163. *The Vibrational Spectra of Acrylonitrile and Perbunan.*

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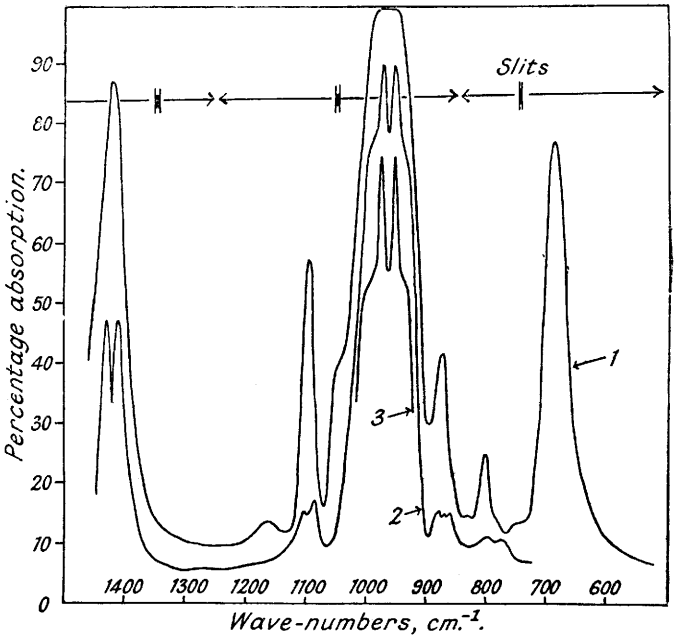
The spectrum of acrylonitrile has been measured over a wide range in the infra-red. A consideration of the results together with Raman data suggests a probable assignment of magnitudes to the normal vibrational modes. The spectrum of a sample of perbunan has also been measured and some suggestions have been made about the structure of this molecule.

A survey has recently been made of the infra-red absorption spectra of a large number of polymeric substances and of their associated monomers and related simple molecules (Thompson and Torkington, *Proc. Roy. Soc.*, in the press). One of the main objects of this work was to decide between different possible molecular structures and to determine the course of several polymeric reactions. In the course of the work the vibrational spectrum of acrylonitrile was measured, not only because of its relationship with the vinyl halides but also since it is a component in the co-polymerisation with butadiene to form the " perbunan " class of synthetic rubber. The moments of inertia of acrylonitrile are fairly small, and it was possible to resolve the rotational contour of some of the absorption bands of the vapour. The use of this band contour and other considerations has made a vibrational analysis possible, leading to a satisfactory assignment of magnitudes to the normal vibration frequencies of the molecule. Some preliminary comments can also be made about the nature of the sample of perbunan studied.

Fig. 1.



(1) 0·08 *mm. liquid;* (2) 7-*cm. cell,* 80 *mm. vapour;* (3) 7-*cm. cell,* 40 *mm. vapour.*

Experimental.

The acrylonitrile was a sample supplied by I.C.I. Ltd., Dyestuffs Division, stabilised over copper powder. It was distilled off before use; b. p. 77—77·5°. Two spectrometers were used, details of which have been described in the previous papers. For the vapour, two absorption cells, 7 cm. and 21 cm. long, were used; for the liquid, layers about 0·1 mm. and 0·05 mm. thick were used.

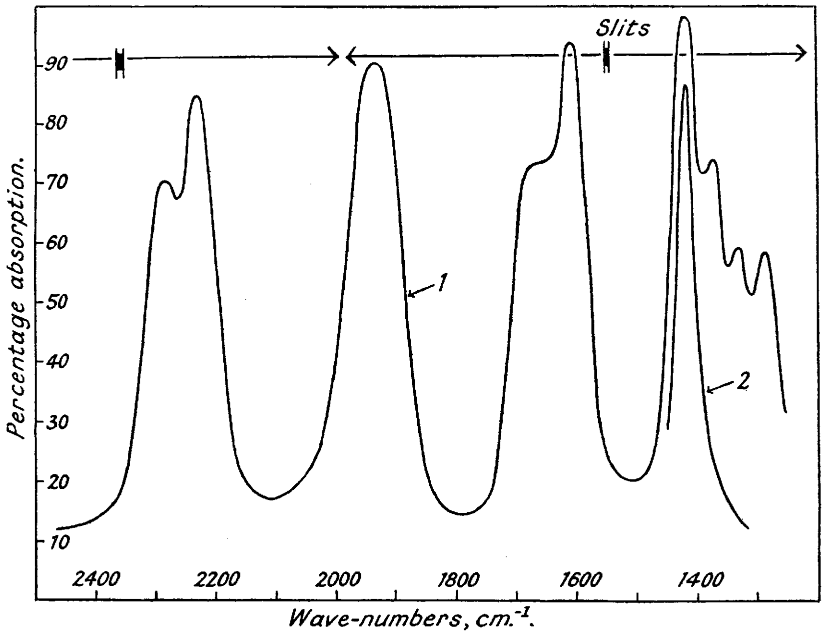
The sample of perbunan was a co-polymer of butadiene with acrylonitrile in the proportion 2 : 1. Films were made by the evaporation of solutions in ethylene dichloride from the surface of mercury. The spectra were measured immediately, since oxidation occurred fairly rapidly.

Results.—The spectrum of acrylonitrile vapour and of a thin film of liquid between 7 and 20μ is shown in Fig. 1, and that of the liquid between 4 and 8μ in Fig. 2. The positions in cm.$^{-1}$ of the absorption bands are summarised in Table I. The Raman data in this table were determined by Reitz and Sabathy (*Sitzungsber. Akad. Wiss. Wien*, 1938, IIb, **146**, 577).

TABLE I.

Infra-red spectrum.		Raman spectrum.
Vapour.	Liquid.	Liquid.
		238(7)
		305(1)
		517(1)
		561(3)
		628(1)
690		688(2)
	742	
782 800	805	
862 870 880	873	878(2)
	ca. 907	
954 971	960 to 980	965(0)
	1038	
1086 1095 1105	1097	1099(2)
		1205(½)
	1288	1275(4)
	1330	
	1372	
1412 1430	1420	1406(4)
	1610	1607(10)
	ca. 1650	
	1938	
	2232	2224(10)
	2283	
		2989(0)

FIG. 2.



(1) 0·20 *liquid;* (2) 0·10 *liquid.*

DISCUSSION.

Acrylonitrile will have 15 normal modes of vibration. These can be analysed, to a first approximation, as follows. There will be 11 motions in the plane of the molecule and 4 out of the plane. Of the eleven planar modes, 5 will involve movements determined essentially by the skeleton C–C–C–N, and 6 will be largely determined by oscillations of C–H bonds. Of the four non-planar modes, one will be controlled by an oscillation of the skeleton and three by movements localised in the C–H bonds. The motions can then be described roughly as follows :

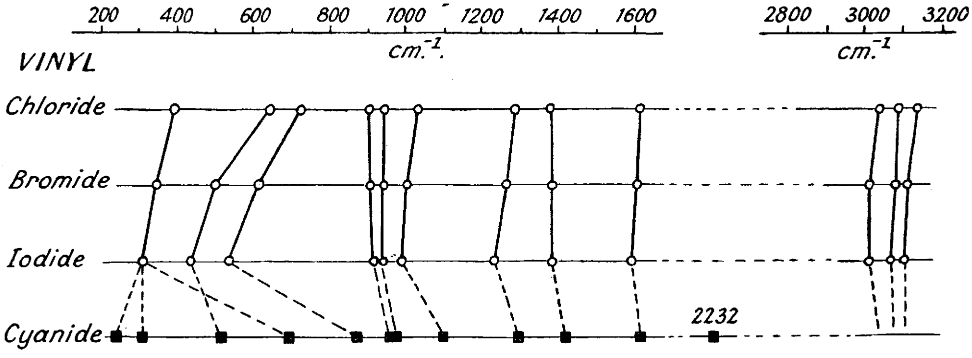
Planar.			Non-planar.
3 C—H	valency vibrations.	1 CH_2 deformation.	1 CH_2 bending.
1 C═C		1 CH_2 rocking.	1 CH bending.
1 C—C		1 CH rocking.	1 twisting.
1 C≡N		2 skeleton deformations.	1 skeleton bending.

We may assume as reasonable interatomic distances : $r_{CH} = 1{\cdot}08$ A., $r_{C=C} = 1{\cdot}35$ A., $r_{C-C} = 1{\cdot}46$ A., and $r_{CN} = 1{\cdot}16$ A., with angles of 120°. The principal moments of inertia are then 18, 170, and 188 × 10^{-40} g.-cm.^{2}, the least axis of inertia being slightly inclined to the direction of the C—C≡N part of the skeleton. The molecule will therefore approximate closely to being a symmetrical rotator, with two equal moments of inertia, and in Gerhard and Dennison's nomenclature (*Physical Rev.*, 1933, **43**, 197), $\beta \sim 9$. For the " parallel " type bands, in which the change of electric moment is parallel to the least axis of inertia, we shall expect absorption bands with three branches (*P*, *Q*, and *R*), the spacing between the pair of outermost maxima (*P–R*) being given by $[S(\beta)/\pi]\sqrt{kT/I_C}$. With a larger moment of inertia, 180 × 10^{-40}, this spacing is about 17 cm.$^{-1}$. The contour of the perpendicular type bands will show a strong central peak, flanked by shoulders of lower intensity. In reality, many of the oscillations will involve changes of electric moment with components along more than one axis of inertia, and the bands observed in these cases will therefore have a hybrid contour.

The infra-red band at 2232 cm.$^{-1}$ is, by analogy with other cyanides, attributed to the planar valency vibration connected with the $C{\equiv}N$ link. Similarly, the band at 1610 is associated with the planar valency vibration of the $C{=}C$ bond. In addition to these values, " coincidences " in the infra-red and Raman spectra are found with the infra-red bands 690, 870, 954, 971, 1095, 1288, 1420. These seven frequencies may be connected with fundamentals. Tentatively, we may assign 1413 to the planar CH_2 deformation, 1288 to the planar CH rocking mode, and 1095 to the planar CH_2 rocking mode. These values fall into line with those of similar vibrations in similar molecules. The contours of the bands at 954 and 971 show that they involve perpendicular type oscillations. These frequencies, moreover, correspond to the pair found at 909, 990 with hydrocarbons containing the vinyl radical (Thompson and Torkington, *loc. cit.*) and at 895, 940 with vinyl chloride. These can be attributed at once to bending motions of the CH_2 and CH radicals. The value 870 may be connected with the planar C–C bond valency vibration, but 690 cannot yet be assigned to a particular mode.

In addition to the above, there will be three valency vibrations associated with C–H bonds, all having values close to 3000 cm.$^{-1}$. This leaves three undetermined frequencies. Raman data show that all cyanides except methyl cyanide have a very low frequency of about 200. Hence 238 is probably a fundamental, and since it does not occur with $(CH_3){-}C{\equiv}N$, it is perhaps the non-planar deformation of the $C{=}C{-}C{\equiv}N$ skeleton. Similarly, 305 is probably a fundamental, and since no infra-red absorption could be detected at 561 and 628, whilst there are signs of feeble absorption at about 19μ (*ca.* 520 cm.$^{-1}$), 517 is taken as the other fundamental. Of the three unassigned fundamentals 305, 517, and 690, two are connected with planar rocking motions of the skeleton, and one is a twisting mode which will be largely determined by motions of the CH_2 about the double bond. It seems most reasonable to assign 305 to one of the rocking modes of the skeleton. Also, 690 is fairly intense in infra-red absorption and so it may not be due to the twisting mode. We should therefore assign 517 to the twisting mode, and 690 to the remaining skeleton deformation.

FIG. 3.



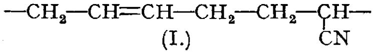
The band contours agree with this assignment. For instance, the bands at 954 and 970 are perpendicular in type, as would be expected for motions out of the plane of the molecule. The infra-red band at 870 is essentially " parallel," with roughly the correct spacing. It is primarily determined by a vibration of the C–C bond; the change of electric moment will have its greatest component along the least axis of inertia.

The above array of fundamentals also satisfactorily explains the other frequencies found in infra-red absorption and in the Raman spectrum, as shown in Table II. In Fig. 3, correlations are shown with the fundamental frequencies of the vinyl halides.

TABLE II.

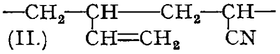
Infra-red.				Raman.	
Frequency.	Interpretation.	Frequency.	Interpretation.	Frequency.	Interpretation.
742	970 − 238	*ca.* 1650	965 + 690	561	870 − 305
ca. 907	690 + 238		954 + 690	628	870 − 238
1038	2 × 517	1938	2 × 970	1205	971 + 238
1330	1095 + 238	2283	1420 + 870		
1372	2 × 690				
	1610 − 238				

The spectrum of a sample of perbunan between 4 and 14μ is shown in Fig. 4. The most intense band is that at 970 cm.$^{-1}$. In the previous papers of this series the spectra of groups of olefinic hydrocarbons were described, from which it was found that characteristic absorption bands exist for the identification of the different classes. Thus, substances containing the vinyl radical have intense bands at about 909 and 990 cm.$^{-1}$, which also appear at slightly displaced frequencies in other vinyl compounds such as the halides. Olefins of the type $R_1{\cdot}CH{:}CHR_2$, on the other hand, show a single strong band at about 965 cm.$^{-1}$. It is clear that the intense band with perbunan at 970 can similarly be attributed to the presence of a structure such as (I), which would arise from 1 : 4-addition of butadiene with acrylonitrile. Perbunan also has a weaker band at 915, and it is possible that any band at 990 would be submerged in the shoulder of the main band at 970. If this were so, it would imply the presence of a structure such as (II), arising from 1 : 2-addition. We might therefore infer that with the sample examined here most of the polymerisation had proceeded by 1 : 4-addition,



$-CH_2-CH=CH-CH_2-CH_2-\underset{CN}{CH}-$

(I.)



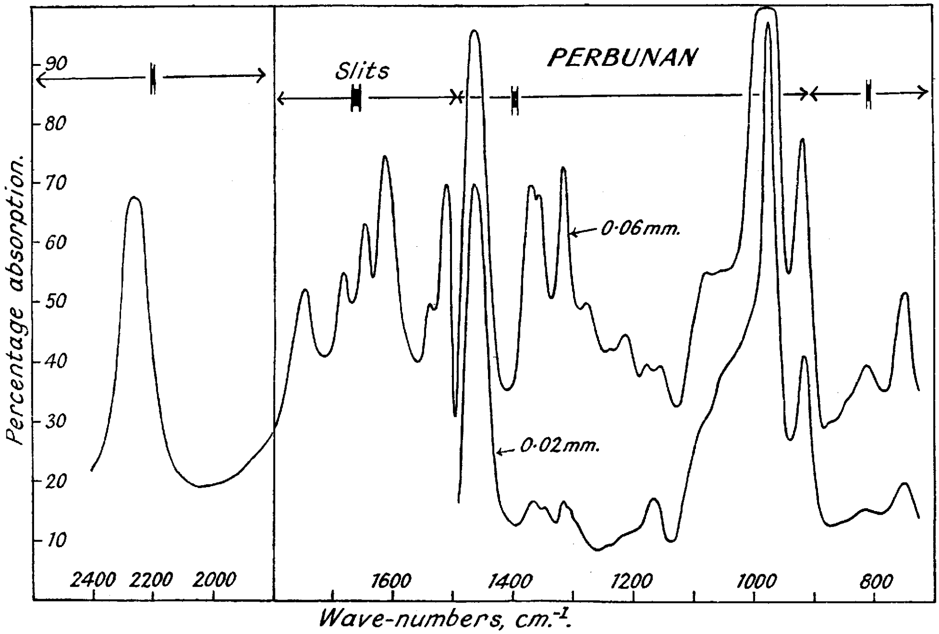
$-CH_2-\underset{CH=CH_2}{CH}-CH_2-\underset{CN}{CH}-$

(II.)

but some by the other course. On the other hand, the interaction of vinyl radicals to form cross linkages would remove the bands due to these radicals.

The sample of perbunan shows a group of bands around 1600, the region of the characteristic C=C bond absorption. This may be consistent with the presence of the different types (I) and (II), and it is also possible that ring closure within the molecule might lead to another slightly different type of C=C bond. The absorption band at 2260 connected with the C≡N linkage vibration is higher with the polymer than with acrylonitrile itself. This might be expected to arise owing to the removal of the neighbouring C=C bond; in methyl cyanide the frequency is about 2250.

Fig. 4.



The presence of the weak band at 1745 cm.$^{-1}$ suggests that a small number of carbonyl groups are present, probably introduced by rapid oxidation while the films were being made. More measurements on other samples and simpler related molecules are needed, however, before more precise deductions about the molecular structure can be made.

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