

## The Vibrational Spectra of Some Metal Borohydrides

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# Intrinsic Viscosity of Linear Polymers

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December 28, 1948

RECENT theoretical developments have led to the proposal of several new expressions relating the intrinsic viscosity of a linear polymer to its molecular weight and structure.<sup>1-4</sup> The following simple interpolation formula, which gives results similar to these, was independently proposed by the author at these laboratories in May, 1947:

$$[\eta] = K_1 Z / (1 + K_2 Z^3), \quad (1)$$

where  $Z$  is the number of links in the polymer chain and in the terminology of Kirkwood and Riseman<sup>5</sup>

$$K_1 = (\xi/\eta_0)(N/3600\text{Mo})b^2, \quad (2)$$

$$K_2 = (\xi/\eta_0)/15\pi\alpha^2b. \quad (3)$$

This expression was chosen because it is the simplest one which at low values of  $Z$  approximates the Staudinger equation in accordance with theory<sup>6-8</sup> and experiment,<sup>9,10</sup> and at high values of  $Z$  approximates the proportionality to  $Z^3$  first suggested by Kuhn.<sup>11</sup> The value of  $K_1$  was taken in accordance with the theory of the Staudinger equation, and the value of  $K_2$  was determined from the consideration that at high values of  $Z$  the solution of convoluted polymer molecules with solvent trapped within their coils should approximate a suspension of Einstein spheres with effective diameter  $D$  equal to  $\alpha R$ , where  $R$ , the root mean square distance between the ends of the chain, is equal to  $bZ^{1/2}$ .

Equation (1) is a remarkably good approximation to the theoretical formula of Kirkwood and Riseman, in which the term  $(1 + K_2 Z^3)^{-1}$  is replaced by

$$\frac{6}{\pi^2} \sum_{k=1}^{\infty} k^{-2} [1 + \lambda_0 (Z/k)^3]^{-1}. \quad (4)$$

The latter expression for values of  $Z$  up to the order of  $10^5$  is approximately equal to  $(1 + 0.76\lambda_0 Z^3)^{-1}$ . The factor 0.76 is correct for  $\lambda_0 Z^3 = 1.5$  and is in error by about 6 percent at the extremes of the range given. It is doubtful whether the precision with which the molecular weight distributions of polymer fractions can be measured is sufficient to provide a distinction between the expression (4) and its approximation. Substituting for  $\lambda_0$  (3) we obtain

$$K_2 = (\xi/\eta_0)0.76/(6\pi^3)^{1/2}b. \quad (5)$$

By comparison with Eq. (3) we obtain 0.72 for the theoretical value of  $\alpha$ , the factor relating the diameter of the equivalent Einstein sphere to the root mean square distance between the chain ends.

Experimental data may readily be fitted to Eq. (1) by plotting  $M/[\eta]$  vs.  $M^{1/2}$  where  $M$  is the molecular weight of the polymer. Osmotic data obtained by the author for acetone solutions of seven fractions of polymethacrylonitrile covering the range 90,000 to 950,000 in  $M_n$  are in accordance with Eq. (1) with  $K_1 = (2.66 \pm 0.21) \times 10^{-4}$  (g/100 ml)<sup>-1</sup>;  $K_2 = (9.4 \pm 1.5) \times 10^{-3}$ . From the ratio of these constants and the value 33.5 for Mo, the mean molecular weight per chain-element, we obtain  $\alpha b = 5.0 \pm 0.3A$ . The value 7.7A for  $b$  was obtained from measurements of the asymmetry of light-scattering by the solutions. Thus the

experimental value for  $\alpha$  is  $0.65 \pm 0.04$ , in approximate agreement with the Kirkwood-Riseman theory. The value of  $\xi/\eta_0$  is 0.9A; thus the effective Stokes' law radius of a chain-element is computed to be 0.05A, comparable to the abnormally low values reported for polystyrene.<sup>3,4</sup>

Weight-average molecular weights computed from light-scattering data were in reasonable agreement with the osmotic molecular weights in the range 90,000 to 400,000; above this range  $M_w$  was larger than  $M_n$  by a factor which increased rapidly as  $M_n$  increased and was of the order of 2 at  $M_n = 10^6$ . In this range and above, the plot of  $M_w/[\eta]$  vs.  $M_w^{1/2}$  deviates rapidly from the similar plot involving  $M_n$ , in the direction of higher values of  $M_w/[\eta]$ . These effects suggest that in the higher molecular-weight range a portion of the solute molecules aggregates into large clusters; the effect of clustering on the value of  $[\eta]$  will be small if the volume of the equivalent Einstein sphere of a cluster is not too greatly different from the sum of the volumes of the equivalent spheres of its constituent solute molecules.

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## The Vibrational Spectra of Some Metal Borohydrides\*

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December 27, 1948

THE infra-red spectra of aluminum, lithium, and sodium borohydrides have been studied by W. C. Price, that of beryllium borohydride by H. C. Longuet-Higgins, and the Raman spectrum of aluminum borohydride by T. F. Young and B. Rice. Details will be published shortly in separate papers, but we here give the main results so far obtained.

TABLE I. Vibrational frequencies in borohydrides.

	B <sub>2</sub> H <sub>6</sub>		Al(BH <sub>4</sub> ) <sub>3</sub>		Be(BH <sub>4</sub> ) <sub>2</sub>	LiBH <sub>4</sub>	NaBH <sub>4</sub>
	I.R. <sup>a</sup>	R. <sup>b</sup>	I.R.	R.	I.R.	I.R.	I.R.
(a)	974 1175 1283	1008 1180	978 1114	977 1122 1156	940 to 1090	1096	1080 (a)
(b)	1604 1850(?) 1984	2102	1450 to 1550 2031 2154	1502 2082	1530 1985 2060 2165	2245 to	2150 to
(c)	2522 2614	2489 2523	2493 2559	2480 2553	2515 2630	2404	2380 (c)

\* See reference 1.  
\*\* See reference 2.

The frequencies of the principal bands occurring in the range 900–2700  $\text{cm}^{-1}$  are shown in Table I, which includes the most recent data on  $\text{B}_2\text{H}_6$  for comparison.<sup>1,2</sup> The frequencies in class (a) are attributed to B-H deformations, and those in class (c) to ordinary B-H stretching modes. The presence of strong absorption around 1500 and 2000  $\text{cm}^{-1}$  in the Be and Al compounds is very strong evidence that these molecules have bridged structures, as suggested already by one of us.<sup>3</sup> In these two molecules there are two groups of frequencies in the range (b); by analogy with diborane, these are probably associated with motion of the bridge hydrogen atoms parallel and perpendicular to the bridge axis, respectively. However, when we pass to the more ionic lithium and sodium borohydrides, these frequencies respectively degenerate into bending and stretching frequencies of the  $\text{BH}_4^-$  ion.

The B-H stretching frequencies in class (c) are probably associated with terminal  $\text{BH}_2$  groups in the Al and Be compounds, but until detailed assignments can be made it would probably be wiser not to draw conclusions as to the relative force constants in these molecules.

Our warmest thanks are due Professor R. S. Mulliken for constant encouragement and help in many ways.

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<sup>2</sup> T. F. Anderson and A. B. Burg, *J. Chem. Phys.* **6**, 586 (1938).

<sup>3</sup> H. C. Longuet-Higgins, *J. Chem. Soc.*, 139 (1946).

### The Infra-Red Spectra of Borine Carbonyl and Tetramethyldiborane\*

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December 27, 1948

THE infra-red spectra of borine carbonyl and of tetramethyldiborane have been obtained in the interval 2 to 25 microns with a Perkin-Elmer spectrometer.

In the spectrum of borine carbonyl ( $\text{H}_3\text{BCO}$ ) the coarse structures of two bands (a strong one at 2440 and a weak one at 810  $\text{cm}^{-1}$ ) have been resolved. In each case the structure is typical of perpendicular-type bands of a symmetric-top molecule, and successive maxima show a distinct intensity alternation of the type strong, weak, weak, strong, . . . which is to be expected in the case of a threefold symmetry axis. These results thus indicate a molecular structure with symmetry  $C_{3v}$ , in agreement with Bauer's electron-diffraction results<sup>1</sup> and with the conclusions of Gordy, Ring, and Burg<sup>2</sup> from microwave rotation spectra. The spacing between adjacent  $Q$ -maxima of the perpendicular bands is 6.7  $\text{cm}^{-1}$  in the case of the 2440- $\text{cm}^{-1}$  band and 3.1  $\text{cm}^{-1}$  for the 810- $\text{cm}^{-1}$  band. Because of the large but uncertain amount of Coriolis coupling which is present, it is difficult to compare these values with the value 8.2  $\text{cm}^{-1}$  to be expected from Bauer's data in the absence of such coupling. The band at 2440  $\text{cm}^{-1}$  can be ascribed to the degenerate B—H stretching vibration, and a

very strong parallel band at 2164  $\text{cm}^{-1}$  is due probably to the corresponding symmetrical vibration.

The spectrum of tetramethyldiborane provides further evidence in support of the bridge structure for diborane ( $\text{B}_2\text{H}_6$ ). The complete absence of other than weak bands at frequencies greater than 1700  $\text{cm}^{-1}$  indicates there are no B—H bonds of the type which gives rise to the very strong bands at 2522 and 2614  $\text{cm}^{-1}$  in diborane;<sup>3</sup> trimethyldiborane, which was also investigated, has, on the other hand, a single strong band at 2509  $\text{cm}^{-1}$ . The strongest band in the tetramethyldiborane spectrum lies at 1602  $\text{cm}^{-1}$  and is almost certainly the analog of the bridge-hydrogen band of diborane at 1604  $\text{cm}^{-1}$ .<sup>3</sup> A weak band at 1968  $\text{cm}^{-1}$  may similarly correspond to the bridge-hydrogen band of  $\text{B}_2\text{H}_6$  at 1984  $\text{cm}^{-1}$ . The analog of the third bridge-hydrogen vibration (probably 1283  $\text{cm}^{-1}$  in diborane), if present, is probably obscured by numerous strong methyl bands in the interval 900 to 1400  $\text{cm}^{-1}$ .

Detailed reports on these spectra and on those of boric acid and dimethyl boric acid will be published later.

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<sup>1</sup> S. H. Bauer, *J. Am. Chem. Soc.* **59**, 1804 (1937).

<sup>2</sup> W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.* **74**, 1191 (1948).

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### Infra-Red Absorption Spectra of Organic Compounds

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December 27, 1948

THE infra-red absorption spectra of some derivatives of methane, ethane, and benzene have been measured in the region from 22 to 39  $\mu$ . The method of measurement in this spectral region has been previously described.<sup>1</sup> All the compounds were measured in the liquid state and the cells were from 0.2 to 1.6 mm in thickness. The observed bands, all of medium or of low intensity, are listed in Table I. The wave numbers listed for the regions of maximum absorption are accurate to about  $\pm 2 \text{ cm}^{-1}$ . The accuracy is sufficient for survey work. One source of error arises from changes in the temperature of the prism. The temperature coefficient of the index of refraction for the TlBr-I prism is  $-0.00016$  as measured in the visible region. Changes in refractive index of these crystals over a period of time have also been observed. Hyde<sup>2</sup> has reported changes in the index of refraction of 0.0048 over a period of a few months. For work of high accuracy the instrument should be calibrated before and after each substance is measured. Methods of annealing recently developed by the Engineer Research and Development Laboratories give promise of producing more stable prisms than those which have been available.

Most of the compounds listed in Table I have been measured in the NaCl and KBr regions. Many bands appear in the region of wave-lengths from 2 to 22  $\mu$ . Carbon tetrachloride in cell thicknesses of 1.0 mm has been investigated with a KBr prism. Bands have been found at 17.59, 18.82, 20.73, and 22.43  $\mu$ . These have all been interpreted in