of 18° C., but also as a working basis Paschen's values for the refractive indices of rock-salt and fluorite were referred to the same standard temperature, tables for this conversion being given in the paper. Most published tables of refractive indices of rock-salt and fluorite have ignored the fact that Paschen's determinations were made at varying temperatures.

A galvanometer of very high sensitiveness was used for registering the energy falling upon the thermopile, and to overcome the effects of electromagnetic disturbances and mechanical vibrations on this instrument constituted some of the chief difficulties of this research. By suitable shielding with 'stalloy' and 'mu metal' the former disturbances were overcome, whilst the mechanical disturbances were nullified by a suspension system which rendered the galvanometer usable at all times, even in a neighbourhood affected by continuous heavy road traffic.

The gases, prepared in a pure state, were passed into one of two observation tubes fitted with rock-salt end-plates, the other tube remaining empty, and these tubes were brought by means of a rocker device alternately into the optical train of radiation from a Nernst filament to which the input of energy was accurately controlled. Observations were made of the energy as it passed first through the empty tube and then through the tube containing gas. This arrangement was preferred to the alternative method of employing one observation tube and exploring sections of the spectrum through this tube when it is alternately empty and filled with gas. In the compensating tube method it is essential that the ends of both tubes shall be in strictly accurate optical alignment.

In all three gases, ammonia, phosphine, and arsine, a main sequence of harmonic oscillation bands is disclosed, but while such a regular departure from true harmonic ratio as Kratzer found in the case of the harmonic oscillation bands of hydrogen chloride is not found in any one of the three individual gases, nearly constant ratios are obtained between each of the corresponding harmonic members of the several gases. The following table illustrates the degree of uniformity of these ratios in the case of the main sequence of oscillation bands :

Band.	Wave Number.			Ratio.	
	Ammonia.	Phosphine.	Arsine.	Phosphine/ Ammonia.	Arsine/ Phosphine.
I.	1630·9	1125·0	1005·4	0·689	0·893
II.	3335·6	2327·2	2121·9	0·697	0·911
III.	5083·9	3413·7	3091·2	0·672	0·905
IV.	6609·4	4560·0	4161·5	0·689	0·912
V.	8250·8	5608·5	5125·6	0·680	0·914
				Mean 0·685	Mean 0·907

The rate of oscillation thus depends upon the mass of the nucleus of the heavy atom of the molecule, and doubtless by assuming a suitable law of force the distance of the atoms from one another could be calculated. It affords also an argument for a similar structure for the molecules of the three gases.

In addition, each of the three gases was found to have a second sequence of harmonics, and phosphine and arsine a sequence peculiar to themselves. Further, there appeared in ammonia a band at 10·55 μ, apparently without harmonics, and members of a series of what were considered to belong to one mode of rotation of the molecules of that gas.

The oscillation frequencies become slower in the order, from ammonia to phosphine and phosphine to arsine, and the wave-number differences in the rotation bands show that the molecules also rotate more and more slowly in the same order.

Consideration is given in the fourth paper to the bearing as regards constitution of the data displayed in the previous paper. The occurrence of harmonics in the oscillation bands has already been

mentioned, and this is considered in conjunction with the determination of the electric moment of the three gases and the temperature coefficient of their dielectric constants as determined by Watson on samples of the same gases.

Hund, from a consideration of the polarisation and laws of force in the case of the ammonia molecule, concluded that when the polarisation reached an equilibrium position, the four ions forming a tetrahedron with equal side faces, this figure was stable. That the ions are separating is shown by the presence of the oscillation bands, and one of the modes of vibration is that of the nitrogen atom against the plane of hydrogen atoms. Hund's condition would then be fulfilled and a tetrahedral structure required for the model. In the case of ammonia and of phosphine, Watson's values for the electric moment clearly support such a view, but in the case of arsine he gets a small value for this and for the temperature coefficient of its dielectric constant. Absorption bands as strong as those of phosphine are found in the spectrum of arsine, and it is argued that the electric moment should not be reckoned as directly measured by the product of the distance of the heavy atom from the three hydrogen atoms and the charges on the ions, but that the effect of the electron shroud, greater in the case of the heaviest of the atoms
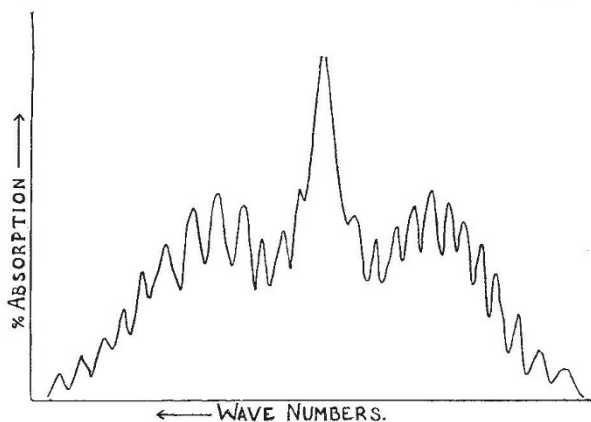

FIG. 1.—Typical band of ammonia, phosphine, or arsine.

(arsenic), comes into play, acting in the opposite direction to the original electric moment. Thus a tetrahedral structure is deduced for all three molecules, though not necessarily of equal height.

Since, in addition to the main sequence of harmonic oscillation bands mentioned above, there occur other sequences, some speculations are made, especially in the case of ammonia, as to the degrees of freedom of the atoms in that molecule of which these sequences may be the reflection. Thus arguments are adduced for assigning the oscillation that may give rise to the band at $10.55\,\mu$, and for the peculiar sequence of bands of ammonia of which

members of a harmonic series appear with the first two members of the sequence absent. The evidence as a whole from these considerations is much more in favour of a tetrahedral than of a coplanar configuration for the molecules of these gases.

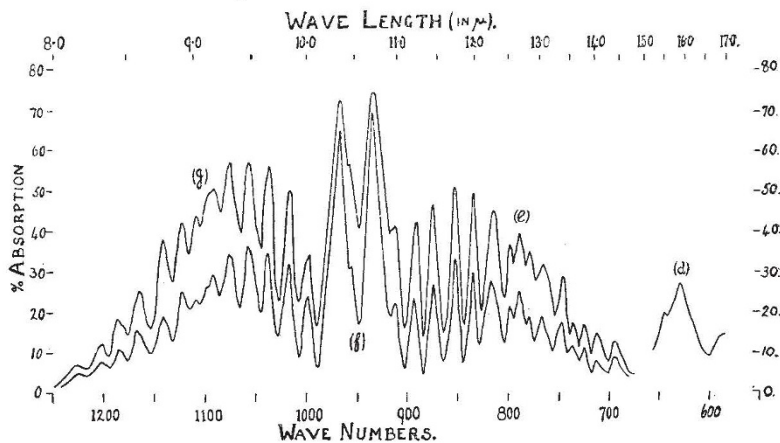While it is recognised that the existence of optically active forms of substituted ammonium

FIG. 2.—Band of ammonia at $10.55\,\mu$. Upper curve at $\frac{1}{4}$ atmosphere, lower curve at $\frac{1}{8}$ atmosphere.

compounds is not decisive on this point, on account of the disturbance caused by the substituting groups, at the same time the work of Ellis and Salant on the infra-red spectrum of amino- and imino-compounds points to the N-H oscillation being connected with what is termed above the main sequence of harmonics, and this view does not conflict with the attribution of other degrees of freedom, some of which correspond to valency bonds, to the other series of oscillation bands in ammonia.

No oscillation bands have been found in these gases similar to that found (and resolved) by Imes and others for hydrogen chloride and characterised by what may be termed P and R branches, with a missing Q or central branch. As a rule, the oscillation bands of ammonia, phosphine, and arsine have P and R branches with a bold central Q branch of absorption. They are usually of the type shown in Fig. 1, which shows a band in which the P and R branches have been resolved to give the rotation fringes.

From the wave number differences, which vary little from band to band for each of the gases, the moment of inertia has been calculated from $J = \dfrac{nh}{4\pi^2\Delta\nu}$, and J has also been calculated from the classical energy relation $\frac{1}{2}J(2\pi\nu)^2 = \frac{3}{2}kT$, ν in this case being the mean difference between the peaks of the Q and the P and R branches. In the following table are given the results of these calculations :

				$J_1 \times 10^{40}$ from Band Structure.	$J_2 \times 10^{40}$ from Energy Relations.
Ammonia	.	.	.	2·78	3·49
Phosphine	.	.	.	4·78	6·24
Arsine	.	.	.	5·53 or 6·51	8·28

The radius of gyration is also calculated from the former set of values of J and compared with those of Rankine, whose radius of mean collision area, as would naturally be expected, is greater than that of the radius of gyration.

The moments of inertia obtained above are thought to have reference to the rotation of the molecule about a line at right angles to the line dropped from the heavy atom on to the plane of the hydrogen atoms and passing through the centre of mass, but in the case of ammonia another and smaller moment of inertia was discovered ($J = 0.35 \times 10^{-40}$). This emerged from a consideration of the band at $10.55\,\mu$ mentioned above, which forms an exception to the usual tripartite bands in these gases. It is shown in Fig. 2. Thus it has a double Q branch, cloven, with a missing rotation member reminiscent of the bands of the halogen hydrides. The wave-number spacing between most of the rotation fringes is similar to that occurring in bands of the main sequence of bands of ammonia, but there are exceptions, or disturbances. The wave-number difference between the disturbance on the R branch (g) and the centre of the two Q branches (f), thence to a disturbance on the P branch (e), and thence to an isolated band beyond (d), is 160 wave-numbers, this last band having a wave-number four times that of a so-called rotation band of ammonia

found by Rubens and Wartenberg about 160 wave-numbers ($63\,\mu$). It is therefore considered that there is here the imposition of another rotation system, and as its moment of inertia is much less, it is attributed to the rotation of the hydrogen atoms round a line dropped perpendicularly from the nitrogen on to the plane of the hydrogen atoms.

Finally, it may be said that while the structure of the three molecules, ammonia, phosphine, and arsine appears to be essentially similar, yet there are features in the infra-red absorption spectrum of ammonia which differ from those of the other two, and while the spectra of phosphine and arsine are very like one another, yet they themselves have features not possessed by ammonia.

As most of the work on these gases was conducted at pressures varying from one to one-sixteenth atmosphere, an opportunity was afforded of observing the effect of pressure on the intensity and on the area of the bands. In view of statements in the literature that such a law as that of Beer, which provides for an exponential decrement of intensity with pressure, does not hold for such a case as this, it was of interest to find that when the bands were well resolved this law was obeyed with remarkable accuracy. This would point to the absorption of the imposed radiation by a comparatively small fraction of the total number of molecules present in the gas.

Health and Sanitation in India.

AN Appendix to the Report of the Royal Commission on Agriculture in India has recently been published,[1] consisting of a concise survey of conditions in each of the presidencies and provinces, eleven in all, of British India. One section of each such survey is devoted to public health and sanitation, and of these it is proposed to give a brief account. The Native States are not included in the survey.

The chief feature brought out by these sections of the volume is the tremendously heavy incidence of certain microbic diseases, such as malaria, cholera, and kala-azar, and the high mortality, or in the case of malaria, the severe deterioration in physical well-being and efficiency caused by them.

As regards malaria, the official figures of deaths directly due to this disease are undoubtedly far too high. Thus in the United Provinces about one million (out of a population of $46\frac{1}{2}$ millions) are reported as dying every year of malaria; but "the village watchman [who is the registration authority] ascribes every case of death which he cannot understand to malaria"; still, the actual number of deaths cannot be less than 100,000 annually. The importance of malaria, however, lies rather (apart from the actual suffering) in the reduction of working efficiency, and in its being a predisposing cause of death from other diseases. Thus (again in the United Provinces) one-fourth of the total population get two attacks of malaria every year, and only

1 per cent receive proper quinine treatment; 25 per cent of the population are totally incapacitated for work for two months, besides having a lowered vitality for the rest of the year. The loss of efficiency for the 18 million workers in the agricultural population of 35 millions is put down at 50 per cent.

For six months of the year the delta of Lower Burma is practically entirely under water, and for months afterwards, shallow pools are left scattered about the country. What this must mean for malaria is easily apprehended; and it is not surprising to learn that malaria undoubtedly reduces the working efficiency of a large part of the rural population. In Bengal, too, it is said that for some three months in every year the capacity for labour of a large proportion of the inhabitants of rural districts, especially in western Bengal, is much impaired by attacks of malaria; and that malaria, in lowering the vitality of mothers, is one of the principal causes of the high rate of infant mortality from which Bengal suffers. Similar remarks are made regarding other provinces also.

Cholera is less widely distributed, and in most parts of India less constantly present than malaria. Bengal suffers more than any other province; the disease reappears year by year, and accounts on the average for rather more than 5 per cent of the total mortality. In the neighbouring province of Bihar and Orissa, the mortality rate from cholera is 2·2 per 1000, and the average mortality is nearly 90,000 annually (out of a population of 38 millions). Yet the disease is easily controllable, given a good