244. *Raman Effect of the Borohydride Ion in Liquid Ammonia.*

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The Raman spectra of solutions of potassium borohydride in liquid ammonia at approximately $-40°$ show, in addition to the frequencies of the solvent, a single polarized shift, $\Delta\nu = 2270 \pm 3$ cm.$^{-1}$, which is attributed to the totally symmetric vibration ν_1 of the regular tetrahedral borohydride (BH_4^-) ion. It is pointed out that, for the isoelectronic species BH_4^-, CH_4, and NH_4^+, the bond-stretching force constant increases in the order given, the increase in going from borohydride ion to methane being markedly greater than that in going from methane to ammonium ion.

THE species borohydride ion, methane, ammonium ion form a simple isoelectronic set, the study of which may give evidence on the question of the dependence of bond properties (force constants, etc.) upon the charge of the central nucleus. Only for methane and ammonium ion have Raman spectra been reported. We have now investigated the borohydride ion in solutions of the potassium salt in liquid ammonia. The choice of solvent was dictated by the instability of the ion in water.

We have observed, in addition to the known spectrum of the solvent, one Raman frequency, $\Delta\nu = 2270$ cm.$^{-1}$, excited both by Hg 4358 Å and by Hg 4046 Å lines. Our experiments show that this frequency is polarized; and it may therefore be confidently assigned to the symmetrical " breathing " frequency $\nu_1(A_1)$ of the regular tetrahedral ion, BH_4^-.

The infrared spectrum of the borohydride ion in solid sodium borohydride, as reported by Price,[1] shows two absorptions: one fairly sharp at 1080 cm.$^{-1}$ and the other a broader band centred at 2270 cm.$^{-1}$. Clearly these are to be identified with the only two infrared-active fundamentals $\nu_4(F_2)$ and $\nu_3(F_2)$, respectively. The corresponding values for the borohydride ion in the lithium salt are [1] 1096 and 2320 cm.$^{-1}$. Frequencies obtained from crystalline salts will be expected to differ somewhat from those for the ion in solution; but it is clear that ν_3 and ν_1 are approximately equal. This is not unexpected in view of the large mass of the boron atom as compared with that of the hydrogen atom. According to the simple valency force field for a regular tetrahedral species, XY_4, ν_3 is always greater than ν_1 but approaches equality with it as the mass ratio m_X/m_Y becomes larger. Observations for a range of molecules and ions bear this out quite well; but it is found that ν_3 may even become slightly less than ν_1 when m_X/m_Y is large, *e.g.*[2] for AlH_4^-.

The approximate equality of ν_3 and ν_1 for the borohydride ion probably makes it impossible to observe the former as a distinct Raman line. It may be noteworthy that, although our experiments were not capable of giving the degree of depolarization exactly, they suggest that $\Delta\nu$ 2270 cm.$^{-1}$ is not completely polarized. This would be in accord with its being mainly due to the completely polarized ν_1 but containing also a contribution from the depolarized shift ν_3.

The other two fundamentals, ν_2 and ν_4, are also permitted in the Raman effect; but they are expected to be very weak, and it is not surprising that we have not observed them. Neither ν_2 nor ν_4 has been observed for the isoelectronic ammonium ion in solution, despite the facts that the concentration of this species in water can be made much greater than for the borohydride ion in liquid ammonia, and that aqueous solutions are much easier to investigate. So also for the isoelectronic methane molecule, ν_2 and ν_4 appear only very feebly even for liquid methane,[3] while ν_4 has never been detected for the gas. The feebleness of these two frequencies should therefore make their observation for the borohydride ion very difficult; but in addition, the value of $\nu_4 = 1080$ from the infrared spectrum is such that its Raman line would be masked by the weak band of liquid ammonia at 1075—1090 cm.$^{-1}$. As to ν_2, which is inactive in infrared absorption, we may use the other three frequencies and calculate an approximate value for it by means of a three-parameter force

[1] Price, *J. Chem. Phys.*, 1949, **17**, 1044.
[2] Lippincott, *ibid.*, p. 1351.
[3] Crawford, Welsh, and Harold, *Canad. J. Phys.*, 1952, **30**, 81.

field. Using the orbital valency field with repulsion between non-bonded atoms [4] and taking the exponent n in the repulsion term as equal to 7, we obtain $\nu_2 = 1065$ cm.$^{-1}$. Thus ν_2 is approximately equal to ν_4, as well as ν_3 being approximately equal to ν_1. The frequencies for the borohydride ion are given in Table 1, together with those of the isolectronic methane molecule and ammonium ion (see Herzberg [5]). It is seen that (i) each

TABLE 1. *Vibrational frequencies of isoelectronic species.*

	$\nu_1 (A_1)$	$\nu_2 (E)$	$\nu_3 (F_2)$	$\nu_4 (F_2)$
BH_4^-	2270	(1065 calc.)	2270	1080
CH_4	2914	1526	3020	1306
NH_4^+	3033	1685	3134	1397

of the frequencies increases regularly from BH_4^- to NH_4^+, *i.e.* as the central positive charge increases; and (ii) for each frequency the increase from BH_4^- to CH_4 is considerably greater than that from CH_4 to NH_4^+.

The changes of the frequencies shown in Table 1 imply corresponding changes in the force constants. Confining our attention to the " breathing " frequencies, ν_1, and using the simple valency force field (without repulsion term) as a sufficiently good approximation for the purposes of this discussion, we obtain the values of the bond-stretching force constant k given in Table 2.

TABLE 2. *Stretching force constants of isoelectronic species.*

	BH_4^-	CH_4	NH_4^+	$AlCl_4^-$	$SiCl_4$	PCl_4^+
ν_1 (cm.$^{-1}$)	2270	2914	3033	349	424	451
$10^{-5}k$ (dynes/cm.)	3·06	5·04	5·46	2·54	3·75	4·24
% increase of k relative to preceding value ...	—	64	8	—	48	13

It is seen that the percentage increase of k in going from BH_4^- to CH_4 is markedly greater than that in going from CH_4 to NH_4^+. This may be connected with the fact that the percentage increase of the central positive charge in going from boron to carbon (20 reckoned on atomic numbers or 33·3 if the two $1s$ electrons are included) is greater than that in going from carbon to nitrogen (16·7 or 25, respectively).

The only other analogous isoelectronic set for which data are available appears to be $AlCl_4^-$, $SiCl_4$, and PCl_4^+. The first of these has been investigated by Gerding and Houtgraaf.[6] The species PCl_4^+, which occurs with PCl_6^- in solid phosphorus pentachloride, has been recently studied by the same workers.[7] For data for $SiCl_4$ see Herzberg.[5] The values of ν_1 and the stretching force constants k are included in Table 2. From a comparison with the corresponding data for BH_4^-, CH_4, and NH_4^+ it is seen that both isoelectronic sets show very similar features. In particular, we note the much larger percentage increase of k in going from the negative ion to the neutral molecule, as compared with going from the latter to the positively charged ion.

EXPERIMENTAL AND RESULTS

Purification of Materials.—The ammonia was generated from the solution, d 0·88, dried, and liquefied by cooling to $-80°$. It was purified by distillation *in vacuo*. The sample of potassium borohydride used was placed at our disposal by Dr. R. E. Richards. Originally supplied by May and Baker, it had been purified by repeated recrystallisation from liquid ammonia.

Preparation of Solutions.—Liquid ammonia was distilled on to solid potassium borohydride *in vacuo* and left a sufficient time at *ca.* $-60°$. The solution so obtained was filtered through a sintered-glass disc at $-60°$ in a suitable all-glass apparatus, care being taken to avoid contact with grease. Finally the solution was poured into the pre-cooled Raman tube through a pre-cooled funnel. Evaporation of ammonia during this process was negligible. The concentration of the solutions used was about 2M.

[4] Heath and Linnett, *Trans. Faraday Soc.*, 1948, **44**, 561, 878.
[5] Herzberg, " Molecular Spectra and Molecular Structure," Van Nostrand, New York, 1945, Vol. 2, p. 167.
[6] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1953, **72**, 21.
[7] *Idem, ibid.*, 1955, **74**, 5.

Photographing of Raman Spectra.—The apparatus was that previously described by Rolfe and Woodward [8] (Toronto-arc excitation, Hilger E 518 spectrograph), slightly modified to take a Raman tube of about 4 ml. capacity. Excellent spectra were obtained with exposure times up to 2 hr., the sample being maintained throughout at approximately $-40°$ by a stream of cold air passing between the Raman tube and a surrounding unsilvered Dewar sleeve. The plates were Kodak Special Scientific (emulsion Oa, sensitivity G). The use of a primary filter of Rhodamine 6 G.D.N. extra was found to be advantageous. The state of polarization of the Raman lines was determined qualitatively by the method of polarized incident light, suitable polaroid cylinders surrounding the Raman tube being used.

Results.—The following Raman spectrum was observed for the solvent, both alone and in the solutions : 1075—1090 cm.$^{-1}$ (weak band), 3214 cm.$^{-1}$ (very strong, polarized), 3298 (very strong, polarized), and 3390 (very strong, depolarized). The weak band was excited by the Hg 4358 Å line only; the other shifts were excited by both Hg 4358 and Hg 4046 Å irradiations. The frequencies were measured in the usual manner, a copper arc being used as standard. The limits of error are estimated to be ± 3 cm.$^{-1}$ for strong lines. The results are in agreement with those of previous workers.[9]

For the solutions of potassium borohydride we observed one Raman frequency, excited by the Hg 4358 Å (medium intensity) and also by the Hg 4046 Å line (weak). The measured $\Delta\nu$ is 2270 cm.$^{-1}$. This frequency was absent for the solvent alone. Spectrograms taken with polarized incident light showed clearly that the line is polarized, but suggest that the degree of polarization is probably greater than zero.

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[8] Rolfe and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1030.
[9] Kinumaki and Aida, *Sci. Reports Tohuku Univ.*, 1954, *A*, **6**, 186.