

430. *The Ultra-violet Absorption Spectra of Phosphine, Arsine, and Stibine.*

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THE ultra-violet absorption spectrum of ammonia consists of a series of predissociation bands between $\lambda 2100$ and 1700 \AA . (Liefson, *Astrophys. J.*, 1926, **63**, 73). For phosphine, three predissociation bands between $\lambda 2200$ and 2300 \AA . have been recorded by Melville (*Nature*, 1932, **129**, 546), the absorption being continuous below $\lambda 2200 \text{ \AA}$. The ultra-violet absorption spectra of arsine and stibine are now recorded, together with further observations on phosphine.

PH_3 was prepared from PH_4I by the action of conc. alkali, AsH_3 by the action of dil. HCl on zinc arsenide, and SbH_3 by dropping a Mg-Sb alloy into ice-cold dil. HCl . The gases were purified by washing with water, drying, and fractional distillation. The spectra were photographed on a Hilger small quartz spectrograph (E. 6), the absorption cells used being (a) a quartz cell 12 cm. long with plane ends, (b) glass tubes 40 or 110 cm. long with quartz windows attached to the ground ends with picein wax. The light source was a Wood's hydrogen tube consuming about $1\frac{1}{2}$ kw.

AsH_3 and PH_3 were stored in large glass bulbs, and SbH_3 , which was used as soon as possible after preptn., was kept in a bulb immersed in liquid air. From their storage vessels the gases were admitted to the previously baked and evacuated absorption tubes up to the required pressure. The photochemical decomp. of these hydrides resulted in the deposition of a solid film on the quartz window nearest the light source, which reduced the transparency of the quartz with exposures of over 15 min. By evacuating the absorption tube after the illumination of the hydride, and making a blank exposure, the solid film was found to diminish the intensity of light transmitted below 2500 \AA ., but it probably would not have masked absorption bands.

With PH_3 two diffuse absorption bands were observed, the best conditions being with the longest (110 cm.) absorption tube filled at atm. press., and with a long exposure (*e.g.*, $3\frac{1}{2}$ hr.). The bands were very faint, their centres being at approx. 2315 and 2290 \AA ., and their width approximately 10 \AA . Below 2270 \AA . the absorption was continuous. Dr. Melville has kindly allowed us to compare these plates with his, and the bands correspond with two of the three recorded by him. On reducing the press. to 3–50 mm. in either the long or the shorter tube, the bands were no longer observed, whereas for NH_3 Liefson (*loc. cit.*) found that at high pressures only a few of the predis-

sociation bands (at longer wave-lengths) were visible, and on reducing the pressure the diffuse band system extended increasingly into the ultra-violet.

With shorter absorption tubes, increased light intensity, or reduced press., the limit of the continuous absorption shifted towards the ultra-violet, partial transmission being obtained down to 2100 Å. In order to verify that the diffuse bands were not due to a secondary decomp. product of PH_3 , the 12-cm. quartz cell was filled with PH_3 at 76 cm. and the absorption spectrum photographed (1 min. exposure). The diffuse bands were not visible. The cell was then illuminated from the side with the hydrogen tube for 6 hr., its position being changed every few min. as a deposit formed on the quartz opposite to the light source. Finally, a further 1 min. absorption exposure was made through the cell. It was identical with the first, showing no trace of the diffuse bands, although considerable photochemical decomp. had taken place. This probably means that the bands are due to the PH_3 molecule rather than to a secondary product, formed in the long exposures needed to show them.

With AsH_3 , a 5-hr. exposure in the 110 cm. tube at 76 cm. (the quartz windows being cleaned three times during the exposure) showed an absorption limit at $\lambda 2390$ Å., but no diffuse bands of the type found for PH_3 could be seen, nor did they appear at lower pressures down to 1.3 cm. either in the long tube or in shorter ones. As before, the apparent absorption limit depended upon the conditions.

For SbH_3 , long exposures were impossible at room temp. owing to its rapid surface decomp. At 90 cm. in the 12-cm. cell and with a 15-min. exposure, the limit of transmission was at $\lambda 2750$ Å. At 8 cm. in the same cell it was at $\lambda 2390$ Å. with a 20-sec. exposure, and at $\lambda 2260$ Å. for the same exposure at a press. of 3 mm. Again, none of these plates gave any definite indication of diffuse absorption bands.

There appears to be a regular gradation in the nature of the absorption spectra of these hydrides with increasing mol. wt., NH_3 having a well-developed predissociation spectrum, PH_3 poorly developed bands, and AsH_3 and SbH_3 only continuous absorption. The actual threshold limits for the photodecomp. cannot be deduced from these results: under comparable conditions there is probably a difference of 200–300 Å. between the limits of continuous absorption of PH_3 and SbH_3 . For PH_3 a threshold at 2100 Å. would correspond with an energy of dissociation of 135,000 cal./g.-mol., and a value of 2400 Å. for SbH_3 would correspond with 118,000 cal./g.-mol. Qualitatively, the results agree with the order of thermal stability of the hydrides, though the thermal decomp. takes place as a surface reaction.

Melville (*loc. cit.*) has recorded the products of decomposition of PH_3 as red P and H_2 . From AsH_3 , H_2 also is formed in the photochemical decomp., together with a brownish-black deposit, which is probably As, but has not been examined for the presence of H.

The authors are indebted to Professor G. I. Finch for the loan of a transformer.