3. The effect of a C-methyl group on the spectrum of 4-dimethylaminoazobenzene and the possible structural relationship between the parent dyes and the polar bound dyes formed *in vivo* are discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Raman Spectra of Germanium Tetrachloride and Lead Tetrachloride

BY JOHN T. NEU AND WILLIAM D. GWINN

The molecules of the type XY_4 have been the subject of considerable investigation and the Raman spectra of a large number of these compounds have been measured and tabulated.[1] Professor Hildebrand[2] has for some time been especially interested in the tetrahalide molecules and has recorded that the distance from the central atom to the halogen atom plotted against the Raman frequencies ν_1 and ν_2 gives generally smooth curves as shown in Fig. 1. The ν_3 frequency for germanium tetrachloride on such a plot, however, shows a considerable deviation from what might be expected. Haun and Harkins[3] have noted a possible alternate value for ν_3, which would give a point closer to the one predicted by the graph. It was, therefore, considered worth while to repeat the determination of the Raman spectrum for germanium tetrachloride and to check the value of ν_3.

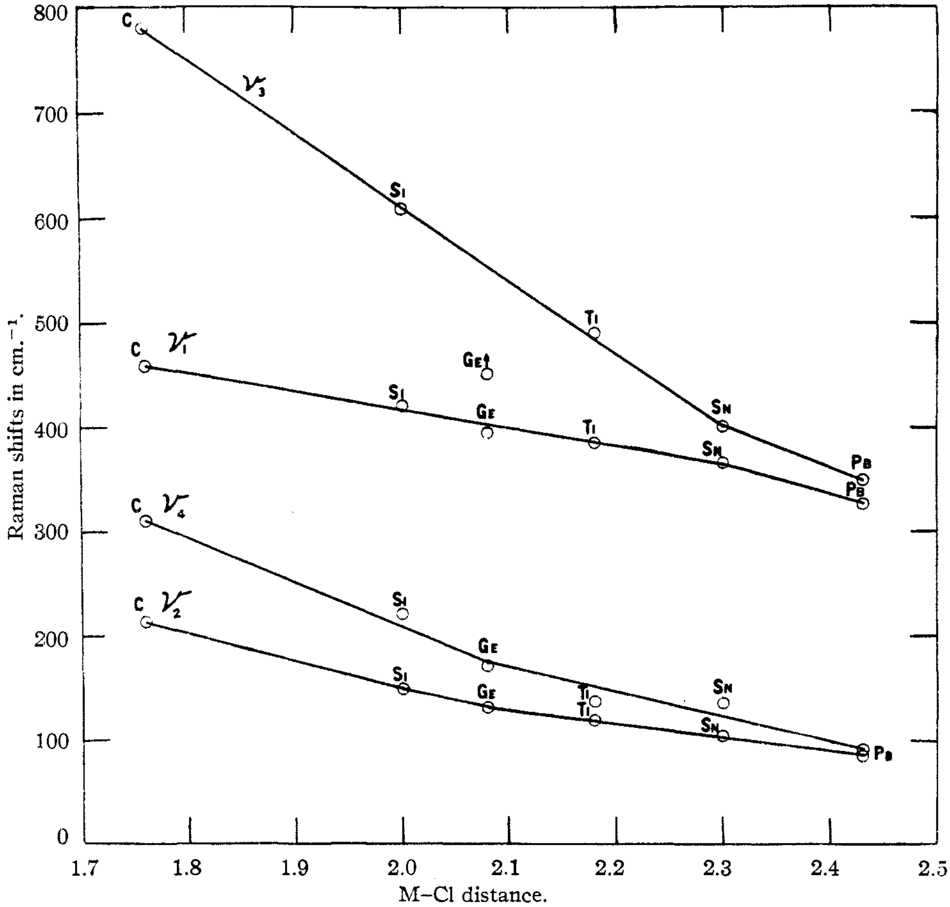

Fig. 1.—Raman frequencies plotted against central atom–chlorine distance in Å.

It also seemed possible that the above-mentioned graph might be used to predict Raman frequencies of tetrahalides where the central atom–halide distance was known. Lead tetrachloride appeared to be a suitable compound with which to verify such a prediction, and at Professor Hildebrand's suggestion, the determination was made

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(1) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, New York, N. Y., 1945.

(2) J. H. Hildebrand, *J. Chem. Phys.*, **15**, 727 (1947).

(3) Haun and Harkins, THIS JOURNAL, **54**, 3971 (1932).

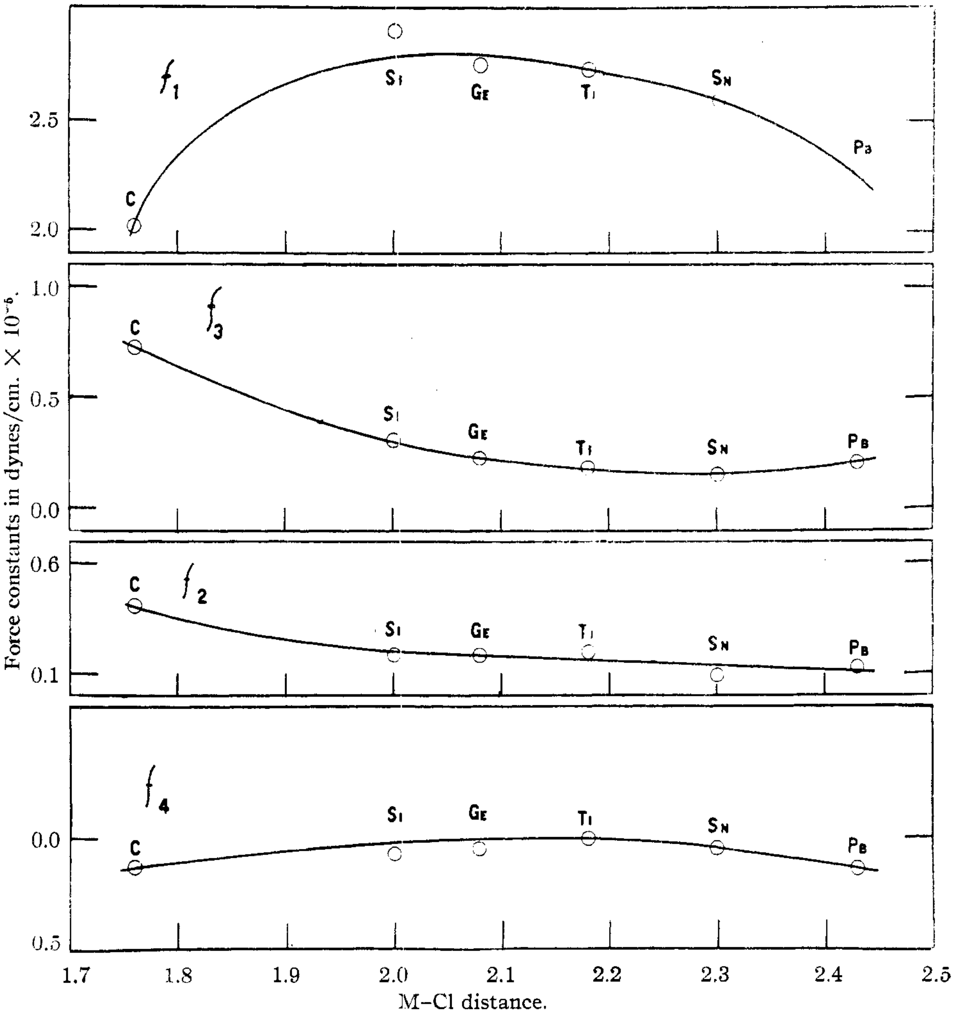

Fig. 2.—Force constants plotted against central atom–chlorine distance in Å.

Experimental

Apparatus.—A Steinheil type GH spectrograph was used with three glass prisms, f/10 collimator and camera lenses, and a slit width of 0.025 mm. Eastman Kodak Co. 103F spectroscopic plates were employed. An iron arc reference spectrum was placed on the plate in such a way that it partially overlapped the Raman spectrum. Shifts were assigned by interpolation from the nearest iron lines. Displacements are tabulated in wave numbers *in vacuo* as determined by conversion of λ in air to wave numbers *in vacuo* from Kayser's "Tabelle der Schwingungszahlen."

The light source consisted of twelve mercury arcs (G.E. type H-2) in a circular arrangement around the sample tube. In the case of germanium tetrachloride, the 4358 Å. line was used for excitation with filter solutions of saturated sodium nitrite, saturated praseodymium chloride, and rhodamine 5GDN extra dye as described by Stamm,[4] interposed between the light source and the sample in three concentric Pyrex cylinders. Lead tetrachloride strongly absorbed the 4358 Å. line and consequently the 5461 Å. line was used for excitation. The outer filter in this case contained saturated sodium chromate, and in the place of the two inner filters a set of baffles was employed to make the incident light essentially perpendicular to the sample tube and hence reduce Rayleigh scattering of the excitation line, thus facilitating detection of Raman shifts close to the exciting line. The exposure required for germanium tetrachloride was approximately equal to that required for carbon tetrachloride, while lead tetrachloride exhibited very strong scattering, due to a close absorption band, and required only about one-fiftieth of the exposure necessary for carbon tetrachloride.

Apparatus for obtaining qualitative polarization data was assembled using a combination of schemes cited by Glockler and Baker.[5] Two horizontal mercury arcs lying in a plane inclined at 45° to the vertical to eliminate differential reflection at the prism surfaces were used in conjunction with baffles to produce planar and perpendicular incident light. A quartz Wollaston prism, inclined so that the axis lay in the plane of the incident light, was placed behind the slit in the collimator tube. With this arrangement, a single exposure gave two representations of the spectrum, one above the other (and shifted slightly), in which the polarized lines appeared less intense in one band than in the other.

Preparation of Compounds.—The lead tetrachloride was prepared by passing chlorine gas into a mixture of lead chloride and concentrated hydrochloric acid cooled to 0°.[6,7] Chloroplumbic acid, H_2PbCl_6, was formed and was converted to the stable insoluble ammonium salt, $(NH_4)_2$-

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[4] R. G. Stamm, *Ind. Eng. Chem. Anal. Ed.*, **17**, 318 (1945).

[5] Glockler and Baker, *J. Chem. Phys.*, **11**, 446 (1943).

[6] V. F. Postmikov and A. I. Speranskiĭ, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 1328 (1940).

[7] Friedrich, *Ber.*, **26**, 1434 (1893).

$PbCl_6$, by addition of ammonium chloride. This salt, when treated with concentrated sulfuric acid at 0°, separated out lead tetrachloride as a dense oily, yellow liquid, which was purified by washing with concentrated sulfuric acid. The liquid was kept at 0° while the Raman spectrum was being taken.

Germanium tetrachloride was made by boiling germanium dioxide with concentrated hydrochloric acid in a stream of hydrogen chloride gas.[8] The escaping hydrogen chloride gas carried the germanium tetrachloride through a water condenser into an acetone–Dry Ice-bath where germanium tetrachloride was frozen out of the gaseous mixture. The product was purified by distillation and treatment with sodium carbonate.

Discussion

Considerable difficulty was encountered in locating the Raman frequencies ν_2 and ν_4 in the case of lead tetrachloride since they lay close to the exciting line and were obscured by the background from it. Plate tracings showed a peak at 90 cm.$^{-1}$, but on only one plate were two separate lines resolved, these appearing at 85 cm.$^{-1}$ and 93 cm.$^{-1}$. The latter values are inclosed in brackets in Table I. The frequencies obtained for lead tetrachloride are in satisfactory agreement with those which would have been predicted by extrapolating the curves in Fig. 1.

TABLE I

RAMAN FREQUENCIES OF GERMANIUM TETRACHLORIDE

Investigator	ν_1	ν_2	ν_3	ν_4
Haun and Harkins[3]	397(10)	132(6)	451(1) or 508	171(6)
Schneider[9]	396	134	453	172
The authors	397(10) P	132(2) D	452(1) D	171(3) D
RAMAN FREQUENCIES OF LEAD TETRACHLORIDE				
The authors	327(10) P	90(3) D [or 85]	348(3) D	90(3) D [or 93]

The Raman shifts obtained for germanium tetrachloride were found to be essentially the same as those found by the two previous investigators (Table I). With long overexposure, however, no trace of a line could be found in the region between 500 cm.$^{-1}$ and 600 cm.$^{-1}$, so it was concluded that the value of 452 cm.$^{-1}$ for ν_3 was the correct one rather than the possible alternate value listed by Haun and Harkins. The deviation of ν_3 may be explained by consideration of the masses of the atoms involved. ν_1 (A_1) and ν_2 (E) represent, respectively, a "breathing" and a bending frequency. Both are independent of the mass of the central atom, while $\nu_3(F_2)$ and $\nu_4(F_2)$ represent vibrations in which the central atom as well as the chlorine atoms are displaced. It would, therefore, be expected that the deviations in the latter two frequencies might occur, as shown by the ν_3 frequency of germanium tetrachloride. In an attempt to eliminate the effect of the mass of the central atom, force constants calculated by the method of Rosenthal[10] rather than frequencies were plotted against the central atom–chlorine distance as shown in Fig. 2. It will be noted that in this plot the germanium tetrachloride shows no marked deviations.

A more complete discussion of the correlation of the Raman spectra with metal–halogen distance is given by Hildebrand.[2]

Summary

For germanium tetrachloride, the correct value of ν_3 is 452 cm.$^{-1}$, and the deviation from the value predicted by plotting the metal–halide distance against Raman shift may be explained by consideration of the mass of the germanium atom. The Raman frequencies of lead tetrachloride are essentially what would have been predicted.

BERKELEY 4, CALIFORNIA RECEIVED JUNE 5, 1948

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[8] Foster, Drennan and Williston, THIS JOURNAL, **64**, 3042 (1942).

[9] K. W. F. Kohlrausch, "Der Smekal-Raman-Effect, Erganzungsband," 1931–1937, J. Springer, Berlin, 1938.

[10] J. E. Rosenthal, *Phys. Rev.*, **45**, 538 (1934); **46**, 730 (1934).

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Synthesis of Aromatic Phosphonic Acids and their Derivatives. II. Some Halobenzene Derivatives

BY GENNADY M. KOSOLAPOFF

Since the scientific literature contains the syntheses of only the *p*-chloro- and the *p*-bromo-benzenephosphonic acids,[1] it was felt advisable to prepare the possible isomers of halo-benzenephosphonic acids containing the principal halogens. This paper describes the syntheses of the *m*- and the *p*-isomers of the chloro-, bromo- and iodobenzenephosphonic acids, and includes the preparation of the related (*p*-chlorobenzene)-(*p*-aminobenzene)-phosphinic acid.

The *p*-chloro derivative was prepared in the manner already described[2] and was used for the preparation of phosphanilic acid according to Bauer,[3] which was readily converted into the *p*-iodo-acid by the diazo-reaction. The preparation of the *p*-bromo-acid was conducted by our modified Michaelis reaction,[2] in the course of which it was found that considerable debromination took place, apparently through the action of the aluminum chloride catalyst.

The *m*-isomers were prepared from benzene-

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[1] Michaelis, *Ann.*, **293**, 193 (1896).

[2] Kosolapoff, THIS JOURNAL, **69**, 2020 (1947).

[3] Bauer, *ibid.*, **63**, 2137 (1941).