Vibrational analysis of the tetrahydroborate and tetradeuterioborate anions, using the data from aqueous solutions, were carried out by the methods outlined in the accompanying paper.[2] The B–H bond length adopted for these calculations, 1.255 Å, has been determined by broad-line nmr.[11] The results, which are summarized in Tables IV and V, show close agreement with those obtained for BH_4^- in liquid ammonia. Apparently either set of force constants may be taken as a reasonable representation of the BH_4^- anion.

Experimental Section

The sensitivity of the compounds to air and moisture required that all manipulations be done in an inert atmosphere of dry N_2, in a drybox, Schlenk line, or in a chemical vacuum line. Most of the sampling and spectroscopic techniques have been described in the accompanying paper,[2] but where differences exist the procedure is given below.

$LiBH_4$ (Alfa Inorganics and ROC/RIC, 99% D) was used without further purification. Diethyl ether (Allied Chemical, anhydrous), tetrahydrofuran (Matheson Coleman and Bell and Fisher Scientific), 1,2-dimethoxyethane (Mallinckrodt) and bis(2-methoxyethyl) ether (Aldrich) were dried and distilled from $LiAlH_4$ or benzophenone ketyl and stored over LiH or Na metal. Pyridine (Baker) was dried and distilled from CaH_2 and isopropyl alcohol (Matheson Coleman and Bell) was similarly purified from Mg metal. D_2O (Bio-Rad) and deionized H_2O were used for the aqueous samples for Raman and infrared work; aqueous NaOD solutions were made by dissolving Na metal into D_2O. Infrared spectra of aqueous solutions were run as thin films on IRtran-2 plates prepared in a glove bag under N_2.

Acknowledgment. This research was initially supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and more recently by a grant from the NSF. Amy Shirk was an NIH Predoctoral Fellow.

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Raman and Infrared Spectra of Tetrahydroaluminate, AlH_4^-, and Tetrahydrogallate, GaH_4^-, Salts

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Abstract: Raman and infrared data of MH_4^- (M = Al, Ga) with monovalent cations Li^+, Na^+, and $(C_2H_5)_4N^+$ for the aluminum salts and Li^+, Na^+, and K^+ for the gallium salts are reported. The data were collected on samples in the solid state and/or ether solutions (diethyl ether, dimethyl ether, tetrahydrofuran, 1,2-dimethoxyethane). Solution data for AlH_4^- are interpreted in terms of three distinct species existing in the various solutions, tightly and loosely bound aggregates and ion pairs. In some solutions, the latter two species exist together in a temperature- and concentration-dependent equilibrium. There is strong evidence against solvent coordination to the AlH_4^- moiety as previously postulated. The previous assignment of $\nu_2(E)$ of AlH_4^- in diethyl ether is discounted and alternative assignments for it are considered. Tentative assignments for the remaining three vibrational modes are made, and a vibrational analysis was carried out. The A_1 stretching frequencies and associated force constants for the group IIIa tetrahydrides show an unusual trend: $BH_4^- > GaH_4^- > AlH_4^-$.

The present work on the vibrational spectra of AlH_4^- and GaH_4^- was designed to elucidate trends in bonding for main group III hydrides. The vibrational spectrum of GaH_4^- has not been studied except for one brief mention of infrared data[1] while that of AlH_4^- has been considered by several workers.[2–6] However, the variation in the AlH_4^- vibrations in the different solvent systems has led to contradictory interpretations in the literature. From the work of Lippincott[2] and of D'Or and Fuger[3] it is known that AlH_4^- is essentially tetrahedral; the Raman and infrared spectra of $LiAlH_4$ in diethyl ether (Et_2O) confirmed such an assignment. By contrast, infrared studies of AlH_4^- in more strongly coordinating ethers such as tetrahydrofuran (THF) and dimethoxydiethyl ether (diglyme) have been interpreted in terms of a six-coordinated $AlH_4(OR_2)_2^-$ moiety.[4,5] Even with $LiAlH_4$ in diethyl ether solution it has been proposed that a five-coordinate species $AlH_4(OR_2)_2^-$ exists.[4] In the Russian work[5] the argument in favor of ether coordination to aluminum is based on the idea that $LiAlH_4$ in diethyl ether displays a spectrum most characteristic of AlH_4^-, and, therefore, the lower Al–H stretching frequencies observed in other solvents arise from ether coordinated AlH_4^-. The German group,[4] however, uses ν_{Al-H} of amine–AlH_3 complexes as a standard for four-coordinated aluminum hydrides.

In the solid state, a single-crystal X-ray diffraction study of $LiAlH_4$[7] shows that the AlH_4^- tetrahedra are slightly distorted. This is in agreement with the splittings observed in the vibrational spectrum of the solid.[5] Claims for a tetrahedral AlH_4^- moiety in the solid state have been made by Semenenko, *et al.*,[6] from the Raman and infrared data for $[R_4N][AlH_4]$, where R = CH_3 and C_2H_5.

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(1) (a) L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *Syn. Inorg. Metal-Org. Chem.*, 1, 37 (1971); (b) L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *J. Gen. Chem. USSR*, 41, 2722 (1971).

(2) E. R. Lippincott, *J. Chem. Phys.*, 17, 1351 (1949).

(3) L. D'Or and J. Fuger, *Bull. Soc. Roy. Sci. Liege*, 25, 14 (1956).

(4) R. Dautel and W. Zeil, *Z. Elektrochem.*, 64, 1234 (1960).

(5) T. G. Adiks, V. V. Gavrilenko, L. I. Zakharkin, and L. A. Ingat'eva, *Zh. Prikl. Spektrosk.*, 6, 806 (1967).

(6) K. N. Semenenko, A. P. Chavgun, V. B. Polyakova, A. L. Dorosinskii, and A. A. Plakhtii, *Russ. J. Inorg. Chem.*, 15, 1504 (1970).

(7) N. Sklar and B. Post, *Inorg. Chem.*, 6, 669 (1967).

Table I. Raman and Ir Data for AlH_4^- (in cm^{-1})[a,b]

	Raman	Ir
$LiAlH_4$–Et_2O	1793 s, p; 1739 w, dp; 763 w (0.6–2.8 *M*)	1740 m; 766 s (0.25 *M*)
$LiAlD_4$–Et_2O	1285 s, p; 546 w (1.6–4.2 *M*)	
$LiAlH_4$–Me_2O	1767 s, p; 1700 w, dp; 764 w (>0.4 *M*)	
$LiAlD_4$–Me_2O	1268 s, p; 1241 w, dp; 546 w	
$NaAlH_4$–Me_2O	1757 s, p; 1702 w, dp; 767 w; 755 sh (~0.5 *M*)	
$NaAlD_4$–Me_2O	1263 p (~1 *M*)	
$LiAlH_4$–THF	1762[d] s, p; 1730[e] s, p; 1692[d] w, dp; 1653[e] w, dp; 764 w (0.1–1 *M*)	1693[d] m; 1652[e] sh; 763 s (0.06–0.4 *M*)
$NaAlH_4$–THF	1755 s, p; 1693 w, dp; 766 w (0.8 *M*)	1692 m; 1652 sh; 1593 w; 755 s; 764 sh (0.1 *M*)
$NaAlD_4$–THF	1257 p (1 *M*)	
$LiAlH_4$–Glyme	1757[d] m, p; 1731[e] s, p; 1648[e] w, dp; 766 w (0.05–0.5 *M*)	
$NaAlH_4$–Glyme	1754[d] s, p; 1732[e] p; 1654[e] w, dp; 764 w (0.25 *M*)	
$[Et_4N][AlH_4](s)$	1757 s; 1684 m; 772 m	1671 m; 760 s
$[Et_4N][AlD_4](s)$	1256 s; 1221 sh; 557 w; 549 w	1219 m; 562 s
$LiAlH_4(s)$[c]	1838 s; 1759 m; 1724 w; 880 w; 783 m; 675 w	1800 sh; 1780; 1645; 890; 810 sh; 700; 465
$NaAlH_4(s)$	1763 s; 1686 ms; 824 mw; 767 w	1678 s; 901 w; 752 s; 688 m

[a] Key: s = strong, m = medium, w = weak, sh = shoulder, p = polarized, dp = depolarized. [b] Concentrations specified in "Results" section. [c] Ir data from A. E. Shirk, 1972, unpublished results. [d] Intensity decreases at lower temperature and/or higher concentration, [e] Intensity increases at lower temperature and/or higher concentration.

Results

Because of the high reactivity of AlH_4^- and GaH_4^- many polar solvents could not be employed; thus the present work was performed with diethyl ether, tetrahydrofuran, dimethyl ether (Me_2O), and 1,2-dimethoxyethane (glyme) as solvents. Ethers provide a reasonable spectral window in the region of Al–H stretching vibrations (1600–1800 cm^{-1}) but sometimes interfere in the deformation region (700–800 cm^{-1}). The GaH_4^- vibrations occur in approximately the same regions as those of AlH_4^-.

Li^+ and Na^+ salts of AlH_4^- were used for the solution spectra, and these and $[(C_2H_5)_4N][AlH_4]$ were studied in the solid state. The Raman and infrared results for AlH_4^- and GaH_4^- are tabulated in Tables I and II, respectively, and some of the systems are also discussed below. For a tetrahedral MX_4 molecule four vibrations are allowed: $\nu_1(A_1)$ and $\nu_2(E)$, the symmetric stretch and deformation, respectively, and $\nu_3(F_2)$ and $\nu_4(F_2)$, the asymmetric stretch and deformation. All four vibrations are Raman active while only the two F_2 modes are infrared active.

Table II. Raman and Infrared Data for GaH_4^- Species (in cm^{-1})

	Raman	Ir
$LiGaH_4$–Et_2O	1830 s, p; 1802 sh, dp	
$LiGaH_4$–Me_2O	1807 s, p; 1766 w, dp; 794 w	
$NaGaH_4(s)$		1760 s, broad, 1720 w; 715 s
$KGaH_4(s)$	1799 s; 1774 sh; 1724 m; 830 s; 765 w	~2030 w; 1773 m; 1720 s; 833 sh; 821 sh; 783 sh; 721 s

$LiAlH_4$ in Diethyl Ether. Raman and infrared spectra of $LiAlH_4$ in Et_2O collected in our laboratory are consistent with these earlier reports,[2,3] with one major exception. The assignment of ν_2 to a 799-cm^{-1} band in the Raman spectrum is erroneous; this band is actually a solvent band as is discussed below. This conclusion is based on the presence of the 799-cm^{-1} feature in the Raman spectra of $LiAlD_4$–Et_2O and pure Et_2O (Figure 1). No other bands which could be attributed to the symmetric AlH_4^- (or AlD_4^-) deformation vibration were observed.

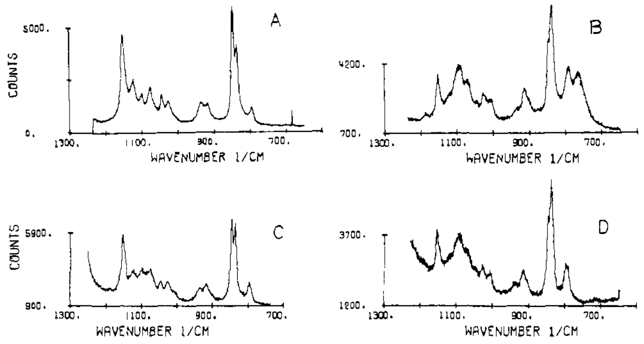

Figure 1. Raman spectra of (A) Et_2O, (B) 2.6 *M* $LiAlH_4$ in Et_2O, (C) 1.6 *M* $LiAlD_4$ in Et_2O, and (D) 2.5 *M* $LiAlD_4$ in Et_2O.

No changes in frequencies were observed with changes in concentration (0.6–2.8 *M* for $LiAlH_4$ and 1.6–4.2 *M* for $LiAlD_4$) and temperature (23, −35, and −83° for 0.6 *M* solution) in the Raman spectra. These frequencies were consistent with those observed in the 0.25 *M* infrared spectrum (Table I). D'Or and Fuger[3] report that the AlH_4^- bands in the infrared spectra remain unchanged in the concentration range 0.03–3.4 *M* which is consistent with our Raman findings; however, Gorin, *et al.*,[8] have recently reported that they find that these infrared bands move to lower frequencies with increasing concentrations (0.41–1.72 *M*) of $LiAlH_4$. Of the two infrared studies we have greater confidence in that of D'Or[3] owing to the agreement with our Raman studies and also owing to reactivity of the hydride solution with the window material, KBr, employed by Gorin and coworkers.

$LiAlH_4$ in THF. Only the infrared data of $LiAlH_4$ in THF have been reported previously; the spectrum supposedly consists of two bands at *ca.* 763 and 1674 cm^{-1}. The latter stretching frequency was thought to indicate that THF is coordinated to the Al atom.[4,5] The infrared data collected in this laboratory on 0.06 and 0.4 *M* solutions show that this 1674-cm^{-1} band is resolvable into an intense band at 1693 cm^{-1} and a shoulder at 1652 cm^{-1}. The Raman spectra (0.1–1 *M*) contain two polarized features at 1762 and 1730 cm^{-1} and two weaker depolarized bands at 1692 and

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[8] P. Gorin, J. C. Marchon, J. Tranchant, S. Kovacevic, and J. P. Marsault, *Bull. Soc. Chim. Fr.*, 3970 (1970).

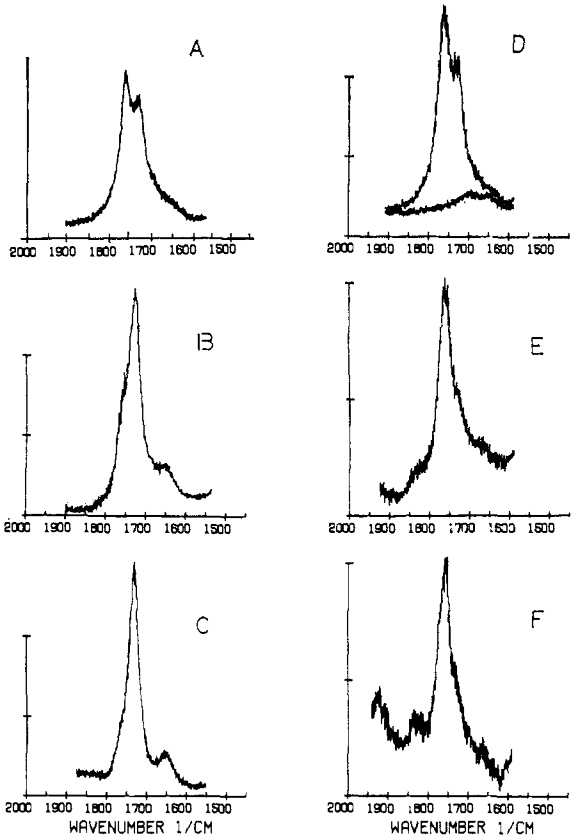

Figure 2. Raman spectra for the Al–H stretch region of $LiAlH_4$ in THF. All spectra are of the $z(y,y)x$ orientation except for the lower inset of (D), which is of the $z(y,z)x$ orientation. The weak bands in the region ~1800–1950 cm^{-1} are attributed to the solvent: (A) 0.9 *M*, 23°; (B) 0.9 *M*, −24°; (C) 0.9 *M*, −60°; (D) 0.4 *M*, 24°; (E) 0.1 *M*, 24°; (F) 0.05 *M*, 24°.

1653 cm^{-1} and a deformation band at 764 cm^{-1}. These data are consistent with our infrared results.

Raman data were collected at 23, −24, and −60° on the 0.4 and 0.1 *M* solutions. The pair of bands at 1762 and 1692 cm^{-1} dominates the spectrum at room temperature and higher concentrations, whereas the 1730 and 1653 cm^{-1} set dominates at −60° (Figure 2). The one deformation band observed appears to be concentration and temperature invariant.

$NaAlH_4$ in THF. The room temperature Raman spectrum of $NaAlH_4$ in THF (0.8 *M*) has bands which correspond to the high-frequency species in the spectrum of the Li^+ salt. Upon cooling the sample to −60°, the polarized 1755-cm^{-1} band becomes asymmetric on the low-frequency side, which hints of another species.

The infrared spectrum of 0.1 *M* solutions is more complex, consisting of a strong absorption at 1692 cm^{-1}, which corresponds to the depolarized feature in the Raman, a nondistinct shoulder at 1652 cm^{-1}, and a weak band at 1593 cm^{-1} (Figure 3). The low-frequency region consists of a band at 755 cm^{-1} and a shoulder at 764 cm^{-1}. The shoulder at 1652 cm^{-1} may also correspond to a small concentration of a lower frequency species existing in solution, but this does not explain the presence of the band at 1595 cm^{-1}. The observance of more than the two expected absorptions in the infrared spectrum (ν_3 and ν_4) may be attributed to a breakdown of the tetrahedral symmetry of AlH_4^-. Another alternative is the assignment of the 1652-cm^{-1} feature as an overtone of the missing ν_2 and the 1593-cm^{-1} band as $\nu_2 + \nu_4$: $2\nu_2 = 1652$, $\nu_2 = 826$, $\nu_2 + \nu_4 = 1593$, $\nu_4 = 767$ cm^{-1}.

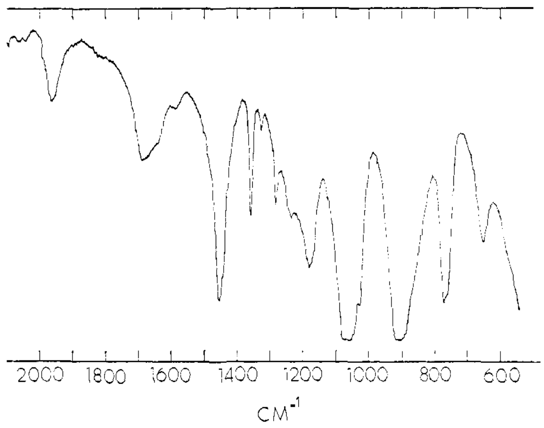

Figure 3. Infrared spectrum of 0.1 *M* $NaAlH_4$ in THF.

$LiAlH_4$ and $NaAlH_4$ in Glyme. The Raman spectrum of $LiAlH_4$ in glyme exhibits concentration and temperature behavior similar to that of $LiAlH_4$ in THF except that the intensity of the pair of lower frequency bands (1731 p, 1648 dp) is greater relative to the higher frequency set for an equivalent solute concentration. The polarized higher frequency band occurs at 1757 cm^{-1}, but its depolarized component was too weak to be measured. The Raman spectrum of $NaAlH_4$ in glyme also exhibits the same behavior. The relative intensities of the two sets of frequencies appear to be intermediate between that of $LiAlH_4$ in THF and glyme.

$[(C_2H_5)_4N][AlH_4](s)$. Using tetramethylammonium and tetraethylammonium salts of AlH_4^-, Semenenko, *et al.*,[6] claimed the observation of all four AlH_4^- fundamentals. $[(C_2H_5)_4N][AlH_4]$ as prepared in our laboratory yielded Raman data consistent with theirs except that, as usual, no ν_2 (reported at 821 cm^{-1}) could be found in the Raman spectrum (Figure 4). The 800-cm^{-1} region is clear except for the 775-cm^{-1} feature, which had been asigned to ν_4, and a band at 794 cm^{-1}, which is assigned to a $[Et_4N]^+$ vibration as it is also present in the $[Et_4N][AlD_4]$ spectrum. The infrared spectrum consists of two bands at 1671 and 760 cm^{-1}, both lower than the Raman values.

GaH_4^-. The GaH_4^- stretching and deformation modes are expected to occur in the regions of *ca.* 1800 and 750 cm^{-1}, respectively, from the reported solid-state infrared data of GaH_4^- stretching frequencies[1] and by analogy to the reported vibrational data for $GaH_3 \cdot N(CH_3)_3$.[9]

Owing to the inherent instability of gallium hydrides, infrared spectra of the solutions were not attempted. Raman spectra of some of the solid samples led to decomposition from laser radiation. The results of the Raman and infrared data collection are tabulated in Table II. As found in the AlH_4^- spectra, a lowering of the Ga–H stretching frequencies is observed with the more polar solvent, from 1830 in Et_2O to 1807 cm^{-1} in Me_2O for ν_1 and 1802 to 1766 cm^{-1} for ν_3. Only one deformation band was observed, at 794 cm^{-1} in the Me_2O solution, but, owing to its low intensity and

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(9) (a) D. F. Shriver, R. L. Amster, and R. C. Taylor, *J. Amer. Chem. Soc.*, 84, 1321 (1962); (b) N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 2, 1036 (1963).

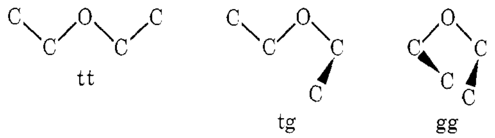
broadness ($\Delta\nu_{1/2}$ = 46 cm^{-1}), it may be an envelope of two or more bands. Solvent bands mask the region above 880 cm^{-1} in Me_2O and 785 cm^{-1} in Et_2O, preventing observation of any other GaH_4^- vibrations which may be present.

The solid-state spectra of $NaGaH_4$ (infrared) and $KGaH_4$ (infrared and Raman) show more bands than the two expected in the infrared region and four expected in the Raman spectrum for a tetrahedral GaH_4^-; furthermore, these bands are very broad, indicating much distortion of the GaH_4^- tetrahedron.

Discussion

The Diethyl Ether Spectrum. The possibility that the 799-cm^{-1} band was a diethyl ether vibration had been considered by D'Or,[3] but, since the feature was relatively more intense in the $LiAlH_4$ solution spectrum than in the pure Et_2O spectrum, it was concluded that the $\nu_2(AlH_4^-)$ assignment was more likely. The corresponding deuteride data as taken in our laboratory show that the 799-cm^{-1} band is in fact an Et_2O band even though the relative intensity change noted by D'Or is real. D'Or has also noted the decrease in intensity of the 1153-cm^{-1} band of Et_2O (a C–O vibration) which he attributed to the formation of $LiAlH_4$–Et_2O complexes. The very large intensity changes in the Et_2O vibrations are actually present throughout most of the solvent spectrum; this effect is enhanced with increasing $LiAlH_4$ concentration though with little, if any, frequency shifts (Figure 1).

Since diethyl ether exists in at least three conformers



interaction of diethyl ether molecules with a solute can lead to a change in conformer population. Krueger and coworkers[10] have assigned the bands in the ir and Raman spectra of Et_2O at room temperature to its various conformers and later reported that in the MgX_2–Et_2O system[11] (X = Br, I) vibrational spectra indicate a change in conformer population from the normally abundant tt to tg or gg conformers. The latter two are sterically more conducive to coordination with Mg^{2+}.

Similarly in the Et_2O–$LiAlH_4$ case, the diethyl ether bands assigned to the tt conformer decrease in intensity with a corresponding increase in the bands assigned to the tg and gg. Here the ether molecules are probably interacting with the lithium cation.

The Nature of AlH_4^- in Ether Solutions. The frequencies of ν_1 and ν_3 observed under various conditions of solvent, concentration, and temperature appear to fall into three classes: 1793 and 1740 cm^{-1}, 1760 and 1690 cm^{-1}, 1730 and 1650 cm^{-1}. Presumably each of these pairs of frequencies corresponds to a different solution species. In all these systems the frequency of the deformation vibration is relatively invariant, at approximately 765 cm^{-1}.

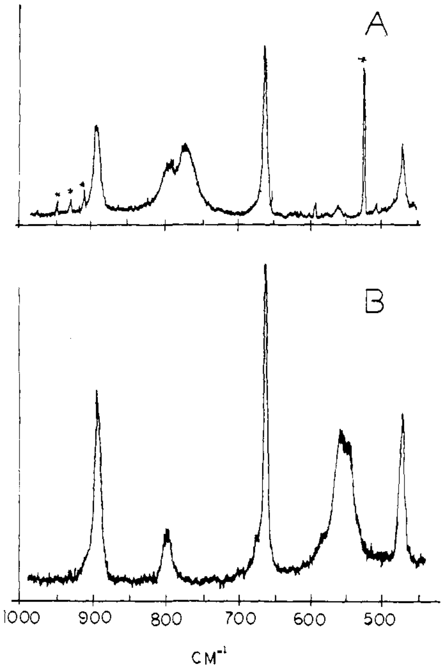


Figure 4. Raman spectra of (A) $[Et_4N][AlH_4]$ and (B) $[Et_4N][AlD_4]$. Peaks labeled with an asterisk (*) are plasma lines of the Ar ion laser.

$LiAlH_4$ in diethyl ether is the only system exhibiting the 1793- and 1740-cm^{-1} stretching frequencies. These frequencies are about 30 cm^{-1} higher than those found for any of the other $MAlH_4$ systems studied except $LiAlH_4$ in the solid state. Yet diethyl ether solutions of $LiAlH_4$ were the first and for a long time the only system on which both Raman and infrared studies had been reported.[2,3] Ironically the frequencies observed in this solvent have long been considered to be representative of the vibrations for free AlH_4^-.

The 1760- and 1690-cm^{-1} species are found for the solutions of $LiAlH_4$ and $NaAlH_4$ in dimethyl ether, tetrahydrofuran, and glyme. (Solid-state data for $[Et_4N][AlH_4]$ and $NaAlH_4$ fall in the same frequency range, 1760 and 1690 cm^{-1}.) In the $LiAlH_4$–THF and $LiAlH_4$– and $NaAlH_4$–glyme solutions, another species has been observed, which exhibits still lower stretching frequencies, 1730 and 1650 cm^{-1}. The equilibrium between the 1760- and 1690-cm^{-1} and 1730- and 1650-cm^{-1} species was observed in the Raman spectra by varying concentration and temperature (23 to −60°). It was found that at higher concentrations and/or lower temperatures the 1730- and 1650-cm^{-1} species grow in intensity at the expense of the higher frequency 1760- and 1690-cm^{-1} species (Figure 2), and these shifts are reversible. For a given concentration and temperature, the equilibrium appears to be shifted further to the 1730- and 1650-cm^{-1} species in $LiAlH_4$–glyme > $NaAlH_4$–glyme > $LiAlH_4$–THF.

Association studies on $LiAlH_4$ in THF solution by boiling point elevation[12] and vapor pressure depression[13] show, as expected, that association increases as concentration of $LiAlH_4$ increases. The dissociation into ionic species is small, as shown from conductivity studies.[14] This is not surprising in view of the low dielectric constants and relatively poor complexing abilities of ethers.

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(10) H. Wieser, W. G. Laidlaw, P. J. Krueger, and H. Fuhrer, *Spectrochim. Acta, Part A*, 24, 1055 (1968).

(11) H. Wieser and P. J. Krueger, *ibid.*, **26**, 1349 (1970).

(12) E. Wiberg, H. Nöth, and R. Uson, *Z. Naturforsch. B*, 11, 487 (1956).

(13) A. E. Shirk, 1972, unpublished results.

(14) N. M. Alpatova, T. N. Dymova, Yu. M. Kessler, and O. R. Osipov, *Russ. Chem. Rev.*, 37, 99 (1968).

The environment of the cation must consist of solvent molecules as well as AlH_4^- anions, even in the case of contact ion pairs. Edgell, *et al.*,[15] have observed the vibrations of alkali metal cations in solution in the far-infrared; these vibrations occur within a given frequency range for a specific cation, with the variations in the frequency being determined by the solvent and anion used. It was concluded that, in THF solutions, these cations vibrated in a cage consisting of solvent and anion molecules held together by ionic forces, the Li^+ vibration occurring in the 373–413-cm^{-1} range and the Na^+ vibration at 184–198 cm^{-1}. The far-infrared spectra of $LiAlH_4$ and $NaAlH_4$ in THF solutions exhibit weak and broad bands at 398 and 193 cm^{-1}, respectively. This consistency with Edgell's results provides direct spectroscopic evidence for cation–AlH_4^- association in our systems.

In tetrahydrofuran solutions of $LiAlH_4$ at *ca.* 65°, molecular weight data indicate a predominance of ion pairs in the concentration range 0.02–0.10 *M* and increasing aggregation above this concentration range.[12] Our own association data[13] obtained at 19°, which may be somewhat imprecise owing to unavoidable systematic errors, indicate a predominance of ion pairs up to *ca.* 0.7 *M*. The interpretation of colligative properties for ionic solutes in low dielectric solvents is open to some uncertainty but the indication is that ion pairs exist at the lower concentrations used in our spectral studies. The Raman spectra of 0.05 and 0.1 *M* $LiAlH_4$ in tetrahydrofuran solution at room temperature show that the 1760- and 1690-cm^{-1} vibrations predominate (Figure 2), therefore we assign this set of vibrations to the ion pair. The 1730- and 1650-cm^{-1} vibrations are in turn assigned to the more associated form of $MAlH_4$ in solution, owing to the increase in the intensity of these vibrations with corresponding increase in hydride concentration. This concentration dependence further rules out the possibility that these spectral features arise from an equilibrium between a solvent separated and contact ion pair as found in the fluorenyl carbanion system.[16] Also, dissociation into ions is considered to be negligible in $MAlH_4$ solutions from the standpoint of the spectroscopically observable species. Thus the species observed in the tetrahydrofuran and glyme solution spectra are thought to be an ion pair and higher aggregate(s), the former associated with the 1760- and 1690-cm^{-1} frequencies, the latter with 1730 and 1650 cm^{-1}. Judging from the temperature dependence, aggregate formation is exothermic. Inspection of Table I shows that the 1760- and 1690-cm^{-1} species are both cation and solvent dependent, with the higher frequency component ranging from 1754 to 1767 cm^{-1}. The 1730- and 1650-cm^{-1} vibrations are essentially independent of the cation and solvent.

The lower Al–H stretching vibrations for the ion aggregates are thought to reflect weaker cation–anion interaction because of known trends for metal halide complexes in the solid state where larger cations generally lead to lower frequencies[17] and also because of the trends observed for AlH_4^- frequencies in the solid state: Li^+, 1838 > Na^+, 1763 > $[Et_4N]^+$, 1757 cm^{-1}. It is possible that the cation–AlH_4^- distances are greater in the aggregate than in the ion pair owing to simple electrostatic interactions.[18] Another possibility is that in the aggregate the cation and anion are separated by solvent molecules. The latter interpretation receives some support from the known trend in cation solvation, $Li^+ > Na^+ > K^+$, etc., and glyme > THF,[16] which parallels the tendency toward formation of the 1730 and 1650 *vs.* the 1760 and 1690 cm^{-1} species: Li, Na–Me_2O $\lesssim$ Na–THF $\ll$ Li–THF < Na–glyme < Li–glyme. This latter interpretation is further supported by the shift from 1755 to 1726 cm^{-1} in ν_1 for $NaAlH_4$ upon addition of the cyclic polyether dicyclohexyl-18-crown-6, which is known to effectively chelate Na^+.[19]

The unusually high stretching frequencies of $LiAlH_4$ in diethyl ether are indicative of a different species existing in this solution. It is known that $LiAlH_4$ is extensively associated in Et_2O solution,[8,20] which is expected in view of its poor coordinating ability and low dielectric constant. In view of the high ν_1 for the aggregate formed in diethyl ether solution, cation–anion interaction is thought to be strongest in this solvent.

It is interesting to speculate on the detailed nature of various ion pair and ion aggregates. Judging from the very high AlH_4^- stretching frequencies and the poor solvating character of diethyl ether, the unique 1973- and 1740-cm^{-1} species of $LiAlH_4$ in diethyl ether is most reasonably attributed to a contact ion aggregate, that is, an aggregate of cations and anions tightly bound together with little shielding of the cation from the anion by the solvent. In contrast, the lower frequency vibrations, 1730 and 1650 cm^{-1}, which are found for aggregates in more polar ethers, are attributed to a decrease in electrostatic cation–anion interaction owing to greater solvation of the cation. This "solvent separated" aggregate may actually represent a series of similar aggregates which are not distinguishable by vibrational spectroscopy. It exists in a concentration- and temperature-dependent equilibrium with the species exhibiting the 1760- and 1690-cm^{-1} vibrations, which is postulated to be a contact ion pair. For all three species existing in these ether solutions, the cation–anion interactions must be fairly weak, however, since no breakdown of the selection rules bases on T_d symmetry is observed.

Dautel and Zeil[4] and Adiks, *et al.*,[5] had proposed that the variations of ν_{AlH} in the infrared solution spectra are due to varying degrees of solvent coordination to Al, which can accommodate a higher coordination number owing to the availability of d orbitals. While this is a possible interpretation of the Al–H stretching frequency shifts, we feel that the interpretation in terms of ion association is more valid. Our interpretation is supported by the observation of similar trends in the stretching frequencies of MBH_4, where ν_{BH} for the lithium salt in diethyl ether solution is much higher than those found in other solution spectra. Furthermore, the Raman spectrum of $LiBH_4$ in diglyme shows a temperature dependence which is similar to that of AlH_4^- in glyme and THF solutions; a sharp and polarized

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[15] W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, Jr., and A. Watts, *J. Amer. Chem. Soc.*, **92**, 2240 (1970).

[16] T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307 (1966).

[17] D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold Ltd., London, 1967, pp 42–43.

[18] E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1961, pp 557, 566. The electrostatic argument given in this reference for an increase in M–X distance from the gas-phase ion pair to the infinite solid may be directly applied to distances in ion pairs *vs.* ion aggregates in solution.

[19] H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971).

[20] E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

Table III. Possible Assignments for AlH_4^- (AlD_4^-) Vibrations[a] (in cm^{-1}) and Calculated Teller–Redlich Product Rule Ratios

System		ν_1	ν_2	ν_3	ν_4	$\nu_1/\nu_1' =$ 1.41	$\nu_2/\nu_2' =$ 1.41	$\nu_3\nu_4/\nu_3'\nu_4' =$ 1.88
$LiAlH_4$–Et_2O	I	1793 (1285)	763 (546)	1740	766	1.40	1.40	
	II	1793 (1285)		1740	764 (546)	1.40		
$LiAlH_4$–Me_2O	I	1767 (1268)	764 (546)	1700 (1241)		1.39	1.40	
	II	1767 (1268)		1700 (1241)	764 (546)	1.39		1.92
$NaAlH_4$–Me_2O	I	1757 (1263)	767	1702	755	1.39		
	II	1757 (1263)		1702	761	1.39		
$NaAlH_4$–THF	I	1756 (1257)	766	1693	770	1.40		
	II	1756 (1257)	(826)[b]	1693	768	1.40		
$[Et_4N][AlH_4]$	I	1757 (1256)	772 (549)	1678 (1220)	760 (560)	1.40	1.41	1.87
	II	1757 (1256)		1678 (1220)	766 (556)	1.40		1.89

[a] Assignment I ν_2 assigned from Raman spectra, ν_4 to that observed in ir; assignment II ν_2 assumed not observed, ν_4 averaged from ir and Raman bands. [b] Calculated from possible overtone and combination bands.

band grows in at 2248 cm^{-1} at lower temperatures while at room temperature only one, intense, polarized band is present at 2307 cm^{-1}.[21] Since the boron atom in BH_4^- cannot increase its coordination number to greater than four, it is not possible for the solvent to coordinate to the boron atom, and ion pair–ion aggregate formation appears to be the only viable alternate for explaining the vibrational data. It is of course possible that the phenomena responsible for the spectral shifts are different for AlH_4^- than for BH_4^-; however, this appears highly unlikely in view of the similarity in the spectra. Another argument against solvent coordination to Al in AlH_4^- is provided by the work of Dilts and Ashby[22] who have found that AlH_4^- does not associate with trialkylamines which are even stronger Lewis bases than the ethers being considered in the present work.

General Assignments. Despite the association of $MAlH_4$ in solution, the AlH_4^- species appears to be sufficiently undistorted so that the vibrations follow those predicted for a tetrahedral moiety. Tentative assignments were made and whenever possible were checked using the Teller–Redlich product rule; these are listed in Table III.

The symmetric stretch, $\nu_1(A_1)$, is easily assigned as the most intense and polarized band in the Raman spectrum, appearing at *ca.* 1760 cm^{-1} for the ion pair (1260 in AlD_4^-) and at 1730 cm^{-1} for the solvent separated aggregate. For the ion pair, $\nu_3(F_2)$ is assigned to the intense feature at *ca.* 1695 cm^{-1} in the infrared spectrum and also to the weak, depolarized band in the Raman spectrum; that for the aggregate occurs at 1650 cm^{-1}. Solvent bands also occur in the 200–1200-cm^{-1} region, hence measurement of ν_3 often was not possible for AlD_4^-.

Two deformation vibrations $\nu_2(E)$ and $\nu_4(F_2)$ are expected but only one was generally observed in the Raman spectrum. Since this band was coincident, or nearly coincident, with that found in the infrared spectrum, the Raman band can also be assigned as ν_4 which leaves no assignment for ν_2. It may be that ν_2 is too weak or diffuse to be observed in the Raman effect; alternatively it is possible that ν_2 is coincident with ν_4. These two alternative assignments will be considered in detail below.

Is ν_2 Missing? In the tetrahedral hydrides known of groups IIIa through Va the ratio $(\nu_2/\nu_4) > 1$ is observed with the separation $(\nu_2 - \nu_4)$ greater for the second period elements (B, C, N) than for the third period. Thus one might expect ν_2 for AlH_4^- to be in the region 895–765 cm^{-1} ($\nu_2 - \nu_4 = 130$ cm^{-1} for BH_4^- in NH_3 solution).[23] In another line of attack, one can calculate the position of ν_2 using various simple force fields to see where ν_2 could be expected to occur. These results are given in Table IV, along with analogous calculations for BH_4^-, where ν_2 is known. For the simple valence force field (SVFF)[24] and orbital valence force field (OVFF)[25] approximations, ν_2 was calculated using the observed ν_1, ν_3, and ν_4 values. Assignment II for $[Et_4N][AlH_4]$ (Table III) and Emery and Taylor's $^{11}BH_4^-$ in liquid ammonia data[23] were used. The ν_2 approximation of Longuet-Higgins and Brown,[26] which was shown to be accurate to ~5% for some MH_4 species, is calculated from a relationship between ν_2 and r_{MH} based on the assumption of a rigid, spherical electronic distribution in a tetrahedral binary hydride. The results in Table IV show that for all three approximations, the calculated value of ν_2 for BH_4^- is lower than the observed frequency. If the same result holds for AlH_4^- then ν_2 would be expected to occur above 850 cm^{-1}.

Table IV. Calculation of $\nu_2(E)$ for AlH_4^- and BH_4^-

	AlH_4^-	BH_4^-
Observed	?	1210
SVFF	835	1122[a]
OVFF	682	916[a]
L-H and B	850	1171[b]

[a] Calculated from observed frequencies of $Na^{11}BH_4$ in NH_3 solution, from ref 22. [b] Value from ref 26b.

Thus it is possible that ν_2 occurs at a frequency higher than that found for ν_4 but is not observable in the Raman spectra. The Raman spectrum of $NaAlH_4$ in the solid state consists of four very broad bands, two each in the stretching and deformation regions. Three of the bands are nearly identical with those found in the Raman spectra of $[Et_4N][AlH_4]$ and many of the $MAlH_4$ solutions (Table I), and the fourth band occurs at 824 cm^{-1} which is assignable as the missing ν_2 vibra-

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(21) A. E. Shirk and D. F. Shriver, *J. Amer. Chem. Soc.*, **95**, 5901 (1973).

(22) J. A. Dilts and E. C. Ashby, *Inorg. Chem.*, **9**, 855 (1970).

(23) A. R. Emery and R. C. Taylor, *J. Chem. Phys.*, **28**, 1029 (1958).

(24) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1962, p 182.

(25) J. W. Linnett and P. J. Wheatley, *Trans. Faraday Soc.*, **45**, 39 (1949).

(26) (a) H. C. Longuet-Higgins and D. A. Brown, *J. Inorg. Nucl. Chem.*, **1**, 60 (1955); (b) D. A. Brown, *J. Chem. Phys.*, **29**, 451 (1958).

tion. However, the broadness and asymmetry of the Raman bands and the multiplicity of the bands observed in the infrared spectrum imply that $NaAlH_4$ is distorted in the solid state, so great faith cannot be placed in this assignment for ν_2.

Another line of evidence for an assignment of ν_2 at a frequency higher than ν_4 comes from the infrared spectrum of $NaAlH_4$ in THF solution, where far more bands occur than the expected two F_2 modes. As discussed earlier in the paper, the two extra bands in the Al–H stretching region may be assigned as combination and overtone bands of ν_2 and ν_4, leading to a calculation of $\nu_2 = 826$ cm^{-1}.

The 821-cm^{-1} band observed by Semenenko[6] for $[Et_4N][AlH_4]$ as ν_2 fits into the above range estimated for the ν_2 vibration, yet the spectra collected in our laboratory display no such feature, nor is there a feature at a frequency of 581 cm^{-1} calculated for $[Et_4N][AlD_4]$.

If ν_2 of AlH_4^- occurs in the 800-cm^{-1} region, it would not be observed in the Et_2O, THF, or glyme solutions owing to strong solvent vibrations above the 765-cm^{-1} deformation band. The spectrum of dimethyl ether is clear to 880 cm^{-1}, however, and no evidence of another feature owing to AlH_4^- was found. Also, in the Raman spectra of $LiAlD_4$ in Et_2O and Me_2O only one band was observed in the deformation region at 546 cm^{-1} in both. Even though the solvent vibrations may mask an AlH_4^- deformation vibration, this vibration would be expected to be observable in the corresponding AlD_4^- spectrum since very few solvent bands occur in the 500–600-cm^{-1} region. There is of course the possibility that the ν_2 vibration is of such low intensity that it is not observed.

Are ν_2 and ν_4 Coincident? It is quite possible that ν_2 is approximately coincident with ν_4. The 765 cm^{-1} band in the Raman spectra is broad, with $\Delta\nu_{1/2} \cong 30$ cm^{-1}, and it is sometimes asymmetric, thus another weaker band could be buried under it. The splitting of the deformation band in $NaAlH_4$–Me_2O (767 w, 755 sh) and $[Et_4N][AlD_4]$ (557 w, 549 w) can be assigned to ν_2 and ν_4 which are not accidentally degenerate in these systems. In general the observed deformation at *ca.* 765 cm^{-1} is remarkably insensitive to its environment, even in THF and glyme solutions where two sets of stretching vibrations are present. In view of this fact, it seems unlikely that the two deformation bands of $NaAlH_4$ in dimethyl ether are due to a splitting of the F_2 vibration.

Two assignments appear likely: assignment I, where ν_2 is attributed to the deformation band observed in the Raman spectrum and ν_4 to that observed in the infrared; and assignment II, where ν_4 is taken as the average of the infrared and Raman frequencies, while ν_2 is assumed to be unobserved. In the case of $LiAlH_4$ and $LiAlD_4$ in Me_2O, assignment II leads to a Teller–Redlich product rule ratio of 1.92 for the F_2 class vibrations which is much higher than the theoretical 1.88 value. Assignment I yields a satisfactory product rule ratio of 1.40 for the E class which is slightly lower than the theoretical 1.41 value. Unfortunately no infrared value for ν_4 could be collected on the highly volatile dimethyl ether solutions. Assignment II for spectral data of $[Et_4N][AlH_4]$ and $[Et_4N][AlD_4]$ leads to a high product ratio of 1.89 for the F_2 vibrations. Alternatively, assigning the Raman bands to ν_2 and the infrared bands to ν_4 leads to a better fit with the theoretical product ratios (see Table III). On this basis the assignment of the Raman band to ν_2 (assignment I) is preferred. It is assumed that the intensity of ν_2 is greater in the Raman effect than that of ν_4. In $NaBH_4$ and $NaBD_4$ in basic aqueous solution ν_2 is slightly more intense than ν_4.[21] It is interesting that ν_4 is absent in the Raman spectrum of $NaBH_4$ and $NaBD_4$ in the solid state but appears in the infrared spectrum, whereas both ν_2 and ν_4 are present in the corresponding spectra of the potassium salts.[27]

The near coincidence of ν_2 and ν_4 has some precedent among transition metal oxo species, MO_4^{n-}. For example, the accidental degeneracy of ν_2 and ν_4 has frequently been postulated, as for ReO_4^- and TcO_4^-, although it has also been argued that in these cases ν_2 is not degenerate with ν_4 but is too weak and diffuse to be observed.[28] In the case of OsO_4, the near coincidence of ν_2 and ν_4 is well documented.[29]

Normal Coordinate Analyses. Normal coordinate analyses were carried out on the two possible assignments of the AlH_4^- ion. The vibrational data of the tetraethylammonium salts in the solid state (Table III) were used as they comprise the only "complete" data set of all the systems studied.

A locally modified version of FPERT[30] was used. The symmetry coordinates for a tetrahedral molecule as tabulated by Cyvin[31] were used, and the potential function employed was in terms of symmetry coordinates S_i and force constants F_{ij}

$$2V = F_{11}S_1^2 + r^2F_{22}S_2^2 + F_{33}S_3^2 + r^2F_{44}S_4^2 + rF_{34}S_3S_4$$

No constraints were necessary as the problem already was overdetermined. The individual eigenvalues were weighted as $w_i = 1/\lambda_i$. The Al–H distance was taken as equal to 1.547 Å as determined for $LiAlH_4$ by Sklar and Post.[7]

The results are given in Tables V and VI. Both assignments yield good fits of calculated and observed frequencies which is not surprising as there is very little difference between the two assignments for the A_1 and F_2 vibrations. Assignment II leads to a larger interaction force constant F_{34} and lowers the value of F_{33} and F_{44}, but the differences between the two sets of results are small and are not considered significant.

Assignment I yields a good fit for the vibrations alternatively assigned to ν_2(E). The force constant F_{22} (0.118 mdyn/Å) is smaller than F_{44} (0.158 mdyn/Å), whereas in the case of BH_4^- the two deformation force constants are approximately equal.[21,23] This is not unreasonable; in the group IV hydrides $F_{22} > F_{44}$ for CH_4 but the reverse is true for SiH_4 and GeH_4.[32] The vibrational analyses do not distinguish between either assignment.

The values of $\nu_1(A_1)$ and F_{11} of BH_4^-, AlH_4^-, and GaH_4^- are listed in Table VII along with those of the group IV tetrahedral hydrides and the ω_e and k_e of the

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(27) K. B. Harvey and N. R. McQuaker, *Can. J. Chem.*, **49**, 3272 (1971).

(28) F. Gonzalez-Vilchez and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1416 (1972), and references therein.

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(30) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. VI," Reports 57–65, Shell Development Co., Emeryville, Calif., 1964.

(31) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Elsevier, Amsterdam, 1968, p 122.

(32) J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964).

Table V. Observed and Calculated Frequencies for $[Et_4N][AlH_4]$

	Assignment I				Assignment II			
	AlH_4^-		AlD_4^-		AlH_4^-		AlD_4^-	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$\nu_1(A_1)$	1757	1763.1	1256	1247.2	1757	1763.1	1256	1247.2
$\nu_2(E)$	772	772.8	549	546.6				
$\nu_3(F_2)$	1678	1678.7	1220	1219.0	1678	1677.2	1220	1221.1
$\nu_4(F_2)$	760	761.6	560	557.8	766	764.2	556	558.3
Average error	A_1 class 7.5 cm^{-1} or 0.52%				7.5 cm^{-1} or 0.52%			
	E class 1.6 cm^{-1} or 0.26%							
	F_2 class 1.4 cm^{-1} or 0.18%				1.5 cm^{-1} or 0.20%			

Table VI. Symmetry Force Constants for Et_4NAlH_4 in mdyn/Å and Potential Energy Distribution for the F_2 Vibrations

	Assignment I	Assignment II		Assignment I	Assignment II
F_{11}	1.845	1.845	F_{44}	0.158	0.163
F_{22}	0.118		F_{34}	0.023	0.059
F_{23}	1.585	1.569			

PED for F_2 block

	Assignment I				Assignment II		
	V_{33}	V_{44}	V_{34}		V_{33}	V_{44}	V_{34}
ν_3	0.993	0.002	0.004	AlH_4^-	0.979	0.005	0.016
ν_4	0.009	1.000	−0.008		0.034	1.009	−0.943
ν_3	0.985	0.007	0.008	AlD_4^-	0.965	0.011	0.024
ν_4	0.017	0.995	−0.012		0.048	1.003	−0.051

Table VII. Comparison of $\nu_1(A_1)$ and F_{11} (mdyn/Å) of Group IIIa and Group IVa Tetrahedral Hydrides and Group IIIa Diatomic Hydrides

MH_4	ν_1, cm^{-1}	F_{11}	State
BH_4^- [a]	2294 (2244)	3.07 (3.02)	Na^+ salt, basic aqueous solution
AlH_4^-	1757	1.84	Et_4N^+ salt, solid state
GaH_4^-	1807	1.94	Li^+ salt, Me_2O solution
CH_4 [b]	2915	5.16	Gas phase
SiH_4 [b]	2187	2.84	Gas phase
GeH_4 [b]	2106	2.65	Gas phase
MH	ω_e	k_e	
BH [c]	2435	3.22	
AlH [c]	1682.57	1.62	
GaH [d]	1604.52	1.51	
InH [c]	1474.7	1.28	

[a] Reference 21; values in parentheses corrected for Fermi resonance. [b] Reference 32. [c] Reference 35. [d] Reference 36.

group III diatomic hydrides for comparison. F_{11} of GaH_4^- was calculated using the 1807-cm^{-1} vibration of $LiGaH_4$ in dimethyl ether solution as $\nu_1(A_1)$. The slightly higher Ga–H stretching force constant for GaH_4^- than for AlH_4^- is expected from the higher frequencies observed for the former. This higher Ga–H stretching frequency has been observed previously in the spectrum of Me_3NGaH_3.[10] It is of interest to note that although the stretching frequency and force constant are higher for the gallium hydride than aluminum hydride, it is generally observed that the gallium compounds decompose more readily. While no comparative thermochemical data are available for these hydrides, Breisacher and Siegel[33] have mass spectrometrically studied the formation of the hydrides of Al, Ga, and In from gas-phase atom reactions and find that the stability of the hydrides decrease in the order $AlH_3 > GaH_3 > InH_3$. The approximate equality of the stretching force constants of AlH_4^- and GaH_4^- is not necessarily indicative of their relative stability toward dissociation, however, since the stretching force constant is a measure of a bond's resistance only to small perturbations in distance from its equilibrium value.

An alternation in properties is common for compounds of elements within each of the main groups III, IV, and V;[34] however, metal–hydrogen frequencies and force constants generally follow a monotonic decrease down a group. For example, F_{11} of group IV MH_4 compounds follows the normal trend, Table VII. Even in the diatomic AlH[35] and GaH[36] molecules, the harmonic vibrational frequencies follow the normal trend, although the difference in ω_e is comparatively small between AlH and GaH; furthermore, the force constants k_e are nearly equal with values 1.6 and 1.5 mdyn/Å for AlH and GaH, respectively. The magnitude of the difference in the stretching force constant in going from period 3 to 4 is much smaller than the large change in going from period 2 and 3; this holds for the group III MH_4^- anions as well as for the diatomic hydrides and the group IV tetrahedral hydrides.[37]

Experimental Section

The sensitivity of the compounds to air and moisture required that all manipulations be done in an inert atmosphere of dry N_2, a drybox, Schlenk line, or in a chemical vacuum line.[38]

Diethyl ether (Allied Chemical, anhydrous), tetrahydrofuran (Matheson Coleman and Bell and Fisher Scientific), and 1,2-dimethoxyethane (Mallinckrodt) were dried and distilled from $LiAlH_4$ or benzophenone ketyl and stored over LiH or Na metal. Dimethyl ether (Matheson) was purified on a chemical vacuum line by passing it through consecutive CaH_2 and −78° traps, condensing the ether in a −196° trap. The gas-phase infrared spectrum was identical with that reported by Kanazawa and Nukada.[39]

$LiAlH_4$ (Metal Hydrides) was purified by filtering a diethyl ether solution through thoroughly outgassed Filter-Aid. The ether was removed under high vacuum, resulting in white $LiAlH_4$ powder. LiH (Matheson Coleman and Bell), NaD (Fluka), and $LiAlD_4$ (Stohler Isotope Chemicals, 99% D) were used without further purification. KH (ROC/RIC) was washed with heptane to remove

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(33) P. Breisacher and B. Siegel, *J. Amer. Chem. Soc.*, **87**, 4255 (1965).

(34) A. L. Allred, *J. Inorg. Nucl. Chem.*, 17, 215 (1961); A. L. Allred and A. L. Hensley, Jr., *ibid.*, 17, 43 (1961).

(35) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, Princeton, N. J., 1950, Table 39.

(36) M. L. Ginter and K. K. Innes, *J. Mol. Spectrosc.*, 7, 64 (1961).

(37) Interestingly, the symmetric stretching frequencies of main group III halides, MX_3, in the gas phase do not fall in a single monotonic order on going down the group: I. R. Beattie and J. R. Horder, *J. Chem. Soc. A*, 2655 (1969).

(38) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, Chapters 1, 5, 7, and 8.

(39) Y. Kanazawa and K. Nukada, *Bull. Chem. Soc. Jap.*, **35**, 612 (1962).

the mineral oil, then dried under vacuum. $[(C_2H_5)_4N]Br$ (Matheson Coleman and Bell, 99%) was dried under vacuum for 24 hr at 50–75°; its infrared spectrum showed no bands due to H_2O. $NaAlH_4$ and $NaGaH_4$ were donated by J. A. Dilts, and dicyclohexyl-18-crown-6 (2,5,8,15,18,21-hexaoxatricyclo$[20.4.0.0^{9,14}]$hexacosane) was donated by B. L. Haymore.

$NaAlD_4$ was prepared according to the reported synthesis for $NaAlH_4$.[40] *Anal.* Calcd for $NaAlD_4$: Na:Al:D, 1.00:1.00:4.00. Found: 0.99:1.00:3.95.

$[(C_2H_5)_4N][AlH_4]$ (and similarly for $[(C_2H_5)_4N][AlD_4]$) was prepared by a modification of Titov's procedure.[41] Finely ground $[Et_4N]Br$ (9.75 g) was added with stirring to a solution of 2.46 g $LiAlH_4$ in 50 ml of THF and allowed to react at room temperature for 2–3 days with stirring. The resulting mixture was filtered, washed with THF, and extracted under N_2 with refluxing THF. A small amount of $LiAlH_4$ was added to the still pot to react with $[Et_4N]Br$, which was also extracted owing to its slight solubility in THF. Crystals of the extracted $[(C_2H_5)_4N][AlH_4]$ were then filtered, washed with THF, and dried, yielding a white solid. *Anal.* Calcd for $C_3H_{20}NAlH_4$: hydridic H, 2.50; Al, 16.73; hydridic H:Al, 4.00. Found: hydridic H, 2.30; Al, 16.14; hydridic H:Al, 3.80; Br^- test negative. Calcd for $C_8H_{20}NAlD_4$: D, 4.87; *Al, 16.32; D:Al, 4.00. Found: D, 4.69;* Al, 16.11; D Al, 3.90; Br^- test negative.

$LiGaH_4$ was prepared by the reaction of $GaCl_3$ with LiH in diethyl ether as reported by Schlesinger, *et al.*[42] *Anal.* Calcd H:Ga, 4.00. Found: H:Ga, 3.97; Cl^- test negative. $KGaH_4$ was prepared *via* an exchange reaction of $LiGaH_4$ with excess KH as reported,[1] substituting glyme for diglyme as the solvent. *Anal.* Found Ga:H, 3.77.

$GaCl_3$ was prepared by allowing Ga metal (MacKay, 99.99%) to react with gaseous HCl (Matheson) as reported.[43]

Analyses. Hydridic hydrogen was determined by hydrolyzing samples in THF or diethyl ether with dilute HCl or H_2O when a halide test was desired. Noncondensable gas (at −196°) was collected for measurement using a Toepler pump.

Ga^{3+} was determined by EDTA titration using Cu-PAN as the indicator.[44] Al^{3+} was determined by EDTA-Zn^{2+} back titration, using Eriochrome Black T as the indicators.[45] Na^+ was determined gravimetrically as the salt $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6.5H_2O$.[46] Concentrations of solutions used in the spectroscopic studies were determined by hydridic hydrogen and/or Al (Ga) analyses on solutions of known volumes.

Infrared Spectra. The far-infrared spectra (450–140 cm^{-1}) were recorded on a Beckman IR-11 and spectra in the region 400–4000 cm^{-1} obtained on a Beckman IR-9. Both instruments were occasionally checked with atmospheric water and CO_2 bands to ensure that the instruments were calibrated to within ±1.0 cm^{-1}. The solution cell for the far-infrared spectra was made of two polyethylene sheets which were heat sealed at the edges and fitted with two syringe needles. Solution spectra for the infrared region were obtained using NaCl or KCl cells of 0.02-mm path length. It was observed that KBr reacted with the hydride solutions. The diethyl ether solutions were kept at 15–20° to prevent evaporation of the solvent by purging the sample compartment of the spectrophotometer with liquid N_2 boil-off. Solid samples were prepared as Nujol mulls between KBr or NaCl plates in the drybox.

Raman Spectra. The Raman data were collected using a Spex 1400-II double monochromator with photon counting detection[47] and occasionally digital data processing. The green 514.5-nm and blue 488.0-nm lines of an argon ion laser (Coherent Radiation Model 52G) were employed as exciting lines. A spectral bandpass of 1.5–2.5 cm^{-1} was employed. All Raman data were collected using the conventional 90° viewing system, with the incident beam taken along the z axis and the collection optics along the x axis. No depolarization ratios were calculated for the solution spectra due to overlapping of peaks. Polarization of a band was determined from two consecutive scans of the region of interest, first with the incident beam polarized in the parallel orientation and the analyzer parallel, $z(y,y)x$, and then with the incident beam parallel and the analyzer perpendicular, $z(y,z)x$.[48]

Solution spectra were obtained using a grease-free high-vacuum solution cell[49] or a 5-mm tube which was sealed off under a partial N_2 atmosphere. All solutions were filtered through a fine frit. Low-temperature Raman spectra were obtained using a cell similar to that reported by Miller and Harney.[50]

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