The Raman Spectra of Arsenic Trichloride and of Its Mixtures

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that the fourth fundamental would lie around 20μ, which was beyond the limit of our instrument. The measurements on C_6H_6, curve (b), were extended only as far out as 15.05μ since this was very near the limit of our instrument and since the wavelength of this last absorption was well known. The vertical lines at the bottom of the graph give the wavelengths and intensities as listed in *Das Ultrarote Spectrum*. The agreement of these two sets of data is very good, however attention is called to several new bands in our curves and to the large discrepancy in the intensities of the band at 8.65μ. A comparison of curves (a) and (b) shows the absence of C_6H_6 in the C_6D_6, in complete agreement with the results of the ultraviolet measurements to be discussed in a later paper. The good agreement between the observed and calculated frequencies of the fundamentals of C_6D_6 is, as will be shown below, excellent support for the present theoretical assumptions concerning the structure of the benzene molecule. Table I presents a summary of the benzene results. The calculated values are by Benedict.

In Fig. 2 and Table II the results on a sample of Eastman Kodak thiophene are presented.

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The Raman spectra from mixtures of AsCl₃ with benzene, carbon tetrachloride, methyl and ethyl alcohol have been investigated. The strong deviations from additivity have been observed for AsCl₃ in alcohols. The shifts are correlated with the strength of the bond As–Cl. A computation of the constants of the molecule AsCl₃ is made which agrees with electronographic data. The geometrical configuration of the molecule AsCl₃ in mixtures undergoes only a slight deformation, but the bond As–Cl is considerably weakened in alcoholic solutions.

1.

INVESTIGATION of Raman spectra of liquid mixtures did not give definite results. In certain cases, the spectrum of mixtures is a strict superposition of the spectra of the components,[1] in other ones various changes have been observed, e.g., the splitting of Raman lines, their shifts and the variation of relative intensities, the disappearance of some frequencies or the appearance of new ones.[2] These deviations from additivity are ascribed to polymerization, to formation of complexes or to solvation. Up to now it has not been possible to establish a clearly expressed connection between the deviations of Raman spectra of mixtures from additivity and the properties of the components of the mixture. In particular, there is no parallelism between deviations from additivity and dipole moments:[3] in certain cases the mixtures with dipole components behave additively, in others additivity is broken in the presence of nonpolar components of the mixture. The question requires thus additional experimental research.

We have examined the Raman spectra of mixtures of arsenic trichloride with benzene, carbon tetrachloride, methyl and ethyl alcohols. The method and detailed results for the two

[1] A. Dadieu and K. W. F. Kohlrausch, Physik. Zeits. **30**, 384 (1929); E. H. L. Meyer, ibid. **32**, 293 (1931); R. E. Whiting and W. H. Martin, Trans. Roy. Soc. Canada **25**, 87 (1931); E. A. Crigler, Phys. Rev. **38**, 1387 (1931); H. H. Voge, J. Chem. Phys. **2**, 264 (1934); S. Leitmann and S. Uchodin, Comptes rendus Acad. USSR **4**, 14 (1934).

[2] A. Dadieu and K. W. F. Kohlrausch, Wien. Ber. **138**, 335 (1929); **139**, 77, 439 (1930); **140**, 293 (1931); E. H. L. Meyer, reference 1; P. Krishnamurti, Ind. J. Phys. **6**, 401 (1931); S. Parthasarths, ibid. **6**, 287 (1931) etc.

[3] For once, such a parallelism was observed for HCl in dipole solvents (W. West and P. Arthur, J. Chem. Phys. **2**, 215 (1934)).

former mixtures were published before,[4] the results for the two latter ones are to appear soon.[5] The accuracy of measurement of the spectra is 1–2 cm^{-1} for sharp Raman lines, for diffuse ones it is reduced to 5 cm^{-1} and less.

The frequencies of benzene, carbon tetrachloride and of both alcohols suffer no changes in mixture with arsenic trichloride. Inversely, the frequencies of the latter are somewhat displaced in the former two solvents, and two of them (372 and 410 cm^{-1}) decrease sharply in alcohols, approximately by the same value (25–30 cm^{-1}) and apparently having no dependence on the concentration (10–50 percent by weight AsCl$_3$). In Table I are represented the

TABLE I.

	AsCl$_3$	AsCl$_3$ +C$_6$H$_6$	AsCl$_3$ +CCl$_4$	AsCl$_3$ +CH$_3$OH	AsCl$_3$ +C$_2$H$_5$OH
I.	159	153	153	154	159
II.	195	191	187	198	198
III.	372	369	382	348	342
IV.	410	401	408	389	388

final average results for the frequencies of AsCl$_3$ in the four mentioned mixtures and in the pure state. For the latter one our measurements are in good agreement with the previous results of other authors.[6]

Thus, in mixture with arsenic trichloride both the nonpolar C$_6$H$_6$ and CCl$_4$ and alcohols, which possess a considerable moment ($M = 1.68$ and 1.74×10^{-18}) suffer no change of their own frequencies. At the time, as the former two have an insignificant influence upon the proper frequencies of AsCl$_3$, the second ones displace them strongly. If we assume these displacements to be due only to the dipole moments of alcohols, it is not clear why the frequencies of the latter are not also displaced in the presence of AsCl$_3$ which possesses a considerable moment.[7] The presence of a considerable moment appears thus

as a necessary but insufficient condition for shifts of the frequencies. It is plausible to assume as a second necessary factor a comparatively weak bond between those parts of molecules which participate in active vibrations. While for the vibrations which define the Raman spectra of benzene and alcohols, the elastic constant of bond lies between $4.3 - 6.3 \times 10^5$ dyne/cm and for CCl$_4$ it is 2.0×10^5 dyne/cm,[8] for vibrations As $-$ Cl in AsCl$_3$ it has only a value 1.7×10^5 dyne/cm.[9] The energy of the bond As $-$ Cl (about 65 Cal.) is also less than the bond-energies in molecules of the solvents for AsCl$_3$ which were studied by us.

The fact that Trumpy[10] has found considerable shifts in the mixtures of dipole halides for both components can be considered as an indirect corroboration of our assumption. Also in these compounds both the elastic constants and the bond energies are considerably smaller than in benzene, carbon tetrachloride and alcohols.[11]

Thus, in mixtures we must expect especially considerable shifts of those frequencies which correspond to the weakest bonds in the presence of a considerable dipole moment for the second component of the mixture. The material given below will show to what extent this conclusion from our observations has a general character.

2.

In order to compute the constants, by which the molecule AsCl$_3$ is characterized, one must proceed from a regular trihedral pyramid, with ion As^{+++} at its top and with ions Cl$^-$ at the bases. Assuming central forces, the computation can be made according to Dennison's equations.[12] The results of the calculation depend upon the way in which the observed frequencies are correlated with possible modes of vibration. We have proceeded from the following assignment of frequencies: $\omega_1 = 410$, $\omega_2 = 159$, $\omega_3 = 372$ and $\omega_4 = 195$, where ω_1 and ω_2 are the single vibrations along the symmetry axis and ω_3 and ω_4 are the double vibrations perpendicular to it.

[4] A. E. Brodskii, A. M. Sack and S. F. Besugly, Sowphys. 5, 146 (1934).

[5] A. E. Brodskii and A. M. Sack, Acta Physicochem. (1935).

[6] P. Daure, Ann. d. Physik 12, 375 (1929); S. Bhagavantam, Ind. J. Phys. 5, 48 (1930) etc.

[7] The orientational calculation of H. Braune and G. Engelbrecht (Zeits. f. physik. Chemie B19, 303 (1932)) gives $\eta = 3.5 \times 10^{-18}$, and from data for densities, refractive indices and dielectric constants (Landolt's Tables) it follows that $\eta = 1.4 \times 10^{-18}$. A comparision with other chlorides and with compounds of As^{+++} indicates likewise a considerable moment of liquid AsCl$_3$.

[8] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, pp. 154, 215.

[9] Cf. below.

[10] B. Trumpy, Zeits. f. Physik 66, 790 (1930); 68, 675 (1931); Det. Kgl. Vid. Selsk. Forh. 4, 102 (1931).

[11] Cf. the juxtaposition of D. A. Andrews and J. W. Murray, J. Chem. Phys. 2, 630 (1934).

[12] D. M. Dennison, Phil. Mag. 1, 195 (1926).

TABLE II.

	β	α	f	f'	$r:h$	$r:s$
Pure AsCl₃	63° 53′	102° 10′	1.70×10⁵	0.73×10⁵	3.54	1.56
AsCl₃+CH₃OH	64° 45′	103° 6′	1.52×10⁵	0.73×10⁵	3.67	1.57
AsCl₃+C₂H₅OH	63° 32′	101° 46′	1.47×10⁵	0.73×10⁵	3.48	1.55

NOTATION: β—the angle between the axis of symmetry of the pyramid and its edge, α—the angle between two bonds As−Cl, f—the elastic constant of the bond As−Cl, f'—the same for the bond Cl−Cl, r—the distance Cl−Cl and s—the distance As−Cl in A.

This assignment gives for the molecule AsCl₃ the constants indicated in the first line of Table II. The resulting values for the constants of the elastic bonds f and f' and for the angle β between the edge As−Cl and the altitude of the pyramid satisfy well all the four Dennison equations. The inverse calculation gives for the frequencies:

436 [410], 150 [159], 387 [372] and 188 [195]

(in brackets are given the mean observed values from Table I). From the angle β we can readily find the ratio $r:h$ of the edge of the base (Cl−Cl) to the altitude, the ratio $r:s$ of the edge of the base to the edge As−Cl and the angle between the two edges As−Cl. These values are likewise given in Table II. The results obtained are in fairly good agreement with the data resulting from electron diffraction[13] which give:

$\alpha = 101°$ [102°]; $\beta = 63°$ [64°]; $r:s = 1.54$ [1.56]

(in brackets are the results of our calculations)· Thus, the conclusions about an inapplicability of Dennison's formulae to the computation of molecule AsCl₃[14] are dubious.

The old data of Bhagavantam[15] disagree equally both with ours and with the electronographic ones. In the recent paper of Howard and Wilson[16] a computation of the constants of the molecule AsCl₃ is made for central as well as valence forces. They obtained for the former model $f = 1.80 \times 10^5$ and $f' = 0.60 \times 10^5$ dyne/cm

[13] L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. 56, 2373 (1934).
[14] Don M. Yost and J. E. Sherborne, J. Chem. Phys. 2, 125 (1934) and Don M. Yost and T. F. Anderson, ibid. 2, 624 (1934). These authors proceed from another assignment of frequencies by analogy with PCl₃ ($\omega_1 = 410, \omega_2 = 193, \omega_3 = 370, \omega_4 = 159$).

in tolerable agreement with our data but an inverse calculation of the frequencies gives a considerable deviation from experimental values.

In order to compute the moments of inertia of the molecule AsCl₃ one must know the distances r and s between Cl−Cl and As−Cl, which cannot be obtained from the Raman spectrum or electronographic data only. Assuming the radii of the ions As⁺⁺⁺ and Cl⁻ to be 0.69 and 1.81A according to Goldschmidt and Pauling and ignoring their deformation, we find $r:s = 1.45$ instead of 1.56 obtained by us. The agreement is sufficiently good; the distances As−Cl and Cl−Cl are to be identified with the sum of radii. Then for both moments of inertia about the symmetry axis and perpendicular to it, the values 765 and 565×10^{-40} will be obtained. Unfortunately the absence of rotational structure did not allow us to verify these values. The moments of inertia computed by us depend in a very strong way upon the errors in values of r—their accuracy is not high.

For the molecule AsCl₃ in its mixtures with alcohols the assumption was made that the pyramid remains regular. The ratio $\omega_1\omega_2/\omega_3\omega_4$ in spite of a considerable change in ω_1 and ω_3 remains nearly constant in mixtures which confirms a very small deformation of the molecule AsCl₃ from the dipoles of the alcohols. Actually, the geometrical constants of the pyramid almost do not change and neither does the constant f'. On the other hand the constant f decreases by 9–13 percent which indicates the weakness of the bond As−Cl. An analogous computation for AsCl₃ in benzene and carbon tetrachloride was not made, because in these cases the shifts from pure AsCl₃ are not outside the limits of possible errors of the values quoted in Table II.

The Raman lines of AsCl₃, in particular ω_3 and ω_4, are very diffuse in alcohols which is due, presumably, to the Stark-effect, caused by the dipoles of the alcohols. In C_6H_6 and CCl_4 this diffusion of the lines is only weakly manifested.

[15] Cf. Kohlrausch, ref. 8., p. 201 (assignment the same as it is by Yost).
[16] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. 2, 630 (1934) (assignment the same as it is by Yost).