

derivatives seem to show slightly larger bathochromic shifts, while among the Vb pentavalent atom compounds, the phosphorus derivatives show larger bathochromic shifts. This may possibly be taken as evidence for the expansion of the valence shell in these two second-row elements.

The ultra-violet spectra of the *o*-, *m*- and *p*-substituted tritylbenzenes also show the vibrational structure of benzene. There is little difference between the spectra of the *p*- and the corresponding *m*-derivatives. The *o*-derivatives seem to exhibit considerable steric interaction. Some of the *p*-substituents which have characteristic absorptions in the ultra-violet, exhibit their absorption maxima at the same wave-lengths as they would in the mono-substituted benzenes. There seems to be little doubt that the *p*-trityl group does not interact with the other substituent or with the benzene ring and that the resonance parameter of the trityl group is approximately zero. Further, the overall electronegativities of the *m*- and *p*-trityl groups were both estimated to be about zero, by a study of the characteristic group frequencies of the *m*- and *p*-derivatives in the infra-red. These conclusions are in accordance with the Hammett reactivity constants of the *m*- and *p*-trityl groups, which have been found to be close to zero by Benkeser and Gosnell⁹.

All the polyphenyl derivatives of IVb and Vb elements show mass effects (decrease in frequency with increase in mass) in their infra-red spectra. The mass effects are marked in the C=C skeletal vibrations, in some of the frequencies due to the mono-substituted phenyl group and in one of the C—H out-of-plane deformation bands (750 cm.⁻¹). The 750 cm.⁻¹ C—H out-of-plane deformation bands of these derivatives show unusual splittings. All these derivatives exhibit bands in the regions 1,440–1,400 cm.⁻¹ and 1,100–1,000 cm.⁻¹, indicating that such frequencies are by no means unique to P Ph or Si Ph groups¹⁰. They might as well be due to some activated ring vibrations.

Further work on these systems is in progress and a detailed report will be published elsewhere at a later date. We wish to thank Prof. R. A. Benkeser of Purdue University for kindly providing the pure samples of the tritylbenzenes.

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¹ Jaffe, H. H., *J. Chem. Phys.*, **22**, 1430 (1954).

² Bowden, K., and Braude, E. A., *J. Chem. Soc.*, 1068 (1952).

³ Mann, F. G., Millar, I. T., and Smith, B. B., *J. Chem. Soc.*, 1130 (1953).

⁴ Jaffe, H. H., and Freedman, L. D., *J. Amer. Chem. Soc.*, **74**, 1069 (1952).

⁵ Robertson, W. W., and Matsen, F. A., *J. Amer. Chem. Soc.*, **72**, 5250 (1950).

⁶ Sklar, A. L., *J. Chem. Phys.*, **7**, 984 (1939).

⁷ Matsen, F. A., et al., *J. Amer. Chem. Soc.*, **72**, 5243, 5248, 5252 (1950).

⁸ Milazzo, G., *Gazz. Chim. Ital.*, **71**, 73 (1941).

⁹ Benkeser, R. A., and Gosnell, R. B., *J. Org. Chem.*, **22**, 327 (1957).

¹⁰ Bellamy, L. J., "The Infrared Spectra of Complex Molecules" (Methuen, London, 1958).

Binding of Water in Ferric Hydrate

A RECENT communication discussed the infra-red spectra and proton magnetic resonance experiments on some hydroxides and hydrous oxides¹. We found in the so-called ferric hydrate OH-groups beside free water (adsorbed), that is to say, this compound may be defined as iron(III) hydroxide. In my own communication, the drawing for the infra-red spectrum (Fig. 1) was incorrect; the centre of gravity of curve I should be between 3.1 and 3.2 μ .

In Table 1 herewith, there are the bands of another precipitate with 19.9 per cent water. This was produced from a solution of ferric nitrate with ammonia.

Table 1

Bands in cm. ⁻¹ (br = broad)	Infra-red spectrum of iron(III) hydroxide		
	I	II	III
	3,300 br	1,625 br	1,030 br
Assignment	OH stretching vibration	H ₂ O bending vibration	OH bending vibration

From the infra-red spectra of the different iron hydroxides², the observed band III is assigned as a bending vibration of the OH-group. The possibility of a combination vibration of the adsorbed water can be excluded. Sometimes this band is split into two. It is possible to calculate³ the Fe—OH distance with the wave-numbers of the bands I and III as ~ 1.90 Å. This value is of the same order of magnitude as the corresponding distance in the other iron hydroxides (namely, γ -FeOOH, 1.97 Å.), and hence the broadening of the bands and the amorphous structure of the compound prejudice the precision of the estimation. The infra-red spectrum of Table 1 may therefore be interpreted as showing that there are OH-groups besides water (adsorbed) in the compound under investigation.

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¹ Glemsler, O., *Nature*, **183**, 943 (1959). Kroon, D., and v. d. Stolpe, C., *Nature*, **183**, 944 (1959).

² Glemsler, O., and Hartert, E., *Z. anorg. allg. Chem.*, **283**, 111 (1956).

³ Hartert, E., and Glemsler, O., *Z. Elektrochem. angew. Physik. Chem.*, **60**, 746 (1956).

PHYSICAL SCIENCES

Geophysical Effects of High-Altitude Nuclear Explosions

PROMINENCE has been given recently to some geophysical effects of the nuclear tests carried out in August 1958 at Johnston Island in the Pacific. According to newspaper reports¹, these tests included high-altitude explosions at heights of the order of 100 miles on August 1 and August 12; for each date the approximate time of the explosion was 1050 U.T. Observations² at Apia, Samoa, show that the test on August 1 coincided with the appearance of an aurora and the occurrence of radio fade-outs at Apia. The special significance of these phenomena is that Apia and Johnston Island lie approximately at opposite ends of a geomagnetic line of force, and the observations at Samoa have been explained³ as due to the generation of charged particles by the test at Johnston Island and the subsequent guidance of the particles along the line of force to produce increased ionization in the lower ionosphere at Apia,