80. *The Vibrational Spectra of the Vinyl Halides.*

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The infra-red absorption spectrum of vinyl iodide has been measured between 3 and 20μ. The frequencies of the absorption bands have been correlated with data from the Raman spectrum, and the rotational contour of the infra-red bands has been examined. Magnitudes have been assigned to all twelve fundamental frequencies, and the fundamentals of vinyl chloride, bromide, and iodide have been compared. The variation in magnitude of a given type of mode as the mass of the halogen atom changes is discussed.

In a previous paper (*Proc. Roy. Soc.*., in press) we have described the infra-red absorption spectra of vinyl chloride and vinyl bromide, and with the help of data on the Raman spectra a plausible assignment of magnitudes to the normal vibration frequencies has been made. The Raman spectrum of vinyl iodide has already been recorded by Kahovec and Kohlrausch (*Z. physikal. Chem.*, 1940, *B*, **46**, 165). The infra-red spectrum of this substance has now been measured, so that a complete assignment of frequencies can now be made, and the whole array of fundamentals of the vinyl halides can be correlated.

Experimental.

Vinyl iodide was prepared by heating ethylene iodide with a solution of sodium ethoxide in ethyl alcohol (Spence, *J. Amer. Chem. Soc.*, 1933, **55**, 1920). The crude product was washed with dilute sodium bisulphite solution and with water, then dried over calcium chloride and redistilled; b. p. 56°. A small amount of ethyl vinyl ether seemed to be formed as a side reaction. This was removed by washing with cold water and quickly separating off the lower layer of vinyl iodide. The removal of the ether was indicated by the disappearance of its infra-red absorption bands.

For measuring the infra-red spectrum two instruments were used. The first was an automatically recording infra-red spectrometer built in this laboratory, and similar in all essentials to that described in previous papers (Thompson and Harris, *Trans. Faraday Soc.*, in press). A Hilger D 88 spectrometer with fluorite and sylvine prisms, and considerably improved resolving power, produced by the introduction of a Schwarz vacuum thermocouple, was used for the regions 3—7μ and 14—20μ. The absorption cell was a glass tube 20 cm. in length with plane sylvine end-plates. Several pressures of the vapour were used.

Results and Discussion.

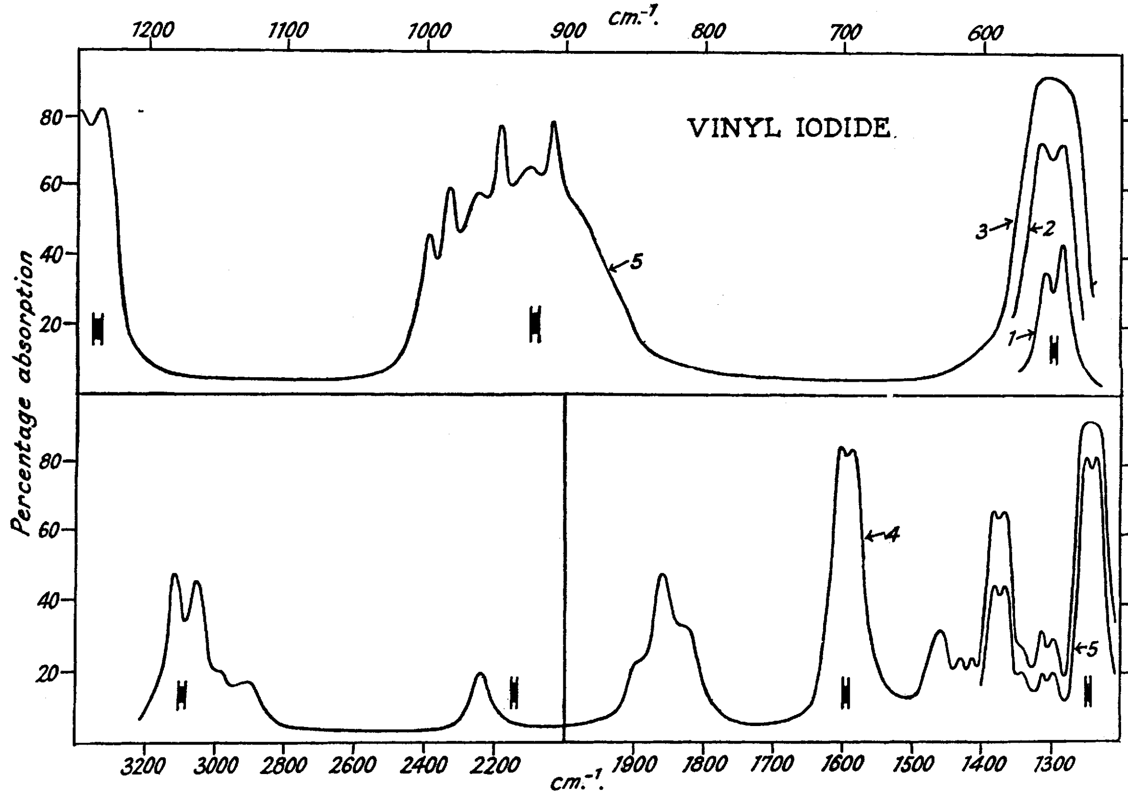
Curves showing the percentage absorption as a function of wave-length are shown in the figure, and the positions of the absorption bands in wave numbers (cm.$^{-1}$) are given in Table I. The Raman displacements recorded by Kahovec and Kohlrausch are given in the same table.

Table I.

Infra-red.	Interpretation.	Raman.
	Fundamental	309
	Fundamental	435
542 557} 550	Fundamental	535
	2 × 435	879
909	Fundamental	
946	Fundamental	
983 997} 990	Fundamental	982
	2 × 550	1098
1235 1250} 1242	Fundamental	1229
1299 1314} 1307	990 + 309	
1345	909 + 435	
1369 1385} 1376	Fundamental	1369
1412 1438} 1425	990 + 435	
1456	909 + 550	
1587 1600} 1593	Fundamental	1581
1825	2 × 909	
1862	909 + 946	
1894	1593 + 309 2 × 946	
	909 + 990	
2242	1242 + 990 Other combinations	
2900	Various combinations	
2995	Fundamental	3003
3050	Fundamental	3062
3115	Fundamental	3092

Vinyl iodide will have nine planar modes of vibration and three non-planar modes, all active in both the Raman and the infra-red spectrum. To a first approximation, the planar vibrations will include three stretching modes, one C=C stretching mode, one C–I stretching mode, and four deformations of the skeleton. These four deformations can be roughly described as a CH_2 deformation, a CH_2 rocking mode, a bending of the $C{=}C{-}I$ skeleton, and a bending of the odd C–H bond. The three non-planar motions will comprise a twisting vibration and two bending motions.

The molecular structure has been examined by Huggill, Coop, and Sutton (*Trans. Faraday Soc.*, 1938, **34** *1518*), who suggested for the molecular parameters: $r_{CC} = 1{\cdot}34$ A., $r_{CI} = 2{\cdot}03$ A., and $C{=}\hat{C}{-}I = 122°$. From these dimensions the three principal moments of inertia will be about 16, 244, and 260 × 10^{-40} g.-cm.^{2}. The molecule therefore approximates closely to being a symmetrical rotator with moments of inertia 16 and 250 × 10^{-40}. In the nomenclature of Gerhard and Dennison (*Physical Rev.*, 1933, **43**, 197), $\beta = 14{\cdot}5$, and in that of Badger and Zumwalt (*J. Chem. Physics*, 1938, **6**, 711), $S = -1{\cdot}0$ and $\rho = 14{\cdot}5$. The *P–R* spacing of a "parallel" type band would then be about 14 cm.$^{-1}$, and the separation of *Q* branches in a "perpendicular" type would be about 3 cm.$^{-1}$. With the resolving power used in the present work the perpendicular bands will be expected to appear as a strong central peak with a shoulder on each side. The least axis of inertia of the molecule will lie obliquely to the main bond directions, but almost parallel to the C–I bond. Some of the planar vibrations will therefore in reality have a hybrid rotational contour; the non-planar vibrations should be "perpendicular" in type.



Path length, 20 *cm.* (1) 20 *mm.*, (2) 50 *mm.*, (3) 140 *mm.*, (4) 140 *mm.*, (5) 25 *mm.*

The observed infra-red bands fall fairly sharply into two types. Those at 909 and 946 have the perpendicular structure, and the others are essentially parallel-type bands in which the *P* and *R* branches are separated by the correct spacing and in which the central *Q* branch is not sufficiently prominent to be properly resolved by means of the present instruments. There are some obvious correlations between the infra-red and the Raman data, as shown in Table I, although, as is often found, the Raman frequencies of the liquid tend to be slightly smaller than the corresponding frequencies with the vapour in the infra-red. When both sets of results are considered together with those given previously for the other vinyl halides, the identification of normal frequencies is seen clearly to be the following: 309, 435, 535, 909, 946, 990, 1229, 1376, 1593, ∼3000, ∼3060, ∼3110.

In Table II the frequencies of all the vinyl halides so far examined are collected together. It is hoped shortly to complete the series by measuring the infra-red spectrum of vinyl fluorides; the corresponding data for vinyl cyanide are in course of publication (Thompson and Torkington, this vol.).

Attention should be drawn to one rather striking feature of the correlations in Table II. With three exceptions there is a definite decrease in the frequency of a given vibration as the mass of the halogen atom increases. These three vibrations, ν_7, ν_{11}, and ν_{12}, each involve the deformation of C–H bonds, and in each case there is a small, though probably real, increase in frequency as the mass of the halogen is increased. This may

TABLE II.

Vinyl halides, $CH_2{=}CH{-}X$.

	Type of vibration.		Chloride.	Bromide.	Iodide.
Planar	C–H stretching	ν_1	3030	3014	3000
	C–H stretching	ν_2	3080	3076	3060
	C–H stretching	ν_3	3130	3100	3110
	C=C stretching	ν_4	1610	1605	1593
	C–X stretching	ν_5	724	615	535
	C–X deformation	ν_6	395	345	309
	CH_2 deformation	ν_7	1370	1377	1376
	deformation	ν_8	1030	1008	990
	deformation	ν_9	1280	1262	1229
	twisting	ν_{10}	622	497	435
Non-planar	C–H deformation	ν_{11}	895	902	909
	C–H deformation	ν_{12}	940	940	946

suggest that electron drifts are caused by the halogen atom, leading to alterations in the bending force constants. If the C–H bonds are stiffened on passing from chlorine to iodine, we should expect an increase in the C–H stretching frequencies, but this does not seem to occur.

The overtone and combination bands found in the infra-red and the Raman spectra of vinyl iodide are very satisfactorily explained by using the above fundamentals, as shown in Table I. In the case of vinyl chloride and bromide, it was possible just to resolve some of the *Q* branches in the bands at about 900 cm.$^{-1}$. The slightly smaller spacing with vinyl iodide has made these not quite resolvable when using the above instruments.

The assignment of fundamentals with the three vinyl halides given above seems sufficiently certain to be used in calculating the thermodynamic properties of these molecules. These calculations will be given in a later paper.

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